

**PART 1 : THE THERMODYNAMICS OF LIQUID  
MIXTURES**

**PART 2 : AN INVESTIGATION INTO THE LOW  
TEMPERATURE BLEACHING OF A  
COTTON NON-WOVEN FABRIC  
USING HYDROGEN PEROXIDE**

**URSULA PENELOPE GOVENDER**

B. Sc. (Hons), University of Natal, Pietermaritzburg

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## **DECLARATION**

The experimental work described in this thesis was carried out in the Department of Chemistry and Applied Chemistry, University of Natal, from March 1992 to December 1993 under the supervision of Professor Trevor Letcher.

These studies represent original work by the author and have not been submitted in any form to another university. Where use was made of work by others, it has been duly acknowledged in the text.

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## ABSTRACT

This thesis is presented in two parts. In part one, the excess molar volumes and the excess molar enthalpies have been determined for several binary systems at 298.15 K using an LKB flow microcalorimeter and/or a 2277 Thermal Activity Monitor and an Anton Paar Digital Densitometer.

The excess molar volumes and excess molar enthalpies,  $V_m^E$  and  $H_m^E$ , have been determined for systems involving an alkanol (1-propanol, 2-propanol) mixed with a hydrocarbon (1-hexene, 1-heptene, 1-octene, 1-hexyne, 1-heptyne, 1-octyne). The results show trends relating to the degree of unsaturation of the hydrocarbon to the position of the hydroxyl group on the alkanol.

The excess molar volumes and excess molar enthalpies,  $V_m^E$  and  $H_m^E$  of {di-n-butylamine + 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 tetrahydrofuran or tetrahydropyran or 1,4 dioxane} have been measured over the whole composition range at the temperature 298.15 K in order to investigate di-n-butylamine - ether interactions. The  $V_m^E$  values for each of the systems studied are negative with the exception of the mixtures of (di-n-butylamine + dibutyl ether or tetrahydrofuran or tetrahydropyran or 1,4 dioxane). The  $H_m^E$  results over the whole mole fraction range are formed endothermically.

Measurements were also made on mixtures involving (a cycloalkane + a pseudo-cycloalkane). The congruency theory was tested for the (cycloalkane + pseudo-cycloalkane) mixture. The cycloalkane mixtures studied here did not satisfy the null test of the congruency principle.

In the second part of this thesis the main aim of the investigation was to apply ambient temperature hydrogen peroxide bleaching techniques to a novel non-woven fabric and to optimize the treatment conditions for this technique.

Five cold-pad batch bleaching formulas were applied to the non-woven and the sample fabrics were analyzed for the following properties

- a) fluidity (measure of degree of degradation of the cotton fibre as a result of the bleaching process)
- b) wettability (absorbency)
- c) whiteness (using instrumental techniques)
- d) inherent fibre surface properties (SEM)

A method was elucidated for the cold batch bleaching of the non-woven which produced a fabric with minimum fibre damage, an acceptable degree of whiteness and excellent absorbency properties. The treatment parameters of time ( $x_1$ ), temperature( $x_2$ ) and hydrogen peroxide concentration ( $x_3$ ) for this method were optimised using a multiple regression analysis for three variables and response surface plots.

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**PART 1**

**THE THERMODYNAMICS OF LIQUID  
MIXTURES**

# CHAPTER 1

## Introduction

Thermodynamics is a useful probe to help better understand molecular interactions in solution<sup>(1)</sup>. In particular experimental excess functions of liquids mixtures are useful in that they provide data to test theories of liquid mixtures and provide a guide for the formulation of new theories<sup>(2)</sup>. For instance, the determination of excess molar enthalpies of aqueous solutions of hydrocarbons is important in understanding and improving the theories of hydrophobic interaction and hence increasing the knowledge into the nature of many biological systems<sup>(3)</sup>. In industry, reliable excess molar enthalpies and excess molar volumes is all important in the design of chemical plants and reactors<sup>(2)</sup>.

The material in the first part of this thesis is concerned with determining excess molar volumes and excess molar enthalpies,  $V_m^E$  and  $H_m^E$  for binary liquid mixtures, with the aim of testing various thermodynamic theories. This work has involved the experimental determination of excess properties for systems concerning molecules not only differing in shape and size, but also with mixtures where one of the components contains multiple bonds.  $V_m^E$  and  $H_m^E$  have been determined for binary systems involving mixtures of (1-alkene or 1-alkyne + an alkanol). The alkanols used were 1-propanol, or 2-propanol. These results were compared to previously reported excess functions for binary mixtures of a 1-alkene, or 1-alkyne with methanol and ethanol, and of an n-alkane with an alkanol, in order to determine the effect of the double bond on the 1-alkene, or the triple bond on the 1-alkyne, on the measured properties.

Excess thermodynamic properties have also been measured for mixtures of {di-n-butylamine (DBA) + an ether}. The various trends and observations have been compared to work previously reported concerning systems involving {tributylamine (TBA)<sup>(97,98)</sup>, or acetonitrile (AN)<sup>(5,6)</sup> + an ether}. The effect of the n-chain ether, the branched ether and the cyclic ether molecules on the results was observed.

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The final set of mixtures investigated in this section involves mixtures of cycloalkanes + pseudo-cycloalkanes. This set of mixtures presented an opportunity to test the principle of congruence.<sup>(112)</sup> The theory of congruence, first proposed by Bronsted and Koefoed,<sup>(111)</sup> is used to correlate and predict several thermodynamic properties, such as activity coefficients, the excess Gibbs free energy of mixing, the excess enthalpy of mixing, and the excess volume of mixing. The results of the cycloalkanes + pseudo-cycloalkanes mixtures were compared to the recently reported<sup>(126)</sup> results for the n-alkane + pseudo-n-alkane mixtures.

## Chapter 2

### Excess Molar Functions of Mixing

#### 2.0 INTRODUCTION

By definition<sup>(1)</sup> the excess molar functions of mixing,  $X_m^E$  for a binary mixture is given by the relation

$$X_m^E = X_{\text{mix}} - X_{\text{mix}}^i \quad 2.1$$

where  $X_{\text{mix}}^i$  is the ideal behaviour of the thermodynamic property  $X$  for the mixing process. Excess functions have been utilized to represent<sup>(2)</sup> the changes in thermodynamic properties of mixing from the ideal behaviour i.e. the deviations from ideality.

In this work the excess molar enthalpies,  $H_m^E$ , and excess molar volumes,  $V_m^E$ , of mixing were determined for the following binary systems: mixtures of an unsaturated hydrocarbon [an 1-alkene or an 1-alkyne] + an alkanol [1-propanol or 2-propanol]; di-n-butylamine (DBA) + an ether [diethyl ether or dipropyl ether or di-1-methyl ethyl ether (IPE) or dibutyl ether or 1,1-dimethyl ethyl methyl ether (TBME) or 1,1-dimethylpropyl methyl ether (TAME) or tetrahydrofuran (THF) or tetrahydropyran (THP) or 1,4-dioxane], over the whole composition range at the temperature 298.15 K.

The results of (an unsaturated hydrocarbon + an alkanol) binary liquid mixture are discussed with reference to cited alkane + alkanol work.<sup>(3,4)</sup> The thermodynamic mixing properties for the (DBA + an ether) are compared to recently reported  $H_m^E$  and  $V_m^E$  results for { acetonitrile (AN)<sup>(5,6)</sup> or tri-butylamine (TBA)<sup>(97,98)</sup> + an ether}. The binary experimental values for {DBA + an ether} are correlated by means of the UNIQUAC and NRTL models.

### 2.1 Excess Molar Volumes of Mixing

The volume change on mixing of binary liquid mixtures,  $V_m^E$ , at constant pressure is of interest to a thermochemist because of two reasons:<sup>(7)</sup>

- a) they serve as accuracy indicators for theories of liquid mixtures dealing with thermodynamic properties, and
- b) from a practical point of view, experimentally reliable results are relatively easy to obtain.<sup>(7)</sup>

#### 2.1.1 Measurement of Excess Molar Volumes

The excess molar volume,  $V_m^E$ , at a concentration of  $x_A$  of component A is defined as<sup>(1)</sup>

$$V_m^E = V_{(\text{mixture})} - \{ x_A V_A^\circ + (1-x_A) V_B^\circ \} \quad 2.2$$

where the last term is the ideal molar volume of the mixture. The volume changes for binary mixtures,  $V_m^E$ , can be determined experimentally in one of two ways, namely (i) indirectly from density ( densitometer or pycnometric) measurements, or (ii) from the more direct dilatometric methods, ie. by measuring the resultant volume change upon mixing of the two components.

Both these experimental methods have been extensively reviewed by Battino,<sup>(7)</sup> Letcher,<sup>(8)</sup> Handa and Benson,<sup>(9)</sup> and by Stokes and Marsh.<sup>(10,11,12)</sup>

##### a) Pycnometer

There is a wealth of reference in the literature of a variety of types of pycnometer.<sup>(13,14,15)</sup> One of the earliest described pycnometer was that of Scatchard, Wood and Mochel<sup>(15)</sup> and is illustrated in fig. 2.1. This single arm pycnometer was used to obtain density measurements with precision of  $0.00001 \text{ g.cm}^{-3}$ . Basically, this pycnometer has a bulb with a capacity of  $11 \text{ cm}^3$ , a 1 mm internal diameter precision capillary with 11 lines lightly etched around the stems, and spaced 1 mm apart.<sup>(15)</sup>

During measurement, the bulb is filled using a hypodermic syringe and cannula and the composition of the mixtures have to be known with a large degree of accuracy. Many

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workers overcame the latter by weighing the two components into the pycnometer.<sup>(14,15)</sup>

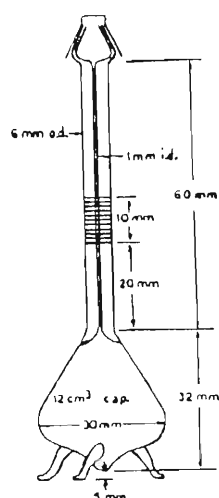


Figure 2.1. Pycnometer of Scatchard et al<sup>15</sup>

Potentially serious errors could arise due to inadequate mixing, evaporation and vapour space composition, however, careful measurements with excellent accuracy and reproducibility have been reported using this technique.<sup>(16)</sup>

Wood and Brausie<sup>(14)</sup> and later Battino<sup>(17)</sup> improved on the accuracy of density measurement by the pycnometer technique by introducing and developing a mixing bottle. Battino's mixing bottle is depicted in fig 2.2. With this bottle potential errors due to evaporation of the samples is minimised. Later a bicapillary pycnometer made of Pyrex glass was developed in the laboratory of Kimura and Takagi.<sup>(18)</sup> This pycnometer had a volume capacity of approximately  $3.6 \text{ cm}^3$ , capillary stems with an internal diameter of  $0.5 \text{ mm}$ . Sharp lines were scored on each stem and magnified by a travelling microscope were used as reference points. The pycnometer was allowed to stand for 20-30 minutes on the balance, before each weighing and the reproducibility for weighing was  $\pm 0.01 \text{ mg}$  - which gave a precision of  $0.00001 \text{ g.cm}^{-3}$  in density measurements.<sup>(18)</sup>

### b) Mechanical Oscillator Densitometers or Density Meters

The remote or external measuring cells were developed to eliminate the inherent sources of error in the pycnometer technique and to achieve the highest possible accuracy and precision



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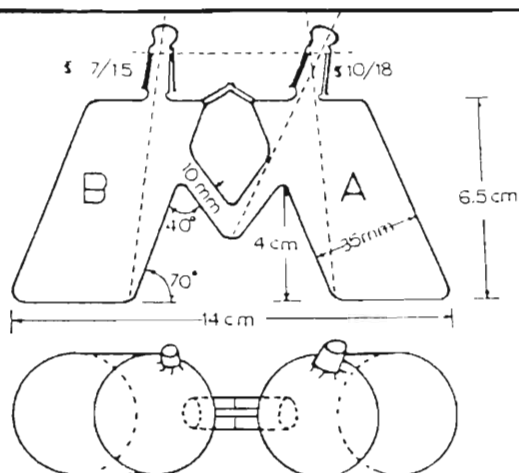


Figure 2.2. Mixing bottle of Battino<sup>17</sup>

of the measurement results.<sup>(19)</sup> The introduction of the remote cells offers a system for liquid measurement according to the oscillating sample tube method.<sup>(20)</sup> The density determination is based, in principle, on measuring the period of oscillation of a vibrating U-shaped sample tube which is either filled with sample or through which the sample is continuously flowing. The accuracy of this method is limited to some extent by four control factors:<sup>(21)</sup> the calibration procedure, the viscosity of the sample, the pressure of the system and the temperature control. The density of the sample is related to the resonance frequency of an electronically excited mechanical oscillator and the period of oscillation of the sample contained in the oscillator.<sup>(21)</sup>

The effective mass ( $M$ ) of the oscillator is composed of its own unknown mass ( $M_o$ ) as well as the unknown mass of the sample, density  $\rho$ , contained in volume  $V$  and is given by

$$M = M_o + V\rho \quad 2.3$$

The resonance frequency is given by

$$2\pi\nu = (c/M)^{1/2} = [c/(M_o + V\rho)]^{1/2} \quad 2.4$$

where the mass  $M$  is attached to a spring of constant elasticity  $c$ , under the condition that the oscillator performs an undamped oscillation.<sup>(9)</sup> Rearranging and making  $\rho$  the subject of the

## Chapter 2: Excess Molar Functions.....

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formulae

$$\rho = -M_o / V + (c/4\pi^2V)(1/v^2) = A + B\tau^2 \quad 2.5$$

where  $\tau = 1/v$ , ie. the period of oscillation, and  $A$  and  $B$  are constants characteristic of the oscillator. Densities are measured relative to a reference material:

$$\rho - \rho_o = B(\tau^2 - \tau_o^2) \quad 2.6$$

where  $\rho_o$  is the density of the reference material and  $\tau_o$  is its corresponding period of oscillation.

In this work, a densitometer containing an external measuring cell designed by Kratky *et al* <sup>(22)</sup> and commercially marketed by Anton Paar (Graz, Austria) is used. It consists of a U-shaped hollow borosilicate glass oscillator or sample tube, mounted in a dual wall glass cylinder filled with a gas of high thermal conductivity to facilitate a rapid temperature equilibration of the sample inside the oscillator.  $B$  from equation 2.6 is determined by obtaining  $\tau$  with two calibration measurements with samples of known densities ie. air and distilled water. The precision obtained in  $\tau$  is  $0.000002\text{Hz}^{-1}$ . Details of the Anton Paar vibrating tube densitometer is given in the experimental section - 2.3.2. Developments by Handa and Benson *et al* <sup>(9)</sup> show that in order to obtain a precision of  $0.001 \text{ cm}^3 \cdot \text{mol}^{-1}$  in  $V_m^E$ , the composition should be precise to five significant figures and density readings precise to six significant places. Further to this, Battino <sup>(7)</sup> reported that the measuring cell temperature must be controlled to  $\pm 0.001 \text{ K}$  to accurately determine densities to  $0.00002 \text{ g} \cdot \text{cm}^{-3}$ .

### c) Direct Measurements - Batch Dilatometers and Continuous Dilution Dilatometers

Highly accurate measurements are obtained by direct measurements using dilatometry, <sup>(1,9)</sup> without the need for time consuming procedures such as pycnometer filling, weighing etc. and errors arising from weight, composition or temperature determination of samples. Direct dilatometric measurement of  $V_m^E$  gives a much higher ratio of accuracy to effort. <sup>(1)</sup> A suitable and simple dilatometer is shown in fig.2.3. <sup>(1)</sup> The dilatometer is filled with a hypodermic

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syringe. Mixing was achieved by gently rocking the dilatometer to and fro. The excess molar volume of mixing,  $V_m^E$ , is given by the relation: (neglecting small terms allowing for the effects of the change of pressure on mixing of the volumes of the liquids and of the mercury)

$$V_m^E = \Delta V / (n_A + n_B) = A\Delta h / (n_A + n_B) \quad 2.7$$

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.

