

# **THERMODYNAMICS OF LIQUID MIXTURES CONTAINING CARBOXYLIC ACIDS**

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*Preface*

I hereby certify that this research is the result of my own investigation, which has not already been accepted in substance for any degree, and is not being concurrently submitted for any other degree. Where use was made of the work of others, it has been duly acknowledged in the text.



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**G G Redhi**

I hereby certify that the above statement is correct.



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**Professor T M Letcher**

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To  
my (late) parents

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*Abstract*

The thesis involves a study of the thermodynamics of ternary liquid mixtures involving carboxylic acids with nitriles, hydrocarbons including cycloalkanes, and water. Carboxylic acids are an important class of compounds with a great number of industrial uses and applications. In many parts of the world the separation of carboxylic acids (in particular acetic and propanoic acid) is an important and desirable task. In South Africa, these carboxylic acids together with many other oxygenates and hydrocarbons are produced by SASOL using the Fischer - Tropsch process. The separation of these acids from hydrocarbons and from water is a commercially lucrative consideration, and is the *raison d'etre* for this study. The work focussed on the use of nitriles in effecting separation by solvent extraction and not by the more common method of distillation. The nitrile compounds were chosen because of their high polarity. The carboxylic acids used in this study always refer to: acetic acid, propanoic acid, butanoic acid, 2-methylpropanoic acid, pentanoic acid and 3-methylbutanoic acid.

The first part of the experimental programme is devoted to the determination of excess molar volumes of mixtures of (a carboxylic acid + nitrile compound), where the nitrile refers to acetonitrile, butanenitrile or benzonitrile, respectively. Densimetry was used to determine the excess molar volumes. The work was done in order to get some idea of the interactions involved between a carboxylic acid and a nitrile.

The second part of the experimental study is concerned with the determination of excess molar enthalpies of mixtures of (a carboxylic acid + nitrile compound), where the nitrile refers to acetonitrile, butanenitrile or benzonitrile, respectively. The excess molar enthalpies were determined using flow microcalorimetry. Again, this work was done in order to gain some insight into the interactions involved between a carboxylic acid and a nitrile.

The third part of the experimental work consists of ternary liquid-liquid equilibria of mixtures of (acetonitrile + a carboxylic acid + heptane or cyclohexane), (benzonitrile + a carboxylic acid + water); and (butanenitrile + a carboxylic acid + water), at 298.15 K. The purpose was to investigate the use of nitriles as solvent extractors in separating carboxylic acids from hydrocarbons and also carboxylic acids from water. Ternary liquid-liquid equilibrium data are

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essential for the design and selection of solvents used in the liquid-liquid extraction process.

The final section deals with the fitting of models of liquid mixtures to the experimental data collected in this work. The NRTL (Non-random, two liquid), UNIQUAC (Universal quasi-chemical), and FBT (Flory-Benson-Treszczanowicz) models were used. The modelling work served three purposes:

- to summarise the experimental data
- to test theories of liquid mixtures
- prediction of related thermodynamic properties

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*List of Symbols*

$V_m$	=	molar volume
$V_m^E$	=	excess molar volume
$H_m$	=	molar enthalpy
$H_m^E$	=	excess molar volume
$n_D$	=	refractive index
$R$	=	pure component volume parameter
$Q$	=	pure component surface parameter
$x_i$	=	mole fraction of $i^{\text{th}}$ component
$T$	=	temperature in Kelvin
$P$	=	pressure
$G^E$	=	excess Gibbs energy per mole
$A$	=	Helmholtz energy
$N$	=	number of molecules
$U_0$	=	potential energy of a lattice containing $N_1 + N_2 + \dots$ molecules
$Z$	=	configurational partition function
$z$	=	lattice coordination number
$\alpha_{12}$	=	parameter in NRTL equation
$\omega$	=	selectivity
$\lambda_i$	=	activity coefficient of component $i$
$\Phi$	=	segment fraction
$\theta_i$	=	area fraction

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$\theta_{ij}$	=	local area fraction of sites belonging to molecule i around sites belonging to molecule j
$\theta$	=	molecular configuration
$\delta$	=	root mean square deviation between calculated and experimental property
$\xi_{ij}$	=	local volume fraction of molecule i in the immediate neighbourhood of molecule j
$w_{12}$	=	potential energy for an interaction 1-2 on a lattice
$W_{12}$	=	molar potential energy of interaction
$\tau$	=	normalized parameter for symmetric systems
$x_1$	=	mole fraction of acetonitrile (or butanenitrile, or benzonitrile)
$x_2$	=	mole fraction of carboxylic acid
$x_3$	=	mole fraction of heptane (or cyclohexane, or water)
$x_1'$	=	mole fraction of acetonitrile (or butanenitrile, or benzonitrile) in water (or hydrocarbon) rich layer
$x_2'$	=	mole fraction of carboxylic acid in water (or hydrocarbon) rich layer
$x_1''$	=	mole fraction of acetonitrile (or butanenitrile, or benzonitrile) in acetonitrile (or butanenitrile, or benzonitrile) rich layer
$x_2''$	=	mole fraction of carboxylic acid in acetonitrile (or butanenitrile, or benzonitrile) rich layer

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## CHAPTER 1

### INTRODUCTION

#### 1.1 THE NEED FOR SYNFUELS AND CHEMICALS IN SOUTH AFRICA

SASOL'S foothold as a global competitor is growing stronger as its competitive advantage in the field of Fischer-Tropsch technology increases in the light of the world's diminishing reserves of crude oil, and the need to use increasing amounts of natural gas. Through the proprietary SASOL Advanced Synthol process, SASOL can convert coal to synthetic crude oil (containing a host of different hydrocarbons and oxygenates), while the SASOL Slurry Phase Distillate reactor can convert natural gas into high-quality low-emissions diesel, (sulphur content < 5 parts per million or 0.0005 %) thereby appeasing the mounting local and international environmental concern for cleaner liquid fuels. SASOL currently supplies 41% of South Africa's liquid fuel requirements ([www.sasol.co.za](http://www.sasol.co.za), 2002). At present most of the synthetic crude oil made by SASOL is burnt as fuel. Many of the components (aromatics, alkenes, alcohols, carboxylic acids etc) are important in the manufacture of plastic and other useful materials. Separation and sale of some of these lucrative and high valued components would add synergistic value to the overall SASOL process.

This study involves an investigation into the feasibility of separation of carboxylic acids from water or hydrocarbons using a nitrile compound. Economically viable separation of these compounds serves a dual purpose: polluted aqueous streams can be cleaned up and high valued chemicals can be produced relatively cheaply. This in turn will save South Africa valuable foreign exchange as many of these compounds are imported.

#### 1.2 SIGNIFICANCE OF EXCESS VOLUMES AND EXCESS ENTHALPIES

Excess volumes and excess enthalpies are two important thermodynamic quantities used in chemical engineering for the design of plant and separation equipment (Sandler, 1989). A knowledge of the thermodynamic non-ideality of liquids and liquid mixtures can often modify a flow sheet substantially (Prausnitz *et al.*, 1986). Typical examples of this are the design of distillation columns, heaters, coolers, condensers and heat exchange equipment

associated with chemical reactors. A good exposition of how chemists and chemical engineers can calculate the phase - equilibrium behaviour of fluid mixtures from thermodynamic data and theories is provided by Prausnitz *et al.* (1986). Excess volumes can, for example, be used to convert thermodynamic properties of mixing determined at constant pressure, to properties at constant volume (Prausnitz *et al.*, 1986).

In addition, excess properties provide information about the molecular interactions and macroscopic behaviour of fluid mixtures which in turn can be used to develop better theories of liquid mixtures. An understanding of the behaviour of liquids can be achieved by studying the properties of their mixtures. These theories are important not only from the point of understanding the nature of liquids and liquid mixtures, but they also enable the interpolation and extrapolation of limited experimental results in order to make reasonable predictions for systems where no experimental data is available. The aim of most theories of mixtures is the prediction of the behaviour of a multicomponent system from the properties of its constituent pure components. Although considerable progress has been made, we are however, still long way from an adequate all embracing theory of liquid and liquid mixtures. This inadequacy is in sharp contrast to the early theories regarding gases and solids.

### 1.3 LIQUID-LIQUID EQUILIBRIA

There has been a resurgence of interest in liquid-liquid extraction (Humphrey *et al.*, 1984), and this appears to be due to:

- Prospects for substantial energy savings compared with distillation when a minor but high density constituent of the feed mixture is to be recovered.
- Possibilities of avoiding temperature damage that might be caused by distillation.
- Development of improved devices for effective equilibration of the liquid phases.
- Better understanding of the principles behind development, design and scale-

up of extraction processes.

Distillation is not always economical when one of several aromatic hydrocarbons must be separated from aliphatic hydrocarbons (Hauschild and Knapp, 1991). It is sometimes practical to use a solvent extraction process to separate such components. This is done by adding a polar solvent. Referring to the rule “like dissolved like” one can expect a mixture of polar solvent, aromatic and paraffinic hydrocarbons to split into two liquid phases, a hydrocarbon- rich phase (the raffinate), and an aromatic-rich phase (the extract). Such ternary liquid-liquid equilibrium data are essential for the design of solvent extraction processes, and for the proper selection of solvents.

#### 1.4 AREA OF RESEARCH COVERED IN THIS THESIS

In the first part of this thesis the excess molar volumes and enthalpies of the binary mixtures (a nitrile compound + a carboxylic acid) were determined at 298.15 K. The nitrile compounds refer to acetonitrile, butanenitrile and benzonitrile. The carboxylic acids always refer to acetic acid, propanoic acid, butanoic acid, 2-methylpropanoic acid, pentanoic acid and 3-methylbutanoic acid.

The excess molar volumes were measured using densimetry and are presented in Chapter 2. The excess molar enthalpies were measured using flow microcalorimetry and are presented in Chapter 3. Both these measurements were made in order to understand the magnitude and effect on these thermodynamic properties, of the mixing process.

In the second part of this thesis the hydrocarbon and water extraction capabilities of acetonitrile, butanenitrile and benzonitrile, respectively, were investigated at 298.15 K. Liquid-liquid equilibrium (LLE) data at 298.15 K were obtained for the following systems:

- (acetonitrile + acetic acid or propanoic acid or butanoic acid or 2-methylpropanoic acid or pentanoic acid or 3-methylbutanoic acid + heptane)
- (acetonitrile + acetic acid or propanoic acid or butanoic acid or 2-methylpropanoic acid or pentanoic acid or 3-methylbutanoic acid + cyclohexane).



- (butanenitrile + acetic acid or propanoic acid or butanoic acid or 2-methylpropanoic acid or pentanoic acid or 3-methylbutanoic acid + water).
- (benzonitrile + acetic acid or propanoic acid or butanoic acid or 2-methylpropanoic acid or pentanoic acid or 3-methylpropanoic acid + water).

In this work we have concentrated on determining the suitability of nitriles as an extraction solvent for the separation of (carboxylic acid - hydrocarbon) mixtures, as well as (carboxylic acid - water) mixtures using liquid-liquid extraction.

The efficient separation of organic acids from aqueous solution is also of economic importance in the chemical industry, for example in the fermentation industry, and many solvents have been tried and tested to improve such recovery (Arce *et al.*, 1995, Briones *et al.*, 1994, Dramur and Tatli, 1993, Fahim *et al.*, 1997). Arce *et al.* (1995) investigated the separation of (propanoic acid - water) mixtures using solvents methyl ethyl ketone and solvents methyl propyl ketone respectively; Briones *et al.* (1994) reported on the separation of (oleic acid - water) mixtures using  $\beta$ -Sitosterol; Dramur and Tatli (1993) investigated the separation of (acetic acid-water) mixtures using phthalic esters viz. dimethyl phthalate and diethyl phthalate, whilst Fahim *et al.* (1997) reported on solvent extraction using hexanol for (acetic acid-water) mixtures. In this work both benzonitrile and butanenitrile have been investigated for their solvent potential in separating (organic acid - water) mixtures.

The LLE work covered in this project was aimed at finding the effect on the phase equilibria of the ternary mixtures (a carboxylic acid + a nitrile compound + a hydrocarbon compound or water) of:

- increasing the carbon chain length of the carboxylic acid.
- increasing carbon chain length of the nitrile compound.

In the final section the question of fitting representative equations to the experimental data, was considered. To the excess volumes data, the Redlich-Kister polynomial as well as FBT (Flory-Benson-Treszczanowicz) theory were applied. For the excess enthalpies, the Redlich-Kister polynomial, as well as UNIQUAC (Universal quasi-chemical), NRTL (Non-random,

two liquid) and FBT(Flory-Benson-Treszczanowicz) theory were applied. The NRTL and UNIQUAC models were applied to all the ternary liquid-liquid equilibrium data.

The structures of the six carboxylic acids as well as three nitrile compounds used in this work are shown in Figure 1.1.

$\text{CH}_3\text{COOH}$	acetic acid
$\text{CH}_3\text{CH}_2\text{COOH}$	propanoic acid
$\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$	butanoic acid
$(\text{CH}_3)_2\text{CHCOOH}$	2-methylpropanoic acid
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH}$	pentanoic acid
$(\text{CH}_3)_2\text{CHCH}_2\text{COOH}$	3-methylbutanoic acid
$\text{CH}_3\text{CN}$	acetonitrile
$\text{C}_6\text{H}_5\text{CN}$	benzonitrile
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CN}$	butanenitrile

**Figure 1.1** Structures of carboxylic acids and nitrile compounds used in this study

## CHAPTER 2

### EXCESS MOLAR VOLUMES

#### 2.1 INTRODUCTION

Excess molar volume data, like many data are more informative and easier to handle when expressed relative to some kind of ideal behaviour (Walas, 1985).

The excess molar volume,  $V_m^E$ , is defined (Maglashan, 1975) as:

$$V_m^E = V_{mixture} - \sum x_i V_i^o \quad (2.1)$$

where  $x_i$  is the mole fraction of component  $i$ ,  $V_{mixture}$  and  $V_i^o$  are the molar volumes of component  $i$  and the mixture respectively. For a binary mixture,

$$V_m^E = V_{mixture} - (x_1 V_1^o + x_2 V_2^o). \quad (2.2)$$

The change in volume on mixing two liquids, especially two polar liquids, 1 and 2 can be attributed to a number of processes (Letcher, 1975): (a) the breakdown of 1 - 1 and 2 - 2 intermolecular interactions which have a positive effect on the volume, (b) the formation of 1 - 2 intermolecular interactions which results in a diminution of the volume of the mixture, (c) packing effects caused by a difference in the size shape of the component species and which may have a positive or negative effect on the particular species involved, and (d) formation of new chemical species.

There is no volume change on mixing two liquids to form a thermodynamically ideal solution at constant temperature and pressure, but a volume change upon mixing two real liquids is observed (Battino, 1971).

Volume changes on mixing of binary liquid mixtures,  $V_m^E$ , at constant pressure and temperature is of interest to chemists and chemical engineers, and is an indicator of the non-idealities present in real mixtures.

There are great difficulties in treating excess volumes and one major problem is the packing effect. However, this has not deterred some theoreticians and a number of theories abound. Examples of these solution theories include Flory - Benson - Treszczanowicz (Treszczanowicz and Benson, 1985) and Extended Real Associated Solution (Heintz, 1985), the former of which is presented in Chapter 7.

## 2.2 MEASUREMENT OF EXCESS MOLAR VOLUMES

The volume changes for binary mixtures,  $V_m^E$ , can be determined experimentally in one of two ways, namely (i) indirectly from density (densitometric or pycnometric) measurements, or (ii) from the more direct dilatometric method, ie. by determining the resultant volume change upon mixing of the two components. A detailed review of both these experimental methods are reported in the literature (Battino, 1971; Letcher, 1975; Handa and Benson, 1979 ; Beath *et al.*, 1969; Pflug and Benson, 1968; Stokes and Marsh, 1972; Marsh, 1980, 1984; and Kumaran and McGlashan, 1977).

### 2.2.1 Direct Determination

In the direct determination, the volume change that occurs when the different liquids are mixed is measured. Direct methods of measurement of  $V_m^E$  include batch dilatometry and continuous dilution dilatometry (Handa and Benson, 1979).

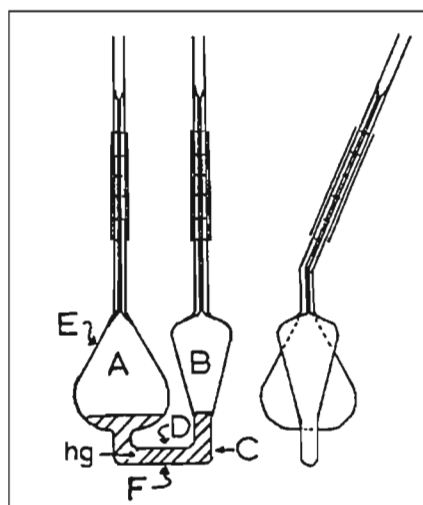
Batch dilatometers are characterized by one composition per loading at a single temperature whilst continuous dilution dilatometers are characterized by a number of compositions per loading at a single temperature.

Dilatometric methods have been used as early as 1887 (Neubeck, 1887), but since then there has been much improvement in the experimental design and efficiency of the dilatometer (Burlew, 1940; Wood and Brusie, 1943; Wirth and LoSourdo, 1968; Washington and Battino, 1968).

#### 2.2.1.1 Batch Dilatometry

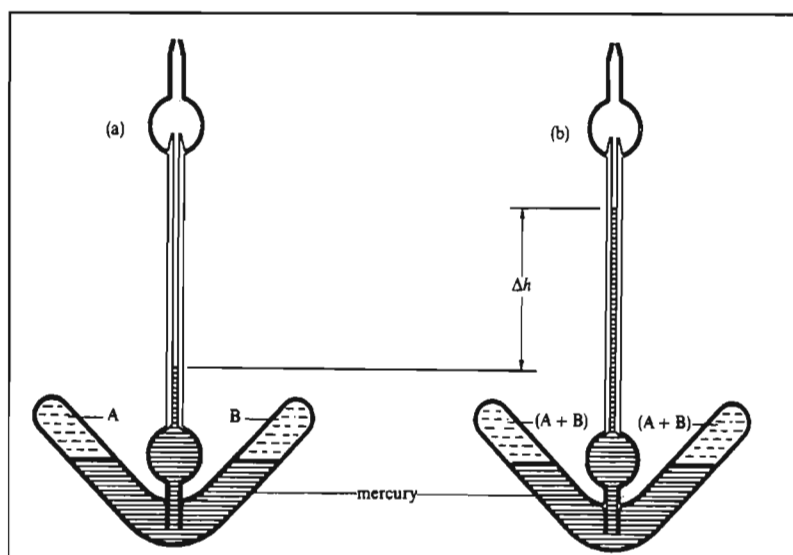
One of the early examples of a design for a single loading dilatometer was the apparatus of Keyser and Hildebrand in the early part of the 20<sup>th</sup> Century (Keyes and Hildebrand, 1917). The apparatus shown in Figure 2.1, consists of a U tube with mercury filling the bottom of the vessel in order to separate the two sample components A and B. Graduated capillaries on the ends of the two tubes provided the means by which the volumes, before and after mixing were determined. The entire mixing vessel was immersed in a thermostatted bath, and thorough mixing was achieved by rocking the apparatus.

It was reported that a precision of  $\pm 0.003 \text{ cm}^3 \cdot \text{mol}^{-1}$  in  $V_m^E$  could be achieved over the temperature range 280 - 350 K (Prausnitz *et al.*, 1986).



**Figure 2.1     The Keyes and Hildebrand Dilatometer**

Another dilatometer of later design is illustrated in Figure 2.2.



**Figure 2.2** A dilatometer for measurements of volume of mixing illustrating (a) before mixing and (b) after mixing.

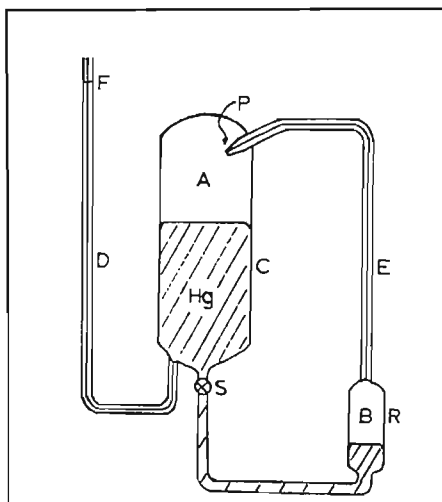
Direct dilatometric measurement of  $V_m^E$  gives a much higher ratio of accuracy to effort (McGlashan, 1979). The dilatometer shown in Figure 2.2 is filled with the aid of a hypodermic syringe. The excess molar volume of mixing,  $V_m^E$  is given (neglecting small terms allowing the effects of the change of pressure on mixing on the volumes of the liquids and of mercury) by the relation

$$V_m^E = \Delta V / (n_A + n_B) = A \Delta h (n_A + n_B) \quad (2.3)$$

Where A is the cross-sectional area of the capillary and  $n_A$  and  $n_B$  are the amounts of substance of A and of B. One possible major source of error in this method is in the determination of the composition as it is necessary to weigh the dilatometer consisting of sample as well as mercury, which results in a large mass. The error associated with taking a difference in large masses is therefore quite significant. Duncan *et al.* (1966) in their reviews, describe methods and modified apparatus in which the precision was found to be  $0.002 \text{ cm}^3 \cdot \text{mol}^{-1}$ .

#### 2.2.1.2 Continuous Dilatometer

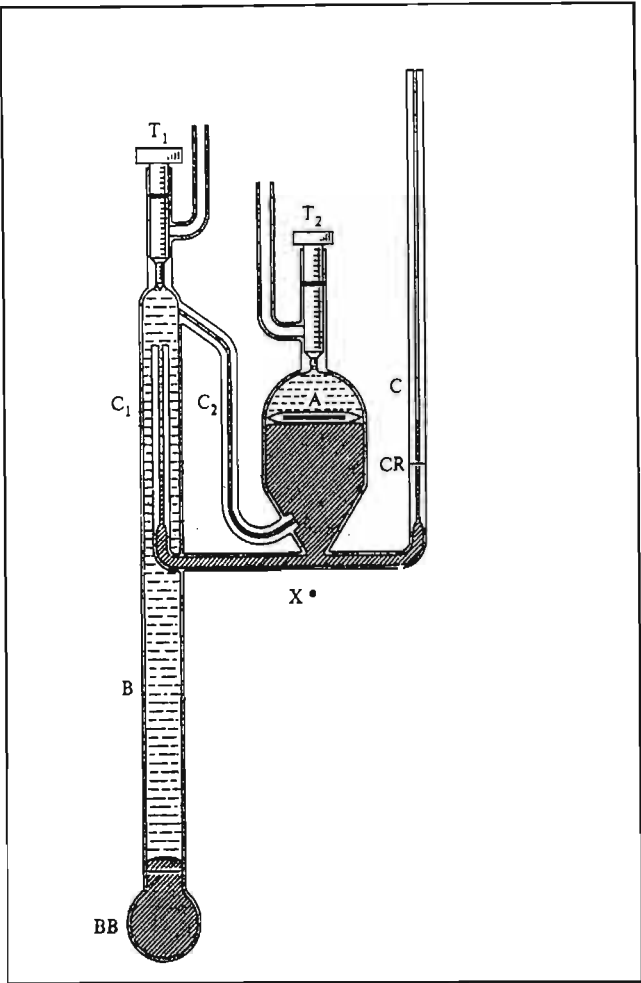
The major advantage of the continuous dilatometer is that it is less time consuming and more data are generated per loading. One of the earliest dilatometer of this type was designed by Geffcken, Kruis and Solana (1937). This dilatometer has been used and modified by many workers (McLure and Swinton, 1965; Watson *et al.*, 1965; Pflug and Benson, 1968; Pasfield, 1965; Beath *et al.*, 1969). The mixing chamber C is initially loaded with pure component A and mercury (as shown in Figure 2.3). The stopcock S leads to reservoir R where pure component B is confined over mercury. The change in the mercury level upon mixing in the calibrated capillary D is read with respect to a reference mark F. The entire apparatus is thermostatted and provision is made for stirring the contents of C. When S is opened mercury from C forces some of the component B into C via the connecting tube E. S is now closed and mixing begins. The change in the level of mercury begins. The change in the level of mercury in capillary D is noted. Successive increments of B are then added in a similar fashion in order to directly determine  $V_m^E$  as a function of composition at one temperature. Volume changes of  $0.0002 \text{ cm}^3$  have reportedly been detected with the above apparatus (Geffcken, Kruis and Solana, 1937).



**Figure 2.3      Continuous dilatometer of Geffcken, Kruis and Solana**

A more recent design of a dilatometer was developed by Kumaran and McGlashan (1977) and is illustrated in Figure 2.4. This dilatometer, an improvement of Bottomley and Scotts (1974) tilting dilatometer allows easier calibration, easier loading, and the measurement of volume changes of any magnitude.

In addition, whereas in the dilution dilatometers of Stokes, Levien and Marsh (1970) and of Bottomley and Scott (1974), the liquid mixture and the pure diluent liquid were separated only through a diffusion boundary in a capillary, with consequent possible errors due to diffusion, in the Kumaran and McGlashan tilting dilatometer the two liquids are separated by mercury at all stages of a run. A standard deviation of  $7 \times 10^{-4} \text{ cm}^3 \cdot \text{mol}^{-1}$  for  $V_m^E$  for this type of dilatometer has been reported (Kumaran and McGlashan, 1977).



**Figure 2.4     The Kumaran and McGlashan dilatometer**

A typical measurement is made by filling (hypodermic syringe) the burette B with one of the pure liquids and the bulb A with the other pure liquid (diluent). The dilatometer is tilted by anticlock wise rotation of its frame so that some mercury flowed from C<sub>1</sub> into B. This displaced mercury in turn forces an equal volume of the diluent liquid through C<sub>2</sub> into bulb A. After mixing, the change in volume is registered as a change in the level of the mercury in the calibrated capillary C. The difference in the heights of the mercury meniscus in C and of the reference mark CR was determined with the aid of a cathetometer. Corrections for changes in pressure arising from changes in mercury levels during measurements had to be made when determining the excess molar volumes.



### 2.2.2 Indirect determination

Density is defined as:

$$\rho = \frac{M}{V} \quad (2.4)$$

where M is the mass of the substance, and V is the volume.

For a binary mixture,  $V_m^E$  is determined from density measurements, calculated using the following equation:

$$V_m^E = \frac{x_1 m_1 + x_2 m_2}{\rho_{\text{mixture}}} - \left( \frac{x_1 m_1}{\rho_1} + \frac{x_2 m_2}{\rho_2} \right) \quad (2.5)$$

where  $x_1$  and  $x_2$  are the mole fractions of components 1 and 2 respectively,  $m_1$  and  $m_2$  are the molar masses of components 1 and 2 respectively, and  $\rho_1$ ,  $\rho_2$ ,  $\rho_{\text{mixture}}$  are the densities of component 1, component 2 and the mixture respectively.

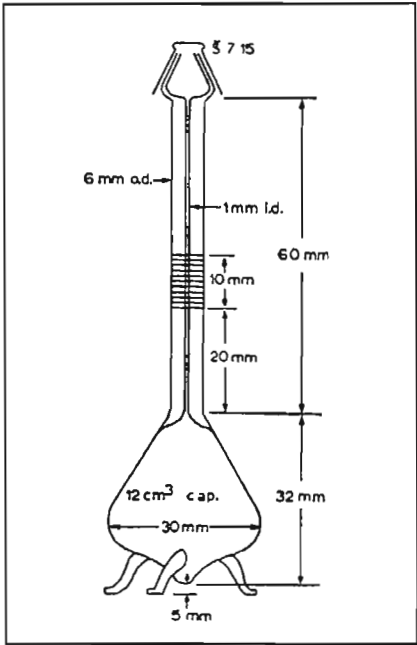
There are a number of different methods of determining densities of liquids. These include pycnometry, magnetic float, and mechanical oscillating densimeters. These different techniques of density determination would now be briefly discussed.

#### 2.2.2.1 Pycnometry

Many types of pycnometers, their characteristics and their handling have been discussed in the literature (Scatchard *et al.*, 1946; Wood and Brusie, 1943; Bauer and Lewin, 1959). One of the earliest documented pycnometers was that used by Wood and Brusie (1943). This pycnometer is illustrated in Figure 2.5. The single arm pycnometer is capable of accuracy of up to one in hundred thousand. This apparatus consisted of a bulb of capacity 1 l cm<sup>3</sup>, a 1 mm internal diameter precision base capillary with eleven lines lightly etched all around the stem and spaced 1 mm apart. A hypodermic syringe and cannula is used to fill the pycnometer during measurement. In the process of determining densities by pycnometry, it is important

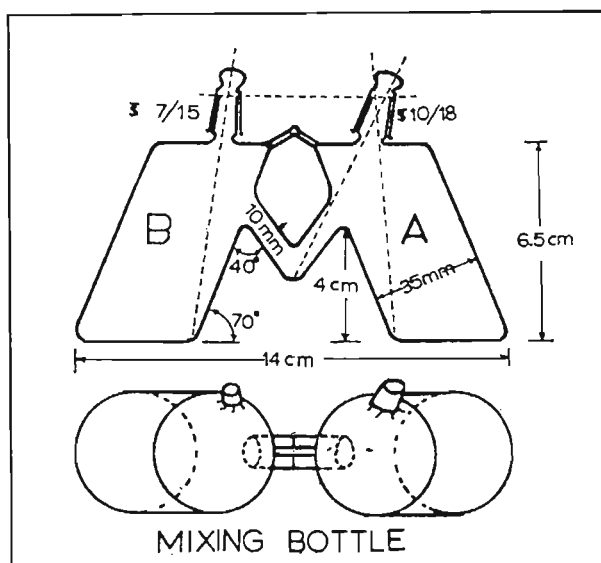
to accurately determine the composition of the mixtures.

Many workers have simply weighed the two components into the pycnometer (Scatchard *et al.*,1946; Walas, 1985).



**Figure 2.5** Single-arm pycnometer of Wood and Brusie

Serious errors could arise due to inadequate mixing of the components, evaporation and vapour space composition. This led to the development of a pycnometer incorporating a mixing bottle (Wood and Brusie, 1943). Some two decades later the design was improved upon (Battino, 1966), and the mixing bottle of Battino is shown in Figure 2.6.

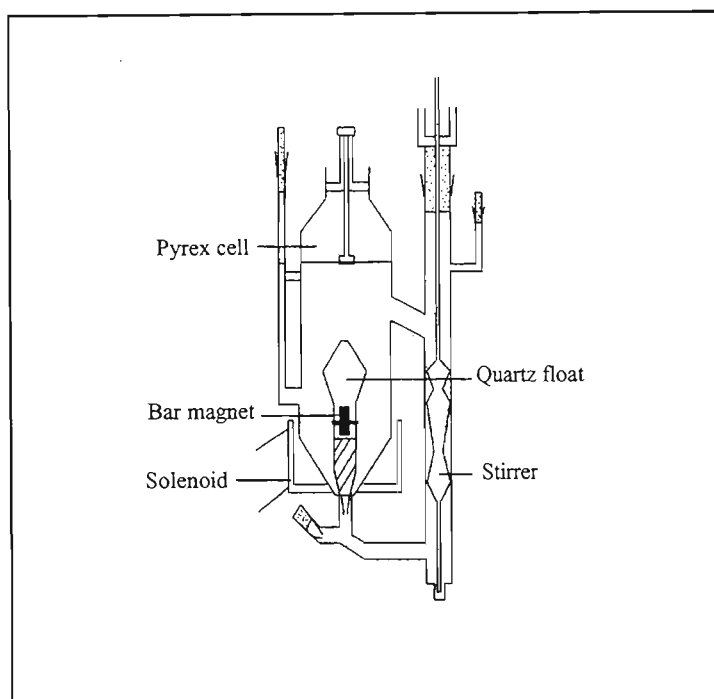


**Figure 2.6**     **Mixing bottle of Battino**

With this mixing bottle potential errors due to inadequate mixing and evaporation of the samples is minimized. Each chamber of Battino's bottle has a capacity of about  $50 \text{ cm}^3$ . These chambers are joined by a 10 mm U-tube in such a way to set them at an angle of 20 degrees to the vertical. The slanting chambers and the relatively large bore of the U-tube facilitates the efficient mixing characteristics of Battino's design. A precision of  $0.00023 \text{ g}\cdot\text{cm}^{-3}$  in density measurements has been reported by Battino (1966).

#### 2.2.2.2     Magnetic float

The magnetic float method of densitometry was designed to give greater accuracy in density measurements. Franks and Smith (1967) describe a modified version of a magnetic float cell originally reported by Lamb and Lee (1913). The pyrex cell with a capacity of approximately  $600 \text{ cm}^3$  was mounted in a thermostatted bath built solely of non-magnetic materials. A precision of density of better than one part in  $10^6$  is reported for the Franks and Smith densitometer and this translates to an accuracy of  $0.001 \text{ cm}^3\cdot\text{mol}^{-1}$  for  $V_m^E$ . The magnetic float densitometer based on the design of Franks and Smith is shown in Figure 2.7.



**Figure 2.7**     **Magnetic float densitometer**

### 2.2.2.3     **Mechanical Oscillating densimeter**

Mechanical oscillating (vibrating tube) densimeters coupled to digital output displays are being widely used in the chemical industry, and research laboratories to measure densities of liquids and liquid mixtures. The frequency of vibration( $\nu$ ) of a constant electrical stimulation is related to the density of the liquid (Handa and Benson, 1979). According to Handa and Benson, the frequency of vibration, of an undamped oscillator (eg. a tube containing liquid sample) connected to a spring of constant elasticity  $c$ , is related to the mass of the oscillator  $M$ , according to the following equation:

$$2\pi\nu = \left( \frac{c}{M} \right)^{\frac{1}{2}} \quad (2.6)$$

If the oscillations were hollow (eg. a tube) then  $M$  would be the sum of the contents in the hollow as well as the true mass of the oscillator ( $M_o$ ). If a liquid with density  $\rho$  fills the hollow (volume  $V$ ), then

$$M = M_o + \rho V \quad (2.7)$$

Substitution for  $M$  into (2.6) and solving for  $\rho$  yields (Handa and Benson, 1979):

$$\rho = -\frac{M_o}{V} + \left( \frac{c}{4\pi^2 V} \right) \left( \frac{1}{v^2} \right) \quad (2.8)$$

$$\text{where } -\frac{M_o}{V} \text{ and } \left( \frac{c}{4\pi^2 V} \right) \text{ are constants.}$$

Equation (2.8) can be written as:

$$\rho = A + B \left( \frac{1}{v} \right)^2 \quad (2.9)$$

$$\text{where } A = -\frac{M_o}{V} \text{ and } B = \left( \frac{c}{4\pi^2 V} \right)$$

The constants A and B are characteristics of the oscillator.  $(1/v)$  is termed the period and is given the symbol  $\tau$ , therefore:

$$\rho = A + B \tau^2 \quad (2.10)$$

Since densities are measured relative to a reference material:

$$\rho - \rho_o = B (\tau^2 - \tau_o^2) \quad (2.11)$$

Where  $\rho_o$  is the density of the reference material (usually the pure solvent, deionised water or air) and  $\tau_o$  is the corresponding period of oscillation.

Commercially available vibrating tube densimeters which can measure density values of up to  $1 \times 10^{-5} \text{ g} \cdot \text{cm}^{-3}$ , are continuously improving the accuracy and precision with which  $V_m^E$  values can be detected (Rowlinson and Swinton, 1982). This implies a possible precision of  $0.003 \text{ cm}^3 \cdot \text{mol}^{-1}$  in the measurement of  $V_m^E$ .

## 2.3 EXPERIMENTAL APPARATUS AND TECHNIQUE

### 2.3.1 Experimental Apparatus

In this work  $V_m^E$  was determined by densimetry using the Anton Paar DMA 602 vibrating tube densimeter for some systems and the Anton Paar DMA 5000 for the other systems. The

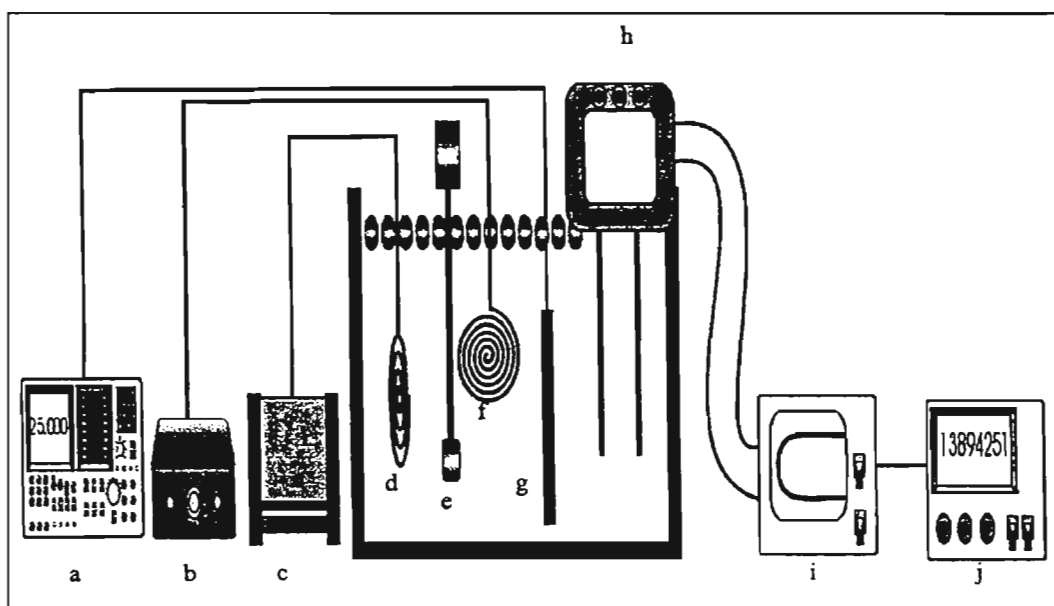
calibrations and techniques used in this study were initially checked by the evaluation of several systems that had been previously published in the literature (McGlashan and Stoekli, 1969; Treszczanowicz and Benson, 1977).

### 2.3.2 The Anton Paar Densimeter

The Anton Paar DMA 602 vibrating tube densimeter coupled to an Anton Paar DMA 60 processing unit was used to determine density measurements. The density determination is based upon the measurement of the oscillations of a vibrating U-shaped sample tube. This tube is filled with the liquid sample mixture and the relationship between the period  $\tau$  and the density of the mixture  $\rho$  is given by

$$\rho = A + B \tau^2 \quad (2.10)$$

The constants A and B are instrument constants for each individual oscillator and can be determined by two calibration measurements with samples of known density, eg. air and deionised water. A schematic representation of the density measuring apparatus is shown in Figure 2.8.



**Figure 2.8** Laboratory arrangement for density determining apparatus [a, Hewlett-Packard quartz thermometer; b, Tronac temperature controller; c, Grants refrigeration unit; d, Cooling probe of refrigeration unit; e, electrical stirrer; f, heating element of Tronac temperature controller; g, thermometer probe; h, pump; i, Anton Paar DMA 602; j, Anton Paar DMA 60]

In this work, the uncertainty in the density occurs due to the fluctuation in the temperature as well as the uncertainty in the period. The uncertainty in the period is a major contributor to the error in the density and results in an uncertainty in the density of less than  $5 \times 10^{-5} \text{ g} \cdot \text{cm}^{-3}$ , and this in turn translates to an error of  $0.005 \text{ cm}^3 \cdot \text{mol}^{-1}$ . The uncertainty in the mass was 0.001 g, and this translates into an error of 0.001 in the mole fraction.

### 2.3.3 Temperature control

The temperature of the Anton Paar DMA 602 densimeter was maintained at  $298.15 \pm 0.002$  K by a system of circulation of water through heaters and coolers. A uniform temperature throughout the water bath was achieved through the use of variable speed mechanical stirrers (e). An auxiliary cooling system comprising a Grants refrigerated bath (c) was used to assist with the temperature control of the main water bath. Water from the secondary bath was pumped via a Haake immersion thermostat unit through an approximately 3 m coiled copper tube, placed inside the main (primary) cooling bath. As the secondary bath was maintained at a temperature of approximately 1 Kelvin below the operating temperature, this set up served to assist the main water bath in temperature maintenance. In both main and secondary water baths, a commercially available corrosion and algae inhibitor was used. In addition the water baths were both covered with spherical polystyrene balls to insulate the water surface against temperature fluctuations as well as minimize evaporation effects.

The thermostat system within the main water bath consisted of a permanent rheostatted immersion heater and a 40 W light bulb connected to a Tronac precision temperature controller. The light bulb set-up is an ingenious contraption as it has a very low thermal heat capacity and facilitates rapid heat transfer. Water from the main water bath was pumped through the water jacked by a submersible pump, and all rubber tubing to and from the densimeter was insulated against heat losses. A Hewlett Packard 2801A quartz thermometer (g) was used to monitor the temperature within the main water bath.

The later model Anton Paar DMA 5000 densimeter which was also used, incorporates an internal thermostat and therefore does not require external temperature control by way of water baths. Two integrated Pt 100 platinum thermometers provides accurate temperature control of 0.001 K.

### 2.3.4 Materials

The purities of all the chemicals were determined using gas-liquid chromatography. A Hewlett-Packard gas chromatograph equipped with a 3393A integrator and a 25 m carbowax capillary column was used. The carboxylic acids and nitrile compounds were stored under 4Å molecular sieves, and analysis by the Karl-Fischer technique showed that the water content was less than 0.01 mass %. The liquids were kept in a dry box before use. A summary of the materials, their suppliers and purities used in this work is given in Table 2.1. Table 2.2 gives the experimental and literature values for densities and refractive indices of the pure compounds.

**Table 2.1**      **Materials used, their suppliers and mass % purities**

COMPOUND	SUPPLIER	% PURITY
acetic acid	Acros	99.5
propanoic acid	Acros	99
butanoic acid	Acros	99
2-methylpropanoic acid	Acros	99.5
pentanoic acid	Acros	99
3-methylbutanoic acid	Acros	99
acetonitrile	Aldrich	>99.5
butanenitrile	Fluka	99
benzonitrile	Sigma Aldrich	99



**Table 2.2      Densities and refractive indices of pure components at T = 298.15 K;  
Refractive indices  $n_D$ , Density  $\rho$**

Component	$n_D$		$\rho / (\text{g}\cdot\text{cm}^{-3})$	
	exp	lit <sup>a</sup>	exp	lit <sup>a</sup>
Acetic acid	1.3697	1.3698	1.0437	1.0439
Propanoic acid	1.3846	1.3843	0.9884	0.9881
Butanoic acid	1.3955	1.3958	0.9535	0.9532
2-Methylpropanoic acid	1.3913	1.3917	0.9431	0.9429
Pentanoic acid	1.4064	1.4060	0.9346	0.9345
3-methylbutanoic acid	1.4019	1.4022	0.9216	0.9219
Acetonitrile	1.3413	1.3416	0.7763	0.7765
Butanenitrile	1.3822	1.3820	0.7866	0.7865
Benzonitrile	1.5252	1.5257	1.0003	1.0006

<sup>a</sup>Riddick *et al.*, (1986).

**2.3.5      Preparation of mixtures**

The pure solvents were initially degassed in an ultrasonic bath for 30 minutes, as aerated solvents tend to give errors in density measurements as well as tend to lead non-reproducible readings. The mixtures were made up in glass flasks of 5 cm<sup>3</sup> volume fitted with ground glass stoppers. Mixtures with compositions spanning the entire mole-fraction scale were made up gravimetrically. Care was taken to first add the least volatile component to the flask, and that the completed mixture left a small space, just large enough to aid mixing in the flask. The mixtures were made up just before injecting into the densimeter, and were shaken vigorously before injection.

**2.3.6      Experimental procedure for instrument**

Prior to each experimental run, the cell was first flushed thoroughly with absolute ethanol (>99.5%) and then acetone. After flushing compressed air was blown through the cell. The value of the constant periodic value,  $\tau$ , for the sample tube filled with air was then noted.

Double deionised Milli-Q water (used as the second calibration standard) was then introduced into the cell by means of a glass syringe, which was fitted with a machined teflon nozzle, ensuring a snug and leak proof fit at the sample cell-syringe junction. The injection process was carried out slowly but steadily, enabling the liquid mixture to properly wet the walls of the cell, and also to alleviate the risk of trapping air bubbles in the U-tube. The sample was always filled past its nodal points and the syringe was left in place at the nodal point during each measurement. The outlet nodal point of the cell was sealed with a teflon plug to reduce evaporation and prevent contamination. The solution mixtures were introduced into the sample cell in exactly the same manner as for the deionised water. Each measuring cycle was allowed to continue until a constant period value was obtained. Period values for water, pure solvents and air were determined between each solution injection, not only for density calculations, but also permitted a continuous check on both sample purity densitometer operation.

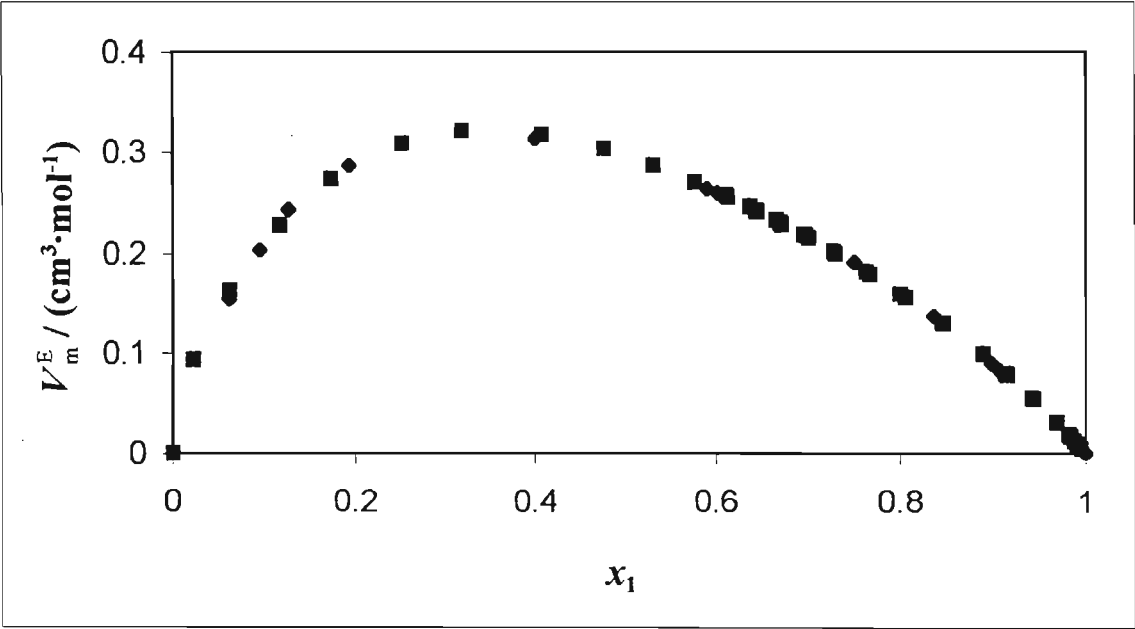
The densities of the mixtures as well as the pure liquids were then determined from the periodic values measured and subsequent application of equation 2.10. Using the density and compositions of these mixtures  $V_m^E$  was determined according to equation 2.5.

### 2.3.7 Validation of the experimental technique

The validity of the technique was established by measuring the excess molar volumes for the mixtures (heptane + propanol) at  $T = 298.15$  K and comparing the results obtained to the literature data for these mixtures (Treszczanowicz and Benson, 1977). A comparison between this work and the literature data is shown in Table 2.3 and graphed in Figure 2.9. The data from this work agreed with the literature data to within  $0.002 \text{ cm}^3 \cdot \text{mol}^{-1}$  which is within the error of this work.

**Table 2.3**      **Comparison of the  $V_m^E$  results obtained in this work with the literature results (Treszczanowicz and Benson, 1977) for mixtures of propanol (1) + heptane (2) at  $T = 298.15$  K.**

$x_1$	$V_m^E(\text{this work})/$ $\text{cm}^3\cdot\text{mol}^{-1}$	$V_m^E(\text{lit.})/$ $\text{cm}^3\cdot\text{mol}^{-1}$
0.000	0.000	0.000
0.061	0.148	0.149
0.125	0.242	0.241
0.193	0.202	0.203
0.400	0.313	0.314
0.590	0.262	0.263
0.601	0.259	0.258
0.750	0.191	0.192
0.835	0.137	0.139
0.897	0.090	0.089
0.906	0.082	0.084
1.000	0.000	0.000



**Figure 2.9**      **Comparison of  $V_m^E$  results from this work with the literature results (Treszczanowicz and Benson, 1977) for the mixtures [propanol (1) +heptane (2)] at  $298.15$  K. ■, literature results; ◆, this work.**

## 2.4 RESULTS

The experimental excess molar volumes,  $V_m^E$  for 18 binary mixtures are presented in the following order:

2.4.1 (acetonitrile + a carboxylic acid) at 298.15 K.

2.4.2 (butanenitrile + a carboxylic acid) at 298.15 K.

2.4.3 (benzonitrile + a carboxylic acid) at 298.15 K.

where carboxylic acid in each case refers to (acetic acid or propanoic acid or butanoic acid or 2-methylpropanoic acid or pentanoic acid or 3-methylbutanoic acid).

The Redlich-Kister (1948) smoothing function:

$$V_m^E = x(1-x) \sum_{r=0}^{r=k} A_r (1-2x)^r \quad (2.12)$$

was fitted to the experimental data by the method of unweighted least squares, and the deviations  $\delta V_m^E$  calculated from the equation:

$$\delta V_m^E / (J \cdot \text{mol}^{-1}) = V_m^E / (J \cdot \text{mol}^{-1}) - x(1-x) \sum_{r=0}^{r=k} A_r (1-2x)^r \quad (2.13)$$

where,  $x$  is the mole fraction of acetonitrile or butanenitrile or benzonitrile, respectively, and  $r = 0, 1, 2$  or  $3$ .

The standard deviation,  $\sigma$  is determined as follows:

$$\sigma = [\sum (V_{m(\text{expt})}^E - V_{m(\text{calc})}^E)^2 / (N - a)]^{\frac{1}{2}}, \quad (2.14)$$

---

where  $N$  is the number of experimental points and  $a$  is the number of fitting coefficients.

For each section (2.4.1 - 2.4.3), tables of results for  $V_m^E$  data, coefficient's  $A_i$  and deviations  $\sigma$  from equation (2.14) are presented. Excess molar volume plots as a function of mole fraction acetonitrile or butanenitrile or benzonitrile have been produced.

2.4.1 Excess Molar Volume Data for Mixtures of [Acetonitrile + a Carboxylic Acid] at 298.15 K

**Table 2.4** Excess molar volumes  $V_m^E$  for the systems: [Acetonitrile (1) + a Carboxylic Acid (2)] and the Deviations,  $\delta V_m^E$ , calculated from equation (2.13) and the parameters of Table 2.5 at the experimental temperature of 298.15 K, as a function of Mole Fraction  $x_1$ .

$x_1$	$V_m^E/\text{cm}^3\cdot\text{mol}^{-1}$	$10^3\cdot\delta V_m^E/\text{cm}^3\cdot\text{mol}^{-1}$	$x_1$	$V_m^E/\text{cm}^3\cdot\text{mol}^{-1}$	$10^3\cdot\delta V_m^E/\text{cm}^3\cdot\text{mol}^{-1}$
Acetic Acid					
0.0489	-0.0846	-11.0	0.6051	-0.3139	-5.0
0.1301	-0.1699	-3.0	0.6656	-0.2814	7.0
0.1602	-0.1889	4.0	0.7464	-0.2411	3.0
0.1719	-0.1997	3.0	0.8071	-0.1923	6.0
0.2283	-0.2413	2.0	0.8509	-0.1681	-8.0
0.3181	-0.2854	3.0	0.9166	-0.0876	6.0
0.4014	-0.3136	-0.9	0.9382	-0.0753	-5.0
0.4871	-0.3301	-6.0	0.9733	-0.0397	-9.0
0.5564	-0.3201	-7.0			
Propanoic Acid					
0.0172	-0.0334	0.2	0.5579	-0.4864	0.3
0.0326	-0.0623	0.3	0.6637	-0.4395	0.2
0.1092	-0.1923	0.1	0.7631	-0.3551	-0.4
0.1383	-0.2355	0.1	0.8386	-0.2648	-0.5
0.1583	-0.2633	0.0	0.8793	-0.2067	-0.2
0.2732	-0.3923	-0.4	0.8942	-0.1838	0.0
0.3845	-0.4673	-0.2	0.9509	-0.0887	1.0
0.4874	-0.4930	0.2			
Butanoic Acid					
0.0422	-0.0365	10.0	0.6433	-0.3864	-0.1
0.1070	-0.1229	-1.0	0.6781	-0.3803	-7.0
0.1624	-0.1901	-7.0	0.7299	-0.3493	-2.0
0.2322	-0.2649	-11.0	0.8109	-0.2774	8.0
0.2908	-0.2856	-19.0	0.8733	-0.2091	7.0
0.3836	-0.3654	-2.0	0.9304	-0.1342	-0.2
0.4541	-0.3990	-3.0	0.9590	-0.0960	-12.0
0.5679	-0.3981	3.0	0.9870	-0.0420	-14.0
2-Methylpropanoic Acid					
0.0518	-0.0456	-6.0	0.6781	-0.2839	-0.7
0.0829	-0.0658	-1.0	0.7210	-0.2712	5.0
0.2300	-0.1712	2.0	0.8045	-0.2008	16.0
0.2959	-0.2096	5.0	0.8677	-0.1578	5.0
0.3780	-0.2586	-2.0	0.9415	-0.0868	-6.0

---

0.4686	-0.2889	-0.6	0.9623	-0.0699	-16.0
0.5794	-0.2999	0.5	0.9850	-0.0346	-12.0
0.6290	-0.3019	-7.0			

## Pentanoic Acid

0.0631	-0.0502	3.0	0.6986	-0.3049	-0.4
0.1299	-0.1189	-6.0	0.7661	-0.2699	7.0
0.2006	-0.1734	-0.6	0.8120	-0.2483	0.2
0.2711	-0.2201	4.0	0.8935	-0.1696	3.0
0.3451	-0.2683	-0.8	0.9340	-0.1247	-6.0
0.4374	-0.2997	-4.0	0.9634	-0.0720	-1.0
0.5132	-0.3231	-3.0	0.9851	-0.0375	-7.0
0.6021	-0.3286	-6.0			

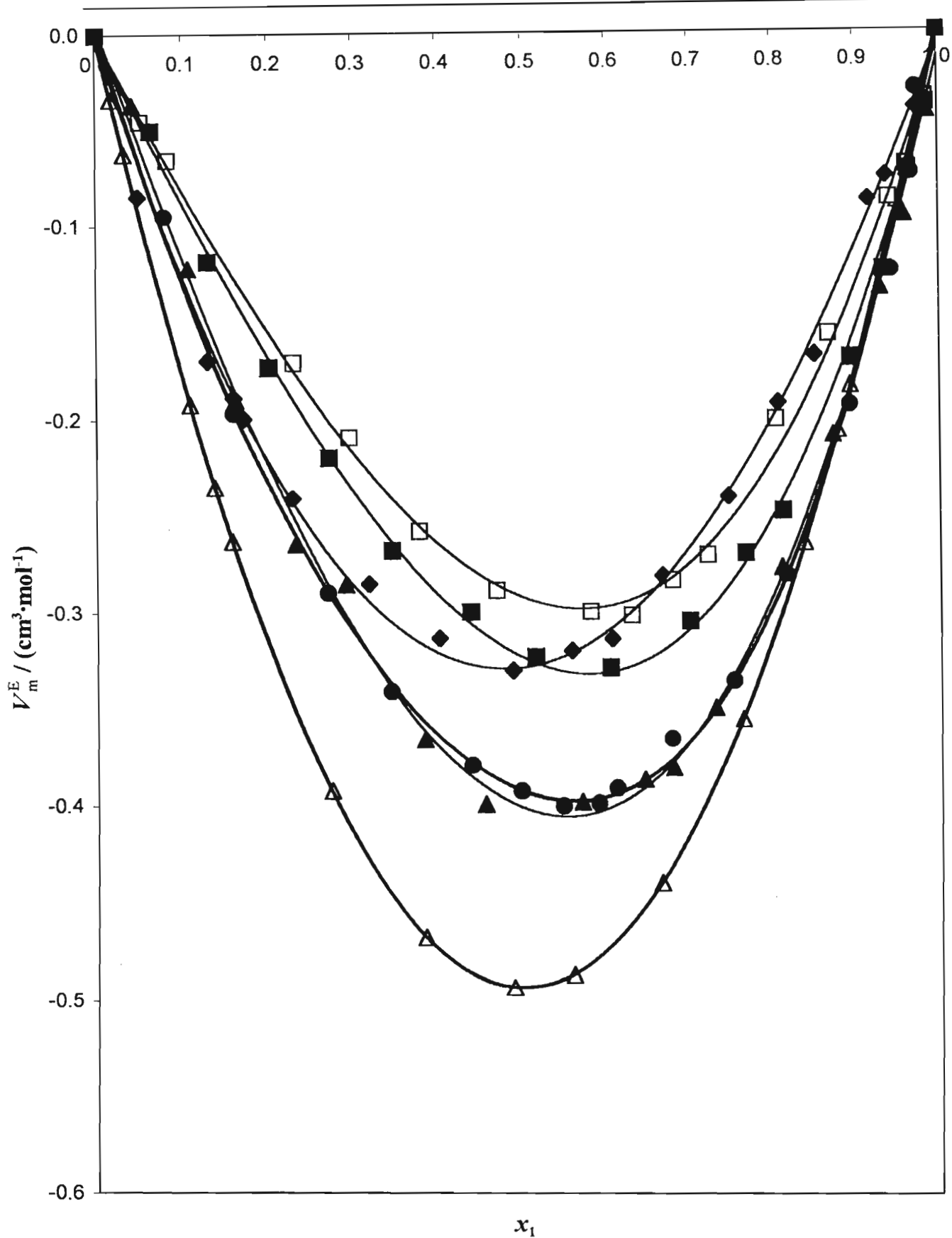
## 3-Methylbutanoic Acid

0.0791	-0.0950	5.0	0.6105	-0.3910	0.1
0.1601	-0.1970	-5.0	0.6766	-0.3653	7.0
0.2694	-0.2899	1.0	0.7520	-0.3356	-2.0
0.3441	-0.3406	0.3	0.8162	-0.2810	1.0
0.4389	-0.3789	2.0	0.8937	-0.1936	-2.0
0.4964	-0.3925	1.0	0.9434	-0.1253	-11.0
0.5456	-0.4002	-3.0	0.9672	-0.0740	-5.0
0.5879	-0.3988	-4.0	0.9737	-0.0298	27.0

**Table 2.5**      **Coefficients  $A_i$  and standard deviations  $\sigma$  from equation (2.14) for the excess molar volumes of systems: [Acetonitrile (1) + a Carboxylic Acid (2)] at 298.15 K.**

Component	$A_0$	$A_1$	$A_2$	$A_3$	$10^2 \cdot \sigma(V_m^E)/$ $\text{cm}^3 \cdot \text{mol}^{-1}$
Acetic Acid	-1.295	-0.017	-0.122	-0.238	0.6
Propanoic Acid	-1.974	-0.002	0.022	-0.032	0.1
Butanoic Acid	-1.597	0.259	-0.058	0.322	0.9
2-Methylpropanoic Acid	-1.179	0.343	0.042	0.031	0.8
Pentanoic Acid	-1.272	0.311	-0.192	0.359	0.5
3-Methylbutanoic Acid	-1.576	0.252	-0.208	0.240	0.9





**Figure 2.10** Excess molar volumes for the systems: [Acetonitrile (1) + a Carboxylic Acid (2)] at 298.15 K, as a function of mole fraction  $x_1$ . Key:  $\Delta$  = Propanoic Acid,  $\blacktriangle$  = Butanoic Acid,  $\bullet$  = 3-Methylbutanoic Acid,  $\blacklozenge$  = Acetic Acid,  $\blacksquare$  = Pentanoic Acid,  $\square$  = 2-Methylpropanoic Acid.

### 2.4.1.1 Discussion: Mixtures of (acetonitrile + a carboxylic acid)

#### This work

The  $V_m^E$  for the mixtures of (acetonitrile + a carboxylic acid) at  $T = 298.15$  K, where a carboxylic acid refers to acetic acid or propanoic acid or butanoic acid or 2-methylpropanoic acid or pentanoic acid or 3-methylbutanoic acid, were investigated to determine the influence the increasing carbon chain length of the carboxylic acids has on the excess molar volumes.

The  $V_m^E$  results are presented in Table 2.4 and plotted in Figure 2.10. The excess molar volumes for all six systems (acetonitrile + a carboxylic acid) are negative over the entire composition range at 298.15 K. The trend in  $V_m^E$  at equimolar concentrations of (acetonitrile + carboxylic acid) mixtures is given in Table 2.6. The excess molar volume minima range from  $-0.493 \text{ cm}^3 \cdot \text{mol}^{-1}$  for equimolar mixtures of (acetonitrile + propanoic acid) to  $-0.292 \text{ cm}^3 \cdot \text{mol}^{-1}$  for equimolar mixtures of (acetonitrile + 2-methylpropanoic acid ).

**Table 2.6**  $V_m^E$  at equimolar concentrations for the mixtures of (acetonitrile + a carboxylic acid) at  $T = 298.15$  K

CARBOXYLIC ACID	$V_m^E / (\text{cm}^3 \cdot \text{mol}^{-1})$
Acetic acid	-0.329
Propanoic acid	-0.493
Butanoic acid	-0.401
2-methylpropanoic acid	-0.292
Pentanoic acid	-0.324
3-methylbutanoic acid	-0.393

The  $V_m^E$  curves are reasonably symmetrical and have minima ranging between  $x_1$  (acetonitrile) = 0.5 to 0.6. The excess molar volumes are most negative in the case of propanoic acid ( $< -0.5 \text{ cm}^3 \cdot \text{mol}^{-1}$ ) and the magnitude decreases in the following order : propanoic acid > butanoic acid ~ 3-methylbutanoic acid > acetic acid ~ pentanoic acid > 2-methylbutanoic acid.

The acids in pure form exist mainly as dimers (Affsprung *et al.*, 1968). The observed negative values for  $V_m^E$  may be explained as follows. The following four-step equilibria which

accompanies the mixing process has been proposed by Lark and Banipal (1985):

- i)  $D - M \rightarrow D + M$
- ii)  $D \rightarrow 2 M$
- iii)  $A-A \rightarrow A + A$
- iv)  $M + A \rightarrow M-A$

where D and M denote a dimer and monomer of the carboxylic acid, respectively, and A represents acetonitrile. The right hand side of the first step suggests a large volume increase. In the second step the volume of the dimer is assumed to be equal to twice the volume of the monomer (Affsprung *et al.*, 1968). Since the third step involves a dissociation, it suggests a volume increase. Due to the formation of a bond in the fourth step a volume contraction is expected. Acetonitrile is a typical aprotic, dipolar organic solvent with a carbon - nitrogen triple bond and an unshared electron pair on the nitrogen atom. X-ray analysis on pure acetonitrile has revealed that the linear acetonitrile dipoles are arranged in antiparallel positions and that definite short range ordering between molecules is due to the dipole - dipole interactions (Brown and Smith, 1962). On the other hand, the carboxylic acids in pure form tend to exist mainly as dimers. In terms of the above proposed mechanism, the overall magnitude of  $V_{m,\min}^E [x_1 \text{CH}_3 \text{CN} + (1 - x_1) \text{RCOOH}]$  is therefore most probably due to the breakdown of the acetonitrile self association (step iii - a positive contribution), the breakdown of the carboxylic acid (dimers) self association (step i and step ii - a positive contribution), and the negative effects of the (acetonitrile - carboxylic acid) association, that is step iv. Step iv outweighs the effects of steps (i + ii + iii) and the association effect is the dominant one. The addition of acetonitrile to any one of the acids first creates monomers by the first two steps resulting in expansion, followed by third step which also contributes to expansion, and thereafter stronger heteromolecular dipole - dipole interactions result in the observed negative  $V_m^E$  values. This argument finds sufficient support from the contractive mixing behaviour of (acetonitrile + methanol) reported by Cibulka *et al.* (1984), as well as for (acetonitrile + 1,1 dimethylketone) reported by Lark and Palta (1979). In the case of (acetonitrile + methanol), a significant amount of dissociation occurs in the case of methanol and the stronger dipole-dipole interactions between methanol and acetonitrile is the dominant effect. For the (acetonitrile + 1,1 dimethylketone) system, the dissociation of the ketone is less than that of the alcohol, and lower heteromolecular dipole-dipole interactions are observed.

Apart from the above proposed mechanism, packing effects can also take place. Unfortunately there is no way of knowing whether the packing effects produce an expansion or contraction. The experimental results show that  $V_m^E$  is negative could be due to an association of the species involved, bringing the molecules closer together, resulting in a diminution or decrease of volume, or it could be due to a sympathetic packing effect of the mixing molecules, or a combination of both effects. It is difficult to separate the volume change contributions due to packing effects from the intermolecular effects. If the packing effects were insignificant, then one might expect the largest  $V_m^E$  contraction for the system (acetonitrile + acetic acid). This is clearly not true, and one must assume that the packing effects as well as dipolar interactions are important.

The dimerization constants for the carboxylic acids is given in Table 2.7.

**Table 2.7**      **Dimerization constants  $K_d$ , for carboxylic acids at  $T = 298.15\text{ K}$**

<b>CARBOXYLIC ACID</b>	<b><math>K_d / (\text{Torr}^{-1})</math></b>
Acetic acid	1.982 <sup>a</sup>
Propanoic acid	2.301 <sup>b</sup>

<sup>a</sup>Affsprung *et al.* (1968)      <sup>b</sup>Apelblat and Kohler (1976)

The dimerization constants ( $K_d$ 's) for the acids tend to increase as the length of the alkyl group of the carboxylic acid increases. The increased  $K_d$  values should reduce the number of available (D-M) trimers, and, accordingly positive contribution to the overall  $V_m^E$  is diminished further. This effect is observed in the case of acetic and propanoic acid, but beyond that, ie. for butanoic acid and higher acids,  $V_m^E$  becomes less negative. This behaviour may also be attributed to the increasing steric hindrance of methyl groups in the carboxylic acids.

It is also found that the position of the minima for  $V_m^E$  (acetonitrile + acetic acid) shifts slowly to the acetonitrile rich region of the mole-fraction scale as the methylation of acetic acid increases. This could be explained by the increasing steric hindrance caused by additional methyl groups. This is further supported by the findings of Cibulka *et al.*, (1984) who have shown that for binary systems containing alkanols and acetonitrile,  $V$  increases in the order  $V^E$  (acetonitrile + normal alkanol) <  $V^E$  (acetonitrile + branched alkanol) <  $V^E$  (acetonitrile + secondary alkanol).

2.4.2 Excess Molar Volume Data for Mixtures of [Butanenitrile + a Carboxylic Acid] at 298.15 K

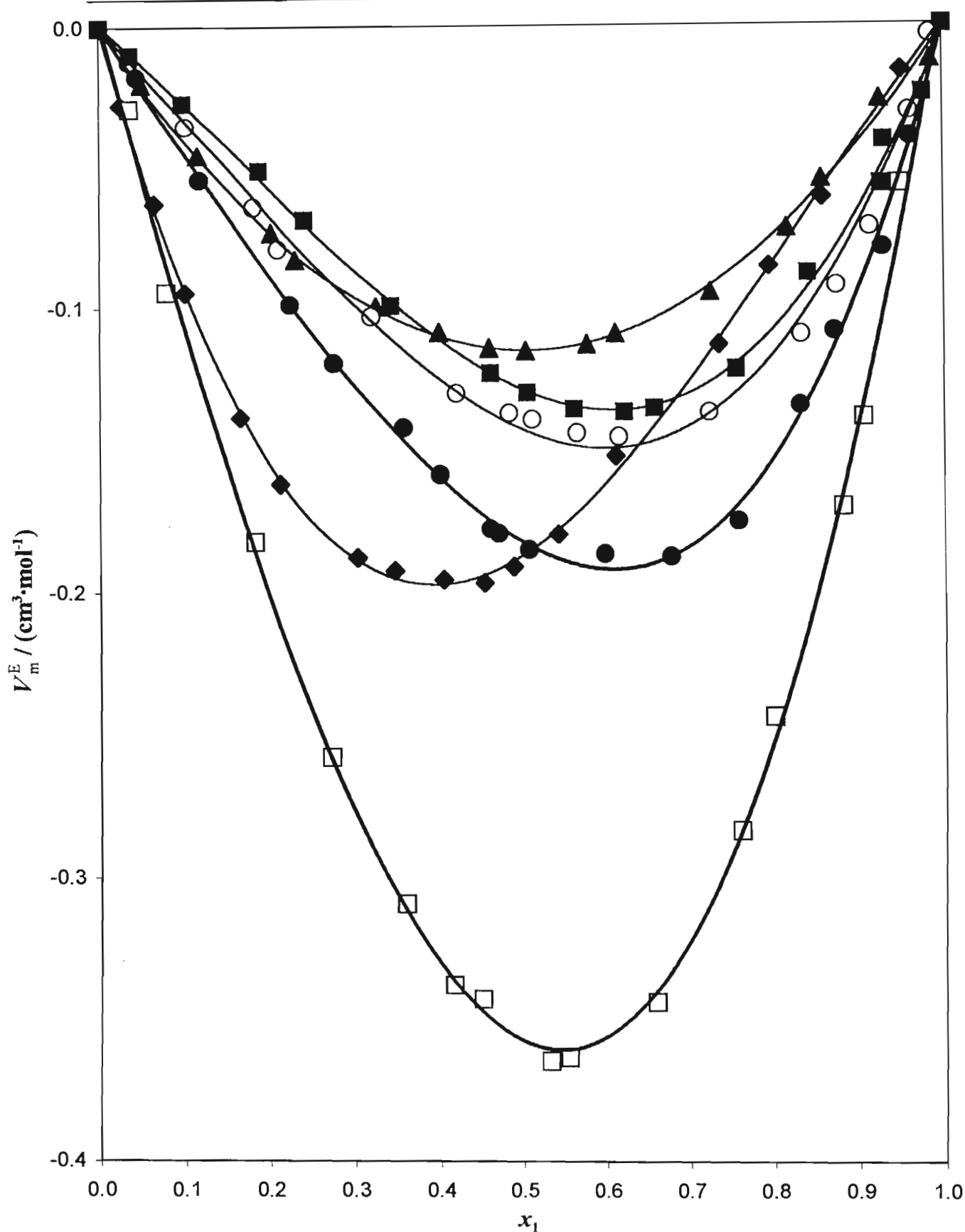
Table 2.8 Excess molar volumes  $V_m^E$  for the systems: [Butanenitrile (1) + a Carboxylic Acid (2)] and the Deviations,  $\delta V_m^E$ , calculated from equation (2.13) and the parameters of Table 2.9 at the experimental temperature of 298.15 K, as a function of Mole Fraction  $x_1$ .

$x_1$	$V_m^E/\text{cm}^3 \cdot \text{mol}^{-1}$	$10^3 \cdot \delta V_m^E/\text{cm}^3 \cdot \text{mol}^{-1}$	$x_1$	$V_m^E/\text{cm}^3 \cdot \text{mol}^{-1}$	$10^3 \delta V_m^E/\text{cm}^3 \cdot \text{mol}^{-1}$
Acetic Acid					
0.0245	-0.0275	-1.0	0.4532	-0.1965	-3.0
0.0645	-0.0629	2.0	0.4887	-0.1909	-2.0
0.1003	-0.0946	-0.1	0.5419	-0.1796	-2.0
0.1646	-0.1387	2.0	0.6120	-0.1523	6.0
0.2129	-0.1618	- 0.8	0.7360	-0.1132	-2.0
0.3035	-0.1876	1.0	0.7952	-0.0855	0.9
0.3467	-0.1923	2.0	0.8589	-0.0613	-3.0
0.4045	-0.1953	1.0	0.9513	-0.0163	3.0
Propanoic Acid					
0.0353	-0.0289	12.3	0.5536	-0.3632	0.3
0.0787	-0.0945	- 7.0	6590	-0.3438	-0.1
0.1819	-0.1822	2.0	0.7610	-0.2834	-0.5
0.2730	-0.2580	-2.0	0.8001	-0.2439	6.0
0.3595	-0.3093	0.1	0.8819	-0.1698	-8.0
0.4160	-0.3378	-2.0	0.9067	-0.0887	-8.0
0.4503	-0.3429	5.0	0.9487	-0.0568	18.0
0.5314	-0.3645	- 2.0			
Butanoic Acid					
0.0493	-0.0200	2.0	0.5770	-0.1130	0.4
0.1151	-0.0457	0.7	0.6119	-0.1092	1.0
0.2028	-0.0731	0.1	0.7256	-0.0948	-2.0
0.2316	-0.0828	- 2.0	0.8161	-0.0721	-3.0
0.3253	-0.0997	-0.1	0.8576	-0.0549	1.0
0.3997	-0.1087	0.9	0.9262	-0.0264	4.0
0.4597	-0.1143	-0.1	0.9855	-0.0126	- 6.0
0.5039	-0.1154	0.0			
2-Methylpropanoic Acid					
0.0351	-0.0122	0.7	0.5647	-0.1443	0.4
0.1012	-0.0352	2.0	0.6159	-0.1457	0.3
0.1811	-0.0643	0.8	0.7240	-0.1370	0.8
0.2109	-0.0790	-4.0	0.8333	-0.1098	-0.9

0.3201	-0.1031	3.0	0.8752	-0.0926	-2.0
0.4200	-0.1301	-0.3	0.9143	-0.0717	-3.0
0.4836	-0.1372	0.2	0.9600	-0.0307	5.0
0.5115	-0.1395	1.0	0.9843	-0.0037	11.0
Pentanoic Acid					
0.0361	-0.0098	-0.9	0.6216	-0.1367	0.2
0.0974	-0.0268	-1.0	0.6575	-0.1355	-0.5
0.1874	-0.0512	1.0	0.7559	-0.1217	-0.2
0.2426	-0.0685	0.8	0.8406	-0.0880	5.0
0.3426	-0.0992	-2.0	0.9274	-0.0567	-7.0
0.4607	-0.1230	0.6	0.9299	-0.0411	7.0
0.5047	-0.1298	0.4	0.9755	-0.0242	-6.0
0.5609	-0.1357	-0.2			
3-Methylbutanoic Acid					
0.0442	-0.0177	2.0	0.5071	-0.1850	- 2.0
0.1173	-0.0545	-2.0	0.5983	-0.1864	5.0
0.2254	-0.0988	-0.2	0.6777	-0.1876	-0.3
0.2765	-0.1195	1.0	0.7586	-0.1749	-6.0
0.3576	-0.1423	5.0	0.8321	-0.1346	3.0
0.4003	-0.1587	0.9	0.9721	-0.1085	6.0
0.4608	-0.1775	-3.0	0.9291	-0.0789	-8.0
0.4705	-0.1793	-3.0	0.9610	-0.0401	2.0

**Table 2.9**      **Coefficients  $A_i$  and standard deviations  $\sigma$  from equation (2.14) for the excess molar volumes of systems: [Butanenitrile (1) + a Carboxylic Acid (2)] at 298.15 K.**

Component	$A_0$	$A_1$	$A_2$	$A_3$	$10^2 \cdot \sigma(V_m^E)/$ $\text{cm}^3 \cdot \text{mol}^{-1}$
Acetic Acid	-0.746	-0.367	-0.006	-0.007	0.2
Propanoic Acid	-1.438	0.322	0.095	-0.171	0.7
Butanoic Acid	-0.462	0.023	0.009	-0.038	0.3
2-Methylpropanoic Acid	-0.557	0.226	-0.116	0.083	0.4
Pentanoic Acid	-0.518	0.263	0.018	0.005	0.4
3-Methylbutanoic Acid	-0.729	0.334	-0.073	0.017	0.4



**Figure 2.11** Excess molar volumes for the systems: [Butanenitrile (1) + a Carboxylic Acid (2)] at 298.15 K, as a function of mole fraction  $x_1$ . Key:  $\blacklozenge$  = Acetic Acid,  $\square$  = Propanoic Acid,  $\blacktriangle$  = Butanoic Acid,  $\circ$  = 2-Methylpropanoic acid,  $\blacksquare$  = Pentanoic Acid,  $\bullet$  = 3-Methylbutanoic Acid.



### 2.4.2.1 Discussion: Mixtures of (butanenitrile + a carboxylic acid)

#### This work

The excess molar volume data for the mixtures of (butanenitrile + a carboxylic acid) at  $T = 298.15\text{ K}$ , where a carboxylic acid refers to acetic acid or propanoic acid or butanoic acid or 2-methylpropanoic acid or pentanoic acid or 3-methylbutanoic acid. In this study the effect of an increase in the nitrile chain length on the excess molar volumes of the acids was investigated.

The  $V_m^E$  results are presented in Table 2.8 and plotted in Figure 2.11.

The excess molar volumes are most negative in the case of propanoic acid ( $< -0.4\text{ cm}^3\cdot\text{mol}^{-1}$ ), and the magnitude decreases in the following order : propanoic acid  $>$  acetic acid  $\sim$  3-methylbutanoic acid  $>$  2-methylpropanoic acid  $>$  pentanoic acid  $>$  butanoic acid.

The negative  $V_m^E$  values may again be explained as follows. The acids in pure form exist mainly as dimers. On mixing of butanenitrile with the carboxylic acids, it is most likely that the same four step mechanism proposed by Lark and Banipal (1985), and discussed in Section 2.4.1.1 applies. In this mechanism acetonitrile is now replaced by the longer chain butanenitrile.

In the proposed mechanism, it is most likely that the addition of butanenitrile to any one of the acids first creates monomers by the first two steps resulting in expansion, followed by the third step which also contributes to expansion, and thereafter stronger heteromolecular dipole - dipole interactions result in the observed negative  $V_m^E$  values. On mixing a carboxylic acid with butanenitrile there are various processes occurring, (a) the breakdown of the butanenitrile - self association (step iii - positive contribution), (b) the breakdown of the carboxylic acid (dimers) self association (step i and step ii - positive enthalpy), and (c) the negative contribution of the (butanenitrile - carboxylic acid) polar - polar association, that is step iv. This type of contractive mixing behaviour has also been observed for (acetonitrile + methanol) reported by Cibulka *et al.* (1984), as well as for (acetonitrile + 1,1 dimethylketone) reported by Lark and Palta (1979).

The excess molar volumes are found to be negative for all six systems over the entire composition range. The  $V_m^E$  (at  $x = 0.5$ ) range from  $-0.115 \text{ cm}^3 \cdot \text{mol}^{-1}$  for equimolar concentrations of (butanenitrile + butanoic acid) mixtures to  $-0.357 \text{ cm}^3 \cdot \text{mol}^{-1}$  for (butanenitrile + propanoic acid) mixtures. (See Table 2.10). The overall negative  $V_m^E$  results obtained in this work indicate that the effect of step iv > steps (i + ii + iii).

The  $V_m^E$  curves obtained are approximately symmetrical and tend to be slightly skewed towards the butanenitrile - rich region of the mole fraction axis, as the carbon number of the carboxylic acid increases.

**Table 2.10**  $V_m^E$  at equimolar concentrations for the mixtures of (butanenitrile + a carboxylic acid) at  $T = 298.15 \text{ K}$ .

CARBOXYLIC ACID	$V_m^E / (\text{cm}^3 \cdot \text{mol}^{-1})$
Acetic acid	-0.187
Propanoic acid	-0.357
Butanoic acid	-0.115
2-methylpropanoic acid	-0.143
Pentanoic acid	-0.129
3-methylbutanoic acid	-0.182

Again, it is also evident that free-volume effects which are primarily due to the difference in size between the components, related to packing effects also make a significant contribution to the negative excess molar volumes. If packing was not an important effect then the magnitude of steps (i + ii + iii) > step iv. Clearly this is not the case and one must conclude that packing effects are also important.

The dimerization constants ( $K_d$ 's) for the acids tend to increase as the length of the alkyl group of the carboxylic acid increases. The increased  $K_d$  values should reduce the number of available (D - M) trimers, and, accordingly positive contribution to the overall  $V_m^E$  is diminished further. This effect partly results in propanoic acid having the most negative  $V_m^E$ . For the higher carboxylic acids there appears to be a progressive contraction in mixing behaviour. This behaviour may also be influenced by the increasing steric hindrance of the

methyl groups, as well as the influence of the longer carbon chain of butanenitrile.

Again, it is difficult to separate the volume change contributions due to packing effects from intermolecular effects. Packing effects can impact either positively or negatively on the excess volumes of the (butanenitrile+ carboxylic acid) mixtures. The negative excess molar volumes obtained is due to either strong association leading to diminution in volume or a packing effect or a combination of these two forces.

It is also found that the position of the minima for  $V_m^E$  (butanenitrile + acetic acid) shifts slowly to the butanenitrile - rich region of the mole fraction scale as the methylation of acetic acid increases. This could possibly be due to free volume effects which are primarily due to the differences in the size between components of the mixtures. The increasing size of the acids in relation to butanenitrile lead to altered dipole-dipole maxima interactions which progressively increase towards the butanenitrile mole fraction scale, as the methylation of acetic acid increases. A similar trend is observed by Pal and Sharma (1998), in their study of mixtures of alkanols with polyethers.

In addition this effect of “shifting minima” could also be influenced by the increase in both the dimerization constants as well as increasing steric hindrance caused by additional methyl groups, and resultant decrease in the association between butanenitrile and higher carbon - number carboxylic acids. Further support of this argument is given by the findings of Cibulka *et al.* (1984) who have shown that for binary systems containing alkanol and acetonitrile,  $V^E$  increases in the order :  $V^E(\text{acetonitrile} + \text{normal alkanol}) < V^E(\text{acetonitrile} + \text{branched alkanol}) < V^E(\text{acetonitrile} + \text{secondary alkanol})$ .

2.4.3 Excess Molar Volume Data for Mixtures of [Benzonitrile + a Carboxylic Acid] at 298.15 K

**Table 2.11** Excess molar volumes  $V_m^E$  for the systems: [Benzonitrile (1) + a Carboxylic Acid (2)] and the Deviations,  $\delta V_m^E$ , calculated from equation (2.13) and the parameters of Table 2.12 at the experimental temperature of 298.15 K, as a function of mole fraction  $x_1$ .

$x_1$	$V_m^E / (\text{cm}^3 \cdot \text{mol}^{-1})$	$10^3 \cdot \delta V_m^E / (\text{cm}^3 \cdot \text{mol}^{-1})$	$x_1$	$V_m^E / (\text{cm}^3 \cdot \text{mol}^{-1})$	$10^3 \cdot \delta V_m^E / (\text{cm}^3 \cdot \text{mol}^{-1})$
Acetic Acid					
0.0200	-0.0179	0.3	0.4568	-0.2257	-3.0
0.0596	-0.0501	2.0	0.5724	-0.2101	-0.3
0.1145	-0.0942	1.0	0.6389	-0.1879	4.0
0.1981	-0.1558	-6.0	0.7140	-0.1650	-2.0
0.2823	-0.1881	2.0	0.8001	-0.1205	2.0
0.3049	-0.1960	2.0	0.8323	-0.1089	-4.0
0.3663	-0.2123	0.7	0.9146	-0.0563	-0.4
0.4052	-0.2195	0.4	0.9621	-0.0195	6.0
Propanoic Acid					
0.0416	-0.0258	23.0	0.6802	-0.2749	-0.1
0.0709	-0.0801	4.0	0.7693	-0.2232	0.1
0.1204	-0.1498	-8.0	0.7553	-0.2297	-3.0
0.1599	-0.1931	-9.0	0.8224	-0.1925	-10.0
0.2430	-0.2578	1.0	0.8669	-0.1435	2.0
0.3288	-0.3098	1.0	0.8927	-0.1181	4.0
0.4324	-0.3380	-0.1	0.9316	-0.0783	5.0
0.5286	-0.3260	5.0	0.9659	-0.0406	4.0
0.6279	-0.2979	0.9			
Butanoic Acid					
0.0569	-0.0642	6.0	0.5447	-0.3589	-0.9
0.0914	-0.1084	2.0	0.5917	-0.3500	-0.4
0.1258	-0.1410	7.0	0.7035	-0.3047	-0.9
0.1730	-0.1932	1.0	0.7912	-0.2499	-6.0
0.1987	-0.2313	-14.0	0.8612	-0.1823	-5.0
0.2859	-0.2893	-5.0	0.9194	-0.1080	3.0
0.3674	-0.3230	5.0	0.9265	-0.0997	2.0
0.4299	-0.3461	3.0	0.9532	-0.0579	9.0
0.4716	-0.3549	2.0			
2-Methylpropanoic Acid					
0.0289	-0.0379	-3.0	0.4899	-0.3780	0.0
0.0752	-0.0919	-4.0	0.5549	-0.3853	-2.0
0.1310	-0.1456	2.0	0.6608	-0.3640	-1.0
0.1756	-0.1832	8.0	0.7789	-0.2879	4.0

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0.2219	-0.2391	6.0	0.8647	-0.2039	1.0
0.3130	-0.2998	2.0	0.9205	-0.1396	-8.0
0.3986	-0.3498	-0.6	0.9437	-0.0928	3.0

## Pentanoic Acid

0.0532	-0.0364	2.0	0.5093	-0.2798	7.0
0.0862	-0.0633	0.2	0.5433	-0.2915	-1.0
0.1002	-0.0752	-1.0	0.5939	-0.2968	-6.0
0.1788	-0.1389	-7.0	0.6203	-0.2872	1.0
0.2186	-0.1495	10.0	0.7023	-0.2689	1.0
0.2997	-0.2134	-4.0	0.8174	-0.2106	-1.0
0.3861	-0.2553	-4.0	0.9183	-0.1102	4.0
0.4407	-0.2685	2.0	0.9556	-0.0706	-4.0

## 3-Methylbutanoic Acid

0.0420	-0.0207	18.0	0.5901	-0.3711	2.0
0.1002	-0.0893	-5.0	0.6318	-0.3696	-0.7
0.1095	-0.0972	11.0	0.7279	-0.3385	-4.0
0.1891	-0.1889	-17.0	0.8261	-0.2649	-6.0
0.3092	-0.2643	2.0	0.8812	-0.1967	-1.0
0.4127	-0.3251	4.0	0.9217	-0.1398	-1.0
0.4614	-0.3499	-0.4	0.9450	-0.0921	9.0
0.5284	-0.3654	3.0	0.9833	-0.0137	19.0
0.5505	-0.3698	1.0			

**Table 2.12**    **Coefficients  $A_i$ , and standard deviations  $\sigma$  from equation (2.14) for the excess molar volumes of systems: [Benzonitrile (1) + a Carboxylic Acid (2)] at T = 298.15 K.**

Component	$A_0$	$A_1$	$A_2$	$A_3$	$10^2 \cdot \sigma(V_m^E)/$ (cm <sup>3</sup> ·mol <sup>-1</sup> )
Acetic Acid	-0.746	-0.367	-0.006	-0.007	0.2
Propanoic Acid	-1.438	0.322	0.095	-0.171	0.7
Butanoic Acid	-0.462	0.023	0.009	-0.038	0.3
2-Methylpropanoic Acid	-0.557	0.226	-0.116	0.083	0.4
Pentanoic Acid	-0.518	0.263	0.018	0.005	0.4
3-Methylbutanoic Acid	-0.729	0.334	-0.073	0.017	0.4

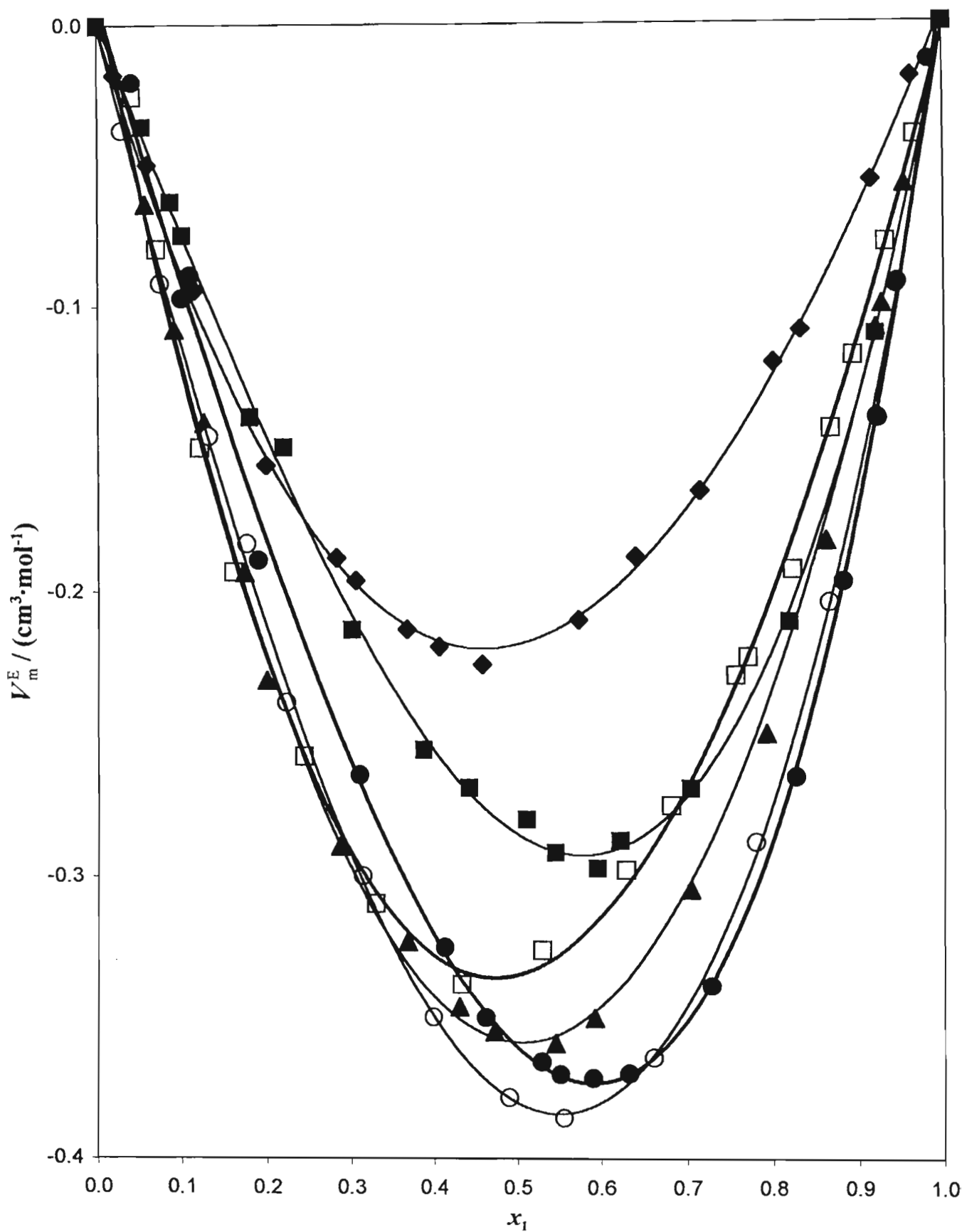


Figure 2.12 Excess molar volumes for the systems: [Benzonitrile (1) + a Carboxylic Acid (2)] at  $T = 298.15 \text{ K}$ , plotted as a function of mole fraction  $x_1$ . Key:  $\blacklozenge$  = Acetic Acid,  $\square$  = Propanoic Acid,  $\blacktriangle$  = Butanoic Acid,  $\circ$  = 2-Methylpropanoic acid,  $\blacksquare$  = Pentanoic Acid,  $\bullet$  = 3-Methylbutanoic Acid

#### 2.4.3.1 Discussion: Mixtures of (benzonitrile + a carboxylic acid)

##### This work

Excess molar volumes for the mixtures of (benzonitrile + acetic acid or propanoic acid or butanoic acid or 2-methylpropanoic acid or pentanoic acid or 3-methylbutanoic acid) at  $T = 298.15$  K are presented in Table 2.11 and plotted as a function of mole fraction benzonitrile in Figure 2.12. In this study, the effect of the aromatic nitrile compound, benzonitrile on the excess molar volumes of binary mixtures of (benzonitrile + a carboxylic acid) was investigated.

The observed results for  $V_m^E$  may be explained as follows. The acids in pure form exist mainly as dimers (Affsprung *et al.*, 1968). It is again likely that the four step equilibria process proposed by (Lark and Banipal, 1985), discussed in 2.4.1.1 accompanies the mixing process. In this equilibria acetonitrile is now replaced by the aromatic benzonitrile

The first step one assumes is accompanied with large volume increases in the right direction ; in the second step the volume of the dimer is assumed to be equal to twice the volume of the monomer (Affsprung *et al.*, 1968). The third step results in an increase in volume. The fourth step is accompanied by a contraction of volume. Benzonitrile is a strongly polar, aromatic solvent with a carbon - nitrogen triple bond and an unshared electron pair on the nitrogen atom. The excess molar curves obtained were interpreted as due to the breakdown of the benzonitrile self association (a positive effect), the breakdown of the carboxylic acid (dimers) self association (a positive effect), and the negative effect of the (benzonitrile - carboxylic acid) polar - polar association.

The excess molar volumes are again found to be negative for all six systems over the entire composition range.

The  $V_m^E$  curves obtained are approximately symmetrical and skewed slightly towards the benzonitrile - rich region of the mole fraction scale. The trend in  $V_m^E$  at equimolar concentrations of (acetonitrile + a carboxylic acid) is given in Table 2.13. The excess molar volume minima range from  $-0.379 \text{ cm}^3 \cdot \text{mol}^{-1}$  for equimolar mixtures of (benzonitrile + 2-methylpropanoic acid) to  $-0.219 \text{ cm}^3 \cdot \text{mol}^{-1}$  for equimolar mixtures of (benzonitrile + acetic



acid).

**Table 2.13**  $V_m^E$  at equimolar concentrations for the mixtures of (benzonitrile + a carboxylic acid) at T = 298.15 K

CARBOXYLIC ACID	$V_m^E / (\text{cm}^3 \cdot \text{mol}^{-1})$
Acetic acid	-0.219
Propanoic acid	-0.335
Butanoic acid	-0.359
2-Methylpropanoic acid	-0.379
Pentanoic acid	-0.285
3-Methylbutanoic acid	-0.360

The excess molar volume is most negative in the case of 2-methylpropanoic acid ( $< -0.4 \text{ cm}^3 \cdot \text{mol}^{-1}$ ), and the magnitude decreases in the following order : 2-methylpropanoic acid  $>$  3-methylbutanoic acid  $>$  butanoic acid  $>$  propanoic acid  $>$  pentanoic acid  $>$  acetic acid. The magnitude of the excess molar volumes tends to increase as the chain length of the carboxylic acid increases, with the exception of pentanoic acid.

When benzonitrile is added to any one of the acids, monomers are first created by the first two steps resulting in expansion, followed by strong heteromolecular dipole-dipole interactions resulting in contraction. This overall effect gives rise to negative volume change, ie. a negative  $V_m^E$ . These results may be compared with the mixing of (acetonitrile + methanol) reported by Cibulka *et al.* (1984), as well for (acetonitrile + 1,1 dimethylketone) reported by Lark and Palta (1979), which also illustrate negative  $V_m^E$  behaviour. It appears that these results all involve the common effect of the formation of the strong dipole-dipole association which exceeds the positive effects of the dissociation of the two species on mixing.

A negative  $V_m^E$  could be due to an association of the species involved, bringing the molecules closer together, resulting in a decrease or contraction of volume, or it could be due to the sympathetic packing effect of the molecule. Packing effects could also contribute either positively or negatively to the excess volumes. The negative  $V_m^E$  results obtained is due to both the intermolecular effects proposed by the four- step mechanism, as well as packing effects.

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It is also found that the position of the minima for  $V_m^E$  (benzonitrile + acetic acid) shifts progressively to the benzonitrile-rich region of the mole fraction scale, as the methylation of acetic acid increases. This could be explained by the increase in both the dimerization constants as well as the increasing steric hindrance caused by the additional methyl groups. The increased dimerization constants should reduce the number of available (D - M) trimers and accordingly positive contribution to the overall  $V_m^E$  is diminished further. This is further supported by the findings of Cibulka *et al.* (1984) who have shown that for binary systems containing alkanol and acetonitrile,  $V^E$  increases in the order:  $V^E$  (acetonitrile + normal alkanol) <  $V^E$  (acetonitrile + branched alkanol) <  $V^E$  (acetonitrile + secondary alkanol).

## CHAPTER 3

### EXCESS MOLAR ENTHALPIES OF MIXING

#### 3.1 INTRODUCTION

The thermodynamic properties  $X$ , such as enthalpy  $H$ , entropy  $S$ , Gibbs energy  $G$ , volume  $V$ , and heat capacity  $C_p$ , of nonelectrolyte mixtures are usually expressed in terms of the excess function  $X^E$  which is the difference between the properties of the mixtures  $X$  and those of the ideal solution (Marsh and O'Hare, 1994). For the mixing process



the difference between the change  $\Delta_{\text{mix}} X_m$  on forming one mole of mixture, and that of forming one mole of ideal mixture  $\Delta_{\text{mix}} X_m^{\text{id}}$  is the molar excess function  $X_m^E$ . Thus,

$$X_m^E = \Delta_{\text{mix}} X_m - \Delta_{\text{mix}} X_m^{\text{id}} \quad (3.2)$$

In terms of enthalpies, the excess molar enthalpy is defined as:-

$$H_m^E = \Delta_{\text{mix}} H_m - \Delta_{\text{mix}} H_m^{\text{id}} \quad (3.3)$$

Calorimeters measure  $\Delta_{\text{mix}} H_m$ , the enthalpy of mixing. As the enthalpy of mixing of an ideal mixture  $\Delta_{\text{mix}} H_m^{\text{id}} = 0$ , a mixing experiment performed in a calorimeter yields the excess enthalpy  $H_m^E$  directly (McGlashan, 1979). From equation (3.3) and  $\Delta_{\text{mix}} H_m^{\text{id}} = 0$ , it is apparent that the molar enthalpy of mixing and the excess enthalpy are identical. These two terms will be used interchangeably in this thesis.

For binary liquid mixtures, the excess molar enthalpies of mixing,  $H_m^E$  may be defined by the relation (Marsh, 1978):

$$H_m^E = G_m^E - T (\partial G_m^E / \partial T) \quad (3.4)$$

implying that  $H_m^E$  can be calculated from a knowledge of  $G_m^E$  and its dependence on temperature. However, this indirect approach for the determination of  $H_m^E$  from  $G_m^E$ , and its temperature dependence, is not considered a satisfactorily accurate method and it has been reported that the errors in  $H_m^E$  derived in this way are at least fifteen times as large as the error in the free energies from which it is derived (Williamson, 1967; Malanowski and Anderko, 1992). More reliable data is obtained by directly measuring  $H_m^E$  using the techniques of calorimetry. Details of these are given later in this Chapter.

The experimentally obtained data are generally fitted to a smoothing equation. The two most common smoothing equations for binary mixtures are the Redlich-Kister equation (Redlich and Kister, 1948):

$$\delta H_m^E = H_m^E - x(1-x) \sum_{r=0}^k A_r (1-2x)^r \quad (3.5)$$

and the Padé approximation or rational function proposed by Malanowski (1974):

$$H_m^E = x_1 x_2 \frac{\sum_{i=0}^n A_i (x_1 - x_2)^i}{1 + \sum_{j=0}^n B_j (x_1 - x_2)^j} \quad (3.6)$$

where  $A_r$  and  $A_i$  refer to the coefficients of the Redlich - Kister function and Padé function respectively. The Redlich - Kister expansion is the less complex expression, but for more complex composition dependencies, the Padé approximation may give better correlation results (Christensen *et al.*, 1988).

Throughout this work the simpler Redlich - Kister equation has been used as the preferred smoothing equation.

### 3.2 CALORIMETRIC MEASURING TECHNIQUES USED TO DETERMINE THE EXCESS MOLAR ENTHALPY

The basic design of any calorimeter involves a knowledge of the masses of the two liquids to be mixed and the temperatures of the liquids before and after mixing. The enthalpy involved can then, in principle, be calculated from a knowledge of heat capacities of the liquids involved and the apparatus. Better still, the excess enthalpy can be determined from a

knowledge of the electrical heat input required to ensure a zero temperature change on mixing (only for endothermic mixing).

Unfortunately, measuring excess enthalpies of mixing is a much more complicated process. Problems involving liquids with high viscosities and liquid pairs involving a large disparity in liquid densities are two of the more serious hurdles that must be overcome if reliable and reproducible results are to be obtained. These problems have been addressed by Raal and Webley (1987).

Firstly, unless the mixing process is continued until the mixed fluid composition is uniform on at least the submicroscopic level (Raal and Webley, 1987), prior to the mixed fluid composition reaching the downstream temperature sensor control, erroneous excess molar enthalpies will be obtained. Complete mixing of the liquids must therefore be achieved in the instrument thoroughly before the mixture reaches the downstream temperature sensor. Although it is likely, though debatable (Nauman and Buffham, 1983) that slow molecular diffusion is necessary to achieve homogeneity on a molecular or near - molecular scale in a stirred fluid, Raal and Webley (1987) point out that stagnant packets or boundary layers not subjected to eddies could be expected to participate in the homogenization process by a diffusional mechanism exponential in time, with a rate constant resulting in a low detector signal magnitude which would be detectable only by very precise instrumentation. Appreciable error would then be introduced into the measuring process, as a result failure to account fully for a very small signal over a relatively long time span. Most microflow calorimeters described in the literature have internal tube diameters, which because of their restricted sizes, do not permit any formation of eddies and hence laminar flow is prevalent (Raal and Webley, 1987). The TAM 2277 flow calorimeter (discussed later in 3.3.1) used in this work incorporates an insert in the mixing vessel to ensure completeness in the mixing of the respective fluids.

The second difficulty is concerned with the interfacial contact between air spaces in the calorimeter and the test liquids as large enthalpy discrepancies become evident due to the vapourization /condensation at the interface. Many of the earlier calorimeters had considerable vapour spaces in the mixing chamber into which the volatile test liquids could evaporate. According to McGlashan (1967) an air space of only  $0.1 \text{ cm}^3$  may give rise to an

error of up to 20 percent in excess molar enthalpies. Subsequently, later calorimeter designs were improved to minimize vapour space in order to assist in the elimination of the evaporation problem. Air spaces may also be formed within the mixing chamber by release of previously dissolved gases from the test liquids. It is also possible that vapours are released forming bubbles when the temperature of a mixture is raised. This problem may be overcome by degassing of the liquids prior to injection into the calorimeter. Furthermore an allowance must be made for volume changes as this could lead to a build-up of internal pressure and erratic results would ensue.

The third factor, concerned only with flow techniques when working under isothermal conditions, is to ensure that equilibration of the liquids is achieved at exactly the temperature of the calorimeter setting, at all flow rates, and independent of fluid heat transfer properties (Raal and Webley, 1987). For exothermic systems (as measured in this work) failure to bring the temperature of the component liquids, if initially colder than the set calorimeter temperature, up to the operating temperature would result in erroneously high values for the measured excess molar enthalpy. Conversely an erroneous low  $H_m^E$  value would be obtained if the fluid is initially at a temperature greater than the operating temperature. Temperature control for the calorimeter used will be discussed further later in this Chapter.

The numerous experimental techniques of excess enthalpy measurements have been comprehensively and critically reviewed by McGlashan (1967), Monk and Wadsö (1968), Marsh (1980), Becker (1980), and again by McGlashan (1984) and most recently by Marsh and O'Hare (1994).

Calorimeters can generally be classified into one of the following types:

- adiabatic
- isothermal
- flow calorimeter

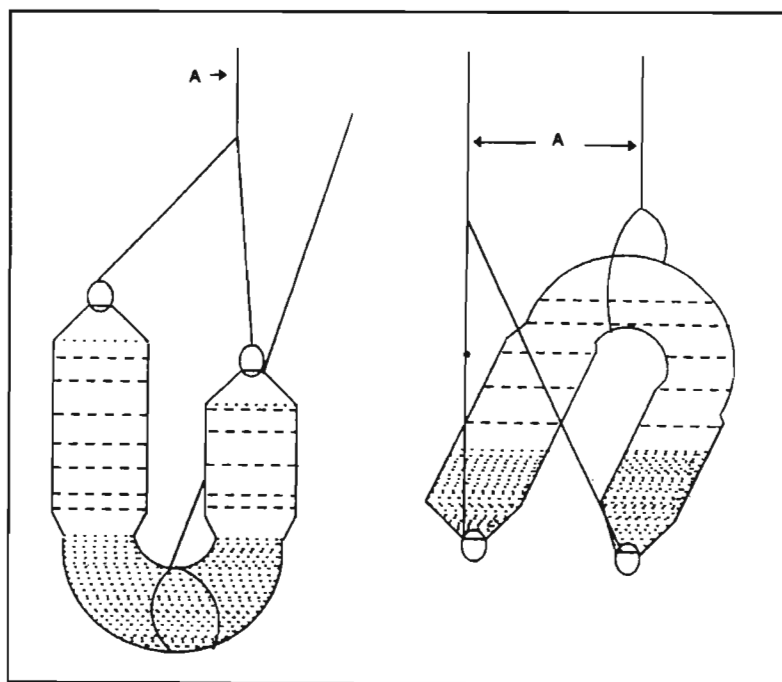
### 3.2.1 Adiabatic Calorimetry

In adiabatic calorimetry a single data point is determined in one loading of the calorimeter

(Rowlinson and Swinton, 1982). In adiabatic calorimetry experiments, the two liquids are mixed in an isolated vessel (vacuum jacket) which is thermally insulated from its surroundings (Skinner and Sturtevant, 1967). If the excess enthalpy is positive, there will be a lowering of the temperature on mixing. This drop in temperature may be nullified by the simultaneous supply of heat. Such a process is considered nearly isothermal and any small differences can be corrected for by observing the temperature change for a calculated supply of energy (Armitage and Morcom, 1969). If  $H_m^E$  is negative, then the mixture warms on mixing. Such exothermic mixing requires two experiments - one to measure the temperature rise on mixing and the other to measure the amount of electrical energy needed to produce such a rise (Armitage and Morcom, 1969).

Results generated by this type of calorimeter obtained from the mixing of liquids producing an exothermic enthalpy are generally unreliable, as a second or calibrating experiment cannot always accurately reproduce the original mixing conditions.

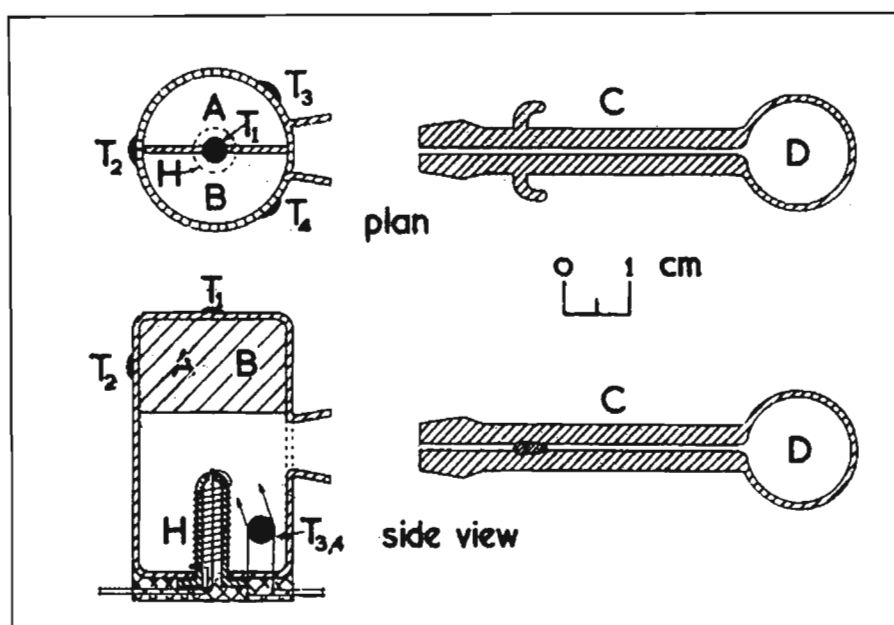
One of earliest batch calorimeters was reported by Hirobe (1925). In this mixing vessel Hirobe attempted to keep vapour spaces as small as possible. Hirobe's mixing vessel is shown in Figure 3.1



**Figure 3.1** Hirobe's mixing vessel

The liquids are initially separated by mercury, and are in contact with vapour spaces, which were kept at a minimum. Mixing is brought about by inversion of the vessel by means of threads, A, shown in the figure above.

Most modern adiabatic calorimeters are based on the apparatus designed by Larkin and McGlashan (1961), shown in Figure 3.2.



**Figure 3.2** Adiabatic Calorimeter of Larkin and McGlashan

The calorimeter of Larkin and McGlashan was one of the first calorimeters designed to eradicate the errors due to the presence of vapour space. However, it did not allow for volume changes that occurred on mixing (Williamson, 1967). The calorimeter consists of a glass mixing vessel with two compartments A and B in its upper half and a side-arm, with capillary C and bulb D which is attached to the vessel through the ground - glass joint E and F. A heating element, H, and four thermistors ( $T_1$ ,  $T_2$ ,  $T_3$ , and  $T_4$ ) distributed over the surface of the mixing vessel form part of the Wheatstone bridge assembly.

The vessel is completely filled with and immersed in a bowl of mercury. The mercury is displaced from the upper compartments by introducing weighed quantities of the mixture through opening A by means of a hypodermic syringe. The loaded vessel with the capillary

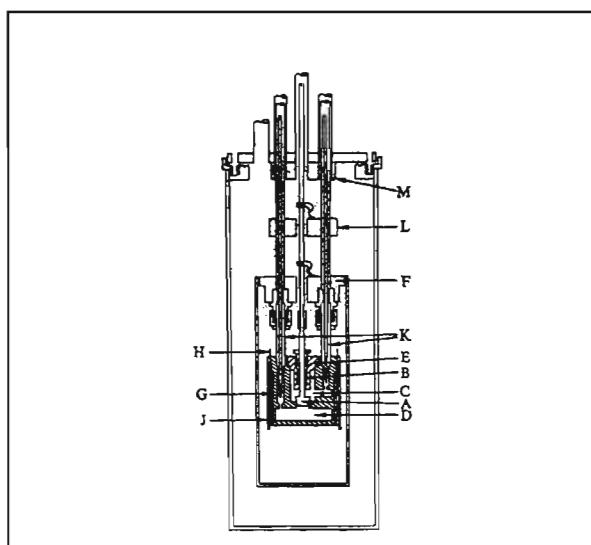


tube C, half filled with mercury and attached at the ground joint F, is placed in an evacuated enclosure with a thermostat until temperature equilibrium is achieved. After temperature equilibrium, the liquids are mixed in the absence of a vapour space by rotation of the apparatus through  $180^\circ$ , the direction of rotation being such that the liquid never comes into contact with the greased joints. The temperature change on mixing is measured by the four thermistors (Larkin and McGlashan, 1961). For endothermic processes, the calorimeter is operated in isoperibolic mode and uses electrical heating to compensate for the heat consumed during the reaction. The electrical heat is added through the resistor (H) and this allows the heat of mixing to be determined accurately. For an exothermic heat of mixing process, a second step in which an equivalent amount of electrical calibration heat needed to produce the same temperature rise as the mixing process is carried out. The heat of mixing and the masses of the liquids are used to calculate  $H_m^E$ . The precision of the instrument has been reported as  $0.7 \text{ J}\cdot\text{mol}^{-1}$  at  $H_{m(\text{max})}^E$  (Larkin and McGlashan, 1961). One of the major limitations of this technique and the subsequent designs is that a considerable amount of time is needed to get a single measurement. In addition it does not readily lend itself to automation. Another problem associated with these calorimeters is that they cannot be used at temperatures below the melting point of mercury. Mercury is used to separate the liquids and obviously if it freezes then mixing is not possible.

A calorimeter designed by Lewis and Stavely (Lewis and Stavely, 1975) several years later, obviated the need to use mercury to separate the liquids but instead a stainless - steel valve was used. Figure 3.3 illustrates the new calorimeter. Liquids with known masses are filled into the upper and lower chambers through the inlet tubes K to C and D using hypodermic syringes. The stainless steel valve is opened and the mixing process is allowed to occur. An electrical heater is used to maintain temperature equilibrium. The heater and a resistance thermometer are housed in the copper sleeve surrounding the mixer vessel. The heat of mixing is given by the magnitude of the electrical calibration heat, and the knowledge of the masses of liquids used and the heat of mixing are used to compute  $H_m^E$ , as given by equation 3.7.

$$H_m^E = \frac{VIt}{\frac{m_1}{M_1} + \frac{m_2}{M_2}} \quad (3.7)$$

where  $m_1$ ,  $m_2$  are the masses of the liquids used, and  $M_1$  and  $M_2$  their corresponding molar masses.  $V$  refers to the potential difference,  $I$  the current strength, and  $t$ , the calibration time. Lewis and Staveland's calorimeter allows for the measurement of the equilibrium vapour pressures of the mixture in the calorimeter, and application of the method of Barker (1953) results in a simultaneous determination of the excess Gibbs function. Due to the corrections necessary for the large vapour spaces present, precision for  $H_m^E$  measurements is not as good as expected and an error of 8 % has been observed.



**Figure 3.3** Batch calorimeter of Lewis and Staveland (A, stainless steel valve; B, invar-teflon-graphite stem seal; C, and D, upper and lower compartments; E, stainless steel body of valve; F, shield support; G, copper sleeve carrying heater and thermometer; H, electrical leads; J, gold-plated radiation shield; L, floating ring; M, copper block)

### 3.2.2 Isothermal Displacement Calorimetry

Up to the early 1960's, enthalpies of mixing, which play an important role in the theoretical and experimental studies of liquid mixtures, were generally measured by batch type calorimeters (McGlashan, 1962). This changed in the 1960's with the introduction of isothermal displacement and flow calorimeters.

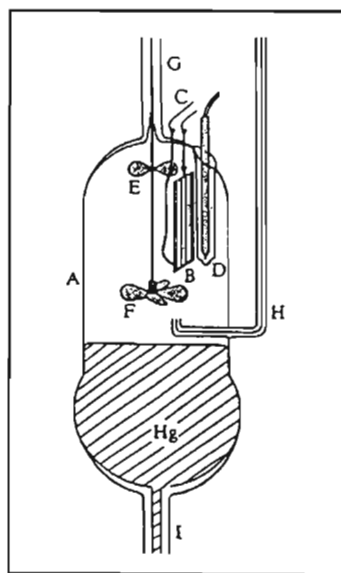
Isothermal displacement calorimetry was introduced in 1961 by Van Ness *et al.* and further developed in succeeding years (Savini *et al.*, 1966). The technique is an important tool for obtaining enthalpies of mixing of liquids at moderate temperatures and ambient pressure. In a displacement calorimeter, the liquid is kept at the same temperature as the environment by controlled heating or cooling. Hence the mixing or dilution process is isothermal. The process of mixing is made rapid and complete by continuous stirring accompanied by steady removal of the energy of stirring by Peltier cooling, in the case of an exothermic process. The liquid diluent can be added in steps, so that a large part of the composition range can be covered in one experiment. Errors due to vaporization and condensation are eliminated by avoiding a vapour space above the liquid. Space for the added liquid and the volume change due to mixing is provided by a movable piston in the Van Ness design (Winterhalter and Van Ness, 1966) and mercury in the mixing vessel of the Armidale design (Ewing *et al.*, 1970). In order to avoid the use of mercury, Stokes later developed a method in which the mixture leaves the vessel, as the diluent is added (Stokes, 1986).

The development by Van Ness and co-workers (Savini *et al.*, 1960 ; Winterhalter *et al.*, 1966) of the isothermal dilution calorimeter represented a giant step in liquid mixture calorimetry. In a striking example of lateral thinking, it eliminated at once all the difficulties and problems which had previously made this field one in which patient doctoral students toiled for years to get results notably different from those of their equally patient, fellows in other laboratories (Marsh and O'Hare, 1994). The problems encountered, and Van Ness's solution to them may be summed up as follows:

- (a) *Compensation for energy lost to or gained from the environment* : The mixture was always kept at the same temperature as the environment ; then no compensation was needed, as the process was isothermal. To achieve these conditions, controlled addition of one liquid to the other was matched by controlled electrical heating in conjunction with a Peltier device for cooling.
- (b) *Ensuring rapid and complete mixing of the liquids* : Continuous stirring rather than merely shaking, tilting or inverting was employed. The energy developed by the stirrer was removed at a steady rate by a Peltier device.

- (c) *Slowness and large material requirements of batch-mixing methods:* With the dilution method, the addition of the second liquid can be stopped as often as desired while readings of total added volume and energy used to maintain constant temperature are taken. Thus one run provides numerous points over one half of the composition range, the other half being obtained by interchanging the components. This resulted in excess enthalpy results being obtained in relatively shorter times than had been previously achieved.
- (d) *Errors due to vapourization or condensation during the mixing process, which are especially significant with highly volatile liquids:* No vapour space was allowed in the mixing vessel, but room for the added liquid was provided for and an allowance was made for the volume change on mixing.

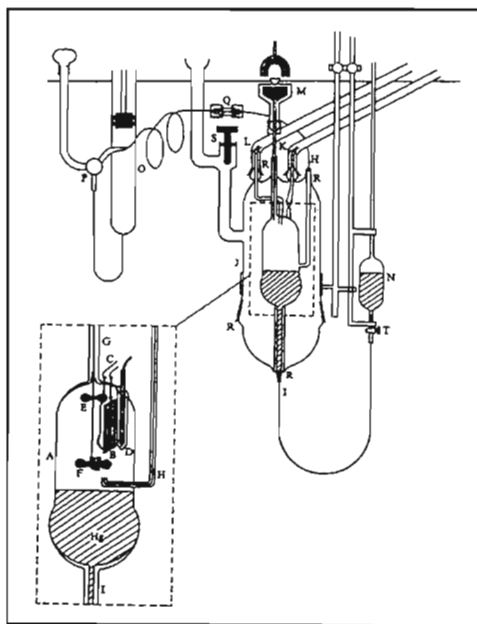
The only essential difference between the Van Ness design and the isothermal displacement calorimeters developed by Marsh, Stokes and co-workers (Stokes *et al.*, 1969 ; Ewing *et al.*, 1970 ; Costigan *et al.*, 1980) in Armidale lies in the solution of problem (d) above. Van Ness used as his mixing vessel a cylindrical Dewar vessel with a lid sliding upward on an O-ring seal to make room for the added liquid. The temperature - sensing thermistor, heating and cooling devices, and stirrer were all supported by the lid, and the added liquid was introduced via a capillary tube passing through the lid into a mercury trap. Figure 3.4 is an illustration of a glass mixing vessel.



**Figure 3.4** Early model glass mixing vessel

The majority of the results published by the Armidale group were made using the mercury displacement method, and the results obtained were reportedly more accurate than the solution displacement method. (Marsh and O'Hare, 1994). A common reaction to the idea of a vessel initially half-full of mercury is "Doesn't the heat capacity of this great mass of mercury greatly reduce the sensitivity of the temperature response to the enthalpy of mixing?" The answer is no since  $C_{p,m}/V_m$ , the heat capacity of mercury per unit volume, is not much more than that of hydrocarbon liquids, and less than that of water or the lower alcohols, so the sensitivity is only about halved at the start of the run (Marsh and O'Hare, 1994), and only slightly compromised during the reaction.

However, in 1985, the “solution displacement” or “mixture displacement method” was developed in order to avoid the use of mercury because of its toxicity (Stokes, 1986; Stokes, 1988), which is a lot simpler in operation, though requiring rather more calculation. A similar method has been reported by Becker and co-workers in 1972 (Becker *et al.*, 1972). In this method the vessel is initially completely filled with one liquid and the other is injected in small pulses. These are well mixed with the vessel contents, which are allowed to escape in similar small pulses at a point remote from the injection site. Figure 3.5 shows the apparatus of Stokes and co-workers (Stokes *et al.*, 1969).



**Figure 3.5** Isothermal displacement calorimeter of Stokes *et al.*

In this calorimeter degassed component 1 is introduced into the mixing chamber via a hypodermic syringe, whilst pure degassed component 2 is added into the piston burette. The liquids are then allowed to equilibrate to the temperature of the apparatus and the vacuum jacket is evacuated. The pure liquid 2 is then pumped into the mixing vessel, and the resulting temperature change is detected by the thermistor. Electrical heat is added via the heater to maintain isothermal conditions. The excess molar enthalpy,  $H_m^E$  is then determined from the calibration heat ( $VIt$ ), together with the volumes of the components  $V_1$  and  $V_2$ , and their respective densities  $\rho_1$  and  $\rho_2$ , as follows:

$$H_m^E = \frac{VIt}{\frac{V_1 \rho_1}{M_1} + \frac{V_2 \rho_2}{M_2}} \quad (3.8)$$

Where  $M_1$  and  $M_2$  denote the molar masses of components 1 and 2 respectively,  $V$ , the potential difference,  $I$ , the current strength, and  $t$ , the calibration time.

### 3.2.3 Flow Calorimetry

Another important, non-batch method used to obtain enthalpies of mixing of liquids is provided by flow calorimetry. Here two liquids flow continuously through a mixing chamber and the resultant thermal effect is measured at constant flow rates and constant pressure. The pressure or temperature of operation can be changed easily, and the method can also be used for gases (Beenakker and Coremans, 1962; Gopal *et al.*, 1989).

The great breakthrough in flow calorimetry took place after 1960. Within a short period, a number of investigators reported the successful construction of flow calorimeters for enthalpies of mixing : in 1966, Rose and Storvick (Rose and Storvick, 1966), in 1967 Stoesser and Gill (Stoesser and Gil, 1967); and in 1968, Monk and Wadsö (Monk and Wadsö, 1968). The first volume of *The Journal of Chemical Thermodynamics* in 1969 marks this development by presenting three papers on newly developed flow calorimeters (Sturtevant and Lyons, 1969; Picker *et al.*, 1969 ; McGlashan and Stoeckli, 1969). Several mixing flow

calorimeters became commercially available (LKB, Setaram). In later years, flow calorimeters were designed for use over wide pressure and temperature changes. The thermochemical group at Brigham Young University in Provo, USA, developed calorimeters for applications at pressures up to 40.5 MPa and temperatures initially to 423K (Christensen *et al.*, 1976) and more recently to 773K (Christensen *et al.*, 1986). Gopal and co-workers (Gopal *et al.*, 1989) extended the technique to liquid-nitrogen temperature, whilst Wormald and co-workers (Wormald *et al.*, 1977) developed a versatile instrument for measurements on liquids, gases and the two phase region at temperatures considerably below ambient.

In recent years a considerable amount of precise information on fluid mixtures has been obtained by flow calorimetry. Benson's group at the National Research Council in Ottawa, Canada, measured excess enthalpies of many organic mixtures (Handa and Benson, 1980) with great precision; these results have been used for testing calorimeter performance. The thermochemical group at Brigham Young University, concentrated on mixtures with such liquified gases as CO<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> (Christensen *et al.*, 1986), important for supercritical fluid extraction and chromatography. Ott (1990) used the method for the examination of phase equilibria, while Gill (1988) and Wadsö (1986) used flow calorimetry to study systems of biological interest as well as determine enthalpies of solution of slightly soluble gases (Gill and Wadsö, 1986).

Recent decades witnessed an increasing interest in the thermodynamic properties of aqueous electrolyte solutions at elevated temperatures and pressures, both from a theoretical as well as technological point of view. Theoretically, properties of aqueous electrolytes at elevated temperatures became interesting because of the influence of structural effects. In this context "structure" means "dynamic structure" as expressed by radial distribution functions, pair correlation functions, etc. In addition there has been a great interest in solution properties in the vicinity of the critical point of the solvent. Technologically, applications to steam generators, supercritical extraction techniques, heat pumps, and to geothermal and oceanographic processes become important. Substantial contributions based on flow calorimetry came from Woods group at the University of Delaware, Newark, USA. Starting with a calorimeter for measuring enthalpies of dilution or mixing up to 373 K (Messikomer and Wood, 1975), Wood and collaborators constructed several calorimeters for measurements at progressively higher temperatures.

In flow mixing calorimetry, two fluids flow continuously through a mixing chamber and the change of enthalpy resulting from the mixing process is measured under steady - state conditions at constant pressure, flow rate, and composition. Flow calorimeters differ in this regard from batch, titration, or displacement calorimeters in which one of the fluids is added (usually incrementally in a batch or displacement calorimeter or continuously in a titration calorimeter) to a reservoir containing a fixed amount of the second component. In general, flow and batch calorimeters directly measure enthalpies of mixing while titration or displacement calorimeters measure a series of enthalpies of dilution which can be summed to give the enthalpy of mixing at the required composition.

A major advantage of the flow calorimeter is that the mixing fluids can be completely contained in a small mixing chamber which has a fast temperature response time. Contact with the atmosphere is avoided, and if complete mixing occurs, only a single phase is present. The absence of a vapour space eliminates a serious source of error which can occur in displacement or batch calorimeters during mixing of volatile liquids.

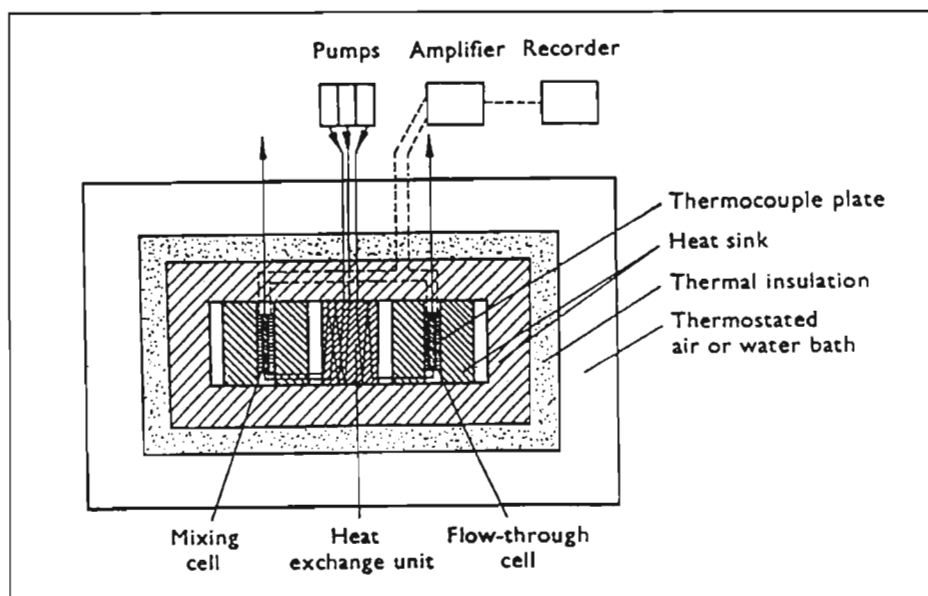
#### 3.2.3.1 Modern Flow Mixing Calorimeters

Flow mixing calorimetry has emerged during the past 25 years as an important method for obtaining accurate values of  $H_m^E$ . This has largely been due to the development of reliable pumps, components such as Peltier devices, improved electronics, and computer control.

Following, their earlier work on aqueous systems, Rose and Storvick (1966) constructed a flow calorimetric apparatus which was the prototype of many modern calorimeters. Liquids were displaced from reservoirs by mercury moved by screw driven pumps and the mixing calorimeter was followed by a heat capacity measuring section. Excess enthalpies of (alcohol and alkane) mixtures were measured with this apparatus.

Stoesser and Gill (1967) reported a sensitive twin-cell calorimeter in 1967. Monk and Wadsö (1968) described a twin cell, heat - flux reaction calorimeter as illustrated in Figure 3.6.





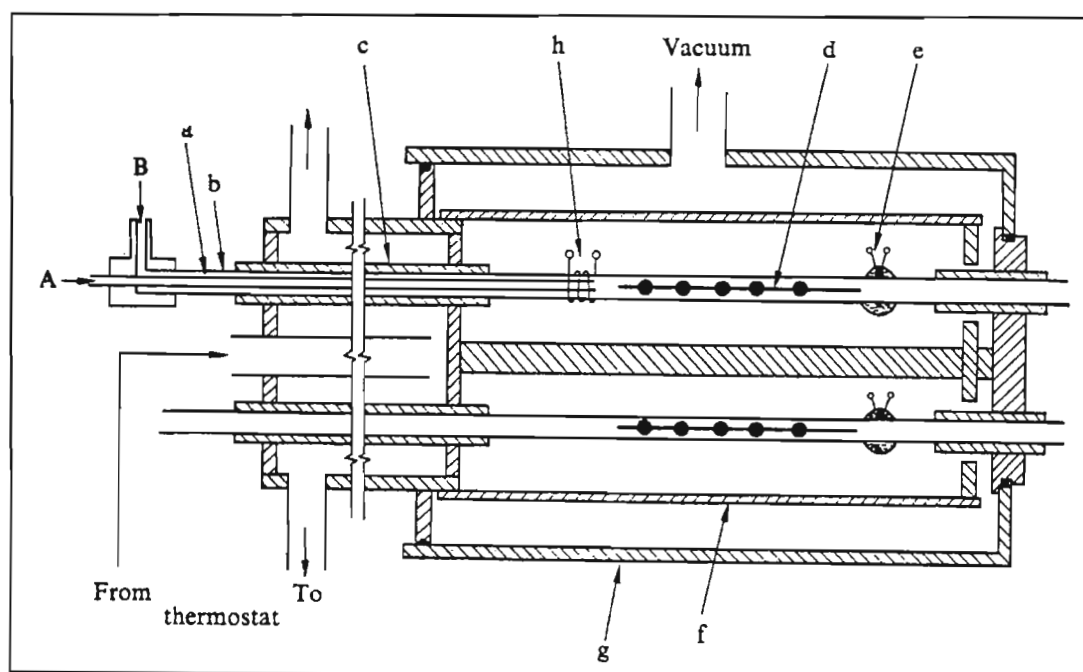
**Figure 3.6** The twin calorimeter of Monk and Wadsö

Monk and Wadsö's calorimeter consisted of a metallic block heat sink containing a heat exchange unit surrounded by a twin arrangement of calorimetric units. The flow reaction cells were each sandwiched between two Peltier (thermopile) devices in contact with heat sinks. Heat evolution or absorption upon the mixing of liquids within the calorimeter is conducted to or from the heat sink via the thermopile generating a proportional current. Efficient liquid mixing in this calorimeter was achieved by the insertion of constrictors into the path of flow. The completeness of mixing was subsequently checked by utilization of the ( $\text{HCl} + \text{NaOH}$ ) system for which the titration curves are well documented. The LKB commercial calorimeter subsequently produced was based on Monk and Wadsö's design.

Christensen and collaborators (1976), constructed a high pressure flow mixing calorimeter capable of operations of up to 40 MPa and 423 K. The calorimeter feature a Peltier device and heater which allowed both positive and negative excess enthalpies to be measured. To attain even higher temperatures, Busey *et al.*, (1984) devised a mixing cell or insert which fitted into a high temperature Calvet calorimeter. It was capable of measurements up to 673 K and 41.5 MPa. Christensen and Izatt (1984) constructed a heat leak calorimeter which was used up to 673 K and 40.5 MPa. A later version of this calorimeter, described by Christensen *et al.*, (1986) used tantalum tubing and operated up to 773 K and 40.5 MPa.

Several new calorimeter designs appeared in 1969. McGlashan and Stoeckli (1969) reported the construction of a single cell flow calorimeter that minimized heat transfer from the mixing zone to the surroundings. It was reported by the authors that this type of instrument gave an error in  $H_m^E$  of about 1 %, in spite of the fact that they did not consider possible heat losses in the heating wires or thermistor leads. Sturtevant and Lyons (1969) designed a similar instrument that required a smaller sample size. However, the error in the determination of  $H_m^E$  was estimated to be 2 %.

Picker and co-workers (1969) reported on adiabatic and isothermal differential flow micro calorimeters with short response times, shown in Figure 3.7. The authors estimate an error of 1 % for their instrument.



**Figure 3.7** Design of adiabatic differential flow calorimeter (a,b, Teflon injection tubes; c, copper tubes to thermostat injected fluids; d, mixing device; e, thermistors; f,g,thermal shields; h, calibration heater)

The two pure liquids to be mixed A and B, flow into the instrument through two concentric Teflon capillary tubes a and b. The outside Teflon tube is smoothly fitted in a copper tube (c) around which thermostatted water is circulated. Mixing of the liquids occur at the end of capillary tube in the mixing device. The temperature of the mixing device is measured with thermistors that are in intimate contact with the mixing vessel. The heat of mixing can be

determined from the temperature measurement and heat capacity. The heat of mixing and the flow rate information are used to calculate  $H_m^E$ .

Raal and Webley (1987) developed an accurate microflow calorimeter that minimized errors arising from energy dissipation as a result of the frictional effects for some of the more viscous as well as non-viscous liquids. The authors paid particular attention to the following basic requirements in order to ensure accurate and reproducible results.

- complete temperature equilibration of the liquids prior to mixing.
- complete and thorough mixing of the component liquids.
- separation of the frictional energy from the excess enthalpy.
- elimination of heat leaks dependent on fluid flow rates and physical properties.
- introduction of an “ease of mixing factor” to counteract the heat measurement errors of difficult-to-mix systems.

The authors compared  $H_m^E$  results for the (cyclohexane + hexane) system from their calorimeter with the results of the IUPAC commission and observed a maximum deviation of only  $0.53 \text{ J}\cdot\text{mol}^{-1}$ .

Raal and Naidoo (1990) later developed a novel differential microflow calorimeter for excess enthalpy measurement on endothermic liquid systems. The instrument design incorporated precise temperature equilibrium of the liquids before mixing, the elimination of flow-rate and physical property - dependent heat leaks, and a differential mode of operation that took into account entropy generation in flows with mixing and friction processes. The authors report good results on this instrument, and an average deviation of only  $0.22 \text{ J}\cdot\text{mol}^{-1}$  for the IUPAC reference standard (cyclohexane + hexane) system, surpassed only by the data of Marsh and Stokes (1969), obtained with their well known batch calorimeter.

The calorimeter design of White, Wood and Biggerstaff (1988) was improved upon by Carter and Wood (1991). The Carter and Wood calorimeter incorporates a three stage preheating system and had the advantage that the heat loss under both reference and sample conditions was identical and hence no heat loss correction was necessary. Error involved in the

measurement with their calorimeter is estimated by the authors to be within 0.2 %.

3.3 EXPERIMENTAL APPARATUS AND TECHNIQUE

3.3.1 Description of the Apparatus used in this Study

The  $H_m^E$  results for the binary liquid mixtures reported in this work were determined using the Thermometric 2277 Thermal Activity Monitor (TAM), a flow-mix microcalorimeter, and is illustrated in Figure 3.8.

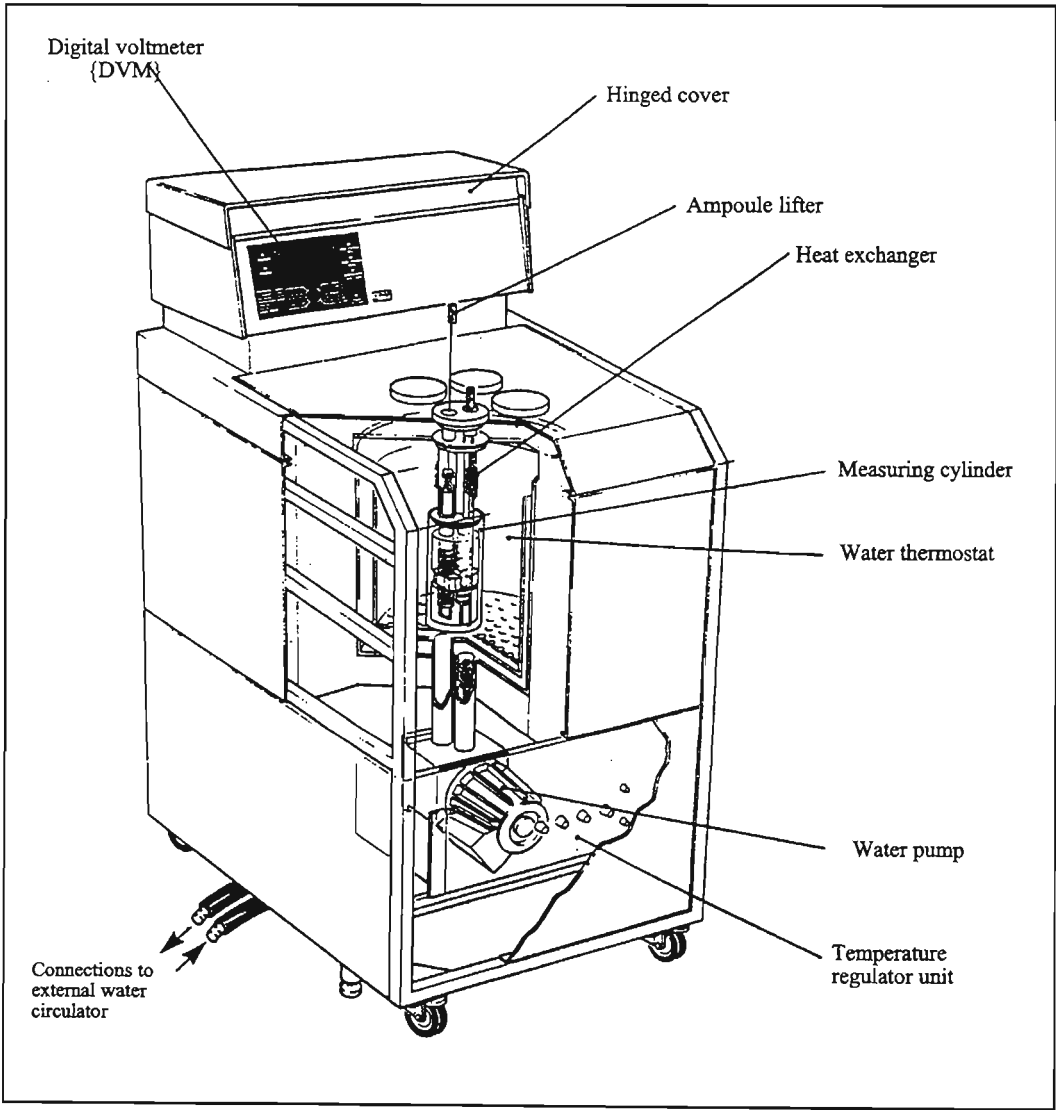
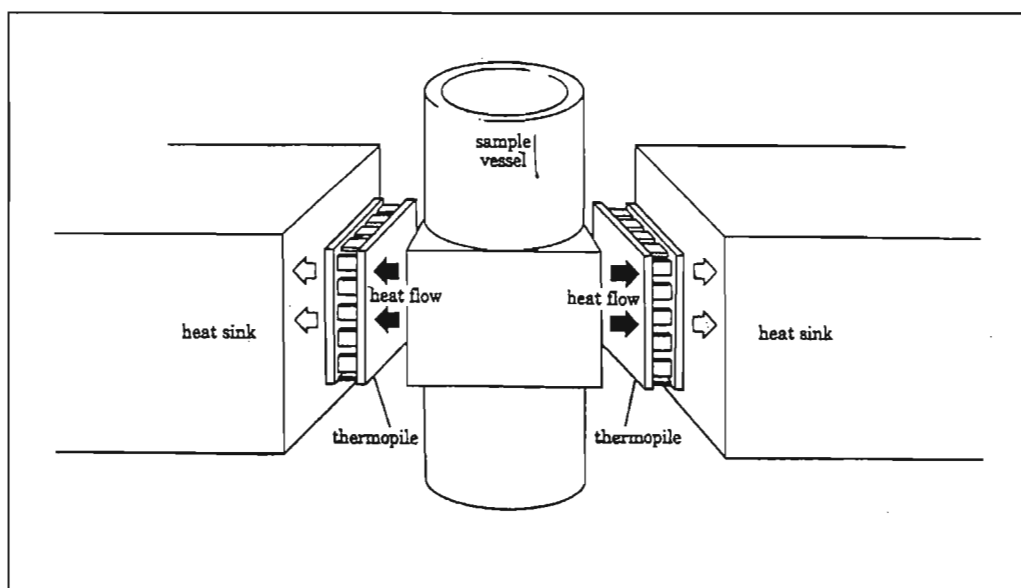


Figure 3.8 Thermometric 2277 Thermal Activity Monitor

### 3.3.1.1 The 2277 Thermal Activity Monitor (TAM) : Principle of Operation

The 2277 Thermal Activity Monitor (TAM) is equipped with an external water circulator (Thermometric 2219 Multi-temp II) and a pair of LKB peristaltic pumps. Continuous heat leakage measurements are conducted in an isothermal system. The system can observe and quantify both exothermic (heat-producing) and endothermic (heat absorbing) processes,

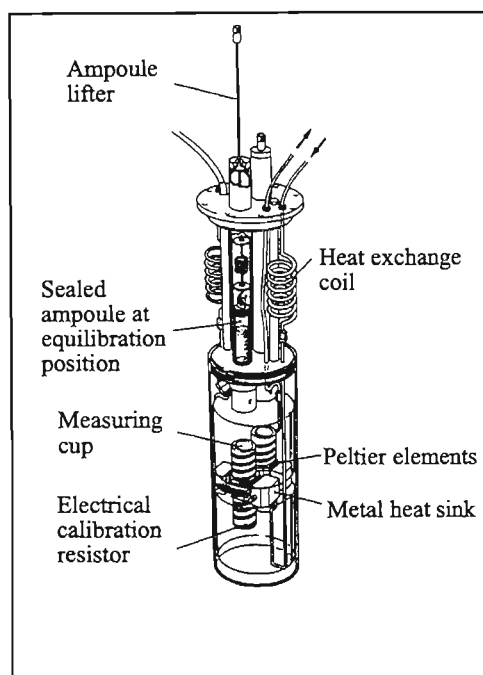
The Thermal Activity Monitor (TAM) utilises the heat flow or heat leakage principles, where heat produced in a thermally - defined vessel flows away in an effort to establish thermal equilibrium with its surroundings. The heat flow principle is illustrated in Figure 3.9.



**Figure 3.9 The Heat Flow Principle**

Exceptional thermal stability is achieved by utilising a 25 litre water thermostat which surrounds the reaction measuring vessels and acts as an infinite heat sink. The temperature of the system is controlled with a solid state temperature controller to within  $\pm 2 \times 10^{-4}$  K, the experimental working range of 278.15 K - 353.15 K.

Samples are presented to the TAM in a combination measuring cylinders (Figure 3.10) which are maintained at constant temperature in the water thermostat.



**Figure 3.10 Combination Measuring Cylinder**

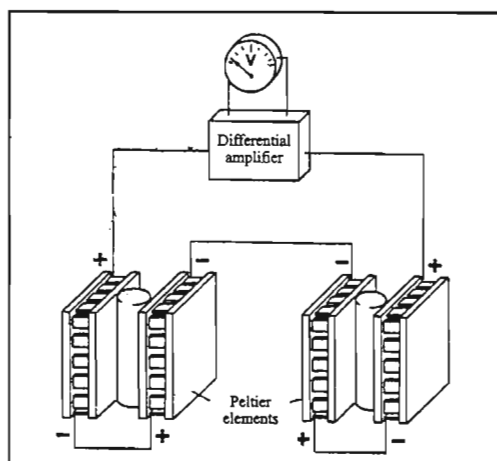
The calorimetric mixing device used in the TAM (Figure 3.10) incorporates a 24 carat gold flow-mix cell, where two different liquids can be mixed. The flow mix cell has a small bore T-piece at the base of the measuring cup where the two incoming flows are mixed. After mixing, the reaction takes place as the mixed flow passes up the spiral around the measuring cup and out to waste.

Measurement takes place in a measuring cup sandwiched between a pair of Peltier thermopile heat sensors. These sensors are in contact with a metal heat sink, and the system is designed so that the main path of the flow of heat to or from the measuring cup is through the Peltier elements. The Peltier elements act as thermoelectric generators capable of responding to temperature gradients of less than  $10^{-6}$  K. These highly sensitive detectors convert the heat energy into a voltage signal proportional to the heat flow  $B$ . This heat transference is directly proportional to the heat of mixing. The vessels, the metal holders and blocks are encased in larger metal blocks which act as the main heat sinks between the heat detection systems and the constant temperature water bath.

Gold tubing (24 carat) is used to convey the liquids to the mixing vessel and flow through vessel. These gold tubes are kept in direct contact via heat exchange coils with the water bath to allow the liquids to equilibrate to the temperature of the system. The gold tubes are also

kept in intimate contact with the main heat sinks ; they are pressed into grooves cut in the heat sinks, and this allows further equilibration to the temperature of the system. The gold tubes are also wound around the holders that house the mixing and flow vessels, and these gold tubes then extend to the mixing vessel and flow vessel. The mixed liquid then leaves the T-piece (24 carat gold) mixing vessel through an outlet also made of gold tubing.

A precision wire wound resistor is located within each measuring cup to initiate a reaction during electrical calibration. This entire assembly is located in a stainless steel canister in the lower part of the measuring cylinder.



**Figure 3.11 Peltier element heat detection system**

The liquids are introduced into the calorimeter by means of LKB peristaltic pumps that pump the liquids via Viton tubing into Teflon tubes, and, internally the gold tubes convey the liquids into the mixing vessel. The outlet tube is also connected externally Teflon tubing.

#### 3.3.1.2 Experimental Procedure

For each experimental run two steps are involved (a) a calibration of the flow rates from the peristaltic pumps. (b) heat of mixing measurement.

Calibration involved two steps, viz. zeroing the instrument and adjusting the amplifiers. Dissolved gases in the liquid components is a serious problem, and degassing of all solvents (by use of an ultrasonic bath) prior to pumping was imperative.

One of the liquids was pumped through both tubes. The aim of this zeroing step is to account for the heat produced during friction. As the same liquids, or a representative mixture was pumped peristaltically through both tubes, the heat of mixing should be zero. The system is then allowed to achieve a steady state, which is when the reading on the display unit stabilizes to a constant value. The output on the display is then, if necessary, adjusted to show zero.

The next step involves adjustment of the calorimeter's amplifiers. This step is carried soon after zeroing the instrument while the liquid is still being pumped through the calorimeter. A defined constant current  $I$ , is applied to the calibration resistor which is in intimate contact with the mixing vessel, and since the resistance  $R$  for the resistor is known, the expected thermal power  $P$ , can be ascertained from the equation:

$$P = I^2 R \quad (3.9)$$

The calorimeter power reading is adjusted accordingly, when necessary. The pumps are now switched off. Calibration for each flow rate is necessary.

The instrument is now ready for the determination of the heat of mixing. The sample liquids were prepared in 25 cm<sup>3</sup> Quickfit conical flasks having narrow necks. Each flask was fitted with modified stoppers and had one 1.8 mm (inner diameter) inlet which was connected by Teflon tubing to the peristaltic pump. This design was efficient in reducing evaporation of the component samples. The mass ( $m_{A, \text{initial}}$  and  $m_{B, \text{initial}}$ ) of these flasks was recorded. The inlet tube of each pump is dried and inserted into the two flasks, and the pumps and a stopwatch are simultaneously started. After the reading on the display has reached a steady state, the power  $P$  produced by the mixing process was recorded. The pumps and the stopwatch are stopped simultaneously, and the respective masses ( $m_{A, \text{final}}$  and  $m_{B, \text{final}}$ ) of two flasks as well as the time elapsed,  $t$ , is also recorded. The masses of the effluent collected after each run were compared to the amounts of the pure liquids consumed, thus serving as a constant check against liquid leaks in the system. For each subsequent run a new flow rate was set and the process carried out as described above.

The excess molar enthalpy  $H_m^E$  is then determined as follows:



$$H_m^E = \frac{P}{F} \quad (3.10)$$

where  $P$  is the power that is displayed on the instrument in mW, and  $F$  is the molar flow rate in moles per second and is determined as:

$$F = \frac{n_A + n_B}{t} \quad (3.11)$$

where,  $n_A$  and  $n_B$  are the number of moles of liquids  $A$  and  $B$  respectively that have flowed through the system in time  $t$ .  $n_A$  and  $n_B$  are calculated as follows:

$$n_A = \frac{m_{A,initial} - m_{A,final}}{M_A} \quad \text{and} \quad n_B = \frac{m_{B,initial} - m_{B,final}}{M_B} \quad (3.12)$$

where  $M_A$  and  $M_B$  are the molar masses of  $A$  and  $B$  respectively, and the mole fraction  $x_A$  is determined as follows:

$$x_A = \frac{n_A}{n_A + n_B} \quad (3.13)$$

$$\text{and } x_A + x_B = 1 \quad (3.14)$$

### 3.3.2 Validation of the Technique

The validity of the technique was established by measuring the excess molar enthalpies for the IUPAC (1970) recommended test system of (cyclohexane + hexane). The results for this system obtained in five different laboratories with three types of isothermal calorimeters showed no systematic discrepancies. The recommended equation at 298.15 K is

$$H_m^E (\text{J} \cdot \text{mol}^{-1}) = x_1(1-x_1) [866.1 - 249.4 (1 - 2x_1) + 97 (1 - 2x_1)^2 - 31.8 (1 - 2x_1)^3] \quad (3.15)$$

where  $x_1$ , is the mole fraction of cyclohexane. Marsh and Stokes (1969) reported very accurate and precise results using an isothermal batch calorimeter with a standard deviation of  $0.09 \text{ J}\cdot\text{mol}^{-1}$ ; Grolier *et al.*, (1975) obtained data with a Picker flow calorimeter with a standard deviation of  $0.35 \text{ J}\cdot\text{mol}^{-1}$ ; McGlashan and Stoeckli (1969), and Siddiqi and Lucas (1982) used an isothermal flow calorimeter and obtained a standard deviation of  $1.1 \text{ J}\cdot\text{mol}^{-1}$  and  $0.78 \text{ J}\cdot\text{mol}^{-1}$ , respectively. The data obtained in this work shows an average deviation of less than  $2 \text{ J}\cdot\text{mol}^{-1}$ , and is in agreement with the literature data of Heintz and Lichtenthaler (1979), who also report an average deviation error of  $2 \text{ J}\cdot\text{mol}^{-1}$ .

### 3.3.3 Preparation of Mixtures

The pure solvents were initially degassed in an ultrasonic bath for 30 minutes. The solvents were prepared in Quickfit conical flasks. Mixtures with compositions spanning the entire composition range were achieved by varying the flow rates of the peristaltic LKB pumps accordingly.

### 3.3.4 Materials

The purities of all the chemicals were determined using gas-liquid chromatography (GLC). A Hewlett-Packard gas chromatograph equipped with a 3393A integrator and a 25 m carbowax capillary column was used. The carboxylic acids, alkane, cycloalkane and nitrile compounds were stored under  $4\text{\AA}$  molecular sieves. Analysis for water content by the Karl Fischer technique showed that in all cases the water content was less than 0.01 mass %. The liquids were kept in a dry box before use. A summary of the materials used in this study, their suppliers and purities is given in Table 3.1.

**Table 3.1** Materials used, their suppliers and mass % purities

COMPOUND	SUPPLIER	%PURITY
Acetic acid	Acros	99.5
Propanoic acid	Acros	99
Butanoic acid	Acros	99
2-Methylpropanoic acid	Acros	99.5
Pentanoic acid	Acros	99
3-Methylbutanoic acid	Acros	99
Acetonitrile	Aldrich	>99.5
Butanenitrile	Fluka	99
Benzonitrile	Sigma Aldrich	99

### 3.4 EXPERIMENTAL RESULTS

The experimental excess molar enthalpies,  $H_m^E$  for 18 binary mixtures are presented in the following order:

3.4.1 (acetonitrile + a carboxylic acid) at 298.15 K.

3.4.2 (butanenitrile + a carboxylic acid) at 298.15 K.

3.4.3 (benzonitrile + a carboxylic acid) at 298.15 K.

where carboxylic acid in each case refers to (acetic acid or propanoic acid or butanoic acid or 2-methylpropanoic acid or pentanoic acid or 3-methylbutanoic acid).

The Redlich-Kister (1948) smoothing function

$$H_m^E = x(1-x) \sum_{r=0}^{r=k} A_r (1-2x)^r \quad (3.16)$$

was fitted to the experimental data by the method of unweighted least squares, and the deviations  $\delta H_m^E$  calculated from the equation.

$$\delta H_m^E / (J \cdot mol^{-1}) = H_m^E / (J \cdot mol^{-1}) - x(1-x) \sum_{r=0}^{r=k} A_r (1-2x)^r \quad (3.17)$$

where,  $x$  is the mole fraction of acetonitrile or butanenitrile or benzonitrile, respectively, and  $r = 0, 1, 2$  or  $3$ .

The standard deviation,  $\sigma$  is determined as follows:

$$\sigma = [\sum (H_{m(expt)}^E - H_{m(calc)}^E)^2 / (N - a)]^{\frac{1}{2}}, \quad (3.18)$$

where  $N$  is the number of experimental points and  $a$  is the number of fitting coefficients.

For each section (3.4.1 - 3.4.3), tables of results for  $H_m^E$  data, coefficient's  $A_i$  and deviations  $\sigma$  from equation (3.18) are presented. Excess molar enthalpy plots as a function of mole fraction acetonitrile or butanenitrile or benzonitrile have been produced.

### 3.4.1 Excess Molar Enthalpy Data for Mixtures of [Acetonitrile + a Carboxylic Acid] at 298.15 K

**Table 3.2 Physical Properties of the Pure Components at T = 298.15 K: Densities,  $\rho$  Refractive Indices,  $n_D$**

Component	$\rho/(\text{g}\cdot\text{cm}^3)$		$n_D$	
	exp	lit <sup>a</sup>	exp	lit <sup>a</sup>
Acetonitrile	0.7763	0.7765	1.3413	1.3416
Acetic acid	1.0437	1.0439	1.3697	1.3698
Propanoic acid	0.9884	0.9881	1.3846	1.3843
Butanoic acid	0.9535	0.9532	1.3955	1.3958
2-Methylpropanoic acid	0.9431	0.9429	1.3913	1.3917
Pentanoic acid	0.9346	0.9345	1.4064	1.4060
3-Methylbutanoic acid	0.9216	0.9219	1.4019	1.4022

<sup>a</sup> Riddick *et al.* (1986)

**Table 3.3**      **Excess molar enthalpies  $H_m^E$  for the systems : [Acetonitrile (1) + a Carboxylic Acid (2)] and the Deviations,  $\delta H_m^E$ , calculated from equation (3.17) and the parameters of Table 3.4 at the experimental temperature of 298.15 K, as a function of Mole Fraction  $x_1$ .**

$x_1$	$H_m^E/\text{J}\cdot\text{mol}^{-1}$	$\delta H_m^E/\text{J}\cdot\text{mol}^{-1}$	$x_1$	$H_m^E/\text{J}\cdot\text{mol}^{-1}$	$\delta H_m^E/\text{J}\cdot\text{mol}^{-1}$
Acetic Acid					
0.0927	96.2	0.1	0.4885	302.4	3.5
0.1409	150.1	6.7	0.5710	284.3	1.6
0.2072	197.3	-3.5	0.6514	247.9	-3.5
0.2787	245.9	-3.5	0.7416	198.3	-4.0
0.3221	267.1	-4.1	0.8090	158.7	0.7
0.3810	291.2	0.2	0.8722	112.3	1.1
0.4460	304.7	4.7	0.9150	79.4	2.7
Propanoic Acid					
0.0920	186.4	8.8	0.5671	620.1	3.4
0.1560	291.0	1.3	0.5993	605.9	0.7
0.2134	375.0	-4.9	0.6517	570.0	-3.5
0.2780	461.1	-6.0	0.7248	494.5	-8.8
0.3407	532.6	-2.6	0.8046	389.9	-3.1
0.3990	581.2	-0.8	0.8878	250.7	6.4
0.4626	617.7	4.4	0.9230	176.3	3.9
0.5057	629.8	7.7			
Butanoic Acid					
0.0890	159.9	-7.1	0.6605	599.6	1.4
0.1448	264.4	0.7	0.6860	575.4	0.0
0.1884	338.3	3.8	0.7141	547.2	1.8
0.2668	452.6	4.1	0.7884	437.7	-3.9
0.3913	580.2	-4.3	0.8201	383.8	-3.6
0.4626	629.2	-0.9	0.8728	298.4	12.7
0.5230	647.4	0.8	0.9067	217.0	3.3
0.5889	634.8	-4.0	0.9377	129.6	-15.1
0.6417	615.6	3.4			
2-Methylpropanoic Acid					
0.1032	276.4	8.5	0.5013	926.8	2.5
0.1870	485.8	0.8	0.5479	922.6	3.2
0.2347	588.7	-8.3	0.6046	896.8	8.9
0.2938	720.7	3.3	0.6531	840.1	0.6
0.3508	801.3	-8.7	0.6827	790.9	-10.5
0.3982	860.0	-7.0	0.7273	718.9	-10.3
0.4417	902.2	-0.5	0.8013	577.9	-0.9
0.4547	918.7	8.5	0.8891	364.7	11.7
0.4571	916.3	5.0	0.9158	273.5	-1.1

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Pentanoic Acid					
0.1197	269.0	-11.0	0.6370	837.8	-3.4
0.1899	418.9	0.1	0.6655	815.9	-2.4
0.2311	501.9	7.2	0.7138	759.6	-0.8
0.2782	583.1	6.9	0.7441	725.1	-13.4
0.4131	765.1	-3.5	0.8076	584.8	5.2
0.4825	831.9	-0.6	0.8487	480.9	6.7
0.5404	858.1	-1.9	0.9029	303.4	-12.1
0.5746	862.9	-0.3	0.9603	118.2	-11.9
0.6211	845.1	-5.3			

3-Methylbutanoic Acid					
0.0895	190.0	-6.9	0.6283	866.9	-0.6
0.1287	270.0	-3.4	0.6731	835.8	-2.3
0.1972	409.1	9.1	0.7177	792.1	5.9
0.2420	486.0	6.2	0.7515	721.9	-9.5
0.3371	632.1	-7.2	0.7835	672.7	4.9
0.4026	730.3	-5.3	0.8207	571.1	-8.3
0.4532	799.6	2.4	0.8529	500.9	9.3
0.5200	857.0	2.7	0.8744	435.9	8.1
0.5902	876.9	1.2	0.9379	206.0	13.4

**Table 3.4**      **Coefficients  $A_r$  and standard deviations  $\sigma$  from equation (3.18) for the excess molar enthalpies of systems: (Acetonitrile (1) + a Carboxylic Acid (2) at T = 298.15 K.**

Component	$A_0$	$A_1$	$A_2$	$A_3$	$\sigma(H_m^E)/J\cdot mol^{-1}$
Acetic Acid	119.0	238.4	-188.9	-215.8	3.7
Propanoic Acid	2486.0	-233.5	-307.6	63.2	5.5
Butanoic Acid	2571.0	-461.5	-416.2	-268.7	6.1
2-Methylpropanoic Acid	3697.0	-221.5	-734.1	-328.1	7.2
Pentanoic Acid	3374.0	-1131.0	-385.8	832.8	7.4
3-Methylbutanoic Acid	3362.0	-1530.0	-351.6	990.1	7.2

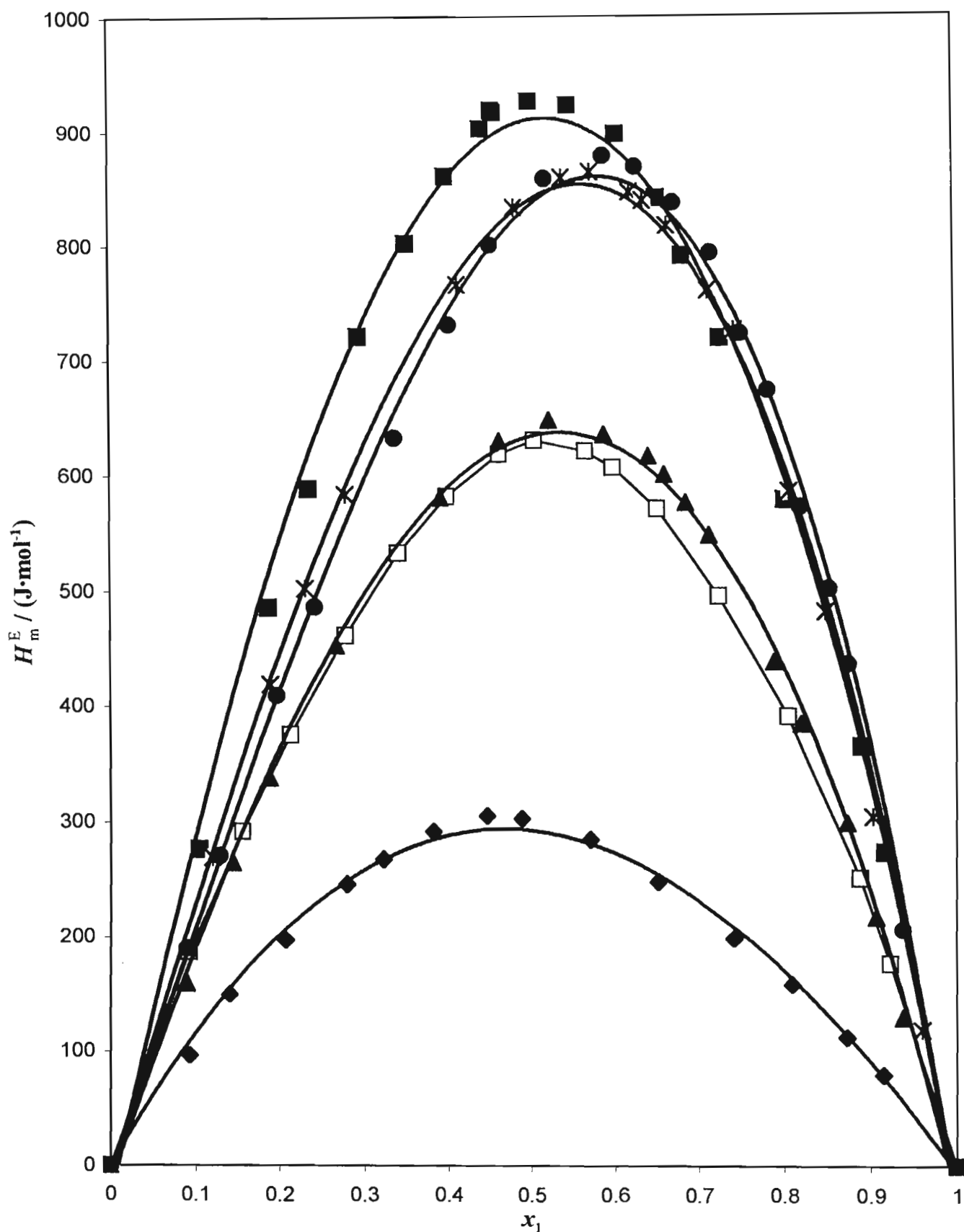
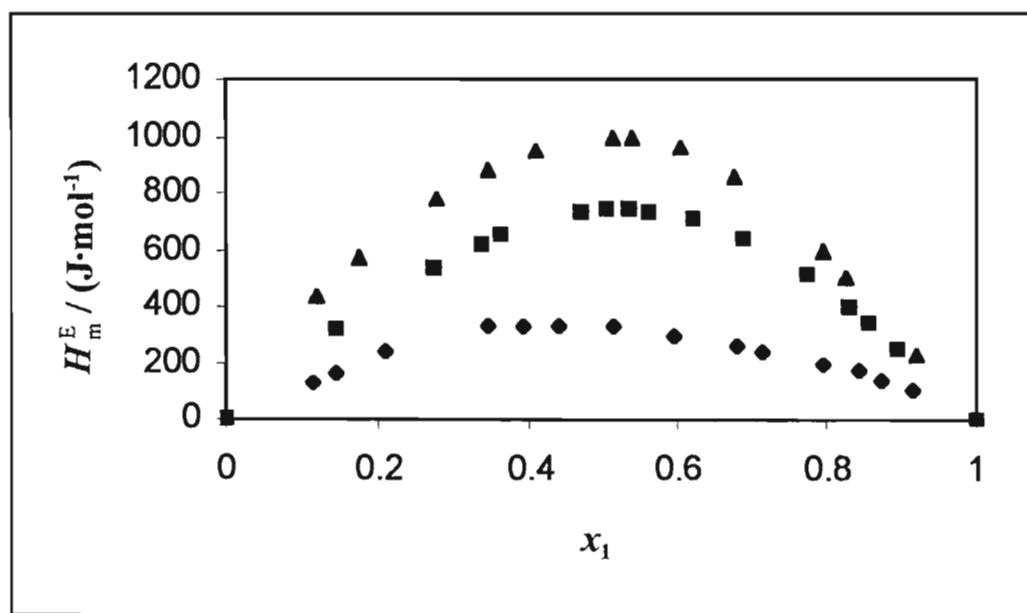


Figure 3.12 Excess molar enthalpies for the systems [Acetonitrile (1) + a Carboxylic Acid (2)] at  $T = 298.15\text{ K}$ , plotted as a function of mole fraction  $x_1$ . Key ◆ = Acetic Acid. □ = Propanoic Acid. ▲ = Butanoic Acid. ■ = 2-Methylpropanoic Acid. × = Pentanoic Acid. ● = 3-Methylbutanoic Acid.



3.4.1.1 *Discussion*Previous Work

The excess enthalpy values for all six of the above systems at 298.15 K have not been reported in the literature. However,  $H_m^E$  for three systems namely (acetonitrile + acetic acid or propanoic acid or 2-methylpropanoic acid) at 308.15 K have been reported by Lark and Banipal (1985) in the literature. The results for their work is plotted in Figure 3.13. Lark and Banipal report a standard deviation of the order of 1% of the measured  $H_m^E$  value which relates to an error of  $10 \text{ J}\cdot\text{mol}^{-1}$  in the worst case. This is not better than the estimated error of  $2 \text{ J}\cdot\text{mol}^{-1}$  reported in this work. Lark and Banipal's results show that the excess molar enthalpies for the mixtures increase with an increase in the carbon chain number of the carboxylic acid. This is consistent with the results obtained in this work. The literature data of Lark and Banipal also show correspondingly higher excess molar enthalpy values at the higher temperature of 308.15 K when compared to the results obtained in this work.



**Figure 3.13** Excess molar enthalpies for the systems [Acetonitrile (1) + a Carboxylic Acid (2)] at 308.15 K (Lark and Banipal, 1985). ◆, acetic acid; ■, propanoic acid; ▲, 2-methylpropanoic acid.

Excess enthalpy measurements have been reported on related systems. Endothermic effects were observed for (acetonitrile and ethylethanoate or propylentanoate or butyl ethanoate by Mato *et al.* (1973), for (acetonitrile + 1 propanol or 2-propanol or butanol) by Nagata and Tamura (1988), and for (acetonitrile + diethyl ether or dipropyl ether or di-1-methylethyl ether or dibutyl ether or 1,1-dimethylethyl methyl ether or 1,1 dimethylpropyl methyl ether or tetrahydropyran) by Letcher and Domanska (1994). The overall endothermic effects seen in the first two mixtures are most probably due to the breakdown of self association between acetonitrile molecules, and ester molecules or between alcohol molecules, whilst in the case of the latter (acetonitrile + ether) mixtures, the positive enthalpy value is due to the breakdown of the acetonitrile self association (positive effect), the positive effect of the breakdown of the ether self association, and the negative effect of the acetonitrile-ether association.

### This Work

The  $H_m^E$  results are presented in Table 3.3 and plotted in Figure 3.12. The excess molar enthalpies for all six systems, namely (acetonitrile + acetic acid or propanoic acid or butanoic acid or 2-methylpropanoic acid or pentanoic acid or 3-methylbutanoic acid) are positive over the entire composition range at 298.15 K. In this study the effect of an increase in the carboxylic acid chain length on the excess molar enthalpies was investigated.

Acetonitrile is a typical aprotic, dipolar simple organic liquid with a carbon-nitrogen triple bond and an unshared electron pair on the nitrogen atom. X-ray analysis on pure acetonitrile has revealed that the linear acetonitrile dipoles are arranged in antiparallel positions and that definite short range ordering between molecules is due to the dipole - dipole interaction (Brown and Smith, 1962).

The carboxylic acids in pure form tend to exist mainly as dimers. However, trimers formed because of strong interaction between dimers and monomers also exist (Affsprung *et al.*, 1968). It is most likely that the following four-step equilibria, proposed by Lark and Banipal (1985) accompanies the mixing process:



- ii)  $D \rightarrow 2 M$
- iii)  $A-A \rightarrow A + A$
- iv)  $M + A \rightarrow M-A$

where D and M denote a dimer and monomer of the carboxylic acid respectively, and A denotes acetonitrile. The overall magnitude of  $H_m^E [x_1 \text{ CH}_3\text{CN} + (1-x_1) \text{RCOOH}]$  is most likely a result of the competition between the four steps, and is therefore most probably due to the breakdown of the acetonitrile self association (step iii - a positive enthalpy), the breakdown of the carboxylic acid (dimers as well as trimers) self association (step i and step ii - a positive enthalpy), and the negative effect of the (acetonitrile - carboxylic acid) association given by step iv. The trend in  $H_m^E$  at equimolar concentrations of (acetonitrile + carboxylic acid) mixtures is given in Table 3.5.

In view of the above equilibria, it is most likely that endothermic contributions from the first three equilibria outweigh possibly small contributions from the last one. This view is supported by Thacker and Rowlinson (1954) who have found evidence of insignificant hydrogen bond formation between acetonitrile and ethanol molecules, resulting in appreciable endothermic mixing of (acetonitrile + ethanol) mixtures arising mainly from the depolymerization of the alcohol.

**Table 3.5**      $H_m^E$  at equimolar concentrations for the mixtures of (acetonitrile + a carboxylic acid) at T = 298.15 K

CARBOXYLIC ACID	$H_m^E / (\text{J} \cdot \text{mol}^{-1})$
Acetic acid	291.9
Propanoic acid	621.9
Butanoic acid	633.3
2-methylpropanoic acid	909.5
Pentanoic acid	837.9
3-methylbutanoic acid	833.1

The  $H_m^E$  curves are all reasonably symmetrical and have maxima for  $x_1$  (acetonitrile) ranging from 0.4 to 0.6 mole fraction units. The excess molar enthalpies are most positive in the case

of 2-methylpropanoic acid, and the magnitude decreases in the order : 2-methylpropanoic acid > 3-methylbutanoic acid ~ pentanoic acid > butanoic acid ~ propanoic acid > acetic acid.

The results of this work indicate in general that the longer the alkyl group of the carboxylic acid, the weaker is the interaction of carboxylic acid with acetonitrile, and it appears as though the long alkyl groups shield the carbonyl oxygen atom of the carboxylic acid from interaction. The results have been interpreted by assuming  $n-\pi$  interactions to occur between the lone pair electrons of the carbonyl oxygen atom (carboxylic acid) and the  $\pi$  electrons of the acetonitrile. This study also indicates that in the case of the branched carboxylic acids, viz., 2-methylpropanoic acid and 3-methylbutanoic acid, the increase in steric crowding due to the methyl groups as well as increasing acid dimerization constants, leads to an increase in the excess enthalpy. This is further supported by Letcher and Domańska (1994) who have found a stronger association of acetonitrile with a branched ether than with a straight chain ether (ROR). They have attributed this result to the inductive effect of the substituted methyl groups increasing the electron density on the oxygen atom of the ether and giving rise to enhanced  $n-\pi$  interactions.

### 3.4.2 Excess Molar Enthalpy Data for Mixtures of [Butanenitrile + a Carboxylic Acid] at 298.15 K

**Table 3.6** Physical Properties of the Pure Components at T = 298.15 K: Densities,  $\rho$  Refractive Indices,  $n_D$

Component	$\rho/(\text{g}\cdot\text{cm}^{-3})$		$n_D$	
	exp	lit <sup>a</sup>	exp	lit <sup>a</sup>
Butanenitrile	0.7866	0.7865	1.3822	1.3820
Acetic acid	1.0437	1.0439	1.3697	1.3698
Propanoic acid	0.9884	0.9881	1.3846	1.3843
Butanoic acid	0.9535	0.9532	1.3955	1.3958
2-Methylpropanoic acid	0.9431	0.9429	1.3913	1.3917
Pentanoic acid	0.9346	0.9345	1.4064	1.4060
3-Methylbutanoic acid	0.9216	0.9219	1.4019	1.4022

<sup>a</sup> Riddick. *et al.* (1986)

**Table 3.7** Excess molar enthalpies  $H_m^E$  for the systems : [Butanenitrile (1) + a Carboxylic Acid (2)] and the Deviations,  $\delta H_m^E$ , calculated from equation (3.17) and the parameters of Table 3.8 at the experimental temperature of 298.15 K, as a function of Mole Fraction  $x_1$ .

$x_1$	$H_m^E/\text{J}\cdot\text{mol}^{-1}$	$\delta H_m^E/\text{J}\cdot\text{mol}^{-1}$	$x_1$	$H_m^E/\text{J}\cdot\text{mol}^{-1}$	$\delta H_m^E/\text{J}\cdot\text{mol}^{-1}$
Acetic Acid					
0.0388	54.8	2.9	0.4611	296.4	-1.6
0.0650	94.6	1.9	0.5659	274.0	-1.0
0.1153	146.2	4.9	0.6398	244.6	-0.6
0.1676	204.8	4.5	0.7134	208.8	2.6
0.2332	246.8	0.1	0.7887	159.4	0.8
0.3229	287.8	1.6	0.8916	83.4	-1.0
0.4151	299.5	-1.1	0.9459	40.9	-1.6
Propanoic Acid					
0.0458	64.2	0.3	0.4991	355.2	0.2
0.1156	149.3	0.2	0.5141	354.5	0.2
0.1653	200.7	-0.0	0.6194	322.2	0.2
0.1946	227.6	-0.0	0.7061	290.9	-0.1
0.2283	255.2	-0.1	0.7939	228.4	-0.4
0.2756	288.2	-0.2	0.8569	171.0	-0.4
0.3398	322.3	-0.2	0.9199	103.2	0.1
0.3950	342.0	-0.1	0.9651	48.4	1.2
0.4425	351.9	0.1			
Butanoic Acid					
0.0549	58.8	0.4	0.6122	365.9	-0.7
0.1312	129.3	-2.9	0.6833	343.4	-1.6
0.1789	175.2	0.7	0.7556	301.1	-0.1
0.2410	226.9	1.7	0.8341	235.0	4.7
0.3035	271.3	0.6	0.8852	174.1	5.3
0.4036	329.5	0.6	0.9225	115.1	-4.6
0.5054	363.2	-0.8	0.9577	59.2	-8.5
0.5586	369.7	-0.5			
2-Methylpropanoic Acid					
0.0827	82.2	0.6	0.6275	392.1	-1.9
0.1521	150.8	0.1	0.6686	382.7	0.5
0.2341	221.0	-6.8	0.7408	353.5	8.9
0.3037	291.8	5.9	0.8347	256.9	-3.3
0.3740	342.9	8.2	0.8831	195.5	-4.2
0.4326	360.1	-5.9	0.9230	138.8	-1.6
0.4975	386.0	-3.4	0.9564	88.8	5.0
0.5641	398.1	-1.2			

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Pentanoic Acid					
0.0855	82.9	-8.9	0.6085	407.0	-2.2
0.1532	164.0	7.1	0.6708	391.7	-1.8
0.2410	235.5	0.9	0.7166	376.7	6.6
0.3402	310.8	-1.2	0.7906	311.5	1.7
0.4548	381.1	1.3	0.8640	225.0	2.2
0.5440	406.2	-1.3	0.9058	156.5	-5.4
0.5957	408.1	-2.2	0.9497	88.3	-1.9
3-Methylbutanoic Acid					
0.0886	85.7	0.3	0.6155	428.3	-0.6
0.1652	153.4	-5.7	0.6694	417.4	0.6
0.2290	225.7	6.5	0.7049	399.9	-1.1
0.3318	309.0	0.3	0.7767	350.4	2.0
0.4328	376.7	-2.7	0.8540	259.1	-0.3
0.4972	412.6	-2.0	0.8985	199.6	6.8
0.5592	425.7	-1.6	0.9453	100.2	-10.6

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**Table 3.8**      **Coefficients  $A_r$  and standard deviations  $\sigma$  from equation (3.18) for the excess molar enthalpies of systems: [Butanenitrile (1) + a Carboxylic Acid (2)] at T = 298.15 K.**

Component	$A_0$	$A_1$	$A_2$	$A_3$	$\sigma(H_m^E)/(\text{J}\cdot\text{mol}^{-1})$
Acetic Acid	1170.0	381.8	17.3	16.4	2.4
Propanoic Acid	1420.0	52.8	13.9	-22.6	0.4
Butanoic Acid	1452.0	-434.5	-65.6	161.2	3.5
2-Methylpropanoic Acid	1560.0	-502.1	-54.9	-47.3	5.1
Pentanoic Acid	1589.0	-624.9	-77.9	257.2	4.4
3-Methylbutanoic Acid	1647.0	-743.7	-83.7	142.3	4.6

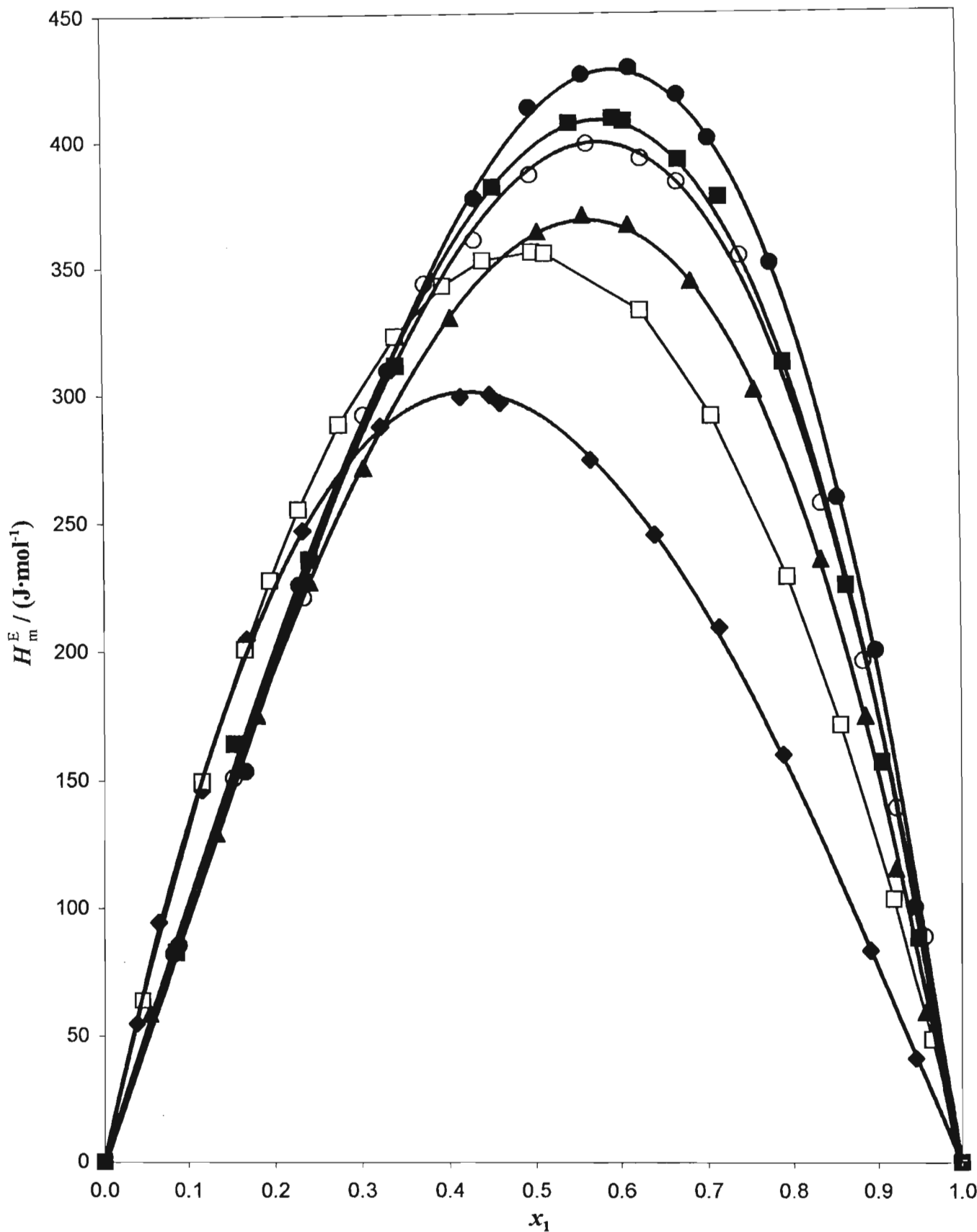


Figure 3.14

Excess molar enthalpies for the systems [Butanenitrile(1) + a Carboxylic Acid (2) at  $T = 298.15 \text{ K}$  plotted as a function of mole fraction  $x_1$ . Key ◆ = Acetic Acid. □ = Propanoic Acid. ▲ = Butanoic Acid. ○ = 2-Methylpropanoic Acid. ■ = Pentanoic Acid. ● = 3-Methylbutanoic Acid.



### 3.4.2.1 Discussion

#### Previous Work

In continuation of the study on the thermodynamic effects of mixtures containing industrially important compounds by Letcher and co-workers (1994, 1996, 1998, 1999, 2000), in this work, the excess molar enthalpies ( $H_m^E$ ) of the six liquid mixtures (butanenitrile + acetic acid or propanoic acid or butanoic acid or 2-methylpropanoic acid or pentanoic acid or 3-methylbutanoic acid) have been determined over the whole composition range at the temperature of  $T = 298.15$  K. Excess enthalpy values for all of the above mixtures at  $T = 298.15$  K have not been previously reported in the literature.

Excess enthalpy measurements have been reported on related systems. Endothermic effects were observed for (butanenitrile + ethanol or butan-1-ol by Garriga *et al.* (1995a) for (butanenitrile - propan-1-ol or propan-2-ol) by Garriga *et al.* (1995b), for (butanenitrile + methanol, + pentan-1-ol, + heptan-1-ol, + nonan-1-ol, or decan-1-ol) by Garriga *et al.* (1996), for (butanenitrile + 2-butanol) by Garriga *et al.* (1997) and, for (butanenitrile + hexan-1-ol or octan-1-ol) by Garriga *et al.* (1995c).

#### This Work

The  $H_m^E$  results are presented in Table 3.7 and plotted in Figure 3.14. The  $H_m^E$  values for the mixtures under investigation are positive over the whole composition range, and the magnitude decreases in the order: 3-methylbutanoic acid > pentanoic acid > 2-methylpropanoic acid > butanoic acid > propanoic acid > acetic acid.  $H_m^E$  ranges from 299 J·mol<sup>-1</sup> for acetic acid to 426 J·mol<sup>-1</sup> for 3-methylbutanoic acid.

Butanenitrile is also a strong, polar solvent with a carbon-nitrogen triple bond and an unshared electron pair on the nitrogen atom.. The carboxylic acids are strongly polar and in pure form tend to exist mainly as dimers (Affsprung *et al.*, 1968). On mixing of butanenitrile with the carboxylic acids it is likely that the same four-step equilibria proposed by Lark and Banipal (1985) is applicable (Section 3.4.1.1). This equilibria, where acetonitrile is replaced by butanenitrile may be used to explain the mixing process. It is likely that endothermic

contributions from the first three steps are the major ones and outweigh possibly small exothermic contributions from the fourth step. The overall magnitude of  $H_m^E$  [ $x_1\text{CH}_3(\text{CH}_2)_2\text{CN} + (1 - x_1)\text{RCOOH}$ ] is therefore most probably due to the breakdown of the butanenitrile self-association (step iii - a positive enthalpy), the breakdown of the carboxylic acid (dimers) self-association (step i and step ii - a positive enthalpy) and the negative effect of the (butanenitrile-carboxylic acid) polar-polar association, given by step iv.

The trend in  $H_m^E$  at equimolar concentrations of (butanenitrile + carboxylic acid) mixtures is given in Table 3.9.

**Table 3.9**  $H_m^E$  at equimolar concentrations for the mixtures of (butanenitrile + a carboxylic acid) at  $T = 298.15\text{ K}$

CARBOXYLIC ACID	$H_m^E / (\text{J} \cdot \text{mol}^{-1})$
Acetic acid	293.0
Propanoic acid	357.2
Butanoic acid	361.6
2-methylpropanoic acid	388.7
Pentanoic acid	396.7
3-methylbutanoic acid	410.2

The results of this work indicate in general that the longer the alkyl group of the carboxylic acid, the weaker is the interaction with butanenitrile, and it most definitely appears as though the long alkyl groups shield the carbonyl oxygen atom of the carboxylic acid from interaction. A similar result has been obtained by Garriga *et al.* (1995c) in the study of (butanenitrile + alcohol) mixtures. The (butanenitrile + carboxylic acid) results have been interpreted by assuming  $n-\pi$  interactions to occur between lone-pair electrons of the oxygen atom and the  $\pi$  electrons of butanenitrile. The results also indicate that in the case of the branched carboxylic acids, viz, 2-methylpropanoic acid and 3-methylbutanoic acid, the increase in steric crowding due to the additional methyl groups, leads to an increase in the excess enthalpy. The position of the maxima for  $H_m^E$  (butanenitrile + acetic acid) shifts slowly to the butanenitrile-rich region of the mole fraction scale as the methylation of acetic acid increases. This could possibly be explained by the increase in both the dimerization constants as well as increasing steric hindrance caused by additional methyl groups. In the case of the dimerization constants,

the increased values should reduce the number of (D-M) trimers in equilibrium, and as can be observed from the proposed four step equilibria, this leads to a decreasing endothermic influence of the carboxylic acid components (steps i and ii) resulting in a slight shift of the maxima to the benzonitrile-rich region of the mole-fraction scale.

Comparative  $H_m^E$  (max) values for mixtures of (butanenitrile + heptane) (McLure and Rodriguez, 1982): and (acetic acid + heptane) (Nagata *et al*, 1975) obtained in the literature are found to be positive and ( $< 1350 \text{ J}\cdot\text{mol}^{-1}$ ) and ( $< 925 \text{ J}\cdot\text{mol}^{-1}$ ) respectively. The relatively small  $H_m^E$  values obtained in this work ( $< 450 \text{ J}\cdot\text{mol}^{-1}$ ) suggest that a significant amount of cross association takes place between the butanenitrile and carboxylic acid components.

From the work by Garriga and co-workers (1995a, 1995b, 1995c) on different alcohols with butanenitrile, it is found that the  $H_m^E$  increases progressively with an increase in the chain length of the alcohol. This may be explained as follows: in mixtures of butanenitrile with an alcohol there is in addition to the hydrogen bond contribution (interaction between the hydroxyl hydrogen of the alcohol and the lone pair of the nitrogen atom in butanenitrile), also an important contribution due to the mixing of the alcohol chain with the butanenitrile which arises from the breaking of strong nitrile-to-nitrile interactions and at a given composition these interactions will be larger in solutions of longer chain alcohols.

### 3.4.3 Excess Molar Enthalpy Data for Mixtures of [Benzonitrile + a Carboxylic Acid] at 298.15 K

**Table 3.10 Physical Properties of the Pure Components at  $T = 298.15 \text{ K}$ : Densities,  $\rho$  Refractive Indices,  $n_D$**

Component	$\rho/(\text{g}\cdot\text{cm}^{-3})$		$n_D$	
	exp	lit <sup>a</sup>	exp	lit <sup>a</sup>
Benzonitrile	1.0003	1.0006	1.3413	1.3416
Acetic acid	1.0437	1.0439	1.3697	1.3698
Propanoic acid	0.9884	0.9881	1.3846	1.3843
Butanoic acid	0.9535	0.9532	1.3955	1.3958
2-Methylpropanoic acid	0.9431	0.9429	1.3913	1.3017
Pentanoic acid	0.9346	0.9345	1.4064	1.4060
3-Methylbutanoic acid	0.9216	0.9219	1.4019	1.4022

<sup>a</sup> Riddick *et al.* (1986)

**Table 3.11** Excess molar enthalpies  $H_m^E$  for the systems : [Benzonitrile (1) + a Carboxylic Acid (2) and the Deviations,  $\delta H_m^E$ , calculated from equation (3.17) and the parameters of Table 3.12 at the experimental temperature of 298.15 K, as a function of Mole Fraction  $x_1$ .

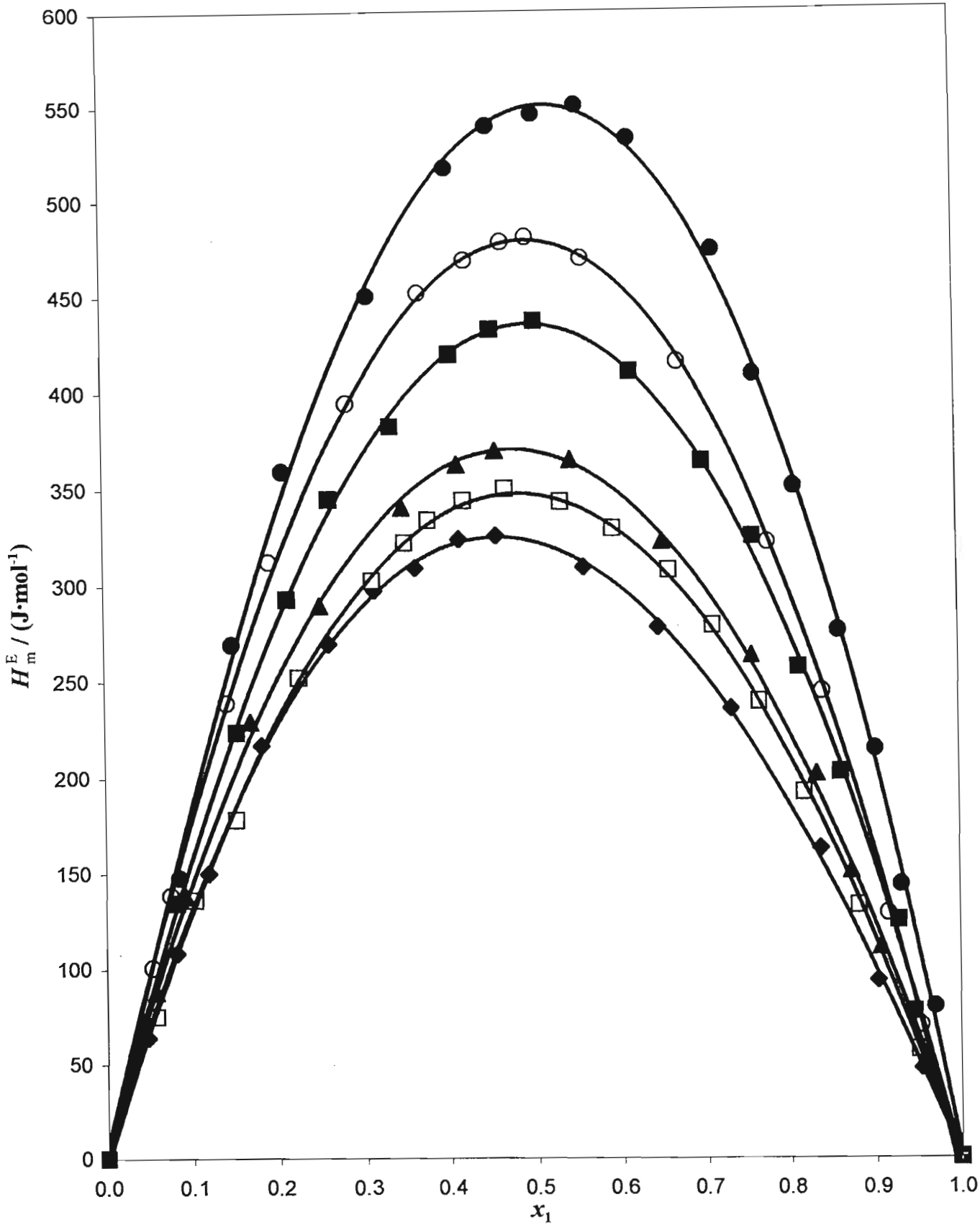
$x_1$	$H_m^E/\text{J}\cdot\text{mol}^{-1}$	$\delta H_m^E/\text{J}\cdot\text{mol}^{-1}$	$x_1$	$H_m^E/\text{J}\cdot\text{mol}^{-1}$	$\delta H_m^E/\text{J}\cdot\text{mol}^{-1}$
Acetic Acid					
0.0475	63.7	-3.0	0.4569	325.3	0.9
0.0813	108.1	-1.3	0.5582	308.7	-1.8
0.1181	150.0	-1.3	0.6449	277.2	-2.0
0.1815	216.7	4.2	0.7311	234.8	2.4
0.2599	269.3	0.3	0.8359	162.0	5.1
0.3133	297.1	1.3	0.9028	93.2	-5.4
0.3623	308.6	-3.8	0.9453	46.9	-1.6
0.4144	323.6	1.4			
Propanoic Acid					
0.0578	74.8	-2.8	0.5324	342.4	-3.0
0.1025	135.9	4.7	0.5933	328.6	-2.9
0.1512	178.0	-4.9	0.6588	306.8	2.1
0.2258	251.9	3.2	0.7088	278.1	2.3
0.3107	301.9	-1.7	0.7652	238.2	1.5
0.3501	321.8	0.1	0.8179	190.9	-1.9
0.3780	333.4	1.6	0.8807	131.9	-0.8
0.4202	343.2	0.6	0.9512	56.5	-0.2
0.4678	349.2	0.8			
Butanoic Acid					
0.0577	88.0	-3.6	0.5440	364.0	1.9
0.0919	137.9	-0.2	0.6513	321.9	-4.7
0.1689	229.1	4.8	0.7563	262.4	1.7
0.2499	289.2	-1.8	0.8324	200.6	6.4
0.3471	339.9	-2.6	0.8721	150.3	-3.4
0.4127	361.7	0.4	0.9065	110.8	-4.8
0.4566	368.9	1.9	0.9621	52.1	3.3
2-Methylpropanoic Acid					
0.0538	100.9	-3.3	0.4953	480.2	0.3
0.0748	138.4	-2.1	0.5598	469.0	-2.4
0.1409	238.7	-2.1	0.6719	414.5	-1.0
0.1928	312.1	6.0	0.7776	321.3	4.5
0.2834	394.1	-0.3	0.8398	243.3	3.3
0.3693	451.3	1.7	0.9151	128.0	-4.4
0.4246	468.4	-2.0	0.9534	69.1	-4.3
0.4664	477.7	-0.7			

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Pentanoic Acid					
0.0821	134.1	0.5	0.6153	409.8	-1.9
0.1523	223.5	-3.3	0.6993	363.0	-1.6
0.2128	292.5	-0.2	0.7589	324.3	8.4
0.2619	344.3	7.5	0.8129	256.0	-5.1
0.3348	382.0	-5.3	0.8603	201.3	-3.5
0.4060	418.9	-0.4	0.9278	124.2	11.6
0.4533	431.6	0.6	0.9457	76.4	-9.5
0.5042	435.9	1.0			
3-Methylbutanoic Acid					
0.0854	147.5	-14.3	0.6170	532.4	3.5
0.1477	269.0	6.5	0.7147	473.3	10.1
0.2091	358.8	11.2	0.7621	408.1	-6.5
0.3087	449.8	-5.1	0.8096	349.9	-4.9
0.4036	516.9	-3.8	0.8597	275.2	-4.2
0.4521	539.3	-0.7	0.9018	213.5	7.4
0.5051	545.5	-4.1	0.9309	142.9	-7.3
0.5562	549.9	2.7	0.9702	79.0	11.2

**Table 3.12** Coefficients  $A_i$  and standard deviations  $\sigma$  from equation (3.18) for the excess molar enthalpies of systems: [Benzonitrile (1) + a Carboxylic Acid (2)] at  $T = 298.15$  K.

Component	$A_0$	$A_1$	$A_2$	$A_3$	$\sigma(H_m^E)/(J \cdot mol^{-1})$
Acetic Acid	1287.0	239.6	7.8	-47.8	3.0
Propanoic Acid	1394.0	90.3	-85.0	29.6	2.6
Butanoic Acid	1469.0	110.8	59.9	101.4	3.7
2-Methylpropanoic Acid	1919.0	48.2	-80.5	208.0	3.3
Pentanoic Acid	1740.0	-5.6	-15.5	84.5	5.8
3-Methylbutanoic Acid	2197.0	-176.9	5.6	29.5	7.9



**Figure 3.15** Excess molar enthalpies for the systems [Benzonitrile (1) + a Carboxylic Acid (2)] at  $T = 298.15 \text{ K}$  plotted as a function of mole fraction  $x_1$ . Key ♦ = Acetic Acid. □ = Propanoic Acid. ▲ = Butanoic Acid. ○ = 2-Methylpropanoic Acid. ■ = Pentanoic Acid. ● = 3-Methylbutanoic Acid.

### 3.4.3.1 Discussion

#### Previous Work

In continuation of the study on the thermodynamic effects of mixtures containing industrially important compounds by Letcher and co-workers (1994, 1996, 1998, 1999, 2000), the excess molar enthalpies ( $H_m^E$ ) for the six liquid mixtures: (Benzonitrile + acetic acid or propanoic acid or butanoic acid or 2-methylpropanoic acid or pentanoic acid or 3-methylbutanoic acid) have been obtained over the whole composition range at the temperature of  $T = 298.15$  K. Literature searches have revealed that excess enthalpy values for all of the above mixtures at  $T = 298.15$  K have not been reported in the literature.

Excess enthalpy measurements have been reported on related systems. Endothermic effects were observed for (benzonitrile + cyclohexane, + benzene, + toluene, or chlorobenzene) by Tanaka *et al.* (1974), and, for (benzonitrile + benzene or toluene) by Wilhelm *et al.* (1998).

#### This Work

The  $H_m^E$  results are presented in Table 3.11 and plotted in Figure 3.15. The  $H_m^E$  values for the mixtures under investigation are positive over the whole composition range, and the magnitude decreases in the order: 3-methylbutanoic acid > 2-methylpropanoic acid > pentanoic acid > butanoic acid > propanoic acid > acetic acid. The  $H_m^E$  curves are all reasonably symmetrical, although somewhat skewed towards the benzonitrile rich-region of the mole fraction scale. The  $H_m^E$  values range from  $325 \text{ J}\cdot\text{mol}^{-1}$  for acetic acid to  $550 \text{ J}\cdot\text{mol}^{-1}$  for 3-methylbutanoic acid.

Benzonitrile is a strongly polar, aromatic solvent with a carbon-nitrogen triple bond and an unshared electron pair on the nitrogen atom. The carboxylic acids are strongly polar and in pure form tend to exist mainly as dimers (Affsprung *et al.*, 1968). The same four-step mechanism proposed by Lark and Banipal (1985) and discussed in 3.4.1.1. is assumed to occur. In this mechanism acetonitrile is replaced by benzonitrile.

It is likely that endothermic contributions from the first three steps are the major ones and



outweigh possibly small exothermic contributions from the fourth step. The overall magnitude of  $H_m^E$  [ $x_1C_6H_5CN + (1 - x_1) RCOOH$ ] is therefore most probably due to the breakdown of the benzonitrile self-association (step iii - a positive enthalpy), the breakdown of the carboxylic acid (dimers) self-association (step i and step ii - positive enthalpy) and the negative effect of the (benzonitrile-carboxylic acid) polar-polar association given by step iv.

The trend in  $H_m^E$  at equimolar concentrations of (benzonitrile + carboxylic acid) mixtures is given in Table 3.13.

**Table 3.13**     $H_m^E$  at equimolar concentrations for the mixtures of (benzonitrile + a carboxylic acid) at T = 298.15 K

CARBOXYLIC ACID	$H_m^E / (J \cdot mol^{-1})$
Acetic acid	322.1
Propanoic acid	346.4
Butanoic acid	368.8
2-methylpropanoic acid	478.5
Pentanoic acid	434.4
3-methylbutanoic acid	549.3

The results of this work indicate that the longer the alkyl group of the carboxylic acid, the weaker is the interaction with benzonitrile, and it appears as though the long alkyl groups shield the carbonyl oxygen atom of the carboxylic acid from interaction. The results have been interpreted by assuming n- $\pi$  interactions to occur between lone-pair electrons of the carbonyl oxygen atom and the  $\pi$  electrons of benzonitrile. The results also indicate that in the case of the branched carboxylic acids, viz., 2-methylpropanoic acid and 3-methylbutanoic acid, the increase in steric crowding due to the additional methyl groups, leads to an increase in the excess enthalpy. A similar effect has been obtained by Letcher and Domańska (1994) in their study of (acetonitrile + ether) mixtures. Letcher and Domańska (1994) have reported that acetonitrile forms a stronger association with a branched ether than a normal ether, and have alluded to the fact that this could well be due to the inductive effect of the substituted methyl groups increasing the electron density on the oxygen atom, resulting in an enhanced n-  $\pi$  interaction.

Comparative  $H_{m,\max}^E$  values for mixtures of (benzonitrile + heptane) (Tanaka *et al.*, 1974) and (acetic acid + heptane) (Nagata *et al.*, 1975), obtained in the literature are found to be positive and ( $< 1400 \text{ J}\cdot\text{mol}^{-1}$ ) and ( $< 925 \text{ J}\cdot\text{mol}^{-1}$ ) respectively. The relatively small  $H_m^E$  values obtained in this work ( $< 550 \text{ J}\cdot\text{mol}^{-1}$ ) suggest that a significant amount of cross association takes place between the benzonitrile and carboxylic acid components.

The position of the maxima for  $H_m^E$  (benzonitrile + acetic acid) shifts slowly to the benzonitrile-rich region of the mole fraction scale as the methylation of acetic acid increases. This could possibly be explained by the increase in both the acid dimerization constants as well as increasing steric hindrance caused by additional methyl groups. In the case of the dimerization constants, the increased values should reduce the number of (D-M) trimers in equilibrium, and from the proposed four step equilibria, this leads to a decreasing endothermic influence of the carboxylic acid components (steps i and ii) resulting in a slight shift of the maxima to the benzonitrile-rich region of the mole-fraction scale.

The  $H_m^E$  work already published involves mixtures of a strongly polar liquid (benzonitrile), with non-polar or slightly polar aromatic and aliphatic compounds. The  $H_m^E$  (max) results obtained are positive and range from  $\sim 1400 \text{ J}\cdot\text{mol}^{-1}$  in the case of cyclohexanol to  $< 70 \text{ J}\cdot\text{mol}^{-1}$  in the case of the aromatic compounds. This could possibly be explained as follows: the large  $H_m^E$  of mixtures of a polar liquid having a large dipole moment with an aliphatic liquid is indicative of self association of the polar molecules. The smaller values of  $H_m^E$  for mixtures of (polar liquid + aromatic liquid), than for mixtures of (polar liquid + aliphatic) liquid are attributed to the dipolar stabilization of polar components in aromatic solution.

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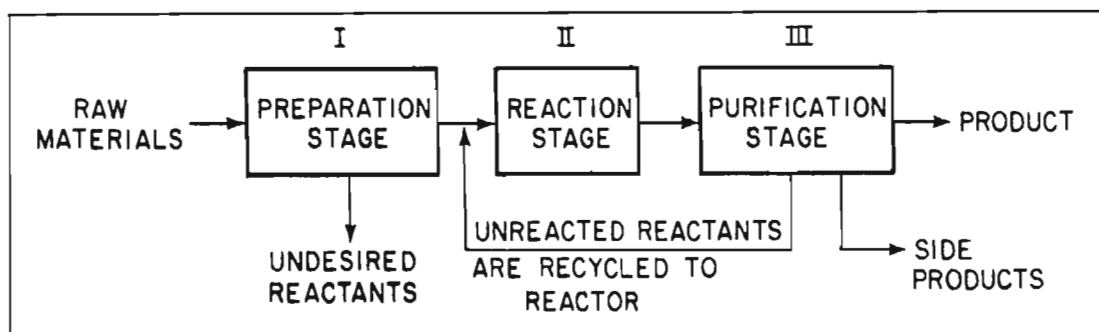
## CHAPTER 4

### THE PHASE-EQUILIBRIUM PROBLEM

#### 4.1 INTRODUCTION

Phase separation is a common industrial, physiological phenomenon and involves the transfer of a substance from one phase to another. This occurs because when two phases are brought into contact, they tend to exchange their constituents until the composition of each phase attains a constant value, and when this state is reached, the phases are said to be in equilibrium. The equilibrium composition of two phases are usually very different from one another, and it is precisely this difference which enables us to separate mixtures by distillation, extraction, and other phase-contacting operations. (Prausnitz *et al.*, 1986).

The final, or equilibrium, phase composition depend on several variables, such as temperature and pressure, and on the chemical nature and concentrations of the substances in the mixture. Phase - equilibrium thermodynamics seeks to establish the relations among the various properties (in particular, temperature, pressure and composition) which ultimately prevail when two or more phases reach a state of equilibrium wherein all tendency for further change has ceased. It is of special interest in chemistry and chemical engineering because so many operations in the manufacture of chemical products consist of phase contacting : extraction, adsorption, distillation, leaching and absorption are essential unit operations in the chemical industry and an understanding of any one of them is based, at least in part, on the science of phase equilibrium. Figure 4.1 below illustrates a typical industrial chemical process in which separations are crucial to the whole process. In a typical large-scale chemical plant, the financial investment for separation operations (Stages I and III) is approximately 50% of the total cost. (Prausnitz *et al.*, 1986).



**Figure 4.1** Scheme of a Chemical Plant

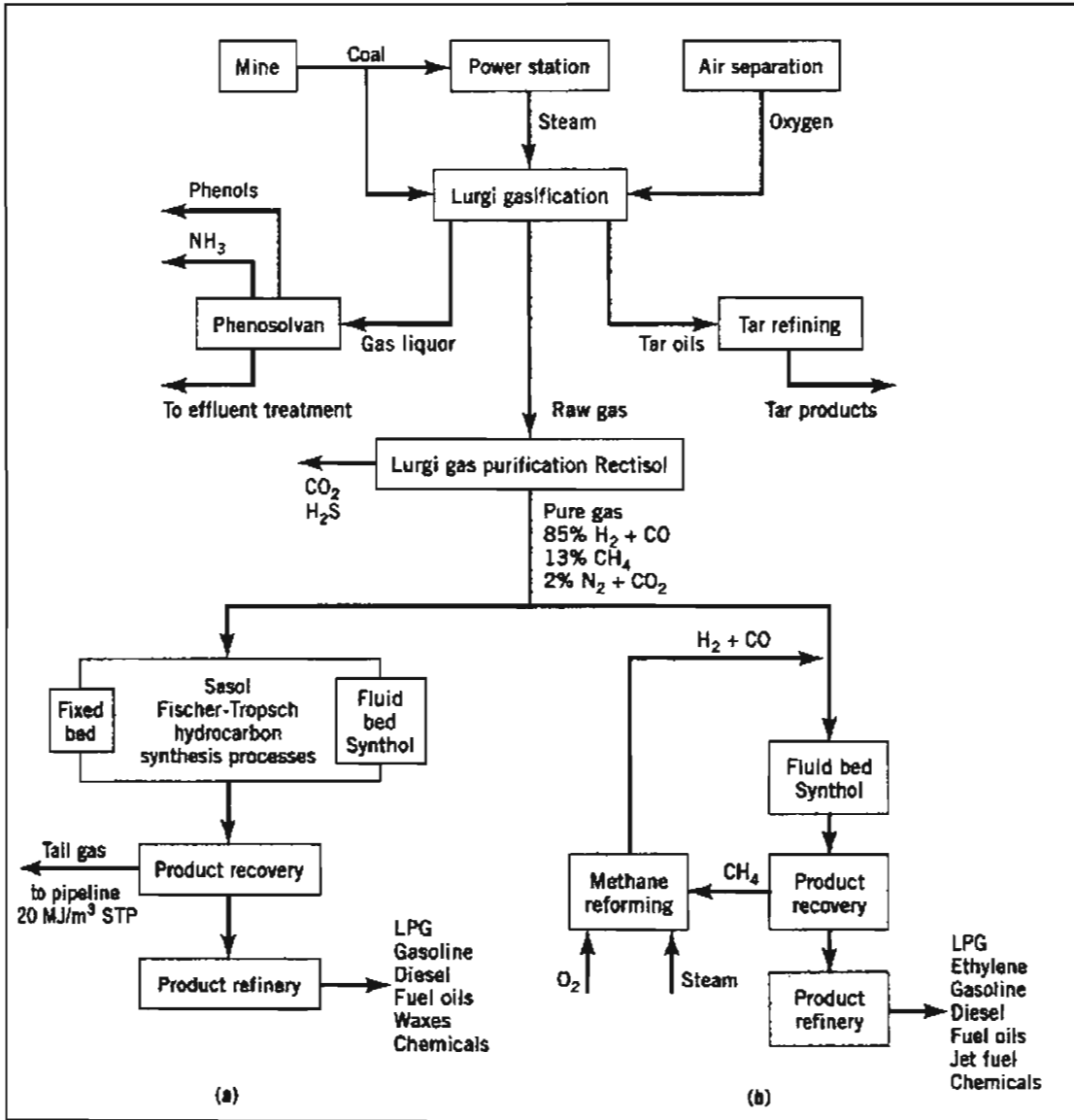
Equilibrium properties are required for the design of separation operations, and these in turn, are essential parts of the typical chemical plant, as shown in Figure 4.1. In this plant the central part stage II is the chemical reactor or "heart" of the plant. But in addition a plant needs a "mouth" (stage I) and a "digestive" system (stage III). Prior to reaction, the reactant must be prepared for reaction, since the raw materials provided by nature are usually mixtures. Separation is often required to separate the desired reactants from other components that are not necessary for, or may interfere with, the reactions. Down stream from the reactor, separation is necessary to separate desired from undesired products and since reaction is not normally complete, it is also necessary to separate the unreacted reactants for recycle.