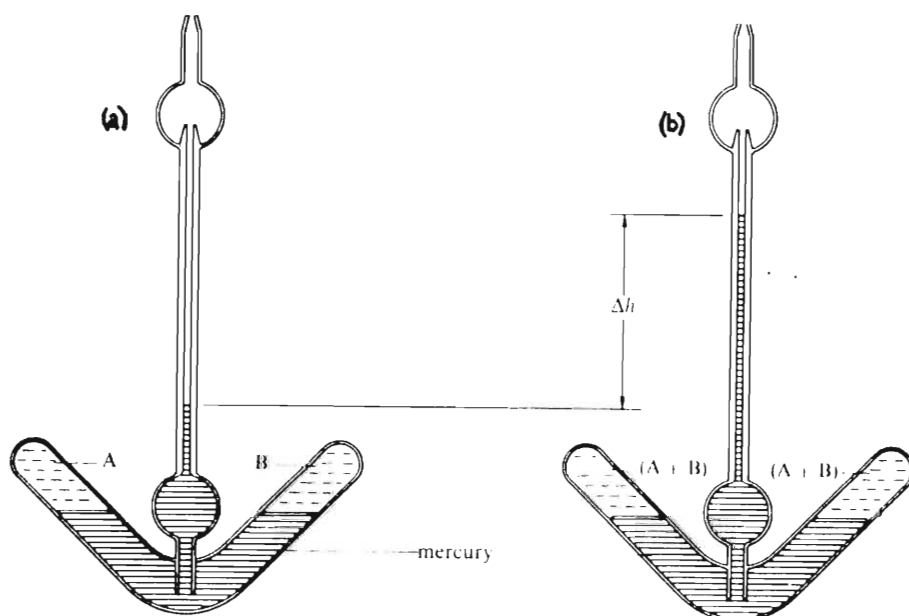


Figure 2.3 A dilatometer for measurements of volume of mixing showing (a) before mixing (b) after mixing<sup>(1)</sup>

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There have been fundamentally two types of dilatometric apparatus designed for the direct measurement of volume change<sup>(9)</sup> : (i) one composition per loading of the apparatus at a single temperature or *batch dilatometers*, and (b) a number of compositions per loading at a single temperature or *continuous dilution dilatometers*.<sup>(9)</sup>

### (i) Batch Dilatometry

One of the early examples of a design for a single loading dilatometer was the apparatus by Keyes and Hildebrand in 1917.<sup>(23)</sup> As seen in fig.2.4, it 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 two arms provided the means by which the volumes, before and after mixing, were determined. The entire mixing vessel was immersed in a thermostatted bath, and mixing was achieved by rocking the apparatus to and fro. It was reported that 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.<sup>(23,7)</sup>

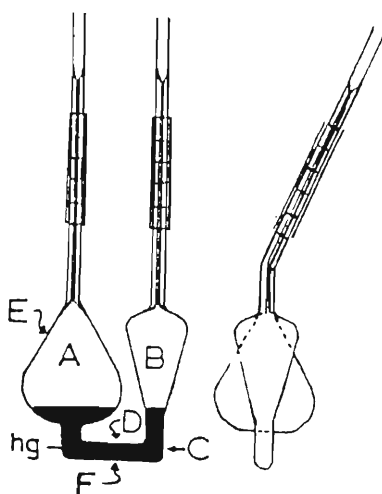


Fig 2.4 Keyes and Hildebrand dilatometer<sup>23</sup>

Duncan, Sheridan and Swinton<sup>(25)</sup> in their reviews, describe methods and a modified dilatometer apparatus in which the precision was found to be  $\pm 0.002 \text{ cm}^3 \cdot \text{mol}^{-1}$  or  $\pm 0.5\%$

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in  $V_m^E$ .<sup>(24,25)</sup>

Errors arising in batch dilatometer include the failure to take into account the a compressibility correction (a 1 % possible error in  $V_m^E$ ), corrections due to temperature fluctuations and the fact that extreme care has to be taken to avoid excessive amounts of grease on the joints.<sup>(26)</sup>

The primary disadvantage of the batch dilatometer was the speed of measurement, ie. each loading of the dilatometer only gave a single  $V_m^E$  reading.

### (ii) Continuous Dilution Dilatometry

The fundamental disadvantage of the batch dilatometer was eliminated by introduction of the many compositions per loading dilatometer ie. dilution dilatometry. The original design of the dilution dilatometer was arguably that by Geffcken, Kruis and Solana.<sup>(27)</sup> It has the mixing chamber C initially loaded with pure component A and mercury (as seen in fig. 2.5). stopcock S leads to reservoir R where pure component B is kept over mercury. The change in the mercury level upon mixing is read directly from the calibrated and graduated capillary D. The entire apparatus is kept in a thermostatted vessel. When S is opened, mercury from C forces some of component B into C via the connecting tube E. S is then closed and mixing begins. The change in level of mercury in capillary D is read directly. Increments of B are added in a similar way in order to determine  $V_m^E$  as a function of composition at one temperature.<sup>(27)</sup>

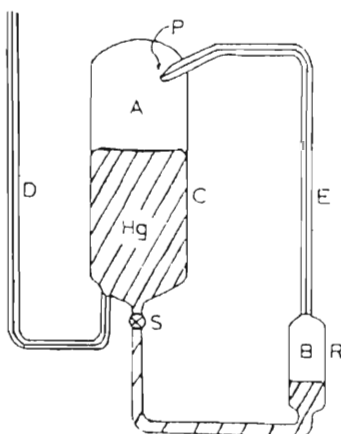


Fig 2.5 Dilution dilatometer of Geffcken, Kruis and Solana<sup>(27)</sup>

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Many workers have modified and adopted Geffcken *et al*'s original design:<sup>(29-34)</sup>

Stokes *et al*<sup>(32)</sup> modified Geffcken *et al*'s design by having component B confined in a burette above which component A is confined in a bulb, both over mercury. The two compartments are attached to a fine stainless steel tube, and known fractions of component B enter into the the bulb (containing A) by means of mercury flowing in the opposite direction via a stopcock. This design facilitates easier loading and usage.<sup>(32)</sup> Kumaran and McGlashan<sup>(33)</sup> designed a tilting dilatometer ; this tilting dilatometer is advantageous in that it reduces error because there are no taps to open and close during a measurement rather- mixing is achieved by tilting.<sup>(33)</sup> This design facilitates easier loading and calibration and allows for measurement of volume changes of any magnitude. Moreover, in the dilatometer designed by Kumaran and McGlashan,<sup>(33)</sup> the two liquids are separated by mercury at all stages of a run instead of only a diffusion boundary in a capillary as in previous dilatometer designs.<sup>(32,34)</sup> The dilatometer designed by Kumaran and McGlashan<sup>(33)</sup> is similar to the one depicted in fig. 2.6 except that capillary C has a larger bore size and it has a calibrated bulb X blown at the bottom of the calibrated burette A. The presence of the bulb X eliminates the need to calibrate the mixing cell B. Before the start of the run, bulb B is filled with mercury and burette A with one of the sample components. After thermal equilibrium and with stopcock  $T_1$  removed, mercury from B is transferred into X thus creating space of known volume in B.<sup>(33)</sup> A standard deviation of  $0.0007 \text{ cm}^3 \cdot \text{mol}^{-1}$  for  $V_m^E$  for this type of dilatometer has been reported.<sup>(33)</sup>

There have been two major reported disadvantages for dilution dilatometers.<sup>(9)</sup> Firstly, relatively large volumes ( $50\text{-}100 \text{ cm}^3$ ) of highly purified components are required; and secondly, specifically for the dilatometers described here<sup>(32,33,34)</sup>, to measure a change in volume at constant pressure, a correction must be made. That is, a change in the height ( $\Delta h$ ) of the mercury meniscus in the capillary causes a change in the mixing cell pressure equal to  $\rho g \Delta h$ , where  $\rho$  = density of mercury. Errors in  $V_m^E$  of 1-2 % can accrue in this manner.<sup>(9)</sup> Tanaka *et al*<sup>(35)</sup> improved on the McGlashan type dilatometer to produce a dilatometer capable of extremely sensitive precision.

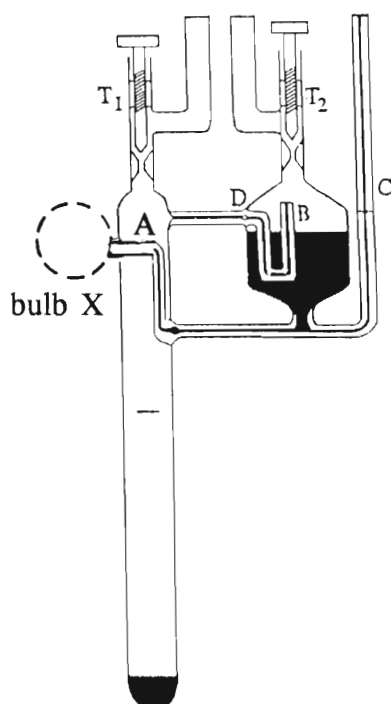


Fig 2.6 Similar designed tilting dilatometer of Kumaran and McGlashan<sup>34</sup>

### 2.1.2 Error Analysis for the $V_m^E$ data obtained from density values used in this work

Appendix 1.1 gives a detailed error analysis. In principle, to obtain a maximum error of  $0.002 \text{ cm}^3 \cdot \text{mol}^{-1}$  in  $V_m^E$ , the masses must be known to a precision of  $0.00001 \text{ g}$ , the  $\tau$  values to  $2 \times 10^{-6} \text{ Hz}^{-1}$  and the densities to  $1 \times 10^{-5} \text{ g} \cdot \text{cm}^{-3}$ .

### 2.2 Excess Molar Enthalpies of Mixing

All chemical and physical reactions have a net heat evolution which gives basic information on the mechanism and extent of reaction, a process which often only calorimetry can detect and measure.<sup>(36)</sup> For binary liquid mixtures, the excess molar enthalpies of mixing,  $H_m^E$ , may in principle,<sup>(37)</sup> be defined by the relation

$$H_m^E = G_m^E - T (\partial G_m^E / \partial T)_p \quad 2.8$$

However, this is not considered a satisfactorily accurate method. It has been reported that the errors in  $H_m^E$  derived in this way are approximately 15 times as large as the error in the free energies from which it is derived.<sup>(2)</sup> For this reason the most precise values of  $H_m^E$  are those measured directly by means of a calorimeter.

In principle, the direct measurement of heats of mixing is quite simple. The basic design involves a cell in which the two liquids are initially separated.<sup>(2)</sup> All that is required is an apparatus in which known quantities of two liquids can be brought to a constant temperature, a thermometer to measure the temperature change when the two liquids are mixed and an electrical heater in which measured amounts of energy can be dissipated in order to calibrate the apparatus.<sup>(2,38,39)</sup> A simple apparatus in which approximate measurements of heats of mixing may be made is shown in fig 2.7.<sup>(2)</sup> Measured quantities of two liquids are placed in the vessels A and B in a thermostat bath. Mixing is brought about by forcing the liquid from A over into B and the temperature change on mixing is measured by the thermometer C. The heat capacity of the apparatus is determined for each experiment by passing a measured current through the heater D of known resistance for a measured time. The enthalpy of mixing is then given by the relation

$$H_m^E = \Delta T_1 / \Delta T_2 (I^2 R t) \quad 2.9$$

where  $\Delta T_1$  is the temperature change on mixing,  $\Delta T_2$  is the temperature rise on calibration,

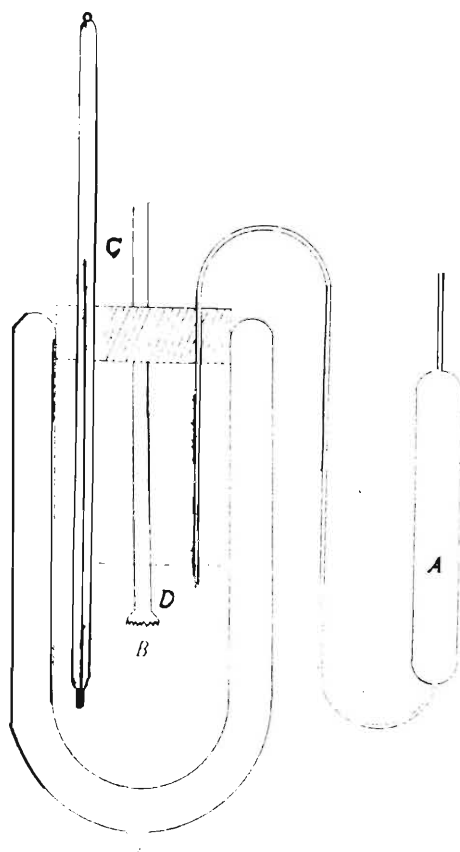


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$R$  is the resistance of the heater,  $I$  is the current of the heater, and  $t$  is the time for which the current flows.<sup>(2)</sup>

The isothermal calorimeters used in this work is a commercial LKB 2107-107 flow microcalorimeter and the Thermometric 2277 Thermal Activity Monitor. The excess molar enthalpies,  $H_m^E$ , were determined for the same binary liquid systems for which the excess molar volumes are reported.



*Fig 2.7 Simple apparatus for measurements of heats of mixing<sup>2</sup>*

### 2.2.1 Calorimetric Measuring Techniques

The enthalpies of mixing are measured in calorimeters of which many types have been described.<sup>(40,41,42)</sup> The most commonly used methods in calorimetry are the adiabatic and isothermal methods. In the adiabatic experiments, the two liquids are mixed in an isolated vessel (i.e vacuum jacket) which is thermally insulated from its surroundings.<sup>(42)</sup> If the excess

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enthalpy,  $H_m^E$  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 difference can be corrected for by observing the temperature change for a calculated supply of electrical energy.<sup>(43)</sup> 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.<sup>(43)</sup>

The single most important point in the design of any calorimeter for the heats of mixing is that when the mixture is formed in a vessel in which there is a vapour space<sup>(2)</sup> there will be on mixing a change in the composition of the vapour corresponding to the changes in the partial pressure of the components in the mixture.<sup>(2)</sup> Corresponding to these changes in vapour composition there will be evaporation and condensation of small quantities of the volatile liquids.<sup>(1,2,42)</sup> When the heat of mixing is small, evaporation or condensation of as little as  $10^{-2}$  to  $10^{-3}$  mole of liquid can produce a heat effect as large or larger than that of the heats of mixing.<sup>(44)</sup> McGlashan<sup>(2)</sup> has reported that vapour spaces of up to  $0.25 \text{ cm}^3$  could lead to an error in  $H_m^E$  of  $\pm 100 \text{ J} \cdot \text{mol}^{-1}$ . For this reason much effort has gone into designing mixing vessels in which vapour spaces are completely eliminated. Accounts in the literature<sup>(45-50)</sup> can be found of all kinds of mixing vessel for calorimeters, such as combustion bomb calorimeters used in the determination of enthalpies of combustion; flame calorimetry used in the determination of enthalpies for sufficiently volatile substances including gases; flow calorimeters used in the measurement of enthalpies of reaction between fluids, microcalorimeters for the measurement of values for  $|H_m^E|$  less than 1 kJ between liquids and "explosion calorimeters" specially designed for the study of reactions between metals at high temperatures.<sup>(1,42)</sup> Hirobe's mixing vessel<sup>(42)</sup> developed in 1914 was arguably the first mixing vessel which attempted to keep vapour spaces as small as possible. Hirobe's mixing vessel is shown in fig. 2.8. The liquids are initially separated by mercury, and in contact with vapour spaces which were kept at a minimum. Mixing comes about by inversion of the vessel by means of the threads, **A** shown in the figure.