#### 4.1.1 The SASOL Process

In 1955 the South African Coal, Oil, and Gas Corporation (SASOL) commercialized the production of liquid fuels utilizing the Fischer-Tropsch technology (Mako and Samuel, 1984). This SASOL I complex has evolved into the streaming of second generation plants known as SASOL II and SASOL III.

The SASOL I process shown in Figure 4.2 (a) combines fixed bed Ruhrchemie-Lurgi Arge reactor units with fluidized-bed Synthol process technology. For SASOL I,  $16000 \text{ tons} \cdot \text{day}^{-1}$  of coal is crushed and gasified with steam and oxygen. After a number of gas purification steps in which by-products and gas impurities are removed, the pure gas is purified in both fixed and fluidized-bed units simultaneously. Conversion to hydrocarbons is higher in the

Synthol unit and the ( $H_2/CO$ ) ratio is also higher. Since the fixed bed Arge reactor favours the formation of straight chain paraffins, there is greater production of diesel and wax fractions than the Synthol unit.



**Figure 4.2** Process flow sheet of (a) SASOL I and (b) the SASOL synfuel process for SASOL II and SASOL III

SASOL I produces a vast array of chemical and fuel products including gasoline. Separation of pure chemicals from mixtures by phase equilibria is an important part of the process.

The 1973 oil crisis resulted in the SASOL II unit, which started in early 1980. This was followed by SASOL III, which was commissioned two years later. The combined annual coal

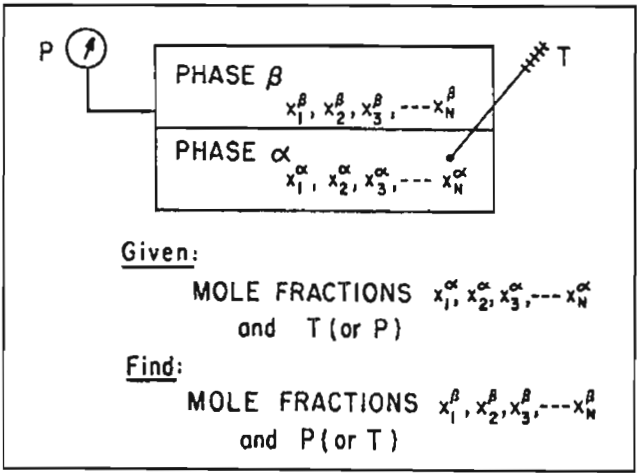
production for SASOL II and III is approximately  $25 \times 10^6$  tons, and these plants together produce approximately  $1.3 \times 10^4 \text{ m}^3$  (ie.80 000 barrels) of transportation fuels per day (Baldwin, 1993 ). The SASOL synfuel process is shown in Figure 4.2 (b). The SASOL II and III plants use only fluid-bed reactor technology, and extensive use of secondary catalytic processing (alkylation, polymerization etc.) is practiced to maximize the production of transportation fuels. Separation by phase equilibrium methods also plays an important part in the production of chemicals.

#### 4.2 ESSENCE OF THE PROBLEM

One needs to relate, quantitatively, the variables which describe the state of equilibrium of two or more homogeneous phases which are free to interchange energy and matter. By a homogeneous phase at equilibrium is meant any region in space where the intensive properties (viz. temperature, density, pressure and composition) are everywhere the same.

It is necessary to describe the state of two or more phases which are free to interact and which have reached a state of equilibrium. Then, given some of the equilibrium properties of the two phases, the next task is to predict the remaining ones.

Figure 4.3 illustrates schematically the type of problem which phase equilibrium thermodynamics seeks to solve. (Prausnitz *et al*, 1986).



**Figure 4.3 Statement of Problem**

Now, suppose that two multicomponent phases  $\alpha$  and  $\beta$ , have reached an equilibrium state and we are given the temperature  $T$  of the two phases and the mole fractions  $x_1^\alpha, x_2^\alpha, \dots$ , of phase  $\alpha$ . Our task, then, is to find the mole fractions  $x_1^\beta, x_2^\beta, \dots$  of phase  $\beta$  and the pressure  $P$  of the system. Alternatively, we might know  $x_1^\alpha, x_2^\alpha, \dots$  and  $P$  and be asked to find  $x_1^\beta, x_2^\beta, \dots$  and  $T$ , or the problem might involve still other combinations of known and unknown variables. The number of intensive properties that must be specified to fix unambiguously the state of equilibrium is given by the Gibbs phase rule. In the absence of chemical reactions, the phase rule is:

Number of independent  
intensive properties

=

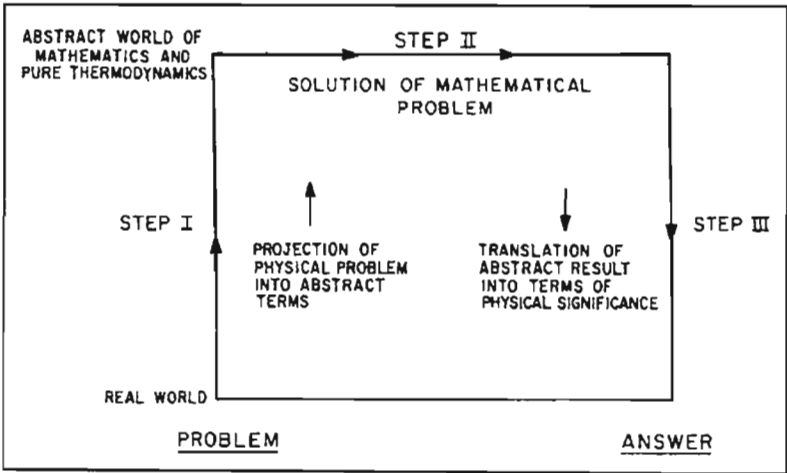
Number of components  
- Number of phases + 2

To solve the problem illustrated in Figure 4.3 one turns to thermodynamics.

4.3     **APPLICATION OF THERMODYNAMICS TO PHASE - EQUILIBRIUM PROBLEMS**

Thermodynamics provides the mathematical framework in which an abstract solution of the phase - equilibrium problem is readily obtained.

The application of thermodynamics to phase equilibria in multi-component systems is shown schematically in Figure 4.4 below. (Prausnitz *et al.*, 1986).



**Figure 4.4     Three-step application of thermodynamics to phase-equilibrium problems**

The real world and the real problem are represented by the lower horizontal line, while the upper horizontal line represents the world of abstraction. The three-step application of thermodynamics to a real problem consists of an indirect mental process, and instead of attempting to solve the real problem within the world of physically realistic variables, the indirect process first projects the problem into the abstract world, then seeks a solution within that world, and finally projects this solution back into physical reality. The solution of a phase equilibrium problem using thermodynamics requires three steps: In step I, the real problem is translated into an abstract mathematical problem; in step II a solution is found to the mathematical problem, and in step III the mathematical solution is translated back into physically meaningful terms.

The essential feature of step I is to define appropriate and useful mathematical functions to facilitate step II. The goal of step II was achieved by the profound insight of Willard Gibbs, who in 1875 defined such a function - the chemical potential. (Gibbs,1961). The mathematical solution of the phase - equilibrium problem is given by the remarkably simple result, that, at equilibrium, the chemical potential of each component must be the same in every phase.

In any problem concerning the equilibrium distribution of some component  $i$  between two phases  $\alpha$  and  $\beta$ , we always begin with the relation

$$\mu_i^\alpha = \mu_i^\beta, \text{ where } \mu \text{ is the chemical potential}$$

Although it can be seen that chemical potential provides a concise condition of equilibrium, unfortunately the chemical potential does not have an immediate equivalent in the physical world and it is therefore desirable to express the chemical potential in terms of some auxiliary function which might be more easily identified with physical reality. Such a function is supplied by the concept of fugacity, and in addition will facilitate certain calculations involved with phase and chemical equilibrium (Kyle, 1984).

In attempting to simplify the abstract equation of chemical equilibrium, G N Lewis first considered the chemical potential of a pure, ideal gas and then generalized to all systems the result he obtained for the ideal case (Lewis and Randall, 1961). Now, for a pure substance  $i$ , the chemical potential is related to the temperature and pressure by the differential equation.



$$d\mu_i = -s_i dT + v_i dP \quad (4.1)$$

where  $s_i \equiv$  molar entropy

$v_i \equiv$  molar volume

From 4.1 
$$\left( \frac{\partial \mu_i}{\partial P} \right)_T = v_i$$

Substituting the ideal - gas equation

$$v_i = \frac{RT}{P} ,$$

and integrating at constant pressure yields:

$$\mu_i = \mu_i^o + RT \ln \frac{P}{P^o} \quad (4.2)$$

Equation (4.2) implies that for an ideal gas, the change in chemical potential in isothermally going from pressure  $P^o$  to pressure  $P$ , is equal to the product of  $RT$  and the logarithm of the pressure ratio  $P/P^o$ . Hence at constant temperature, the change in the abstract, thermodynamic quantity  $\mu$  is a simple logarithmic function of the physically real quantity, pressure.

However, equation (4.2) is valid only for pure, ideal gases. To generalize equation (4.2), Lewis defined a function  $f$ , called the fugacity, by writing for an isothermal change for any component in any system, whether solid, liquid or gas, pure or mixed, ideal or not,

$$\mu = \mu_i^o + RT \ln \frac{f_i}{f_i^o} \quad (4.3)$$

While either  $\mu_i^o$  or  $f_i^o$  is arbitrary, both may not be chosen independently; when one is chosen the other is fixed.

For a pure, ideal gas, the fugacity is equal to the pressure, and for a component  $i$  in a mixture of ideal gases, it is equal to its partial pressure  $y_i P$ . Since all systems pure or mixed approach ideal - gas behaviour at very low pressures, the definition of fugacity is completed by the

limit.

$$\frac{f_i}{y_i P} \rightarrow 1 \text{ as } P \rightarrow 0 \quad (4.4)$$

where  $y_i$  is the mole fraction of

Lewis called the ratio  $f/f^\circ$ , the activity, designated by the symbol  $a$ . The activity of a substance gives an indication of how "active" a substance is relative to its standard state since it provides a measure of the difference between the substance's chemical potential at the state of interest and that at its standard state. The ideal gas is not only a limiting case for thermodynamic convenience but corresponds to a well developed physical model based on the kinetic theory of matter. The concept of fugacity, therefore, helps to make the transition from pure thermodynamics to the theory of intermolecular forces; if the fugacity is a "corrected pressure", these corrections are due to nonidealities, which possibly can be interpreted by molecular considerations.

For phases  $\alpha$  and  $\beta$ , respectively, equation (4.3) reduces to

$$\mu_i^\alpha = \mu_i^{\circ\alpha} + RT \ln \frac{f_i^\alpha}{f_i^{\circ\alpha}} \quad (4.5)$$

$$\text{and } \mu_i^\beta = \mu_i^{\circ\beta} + RT \ln \frac{f_i^\beta}{f_i^{\circ\beta}} \quad (4.6)$$

Substituting (4.5) and (4.6) into the equilibrium relation  $\mu_i^\alpha = \mu_i^\beta$  yields:-

$$\mu_i^{\circ\alpha} + RT \ln \frac{f_i^\alpha}{f_i^{\circ\alpha}} = \mu_i^{\circ\beta} + RT \ln \frac{f_i^\beta}{f_i^{\circ\beta}} \quad (4.7)$$

Now consider two cases. Firstly, suppose that the standard states for the two phases are the same, that is suppose  $\mu_i^{\circ\alpha} = \mu_i^{\circ\beta}$ .

(4.8)

It then follows that (4.7) reduces to:-

$$f_i^{\circ\alpha} = f_i^{\circ\beta} \quad (4.9)$$

Equations (4.7), (4.8) and (4.9) give a new form of the fundamental equation of phase equilibrium, that is

$$f_i^\alpha = f_i^\beta \quad (4.10)$$

Secondly, suppose that the standard states for the two phases are at the same temperature, but not at the same pressure and composition. In this case we use an exact relation between the two standard states:

$$\mu_i^{\circ\alpha} = \mu_i^{\circ\beta} + RT \ln \frac{f_i^{\circ\alpha}}{f_i^{\circ\beta}} \quad (4.11)$$

Substituting (4.11) into (4.7), we have again

$$f_i^\alpha = f_i^\beta \quad (4.10)$$

Equation (4.10) tells us that the equilibrium condition in terms of chemical potentials can be replaced without loss of generality by an equation which says that for any species  $i$ , the fugacities must be the same in all phases. The condition that the activities must be equal holds only for the special case where the standard states in all phases are the same.

Now if phase  $\alpha$  is vapour and  $\beta$  is liquid, equation (4.10) is rewritten in terms of the vapour phase fugacity coefficient  $\Psi_i$ , the liquid phase activity coefficient  $\gamma_i$ , and the liquid phase reference fugacity  $f_i^\circ$ :

$$\Psi_i x_i^\alpha P = \gamma_i x_i^\beta f_i^\circ \quad i = 1, 2, \dots, N \quad (4.12)$$

where  $N$  is the total number of components in the mixture.

If both phases are liquid, ie. mole fraction given by  $x_i^\alpha$  and  $x_i^\beta$ , equation (4.10) is now given by:

$$x_i^\alpha \gamma_i^\alpha = x_i^\beta \gamma_i^\beta \quad i = 1, 2, \dots, N \quad (4.13)$$

At pressures up to a few atmospheres, the fugacity coefficients and reference fugacities are readily calculated using the virial equation in conjunction with second virial coefficients

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obtained from experimental information or generalized correlations.

In reality, at these low pressures  $\Psi_i$  is often nearly unity and  $f_i^\circ$  is nearly the pure component vapour pressure at the same temperature as the mixture. Therefore, to answer the question stated in connection with the phase equilibrium problem, one is left with the problem of establishing a relation for the activity coefficients as function of composition  $x_i$  and temperature  $T$  (Fredenslund *et al*, 1977).

## CHAPTER 5

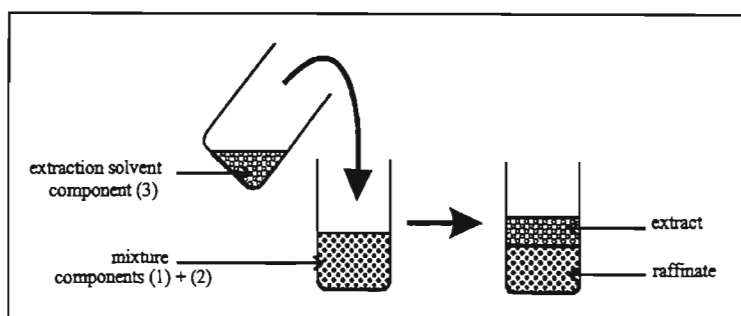
## LIQUID-LIQUID EQUILIBRIUM

## 5.1 INTRODUCTION

Liquid-liquid extraction in its simplest form is a process for separating two components in solution by their distribution between two immiscible liquid phases, after the addition of a third component. The liquid which is added to the solution to bring about the extraction is known as the solvent or entrainer. This solvent takes up part of the components of the original solution and forms an immiscible layer with the remaining solution. The solvent layer is called the *extract*, and the other layer composed of the remainder of the original solution plus some of the solvent, is termed the *raffinate* (Peters, 1984).

The separation of the components of a liquid mixture by treatment with a solvent in which one or more of the desired components is preferentially soluble is known as liquid-liquid extraction - an operation which is used for example, in the processing of coal tar liquids and in the production of fuels in the nuclear industry, and which has been applied extensively to the separation of hydrocarbons in the petroleum industry (Coulson *et al.*, 1985). In the operation it is essential that the liquid - mixture feed and solvent are at least partially if not completely immiscible, and in essence, three stages are involved:

- a. bringing the feed mixture and the solvent into intimate contact,
- b. separation of the resulting two phases,
- c. removal and recovery of the solvent from each phase.



**Figure 5.1** Principle of liquid-liquid extraction

## 5.2 USES FOR LIQUID-LIQUID EXTRACTION

Liquid-liquid extraction is used primarily when distillation is impractical or too costly to use. It may be more practical than distillation when the relative volatility for two components falls between 1.0 and 1.2. In addition, liquid extraction may be more economical than distillation or steam-stripping a dissolved impurity from waste-water when the relative volatility of the solute to water is less than 4 (Perry and Green, 1997). An investigation by Robbins (1980) has found that liquid-liquid extraction was economically more attractive than carbon-bed or resin-bed adsorption as a pretreatment process for waste water detoxification before biotreatment. In other cases the components to be separated may be heat sensitive like antibiotics, or relatively nonvolatile like mineral salts, and liquid-liquid extraction may provide the most cost effective separation process. An extraction process usually requires:

- i. liquid-liquid extraction
- ii. solvent recovery
- iii. raffinate desolventizing (or separation)

Several cases of cost-effective liquid-liquid extraction processes have been employed in the chemical industry. Examples include the recovery of acetic acid from water using ethyl ether or ethyl acetate (Brown, 1963), in the separation of aromatics from aliphatics, the extraction solvent tetraethylene glycol is used (Symoniak *et al.*, 1981). Other extraction solvents used in liquid-liquid extraction include sulfolane, N-methyl-2-pyrrolidone, quinoline and dimethyl sulfoxide.

## 5.3 PREFERRED PROPERTIES OF SOLVENTS TO BE USED FOR LIQUID-LIQUID EXTRACTION

### 5.3.1 Selectivity

The selectivity or relative separation,  $\omega$ , of a solvent is a measure of the ability of a solvent to separate a mixture into its individual components (Perry and Green, 1997). The selectivity is defined as the ratio of the mole fraction of two components in one phase, divided by the ratio of the mole fractions of the same two components in the other phase, and is given by:

$$\omega = (x_2/x_1)_{\text{phase 1}} / (x_2/x_1)_{\text{phase 2}}; \quad (5.1)$$

Where  $x_2$  and  $x_1$  refer to the mole fractions of the components to be separated. The separation power of a liquid-liquid system is governed by the deviation of the selectivity  $\omega$ , from unity. For an effective separation of components between the two liquid phases,  $\omega$ , must be greater or less than unity, whereas for  $\omega = 1$ , no separation is possible, ie. the composition of both phases is identical. At the plait point the selectivity is 1. For a few systems  $\omega$  tends to be substantially constant, though more usually it varies with concentrations (Coulson *et al.*, 1985).

### 5.3.2 Distribution Coefficient

The distribution coefficient (or partition coefficient) is another useful parameter, and is defined as the mole fraction of solute in the extract phase divided by the mole fraction of the same solute in the raffinate phase, at equilibrium (Perry and Green, 1997).

$$K = \frac{x_{23}}{x_{21}} \quad (5.2)$$

Where  $x_{23}$  is the mole fraction of component 2 in the phase that is rich in component 3 and  $x_{21}$  is the mole fraction of component 2 in the phase that is rich in phase 1. The distribution coefficient,  $K$ , for a chosen solute should preferably be high, so that a low ratio of extraction solvent to feed solvent may be utilized for an effective liquid-liquid separation.

### 5.3.3 Recoverability

The extraction solvent should be easy to recover from the extract stream as well as the raffinate stream after the extraction process. Since distillation is often used, the relative volatility of the extraction-solvent to non-solvent components should be significantly greater or less than unity. The relative volatility,  $\alpha_{13}$  is defined as (Coulson *et al.*, 1985):

$$x_{13} = \frac{P_1 \gamma_1}{P_3 \gamma_3} \quad (5.3)$$

Where  $P_1$  and  $P_3$  are the vapour pressures of the two components to be separated using distillation and  $\gamma_1$  and  $\gamma_3$  are the respective activity coefficients of the two components. The relative volatility ratio has the same significance in distillation as the selectivity ratio has in extraction.

#### 5.3.4 Capacity

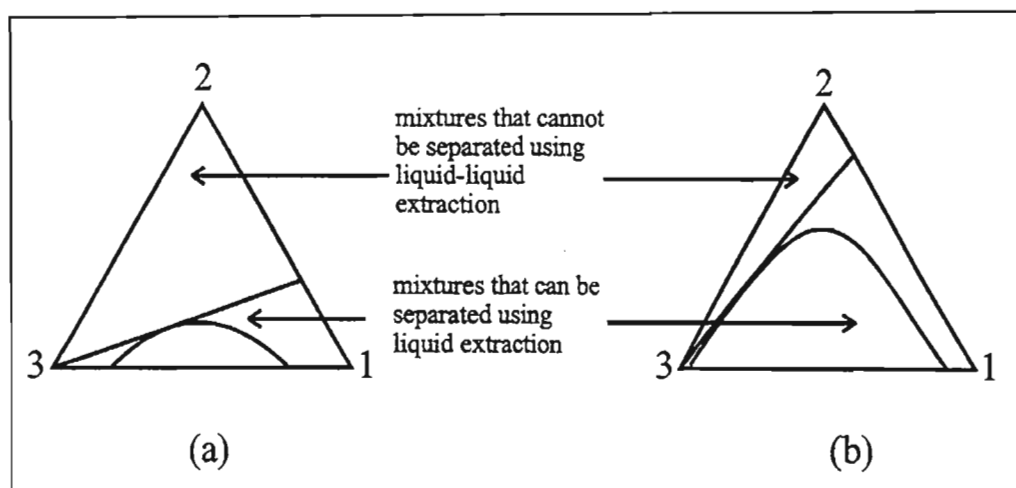
This property refers to the maximum loading of solute per mole fraction of solvent in the extraction solvent-rich phase (Perry and Green, 1997) and is an indication of the magnitude of the two-phase envelope that will form for a particular system. The formation of a two-phase mixture is crucial to the usage of liquid-liquid extraction processes. For a Type I system, ie. a system in which only *one* of the binary pairs is immiscible, capacity data is deduced from the plait point in a ternary diagram and at the solubility limit for a Type II system (system in which *two* of the binary pairs are immiscible). For an extraction solvent or entrainer of high capacity, small quantities of it would be needed for efficient separation (Treybal, 1963). It must be noted that selectivity and capacity are generally inversely related and in choosing a suitable entrainer there is a trade-off between selectivity and capacity factors.

#### 5.3.5 Solvent Solubility

A low solubility of the extraction solvent (compound 1) in one of the components (compounds 2 or 3) is desirable (Perry and Green, 1997). A low solubility of feed solvent in the extract or raffinate leads to a high relative separation and, generally to low solute recovery costs.

A ternary phase diagram with a large two-phase region implies a relatively high mutual insolubility of the three components in the ternary mixture. This is an advantage as the useful composition range over which the extraction solvent or entrainer can be utilized is large (See Figure 5.2).





**Figure 5.2** (a) Ternary liquid-liquid phase diagram with a small two-phase (envelope) region. (b) Ternary liquid-liquid phase diagram region with a large two-phase (envelope) region.

In Figure 5.2b there is a large composition range of mixtures of 2 and 3 which can be separated, whereas in Figure 5.2a a much narrower range of composition of mixtures of 2 and 3 can be separated by liquid-liquid extraction. An example of a system showing Figure 5.2b type behaviour is the system [sulfolane + benzene + decane], reported by Letcher *et al.* (1996)

### 5.3.6 Density

The difference in densities between the two liquid phases (conjugate phases) in equilibrium affects the counter current rates that can be achieved in extraction equipment as well as the coalescence rates (Perry and Green, 1997). Ideally there should be a large difference in the densities of the conjugate phases to ensure a rapid disengagement of phases (Rawat *et al.*, 1972).

### 5.3.7 Viscosity

In general, liquids which possess the highest solvent power, yield solutions of lowest viscosity and the fluidity of a solution is an indirect measure of the solvent power of the solvent (Rawat *et al.*, 1972).

Many poor solvents become better solvents on being mixed with other components, whilst

on the other hand addition of certain components to solvents, result in loss of solvent properties. It is found that liquids having small molecules are better dispensing media and give solutions of low viscosity. After the given solvent is loaded with a certain amount of hydrocarbons, it loses its selective properties.

#### 5.3.8 Interfacial Tension

A good extraction solvent should have a high interfacial tension (Lo *et al.*, 1982). This promotes rapid coalescence and ensures the rapid disengagement of the two phases.

#### 5.3.9 Toxicity

Low toxicity from solvent-vapour inhalation or skin contact is essential as with modern industrial plants, where conditions in the work place must today conform to high standards. In addition, for aqueous systems, when extraction is used as a pretreatment for waste water before it enters a biotreatment plant and with final effluent discharge to a stream, lake or out to sea, low toxicity to fish and bioorganisms is vital. It is often found that solvent toxicity is low when water solubility is high (Perry and Green, 1997).

#### 5.3.10 Chemical Characteristics

Rawat *et al.*, (1972) have reported that most good extraction solvents are small in molecular size with functional groups arranged in such a way that high polarity results. Prausnitz and Anderson (1961) also point out that selectivity depends primarily on the difference in molar volumes of the hydrocarbons to be separated and on the polar energy density of the solvents. In cases where chemical effects are important or where the molar volumes of the hydrocarbons to be separated are only slightly different, selectivity also depends on the relative ability of the hydrocarbons in acting as electron donors and on the ability of the solvent to act as an electron acceptor in forming acid-base complexes. The molecular volumes of good extraction solvents should be low, ie. less than  $150 \text{ cm}^3 \cdot \text{mol}^{-1}$  (Rawat *et al.*, 1972).

An extraction solvent should also have the following characteristics (Rawat *et al.*, 1972):

- high boiling point
- low melting point
- density range 1.0 to 1.3 g·cm<sup>-3</sup>
- high thermal and chemical stability
- it should be non-corrosive
- low latent heat and specific heat

#### 5.3.11 Availability and Cost

Another important factor which determines the economic viability of liquid-liquid extraction potential of a prospective solvent is its ease of availability and unit cost. The latter factor is particularly important if high solvent loading is to be used to attain high efficiency.

### 5.4 REPRESENTATION OF TERNARY LIQUID-LIQUID EQUILIBRIA

#### 5.4.1 The Phase Rule

In one of the most elegant calculations in the field of chemical thermodynamics, J W Gibbs deduced the phase rule which is a general relation between the variance (or number of degrees of freedom)  $F$ , the number of components  $C$ , and the number of phases  $P$  at equilibrium for a system of any composition:

$$F = C - P + 2 \quad (5.4)$$

The variance  $F$  of a system refers to the number of intensive variables that can be changed independently without disturbing the number of phases in equilibrium. For a three component system (this work):

$$F = 5 - P \quad (5.5)$$

Holding the temperature and pressure constant leaves two degrees of freedom, viz. the mole fraction of two of the components.

5.4.2 Triangular Phase Diagrams

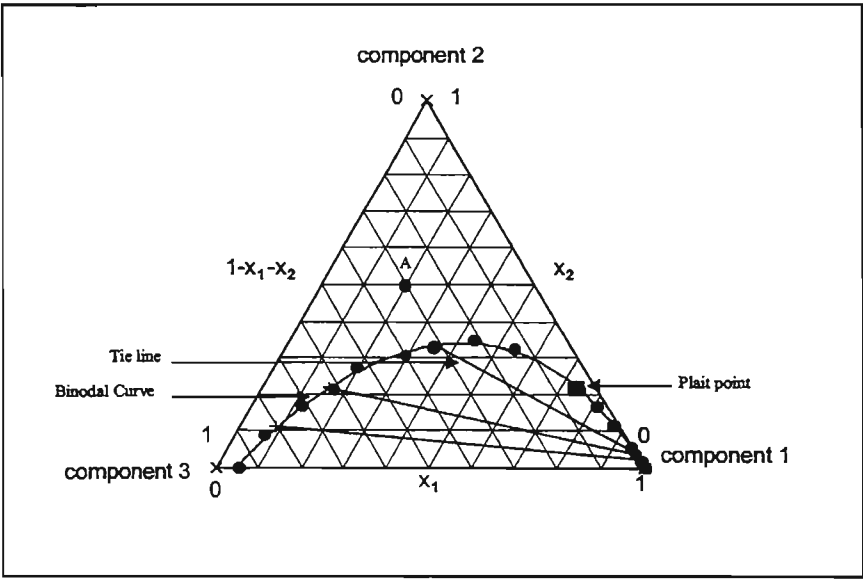
One of the best ways of showing how phase equilibria vary with the composition of the system is to use a triangular phase diagram. The currently used geometrical representation was introduced by Roozeboom in 1894. He introduced the equilateral “Gibbs triangle” with lines ruled parallel to each side.

The mole fractions of the three components of a ternary system ( $C = 3$ ) satisfy:

$$x_A + x_B + x_C = 1 \tag{5.6}$$

A phase diagram drawn as an equilateral triangle ensures that this property is satisfied automatically because the sum of the distances to a point inside an equilateral triangle measured parallel to the edges is equal to the length of the side of the triangle, and that side may be taken to have unit length.

In this work ternary liquid-liquid equilibria data are represented on triangular diagrams as shown in Figure 5.3.



**Figure 5.3 Representation of ternary liquid-liquid equilibrium data using a triangular phase diagram.**

In the ternary phase diagram above the region below the binodal curve indicates the mixtures that are not completely miscible, and results in the formation of two separate phases. The area

above the binodal curve indicates the area where the three components are completely miscible (single phase) and therefore no phase separation occurs. The tie-lines in the two phase regions are constructed experimentally by determining the compositions of the two phases (conjugate) that are in equilibrium, and marking the points on a phase diagram (see Figure 5.3). The line joining the two points is the tie line. The locus of the tie-line extremities is the binodal curve. The plait (or critical) point is a point on the binodal curve where the composition of the two phases in equilibrium become identical.

5.4.3 Classification of the Equilibrium (Binodal) Curve in a Ternary System

There is a greater variety of binodal (equilibrium) curves for a ternary system, than for a binary system (Novak *et al.*, 1987). The system can be divided into three basic groups whose combinations yield the remaining more complicated types.

The first group includes systems containing only two-phase regions formed from the corresponding binary systems, as shown in Figure 5.4.

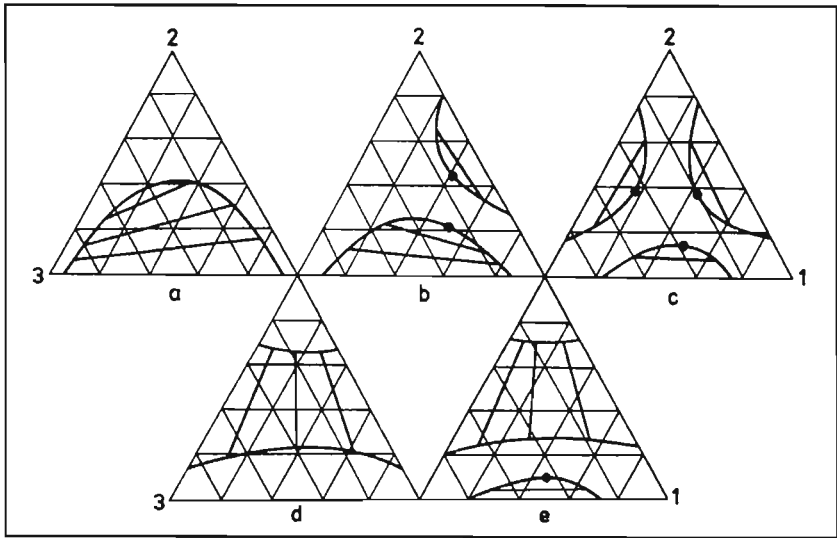
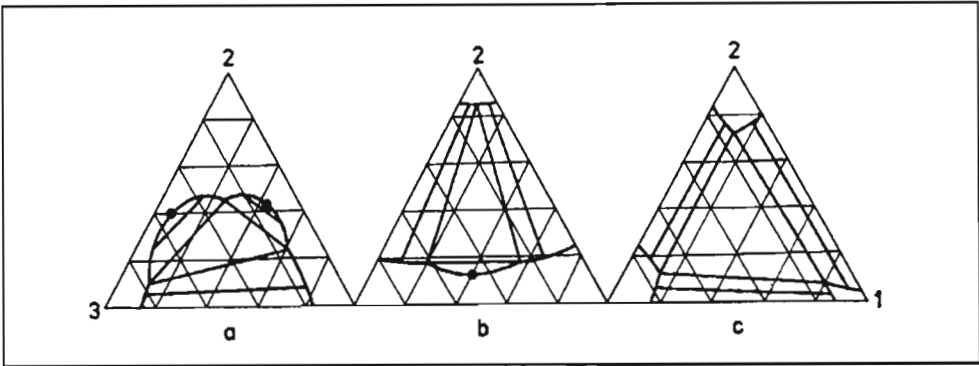


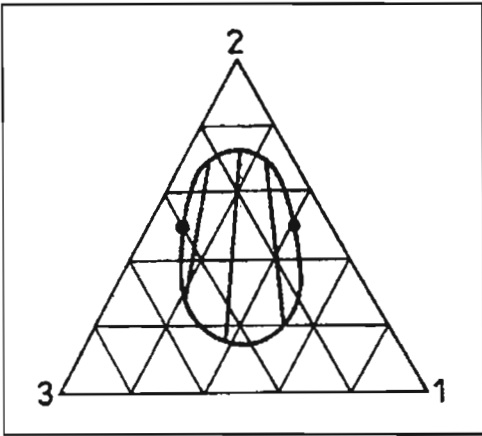
Figure 5.4 Basic types of Ternary Systems with a two-phase region.

The second group consists of systems with a three-phase region, illustrated in Figure 5.5 below.



**Figure 5.5     Basic types of Ternary Systems with a three phase region.**

The third group represents systems with a closed limited miscibility region (island curve) as in Figure 5.6 below.



**Figure 5.6     A system with a closed limiting miscibility curve (island curve).**

A ternary system consists of three binary systems, and if only one binary pair is not completely miscible (or heterogeneous), then a ternary diagram such as that represented in Figure 5.4a is obtained. Systems in which two of the binary pairs are not completely miscible are shown in Figures 5.4b and 5.4d. Ternary systems with all three binary pairs not completely miscible are shown in Figures 5.4c, 5.4e and 5.5c. An example of a system with all three binaries completely miscible, but having a closed limiting miscibility (two-phases) curve or island curve is shown in Figure 5.6.

Treybal (1963), designated those systems represented by Figure 5.4a as Type I systems, and systems shown in Figure 5.4d as Type II. Figure 5.5c represents a Type III system, that is a

ternary system in which all of the binary pairs are immiscible, according to this scheme. According to Sorenson *et al.*(1979) most of ternary systems reported in the literature are of Type I. In this work, all of the systems studied are of Type I.

## 5.5 EXPERIMENTAL TECHNIQUES

### 5.5.1 Introduction

In principle the measurement of phase equilibria involves simply the measurements of pressure, temperature, phase compositions and phase amounts. In practice, however, it is not a simple matter to obtain experimental data of high accuracy. Care must be taken to assure that equilibrium really exists, that the temperature and pressure are measured at the position where equilibrium really exists, and that the taking of samples for analysis does not disturb the equilibrium appreciably (Walas,1985).

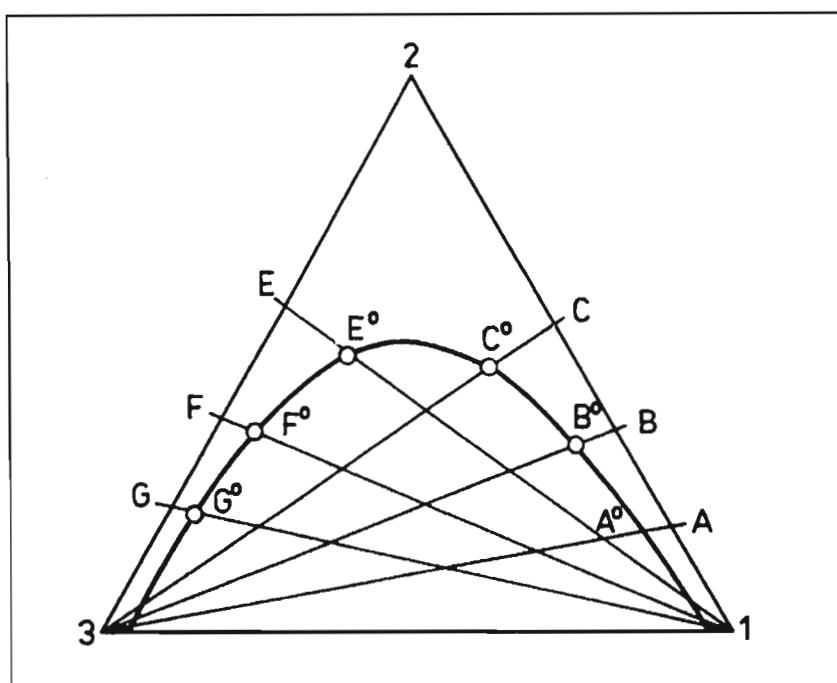
### 5.5.2 Determination of The Binodal Curve in a Ternary System

#### 5.5.2.1 The Titration Method

Although the binodal curve does not yield complete information on phase equilibria since it defines only the heterogeneous region, it can be used to determine the composition of the conjugate phases when other properties of the system studied are known (Novak *et al.*, 1987). The usual or classical method of determining the tie-lines and the binodal curve is to make a lot of mixtures of unlimited miscibility, let them reach equilibrium, analyse each of the layers by GLC, and then mark the concentrations of the liquids in equilibrium. Joining all the experimental points relating to a system in equilibrium gives the tie-lines, and joining all the points gives the binodal curve on a ternary graph. In this work the titration method, adapted from that of Briggs and Comings (1943), and modified by Letcher *et al.*(1989), was used. Here the binodal curve was first determined, followed by an analysis using refractive index or density, in order to determine the tie-lines.

A number of mixtures of substances with unlimited miscibility (1+2) or (2+3) are prepared - see Figure 5.7. Then the third, or first component is added to a known amount of the mixture

from a microburette until the appearance of turbidity occurs. If, for example, one begins with mixture B in Figure 5.7, addition of substance 3 leads to movement along line B 3 and turbidity occurs for a mixture with composition corresponding to point B°. If component 1 is added to mixture F, then, point F° is obtained. Thus from a knowledge of the amounts of substances required for phase separation, the binodal curve is constructed. The titration method was developed for the situation when one of the three components is a non-volatile liquid and hence difficult to analyse by GLC.



**Figure 5.7** Determination of the binodal curve by the titration method

#### 5.5.2.2 The Direct Analytical Method

In the direct analytical method, a procedure (useful for systems with greater numbers of components) mixtures whose overall compositions lie in the two phase (heterogeneous) region are made up. The heterogeneous mixture is then stirred vigorously for a sufficiently long time at constant temperature, and, after phase separation, samples are taken for analysis. Here conditions are rather more complicated than in binary systems, as the content of at least two (and in general  $N-1$ ) components must be determined in each phase. The analytical determination of the tie lines is carried out using a combination of various physical and chemical methods. Gas chromatography can be used successfully here (Moriyoshi *et al.*,



1989). The tie lines are determined directly (the composition of the two phases being determined by peak area comparison) and there is no need to determine the tie-lines separately. The binodal curve is thus drawn through the extreme points on each of the tie-lines.

In practice, liquid-liquid equilibria for systems containing more than three components can only be measured by the direct analytical method (Novak *et al.*, 1987)

### 5.5.3 Determination of the Tie-lines in Ternary Systems Using the Binodal Curve

#### 5.5.3.1 Introduction

If the shape of the binodal curve and further properties are known (eg. refractive index, density), measurement of these properties in the equilibrium phase permits determination of the corresponding position on the binodal curve and thus the tie-line can be found. Otherwise, it is sufficient to determine the concentration of only one of the components in both phases, which yield their composition.

#### 5.5.3.2 Karl-Fisher titration

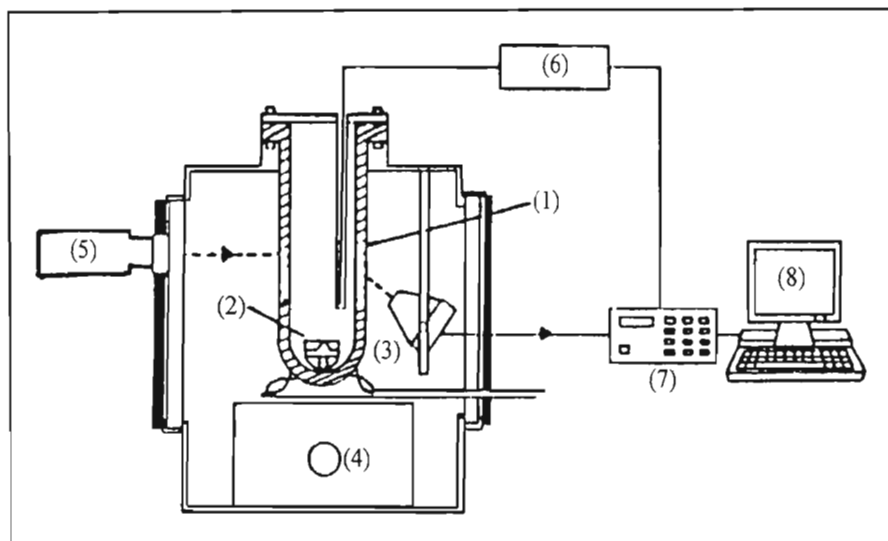
As an alternative to the refractive index method, the tie-lines could also be obtained using the Karl Fischer method, provided one of the components is water (Skoog *et al.*, 1991). In this method the Karl Fischer reagent is used to titrate against the water in each phase. In this way the aqueous content of each phase can be determined, and these are then located on the binodal curve and the corresponding tie-lines drawn.

There are several variations of the basic technique depending upon the solubility of the material, the state in which water is retained and the physical state of the sample.

#### 5.5.3.3 Laser-light scattering technique

A fairly recently developed laser light scattering technique is available for the determination of mutual solubilities in liquid systems (Benjamin *et al.*, 1993). A schematic diagram of the

apparatus is shown in Figure 5.8.



**Figure 5.8** A schematic diagram of apparatus for mutual solubility measurements. [(1) equilibrium vessel (pressure glass with film heater), (2) stirrer chip, (3) light sensor (selenium cell), (4) magnetic stirrer, (5) optical system (He-Ne laser), (6) thermometer, (7) digital multimeter, (8) personal computer]

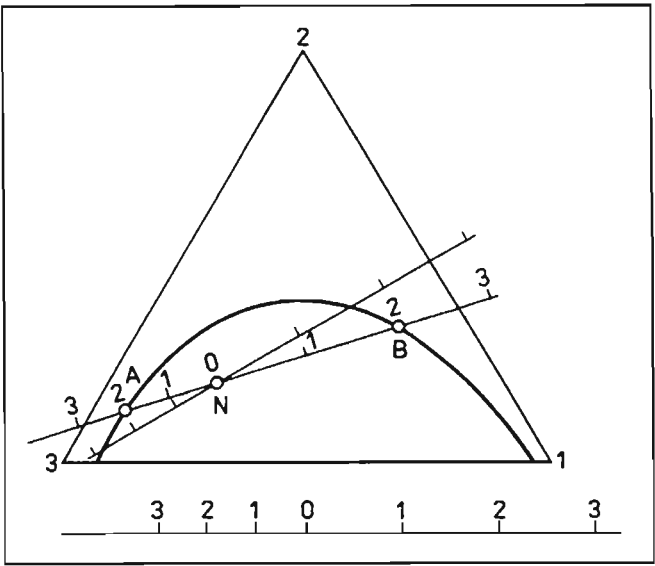
From a plot of intensity of light scattering versus temperature of sample under investigation, the experimental cloud point could be determined and the solubility curve obtained.

#### 5.5.3.4 Method based on Mass Balance and the Lever Rule

The method based on mass balance and the lever rule permits determination of the tie-lines without analysis (Novak *et al.*, 1987). A heterogeneous mixture is prepared with a composition corresponding eg. to a point N (Figure 5.9). Both co-existing phases are then separated in a thermostatted separating funnel and weighed. Assuming for eg. that the turbid phase richer in substance (1) is present in twice the amount of the turbid phase richer in substance (3).

A scale is prepared to assist in the evaluation (here in a ratio of 1:2 see Figure 5.9). Point O is placed over point N and the scale is turned until a position is found such that the same numerical value is obtained on both branches at points intersecting the binodal curve. Care should be taken that the binodal curve is plotted in mass fractions as the masses of both

phases are compared in the experiment.

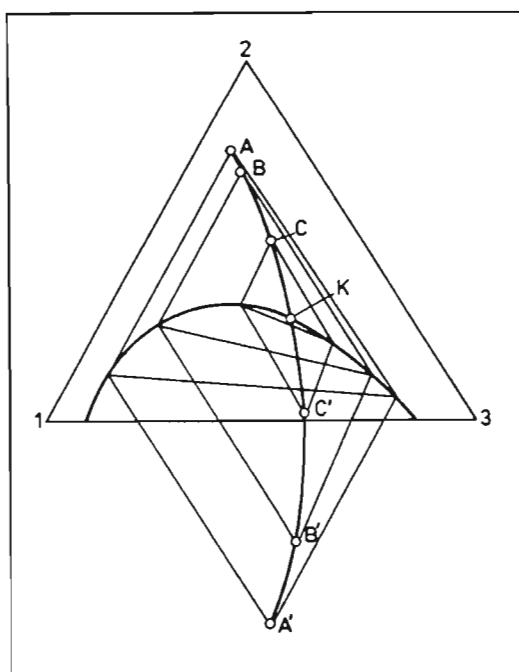


**Figure 5.9** Application of the lever rule to determination of the compositions of the equilibrium phases (tie-lines) when the binodal curve is known

**5.5.4 Determination of the critical point (plait point) in three component systems**

**5.5.4.1 The Coolidge method**

In this method the critical point is found geometrically by extrapolating the experimental tie-lines. Coolidge recommends constructing two triangles on each tie-line (see Figure 5.10), whose sides are parallel with those of the concentration triangle (Washburn,1928). A smooth curve connecting the apices of the triangle passes through the binodal curve in the critical point K.



**Figure 5.10** Determination of the critical point by the Coolidge method

In non-symmetrical systems, the curve obtained intersects the binodal curve at a small angle, and determination of the intercept is quite imprecise. It is then preferable to construct isosceles triangles above and below the tie-line with arms equal to between 60 and 75% of the length of the tie line (depending on the size of the triangle).

#### 5.5.4.2 The Treybal method

The Treybal method (1946) involves obtaining a linear plot of

$$\log \left[ \frac{x_1''}{x_2''} \right] \text{ vs } \log \left[ \frac{x_1'}{x_3'} \right] \quad (5.7)$$

where in the case of the acetonitrile-carboxylic acid-heptane system, for example:

- $x_1''$  = mole fraction of carboxylic acid in the acetonitrile-rich phase
- $x_1'$  = mole fraction of carboxylic acid in the heptane-rich phase
- $x_3'$  = mole fraction of heptane in the heptane-rich phase
- $x_2''$  = mole fraction of acetonitrile in the acetonitrile-rich phase

A curve results from the plot of  $\log \left[ \frac{x_1}{x_2} \right]$  vs  $\log \left[ \frac{x_1}{x_3} \right]$  where  $x_1$ ,  $x_2$  and  $x_3$  are the mole

fractions of a carboxylic acid, acetonitrile, and heptane respectively, for a point on the binodal curve.

The plait point is then given by the intersection of the plot of

$$\left[ \log \frac{x_1''}{x_2''} \text{ vs } \log \frac{x_1'}{x_3'} \right] \quad \text{with} \quad \left[ \log \frac{x_1}{x_2} \text{ vs } \log \frac{x_1}{x_3} \right]$$

## 5.6 EXPERIMENTAL SECTION

### 5.6.1 Samples used

The purities of all the chemicals were determined using gas-liquid chromatography (GLC). The carboxylic acids, viz. acetic acid, propanoic acid, butanoic acid, 2-methylpropanoic acid, pentanoic acid, 3-methylbutanoic acid; the nitrile compounds, viz. acetonitrile, benzonitrile, butanenitrile; as well as heptane and cyclohexane were all stored under 4Å molecular sieves before use. Analysis for moisture content by the Karl-Fischer technique showed that in all cases the water content was less than 0.01 mass %. Milli-Q purified water was used in all cases. A summary of the materials, their suppliers and purities, used in this work is given in Table 5.1

**Table 5.1**      **Materials used, their suppliers and mass % purities**

COMPOUND	SUPPLIER	MASS % PURITY
acetic acid	Acros	99.5
propanoic acid	Acros	99
butanoic acid	Acros	99
2-methylpropanoic acid	Acros	99
pentanoic acid	Acros	99
3-methylbutanoic acid	Acros	99
acetonitrile	Sigma Aldrich	> 99.5
benzonitrile	Fluka	99
heptane	Sigma Aldrich	> 99.5
cyclohexane	BDH Chemicals	99

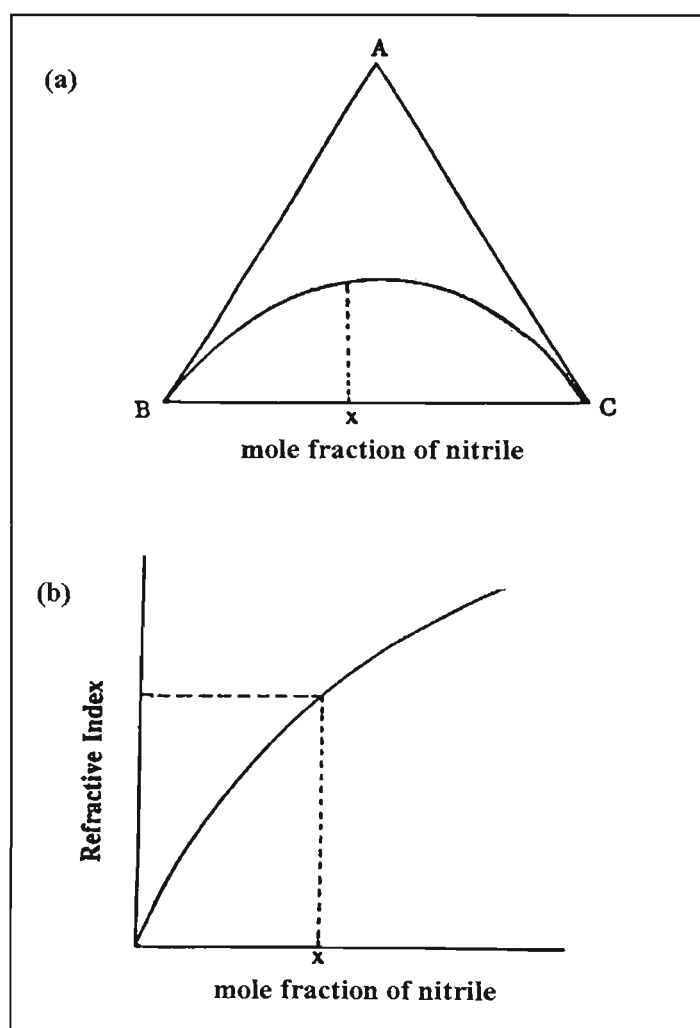
### 5.6.2 Procedure

In this study, the "method of titrations", that is a method adapted from that of Briggs and Comings (1943) and developed by Letcher *et al.* (1989) was used to determine the ternary liquid-liquid equilibrium data. Here the binodal curve is first obtained and the tie-lines are then determined. The points on the binodal curve were obtained in the following way:- a mixture of two of the miscible components, that is (a nitrile + a carboxylic acid) were prepared accurately by weighing. The mixtures were then left to equilibrate in a stirred water bath maintained at  $298.15\text{ K} \pm 0.01\text{ K}$ , by means of a Tronac temperature controller used in conjunction with a calibrated Hewlett-Packard quartz thermometer, for at least an hour. The third component, viz. hydrocarbon (or water), was then added dropwise from a weighed gas tight syringe until the mixture turned cloudy. The syringe was then weighed again to determine the mass of the hydrocarbon (or water) added. To ensure the maintenance of only one phase for refractive index measurements, a measured drop of carboxylic acid was added in each-case. At the hydrocarbon-rich (or water-rich) end of the binodal curve the binary mixture was made up of hydrocarbon (or water) and an acid, and the third component added was the nitrile.

The refractive index of the clear mixture was then measured using a Bellingham and Stanley RFM 90 refractometer set at  $25.5^\circ\text{C}$  for all the ternary systems. A standard "calibration curve" for each system was obtained by relating the refractive index of each mixture on the

co-existence curve, to a composition which was determined by dropping a perpendicular from the co-existence curve to the nitrile mole fraction axis.

The tie-lines were determined from carefully made up solutions in the immiscible regions of the phase diagram. The samples were then well shaken and left in a controlled water bath at  $298.15\text{ K} \pm 0.1\text{ K}$  for at least 24 hours to facilitate phase separation and to ensure equilibrium. Samples of the separated phases were then withdrawn using warmed, gas tight syringes and analysed immediately using the refractive index method. The refractive indices of the different phases were then related to compositions on the binodal curve by linear interpolation of the refractive indices against the nitrile axis using Figure 5.11(b). Each tie-line was checked to ensure that the line joining the two points representing the compositions of the solution pairs at equilibrium, passed through the composition of the overall mixture.



**Figure 5.11** The refractive index method for drawing tie-lines using 5.11(a) the binodal curve and 5.11(b) the calibration curve

### 5.7 FITTING MATHEMATICAL EQUATIONS TO THE BINODAL CURVE DATA

For a ternary liquid mixture with only one pair of immiscible liquids, the equation of Hlavatý (1972) has until fairly recently been the only successful method in fitting an equation to the binodal curve.

Three equations have been fitted to the ternary data for each system following the work of Hlavatý (1972).

The coefficients  $A_i$  relate to a modified Hlavatý equation :

$$x_2 = A_1 x_A \ln x_A + A_2 x_B \ln x_B + A_3 x_A x_B \quad (5.8)$$

Unfortunately, the independent variables are highly correlated and slight changes in binodal curve data produce large changes in the magnitudes of the coefficients  $A_1$ ,  $A_2$  and  $A_3$ .

A better fitting equation proposed by Letcher *et al.* (1989), which does not suffer from this disadvantage is the  $\beta$ -density function equation. The coefficients  $B_i$  relate to a  $\beta$ -function equation:

$$x_2 = B_1 (1 - x_A)^{B_2} x_A^{B_3} \quad (5.9)$$

Another equation also proposed by the same workers (Letcher *et al.*, 1986), which does not suffer the disadvantage of being highly correlative is, the logarithmic-gamma equation. This equation was chosen because the binodal curves are similar in shape to the densities of the logarithmic-gamma distribution which have been obtained by Schultz and Crouse (1973), to describe the distribution of mass fractions of a body subjected to successive random divisions of its randomly divided parts. The coefficients  $C_i$  relate to the log  $\gamma$  equation:

$$x_2 = C_1 (-\ln x_A)^{C_2} x_A^{C_3} \quad (5.10)$$

$$\text{where } x_A = (x_1 + 0.5 x_2 - x_1^0) / (x_{11}^0 - x_1^0) \quad (5.11)$$

$$x_B = (x_{11}^0 - x_1 - 0.5 x_2) / (x_{11}^0 - x_1^0) \quad (5.12)$$

and in the case of the ternary system (acetonitrile + a carboxylic acid + heptane) for instance  $x_1$  refers to the mole fraction composition of the acetonitrile,  $x_2$  refers to the mole fraction of a carboxylic acid and  $x_{11}^0$  and  $x_1^0$  are the values of  $x_1$  on the binodal curve which cuts the  $x_2 = 0$  axis and have been used to summarize the binodal curve data.



Equations 5.10 - 5.12 have been fitted to the binodal curves with the standard deviations  $\sigma$ . This is defined as :

$$\sigma = \left[ \sum [x_2(\text{calc}) - x_2(\text{exp})]^2 / (n - 3) \right]^{1/2} \quad (5.13)$$

where  $n$  is the number of data points and 3 is the number of estimated coefficients. (Sen and Srivastava, 1990). The standard errors is defined by Sen and Srivastava (1990) as the square root of the variance of the estimated coefficients.

## 5.8 EXPERIMENTAL RESULTS

The experimental liquid-liquid equilibrium data are presented in the following order:

- 5.8.1 [Acetonitrile (1) + a Carboxylic Acid (2) + Heptane (3)] at 298.15 K.
- 5.8.2 [Acetonitrile (1) + a Carboxylic Acid (2) + Cyclohexane (3)] at 298.15 K.
- 5.8.3 [Benzonitrile (1) + a Carboxylic Acid (2) + Water (3)] at 298.15 K.
- 5.8.4 [Butanenitrile (1) a Carboxylic Acid (2) + Water (3)] at 298.15 K.

In each case a carboxylic acid refers to (acetic acid or propanoic acid or butanoic acid or 2-methylpropanoic acid or pentanoic acid or 3-methylbutanoic acid).

The main purpose of this section is to investigate the use of nitriles as solvent extractors in the separation of :

- carboxylic acids from alkanes
- carboxylic acids from cycloalkanes
- carboxylic acids from water.

For each section tables of results for binodal curve data, calibration curve data, distribution curve data, as well as ternary phase diagrams are presented.

### 5.8.1 Liquid-liquid equilibria for mixtures of [Acetonitrile + a Carboxylic acid + Heptane] at 298.15 K

**Table 5.2** Physical Properties of the Pure Components at 298.15 K; Molar Volumes,  $V_m$ , Refractive Indices,  $n_D$ , Volume and Surface Parameters,  $R$  and  $Q$ .

Component	$V_m/\text{cm}^3 \cdot \text{mol}^{-1}{}^a$	$n_D$		$R^b$	$Q^b$
		exp	lit. <sup>a</sup>		
acetonitrile	52.87	1.3413	1.3416	1.870	1.724
acetic acid	57.53	1.3697	1.3698	2.202	2.072
propanoic acid	74.97	1.3846	1.3843	2.877	2.612
butanoic acid	92.43	1.3955	1.3958	3.551	3.152
2-methylpropanoic acid	93.44	1.3913	1.3917	3.550	3.148
pentanoic acid	109.29	1.4064	1.4060	4.226	3.692
3-methylbutanoic acid	110.54	1.4019	1.4022	4.225	3.688
heptane	147.47	1.3851	1.3851	5.174	4.396

<sup>a</sup> Riddick *et al.* (1986). <sup>b</sup> Gmehling *et al.* (1993)

**Table 5.3      Compositions of Points on the Binodal Curve at 298.15 K for the systems: [Acetonitrile (1) + a Carboxylic Acid (2) + Heptane (3)], Equilibrium Mole Fraction,  $x_1$ , and  $x_2$ .**

$x_1$	$x_2$		$x_1$	$x_2$
Acetic Acid				
0.956	0.004		0.103	0.786
0.942	0.017		0.051	0.780
0.915	0.041		0.023	0.702
0.824	0.133		0.180	0.706
0.743	0.216		0.011	0.560
0.689	0.270		0.007	0.388
0.598	0.362		0.006	0.305
0.504	0.448		0.005	0.211
0.400	0.547		0.004	0.060
0.252	0.682		0.003	0.014
0.191	0.732			
Propanoic Acid				
0.952	0.010		0.362	0.385
0.943	0.016		0.329	0.380
0.928	0.031		0.270	0.361
0.844	0.110		0.216	0.330
0.768	0.178		0.161	0.288
0.715	0.222		0.113	0.225
0.621	0.290		0.070	0.145
0.511	0.353		0.038	0.062
0.441	0.377		0.019	0.004
Butanoic Acid				
0.951	0.011		0.335	0.289
0.917	0.046		0.255	0.264
0.854	0.095		0.186	0.234
0.787	0.145		0.124	0.184
0.742	0.179		0.082	0.140
0.649	0.238		0.034	0.065
0.506	0.292		0.006	0.004
0.401	0.299			
2-Methylpropanoic Acid				
0.953	0.008		0.345	0.293
0.945	0.014		0.264	0.275
0.925	0.032		0.190	0.248
0.858	0.093		0.152	0.223
0.788	0.147		0.114	0.186
0.737	0.179		0.064	0.131
0.642	0.237		0.031	0.064
0.511	0.284		0.013	0.009
0.411	0.298			

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Pentanoic Acid			
0.956	0.004	0.376	0.269
0.946	0.012	0.298	0.261
0.935	0.025	0.223	0.239
0.874	0.072	0.145	0.201
0.806	0.122	0.120	0.181
0.774	0.143	0.075	0.135
0.755	0.156	0.036	0.070
0.663	0.205	0.007	0.005
0.519	0.250		
3-Methylbutanoic Acid			
0.966	0.004	0.455	0.265
0.947	0.012	0.377	0.270
0.939	0.024	0.224	0.244
0.875	0.079	0.153	0.202
0.807	0.126	0.095	0.151
0.759	0.158	0.047	0.084
0.665	0.205	0.009	0.006
0.529	0.250		

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**Table 5.4      Calibration Curve Data at 298.15 K for the systems : [Acetonitrile (1) + a Carboxylic Acid (2) + Heptane (3)], Equilibrium Mole Fraction,  $x_1$ , Refractive Index,  $n_D$**

$x_1$	$n_D$	$x_1$	$n_D$
Acetic Acid			
1.000	1.3413	0.252	1.3666
0.956	1.3444	0.191	1.3678
0.942	1.3458	0.103	1.3691
0.915	1.3469	0.051	1.3704
0.824	1.3505	0.023	1.3736
0.743	1.3533	0.180	1.3762
0.689	1.3550	0.011	1.3773
0.598	1.3579	0.006	1.3782
0.504	1.3602	0.003	1.3829
0.400	1.3631	0.000	1.3851
Propanoic Acid			
1.000	1.3413	0.362	1.3744
0.952	1.3455	0.329	1.3756
0.943	1.3465	0.270	1.3770
0.928	1.3476	0.216	1.3787
0.844	1.3531	0.161	1.3801
0.768	1.3578	0.113	1.3816
0.715	1.3603	0.070	1.3827
0.621	1.3648	0.038	1.3834
0.511	1.3692	0.019	1.3842
0.441	1.3712	0.000	1.3851
Butanoic Acid			
1.000	1.3413	0.335	1.3801
0.951	1.3462	0.255	1.3811
0.917	1.3502	0.186	1.3821
0.854	1.3556	0.124	1.3829
0.787	1.3607	0.082	1.3834
0.742	1.3638	0.034	1.3839
0.649	1.3676	0.006	1.3849
0.506	1.3746	0.000	1.3851
0.401	1.3779		

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2-Methylpropanoic Acid				
1.000	1.3413	0.345	1.3775	
0.953	1.3460	0.264	1.3796	
0.945	1.3466	0.190	1.3813	
0.925	1.3485	0.152	1.3817	
0.858	1.3539	0.114	1.3824	
0.788	1.3587	0.064	1.3830	
0.737	1.3621	0.031	1.3835	
0.642	1.3669	0.013	1.3847	
0.511	1.3723	0.000	1.3851	
0.411	1.3746			
Pentanoic Acid				
1.000	1.3413	0.376	1.3804	
0.956	1.3460	0.298	1.3813	
0.946	1.3472	0.223	1.3817	
0.935	1.3494	0.145	1.3823	
0.874	1.3569	0.120	1.3828	
0.806	1.3623	0.075	1.3831	
0.774	1.3648	0.036	1.3826	
0.755	1.3664	0.007	1.3846	
0.663	1.3721	0.000	1.3851	
0.519	1.3782			
3-Methylbutanoic Acid				
1.000	1.3413	0.455	1.3784	
0.966	1.3455	0.377	1.3794	
0.947	1.3469	0.224	1.3812	
0.939	1.3484	0.153	1.3821	
0.875	1.3548	0.095	1.3827	
0.807	1.3610	0.047	1.3832	
0.759	1.3645	0.009	1.3848	
0.665	1.3704	0.000	1.3851	
0.529	1.3761			

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**Table 5.5      Composition of the Conjugate Solutions,  $x_1'$ ,  $x_2'$ , and  $x_1''$ ,  $x_2''$ , at 298.15 K, Refractive Index,  $n_D$ .**

hydrocarbon- rich			acetonitrile-rich		
$x_1'$	$x_2'$	$n_D$	$x_1''$	$x_2''$	$n_D$
Acetonitrile (1) + Acetic Acid (2) + Heptane (3)					
0.002	0.006	1.3836	0.917	0.042	1.3468
0.004	0.142	1.3813	0.681	0.279	1.3353
0.006	0.281	1.3782	0.388	0.557	1.3634
0.007	0.370	1.3780	0.192	0.732	1.3678
0.009	0.463	1.3776	0.085	0.782	1.3696
Acetonitrile (1) + Propanoic Acid (2) + Heptane (3)					
0.021	0.001	1.3841	0.936	0.024	1.3470
0.033	0.052	1.3836	0.811	0.140	1.3551
0.050	0.098	1.3831	0.643	0.275	1.3637
0.060	0.123	1.3829	0.455	0.373	1.3708
0.079	0.165	1.3825	0.289	0.370	1.3765
Acetonitrile (1) + Butanoic Acid (2) + Heptane (3)					
0.014	0.022	1.3846	0.875	0.078	1.3538
0.025	0.045	1.3842	0.742	0.179	1.3638
0.030	0.059	1.3840	0.566	0.275	1.3717
0.038	0.073	1.3838	0.454	0.299	1.3762
0.040	0.081	1.3837	0.300	0.281	1.3805
Acetonitrile (1) + 2-Methylpropanoic Acid (2) + Heptane (3)					
0.015	0.018	1.3846	0.905	0.050	1.3501
0.018	0.027	1.3844	0.721	0.189	1.3629
0.020	0.032	1.3842	0.477	0.288	1.3731
0.021	0.038	1.3841	0.358	0.292	1.3769
0.026	0.046	1.3838	0.169	0.227	1.3815
Acetonitrile (1) + Pentanoic Acid (2) + Heptane (3)					
0.01	0.017	1.3845	0.920	0.035	1.3513
0.012	0.027	1.3844	0.799	0.130	1.3628
0.019	0.038	1.3842	0.578	0.238	1.3757
0.020	0.047	1.3841	0.390	0.270	1.3802
0.028	0.059	1.3838	0.274	0.258	1.3814
Acetonitrile (1) + 3-Methylbutanoic Acid (2) + Heptane (3)					
0.010	0.012	1.3848	0.905	0.053	1.3518
0.012	0.019	1.3847	0.715	0.184	1.3673
0.017	0.028	1.3845	0.548	0.247	1.3753
0.020	0.034	1.3843	0.336	0.270	1.3799
0.021	0.040	1.3842	0.240	0.247	1.3810



**Table 5.6**      **Coefficients  $A_i$ ,  $B_i$ , and  $C_i$  in Equations (5.8) - (5.10), at 298.15 K.**

Hlavatý	$\beta$	logy
Acetonitrile (1) + Acetic Acid (2) + Heptane (3)		
$A_1 = 0.254$	$B_1 = 4.235$	$C_1 = 3.831$
$A_2 = 0.686$	$B_2 = 1.271$	$C_2 = 1.229$
$A_3 = 4.309$	$B_3 = 1.215$	$C_3 = 1.682$
$\sigma = 0.022$	$\sigma = 0.020$	$\sigma = 0.022$
Acetonitrile (1) + Propanoic Acid (2) + Heptane (3)		
$A_1 = 0.297$	$B_1 = 1.633$	$C_1 = 1.523$
$A_2 = -0.269$	$B_2 = 0.925$	$C_2 = 0.896$
$A_3 = 1.552$	$B_3 = 1.182$	$C_3 = 1.531$
$\sigma = 0.010$	$\sigma = 0.009$	$\sigma = 0.010$
Acetonitrile (1) + Butanoic Acid (2) + Heptane (3)		
$A_1 = -0.018$	$B_1 = 1.001$	$C_1 = 3.831$
$A_2 = -0.473$	$B_2 = 0.766$	$C_2 = 1.229$
$A_3 = 0.492$	$B_3 = 1.001$	$C_3 = 1.682$
$\sigma = 0.006$	$\sigma = 0.007$	$\sigma = 0.008$
Acetonitrile (1) + 2-Methylpropanoic Acid (2) + Heptane (3)		
$A_1 = -0.140$	$B_1 = 0.945$	$C_1 = 0.891$
$A_2 = -0.456$	$B_2 = 0.759$	$C_2 = 0.736$
$A_3 = 0.355$	$B_3 = 0.915$	$C_3 = 1.200$
$\sigma = 0.004$	$\sigma = 0.005$	$\sigma = 0.007$
Acetonitrile (1) + Pentanoic Acid (2) + Heptane (3)		
$A_1 = -0.102$	$B_1 = 0.883$	$C_1 = 0.830$
$A_2 = -0.341$	$B_2 = 0.792$	$C_2 = 0.768$
$A_3 = 0.460$	$B_3 = 0.924$	$C_3 = 1.221$
$\sigma = 0.004$	$\sigma = 0.004$	$\sigma = 0.003$
Acetonitrile (1) + 3-Methylbutanoic Acid (2) + Heptane (3)		
$A_1 = -0.023$	$B_1 = 0.966$	$C_1 = 0.904$
$A_2 = -0.261$	$B_2 = 0.847$	$C_2 = 0.821$
$A_3 = 0.692$	$B_3 = 0.982$	$C_3 = 1.297$
$\sigma = 0.005$	$\sigma = 0.005$	$\sigma = 0.004$

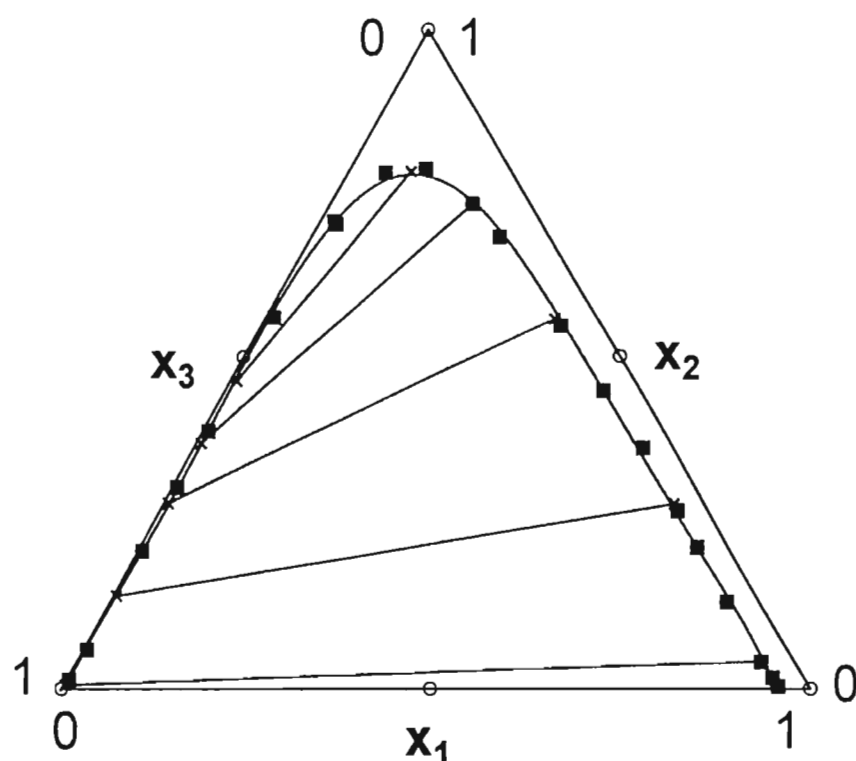


Figure 5.12 Liquid-liquid equilibrium data for the system [acetonitrile (1) + acetic acid (2) + heptane (3)] at 298.15 K.

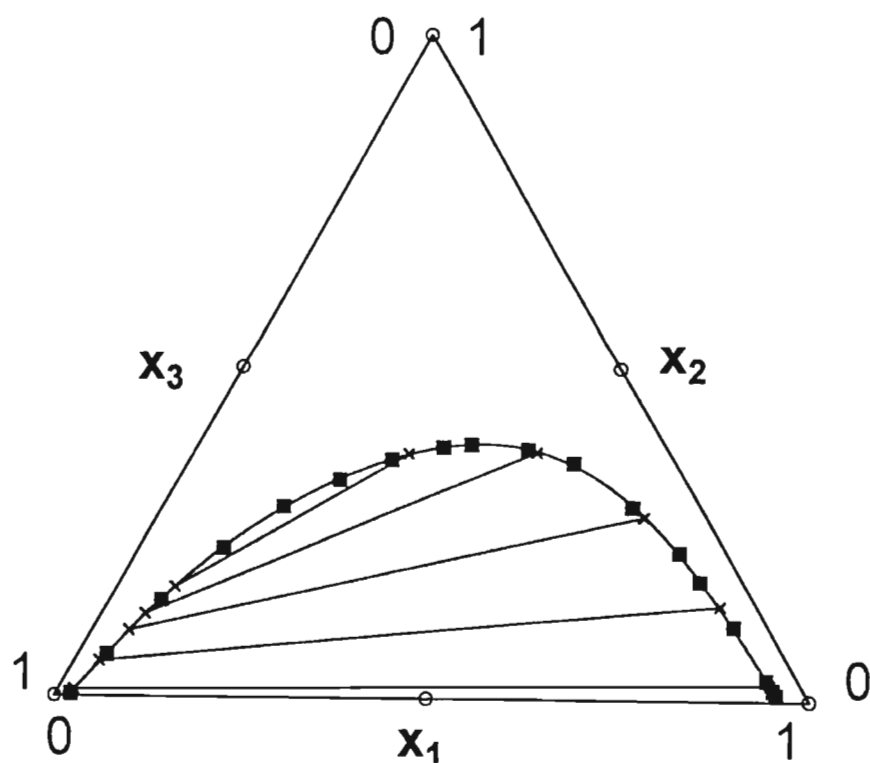


Figure 5.13 Liquid-liquid equilibrium data for the system [acetonitrile (1) + propanoic acid (2) + heptane (3)] at 298.15 K.

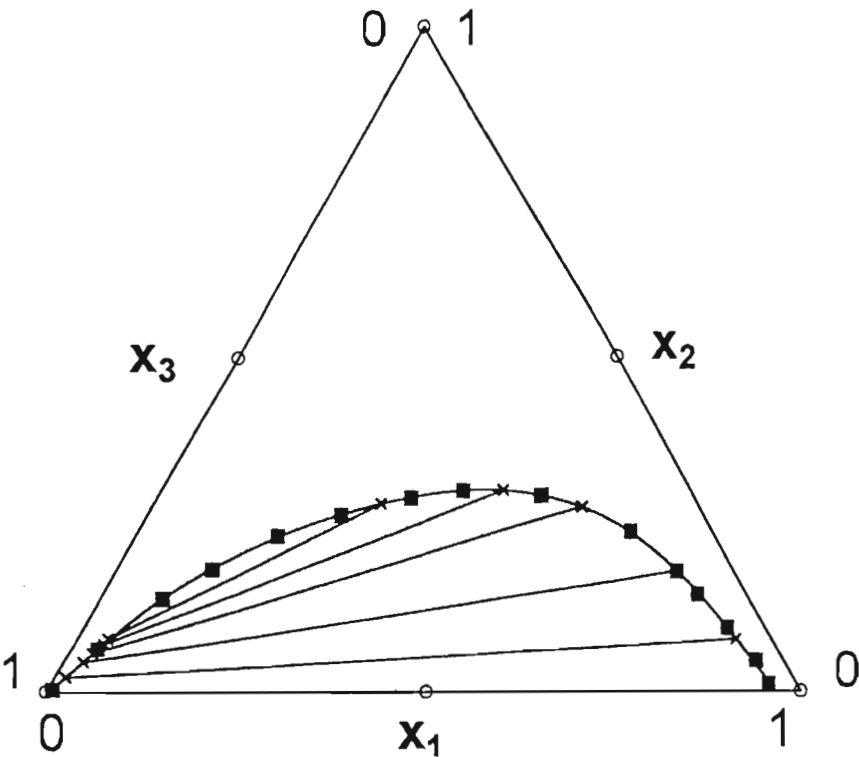


Figure 5.14 Liquid-liquid equilibrium data for the system [acetonitrile (1) + butanoic acid (2) + heptane (3)] at 298.15 K.

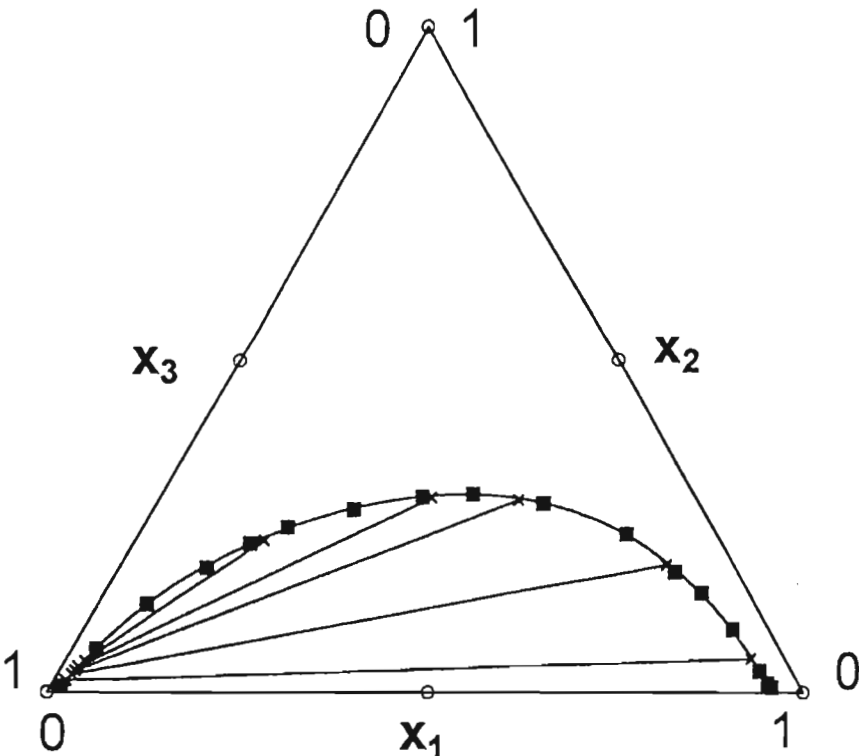


Figure 5.15 Liquid-liquid equilibrium data for the system [acetonitrile (1) + 2-methylpropanoic acid (2) + heptane (3)] at 298.15 K.

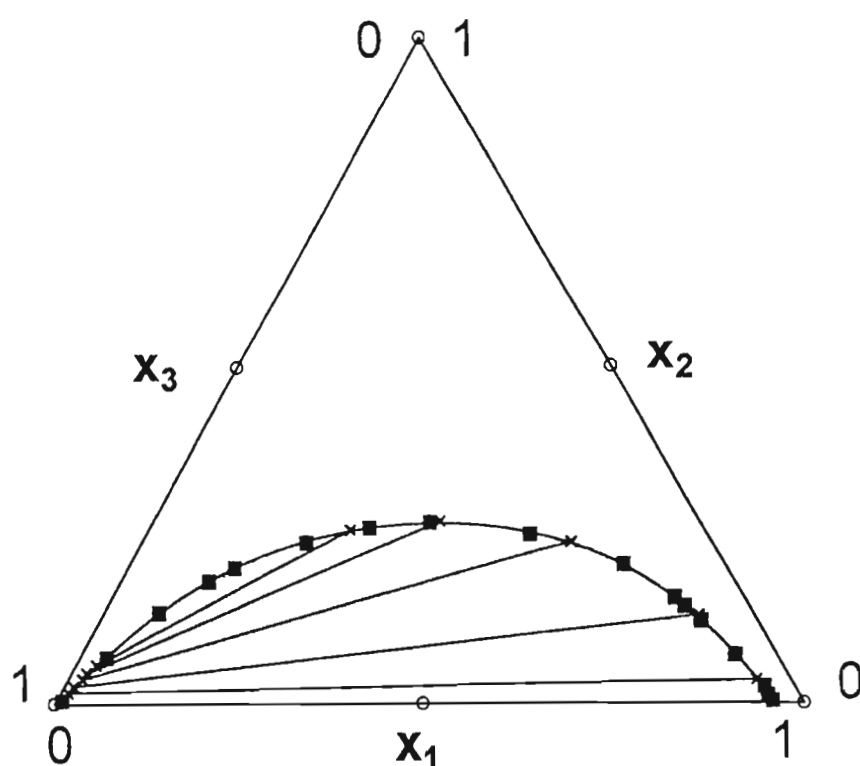


Figure 5.16 Liquid-liquid equilibrium data for the system [acetonitrile (1) + pentanoic acid (2) + heptane (3)] at 298.15 K.

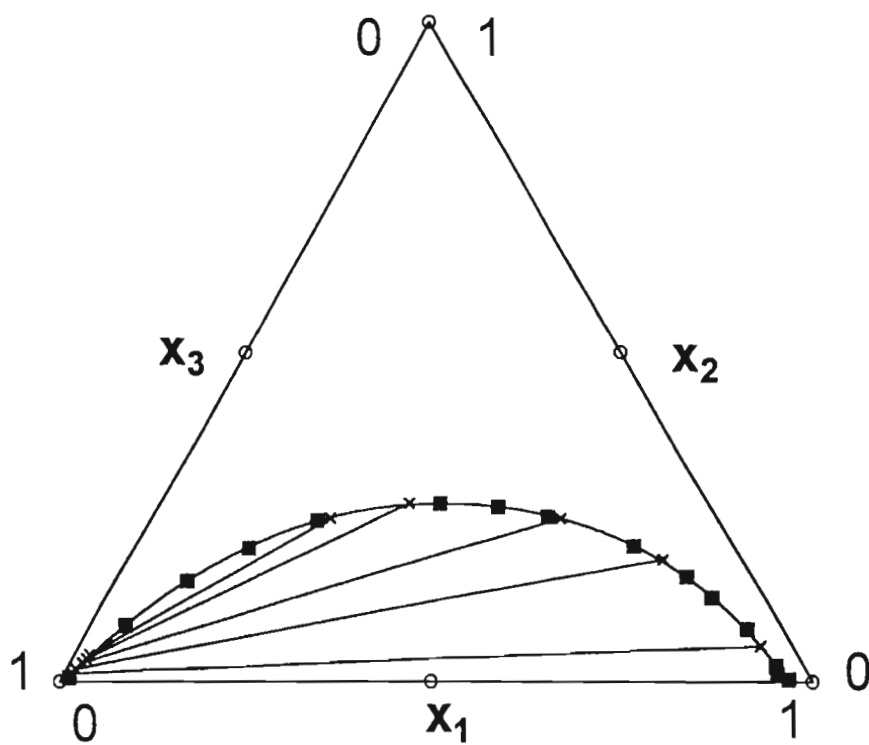
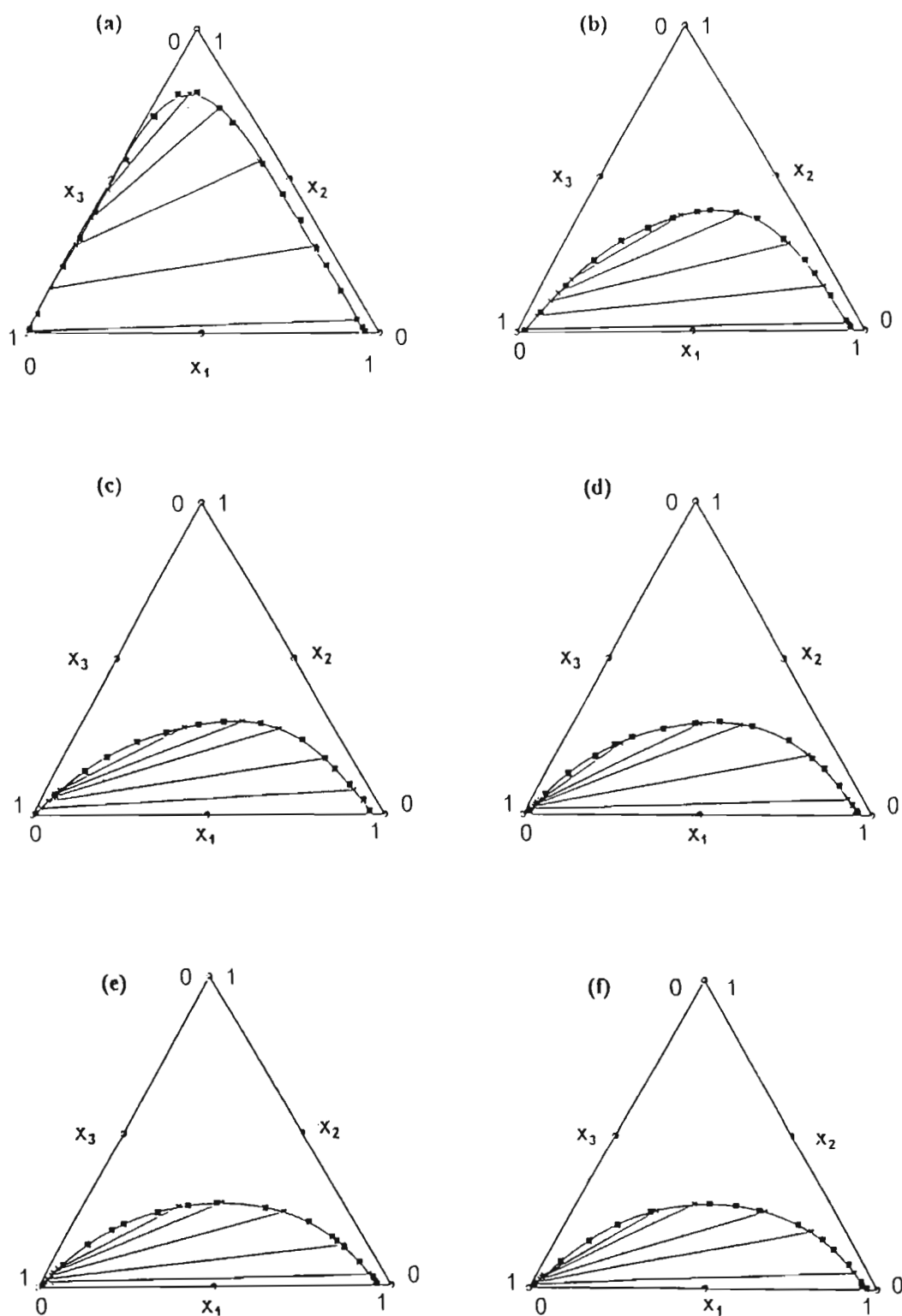


Figure 5.17 Liquid-liquid equilibrium data for the system [acetonitrile (1) + 3-methylbutanoic acid (2) + heptane (3)] at 298.15 K.



**Figure 5.18** Summary of liquid-liquid equilibrium data for the following systems at 298.15 K: (a) acetonitrile(1) + acetic acid(2) + heptane (3); (a) acetonitrile(1) + propanoic acid(2) + heptane (3); (c) acetonitrile(1) + butanoic acid(2) + heptane (3); (d) acetonitrile(1) + 2-methylpropanoic acid(2) + heptane (3); (e) acetonitrile(1) + pentanoic acid(2) + heptane (3); (e) acetonitrile(1) + 3-methylbutanoic acid(2) + heptane (3). [Key: (■) experimental points; (×) experimental tie-lines]

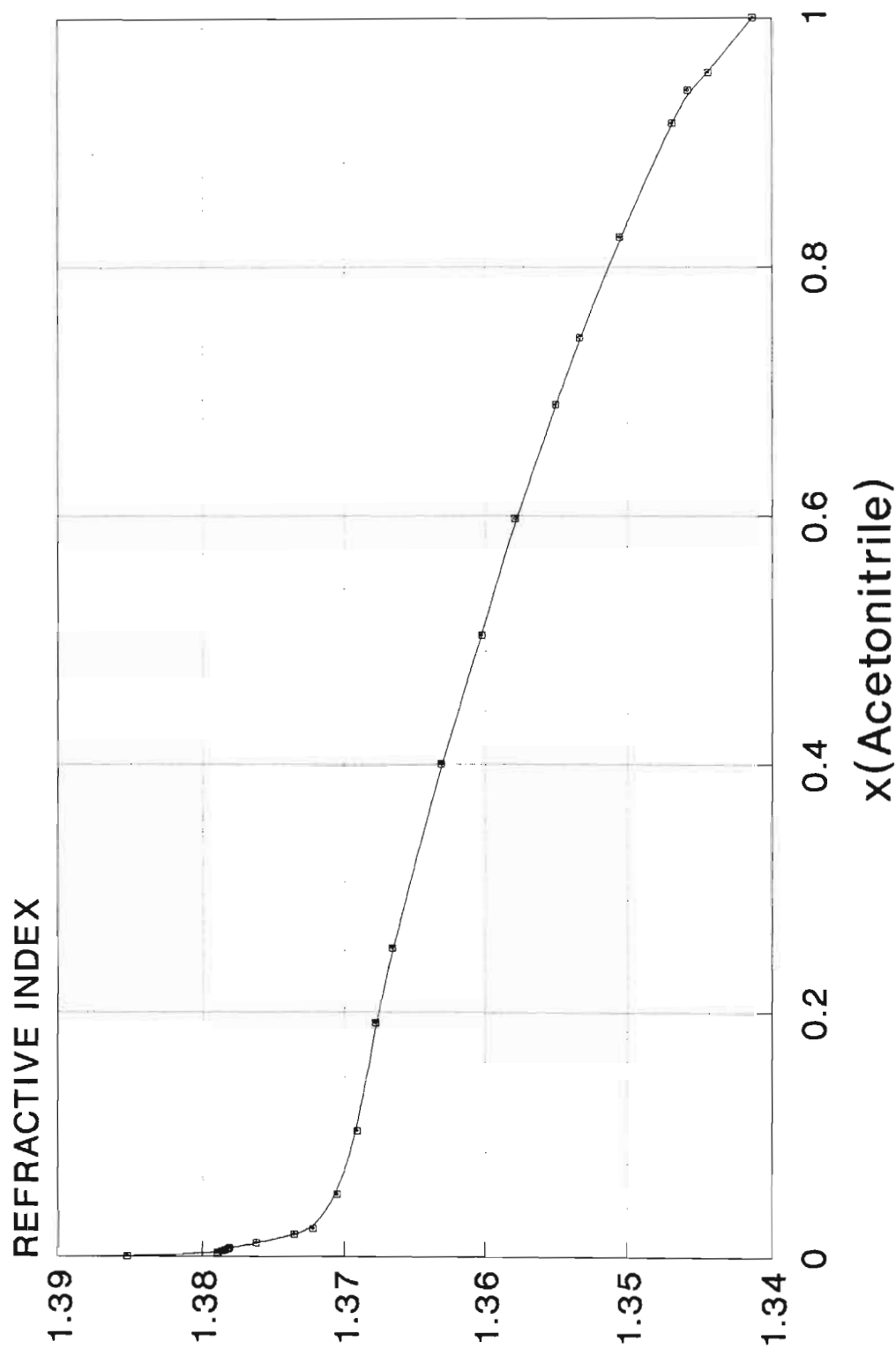


Figure 5.19 Calibration curve for (acetonitrile + acetic acid + heptane) system at 298.15 K.

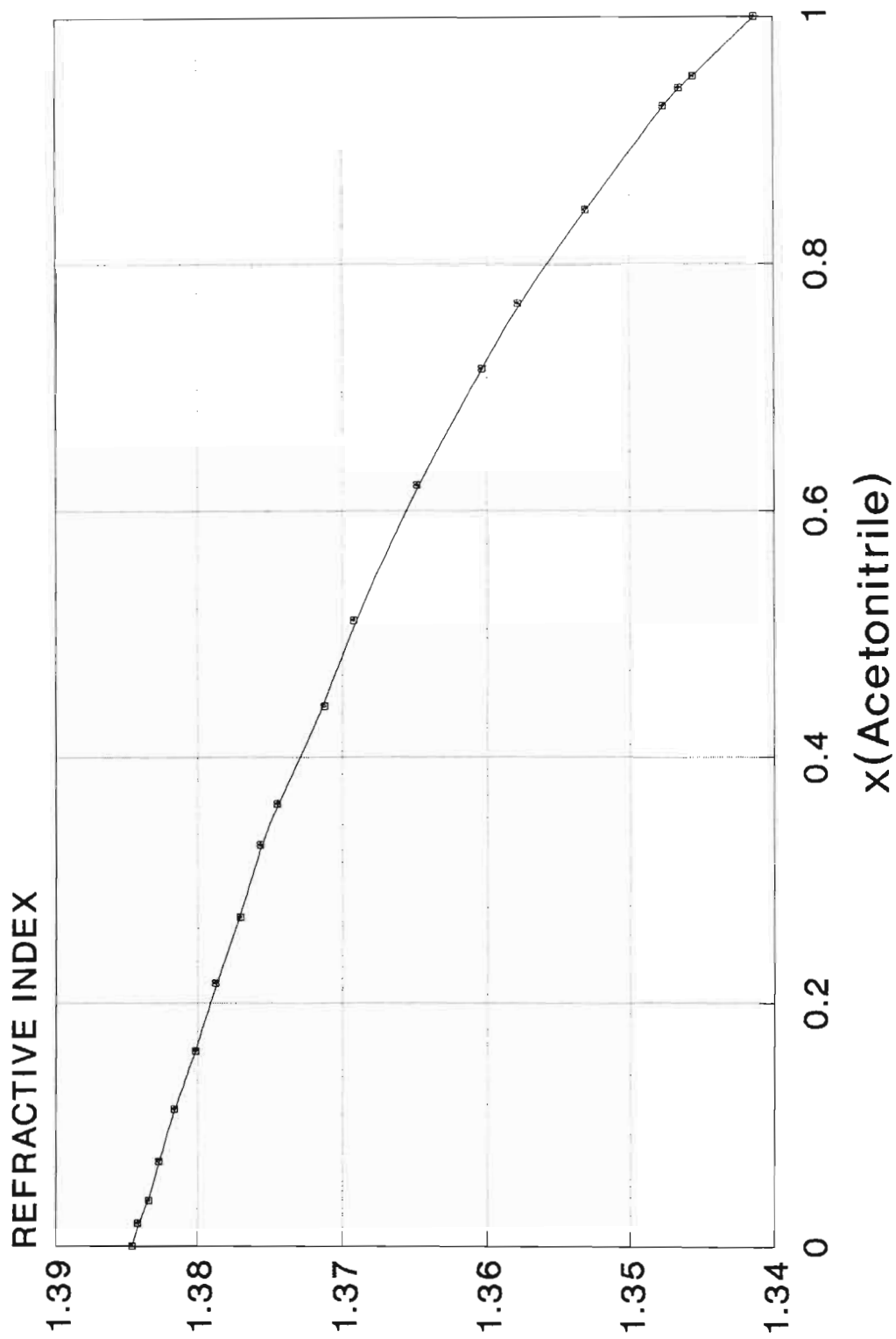


Figure 5.20 Calibration curve for (acetonitrile + propanoic acid + heptane) system at 298.15 K.

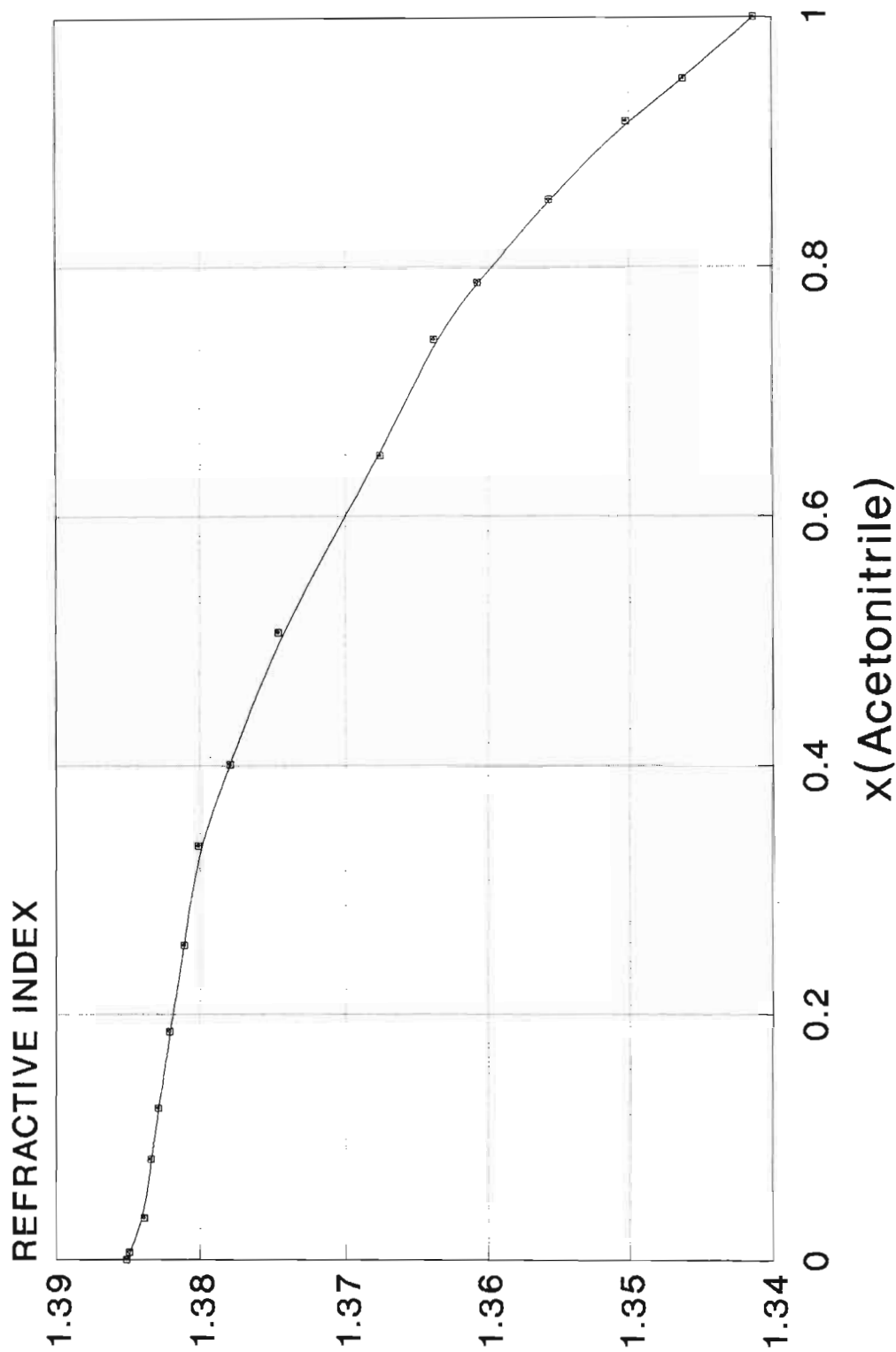


Figure 5.21 Calibration curve for (acetonitrile + butanoic acid + heptane) system at 298.15 K.



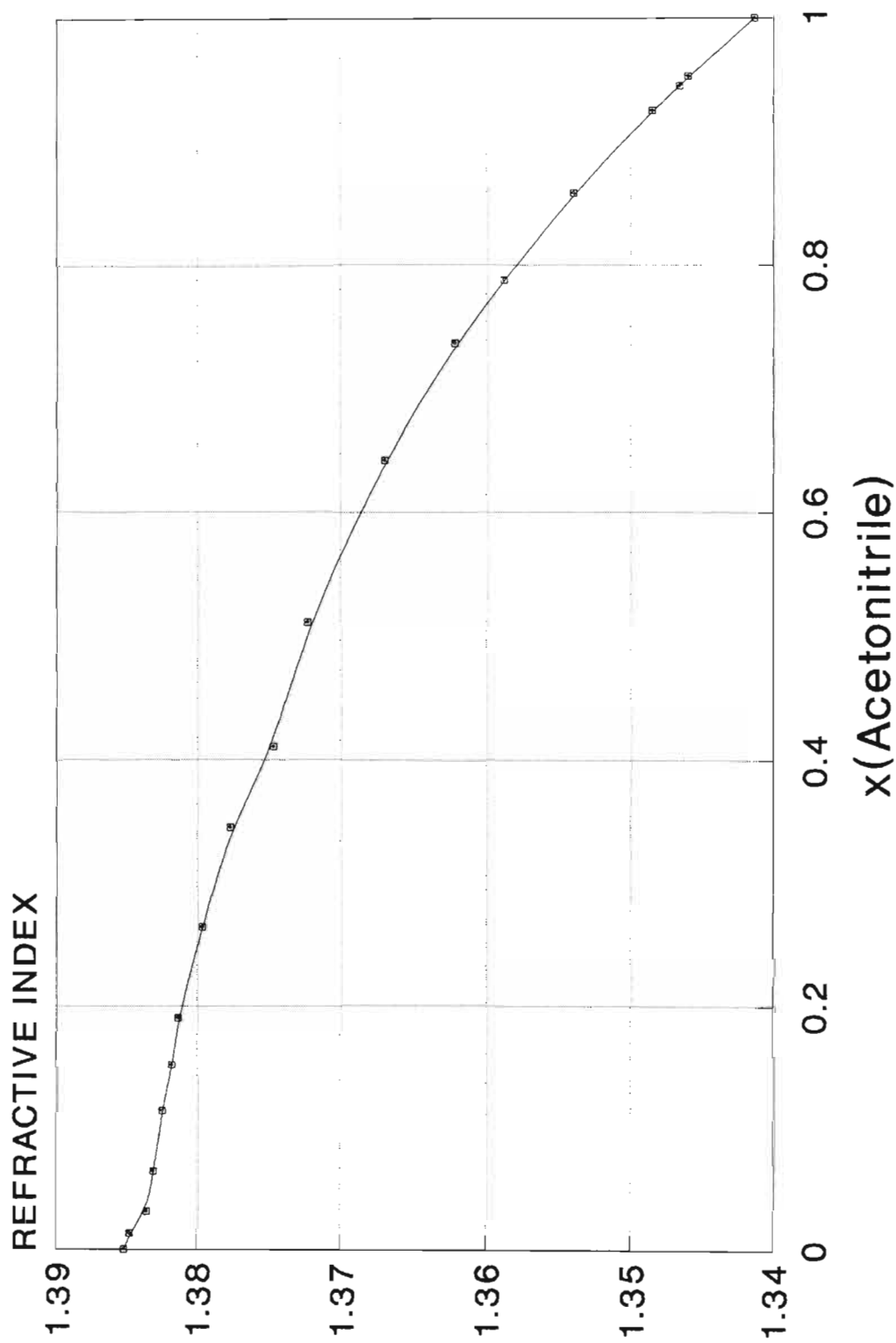


Figure 5.22 Calibration curve for (acetonitrile + 2-methylpropanoic acid + heptane) system at 298.15 K.

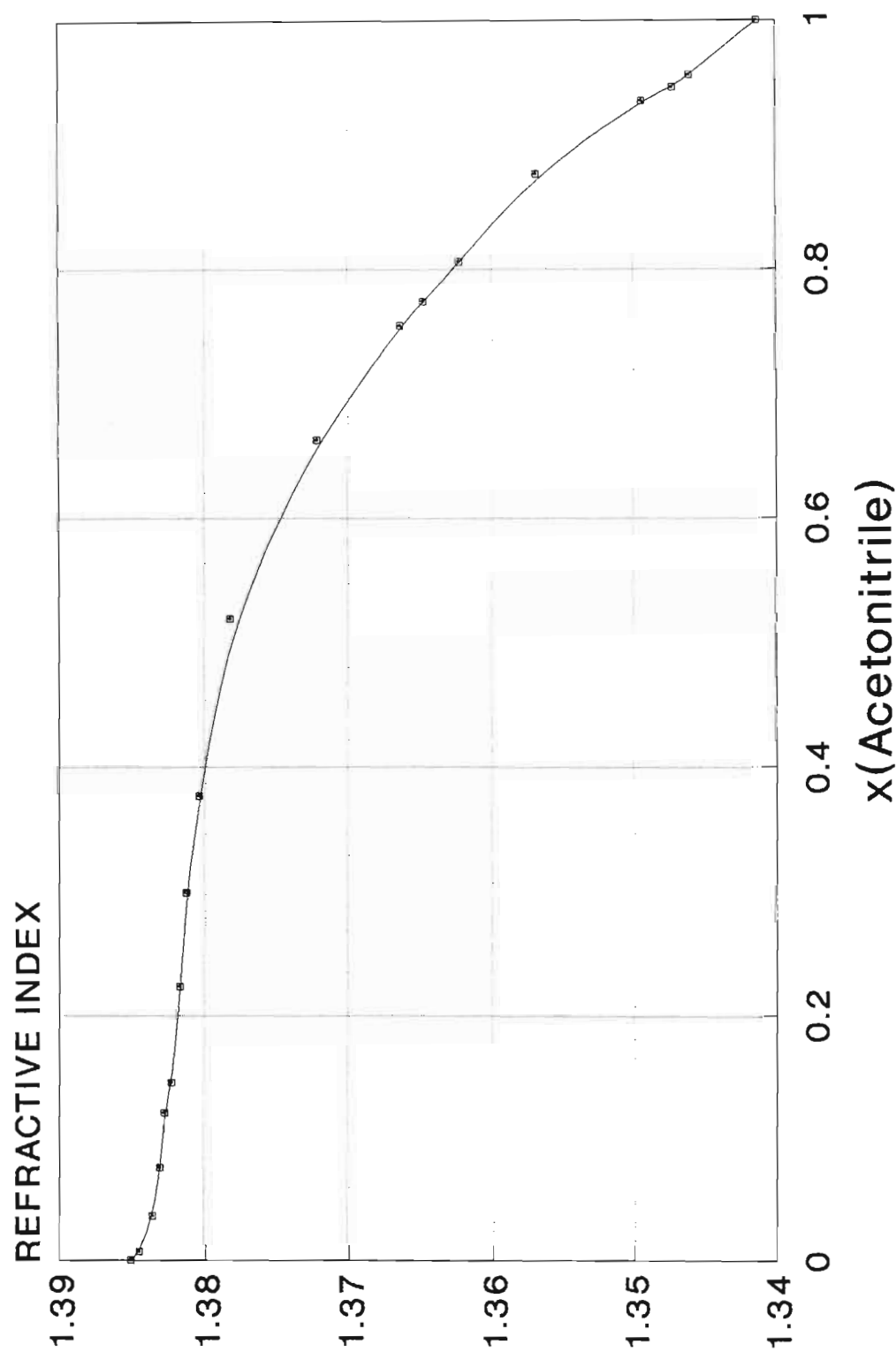


Figure 5.23 Calibration curve for (acetonitrile + pentanoic acid + heptane) system at 298.15 K.

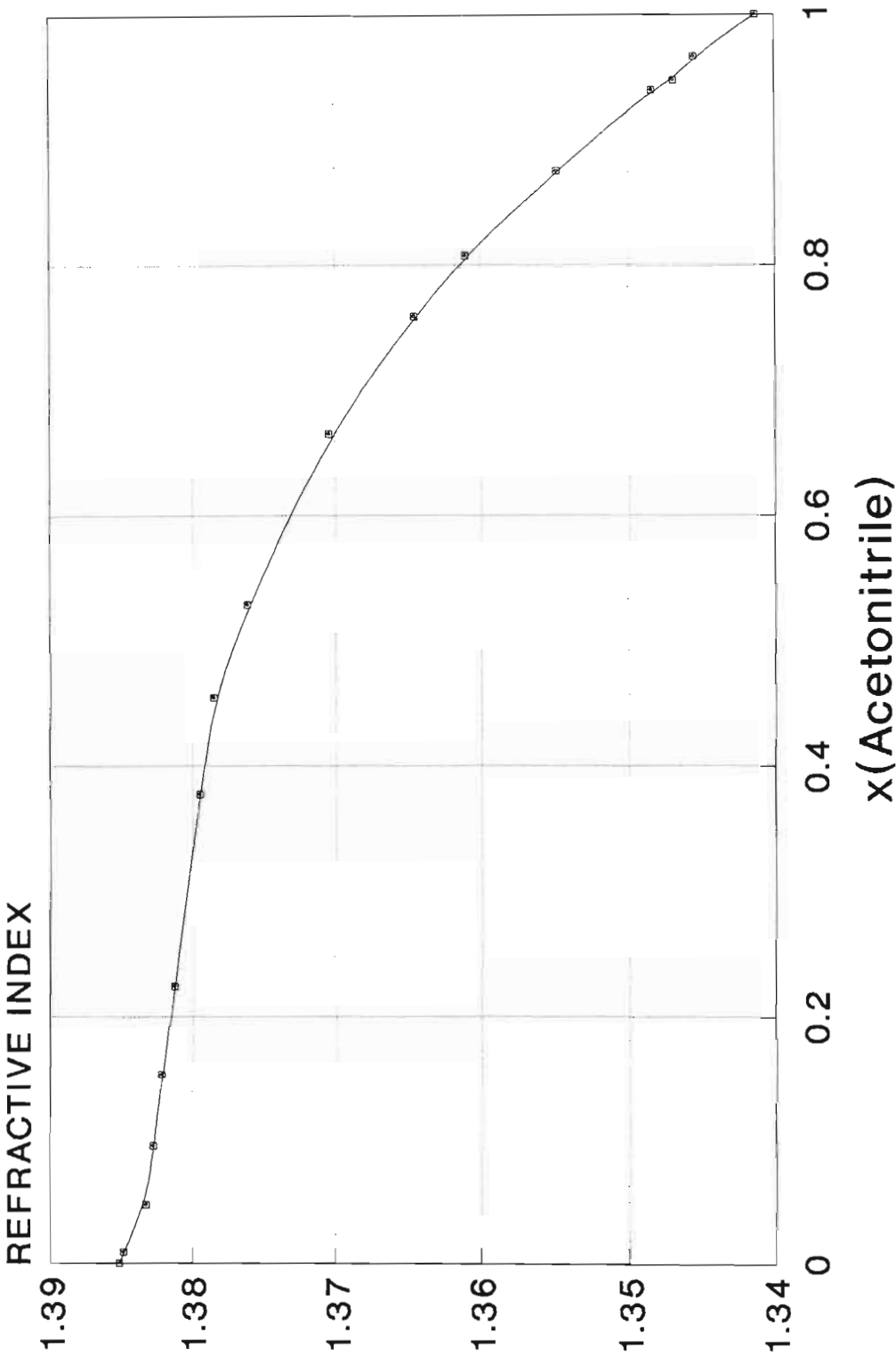


Figure 5.24 Calibration curve for (acetonitrile + 3-methylbutanoic acid + heptane) system at 298.15 K.

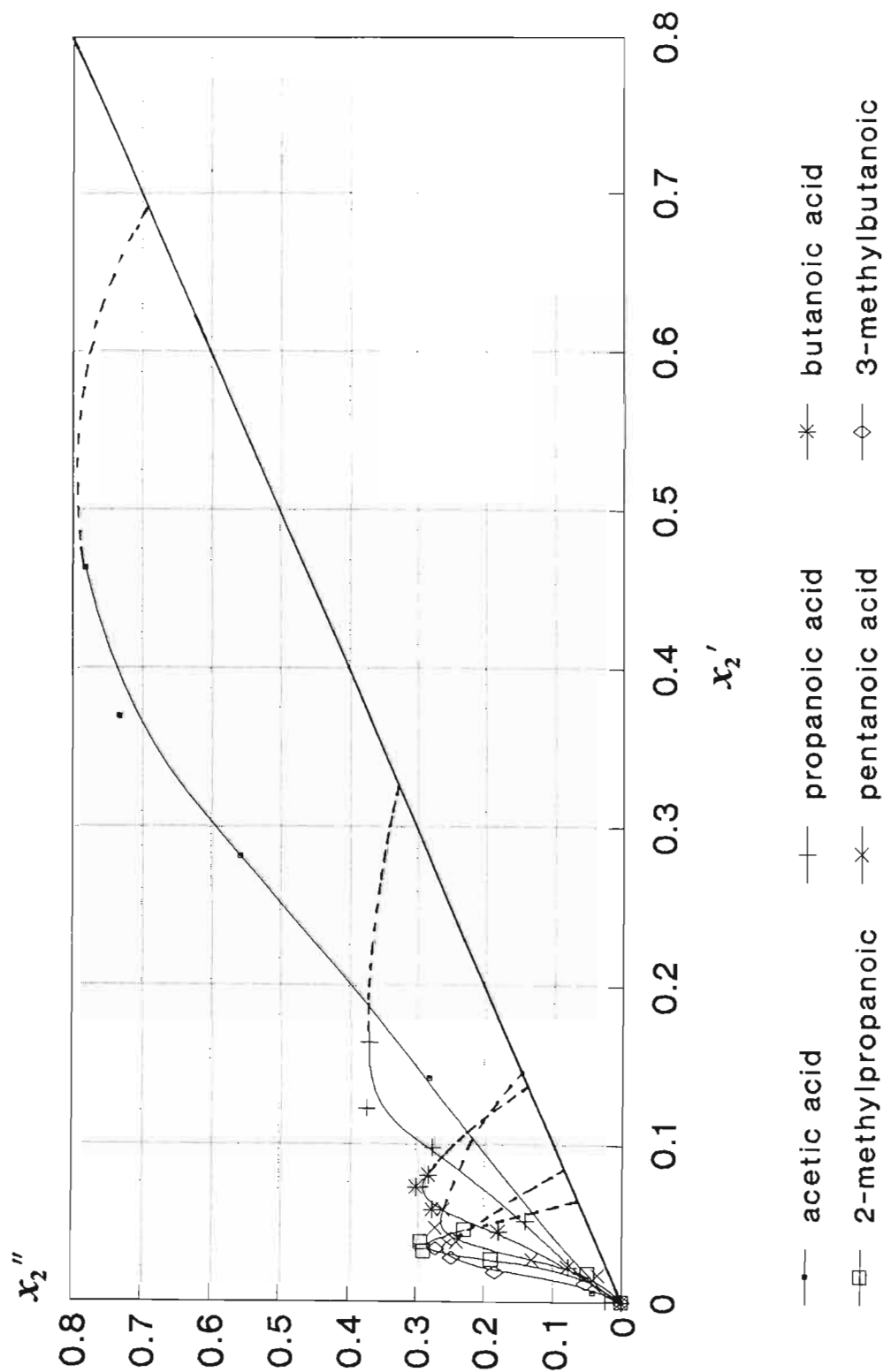


Figure 5.25 A plot of  $x_2''$  against  $x_2'$  showing the relative solubilities of the carboxylic acid in the acetonitrile-rich and heptane-rich layers.

**Table 5.7**      **Representative selectivity values of acetonitrile for the separation of carboxylic acids from heptane at 298.15 K, using equation 5.14**

Carboxylic acid	Selectivity ( $\omega$ )
acetic acid	26
propanoic acid	29
butanoic acid	27
2-methylpropanoic acid	36
pentanoic acid	32
3-methylbutanoic acid	41

### 5.8.1.1 Discussion

#### Previous Work

Liquid - liquid equilibria (LLE) data on a number of ternary mixtures containing acetonitrile have been published in the literature: (acetonitrile + benzene + heptane) at  $T = 318.15$  K by Palmer and Smith (1972) ; (acetone + ethanol or 1-propanol + hexane or heptane or octane) at  $298.15$  K by Nagata (1987); and (acetonitrile + benzene or toluene + cyclohexane) at  $298.15$  K and  $318.15$  K by Nagata and Ohta (1983).

#### This Work

The binodal curves in Figure 5.18 (a) - (f) show that the solubility of heptane in (acetonitrile + acetic acid or propanoic acid or 2 methylpropanoic acid or pentanoic acid or 3-methylbutanoic acid) is very much dependent on the type of acid. Figure 5.25 shows a plot of the relative solubilities of the carboxylic acid in the acetonitrile - rich and heptane - rich layers. The partitioning of a carboxylic acid between heptane and acetonitrile is shown to be dependent on both the length and structure of the carbon chain of the carboxylic acid. In the ternary systems heptane is most soluble in the systems containing butanoic acid, 2-methylpropanoic acid, pentanoic acid or 3-methylbutanoic acid. For a particular carboxylic acid, heptane is more soluble in acetonitrile for mixtures containing propanoic acid than for mixtures containing acetic acid.

The shapes of the binodal curves for (acetonitrile + a carboxylic acid + heptane) are skewed towards the heptane axis. Figure 5.18 shows that the areas of the two phase heterogeneous region for the carboxylic acid mixtures decrease in the following order : 3-methylbutanoic acid ~ pentanoic acid < 2-methylpropanoic acid < butanoic acid < propanoic acid < acetic acid. This implies that the mutual solubility of the components is increased as the carbon chain length of the acid is increased and also that heptane is most soluble in the (acetonitrile - 3-methylbutanoic acid) or (acetonitrile - pentanoic acid) mixture and least soluble in the (acetonitrile - acetic) acid mixture.

The relative solubility of an acid in acetonitrile or the alkane is evident from the tie lines. The

slopes of the tie lines obtained in this work show that all the acids are more soluble in the acetonitrile - rich mixture than the alkane - rich mixtures. For the C5 acids the gradient of the tie lines for 3-methylbutanoic acid is greater than those for pentanoic acid. This could be attributable to the greater solubilizing effect of the two methyl groups on the terminal carbon of 3-methylbutanoic acid as opposed to its straight chain isomer. A similar effect is noted for 2-methylpropanoic as compared to butanoic acid.

The mutual solubility of heptane in acetonitrile and acid mixtures is very much dependent on the length and structure of the carbon chains of the carboxylic acid. Acetic acid, with two carbons is too short a carbon chain to act as a suitable bridging agent between acetonitrile and heptane. Mutual solubility of the carboxylic acids progressively increases with an increase in the length of alkyl chain of the acids. Pentanoic acid and 3-methyl-butanoic acid, two C5 acids, are the best bridging agents of the acids discussed here.

The slopes of the tie lines are very important when investigating phase separation effects. From Figure 5.18, it can be seen for all acids higher than acetic acid, phase separation results in a heptane - rich phase containing over 90 mol % heptane.

Branching of the carbon chain improves the mutual solubility effect and both 2-methylpropanoic acid and 3-methylbutanoic acid show similar solubility to their corresponding straight chain analogues in spite of their non-linear structures. The minimum concentration of a carboxylic acid that is soluble in any concentration of (heptane + acetonitrile) mixtures decreases progressively from acetic acid (0.79 mole fraction) to propanoic acid (0.39), to butanoic acid (0.30), and to 2-methylpropanoic acid (0.29). For the remaining higher order acids, viz., pentanoic acid and its isomer 3-methylbutanoic acid, the minimum concentrations of these acids which are soluble in any (heptane + acetonitrile) mixtures are both almost 0.27 mole fraction.

The effectiveness of extraction of a carboxylic acid (2) by acetonitrile is given by its selectivity  $\omega$  (Letcher *et al.*, 1996), which is a measure of the ability of acetonitrile to separate the carboxylic acid(2) from heptane(3):

$$\omega = \frac{\text{distribution coefficient of carboxylic acids}}{\text{distribution coefficient of heptane}}$$

$$\omega = \frac{(x_2/x_3)_{\text{acetonitrile-rich phase}}}{(x_2/x_3)_{\text{heptane-rich phase}}} \quad (5.14)$$

where  $x_2$  refers to the mole fraction of the carboxylic acid, and  $x_3$  the mole fraction of heptane.

Table 5.7 gives the selectivity values for the separation of carboxylic acids from heptane using acetonitrile. Representative values of selectivity for the middle of the area of the measured tie lines are 26, 29, 27, 36, 32 and 41 for acetic acid, propanoic acid, butanoic acid, 2-methylpropanoic acid, pentanoic acid and 3-methylbutanoic acid respectively. From the selectivity data, it can be concluded that the separation of all the carboxylic acids from heptane by extraction is feasible. It can also be concluded that acetonitrile is an especially good component for the separation of mixtures of heptane and 2-methylpropanoic acid or heptane and 3-methylbutanoic acid.

The modified Hlavaty, beta and logy equations were fitted to the experimental binodal data. The  $\beta$  function gave the best overall fit as compared to the modified Hlavaty equation and logy function.



5.8.2 Liquid-liquid equilibria for mixtures of [acetonitrile + a carboxylic acid + cyclohexane] at 298.15 K

**Table 5.8** Physical Properties of the Pure Components at 298.15 K; Molar Volumes,  $V_m$ , Refractive Indices,  $n_D$ , Volume and Surface Parameters,  $R$  and  $Q$ .

Component	$V_m/(\text{cm}^3 \cdot \text{mol}^{-1})^a$	$n_D$		$R^b$	$Q^b$
		exp	lit. <sup>a</sup>		
acetonitrile	52.87	1.3413	1.3416	1.870	1.724
acetic acid	57.53	1.3697	1.3698	2.202	2.072
propanoic acid	74.97	1.3846	1.3843	2.877	2.612
butanoic acid	92.43	1.3955	1.3958	3.551	3.152
2-methylpropanoic acid	93.44	1.3913	1.3917	3.550	3.148
pentanoic acid	109.29	1.4064	1.4060	4.226	3.692
3-methylbutanoic acid	110.54	1.4019	1.4022	4.225	3.688
cyclohexane	108.75	1.4237	1.4235	4.046	3.240

<sup>a</sup> Riddick *et al.*(1986)

<sup>b</sup> Gmehling *et al.*(1993)

**Table 5.9      Compositions of Points on the Binodal Curve at 298.15 K for the systems: [Acetonitrile (1) + a Carboxylic Acid (2) + Cyclohexane (3)], Equilibrium Mole Fraction,  $x_1$ ,  $x_2$ .**

$x_1$	$x_2$		$x_1$	$x_2$
Acetic Acid				
0.939	0.000		0.276	0.606
0.910	0.027		0.217	0.655
0.885	0.051		0.185	0.676
0.797	0.133		0.163	0.688
0.708	0.219		0.093	0.694
0.662	0.259		0.059	0.599
0.572	0.348		0.053	0.450
0.475	0.439		0.050	0.314
0.451	0.459		0.048	0.246
0.378	0.522		0.046	0.135
0.330	0.568		0.044	0.000
Propanoic Acid				
0.939	0.000		0.336	0.325
0.931	0.010		0.259	0.307
0.889	0.040		0.184	0.249
0.816	0.103		0.126	0.179
0.725	0.173		0.093	0.129
0.673	0.207		0.064	0.067
0.575	0.263		0.044	0.000
0.456	0.313			
Butanoic Acid				
0.939	0.000		0.413	0.241
0.919	0.014		0.376	0.244
0.896	0.031		0.300	0.239
0.837	0.076		0.249	0.220
0.742	0.137		0.164	0.172
0.684	0.169		0.111	0.110
0.578	0.211		0.069	0.050
0.501	0.234		0.044	0.000
2-Methylpropanoic Acid				
0.939	0.000		0.426	0.239
0.916	0.016		0.346	0.250
0.888	0.036		0.274	0.242
0.813	0.087		0.196	0.218
0.729	0.137		0.136	0.173
0.684	0.165		0.090	0.124
0.575	0.213		0.070	0.081
0.499	0.231		0.044	0.000

$x_1$	$x_2$	$x_1$	$x_2$
Pentanoic Acid			
0.939	0.000	0.446	0.201
0.915	0.016	0.379	0.205
0.890	0.033	0.320	0.201
0.834	0.068	0.259	0.192
0.741	0.119	0.171	0.158
0.695	0.143	0.129	0.125
0.576	0.181	0.084	0.071
0.495	0.196	0.044	0.000
3-Methylbutanoic Acid			
0.939	0.000	0.381	0.205
0.918	0.014	0.330	0.202
0.902	0.025	0.268	0.196
0.831	0.067	0.188	0.167
0.751	0.117	0.135	0.136
0.697	0.143	0.087	0.092
0.585	0.181	0.065	0.056
0.503	0.197	0.044	0.000
0.427	0.201		

**Table 5.10      Calibration Curve Data at 298.15 K for the systems : [Acetonitrile (1) + a Carboxylic Acid (2) + Cyclohexane (3)], Equilibrium Mole Fraction,  $x_1$ , Refractive Index,  $n_D$ .**

$x_1$	$n_D$	$x_1$	$n_D$
Acetic Acid			
1.000	1.3413	0.330	1.3702
0.939	1.3487	0.276	1.3716
0.910	1.3508	0.217	1.3732
0.885	1.3521	0.185	1.3766
0.797	1.3547	0.163	1.3788
0.708	1.3582	0.093	1.3914
0.662	1.3595	0.059	1.3996
0.572	1.3630	0.053	1.4015
0.475	1.3660	0.048	1.4030
0.451	1.3673	0.044	1.4050
0.378	1.3689	0.000	1.4237
Propanoic Acid			
1.000	1.3413	0.336	1.3913
0.939	1.3492	0.259	1.3971
0.931	1.3511	0.184	1.4032
0.889	1.3535	0.126	1.4096
0.816	1.3584	0.093	1.4139
0.725	1.3632	0.064	1.4172
0.673	1.3679	0.044	1.4196
0.575	1.3736	0.000	1.4237
0.456	1.3819		
Butanoic Acid			
1.000	1.3413	0.413	1.3913
0.939	1.3492	0.376	1.3948
0.919	1.3512	0.300	1.3989
0.896	1.3549	0.249	1.4018
0.837	1.3598	0.164	1.4085
0.742	1.3678	0.111	1.4132
0.684	1.3719	0.069	1.4162
0.578	1.3798	0.044	1.4196
0.501	1.3845	0.000	1.4237

$x_I$	$n_D$	$x_I$	$n_D$
2-Methylpropanoic Acid			
1.000	1.3413	0.426	1.3890
0.939	1.3492	0.346	1.3939
0.916	1.3517	0.274	1.3991
0.888	1.3543	0.196	1.4047
0.813	0.3594	0.136	1.4090
0.729	0.3674	0.090	1.4143
0.684	0.3708	0.070	1.4161
0.575	1.3786	0.044	1.4196
0.499	1.3839	0.000	1.4237
Pentanoic Acid			
1.000	1.3413	0.446	1.3948
0.939	1.3492	0.379	1.3978
0.915	1.3521	0.320	1.4012
0.890	1.3547	0.259	1.4047
0.834	1.3609	0.171	1.4101
0.741	1.3702	0.129	1.4135
0.695	1.3749	0.084	1.4167
0.576	1.3841	0.044	1.4196
0.495	1.3897	0.000	1.4237
3-Methylbutanoic Acid			
1.000	1.3413	0.381	1.3964
0.939	1.3492	0.330	1.3990
0.918	1.3518	0.268	1.4032
0.902	1.3539	0.188	1.4083
0.831	1.3611	0.135	1.4111
0.751	1.3698	0.087	1.4155
0.697	1.3736	0.065	1.4176
0.585	1.3822	0.044	1.4196
0.503	1.3873	0.000	1.4237
0.427	1.3931		

**Table 5.11** Composition of the Conjugate Solutions,  $x_1'$ ,  $x_2'$ , and  $x_1''$ ,  $x_2''$ , at 298.15 K.

cyclohexane- rich			acetonitrile-rich		
$x_1'$	$x_2'$	$n_D$	$x_1''$	$x_2''$	$n_D$
Acetonitrile (1) + Acetic Acid (2) + Cyclohexane (3)					
0.045	0.046	1.4043	0.779	0.154	1.3559
0.046	0.151	1.4039	0.655	0.274	1.3598
0.048	0.263	1.4032	0.499	0.421	1.3657
0.049	0.340	1.4029	0.347	0.551	1.3699
0.052	0.515	1.4019	0.171	0.684	1.3779
Acetonitrile (1) + Propanoic Acid (2) + Cyclohexane (3)					
0.046	0.028	1.4191	0.812	0.108	1.3586
0.074	0.084	1.4159	0.683	0.202	1.3664
0.081	0.120	1.4151	0.527	0.286	1.3773
0.101	0.144	1.4128	0.423	0.319	1.3846
0.132	0.189	1.4093	0.329	0.321	1.3913
Acetonitrile (1) + Butanoic Acid (2) + Cyclohexane (3)					
0.046	0.008	1.4189	0.836	0.075	1.2094
0.051	0.018	1.4184	0.767	0.122	1.2591
0.069	0.051	1.4166	0.604	0.203	1.3369
0.086	0.079	1.4151	0.460	0.239	1.3743
0.095	0.084	1.4142	0.349	0.244	1.3911
Acetonitrile (1) + 2-Methylpropanoic Acid (2) + Cyclohexane (3)					
0.046	0.005	1.4189	0.808	0.092	1.3608
0.050	0.019	1.4184	0.759	0.122	1.3646
0.057	0.041	1.4177	0.596	0.205	1.3772
0.061	0.060	1.4172	0.455	0.244	1.3871
0.080	0.107	1.4152	0.277	0.247	1.3985
Acetonitrile (1) + Pentanoic Acid (2) + Cyclohexane (3)					
0.048	0.008	1.4195	0.829	0.071	1.3615
0.059	0.031	1.4186	0.734	0.126	1.3709
0.066	0.047	1.4180	0.549	0.189	1.3866
0.083	0.074	1.4167	0.373	0.205	1.3982
0.089	0.084	1.4162	0.267	0.192	1.4044
Acetonitrile (1) + 3-Methylbutanoic Acid (2) + Cyclohexane (3)					
0.048	0.009	1.4189	0.823	0.078	1.3624
0.050	0.020	1.4187	0.716	0.142	1.3722
0.061	0.045	1.4177	0.545	0.188	1.3850
0.076	0.068	1.4164	0.370	0.204	1.3966
0.081	0.082	1.4160	0.256	0.193	1.4039

**Table 5.12**      **Coefficients  $A_i$ ,  $B_i$ , and  $C_i$  in Equations (5.8)-(5.10), at 298.15 K.**

Hlavatý	$\beta$	$\log \gamma$
Acetonitrile (1) + Acetic acid (2) + Cyclohexane (3)		
$A_1 = 1.001$	$B_1 = 3.271$	$C_1 = 3.026$
$A_2 = 1.234$	$B_2 = 1.210$	$C_2 = 1.187$
$A_3 = 5.721$	$B_3 = 1.200$	$C_3 = 1.658$
$\sigma = 0.020$	$\sigma = 0.029$	$\sigma = 0.027$
Acetonitrile (1) + Propanoic acid (2) + Cyclohexane (3)		
$A_1 = 0.140$	$B_1 = 1.045$	$C_1 = 0.992$
$A_2 = -0.074$	$B_2 = 0.850$	$C_2 = 0.838$
$A_3 = 1.386$	$B_3 = 0.946$	$C_3 = 1.266$
$\sigma = 0.004$	$\sigma = 0.010$	$\sigma = 0.010$
Acetonitrile (1) + Butanoic acid (2) + Cyclohexane (3)		
$A_1 = 0.008$	$B_1 = 1.058$	$C_1 = 0.974$
$A_2 = -0.114$	$B_2 = 1.001$	$C_2 = 0.977$
$A_3 = 0.842$	$B_3 = 1.053$	$C_3 = 1.414$
$\sigma = 0.003$	$\sigma = 0.005$	$\sigma = 0.006$
Acetonitrile (1) + 2-Methylpropanoic acid (2) + Cyclohexane (3)		
$A_1 = -0.167$	$B_1 = 0.972$	$C_1 = 0.905$
$A_2 = -0.098$	$B_2 = 0.990$	$C_2 = 0.968$
$A_3 = 0.6395$	$B_3 = 0.929$	$C_3 = 1.296$
$\sigma = 0.003$	$\sigma = 0.004$	$\sigma = 0.005$
Acetonitrile (1) + Pentanoic acid (2) + Cyclohexane (3)		
$A_1 = -0.139$	$B_1 = 0.786$	$C_1 = 0.736$
$A_2 = -0.133$	$B_2 = 0.950$	$C_2 = 0.930$
$A_3 = 0.452$	$B_3 = 0.939$	$C_3 = 1.295$
$\sigma = 0.002$	$\sigma = 0.004$	$\sigma = 0.004$
Acetonitrile (1) + 3-Methylbutanoic acid (2) + Cyclohexane (3)		
$A_1 = -0.193$	$B_1 = 0.756$	$C_1 = 0.698$
$A_2 = -0.163$	$B_2 = 0.942$	$C_2 = 0.919$
$A_3 = 0.336$	$B_3 = 0.884$	$C_3 = 1.222$
$\sigma = 0.003$	$\sigma = 0.005$	$\sigma = 0.006$

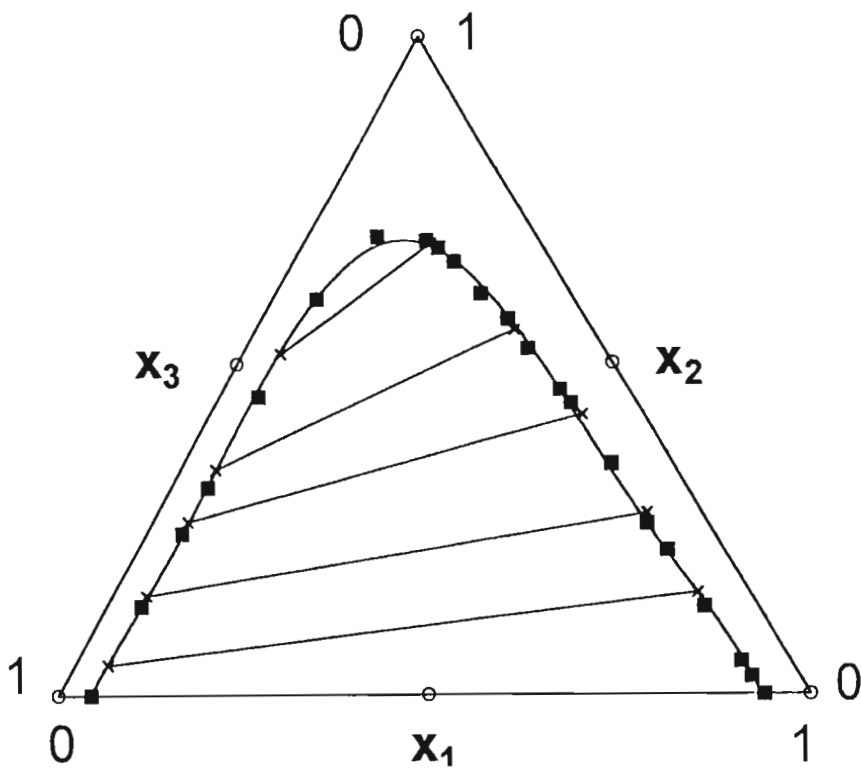


Figure 5.26 Liquid-liquid equilibrium data for the system [acetonitrile (1) + acetic acid (2) + cyclohexane (3)] at 298.15 K.

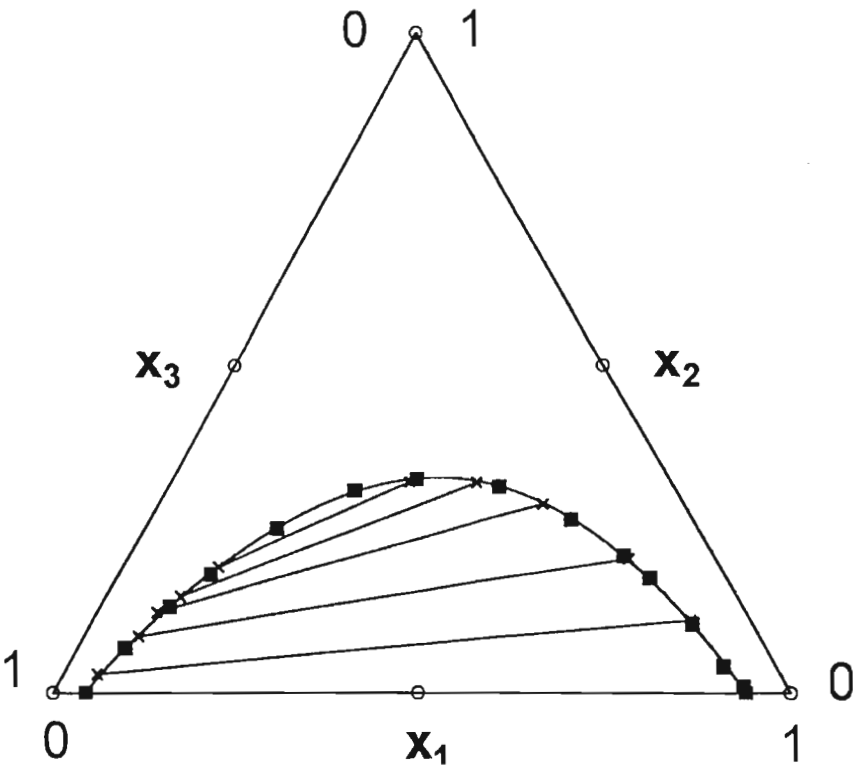


Figure 5.27 Liquid-liquid equilibrium data for the system [acetonitrile (1) + propanoic acid (2) + cyclohexane (3)] at 298.15 K.



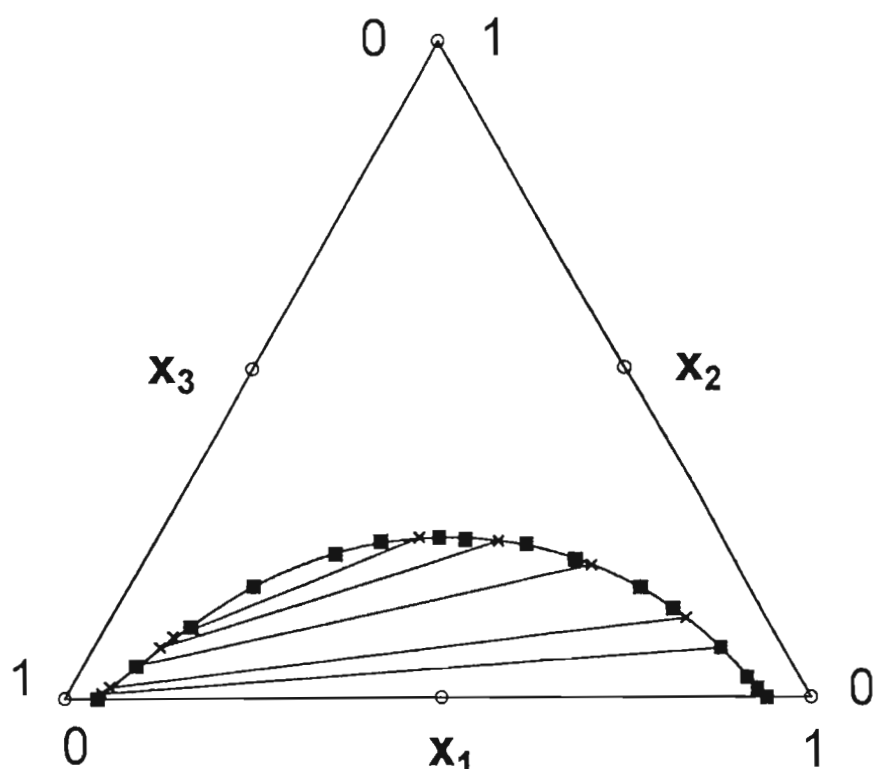


Figure 5.28 Liquid-liquid equilibrium data for the system [acetonitrile (1) + butanoic acid (2) + cyclohexane (3)] at 298.15 K.

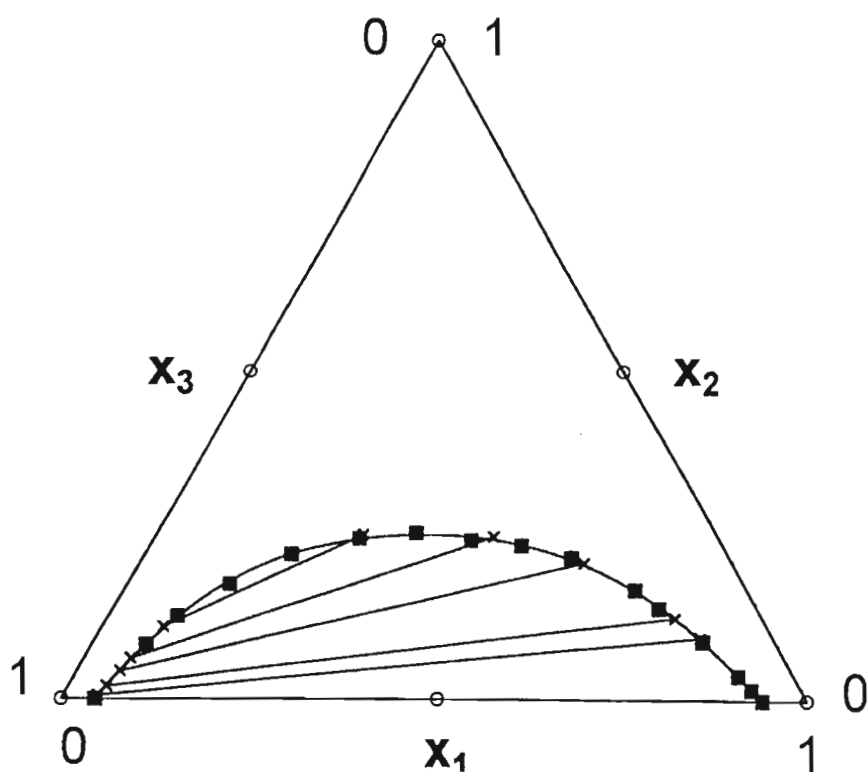


Figure 5.29 Liquid-liquid equilibrium data for the system [acetonitrile (1) + 2-methylpropanoic acid (2) + cyclohexane (3)] at 298.15 K.

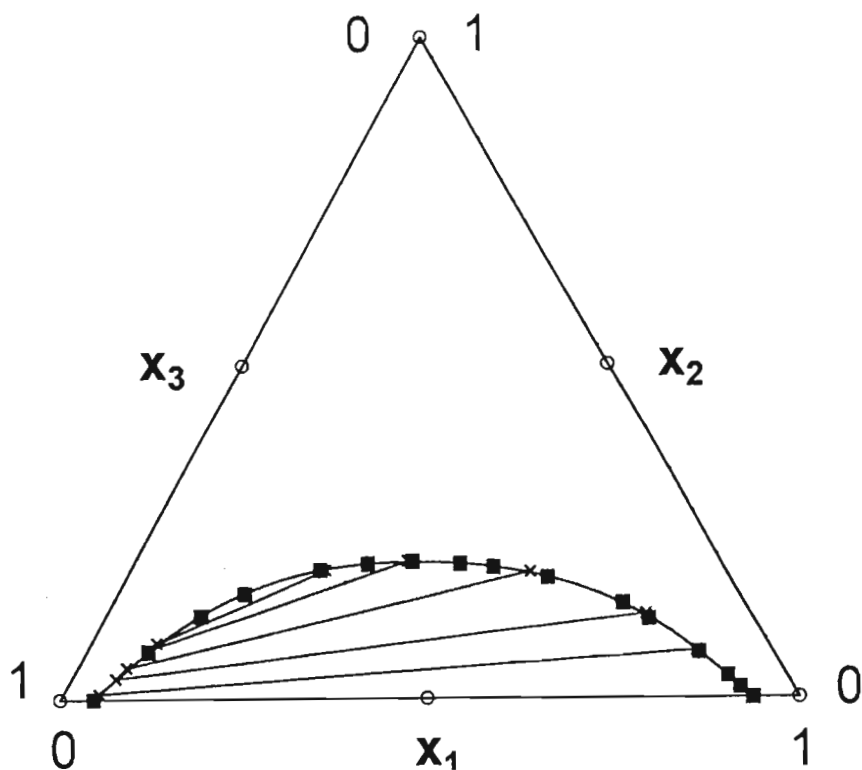


Figure 5.30 Liquid-liquid equilibrium data for the system [acetonitrile (1) + pentanoic acid (2) + cyclohexane (3)] at 298.15 K.

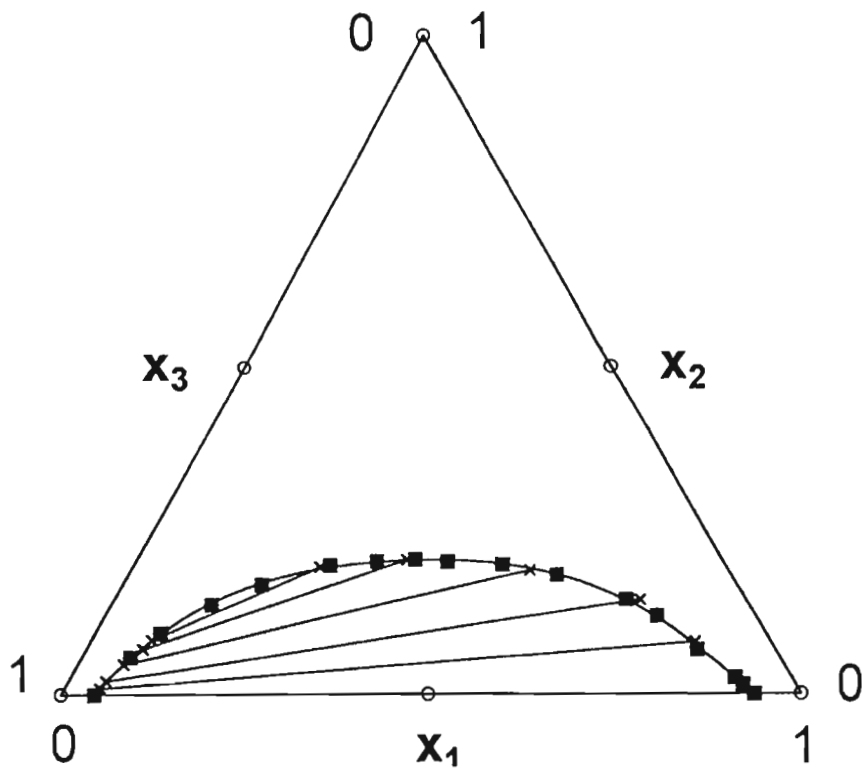
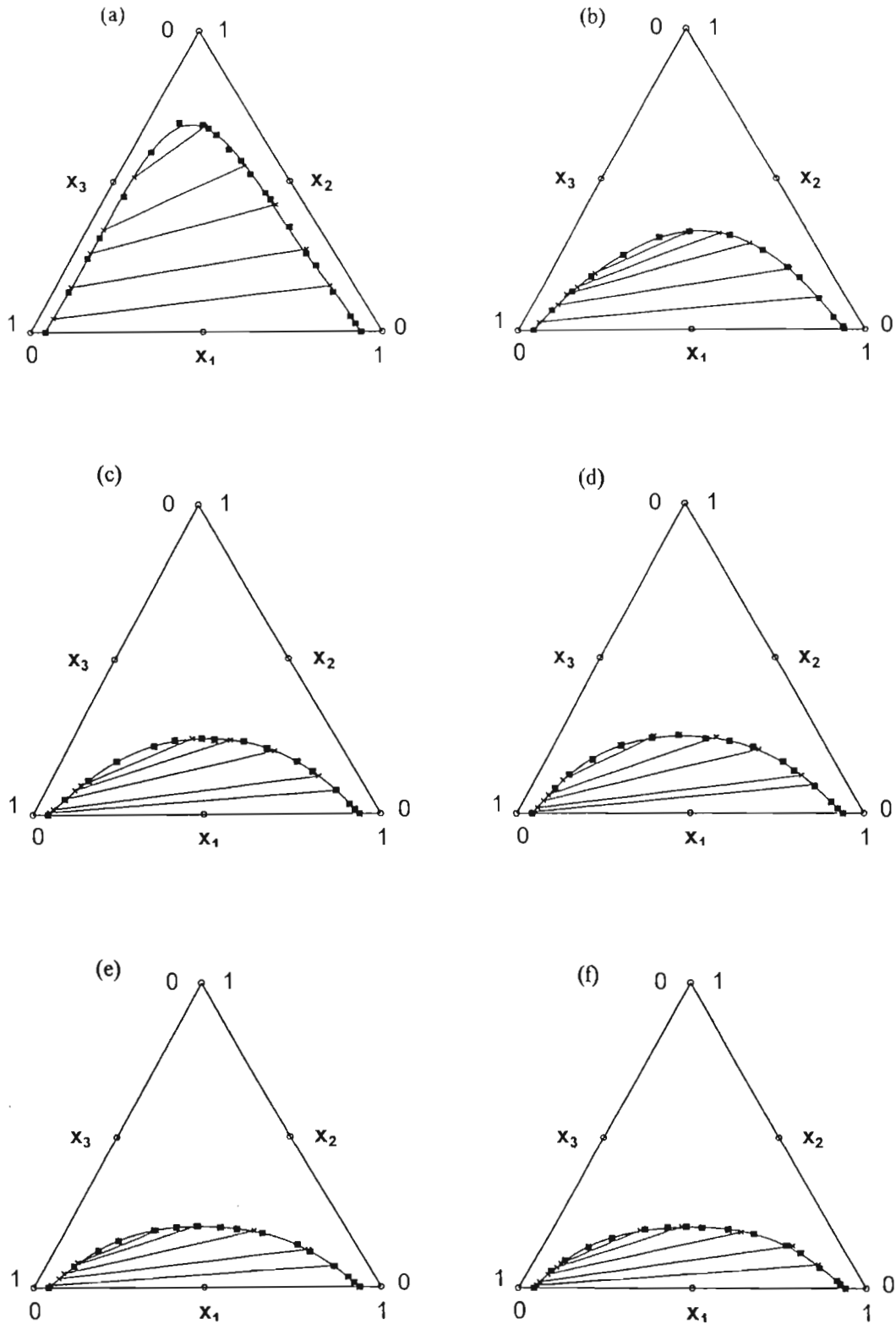


Figure 5.31 Liquid-liquid equilibrium data for the system [acetonitrile (1) + 3-methylbutanoic acid (2) + cyclohexane (3)] at 298.15 K.



**Figure 5.32** Summary of liquid-liquid equilibrium data for the following systems at 298.15 K: (a) acetonitrile(1) + acetic acid(2) + cyclohexane(3); (a) acetonitrile(1) + propanoic acid(2) + cyclohexane (3); (c) acetonitrile(1) + butanoic acid(2) + cyclohexane(3); (d) acetonitrile(1) + 2-methylpropanoic acid(2) + cyclohexane (3); (e) acetonitrile(1) + pentanoic acid(2) + cyclohexane (3); (e) acetonitrile(1) + 3-methylbutanoic acid(2) + cyclohexane (3). [Key: (■) experimental points; (×) experimental tie-lines]

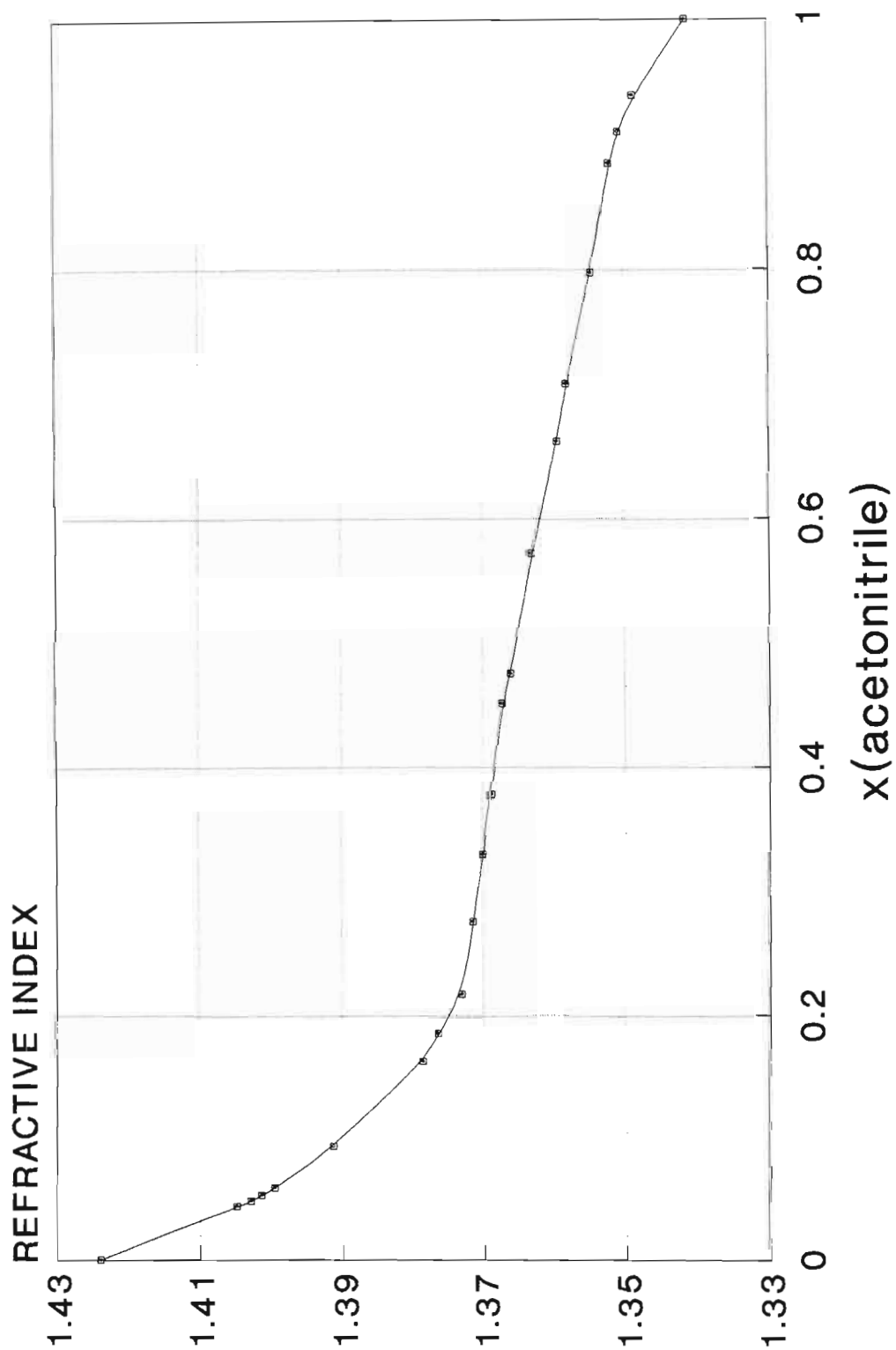


Figure 5.33 Calibration curve for (acetonitrile + acetic acid + cyclohexane) system at 298.15 K.

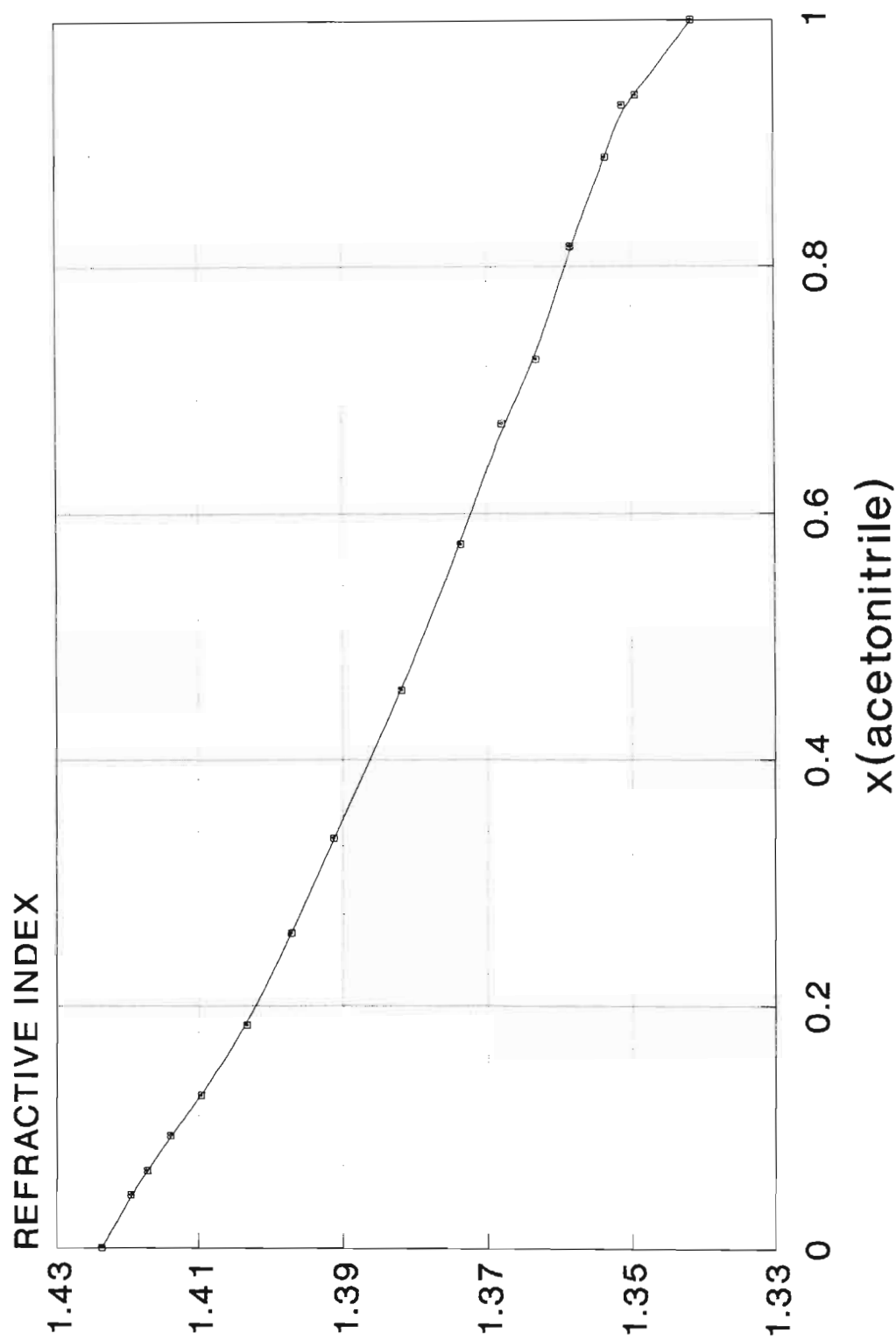


Figure 5.34 Calibration curve for (acetonitrile + propanoic acid + cyclohexane) system at 298.15 K.

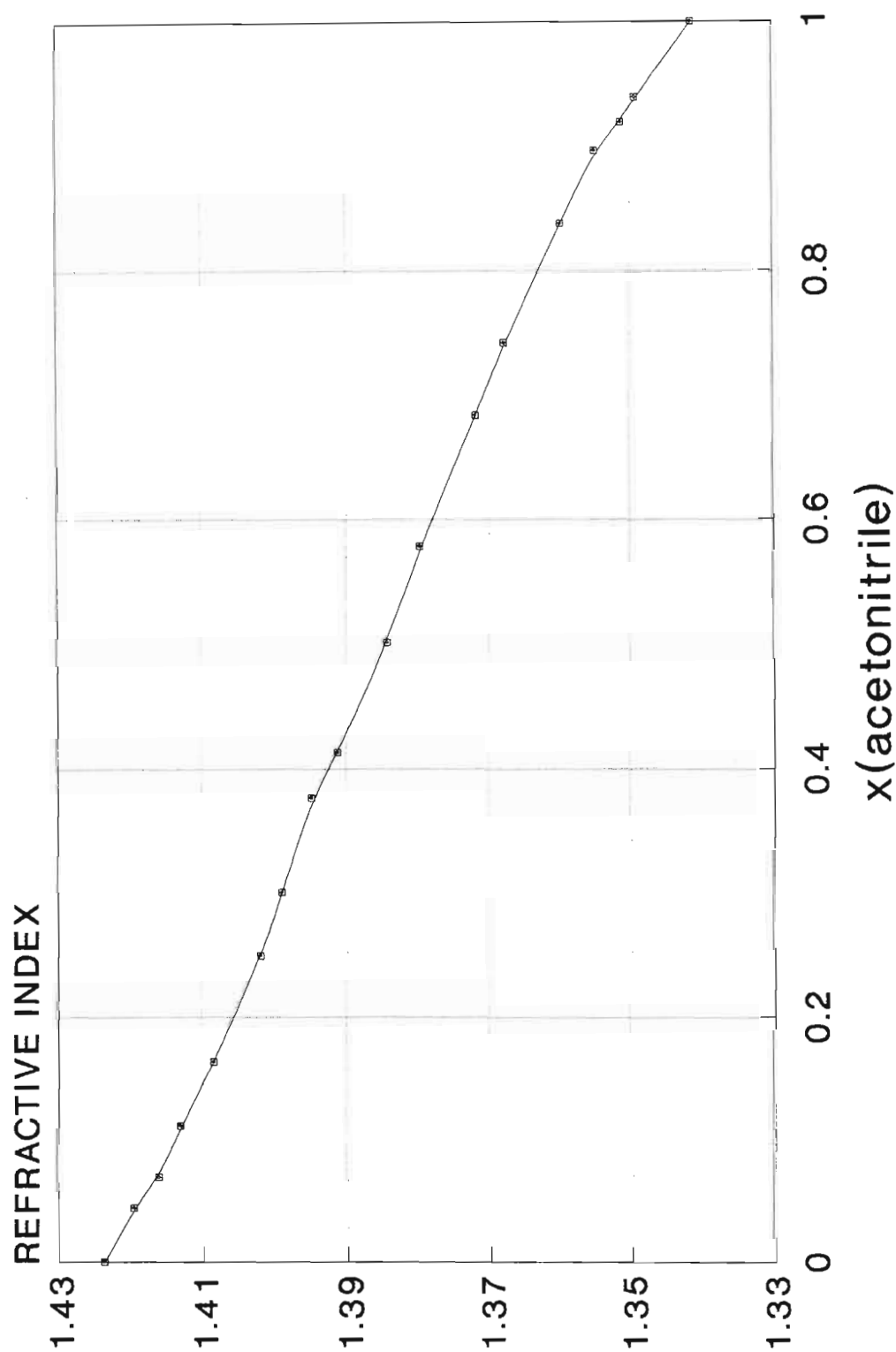


Figure 5.35 Calibration curve for (acetonitrile + butanoic acid + cyclohexane) system at 298.15 K.

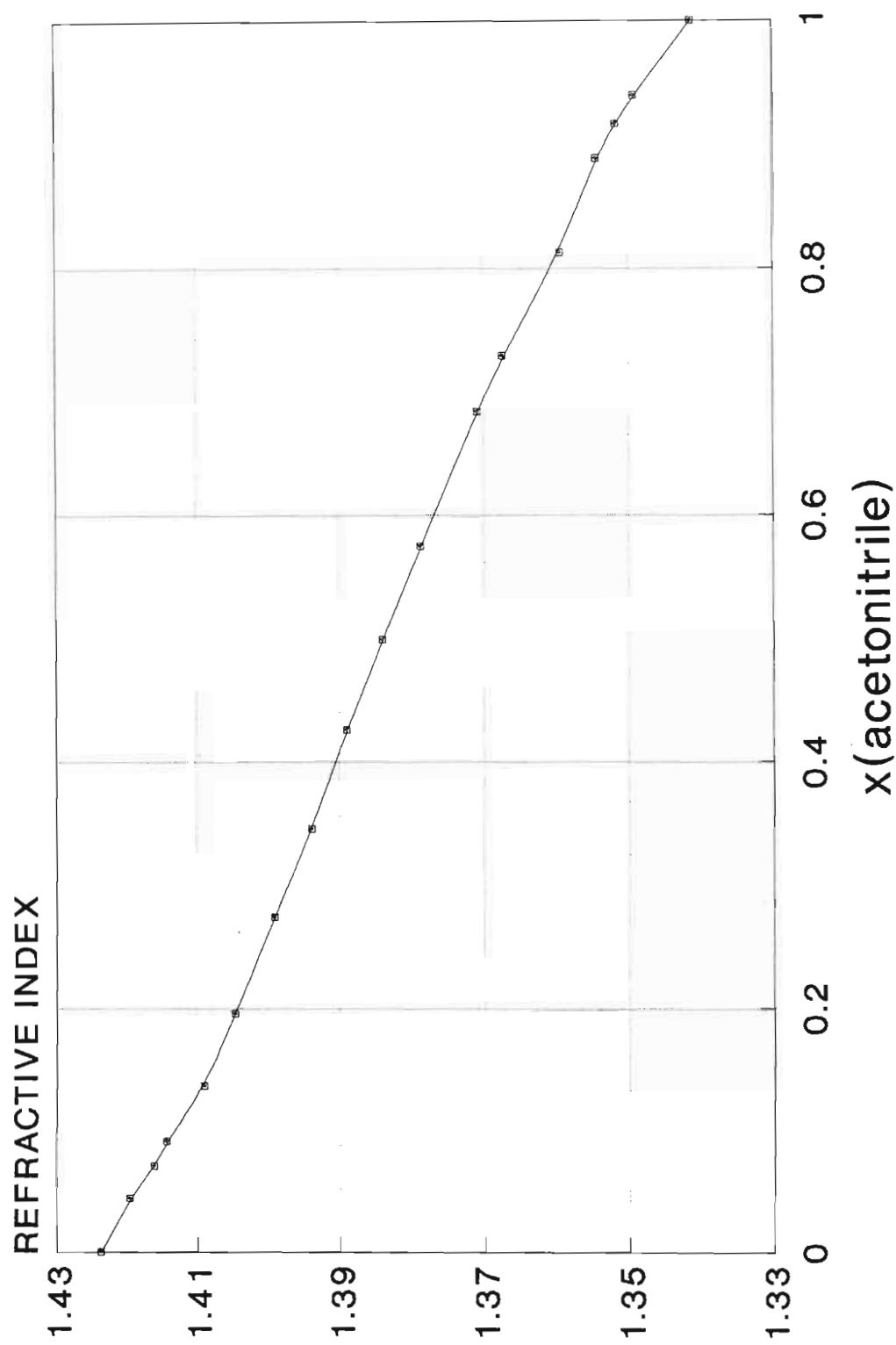
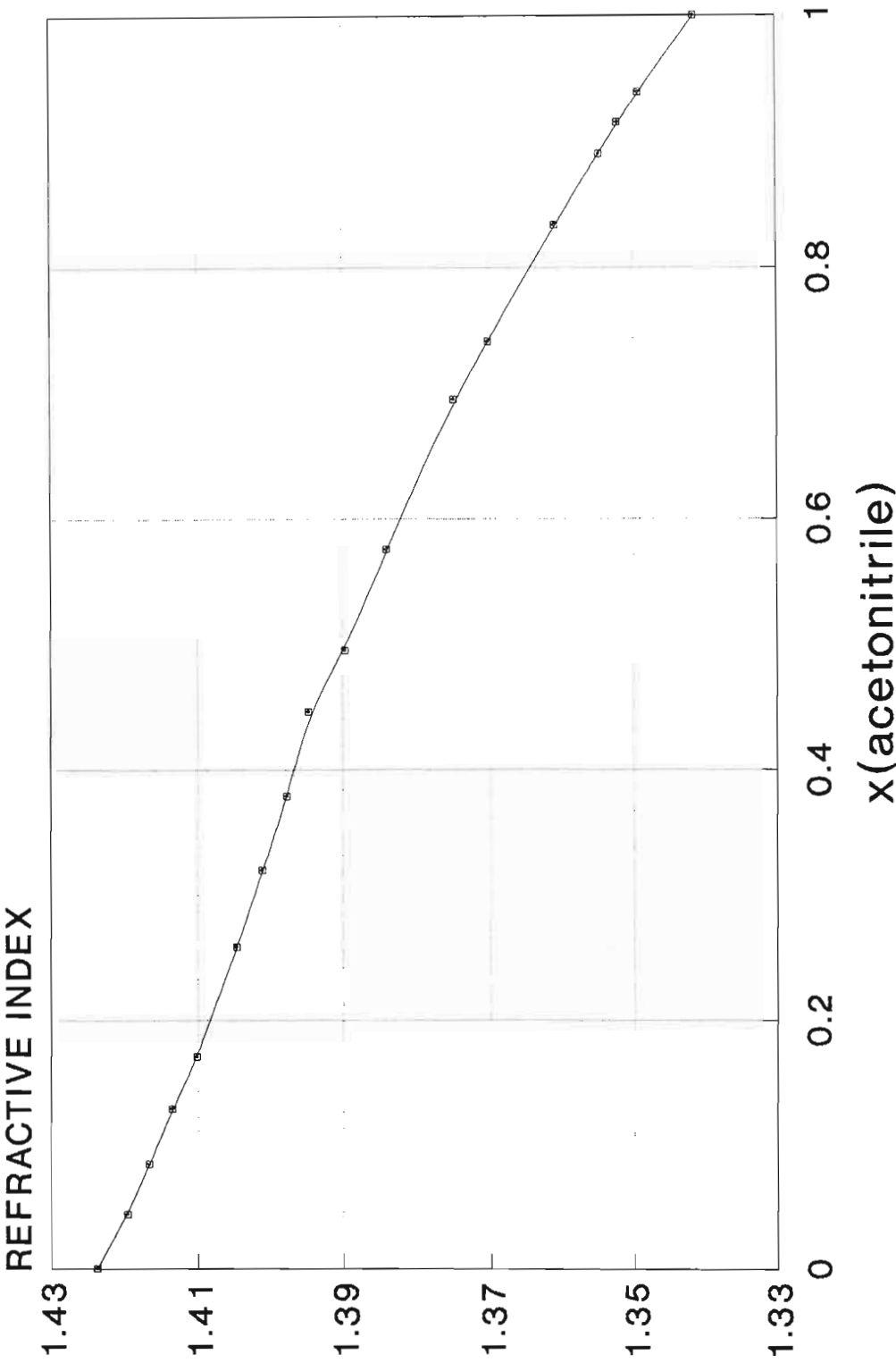


Figure 5.36 Calibration curve for (acetonitrile + 2-methylpropanoic acid + cyclohexane) system at 298.15 K.



**Figure 5.37** Calibration curve for (acetonitrile + pentanoic acid + cyclohexane) system at 298.15 K.



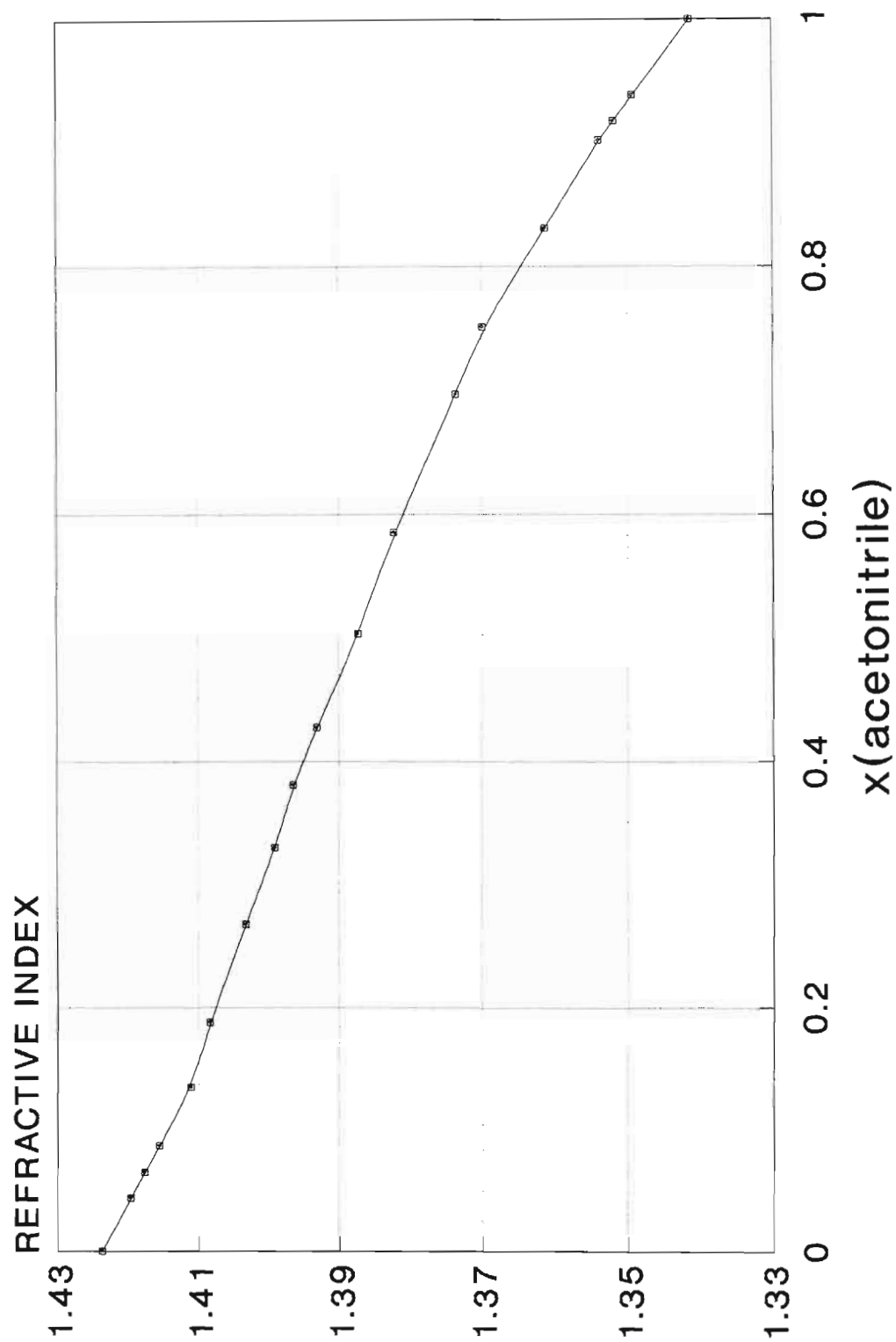


Figure 5.38 Calibration curve for (acetonitrile + 3-methylbutanoic acid + cyclohexane) system at 298.15 K.

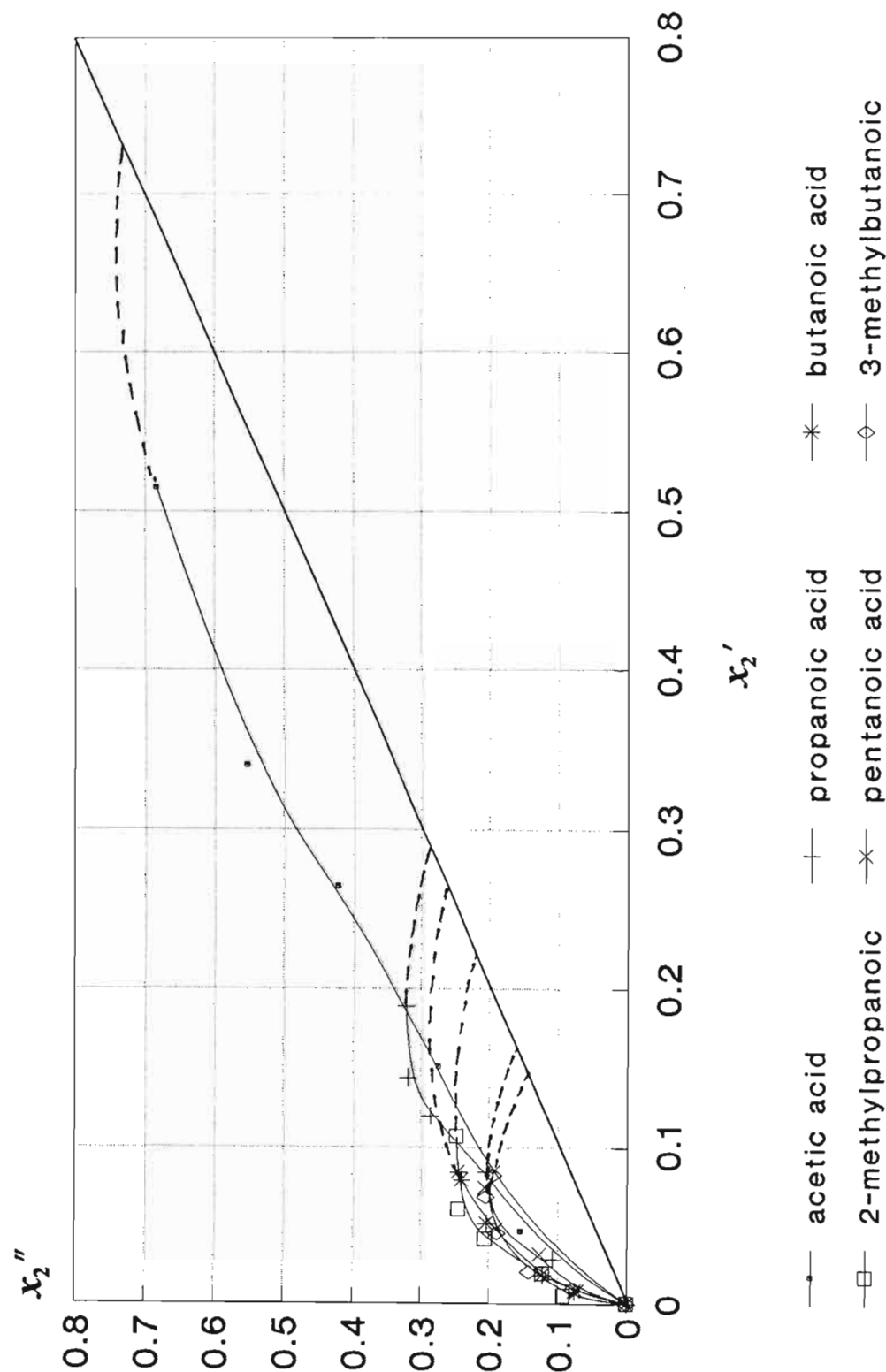


Figure 5.39 A plot of  $x_2''$  against  $x_2'$  showing the relative solubilities of the carboxylic acid in the acetonitrile-rich and cyclohexane-rich layers.

**Table 5.13**     **Representative selectivity values of acetonitrile for the separation of carboxylic acids from cyclohexane at 298.15 K, using equation 5.15**

Carboxylic acid	Selectivity ( $\omega$ )
acetic acid	13
propanoic acid	10
butanoic acid	18
2-methylpropanoic acid	23
pentanoic acid	14
3-methylbutanoic acid	14

### 5.8.2.1 Discussion of Ternary Systems involving acetonitrile / carboxylic acid / cyclohexane at 298.15 K

#### Previous Work

Liquid - liquid equilibria (LLE) data on related systems have been reported in the literature : (acetonitrile + benzene + heptane) at  $T = 298.15$  K by Palmer and Smith (1972), (acetonitrile + ethanol or 1-propanol + hexane or heptane, or octane) at  $T = 298.15$  K by Nagata (1987), (acetonitrile + benzene or toluene + cyclohexane) at  $T = 298.15$  K and  $T = 318.15$  K by Nagata and Ohta (1983). None of the data presented in this section have been published in the literature.

#### This Work

The amount of hydrocarbon that is miscible with an (acetonitrile + carboxylic acid) mixture is dependent on the carbon number and type of carboxylic acid. In the ternary systems, illustrated in Figure 5.32(a) - (f), it can be observed that cyclohexane is most soluble in the systems containing butanoic acid, 2-methylpropanoic acid, pentanoic acid, or 3-methylbutanoic acid. It is again found from Figure 5.32(a) - (f) that for a particular carboxylic acid, the solubility of cyclohexane in acetonitrile is inversely related to the area of the two phase region.

The shapes of the binodal curves for (acetonitrile + carboxylic acid + cyclohexane) system show less skewing towards the cyclohexane axis than that of the (acetonitrile + carboxylic acid + heptane) system. Figures 5.32(a) - (f) show that the area of the two - phase heterogeneous region for the carboxylic acid mixtures increases in the order:

3-methylbutanoic acid  $\sim$  pentanoic acid < 2-methylpropanoic acid < butanoic acid < propanoic acid < acetic acid.

The partitioning of the carboxylic acid between the cyclohexane - rich and acetonitrile - rich layers for six of the systems is expressed in Figure 5.39, where the mole fraction of each carboxylic acid in the conjugate layers has been plotted. All the carboxylic acids are more soluble in the acetonitrile layer than the cyclohexane layer.

From Figure 5.32 it can be deduced that the single phase homogeneous region increases as the carbon chain length of the acid is increased, and it is found that cyclohexane is most soluble in the (3-methylbutanoic acid + acetonitrile) or (pentanoic acid + acetonitrile) mixture, and least soluble in the (acetic acid + acetonitrile) mixture.

The relative solubility of a carboxylic acid in acetonitrile or cyclohexane is evident from the tie-lines. The gradients of the tie-lines obtained in this study show that all the acids are more soluble in the acetonitrile than the alkane (hydrocarbon) mixture. For the C5 acids, the gradient of the tie-lines for 3-methylbutanoic acid is significantly greater than those for pentanoic acid. This could possibly be attributed to the greater solubilizing effect of the two methyl groups on the terminal carbon of 3-methylbutanoic acid as opposed to its straight-chain isomer. A similar effect is noted for 2-methylpropanoic acid as compared to butanoic acid, and this indicates that 2-methylpropanoic acid shows a more profound solubility preference for the acetonitrile than cyclohexane, as opposed to its straight chain isomer.

The relatively large two-phase heterogeneous region for the (acetonitrile + acetic acid + cyclohexane) system suggests that the entrainer acetonitrile has high capacity or loading of solute per mole fraction of the solvent (acetonitrile), that is small quantities of it would be needed for efficient separation.

It is also evident that branching of the carbon chain improves appreciably the mutual solubility effect and both 2-methylpropanoic acid and 3-methylbutanoic acid show very similar solubility characteristics.

The minimum concentration of a carboxylic acid that is soluble in any concentration of cyclohexane + acetonitrile) mixtures again decreases substantially from acetic acid (0.69 mole fraction), to propanoic acid (0.33 mole fraction), to butanoic acid (0.24 mole fraction), and to 2-methylpropanoic acid (0.25 mole fraction). The remaining higher order acids, viz., pentanoic and 3-methylbutanoic show reduced solubility in (cyclohexane + acetonitrile) mixture at a minimum value of approximately 0.21 mole fraction.

The effectiveness of extraction of a carboxylic acid(2) from cyclohexane(3):

$$\omega = \frac{\text{distribution coefficient of carboxylic acids}}{\text{distribution coefficient of cyclohexane}}$$

$$\omega = \frac{(x_2 / x_3)_{\text{acetonitrile-rich phase}}}{(x_2 / x_3)_{\text{cyclohexane-rich phase}}} \quad (5.15)$$

where  $x_2$  refers to the mole fraction of the carboxylic acid and  $x_3$ , the mole fraction of the cyclohexane. From Table 5.13, representative values of selectivity for the middle of the area of the measured tie-lines are (13, 10, 18, 23, 14 and 14) for (acetic acid, propanoic acid, butanoic acid, 2-methylpropanoic acid, pentanoic acid, and 3-methylpropanoic acid), respectively. From these values it can be concluded that the separation of all the carboxylic acids from cyclohexane by extraction is feasible. It can also be concluded that acetonitrile is an especially good component for the separation of mixtures of cyclohexane and 2-methylpropanoic acid or cyclohexane and butanoic acid.

Comparing the ternary diagrams for all the systems (acetonitrile + a carboxylic acid + cyclohexane) discussed presently, with the ternary diagrams for (acetonitrile + acetic acid or propanoic acid or butanoic acid or 2-methylpropanoic acid, or pentanoic acid or 3-methylpropanoic acid + heptane), it is found that replacing heptane with cyclohexane always results in a decrease in the area of the two-phase heterogeneous region and a corresponding decrease in the slope of the tie-lines. This implies that the solvent acetonitrile has a higher solubility, but lower solvent power (capacity) for (carboxylic acid + cyclohexane) mixtures, at the same temperature and pressure conditions. Acetonitrile is thus a better solvent for extracting carboxylic acids from heptane than from cyclohexane.

The standard deviations  $\sigma$  of the three fitted equations to the binodal curves, viz. the modified Hlavatý, beta and  $\log \gamma$ , again show that all are capable of fitting binodal curve data points. The modified Hlavatý equation gave the best fit, and for all six of the ternary systems, lower standard deviations ( $\sigma$ ) were obtained.

5.8.3    **Liquid-liquid equilibria for mixtures of [benzonitrile + a carboxylic acid + water]  
at 298.15 K**

**Table 5.14    Physical Properties of the Pure Components at T = 298.15 K; Molar Volumes,  $V_{\text{mi}}$ , Refractive Indices,  $n_{\text{D}}$ , Volume and Surface Parameters,  $R$  and  $Q$ .**

Component	$V_{\text{mi}}/(\text{cm}^3 \cdot \text{mol}^{-1})^a$	$n_{\text{D}}$		$R^b$	$Q^b$
		exp	lit. <sup>a</sup>		
benzonitrile	103.06	1.5260	1.5257	3.991	2.996
acetic acid	57.53	1.3697	1.3698	2.202	2.072
propanoic acid	74.97	1.3846	1.3843	2.877	2.612
butanoic acid	92.43	1.3955	1.3958	3.551	3.152
2-methylpropanoic acid	93.44	1.3913	1.3917	3.550	3.148
pentanoic acid	109.29	1.4064	1.4060	4.226	3.692
3-methylbutanoic acid	110.54	1.4019	1.4022	4.225	3.688
water	18.07	1.3325	1.3325	0.920	1.400

<sup>a</sup> Riddick *et al.*  
<sup>b</sup> Gmehling *et al.*

**Table 5.15      Compositions of Points on the Binodal Curve at T = 298.15 K for the systems : [Benzonitrile (1) + a Carboxylic Acid (2) + Water (3)], Equilibrium Mole Fraction,  $x_1$ ,  $x_2$ .**

$x_1$	$x_2$	$x_1$	$x_2$
Acetic Acid			
0.946	0.000	0.155	0.277
0.866	0.044	0.106	0.268
0.779	0.092	0.060	0.244
0.701	0.136	0.042	0.225
0.595	0.181	0.018	0.180
0.514	0.221	0.004	0.105
0.429	0.255	0.002	0.054
0.348	0.273	0.000	0.000
0.237	0.282		
Propanoic Acid			
0.946	0.000	0.220	0.285
0.868	0.052	0.168	0.268
0.832	0.075	0.115	0.242
0.754	0.121	0.062	0.188
0.677	0.163	0.034	0.144
0.597	0.199	0.022	0.122
0.502	0.233	0.013	0.102
0.432	0.252	0.009	0.071
0.310	0.280	0.000	0.000
Butanoic Acid			
0.946	0.000	0.130	0.334
0.879	0.046	0.098	0.321
0.809	0.086	0.074	0.309
0.706	0.138	0.048	0.277
0.563	0.212	0.026	0.234
0.506	0.241	0.013	0.171
0.395	0.292	0.005	0.126
0.294	0.328	0.002	0.063
0.207	0.347	0.000	0.000
2-Methylpropanoic Acid			
0.946	0.000	0.120	0.392
0.876	0.045	0.089	0.387
0.819	0.086	0.059	0.359
0.660	0.182	0.038	0.330
0.593	0.220	0.030	0.306
0.522	0.258	0.010	0.240
0.425	0.312	0.005	0.154
0.315	0.359	0.002	0.067
0.234	0.380	0.000	0.000



$x_1$	$x_2$	$x_1$	$x_2$
0.162	0.396		
Pentanoic Acid			
0.946	0.000	0.342	0.380
0.883	0.049	0.258	0.426
0.830	0.085	0.214	0.448
0.820	0.090	0.145	0.447
0.684	0.184	0.111	0.489
0.558	0.259	0.080	0.501
0.491	0.298	0.054	0.512
0.408	0.346	0.000	0.527
3-Methylbutanoic Acid			
0.946	0.000	0.272	0.397
0.850	0.065	0.219	0.422
0.803	0.097	0.165	0.449
0.716	0.152	0.127	0.468
0.559	0.247	0.093	0.484
0.529	0.261	0.051	0.502
0.425	0.319	0.030	0.512
0.363	0.350	0.000	0.518

**Table 5.16      Calibration Curve Data at T = 298.15 K for the systems : [Benzonitrile (1) + a Carboxylic Acid (2) + Water (3)], Equilibrium Mole Fraction,  $x_1$ , Refractive Index,  $n_D$ .**

$x_1$	$n_D$	$x_1$	$n_D$
Acetic Acid			
1.000	1.5260	0.155	1.4274
0.866	1.5200	0.106	1.4124
0.799	1.5140	0.060	1.3955
0.595	1.4975	0.042	1.3867
0.514	1.4849	0.018	1.3720
0.429	1.4764	0.003	1.3540
0.348	1.4652	0.000	1.3325
0.237	1.4480		
Propanoic Acid			
1.000	1.5260	0.220	1.4437
0.868	1.5196	0.115	1.4193
0.832	1.5161	0.062	1.4010
0.754	1.5101	0.034	1.3846
0.677	1.5014	0.022	1.3757
0.597	1.4931	0.013	1.3682
0.502	1.4846	0.005	1.3570
0.432	1.4773	0.000	1.3325
0.310	1.4602		
Butanoic Acid			
1.000	1.5260	0.130	1.4251
0.879	1.5204	0.098	1.4175
0.809	1.5161	0.074	1.4107
0.706	1.5036	0.048	1.4024
0.563	1.4894	0.026	1.3918
0.506	1.4822	0.013	1.3665
0.395	1.4685	0.005	1.3550
0.294	1.4542	0.000	1.3325
0.207	1.4398		
2-Methylpropanoic Acid			
1.000	1.5260	0.120	1.4193
0.876	1.5204	0.089	1.4122
0.819	1.5172	0.059	1.4046
0.660	1.5002	0.038	1.3977
0.593	1.4892	0.030	1.3870
0.522	1.4825	0.010	1.3672
0.425	1.4684	0.005	1.3554
0.315	1.4543	0.000	1.3325
0.234	1.4408		
0.162	1.4285		

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Pentanoic Acid			
1.000	1.5260	0.258	1.4502
0.883	1.5228	0.214	1.4442
0.830	1.5204	0.145	1.4323
0.820	1.5179	0.111	1.4261
0.684	1.5061	0.080	1.4121
0.558	1.4928	0.054	1.3993
0.491	1.4871	0.034	1.3804
0.408	1.4747	0.000	1.3325
0.342	1.4621		
3-Methylbutanoic Acid			
1.000	1.5260	0.272	1.4478
0.850	1.5210	0.219	1.4411
0.833	1.5176	0.165	1.4296
0.716	1.5051	0.127	1.4234
0.559	1.4916	0.093	1.4174
0.529	1.4852	0.051	1.4002
0.425	1.4728	0.030	1.3751
0.363	1.4606	0.000	1.3325

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**Table 5.17**    **Composition of the Conjugate Solutions,  $x_1'$ ,  $x_2'$ , and  $x_1''$ ,  $x_2''$ , at T = 298.15 K, Refractive Index,  $n_D$**

water- rich			benzonitrile-rich		
$x_1'$	$x_2'$	$n_D$	$x_1''$	$x_2''$	$n_D$
Benzonitrile (1) + Acetic Acid (2) + Water (3)					
0.001	0.009	1.3397	0.924	0.012	1.5226
0.001	0.037	1.3397	0.742	0.114	1.5108
0.002	0.055	1.3468	0.549	0.206	1.4903
0.003	0.091	1.3540	0.380	0.262	1.4696
0.011	0.130	1.3636	0.229	0.280	1.4460
Benzonitrile (1) + Propanoic Acid (2) + Water (3)					
0.002	0.010	1.3423	0.878	0.046	1.5202
0.004	0.019	1.3521	0.641	0.179	1.4977
0.006	0.028	1.3582	0.456	0.247	1.4798
0.009	0.040	1.3620	0.282	0.284	1.4551
0.010	0.049	1.3632	0.192	0.281	1.4372
Benzonitrile (1) + Butanoic Acid (2) + Water (3)					
0.001	0.002	1.3370	0.899	0.031	1.5213
0.001	0.015	1.3370	0.727	0.130	1.5061
0.002	0.024	1.3415	0.531	0.232	1.4854
0.002	0.041	1.3415	0.319	0.320	1.4577
0.003	0.074	1.3460	0.160	0.337	1.4308
Benzonitrile (1) + 2-Methylpropanoic Acid (2) + Water (3)					
0.001	0.002	1.3371	0.891	0.039	1.5211
0.001	0.012	1.3371	0.687	0.166	1.5031
0.001	0.029	1.3371	0.440	0.300	1.4706
0.002	0.050	1.3417	0.259	0.378	1.4449
0.004	0.110	1.3508	0.130	0.394	1.4215
Benzonitrile (1) + Pentanoic Acid (2) + Water (3)					
0.001	0.001	1.3339	0.846	0.073	1.5211
0.002	0.003	1.3353	0.561	0.258	1.4931
0.002	0.005	1.3353	0.348	0.377	1.4632
0.003	0.007	1.3367	0.209	0.448	1.4433
0.003	0.009	1.3367	0.062	0.508	1.4032
Benzonitrile (1) + 3-Methylbutanoic Acid (2) + Water (3)					
0.001	0.001	1.3339	0.865	0.055	1.5215
0.002	0.002	1.3353	0.574	0.235	1.4929
0.004	0.005	1.3382	0.369	0.350	1.4618
0.006	0.006	1.3410	0.230	0.419	1.4425
0.007	0.008	1.3424	0.031	0.509	1.3763

**Table 5.18** Coefficients  $A_i$ ,  $B_i$ , and  $C_i$  in Equations (5.8)-(5.10), at  $T = 298.15$  K

Hlavatý	$\beta$	$\log \gamma$
Benzonitrile (1) + Acetic acid (2) + Water (3)		
$A_1 = -0.587$	$B_1 = 1.017$	$C_1 = 0.903$
$A_2 = 0.111$	$B_2 = 1.117$	$C_2 = 1.071$
$A_3 = 0.447$	$B_3 = 0.747$	$C_3 = 1.134$
$\sigma = 0.005$	$\sigma = 0.006$	$\sigma = 0.004$
Benzonitrile (1) + Propanoic acid (2) + Water (3)		
$A_1 = -0.431$	$B_1 = 0.924$	$C_1 = 0.834$
$A_2 = -0.019$	$B_2 = 0.979$	$C_2 = 0.940$
$A_3 = 0.482$	$B_3 = 0.763$	$C_3 = 1.101$
$\sigma = 0.003$	$\sigma = 0.003$	$\sigma = 0.003$
Benzonitrile (1) + Butanoic acid (2) + Water (3)		
$A_1 = -0.53$	$B_1 = 1.130$	$C_1 = 1.023$
$A_2 = 0.285$	$B_2 = 1.071$	$C_2 = 1.036$
$A_3 = 0.960$	$B_3 = 0.755$	$C_3 = 1.139$
$\sigma = 0.010$	$\sigma = 0.013$	$\sigma = 0.010$
Benzonitrile (1) + 2-Methylpropanoic acid (2) + Water (3)		
$A_1 = -0.518$	$B_1 = 1.478$	$C_1 = 1.339$
$A_2 = 0.419$	$B_2 = 1.168$	$C_2 = 1.132$
$A_3 = 1.364$	$B_3 = 0.824$	$C_3 = 1.252$
$\sigma = 0.012$	$\sigma = 0.013$	$\sigma = 0.010$
Benzonitrile (1) + Pentanoic acid (2) + Water (3)		
$A_1 = -0.139$	$B_1 = 0.786$	$C_1 = 0.736$
$A_2 = -0.133$	$B_2 = 0.950$	$C_2 = 0.930$
$A_3 = 0.452$	$B_3 = 0.939$	$C_3 = 1.295$
$\sigma = 0.002$	$\sigma = 0.004$	$\sigma = 0.004$
Benzonitrile (1) + 3-Methylbutanoic acid (2) + Water (3)		
$A_1 = -0.193$	$B_1 = 0.756$	$C_1 = 0.698$
$A_2 = -0.163$	$B_2 = 0.942$	$C_2 = 0.919$
$A_3 = 0.336$	$B_3 = 0.884$	$C_3 = 1.222$
$\sigma = 0.003$	$\sigma = 0.005$	$\sigma = 0.006$

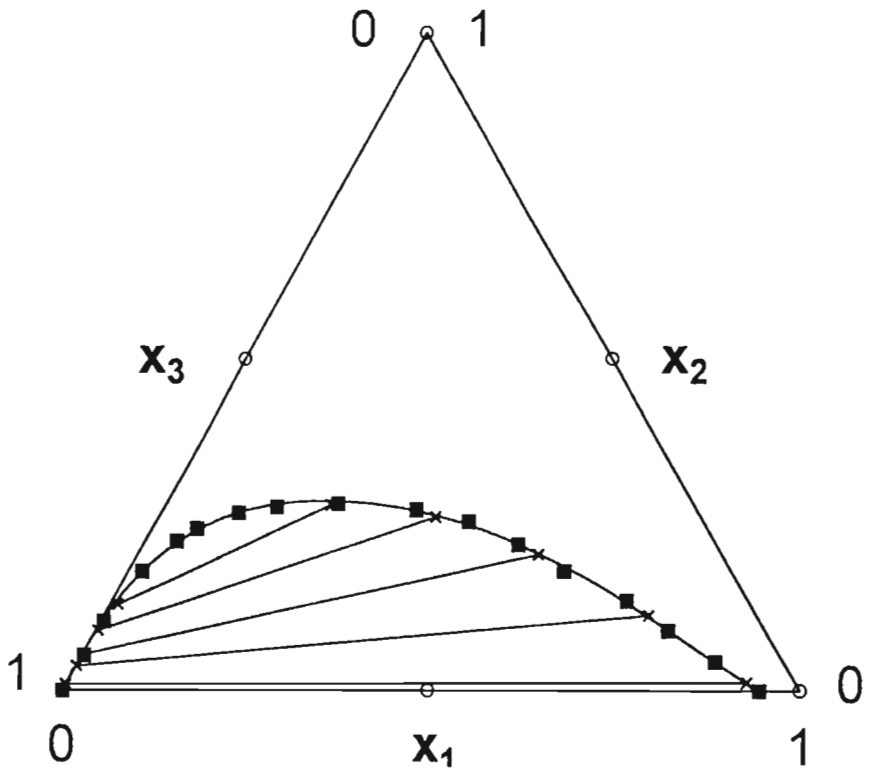


Figure 5.40 Liquid-liquid equilibrium data for the system [benzonitrile(1) + acetic acid(2) + water (3)] at 298.15 K.

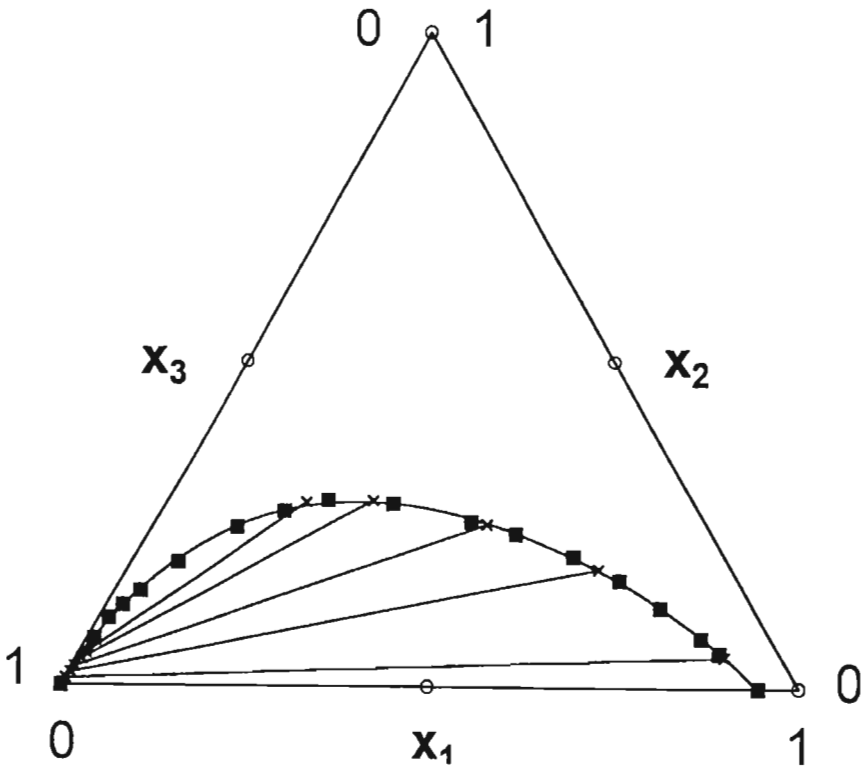


Figure 5.41 Liquid-liquid equilibrium data for the system [benzonitrile(1) + propanoic acid(2) + water (3)] at 298.15 K.

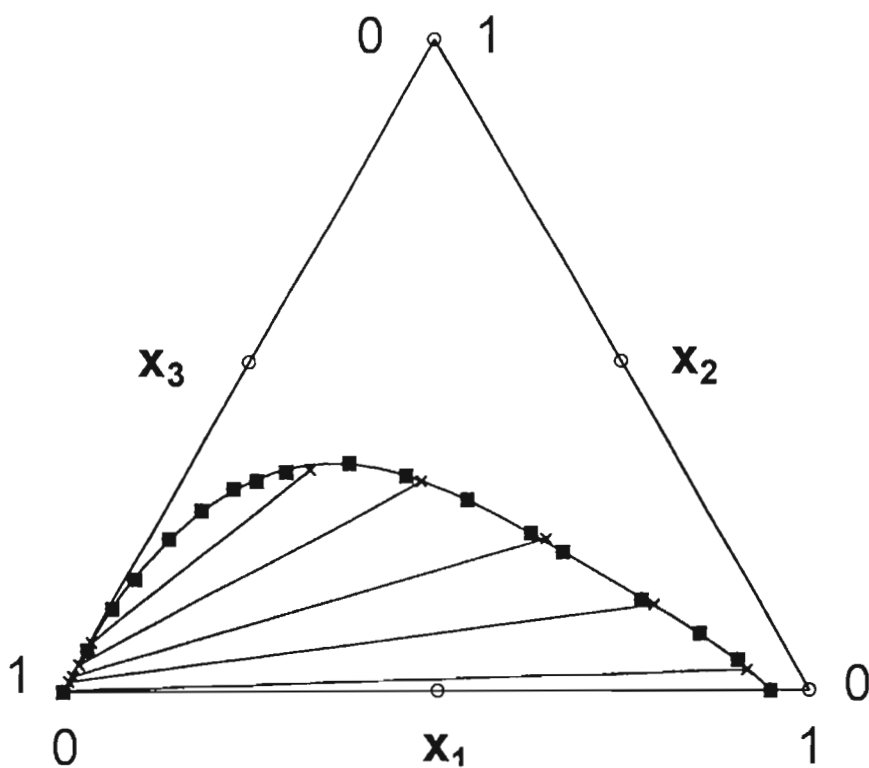


Figure 5.42 Liquid-liquid equilibrium data for the system [benzonitrile (1) + butanoic acid (2) + water (3)] at 298.15 K.

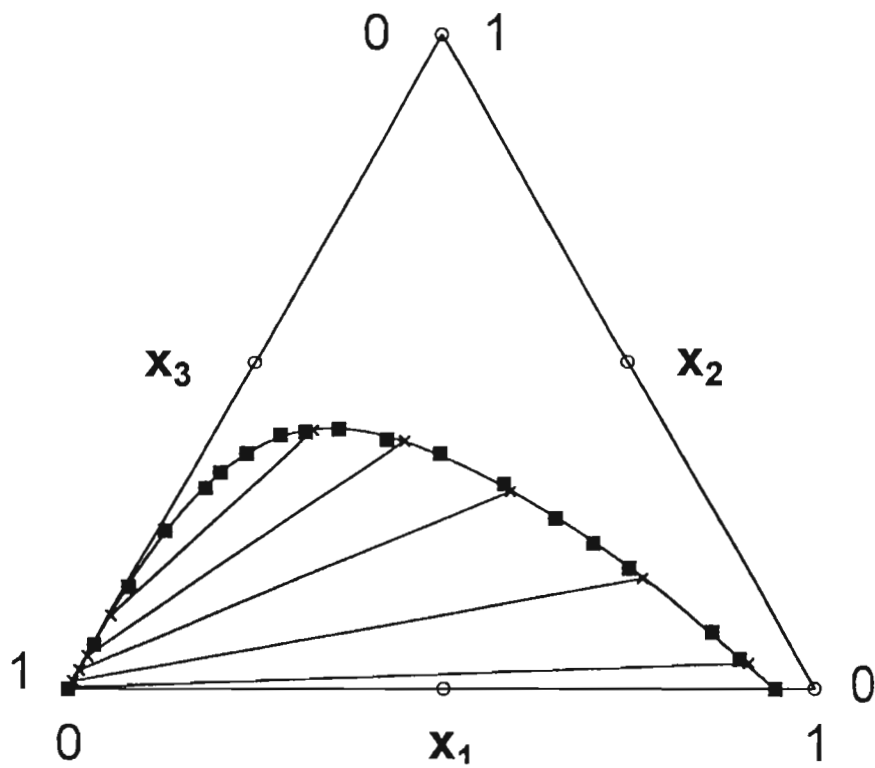


Figure 5.43 Liquid-liquid equilibrium data for the system [benzonitrile (1) + 2-methylpropanoic acid (2) + water (3)] at 298.15 K.

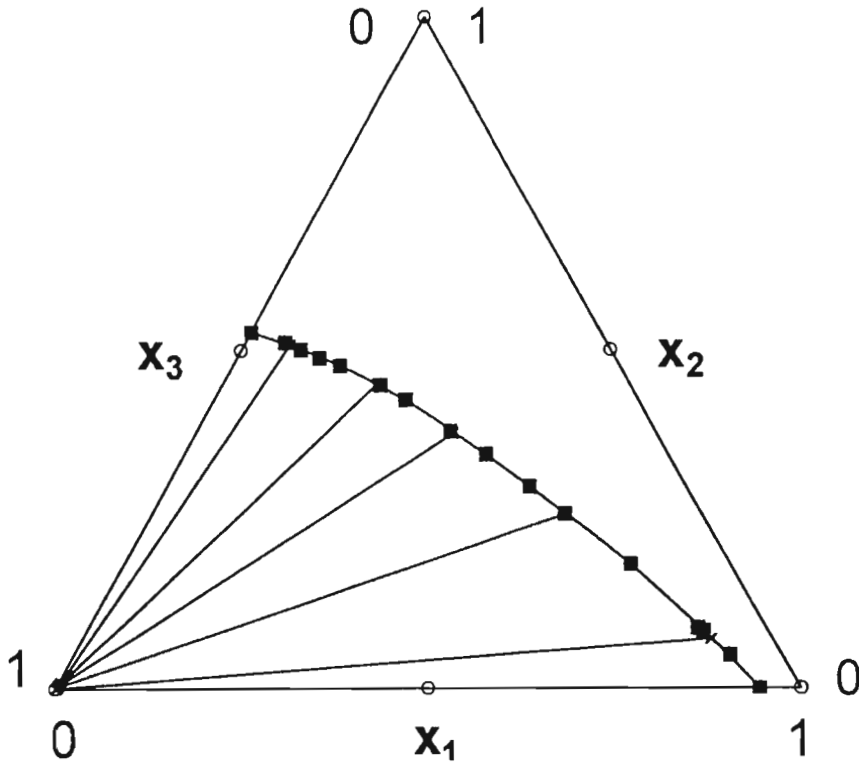


Figure 5.44 Liquid-liquid equilibrium data for the system [benzonitrile (1) + pentanoic acid (2) + water (3)] at 298.15 K.

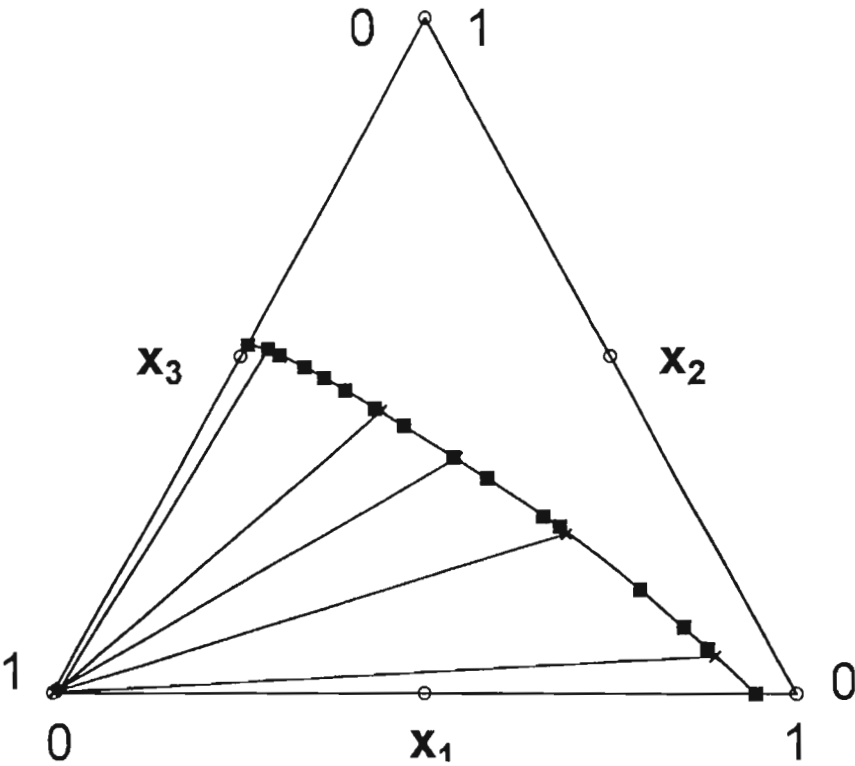
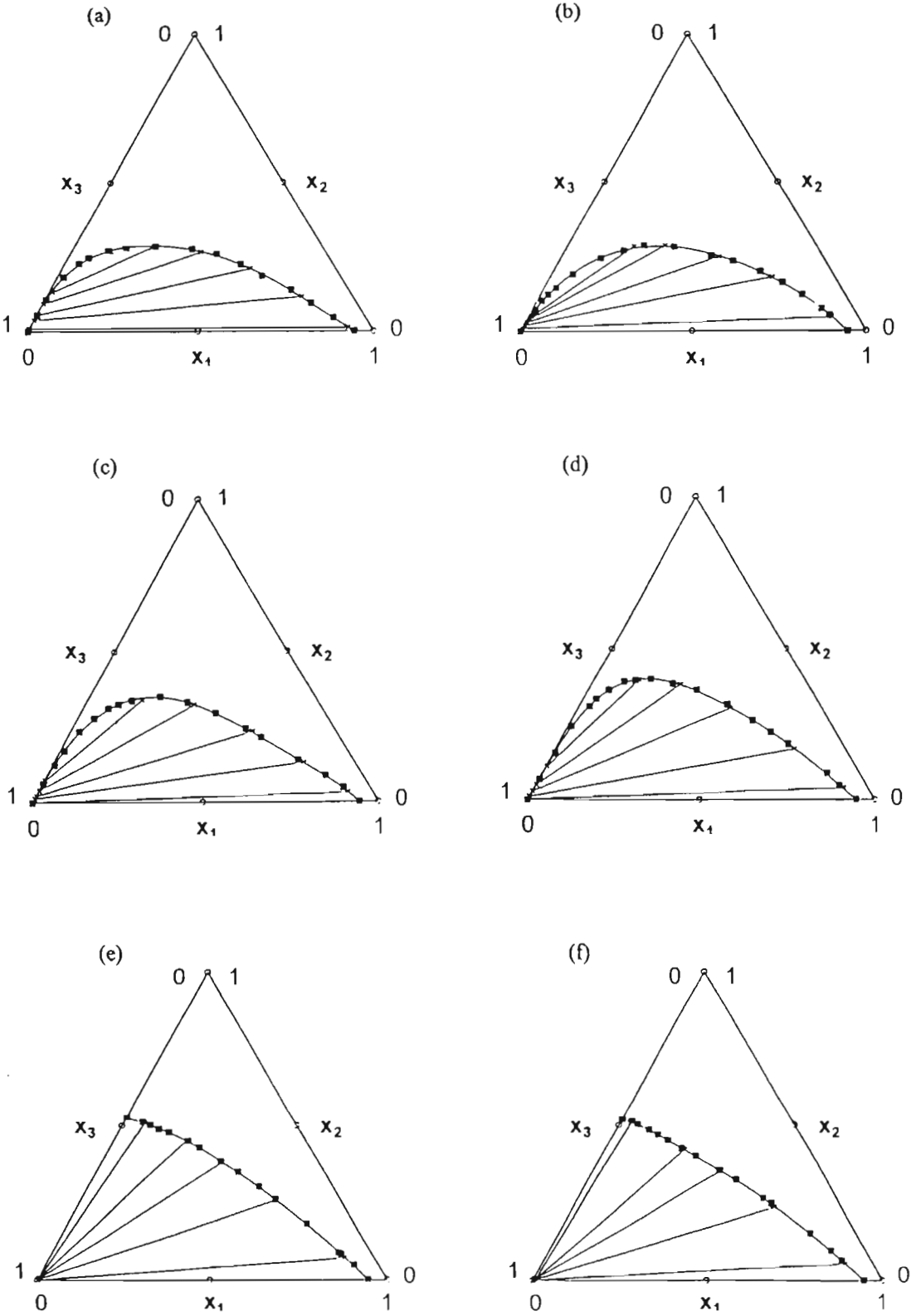


Figure 5.45 Liquid-liquid equilibrium data for the system [benzonitrile (1) + 3-methylbutanoic acid (2) + water (3)] at 298.15 K.