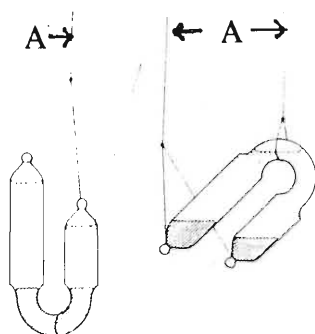


Fig 2.8 Hirobe's mixing vessel<sup>42</sup>

Modified designs but with more attention focused on the reduction of the effects of vapour spaces have been developed by later workers.<sup>(51,52)</sup> One of the major advancements in the developments of mixing vessels was the one introduced by van der Waals in 1950<sup>(53)</sup> for his heats of mixing measurements and is shown in fig. 2.9. It was made of brass and the liquids were introduced into compartments A and B and isolated by means of a ground in stopper K. The lid was screwed on against the packing L. Mixing was brought about by manipulation of nylon threads from outside the calorimeter so as to invert the vessel and displace K.

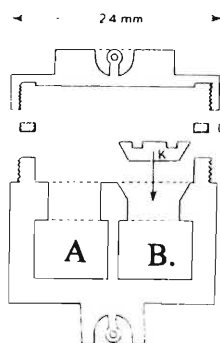


Fig 2.9 Van der Waals's mixing vessel<sup>53</sup>

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The mixing vessel of McGlashan and Larkin<sup>(54)</sup>, developed in 1961, is shown in fig. 2.10. This was one of the first calorimeters suitable for enthalpies of measurement as it eradicates the errors due to the presence of vapour space and it did not allow for volume changes that occurred on mixing.<sup>(2,54)</sup> The vessel consists of two compartments A and B in its upper half, and a capillary C with bulb D which can be attached to the vessel through the ground glass joint E and F. A heating element, H, and four thermistors ( $T_1$  to  $T_4$ ) distributed over the surface of the mixing vessel forms part of the Wheatstone bridge assembly. The vessel is filled completely with and immersed in a bowl of mercury. The mercury is displaced from the upper compartments by introducing weighed quantities of the mixture through the opening on 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 within a thermostat until temperature is achieved. After temperature equilibration, 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.<sup>(54)</sup> The accuracy of the apparatus has been quoted at  $0.7 \text{ J.mol}^{-1}$  of the maximum value of  $H_m^E$ .<sup>(37,54)</sup> One of the major disadvantages of this technique and the subsequent designs is that it takes a long time to get a single measurement and the method cannot be readily automated.

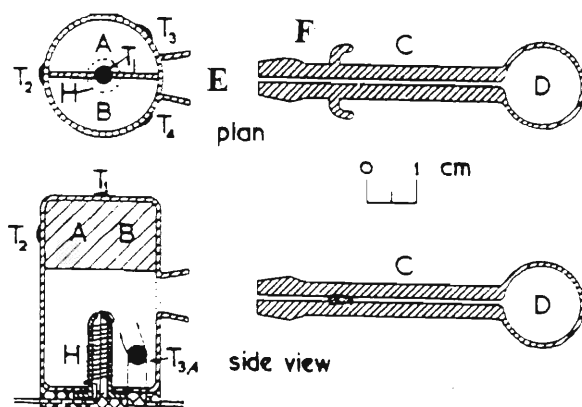


Fig 2.10 Adiabatic calorimeter of McGlashan and Larkin<sup>54</sup>

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For the most precise measurements in which enthalpies of mixing are determined with an accuracy of  $\pm 0.05 \text{ J}\cdot\text{mol}^{-1}$  flow microcalorimetry was developed and advanced.<sup>(55,59)</sup> Basically, in flow microcalorimetry, two liquids are injected at a steady known rate into a mixing vessel, where complete mixing is achieved in the absence of a vapour space.<sup>(2)</sup> The excess enthalpy is related to the power output of the heating element and the molar flow rates of the two components<sup>(37)</sup> (refer to experimental section for details). The advantage of the flow microcalorimeter is that it produces rapid, sensitive results; that both endothermic and exothermic mixing reactions can be studied, and that only small quantities (often less than  $50 \text{ cm}^3$  of each liquid) are needed for each experimental run.<sup>(1)</sup> No modern flow microcalorimeter allows any vapour space whatsoever with a resulting precision of 1% or better being achieved.<sup>(60-62)</sup> A flow microcalorimeter can be modified to be either adiabatic or isothermal.<sup>(63)</sup> The adiabatic condition is achieved when the flow cell and the temperature sensitive elements are thermally insulated from their surroundings. In the isothermal mode, the heat of mixing in the reaction vessel is transferred to the heat sink.<sup>(63)</sup>

A general description of the history of flow microcalorimeter designs as well as the working principles of flow microcalorimeters (both isothermal and adiabatic) is given by Monk and Wadsö in their review.<sup>(64)</sup> Amongst the earliest of these designs was that of McGlashan and Stoeckli.<sup>(65)</sup> It was reported that this type of instrument gave an error in  $H_m^E$  of  $\pm 1\%$ .<sup>(65)</sup> One major drawback in this instrument was that it required a large sample volume to cover the whole composition range. Furthermore, heat leaks inherent in the design of the instrument was not compensated for in the final calculation.<sup>(64,65)</sup>

A twin conduction calorimeter designed in the laboratory of Monk and Wadsö<sup>(64)</sup> and later commercialised by the LKB company (presently taken over by Thermometric) served to eradicate some of the uncertainties produced by the McGlashan *et al*<sup>(65)</sup> type calorimeter. Basically the apparatus consists of a metal block heat sink, containing a centrally located heat exchanger unit surrounded by calorimetric units in a twin arrangement. The calorimetric units comprise two flow reaction cells surrounded by surface thermopiles in contact with primary heat sinks. The heat sinks are thermally isolated and immersed in a water bath. Heat evolved or absorbed during the mixing process is thus conducted to or from a heat sink

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arrangement through the semi-conductor thermopiles. Peristaltic pumps were used to introduce the liquids into the mixing cell.<sup>(64)</sup>

Work done by Hsu and Clever<sup>(66)</sup> on the instrument developed by Monk and Wadsö<sup>(64)</sup> showed that errors could arise from flow rate variation required to cover the complete mole fraction composition range. Errors of  $\pm 20 \text{ J.mol}^{-1}$  in  $H_m^E$ <sup>(66)</sup> was reported using the recommended IUPAC<sup>(67)</sup> test system (i.e cyclohexane + n-hexane). This error was not accounted for in  $H_m^E$  determinations. This error becomes more substantial and serious in the dilute mole fraction range where  $H_m^E$  is small and the sample liquid flow rates are near their limits.<sup>(66)</sup>

Further recent designs of flow microcalorimeters include that of Randzio and Tomaszkiwicz(1980)<sup>(56)</sup>, Siddiqi and Lucas (1982)<sup>(68)</sup> and Christensen *et al* (1981,<sup>(45)</sup> 1976<sup>(46)</sup>). In all of these designs frictional effects (i.e in difficult to mix systems the principle measurement in the mixing cell is usually regulated via temperature measurements from thermocouples; there is a small temperature rise due to viscous dissipation in the mixing and reference arms of the calorimeter- this temperature difference gives rise to errors due to frictional effects) were simply neglected and have been shown to produce substantial error if not carefully corrected or designed for.<sup>(69)</sup>

Raal and Webley<sup>(69)</sup>, in their recent design of a new differential microflow calorimeter considered the following points as important requirements for the present day microcalorimeter design: ( in addition to the absence of vapour space and careful composition control)

- (a) Carefully designed equilibrators preceding the mixing cell and producing both components at exactly the set calorimeter temperature at all flow rates
- (b) accurate separation of frictional energy from the desired excess enthalpy and
- (c) the elimination of heat leaks dependant on fluid flow rates and physical properties.

Accommodating all the above pointers, Raal and Webley<sup>(69)</sup> designed a differential microflow

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calorimeter capable of producing  $H_m^E$  with an accuracy of  $0.53 \text{ J}\cdot\text{mol}^{-1}$ . They have reported results for the (cyclohexane + n-hexane) binary liquid system (the IUPAC recommended test system)<sup>(67)</sup> which are in excellent agreement with the data of Marsh and Stokes<sup>(70)</sup> and is superior in precision and accuracy to those of Grolier<sup>(57)</sup> (Picker type calorimeter), and McGlashan and Stoeckli.<sup>(65)</sup>

The most recent developments<sup>(71,72)</sup> by workers such as Randzio<sup>(56)</sup> and his research team are on instrument capable of measuring  $H_m^E$  at high temperatures and pressures as well as instruments designed to cope with very viscous systems.

## 2.3 EXPERIMENTAL

### 2.3.1 Materials

All the liquids used in this work were tested for impurities by GCMS and glc and were kept in a dry box before use. Some of the liquids were purified according to recommended methods.<sup>(73)</sup> A summary of the materials, their suppliers and purities used in this work are given in Table 2.1.

The alkenes and alkynes were fractionally distilled before use. Glc analysis of the 1-alkenes and 1-alkynes shows that the impurity content was less than 0.5 mol percent. The alkanols were purified repeatedly using previously established methods<sup>(74)</sup> in the following manner: they were refluxed over magnesium turnings and iodine for 30 minutes and then distilled through a 150 mm lagged glass fragment-packed column. The water impurity content in the alkanols was determined by Karl Fischer titrations to be less than 0.02 mole percent. Glc analyses indicated a purity of  $>99.8$  mole percent for all the alcohols. The densities of the of the 1-propanol and 2-propanol at 298.15 K was found to be  $0.7998$  and  $0.7815 \text{ g}\cdot\text{cm}^{-3}$ , respectively. Di-n-butylamine (DBA) was used without any further purification. The ethers were distilled before use and dried using 0.4 nm molecular sieves and degassed before measurement. The ethers were also analyzed for their water contamination before use and in all cases the mole fraction of  $\text{H}_2\text{O}$  was determined to be  $< 0.0001$ . Analysis of the ethers and the di-n-butylamine done by g.l.c. indicated that the total mole fractions of impurities was  $< 0.002$  for each of the liquids xcept dipropyl ether and  $< 0.006$  for dipropyl ether.

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Distillation of the dipropyl ether did not improve the purity and the cost of purchasing pure dipropyl ether was prohibitive. A Varian GCMS and a Hewlett-Packard 5891A gas chromatograph equipped with a 3393A integrator and a 25m carbowax 20Mc capillary column was used. All the solvents were kept in a dry-box containing silica-gel and a double access door.

**Table 2.1.** *Materials used, their suppliers and purities*

<i>Compound</i>	<i>Supplier</i>	<i>Purity (mole %)</i>
1-hexene	Aldrich	99.8
1-heptene	Aldrich	99.8
1-octene	Aldrich	99.5
1-hexyne	Aldrich	99.5
1-heptyne	Aldrich	99.5
1-octyne	Aldrich	99.6
propan-1-ol	BDH	99.8
propan-2-ol	BDH	99.7
cyclo-5	Fluka	>99
cyclo-6	Polychem	99.0
cyclo-7	Aldrich	>99
cyclo-8	Janssen Chimica	>99



Table 2.1 *continued*

<i>Compound</i>	<i>Supplier</i>	<i>Purity (mole %)</i>
cyclo-10	Fluka	> 99
DBA	Janssen Chimica	> 99
diethyl ether	Janssen Chimica	98+
dipropyl ether	Janssen Chimica	> 99
dibutyl ether	Janssen Chimica	99+
isopropyl ether	Riedel-deHaën	98+
TAME	Aldrich	> 99
TBME	Janssen Chimica	99.5
THF	Riedel-deHaën	> 99
THP	Janssen Chimica	> 99
1.4 dioxane	Merck	> 99

### 2.3.2 Apparatus Details

The  $H_m^E$  and  $V_m^E$  results for the binary liquid mixtures reported in this work were determined using the commercially available LKB 2107-101 and Thermometric 2277 Thermal Activity flow-mix microcalorimeter and an Anton Paar DMA 601 vibrating tube densitometer, respectively.

### 2.3.2.1 Equipment Description

#### a) $V_m^E$ measurements - Anton Paar DMA 601 vibrating tube densitometer

##### (i) Principle of operation

The laboratory arrangement for the densitometer is shown schematically in fig. 2.11. The measuring cell is contained in its own separate housing and is thermally separated from the electronics. The oscillator or sample tube (see fig. 2.12) is made out of borosilicate glass and is fused into a dual wall glass cylinder. The space between the U-shaped sample tube and the inner wall of the dual wall is filled with a gas of high thermal conductivity to facilitate a rapid temperature equilibration of the sample inside the oscillator with the thermostat liquid which flows through the dual wall cylinder around the sample tube. An additional shorter capillary tube inside the inner space of the dual wall cylinder is for the accurate determination of the measuring cell temperature by means of a temperature sensor. This capillary tube has a wall thickness of about 0.2 mm to assure good heat transfer. In operation, the sample tube is completely filled with  $\pm 0.7$  ml of sample substance then electronically excited and density measurements are determined precisely by measurement of the period of oscillation of the sample tube. The following relationship exists between the period,  $\tau$  and the density  $\rho$  :<sup>(75)</sup>

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

where  $A$  and  $B$  are instrument constants that are determined through calibration measurements with substances of known density.