**Figure 5.46** Summary of liquid-liquid equilibrium data for the following systems at 298.15 K: (a) benzonitrile(1) + acetic acid(2) + water(3); (b) benzonitrile(1) + propanoic acid(2) + water(3); (c) benzonitrile(1) + butanoic acid(2) + water(3); (d) benzonitrile(1) + 2-methylpropanoic acid(2) + water (3); (e) benzonitrile(1) + pentanoic acid(2) + water(3); (f) benzonitrile(1) + 3-methylbutanoic acid(2) + water(3). [Key: (■) experimental points; (×) experimental tie-lines]

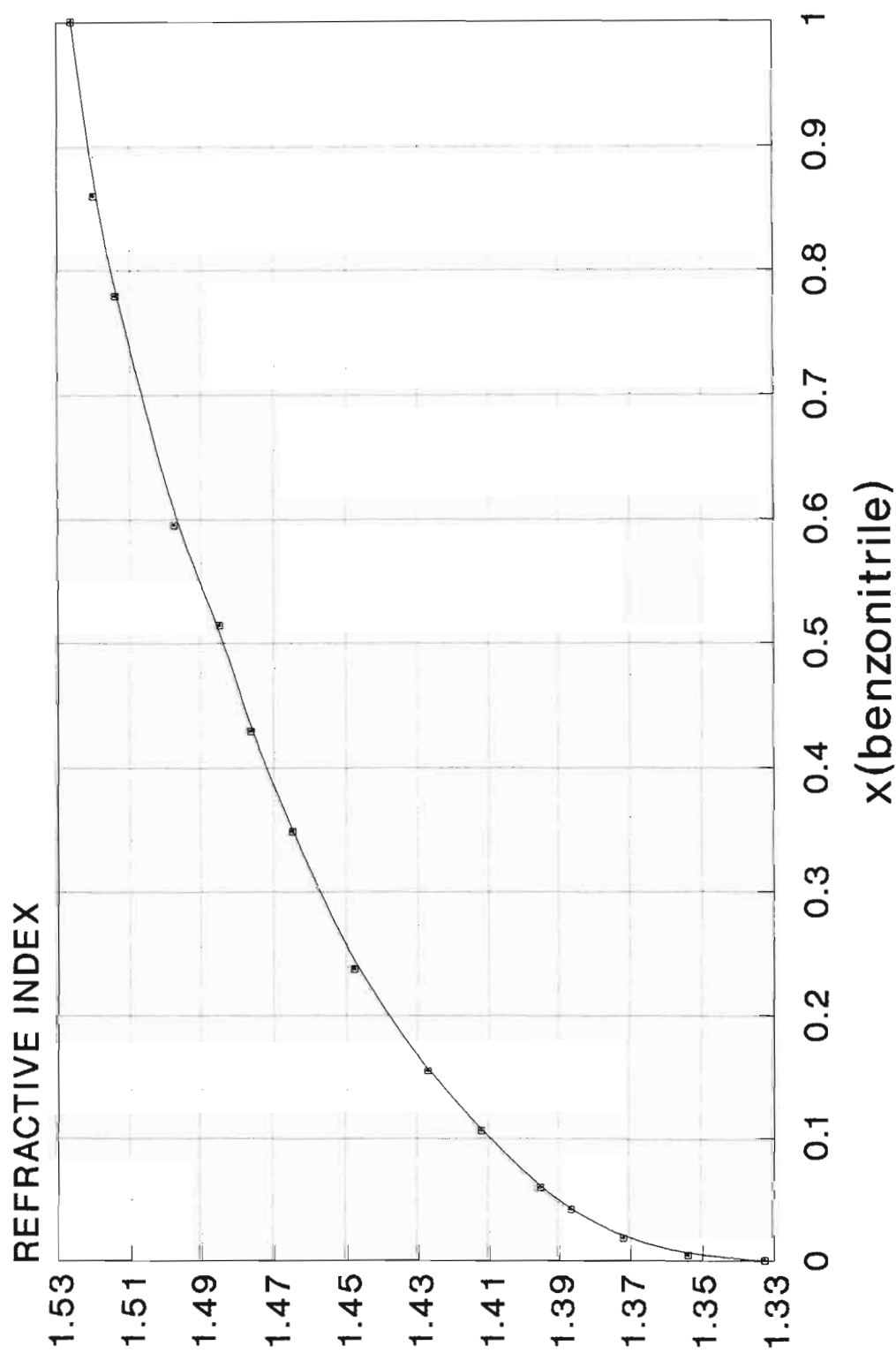


Figure 5.47 Calibration curve for (benzonitrile + acetic acid + water) system at 298.15 K.

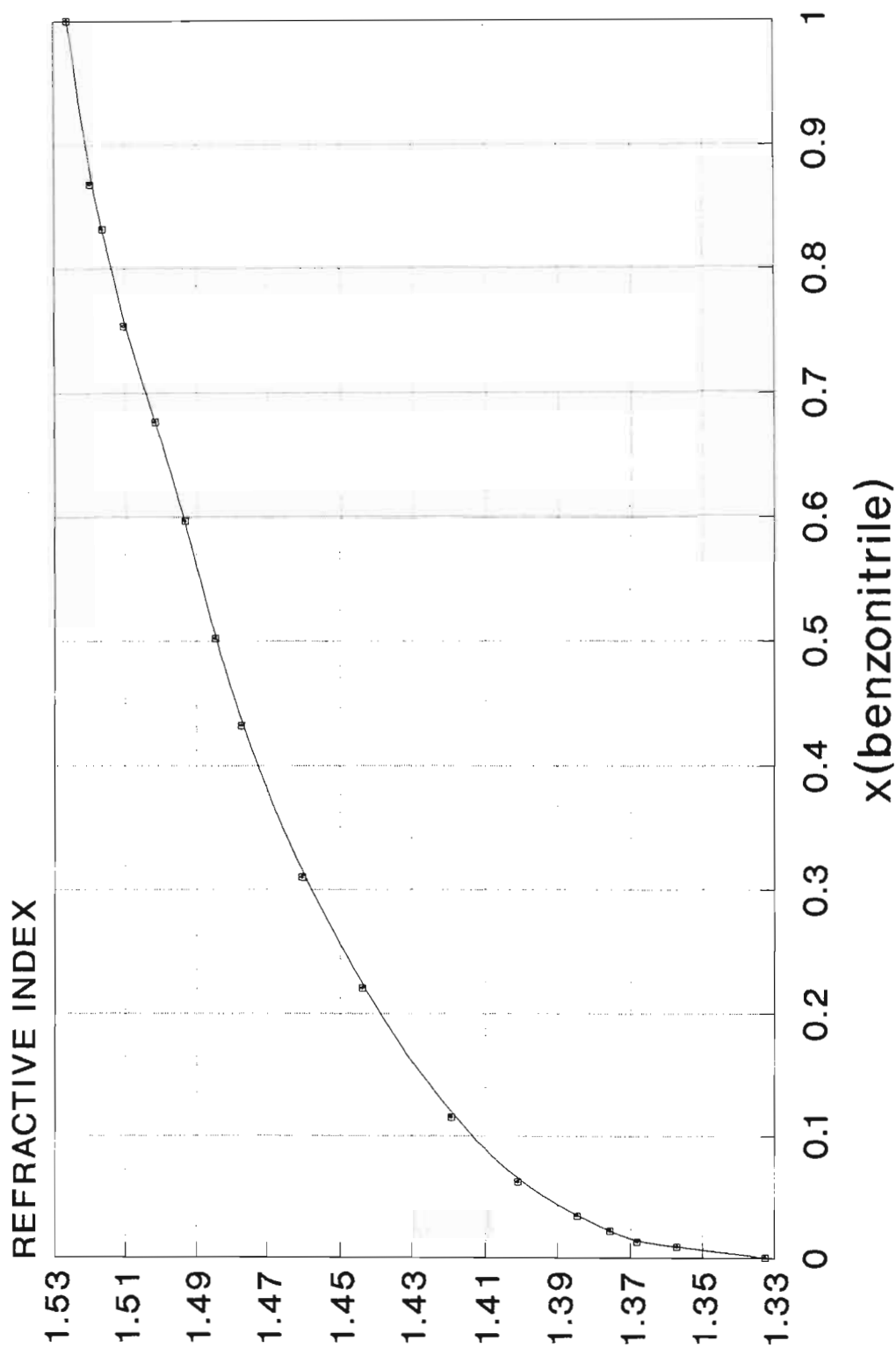


Figure 5.48 Calibration curve for (benzonitrile + propanoic acid + water) system at 298.15 K.

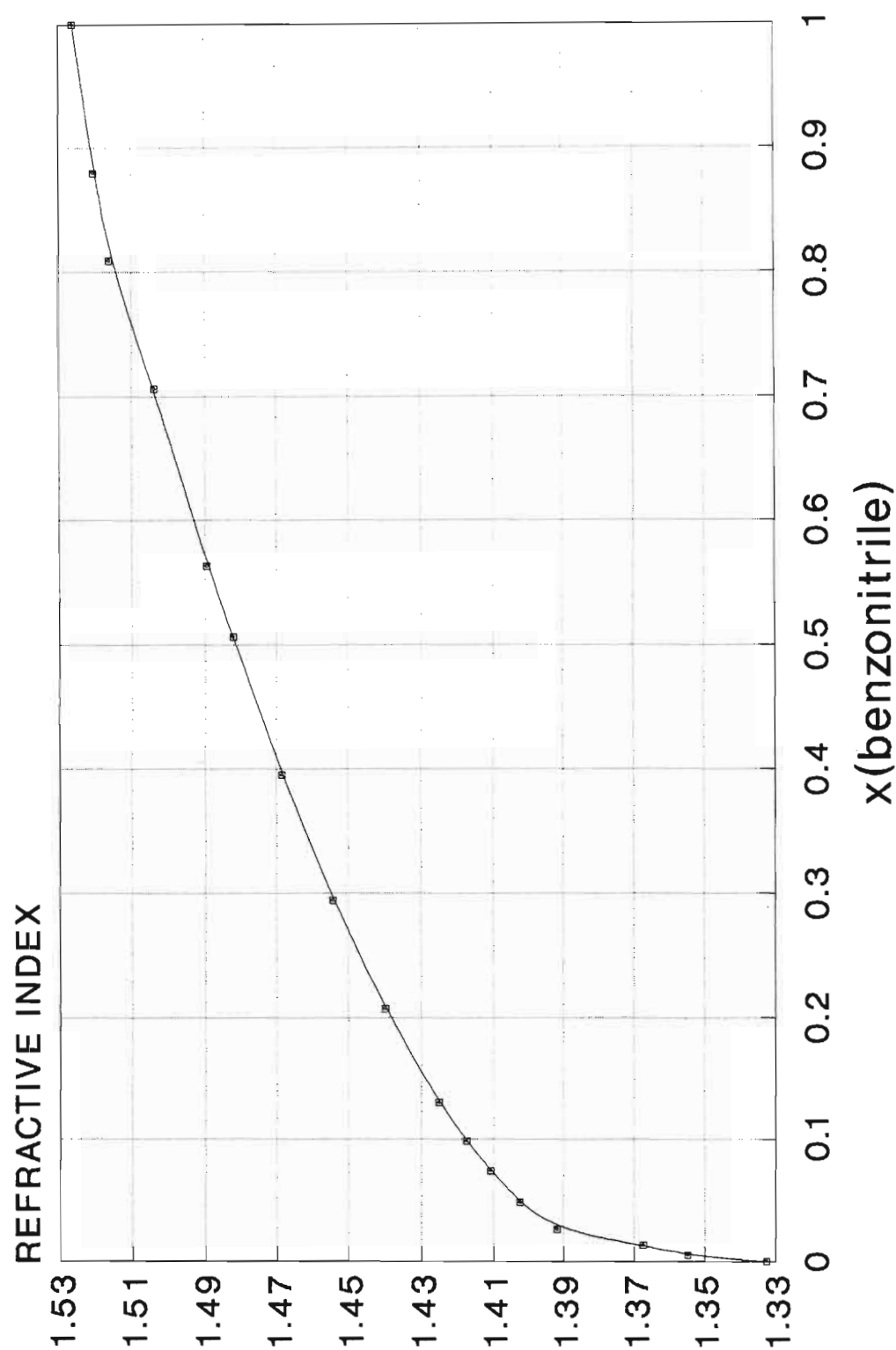


Figure 5.49 Calibration curve for (benzonitrile + butanoic acid + water) system at 298.15 K.

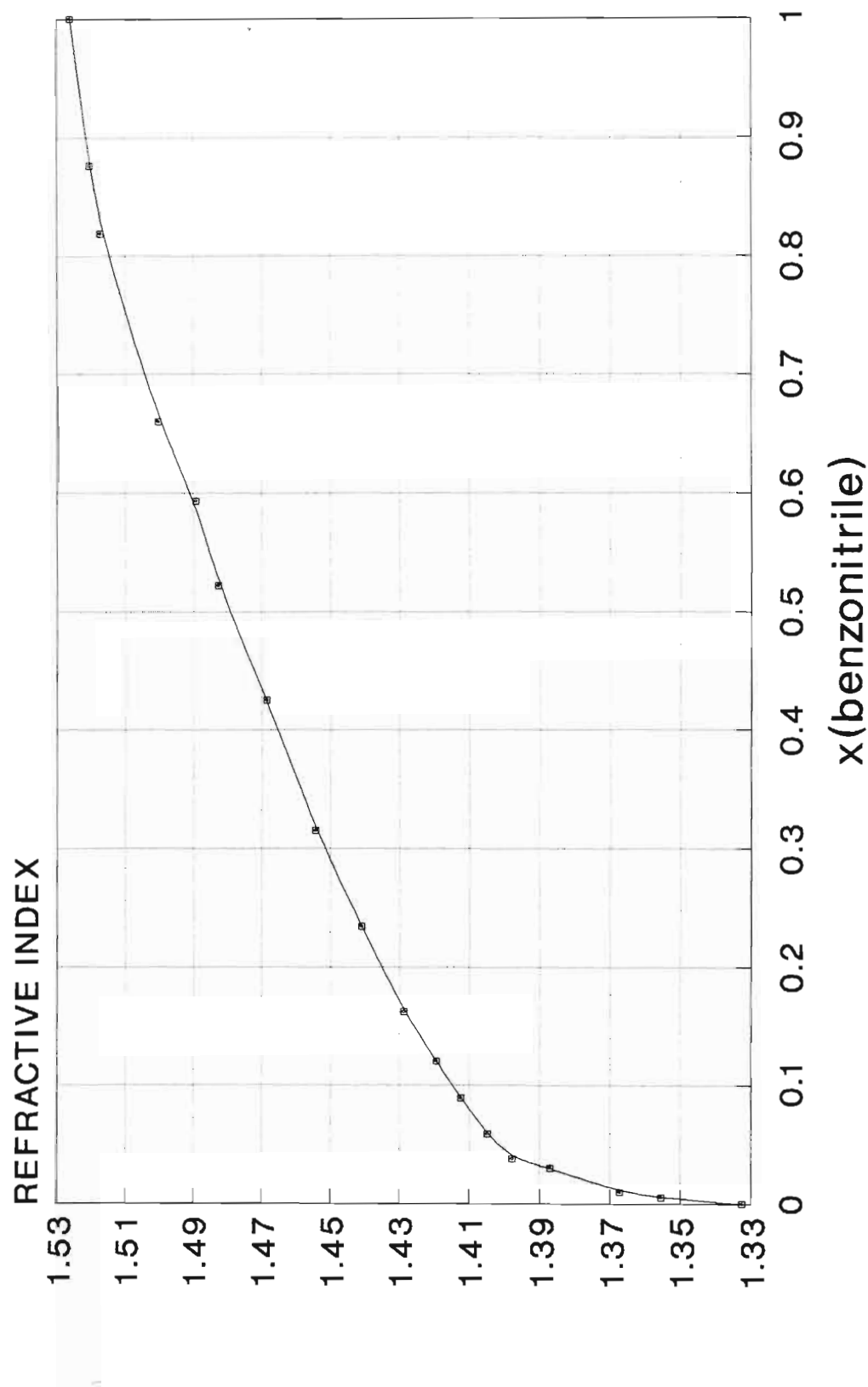


Figure 5.50 Calibration curve for (benzonitrile + 2-methylpropanoic acid + water) system at 298.15 K.

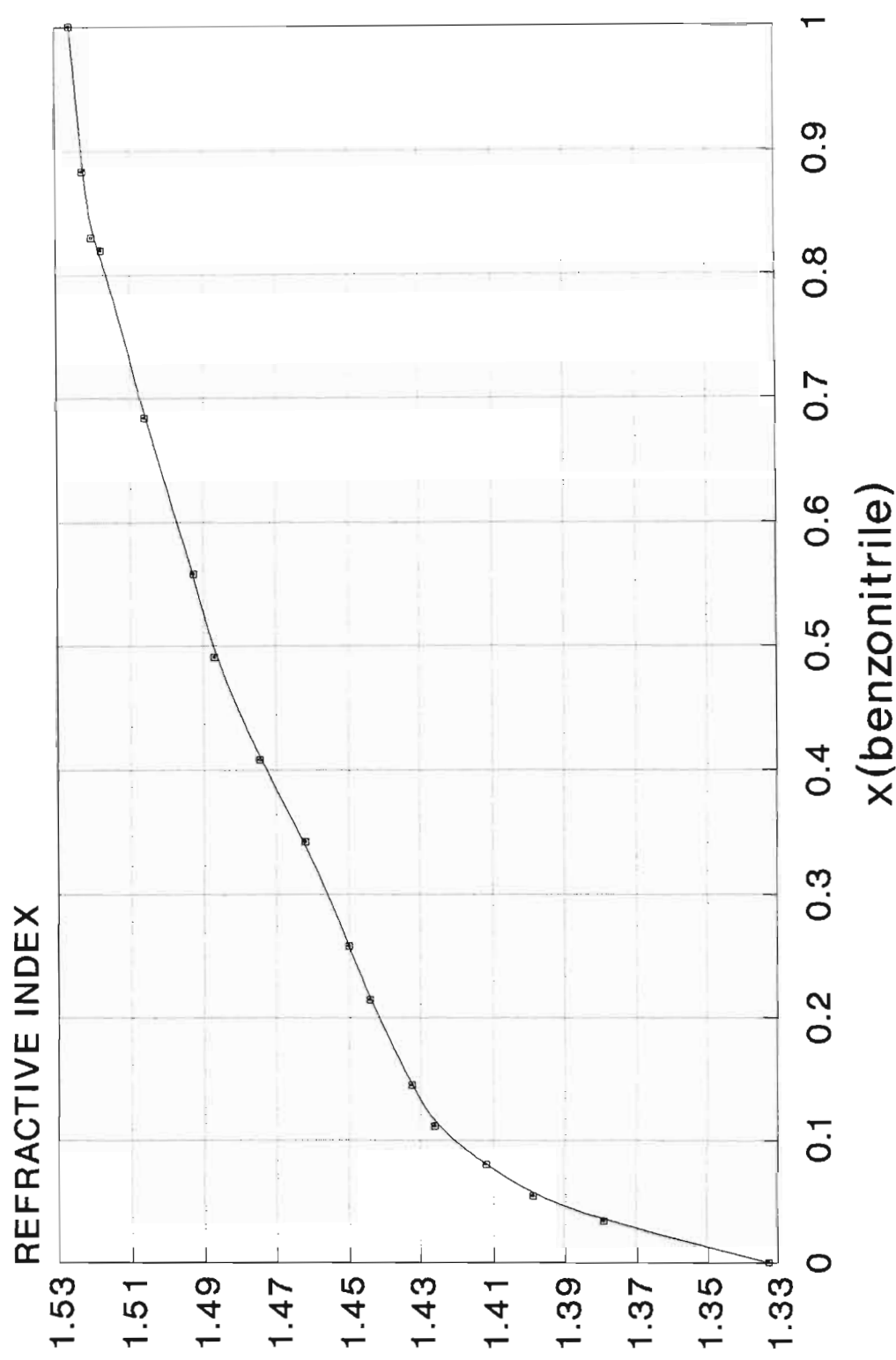


Figure 5.51 Calibration curve for (benzonitrile + pentanoic acid + water) system at 298.15 K.

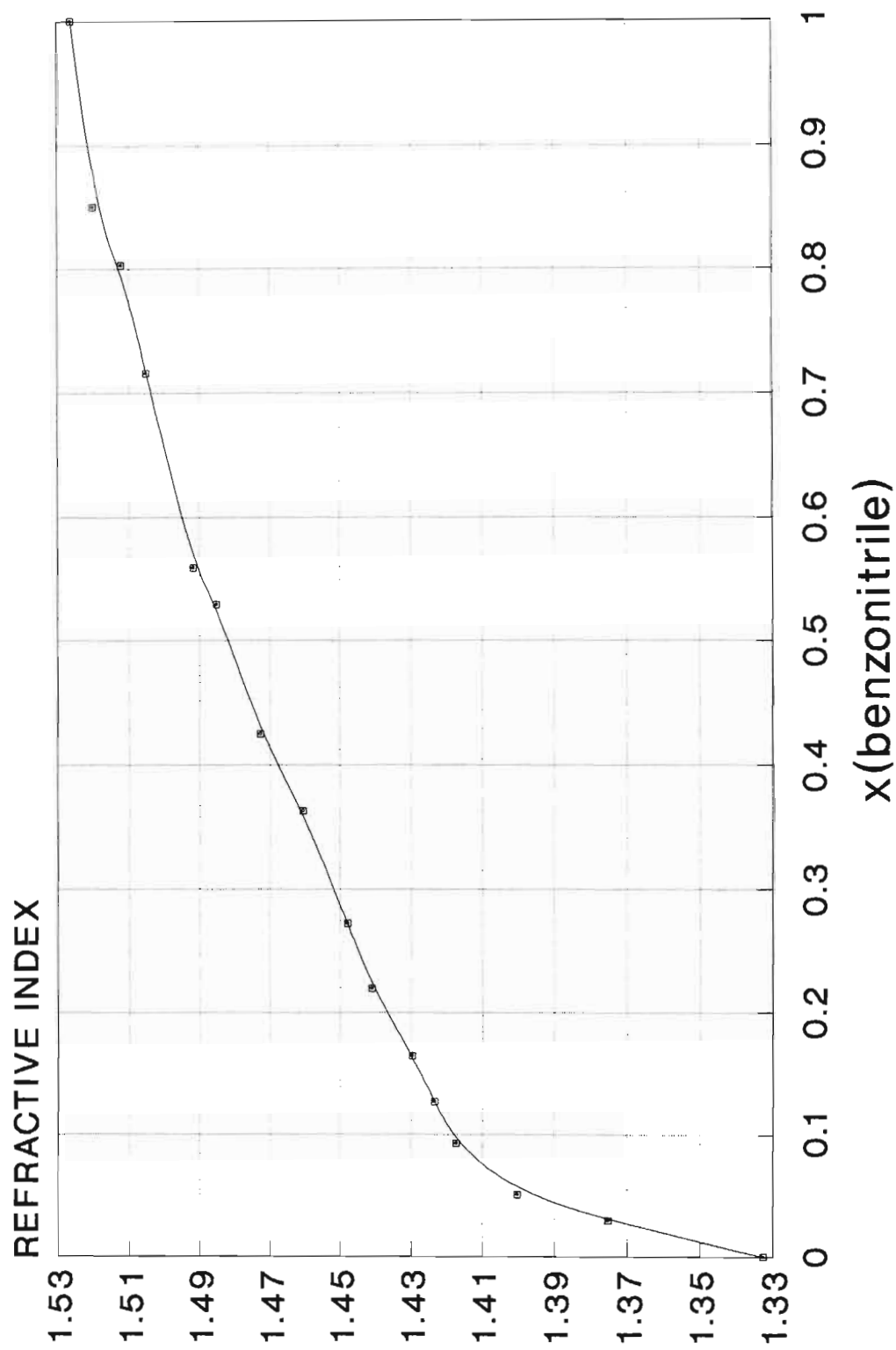
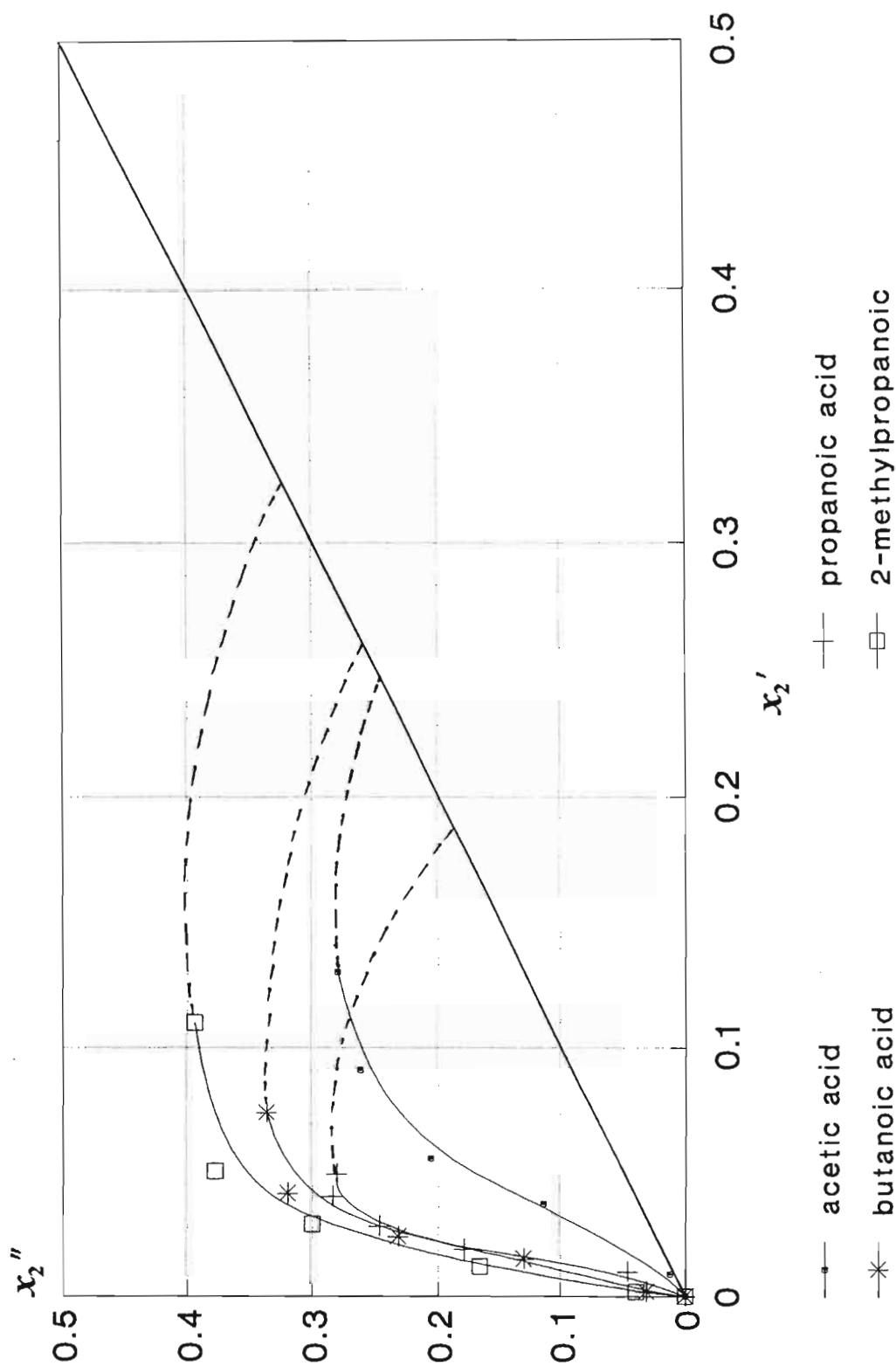


Figure 5.52 Calibration curve for (benzonitrile + 3-methylbutanoic acid + water) system at 298.15 K.



**Figure 5.53** A plot of  $x_2''$  against  $x_2'$  showing the relative solubilities of the carboxylic acid in the benzonitrile-rich and water-rich layers.



**Table 5.19**     **Representative selectivity values of benzonitrile for the separation of carboxylic acids from water at 298.15 K, using equation 5.16**

Carboxylic acid	Selectivity ( $\omega$ )
acetic acid	14
propanoic acid	29
butanoic acid	40
2-methylpropanoic acid	39
pentanoic acid	272
3-methylbutanoic acid	247

### 5.8.3.1 Discussion of Ternary Systems [Benzonitrile(1) + a Carboxylic Acid(2) + Water(3)] at 298.15 K

#### Previous Work

Liquid-Liquid equilibria (LLE) data on related ternary systems have been reported in the literature : (water + benzonitrile + methanol) by Botto *et al.* (1989), (water + benzonitrile + ethanol or 1-propanol) by Grande *et al.* (1995), (water + benzonitrile + 2-propanol or 1-butanol) by Grande *et al.* (1996), (water + benzonitrile + N, N-dimethylformamide or N-methylformamide by Grande *et al.* (1998), and, for (water + benzonitrile + acetonitrile or propionitrile) by Grande *et al.* (2000). To the best of our knowledge no liquid-liquid equilibria data has been reported on (benzonitrile + carboxylic acids + water) systems in the literature.

#### This Work

In this work precise new LLE data have been obtained for (benzonitrile + acetic acid or propanoic acid or butanoic acid or 2-methylpropanoic acid or pentanoic acid or 3-methylbutanoic acid + water) at 298.15 K.

The binodal curves in Figure 5.46 (a) - (f) show that the solubility of water in (benzonitrile + carboxylic acid) mixtures is very much dependant on the type of acid. In the ternary systems investigated, water is most soluble in the systems containing acetic acid, propanoic acid, and to a slightly lesser extent butanoic acid and 2-methylpropanoic acid.

Figure 5.46(a) - (f) also indicates that the area of the two-phase heterogenous region for the carboxylic acid mixtures increases in the order : acetic acid ~ propanoic acid < butanoic acid < 2-methylpropanoic acid < pentanoic acid ~ 3-methylbutanoic acid. This implies that the mutual solubility of the ternary components is decreased as the carbon chain length is progressively increased. Water is most soluble in the benzonitrile - acetic acid or benzonitrile - propanoic acid mixtures.

The shapes of the binodal curves for benzonitrile + acetic acid or propanoic acid or butanoic

acid or 2-methylpropanoic acid + water, show a large skewing towards the water axis. The partitioning of the carboxylic acids between the water - rich and benzonitrile - rich layers for all of the systems studied is illustrated in Figure 5.53, where the mole fraction of each carboxylic acid in the conjugate layers has been plotted. Figure 5.53 shows that all the carboxylic acids are more soluble in benzonitrile than water.

The maximum solubility of benzonitrile in water is 0.946 mole fraction. The minimum concentration (in mole fraction) for the solubility of the carboxylic acids over the whole composition range, in the mixture (benzonitrile + a carboxylic acid + water) was found to be 0.282, 0.285, 0.347, 0.392, 0.527 and 0.518 for acetic acid, propanoic acid, butanoic acid, 2-methylpropanoic acid, pentanoic acid and 3-methylbutanoic acid respectively.

The relative solubility of an acid in water or in benzonitrile can be observed from the tie lines. It can be seen that in all cases, the acids are more soluble in the benzonitrile - rich phase, with a large skewing towards the water axis. For the C4 acids, the gradient of the tie-lines for 2-methylpropanoic acid is significantly greater than those for butanoic acid. This could be attributable to the greater solubilising effect of the two methyl groups on the terminal carbon of 2-methylpropanoic acid as opposed to its straight chain isomer. A similar effect is noted for 3-methylbutanoic acid when compared to pentanoic acid.

The mutual solubility of water in benzonitrile is very much dependent on the length and structure of the carbon chains of the carboxylic acid. Acetic acid with just two carbons is the best bridging agent of the carboxylic acids investigated here. Propanoic acid, with three carbon atoms shows slightly lower mutual solubility of water in benzonitrile. For the C4 acids, butanoic acid shows slightly better mutual solubility characteristics of water in benzonitrile, when compared to 2-methylpropanoic acid. This could possibly be due to steric effects of the two methyl group on the terminal carbon of 2-methylpropanoic acid. For the C5 carboxylic acids on the other hand, it appears that the alkyl chains are too long to act as effective bridging agents, resulting in both C5 acids being not soluble in water at all concentrations.

The effectiveness of extraction of a carboxylic acid (2) by benzonitrile (3) is given by its selectivity  $\omega$  (Letcher *et al.*, 1996), which is a measure of the ability of benzonitrile to

separate the carboxylic acid (2) from water:

$$\omega = \frac{\text{distribution coefficient of carboxylic acids}}{\text{distribution coefficient of water}}$$

$$\omega = \frac{(x_2 / x_3)_{\text{benzonitrile-rich phase}}}{(x_2 / x_3)_{\text{water-rich phase}}} \quad (5.16)$$

where  $x_2$  refers to the mole fraction of carboxylic acid and  $x_1$ , the mole fraction of water. Table 5.19 gives selectivity values of benzonitrile for the extraction of carboxylic acids from water. Representative values of selectivity for the middle of the area of the measured tie-lines are 14, 29, 40, 39, 272 and 247 for acetic acid, propanoic acid, butanoic acid, 2-methyl propanoic acid, pentanoic acid and 3-methylbutanoic acid respectively. From the selectivity data, it can be concluded that the separation of all the carboxylic acids from water by extraction is feasible. It can also be concluded that benzonitrile is an especially good component for the separation of mixtures of water and 3-methylbutanoic acid.

The standard deviations,  $\sigma$  of the three fitted equations to the binodal curves, viz. the modified Hlavatý, beta and  $\log \gamma$  equations again show that all are capable of fitting the binodal curve data points. The Hlavatý equation gave the best overall fit as compared to the  $\beta$  function equation and the  $\log \gamma$  function.

5.8.4    **Liquid-liquid equilibria for mixtures of butanenitrile + a carboxylic acid + water at 298.15 K**

**Table 5.20    Physical Properties of the Pure Components at 298.15 K; Molar Volumes,  $V_{mi}$ , Refractive Indices,  $n_D$ , Volume and Surface Parameters,  $R$  and  $Q$ .**

Component	$V_{mi}/(\text{cm}^3 \cdot \text{mol}^{-1})^a$	$n_D$		$R^b$	$Q^b$
		exp	lit. <sup>a</sup>		
butanenitrile	87.87	1.3822	1.3820	3.219	2.804
acetic acid	57.53	1.3697	1.3698	2.202	2.072
propanoic acid	74.97	1.3846	1.3843	2.877	2.612
butanoic acid	92.43	1.3955	1.3958	3.551	3.152
2-methylpropanoic acid	93.44	1.3913	1.3917	3.550	3.148
pentanoic acid	109.29	1.4064	1.4060	4.226	3.692
3-methylbutanoic acid	110.54	1.4019	1.4022	4.225	3.688
water	18.07	1.3325	1.3325	0.9200	1.400

<sup>a</sup> Riddick *et al.*(1986)

<sup>b</sup> Gmehling *et al.*(1993)

**Table 5.21** Compositions of Points on the Binodal Curve at 298.15 K for the systems: [Butanenitrile (1) + a Carboxylic Acid (2) + Water (3)], Equilibrium Mole Fraction,  $x_1$ ,  $x_2$ .

$x_1$	$x_2$		$x_1$	$x_2$
Acetic Acid				
0.904	0.000		0.283	0.183
0.856	0.021		0.226	0.180
0.780	0.055		0.161	0.172
0.704	0.086		0.102	0.149
0.621	0.114		0.048	0.112
0.523	0.140		0.032	0.092
0.439	0.161		0.012	0.052
0.351	0.179		0.000	0.000
Propanoic Acid				
0.904	0.000		0.265	0.208
0.836	0.030		0.195	0.201
0.739	0.071		0.147	0.169
0.606	0.126		0.101	0.150
0.545	0.146		0.062	0.115
0.461	0.174		0.038	0.084
0.383	0.193		0.007	0.019
0.336	0.202		0.000	0.000
Butanoic Acid				
0.904	0.000		0.235	0.270
0.832	0.035		0.195	0.275
0.745	0.074		0.156	0.272
0.699	0.097		0.109	0.258
0.633	0.128		0.066	0.237
0.530	0.169		0.030	0.185
0.466	0.198		0.014	0.125
0.361	0.239		0.005	0.066
0.271	0.262		0.000	0.000
2-Methylpropanoic Acid				
0.904	0.000		0.210	0.302
0.799	0.060		0.144	0.311
0.715	0.099		0.056	0.298
0.640	0.135		0.017	0.260
0.566	0.166		0.012	0.241
0.467	0.209		0.006	0.195
0.382	0.242		0.004	0.154
0.290	0.279		0.003	0.089
0.253	0.289		0.000	0.000

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Pentanoic Acid			
0.904	0.000	0.428	0.278
0.849	0.035	0.349	0.318
0.783	0.074	0.268	0.355
0.722	0.113	0.192	0.387
0.657	0.151	0.094	0.430
0.574	0.198	0.034	0.453
0.515	0.230	0.000	0.459
3-Methylbutanoic Acid			
0.904	0.000	0.439	0.254
0.851	0.032	0.360	0.291
0.799	0.062	0.271	0.330
0.746	0.094	0.195	0.363
0.664	0.137	0.099	0.399
0.587	0.181	0.048	0.410
0.529	0.211	0.000	0.419

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**Table 5.22**    **Calibration Curve Data at 298.15 K for the systems : [Butanenitrile (1) + a Carboxylic Acid (2) + Water (3)], Equilibrium Mole Fraction,  $x_1$ , Refractive Index,  $n_D$ .**

$x_1$	$n_D$	$x_2$	$n_D$
Acetic Acid			
1.000	1.3822	0.283	1.3743
0.856	1.3811	0.161	1.3698
0.704	1.3798	0.102	1.3659
0.621	1.3787	0.048	1.3590
0.523	1.3778	0.032	1.3550
0.439	1.3770	0.012	1.3451
0.351	1.3762	0.000	1.3325
Propanoic Acid			
1.000	1.3822	0.265	1.3775
0.836	1.3819	0.147	1.3705
0.739	1.3811	0.062	1.3611
0.606	1.3805	0.038	1.3552
0.545	1.3802	0.007	1.3380
0.461	1.3795	0.000	1.3325
0.383	1.3789		
Butanoic Acid			
1.000	1.3822	0.235	1.3700
0.832	1.3813	0.195	1.3668
0.745	1.3802	0.156	1.3639
0.633	1.3781	0.109	1.3563
0.530	1.3748	0.066	1.3499
0.466	1.3740	0.030	1.3413
0.361	1.3728	0.000	1.3325
0.271	1.3711		
2-Methylpropanoic Acid			
1.000	1.3822	0.290	1.3716
0.904	1.3811	0.253	1.3704
0.799	1.3799	0.210	1.3681
0.715	1.3790	0.144	1.3621
0.640	1.3779	0.056	1.3472
0.566	1.3760	0.017	1.3376
0.467	1.3748	0.000	1.3325
0.382	1.3731		



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Pentanoic Acid			
1.000	1.3822	0.428	1.3633
0.849	1.3765	0.349	1.3611
0.783	1.3742	0.268	1.3594
0.722	1.3728	0.192	1.3578
0.657	1.3707	0.094	1.3508
0.574	1.3676	0.034	1.3415
0.515	1.3653	0.000	1.3325
3-Methylbutanoic Acid			
1.000	1.3822	0.439	1.3591
0.851	1.3755	0.360	1.3568
0.799	1.3732	0.271	1.3547
0.746	1.3713	0.195	1.3525
0.664	1.3681	0.099	1.3470
0.587	1.3649	0.048	1.3402
0.529	1.3625	0.000	1.3325

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**Table 5.23**      **Composition of the Conjugate Solutions,  $x_1'$ ,  $x_2'$ , and  $x_1''$ ,  $x_2''$ , at 298.15 K, Refractive Index,  $n_D$**

water- rich			butanenitrile-rich		
$x_1'$	$x_2'$	$n_D$	$x_1''$	$x_2''$	$n_D$
Butanenitrile (1) + Acetic Acid (2) + Water (3)					
0.001	0.003	1.3336	0.797	0.049	1.3806
0.002	0.012	1.3346	0.608	0.120	1.3786
0.005	0.026	1.3378	0.451	0.161	1.3771
0.010	0.042	1.3430	0.335	0.180	1.3758
0.024	0.081	1.3510	0.198	0.179	1.3712
Butanenitrile (1) + Propanoic Acid (2) + Water (3)					
0.002	0.006	1.3341	0.860	0.021	1.3819
0.004	0.011	1.3356	0.689	0.093	1.3809
0.008	0.021	1.3386	0.558	0.144	1.3804
0.010	0.030	1.3397	0.411	0.187	1.3791
0.019	0.051	1.3447	0.298	0.204	1.3779
Butanenitrile (1) + Butanoic Acid (2) + Water (3)					
0.001	0.008	1.3330	0.803	0.047	1.3811
0.002	0.013	1.3333	0.578	0.150	1.3763
0.003	0.018	1.3336	0.413	0.219	1.3734
0.003	0.026	1.3336	0.297	0.258	1.3718
0.004	0.034	1.3339	0.210	0.271	1.3681
Butanenitrile (1) + 2-Methylpropanoic Acid (2) + Water (3)					
0.001	0.009	1.3327	0.766	0.074	1.3798
0.002	0.023	1.3330	0.549	0.173	1.3758
0.002	0.033	1.3330	0.401	0.236	1.3737
0.002	0.049	1.3330	0.239	0.294	1.3696
0.003	0.070	1.3333	0.184	0.307	1.3660
Butanenitrile (1) + Pentanoic Acid (2) + Water (3)					
0.001	0.001	1.3329	0.835	0.042	1.3761
0.003	0.002	1.3335	0.641	0.160	1.3701
0.005	0.004	1.3341	0.473	0.255	1.3643
0.005	0.006	1.3341	0.250	0.361	1.3593
0.006	0.008	1.3343	0.051	0.442	1.3447
Butanenitrile (1) + 3-Methylbutanoic Acid (2) + Water (3)					
0.001	0.001	1.3330	0.811	0.056	1.3738
0.002	0.003	1.3332	0.601	0.167	1.3654
0.004	0.005	1.3336	0.418	0.265	1.3585
0.006	0.007	1.3340	0.210	0.359	1.3530
0.009	0.008	1.3345	0.038	0.410	1.3394

**Table 5.24** Coefficients  $A_i$ ,  $B_i$ , and  $C_i$  in Equations (5.8)-(5.10), at 298.15 K.

Hlavatý	$\beta$	logy
Butanenitrile (1) + Acetic acid (2) + Water (3)		
$A_1 = -0.363$	$B_1 = 0.622$	$C_1 = 0.553$
$A_2 = 0.022$	$B_2 = 1.056$	$C_2 = 1.014$
$A_3 = 0.232$	$B_3 = 0.751$	$C_3 = 1.109$
$\sigma = 0.002$	$\sigma = 0.003$	$\sigma = 0.001$
Butanenitrile (1) + Propanoic acid (2) + Water (3)		
$A_1 = -0.161$	$B_1 = 0.874$	$C_1 = 0.726$
$A_2 = 0.206$	$B_2 = 1.195$	$C_2 = 1.119$
$A_3 = 0.857$	$B_3 = 0.937$	$C_3 = 1.298$
$\sigma = 0.004$	$\sigma = 0.004$	$\sigma = 0.003$
Butanenitrile (1) + Butanoic acid (2) + Water (3)		
$A_1 = -0.516$	$B_1 = 1.060$	$C_1 = 0.915$
$A_2 = 0.282$	$B_2 = 1.246$	$C_2 = 1.187$
$A_3 = 0.687$	$B_3 = 0.821$	$C_3 = 1.237$
$\sigma = 0.007$	$\sigma = 0.009$	$\sigma = 0.006$
Butanenitrile (1) + 2-Methylpropanoic acid (2) + Water (3)		
$A_1 = -0.780$	$B_1 = 1.092$	$C_1 = 0.958$
$A_2 = 0.207$	$B_2 = 1.203$	$C_2 = 1.150$
$A_3 = 0.310$	$B_3 = 0.753$	$C_3 = 1.166$
$\sigma = 0.012$	$\sigma = 0.015$	$\sigma = 0.013$
Butanenitrile (1) + Pentanoic acid (2) + Water (3)		
$A_1 = -2.232$	$B_1 = 0.797$	$C_1 = 0.771$
$A_2 = -0.231$	$B_2 = 0.982$	$C_2 = 0.971$
$A_3 = -1.988$	$B_3 = 0.193$	$C_3 = 0.608$
$\sigma = 0.005$	$\sigma = 0.002$	$\sigma = 0.002$
Butanenitrile (1) + 3-Methylbutanoic acid (2) + Water (3)		
$A_1 = -2.033$	$B_1 = 0.736$	$C_1 = 0.711$
$A_2 = -0.216$	$B_2 = 0.978$	$C_2 = 0.967$
$A_3 = -1.812$	$B_3 = 0.206$	$C_3 = 0.619$
$\sigma = 0.004$	$\sigma = 0.001$	$\sigma = 0.002$

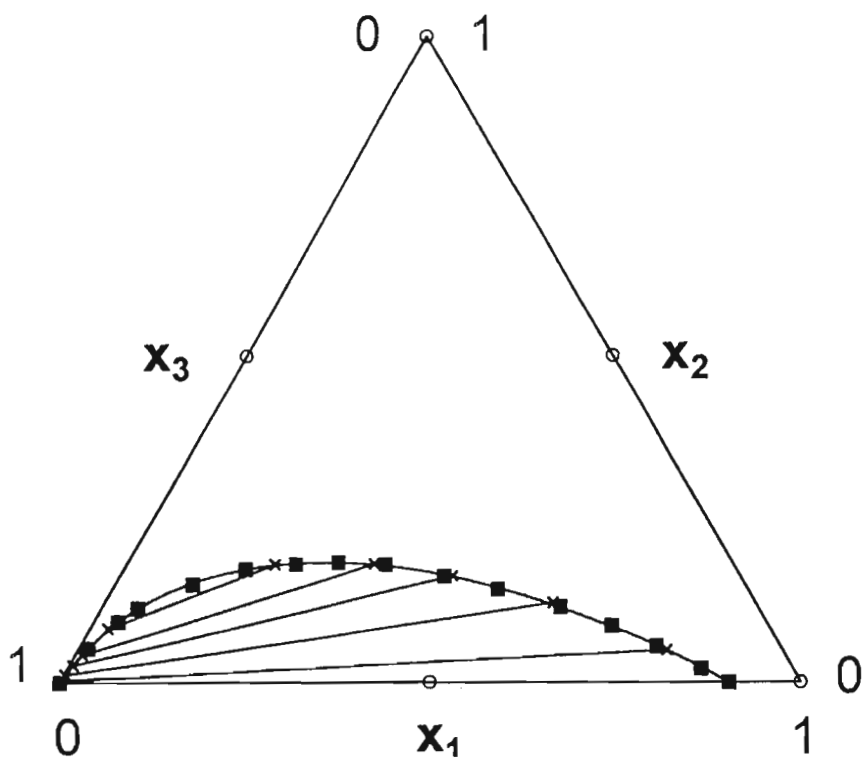


Figure 5.54 Liquid-liquid equilibrium data for the system [butanenitrile (1) + acetic acid (2) + water (3)] at 298.15 K.

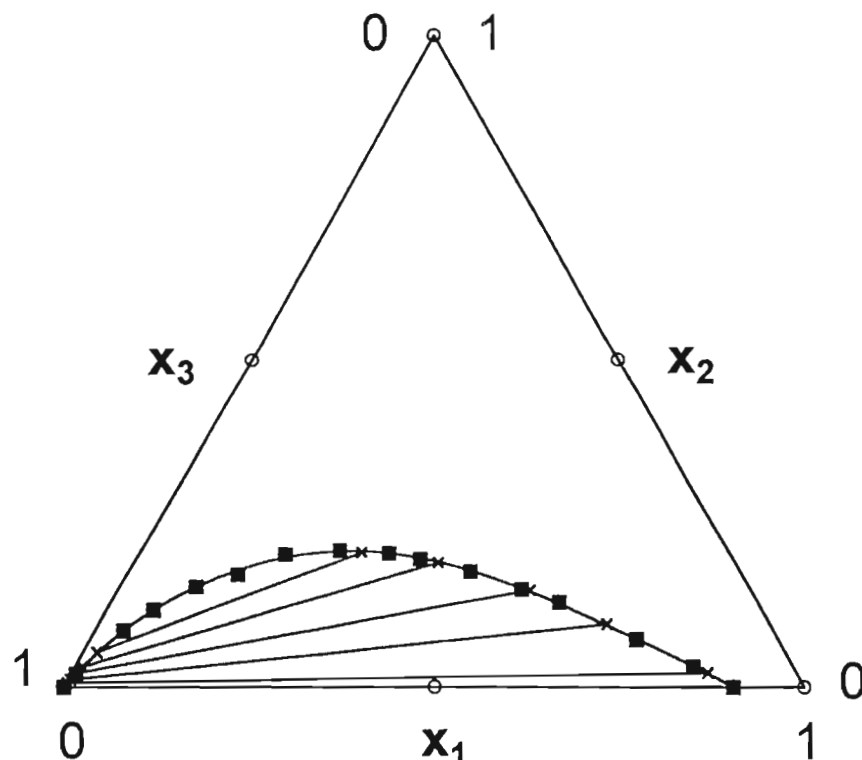


Figure 5.55 Liquid-liquid equilibrium data for the system [butanenitrile(1) + propanoic acid(2) + water (3)] at 298.15 K.

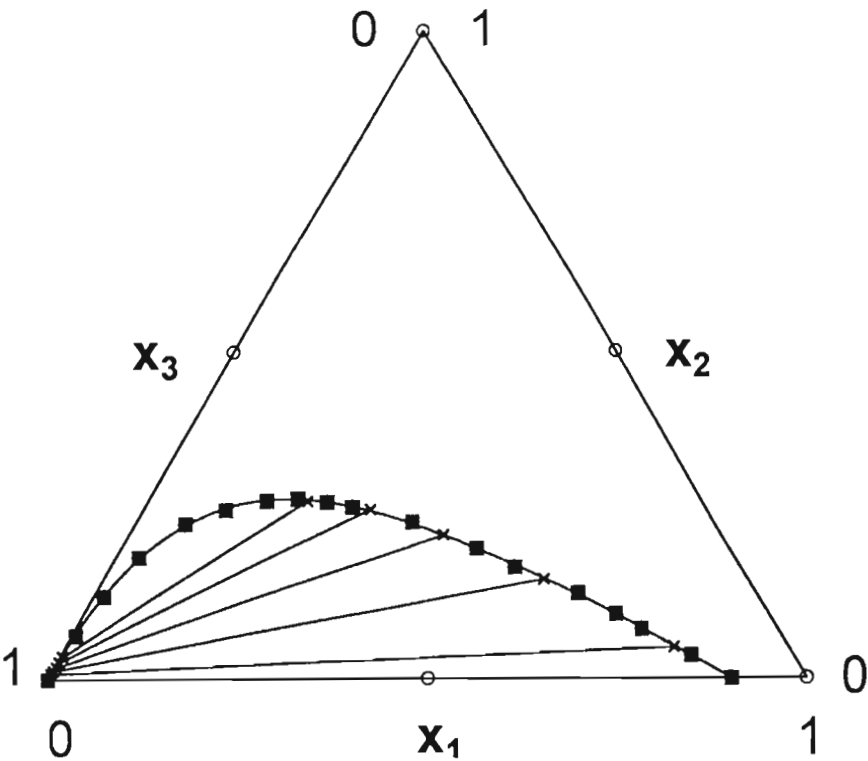


Figure 5.56 Liquid-liquid equilibrium data for the system [butanenitrile (1) + butanoic acid (2) + water (3)] at 298.15 K.

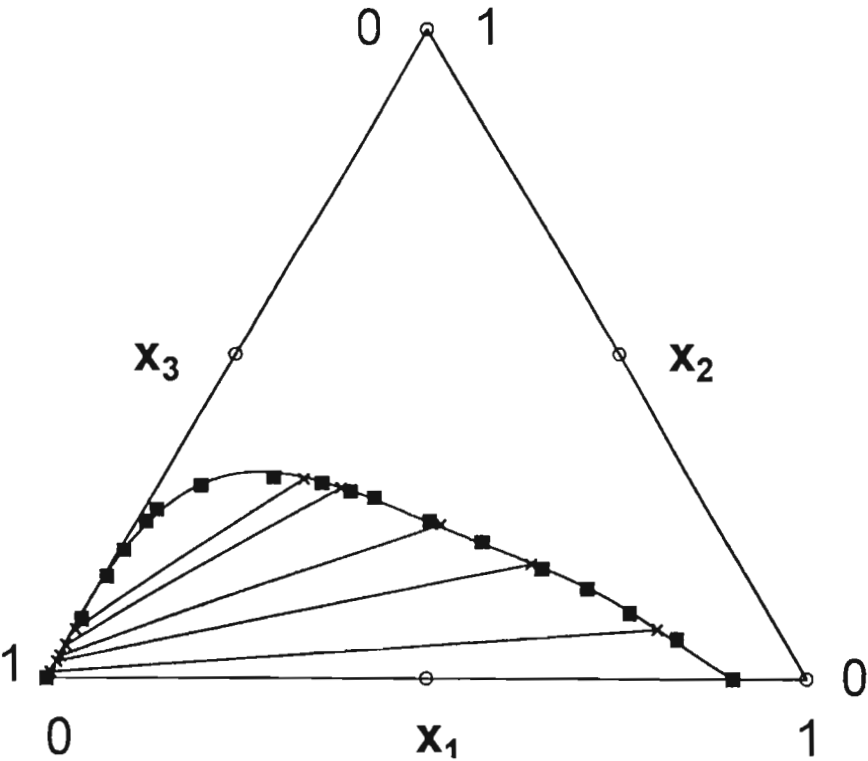


Figure 5.57 Liquid-liquid equilibrium data for the system [butanenitrile (1) + 2-methylpropanoic acid (2) + water (3)] at 298.15 K.

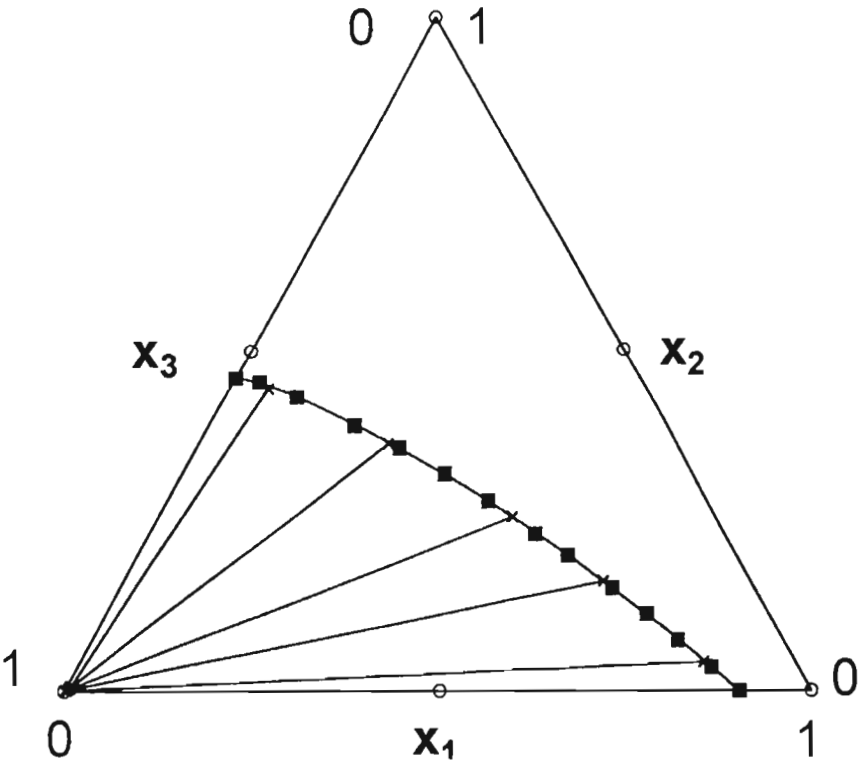


Figure 5.58 Liquid-liquid equilibrium data for the system [butanenitrile (1) + pentanoic acid (2) + water (3)] at 298.15 K.

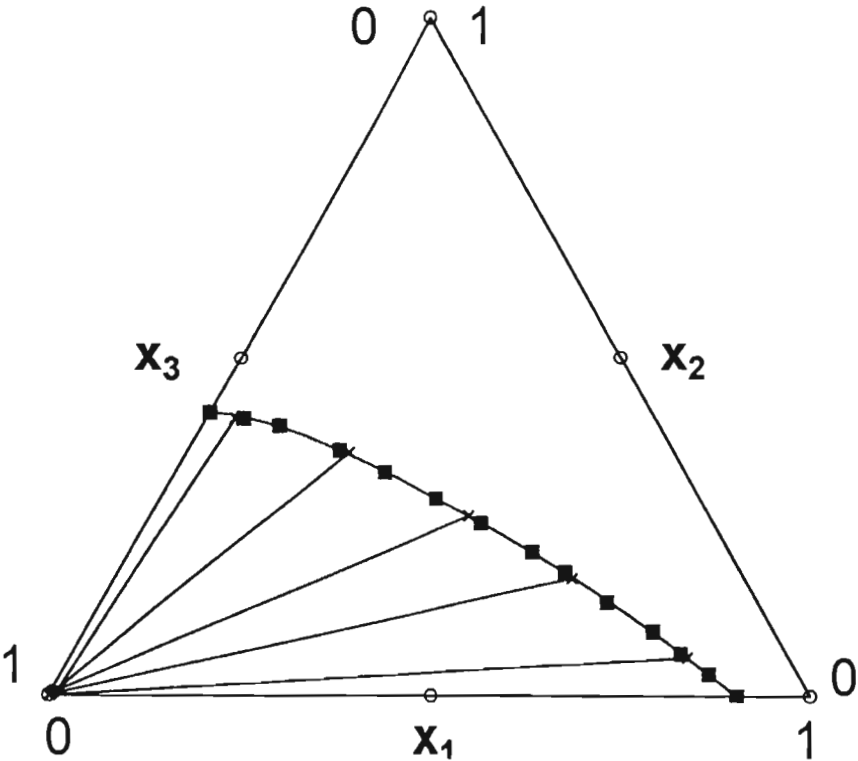
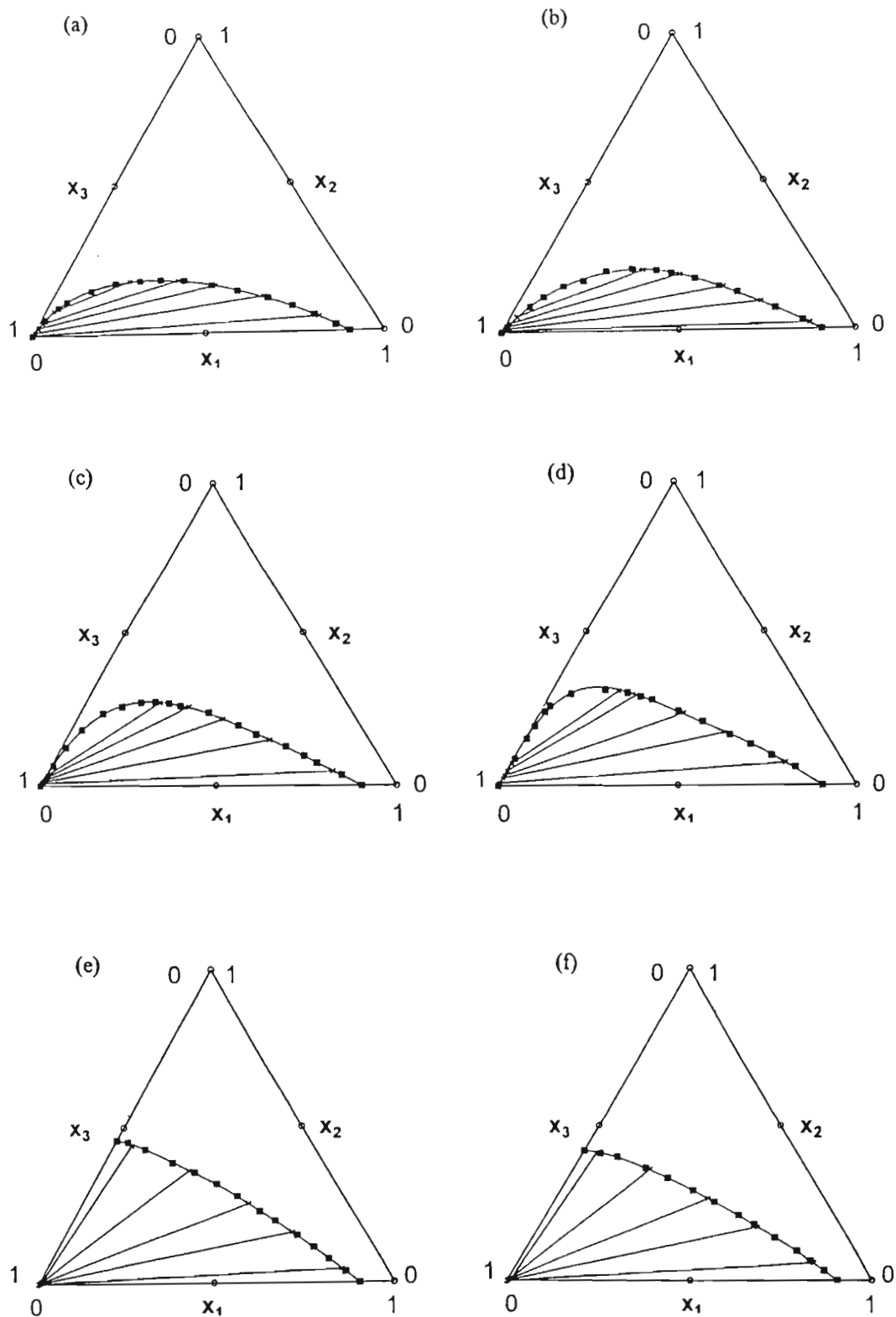


Figure 5.59 Liquid-liquid equilibrium data for the system [butanenitrile (1) + 3-methylbutanoic acid (2) + water (3)] at 298.15 K.



**Figure 5.60** Summary of liquid-liquid equilibrium data for the following systems at 298.15 K: (a) butanenitrile(1) + acetic acid(2) + water(3); (a) butanenitrile(1) + propanoic acid(2) + water(3); (c) butanenitrile(1) + butanoic acid(2) + water(3); (d) butanenitrile(1) + 2-methylpropanoic acid(2) + water(3); (e) butanenitrile(1) + pentanoic acid(2) + water(3); (e) butanenitrile(1) + 3-methylbutanoic acid(2) + water(3). [Key: (■) experimental points; (×) experimental tie-lines]

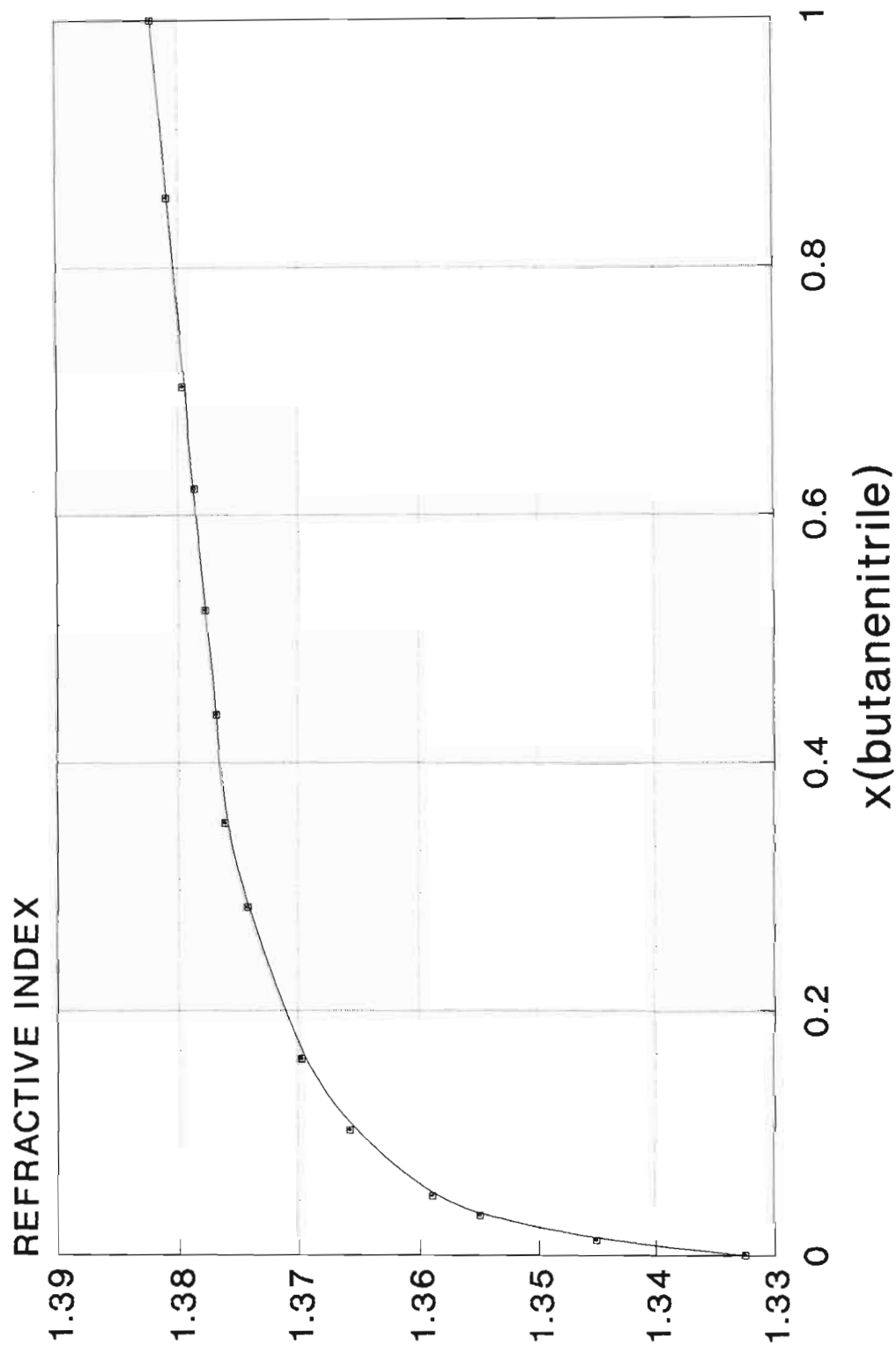


Figure 5.61 Calibration curve for (butanenitrile + acetic acid + water) system at 298.15 K.



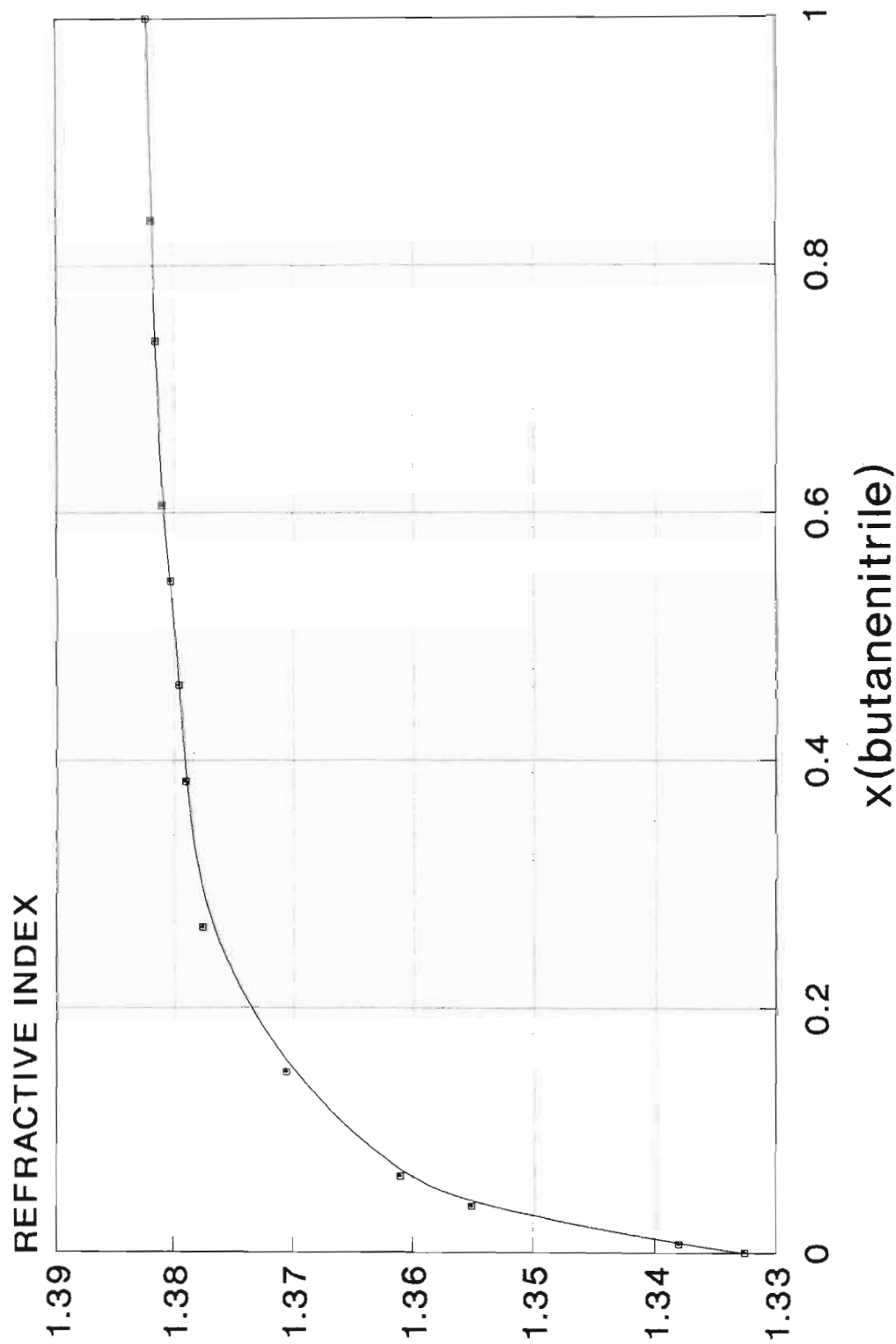


Figure 5.62 Calibration curve for (butanenitrile + propanoic acid + water) system at 298.15 K.

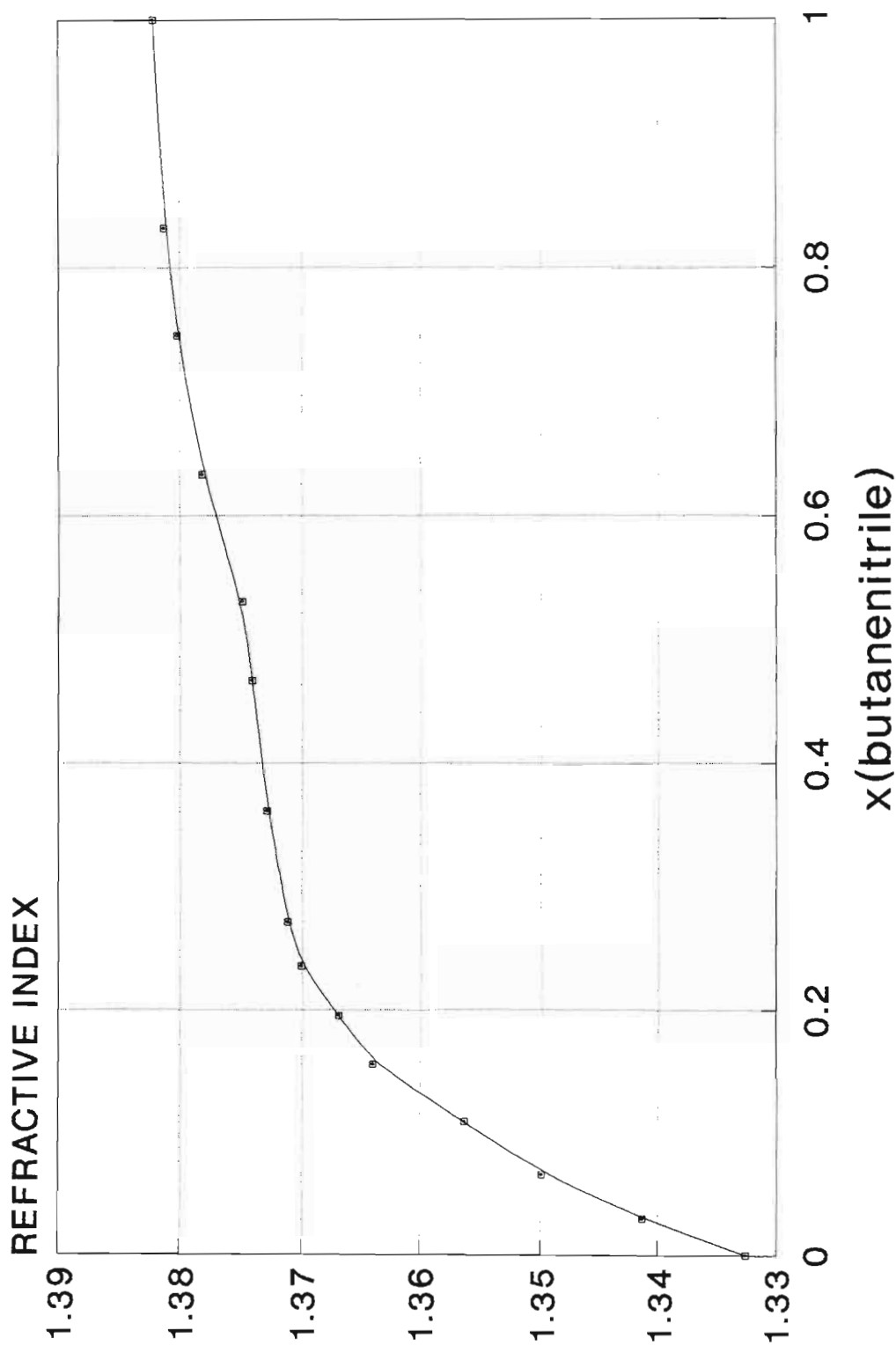


Figure 5.63 Calibration curve for (butanenitrile + butanoic acid + water) system at 298.15 K.

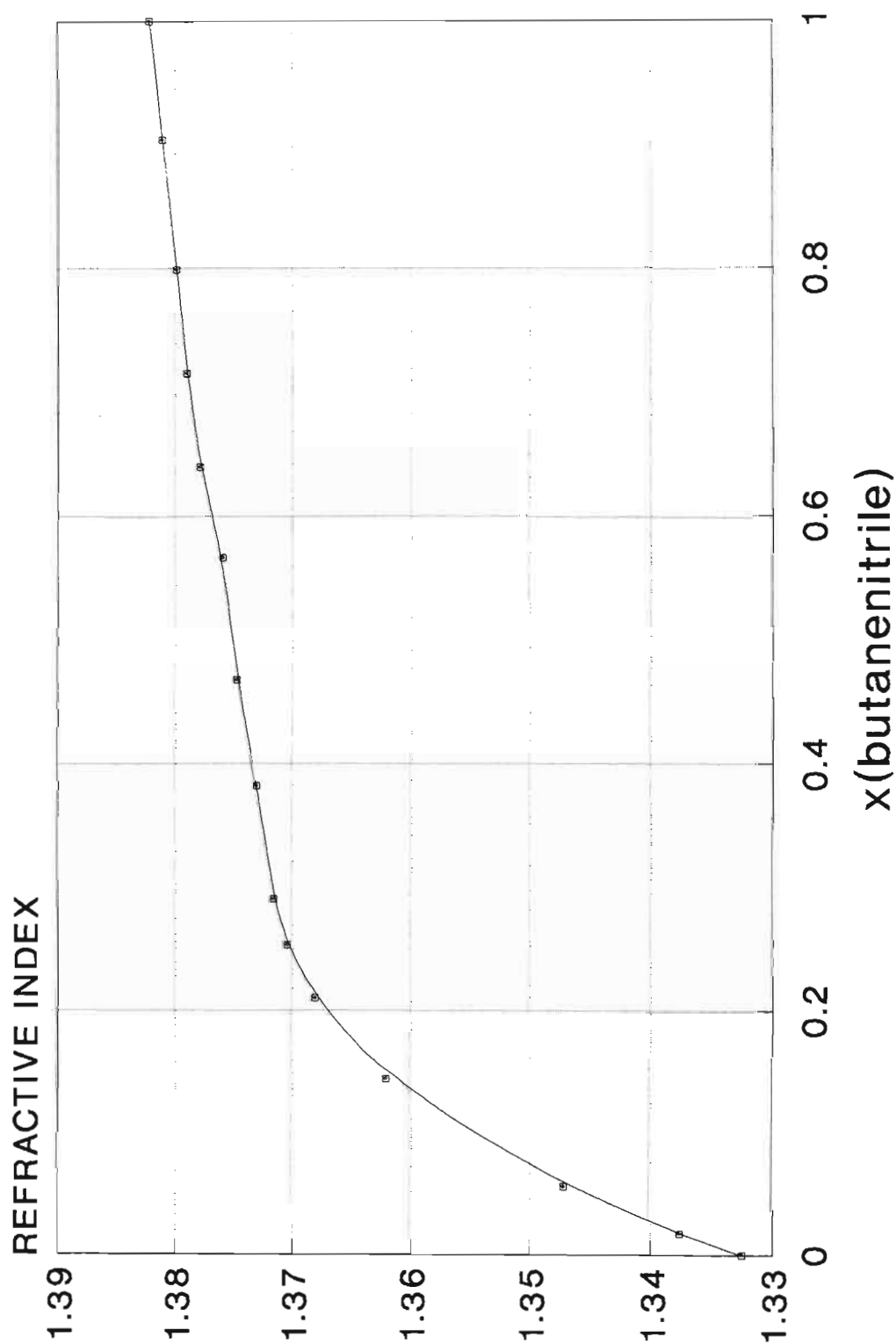


Figure 5.64 Calibration curve for (butanenitrile + 2-methylpropanoic acid + water) system at 298.15 K.

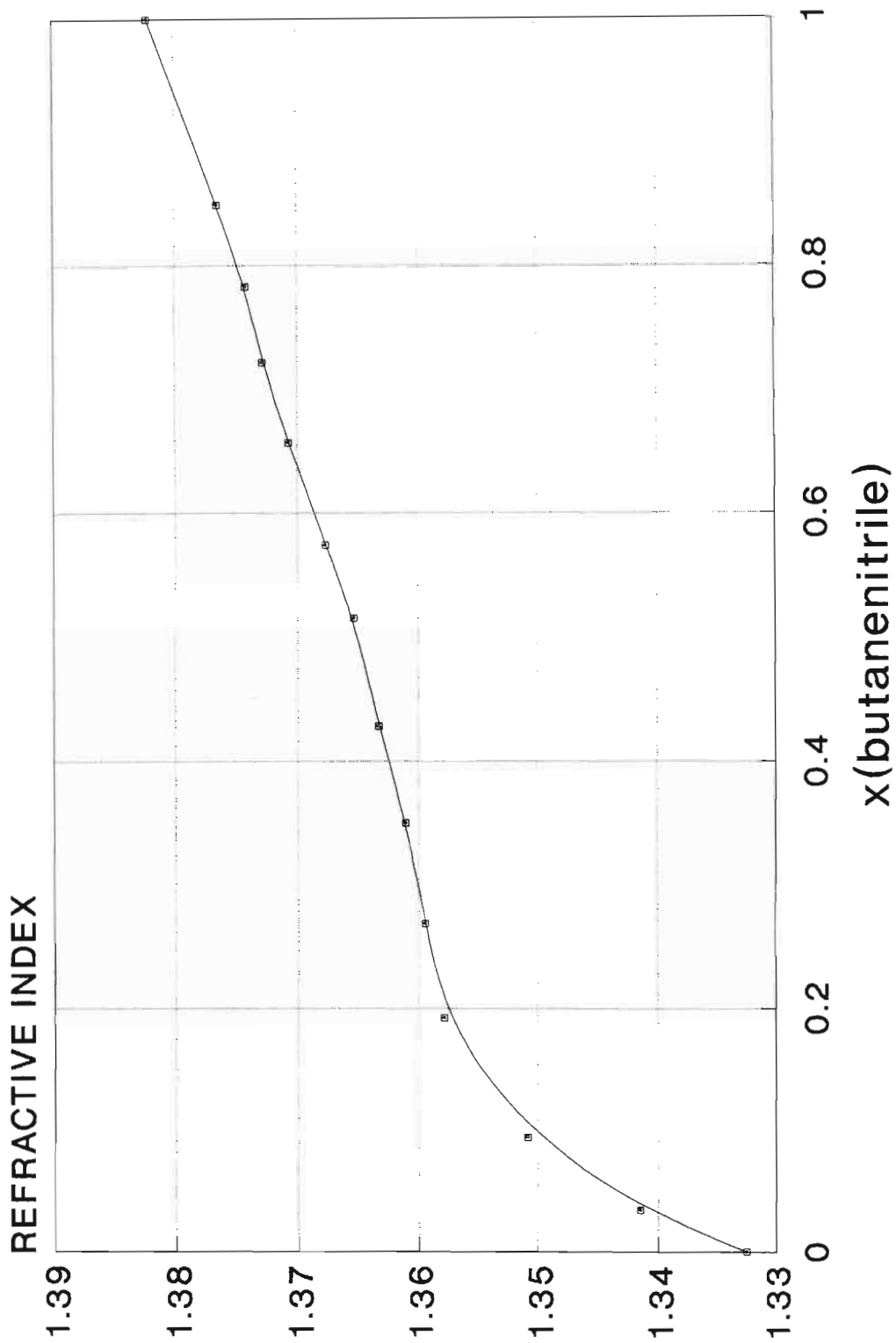


Figure 5.65 Calibration curve for (butanenitrile + pentanoic acid + water) system at 298.15 K.

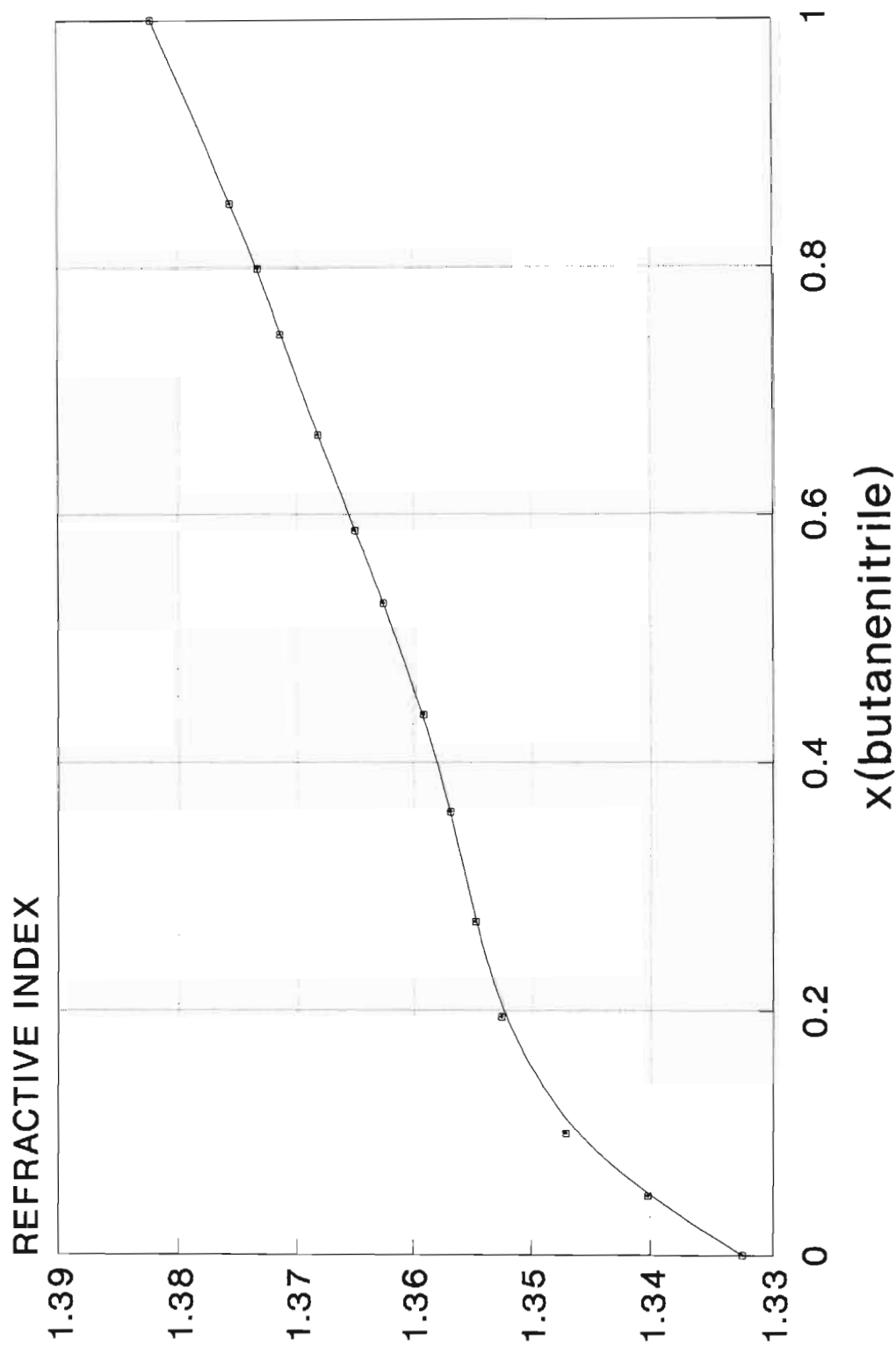
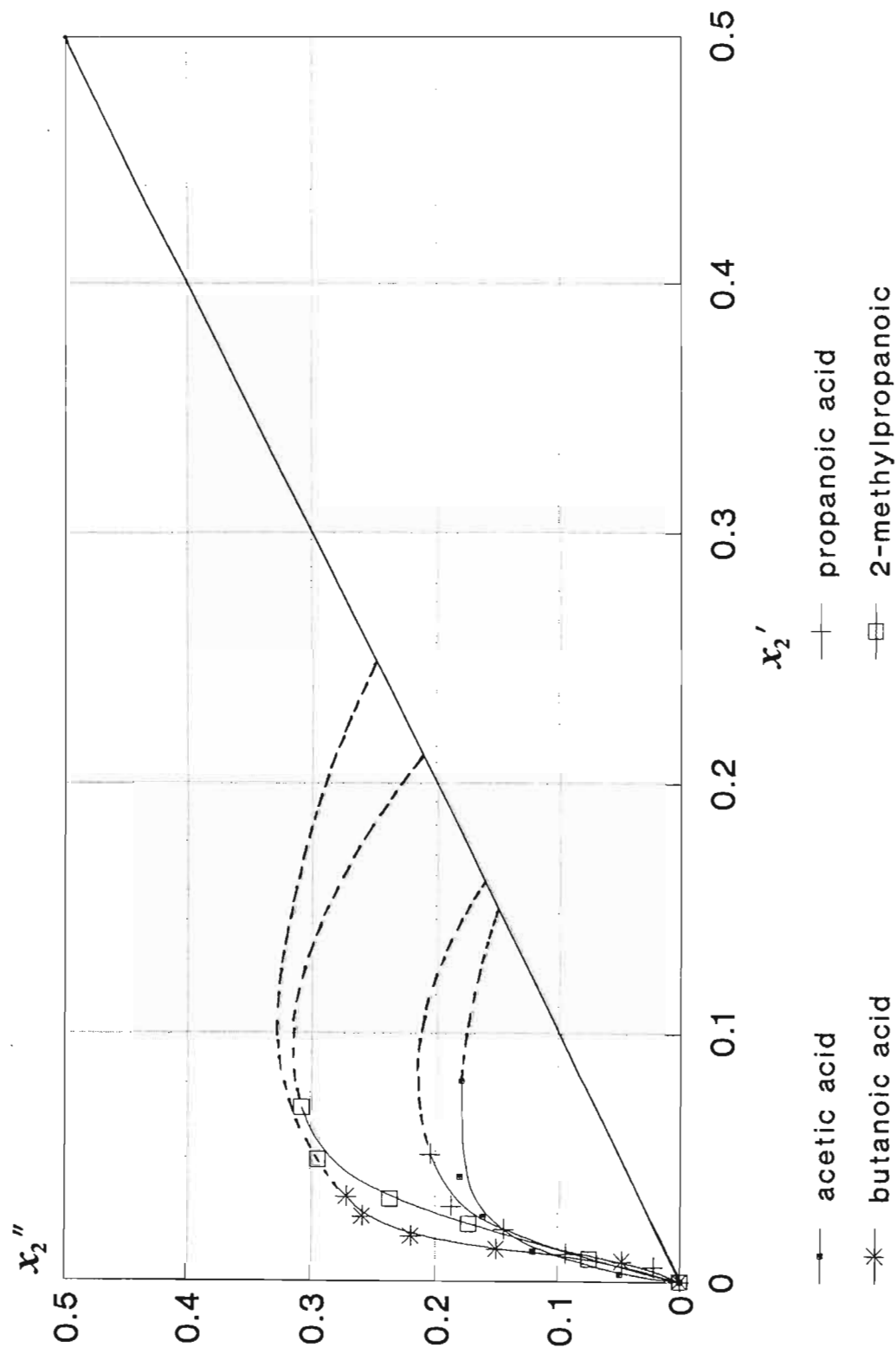


Figure 5.66 Calibration curve for (butanenitrile + 3-methylbutanoic acid + water) system at 298.15 K.



**Figure 5.67** A plot of  $x_2''$  against  $x_2'$  showing the relative solubilities of the carboxylic acid in the butanenitrile-rich and water-rich layers.

**Table 5.25**    **Representative selectivity values of butanenitrile for the separation of carboxylic acids from water at 298.15 K, using equation 5.17**

Carboxylic acid	Selectivity ( $\omega$ )
acetic acid	15
propanoic acid	22
butanoic acid	32
2-methylpropanoic acid	19
pentanoic acid	232
3-methylbutanoic acid	165

#### 5.8.4.1 Discussion of Ternary Systems [Butanenitrile(1) + a Carboxylic Acid(2) + Water(3)] at $T = 298.15\text{ K}$

##### Previous Work

Butanenitrile is another nitrile compound which is becoming important in the manufacture of imminium salts (with interesting biological properties) and of piperidine alkaloid precursors (used in the pharmaceutical industry) (Caram *et al.*, 1984; Saminego *et al.*, 1994; Rodriguez *et al.*, 1995). A literature search has shown that liquid-liquid equilibria (LLE) on related systems have been scarce. Liquid-liquid equilibria on (butanenitrile + hydrocarbons + water) has been investigated by Naicker (2000).

##### This Work

In this study new precise LLE data are presented for the following systems at 298.15 K : (butanenitrile + acetic acid or propanoic acid or butanoic acid or 2-methylpropanoic acid or pentanoic acid or 3-methylbutanoic acid + water.

The slopes of the binodal curves obtained in Figure 5.60 (a)-(f) again show that the solubility of water in (butanenitrile + a carboxylic acid) mixture is very much dependent on the carbon number and type of the carboxylic acid. Water is most soluble in the systems containing the shorter chain acetic acid and propanoic acid. Similar results were obtained for the previous work: (benzonitrile + a carboxylic acid + water), as well as results obtained by Letcher *et al.* (1992), for mixtures of diisopropyl ether + an alkanol + water.

Figure 5.60 shows that the area of the two-phase heterogeneous region for the carboxylic acid mixtures decreases in the order : acetic acid < propanoic acid < butanoic acid < 2-methylpropanoic acid < 3-methylbutanoic acid < pentanoic acid. This implies that the mutual solubility of the components is decreased with a corresponding increase in the carbon chain length of the respective acids, and also that water is most soluble in the (butanenitrile + acetic acid) mixture, but least soluble in the (butanenitrile + pentanoic acid) mixture.

The slopes of the binodal curves for butanoic acid, 2-methylpropanoic acid, pentanoic acid



and 3-methylbutanoic acid show a skewing towards the water axis.

The relative solubility of an acid in butanenitrile or water is evident from the tie-lines. The slope of the tie lines obtained in this work show that all the acids are more soluble in the butanenitrile than the water mixture. For the C4 acids, the gradient of the tie-lines for 2-methylpropanoic acid is significantly greater than those for butanoic acid. This could be attributable to the greater solubilising effect of the two electron releasing methyl groups on the terminal carbon of 2-methylpropanoic acid as opposed to its straight chain isomer. A similar effect is noted for 3-methylbutanoic acid when compared to pentanoic acid.

From the LLE data presented here, it is found that an increase in the concentration of the acids results in an increase in water solubility in the organic phase and a decrease in butanenitrile solubility in the aqueous phase.

The effectiveness of extraction of a carboxylic acid (2) by butanenitrile is given by its selectivity  $\omega$ , which is a measure of the ability of butanenitrile to separate the carboxylic acid (2) from water(3) (Letcher *et al.*, 1996):

$$\omega = \frac{\text{distribution coefficient of carboxylic acids}}{\text{distribution coefficient of water}}$$

$$\omega = \frac{(x_2 / x_3)_{\text{butanenitrile-rich phase}}}{(x_2 / x_3)_{\text{water-rich phase}}} \quad (5.17)$$

where  $x_2$  refers to the mole fraction of carboxylic acid, and  $x_3$  the mole fraction of water. Representative values of selectivity for the middle of the area of the measured tie - lines are given in Table 5.25. The selectivity values obtained are 15, 22, 32, 19, 232, and 165 for acetic acid, propanoic acid, butanoic acid, 2-methylpropanoic acid, pentanoic acid and 3-methylbutanoic acid respectively. From the selectivity data, it can be concluded the separation of all the carboxylic acids from water by extraction is feasible. It can also be concluded that butanenitrile is an especially good solvent for the separation of mixtures of (water and pentanoic acid) or (water and 3-methylbutanoic acid)

Comparing the ternary diagrams for all the systems done in this work with the diagrams for (benzonitrile + acetic acid or propanoic acid or butanoic acid or 2-methylpropanoic acid or pentanoic acid or 3-methylbutanoic acid + water), it is found that replacing butanenitrile with benzonitrile always results in an increase in the two-phase heterogeneous region and a corresponding increase in the tie-line gradients. This implies that the solvent butanenitrile has a higher solubility, but lower solvent power (capacity) for (carboxylic acid + water) mixtures as compared to the solvent benzonitrile for (carboxylic acid + water) mixtures, at the same temperature and pressure conditions. Benzonitrile is thus the better solvent for extraction of carboxylic acids from water.

Again, three equations viz., the modified Hlavaty, beta and  $\log \gamma$  equations were fitted to the binodal curve data. The  $\log \gamma$  function gave the best overall fit compared to the  $\beta$  function equation and modified Hlavaty equation.

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## CHAPTER 6

### MIXTURES OF MOLECULAR LIQUIDS

#### 6.1 INTRODUCTION

The finite compressibility and the relatively high density which characterises liquids in general, point to the existence of repulsive and attractive intermolecular forces. Although the bulk properties of liquids (for eg. boiling points, thermal conductivities etc.) may also be used in principle to classify them, a much better classification is made according to the intermolecular forces.

It is useful to distinguish between the following classes of liquids: simple fluids (eg. Argon), non-polar molecular liquids (eg. hexane), polar molecular liquids (eg. acetonitrile), hydrogen bonded molecular liquids (eg. carboxylic acids), ionic liquids or molten salts (eg. potassium chloride), and liquid metals (eg. lead). Many of the unusual and interesting properties of molecular liquids are supposed to come from the fact that the anisotropy of the interaction between molecules is responsible for the development of a characteristic short range order, which is very much different from the one encountered in simple liquids, where the mean number of neighbours is so high that on average, its distribution has some sort of symmetry. On the other hand, in molecular liquids, nearest neighbour molecules do interact differently depending on their molecular orientation.

This chapter on the Theory of Molecular Mixtures applies the tools of statistical mechanics and thermodynamics to the equilibrium properties of molecular liquid mixtures, so that reactions and interactions phenomenologically described can also be better understood, and made the basis for the solution theories presented in Chapter 7.

#### 6.2 INTRODUCTION : SIMPLE MIXTURES

Simple mixtures are defined as those in which the nominal components are identical with the actual species in the pure liquids as well as in the mixture. This excludes all the cases where

the molecules of one or more of the components associate either among themselves (self association) or mutually with those of another component (solvent, adduct formation), or dissociate - the latter case being rare in mixtures of molecular liquids. This leaves under consideration all those cases where the interactions between the molecules are governed by dispersion forces and by weak dipole interactions, and where the assumption of random mixing is valid.

### 6.2.1 Ideal Mixtures

The decision on whether a given system is ideal, and obeys the laws of ideal mixing depends on the precision with which the experimental data can be obtained. It is often valid to state that within the experimental errors a system is ideal, but closer examinations may reveal slight deviations. Thus, the system (1,2- dibromoethane + 1,2 - dibromopropane) at 85°C (Zawidzki, 1900) was often quoted as an example of an ideal system (Guggenheim, 1952), but it does show deviations (Williamson, 1967). A system may be (nearly) ideal at one temperature and total pressure, and show deviations under different conditions. A necessary (but not sufficient) condition for ideal mixing (if the vapour mix ideally) is

$$\Delta p/p = [p_{obs} - (x_1 p_1^* + x_2 p_2^*)] / p_{obs} = 0 \quad (6.1)$$

where  $p_i \equiv$  vapour pressure of component  $i$  and  $x_i \equiv$  mole fraction of component  $i$ .

This condition is satisfied within very narrow limits for mixtures of isotopically substituted liquids with moderate mass differences, but is valid also within  $\pm 0.005$  for other mixtures. Even if equation (6.1) is obeyed, it is possible that  $g^E \neq 0$ , since the vapour is not a perfect gas mixture.

### 6.2.2 Athermal Mixtures

Most real systems, which deviate from the ideal mixing laws, have non-zero enthalpies of mixing, but there is a class called athermal mixtures (Guggenheim, 1952) which obey (within the experimental errors) the law : over a certain temperature range.

$$H^E(x_i) = 0 \quad (6.2)$$

(where  $H^E$  refers to the excess enthalpy and  $x_i$  refers to mole fraction of component  $i$ ).

For such systems the excess Gibbs energy is given entirely by the entropy contribution

$$G^E = -TS^E \quad (6.3)$$

Even if there are no real systems obeying (6.2) and (6.3), these expressions may be used as points of reference to which systems having small  $H^E$  but large  $S^E$  may be referred. Such a situation may arise when the interactions between the molecules of each of the components are very similar, so that they are similar also in the mixture, but there is a large discrepancy in sizes between the molecules resulting in their mixing being not completely random. The maximum entropy of mixing is therefore not achieved, and  $S^E$  differs from zero. It follows from (6.2), for the random mixing model, to a good approximation (Hildebrand and Scott, 1950), that the excess volume  $V^E = 0$ . The volume change of mixing is given by:

$$\begin{aligned} V^M &= (\partial G^M / \partial P) \\ &\approx (\partial U^M / \partial P) - T (\partial S^M / \partial P) \quad (\text{at } T, P = P_0) \end{aligned} \quad (6.4)$$

where the approximate equality is due to the Gibbs energy of mixing,  $G^M$  and Helmholtz energy,  $A^M$  differing only to the second order in  $V^E$ . The last term in (6.4) equals zero, since for random mixing the entropy depends only on the composition. The first term can be written as:

$$\begin{aligned} (\partial U^M / \partial P) &= (\partial V_0 / \partial P) (\partial U^M / \partial V_0) \\ &= -\kappa_0 V_0 (U^M / \partial V_0) \\ &= -\kappa_0 V_0 [\partial U^M / \partial V_0] - (\sum \partial U_i^* / \partial V_0) \\ &\approx -\kappa_0 V_0 [\partial U_m / V_0 + \sum \partial U_i^* / V_0] \\ &= \kappa_0 U^M \end{aligned} \quad (6.5)$$

at constant  $T$ , and at low  $P (=P_0)$ , where the compressibility is  $\kappa_0$  and the volume is  $V_0$ . The approximate substitution  $-U/V$  for  $(\partial U / \partial V)_T$  has been justified on empirical grounds (Hildebrand and Scott, 1950). The volume change on mixing is thus proportional to the internal-energy change, and since the latter is zero, by (6.2), the former is also zero.

The simplest way to obtain the excess entropy  $S^E$  is from considerations of free volumes (Hildebrand, 1947). The entropy change for any expansion from a free volume  $V_{\text{initial}}^f$  to a free volume  $V_{\text{final}}^f$ , where the free volume is the volume accessible to the molecule, is:

$$\Delta S = nR \ln(V_{\text{final}}^f / V_{\text{initial}}^f) \quad (6.6)$$

Therefore, in a mixing process where molecules of component 1, which were initially confined to the free volume  $n_1 V_1^f$ , have access to the volume  $n_1 V_1^f + n_2 V_2^f$ , and similarly for components 2, the entropy of mixing is:

$$S^M = -R \left[ n_1 \ln \frac{n_1 V_1^f}{n_1 V_1^f + n_2 V_2^f} + n_2 \ln \frac{n_2 V_2^f}{n_1 V_1^f + n_2 V_2^f} \right] \quad (6.7)$$

or, per mole of mixture.

$$S^M = -R[x_1 \ln x_1 / (x_1 + r x_2) + x_2 \ln r x_2 / (x_1 + r x_2)] \quad (6.8)$$

where  $r = V_2^f / V_1^f$  is the ratio of the free volumes. Now the free volume is the total volume minus the excluded, or occupied volume. If the free volume is assumed to be proportioned to the total volume, and the same proportionality factor is assumed to apply to the two components, it is then possible to set  $r = V_2^* / V_1^*$ , and (6.8) reduces to

$$S^M = -R[x_1 \ln \phi_2] \quad (6.9)$$

Alternatively,  $r$  may be taken as an arbitrary parameter and (6.8) can be stated in terms of  $z$ -fractions, ie.:

$$S^M = R[x_1 \ln z_1 + x_2 \ln z_2] \quad (6.10)$$

$$\text{where } z_1 = \frac{x_1}{(x_1 + r x_2)}$$

$$\text{and } z_2 = \frac{r x_2}{(x_1 + r x_2)}$$

The expressions (6.9) and (6.10) lead to  $S^E > 0 > G^E$ .

### 6.2.3 Regular mixtures

Another simplified case is that in which random mixing is assumed but a finite energy of mixing is allowed. There must be some upper limit to this energy change since for strong interactions which are different in the pure components and in the mixture, the assumption of random mixing is unrealistic.

The stipulation  $S_v^E(x_i) = 0$  is made, and a finite, but small  $V^E$  is permitted. The theory of regular mixtures has very little to say about the magnitude of  $V^E$ , and only those cases where second-order terms in the excess volume are negligible will be considered, so that

$$\begin{aligned} G_p^E &= a_v^E - (2\kappa_m V_m)^{-1} V^{E2} + \dots \\ &\approx a_v^E \\ &\approx u_v^E \end{aligned} \quad (6.11)$$

$$\text{but } H_p^E = U_v^E + T(\alpha_m/\kappa_m)V^E + \dots \quad (6.12)$$

$$S_p^E = S_v^E + (\alpha_m/\kappa_m)V^E + \dots \approx (\alpha_m/\kappa_m)V_o^E \sim 0 \quad (6.13)$$

the last approximate equality holding only for negligible  $V^E$ . In that case,  $G^E = H^E$  and  $S^E = 0$ .

### 6.2.4 General phenomenology of non-ideal mixtures

The approximation of athermal solutions ( $H^E = 0$ ) and of regular solutions ( $S^E = 0$ ) are identical limiting cases, and real solutions usually have non-zero values of both  $S^E$  and  $H^E$ . Several empirical equations have been proposed, recognising the effects of unequal sizes of the molecules (configurational) and of their mutual interactions. Generally, the excess Gibbs energy is written as the sum  $G^E = G_{\text{conf}}^E + G_{\text{inter}}^E$ , which leads to corresponding values of the excess chemical potential and the activity coefficient

$$\ln f_i = \ln f_{i,\text{conf}} + \ln f_{i,\text{inter}} \quad (6.14)$$

One way to deal with the interaction energy is to start from the two-liquid approximation and include it in a Boltzmann factor that weights the probability of finding a molecule of component 1 or component 2 in the immediate vicinity of a given molecule. According to

Wilson (1964), the ratio of probabilities of finding the same kind of molecule,  $x_{ii}$ , to that of finding a different molecule,  $x_{ij}$  equals the ratio of the bulk mole fractions weighted appropriately:

$$(x_{ii}/x_{ij}) = [x_i \exp (-\langle \varepsilon_{ii} \rangle / kT)] / [x_j \exp (-\langle \varepsilon_{ij} \rangle / kT)] \quad (6.15)$$

where the average potential energies  $\langle \varepsilon \rangle$  are assumed to be independent of  $r$  and treated as free parameters, where  $r$  is the distance between particles.

Local volume fraction  $\Phi$  are then defined as

$$\Phi = x_{ii} V_i^* / (x_{ii} V_i^* + x_{ij} V_j^*) \quad (6.16)$$

and these replace the mole fractions in the expression for the entropy of mixing (6.9) yielding the excess Gibbs energy.

$$G^E = RT [x_1 \ln(\Phi/x_1) + x_2 \ln(\Phi/x_2)] \quad (6.17)$$

and upon substitution of the values of  $x_{ii}$  and  $x_{ij}$  from (6.15) in  $\Phi_i$  of (6.16) and (6.17), the expression:

$$G^E = -RT \ln [x_1 (\ln x_1 + x_2 \Lambda_{12}) + x_2 \ln (x_2 + x_1 \Lambda_{21})] \quad (6.18)$$

is obtained, where

$$\Lambda_{12} = (V_2^*/V_1^*) \exp [(\langle \varepsilon_{11} \rangle - \langle \varepsilon_{12} \rangle) / kT] \quad (6.19a)$$

$$\Lambda_{21} = (V_1^*/V_2^*) \exp [(\langle \varepsilon_{22} \rangle - \langle \varepsilon_{12} \rangle) / kT] \quad (6.19b)$$

The parameters  $\Lambda$  are thus functions of  $r$  and  $T$  with two free parameters  $(\langle \varepsilon_{11} \rangle - \langle \varepsilon_{12} \rangle) / k$  and  $(\langle \varepsilon_{22} \rangle - \langle \varepsilon_{12} \rangle) / k$ . Wilsons equations is thus useful for fitting data, but not for predicting activity coefficients of new systems.

### 6.3 ASSOCIATED MIXTURES

Associated mixtures are defined as those in which there is chemical evidence (usually extra-thermodynamic such as spectroscopic, evidence) for the association of the particles of at least one of the components, either with each other (self association), or with those of another component (mutual association or adduct formation). It is possible to approach the description of such mixtures in terms of the properties of the components in a formal thermodynamic manner, or with respect to the molecular interactions, such as dipole



interactions, hydrogen bonding, coordinative bond formation etc. The association may be treated in terms of a definite chemical reaction (or a set of reactions) to which an equilibrium constant (or constants) and standard changes of thermodynamic quantities, such as enthalpy, per mole of reaction can be assigned.

In the following, mainly nominally binary mixtures of component 1 (having molecules of type  $(A)$  and of component 2 (having molecules of type  $(B)$ ) will be discussed. Extension to multicomponent systems is straightforward. In the general case of association to species  $A_i$ ,  $B_j$  and  $A_m B_n$  the total number of moles ( $n_1$  and  $n_2$ ) will be given by:

$$n_1 = \sum_i i n_{A_i} + \sum_m \sum_n m n_{A_m B_n} \quad (6.20)$$

$$n_2 = \sum_j j n_{B_j} + \sum_m \sum_n m n_{A_m B_n} \quad (6.21)$$

A fundamental relationship which is valid in all cases of association, relates the chemical potentials  $u_1$  and  $u_2$  of the nominal components to those of the corresponding non-associated (monomeric) molecular species  $A$  and  $B$  (Prigogine and Defay, 1954). This is based on the fact that equilibrium occurs among the species so that for  $A_i \rightleftharpoons iA$ ,  $\mu_{A_i} = i\mu_A$  etc. At constant temperature and pressure, the total differential of the Gibbs energy is:

$$\begin{aligned} dG &= \sum_i \mu_{A_i} dn_{A_i} + \sum_j \mu_{B_j} dn_{B_j} + \sum_m \sum_n \mu_{A_m B_n} dn_{A_m B_n} \\ &= \mu_A \sum_i i dn_{A_i} + \mu_B \sum_j j dn_{B_j} + \mu_A \sum_m \sum_n m dn_{A_m B_n} + \mu_B \sum_m \sum_n n dn_{A_m B_n} \\ &\quad + m_B \sum_m \sum_n n dn_{A_m B_n} \\ &= \mu_A dn_1 + \mu_B dn_2 \end{aligned} \quad (6.22)$$

On the other hand, for a binary mixture at constant  $T$  and  $P$

$$dG = \mu_1 dn_1 + \mu_2 dn_2 \quad (6.23)$$

which leads to the identities

$$\mu_1 = \mu_A \quad \mu_2 = \mu_B \quad (6.24)$$

The chemical potentials of the components are thus equal to those of the monomers, a result which is independent of the ideality or otherwise of the mixture and of the nature of association.

A further result from expressing the chemical potential in terms of the nominal components and in terms of the monomeric species is:

$$\mu = \mu_1^\circ + RT \ln x_1 f_1 = \mu_A = \mu_A^\circ + RT \ln x_A f_A \quad (6.25)$$

and similarly for the component 2, ie. (B). Elimination of the standard chemical potentials is made by setting  $x_1 = 1$  for the pure component 1, and denoting  $x_A f_A$  as  $x_A^* f_A^*$  in this state. It then follows:

$$f_1 = x_A f_A / x_1 x_A^* f_A^* \quad (6.26a)$$

$$f_2 = x_B f_B / x_2 x_B^* f_B^* \quad (6.26b)$$

as the general expression for the activity coefficient of the nominal components. For ideal associated mixtures  $f_A = f_A^* = f_B = f_B^* = 1$ , so that  $f_1$  (ideal associated solution)  $= x_A / x_1 x_A^*$  etc., while for non-ideal mixtures, the activity coefficients of the monomeric species must be assigned proper values.

### 6.3.1 Ideal associated mixture

Dolezalek (1908) has shown that deviations from Raoult's Law for liquid mixtures can often be explained by association, assuming the association products and the other particles to mix ideally. Kehiaian and Sosnkowska - Kehiaian (1963) examined in detail the formal thermodynamic consequences of such an assumption. The following two simple cases will be treated.

Case (1) : Self Association of  $A$  to dimers  $A_2$ , so that the mixture involves the species  $A, A_2$

and  $B$ .

Case (2) : Mutual association of  $A$  and  $B$  to form  $AB$ , so that the mixture involves the species  $A$ ,  $AB$  and  $B$ .

Case (1) The chemical equilibrium  $2A \rightleftharpoons A_2$  is characterised by the equilibrium constant  $K_2 = x_{A_2}/x_A^2$  which can be written in terms of the mole fractions of the nominal components, ie.  $x_1$ , as

$$K_2 = \xi / [x_1 - \xi(2-x_1)]^2 \quad (6.27)$$

where  $\xi$  = fraction of self-associated species (dimers)

$$\text{Now } \xi = \frac{x_1}{2 - x_1} - \frac{[4K_2 x_1 (2 - x_1) + 1]^{\frac{1}{2}} - 1}{2K_2 (2 - x_1)^2} \quad (6.28)$$

For pure component 1,  $x_1 = 1$  and  $\xi^*$  of the dimer and  $x_A^*$  of the monomer are obtained as

$$\xi = 1 - \xi^* [(4K_2 + 1)^{\frac{1}{2}} - 1]/2K_2 \quad (6.29a)$$

$$x_A^* = 1 - \xi^* = [(4K_2 + 1)^{\frac{1}{2}} - 1]/2K_2 \quad (6.28b)$$

For increasing values of  $K_2$  the maximum possible value of  $\xi$  is obtained for any  $x_1$  from (6.28) as  $x_1/(2-x_1)$  for  $K \rightarrow \infty$ , and the slope  $(\partial\xi/\partial x_1)_{T,P}$  is always positive, except at  $x_1 = 0$ , where it is zero.

The molar Gibbs energy of the mixture is:

$$\begin{aligned} G_m &= x_1 (\mu_A^\circ + RT \ln x_A) + x_2 (\mu_B^\circ + RT \ln x_B) \\ &= x_1 (\mu_1^\circ + RT \ln x_1) + x_2 (\mu_2^\circ + RT \ln x_2) \\ &\quad + RTx_1 \ln (x_A/x_A^* x_1) + RTx_2 \ln (x_B/x_2) \end{aligned} \quad (6.30)$$

since  $\mu_2^\circ = \mu_B^\circ$  (as  $\mu_B^\circ = 1$ ) but  $\mu_1^\circ = \mu_A^\circ + RT \ln x_A^*$

The first two terms of (6.30) are the ideal Gibbs energy of mixing, and the last two are the excess Gibbs energy. The activity coefficients of the nominal components are:

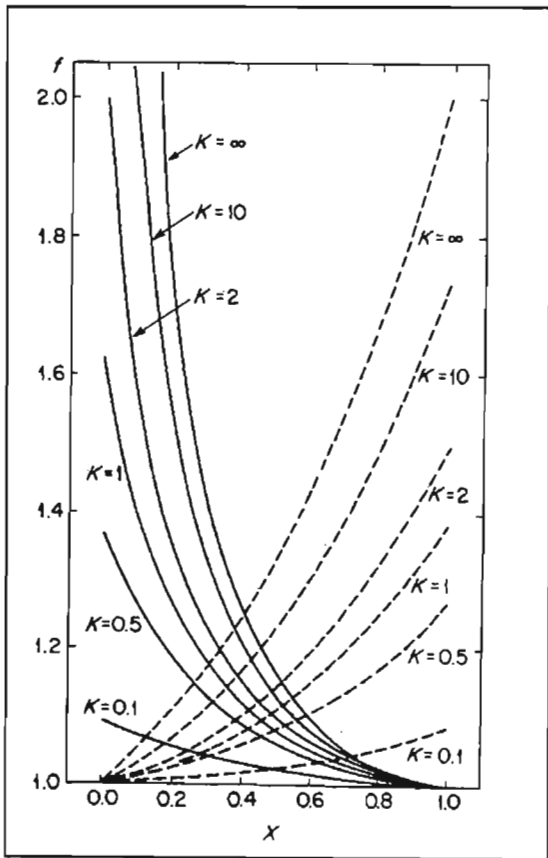
$$f_1 = x_A/x_A^* x_1 = [x_1 - \xi(2 - x_1)]/[x_1(1 - \xi^*)] > 1 \quad (6.31a)$$

$$f_2 = x_B/x_2 = 1 + \xi > 1 \quad (6.31b)$$

and since  $x_A \geq x_A^* x_1$  and  $x_B > x_2$ , both activity coefficients are always larger than unity and  $G^E > 0$  over the whole composition range. The value of  $\xi$  from (6.28) may be substituted in (6.31) to give  $f_1$  and  $f_2$  in terms of  $x_1$  and  $k_2$ . The limiting values of the activity coefficients at infinite dilution are:

$$\lim f_1 (x_1 \rightarrow 0) = 1/(1 - \xi^*) \quad (6.32a)$$

$$\lim f_2 (x_1 \rightarrow 1) = 1 + \xi^* \quad (6.32b)$$



**Figure 6.1** Activity coefficients of the nominal components in an ideal associated mixture of type  $A + A_2 + B$  (self dimerization), plotted against the nominal composition  $x_1$  and parameter  $K$ .

*Case (2)* The chemical equilibrium  $A + B \rightleftharpoons AB$  is symmetrical in the components, hence it is expected that all the excess functions will also be symmetrical. The equilibrium constant  $K_{AB}$  can be written in terms of the nominal components, ie.  $x_1$

$$K_{AB} = \zeta / [x_1 (1 - x_1) (1 + \zeta)^2 - \zeta] \quad (6.33)$$

where  $\zeta = x_{AB}$ , the fraction of adduct

$$\text{Now } \zeta = \frac{K_{AB} + 1}{2K_{AB}x_1(1-x_1)} - 1 - \left[ \left( \frac{K_{AB} + 1}{2K_{AB}x_1(1-x_1)} - 1 \right)^2 - 1 \right]^{\frac{1}{2}} \quad (6.34)$$

For the pure components,  $\zeta = 0$  and  $x_A^* = x_1^* = 1$ , and similarly  $x_B^* = x_2 = 1$ .

The molar Gibbs energy is given by

$$\begin{aligned} G_m &= x_1 (\mu_A^\circ + RT \ln x_A) + x_2 (\mu_B^\circ + RT \ln x_B) \\ &= x_1 (\mu_1^\circ + RT \ln x_1) + x_2 (\mu_2^\circ + RT \ln x_2) \\ &= x_1 (\mu_1^\circ + RT \ln x_1) + x_2 (\mu_2^\circ + RT \ln x_2) + RTx_1 \ln(x_A/x_1) \\ &\quad + RTx_2 \ln(x_B/x_2) \end{aligned} \quad (6.35)$$

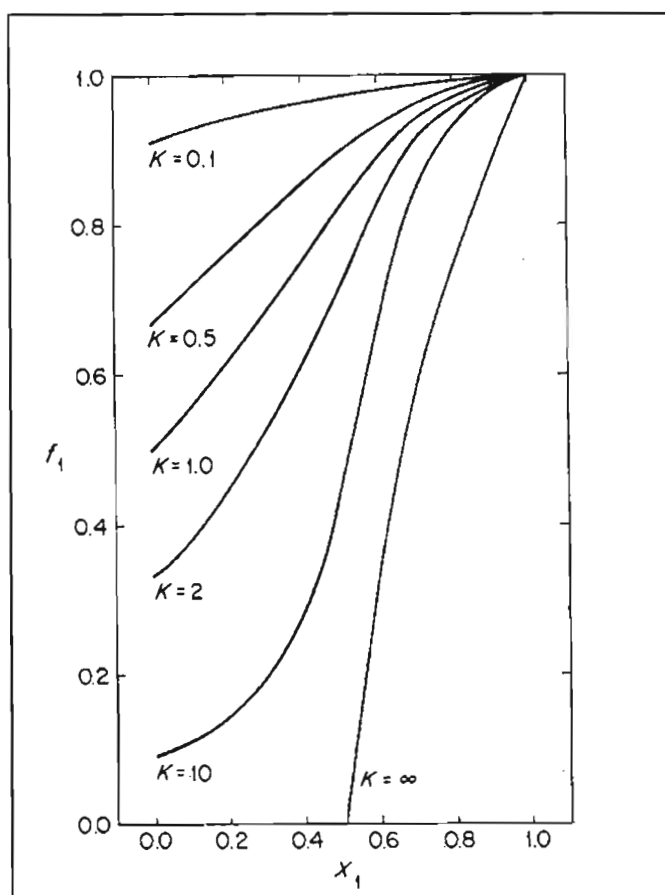
Since in this case  $\mu_1^\circ = \mu_A^\circ$  and  $\mu_2^\circ = \mu_B^\circ$

$$\begin{aligned} G^E/RT &= x_1 \ln(x_A/x_1) + x_2 \ln(x_B/x_2) \\ &= x_1 \ln[1 - (1-x_1)\zeta/x_1] + (1-x_1) \ln[1 - x_1 \zeta/(1-x_1)] \end{aligned} \quad (6.36)$$

Since  $x_A < x_1$  and  $x_B < x_2$ , the excess Gibbs energy is always negative, and so are the deviations from Raoult's law for the nominal components.

$$f_1 = x_A/x_1 = 1 - \zeta(1-x_1)/x_1 < 1 \quad (6.37a)$$

$$f_2 = x_B/x_2 = 1 - \zeta x_1 / (1-x_1) / x_1 < 1 \quad (6.37b)$$



**Figure 6.2** Activity coefficients of the nominal components in an ideal associated mixture of type A + AB + B (adduct formation), plotted against the nominal composition  $x_1$  with parameter  $K_{AB}$

### 6.3.2 Athermal associated mixtures

If the effects of the difference in size of the molecular species is recognised in addition to the effects of association, but the mixing process itself is assumed to proceed without a thermal effect beyond that of the chemical reactions, athermal associated mixtures result (Kehiaian and Treszczanowicz, 1966). The general associated species is  $A_m B_n$ , and the equilibrium condition  $\mu_{AmBn} = m\mu_A + n\mu_B$  holds, and further,  $H^M(A_m B_n) = 0$  and Flory's approximation is used for the molar entropy viz.

$S^M(A_m B_n) = -R \sum x_{AmBn} \ln \phi_{AmBn}$ , with the additional assumption that the standard volume change of the reaction,  $\Delta V_{mn}^\circ = V_{AmBn}^\circ - mV_A^\circ - nV_B^\circ = 0$  (this implies that  $V^E = 0$ ). From the latter relationship it follows that  $\phi_{AmBn}/x_{AmBn} = m(\phi_A/x_A) + n(\phi_B/x_B)$

The equilibrium constant in terms of volume fraction is

$$K_{mn(\varphi)} = \varphi_{AmBn} / \varphi_A^m \varphi_B^n = K_{mn} e^{m+n-1} \quad (6.38)$$

where  $K_{mn}$  is the thermodynamic constant which is independent of composition.

The activity coefficient of the actual general species is:

$$\begin{aligned} \ln f_{AmBn} &= \ln [m(\varphi_A/x_A) + n(\varphi_B/x_B)] + 1 \\ &\quad - [m(\varphi_A/x_A) + n(\varphi_B/x_B)] \end{aligned} \quad (6.39)$$

Expression (6.39) with the values (m,n)=(1,0) for the monomer *A* and (0,1) for the monomer *B*, may be used with (6.25) and the equilibrium condition for the chemical potentials, to give the activity coefficients of the nominal components as :

$$f_1 = \varphi_A (x_1 \varphi_A^*)^{-1} \exp [(\varphi_A^*/x_A^*) - (\varphi_A / x_A)] \quad (6.40)$$

$$f_2 = \varphi_B (x_2 \varphi_B^*)^{-1} \exp [(\varphi_B^*/x_B^*) - (\varphi_B / x_B)] \quad (6.41)$$

The activity coefficient for component 1 is obtained from 6.40 as:

$$\begin{aligned} \ln f_1 &= [\ln (\varphi_1/x_1) + 1 - (\varphi_1/x_1)] + \ln (\varphi_1/x_1) + \ln (\varphi_A^*/\varphi_1 \varphi_A^*) \\ &\quad - \frac{1}{2} (\varphi_{A1}^* - \varphi_{A2}) \end{aligned} \quad (6.42)$$

The first term in the square brackets is the contribution from the non-associated athermal interactions.

### 6.3.3 Regular associated mixtures

An approximation to the behaviour of actual systems, better than that of athermal associated mixtures, is that of the regular associated mixture which allows for finite enthalpies of mixing of the actual components of the associated mixture.

In the system  $A + A_2 + B$ , equation (6.27) for the equilibrium constant in ideal mixtures must be modified for the regular mixtures to give:

$$K_2 = \xi [x_1 - \xi(2-x_1)]^{-2} \exp[-\alpha(1-x_1)(2-x_1)(1+\xi)^2/RT] \quad (6.43)$$

and in the system  $A + AB + B$ , equation (6.33) must be correspondingly modified to

$$K_{AB} = \zeta [x_1 - (1-x_1)(1+\zeta)^2 - \zeta]^{-1} \exp[-\alpha \{1-x_1(1-x_1)(1+\zeta)^2/RT\}] \quad (6.44)$$

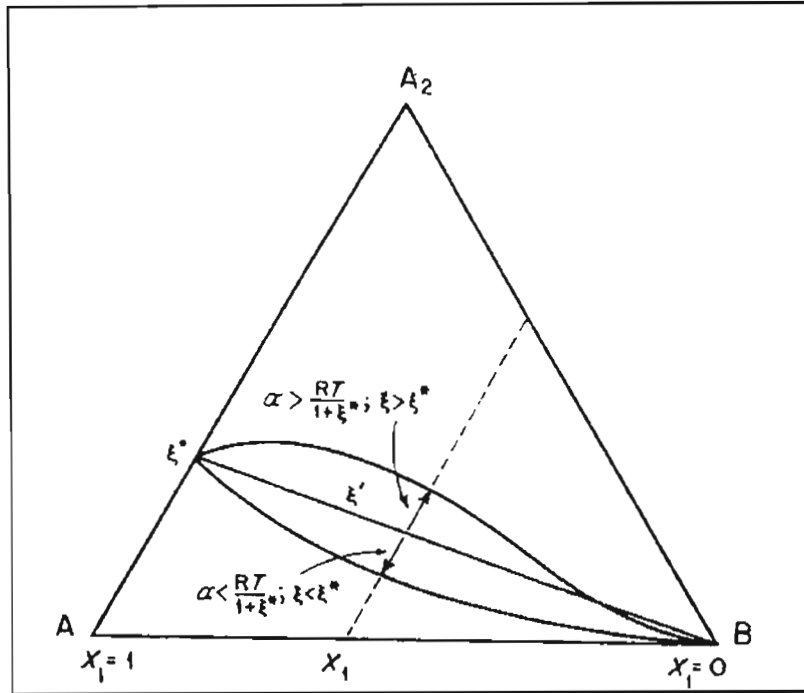
The exponential terms thus correct for the non-ideality of the interactions, namely for the non specific interaction of  $A$  and  $B$ . These non-specific interactions have interesting consequences. For instance, ideal mixtures, even if associated, cannot split into two immiscible phases (Prigogine and Defay, 1954). Suppose that an ideal mixture contains species  $A, B$  and  $A_m B_n$  in two phases ' and ". Since  $\mu_A' = \mu_1' = \mu_1'' = \mu_A''$ , and since in ideal solutions  $\mu_A' = \mu_A^{\circ'} + RT \ln x_A'$ ,  $\mu_A'' = \mu_A^{\circ''} + RT \ln x_A''$  and  $\mu_A^{\circ'} = \mu_A^{\circ''} = \mu_A^{\circ}$ , it follows that  $x_A' = x_A''$ . Similar considerations apply to component 2, and  $x_B' = x_B''$ . Similar considerations apply to component 2, and  $x_B' = x_B^{\circ}$  so that necessarily also  $x'_{AmBn} = x''_{AmBn}$  for all  $m$  and  $n$ , as  $x_{AmBn} = K_{mn} x_m^A x_n^B$  and  $K_{mn}$  is independent of the composition in ideal mixtures. But if the mole fractions of all the species are identical in the two phases ' and ", these are identical in all respects, and constitute but one homogeneous phase.

Another interesting consequence of the non-ideality is the possibility of an associating substance to show increasing association when diluted with another inert substance, contrary to the expectation from ideal mixtures, where dissociation always follows dilution.

Consider the system  $A + A_2 + B$ , Figure 6.3, where pure component 1 contains a mole fraction  $\xi^*$  of dimers. On dilution with the second component B, the mole fraction of dimers would become  $\xi' = \xi^* (1 - x_B) = \xi^* x_1 / (1 + (1 - x_1) \xi^*)$ , if the association equilibrium were "frozen". The real dimer mole fraction on  $x_1$  in such a manner that

$$\begin{aligned} \lim (\partial \xi / \partial x_1)_{x_1=0} &= 0 \\ \lim (\partial \xi / \partial x_1)_{x_1=1} &= \xi^* [2 - \alpha (1 - \xi^{*2}) / RT] \end{aligned} \quad (6.45)$$





**Figure 6.3** The dimer fraction  $\xi$  in a regular self associated mixture of type  $A + A_2 + B$  as a function of the nominal composition  $x_1$  and the energy parameter  $\alpha$ .

From Figure 6.3, it can be seen that for the pure component 1, the dimer fraction is  $\xi^*$ , and the line  $\xi'$  indicates this fraction if the equilibrium were frozen on dilution with component 2 or B. Depending on the value of  $\alpha$ , more dimers are formed,  $\xi > \xi^*$  or fewer are formed, in the real equilibrium mixture, at a given nominal composition  $x_1$ .

For the “frozen” dimers:

$$\begin{aligned} \lim (\partial \xi' / \partial x_1)_{x_1=0} &= \xi^* / (1 + \xi^*) \\ \lim (\partial \xi' / \partial x_1)_{x_1=1} &= \xi^* / (1 + \xi^*) \end{aligned} \quad (6.46)$$

In dilute solutions of component 1, therefore, the equilibrium lines lie below the frozen line, and the dimers must dissociate. In concentrated solutions, however, if  $\alpha > RT/(1 + \xi^*)$ , the “frozen” lines lie below the equilibrium line, so that more dimers must be formed by association, and  $\xi > \xi^*$  when some diluent B is added to a component A.

Treszczanowicz and Kehiaian (1966) in their work on regular associated mixtures, assumed that only the monomers A and B interact non-specifically, but not the monomers A with the

oligomers  $A_n$ , or with adducts  $A_m B_n$ , etc. This is rather restrictive (Marcus, 1977) and it is more reasonable to take  $\alpha$  as representing an average between the homomolecular and heteromolecular interactions (eg.  $\alpha_{A,A}$ ,  $\alpha_{B,B}$ ,  $\alpha_{A,B}$ ,  $\alpha_{A,AB}$ ,  $\alpha_{B,AB}$ ,  $\alpha_{AB,AB}$  in the ternary system  $A + AB + B$ ). Following Prigogine and Defay (1954), this average non specific interaction energy is defined so that it will contribute a term  $(\alpha x_1 x_2)$  to the excess Gibbs energy of the system, which may be written as

$$G^E = x_1 RT \ln (x_A/x_1 x_A^*) + x_2 RT \ln(x_B / x_2 x_B^*) + (\alpha x_1 x_2) \quad (6.47)$$

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## CHAPTER 7

### NON-ELECTROLYTE SOLUTION THEORY AND APPLICATION

#### 7.1 INTRODUCTION

A significant fraction of chemical process design is concerned with separation of fluid mixtures by diffusional operations. All design methods for such separations require quantitative estimates of fluid-phase equilibria, and liquid phase activity coefficients must be known. In those fortunate cases where phase equilibrium data are available, such estimates can usually be made with ease.

In many other cases, however, where the required experimental data are not available, it is difficult to make even rough estimates on a rational basis. Predictive models have therefore been developed towards alleviating this common problem in chemical process design. Three models will be discussed, namely NRTL (non-random, two liquid), UNIQUAC (universal quasi-chemical), and FBT (Flory-Benson-Treszczanowicz).

In the NRTL (Renon and Prausnitz, 1968) equation, consideration is given to the prediction of ternary vapour-liquid and ternary liquid-liquid equilibria based on binary data. UNIQUAC (Abrams and Prausnitz, 1975) is applicable to multicomponent mixtures of non-polar and polar liquids (including those that participate in hydrogen bonding) as encountered in typical chemical and petrochemical processes.

#### 7.2 THE NRTL (NON-RANDOM, TWO-LIQUID) EQUATION

##### 7.2.1 Introduction

Interpolation and extrapolation of thermodynamic data for liquid mixtures are common necessities to the phase-equilibrium chemist. The model of ideal solutions is useful for providing a first approximation and a reference, but deviations from ideality are frequently large. These deviations are expressed by excess functions which depend on the concentrations

of the components and on the temperature (Renon and Prausnitz, 1968).

As shown by Wohl (1946), excess functions have commonly been expressed by algebraic expansions of mole fractions with arbitrary, temperature dependent coefficients which are obtained by fitting experimental data. In these expansions, as many terms and parameters as necessary are introduced in order to represent the experimental data.

Later Wilson (1964) showed that the excess Gibbs energy could be conveniently expressed by an algebraic function of local composition and in his final equation Wilson used local volume fractions. Subsequently Orye and Prausnitz (1965) showed that Wilson's equation is useful for representing equilibrium data for a wide variety of liquid mixtures.

### 7.2.2 The Wilson and Heil Equations

To take into account non-randomness in liquid mixtures, Wilson (1964) suggested a relation between local mole fraction  $x_{11}$  of molecules 1 and local mole fraction  $x_{21}$  of molecules 2, which are in the immediate neighbourhood of molecule 1:

$$\frac{x_{21}}{x_{11}} = \frac{x_2 \exp(-g_{21}/RT)}{x_1 \exp(-g_{11}/RT)} \quad (7.1)$$

where  $g_{21}$  and  $g_{11}$  are, respectively energies of interaction between a 1-2 and 1-1 pair of molecules ( $g_{12} = g_{21}$ ). The overall mole fractions in the mixture are  $x_1$  and  $x_2$ . Wilson obtained an expression for the excess Gibbs energy by analogy with the Flory-Huggins expression for athermal mixtures, where he replaces overall volume fractions by local volume fractions:

$$G^E/RT = x_1 \ln(\xi_{11}/x_1) + x_2 \ln(\xi_{22}/x_2) \quad (7.2)$$

where the local volume fractions  $\xi_{11}$  and  $\xi_{22}$  are derived from equation (7.1):

$$\xi_{11} = \frac{x_1}{x_1 + x_2(v_2/v_1) \exp(-(g_{21} - g_{11})/RT)} \quad (7.3)$$

$$\xi_{22} = \frac{x_2}{x_2 + x_1(v_1/v_2) \exp(-(g_{12} - g_{22})/RT)} \quad (7.4)$$

where the  $v$ 's are the molar volumes.

Heil (1966) pursued the original analogy further and proposed an expression for the excess Gibbs energy similar to the Flory-Huggins equation for athermal mixtures. The Heil equation was derived for polymer solutions of small molecules:

$$\begin{aligned} G^E/RT = & x_1 \ln(\xi_{11}/x_1) + x_2 \ln(\xi_{22}/x_2) \\ & + \frac{g_{21} - g_{11}}{RT} x_1 \xi_{21} + \frac{g_{12} - g_{22}}{RT} x_2 \xi_{12} \end{aligned} \quad (7.5)$$

where  $\xi_{21} = 1 - \xi_{11}$  and  $\xi_{12} = 1 - \xi_{22}$

Both equations (7.2) and (7.5) are useful semi-empirical relations for thermodynamic excess functions : both equations contain only two adjustable parameters per binary,  $(g_{21} - g_{11})$  and  $(g_{12} - g_{22})$ , and both are readily generalized into solutions containing any number of components.

### 7.2.3 The Non-Random, Two Liquid Equation

To define the local composition, an assumption similar to that of the quasichemical theory of Guggenheim (1952) is made. To obtain an expression for the excess Gibbs energy, Scott's two liquid theory of binary mixtures (1956) can be used. To take into account non randomness of mixing, it is assumed that the relation between the local fraction  $x_{21}$  and  $x_{11}$  is given by a modification of equation (7.1).

$$\frac{x_{21}}{x_{11}} = \frac{x_2 \exp(-\alpha_{12}g_{21}/RT)}{x_1 \exp(-\alpha_{12}g_{11}/RT)} \quad (7.6)$$

where  $\alpha_{12}$  is a constant characteristic of the non-randomness of the mixture. Interchanging subscripts 1 and 2, also yields:

$$\frac{x_{12}}{x_{22}} = \frac{x_1 \exp(-\alpha_{12}g_{12}/RT)}{x_2 \exp(-\alpha_{12}g_{22}/RT)} \quad (7.7)$$

The local mole fractions are related by:

$$x_{21} + x_{11} = 1 \quad (7.8)$$

$$x_{12} + x_{22} = 1 \quad (7.9)$$

To show the similarity of our assumption with that of the quasichemical theory, the product of equations (7.6) and (7.7) (noting that  $g_{12} = g_{21}$ ) is taken and the resultant relationship is :

$$\frac{x_{21}}{x_{11}} = \frac{x_{12}}{x_{22}} = \exp[-\alpha_{12}(2g_{12} - g_{11} - g_{22})/RT] \quad (7.10)$$

Equations (7.8) and (7.9) substituted into equation (7.7) yields

$$x_{21}x_{12} = (1 - x_{21})(1 - x_{12}) \exp[-\alpha_{12}(2g_{12} - (2g_{12} - g_{11} - g_{22}))/RT] \quad (7.11)$$

On the other hand, the assumption of non-randomness in the quasichemical theory of Guggenheim (1952) can be written as

$$x_{21}x_{12} = (1 - x_{21})(1 - x_{12}) \exp[-\frac{1}{z}(2W_{12} - W_{11} - W_{22})/RT] \quad (7.12)$$

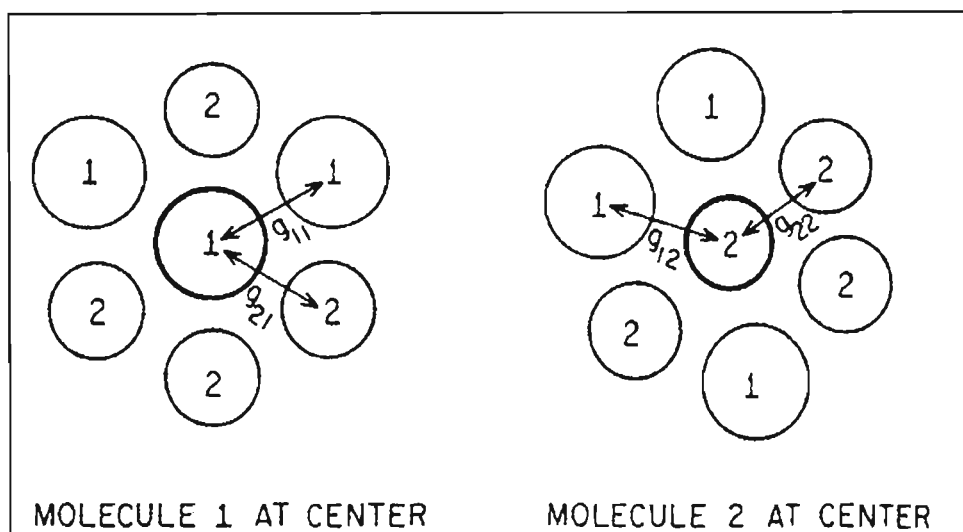
where  $z$  is the co-ordination number of the lattice and  $W_{12}$ ,  $W_{11}$ ,  $W_{22}$  are, respectively, the molar potential energies of interaction 1-2, 1-1, and 2-2 pairs. Comparison of equations (7.11) and (7.12) shows the similarity between the two assumptions;  $\alpha_{12}$  is the substitute for  $(1/z)$ . However, the energies  $g_{ij}$  in equation (7.11) are Gibbs energies, whereas the energies  $W_{ij}$  in equation (7.12) are potential energies.

From equations (7.6) and (7.8), we obtain for the local mole fractions

$$x_{21} = \frac{x_2 \exp[-\alpha_{12}(g_{21} - g_{11})/RT]}{x_1 + x_2 \exp[-\alpha_{12}(g_{21} - g_{11})/RT]} \quad (7.13)$$

and similarly from equations (7.7) and (7.9)

$$x_{12} = \frac{x_1 \exp[-\alpha_{12}(g_{12} - g_{22})/RT]}{x_2 + x_1 \exp[-\alpha_{12}(g_{12} - g_{22})/RT]} \quad (7.14)$$



**Figure 7.1** Two types of cells according to Scott's two liquid theory of binary mixtures

Equations (7.13) and (7.14) are now introduced into the two-liquid theory of Scott which assumes that there are two kinds of cells in a binary mixture : one for molecules 1 and one for molecules 2, as shown in Figure 7.1. For cells containing molecules 1 at their centres, the residual Gibbs energy (that is, compared with the ideal gas at the same temperature, pressure and composition) is the sum of all the residual Gibbs energies for two-body interactions experienced by the centre molecule 1. The residual Gibbs energy for a cell containing molecule 1 at its centre is  $g^{(1)}$  and it is given by

$$g^{(1)} = x_{11}g_{11} + x_{21}g_{21} \quad (7.15)$$

If one considers pure liquid 1,  $x_{11} = 1$  and  $x_{21} = 0$ . In this case the residual Gibbs energy for a cell containing a molecule 1 at its centre,

$$g^{(1)}_{\text{pure}}, \text{ is } g^{(1)}_{\text{pure}} = g_{11} \quad (7.16)$$

Similarly, for a cell containing a molecule 2 at its centre

$$g^{(2)} = x_{12}g_{12} + x_{22}g_{22} \quad (7.17)$$

and

$$g^{(2)}_{\text{pure}} = g_{22} \quad (7.18)$$

The molar excess Gibbs energy for a binary solution is the sum of two changes in residual Gibbs energy: firstly, that of transferring  $x_1$  molecules from a cell of the pure liquid 1 into a

cell 1 of the solution  $(g^{(1)} - g_{\text{pure}}^{(1)})x_1$ , and secondly, that of transferring  $x_2$  molecules from a cell of the pure liquid 2 into a cell 2 of the solution,

$$(g^{(2)} - g_{\text{pure}}^{(2)})x_2.$$

$$\text{Therefore, } G^E = x_1(g^{(1)} - g_{\text{pure}}^{(1)}) + x_2(g^{(2)} - g_{\text{pure}}^{(2)}) \quad (7.19)$$

Substituting equations (7.8), (7.9), (7.15), (7.16), (7.17) and (7.18) into equation (7.19), yields:

$$G^E = x_1x_{21}(g_{21} - g_{11}) + x_2x_{12}(g_{12} - g_{22}) \quad (7.20)$$

where  $x_{21}$  and  $x_{12}$  are given by equations (7.13) and (7.14).

Equation (7.20), coupled with equations (7.13) and (7.14), is called the NRTL (non-random, two liquid) equation.

The activity coefficients for of the NRTL equation are found by differentiation of equation (7.20). Proceeding:

$$\ln \gamma_1 = x_2^2 \left( \tau_{21} \frac{\exp(-2\alpha_{12}\tau_{21})}{[x_1 + x_2 \exp(-\alpha_{12}\tau_{21})]^2} + \tau_{12} \frac{\exp(-\alpha_{12}\tau_{12})}{[x_2 + x_1 \exp(-\alpha_{12}\tau_{12})]^2} \right) \quad (7.21)$$

$$\ln \gamma_2 = x_1^2 \left( \tau_{12} \frac{\exp(-2\alpha_{12}\tau_{12})}{[x_2 + x_1 \exp(-\alpha_{12}\tau_{12})]^2} + \tau_{21} \frac{\exp(-\alpha_{12}\tau_{21})}{[x_1 + x_2 \exp(-\alpha_{12}\tau_{21})]^2} \right) \quad (7.22)$$

$$\text{where } \tau_{12} = (g_{12} - g_{22})/RT \quad (7.23)$$

$$\tau_{21} = (g_{21} - g_{11})/RT \quad (7.24)$$

with  $g_{12} = g_{21}$

For strongly non-ideal mixtures and especially for partially immiscible systems, the NRTL often provides a good representation of experimental data provided that care is exercised in data reduction to obtain the adjustable parameters.

For a solution of m-components, the NRTL equation is:



$$\frac{G^E}{RT} = \sum_{i=1}^m x_i \frac{\sum_{j=1}^m \tau_{ji} G_{ji} x_j}{\sum_{\ell=1}^m G_{\ell i} x_{\ell}} \quad (7.25)$$

$$\tau_{ji} = \frac{g_{ji} - g_{ii}}{RT} \quad (7.26)$$

$$G_{ji} = \exp(-x_{ji} \tau_{ji}) \quad (a_{ji} = a_{ij}) \quad (7.27)$$

The activity coefficient for a component i is given by

$$\ln \gamma_i = \frac{\sum_{j=1}^m \tau_{ji} G_{ji} x_j}{\sum_{j=1}^m G_{ji} x_j} + \sum_{j=1}^m \frac{x_j G_{ij}}{\sum_{\ell=1}^m G_{\ell j} x_{\ell}} \left( \tau_{ij} - \frac{\sum_{r=\ell}^m x_r \tau_{rj} G_{rj}}{\sum_{\ell=1}^m G_{ij} x_{\ell}} \right) \quad (7.28)$$

Equations (7.25) - (7.28) contain only parameters obtained from binary data.

#### 7.2.4 Symmetric Systems

Those binary systems for which the excess Gibbs energy is not changed, if one changes  $x$  to  $(1-x)$ , are called symmetric. It is also assumed that molar volumes  $v_2 = v_1$ . The condition for symmetry in the local composition equations is the equality of the parameters  $\tau_{12}$  and  $\tau_{21}$ , and it is found that

$$\tau_{12} = \tau_{21} < \tau \quad (7.29)$$

The van Laar equation can be written in the form

$$G^E/RT = \frac{2Ax_1x_2}{Ax_1 + Bx_2} \quad (7.30)$$

where A and B are temperature dependent parameters. For a symmetric system  $A = B$ ,

equation (7.30) is then identical with the two suffix Margules and Redlich - Kister equations.

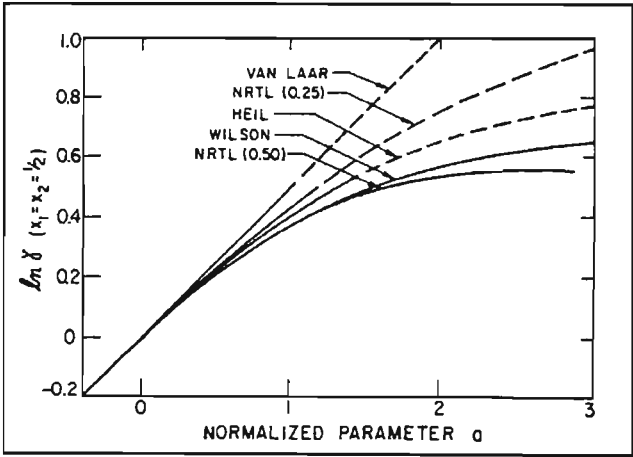
For the NRTL equation one needs to specify the constant  $\alpha_{12}$ . In comparison if one considers two values of  $\alpha_{12}$ , namely 0.50 and 0.25, the two corresponding equations are designated, respectively, by NRTL (0.50) and NRTL (0.25).

The parameter  $a$  is defined as follows:-

- $a$  = A for the van Laar equation
- $a$  =  $2\tau$  for Heils equation
- $a$  =  $\tau$  for Wilsons equation and the NRTL equation

All these equations become asymptotically equivalent for small values of the parameter  $a$  . In each case, the first term in the power series expansion of  $G^E/RT$  in terms of  $a$  is  $2ax_1x_2$ .

The activity coefficient at infinite dilution is a monotonic, increasing function of  $a$  for all the equations considered above; therefore the parameter  $a$  is also a measure of the degree of nonideality of the mixture. Figure 7.2 shows the variation of  $a$  with the activity coefficient of an equimolar mixture, indicating also the minimum value of  $a$  which is required for phase splitting.



**Figure 7.2** Activity coefficient for symmetric mixture as a function of normalized parameter  $a$ .

7.2.5 Liquid-Liquid Equilibria

While the Wilson equation is not applicable to liquid-liquid systems, the Heil and the NRTL ( $0.2 < \alpha < 0.47$ ) equations can be used to represent thermodynamic properties of binary

mixtures with two liquid phases. It is possible to calculate the parameters from experimental compositions of the two equilibrated liquid phases.

With the local composition equations, prediction of the properties of multicomponent systems is possible without any additional ternary or higher order parameters. For the NRTL equation, the excess Gibbs energy is derived from the two-liquid theory by taking into account only two-body interactions, and there is no need to introduce higher order interactions in the treatment of multicomponent systems when they were neglected for binary mixtures.

The NRTL equation is a good and general equation for the prediction of ternary vapour liquid as well ternary liquid-liquid equilibria using only data for binary mixtures, but no ternary constant, if the optimum value of  $x_{12}$  for each binary is chosen.

### 7.3 THE UNIQUAC EQUATION

A critical examination of the derivation of the NRTL shows that this equation is more suitable to excess enthalpy  $H^E$  than to Gibbs energy  $G^E$  (Renon and Prausnitz, 1969). Also, since experimental data for typical binary mixtures are usually not sufficiently available or precise to yield three meaningful binary parameters, attempts were made to derive a two parameter equation for  $G^E$  which retains at least some of the advantages of the Wilson equation without, however being restricted to completely miscible mixtures. Abrams et al.(1975) derived an equation which, in a sense, extends the quasi - chemical theory of Guggenheim for non-random mixtures to solutions containing molecules of different size. This extension was therefore called the universal quasi-chemical theory or, in short UNIQUAC.

In this work, the theory of Guggenheim is extended to mixtures containing molecules of different size and shape by utilizing the local - composition concept of Wilson (1964).

#### 7.3.1 Partition Function for a Binary Liquid Mixture

Following Guggenheim (1952), it was postulated by Abrams and Prausnitz that a liquid can be represented by a three-dimensional lattice of equi-spaced lattice sites; the volume in the immediate vicinity of a site is called a cell. Each molecule in the liquid is divided into attached segments such that each segment occupies one cell. The total number of cells is

equal to the total number of segments. (A possible refinement where some cells are unoccupied - holes, is not used here). The configurational partition function  $Z$  is given by:

$$Z = Z_{\text{lattice}} \cdot Z_{\text{cell}} \quad (7.31)$$

where  $Z_{\text{lattice}}$  refers to the situation where the centre of every segment is coincident with a lattice site and where  $Z_{\text{cell}}$  provides those contributions to  $Z$  which are caused by motions of a segment about this central position. In mixtures of nonelectrolyte liquids removed from critical conditions, it is assumed that for each component  $Z_{\text{cell}}$  is independent of composition. For a binary mixture containing  $N_1$  molecules of component 1 and  $N_2$  molecules of component 2, the Helmholtz energy of mixing is then given by:

$$\Delta A = -kT \ln \frac{Z_{\text{lattice}}(N_1 N_2)}{Z_{\text{lattice}}(N_1, 0) Z_{\text{lattice}}(0, N_2)} \quad (7.32)$$

where  $k$  = Boltzmann's constant.

The molar excess Gibbs energy  $g^E$  is given by:

$$G^E \approx a^E = \frac{\Delta A}{n_1 + n_2} - RT(x_1 \ln x_1 + x_2 \ln x_2) \quad (7.33)$$

where  $R$  = universal gas constant

$x$  = mole fraction

$n$  = number of moles

Following Guggenheim, the lattice partition function is given by

$$Z_{\text{lattice}} = \sum_{\text{all } \Theta} w(\Theta) \exp[-U_o(\Theta)/kT] \quad (7.34)$$

where  $w$  = is the combinatorial factor (number of ways that the molecule can be arranged in space).

$U_o$  = potential energy of the lattice - i.e. the energy required to remove all molecules from the lattice;  $U_o$  is closely related to the energy of isothermal vapourization from the liquid to the ideal - gas state.

Both  $w$  and  $U_o$  depend on the molecular configuration of the mixture, designated by the variable  $\Theta$ . The summation in equation (7.34) is over all possible  $\Theta$ , that is over all values

of  $\Theta$  which are permitted within the constraints of the overall stoichiometry.

Since Guggenheim was concerned with mixtures of spherical molecules having the same size, he used for  $\Theta$  the quantity  $N_{12}$  which is the number of nearest neighbours, where one neighbour is a molecule of component 1 and the other a molecule of component 2.  $N_{12}$  depends not only on  $N_1$  and  $N_2$  but also on the microscopic structure of the solution; if there is a tendency to segregate where like molecules want to be near each other,  $N_{12}$  is relatively small. On the other hand, if there is a tendency for the molecules to mix randomly without regard to identity,  $N_{12}$  is relatively large.

For mixtures of polysegmented molecules differing in size and shape,  $N_{12}$  is not an appropriate variable for describing the micro-composition of the lattice. For such mixtures the use of the local area fraction is proposed (Abrams and Prausnitz, 1975).

### 7.3.2 Local Area Fraction

A molecule of component 1 is represented by a set of bonded segments; the number of segments per molecule is  $r_1$ . While all segments, by definition, have the same size, they differ in their external contact area. For a molecule of component 1, the number of external nearest neighbours is given by  $zq_1$  where  $z$  is the co-ordination number of the lattice and  $q_1$  is a parameter proportional to the molecules external surface area. Similarly, for a molecule of component 2, we have structural parameters  $r_2$  and  $q_2$ .

Attention will now be focussed on the composition of a region in the immediate vicinity of a molecule 1. The local area fraction  $\Theta_{21}$  is the fraction of external sites around molecule 1 which are occupied by segments of molecule 2. Similarly, local area fraction  $\Theta_{11}$  is the fraction of external sites around molecule 1 which are occupied by segments of another molecule 1. When attention is focussed on the composition of a region in the immediate vicinity of a molecule 2, similar definitions hold for  $\Theta_{12}$  and  $\Theta_{22}$ . For a binary mixture, therefore there are four local fractions which describe the microstructure of the lattice; however, only two of these are independent because

$$\Theta_{11} + \Theta_{21} = 1 \quad (7.35)$$

$$\Theta_{12} + \Theta_{22} = 1 \quad (7.36)$$

The lattice energy  $U_o$  is the sum of all interaction energies between pairs of non-bonded segments.

$$-U_o = \left( \frac{z}{2} \right) q_1 N_1 (\Theta_{11} U_{11} + \Theta_{21} U_{21}) + \left( \frac{z}{2} \right) q_2 N_2 (\Theta_{22} U_{22} + \Theta_{12} U_{12}) \quad (7.37)$$

where  $U_{ij}$  characterizes the energy of interaction between sites  $i$  and  $j$ . For convenience let

$$u_{ij} = \left( \frac{z}{2} \right) U_{ij}. \quad \text{Equation (7.37) then becomes}$$

$$-U_o = q_1 N_1 (\Theta_{11} u_{11} + \Theta_{21} u_{21}) + q_2 N_2 (\Theta_{22} u_{22} + \Theta_{12} u_{12}) \quad (7.38)$$

The negative sign on the left hand side of equations (7.37) and (7.38) follows from the convention that the potential energy of the ideal - gas state (infinite separation between molecules) is taken as zero. In a given molecule, all segments are not necessarily chemically identical. Energy parameters  $u_{ij}$ , therefore represent averages since subscripts  $i$  and  $j$  refer to components, that is molecules of type  $i$  and  $j$ .

### 7.3.3 Combinatorial Factors

For a given set of local area fractions, one must calculate the number of possible configurations or microstructures for a mixture of  $N_1$  molecules of component 1 and  $N_2$  molecules of component 2.

There is no exact method available for solving this combinatorial problem, and an approximation analogous to that used by Guggenheim is attempted.

Assume that

$$w = w_1 w_2 h(N_1 N_2) \quad (7.39)$$

where  $w_i$  refers to the number of configurations associated with a site occupied by a segment of molecule  $i$  ( $i = 1, 2$ ). The function  $h$  depends on  $N_1$  and  $N_2$ ; it is introduced as a normalization factor to assure that the combinatorial factor  $w$  satisfies a physically reasonable boundary condition. For the boundary condition, the combinatorial factor of Staverman (1950) for mixtures of molecules with arbitrary size and shape but no attractive forces, is

chosen - Staverman's formula is very similar to that of Flory - Huggins.

The number of distinguishable configurations  $w_1$  and  $w_2$  are approximated by:

$$w_1 = \frac{(q_1 N_1 \theta_{11} + q_2 N_2 \theta_{12})!}{(q_1 N_1 \theta_{11})! (q_1 N_1 \theta_{21})!} \quad (7.40)$$

$$w_2 = \frac{(q_2 N_2 \theta_{22} + q_1 N_1 \theta_{21})!}{(q_2 N_2 \theta_{22})! (q_2 N_2 \theta_{12})!} \quad (7.41)$$

Co-ordination number  $z$

does not appear in equations (7.40) and (7.41) because it is not possible to permute independently all of the nearest neighbour about a lattice site.

To find  $h$ , we consider the athermal case (all  $u_{ij} = 0$  and  $U_o = 0$ ). The maximum term in the summation is found by separate differentiations with respect to  $\Theta_{11}$  and  $\Theta_{12}$  and by setting the results equal to zero. Omitting mathematical details, it is found that the average local area fractions for an athermal mixture are given by

$$\theta_{11}^{(0)} = \frac{q_1 N_1}{q_1 N_1 + q_2 N_2} \quad (7.42)$$

$$\theta_{22}^{(0)} = \frac{q_2 N_2}{q_1 N_1 + q_2 N_2} \quad (7.43)$$

The superscript (0) denotes zeroth approximation (that is, athermal mixture). Mass-balance

constraints give  $\theta_{12}^{(0)} = \theta_{11}^{(0)} = \theta_1 = \frac{q_1 N_1}{q_1 N_1 + q_2 N_2}$  (7.44)

$$\theta_{21}^{(0)} = \theta_{22}^{(0)} = \theta_2 = \frac{q_2 N_2}{q_1 N_1 + q_2 N_2} \quad (7.45)$$

In the zeroth approximation, therefore, the average local area fractions are the same as the average area fractions denoted by  $\Theta_1$  and  $\Theta_2$ .

The normalization factor  $h$  can now be found by substituting equations (7.40) to (7.43) into equation (7.39) yielding:

$$h(N_1, N_2) = \frac{w^{(0)}(q_1 N_1 \theta_{11}^{(0)})! (q_1 N_1 \theta_{21}^{(0)})! (q_2 N_2 \theta_{22}^{(0)})! (q_2 N_2 \theta_{12}^{(0)})!}{(q_1 N_1 \theta_{11}^{(0)} + q_2 N_2 \theta_{12}^{(0)})! (q_2 N_2 \theta_{22}^{(0)} + q_1 N_1 \theta_{21}^{(0)})!} \quad (7.46)$$

where  $w^{(0)}$  is the combinatorial factor given by Staverman (1950).

Having found  $h$  as outlined above, one now proceeds to find the next approximation for the average local fractions for the nonathermal case, that is where  $\mu_{ij} \neq 0$ .

#### 7.3.4 Average local area fractions in nonathermal mixtures

The summation in equation (7.34) is replaced by its maximum term. Equations (7.39), (7.40) and (7.41) are used again but in this approximation  $U_o$  (equation 7.37) is not set equal to zero. Equation (7.46) is retained. The resulting expression for  $Z_{\text{lattice}}$  is separately differentiated with respect to  $\Theta_{11}$  and  $\Theta_{22}$  and the results are set equal to zero. Again using the constraining equations (7.35) and (7.36), but omitting mathematical details, it is found that the average local area fractions are given by:

$$\theta_{11}^{(1)} = \frac{\theta_1}{\theta_1 + \theta_2 \exp \frac{-(u_{21} - u_{11})}{RT}} \quad (7.47)$$

$$\text{and} \quad \theta_{22}^{(1)} = \frac{\theta_2}{\theta_2 + \theta_1 \exp \frac{-(u_{12} - u_{22})}{RT}} \quad (7.48)$$

where  $u_{ij}$  is expressed in units of Joules per mole and where superscript (1) denotes first



approximation and  $\Theta_1$  and  $\Theta_2$  are average area fractions defined by (7.44) and (7.45). In mixtures that are not athermal, therefore, the average local area fractions are not the same as the average area fractions.

Substituting equations (7.32), (7.34), (7.38), (7.39) to (7.41), and (7.46) to (7.48) into equations (7.33) we obtain the desired result:

$$G^E = G^E (\text{combinatorial}) + G^E (\text{residual}) \quad (7.49)$$

where

$$\frac{G^E (\text{combinatorial})}{RT} = x_1 \ln \frac{\Phi_1}{x_1} + x_2 \ln \frac{\Phi_2}{x_2} + z/2 \left( q_1 x_1 \ln \frac{\theta_1}{\Phi_1} + q_2 x_2 \ln \frac{\theta_2}{\Phi_2} \right) \quad (7.50)$$

$$\text{and } \frac{G^E (\text{residual})}{RT} = -qx [\ln \theta_1 + \theta_2 \tau_{21}] - q_2 x_2 \ln [\theta_2 + \theta_1 \tau_{12}] \quad (7.51)$$

$$\text{where } \tau_{21} = \exp \left( - \left[ \frac{u_{21} - u_{11}}{RT} \right] \right)$$

$$\tau_{12} = \exp \left( - \left[ \frac{u_{12} - u_{22}}{RT} \right] \right) \quad (7.52)$$

In equation (7.50),  $\Phi$  is the average segment fraction:

$$\Phi_1 = \frac{x_1 r_1}{x_1 r_1 + x_2 r_2} \text{ and } \Phi_2 = \frac{x_2 r_2}{x_1 r_1 + x_2 r_2} \quad (7.53)$$

Equations (7.49) to (7.51) contain pure-component structural parameters  $r_1, r_2, q_1$  and  $q_2$ ; these are evaluated from bond angles and bond distances as discussed below.

It is also noted that the expression for  $G^E$  (combinatorial) contains two composition variables:

the average area fraction  $\Theta$  and the average segment fraction  $\Phi$ . However, the expression  $G^E$  (residual) contains only one composition variable : the average area fraction  $\Theta$ . There are no adjustable binary parameters in equation (7.50), but there are two adjustable binary parameters in (7.51) :  $(u_{21} - u_{11})$  and  $(u_{12} - u_{22})$ . From the derivation of equations (7.49) to (7.51) it follows that  $u_{21} = u_{12}$ .

### 7.3.5 Evaluation of pure-component structural parameters $r$ and $q$

The structural parameters  $r$  and  $q$  are, respectively, the van der Waals volume and area of the molecule relative to those of a standard segment.

$$r_i = V_{w_i}/V_{w_s} \quad (7.54)$$

$$q_i = Aw_i/Aw_s \quad (7.55)$$

where  $V_{w_i}$  and  $Aw_i$  are the van der Waals volumes and areas of the molecule given by Bondi (1968), and where  $V_{w_s}$  and  $Aw_s$  are the van der Waals volume and area of a standard segment. The choice of a standard segment is arbitrary, and here it is defined as a sphere such that for a linear polymethylene molecule of infinite length the identity :

$$(z/2) (r-q) = r - 1 \quad (7.56)$$

is satisfied. The co-ordination number  $z$  is set equal to 10. The volume of the standard sphere in terms of its radius  $Rw_s$  is given by

$$V_{w_s} = \frac{4}{3} \pi Rw_s^3 \quad (7.57)$$

and the area by:

$$Aw_s = 4\pi Rw_s^2 \quad (7.58)$$

The van der Waals volume and area of an  $n$ -mer of polymethylene are  $n$  times the volume and area of a methylene group as given by Bondi (1968); that is

$$V_{w_i} = n(10.23) \text{ cm}^3 \cdot \text{mol}^{-1} \quad (7.59)$$

$$Aw_i = n(1.35) \times 10^9 \text{ cm}^2 \cdot \text{mol}^{-1} \quad (7.60)$$

Substitution of equations (7.54), (7.55) and (7.57) to (7.60) into (7.56) as  $n$  tends to infinity yields an equation which fixes  $Rw_s = 10.95 \times 10^{15} \text{ cm} \cdot \text{mol}^{-1}$ . Substitution into equations (7.57) and (7.58) yields a standard segment volume  $15.17 \text{ cm}^3 \cdot \text{mol}^{-1}$  and a standard segment area of  $2.5 \times 10^9 \text{ cm}^2 \cdot \text{mol}^{-1}$ . Equations (7.54) and (7.55) then become

$$r_i = V w_i / 15.17 \quad (7.54a)$$

$$q_i = A w_i / 2.5 \times 10^9 \quad (7.55a)$$

### 7.3.6 Application to binary and multicomponent systems

Equations (7.49) to (7.51) give the excess Gibbs energy for a binary mixture in terms of two adjustable binary parameters and two pure-component structural parameters per component,  $r$  and  $q$ .

Activity coefficients are readily found by differentiation as indicated by the equation:

$$RT \ln \gamma_i = \left( \frac{\partial n_T G^E}{\partial n_i} \right)_{T, P, n_j (j \neq i)} \quad (7.61)$$

For a binary mixture, activity coefficient  $\gamma_i$  is given by

$$\begin{aligned} \ln \gamma_1 = \ln \Phi_1 / x_1 + (z/2) q_1 \ln \frac{\theta_1}{\Phi_1} + \Phi_2 \left( \ell_1 - \frac{r_1}{r_2} \ell_2 \right) \\ - q_1 \ln(\Theta_1 + \Theta_2 \tau_{21}) + \Theta_2 q_1 \left( \frac{\tau_{21}}{\theta_1 + \theta_2 \tau_{21}} - \frac{\tau_{12}}{\theta_2 + \theta_1 \tau_{12}} \right) \end{aligned} \quad (7.62)$$

where  $\ell_1 = (z/2) (r_1 - q_1) - (r_1 - 1)$

$$\ell_2 = (z/2) (r_2 - q_2) - (r_2 - 1) \quad (7.62a)$$

For component 2,  $\gamma_2$  can be found by interchanging subscripts 1 and 2.

The derivation of equation (7.49) is readily extended to mixtures containing three or more components without additional assumptions. For the multicomponent case, equations (7.50) and (7.51) become:

$$\frac{G^E (\text{combinatorial})}{RT} = \sum x_i \ln \frac{\Phi_i}{x_i} + \frac{z}{2} \sum_i q_i x_i \ln \frac{\theta_i}{\Phi_i} \quad (7.50a)$$

$$\frac{G^E(\text{residual})}{RT} = -\sum_i q_i x_i \ln \left( \sum_j \theta_j \tau_{ji} \right) \quad (7.51a)$$

$$\text{where } \tau_{ji} = \exp \left[ \left( \frac{u_{ji} - \mu_{ii}}{RT} \right) \right] \quad (7.52a)$$

and the activity coefficient for component  $i$  becomes

$$\ln \gamma_i = \ln \frac{\Phi_i}{x_i} + \left( \frac{z}{2} \right) q_i \ln \left( \frac{\theta_i}{\Phi_i} \right) + \ell_i - \frac{\Phi_i}{x_i} \sum_j x_j \ell_j$$

$$- q_i \ln \left( \sum_j \theta_j \tau_{ji} \right) + q_i - q_i \sum_j \frac{\theta_j \tau_{ij}}{\sum_k \theta_k \tau_{kj}} \quad (7.62b)$$

$$\text{where } \ell_j = (z/2) (r_j - q_j) - (r_j - 1) \quad (7.63a)$$

and where the average area fraction  $\Theta$  and the average segment fraction  $\Phi$  are defined by

$$\theta_i = \frac{q_i N_i}{\sum_j q_j N_j} = \frac{q_i x_i}{\sum_j q_j x_j} \quad (7.64)$$

$$\text{and } \Phi_i = \frac{r_i N_i}{\sum_j r_j N_j} = \frac{r_i x_i}{\sum_j r_j x_j} \quad (7.65)$$

Since the derivation of equation (7.62) is based on a generalization or extension of Guggenheims quasi-chemical model, equation (7.62) is referred to by the name UNIQUAC (universal quasi-chemical).

Thus in the UNIQUAC model there are two contributions. The combinatorial term which is evaluated using group contributions to compute the size parameters, and the residual term which has two adjustable parameters for each binary system that is to be fit to experimental data.

## 7.4 THE FLORY-BENSON-TRESZCZANOWICZ (FBT) MODEL

### 7.4.1 Introduction

Many attempts have been made to describe the thermodynamic properties of associated mixtures using lattice models. Those based on a chemical association reaction can be classified generally according to the thermodynamic type of the mixture (Kehiaian and Treszczanowicz, 1969); ideal, regular, athermal (Kehiaian and Treszczanowicz, 1968 ; Treszczanowicz, 1973 a, b) and non-thermal (Treszczanowicz and Treszczanowicz, 1973, 1975, 1981 ; Treszczanowicz *et al.*, 1973, 1981a ; Chen and Bagley, 1978 ; Nath and Bender, 1981 ; Brandani, 1983), assumed for the real species (ie. monomers and multimers) in the mixtures. In evaluating the model parameters, the thermodynamic properties of the mixtures are usually described without taking into account the properties of the pure component liquids (Kehiaian, 1972 ; Nath and Bender, 1981). Moreover, associated mixture models based exclusively on lattice theories are ill-suited for treating volume properties (ie. excess volumes, compressibilities and expansivities) since considerations are limited to the effect of H-bond breaking and formation as described by the association reaction (Treszczanowicz and Benson, 1985). For an ideal or athermal associated mixture, the purely chemical effect is insufficient to compensate for the composing effects of free volume and non-specific interactions existing in real mixtures and to fit the complex composition dependence of their excess volumes.

Despite their inadequacies, “chemical” lattice theories of associated mixtures have proved useful in describing and predicting the excess Gibbs function, enthalpy, entropy, and heat capacity as functions of temperature and composition for mixtures formed from self-associated and inert components. They also provide a basis for correlating the association constants of homologous series of self-associated liquids such as alkanols (Kehiaian, 1972 ; Treszczanowicz *et al.*, 1973), and also suggest precise conditions for separating the excess properties into independent chemical and physical contributions (Treszczanowicz and Treszczanowicz, 1981).

Usually the excess thermodynamic functions of an associated mixture are represented as sums of chemical and physical contributions.

$$X^E = X^E_{\text{chem}} + X^E_{\text{phy}} \quad (7.66)$$

where  $X = G, H, S, C_p, V$  etc. are, respectively, the molar Gibbs function, enthalpy, entropy, isobaric heat capacity, volume, etc. For non-athermal associated mixtures, the chemical and combinatorial contributions arise from the combinatorial part of the non-athermal excess Gibbs function expressed in terms of the real species in the mixture, and their mathematical shape as a function of composition depends in detail on the chemical equilibria considered. On the other hand the physical contribution arises from that part of the excess Gibbs function due to non-specific interactions. These contributions are additive and independent if it is assumed that the associating or bonding groups (such as the OH groups in alkanols) are the same as far as non-specific interactions are concerned, whether they are located in a monomer or bonded in a multimer. On the basis of this assumption it is possible to express the physical contribution as a function simply of the nominal (stoichiometric) component composition, as in the case of a non-associated mixture. If the Flory-Huggins theory is used, the physical term takes the Scatchard-Hildebrand form (Treszczanowicz and Treszczanowicz, 1981). However, many authors replace this more or less arbitrarily, by other relations : Liebermann and Wilhelm (1975) used the Bruin relation ; Nitta and Katayama (1973) used solubility parameters; Nagata and Kawamura (1977) and Nagata (1978) used local composition concepts.

The inadequacies of lattice models noted above with regard to volume properties led workers to consider a theory based on an equation of state. The new Flory theory (Flory, 1965; Orwoll and Flory, 1967) is convenient for this purpose because of its relative simplicity and the availability of experimental results needed to evaluate the parameters of the pure components. However, a rigorous mathematical solution starting from the partition function (or Gibbs function) of the mixture in terms of the real species is presently not feasible, due to the need to establish mixing rules between the model parameters for these species and to define hypothetical pure state characteristic parameters (temperature  $T^*$ , pressure  $p^*$  and molar volume  $V^*$ ) of the multimers, and also to correlate them with the molecular structure.

Therefore, the FBT model adopted a much simpler approach, in which the association parameters and the interaction parameters  $X_{12}$  are calculated from properties of the mixture, and the characteristic parameters of the components are estimated from properties of the pure liquids. Accordingly, the treatment does not give a description of the pure alkanol in terms of association, but does not take into account free volume and other equation of state effects.

Brandani and Prausnitz (1981) have used a somewhat similar treatment, consisting of an association model, combined with non-specific interaction and free volume terms described by an equation of state, to correlate the vapour-liquid equilibria of some associated mixtures.

#### 7.4.2 FBT Theory

The excess Gibbs function  $G^E$  (and excess entropy  $S^E$ ) of a binary associated mixture is assumed to be a sum of three additive and independent contributions viz., combinatorial, chemical and physical.

$$G^E = G_{\text{comb}}^E + G_{\text{chem}}^E + G_{\text{phys}}^E \quad (7.67)$$

The combinatorial contribution is described by the Flory-Huggins athermal mixture theory and formally is part of an athermal associated or a Flory model. Derivatives of  $G^E$ , such as  $X^E = H^E$ ,  $V^E$ ,  $C_p^E$ , etc are sums of two contributions - chemical and physical, as given by eq.(7.66).

The Flory-Benson-Treszczanowicz model describes the excess properties of a binary solution in terms of two contributions (Treszczanowicz and Benson, 1985). The first term describes the physical contribution to the excess property and the second term describes the chemical contribution to the excess property. The physical contribution is due to weak van der Waals intermolecular interactions as well as free volume effects, whilst the chemical contribution is due to hydrogen bonding. Flory's theory (Flory, Orwoll and Vrij, 1964 ; Eichinger and Flory, 1968) is used to describe the physical contribution, and, the chemical contribution is described by an athermal associated mixture model with a Mecke-Kempler (Bondi, 1968 ; Treszczanowicz, 1973a ; Treszczanowicz 1973b ; Treszczanowicz and Treszczanowicz, 1975; Treszczanowicz and Treszczanowicz, 1981) mode of association. The excess molar enthalpy,  $H_m^E$  and the excess molar volume,  $V_m^E$  in terms of these two contributions are:

$$H_m^E = H_{(\text{mk})}^E + H_{(\text{F})}^E, \quad (7.68)$$

$$\text{and } V_m^E = V_{(\text{MK})}^E + V_{(\text{F})}^E \quad (7.69)$$

where  $H_{(\text{F})}^E$  is the excess molar enthalpy derived from the Flory theory (Batchelor *et al.*, 1959) and is given by:

$$H_m^E = x_1 P_1^* V_1^* [\tilde{V}_1 - (1/\tilde{V})] + x_2 P_2^* V_2^* [\tilde{V}_2 - (1/\tilde{V})] + x_1 P_1^* X_{12} / \tilde{V} \quad (7.70)$$

where  $P_i^*$  = characteristic pressure of component  $i$

$V_i^*$  = characteristic volume of component  $i$

$\tilde{V}_i$  = reduced volume of component  $i$

$X_{12}$  = Flory interaction parameter characteristic of mixture 1 and 2.

$V_{(F)}^E$  is the excess molar enthalpy derived from the Flory theory (Flory *et al.*, 1964) and is given by:

$$V_m^E = \frac{(x_1 V_1^* + x_2 V_2^*)(\phi_1 \tilde{V}_1 + \phi_2 \tilde{V}_2)^{\frac{7}{3}} (\tilde{T} - \tilde{T}^0)}{\frac{4}{3} - (\phi_1 \tilde{V}_1 + \phi_2 \tilde{V}_2)^{\frac{1}{3}}} \quad (7.71)$$

where  $\phi_i$  = segment fraction

$\tilde{T}^0$  = ideal reduced temperature

$\tilde{T}$  = reduced temperature of component  $i$

the reduced volume of component  $i$ ,  $\tilde{V}_i$  is:

$$\tilde{V}_i = \left( \frac{1 + \frac{4}{3} \alpha_i T}{1 + \alpha_i T} \right) \quad (7.72)$$

where  $\alpha_i$  is the thermal expansion coefficient of  $i$  and  $T$  the absolute temperature. The characteristic volume,  $V_i^*$  is calculated from the reduced volume,  $\tilde{V}_i$  and the molar volume,

$V_i$  of component  $i$  as follows:

$$V_i^* = \frac{\tilde{V}_i}{V_i} \quad (7.73)$$

The  $H_{(MK)}^E$  is the excess molar enthalpy derived from the Mecke-Kempton model and is given as follows:

$$H_{(MK)}^E = \Delta h^0 x_1 \cdot h(K^0, \phi_1) \quad (7.74)$$

where  $\Delta h^0$  is the molar enthalpy of association.

The  $V_{(MK)}^E$  is the excess molar volume derived from the Mecke-Kempton model and is given as follows:



$$V_{(\text{MK})}^{\text{E}} = \Delta v^{\circ} x_1 \cdot h(K^{(\phi)}, \phi_1) \quad (7.75)$$

where  $\Delta v^{\circ}$  is the molar volume of association,

The segment fraction  $\phi_1$  is defined as:

$$\phi_1 = 1 - \phi_2 \quad (7.76)$$

$$\text{where } \phi_2 = \frac{x_2 V_2^*}{x_1 V_1^* + x_2 V_2^*} \quad (7.77)$$

The segment fraction  $\phi_1$  is calculated from equation (7.74)

$$h(K^{(\phi)}, \phi_1) = \frac{[\phi_1 \ln(1 + K^{(\phi)}) - \ln(1 + K^{(\phi)} \cdot \phi_1)]}{K^{(\phi)} \phi_1} \quad (7.78)$$

where,  $K^{(\phi)}$  is the equilibrium constant that characterizes the association in the mixture.  $K^{(\phi)}$  is defined by the following equation:

$$\ln K^{(\phi)} = 1 + \ln(k_H / r_1) \quad (7.79)$$

where

$$k_H = \exp \left( -\frac{\Delta h^{\circ} - T \Delta s^{\circ}}{RT} \right) \quad (7.80)$$

and

$$r_1 = \frac{V_1^*}{17.12} \quad (7.81)$$

where  $\Delta s^{\circ}$  is the molar entropy of association and  $V_1^*$  is the characteristic molar volume of component 1 and is determined using equation (7.73). The model therefore has four parameters that are characteristic of the mixture,  $X_{12}$  from the physical contribution due to Flory's theory,  $\Delta h^{\circ}$ ,  $\Delta v^{\circ}$  and  $\Delta s^{\circ}$  from the chemical contribution due to the Mecke-Kempter model. Instead of  $\Delta s^{\circ}$  the fourth parameter can be  $K^{(\phi)}$  in which case  $\Delta s^{\circ}$  can be calculated from equation (7.80).

In this work the Flory-Benson-Treszczanowicz model was applied to the excess molar volumes and excess molar enthalpies for the mixtures (a nitrile compound + a carboxylic acid) at  $T = 298.15 \text{ K}$  and  $p = 0.1 \text{ MPa}$ .

### 7.5 APPLICATION OF THE NRTL AND UNIQUAC MODELS TO THE EXCESS MOLAR ENTHALPIES FOR MIXTURES OF A [NITRILE COMPOUND + A CARBOXYLIC ACID]

Two thermodynamic models, namely the nonrandom two-liquid equation NRTL (Renon and Pransnitz, 1968) and the universal quasichemical equation UNIQUAC (Abrams and Pransnitz, 1975) were both fitted to the excess molar enthalpy data for liquid mixture of (a nitrile compound + a carboxylic acid compound) at  $T = 298.15$  K, that were presented in Chapter 3. The interaction parameters for each model were determined with the aid of MATHCAD 8 worksheets.

The UNIQUAC surface area and volume parameters for the compounds are presented in Table 7.1.

**Table 7.1 Physical Properties of the Pure Components at 298.15 K; Molar Volumes,  $V_{mi}$ , Refractive Indices,  $n_D$ , Volume and Surface Parameters,  $R$  and  $Q$ .**

Component	$V_{mi}/\text{cm}^3 \cdot \text{mol}^{-1}$ <sup>a</sup>	$n_D$		$R^b$	$Q^b$
		exp	lit. <sup>a</sup>		
acetonitrile	52.87	1.3413	1.3416	1.870	1.724
acetic acid	57.53	1.3697	1.3698	2.202	2.072
propanoic acid	74.97	1.3846	1.3843	2.877	2.612
butanoic acid	92.43	1.3955	1.3958	3.551	3.152
2-methylpropanoic acid	93.44	1.3913	1.3917	3.550	3.148
pentanoic acid	109.29	1.4064	1.4060	4.226	3.692
3-methylbutanoic acid	110.54	1.4019	1.4022	4.225	3.688
benzonitrile	103.06	1.5260	1.5257	3.991	2.996
butanenitrile	87.87	1.3822	1.3820	3.219	2.804

<sup>a</sup> Riddick *et al.* (1986). <sup>b</sup> Gmehling *et al.* (1993)

### 7.5.1 Application of the NRTL and UNIQUAC models to the excess molar enthalpies for mixtures of (acetonitrile + a carboxylic acid) at T = 298.15 K.

For the NRTL model the non-randomness parameter  $\alpha_{ij}$  was set at a value of 0.2. The NRTL interaction parameters  $g_{12} - g_{22}$  and  $g_{21} - g_{11}$  are given in Table 7.2 together with the standard deviations. The UNIQUAC interaction parameters  $\Delta u_{12}$  and  $\Delta u_{21}$  are also given in Table 7.2 together with the corresponding standard deviations. The standard deviation  $\sigma$  for the NRTL and the UNIQUAC models is defined as:

$$\sigma = [\Sigma(H_{m(\text{expt})}^E - H_{m(\text{calc})}^E)^2/N]^{1/2} \quad (7.82)$$

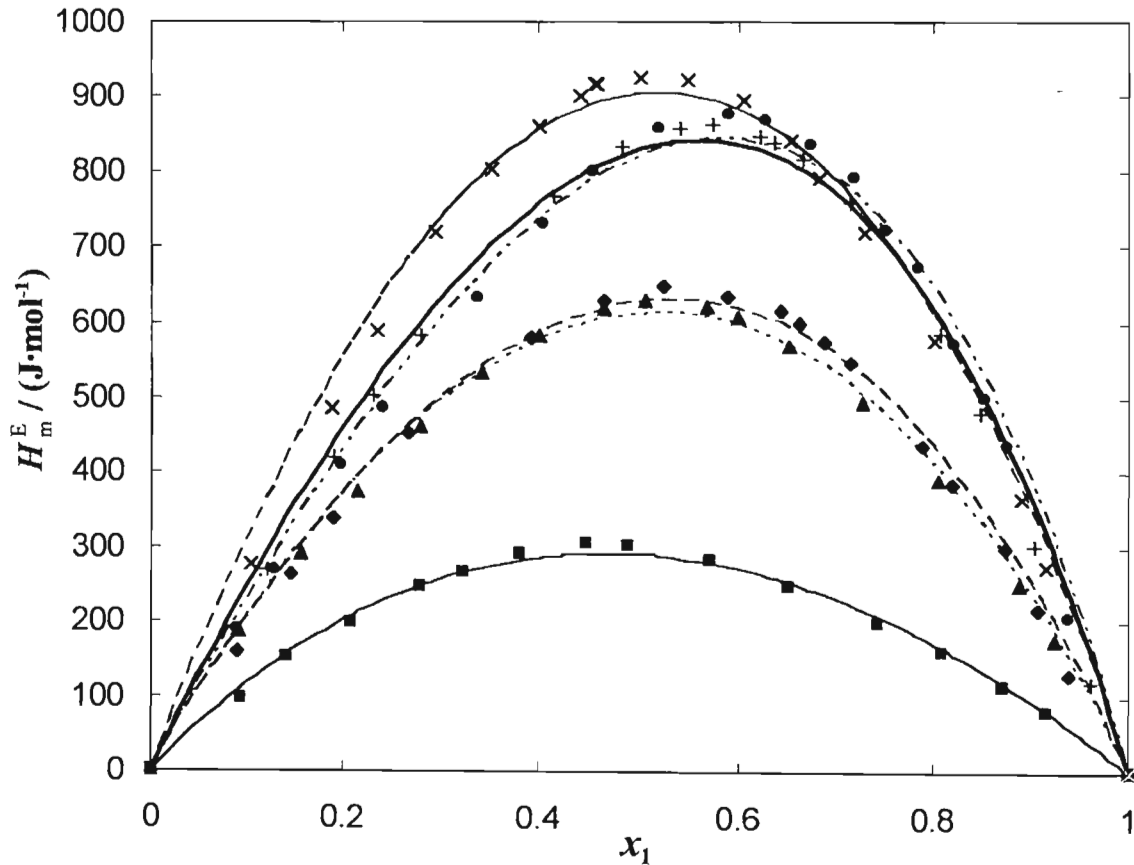
where N is the number of experimental data points.

The results of fitting the NRTL model and the UNIQUAC model to the excess molar enthalpy data for the mixtures of (acetonitrile + acetic acid or propanoic acid or butanoic acid or 2-methylpropanoic acid or pentanoic acid or 3-methylbutanoic acid) are plotted in Figures 7.3 and 7.4.

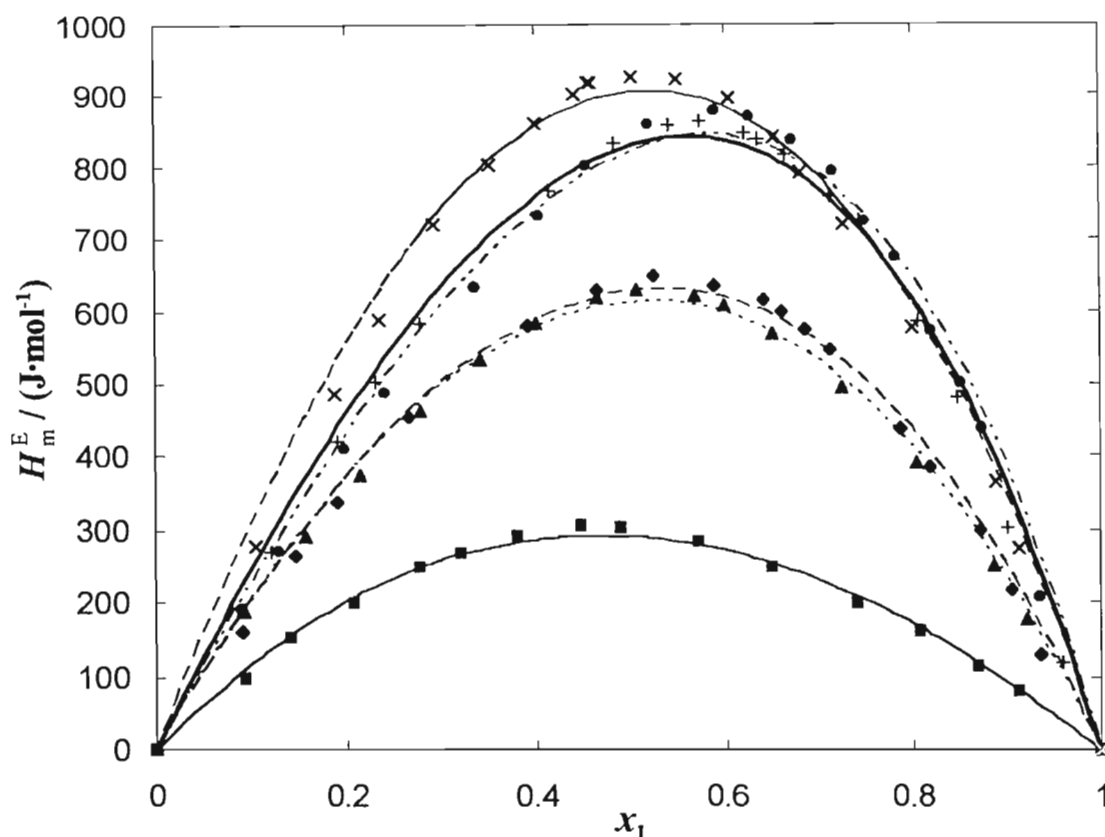
**Table 7.2** Correlation of the excess molar enthalpies for the systems: [acetonitrile (1) + a carboxylic acid (2)] at 298.15 K by means of the NRTL and UNIQUAC equations: values of interaction parameters and measures of deviations.

Component	NRTL <sup>a</sup>			UNIQUAC		
	$g_{12}-g_{22}$	$g_{21}-g_{11}$	$\sigma/\text{J}\cdot\text{mol}^{-1}$	$\Delta u_{12}$	$\Delta u_{21}$	$\sigma/\text{J}\cdot\text{mol}^{-1}$
	$\text{J}\cdot\text{mol}^{-1}$			$\text{J}\cdot\text{mol}^{-1}$		
Acetic Acid	- 146.4	1489.0	7.5	-154.5	941.1	7.4
Propanoic Acid	2343.0	353.9	10.9	365.9	1009.0	11.9
Butanoic Acid	2894.0	-7.8	15.9	214.2	1105.0	16.8
2-Methylpropanoic Acid	3055.0	1074.0	22.8	441.9	1627.0	24.9
Pentanoic Acid	4576.0	-255.2	22.0	462.2	1201.0	25.6
3-Methylbutanoic Acid	5419.0	-663.6	24.4	674.6	958.4	29.9

<sup>a</sup>Calculated with  $\alpha_{12}=0.2$



**Figure 7.3** Excess molar enthalpies for the mixtures [acetonitrile (1) + a carboxylic acid (2)] at 298.15 K and the results calculated using the NRTL model. (■, acetic acid; ◆, butanoic acid; ▲, propanoic acid; ●, 2-methylpropanoic acid; +, pentanoic acid; ×, 3-methylbutanoic acid; lines represent the model fit)



**Figure 7.4** Excess molar enthalpies for the mixtures [acetonitrile (1) + a carboxylic acid (2)] at 298.15 K and the results calculated using the UNIQUAC model. (■, acetic acid; ◆, butanoic acid; ▲, propanoic acid; ●, 2-methylpropanoic acid; +, pentanoic acid; ×, 3-methylbutanoic acid; lines represent the model fit)

As can be observed from Table 7.2, both the NRTL and UNIQUAC models correlate the excess molar enthalpy data for the mixtures of (acetonitrile + a carboxylic acid) reasonably well, with  $\sigma$  better than  $25 \text{ J}\cdot\text{mol}^{-1}$  and  $30 \text{ J}\cdot\text{mol}^{-1}$  respectively. This is not better than the correlation provided by the Redlich-Kister equation, where a standard deviation value of better than  $8 \text{ J}\cdot\text{mol}^{-1}$  was achieved. Both models correlate the excess molar enthalpy data for the mixtures equally well.

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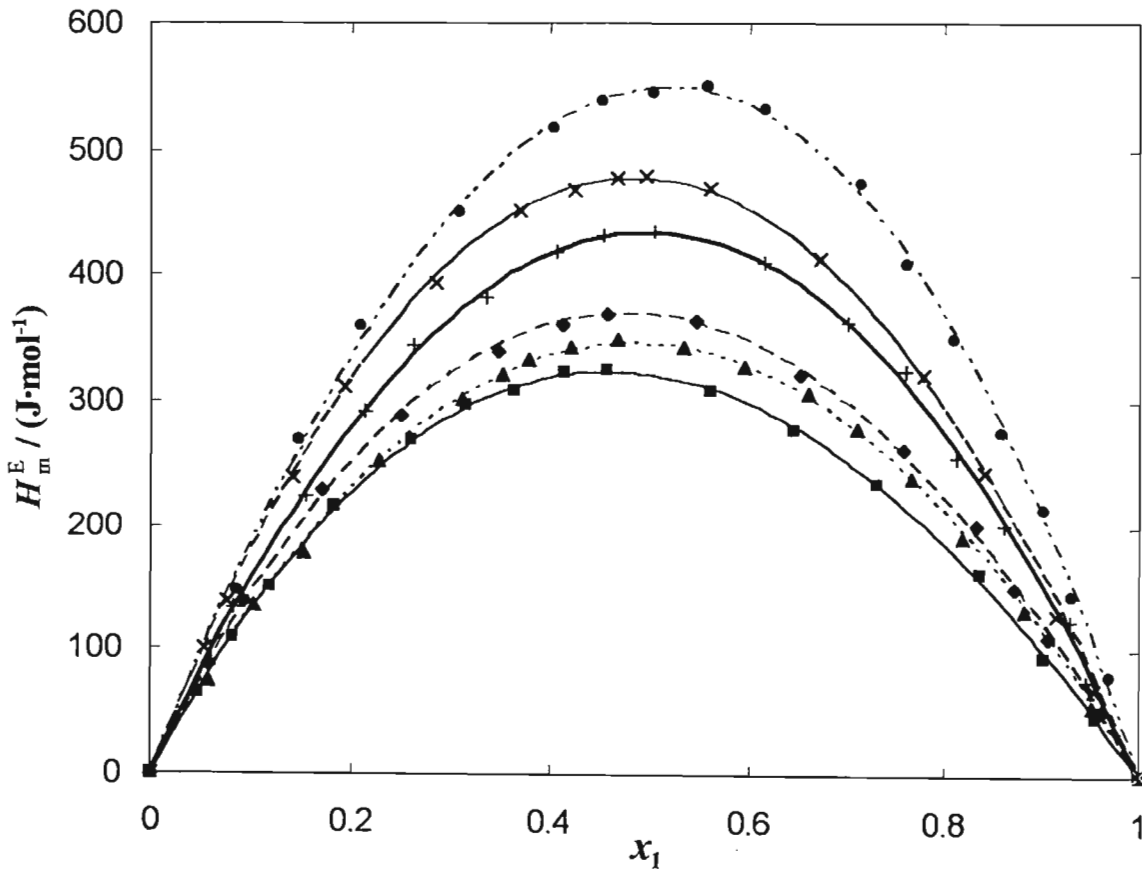
**7.5.2 Application of the NRTL and UNIQUAC models to the excess molar enthalpies for mixtures of (benzonitrile + a carboxylic acid) at T = 298.15 K.**

The binary interaction parameters for fitting the NRTL and UNIQUAC models to the excess molar enthalpies for the mixtures of (benzonitrile + a carboxylic acid) at T = 298.15 K are presented in Table 7.3. The results of fitting the NRTL model and the UNIQUAC model to the excess enthalpy data for the mixtures of (benzonitrile + a carboxylic acid) are graphed in Figures 7.5 and 7.6. The standard deviations,  $\sigma$  which are calculated according to equation (7.82) are reported in Table 7.3. Both the NRTL and UNIQUAC models fitted the excess molar enthalpy data well, with  $\sigma$  better than 7 J·mol<sup>-1</sup> in the case of both models.

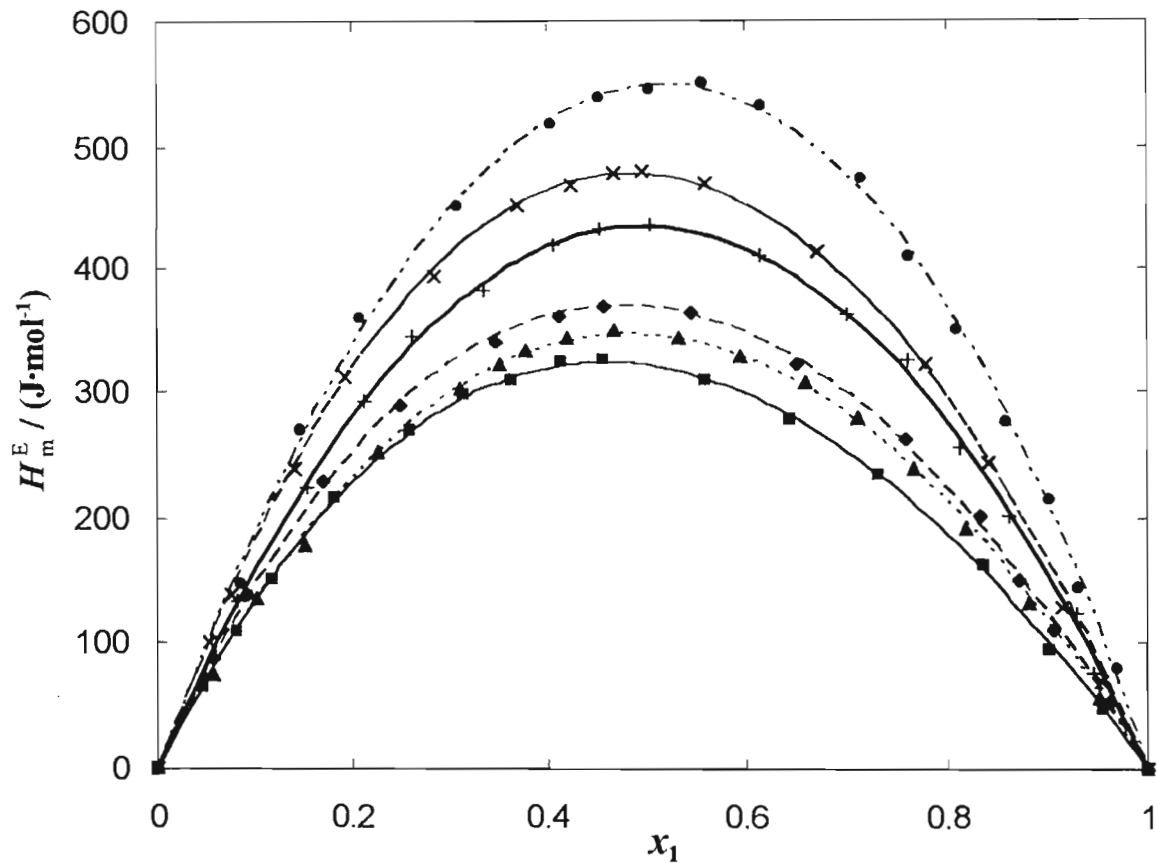
**Table 7.3**      **Correlation of the excess molar enthalpies for the systems : [Benzonitrile (1) + a Carboxylic Acid (2)] at 298.15 K by means of the NRTL and UNIQUAC equations: values of parameters and measures of deviations.**

Component	NRTL <sup>a</sup>			UNIQUAC		
	$g_{12}-g_{22}$	$g_{21}-g_{11}$	$\sigma/\text{J}\cdot\text{mol}^{-1}$	$\Delta u_{12}$	$\Delta u_{21}$	$\sigma/\text{J}\cdot\text{mol}^{-1}$
	$\text{J}\cdot\text{mol}^{-1}$			$\text{J}\cdot\text{mol}^{-1}$		
Acetic Acid	-222.9	1759.0	2.8	312.4	241.3	3.0
Propanoic Acid	320.1	1177.0	3.5	253.1	269.3	3.6
Butanoic Acid	214.0	1427.0	3.8	35.8	583.1	3.8
2-Methylpropanoic Acid	684.4	1397.0	4.8	114.6	573.2	4.8
Pentanoic Acid	944.8	892.4	5.2	3.8	581.5	5.2
3-Methylbutanoic Acid	2075.0	316.9	6.9	283.5	431.9	6.9

<sup>a</sup>Calculated with  $\alpha_{12}=0.2$



**Figure 7.5**      **Excess molar enthalpies for the mixtures [benzonitrile (1) + a carboxylic acid (2)] at 298.15 K calculated using the NRTL model. (■, acetic acid; ◆, butanoic acid; ▲, propanoic acid; ●, 2-methylpropanoic acid; +, pentanoic acid; ×, 3-methylbutanoic acid; lines represent the model fit)**



**Figure 7.6** Excess molar enthalpies for the mixtures [benzonitrile (1) + a carboxylic acid (2)] at 298.15 K calculated using the UNIQUAC model. (■, acetic acid; ◆, butanoic acid; ▲, propanoic acid; ●, 2-methylpropanoic acid; +, pentanoic acid; ×, 3-methylbutanoic acid; lines represent the model fit)



### 7.5.3 Application of the NRTL and UNIQUAC models to the excess molar enthalpies for mixtures of (butanenitrile + a carboxylic acid) at $T = 298.15\text{ K}$

In fitting the NRTL model the non-randomness parameter,  $\alpha_{12}$  was set at 0.4. The NRTL interaction parameters,  $\alpha_{12}$  was set at 0.4. The NRTL interaction parameters,  $g_{12} - g_{22}$  and  $g_{21} - g_{11}$  are given in Table 7.4 together with the corresponding standard deviations  $\sigma$ . The UNIQUAC interaction parameters  $\Delta U_{12}$  and  $\Delta U_{21}$  are also given in Table 7.4 together with the corresponding standard deviations. The standard deviations for both the NRTL and UNIQUAC models are calculated according to equation (7.82).

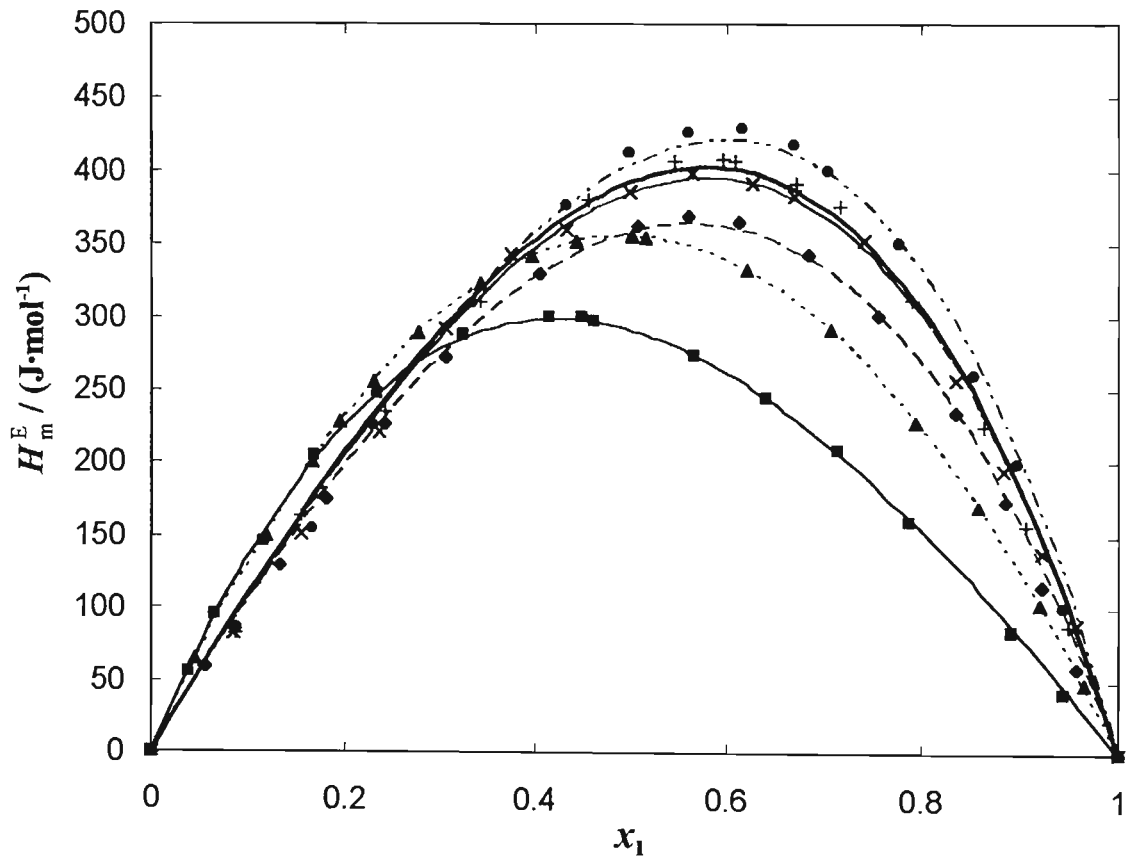
The results of fitting the NRTL and UNIQUAC models to the excess molar enthalpy data for the mixtures of (butanenitrile + acetic acid or propanoic acid or butanoic acid or 2-methylpropanoic acid or pentanoic acid or 3-methylbutanoic acid) are plotted in Figures 7.7 and 7.8.

The NRTL and UNIQUAC models correlate the excess molar enthalpy data for the mixtures of (butanenitrile + a carboxylic acid) reasonably well with  $\sigma$  better than  $10\text{ J}\cdot\text{mol}^{-1}$  and  $12\text{ J}\cdot\text{mol}^{-1}$  respectively. However, the correlation provided by the Redlich-Kister polynomial is significantly better with a standard deviation of less than  $6\text{ J}\cdot\text{mol}^{-1}$ .

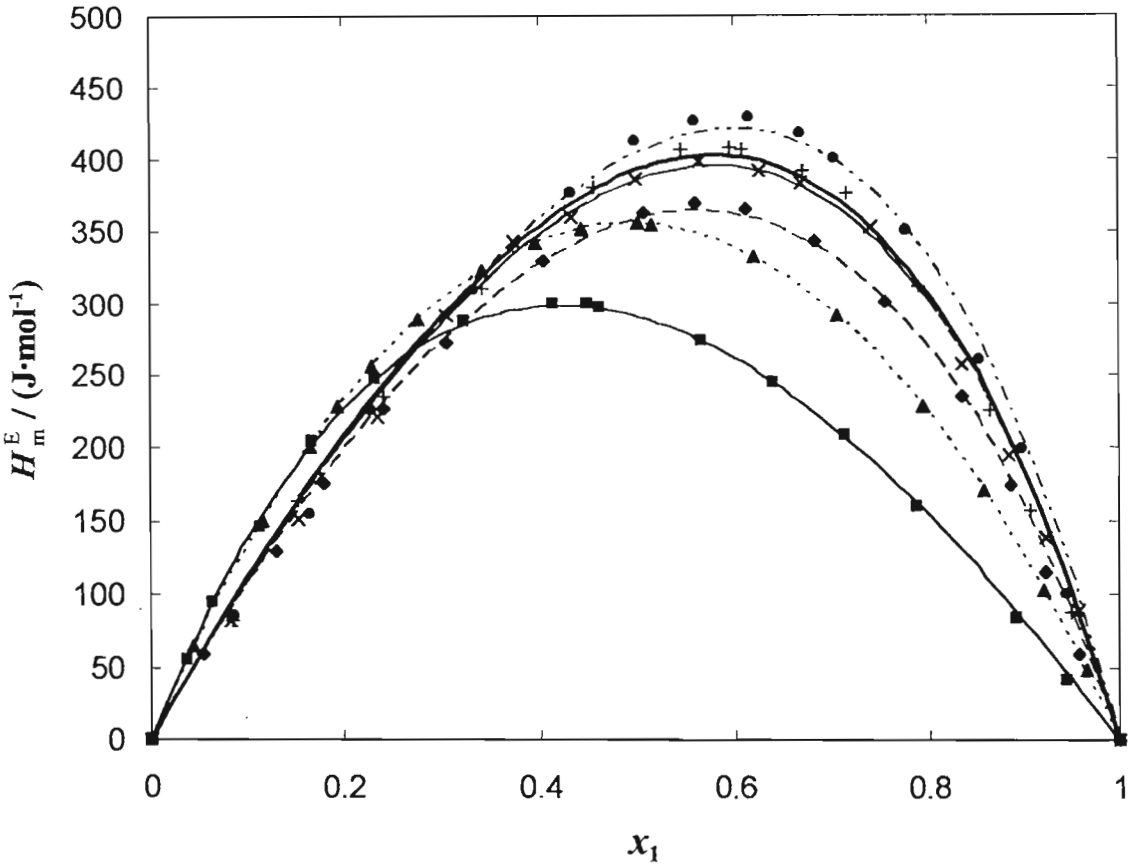
**Table 7.4** Correlation of the excess molar enthalpies for the systems : [butanenitrile(1) + a carboxylic acid(2) at T = 298.15K by means of the NRTL and UNIQUAC equations : values of parameters and measures of deviations.