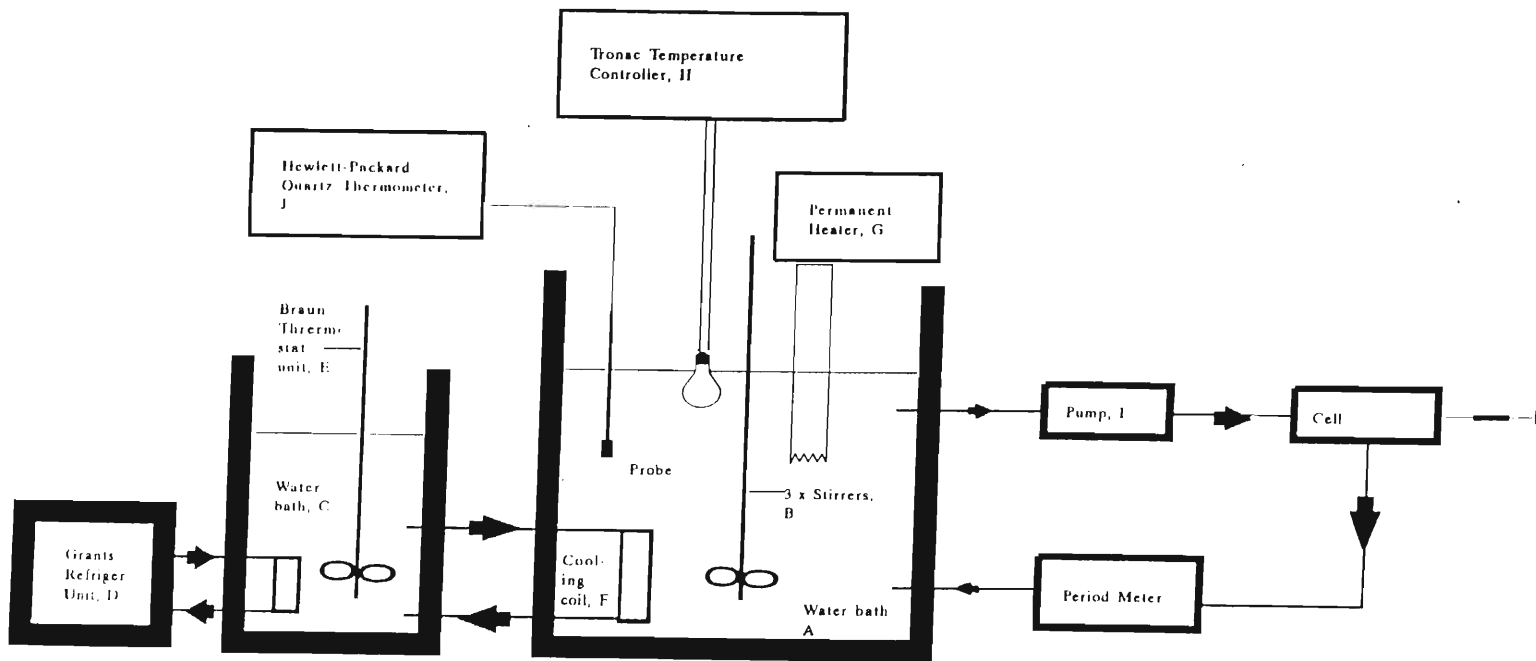
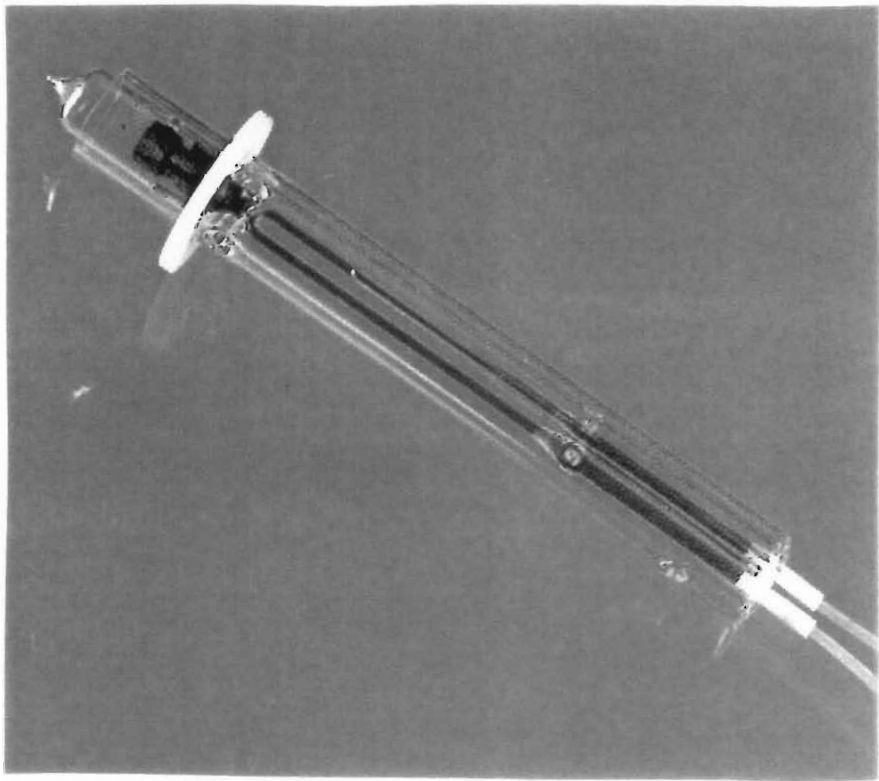


fig. 2.11. : Laboratory arrangement.



*Fig 2.12 The sample tube or oscillator used for density measurements*

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### *(ii) Theory of Density Measurement*

The density determination for liquids is based on the electronic measurement of frequency or equivalently frequency.<sup>(75)</sup> The sample is introduced into a device that is capable of oscillating, and the natural frequency of the oscillating device is influenced by the mass and therefore the density of the sample. The oscillator is electronically excited to oscillate in an undamped fashion<sup>(20)</sup> and the direction of oscillation is perpendicular to a plane through the inlet and outlet opening of the sample tube. The natural frequency of the oscillating device is only influenced by that precisely defined volume proportion of the sample that fills the oscillator up to its nodal points (inlet and outlet points). Thus the relationship between sample mass and natural frequency of the oscillator can be transferred without error to the sample density.

If we consider an equivalent system consisting of a hollow body oscillator with the mass  $M$ , which is suspended on a spring with a spring constant  $c$ . Its volume,  $V$  is assumed to be filled by a sample of density  $\rho$ .

The natural frequency  $f$  of such a system is then given by

$$f = \frac{1}{2 \Pi} \sqrt{\frac{c}{M + \rho \cdot V}} \quad 2.10$$

and therefore the period of oscillation  $\tau$  is given by

$$\tau = 2 \Pi \sqrt{\frac{M + \rho \cdot V}{c}} \quad 2.11$$

After this expression is squared and simplified by

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$$B = \frac{4 \Pi^2 \cdot V}{c} \quad ; \quad A = - \left( \frac{4 \Pi^2 \cdot M}{c} \right) \quad 2.12$$

one obtains

$$\rho = A + B' \cdot \tau^2 \quad \text{where } B' = 1/B \quad 2.13$$

Therefore, the following applies for the density difference of two samples:

$$\rho_1 - \rho_2 = B' (\tau_1^2 - \tau_2^2); \quad \text{and } B' = 1/B \quad 2.14$$

Constants *A* and *B* contain the spring constants of the oscillator as well as the empty oscillator's mass and that volume of the sample which participates in the oscillation. These constants are instrument constants for each individual oscillator and can be determined by two calibration measurements with samples of known density (e.g. air and deionised water). An unknown sample density,  $\rho_x$  with a period value,  $\tau_x$  is thus determined by the analog equation:

$$\rho_x = B' (\tau_x^2 - \tau_{\text{H}_2\text{O}}^2) + \rho_{\text{H}_2\text{O}} \quad 2.15$$

where water is the calibrating substance.

A prerequisite for measurements of high accuracy is an unquestionable temperature equilibration after the sample is introduced into the sample tube.<sup>(75)</sup> A shorter capillary tube inside the inner space of the dual wall cylinder is for the accurate determination of the measuring cell temperature by means of a temperature sensor (e.g. a thermistor). The achievable accuracy depends on the achievable operating temperature. A good external thermostat with a temperature stability of  $\pm 0.01$  °C can yield an uncertainty in the density measurement of approximately  $\pm 3 \times 10^{-6}$  g·cm<sup>3</sup>.<sup>(75)</sup> For this reason, the temperature stability was controlled to within 0.001 K in this work. In addition, errors can occur during

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sample injection into the sample cell when, for example the sample is introduced too fast, which generates air bubbles which results in a fluctuating and therefore inconsistent  $\tau$  value. Precautions must be taken during sample introduction to ensure no entrapment of air.

### *(iii) Temperature Control*

A diagrammatic representation of the temperature control system is shown in fig. 2.11. A uniform temperature throughout the bath was achieved through the use of two variable speed mechanical stirrers, B. An auxiliary cooling system, C, comprised a 50 litre water bath cooled by a Grants refrigeration coil, D, was incorporated to assist with the temperature control of the main water bath. Water from this auxiliary bath was pumped via a Haak immersion thermostat unit, E, at a rate of  $2.8 \text{ litre} \cdot \text{min}^{-1}$  through a four metre coiled copper tube, F, (12 mm i.d) placed inside the primary cooling bath. Since the auxiliary bath was maintained at a temperature of approximately 1 K below the operating temperature, this arrangement served to assist the main water bath in temperature maintenance. The thermostat liquid used for both the auxiliary and the main water bath was distilled water treated with a commercially available corrosion and algae inhibitor.

The thermostat system within the main water bath consisted of a permanent rheostated immersion heater, G, delivering up to 4 W, and a 100 W light bulb connected to a Tronac temperature controller, H. Water from the primary water bath was pumped through the water jacket by a submersible pump, I, at a rate of  $3.4 \text{ litre} \cdot \text{min}^{-1}$ . All rubber tubing to and from the densitometer was insulated to reduce heat losses. A Hewlett Packard 2801A quartz thermometer, J, calibrated as discussed in Appendix 1.2 was employed to monitor the temperature within the main bath. A Paar digital thermometer, linked to a thermocouple, was used to monitor the temperature in the cell.

### *(iv) Operation procedure for instrument and actual sample measurement*

Before any experimental measurements were made, complete temperature equilibration was achieved by allowing a warm up time of at least 30 minutes. Prior to each experimental run, the cell was flushed thoroughly with absolute ethanol (>99 %) and then acetone. After flushing, compressed air was blown through the cell. A constant period value,  $\tau$ , for the

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sample tube filled with air (in this case, the value for  $\tau_A = \pm 1.762623$ ) was obtained. Double distilled pre-boiled water (used as the calibrated standard sample) was then introduced into the cell by means of a glass syringe, which is equipped with a machined teflon nozzle, ensuring a leak-proof fit at the sample cell-syringe junction. The injection process was carried out slowly, enabling the liquid to properly wet the walls of the cell, and thus reducing 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 inlet nodal point during each measurement. The outlet nodal point of the cell was sealed with a teflon plug to reduce evaporation. The solution mixtures were introduced into the sample cell in exactly the same manner as the distilled water above.

With the cell illumination light off, the photoelectric portion of the excitation system was automatically activated. Each measuring cycle was allowed to continue until a constant period value was obtained. Period values for water (reference substance) pure solvents and air were determined between each solution injection. These values were not only required for the density calculations, but also permitted a continuous check on both the sample purity and the densitometer operation. The precision of  $\tau$ , judged by the repeated measurements for the same solution at different times, was estimated to be better than  $2 \times 10^6 \text{ Hz}^{-1}$ .

### *(v) Preparation of mixtures*

The pure solvents were degassed before sample solutions were made up by immersing the them in a sonic bath for 20 minutes.

The mixtures were made up in five  $\text{cm}^3$  flasks fitted with ground glass stoppers. Care was taken to first add the least volatile component to the flask, and that the completed mixture left a small vapour - just large enough to aid mixing. The mixtures were made up shortly before injecting into the densitometer, and were given a vigorous shake before injection.



### (b) $H_m^E$ measurements - LKB 2107 microcalorimeter and the 2277 Thermal Activity Monitor

#### (i) Principle of operation

The isothermal flow-mix measuring cylinder for the LKB calorimeter used in this work is shown diagrammatically in fig. 2.13. The mixing vessel, a, has two separate inlets and comprises a bifilar spiral-wound 24 carat gold tube of 1 mm i.d. and with a volume of 0.5 cm<sup>3</sup>. The design is such that adequate mixing is achieved with no vapour space. The mixing vessel is in thermal contact with a pair of matched thermocouples in the thermopiles, B, and an aluminium heat-sink assembly, C, and with heat sink compound covering all the surfaces of these items. An exothermic reaction results in heat flow to the heat sink assembly, while the opposite effect is observed for endothermic reactions. In each case the resultant temperature difference is detected by the thermopile positioned between the vessel and the heat sink. The output from the thermopiles is amplified and fed to a digital readout system and a Perkin-Elmer 561 chart recorder.

The aluminium block heat sink assembly is contained within an insulated housing. A heater and a temperature sensor are mounted within the main heat sink. The entire arrangement is contained within an LKB thermostat which comprises a thermostatically controlled air bath. To maintain the temperatures required for this investigation. Water cooled to 287 K by a Labcon Thermostat unit, was pumped through at a rate of 500 cm<sup>3</sup> · min<sup>-1</sup>.

The LKB was used in conjunction with an LKB control unit. This incorporates a power supply capable of providing an adjustable current to the calibration heaters contained within the insulated mixing vessel assembly, and a facility for heating and monitoring the temperature of the calorimeter heat sink assembly. This heating facility helps to reduce the equilibration time of the apparatus during "startup" or when raising the operating temperature

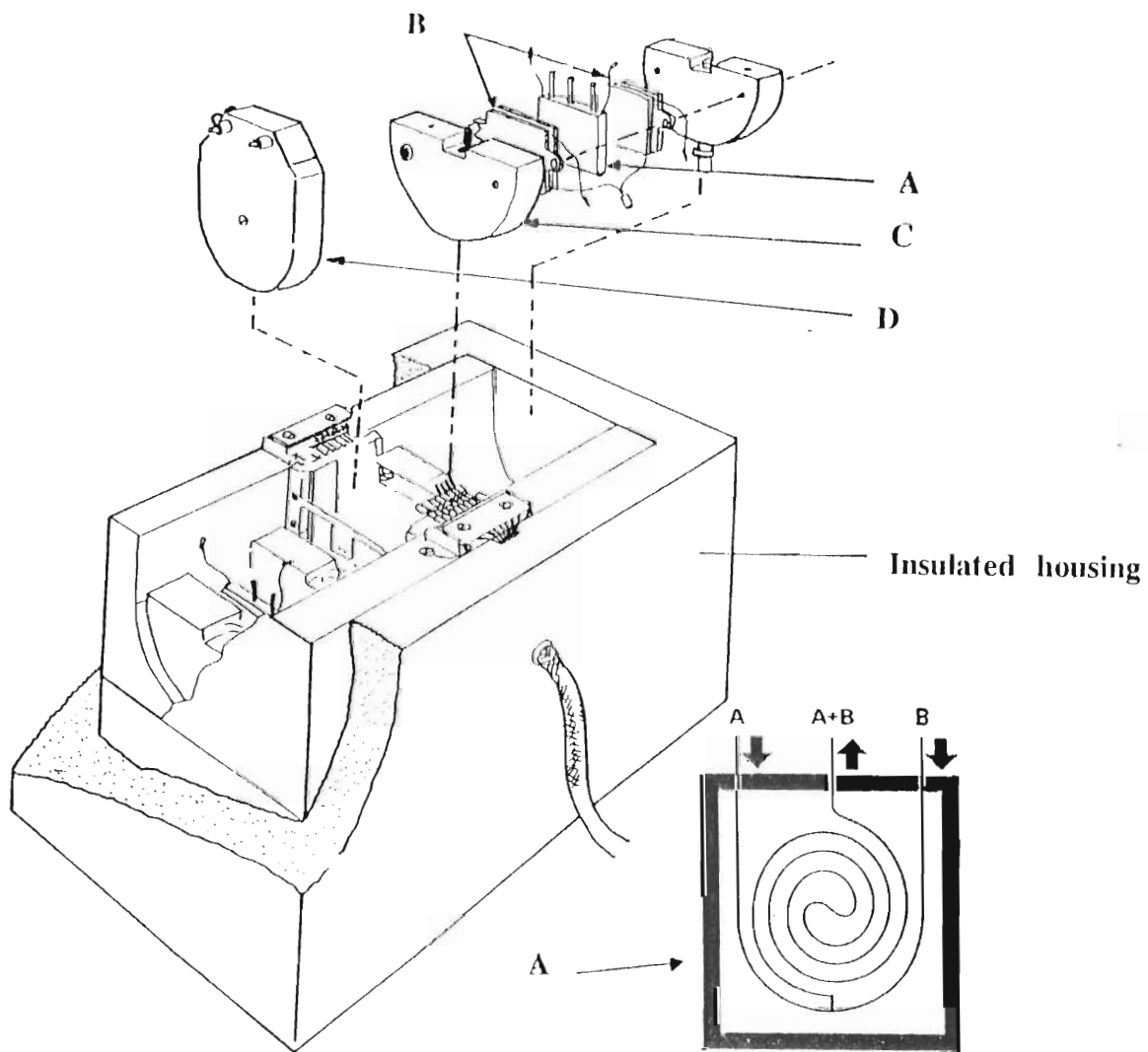


Fig. 2.13 Representation of the LKB microcalorimeter and the exploded view of the flow cell taken from LKB manual