Component	NRTL <sup>a</sup>			UNIQUAC		
	$g_{12}-g_{22}$	$g_{21}-g_{11}$	$\sigma/\text{J}\cdot\text{mol}^{-1}$	$\Delta u_{12}$	$\Delta u_{21}$	$\sigma/\text{J}\cdot\text{mol}^{-1}$
	$\text{J}\cdot\text{mol}^{-1}$			$\text{J}\cdot\text{mol}^{-1}$		
Acetic Acid	-87.7	1722.0	2.8	-104.0	703.3	3.7
Propanoic Acid0	775.1	799.7	0.4	287.4	269.3	0.5
Butanoic Acid	2186.0	-288.2	5.9	758.5	-151.7	6.3
2-Methylpropanoic Acid	2582.0	-372.9	6.5	955.4	-236.9	7.2
Pentanoic Acid	2590.0	-348.7	8.6	723.6	-113.1	9.7
3-Methylbutanoic Acid	3002.0	-453.2	9.3	946.1	-233.7	11.4

<sup>a</sup>Calculated with  $\alpha_{12} = 0.4$



**Figure 7.7** Excess molar enthalpies for the mixtures [butanenitrile (1) + a carboxylic acid (2)] at 298.15 K calculated using the NRTL model. (■, acetic acid; ◆, butanoic acid; ▲, propanoic acid; ●, 2-methylpropanoic acid; +, pentanoic acid; ×, 3-methylbutanoic acid; lines represent the model fit)



**Figure 7.8** Excess molar enthalpies for the mixtures [butanenitrile (1) + a carboxylic acid (2)] at 298.15 K calculated using the UNIQUAC model. (■, acetic acid; ◆, butanoic acid; ▲, propanoic acid; ●, 2-methylpropanoic acid; +, pentanoic acid; ×, 3-methylbutanoic acid; lines represent the model fit)

### 7.6 APPLICATION OF THE FLORY-BENSON-TRESZCZANOWICZ (FBT) MODEL TO THE EXCESS MOLAR VOLUMES AND EXCESS MOLAR ENTHALPIES FOR MIXTURES OF A [NITRILE COMPOUND + A CARBOXYLIC ACID]

The FBT model was applied to the excess molar volume and excess molar enthalpy data reported in Chapter 3 and Chapter 4 respectively, for the mixtures of a (nitrile compound + a carboxylic acid) at  $T = 298.15$  K. The four adjustable parameters of the FBT model, viz.  $X_{AB}$ ,  $\Delta h^\circ$ ,  $\Delta v^\circ$ , and  $\Delta s^\circ$  were determined by fitting the model to the excess molar volume and excess molar enthalpy data simultaneously using a MATHCAD 8.0 worksheet. These adjustable parameters and their significance have been described earlier in Section 7.4. The agreement between the experimental values and the values calculated from the FBT model for the excess molar volume are given by the standard deviations,  $\delta V_M^E$  and  $\delta H_M^E$  respectively. These are defined as:

$$\delta V_m^E = \left[ \sum (V_{m(\text{exp})}^E - V_{m(\text{calc})}^E)^2 / N \right]^{1/2} \quad (7.83)$$

and

$$\delta H_m^E = \left[ \sum (H_{m(\text{exp})}^E - H_{m(\text{calc})}^E)^2 / N \right]^{1/2} \quad (7.84)$$

where N refers to the number of experimental data points.

The pure component properties required for the application of the FBT model are the thermal expansion coefficient, the isothermal compressibility and the molar volumes. These data are reported in Table 7.5.

**Table 7.5** Molar masses,  $M$ , Densities,  $\rho$ , thermal expansion coefficients,  $\alpha$ , isothermal compressibility,  $\kappa_T$ , for the nitrile compounds and carboxylic acids used in this work.

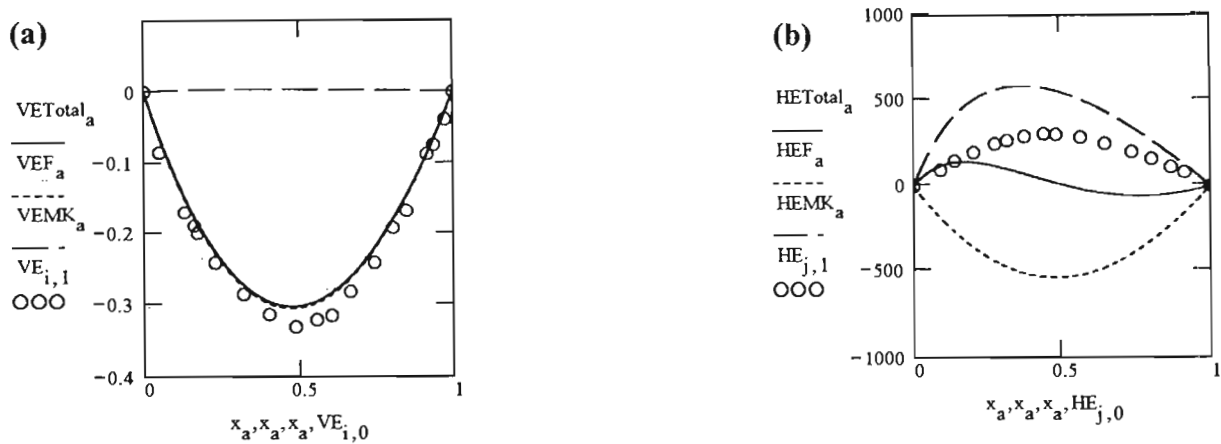
Component	$M/\text{g}\cdot\text{mol}^{-1}$	$\rho^a/\text{g}\cdot\text{cm}^{-3}$	$\alpha\cdot 10^3/\text{K}^{-1}$	$\kappa_T\cdot 10^3/\text{MPa}$
Acetonitrile	41.05	0.7764	1.372 <sup>a</sup>	1.116 <sup>a</sup>
Butanenitrile	69.11	0.7865	1.158 <sup>b</sup>	0.981 <sup>c</sup>
Benzonitrile	103.12	1.0006	0.890 <sup>c</sup>	0.611 <sup>c</sup>
Acetic acid	60.05	1.0439	1.068 <sup>d</sup>	1.015 <sup>d</sup>
Propanoic acid	74.08	0.9881	1.076 <sup>d</sup>	0.967 <sup>d</sup>
Butanoic acid	88.11	0.9532	1.026 <sup>d</sup>	0.906 <sup>d</sup>
2-Methylpropanoic acid	88.11	0.9429	1.026	0.906
Pentanoic acid	102.13	0.9345	0.965 <sup>d</sup>	0.829
3-methylbutanoic acid	102.13	0.9219	0.965	0.829

<sup>a</sup> Riddick *et al.*(1986).<sup>c</sup> Uosaki *et al.*(1990)<sup>b</sup> TRC Thermodynamic Tables (1988)<sup>d</sup> Vong, W., Tsai, F.(1997)**7.6.1 Application of the FBT model to the excess molar volumes and enthalpies for mixtures of (acetonitrile + a carboxylic acid) at  $T = 298.15$  K.**

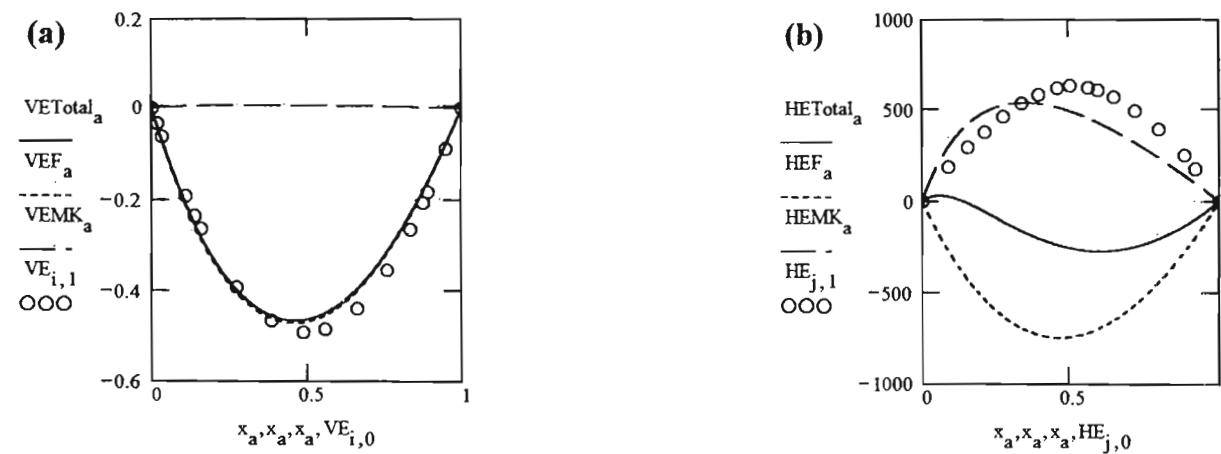
The Flory-Benson-Treszczanowicz model was fitted to the excess molar volumes and excess molar enthalpies for the mixtures (acetonitrile + acetic acid or propanoic acid or butanoic acid or 2-methylpropanoic acid or pentanoic acid or 3-methylbutanoic acid) at  $T = 298.15$  K. The four adjustable parameters  $XAB$ ,  $\Delta h^\circ$ ,  $\Delta v^\circ$  and  $\Delta s^\circ$  and the results of the correlation are illustrated in Table 7.6. Figures 7.9 - 7.15 give a plot of the results.

**Table 7.6** Correlation of the excess molar volumes and enthalpies for the systems : [acetonitrile (1) + a carboxylic acid (2)] at 298.15 K by means of the FBT model : values of interaction parameters and measures of deviations

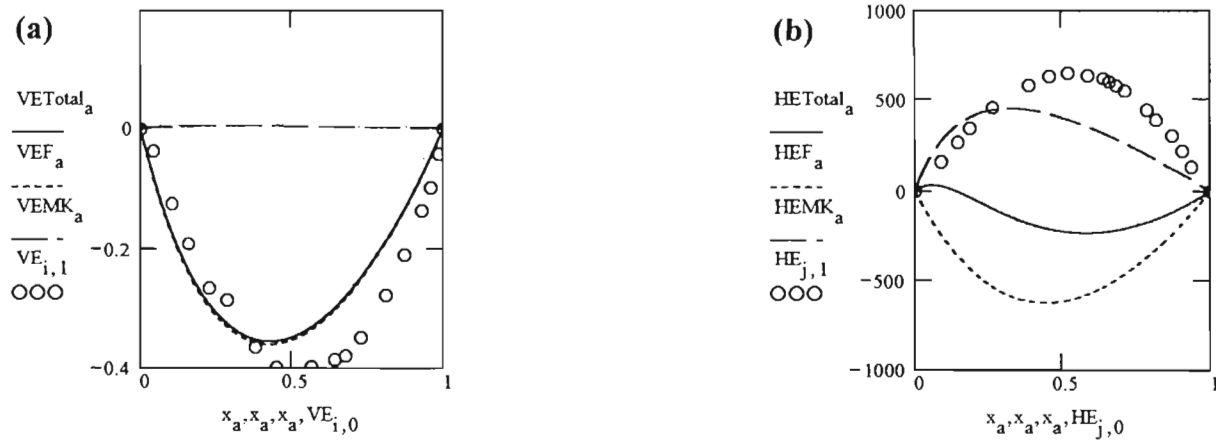
Component	$\frac{XAB}{J\cdot\text{cm}^{-3}}$	$\frac{\Delta h^\circ}{\text{kJ}\cdot\text{mol}^{-1}}$	$\frac{\Delta v^\circ}{\text{cm}^3\cdot\text{mol}^{-1}}$	$\frac{\Delta s^\circ}{J\cdot\text{K}^{-1}}$	$\frac{\delta H_m^E}{J\cdot\text{mol}^{-1}}$	$\frac{\delta V_m^E}{\text{cm}^3\cdot\text{mol}^{-1}}$
Acetic acid	-46	-8.1	0.04	-18	196	0.019
Propanoic acid	-56	-8.5	-0.1	-18	642	0.024
Butanoic acid	-39	-8.5	-0.1	-16	617	0.061
2-Methylpropanoic Acid	-30	-11.9	-0.2	-28	656	0.052
Pentanoic acid	-30	-13.5	-0.2	-26	671	0.064
3-Methylbutanoic acid	-36	-11.9	-0.5	-24	747	0.071



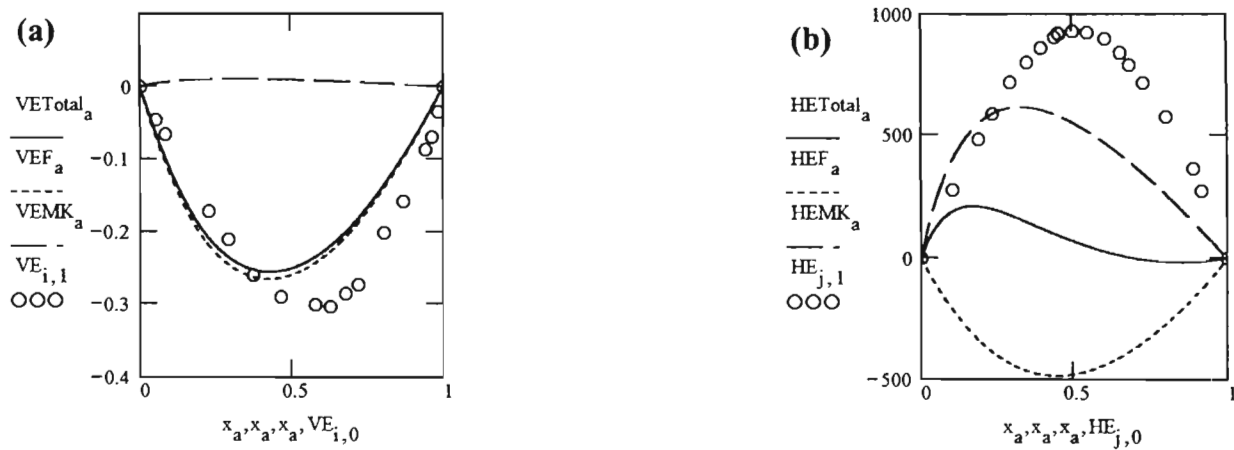
**Figure 7.9** Results of fitting the FBT model to excess molar volumes(a) and excess molar enthalpies(b) for mixtures of (acetonitrile + acetic acid) at  $T = 298.15\text{ K}$  \_\_\_\_\_, from FBT theory; \_\_\_\_\_, chemical contribution; ..... , physical contribution; ○, experimental data.



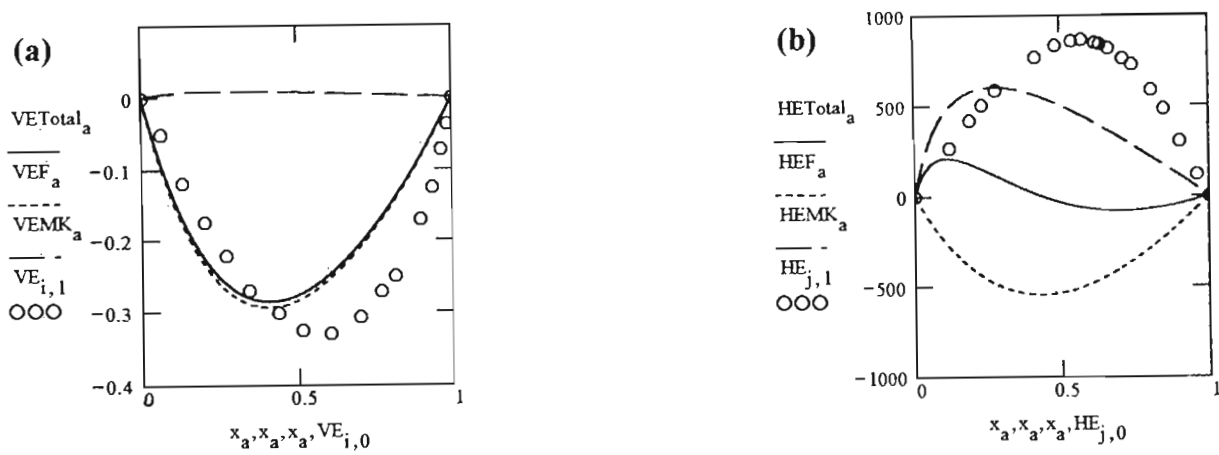
**Figure 7.10** Results of fitting the FBT model to excess molar volumes(a) and excess molar enthalpies(b) for mixtures of (acetonitrile + propanoic acid) at  $T=298.15\text{ K}$  \_\_\_\_\_, from FBT theory; \_\_\_\_\_, chemical contribution; ..... , physical contribution; ○, experimental data.



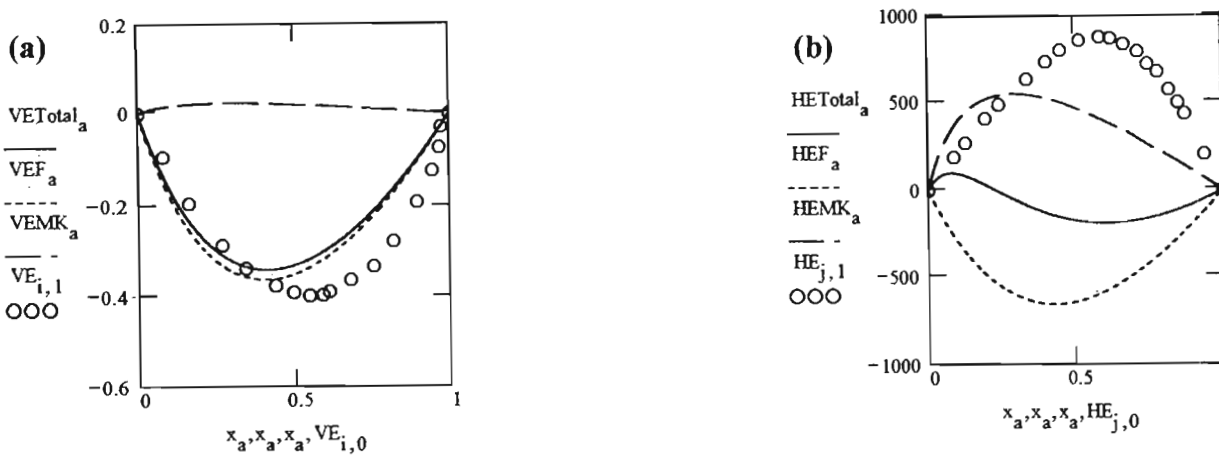
**Figure 7.11** Results of fitting the FBT model to excess molar volumes(a) and excess molar enthalpies(b) for mixtures of (acetonitrile + butanoic acid) at  $T=298.15$  K \_\_\_\_\_, from FBT theory; \_\_\_\_\_, chemical contribution; ....., physical contribution; ○, experimental data.



**Figure 7.12** Results of fitting the FBT model to excess molar volumes(a) and excess molar enthalpies(b) for mixtures of (acetonitrile + 2-methylpropanoic acid) at  $T=298.15$  K \_\_\_\_\_, from FBT theory; \_\_\_\_\_, chemical contribution; ....., physical contribution; ○, experimental data.



**Figure 7.13** Results of fitting the FBT model to excess molar volumes(a) and excess molar enthalpies(b) for mixtures of (acetonitrile + pentanoic acid) at  $T=298.15$  K \_\_\_\_\_ , from FBT theory; \_ \_ \_ \_ , chemical contribution; ..... , physical contribution;  $\circ$ , experimental data.



**Figure 7.14** Results of fitting the FBT model to excess molar volumes(a) and excess molar enthalpies(b) for mixtures of (acetonitrile + 3-methylbutanoic acid) at  $T=298.15$  K \_\_\_\_\_ , from FBT theory; \_ \_ \_ \_ , chemical contribution; ..... , physical contribution;  $\circ$ , experimental data.

The FBT model is able to simultaneously describe the excess molar volume and excess molar enthalpy for the mixtures (acetonitrile + acetic acid or propanoic acid or butanoic acid or 2-methylbutanoic acid or pentanoic acid or 3-methylbutanoic acid) in a qualitative and quantitative manner. In particular the model predicts the excess molar data reasonably well and it also reproduces the shape of the excess molar volume curves satisfactorily.

In terms of the FBT model the greatest contribution to the excess molar volumes for the



mixtures (acetonitrile + a carboxylic acid) is the physical contribution which is primarily due to dipole-dipole as well as van der Waals types of interactions.

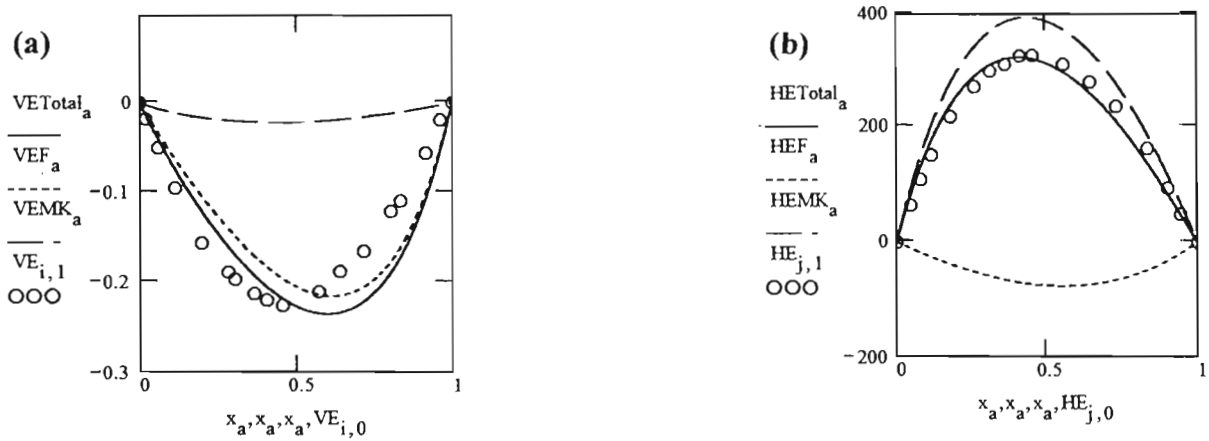
The FBT model also predicts that the major contribution to the excess molar enthalpy is the chemical interaction. This prediction factor is well supported by the fact that strong hydrogen bonding dominates the excess molar enthalpies for these mixtures.

7.6.2 Application of the FBT model to the excess molar volumes and enthalpies for mixtures of (benzonitrile + a carboxylic acid) at T = 298.15 K

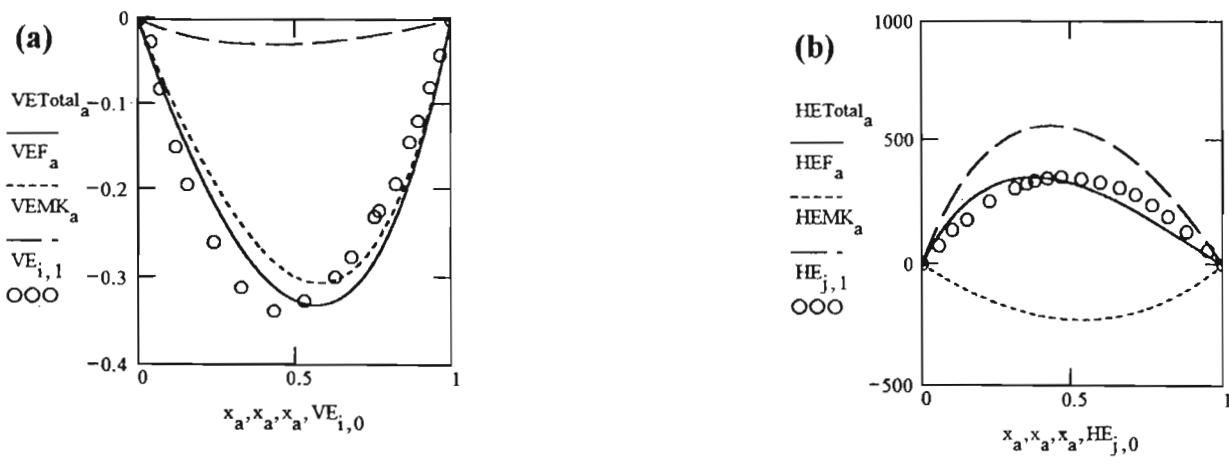
The Flory-Benson-Treszczanowicz model was fitted to the excess molar volumes and enthalpies for mixtures of (benzonitrile + acetic acid or propanoic acid or butanoic acid or 2-methylpropanoic acid or pentanoic acid or 3-methylbutanoic acid) at T = 298.15 K. The four adjustable parameters  $X_{AB}$ ,  $\Delta h^\circ$ ,  $\Delta v^\circ$  and  $\Delta s^\circ$  as well as the results of the correlation are illustrated in Table 7.7. The results are plotted in Figures 7.15 - 7.20.

**Table 7.7** Correlation of the excess molar volumes and enthalpies for the systems : [benzonitrile(1) + a carboxylic acid(2)] at 298.15 K by means of the FBT model : values of interaction parameters and measures of deviations

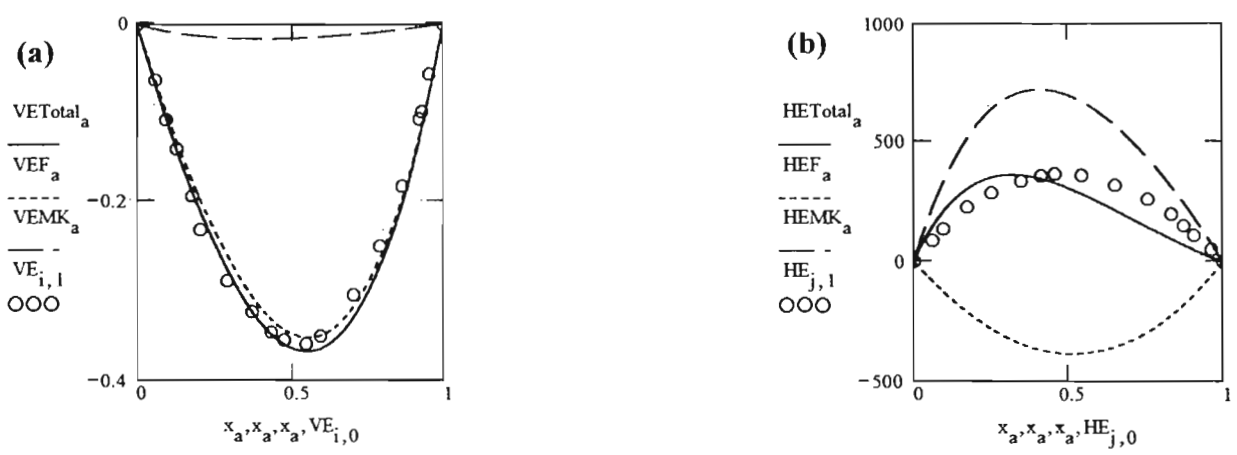
Component	$\frac{X_{AB}}{J \cdot cm^{-3}}$	$\frac{\Delta h^\circ}{kJ \cdot mol^{-1}}$	$\frac{\Delta v^\circ}{cm^3 \cdot mol^{-1}}$	$\frac{\Delta s^\circ}{J \cdot K^{-1}}$	$\frac{\delta H_m^E}{J \cdot mol^{-1}}$	$\frac{\delta V_m^E}{cm^3 \cdot mol^{-1}}$
Acetic acid	-5	-3.5	0.2	0.4	17	0.036
Propanoic acid	-13	-5.9	0.3	-9	43	0.035
Butanoic acid	-19	-8.5	0.2	-16	71	0.015
2-Methylpropanoic Acid	-15	-8.4	0.01	-16	85	0.008
Pentanoic acid	-17	-9.2	-0.1	-18	124	0.016
3-Methylbutanoic acid	-21	-7.2	-0.1	-8	365	0.033



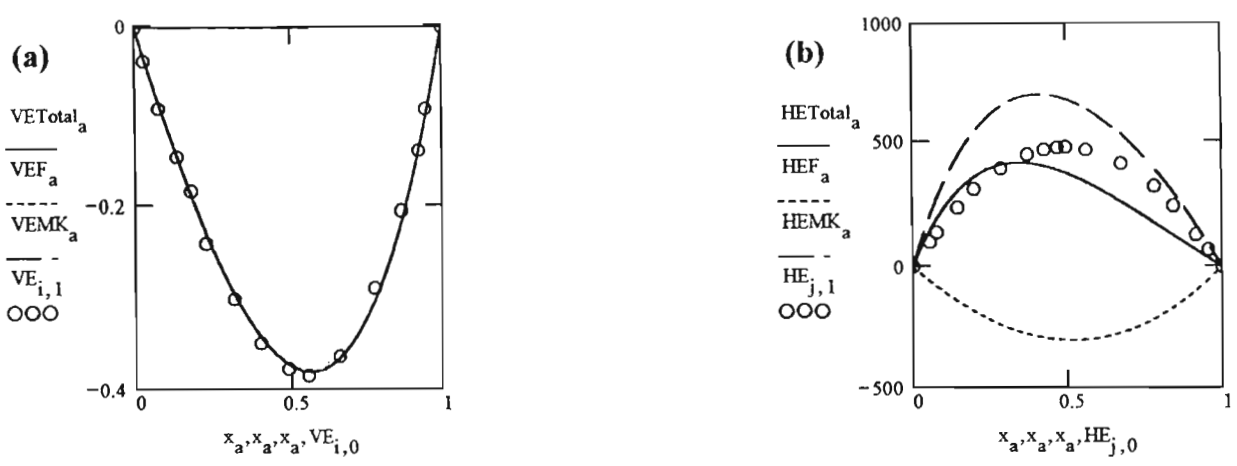
**Figure 7.15** Results of fitting the FBT model to excess molar volumes(a) and excess molar enthalpies(b) for mixtures of (benzonitrile + acetic acid) at  $T = 298.15 \text{ K}$  \_\_\_\_\_, from FBT theory; \_\_\_\_\_, chemical contribution; ..... , physical contribution;  $\circ$ , experimental data.



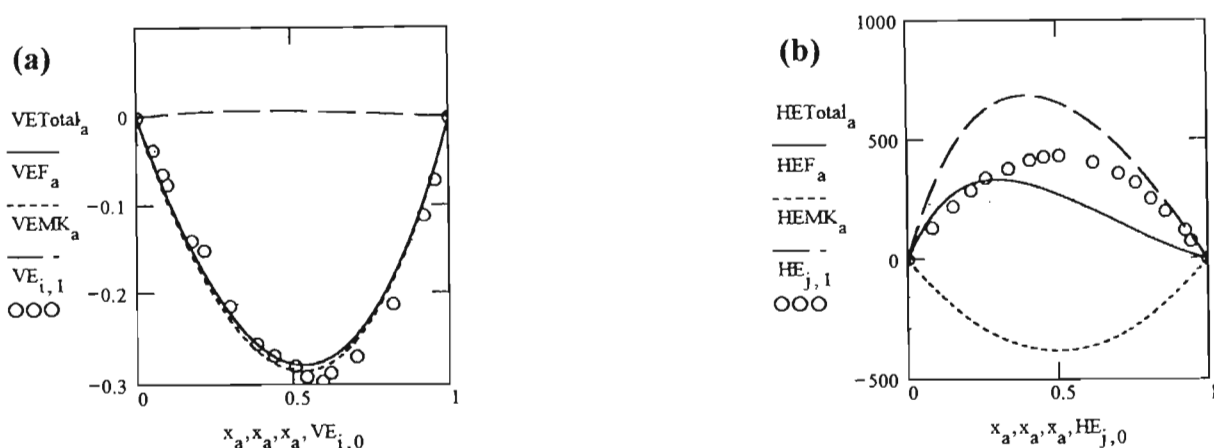
**Figure 7.16** Results of fitting the FBT model to excess molar volumes(a) and excess molar enthalpies(b) for mixtures of (benzonitrile + propanoic acid) at  $T=298.15 \text{ K}$  \_\_\_\_\_, from FBT theory; \_\_\_\_\_, chemical contribution; ..... , physical contribution;  $\circ$ , experimental data.



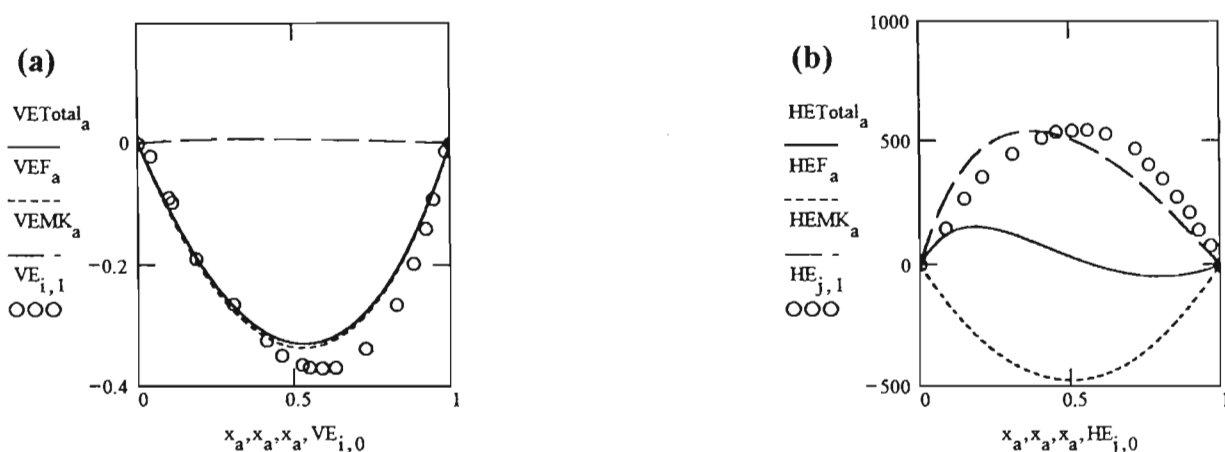
**Figure 7.17** Results of fitting the FBT model to excess molar volumes(a) and excess molar enthalpies(b) for mixtures of (benzonitrile + butanoic acid) at  $T=298.15$  K \_\_\_\_\_, from FBT theory; \_ \_ \_ \_ , chemical contribution; ....., physical contribution;  $\circ$ , experimental data.



**Figure 7.18** Results of fitting the FBT model to excess molar volumes(a) and excess molar enthalpies(b) for mixtures of (benzonitrile + 2-methylpropanoic acid) at  $T=298.15$  K \_\_\_\_\_, from FBT theory; \_ \_ \_ \_ , chemical contribution; ....., physical contribution;  $\circ$ , experimental data.



**Figure 7.19** Results of fitting the FBT model to excess molar volumes(a) and excess molar enthalpies(b) for mixtures of (benzonitrile + pentanoic acid) at  $T=298.15$  K \_\_\_\_\_, from FBT theory; \_\_\_\_\_, chemical contribution; \_\_\_\_\_, physical contribution;  $\circ$ , experimental data.



**Figure 7.20** Results of fitting the FBT model to excess molar volumes(a) and excess molar enthalpies(b) for mixtures of (benzonitrile + 3-methylbutanoic acid) at  $T=298.15$  K \_\_\_\_\_, from FBT theory; \_\_\_\_\_, chemical contribution; \_\_\_\_\_, physical contribution;  $\circ$ , experimental data.

The FBT model is able to fit the excess molar volumes for all the mixtures (benzonitrile + a carboxylic acid) investigated in this work, in both a qualitative as well as quantitative manner. However, in the case of the excess molar enthalpy, the precision of the fit decreases considerably as the chain length of the carboxylic acid increases.

In terms of the FBT model, the dominant contribution to the excess molar volumes for the mixtures (benzonitrile + a carboxylic acid) is the physical contribution which occurs mainly due to dipole-dipole as well as van der Waals type of interactions.

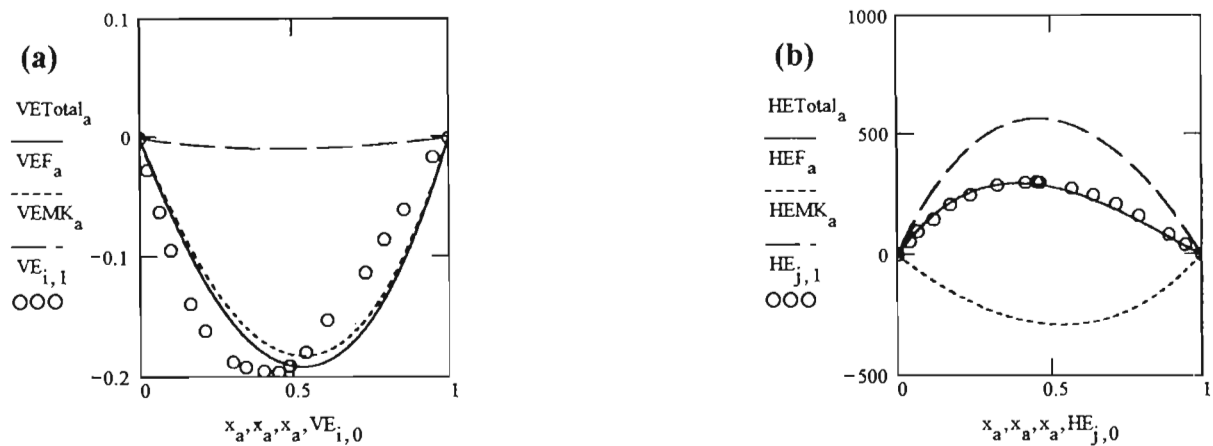
From Figures 7.15 - 7.20 it can be seen that for the excess molar enthalpy, the FBT model predicts the chemical contribution as the major contribution. This implies that hydrogen bonding dominates the excess molar enthalpy for the mixtures (benzonitrile + a carboxylic acid).

### 7.6.3 Application of the FBT model to the excess molar volumes and enthalpies for mixtures of (butanenitrile + a carboxylic acid) at T=298.15 K

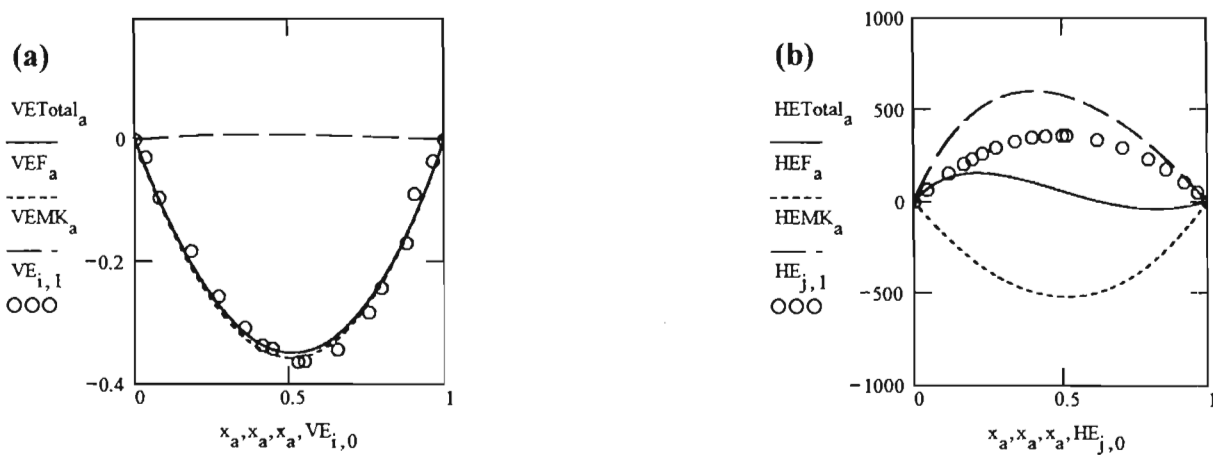
The Flory-Benson-Treszczanowicz model was fitted to the excess molar volumes and enthalpies for mixtures of (butanenitrile + acetic acid or propanoic acid or butanoic acid or 2-methylpropanoic acid or pentanoic acid or 3-methylbutanoic acid) at T = 298.15 K. The four adjustable parameters  $X_{AB}$ ,  $\Delta h^\circ$ ,  $\Delta v^\circ$  and  $\Delta s^\circ$  as well as the results of the correlation are illustrated in Table 7.8. The results are plotted in Figures 7.21 - 7.26

**Table 7.8** Correlation of the excess molar volumes and enthalpies for the systems : [butanenitrile(1) + a carboxylic acid(2)] at 298.15 K by means of the FBT model : values of interaction parameters and measures of deviations

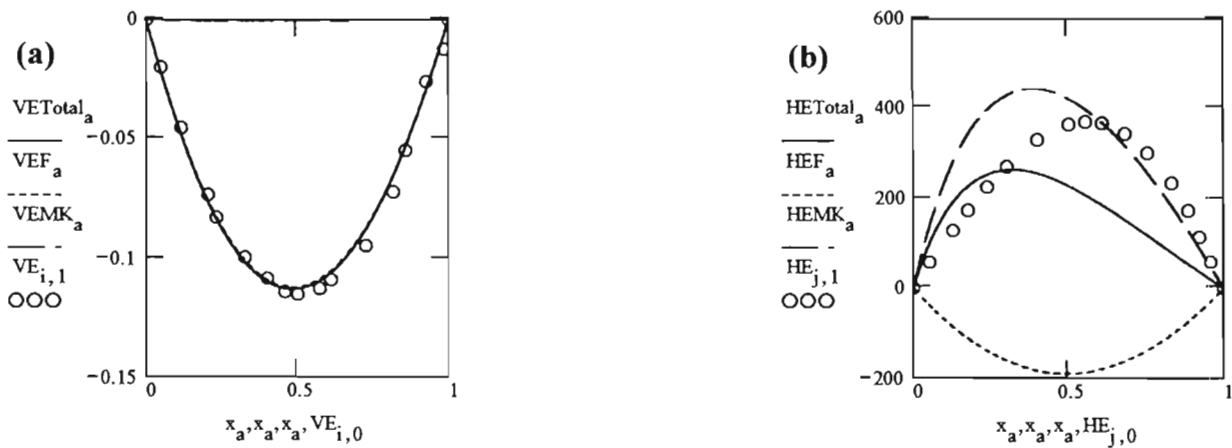
Component	$\frac{X_{AB}}{J \cdot cm^{-3}}$	$\frac{\Delta h^\circ}{kJ \cdot mol^{-1}}$	$\frac{\Delta v^\circ}{cm^3 \cdot mol^{-1}}$	$\frac{\Delta s^\circ}{J \cdot K^{-1}}$	$\frac{\delta H_m^E}{J \cdot mol^{-1}}$	$\frac{\delta V_m^E}{cm^3 \cdot mol^{-1}}$
Acetic acid	-21	-6.1	-0.1	-14	13	0.030
Propanoic acid	-16	-7.1	-0.16	-12	63	0.130
Butanoic acid	-10	-6.1	-0.01	-8.5	113	0.004
2-Methylpropanoic Acid	-12	-7.1	-0.1	-12	127	0.020
Pentanoic acid	-10	-7.1	-0.2	-10	166	0.022
3-Methylbutanoic acid	-14	-7.1	-0.2	-10	235	0.029



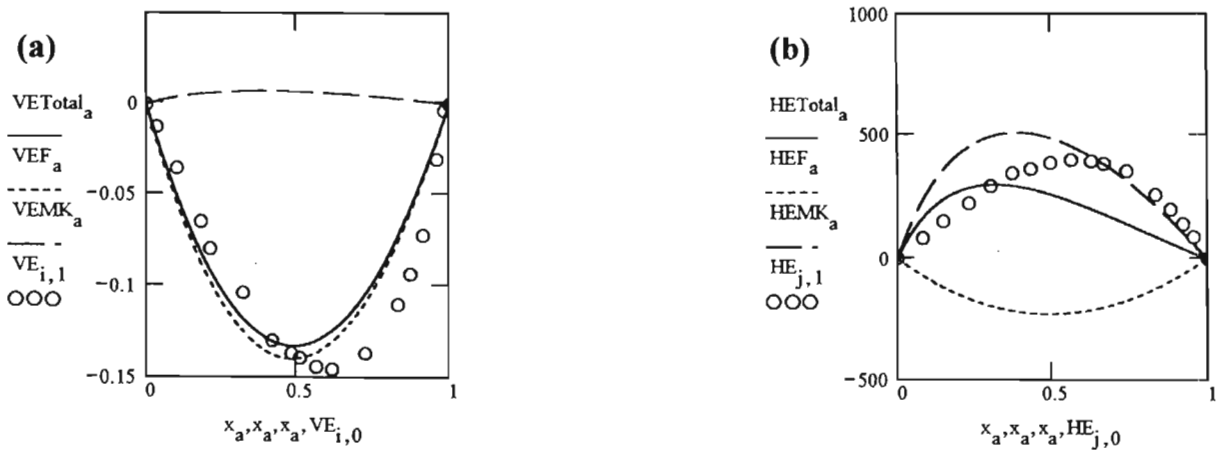
**Figure 7.21** Results of fitting the FBT model to excess molar volumes(a) and excess molar enthalpies(b) for mixtures of (butanenitrile + acetic acid) at  $T = 298.15\text{ K}$  \_\_\_\_\_, from FBT theory; \_\_\_\_\_, chemical contribution; ....., physical contribution; ○, experimental data.



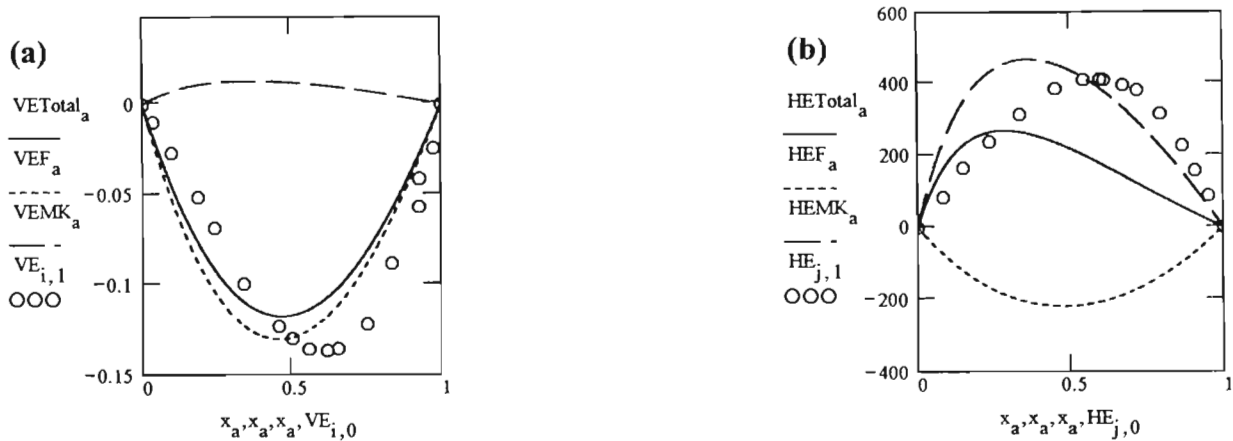
**Figure 7.22** Results of fitting the FBT model to excess molar volumes(a) and excess molar enthalpies(b) for mixtures of (butanenitrile + propanoic acid) at  $T = 298.15\text{ K}$  \_\_\_\_\_, from FBT theory; \_\_\_\_\_, chemical contribution; ....., physical contribution; ○, experimental data.



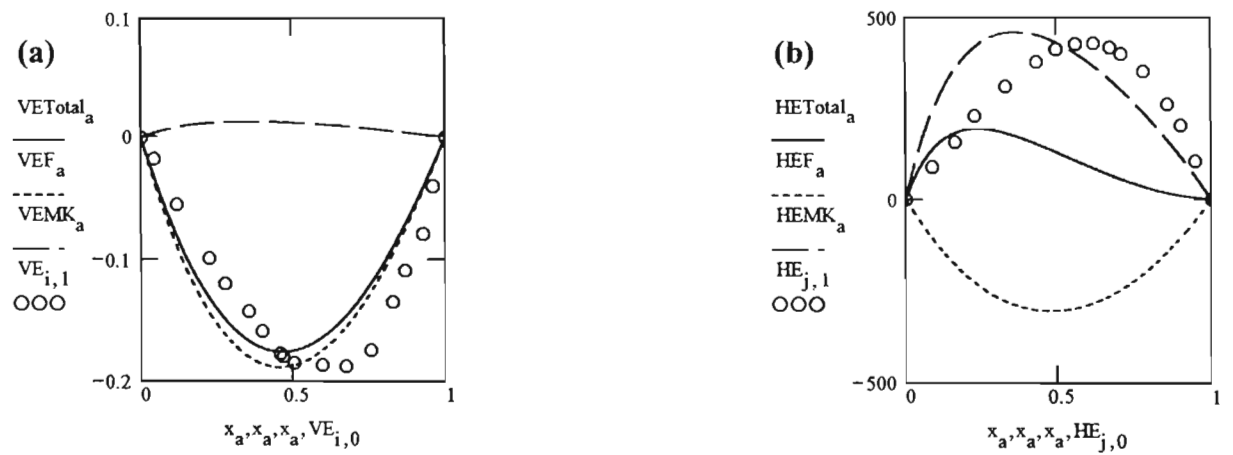
**Figure 7.23** Results of fitting the FBT model to excess molar volumes(a) and excess molar enthalpies(b) for mixtures of (butanenitrile + butanoic acid) at  $T=298.15$  K \_\_\_\_\_, from FBT theory; \_\_\_\_\_, chemical contribution; ....., physical contribution;  $\circ$ , experimental data.



**Figure 7.24** Results of fitting the FBT model to excess molar volumes(a) and excess molar enthalpies(b) for mixtures of (butanenitrile + 2-methylpropanoic acid) at  $T=298.15$  K \_\_\_\_\_, from FBT theory; \_\_\_\_\_, chemical contribution; ....., physical contribution;  $\circ$ , experimental data.



**Figure 7.25** Results of fitting the FBT model to excess molar volumes(a) and excess molar enthalpies(b) for mixtures of (butanenitrile + pentanoic acid) at  $T=298.15\text{ K}$  \_\_\_\_\_, from FBT theory; \_\_\_\_\_, chemical contribution; ....., physical contribution;  $\circ$ , experimental data.



**Figure 7.26** Results of fitting the FBT model to excess molar volumes (a) and excess molar enthalpies (b) for mixtures of (butanenitrile + 3-methylbutanoic acid) at  $T=298.15\text{ K}$  \_\_\_\_\_, from FBT theory; \_\_\_\_\_, chemical contribution; ....., physical contribution;  $\circ$ , experimental data.

The FBT model is able to simultaneously describe the excess molar volume and the excess molar enthalpy for the mixtures (butanenitrile + a carboxylic acid) in both a qualitative and quantitative manner in the case of the excess molar volumes. However, the standard deviation for the FBT correlation for excess molar enthalpy decreases progressively as the carbon chain length of the carboxylic acid increases. A similar effect is noted in the case of the excess molar enthalpy for (benzonitrile + a carboxylic acid).



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It is found that the physical term dominates the FBT model in the case of the excess molar volumes.

In the case of the excess molar enthalpy, the major contribution in terms of the FBT model is the chemical term. This is indicative of the strong hydrogen bonding which dominates the excess molar enthalpy for the mixtures (butanenitrile + a carboxylic acid).

## 7.7 APPLICATION OF THE NRTL AND UNIQUAC MODELS TO TERNARY LIQUID-LIQUID EQUILIBRIA

### 7.7.1 Ternary systems involving (acetonitrile + a carboxylic acid + heptane) at 298.15 K)

Thermodynamic models such as the non-random two liquid equation, NRTL (Renon and Pransnitz, 1968), and the universal quasichemical equations UNIQUAC (Abrams and Pransnitz, 1975), have been used to correlate the experimental tie - line data for the systems : (acetonitrile + acetic acid or propanoic acid or butanoic acid or 2-methylpropanoic acid or pentanoic acid or 3-methylbutanoic acid + heptane) at 298.15 K.

The equations and algorithms used in the calculation of the composition of the liquid phases follows the method used by Walas (1985). The data was correlated using a computer programme (Appendix 1) that minimized the objective function  $F(P)$ . The objective function used to minimize the difference between the experimental and calculated concentrations is defined as:

$$F(P) = \sum_{i=1}^n [x_{1i}'^{\text{exp}} - x_{1i}'^{\text{calc}}(P, T)]^2 + [x_{2i}'^{\text{exp}} - x_{2i}'^{\text{calc}}(P, T)]^2 + [x_{1i}''^{\text{exp}} - x_{1i}''^{\text{calc}}(P, T)]^2 + [x_{2i}''^{\text{exp}} - x_{2i}''^{\text{calc}}(P, T)]^2 \quad (7.85)$$

where  $P$  is the set of parameters vector,  $n$  is the number of experimental points,  $x_{1i}'^{\text{exp}}$ ,  $x_{2i}'^{\text{exp}}$  and  $x_{1i}'^{\text{cal}}$  (PT),  $x_{2i}'^{\text{cal}}$  are the experimental and calculated mole fractions of one phase, and  $x_{1i}''^{\text{exp}}$ ,  $x_{2i}''^{\text{exp}}$ , and  $x_{1i}''^{\text{cal}}$  (P,T),  $x_{2i}''^{\text{cal}}$  (P,T) are the experimental and calculated mole fractions of

the second phase. The pure component structural parameters  $r$  (volume parameter) and  $q$  (surface parameter) in the UNIQUAC equation were obtained from the tables of modified UNIFAC, published by Gmehling *et al.* (1993). The UNIQUAC surface area and volume parameters for all the components is given in Table 7.9.

**Table 7.9      Physical Properties of the Pure Components at 298.15 K; Molar Volumes,  $V_{mi}$ , Refractive Indices,  $n_D$ , Volume and Surface Parameters,  $R$  and  $Q$ .**

Component	$V_{mi}/\text{cm}^3 \cdot \text{mol}^{-1}{}^a$	$n_D$		$R^b$	$Q^b$
		exp	lit. <sup>a</sup>		
acetonitrile	52.87	1.3413	1.3416	1.870	1.724
acetic acid	57.53	1.3697	1.3698	2.202	2.072
propanoic acid	74.97	1.3846	1.3843	2.877	2.612
butanoic acid	92.43	1.3955	1.3958	3.551	3.152
2-methylpropanoic acid	93.44	1.3913	1.3917	3.550	3.148
pentanoic acid	109.29	1.4064	1.4060	4.226	3.692
3-methylbutanoic acid	110.54	1.4019	1.4022	4.225	3.688
benzonitrile	103.06	1.5260	1.5257	3.991	2.996
butanenitrile	87.87	1.3822	1.3820	3.219	2.804
heptane	147.47	1.3851	1.3852	5.174	4.396
cyclohexane	108.75	1.4237	1.4235	4.046	3.240
water	18.07	1.3325	1.3325	0.920	1.400

<sup>a</sup> Riddick *et al.* (1986). <sup>b</sup> Gmehling *et al.* (1993)

For the NRTL model the third randomness parameter  $\alpha_{ij}$  was set at a value of 0.2. The parameters calculated in this way,  $g_{ij} - g_{ji}$ ,  $g_{ji} - g_{ii}$  and  $\Delta u_{ij}$ ,  $\Delta u_{ji}$  for the NRTL and UNIQUAC, respectively are shown in Table 7.10. The model correlation parameters, together with the root mean square values are included in Table 7.10. The rms value defined below, can be taken as a measure of the precision of the correlations.

$$rms = \left( \sum_i \sum_\ell \sum_m [x_{i\ell m}^{\text{exp}} - x_{i\ell m}^{\text{cal}}]^2 / 6k \right)^{\frac{1}{2}} \quad (7.86)$$

where  $x$  is the mole fraction,  $k$  the number of tie-lines, and the subscripts  $i$ ,  $\ell$  and  $m$  designate the component, phase and tie-line respectively.

**Table 7.10** Values of the Parameters for the NRTL and UNIQUAC Equations, Determined from Ternary Liquid-Liquid Equilibria for the systems: Acetonitrile (1) + a Carboxylic Acid (2) + Heptane (3) as Well as the Calculated Root Mean Square Deviation, rms<sup>b</sup>.

component <i>i-j</i>	parameters(J·mol <sup>-1</sup> )			
	NRTL <sup>a</sup>		UNIQUAC	
	$g_{ij} - g_{jj}$	$g_{ji} - g_{ii}$	$\Delta u_{ij}$	$\Delta u_{ji}$
Acetonitrile (1) + Acetic Acid (2) + Heptane (3)				
	(0.003)		(0.227)	
1-2 2-1	-2360.27	6107.47	0.20	0.23
1-3 3-1	3606.27	15248.29	-0.10	0.03
2-3 3-2	7038.95	-707.69	-8.59	8.53
Acetonitrile (1) + Propanoic Acid (2) + Heptane (3)				
	(0.006)		(0.021)	
1-2 2-1	4693.46	11522.21	-338.94	40853.60
1-3 3-1	6928.49	6076.73	68.66	10939.72
2-3 3-2	916.90	9840.28	619.13	2510.25
Acetonitrile (1) + Butanoic Acid (2) + Heptane (3)				
	(0.019)		(0.242)	
1-2 2-1	66013.37	14504.09	-21.81	-97.54
1-3 3-1	4724.83	6077.16	98.28	78.39
2-3 3-2	4227.85	3160.78	-100.16	18.73
Acetonitrile (1) + 2-Methylpropanoic Acid (2) + Heptane (3)				
	(0.013)		(0.051)	
1-2 2-1	-4705.61	20825.59	-2859.04	-1391.75
1-3 3-1	6819.80	4903.75	1541.87	4593.31
2-3 3-2	-2445.64	8426.63	-309.47	-1549.41
Acetonitrile (1) + Pentanoic Acid (2) + Heptane (3)				
	(0.003)		(0.018)	
1-2 2-1	-43.94	8800.71	1628.90	21818.88
1-3 3-1	6537.71	7980.18	1864.77	40216.15
2-3 3-2	-2709.08	11811.35	-2317.15	12027.50

Acetonitrile (1) + 3-Methylbutanoic Acid (2) + Heptane (3)				
	(0.022)		(0.233)	
1-2 2-1	50216.71	24207.70	2.79	49.45
1-3 3-1	4604.56	5987.53	99.65	70.01
2-3 3-2	4781.79	4074.60	-224.95	-10.01

<sup>a</sup>Calculated with  $\alpha_{ij} = 0.2$ .

<sup>b</sup>The rms deviations are given in parenthesis

The NRTL model correlates the tie-line data for mixtures of (acetonitrile + acetic acid or propanoic acid or butanoic acid or 2-methylpropanoic acid or pentanoic acid or 3-methylpropanoic acid or + heptane) at T = 298.15 K to within 0.019 mole fraction, whilst the UNIQUAC model correlates the same data to within 0.242 mole fraction in the worst case. From Table 7.10 it is evident that the NRTL model provides a much better fit to the experimental data than the UNIQUAC model.

### 7.7.2 Ternary systems involving (acetonitrile + a carboxylic acid + cyclohexane) at 298.15 K

The NRTL (Renon and Prausnitz, 1968) and the UNIQUAC (Abrams and Prausnitz, 1975) models, have again been used to correlate the experimental data for the six ternary systems discussed here. The systems are (acetonitrile + acetic acid or propanoic acid or butanoic acid or 2-methylpropanoic acid or pentanoic acid or 3-methylbutanoic acid + cyclohexane). The equations and algorithms used in the calculation of the composition of the liquid phases follows the method used by Walas (1985). The objective function  $F(P)$  was used to minimize the differences between the experimental and calculated concentrations:

$$F(P) = \sum_{i=1}^n [x_{li}'^{\text{exp}} - x_{li}'^{\text{calc}}(P, T)]^2 + [x_{2i}'^{\text{exp}} - x_{2i}'^{\text{calc}}(P, T)]^2 + [x_{li}''^{\text{exp}} - x_{li}''^{\text{calc}}(P, T)]^2 + [x_{2i}''^{\text{exp}} - x_{2i}''^{\text{calc}}(P, T)]^2 \quad (7.85)$$

where  $P$  is the set of parameters vector,  $n$  is the number of experimental points,  $x_{li}'^{\text{exp}}$ ,  $x_{2i}'^{\text{exp}}$  and  $x_{li}'^{\text{cal}}(P, T)$ ,  $x_{2i}'^{\text{cal}}(P, T)$  are the experimental and calculated mole fractions of the second phase.

The pure component structural parameters  $R$  (volume parameter) and  $Q$  (surface parameter) in the UNIQUAC equation were obtained from the tables of Modified UNIFAC, published by Gmehling *et al.* (1993). The UNIQUAC, surface area and volume parameters for all the components is given in Table 7.9.

For the NRTL model, the third non-randomness parameter,  $\alpha_{ij}$  was set at a value of 0.3 for the systems (acetonitrile + propanoic acid or butanoic acid + cyclohexane). For the other four system,  $\alpha_{12} = 0.2$  provided the best fit. The calculated binary parameters for the NRTL and UNIQUAC equations, together with their respective calculated root mean square (rms) deviations are given in Table 7.11. The rms values which can be taken as a measure of the precision of the correlations:

$$rms = \left( \sum_i \sum_\ell \sum_m [x_{ilm}^{\text{exp}} - x_{ilm}^{\text{calc}}]^2 / 6k \right)^{\frac{1}{2}} \quad (7.86)$$

where  $x$  is the mole fraction,  $k$  the number of tie-lines, the subscripts  $i$ ,  $\ell$ , and  $m$  denote the component, phase and tie-line respectively.

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As can be observed from Table 7.11, the correlation obtained with the NRTL model is substantially better than that obtained with the UNIQUAC model : the average root mean square deviation phase composition error was 0.007 for NRTL as compared to 0.194 for UNIQUAC.

**Table 7.11** Values of the Parameters for the NRTL and UNIQUAC Equations, Determined from Ternary Liquid-Liquid Equilibria for the systems Acetonitrile (1) + a Carboxylic Acid (2) + Cyclohexane (3) as Well as the Calculated Root Mean Square Deviation, rms<sup>c</sup>.

component <i>i-j</i>	parameters/(J.mol <sup>-1</sup> )			
	NRTL		UNIQUAC	
	$g_{ij} - g_{jj}$	$g_{ji} - g_{ii}$	$\Delta u_{ij}$	$\Delta u_{ji}$
Acetonitrile (1) + Acetic Acid (2) + Cyclohexane (3) (0.008) <sup>a</sup> (0.136)				
1-2 2-1	-3794.08	11039.45	-2506.47	-517.62
1-3 3-1	3382.44	5928.67	-1158.91	612.19
2-3 3-2	7785.07	-751.21	34.47	809.88
Acetonitrile (1) + Propanoic Acid (2) + Cyclohexane (3) (0.003) <sup>b</sup> (0.201)				
1-2 2-1	4335.66	8673.43	-9.96	-21.68
1-3 3-1	5330.43	5377.18	25.13	31.54
2-3 3-2	1130.07	9535.61	9.84	53.29
Acetonitrile (1) + Butanoic Acid (2) + Cyclohexane (3) (0.009) <sup>b</sup> (0.214)				
1-2 2-1	4652.39	25803.66	-5.30	-5.69
1-3 3-1	4700.05	5870.98	25.22	25.21
2-3 3-2	-1376.89	11944.24	25.20	8.36
Acetonitrile (1) + 2-Methylpropanoic Acid (2) + Cyclohexane (3) (0.003) <sup>a</sup> (0.219)				
1-2 2-1	4305.09	-4783.49	-13.95	-6.03
1-3 3-1	4834.16	4904.67	218.54	12.05
2-3 3-2	-3316.72	8270.11	9.76	11.43
Acetonitrile (1) + Pentanoic Acid (2) + Cyclohexane (3) (0.013) <sup>a</sup> (0.196)				
1-2 2-1	11030.55	-8127.75	-3.57	-2.78
1-3 3-1	5838.17	3905.44	2.70	27.47
2-3 3-2	-4886.81	7979.35	6.25	3.82



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Acetonitrile (1) + 3-Methylbutanoic Acid (2) + Cyclohexane (3)				
	(0.008) <sup>b</sup>		(0.198)	
1-2 2-1	9435.54	-6564.35	3.32	-13.73
1-3 3-1	4855.41	6894.60	-26.36	5.04
2-3 3-2	57961.02	5014.84	7.59	33.04

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<sup>a</sup>Calculated with  $\alpha_{ij} = 0.2$ .

<sup>b</sup>Calculated with  $\alpha_{ij} = 0.3$ .

<sup>c</sup>The rms deviations are given in parenthesis

### 7.7.3 Ternary systems involving (benzonitrile + a carboxylic acid + water) at 298.15 K

The NRTL (Renon and Prausnitz, 1968) and UNIQUAC (Abrams and Prausnitz, 1975) thermodynamic models have been used to correlate the experimental data for the following six ternary systems: (benzonitrile + acetic acid or propanoic acid or butanoic acid or 2-methylpropanoic acid or pentanoic acid or 3-methylbutanoic acid + water) at 298.15 K. The equations and algorithms used in the calculation of the equilibrium composition of liquid phase follows the method used by Walas (1985). The data was correlated using a computer program (Appendix 1) that minimized the objective function  $F(P)$ . The objective function  $F(P)$  is given by:

$$F(P) = \sum_{i=1}^n [x_{1i}'^{\text{exp}} - x_{1i}'^{\text{calc}}(P, T)]^2 + [x_{2i}'^{\text{exp}} - x_{2i}'^{\text{calc}}(P, T)]^2 + [x_{1i}''^{\text{exp}} - x_{1i}''^{\text{calc}}(P, T)]^2 + [x_{2i}''^{\text{exp}} - x_{2i}''^{\text{calc}}(P, T)]^2 \quad (7.85)$$

where  $P$  is the set of parameters vector,  $n$  is the number of experimental points,  $x_{1i}'^{\text{exp}}$ ,  $x_{2i}'^{\text{exp}}$  and  $x_{1i}'^{\text{cal}}$  ( $P, T$ ),  $x_{2i}'^{\text{cal}}$  ( $P, T$ ) are the experimental and calculated mole fractions of one phase, and,  $x_{1i}''^{\text{exp}}$ ,  $x_{2i}''^{\text{exp}}$  and  $x_{1i}''^{\text{cal}}$  ( $P, T$ ),  $x_{2i}''^{\text{cal}}$  ( $P, T$ ) are the experimental and calculated mole fractions of the second phase.

The pure component structural parameters  $R$  (volume parameter) and  $Q$  (Surface parameter) in the UNIQUAC equation were obtained from the tables of modified UNIFAC, published by Gmehling *et al.* (1993). The UNIQUAC surface area and volume parameters for all the components is given in Table 7.9.

The third non-randomness parameter  $\alpha_{ij}$ , with respect to the NRTL model was set at 0.2, 0.3 and 0.4 for the systems: (benzonitrile + acetic acid or propanoic acid or pentanoic acid + water), (benzonitrile + butanoic acid or 2-methylpropanoic acid + water) and (benzonitrile + 3-methylbutanoic acid + water) respectively. The binary parameters  $g_{ij}$  -  $g_{ji}$ ,  $g_{ji}$  -  $g_{ii}$  and  $\Delta u_{ij}$ ,  $\Delta u_{ji}$ , together with the corresponding rms values for the NRTL and UNIQUAC models are respectively shown in Table 7.12. The rms value defined below, can be taken as a measure of the precision of the correlations:

$$rms = (\sum_i \sum_\ell \sum_m [x_{ilm}^{exp} - x_{ilm}^{calc}]^2 / 6k)^{\frac{1}{2}}$$

where  $x$  is the mole fraction,  $k$  the number of tie-lines, and the subscripts  $i$ ,  $\ell$ , and  $m$  designate the component, phase and tie-line respectively.

The NRTL model correlates the tie-line data for the mixtures of (benzonitrile + acetic acid or propanoic acid or butanoic acid or 2-methylpropanoic acid or pentanoic acid or 3-methylbutanoic acid + water) at  $T = 298.15$  K to within 0.016 mole fraction, whilst the UNIQUAC model correlates the same data to within 0.386 mole fraction. It is evident from Table 7.12 that the correlation obtained with the NRTL model is significantly better than that obtained with the UNIQUAC model: the average root mean square deviation phase composition error was 0.005 for NRTL as compared to 0.343 for UNIQUAC.

**Table 7.12** Values of the Parameters for the NRTL and UNIQUAC Equations, Determined from Ternary Liquid-Liquid Equilibria for the systems Benzonitrile (1) + a Carboxylic Acid (2) + Water (3) as Well as the Calculated Root Mean Square Deviation, rms<sup>d</sup>.

component <i>i-j</i>	parameters/(J.mol <sup>-1</sup> )			
	NRTL		UNIQUAC	
	$g_{ij} - g_{jj}$	$g_{ji} - g_{ii}$	$\Delta u_{ij}$	$\Delta u_{ji}$
Benzonitrile (1) + Acetic Acid (2) + Water (3)				
	(0.004) <sup>a</sup>		(0.398)	
1-2 2-1	-1705.57	964.02	438.67	30283.78
1-3 3-1	3270.31	-14218.41	-3.98	1294.84
2-3 3-2	-5614.85	-10757.43	-5813.13	507.28
Benzonitrile (1) + Propanoic Acid (2) + Water (3)				
	(0.016) <sup>a</sup>		(0.368)	
1-2 2-1	-6999.29	12526.14	-0.14	0.02
1-3 3-1	3325.53	5863.67	-0.01	0.17
2-3 3-2	-1921.07	6199.22	0.47	0.41
Benzonitrile (1) + Butanoic Acid (2) + Water (3)				
	(0.008) <sup>b</sup>		(0.288)	
1-2 2-1	771.27	-3087.68	0.19	0.18
1-3 3-1	6045.69	8464.33	0.17	0.02
2-3 3-2	4102.52	3270.97	2.09	-0.95
Benzonitrile (1) + 2-Methylpropanoic Acid (2) + Water (3)				
	(0.001) <sup>b</sup>		(0.389)	
1-2 2-1	-2647.82	1683.40	0.03	0.20
1-3 3-1	5784.46	13424.35	0.16	0.02
2-3 3-2	-619.65	5990.99	0.70	0.45
Benzonitrile (1) + Pentanoic Acid (2) + Water (3)				
	(0.013) <sup>a</sup>		(0.387)	
1-2 2-1	11030.55	-8127.75	-0.08	-0.41
1-3 3-1	5838.17	3905.44	0.19	0.35
2-3 3-2	-4886.81	7979.35	0.36	0.02

Benzonitrile (1) + 3-Methylbutanoic Acid (2) + Water (3)				
	(0.008) <sup>c</sup>		(0.383)	
1-2 2-1	9435.54	-6564.35	-0.28	-0.27
1-3 3-1	4855.41	6894.60	-0.21	0.06
2-3 3-2	57961.02	5014.84	0.15	-0.08

<sup>a</sup>Calculated with  $\alpha_{ij} = 0.2$

<sup>b</sup>Calculated with  $\alpha_{ij} = 0.3$

<sup>c</sup>Calculated with  $\alpha_{ij} = 0.4$

<sup>d</sup>The rms deviations are given in parenthesis

#### 7.7.4 Ternary systems involving (butanenitrile + a carboxylic acid + water) at 298.15K

The NRTL (Renon and Prausnitz, 1968) and the UNIQUAC (Abrams and Prausnitz, 1975) models have been used to correlate the experimental data for the six ternary systems viz. (butanenitrile + acetic acid or propanoic acid or butanoic acid or 2-methylpropanoic acid or pentanoic acid or 3-methylbutanoic acid + water. The equations and algorithms used in the calculation of the composition of the liquid phases follows the method used by Walas (1985). The objective function  $F(P)$  used is identical to that described in Section 7.6.1 and given by equation (7.85).

The pure component structural parameters  $R$  (volume parameter) and  $Q$  (surface parameter) in the UNIQUAC equation were obtained from the tables of Modified UNIFAC, published by Gmehling *et al* (1993). The UNIQUAC surface area and volume parameters for all the components is given in Table 7.9.

For the NRTL model the third non-randomness parameter  $x_{ij}$  was set at a value of 0.2, 0.3 and 0.7 for the systems : (butanenitrile + propanoic acid or butanoic acid + water), (butanenitrile + acetic acid or 2-methylpropanoic acid or pentanoic acid + water) and (butanenitrile + 3-methylbutanoic acid + water) respectively. The binary interaction parameters  $g_{ij} - g_{jj}$ ,  $g_{ji} - g_{ii}$  for the NRTL model, and  $\Delta u_{ij}$ ,  $\Delta u_{ji}$  for the UNIQUAC model together with their corresponding rms values are shown in Table 7.13. The rms value defined below, can be taken as a measure of the precision of the correlations:

$$rms = \left( \sum_i \sum_l \sum_m [x_{ilm}^{exp} - x_{ilm}^{calc}]^2 / 6k \right)^{\frac{1}{2}} \quad (7.86)$$

where  $x$  is the mole fraction,  $k$  the number of tie-lines and the subscript  $i$ ,  $\ell$ , and  $m$  denote the component, phase and tie-line, respectively.

The NRTL model correlates the tie-line data for mixtures of (butanenitrile + acetic acid or propanoic acid or butanoic acid or 2-methylpropanoic acid or pentanoic acid or 3-methylbutanoic acid + water) at  $T = 298.15$  K to within 0.002 mole fraction in the best case and 0.035 mole fraction in the worst case. The same experimental tie-line data correlated by

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the UNIQUAC model yields a best fit of 0.202 mole fraction, and worst case of 0.343 mole fraction. As can be observed from Table 7.13, the correlation obtained with the NRTL model is significantly better than that obtained with the UNIQUAC model : the average root mean square deviation phase composition error was 0.019 for NRTL as compared to 0.284 for UNIQUAC.

**Table 7.13** Values of the Parameters for the NRTL and UNIQUAC Equations, Determined from Ternary Liquid-Liquid Equilibria for the systems Butanenitrile (1) + a Carboxylic Acid (2) + Water (3) as Well as the Calculated Root Mean Square Deviation, rms<sup>d</sup>.

component <i>i-j</i>	parameters/(J·mol <sup>-1</sup> )			
	NRTL		UNIQUAC	
	$g_{ij} - g_{ji}$	$g_{ji} - g_{ii}$	$\Delta u_{ij}$	$\Delta u_{ji}$
Butanenitrile (1) + Acetic Acid (2) + Water (3) (0.005) <sup>b</sup> (0.309)				
1-2 2-1	-11496.76	-4989.76	-253.22	2514.31
1-3 3-1	3002.82	12995.88	1752.66	653.24
2-3 3-2	1898.29	-10133.30	443.27	-3567.83
Butanenitrile (1) + Propanoic Acid (2) + Water (3) (0.003) <sup>a</sup> (0.202)				
1-2 2-1	-13140.99	4741.70	-3375.08	4931.77
1-3 3-1	1845.97	11861.74	6473.98	3597.85
2-3 3-2	-6343.77	4755.57	1187.91	1700.63
Butanenitrile (1) + Butanoic Acid (2) + Water (3) (0.035) <sup>a</sup> (0.312)				
1-2 2-1	-3897.86	-1311.74	-2997.74	-181.14
1-3 3-1	2409.04	3557.25	1346.85	1027.53
2-3 3-2	-2561.32	4941.43	-562.41	1134.26
Butanenitrile (1) + 2-Methylpropanoic Acid (2) + Water (3) (0.015) <sup>b</sup> (0.276)				
1-2 2-1	-3857.25	227.35	-2868.95	-70.69
1-3 3-1	3552.27	5874.44	1058.82	1249.86
2-3 3-2	-1388.06	3705.97	-334.71	693.24
Butanenitrile (1) + Pentanoic Acid (2) + Water (3) (0.002) <sup>b</sup> (0.343)				
1-2 2-1	3854.86	3388.49	-3584.58	84.36
1-3 3-1	4035.78	11466.06	1090.62	892.71
2-3 3-2	-812.59	13617.87	217.19	1241.60



Butanenitrile (1) + 3-Methylbutanoic Acid (2) + Water (3)				
	(0.029) <sup>c</sup>		(0.261)	
1-2 2-1	35369.09	1500.52	-5270.05	-1235.69
1-3 3-1	4702.11	5555.17	1088.43	1139.58
2-3 3-2	3279.90	3774.56	114.05	3217.57

<sup>a</sup>Calculated with  $\alpha_{ij} = 0.2$

<sup>b</sup>Calculated with  $\alpha_{ij} = 0.3$

<sup>c</sup>Calculated with  $\alpha_{ij} = 0.7$

<sup>d</sup>The rms deviations are given in parenthesis

## CHAPTER 8

### CONCLUSIONS

In this chapter, the experimental work presented in Chapter 2, Chapter 3, Chapter 5 and Chapter 7 is summarized.

#### 8.1 CHAPTER 2 : EXCESS MOLAR VOLUMES

In chapter 2, the excess molar volumes for 18 binary mixtures have been determined. The systems are:

- (a) (acetonitrile + acetic acid or propanoic acid or butanoic acid or 2-methylpropanoic acid or pentanoic acid or 3-methylbutanoic acid).
- (b) (butanenitrile + acetic acid or propanoic acid or butanoic acid or 2-methylpropanoic acid or pentanoic acid or 3-methylbutanoic acid).
- (c) (benzonitrile + acetic acid or propanoic acid or butanoic acid or 2-methylpropanoic acid or pentanoic acid or 3-methylbutanoic acid).

##### 8.1.1 Excess molar volumes for mixtures of (acetonitrile + a carboxylic acid)

Of the six systems studied under the binary system (acetonitrile + a carboxylic acid),  $V_m^E$  results for the systems (acetonitrile + acetic acid or propanoic acid or 2-methylpropanoic acid) have previously been reported by Lark and Banipal (1985). In all cases the results obtained in this study are within  $0.005 \text{ cm}^3 \cdot \text{mol}^{-1}$  of their values.

The excess molar volumes for all six systems are plotted in Figure 2.10. The results are negative for all six systems over the entire composition range at 298.15 K. The  $V_m^E$  minima range from  $-0.4930 \text{ cm}^3 \cdot \text{mol}^{-1}$  for (acetonitrile + propanoic acid) mixtures to  $-0.3019 \text{ cm}^3 \cdot \text{mol}^{-1}$  for (acetonitrile + 2-methylpropanoic acid) mixtures, and have minima mole fraction  $x_1$  (acetonitrile) which lie between  $x_1 = -0.493 \text{ cm}^3 \cdot \text{mol}^{-1}$  and  $-0.292 \text{ cm}^3 \cdot \text{mol}^{-1}$ .

The observed results for  $V_m^E$  may be explained as follows. The acids in pure form exist mainly as dimers (Affsprung *et.al*, 1968). The following four-step equilibria accompanies the mixing process (Lark and Banipal, 1985):

- i)  $D - M \rightarrow D + M$
- ii)  $D \rightarrow 2 M$
- iii)  $\text{Acetonitrile-Acetonitrile} \rightarrow \text{Acetonitrile} + \text{Acetonitrile}$
- iv)  $M + \text{Acetonitrile} \rightarrow M\text{-Acetonitrile}$

where D and M denote a dimer and monomer of the carboxylic acid respectively. The first process is most likely accompanied by a volume increase in the right direction, the second is isochoric, ie., the volume of the dimer is assumed to be equal to twice the volume of the monomer (Affsprung *et al.*, 1968). The dissociation of acetonitrile in the third step suggests a volume increase. The fourth step involving the association of acetonitrile with the acid is most likely accompanied by a contraction in volume. The addition of acetonitrile to any one of the acids first creates monomers by the first two steps resulting in expansion, the third step also involves expansion, followed by strong heteromolecular dipole-dipole interactions resulting in contraction. The overall effect is one of negative volume change ie. a negative  $V_m^E$ . These results may be compared with the mixing of (acetonitrile + methanol) reported by Cibulka *et al.* (1984) as well as for (acetonitrile + 1,1 dimethylketone) reported by Lark and Palta (1979), which also result in a negative  $V_m^E$ . It is possible that these results all involve the common effect of the formation of a strong dipole-dipole association which outweighs the positive effects of the dissociation of the two species on mixing.

However from the nature of the experimental  $V_{m, \min}^E$  results obtained, it is also evident that in addition to the proposed four- step mechanism, packing effects are also possible. Free-volume effects which are primarily due to the difference in size between the components, linked to packing effects also make a significant contribution to the negative excess molar volumes.

It is found that the position of the minima for  $V_m^E$  (acetonitrile + acetic acid) shifts progressively to the acetonitrile-rich region of the mole fraction scale as the methylation of acetic acid increases. This could be explained by the increase in both the dimerization constants as well as the increasing steric hindrance caused by the additional methyl groups.

The increased dimerization constants should reduce the number of available (D - M) trimers and accordingly positive contribution to the overall  $V_m^E$  is diminished further. This is further supported by the findings of Cibulka *et al.* (1984) who have shown that for binary systems containing alkanol and acetonitrile, steric hindrance plays an important part with the result that  $V^E$  increases in the order:  $V^E$  (acetonitrile + normal alkanol) <  $V^E$  (acetonitrile + branched alkanol) <  $V^E$  (acetonitrile + secondary alkanol).

### 8.1.2 Excess molar volumes for mixtures of (butanenitrile + a carboxylic acid)

Excess molar volumes have been determined for the following binary mixtures: (butanenitrile + acetic acid or propanoic acid or butanoic acid or 2-methylpropanoic acid or pentanoic acid or 3-methylbutanoic acid) at 298.15 K. Excess molar values for none of the above mixtures have been previously reported in the literature.

The excess molar volumes for all the above systems are plotted in Figure 2.11. The results are again negative for all the systems over the entire composition range at 298.15 K. The excess molar volumes are most negative in the case of propanoic acid ( $< -0.4 \text{ cm}^3 \cdot \text{mol}^{-1}$ ) and the magnitude decreases in the following order : propanoic acid > acetic acid  $\sim$  3-methylbutanoic acid > 2-methylpropanoic acid > pentanoic acid > butanoic acid.

The negative excess molar volumes is an indication of the fairly strong association of the butanenitrile and carboxylic acid molecules through strong dipole-dipole interaction of the CN group, and to a lesser effect hydrogen bonding via the OH group.

The four- step equilibria (Section 8.1.1) proposed by Lark and Banipal may again be used to explain the observed  $V_m^E$  results for the strongly polar (butanenitrile + carboxylic acid) mixtures.

From the experimental  $V_m^E$  results obtained it is also possible that in addition to the proposed four-step mechanism, packing effects are also possible. Unfortunately it is not possible to determine whether packing effects produce an expansion or contraction. From the related  $H_m^E$  results obtained it appears that the first three steps of the proposed four-step mechanism are the main contributors. This suggests that packing effects may play an important part in the

excess molar volumes for mixtures of (butanenitrile + a carboxylic acid)

It is again found that the position of the minima for  $V_m^E$  (butanenitrile + acetic acid) shifts slowly to the butanenitrile - rich region of the mole fraction scale as the methylation of acetic acid increases. This could possibly be explained by the increase in both the dimerization constants as well as the increasing steric hindrance caused by the additional methyl groups and the resultant decrease in the association between butanenitrile and carboxylic acid. Alternatively, this effect could be due to the free-volume effects, which result primarily from the difference in the size between the components of the mixtures. The increasing size differences lead to altered dipole-dipole maxima interactions which progressively increase towards the butanenitrile mole-fraction scale, as the methylation of acetic acid increases. A similar trend is observed by Pal and Sharma (1998) in their study of mixtures of alkanols with polyethers.

### 8.1.3 Excess molar volumes for mixtures of (benzonitrile + a carboxylic acid)

Excess molar volumes for six binary systems, viz., (benzonitrile + acetic acid or propanoic acid or butanoic acid or 2-methylpropanoic acid or pentanoic acid or 3-methylbutanoic acid) at 298.15 K have been determined. Data for all of the above mixtures contribute new information to the literature.

The excess molar volumes for all six systems are negative. The excess molar volumes are most negative in the case of 2-methylpropanoic acid ( $< -0.4 \text{ cm}^3 \cdot \text{mol}^{-1}$ ) and the magnitude decreases in the following order: 2-methylpropanoic acid > 3-methylbutanoic acid > butanoic acid > propanoic acid > pentanoic acid > acetic acid.

From the experimental  $V_m^E$  results obtained, it is also likely that volume change contributions due to both packing effects as well as intermolecular effects are responsible for the above trend in the excess molar volumes. It is not possible to determine whether the packing effect produces an expansion or contraction.  $H_m^E$  results obtained suggest that the first three steps of the proposed 4-step mechanism are responsible for the endothermic results obtained for mixtures of (benzonitrile + a carboxylic acid). This lends further support to the packing effect being an important factor in the analysis of the  $V_m^E$  results obtained. The negative excess

molar volumes also indicates association between the benzonitrile and carboxylic acid molecules through strong dipole-dipole interaction of the CN group as well as hydrogen bonding through the OH group.

It is found that the position of the minima for  $V_m^E$  (benzonitrile + acetic acid) shifts progressively to the benzonitrile-rich region of the mole fraction scale as the methylation of acetic acid increases. This could be explained by the increase in both the dimerization constants as well as the increasing steric hindrance caused by the additional methyl groups. The increased dimerization constants should reduce the number of available (D - M) trimers and accordingly positive contribution to the overall  $V_m^E$  is diminished further. This is further supported by the findings of Cibulka *et al.* (1984) who have shown that for binary systems containing alkanol and acetonitrile, steric hindrance is an important factor and have found that  $V^E$  increases in the order:  $V^E$  (acetonitrile + normal alkanol) <  $V^E$  (acetonitrile + branched alkanol) <  $V^E$  (acetonitrile + secondary alkanol).

The excess molar volumes for mixtures of (a nitrile compound + a carboxylic acid) with respect to the nitrile compound increase in the order : butanenitrile < benzonitrile < acetonitrile. It is found that the association and packing effects for the smaller acetonitrile molecules is more favourable than for the larger aromatic benzonitrile molecule. The longer chained butanenitrile molecule shows the lowest  $V_m^E$  values, and this could possibly be due to bulkiness of the molecule which impacts poorly on the packing and intermolecular forces at play in the (butanenitrile-acid) mixtures.

## 8.2 CHAPTER 3 : EXCESS MOLAR ENTHALPIES

In Chapter 3, the excess molar enthalpies for 18 binary mixtures have been determined. The systems are:

- (a) (acetonitrile + acetic acid or propanoic acid or butanoic acid or 2-methylpropanoic acid or pentanoic acid or 3-methylbutanoic acid).
- (b) (butanenitrile + acetic acid or propanoic acid or butanoic acid or 2-methylpropanoic acid or pentanoic acid or 3-methylbutanoic acid).

- (c) (benzonitrile + acetic acid or propanoic acid or butanoic acid or 2-methylpropanoic acid or pentanoic acid or 3-methylbutanoic acid)

### 8.2.1 Excess molar enthalpies for mixtures of (acetonitrile + a carboxylic acid)

The  $H_m^E$  values for the six mixtures (acetonitrile + acetic acid or propanoic acid or butanoic acid or 2-methylpropanoic acid or pentanoic acid or 3-methylbutanoic acid) are positive over the whole composition range and the magnitude decreases in the order: 2-methylpropanoic acid > 3 methylbutanoic acid ~ pentanoic acid > butanoic acid ~ propanoic acid > acetic acid.

It is most likely that the following four-step equilibria proposed by Lark and Banipal (1985) accompanies the mixing process:

- i)  $D - M \rightarrow D + M$
- ii)  $D \rightarrow 2 M$
- iii)  $\text{Acetonitrile-Acetonitrile} \rightarrow \text{Acetonitrile} + \text{Acetonitrile}$
- iv)  $M + \text{Acetonitrile} \rightarrow M\text{-Acetonitrile}$

where D and M represent a dimer and monomer of the carboxylic acid respectively. As the overall  $H_m^E$  values are positive, it appears that steps(i + ii + iii) outweigh step iv. The excess molar enthalpies range from 304 J·mol<sup>-1</sup> for acetic acid to 926 J·mol<sup>-1</sup> for 2-methylpropanoic acid. This indicates that the positive endothermic effects due to the dissociation of acetonitrile, and the dissociation of the acids, are the dominant effects in these mixtures.

The results of this work indicate in general that the longer the alkyl group of the carboxylic acid, the weaker is the interaction with acetonitrile, and it appears as though the long alkyl groups shield the carbonyl oxygen atom of the carboxylic acid from interaction.

### 8.2.2 Excess molar enthalpies for mixtures of (a butanenitrile + a carboxylic acid)

In this work new excess molar enthalpy data have been obtained for the following six binary mixtures (butanenitrile + acetic acid or propanoic acid or butanoic acid or 2-methylpropanoic acid or pentanoic acid or 3-methylbutanoic acid) at 298.15 K.

The  $H_m^E$  values for the mixtures under investigation are positive over the whole composition range and the magnitude decreases in the order : 3-methylbutanoic acid > butanoic acid > pentanoic acid > 2-methylpropanoic acid > butanoic acid > propanoic acid > acetic acid.

Butanenitrile is a strong polar solvent whilst the carboxylic acids although strongly polar, exist mainly as dimers in pure form. It is most likely that the same four-step mechanism proposed by Lark and Banipal (1985) as given in Section 8.1.1 also applies to the mixing process of (butanenitrile + a carboxylic acid). In this mechanism butanenitrile is now substituted for acetonitrile. The overall magnitude of  $H_{m,max}^E \{CH_3(CH_2)_2 CN + RCOOH\}$  is positive, and is most probably due to the breakdown of the butanenitrile self-association (an endothermic effect), the breakdown of the carboxylic acid (dimers) self association (an endothermic effect), and the exothermic effect of the (butanenitrile-carboxylic acid) polar-polar association. Again it appears that the collective endothermic effects of the first three steps of the mechanism outweigh the exothermic influence of the fourth step.

Comparative  $H_{m,max}^E$  values for (butanenitrile + heptane) by McLure and Rodriguez (1982), and (acetic acid + heptane) by Nagata *et al.* (1975), obtained in the literature are found to be positive and  $< 1350 \text{ J}\cdot\text{mol}^{-1}$  and  $< 925 \text{ J}\cdot\text{mol}^{-1}$  respectively, indicating that there is a dissociation effect for both the nitrile and the acid. The relatively small  $H_m^E$  values obtained in this work ( $< 450 \text{ J}\cdot\text{mol}^{-1}$ ) suggest that a significant amount of cross-association takes place between the butanenitrile and carboxylic acid components.

The results of this work again indicate in general that the longer the alkyl groups of the carboxylic acid, the weaker is the interaction with the nitrile compound. It appears as though the long alkyl groups shield the carbonyl oxygen atom of the carboxylic acid from interaction with the butanenitrile molecule. The results have been interpreted by assuming  $n-\pi$  interactions to occur between lone-pair electrons of the oxygen atom and the  $\pi$  electrons of butanenitrile.

### 8.2.3 Excess molar enthalpies for mixtures of (benzonitrile + a carboxylic acid)

In this work excess molar enthalpy data have been determined for the mixtures of (benzonitrile + acetic acid or propanoic acid or butanoic acid or 2-methylbutanoic acid) at



298.15 K. All of the six systems investigated contribute new information to the literature.

The four-step mechanism proposed by Lark and Banipal (1985) and given in Section 8.1.1, is most likely to apply to the (benzonitrile + carboxylic acid) system. In this mechanism acetonitrile is now replaced by benzonitrile. The  $H_m^E$  results obtained are endothermic and again suggest that the collective endothermic effects of the first three steps preponderate that of the fourth step.

The magnitude of the  $H_m^E$  values for the mixtures under investigation decrease in the following order : 3 methylbutanoic acid > 2-methylpropanoic acid > pentanoic acid > butanoic acid > propanoic acid > acetic acid. There appears to be a inverse correlation between the length of the alkyl group of the carboxylic acid and the degree of interaction with the benzonitrile as observed from Table 3.9.

The excess molar enthalpies are found to be positive for all the six systems. The enthalpies are fairly small, ranging from  $325 \text{ J}\cdot\text{mol}^{-1}$  to  $\sim 550 \text{ J}\cdot\text{mol}^{-1}$ . The small magnitude of  $H_m^E$  may be attributed to the appreciable degree of cross-association occurring between the benzonitrile and carboxylic acid molecules. This is further supported by  $H_{m,\max}^E$  values for mixtures of (benzonitrile + heptane) reported by Tanaka *et al.* (1974), and for mixtures of (acetic acid + heptane) determined by Nagata *et al.* (1975), who have reported values of ( $< 1400 \text{ J}\cdot\text{mol}^{-1}$ ) and ( $< 925 \text{ J}\cdot\text{mol}^{-1}$ ) respectively.

It is also found that the position of the maxima for  $H_m^E$  (benzonitrile + acetic acid) shifts progressively to the benzonitrile - rich region of the mole fraction scale as the methylation of acetic acid increases. This is possibly due to steric hindrance of the crowding methyl groups - leading to greater dipole-dipole interactions.

The excess molar enthalpies for mixtures of (acetonitrile or butanenitrile or benzonitrile + a carboxylic acid) with respect to the nitrile compound, increases in the order:



It appears that as the number of carbon atoms in the nitrile compound decreases in the series, the  $H_m^E$  increases. This is most likely attributable to the following. As the overall magnitude of  $H_{m,\max}^E$  is due to the breakdown of the nitrile self-association (a positive enthalpy), the

breakdown of the carboxylic acid (dimers) self-association (a positive enthalpy) and the negative enthalpy of the (nitrile -carboxylic acid) polar-polar association, it appears that the dissociation term is greatest for smaller, less bulky molecules like acetonitrile and lower for the larger molecules. The aromatic molecule benzonitrile would have a higher dissociation contribution than the long chained and bulky butanenitrile molecule. It is also likely that the degree of cross-association between the nitrile and carboxylic acid molecules, which is also influenced by the size of the molecules, has a profound effect on the magnitude of  $H_m^E$  values.

### 8.3 CHAPTER 5 : TERNARY LIQUID - LIQUID EQUILIBRIA

In this study precise new liquid - liquid equilibria data have been produced for the following systems at 298.15 K.

- (a) (Acetonitrile + acetic acid or propanoic acid or butanoic acid or 2-methylpropanoic acid or pentanoic acid or 3-methylbutanoic acid + heptane).
- (b) (Acetonitrile + acetic acid or propanoic acid or butanoic acid or 2-methylpropanoic acid or pentanoic acid or 3-methylbutanoic acid + cyclohexane)
- (c) (Benzonitrile + acetic acid or propanoic acid or butanoic acid or 2-methylpropanoic acid or pentanoic acid or 3-methylbutanoic acid + water).
- (d) (Butanenitrile + acetic acid or propanoic acid or butanoic acid or 2-methylpropanoic acid or pentanoic acid or 3-methylbutanoic acid + water).

#### 8.3.1 Liquid - liquid equilibria for mixtures of (acetonitrile + a carboxylic acid + heptane)

Liquid - liquid equilibria for the six ternary mixtures : (acetonitrile + acetic acid or propanoic acid or butanoic acid or 2-methylpropanoic acid or pentanoic acid or 3-methylbutanoic acid + heptane) were determined at 298.15 K.

Figure 5.18 shows that the area of the two-phase heterogeneous region for the carboxylic acid mixtures decreases in the order: 3-methylbutanoic acid ~ pentanoic acid < 2-methylpropanoic acid < butanoic acid < propanoic acid < acetic acid. The mutual solubility of the components is increased as the carbon chain length of the carboxylic acid is increased. This implies that heptane is most soluble in the carboxylic acid - acetonitrile blends containing pentanoic acid or 3-methylbutanoic acid.

The slope of the tie lines obtained show that all the acids are more soluble in the acetonitrile than the alkane (heptane) mixture. In particular the slopes of the tie lines are steeper for the acetic acid system than in the corresponding propanoic acid system, and this suggests that the separation of acetic acid from heptane by extraction with acetonitrile can be achieved in fewer stages than the separation of propanoic acid from heptane.

The separation of a carboxylic acid from heptane by extraction with acetonitrile is feasible as can be ascertained from the distribution and selectivity data. The four carboxylic acids butanoic acid, 2-methylpropanoic acid, pentanoic acid and 3-methylbutanoic acid are better solvents for the (acetonitrile + heptane) mixtures than are the other carboxylic acids. Acetonitrile has the highest solvent power (capacity) for (acetic acid + heptane) mixtures.

The standard deviations,  $\sigma$  of the three fitted equations for the binodal curves, viz. the modified Hlavatý,  $\beta$  and  $\log \gamma$  show that all are capable of fitting binodal curve data points (Table 5.6). However, the  $\beta$  function equation gave the best overall correlation as compared to the Hlavatý equation and  $\log \gamma$  function.

### 8.3.2 Liquid-liquid equilibria for mixtures of (acetonitrile + a carboxylic acid + cyclohexane)

Liquid - liquid equilibria for the ternary mixtures : (acetonitrile + acetic acid or propanoic acid or butanoic acid or 2-methylpropanoic acid or pentanoic acid or 3-methylbutanoic acid + cyclohexane) were determined at 298.15 K. All the ternary systems stated above contribute new solubility data to the literature.

In the ternary systems cyclohexane is most soluble in the systems containing butanoic acid,

2-methylpropanoic acid, pentanoic acid or 3-methylbutanoic acid. Cyclohexane is more soluble in acetonitrile for mixture containing propanoic acid than for mixtures containing acetic acid.

The area of the two-phase heterogeneous region for the carboxylic acid mixtures increases in the order : 3-methylbutanoic acid ~ pentanoic acid < 2-methylpropanoic acid < butanoic acid < propanoic acid < acetic acid. The mutual solubility of the components is increased as the carbon chain length of the acid is increased. Cyclohexane is most soluble in (acetonitrile + 3-methylbutanoic acid), or (acetonitrile + pentanoic acid), and least soluble in (acetonitrile + acetic acid) mixtures.

The slopes of the tie-lines show that all the acids are more soluble in the acetonitrile than the alkane (hydrocarbon) mixture. The gradient of the tie-lines for 3-methylbutanoic acid is significantly greater than those pentanoic acid. This is attributable to the greater solubilizing effect of the two methyl groups on the terminal carbon of 3-methylbutanoic as opposed to its straight - chain isomer. A similar effect is noted for 2-methylpropanoic acid as compared to butanoic acid.

The separation of carboxylic acid from cyclohexane by extraction with acetonitrile is feasible as can be observed from the distribution and selectivity data. It can also be concluded that acetonitrile is an especially good component for the separation of mixtures of (cyclohexane and 2-methylpropanoic acid) or (cyclohexane and butanoic acid).

The solvent acetonitrile has a higher solubility, but lower solvent power (capacity) for (carboxylic acid + cyclohexane) mixtures, as opposed to (carboxylic acid + heptane) mixtures at the same temperature and pressure. Acetonitrile is thus a better solvent for extracting carboxylic acids from heptane than from cyclohexane.

The Hlavatý equation gave the best overall fit to the experimental binodal curve data for the six ternary systems.

### 8.3.3 Liquid - liquid equilibria for mixtures of (benzonitrile + a carboxylic acid + water)

The efficient separation of organic acids from aqueous solutions is of importance in the fermentation industry (Arce *et al.*, 1995; Briones *et al.*, 1994; Fahim *et al.*, 1997). In this work benzonitrile is used as a solvent in the separation of carboxylic acids from water.

Liquid - liquid equilibria for the six ternary mixtures : (benzonitrile + acetic acid or propanoic acid or butanoic acid or 2-methylpropanoic acid or pentanoic acid or 3-methylbutanoic acid + water) were determined at 298.15 K.

It is found that water is most soluble in the systems containing acetic acid or propanoic acid or butanoic acid or 2-methylpropanoic acid.

The area of the two-phase heterogeneous region for the carboxylic acid mixtures increases in the order: acetic acid ~ propanoic acid < butanoic acid < 2-methylpropanoic acid < pentanoic acid ~ 3-methylbutanoic acid. The mutual solubility of the components is decreased as the carbon chain length of the acid is increased.

The gradient of the tie-lines obtained in this work show that all the acids are more soluble in benzonitrile than water. In addition it is found that the solubility of the carboxylic acid in the water-rich phase decreases as the carbon chain length increases.

The selectivity ranges from 14 to 272, which implies that the separation of all the carboxylic acids from water by extraction is feasible. The selectivity generally increases as the carbon chain length of the carboxylic acid increases. It is evident that it is easier to separate the higher order carboxylic acid - water mixtures than the lower order carboxylic acid - water mixtures.

The Hlavatý equation gave the best fit to the experimental binodal curve data for the six ternary systems (standard deviations range from 0.002 to 0.010 mole fraction).

#### 8.3.4 Liquid-liquid equilibria for mixtures of (butanenitrile + a carboxylic acid + water)

Again, the efficient separation of organic acids from aqueous solutions is of importance in the fermentation industry (Arce *et al.*, 1995; Briones *et al.*, 1994; Fahim *et al.*, 1997). In this work butanenitrile is used as a solvent in the separation of carboxylic acids from water.

The shape of the binodal curves and the slopes of the tie-lines (Figure 5.60) show that the solubility of water in (butanenitrile + a carboxylic acid) mixture is very much dependent on the carbon number and type of carboxylic acid. In the ternary systems water is most soluble in the systems containing acetic acid and propanoic acid.

Figure 5.60 shows that the area of the two phase region decreases in the order: acetic acid < propanoic acid < butanoic acid < 2-methylpropanoic acid < 3-methylbutanoic acid < pentanoic acid. It is again found that the mutual solubility of the components is increased as the carbon chain length of the acid is decreased.

The slope of the tie-lines obtained in this work show that all the acids are more soluble in the butanenitrile than the water mixture. The slope of tie-lines for 2-methylpropanoic acid is significantly greater than those for butanoic acid, and this could be attributable to the greater solubilizing effect of the two methyl groups on the terminal carbon of 2-methylpropanoic acid as opposed to its straight chain isomer. It also suggests that the separation of 2-methylpropanoic acid from water by extraction with butanenitrile can be achieved in fewer stages than the corresponding separation of butanoic acid from water.

The separation of all the carboxylic acids from water by extraction with butanenitrile is feasible as can be concluded from the distribution and selectivity data. It can also be concluded that butanenitrile is an especially good solvent for the separation of mixtures of (water and pentanoic acid) or (water and 3-methylbutanoic acid).

Comparing the ternary diagrams for all the systems done in this work, with the diagrams for (benzonitrile + a carboxylic acid + water), it is found that the solvent butanenitrile has a higher solubility but lower solvent power (capacity) for (carboxylic acid + water) mixtures as

compared to the solvent benzonitrile for (carboxylic acid + water) mixtures at the same temperature and pressure conditions. Benzonitrile is thus the better solvent for extraction of carboxylic acids from water.

Of the three equations fitted to the binodal curve, viz. Hlavatý,  $\beta$  equation, and  $\log \gamma$  equation, the  $\log \gamma$  equation gave the best fit with an average standard deviation of 0.005 mole fraction.

#### 8.4 CHAPTER 7 : SOLUTION THEORY

In Chapter 7 some theories for non-electrolyte solutions were applied to the data presented in the earlier Chapters.

- The NRTL and UNIQUAC models were applied to the excess molar enthalpies for mixtures of (acetonitrile + a carboxylic acid) at  $T = 298.15$  K. The models were able to describe the data to within 25 and 30  $\text{J}\cdot\text{mol}^{-1}$  for the NRTL and UNIQUAC equations respectively, which is not as good as the correlation of the Redlich-Kister equation which is better than 8  $\text{J}\cdot\text{mol}^{-1}$ . This is consistent with what has been reported in the literature for mixtures of type polar (nitrile) + polar (carboxylic acids).
- The NRTL and UNIQUAC models were also fitted to the excess molar enthalpies for mixture of (butanenitrile + a carboxylic acid) at  $T = 298.15$  K. Both the NRTL and UNIQUAC models fitted the excess molar enthalpy data well with standard deviations of less than 9.3  $\text{J}\cdot\text{mol}^{-1}$  and 11.5  $\text{J}\cdot\text{mol}^{-1}$  respectively. However, the NRTL model fitted the data comprehensively better than the UNIQUAC model in all cases. The Redlich -Kister correlation gave a standard deviation error of less than 5.1  $\text{J}\cdot\text{mol}^{-1}$ .
- Application of the NRTL and UNIQUAC models to the excess molar enthalpies for mixtures of (benzonitrile + a carboxylic acid) at  $T = 298.15$  K, yielded standard deviations of (2.8 - 6.9)  $\text{J}\cdot\text{mol}^{-1}$  and (3.0 - 6.9)  $\text{J}\cdot\text{mol}^{-1}$  respectively. This is comparable to the correlation of the Redlich-Kister equation (2.6 - 7.9)  $\text{J}\cdot\text{mol}^{-1}$ . The average standard deviations for the correlations obtained were 4.50, 4.55 and 4.38  $\text{J}\cdot\text{mol}^{-1}$  for the NRTL, UNIQUAC and Redlich Kister correlations respectively.

Both the NRTL and UNIQUAC models correlate well with the experimental data. It must be noted that the Redlich-Kister equation is simply a fitting function and does not have a theoretical basis. Furthermore the number of parameters are chosen to provide a very good fit of the experimental data.

- The FBT model was applied to the excess molar volumes and excess molar enthalpies for the mixtures (acetonitrile + a carboxylic acid). The model correlates the excess molar enthalpy and excess molar volume data reasonably well. The standard deviation for the correlation of the excess molar volume is better than  $0.08 \text{ cm}^3 \cdot \text{mol}^{-1}$ , which is significantly higher than the correlation produced by the Redlich-Kister equation, where a standard deviation value of less than  $0.01 \text{ cm}^3 \cdot \text{mol}^{-1}$  was obtained. The model is not able to reproduce the symmetry of the excess molar enthalpy perfectly. This results in high standard deviation for the excess molar enthalpy ( $\delta H_m^E < 750 \text{ J} \cdot \text{mol}^{-1}$ ), which again is higher than the correlation achieved with the Redlich-Kister equation ( $\delta H_m^E < 8 \text{ J} \cdot \text{mol}^{-1}$ ). Due to the positive molar enthalpy values and negative molar volumes obtained experimentally, it was found that by trying to improve the correlation for the excess molar volumes, a corresponding decrease in correlation gave rise to an increase in the standard deviations for the excess molar enthalpies. The FBT model also indicated that the greatest contribution to the excess molar enthalpy is due to the contribution given by the Mecke-Kempton model for the hydrogen bonded species. This is supported by the strong hydrogen bonding occurring in the carboxylic acid molecules.
- The FBT model was also applied to the excess molar volumes and excess molar enthalpies for the six mixtures (benzonitrile + a carboxylic acid). It was found that the model correlated the excess molar volume data reasonably well with a standard deviation of better than  $0.04 \text{ cm}^3 \cdot \text{mol}^{-1}$ . However, this result is significantly higher than that obtained with the Redlich-Kister equation ( $\delta V_m^E < 0.007 \text{ cm}^3 \cdot \text{mol}^{-1}$ ). It was also found that the FBT model was not able to perfectly fit the experimental enthalpy data in the majority of cases for the above mixtures. As a result, a standard deviation of less than  $366 \text{ J} \cdot \text{mol}^{-1}$  was obtained in the worst case, and this is not as good as the



correlation obtained with the Redlich-Kister equation ( $\delta H_m^E < 8 \text{ J}\cdot\text{mol}^{-1}$ ). The higher  $\delta H_m^E$  obtained in the case of the FBT model can be attributed to the failure of the model to perfectly produce the symmetry of the excess molar enthalpy curves. The FBT model has also shown that the dominant contribution to the excess molar enthalpy data is the chemical contribution, whereas in the case of the excess molar volume data, the physical contribution is the main influence.

- The FBT model was also applied to the excess molar volumes and excess molar enthalpies for the mixtures (butanenitrile + a carboxylic acid). The model correlated the excess molar volume data reasonably well, with a standard deviation of less than  $0.14 \text{ cm}^3\cdot\text{mol}^{-1}$ , but this is not as good as the correlation of the Redlich-Kister equation ( $\delta V_m^E < 0.007 \text{ cm}^3\cdot\text{mol}^{-1}$ ). The FBT model correlates the excess molar enthalpy data very satisfactorily. The model however fails to calculate the symmetry of the experimental enthalpy curves perfectly, and this results in a standard deviation of  $235 \text{ J}\cdot\text{mol}^{-1}$  in the worst case. The FBT model predicts that the major contribution to the excess molar enthalpy data is the chemical contribution, given by the Mecke-Kempton model for hydrogen bonded species. For the excess molar volume data, the physical term is the major contribution and this involves the effect of non-specific interaction between the real molecular species in the mixture, together with free volume effects (Treszczanowicz and Benson, 1985).
- The ability of the FBT model to correlate the excess molar volume and excess molar enthalpy data has been reported previously in the literature for several types of mixtures (Letcher *et al.*, 1998a, 2000a; Treszczanowicz and Treszczanowicz, 1994, 1997; Kasprzycka - Guttman *et al.*, 1995, 1996; Naicker, 2000). This work represents the first attempt at using the model to represent the data for mixtures of the type (a nitrile compound + a carboxylic acid). The failure of the model to perfectly reproduce the symmetry of the excess enthalpy data has been noted in the literature.
- The NRTL and UNIQUAC models were also applied to the ternary liquid-liquid equilibria for mixtures of (acetonitrile + a carboxylic acid + heptane) at  $T = 298.15 \text{ K}$ .

The models were able to correlate the tie-line data reasonably well to better than 0.02 mole fraction in the case of the NRTL model, and better than 0.25 mole fraction in the case of the UNIQUAC model. This is not as good as the experimental uncertainty. As can be observed from Table 7.10, the correlation obtained with the NRTL model is significantly better than that obtained with the UNIQUAC model: the average root mean square deviation phase composition error was 0.011 mole fraction for NRTL and 0.132 mole fraction for UNIQUAC.

- The NRTL and UNIQUAC models were also applied to the liquid-liquid equilibrium data for mixtures of (acetonitrile + a carboxylic acid + cyclohexane) at 298.15 K. The NRTL equation fitted the experimental data better than the UNIQUAC equation: the average mean was 0.007 mole fraction for NRTL as compared with 0.194 mole fraction for UNIQUAC.
- Equations relating to the NRTL and UNIQUAC models have been fitted to the experimental tie line data for liquid mixture of (benzonitrile + a carboxylic acid + water) at 298.15 K. The NRTL equation fitted the experimental data better than the UNIQUAC equation: the average mean square deviation phase composition error was 0.008 mole fraction for the NRTL as compared with 0.343 mole fraction for UNIQUAC.
- The NRTL and UNIQUAC models have also been applied to the liquid-liquid equilibrium data for mixtures of (butanenitrile + a carboxylic acid + water) at 298.15 K. Both the models were able to correlate the tie-line data reasonably well. In the case of the NRTL model, the correlation was better than 0.04 mole fraction, and a correlation of better than 0.35 mole fraction was obtained with UNIQUAC model. This was not better than the experimental uncertainty of 0.001 mole fraction. As can be observed from Table 7.13 the correlation obtained with the NRTL model is significantly better than that obtained with the UNIQUAC model: the average root mean square deviation phase composition error was 0.015 mole fraction for the NRTL and 0.284 mole fraction for UNIQUAC.

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- Future work - the ERAS (extended real associated solution) model which combines the equation of state approach with solution theories that account for the effect of associating components, needs to be fitted to the excess molar enthalpies and excess molar volumes for the (nitriles + carboxylic acid) mixtures. It would be interesting to see if better correlations for the A-A, B-B and A-B interactions of these strongly polar and associating mixtures could be obtained with the ERAS model, than that obtained with the FBT model.

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## APPENDIX 1

## LLE PROGRAM

```

C      LIBRARY 'OPEN2.OBJ'
      IMPLICIT REAL*8 (A-H,O-Z)
      CHARACTER*1 FO(11)
      INTEGER*2 NN,NS,NT,NM,KV1,NPHAS,L,NNN,KGRA
      REAL*4 W,D,R3,Q3,T,Z
      CHARACTER*40 TEXT(600),TEXT1
      CHARACTER*40 INFIL,OUTFIL
      CHARACTER*4 AMODEL(2),POS(4)
      CHARACTER*78 INBUF,XBUF
      CHARACTER*1 AC2(17)
      COMMON/C3/Q(3),R(3),PAR(3,3),TAU(3,3),G(3,3),ALP(3,3)
      COMMON/CFUNC1/TC(15),Q2(15,3),R2(15,3),P(15,3,3),
      *ALPHA(15,3,3),YEXP(15,40,4),SEP1(15),SEP2(15),PEN
      COMMON/CFUNC2/NP1(32,15),NP2(32,15),NTIE(15),MODEL,NTT,NOB,ND,KONP
      COMMON/CGEN/ZEXP(40,6),YMAT(15,120,4),CRAL(15,40),MIN(15,40),NEXP,
*KGIT(15),NR(15,120),IC(15),NITE(120)
      COMMON/CBINOD/STEP,YY1(15),YY3(15),NDAT(15)
      COMMON/CKTYP/KTYP(15)
      COMMON/OUTPAR/IOUT
      DIMENSION X(32),PE(6),Z(40,3,2),
*      R3(600),Q3(600),NCEY(17),NCEZ(17)
      DIMENSION NC(15,3),IFUN(6),KK(4),MA(6),IPC(15,17),KO(6),NNN(1600)
      DIMENSION MCOM(17),MC1(17),MC2(17),MP1(31),MP2(31),IS(31),NM(3)
      DIMENSION XY1(31),XY2(31),ALF(31),YEXP1(6),ST(6)
      DATA AMODEL/'UNIQ','NRTL'/
      DATA POS/' ','L ','U ','R '/
      DATA KK/1,3,2,4/
      IN1=31
      IN3=33
C *****DEFINITION OF IN/OUT UNITS
C THIS PROGRAM NEEDS FOLLOWING UNITS:
C UNIT 1  CONSOLE IN/OUT
C UNIT 4  DATA FILE IN
C UNIT 7  RESULT FILE OUT
C UNIT 31 LLEAUX IN -NOT USED IN PC VERSION-
C UNIT 33 DATLLE3 IN -NOT USED IN PC VERSION-
C MAKE YOUR OWN SUBROUTINE OPEN2
C   CALL OPEN2
C
C INPUT CARDS
C

```

```

WRITE(*,*) ' ENTER NAME OF INPUTFILE '
READ(*, '(A)') INFIL
OPEN(4, FILE=INFIL)
READ(4, *) IOUT
IF(IOUT.NE. 0) THEN
  WRITE(*,*) ' ENTER NAME OF OUTPUT FILE '
  READ(*, '(A)') OUTFIL
  IOUT = 12
  OPEN(IOUT, FILE=OUTFIL)
ELSE
  IOUT=6
ENDIF
WRITE(6,9992) IOUT
9992 FORMAT(1H1,///, ' IOUT =', I3,/, ' IF IOUT = 0 : OUTPUT ONLY ON UNIT
*6',/, ' IF IOUT <>0 : OUTPUT ON BOTH UNIT 6 AND 12',/)
WRITE(6,915)
IF(IOUT.NE. 6) WRITE(IOUT,915)
WRITE(6,965)
IF(IOUT.NE. 6) WRITE(IOUT,965)
READ(4,*)MODEL,ND,MC,MP,NCAL,NCE
WRITE(6,981)MODEL,ND,MC,MP,NCAL,NCE
IF(IOUT.NE. 6) WRITE(IOUT,981)MODEL,ND,MC,MP,NCAL,NCE
DO 15 I=1,ND
15 READ(4,*)NDAT(I),SEP1(I),SEP2(I),YY1(I),YY3(I)
WRITE(6,982)(NDAT(I),SEP1(I),SEP2(I),YY1(I),YY3(I),I=1,ND)
IF(IOUT.NE. 6) WRITE(IOUT,982)(NDAT(I),SEP1(I),SEP2(I),YY1(I),
*YY3(I),I=1,ND)
C READ(4,*)(MC1(I),AC2(I),I=1,MC)
READ(4,*)INBUF
IX=0
XBUF=' '
DO 10 I=1,78
IF(INBUF(I:I).EQ. ' ') GOTO 10
IX=IX+1
XBUF(IX:IX)=INBUF(I:I)
10 CONTINUE
READ(XBUF, '(17(I1,A1))')(MC1(I),AC2(I),I=1,MC)
WRITE(6,983)(MC1(I),AC2(I),I=1,MC)
IF(IOUT.NE. 6) WRITE(IOUT,983)(MC1(I),AC2(I),I=1,MC)
DO 16 I=1,MP
MP1(I)=0
MP2(I)=0
XY1(I)=0.D0
XY2(I)=0.D0
ALF(I)=0.D0
16 READ(4,*)MP1(I),MP2(I),XY1(I),XY2(I),ALF(I)
WRITE(6,984)(MP1(I),MP2(I),XY1(I),XY2(I),ALF(I),I=1,MP)
IF(IOUT.NE. 6) WRITE(IOUT,984)(MP1(I),MP2(I),XY1(I),XY2(I),
*ALF(I),I=1,MP)
DO 17 I=1,NCAL
IFUN(I)=0
KO(I)=0
MA(I)=0
PE(I)=0.D0
ST(I)=0.D0

```

```

17  READ(4,*)IFUN(I),KO(I),MA(I),PE(I),ST(I)
    WRITE(6,964)(IFUN(I),KO(I),MA(I),PE(I),ST(I),I=1,NCAL)
    IF(IOUT.NE.6) WRITE(IOUT,964)(IFUN(I),KO(I),MA(I),PE(I),ST(I),
    *I=1,NCAL)
C
C READ COMPONENT CONSTANTS
C
    ICMP=0
    IF(NCE.EQ.0)GOTO 853
    NCEX=0
854  READ(4,*)NN,R1,Q1,TEXT1
    WRITE(6,994)NN,R1,Q1,TEXT1
    IF(IOUT.NE.6) WRITE(IOUT,994)NN,R1,Q1,TEXT1
    IF(R1.GT.-1.D-14)GOTO 855
    NCEX=NCEX+1
    NCEY(NCEX)=-R1
    NCEZ(NCEX)=NN
    GOTO 856
855  ICMP=ICMP+1
    R3(ICMP)=R1
    Q3(ICMP)=Q1
    TEXT(ICMP)=TEXT1
    NNN(NN+1500)=ICMP
856  IF(ICMP+NCEX.LT.NCE)GOTO 854
853  IF(ICMP.GE.MC)GOTO 360
860  ICMP=ICMP+1
    READ(IN1)NN,W,D,TEXT(ICMP),(FO(I),I=1,11),
    *R3(ICMP),Q3(ICMP)
    NNN(NN)=ICMP
    IF(NN.NE.1500)GOTO 860
C
C READ EXPERIMENTAL DATA
C
360  DO 743 I=1,ND
    IF(NDAT(I).GE.2000)GOTO 851
850  READ(IN3)NS,NT,(NM(J),J=1,3),KV1,NPHAS,KGRA,L,T,
    *(((Z(I1,J,K),K=1,2),J=1,NPHAS),I1=1,NT)
    IF(NS.LT.NDAT(I))GOTO 850
    GOTO 852
851  READ(4,*)(NM(J),J=1,3),NT,KV1,T
    WRITE(6,996)(NM(J),J=1,3),NT,KV1,T
    IF(IOUT.NE.6) WRITE(IOUT,996)(NM(J),J=1,3),NT,KV1,T
    DO 861 J=1,3
    KON=0
    IF(NCEX.EQ.0)GOTO 861
    DO 862 K=1,NCEX
    IF(NM(J).NE.NCEZ(K))GOTO 862
    NM(J)=NCEY(K)
    KON=1
862  CONTINUE
861  IF(KON.EQ.0)NM(J)=NM(J)+1500
    DO 18 I1=1,NT
18  READ(4,*)((Z(I1,J,K),K=1,2),J=1,2)
    WRITE(6,998)((Z(I1,J,K),K=1,2),J=1,2),I1=1,NT)
    IF(IOUT.NE.6) WRITE(IOUT,998)((Z(I1,J,K),K=1,2),J=1,2),
    *I1=1,NT)

```

```

852  NTIE(I)=NT
      TC(I)=T
      KTYP(I)=KV1
      DO 863 J=1,3
863  NC(I,J)=NM(J)
      IF(MODEL.NE.1)GOTO 797
      DO 705 I1=1,3
      Q2(I,I1)=Q3(NNN(NC(I,I1)))
705  R2(I,I1)=R3(NNN(NC(I,I1)))
797  DO 743 J=1,NT
      YEXP(I,J,1)=Z(J,1,1)/100.D0
      YEXP(I,J,2)=Z(J,1,2)/100.D0
      YEXP(I,J,3)=Z(J,2,1)/100.D0
743  YEXP(I,J,4)=Z(J,2,2)/100.D0
      WRITE(6,915)
      IF(IOUT.NE.6) WRITE(IOUT,915)
      WRITE(6,934)(AMODEL(MODEL),I=1,16)
      IF(IOUT.NE.6) WRITE(IOUT,934)(AMODEL(MODEL),I=1,16)

```

C

C DEFINITION OF PARAMETERS

C

```

      DO 407 I=1,ND
      DO 407 J=1,3
      P(I,J,J)=0.D0
407  ALPHA(I,J,J)=0.D0
      DO 400 I=1,MC
      DO 803 J=1,3
803  IF(AC2(I).EQ.POS(J+1))MC2(I)=J
400  MCOM(I)=NC(MC1(I),MC2(I))
      M=0
      N=0
      DO 403 I=1,MP
      IF(ALF(I).LT.1.D-14)ALF(I)=.2D0
      IF(MP1(I).GT.0)GOTO 402
      MP1(I)=-MP1(I)
      M=M+2
      IS(I)=-1
      GOTO 406
402  N=N+2
      IS(I)=1
      DO 410 J=1,ND
      NP1(N-1,J)=0
      NP2(N-1,J)=0
      NP1(N,J)=0
410  NP2(N,J)=0
406  MP1(I)=MCOM(MP1(I))
      MP2(I)=MCOM(MP2(I))
      DO 403 J=1,ND
      I1=0
      I2=0
      DO 417 L=1,MC
417  IPC(J,L)=0
      DO 404 K=1,3
      DO 401 L=1,MC
401  IF(NC(J,K).EQ.MCOM(L))IPC(J,L)=K
      IF(NC(J,K).EQ.MP1(I))I1=K

```

```

404   IF(NC(J,K).EQ.MP2(I))I2=K
      IF(I1.EQ.0.OR.I2.EQ.0)GOTO 403
      P(J,I1,I2)=XY1(I)
      P(J,I2,I1)=XY2(I)
      ALPHA(J,I1,I2)=ALF(I)
      ALPHA(J,I2,I1)=ALF(I)
      IF(IS(I).NE.1)GOTO 403
      NP1(N-1,J)=I1
      NP2(N-1,J)=I2
      NP1(N,J)=I2
      NP2(N,J)=I1
      X(N-1)=XY1(I)
      X(N)=XY2(I)
403   CONTINUE
C
C WRITE COMPONENTS
C
      WRITE(6,915)
      IF(IOUT.NE.6) WRITE(IOUT,915)
      IF(MODEL.EQ.1)WRITE(6,969)
      IF(MODEL.EQ.1.AND.IOUT.NE.6) WRITE(IOUT,969)
      IF(MODEL.EQ.2)WRITE(6,985)
      IF(MODEL.EQ.2.AND.IOUT.NE.6) WRITE(IOUT,985)
      DO 805 I=1,MC
      IF(MODEL.NE.1)GOTO 411
      WRITE(6,970)I,TEXT(NNN(MCOM(I))),R3(NNN(MCOM(I))),
      *Q3(NNN(MCOM(I)))
      IF(IOUT.NE.6) WRITE(IOUT,970)I,TEXT(NNN(MCOM(I))),
      *R3(NNN(MCOM(I))),Q3(NNN(MCOM(I)))
      GOTO 805
411   WRITE(6,970)I,TEXT(NNN(MCOM(I)))
      IF(IOUT.NE.6) WRITE(IOUT,970)I,TEXT(NNN(MCOM(I)))
805   CONTINUE
C
C CHECK FOR MISSING COMPONENTS
C
      DO 799 I=1,ND
      DO 799 J=1,3
      IKON=0
      DO 800 K=1,MC
800   IF(NC(I,J).EQ.MCOM(K))IKON=1
      IF(IKON.EQ.0)WRITE(6,979)NDAT(I)
      IF(IKON.EQ.0.AND.IOUT.NE.6)WRITE(IOUT,979)NDAT(I)
799   CONTINUE
C
C WRITE POSITION OF COMPONENTS IN INDIVIDUAL DATA SETS
C
      WRITE(6,915)
      IF(IOUT.NE.6) WRITE(IOUT,915)
      WRITE(6,975)
      IF(IOUT.NE.6) WRITE(IOUT,975)
      WRITE(6,976)(NDAT(I),I=1,ND)
      IF(IOUT.NE.6) WRITE(IOUT,976)(NDAT(I),I=1,ND)
      WRITE(6,912)
      IF(IOUT.NE.6) WRITE(IOUT,912)
      DO 416 I=1,MC

```



```

        WRITE(6,977)I,(POS(IPC(J,I)+1),J=1,ND)
416    IF(IOUT.NE. 6) WRITE(IOUT,977)I,(POS(IPC(J,I)+1),J=1,ND)
C
C CHECK FOR MISSING PARAMETER PAIRS
C
        DO 801 I=1,ND
        DO 801 J=1,3
        DO 801 K=1,3
        IF(J.EQ.K)GOTO 801
        IKON=0
        DO 802 L=1,MP
        IF(NC(I,J).EQ.MP1(L).AND.NC(I,K).EQ.MP2(L))IKON=1
802    IF(NC(I,J).EQ.MP2(L).AND.NC(I,K).EQ.MP1(L))IKON=1
        IF(IKON.EQ.0)WRITE(6,980)NDAT(I)
        IF(IKON.EQ.0.AND.IOUT.NE.6)WRITE(IOUT,980)NDAT(I)
801    CONTINUE
C
C WRITE PARAMETERS TO BE KEPT CONSTANT
C
        IF(M.EQ.0)GOTO 412
        WRITE(6,915)
        IF(IOUT.NE. 6) WRITE(IOUT,915)
        WRITE(6,971)
        IF(IOUT.NE. 6) WRITE(IOUT,971)
        IF(MODEL.EQ.1)WRITE(6,987)
        IF(MODEL.EQ.1.AND.IOUT.NE.6)WRITE(IOUT,987)
        IF(MODEL.EQ.2)WRITE(6,972)
        IF(MODEL.EQ.2.AND.IOUT.NE.6)WRITE(IOUT,972)
        DO 413 I=1,MP
        IF(IS(I).NE.-1)GOTO 413
        IF(MODEL.NE.1)GOTO 513
        WRITE(6,973)TEXT(NNN(MP1(I))),
        *TEXT(NNN(MP2(I))),XY1(I),XY2(I)
        IF(IOUT.NE. 6) WRITE(IOUT,973)TEXT(NNN(MP1(I))),
        *TEXT(NNN(MP2(I))),XY1(I),XY2(I)
        GOTO 413
513    WRITE(6,973)TEXT(NNN(MP1(I))),
        *TEXT(NNN(MP2(I))),XY1(I),XY2(I),ALF(I)
        IF(IOUT.NE. 6) WRITE(IOUT,973)TEXT(NNN(MP1(I))),
        *TEXT(NNN(MP2(I))),XY1(I),XY2(I),ALF(I)
413    CONTINUE
C
C WRITE INITIAL GUESS AT PARAMETERS TO BE ESTIMATED
C
412    IF(N.EQ.0)GOTO 414
        WRITE(6,915)
        IF(IOUT.NE. 6) WRITE(IOUT,915)
        IF(MODEL.NE.1)GOTO 808
        WRITE(6,986)
        IF(IOUT.NE. 6) WRITE(IOUT,986)
        WRITE(6,987)
        IF(IOUT.NE. 6) WRITE(IOUT,987)
        GOTO 809
808    WRITE(6,974)
        IF(IOUT.NE. 6) WRITE(IOUT,974)

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      WRITE(6,972)
      IF(IOUT.NE. 6) WRITE(IOUT,972)
809    K=0
      DO 415 I=1,MP
      IF(IS(I).NE.1)GOTO 415
      K=K+2
      IF(MODEL.NE.1)GOTO 806
      WRITE(6,973)TEXT(NNN(MP1(I))),TEXT(NNN(MP2(I))),
      *X(K-1),X(K)
      IF(IOUT.NE. 6) WRITE(IOUT,973)TEXT(NNN(MP1(I))),
      *TEXT(NNN(MP2(I))),X(K-1),X(K)
      GOTO 415
806    WRITE(6,973)TEXT(NNN(MP1(I))),TEXT(NNN(MP2(I))),
      *X(K-1),X(K),ALF(I)
      IF(IOUT.NE. 6) WRITE(IOUT,973)TEXT(NNN(MP1(I))),
      *TEXT(NNN(MP2(I))),X(K-1),X(K),ALF(I)
415    CONTINUE
C
C WRITE EXPERIMENTAL DATA FOR EACH DATA SET
C
414    DO 794 I=1,ND
      WRITE(6,915)
      IF(IOUT.NE. 6) WRITE(IOUT,915)
      WRITE(6,916)NDAT(I)
      IF(IOUT.NE. 6) WRITE(IOUT,916)NDAT(I)
      WRITE(6,978)(TEXT(NNN(NC(I,J))),J=1,3)
      IF(IOUT.NE. 6) WRITE(IOUT,978)(TEXT(NNN(NC(I,J))),
      *J=1,3)
      WRITE(6,907)TC(I),KTYP(I)
      IF(IOUT.NE. 6) WRITE(IOUT,907)TC(I),KTYP(I)
      WRITE(6,902)
      IF(IOUT.NE. 6) WRITE(IOUT,902)
      NT=NTIE(I)
      DO 702 J=1,NT
      DO 703 K=1,4
703    YEXP1(K)=YEXP(I,J,KK(K))
      YEXP1(5)=1.D0-YEXP1(1)-YEXP1(3)
      YEXP1(6)=1.D0-YEXP1(2)-YEXP1(4)
      WRITE(6,906)J,(YEXP1(K),K=1,6)
702    IF(IOUT.NE. 6) WRITE(IOUT,906)J,(YEXP1(K),K=1,6)
      IF(SEP1(I).GT.1.D-14)WRITE(6,931)SEP1(I)
      IF(SEP1(I).GT.1.D-14.AND.IOUT.NE.6)WRITE(IOUT,931)SEP1(I)
      IF(SEP2(I).GT.1.D-14)WRITE(6,932)SEP2(I)
794    IF(SEP2(I).GT.1.D-14.AND.IOUT.NE.6)WRITE(IOUT,932)SEP2(I)
C
C EXECUTION ACCORDING TO IFUN(I)
C
      DO 780 I5=1,NCAL
      IF(LABS(IFUN(I5)).EQ.1)GOTO 795
      WRITE(6,915)
      IF(IOUT.NE. 6) WRITE(IOUT,915)
      STEP=ST(I5)
      IF(STEP.LT.1.D-14)STEP=.02D0
      WRITE(6,933)STEP
      IF(IOUT.NE. 6) WRITE(IOUT,933)STEP

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795  IF(IFUN(I5).GE.3)GOTO 729
      WRITE(6,915)
      IF(IOUT.NE. 6) WRITE(IOUT,915)
      MAXF=MA(I5)
      KONP=KO(I5)
      PEN=PE(I5)
      WRITE(6,919)MAXF,PEN
      IF(IOUT.NE. 6) WRITE(IOUT,919)MAXF,PEN
      NOB=1
      IF(ABS(IFUN(I5)).EQ.2)NOB=2
      IF(IFUN(I5).GT.0)GOTO 730
C
C NELDER-MEAD
C
      IF(NOB.EQ.1)WRITE(6,917)
      IF(NOB.EQ.1.AND.IOUT.NE.6)WRITE(IOUT,917)
      IF(NOB.EQ.2)WRITE(6,918)
      IF(NOB.EQ.2.AND.IOUT.NE.6)WRITE(IOUT,918)
      DO 804 I=1,N
804  IF(DABS(X(I)).LT.1.D-10)X(I)=100.D0
      CALL NELDER(N,MAXF,X)
      GOTO 791
C
C MARQUARDT
C
730  IF(NOB.EQ.1)WRITE(6,921)
      IF(NOB.EQ.2)WRITE(6,922)
      CALL MARQ(N,MAXF,X)
C
C WRITE ESTIMATED PARAMETERS
C
791  WRITE(6,915)
      IF(IOUT.NE. 6) WRITE(IOUT,915)
      IF(MODEL.NE.1)GOTO 810
      WRITE(6,988)
      IF(IOUT.NE. 6) WRITE(IOUT,988)
      WRITE(6,987)
      IF(IOUT.NE. 6) WRITE(IOUT,987)
      GOTO 811
810  WRITE(6,956)
      IF(IOUT.NE. 6) WRITE(IOUT,956)
      WRITE(6,972)
      IF(IOUT.NE. 6) WRITE(IOUT,972)
811  K=0
      DO 418 I=1,MP
      IF(IS(I).NE.1)GOTO 418
      K=K+2
      IF(MODEL.NE.1)GOTO 807
      WRITE(6,973)TEXT(NNN(MP1(I))),TEXT(NNN(MP2(I))),
      *X(K-1),X(K)
      IF(IOUT.NE. 6) WRITE(IOUT,973)TEXT(NNN(MP1(I))),
      *TEXT(NNN(MP2(I))),X(K-1),X(K)
      GOTO 418
807  WRITE(6,973)TEXT(NNN(MP1(I))),TEXT(NNN(MP2(I))),
      *X(K-1),X(K),ALF(I)
      IF(IOUT.NE. 6) WRITE(IOUT,973)TEXT(NNN(MP1(I))),

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      *TEXT(NNN(MP2(I))),X(K-1),X(K),ALF(I)
418  CONTINUE
      GOTO 780

C
C WRITE RESULTS FOR EACH DATA SET
C
729  DO 701 I=1,ND
      IF(IOUT.NE. 6) WRITE(IOUT,915)
      WRITE(6,915)
      WRITE(6,924)NDAT(I)
      IF(IOUT.NE. 6) WRITE(IOUT,924)NDAT(I)
      WRITE(6,978)(TEXT(NNN(NC(I,J))),J=1,3)
      IF(IOUT.NE. 6) WRITE(IOUT,978)(TEXT(NNN(NC(I,J))),
      *J=1,3)
      NEXP=NTIE(I)
      DO 710 J=1,3
      IF(MODEL.NE.1)GOTO 798
      Q(J)=Q2(I,J)
      R(J)=R2(I,J)
798  DO 710 K=1,3
      TAU(J,K)=P(I,J,K)/(TC(I)+273.15D0)
      ALP(J,K)=ALPHA(I,J,K)
      G(J,K)=DEXP(-ALP(J,K)*TAU(J,K))
710  PAR(J,K)=DEXP(-TAU(J,K))
      CALL BINOD(MODEL,I)
      IF(KGIT(I).EQ.0)GOTO 701
      DO 788 J=1,NEXP
      DO 790 K=1,4
790  ZEXP(J,K)=YEXP(I,J,K)
      ZEXP(J,5)=1.D0-ZEXP(J,1)-ZEXP(J,2)
788  ZEXP(J,6)=1.D0-ZEXP(J,3)-ZEXP(J,4)
      CALL COMPA(I)
      CALL OUTLIN(I,MODEL,IFUN(I5))
701  CONTINUE
780  CONTINUE
      STOP
C900  FORMAT(6I3)
C901  FORMAT(I4,6X,4F10.1)
902  FORMAT(26X,'EXPERIMENTAL TIE LINES IN MOLE PCT',/,3X,'EXP',9X,
      *,
      *' TIE LINE',
      *7X,'LEFT COMPONENT',5X,'UPPER COMPONENT',5X,'RIGHT COMPONENT',/,
      *' NUMBER',7X,3('PHASE 1 PHASE 2 '),/)
906  FORMAT(1X,I5,7X,3(2P2F9.4,2X))
907  FORMAT(' TEMPERATURE = ',F7.2,' DEG C          TYPE OF SYSTEM = ',
      *I1,/)
912  FORMAT(' ')
C913  FORMAT(3I3,1X,2F10.1)
915  FORMAT(/,1X,79('*'))/
916  FORMAT(' EXPERIMENTAL DATA FOR DATA SET NUMBER',I5,' :',/)
917  FORMAT(' PARAMETER ESTIMATION USING NELDER-MEAD AND THE ACTIVITY O
      *BJECTIVE FUNCTION :',/)
918  FORMAT(' PARAMETER ESTIMATION USING NELDER-MEAD AND THE CONCENTRAT
      *ION OBJECTIVE FUNCTION :',/)
919  FORMAT(' STOP CRITERIA :   MAXF = ',I4,/,)

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      * PENALTY FUNCTION : PEN = ',G10.3,/)
921  FORMAT(' PARAMETER ESTIMATION USING MARQUARDT AND THE ACTIVITY
      OBJECTIVE FUNCTION :',/)
922  FORMAT(' PARAMETER ESTIMATION USING MARQUARDT AND THE
CONCENTRATION
      OBJECTIVE FUNCTION :',/)
924  FORMAT(' RESULTS FOR DATA SET NUMBER',I5,' :',/)
931  FORMAT(/, ' X(PHASE 1)/X(PHASE 2) FOR UPPER COMPONENT IN INFINITE DILUTION
      SHOULD BE',G12.4)
932  FORMAT(/, ' X(PHASE 1)/X(PHASE 2) FOR LEFT COMPONENT IN INFINITE DILUTION
      SHOULD BE',G12.4)
933  FORMAT(' STEP USED TO CONSTRUCT THE BINODAL CURVE = ',F7.4,
      * MOLE FRACTION')
934  FORMAT(16(1X,A4))
956  FORMAT(' ESTIMATED PARAMETERS (ALPHA CONSTANT) :',/)
964  FORMAT(7X,'E',11X,3I3,1X,2G12.5)
965  FORMAT(' INPUT :',/, ' USERS MANUAL INPUT DATA (FORMAT NOT AS IN
INPUT)',/)
C967  FORMAT(17(I2,A1))
C968  FORMAT(2I3,4X,3F10.1)
969  FORMAT(' COMPONENTS INVOLVED IN THE TREATED DATA SET(S) :',/, '
COMPONENT',45X,'UNQUAC UNQUAC',/, ' NUMBER',50X,'R',9X,
*Q',/)
970  FORMAT(1X,I5,5X,A40,3X,F8.4,F9.3)
971  FORMAT(' PARAMETERS TO BE KEPT CONSTANT :',/)
972  FORMAT(' COMPONENT I',29X,'COMPONENT J',33X,'A(I,J)',8X,
      *A(J,I)',9X,'ALPHA',/,85X,'KELVIN',8X,'KELVIN',/)
973  FORMAT(1X,A40,A40,2G14.5,F11.4)
974  FORMAT(' INITIAL GUESS AT PARAMETERS TO BE ESTIMATED (ALPHA CONSTA
      *NT) :',/)
975  FORMAT(' POSITION (L=LEFT,U=UPPER,R=RIGHT) OF EACH COMPONENT IN TH
      *E INDIVIDUAL DATA SETS:',/)
976  FORMAT(' COMPONENT',4X,'POSITION IN DATA SET NUMBER',/, ' NUMBER',
      *6X,15I5)
977  FORMAT(1X,I5,10X,15(1X,A4))
978  FORMAT(' LEFT COMPONENT = ',A40,/, ' UPPER COMPONENT = ',A40,
      */, ' RIGHT COMPONENT = ',A40,/)
979  FORMAT(' A COMPONENT OF DATA SET NUMBER ',I4,' HAS BEEN FORGOTTEN
      *IN THE INPUT')
980  FORMAT(' A COMPONENT PAIR OF DATA SET NUMBER ',I4,' HAS BEEN FORGO
      *TTEN IN THE INPUT')
981  FORMAT(7X,'A',11X,6I3)
982  FORMAT(7X,'B',11X,I4,6X,4G12.5)
983  FORMAT(7X,'C',11X,17(I2,A1))
984  FORMAT(7X,'D',11X,2I3,4X,3G12.5)
985  FORMAT(' COMPONENTS INVOLVED IN THE TREATED DATA SET(S) :',/, '
      * COMPONENT',45X,' ',/, ' NUMBER',50X,' ',9X,
      * ',/)
986  FORMAT(' INITIAL GUESS AT PARAMETERS TO BE ESTIMATED :',/)
987  FORMAT(' COMPONENT I',29X,'COMPONENT J',33X,'A(I,J)',8X,
      *A(J,I)',9X,' ',/,85X,'KELVIN',8X,'KELVIN',/)
988  FORMAT(' ESTIMATED PARAMETERS :',/)
C993  FORMAT(I4,6X,2F10.1,10A4)
994  FORMAT(7X,'F',11X,I4,6X,2G12.5,A40)
C995  FORMAT(5I4,F10.1)
996  FORMAT(7X,'G',11X,5I4,G12.5)

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C997  FORMAT(4F10.1)
998   FORMAT(7X,'G',11X,4G12.5)
      END
      SUBROUTINE OUTLIN(NS,MODEL,KONP)
      IMPLICIT REAL*8 (A-H,O-Z)
      COMMON/CGEN/ZEXP(40,6),YMAT(15,120,4),CRAL(15,40),MIN(15,40),NEXP,
      *KGIT(15),NR(15,120),IC(15),NITE(120)
      COMMON/CKTYP/KTYP(15)
      COMMON/OUTPAR/IOUT
      DIMENSION K(6),XDIS1(40),XDIS2(40),BET(120),X1(3),X2(3),
      *ACT1(3),ACT2(3),DACT1(3,3),DACT2(3,3),PACT1(3,16),PACT2(3,16)
      DIMENSION XBET1(40),XBET2(40),CBET1(40),CBET2(40)
      DIMENSION SUM1(6),ZCAL(6),ZDIF(6),YMAT1(6)
      DATA K/1,3,2,4,5,6/

C
C FIND DEVIATION OF X2(PHASE 1)/X2(PHASE 2)
C
      X1(1)=YMAT(NS,1,1)
      X2(1)=YMAT(NS,1,3)
      X1(2)=1.D-6
      X2(2)=1.D-6
      NSEP=1
81    IF(MODEL.NE.1)GOTO 73
      CALL UNIQ2(3,X1,ACT1,DACT1,PACT1,0)
      CALL UNIQ2(3,X2,ACT2,DACT2,PACT2,0)
      GOTO 74
73    CALL NRTL2(3,X1,ACT1,DACT1,PACT1,0)
      CALL NRTL2(3,X2,ACT2,DACT2,PACT2,0)
74    IF(NSEP.EQ.2)GOTO 82
      BET1=ACT2(2)/ACT1(2)
      BET(1)=BET1
      NGIT=KGIT(NS)
      DO 7 I=2,NGIT
7    BET(I)=YMAT(NS,I,2)/YMAT(NS,I,4)
      DO 5 I=1,NEXP
      XDIS1(I)=0.D0
      XDIS2(I)=0.D0
      CBET1(I)=0.D0
      CBET2(I)=0.D0
      XBET1(I)=0.D0
      XBET2(I)=0.D0
      IF(ZEXP(I,4).LT.1.D-14)GOTO 5
      MI=0
      DO 6 J=2,NGIT
6    IF(MI.EQ.0.AND.YMAT(NS,J,4).GT.ZEXP(I,4))MI=J
      IF(MI.EQ.0)GOTO 5
      FR=(ZEXP(I,4)-YMAT(NS,MI-1,4))/(YMAT(NS,MI,4)-YMAT(NS,MI-1,4))
      CBET1(I)=BET(MI-1)+FR*(BET(MI)-BET(MI-1))
      XBET1(I)=ZEXP(I,2)/ZEXP(I,4)
      XDIS1(I)=(CBET1(I)-XBET1(I))/XBET1(I)*100.D0
5    CONTINUE
C
C FIND DEVIATION OF X1(PHASE 1)/X1(PHASE 2)
C
      BET2=0.D0
      IF(IC(NS).NE.2)GOTO 8

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      X1(2)=YMAT(NS,NGIT,2)
      X2(2)=YMAT(NS,NGIT,4)
      X1(1)=1.D-6
      X2(1)=1.D-6
      NSEP=2
      GOTO 81
82    BET2=ACT2(1)/ACT1(1)
      BET(NGIT)=BET2
      NGIT1=NGIT-1
      DO 12 I=1,NGIT1
12    BET(I)=YMAT(NS,I,1)/YMAT(NS,I,3)
      DO 9 I=1,NEXP
      IF(ZEXP(I,3).LT.1.D-14)GOTO 9
      MI=0
      DO 11 J=2,NGIT
11    IF(MI.EQ.0.AND.YMAT(NS,J,4).GT.ZEXP(I,4))MI=J
      IF(MI.EQ.0)GOTO 9
      FR=(ZEXP(I,4)-YMAT(NS,MI-1,4))/(YMAT(NS,MI,4)-YMAT(NS,MI-1,4))
      CBET2(I)=BET(MI-1)+FR*(BET(MI)-BET(MI-1))
      XBET2(I)=ZEXP(I,1)/ZEXP(I,3)
      XDIS2(I)=(CBET2(I)-XBET2(I))/XBET2(I)*100.DO
9     CONTINUE
C
C PRINT BINODAL CURVE
C
8     WRITE(6,950)IC(NS)
      IF(IOUT.NE.6) WRITE(IOUT,950)IC(NS)
950   FORMAT(' TYPE OF CALCULATED BINODAL CURVE = ',I2,/)
      NLIN=NGIT
      IF(IC(NS).EQ.1)NLIN=NLIN+1
      WRITE(6,951)
      IF(IOUT.NE.6) WRITE(IOUT,951)
951   FORMAT(16X,'CALCULATED TIE LINES IN MOLE PCT (FOR INTERPOLATION)',/,3X,
        *'NUMBER',5X,'_____
        *____',/,
        *5X,'OF',8X,'LEFT COMPONENT',5X,'UPPER COMPONENT',5X,
        *'RIGHT COMPONENT',/,1X,'ITERATIONS',3X,
        *3('PHASE 1 PHASE 2  '),/)
      DO 84 I=1,NLIN
      DO 85 J=1,4
85    YMAT1(J)=YMAT(NS,I,K(J))
      YMAT1(5)=1.D0-YMAT1(1)-YMAT1(3)
      YMAT1(6)=1.D0-YMAT1(2)-YMAT1(4)
      IF(IOUT.NE.6) WRITE(IOUT,112)NITE(I),(YMAT1(J),J=1,6)
84    WRITE(6,112)NITE(I),(YMAT1(J),J=1,6)
112   FORMAT(1X,I6,5X,3(2P2F9.4,2X))
C
C PRINT DEVIATION OF DISTRIBUTION RATIOS
C
      IF(KONP.LE.3)RETURN
      WRITE(6,113)
      IF(IOUT.NE.6) WRITE(IOUT,113)
113   FORMAT(/, ' DEVIATION BETWEEN CALCULATED (INTERPOLATED) AND EXPERI
        *MENTAL DISTRIBUTION RATIOS : ',/)
      IF(KTYP(NS).EQ.1)WRITE(6,114)
      IF(KTYP(NS).EQ.1.AND.IOUT.NE.6)WRITE(IOUT,114)

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114  FORMAT(23X,'UPPER COMPONENT',38X,'          ',/,
      *9X, 5X,'          ',/,
      *3X,'EXP',3X, 5X,'X(PHASE 2)',9X,'X(PHASE 1)/X(PHASE 2)',8X,/,
      *1X,'TIE LINE', 5X,'          ',3X,'          ',
      *          ',/,
      *2X,'NUMBER',1X, 6X,'CALC=EXP',6X,'EXP',6X,'CALC',2X,
      *'(CALC-EXP)/EXP*100',/)
      IF(KTYP(NS).EQ.2.AND.IOUT.NE.6)WRITE(IOUT,110)
110  FORMAT(23X,'UPPER COMPONENT',38X,'LEFT COMPONENT',/,
      *9X,2(5X,'          '),/,
      *3X,'EXP',3X,2(5X,'X(PHASE 2)',9X,'X(PHASE 1)/X(PHASE 2)',8X),/,
      *1X,'TIE LINE',2(5X,'          '),3X,'          ',
      *          '),/,
      *2X,'NUMBER',1X,2(6X,'CALC=EXP',6X,'EXP',6X,'CALC',2X,
      *'(CALC-EXP)/EXP*100'),/)
      NEX1=0
      DO 83 I=1,NEXP
      IF(ZEXP(I,4).GT.1.D-10.AND.XBET1(I).LT.1.D-10)GOTO 201
      NEX1=NEX1+1
      IF(KTYP(NS).EQ.2)GOTO 200
      WRITE(6,111)I,ZEXP(I,4),XBET1(I),CBET1(I),XDIS1(I)
      IF(IOUT.NE.6)WRITE(IOUT,111)I,ZEXP(I,4),XBET1(I),CBET1(I),
      *XDIS1(I)
      GOTO 83
200  WRITE(6,111)I,ZEXP(I,4),XBET1(I),CBET1(I),XDIS1(I),
      *          ZEXP(I,3),XBET2(I),CBET2(I),XDIS2(I)
      IF(IOUT.NE.6)WRITE(IOUT,111)I,ZEXP(I,4),XBET1(I),CBET1(I),
      *          XDIS1(I),ZEXP(I,3),XBET2(I),CBET2(I),XDIS2(I)
111  FORMAT(1X,I5,3X,2(2PF13.4,2X,0P2F9.2,F13.1,7X))
      GOTO 83
201  XBET1(I)=ZEXP(I,2)/ZEXP(I,4)
      IF(KTYP(NS).EQ.2)GOTO 202
      WRITE(6,115)I,ZEXP(I,4),XBET1(I)
      IF(IOUT.NE.6)WRITE(IOUT,115)I,ZEXP(I,4),XBET1(I)
      GOTO 83
202  XBET2(I)=ZEXP(I,1)/ZEXP(I,3)
      WRITE(6,115)I,ZEXP(I,4),XBET1(I),ZEXP(I,3),XBET2(I)
      IF(IOUT.NE.6)WRITE(IOUT,115)I,ZEXP(I,4),XBET1(I),ZEXP(I,3),
      *XBET2(I)
115  FORMAT(1X,I5,3X,2(2PF13.4,2X,0PF9.2,6X,'*',13X,'*',8X))
83  CONTINUE
      BE1=0.D0
      BE2=0.D0
      DO 80 I=1,NEX1
      BE1=BE1+XDIS1(I)**2
80  BE2=BE2+XDIS2(I)**2
      BE1=DSQRT(BE1/NEX1)
      BE2=DSQRT(BE2/NEX1)
      IF(KTYP(NS).EQ.2)GOTO 203
      WRITE(6,108)BE1
      IF(IOUT.NE.6)WRITE(IOUT,108)BE1
      WRITE(6,106)BET1
      IF(IOUT.NE.6)WRITE(IOUT,106)BET1
      GOTO 204
203  WRITE(6,108)BE1,BE2
      IF(IOUT.NE.6)WRITE(IOUT,108)BE1,BE2

```



```

108  FORMAT(/,1X,'ROOT MEAN SQUARE',F38.1,F53.1)
      WRITE(6,106)BET1,BET2
      IF(IOUT.NE. 6) WRITE(IOUT,106)BET1,BET2
106  FORMAT(/,1X,'INFINITE DILUTION',F24.2,F53.2)
C
C PRINT DEVIATION OF EACH CONCENTRATION
C
204  IF(KONP.LE.4)RETURN
      WRITE(6,952)
      IF(IOUT.NE. 6) WRITE(IOUT,952)
      WRITE(6,911)
      IF(IOUT.NE. 6) WRITE(IOUT,911)
      DO 3 I=1,6
3      SUM1(I)=0.D0
      SUM2=0.D0
      DO 1 N=1,NEXP
      SUM=0.D0
      DO 55 I=1,4
55      ZCAL(I)=YMAT(NS,MIN(NS,N),I)+CRAL(NS,N)*(YMAT(NS,MIN(NS,N)+1,I)-
        *YMAT(NS,MIN(NS,N),I))
      ZCAL(5)=1.D0-ZCAL(1)-ZCAL(2)
      ZCAL(6)=1.D0-ZCAL(3)-ZCAL(4)
      DO 2 I=1,6
      ZDIF(I)=ZCAL(I)-ZEXP(N,I)
      SUM=SUM+ZDIF(I)**2
2      SUM1(I)=SUM1(I)+ZDIF(I)**2
      SUM2=SUM2+SUM
      SUM=DSQRT(SUM/6.D0)
      WRITE(6,912)(ZEXP(N,K(J)),J=1,6)
      IF(IOUT.NE. 6) WRITE(IOUT,912)(ZEXP(N,K(J)),J=1,6)
      WRITE(6,913)(ZCAL(K(J)),J=1,6)
      IF(IOUT.NE. 6) WRITE(IOUT,913)(ZCAL(K(J)),J=1,6)
      IF(IOUT.NE. 6) WRITE(IOUT,914)(ZDIF(K(J)),J=1,6),SUM
1      WRITE(6,914)(ZDIF(K(J)),J=1,6),SUM
      DO 4 I=1,6
4      SUM1(I)=DSQRT(SUM1(I)/NEXP)
      SUM2=DSQRT(SUM2/6.D0/NEXP)
      WRITE(6,915)(SUM1(K(J)),J=1,6),SUM2
      IF(IOUT.NE. 6) WRITE(IOUT,915)(SUM1(K(J)),J=1,6),SUM2
911  FORMAT(/,32X,'LEFT COMPONENT',10X,'UPPER COMPONENT',10X,
        *'RIGHT COMPONENT',
        *8X,'CALC-EXP',/,30X,3('PHASE 1  PHASE 2          '), ' RMS ',/)
912  FORMAT(' EXPERIMENTAL TIE LINE ',3X,3(2P2F11.4,3X))
913  FORMAT(' CALCULATED TIE LINE ',5X,3(2P2F11.4,3X))
914  FORMAT(' CALC-EXP',17X,3(2P2F11.4,3X),2PF11.4,/)
915  FORMAT(/,' CALC-EXP ROOT MEAN SQUARE',3(2P2F11.4,3X),2PF11.4)
952  FORMAT(/,' DEVIATION BETWEEN CALCULATED (INTERPOLATED) AND EXPERI
        *MENTAL CONCENTRATIONS IN MOLE PCT :')
      RETURN
      END
      SUBROUTINE BINOD(MODEL,NS)
      IMPLICIT REAL*8 (A-H,O-Z)
      COMMON/CGEN/ZEXP(40,6),YMAT(15,120,4),CRAL(15,40),MIN(15,40),NEXP,
        *KGIT(15),NR(15,120),IC(15),NITE(120)
      COMMON/CBISO/NIC1,NIC2,IC1(120),IC2(120)
      COMMON/CBINOD/STEP,YY1(15),YY3(15),NDAT(15)

```

```

COMMON/OUTPAR/IOUT
DIMENSION Y(4),YOLD(4),DY(4),DYOLD(4),DMAT(4,4)
DO 1 I=1,4
DO 1 J=1,4
1  DMAT(I,J)=0.D0
IRUND=200
IC(NS)=0
NOLD=2
N=0
NIC1=0
NIC2=0
Y(1)=1.D0-YY3(NS)/100.D0
Y(2)=0.D0
Y(3)=YY1(NS)/100.D0
Y(4)=0.D0
C
C CALCULATE TIE LINE N+1
C
12  CALL SOLVE(MODEL,Y,DY,NOLD,NEW,NITER,N)
    IF(NITER.LE.10)GOTO 16
C
C CONVERGENCE FAILURE
C
    IF(N.GT.0)GOTO 19
    IC(NS)=-10
    WRITE(6,902)NDAT(NS)
    IF(IOUT.NE.6) WRITE(IOUT,902)NDAT(NS)
    GOTO 3
19  IF(IHALF.LT.5)GOTO 20
    IC(NS)=-10
    GOTO 3
20  IHALF=IHALF+1
    ST=ST/2.D0
    GOTO 17
C
C CONVERGENCE OBTAINED
C
16  IF(DABS(Y(1)-Y(3))+DABS(Y(2)-Y(4)).GT.1.D-8)GOTO 21
    IF(N.GT.0)GOTO 19
    WRITE(6,903)NDAT(NS)
    IF(IOUT.NE.6) WRITE(IOUT,903)NDAT(NS)
    GOTO 3
21  N=N+1
    NITE(N)=NITER
    NR(NS,N)=NOLD
    IHALF=0
    DO 2 I=1,4
2  YMAT(NS,N,I)=Y(I)
    IF(IC(NS).EQ.2.AND.Y(1).LT.1.D-10)GOTO 3
C
C FIND COEFFICIENTS OF THIRD DEGREE POLYNOMIUM TO EXTRAPOLATE
C BINODAL CURVE
C
    DYMAX=DABS(DY(NEW))
    DO 4 I=1,4
4  DY(I)=DY(I)/DYMAX

```

```

      IF(N.EQ.1)GOTO 5
      STAP=DABS(Y(NEW)-YOLD(NEW))
      IF(DY(NEW)*DYOLD(NEW).GT.0.D0)GOTO 6
      DO 7 I=1,4
7      DY(I)=-DY(I)
6      IF(NEW.EQ.NOLD)GOTO 8
      RR=DY(NEW)/DYOLD(NEW)
      DO 9 I=1,4
9      DYOLD(I)=DYOLD(I)*RR
8      DO 10 I=1,4
      Z=(YOLD(I)-Y(I))/STAP
      DMAT(I,3)=(3.D0*Z+2.D0*DY(I)+DYOLD(I))/STAP
10     DMAT(I,4)=(2.D0*Z+DY(I)+DYOLD(I))/STAP**2
5      ST=RUND(Y(NEW),DY(NEW),STEP,IRUND)
      DO 18 I=1,4
      DMAT(I,1)=Y(I)
      DMAT(I,2)=DY(I)
      YOLD(I)=Y(I)
18     DYOLD(I)=DY(I)
C
C INITIAL GUESS AT NEXT TIE LINE
C
17     DO 11 I=1,4
      Y(I)=DMAT(I,4)
      DO 11 J=1,3
11     Y(I)=ST*Y(I)+DMAT(I,4-J)
      IF(IHALF.GT.0)GOTO 12
C
C CHECK FOR END OF BINODAL CURVE
C
      CALL TERM(Y,DMAT,IC(NS),NEW)
      NOLD=NEW
      IF(IC(NS).EQ.0.OR.IC(NS).EQ.2)GOTO 12
C
C END OF BINODAL CURVE
C
3      KGIT(NS)=N
      IF(N.EQ.0)RETURN
      IF(IC(NS).NE.1)GOTO 13
      N=N+1
      DO 14 I=1,4
14     YMAT(NS,N,I)=Y(I)
      NITE(N)=0
13     IF(NIC1.GT.0)WRITE(6,900)IC1(1),IC1(NIC1),NDAT(NS)
      IF(NIC1.GT.0.AND.IOUT.NE.6)WRITE(IOUT,900)IC1(1),IC1(NIC1),
      *NDAT(NS)
      IF(NIC2.GT.0)WRITE(6,901)IC2(1),IC2(NIC2),NDAT(NS)
      IF(NIC2.GT.0.AND.IOUT.NE.6)WRITE(IOUT,901)IC2(1),IC2(NIC2),
      *NDAT(NS)
900    FORMAT(/,' FALSE SOLUTION IN PHASE 1 FOR CALCULATED TIE LINES ',
      *I3,' TO ',I3,' OF DATA SET NUMBER ',I4,/)
901    FORMAT(/,' FALSE SOLUTION IN PHASE 2 FOR CALCULATED TIE LINES ',
      *I3,' TO ',I3,' OF DATA SET NUMBER ',I4,/)
902    FORMAT(/,' THE BASE LINE CALCULATION DID NOT CONVERGE IN 10 ITERAT
      *IONS FOR DATA SET NUMBER ',I4,/)

```

```

903  FORMAT(/,' THE CALCULATED CONCENTRATIONS ON THE BASE LINE ARE IDEN
      *TICAL IN THE TWO PHASES FOR DATA SET NUMBER ',I4,/)
      RETURN
      END
      SUBROUTINE SOLVE(MODEL,Y,DY,NOLD,NEW,NITER,N)
      IMPLICIT REAL*8(A-H,O-Z)
      COMMON/CBISO/NIC1,NIC2,IC1(120),IC2(120)
      COMMON/OUTPAR/IOUT
      DIMENSION Y1(3),Y2(3),ACT1(3),ACT2(3),DACT1(3,3),DACT2(3,3),
      *PACT(3,16)
      DIMENSION Y(4),DY(4),AMAT(3,5)
      DIMENSION INO(3)
      NITER=0

C
C CONVERGE THE TIE LINE CORRESPONDING TO Y(NOLD) AND
C FIND THE DERIVATIVES OF THE CONCENTRATIONS WITH RESPECT TO Y(NOLD)
C
11   NITER=NITER+1
      IF(NITER.GT.10)RETURN
      DO 2 I=1,4
2     IF(Y(I).LT.0.D0)Y(I)=0.D0
      DO 3 I=1,2
      Y1(I)=Y(I)
3     Y2(I)=Y(I+2)
      IF(MODEL.NE.1)GOTO 4
      CALL UNIQ2(3,Y1,ACT1,DACT1,PACT,1)
      CALL UNIQ2(3,Y2,ACT2,DACT2,PACT,1)
      GOTO 5
4     CALL NRTL2(3,Y1,ACT1,DACT1,PACT,1)
      CALL NRTL2(3,Y2,ACT2,DACT2,PACT,1)
5     J=0
      DO 6 I=1,4
      IF(I.EQ.NOLD)GOTO 6
      J=J+1
      INO(J)=I
6     CONTINUE
      DO 7 I=1,3
      DO 7 J=1,2
      AMAT(I,J)=DACT1(I,J)-DACT1(I,3)
7     AMAT(I,J+2)=DACT2(I,3)-DACT2(I,J)
      DO 8 I=1,3
      AMAT(I,5)=AMAT(I,NOLD)
      DO 9 J=1,3
9     AMAT(I,J)=AMAT(I,INO(J))
8     AMAT(I,4)=ACT1(I)-ACT2(I)
      CALL GAUSL(3,5,3,2,AMAT)
      RES=0.D0
      DO 10 I=1,3
      Y(INO(I))=Y(INO(I))-AMAT(I,4)
      DY(INO(I))=-AMAT(I,5)
10    RES=RES+AMAT(I,4)**2
      IF(RES.GT.1.D-10)GOTO 11
C

```

## C CHECK FOR FALSE SOLUTION

```

C
      IZ=0
      DO 14 I=1,2
      IF(Y1(I).LT.1.D-14)IZ=1
14    IF(Y2(I).LT.1.D-14)IZ=1
      IF(IZ.EQ.1)GOTO 13
      CALL GMIX(3,Y1,ACT1,DACT1,ICVEX)
      IF(ICVEX.EQ.1)GOTO 15
      NIC1=NIC1+1
      IC1(NIC1)=N+1
15    CALL GMIX(3,Y2,ACT2,DACT2,ICVEX)
      IF(ICVEX.EQ.1)GOTO 13
      NIC2=NIC2+1
      IC2(NIC2)=N+1

```

C

## C FIND NEW, THE NUMBER OF THE CONCENTRATION WITH GREATEST DERIVATIVE

```

C
13    DY(NOLD)=1.D0
      NEW=NOLD
      DYMAX=1.D0
      DO 12 I=1,4
      IF(DABS(DY(I)).LE.DYMAX)GOTO 12
      NEW=I
      DYMAX=DABS(DY(I))
12    CONTINUE
      RETURN
      END
      SUBROUTINE GMIX(NK,X,ACT,DACT,ICVEX)
      IMPLICIT REAL*8(A-H,O-Z)
      COMMON/OUTPAR/IOUT
      DIMENSION X(3),DG(2),DDG(2,2),ACT(3),DACT(3,3)

```

C

## C CHECK FOR STABILITY OF EACH PHASE

C

```

      ICVEX=1
      X(3)=1.D0-X(1)-X(2)
      DO 1 I=1,NK
1    IF(X(I).LT.1.D-15) X(I)=1.D-15
      DO 5 I=1,NK
      DO 5 J=1,NK
5    DACT(I,J)=DACT(I,J)/ACT(I)
      IF(NK.EQ.3) GOTO 9
      DDG(2,2)=DACT(2,2)-DACT(1,2)-DACT(2,1)+DACT(1,1)
      GOTO 30
9    DO 20 I=2,NK
      II=I-1
      DO 20 J=2,NK
      JJ=J-1
20   DDG(II,JJ)=DACT(I,J)-DACT(1,J)-DACT(II,1)+DACT(1,1)
      IF(X(1).LE.1.D-12.OR.X(2).LE.1.D-12) GOTO 30
      DET=DDG(1,1)*DDG(2,2)-DDG(2,1)*DDG(2,1)
      IF(DET.LE.0.D0.OR.DDG(1,1).LE.0.D0.OR.DDG(2,2).LE.0.D0) ICVEX=-1
      GOTO 100
30   CONTINUE
      IF(DDG(2,2).LE.0.D0) ICVEX=-1

```

```

100  CONTINUE
      RETURN
      END
      FUNCTION RUND(Y,DY,S,IRUND)
      IMPLICIT REAL*8(A-H,O-Z)
C
C FIND ROUND VALUE FOR CONCENTRATION STEP
C
      X=Y+S*DY+1.D-8*DY**2
      IX=IRUND*X
      Z=DBLE(IX)/IRUND-Y
      RUND=DABS(Z)
      RETURN
      END
      SUBROUTINE TERM(Y,DMAT,ICOND,NEW)
      IMPLICIT REAL*8(A-H,O-Z)
      COMMON/OUTPAR/IOUT
      DIMENSION Y(4),DMAT(4,4),A(4)
C
C CHECK FOR END OF BINODAL CURVE
C
      IF(Y(1).LT.1.D-14.OR.Y(3).LT.1.D-14)GOTO 1
      IF(Y(1)+Y(2).GT.1.D0.OR.Y(3)+Y(4).GT.1.D0)GOTO 2
      IF(Y(1)+Y(2)-.01D0.LT.Y(3)+Y(4).AND.Y(1)-.01D0.LT.Y(3))GOTO 3
      RETURN
1     ICOND=2
      DS=DMAT(1,1)/(DMAT(1,1)-Y(1))
      DO 5 I=1,4
5     Y(I)=DMAT(I,1)+DS*(Y(I)-DMAT(I,1))
      Y(1)=0.D0
      NEW=1
      RETURN
2     ICOND=-2
      RETURN
3     ICOND=1
      ND=2+NEW
      IF(ND.GT.4)ND=ND-4
      DO 6 I=1,4
6     A(I)=DMAT(NEW,I)-DMAT(ND,I)
      DS=0.D0
      NITER=0
7     NITER=NITER+1
      IF(NITER.LE.10)GOTO 8
      ICOND=-1
      RETURN
8     F=((A(4)*DS+A(3))*DS+A(2))*DS+A(1)
      DF=(3.D0*A(4)*DS+2.D0*A(3))*DS+A(2)
      DF=-F/DF
      DS=DS+DF
      IF(DABS(DF).GT.1.D-6)GOTO 7
      DO 9 I=1,4
      Y(I)=DMAT(I,4)
      DO 9 J=1,3
9     Y(I)=Y(I)*DS+DMAT(I,4-J)
      RETURN
      END

```

```

SUBROUTINE COMPA(NS)
  IMPLICIT REAL*8 (A-H,O-Z)
  COMMON/CGEN/ZEXP(40,6),YMAT(15,120,4),CRAL(15,40),MIN(15,40),NEXP,
  *KGIT(15),NR(15,120),IC(15),NITE(120)
  COMMON/OUTPAR/IOUT
C
C FIND FOR EACH EXPERIMENTAL TIE LINE THE TWO CLOSEST CALCULATED,
C MIN AND MIN+1, AND THE INTERPOLATION FACTOR
C
  NGIT1=KGIT(NS)-1
  DO 1 N=1,NEXP
    RESMIN=1000.D0
    DO 2 I=1,NGIT1
      RES=0.D0
      DO 3 J=1,4
3      RES=RES+(YMAT(NS,I,J)-ZEXP(N,J))**2
      RES=RES+(1.D0-YMAT(NS,I,1)-YMAT(NS,I,2)-ZEXP(N,5))**2
      *      +(1.D0-YMAT(NS,I,3)-YMAT(NS,I,4)-ZEXP(N,6))**2
      IF(RES.GT.RESMIN)GOTO 2
      RESMIN=RES
      NMIN=I
2      CONTINUE
      MIN(NS,N)=NMIN
      CRAL(NS,N)=0.D0
      CALL INTER(N,NMIN,ALF,NS)
      IF(ALF.GT.0.D0.AND.ALF.LT.1.D0)GOTO 4
      IF(NMIN.EQ.1)GOTO 1
      IF(ALF.LT.0.D0)GOTO 5
      MIN(NS,N)=NMIN+1
      GOTO 1
5      CALL INTER(N,NMIN-1,ALF,NS)
      IF(ALF.GT.1.D0)GOTO 1
      MIN(NS,N)=NMIN-1
4      CRAL(NS,N)=ALF
1      CONTINUE
      RETURN
      END
      SUBROUTINE INTER(N,I,ALF,NS)
        IMPLICIT REAL*8 (A-H,O-Z)
        COMMON/CGEN/ZEXP(40,6),YMAT(15,120,4),CRAL(15,40),MIN(15,40),NEXP,
        *KGIT(15),NR(15,120),IC(15),NITE(120)
        COMMON/OUTPAR/IOUT
        DIMENSION YMAT1(6),YMAT2(6)
C
C FIND THE INTERPOLATION FACTOR
C
        SS=0.D0
        SD=0.D0
        DO 2 J=1,4
          YMAT1(J)=YMAT(NS,I,J)
2          YMAT2(J)=YMAT(NS,I+1,J)
          YMAT1(5)=1.D0-YMAT1(1)-YMAT1(2)
          YMAT1(6)=1.D0-YMAT1(3)-YMAT1(4)
          YMAT2(5)=1.D0-YMAT2(1)-YMAT2(2)
          YMAT2(6)=1.D0-YMAT2(3)-YMAT2(4)
          DO 1 J=1,6

```

```

      D1=YMAT2(J)-YMAT1(J)
      D2=ZEXP(N,J)-YMAT1(J)
      SS=SS+D1*D1
1      SD=SD+D1*D2
      ALF=SD/SS
      RETURN
      END
      SUBROUTINE NELDER(NPAR,MAXF,XX)
      IMPLICIT REAL*8 (A-H,O-Z)
      COMMON/CGEN/ZEXP(40,6),YMAT(15,120,4),CRAL(15,40),MIN(15,40),NEXP,
      *KGIT(15),NR(15,120),IC(15),NITE(120)
      COMMON/CFUNC2/NP1(32,15),NP2(32,15),NTIE(15),MODEL,NIT,NOB,ND,KONP
      COMMON/OUTPAR/IOUT
      DIMENSION X(33,32),F(33),XB(32),XS(32),XM(32),XR(32),XE(32),XK(32)
      DIMENSION XX(32)
      ISTOP=0
      ALFA=1.
      BETA=0.5
      GAMMA=2.
      RMS=0.D0

C
C CALCULATION OF RESIDUALS F IN THE INITIAL MATRIX X
C
      NN=NPAR+1
      N=NPAR
      DO 250 I=1,NPAR
250      X(1,I)=XX(I)
      DO 201 J=2,NN
      DO 201 I=1,N
      IF(J-I-1)202,203,202
203      X(J,I)=1.1*X(1,I)
      GO TO 201
202      X(J,I)=X(1,I)
201      CONTINUE
      DO 1 J=1,NN
      DO 21 I=1,N
21      XX(I)=X(J,I)
      CALL FUNC(NPAR,0,XX,FF,SREX,SSQDIS,SSQPUN)
      WRITE(6,711)(XX(I),I=1,N)
      IF(IOUT.NE.6) WRITE(IOUT,711)(XX(I),I=1,N)
711      FORMAT(' PARAMETERS = ',8G13.5)
      WRITE(6,712)FF,RMS,(IC(I),I=1,ND)
      IF(IOUT.NE.6) WRITE(IOUT,712)FF,RMS,(IC(I),I=1,ND)
712      FORMAT(' SSQ          = ',G13.5,'          RMS = ',G13.5,
      *'          BINOD = ',15I3)
      WRITE(6,713)SREX,SSQDIS,SSQPUN
      IF(IOUT.NE.6) WRITE(IOUT,713)SREX,SSQDIS,SSQPUN
713      FORMAT(27X,'          SSQX = ',G13.5,'          SSQDIS = ',G13.5,
      *'          SSQPEN = ',G13.5)
      1      F(J)=FF
      NF=NN

C
C ESTIMATION OF THE LOWEST F = FB
C
25      FB=F(1)
      DO 98 I=1,N

```



```

98   XB(I)=X(1,I)
      JB=1
      DO 31 J=2,NN
      IF(FB-F(J))31,31,108
108  FB=F(J)
      JB=J
      DO 41 I=1,N
41   XB(I)=X(J,I)
31   CONTINUE
C
C STORAGE OF THE FINAL PARAMETERS
C
      IF(ISTOP.EQ.0)GOTO 834
      CALL FUNC(NPAR,0,XB,FB,SREX,SSQDIS,SSQPUN)
      WRITE(6,711)(XB(I),I=1,N)
      IF(IOUT.NE.6) WRITE(IOUT,711)(XB(I),I=1,N)
      WRITE(6,712)FB,RMS
      IF(IOUT.NE.6) WRITE(IOUT,712)FB,RMS
      WRITE(6,713)SREX,SSQDIS,SSQPUN
      IF(IOUT.NE.6) WRITE(IOUT,713)SREX,SSQDIS,SSQPUN
      DO 835 I=1,N
835  XX(I)=XB(I)
      IF(ISTOP.EQ.1)GOTO 860
      IF(ISTOP.EQ.2)GOTO 861
C
C ESTIMATION OF THE HIGHEST F = FS
C
834  FS=F(1)
      DO 51 I=1,N
51   XS(I)=X(1,I)
      JS=1
      DO 61 J=2,NN
      IF(FS-F(J))111,61,61
111  FS=F(J)
      JS=J
      DO 71 I=1,N
71   XS(I)=X(J,I)
61   CONTINUE
C
C CALCULATION OF THE CENTROID XM EXCLUDING XS
C
      DO 81 I=1,N
81   XM(I)=-XS(I)
      DO 9 J=1,NN
      DO 122 I=1,N
122  XM(I)=XM(I)+X(J,I)
9    CONTINUE
      DO 121 I=1,N
121  XM(I)=XM(I)/DBLE(N)
C
C REFLECTION
C
      DO 131 I=1,N
131  XR(I)=XM(I)+ALFA*(XM(I)-XS(I))
      CALL FUNC(NPAR,0,XR,FR,SREX,SSQDIS,SSQPUN)
      WRITE(6,711)(XR(I),I=1,N)

```

```

      IF(IOUT.NE. 6) WRITE(IOUT,711)(XR(I),I=1,N)
      WRITE(6,712)FR,RMS
      IF(IOUT.NE. 6) WRITE(IOUT,712)FR,RMS
      WRITE(6,713)SREX,SSQDIS,SSQPUN
      IF(IOUT.NE. 6) WRITE(IOUT,713)SREX,SSQDIS,SSQPUN
      NF=NF+1
C
C EXPANSION
C
      IF(FR-FB)141,151,151
141  DO 161 I=1,N
161  XE(I)=XM(I)+GAMMA*(XR(I)-XM(I))
      CALL FUNC(NPAR,0,XE,FE,SREX,SSQDIS,SSQPUN)
      WRITE(6,711)(XE(I),I=1,N)
      IF(IOUT.NE. 6) WRITE(IOUT,711)(XE(I),I=1,N)
      WRITE(6,712)FE,RMS
      IF(IOUT.NE. 6) WRITE(IOUT,712)FE,RMS
      WRITE(6,713)SREX,SSQDIS,SSQPUN
      IF(IOUT.NE. 6) WRITE(IOUT,713)SREX,SSQDIS,SSQPUN
      NF=NF+1
      IF(FE-FB)17,18,18
17  DO 19 I=1,N
      X(JS,I)=XE(I)
19  XS(I)=XE(I)
      F(JS)=FE
C
C STOP CRITERIA
C
27  IF(NF.LT.MAXF)GOTO 840
      ISTOP=1
      GOTO 25
860  WRITE(6,500)NF
      IF(IOUT.NE. 6) WRITE(IOUT,500)NF
500  FORMAT(/,' NUMBER OF FUNCTION EVALUATIONS = ',I4)
      RETURN
840  FM=0.
      DO 20 J=1,NN
20  FM=FM+F(J)
      FM=FM/DBLE(NN)
      FRMS=0.
      DO 22 J=1,NN
22  FRMS=(F(J)-FM)**2+FRMS
      RMS=DSQRT(FRMS/DBLE(N))
      IF(RMS.GT.1.D-6)GOTO 25
      ISTOP=2
      GOTO 25
861  WRITE(6,501)RMS
      IF(IOUT.NE. 6) WRITE(IOUT,501)RMS
501  FORMAT(/,' NELDER-MEAD STANDARD ERROR = ',G10.3)
      RETURN
C
C NEW SIMPLEX, FE GREATER THAN FB
C
18  DO 26 I=1,N
      X(JS,I)=XR(I)
26  XS(I)=XR(I)

```

```

      F(JS)=FR
      FS=FR
      GO TO 27
C
C NEW SIMPLEX, FR GREATER THAN FB
C
151 DO 30 J=1,NN
      IF(J-JS)28,30,28
28   IF(FR-F(J))18,18,30
30   CONTINUE
      IF(FR-FS)91,91,32
91   DO 33 I=1,N
      X(JS,I)=XR(I)
33   XS(I)=XR(I)
      F(JS)=FR
      FS=FR
32   DO 34 I=1,N
34   XK(I)=XM(I)+BETA*(XS(I)-XM(I))
      CALL FUNC(NPAR,0,XK,FK,SREX,SSQDIS,SSQPUN)
      WRITE(6,711)(XK(I),I=1,N)
      IF(IOUT.NE.6) WRITE(IOUT,711)(XK(I),I=1,N)
      WRITE(6,712)FK,RMS
      IF(IOUT.NE.6) WRITE(IOUT,712)FK,RMS
      WRITE(6,713)SREX,SSQDIS,SSQPUN
      IF(IOUT.NE.6) WRITE(IOUT,713)SREX,SSQDIS,SSQPUN
      NF=NF+1
C
C NEW SIMPLEX AFTER CONTRACTION
C
      IF(FK-FS)35,35,36
35   DO 37 I=1,N
      X(JS,I)=XK(I)
37   XS(I)=XK(I)
      F(JS)=FK
      FS=FK
      GO TO 27
36   DO 38 J=1,NN
      DO 39 I=1,N
39   X(J,I)=(X(J,I)+XB(I))/2.
38   CONTINUE
      GO TO 27
      END
      SUBROUTINE MARQ(N,MAXF,X)
      IMPLICIT REAL*8(A-H,O-Z)
      COMMON/CMAR/GRAD(32),XJTJ(32,32),H(15,240)
      COMMON/CGEN/ZEXP(40,6),YMAT(15,120,4),CRAL(15,40),MIN(15,40),NEXP,
      *KGIT(15),NR(15,120),IC(15),NITE(120)
      COMMON/CFUNC1/TC(15),Q2(15,3),R2(15,3),P(15,3,3),
      *ALPHA(15,3,3),YEXP(15,40,4),SEP1(15),SEP2(15),PEN
      COMMON/CFUNC2/NP1(32,15),NP2(32,15),NTIE(15),MODEL,NIT,NOB,ND,KONP
      COMMON/OUTPAR/IOUT
      DIMENSION DX(32),X(32),Y(32),XNY(32),A(32,32)
      XLAMB=.0001D0
      SREL=1.D0
C

```

## C RESIDUAL FOR INITIAL PARAMETERS

```

C
  CALL FUNC(N,0,X,SRES,SREX,SSQDIS,SSQPUN)
  IEVAL=1
  SSQ=SRES
  WRITE(6,710)SSQ,(IC(I),I=1,ND)
  IF(IOUT.NE.6) WRITE(IOUT,710)SSQ,(IC(I),I=1,ND)
710  FORMAT(' SSQSTART  = ',G13.5,'      BINOD = ',15I3)
  WRITE(6,713)SREX,SSQDIS,SSQPUN
  IF(IOUT.NE.6) WRITE(IOUT,713)SREX,SSQDIS,SSQPUN
713  FORMAT(27X,'      SSQX = ',G13.5,'  SSQDIS = ',G13.5,
  *'  SSQPEN = ',G13.5)
  WRITE(6,711)(X(I),I=1,N)
  IF(IOUT.NE.6) WRITE(IOUT,711)(X(I),I=1,N)
711  FORMAT(' PARAMETERS = ',8G13.5)
  NEW=1

```

C  
C CALCULATION OF GRAD AND XJTJ

```

C
10  DO 67 I=1,N
    GRAD(I)=0.D0
    DO 67 J=1,N
67  XJTJ(I,J)=0.D0
    CALL FUNC(N,1,X,DUMMY,DUMMY,DUMMY,DUMMY)

```

C  
C CHOLESKY DECOMPOSITION

```

C
49  DO 41 I=1,N
    DO 40 J=1,N
    40  A(I,J)=XJTJ(I,J)
    41  A(I,I)=A(I,I)+XLAMB
    CALL CHOL(N,A)

```

C  
C CALCULATION OF PARAMETER INCREMENTS

```

C
  Y(1)=-GRAD(1)/A(1,1)
  DO 81 I=2,N
  SUM=0.D0
  II=I-1
  DO 80 J=1,II
80  SUM=SUM+A(I,J)*Y(J)
81  Y(I)=(-GRAD(I)-SUM)/A(I,I)
  DX(N)=Y(N)/A(N,N)
  DO 85 I=2,N
  II=N-I+1
  SUM=0.D0
  III=II+1
  DO 84 J=III,N
84  SUM=SUM+A(J,II)*DX(J)
85  DX(II)=(Y(II)-SUM)/A(II,II)
  DO 90 I=1,N
90  XNY(I)=X(I)+DX(I)

```

C  
C RESIDUAL FOR NEW PARAMETERS

```

C
  CALL FUNC(N,0,XNY,SRES,SREX,SSQDIS,SSQPUN)

```

```

        IEVAL=IEVAL+1
        SSQNY=SRES
        IF(IEVAL.GE.MAXF)GOTO 122
C
C ESTIMATION OF ACTUAL AND THEORETICAL IMPROVEMENT OF RESIDUAL
C
        SQ1=0.D0
        SQ2=0.D0
        DO 110 I=1,N
        SQ1=SQ1+DX(I)**2
        SQ2=SQ2-DX(I)*GRAD(I)
110      CCAL=SSQ-SSQNY
        CPRE=SQ2+XLAMB*SQ1
        CALPRE=CCAL/CPRE
        IF(NEW.EQ.0)GOTO 802
        WRITE(6,716)
        IF(IOUT.NE.6) WRITE(IOUT,716)
716      FORMAT(' ')
        WRITE(6,714)(GRAD(I),I=1,N)
        IF(IOUT.NE.6) WRITE(IOUT,714)(GRAD(I),I=1,N)
714      FORMAT(' GRADIENT  = ',8G13.5)
802      IF(ND.GT.8)GOTO 129
        WRITE(6,715)SSQNY,XLAMB,CALPRE,(IC(I),I=1,ND)
        IF(IOUT.NE.6) WRITE(IOUT,715)SSQNY,XLAMB,CALPRE,(IC(I),I=1,ND)
715      FORMAT(' SSQNEW  = ',G13.5,'  XLAMB = ',G13.5,'  CALPRE = ',
        *,G13.5,'  BINOD = ',8I3)
        GOTO 128
129      WRITE(6,715)SSQNY,XLAMB,CALPRE,(IC(I),I=1,8)
        IF(IOUT.NE.6) WRITE(IOUT,715)SSQNY,XLAMB,CALPRE,(IC(I),I=1,8)
        WRITE(6,719)(IC(I),I=9,ND)
        IF(IOUT.NE.6) WRITE(IOUT,719)(IC(I),I=9,ND)
719      FORMAT(92X,7I3)
128      WRITE(6,713)SREX,SSQDIS,SSQPUN
        IF(IOUT.NE.6) WRITE(IOUT,713)SREX,SSQDIS,SSQPUN
C
C CHANGE LAMBDA
C
        IF(DABS(CALPRE-1.D0).LT..01)XLAMB=XLAMB/3.D0
        IF(CALPRE.GT..75D0)XLAMB=XLAMB/3.D0
        IF(CALPRE.LT..25D0)XLAMB=XLAMB*3.D0
        IF(CALPRE.LT.0.D0)XLAMB=XLAMB*10.D0
        IF(XLAMB.GE.1.D4)GOTO 122
        IF(CALPRE.GT.0.D0)GOTO 120
        NEW=0
        GOTO 49
C
C ACCEPTANCE OF NEW PARAMETERS
C
120      SREL=0.D0
        DO 130 I=1,N
        SREL=SREL+((X(I)-XNY(I))/XNY(I))**2
130      X(I)=XNY(I)
        SREL=DSQRT(SREL/N)
        SSQOLD=SSQ
        SSQ=SSQNY
        WRITE(6,711)(X(I),I=1,N)

```

```

        IF(IOUT.NE.6) WRITE(IOUT,711)(X(I),I=1,N)
        NEW=1
C
C STOP CRITERION
C
        IF(SSQOLD-SSQ.GT.SSQOLD*.01D0)GOTO 10
122      GNORM=0.D0
        DO 140 I=1,N
140      GNORM=GNORM+GRAD(I)**2
        GNORM=DSQRT(GNORM)
        IF(GNORM.GT.1.D-8)GOTO 121
        WRITE(6,705)GNORM
        IF(IOUT.NE.6) WRITE(IOUT,705)GNORM
705      FORMAT(/,' NORM OF GRADIENT = ',G10.3)
        RETURN
121      IF(SREL.GT.1.D-5)GOTO 119
        WRITE(6,706)SREL,GNORM
        IF(IOUT.NE.6) WRITE(IOUT,706)SREL,GNORM
706      FORMAT(/,' ROOT MEAN SQUARE OF RELATIVE PARAMETER CHANGE = ',G10.3
        *,'  NORM OF GRADIENT = ',G10.3)
        RETURN
119      IF(XLAMB.LT.1.D4) GOTO 999
        WRITE(6,704)XLAMB,GNORM
        IF(IOUT.NE.6) WRITE(IOUT,704)XLAMB,GNORM
704      FORMAT(/,' THE MARQUARDT PARAMETER = ',G10.3,
        *,'  NORM OF GRADIENT = ',G10.3)
        GOTO 123
999      IF(IEVAL.LT.MAXF) GOTO 10
        WRITE(6,703)IEVAL,GNORM
        IF(IOUT.NE.6) WRITE(IOUT,703)IEVAL,GNORM
703      FORMAT(/,' NUMBER OF FUNCTION EVALUATIONS = ',I4,
        *,'  NORM OF GRADIENT = ',G10.3)
123      DO 124 I=1,N
        DO 124 J=1,ND
124      IF(NP1(I,J).NE.0)P(J,NP1(I,J),NP2(I,J))=X(I)
        RETURN
        END
        SUBROUTINE CHOL(N,A)
        IMPLICIT REAL*8(A-H,O-Z)
        COMMON/OUTPAR/IOUT
        DIMENSION A(32,32)
C
C CHOLESKY DECOMPOSITION
C
        DO 50 I=1,N
        I1=I-1
        IF(I1.EQ.0) GOTO 30
        DO 20 J=I,N
        DO 20 K=1,I1
20      A(I,J)=A(I,J)-A(I,K)*A(J,K)
30      A(I,I)=DSQRT(A(I,I))
        IF(I.EQ.N) GOTO 100
        J1=I+1
        DO 50 J=J1,N
50      A(J,I)=A(I,J)/A(I,I)
100     RETURN

```

```

END
SUBROUTINE FUNC(N,NDIF,X,SRES,SREX,SSQDIS,SSQPEN)
IMPLICIT REAL*8 (A-H,O-Z)
COMMON/C3/Q(3),R(3),PAR(3,3),TAU(3,3),G(3,3),ALP(3,3)
COMMON/CGEN/ZEXP(40,6),YMAT(15,120,4),CRAL(15,40),MIN(15,40),NEXP,
*KGIT(15),NR(15,120),IC(15),NITE(120)
COMMON/CFUNC1/TC(15),Q2(15,3),R2(15,3),P(15,3,3),
*ALPHA(15,3,3),YEXP(15,40,4),SEP1(15),SEP2(15),PEN
COMMON/CFUNC2/NP1(32,15),NP2(32,15),NTIE(15),MODEL,NIT,NOB,ND,KONP
COMMON/STYR/LIST(16,2),NPAR
COMMON/CMAR/GRAD(32),XJTJ(32,32),H(15,240)
COMMON/CNPA/DR1(15),DDR1(15,16),DR2(15),DDR2(15,16),NPA(16)
COMMON/CTCK/TCK
COMMON/OUTPAR/IOUT
DIMENSION X1(3),X2(3),ACT1(3),ACT2(3),DACT1(3,3),DACT2(3,3),
*PACT1(3,16),PACT2(3,16),F(3),X(32),XJAC(3,32),YMAT1(6),YMAT2(6)
C
C PARAMETERS TRANSFERRED FROM X TO P
C
      DO 10 I=1,N
      DO 10 J=1,ND
10    IF(NP1(I,J).NE.0)P(J,NP1(I,J),NP2(I,J))=X(I)
      SRES=0.D0
      SREX=0.D0
      SSQDIS=0.D0
      SSQPEN=0.D0
C
C RECALL EXPERIMENTAL DATA
C
      DO 80 NS=1,ND
      IC(NS)=0
      NPAR=0
      DO 15 I=1,N
C      WRITE(1,*)'NP1(',I,NS,')=' ,NP1(I,NS)
      IF(NP1(I,NS).EQ.0)GOTO 15
      NPAR=NPAR+1
C      WRITE (1,*)'N=',N,'NPAR=',NPAR,'I=',I,'NS=',NS
      LIST(NPAR,1)=NP1(I,NS)
      LIST(NPAR,2)=NP2(I,NS)
      NPA(NPAR)=I
15    CONTINUE
      TCK=TC(NS)+273.15D0
      DO 20 I=1,3
      IF(MODEL.NE.1)GOTO 98
      Q(I)=Q2(NS,I)
      R(I)=R2(NS,I)
98    DO 20 J=1,3
      TAU(I,J)=P(NS,I,J)/TCK
      ALP(I,J)=ALPHA(NS,I,J)
      G(I,J)=DEXP(-ALP(I,J)*TAU(I,J))
20    PAR(I,J)=DEXP(-TAU(I,J))
      NEXP=NTIE(NS)
      DO 31 I=1,NEXP
      DO 30 J=1,4
30    ZEXP(I,J)=YEXP(NS,I,J)
      ZEXP(I,5)=1.D0-ZEXP(I,1)-ZEXP(I,2)

```

```

31  ZEXP(I,6)=1.D0-ZEXP(I,3)-ZEXP(I,4)
C
C RESIDUAL FOR ACTIVITY OBJECTIVE FUNCTION
C
      IF(NOB.NE.1)GOTO 71
      E=1.D-10
      DO 61 NT=1,NEXP
      DO 62 I=1,2
      X1(I)=ZEXP(NT,I)
62  X2(I)=ZEXP(NT,I+2)
      IF(MODEL.NE.1)GOTO 63
      CALL UNIQ2(3,X1,ACT1,DACT1,PACT1,-2)
      CALL UNIQ2(3,X2,ACT2,DACT2,PACT2,-2)
      GOTO 64
63  CALL NRTL2(3,X1,ACT1,DACT1,PACT1,-2)
      CALL NRTL2(3,X2,ACT2,DACT2,PACT2,-2)
64  DO 65 I=1,3
      SN=ACT1(I)+ACT2(I)+E
      F(I)=(ACT1(I)-ACT2(I))/SN
      SREX=SREX+F(I)**2
      DO 86 J=1,N
86  XJAC(I,J)=0.D0
      DO 65 J=1,NPAR
65  XJAC(I,NPA(J))=(PACT1(I,J)-PACT2(I,J)-F(I)*(PACT1(I,J)+PACT2(I,J))
      *)/SN
C
C GRAD AND XJTJ FOR ACTIVITY OBJECTIVE FUNCTION
C
      IF(NDIF.EQ.0) GOTO 66
      DO 45 K=1,3
      DO 45 I=1,N
      GRAD(I)=GRAD(I)+F(K)*XJAC(K,I)
      DO 45 J=1,N
      XJTJ(I,J)=XJTJ(I,J)+XJAC(K,I)*XJAC(K,J)
45  XJTJ(J,I)=XJTJ(I,J)
66  CONTINUE
61  CONTINUE
      GOTO 80
C
C RESIDUAL FOR CONCENTRATION OBJECTIVE FUNCTION
C
71  IF(NDIF.EQ.1)GOTO 72
      CALL BINOD(MODEL,NS)
      IF(KGIT(NS).GT.0)GOTO 94
      SRES=1.D6
      RETURN
94  CALL COMPA(NS)
      IF(KONP.NE.0)CALL OUTLIN(NS,MODEL,KONP)
      DO 40 I=1,NEXP
      CR=CRAL(NS,I)
      MI=MIN(NS,I)
      DO 41 J=1,4
      YMAT1(J)=YMAT(NS,MI,J)
41  YMAT2(J)=YMAT(NS,MI+1,J)
      YMAT1(5)=1.D0-YMAT1(1)-YMAT1(2)
      YMAT1(6)=1.D0-YMAT1(3)-YMAT1(4)

```



```

      YMAT2(5)=1.D0-YMAT2(1)-YMAT2(2)
      YMAT2(6)=1.D0-YMAT2(3)-YMAT2(4)
      DO 40 J=1,6
      YM=YMAT1(J)
      YM1=YMAT2(J)
      H(NS,6*(I-1)+J)=ZEXP(I,J)-YM-CR*(YM1-YM)
40    SREX=SREX+H(NS,6*(I-1)+J)**2
C
C RESIDUAL CONTRIBUTION FROM DISTRIBUTION RATIO
C
      IF(SEP1(NS).LT.1.D-14)GOTO 76
      X1(1)=YMAT(NS,1,1)
      X2(1)=YMAT(NS,1,3)
      X1(2)=1.D-6
      X2(2)=1.D-6
      NSEP=1
81    IF(MODEL.NE.1)GOTO 73
      CALL UNIQ2(3,X1,ACT1,DACT1,PACT1,-2)
      CALL UNIQ2(3,X2,ACT2,DACT2,PACT2,-2)
      GOTO 74
73    CALL NRTL2(3,X1,ACT1,DACT1,PACT1,-2)
      CALL NRTL2(3,X2,ACT2,DACT2,PACT2,-2)
74    IF(NSEP.EQ.2)GOTO 82
      DR1(NS)=DLOG(SEP1(NS)*ACT1(2)/ACT2(2))
      DO 75 I=1,NPAR
75    DDR1(NS,I)=PACT1(2,I)/ACT1(2)-PACT2(2,I)/ACT2(2)
      GOTO 78
76    DR1(NS)=0.D0
      DO 77 I=1,NPAR
77    DDR1(NS,I)=0.D0
78    IF(SEP2(NS).LT.1.D-14)GOTO 79
      X1(2)=YMAT(NS,KGIT(NS),2)
      X2(2)=YMAT(NS,KGIT(NS),4)
      X1(1)=1.D-6
      X2(1)=1.D-6
      NSEP=2
      GOTO 81
82    DR2(NS)=DLOG(SEP2(NS)*ACT1(1)/ACT2(1))
      DO 83 I=1,NPAR
83    DDR2(NS,I)=PACT1(1,I)/ACT1(1)-PACT2(1,I)/ACT2(1)
      GOTO 84
79    DR2(NS)=0.D0
      DO 85 I=1,NPAR
85    DDR2(NS,I)=0.D0
84    SSQDIS=SSQDIS+DR1(NS)**2+DR2(NS)**2
      GOTO 80
C
C GRAD AND XJTJ FOR CONCENTRATION OBJECTIVE FUNCTION
C
72    CALL DERGIT(MODEL,NS)
      CALL DERFUN(N,NS)
80    CONTINUE
      IF(NDIF.EQ.1)GOTO 93
C
C RESIDUAL CONTRIBUTION FROM PENALTY FUNCTION
C

```

```

      DO 91 I=1,N
91      SSQPEN=SSQPEN+PEN*X(I)**2
      SRES=SREX+SSQDIS+SSQPEN
      RETURN
C
C GRAD AND XJTJ CONTRIBUTION FROM PENALTY FUNCTION
C
93      DO 90 I=1,N
      GRAD(I)=GRAD(I)+PEN*X(I)
90      XJTJ(I,I)=XJTJ(I,I)+PEN
      RETURN
      END
      SUBROUTINE DERGIT(MODEL,NS)
      IMPLICIT REAL*8 (A-H,O-Z)
      COMMON/CXDER/XDER(120,4,16)
      COMMON/CGEN/ZEXP(40,6),YMAT(15,120,4),CRAL(15,40),MIN(15,40),NEXP,
      *KGIT(15),NR(15,120),IC(15),NITE(120)
      COMMON/STYR/LIST(16,2),NPAR
      COMMON/OUTPAR/IOUT
      DIMENSION X1(3),X2(3),ACT1(3),ACT2(3),DACT1(3,3),DACT2(3,3)
      DIMENSION PACT1(3,16),PACT2(3,16),SMAT(3,4),DMAT(3,19)
C
C DERIVATIVES OF CALCULATED TIE LINES WITH RESPECT TO PARAMETERS
C
      NGIT=KGIT(NS)
      DO 100 K=1,NGIT
      DO 5 I=1,4
      DO 5 J=1,NPAR
5      XDER(K,I,J)=0.D0
      DO 10 N=1,NEXP
      IA=MIN(NS,N)
      IB=IA
      IF(CRAL(NS,N).GT.1.D-14)IB=IA+1
      IF(K.NE.IA.AND.K.NE.IB)GOTO 10
      DO 30 J=1,2
      X1(J)=YMAT(NS,K,J)
30      X2(J)=YMAT(NS,K,J+2)
      IF(MODEL.NE.1)GOTO 35
      CALL UNIQ2(3,X1,ACT1,DACT1,PACT1,-1)
      CALL UNIQ2(3,X2,ACT2,DACT2,PACT2,-1)
      GOTO 38
35      CALL NRTL2(3,X1,ACT1,DACT1,PACT1,-1)
      CALL NRTL2(3,X2,ACT2,DACT2,PACT2,-1)
38      DO 40 I=1,3
      DO 40 J=1,2
      SMAT(I,J)=DACT1(I,J)-DACT1(I,3)
40      SMAT(I,J+2)=DACT2(I,3)-DACT2(I,J)
      JNO=0
      DO 45 J=1,4
      IF(J.EQ.NR(NS,K))GOTO 45
      JNO=JNO+1
      DO 50 I=1,3
50      DMAT(I,JNO)=SMAT(I,J)
45      CONTINUE
      DO 60 I=1,3
      DO 60 J=1,NPAR

```

```

60    DMAT(I,J+3)=PACT2(I,J)-PACT1(I,J)
      CALL GAUSL(3,19,3,NPAR,DMAT)
      INO=0
      DO 70 I=1,4
        IF(I.EQ.NR(NS,K))GOTO 70
        INO=INO+1
      DO 75 J=1,NPAR
75    XDER(K,I,J)=DMAT(INO,J+3)
70    CONTINUE
10    CONTINUE
100   CONTINUE
      RETURN
      END
      SUBROUTINE DERFUN(NPX,NS)
      IMPLICIT REAL*8 (A-H,O-Z)
      COMMON/CNPA/DR1(15),DDR1(15,16),DR2(15),DDR2(15,16),NPA(16)
      COMMON/CXDER/XDER(120,4,16)
      COMMON/CMAR/GRAD(32),XJTJ(32,32),H(15,240)
      COMMON/CGEN/ZEXP(40,6),YMAT(15,120,4),CRAL(15,40),MIN(15,40),NEXP,
      *KGIT(15),NR(15,120),IC(15),NITE(120)
      COMMON/STYR/LIST(16,2),NPAR
      COMMON/OUTPAR/IOUT
      DIMENSION X(2,6),DX(2,6),Z(6),XJAC(6,32)

C
C GRAD AND XJTJ CONTRIBUTION FROM DISTRIBUTION RATIO
C
      DO 101 I=1,NPAR
        GRAD(NPA(I))=GRAD(NPA(I))+DR1(NS)*DDR1(NS,I)+DR2(NS)*DDR2(NS,I)
        DO 101 J=1,NPAR
101    XJTJ(NPA(I),NPA(J))=XJTJ(NPA(I),NPA(J))+DDR1(NS,I)*DDR1(NS,J)
        *+DDR2(NS,I)*DDR2(NS,J)

C
C CALCULATION OF GRAD AND XJTJ
C
      DO 100 N=1,NEXP
        ALF=CRAL(NS,N)
        IA=MIN(NS,N)
        IB=IA
        IF(ALF.GT.1.D-14)IB=IA+1
        DO 10 J=1,4
          X(1,J)=YMAT(NS,IA,J)
10    X(2,J)=YMAT(NS,IB,J)
          X(1,5)=1.D0-X(1,1)-X(1,2)
          X(1,6)=1.D0-X(1,3)-X(1,4)
          X(2,5)=1.D0-X(2,1)-X(2,2)
          X(2,6)=1.D0-X(2,3)-X(2,4)
          DO 11 J=1,6
11    Z(J)=ZEXP(N,J)
          DO 51 I=1,6
            DO 51 J=1,NPX
51    XJAC(I,J)=0.D0
            DO 50 NP=1,NPAR
              DO 60 J=1,2
                I=IA
                IF(J.EQ.2)I=IB
                DO 65 K=1,4

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65   DX(J,K)=XDER(I,K,NP)
    DX(J,5)=-DX(J,1)-DX(J,2)
60   DX(J,6)=-DX(J,3)-DX(J,4)
    SA=0.D0
    SB=0.D0
    DO 30 J=1,6
    D=X(1,J)-X(2,J)
    DZ=Z(J)-X(1,J)
    DDX=DX(1,J)-DX(2,J)
    SA=SA+D*DZ
30   SB=SB+D*(2.D0*ALF*DDX-DX(1,J))+DZ*DDX
    IF(DABS(SA).LT.1.D-14)SA=1.D0
    Q=SB/SA
    DO 50 J=1,6
50   XJAC(J,NPA(NP))=-DX(1,J)+ALF*(DX(1,J)-DX(2,J)+(X(1,J)-X(2,J))*Q)
    DO 80 NN=1,6
    DO 80 I=1,NPX
    GRAD(I)=GRAD(I)+XJAC(NN,I)*H(NS,(N-1)*6+NN)
    DO 80 J=I,NPX
    XJTJ(I,J)=XJTJ(I,J)+XJAC(NN,I)*XJAC(NN,J)
80   XJTJ(J,I)=XJTJ(I,J)
100  CONTINUE
    RETURN
    END
    SUBROUTINE UNIQ2(NK,X,ACT,DACT,PACT,NOAC)
    IMPLICIT REAL*8(A-H,O-Z)
    COMMON/C3/Q(3),R(3),PAR(3,3),TAU(3,3),G(3,3),ALP(3,3)
    COMMON/STYR/LIST(16,2),NPAR
    COMMON/CTCK/TCK
    COMMON/OUTPAR/IOUT
    DIMENSION X(3),ACT(3),DACT(3,3),THETA(3),PHI(3),THS(3),PACT(3,16)
    DIMENSION QI(3),QIX(3),RI(3),PARA(3,3),PARB(3,3),GAM(3),QID(3)

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C

C CALCULATION OF ACTIVITIES AND DERIVATIVES OF ACTIVITIES WITH RESPECT  
C TO CONCENTRATIONS AND PARAMETERS USING THE UNIQUAC EQUATION

C

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    X(3)=1.-X(1)-X(2)
    IF (X(3).LT.0.) X(3)=0.
    NCOR=5
    THETS=0.
    PHS=0.
    DO 10 I=1,NK
    THETA(I)=Q(I)*X(I)
    THETS=THETS+THETA(I)
    PHI(I)=R(I)*X(I)
10   PHS=PHS+PHI(I)
    DO 20 I=1,NK
    THETA(I)=THETA(I)/THETS
    PHI(I)=PHI(I)/PHS
    RI(I)=R(I)/PHS
    QIX(I)=Q(I)/THETS
    QI(I)=RI(I)/QIX(I)
20   QID(I)=1.-QI(I)
    DO 30 I=1,NK
    THS(I)=0.D0
    DO 30 J=1,NK

```

```

30  THS(I)=THS(I)+PAR(J,I)*THETA(J)
    DO 40 I=1,NK
      GA=1.-RI(I)
      VAL=DLOG(QI(I)**NCOR*THS(I))
      GB=NCOR*QID(I)+VAL-1
      DO 45 J=1,NK
        PARA(I,J)=PAR(I,J)/THS(J)
        PARB(I,J)=PARA(I,J)*THETA(J)
45  GB=GB+PARB(I,J)
      GAM(I)=DEXP(GA-Q(I)*GB)*RI(I)
40  ACT(I)=X(I)*GAM(I)
    IF(NOAC.EQ.0)RETURN
    IF (NOAC.EQ.-2) GO TO 65
    DO 50 I=1,NK
      DO 50 J=1,NK
        PSUM=1.-PARA(I,J)-PARA(J,I)
        DO 55 K=1,NK
55  PSUM=PSUM+PARA(I,K)*PARB(J,K)
        PSUM=PSUM-NCOR*QID(I)*QID(J)
        DACT(I,J)=Q(I)*QIX(J)*PSUM+RI(I)*RI(J) - RI(I) -RI(J)
50  DACT(J,I)=DACT(I,J)
      DO 60 I=1,NK
        DO 60 J=1,NK
          DACT(I,J)=ACT(I)*DACT(I,J)
          IF (J.EQ.I) DACT(I,J)=DACT(I,J)+GAM(I)
60  CONTINUE
      IF(NOAC.GT.0)RETURN
65  DO 70 I=1,NK
      PRD=ACT(I)*Q(I)
      DO 80 JK=1,NPAR
        J=LIST(JK,1)
        K=LIST(JK,2)
        Z=THETA(J)*PARB(I,K)
        IF (J.EQ.I) Z=Z-THETA(K)
        IF (K.EQ.I) Z=Z-THETA(J)
        ZZ=PRD*Z/THS(K)
80  PACT(I,JK)=-ZZ*PAR(J,K)/TCK
70  CONTINUE
    RETURN
    END
    SUBROUTINE NRTL2(NK,X,ACT,DACT,PACT,NOAC)
    IMPLICIT REAL*8 (A-H,O-Z)
    COMMON/C3/Q(3),R(3),PAR(3,3),TAU(3,3),G(3,3),ALP(3,3)
    COMMON/STYR/LIST(16,2),NPAR
    COMMON/CTCK/TCK
    COMMON/OUTPAR/IOUT
    DIMENSION X(3),ACT(3),DACT(3,3),GAM(3),G1(3,3),TAU1(3,3),S(3,3)
    DIMENSION G2(3,3),PACT(3,16),A1(3),B1(3)

C
C CALCULATION OF ACTIVITIES AND DERIVATIVES OF ACTIVITIES WITH RESPECT
C TO CONCENTRATIONS AND PARAMETERS USING THE NRTL EQUATION
C
    X(3)=1.-X(1)-X(2)
    IF (X(3).LT.0.) X(3)=0.
    DO 20 I=1,NK
      AA=0.D0

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```

      BB=0.D0
      DO 30 J=1,NK
      Z=G(J,I)*X(J)
      AA=AA+Z
30     BB=BB+Z*TAU(J,I)
      A1(I)=AA
      B1(I)=BB
      GAM(I)=BB/AA
      DO 20 J=1,NK
      G1(J,I)=G(J,I)/AA
      TAU1(J,I)=TAU(J,I)-GAM(I)
      G2(J,I)=G1(J,I)*TAU1(J,I)
20     S(J,I)=X(I)*G2(J,I)
      DO 40 I=1,NK
      DO 50 J=1,NK
50     GAM(I)=GAM(I)+S(I,J)
      GAM(I)=DEXP(GAM(I))
40     ACT(I)=X(I)*GAM(I)
      IF(NOAC.EQ.0)RETURN
      IF(NOAC.EQ.-2)GOTO 75
      DO 60 I=1,NK
      DO 60 J=1,NK
      SUM=G2(J,I)+G2(I,J)
      DO 65 K=1,NK
65     SUM=SUM-G1(I,K)*S(J,K)-G1(J,K)*S(I,K)
      DACT(I,J)=SUM
60     DACT(J,I)=SUM
      DO 70 I=1,NK
      DO 70 J=1,NK
      DACT(I,J)=DACT(I,J)*ACT(I)
      IF(J.EQ.I)DACT(I,I)=DACT(I,I)+GAM(I)
70     CONTINUE
      IF(NOAC.GT.0)RETURN
75     DO 81 JK=1,NPAR
      J=LIST(JK,1)
      K=LIST(JK,2)
      DD=X(J)*X(K)*G(J,K)/A1(K)**2
      E1=1.D0-ALP(J,K)*TAU(J,K)
      C1=ALP(J,K)*B1(K)
      C2=E1+2.D0*C1/A1(K)
      C4=G(J,K)/A1(K)*(E1+C1/A1(K))
      DO 80 I=1,NK
      ZZ=DD*G(I,K)*(TAU(I,K)*ALP(J,K)-C2)
      IF(J.EQ.I)ZZ=ZZ+X(K)*C4
      IF(K.EQ.I)ZZ=ZZ+X(J)*C4
80     PACT(I,JK)=ZZ*ACT(I)/TCK
81     CONTINUE
      RETURN
      END
      SUBROUTINE GAUSL(ND,NCOL,N,NS,A)
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION A(ND,NCOL)

C
C      GAUSL SOLVES A*X=B, WHERE A IS N*N AND B IS N*NS, BY GAUSSIAN
C      ELIMINATION WITH PARTIAL PIVOTING. THE MATRIX (OR VECTOR) B
C      IS PLACED ADJACENT TO A IN COLUMNS N+1 TO N+NS.

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C      A IS DESTROYED, AND THE RESULTING MATRIX X REPLACES B
C
      N1=N+1
      NT=N+NS
      IF (N .EQ. 1) GO TO 50
C      START ELIMINATION
      DO 10 I=2,N
      IP=I-1
      I1=IP
      X=DABS(A(I1,I1))
      DO 11 J=I,N
      IF (DABS(A(J,I1)) .LT. X) GO TO 11
      X=DABS(A(J,I1))
      IP=J
11     CONTINUE
      IF (IP .EQ. I1) GO TO 13
C      ROW INTERCHANGE
      DO 12 J=I1,NT
      X=A(I1,J)
      A(I1,J)=A(IP,J)
12     A(IP,J)=X
13     DO 10 J=I,N
      IF(DABS(A(I1,I1)).LT.1.D-10)A(I1,I1)=1.D0
      X=A(J,I1)/A(I1,I1)
      DO 10 K=I,NT
10     A(J,K)=A(J,K) - X*A(I1,K)
C      ELIMINATION FINISHED, NOW BACKSUBSTITUTION
50     DO 20 IP=1,N
      I=N1-IP
      DO 20 K=N1,NT
      IF(DABS(A(I,I)).LT.1.D-10)A(I,I)=1.D0
      A(I,K) = A(I,K)/A(I,I)
      IF (I .EQ. 1) GO TO 20
      I1=I-1
      DO 25 J=1,I1
25     A(J,K) = A(J,K) - A(I,K)*A(J,I)
20     CONTINUE
      RETURN
      END

```