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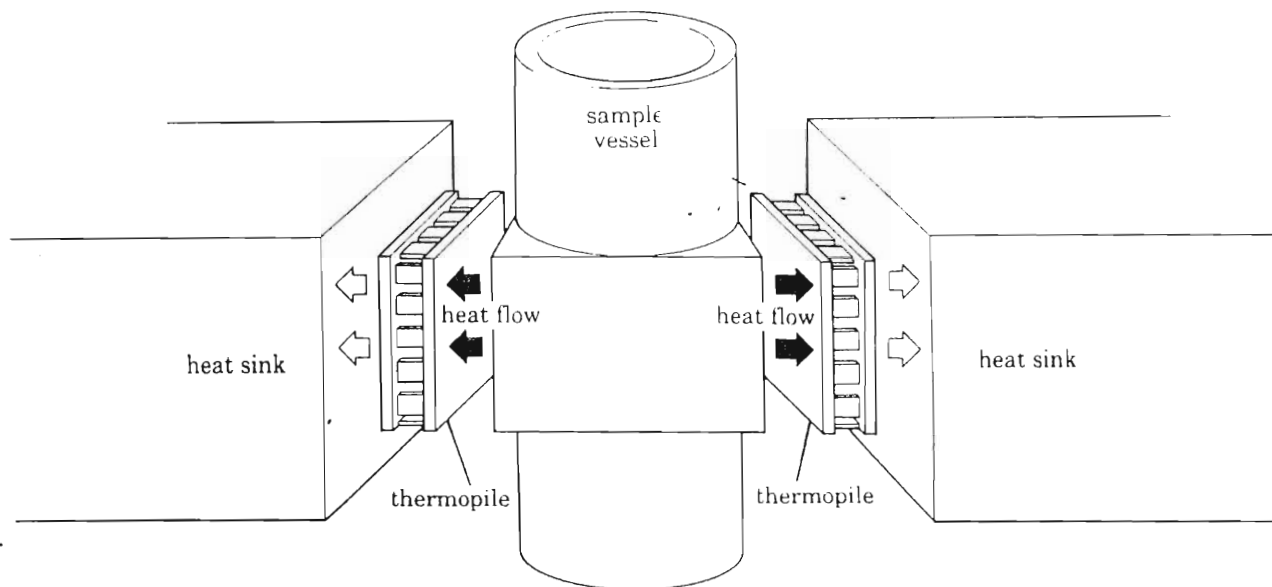
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and was always switched off when measurements with the instrument were made.

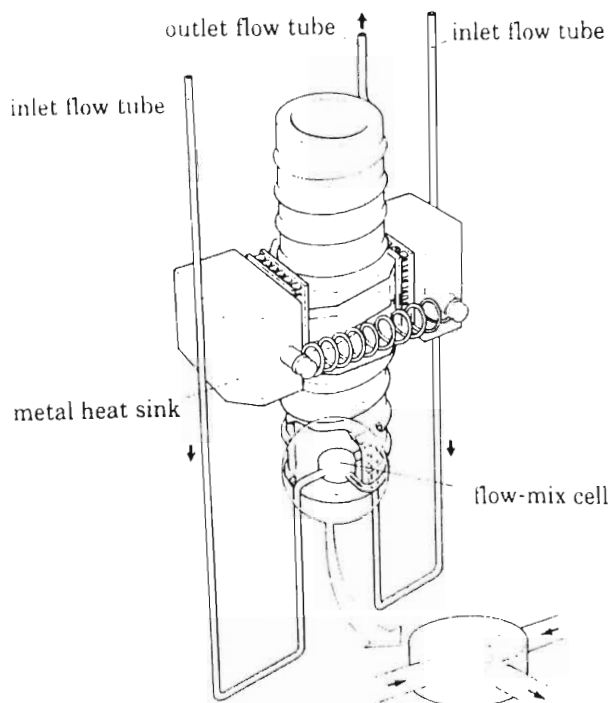
Since liquids entering the microcalorimeter are required to be within 0.05 K of the experimental temperature, they were first routed through an external heat exchanger fitted into a recess in the bottom of the air bath of the thermostat unit and then through the internal heat exchangers, D, situated inside the insulated housing containing the mixing vessel assembly. Samples were introduced using two Jubilee peristaltic pumps, capable of stable flow rates ranging from 0.03 - 2.0 cm<sup>3</sup> · min<sup>-1</sup>. Viton tubing, 1.5 mm *i.d.*, and teflon tubing, 1.2 mm *i.d* were used in the pumps and flow lines respectively. The temperature inside the microcalorimeter was monitored by a Hewlett Packard 2804 A quartz thermometer and was found to be constant to within 0.01 K.

The 2277 Thermal Activity Monitor equipped with an external thermostatic water circulator (Thermometric 2219 Multi-temp II) and a pair of Eldex variable speed piston pumps capable of stable flow rates ranging from 0.05 to 3 ml · min<sup>-1</sup> was used in conjunction with the LKB microcalorimeter for the (DBA + ether) work. The Viton tubing necessary for the operation of the peristaltic pumps were not suitable as they were not sufficiently resistant to some of the solvents, particularly THF and the secondary amine. In addition the LKB microcalorimeter was considered not sufficiently accurate for precise excess enthalpy determinations in the 1 to 50 J · mol<sup>-1</sup> (microwatt) range.

The Thermal Activity Monitor (TAM), utilises the heat flow or heat leakage principle where heat produced in a thermally defined vessel flows away in an effort to establish thermal equilibrium with its surroundings (fig.2.14(a)). The calorimetric mixing device used in the TAM (fig. 2.14(b)), has a 24 carat gold flow-mix cell, A, where 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, B, around the measuring cup and out to waste. The measuring cup is sandwiched between a pair of Peltier thermopile heat sensors. These sensors are in contact with a metal heat sink. The system is designed so that the main path



(a)



(b)

Fig. 2.14 (a) Representation of the heat flow principle used in the TAM and (b) the flow-mix measuring cup in the TAM taken from TAM manual

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for 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 one millionth of a degree celsius. These highly sensitive detectors convert the heat energy into a voltage signal proportional to the heat flow. Results are presented as a measure of the thermal energy produced by sample per unit of time.

Results are quantified where known power values are passed through built in precision resistors. Precision wire wound resistors (C in fig. 2.14(b)) are located within each measuring cup to represent a reaction during electrical calibration. The calibration resistors is integral with the measuring cup, to simulate as near as possible, the position of the reaction. This ensures that the output from the detector will be, as near as possible, identical to the output when the same power is dissipated from the resistor as from the sample. During calibration, a known current is passed through the appropriate channel heater resistor, and because the resistor value is known, a specific thermal power gives a calibration level which may then be used to determine quantitative experimental results. A typical calibration (A) and experimental (B) recorder output is shown in fig. 2.15.

This entire assembly is located in a stainless steel cylinder. Each cylinder has two measuring cup assemblies just described; the Peltier elements in each measuring cup are connected in series but in opposition so that the resultant signal represents the difference in the heat flow from the two measuring cups. This design allows one measurement cup assembly to be used for the sample and the other to be used as the blank.

This instrument is suitable for the solvents used in this investigation as ,outside the calorimeter unit the liquids are in contact with the Teflon (tubes and the tips of the pistons) and glass only. Inside contacts are the gold tube of the heat exchanger and the mixing cell and the teflon tubes. Samples were introduced into the cell using two Eltron piston pumps capable of producing flow rates from  $0.5$  to  $3.0 \text{ cm}^3 \cdot \text{min}^{-1}$ .

The sensitivity and high level of precision of the TAM is largely due to the stability of the

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infinite heat sink which surrounds the measuring cylinders. This heat sink is formed by a closed 25 litre thermostatted water bath, maintained to  $\pm 2 \times 10^{-4}$  °C within the experimental range. Water is continuously circulated by pumping upwards into a cylindrical stainless steel tank, where it overflows into a similar but larger outer tank. The pump then re-circulates the water from the outer tank back into the inner tank. Several interactive controlling systems work together to maintain the water at a constant temperature. Two thermistors monitor the water temperature whose signals are fed to an electronic temperature regulator unit. The 25 litre thermostat is filled with deionised water and a corrosion inhibitor containing sodium nitrate, sodium metasilicate and benzotriazole.

### *(iii) Operation procedure and actual sample measurement*

For both instruments, an initial equilibration time of at least three days was required. Power to the equipment was left on continuously for the duration of the experimental determinations to ensure that thermal equilibrium was maintained in the temperature control units. The flow lines were filled with water overnight. In the morning absolute ethanol was pumped through each flow line at a rate of  $5 \text{ cm}^3 \cdot \text{min}^{-1}$  for 15 minutes before introduction of the component liquids.

For the LKB microcalorimeter, the two inlets were separately flushed and primed with the two degassed sample components. A typical recorder output as a function of time for a steady state  $H_m^E$  measurement is represented in fig.2.16. Section A represents the steady state baseline obtained without any fluid flowing through the mixing vessel. This was always recorded before commencing a set of experimental measurements. Since accurate time elapse values were required for the determination of sample flow rates, the pumps and the stopwatch were activated simultaneously. Pumping of the samples was continued until a new steady state was reached, depicted by the baseline deflection, B, in fig. 2.16. Thereafter a calibration current to the calibration heater was applied in order to nullify this deflection, in the case of an endothermic reaction restoring the original baseline. In the case of an

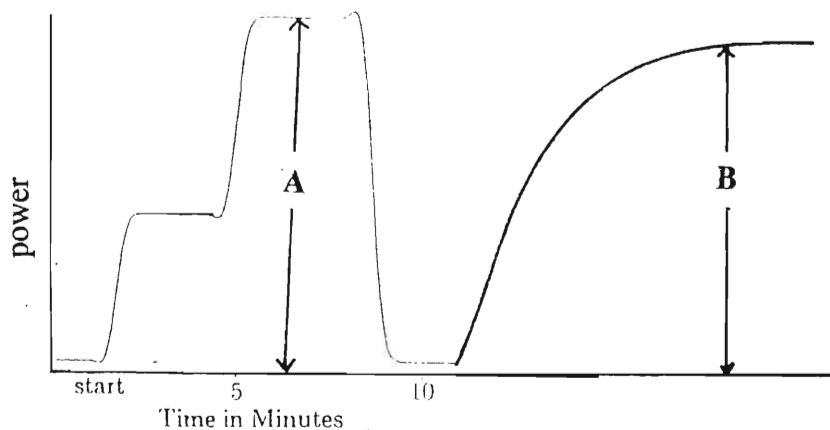


Fig. 2.15 A typical calibration and experimental recorder output for the TAM

exothermic reaction, enough current was applied to reproduce this baseline deflection, B. In practice, noise and non-uniform flow rates resulting from the peristaltic pumps operating at low speeds produced regular baseline deflections on the recorder. The current was thus always adjusted to a point where the spread about the mean value on the deflected baseline was reproduced about the zero flow-baseline.

Once the original baseline had been regained, both pumps were switched off. The molar flow rates  $f_1$  and  $f_2$  were determined by weighing the two component flasks before and after each experimental run. From these masses and the time elapsed for the experiment, the molar flow rates were determined. A Mettler AE240 electronic balance, accurate to 0.001 mg was used for the mass determinations.

For the TAM, due to the sensitivity of the instrument and the absence of a control unit containing an inbuilt current supply, calibration at the individual flow rates was necessary. This involved flushing one of the component solvents through both the inlet tubings at a flow rate similar to that for the actual experimental determination. A known current,  $I$ , from an external power source is simultaneously passed through the inbuilt resistor and because  $R$  for the resistor is known, the expected thermal power,  $P$ , can be obtained from the equation

$$P = I^2 R$$

2.16

and the calorimeter power reading is adjusted accordingly. Both the pumps, the external power supply were then switched off, the baseline was allowed to return to zero and flow of the second sample component in one of the lines was initiated for sufficient time to coat the tubing. Experiments were then carried out according to a method similar to that of the LKB microcalorimeter with the flow-rates exactly like those used in the calibration.

### *(iii) Preparation of Mixtures*

The sample liquids were prepared in 25 cm<sup>3</sup> Quickfit conical flasks fitted with modified B 14 stoppers - which had one 1.8 mm *i.d.* inlet connected by teflon tubing to the pump. This design was efficient in reducing evaporation of the component samples hence reducing the problem of co-existing liquid and gaseous phases. The masses of the effluent collected after each run were compared to the amounts of pure component consumed, thus serving as a constant check against liquid leaks in the system. For each new run, a new pumping rate was set and the process carried out as described.

During some experiments air bubbles were seen in the outlet tube and were disclosed on the recorder as sudden decreases or increases in the steady state line. These were thought to originate from gas bubbles present in the sample components. Hence degassing of all solvents prior to an experimental run was imperative.

### *(iv) Friction Effects and Flow rate determinations*

The friction effects due to flow of the solvents and the characteristics of the sample components towards the teflon tubing have to be corrected for in the LKB 2107 microcalorimeter. This correction was not necessary in the TAM as the calibration took these factors into account. For an experimental run done on the LKB microcalorimeter, the values of the baseline deflections,  $\theta_B$ , and the corresponding currents,  $I$ , required to nullify these deflections were plotted for each system. (see fig.2.16) In each case the resulting graph together with the graph for the mixture from each run were employed to adjust the experimental readings for the frictional effects.



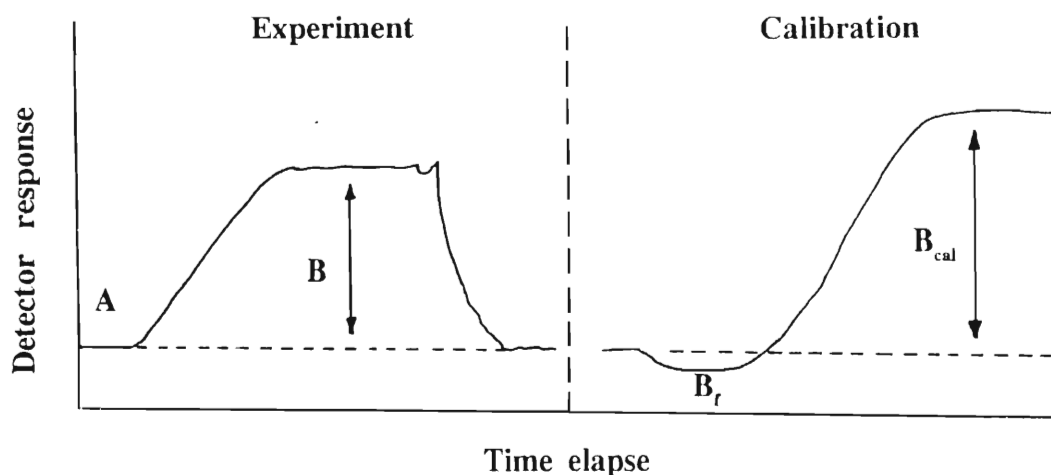


Fig. 2.16 A typical calibration and experimental recorder output for the LKB microcalorimeter

These calibrations were carried out collectively at the end of a series of experimental runs for a system. Each calibration involved purging the mixing vessel with the effluent from a particular run. With the same pumping parameters as were employed for that particular run, any heating effect due to friction exhibited a deflection,  $B_f$ , in fig 2.16. The experimental detector voltage shift was thus corrected to

$$B_o = B - B_f \quad 2.17$$

The indicated calibration current,  $I_{cal}$ , corresponding to  $B_o$ , was then interpolated from the experimentally determined graph and was passed through the calorimeter heater, thereby producing a baseline deflection corresponding to  $B_{cal}$  in fig 2.16. The excess molar enthalpy was thus calculated from

$$H_m^E = \{B_o(I_{cal})^2 R\} / B_{cal} / (f_1 + f_2) \quad 2.18$$

where  $R$  is the resistance heater. It is however, observed that  $B_o \approx B_{cal}$  for flow rates less than  $0.80 \text{ cm}^3 \cdot \text{min}^{-1}$ .<sup>(82)</sup> Since the majority of the experimental runs were carried out at flow

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rates less than this, the above calibration procedure became unnecessary in many cases and  $H_m^E$  was then determined by

$$H_m^E = (I_{cal}^2 R) / (f_1 + f_2) \quad 2.19$$

For exothermic reactions, the steady state deflection,  $B$ , was noted and a current,  $I$ , was applied to double this deflection. Heating due to frictional effects would once again produce a deflection,  $B_f$ , and hence equation 2.17 becomes

$$B_o = B + B_f \quad 2.20$$

The TAM was, however, found to give more precise results for small endothermic and exothermic reactions and hence for most of the systems discussed in this work it was the instrument of choice.

### (v) Test systems

The excess enthalpies of the nonviscous system (cyclohexane + n-hexane) has recently been recommended by the IUPAC<sup>(67)</sup> Commission on Thermodynamics and Thermochemistry(1970) for checking calorimeter accuracy and data, since results for this system obtained in five different laboratories with three types of isothermal calorimeters shows no systematic discrepancies.

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The recommended equation at 298.15 K is

$$H_m^E(\text{J} \cdot \text{mol}^{-1}) = x_1(1-x_1)[866.1 - 249.4(1-2x_1) + 97.0(1-2x_1)^2 - 31.8(1-2x_1)^3] \quad 2.21$$

where  $x_1$  is the mole fraction of cyclohexane. Marsh and Stokes<sup>(70)</sup> reported very accurate and precise results using an isothermal batch calorimeter with a standard deviation of 0.09 J·mol<sup>-1</sup>; Grolier *et al*<sup>(57)</sup> obtained data with a Picker flow calorimeter with a standard deviation of 0.35 J·mol; McGlashan and Stoeckli,<sup>(47)</sup> and Siddiqi and Lucas<sup>(68)</sup> used an isothermal flow calorimeter and obtained a standard deviation of 1.1 J·mol and 0.78 J·mol respectively. The accuracy and precision for this work was estimated from the data sets obtained for the (cyclohexane + benzene) system and the standard deviation for these results and those interpolated from the IUPAC equation is 1.0 J·mol<sup>-1</sup>. This data shows equal and superior precision to that of McGlashan and Stoeckli.<sup>(47)</sup>

## 2.4 RESULTS

The measured excess volumes,  $V_m^E$ , and the measured excess enthalpies,  $H_m^E$ , are given in Tables 2.2 - 2.4 and Table 2.8 - 2.10, respectively. Each of the measured properties,  $X_m^E$ , are given together with the deviations,  $\delta X_m^E$ , calculated from the Redlich-Kister polynomial

$$\delta X_m^E = X_m^E - x(1-x) \sum_{r=0}^n Y_r (1-2x)^r \quad 2.22$$

where  $x$  refers to the mole fraction,  $X$  refers to either  $V$  or  $H$  and  $Y_r$  refers to either  $B_r$  or  $A_r$ , respectively. The coefficients  $Y_r$  are estimated by the method of unweighed least squares and are given in Table 2.5 - 2.7 and 2.11 - 2.13, respectively. The *Statgraphics 3.0* package was used to calculate these coefficients, and  $\delta$ . The  $V_m^E$  results were calculated using a GWBASIC program - the details of which are given in *Appendix 1.3*.

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**TABLE 2.2** Excess molar volumes,  $V_m^E$ , for binary mixtures of 1-hexene, 1-heptene and 1-octene with 1-propanol and 2-propanol and the deviations,  $\delta V_m^E$  calculated from equation.2.22 at the temperature 298.15 K

$x$	$V_m^E$ $\text{cm}^3 \cdot \text{mol}^{-1}$	$\delta V_m^E \cdot 10^3$ $\text{cm}^3 \cdot \text{mol}^{-1}$	$x$	$V_m^E$ $\text{cm}_3 \cdot \text{mol}^{-1}$	$\delta V_m^E \cdot 10^3$ $\text{cm}^3 \cdot \text{mol}^{-1}$	$x$	$V_m^E$ $\text{cm}^3 \cdot \text{mol}^{-1}$	$\delta V_m^E \cdot 10^3$ $\text{cm}^3 \cdot \text{mol}^{-1}$
$x1\text{-C}_6\text{H}_{12} + (1-x)1\text{-C}_3\text{H}_7\text{OH}$								
0.0394	-0.032	1.0	0.3773	-0.038	-5.0	0.8027	0.116	6.0
0.1273	-0.071	10.0	0.4837	0.012	28.0	0.8362	0.112	-2.0
0.1995	-0.081	-15.0	0.5917	0.056	-35.0	0.9100	0.084	-7.0
0.2673	-0.071	4.0	0.7237	0.108	15.0			
$x1\text{-C}_7\text{H}_{14} + (1-x)1\text{-C}_3\text{H}_7\text{OH}$								
0.0276	-0.001	-7.0	0.4013	0.123	-6.0	0.8314	0.180	4.0
0.0779	0.001	-32.0	0.4706	0.154	-9.0	0.8736	0.151	-5.0
0.1747	0.031	37.0	0.5563	0.189	10.0	0.9276	0.100	-3.0
0.3181	0.084	-9.0	0.6964	0.214	2.0			
$x1\text{-C}_8\text{H}_{16} + (1-x)1\text{-C}_3\text{H}_7\text{OH}$								
0.0492	0.023	-21.0	0.3195	0.179	-30.0	0.6133	0.270	-6.0
0.0900	0.053	31.0	0.4401	0.230	25.0	0.7134	0.278	-3.0
0.1673	0.100	9.0	0.5232	0.253	20.0	0.8703	0.225	17.0
0.2333	0.137	-15.0						

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Table 2.2. continued

$x$	$\frac{V_m^E}{\text{cm}^3 \cdot \text{mol}^{-1}}$	$\frac{\delta V_m^E \cdot 10^3}{\text{cm}^3 \cdot \text{mol}^{-1}}$	$x$	$\frac{V_m^E}{\text{cm}^3 \cdot \text{mol}^{-1}}$	$\frac{\delta V_m^E \cdot 10^3}{\text{cm}^3 \cdot \text{mol}^{-1}}$	$x$	$\frac{V_m^E}{\text{cm}^3 \cdot \text{mol}^{-1}}$	$\frac{\delta V_m^E \cdot 10^3}{\text{cm}^3 \cdot \text{mol}^{-1}}$
$x1\text{-C}_6\text{H}_{12} + (1-x)2\text{-C}_3\text{H}_7\text{OH}$								
0.0557	0.021	1.0	0.3694	0.276	-28.0	0.7268	0.397	23.0
0.1294	0.061	-27.0	0.4987	0.382	-22.0	0.8254	0.296	-37.0
0.1950	0.115	8.0	0.6039	0.427	18.0	0.8910	0.205	16.0
0.2680	0.185	44.0						
$x1\text{-C}_7\text{H}_{14} + (1-x)2\text{-C}_3\text{H}_7\text{OH}$								
0.0566	0.069	-33.0	0.3505	0.393	-2.0	0.7241	0.492	22.0
0.1031	0.131	19.0	0.4667	0.480	-9.0	0.8704	0.312	2.0
0.1886	0.227	-13.0	0.6027	0.525	-14.0	0.9409	0.160	-20.0
0.2516	0.299	23.0						
$x1\text{-C}_8\text{H}_{16} + (1-x)2\text{-C}_3\text{H}_7\text{OH}$								
0.0419	0.074	-1.0	0.3305	0.434	15.0	0.7012	0.529	-14.0
0.0916	0.153	-1.0	0.4383	0.511	-7.0	0.8534	0.363	36.0
0.1633	0.253	3.0	0.5435	0.555	2.0	0.9401	0.170	-38.0
0.2304	0.332	-10.0						

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**TABLE 2.3** Excess molar volumes,  $V_m^E$ , for binary mixtures of 1-hexyne, 1-heptyne and 1-octyne with 1-propanol and 2-propanol and the deviations,  $\delta V_m^E$  calculated from equation 2.22 at the temperature 298.15 K

$x$	$V_m^E$ $\text{cm}^3 \cdot \text{mol}^{-1}$	$\delta V_m^E \cdot 10^3$ $\text{cm}^3 \cdot \text{mol}^{-1}$	$x$	$V_m^E$ $\text{cm}^3 \cdot \text{mol}^{-1}$	$\delta V_m^E \cdot 10^3$ $\text{cm}^3 \cdot \text{mol}^{-1}$	$x$	$V_m^E$ $\text{cm}^3 \cdot \text{mol}^{-1}$	$\delta V_m^E \cdot 10^3$ $\text{cm}^3 \cdot \text{mol}^{-1}$
$x1\text{-C}_6\text{H}_{10} + (1-x)1\text{-C}_3\text{H}_7\text{OH}$								
0.0637	-0.054	2.0	0.5097	-0.085	0.0	0.7558	-0.050	1.0
0.1123	-0.083	-3.0	0.6332	-0.073	0.0	0.8260	-0.033	0.0
0.2544	-0.094	3.0	0.7128	-0.060	0.0	0.9009	-0.015	-1.0
0.3968	-0.092	-1.0						
$x1\text{-C}_7\text{H}_{12} + (1-x)1\text{-C}_3\text{H}_7\text{OH}$								
0.0509	-0.036	-4.0	0.3495	-0.034	-2.0	0.7378	0.059	-1.0
0.0997	-0.047	2.0	0.4721	0.001	1.0	0.8037	0.065	0.0
0.1811	-0.055	2.0	0.5744	0.028	1.0	0.8771	0.060	0.0
0.2497	-0.052	0.0						
$x1\text{-C}_8\text{H}_{14} + (1-x)1\text{-C}_3\text{H}_7\text{OH}$								
0.0400	-0.013	2.0	0.3277	-0.005	-7.0	0.6815	0.089	-2.0
0.0899	-0.025	0.0	0.4429	0.039	6.0	0.7830	0.096	-2.0
0.1657	-0.026	0.0	0.5386	0.061	1.0	0.8906	0.080	3.0
0.2248	-0.017	2.0						

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TABLE 2.3 continued

$x$	$V_m^E$ cm <sup>3</sup> ·mol <sup>-1</sup>	$\delta V_m^E \cdot 10^3$ cm <sup>3</sup> ·mol <sup>-1</sup>	$x$	$V_m^E$ cm <sup>3</sup> ·mol <sup>-1</sup>	$\delta V_m^E \cdot 10^3$ cm <sup>3</sup> ·mol <sup>-1</sup>	$x$	$V_m^E$ cm <sup>3</sup> ·mol <sup>-1</sup>	$\delta V_m^E \cdot 10^3$ cm <sup>3</sup> ·mol <sup>-1</sup>
$x1-C_6H_{10} + (1-x)2-C_3H_7OH$								
0.0560	-0.012	-5.0	0.2954	0.102	0.0	0.7737	0.203	9.0
0.0779	-0.010	-5.0	0.3899	0.155	-2.0	0.8970	0.110	-3.0
0.1129	0.117	2.0	0.5284	0.209	-4.0	0.8425	0.151	-4.0
0.2067	0.055	6.0	0.6151	0.226	0.0			
$x1-C_7H_{12} + (1-x)2-C_3H_7OH$								
0.0356	0.007	2.0	0.3668	0.188	-7.0	0.7319	0.258	-5.0
0.1008	0.025	-3.0	0.5033	0.262	3.0	0.8506	0.195	0.0
0.1889	0.084	3.0	0.5840	0.282	4.0	0.9205	0.126	3.0
0.2523	0.125	2.0						
$x1-C_8H_{14} + (1-x)2-C_3H_7OH$								
0.0939	0.036	2.0	0.4548	0.266	0.0	0.7899	0.236	0.0
0.1678	0.076	-2.0	0.5555	0.296	-3.0	0.8561	0.174	-3.0
0.2377	0.125	-2.0	0.6969	0.290	3.0	0.9322	0.094	2.0
0.3422	0.205	4.0						



## Chapter 2: Excess Molar Functions.....

**TABLE 2.4** Excess molar volumes,  $V_m^E$ , for (di-n-butylamine + an ether) and the deviations,  $\delta V_m^E$  calculated from equation 2.22 at the temperature 298.15 K

$x$	$V_m^E$ $\text{cm}^3 \cdot \text{mol}^{-1}$	$V_m^E \cdot 10^3$ $\text{cm}^3 \cdot \text{mol}^{-1}$	$x$	$V_m^E$ $\text{cm}^3 \cdot \text{mol}^{-1}$	$\delta V_m^E \cdot 10^3$ $\text{cm}^3 \cdot \text{mol}^{-1}$	$x$	$V_m^E$ $\text{cm}^3 \cdot \text{mol}^{-1}$	$\delta V_m^E \cdot 10^3$ $\text{cm}^3 \cdot \text{mol}^{-1}$
$x(\text{C}_4\text{H}_9)_2\text{NH} + (1-x)(\text{C}_2\text{H}_5)_2\text{O}$								
0.0250	-0.0554	-4.0	0.2348	-0.2902	4.0	0.5952	-0.3062	-1.6
0.0329	-0.0651	1.2	0.2926	-0.3195	1.5	0.6541	-0.2751	1.1
0.0592	-0.1152	-3.2	0.3371	-0.3367	-2.8	0.6901	-0.2534	1.8
0.0905	-0.1621	-3.3	0.3937	-0.3429	-1.1	0.7492	-0.2142	0.8
0.0931	-0.1651	-2.7	0.4402	-0.3431	-1.3	0.7991	-0.1752	1.0
0.1247	-0.2012	0.6	0.4951	-0.3352	-0.2	0.8057	-0.1686	2.2
0.1603	-0.2338	4.9	0.5395	-0.3254	-1.1	0.9062	-0.0882	-5.4
0.1983	-0.2698	0.5						
$x(\text{C}_4\text{H}_9)_2\text{NH} + (1-x)(\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{O}$								
0.0706	-0.0023	-1.0	0.4321	-0.1020	-1.8	0.7723	-0.0694	-5.1
0.1193	-0.0398	-2.1	0.4694	-0.1026	-2.3	0.8194	-0.0535	1.5
0.1641	-0.0546	-2.2	0.5058	-0.0992	-0.2	0.8562	-0.0475	-0.7
0.2097	-0.0613	4.9	0.5382	-0.0968	0.1	0.8932	-0.0381	-0.6
0.2768	-0.0798	2.9	0.6028	-0.0866	3.8	0.9389	-0.0208	3.0
0.3319	-0.0912	1.1	0.6722	-0.0802	0.9	0.9602	-0.0182	-1.8
0.3714	-0.1003	-3.4	0.7189	-0.0716	2.1			

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Table 2.4 - continued

$x$	$V_m^E$ cm <sup>3</sup> ·mol <sup>-1</sup>	$\delta V_m^E \cdot 10^3$ cm <sup>3</sup> ·mol <sup>-1</sup>	$x$	$V_m^E$ cm <sup>3</sup> ·mol <sup>-1</sup>	$\delta V_m^E \cdot 10^3$ cm <sup>3</sup> ·mol <sup>-1</sup>	$x$	$V_m^E$ cm <sup>3</sup> ·mol <sup>-1</sup>	$\delta V_m^E \cdot 10^3$ cm <sup>3</sup> ·mol <sup>-1</sup>
$x(\text{C}_4\text{H}_9)_2\text{NH} + (1-x)\{(\text{CH}_3)_2\text{CH}\}_2\text{O}$								
0.0100	-0.0305	1.1	0.2420	-0.3225	8.3	0.6231	-0.3462	4.0
0.0698	-0.1308	3.0	0.2923	-0.3652	-1.7	0.6942	-0.3074	-1.5
0.1082	-0.1903	-0.4	0.3581	-0.3916	-0.8	0.7370	-0.2729	0.8
0.1305	-0.2210	-1.9	0.4035	-0.4014	-1.2	0.8152	-0.2062	-0.1
0.1612	-0.2583	-2.8	0.4318	-0.4048	-2.5	0.8682	-0.1562	-1.5
0.1964	-0.2921	-0.2	0.4957	-0.3993	-2.2	0.9248	-0.0959	-0.1
0.2302	-0.3225	-0.9	0.5621	-0.3762	2.2	0.9748	-0.0427	-1.6
$x(\text{C}_4\text{H}_9)_2\text{NH} + (1-x)(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_2\text{O}$								
0.0256	0.0040	2.2	0.3868	0.0257	-3.5	0.6814	0.0195	-0.8
0.0393	0.0042	1.2	0.4387	0.0279	-1.6	0.7018	0.0202	1.1
0.1125	0.0123	2.2	0.4521	0.0304	1.0	0.7621	0.0183	2.7
0.1784	0.0167	-0.1	0.4533	0.0387	0.7	0.7933	0.0102	-3.6
0.2157	0.0176	-2.6	0.5027	0.0292	-3.0	0.8289	0.0110	-0.7
0.2218	0.0182	-2.5	0.5552	0.0237	-0.8	0.9242	0.0075	1.7
0.2905	0.0297	4.0	0.5811	0.0247	-0.9	0.9586	0.0049	1.5
0.3249	0.0243	-3.1	0.6177	0.0229	-0.9	0.9886	0.0017	0.7

Chapter 2: Excess Molar Functions.....

Table 2.4 - continued

$x$	$V_m^E$	$\delta V_m^E \cdot 10^3$	$x$	$V_m^E$	$\delta V_m^E \cdot 10^3$	$x$	$V_m^E$	$\delta V_m^E \cdot 10^3$
	$\text{cm}^3 \cdot \text{mol}^{-1}$	$\text{cm}^3 \cdot \text{mol}^{-1}$		$\text{cm}^3 \cdot \text{mol}^{-1}$	$\text{cm}^3 \cdot \text{mol}^{-1}$		$\text{cm}^3 \cdot \text{mol}^{-1}$	$\text{cm}^3 \cdot \text{mol}^{-1}$
$x(\text{C}_4\text{H}_9)_2\text{NH} + (1-x)\text{CH}_3\text{C}(\text{CH}_3)_2\text{OCH}_3$								
0.0483	-0.0328	-1.3	0.3925	-0.1359	-0.2	0.6951	-0.1098	-3.6
0.0829	-0.0517	0.4	0.3951	-0.1358	-0.1	0.7129	-0.1029	-0.8
0.1663	-0.0928	-1.5	0.4582	-0.1356	0.6	0.7385	-0.0944	1.4
0.1986	-0.1024	0.2	0.5197	-0.1307	2.2	0.7882	-0.0819	0.2
0.2434	-0.1129	2.3	0.5624	-0.1265	2.2	0.8361	-0.0692	-2.3
0.2552	-0.1156	2.4	0.6291	-0.1211	-2.0	0.8669	-0.0519	
0.3055	-0.1318	-4.4	0.6741	-0.1103	0.4	0.9262	-0.0324	-0.1
0.3461	-0.1328	-0.4						
$x(\text{C}_4\text{H}_9)_2\text{NH} + (1-x)\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)_2\text{OCH}_3$								
0.0209	-0.0092	-3.8	0.3470	-0.0214	2.7	0.7175	-0.0230	2.0
0.0821	-0.0186	-2.2	0.4010	-0.0243	-0.5	0.7687	-0.0232	0.9
0.1152	-0.0202	-0.2	0.4454	-0.0256	-2.0	0.8054	-0.0230	-0.3
0.2005	-0.0233	0.9	0.4931	-0.0263	-2.5	0.8135	-0.0217	0.6
0.2204	-0.0237	0.9	0.5501	-0.0278	-3.6	0.8762	-0.0197	-1.9
0.3016	-0.0235	1.0	0.6260	-0.0233	1.6	0.9288	-0.0139	-2.1
0.3085	-0.0238	0.7	0.6789	-0.0230	2.2			

Chapter 2: Excess Molar Functions.....

Table 2.4 - continued

$x$	$V_m^E$ cm <sup>3</sup> ·mol <sup>-1</sup>	$\delta V_m^E \cdot 10^3$ cm <sup>3</sup> ·mol <sup>-1</sup>	$x$	$V_m^E$ cm <sup>3</sup> ·mol <sup>-1</sup>	$\delta V_m^E \cdot 10^3$ cm <sup>3</sup> ·mol <sup>-1</sup>	$x$	$V_m^E$ cm <sup>3</sup> ·mol <sup>-1</sup>	$\delta V_m^E \cdot 10^3$ cm <sup>3</sup> ·mol <sup>-1</sup>
$x(\text{C}_4\text{H}_9)_2\text{NH} + (1-x) \text{c}-(\text{CH}_2)_4\text{O}$								
0.0435	0.0215	0.4	0.2953	0.0896	0.0	0.6104	0.0792	-0.6
0.0846	0.0382	-0.2	0.3533	0.0967	2.5	0.6378	0.0764	0.4
0.1080	0.0508	3.7	0.3538	0.0965	2.3	0.7004	0.0673	1.3
0.1150	0.0575	8.0	0.3845	0.0947	-0.5	0.7557	0.0521	-3.9
0.1546	0.0556	-6.5	0.4490	0.0946	0.1	0.8159	0.0491	5.0
0.1568	0.0578	-4.9	0.4786	0.0920	-1.1	0.8842	0.0307	1.5
0.1691	0.0647	-1.4	0.5221	0.0892	-0.6	0.9179	0.0218	0.5
0.2032	0.0706	-3.9	0.5492	0.0861	-1.1	0.9220	0.0156	-4.7
0.2421	0.0862	4.0						
$x(\text{C}_4\text{H}_9)_2\text{NH} + (1-x)\text{c}-(\text{CH}_2)_5\text{O}$								
0.0476	0.0310	0.6	0.4468	0.1298	-0.4	0.8260	0.0596	2.2
0.0926	0.0544	0.7	0.4610	0.1285	-1.8	0.8438	0.0379	-13.0
0.1632	0.0842	2.1	0.4884	0.1344	4.5	0.8780	0.0449	6.4
0.2107	0.0932	-3.5	0.5627	0.1253	0.7	0.9245	0.0285	6.4
0.2753	0.1134	1.5	0.6297	0.1147	0.5	0.9482	0.0103	-4.0
0.3262	0.1208	0.2	0.6804	0.1032	0.2	0.9693	0.0133	5.3
0.3675	0.1237	-1.9	0.7122	0.0961	1.6	0.9733	0.0073	0.4
0.4038	0.1274	-1.1	0.7768	0.0725	-2.0	0.9877	0.0014	-1.6

Chapter 2: Excess Molar Functions.....

Table 2.4 - continued

$x$	$V_m^E$ $\text{cm}^3 \cdot \text{mol}^{-1}$	$\delta V_m^E \cdot 10^3$ $\text{cm}^3 \cdot \text{mol}^{-1}$	$x$	$V_m^E$ $\text{cm}^3 \cdot \text{mol}^{-1}$	$\delta V_m^E \cdot 10^3$ $\text{cm}^3 \cdot \text{mol}^{-1}$	$x$	$V_m^E$ $\text{cm}^3 \cdot \text{mol}^{-1}$	$\delta V_m^E \cdot 10^3$ $\text{cm}^3 \cdot \text{mol}^{-1}$
$x(\text{C}_4\text{H}_9)_2\text{NH} + (1-x)c\text{-(CH}_2)_2\text{O(CH}_2)_2\text{O}$								
0.0177	0.0390	0.4	0.2837	0.4137	3.3	0.7178	0.3702	10.0
0.0323	0.0786	9.6	0.3402	0.4465	-0.1	0.7476	0.3352	4.1
0.0693	0.1425	2.5	0.3813	0.4658	1.2	0.7922	0.2892	6.8
0.0978	0.1803	-9.1	0.4052	0.4762	4.4	0.8307	0.2347	-1.2
0.1127	0.2165	3.1	0.4365	0.4882	10.4	0.8786	0.1692	-4.1
0.1629	0.2801	-5.6	0.4948	0.4722	-6.2	0.9232	0.1232	11.9
0.2123	0.3467	1.9	0.5482	0.4602	-6.9	0.9303	0.0912	-10.0
0.2244	0.3508	-6.8	0.6014	0.4321	-12.9	0.9611	0.0420	-14.7
0.2365	0.3736	4.0	0.6516	0.4133	-1.1			

## Chapter 2: Excess Molar Functions.....

**TABLE 2.5.** Coefficients  $B_r$  from equation 2.22 and standard deviations  $\sigma^a$  for  $\{ (x1C_kH_{2k})$  or  $(x1-C_kH_{2k-2}) + (1-x)1-C_3H_7OH\}$  at the temperature 298.15 K

Compound	$B_0$	$B_1$	$B_2$	$B_3$	$\sigma \cdot 10^2$ cm <sup>3</sup> ·mol <sup>-1</sup>
$x C_6H_{12}$	0.068	-1.015	0.126	-	-
$x C_7H_{14}$	0.670	-0.827	0.142	-	-
$x C_8H_{16}$	0.980	-0.538	0.624	-0.633	-
$x C_6H_{10}$	-0.339	-0.122	-0.239	-0.469	0.2
$x C_7H_{12}$	0.030	-0.532	-0.007	-0.282	0.2
$x C_8H_{14}$	0.197	-0.549	0.101	-0.212	0.4

<sup>a</sup>: given by equation  $\sigma = [\Sigma(V_{m(\text{exp})}^E - V_{m(\text{calc})}^E)^2 / (n - k - 1)]^{1/2}$ .

## Chapter 2: Excess Molar Functions.....

**TABLE 2.6.** Coefficients  $B_r$  from equation 2.22 and standard deviations  $\sigma^a$  for  $\{ (x1C_kH_{2k})$   
or  $(x1-C_kH_{2k-2}) + (1-x)2-C_3H_7OH\}$  at the temperature 298.15 K

Compound	$B_0$	$B_1$	$B_2$	$B_3$	$\sigma \cdot 10^2$ $\text{cm}^3 \cdot \text{mol}^{-1}$
$x C_6H_{12}$	1.540	-1.239	-0.383	0.378	-
$x C_7H_{14}$	1.994	-0.922	0.182	-	-
$x C_8H_{16}$	2.165	-0.736	0.389	-	-
$x C_6H_{10}$	0.819	-0.644	-0.314	-0.188	0.5
$x C_7H_{12}$	1.031	-0.663	-0.089	-0.247	0.5
$x C_8H_{14}$	1.140	-0.687	0.324	-0.061	0.3

<sup>a</sup>: given by equation  $\sigma = [\Sigma(V_{m(\text{exp})}^E - V_{m(\text{calc})}^E)^2 / (n - k - 1)]^{1/2}$ .

## Chapter 2: Excess Molar Functions.....

**Table 2.7** Coefficients  $B_r$  and standard deviations  $\sigma^a$  for  $\{x(\text{C}_4\text{H}_9)_2\text{NH} + (1-x)\text{ROR}'\}$  at the temperature 298.15 K by equation 2.22

ROR'	$B_0$	$B_1$	$B_2$	$B_3$	$\sigma \cdot 10^2$ cm <sup>3</sup> ·mol <sup>-1</sup>
CH <sub>3</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>3</sub>	-1.3363	-0.4004	-0.1688	-0.2774	0.3
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> O(CH <sub>2</sub> ) <sub>2</sub> CH <sub>3</sub>	-0.3970	-0.0933	0.0407	0.1949	0.3
CH <sub>3</sub> CH(CH <sub>3</sub> )OCH(CH <sub>3</sub> )CH <sub>3</sub>	-0.0127	-1.5343	-0.3919	0.0096	0.2
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> O(CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>	0.1141	0.0521	-0.0377	-0.0664	0.3
CH <sub>3</sub> C(CH <sub>3</sub> ) <sub>2</sub> OCH <sub>3</sub>	0.0029	-0.5489	-0.1275	-0.1052	0.2
CH <sub>3</sub> CH <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub> OCH <sub>3</sub>	-0.0951	0.0119	-0.1452	-0.0525	0.2
<i>c</i> -(CH <sub>2</sub> ) <sub>4</sub> O	0.3666	0.1483	0.0329	-0.2969	0.3
<i>c</i> -(CH <sub>2</sub> ) <sub>5</sub> O	0.5180	0.0859	-0.0480	0.1532	0.4
<i>c</i> -(CH <sub>2</sub> ) <sub>2</sub> O(CH <sub>2</sub> ) <sub>2</sub> O	1.9111	0.2517	-0.0616	0.1391	0.7

<sup>a</sup>: given by equation  $\sigma = [\Sigma(V_{m(\text{exp})}^E - V_{m(\text{calc})}^E)^2 / (n - k)]^{1/2}$ .



## Chapter 2: Excess Molar Functions.....

**Table 2.8.** Excess molar enthalpies,  $H_m^E$  for binary mixtures of 1-hexene, 1-heptene and 1-octene with 1-propanol and 2-propanol and the deviations,  $\delta H_m^E$  calculated from equation 2.22 at 298.15 K.

$x$	$\overline{H_m^E}$ J·mol <sup>-1</sup>	$\overline{\delta H_m^E}$ J·mol <sup>-1</sup>	$x$	$\overline{H_m^E}$ J·mol <sup>-1</sup>	$\overline{\delta H_m^E}$ J·mol <sup>-1</sup>	$x$	$\overline{H_m^E}$ J·mol <sup>-1</sup>	$\overline{\delta H_m^E}$ J·mol <sup>-1</sup>
$x1-C_6H_{12} + (1-x)1-C_3H_7OH$								
0.0518	75.6	0.2	0.3409	428.8	-1.5	0.7014	655.2	-1.4
0.0836	119.2	-0.3	0.4222	510.7	-1.9	0.7489	640.5	4.2
0.1202	168.5	0.0	0.5052	588.2	3.3	0.8016	585.3	-1.2
0.1895	255.6	-0.9	0.5956	639.8	-1.5	0.8722	461.4	-0.8
0.2518	332.3	1.4	0.6636	658.2	-1.1	0.9334	285.7	0.2
0.2944	380.8	1.3						
$x1-C_7H_{14} + (1-x)1-C_3H_7OH$								
0.0559	90.2	1.7	0.4533	598.9	2.9	0.7768	664.8	-1.0
0.0928	144.4	-0.6	0.5317	662.8	1.2	0.7932	647.4	0.3
0.1655	252.4	1.1	0.6157	705.8	-1.4	0.8206	611.5	3.8
0.2072	305.2	-3.7	0.6824	713.5	-2.6	0.9007	420.8	-1.8
0.2807	408.1	3.4	0.7352	699.8	0.9	0.9536	228.2	-0.7
0.3746	511.8	-3.5						
$x1-C_8H_{16} + (1-x)1-C_3H_7OH$								
0.0944	169.6	-0.7	0.4798	667.7	0.2	0.7504	730.6	1.6
0.1361	239.9	0.5	0.5387	712.8	0.0	0.8226	640.4	1.0
0.1773	303.8	-0.1	0.6116	749.8	-0.6	0.8612	560.2	1.1
0.2539	414.4	0.3	0.6848	759.0	0.6	0.9033	435.6	-3.7
0.4005	591.0	-0.1	0.7094	750.4	-1.7	0.9568	230.1	1.9

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Table 2.8- continued

$x$	$\overline{H_m^E}$ J·mol <sup>-1</sup>	$\overline{\delta H_m^E}$ J·mol <sup>-1</sup>	$x$	$\overline{H_m^E}$ J·mol <sup>-1</sup>	$\overline{\delta H_m^E}$ J·mol <sup>-1</sup>	$x$	$\overline{H_m^E}$ J·mol <sup>-1</sup>	$\overline{\delta H_m^E}$ J·mol <sup>-1</sup>
$x1-C_6H_{12} + (1-x)2-C_3H_7OH$								
0.0736	151.4	-0.5	0.3294	636.5	0.7	0.6756	863.5	-4.9
0.1446	308.5	3.7	0.3489	660.9	-3.1	0.7044	859.7	0.5
0.1975	412.8	-0.1	0.4357	763.5	0.1	0.7647	811.7	-3.1
0.2556	521.5	0.9	0.5265	838.2	4.1	0.8335	704.6	-2.8
0.2812	560.4	-3.3	0.5734	862.2	5.1	0.9066	502.2	6.8
$x1-C_7H_{14} + (1-x)2-C_3H_7OH$								
0.0808	192.4	0.5	0.4455	830.7	3.5	0.7736	833.8	0.1
0.1432	344.8	2.7	0.4677	846.2	1.6	0.8062	786.1	-0.4
0.1814	428.6	-0.7	0.4955	862.0	-1.5	0.8516	690.7	-0.9
0.2526	571.0	-1.6	0.5594	894.7	0.2	0.9055	516.2	-4.5
0.3066	662.7	-1.1	0.6655	904.3	0.0	0.9449	352.6	8.8
0.3304	696.9	-2.0	0.7405	866.7	-0.7			
$x1-C_8H_{16} + (1-x)2-C_3H_7OH$								
0.0736	209.4	3.4	0.3133	726.4	1.3	0.6142	952.5	0.1
0.1144	314.8	0.0	0.3970	831.3	-0.4	0.6926	935.5	0.1
0.1425	382.4	-3.3	0.4574	885.7	-1.2	0.7759	858.4	-0.6
0.1622	433.7	0.5	0.5188	926.9	0.9	0.8326	752.7	-2.1
0.2429	605.0	-0.4	0.5333	933.7	0.9	0.9059	528.9	2.7
0.2590	635.2	-0.1						

Chapter 2: Excess Molar Functions.....

Table 2.9 Excess molar enthalpies,  $H_m^E$  for binary mixtures of 1-hexyne, 1-heptyne and 1-octyne with 1-propanol and 2-propanol and the deviations,  $\delta H_m^E$  calculated from equation 2.22 at 298.15 K.

$x$	$\overline{H_m^E}$ J·mol <sup>-1</sup>	$\overline{\delta H_m^E}$ J·mol <sup>-1</sup>	$x$	$\overline{H_m^E}$ J·mol <sup>-1</sup>	$\overline{\delta H_m^E}$ J·mol <sup>-1</sup>	$x$	$\overline{H_m^E}$ J·mol <sup>-1</sup>	$\overline{\delta H_m^E}$ J·mol <sup>-1</sup>
$x1-C_6H_{10} + (1-x)1-C_3H_7OH$								
0.0827	154.6	-4.6	0.3826	658.2	-5.4	0.7359	944.4	-1.6
0.1182	225.8	-0.1	0.4458	740.4	-5.1	0.7569	4892.0	-3.8
0.1434	276.3	4.0	0.5463	849.6	1.1	0.8045	851.5	-2.2
0.1545	290.1	-2.5	0.5756	869.2	-1.6	0.8642	745.6	-4.8
0.2016	379.4	2.7	0.6538	914.7	5.5	0.9012	648.7	4.8
0.2513	467.4	5.6	0.6928	921.7	7.5			
$x1-C_7H_{12} + (1-x)1-C_3H_7OH$								
0.0652	126.2	-19.5	0.4526	775.2	-2.9	0.7715	916.3	7.2
0.1543	255.8	0.5	0.5032	839.7	0.7	0.7874	898.6	4.7
0.1753	339.6	5.4	0.5658	891.9	-6.0	0.8363	822.4	-2.9
0.2558	470.9	6.1	0.6318	931.2	-5.0	0.8721	741.8	-7.4
0.3668	654.8	1.2	0.7015	941.0	-3.1	0.9502	450.7	2.3
0.4370	760.8	3.5	0.7525	929.2	5.6			
$x1-C_8H_{14} + (1-x)1-C_3H_7OH$								
0.0887	192.2	10.8	0.4940	850.7	-2.5	0.7553	950.8	0.6
0.1762	359.6	6.0	0.4969	861.2	4.9	0.8302	857.2	-8.2
0.2001	399.4	0.4	0.6214	957.2	2.5	0.8596	800.7	-5.4
0.3283	615.6	-9.1	0.6532	965.0	-1.1	0.9664	789.6	0.0
0.3997	726.3	-7.5	0.6998	976.2	6.3	0.9502	454.2	5.8
0.4091	746.2	-0.8	0.7050	975.8	6.5			

## Chapter 2: Excess Molar Functions.....

Table 2.9- continued

$x$	$H_m^E$	$\delta H_m^E$	$x$	$H_m^E$	$\delta H_m^E$	$x$	$H_m^E$	$\delta H_m^E$
	$J \cdot mol^{-1}$	$J \cdot mol^{-1}$		$J \cdot mol^{-1}$	$J \cdot mol^{-1}$		$J \cdot mol^{-1}$	$J \cdot mol^{-1}$
$x1-C_6H_{10} + (1-x)2-C_3H_7OH$								
0.0637	198.9	-10.7	0.3706	943.8	1.2	0.6578	1127.8	-4.3
0.1457	451.3	-0.3	0.4265	1019.4	-2.4	0.7098	1196.5	-1.6
0.1992	590.8	-1.2	0.5062	1104.2	2.3	0.7538	1047.6	0.4
0.2831	785.9	2.8	0.5997	1140.9	-0.4	0.8685	796.8	12.7
0.3220	864.2	5.0	0.6280	1138.7	-1.6	0.9102	608.9	-9.7
$x1-C_7H_{12} + (1-x)2-C_3H_7OH$								
0.0970	342.9	-0.6	0.4736	1107.6	3.4	0.7084	1119.6	-4.3
0.1200	406.7	-8.6	0.4805	1109.6	-0.7	0.7816	1027.7	3.0
0.2559	768.6	-0.6	0.5802	1160.5	-3.6	0.8025	986.5	4.1
0.3635	972.1	2.7	0.6115	1163.2	-3.7	0.8593	836.0	9.7
0.3833	1007.4	8.5	0.6534	1152.7	-6.0	0.9462	407.7	-11.2
$x1-C_8H_{14} + (1-x)2-C_3H_7OH$								
0.0749	284.2	-7.0	0.4724	1129.8	3.8	0.7514	1089.7	-1.4
0.1714	594.8	-2.6	0.5017	1158.7	3.2	0.8037	1004.5	7.9
0.2511	798.0	0.5	0.5532	1177.8	-3.1	0.8412	898.2	-1.8
0.3123	926.2	4.8	0.6098	1189.0	0.5	0.8482	885.8	7.0
0.3656	1013.9	4.3	0.6768	1159.0	-7.1	0.9135	610.2	-7.3

## Chapter 2: Excess Molar Functions.....

**Table 2.10.** Excess molar enthalpies,  $H_m^E$ , for (di-n-butylamine + an ether) and the deviations,  $\delta H_m^E$ , calculated from equation 2.22 at the temperature 298.15 K.

$x$	$H_m^E$ J·mol <sup>-1</sup>	$\delta H_m^E$ J·mol <sup>-1</sup>	$x$	$H_m^E$ J·mol <sup>-1</sup>	$\delta H_m^E$ J·mol <sup>-1</sup>	$x$	$H_m^E$ J·mol <sup>-1</sup>	$\delta H_m^E$ J·mol <sup>-1</sup>
$x(C_4H_9)_2NH + (1-x)(C_2H_5)_2O$								
0.0702	16.50	1.5	0.4123	55.05	2.3	0.6882	37.48	-1.6
0.1006	21.20	0.4	0.4213	56.25	3.3	0.7319	34.65	0.4
0.1510	27.02	-2.4	0.4712	53.14	0.3	0.7528	30.71	-1.0
0.1707	30.58	-1.9	0.5207	51.90	-0.1	0.7895	28.21	-1.1
0.2048	36.69	-0.6	0.5340	59.93	-1.1	0.8132	23.75	-0.3
0.2807	46.20	0.5	0.5887	47.82	-0.1	0.8602	21.25	3.4
0.3478	50.40	-0.1	0.6425	39.65	-3.9	0.9504	7.05	1.1
0.3499	51.05	0.4						
$x(C_4H_9)_2NH + (1-x)(CH_3CH_2CH_2)_2O$								
0.0825	16.42	-1.9	0.3759	65.90	2.0	0.6502	62.17	0.6
0.1187	24.86	-1.0	0.4204	66.14	-0.6	0.7052	55.82	0.4
0.1270	28.56	1.0	0.4501	66.28	-1.7	0.7445	49.13	-0.3
0.1465	33.94	2.5	0.4553	66.67	-1.5	0.7961	42.70	0.8
0.1942	41.18	0.9	0.5427	67.80	-0.4	0.8242	38.42	1.5
0.2862	53.00	-1.4	0.5881	67.50	1.2	0.8550	29.76	-2.9
0.3264	60.04	0.8	0.6433	63.80	1.6	0.8552	28.15	-1.3
0.3588	61.02	-1.4						

Chapter 2: Excess Molar Functions.....

Table 2.10- continued

$x$	$\overline{H_m^E}$ J·mol <sup>-1</sup>	$\overline{\delta H_m^E}$ J·mol <sup>-1</sup>	$x$	$\overline{H_m^E}$ J·mol <sup>-1</sup>	$\overline{\delta H_m^E}$ J·mol <sup>-1</sup>	$x$	$\overline{H_m^E}$ J·mol <sup>-1</sup>	$\overline{\delta H_m^E}$ J·mol <sup>-1</sup>
$x(\text{C}_4\text{H}_9)_2\text{NH} + (1-x)\{(\text{CH}_3)_2\text{CH}\}_2\text{O}$								
0.0952	12.28	1.0	0.4260	29.07	-1.6	0.7089	29.16	-0.1
0.1053	14.25	2.0	0.4399	31.16	0.2	0.7317	27.78	-0.4
0.2502	23.53	0.1	0.5162	32.97	0.9	0.7629	27.69	1.1
0.2872	23.62	-1.8	0.5678	31.83	-0.3	0.7693	27.51	1.4
0.3478	27.82	-0.3	0.5826	32.82	0.7	0.8622	17.29	-1.5
0.3547	27.98	-0.4	0.6341	32.14	0.7	0.9241	9.01	-2.6
0.3578	28.87	0.3						
$x(\text{C}_4\text{H}_9)_2\text{NH} + (1-x)(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_2\text{O}$								
0.0742	16.98	-0.2	0.3515	68.33	1.2	0.5211	70.45	-1.8
0.0839	20.99	1.6	0.3672	69.02	0.5	0.5960	68.65	1.3
0.1012	21.16	-2.2	0.3769	68.32	-1.0	0.6365	65.09	2.0
0.1220	29.95	1.2	0.3917	70.94	0.5	0.7013	50.92	-3.1
0.1471	32.95	-0.6	0.4202	74.87	2.9	0.7637	43.20	-0.2
0.1535	35.03	0.1	0.4875	76.02	2.9	0.8478	29.55	2.1
0.1622	37.27	0.4	0.4983	71.71	-1.2	0.8624	21.91	-2.6
0.2578	52.57	-2.2	0.5062	71.83	-0.9	0.9176	16.44	2.5
0.3391	64.60	-1.2	0.5099	71.10	-1.5			

Chapter 2: Excess Molar Functions.....

Table 2.10 - continued

$x$	$\overline{H_m^E}$ J·mol <sup>-1</sup>	$\overline{\delta H_m^E}$ J·mol <sup>-1</sup>	$x$	$\overline{H_m^E}$ J·mol <sup>-1</sup>	$\overline{\delta H_m^E}$ J·mol <sup>-1</sup>	$x$	$\overline{H_m^E}$ J·mol <sup>-1</sup>	$\overline{\delta H_m^E}$ J·mol <sup>-1</sup>
$x(\text{C}_4\text{H}_9)_2\text{NH} + (1-x)\text{CH}_3\text{C}(\text{CH}_3)_2\text{OCH}_3$								
0.0739	25.59	-2.5	0.4079	82.01	0.7	0.7085	54.25	0.2
0.1122	35.94	2.4	0.4512	88.10	6.3	0.7692	43.20	1.1
0.1805	50.02	-0.7	0.4904	85.53	4.7	0.8274	32.68	2.5
0.2649	66.96	-0.3	0.5580	76.16	0.1	0.8986	22.78	6.8
0.2670	65.65	-2.0	0.5851	75.48	2.3	0.9094	22.37	8.4
0.3097	68.01	-5.7	0.6498	66.70	2.5	0.9985	1.57	
0.3988	80.44	-0.5						
$x(\text{C}_4\text{H}_9)_2\text{NH} + (1-x)\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)_2\text{OCH}_3$								
0.0328	9.11	2.9	0.3855	42.75	-2.3	0.6382	39.70	0.7
0.1226	21.54	0.4	0.4503	42.86	-2.7	0.6643	35.57	-1.5
0.1354	24.87	1.9	0.4764	43.95	-1.5	0.6992	35.37	1.2
0.1887	30.12	0.2	0.5567	44.68	1.2	0.7495	28.96	-0.4
0.2205	33.02	-0.4	0.5867	44.50	2.4	0.7911	24.60	-0.4
0.2568	37.63	0.7	0.5922	44.48	2.7	0.8013	23.08	-0.8
0.3461	41.56	-1.4	0.6148	42.47	2.0	0.8676	13.59	-2.7

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Table 2.10 - continued

$x$	$\overline{H_m^E}$ J·mol <sup>-1</sup>	$\overline{\delta H_m^E}$ J·mol <sup>-1</sup>	$x$	$\overline{H_m^E}$ J·mol <sup>-1</sup>	$\overline{\delta H_m^E}$ J·mol <sup>-1</sup>	$x$	$\overline{H_m^E}$ J·mol <sup>-1</sup>	$\overline{\delta H_m^E}$ J·mol <sup>-1</sup>
$x(\text{C}_4\text{H}_9)_2\text{NH} + (1-x) \text{c}-(\text{CH}_2)_4\text{O}$								
0.0700	42.38	0.8	0.4132	111.20	0.7	0.7127	67.53	-0.5
0.0952	49.98	-3.7	0.4526	108.90	0.5	0.7628	54.99	-2.0
0.1311	71.04	2.4	0.4871	107.57	2.1	0.8113	47.07	1.3
0.2021	89.84	-0.9	0.5374	98.19	-1.3	0.8545	34.91	-0.6
0.2811	106.71	1.5	0.5802	93.14	-0.1	0.8893	29.20	2.1
0.3297	106.97	-2.6	0.6308	85.38	0.9	0.9352	17.18	1.3
0.3659	111.80	0.9	0.6633	76.15	-2.1			
$x(\text{C}_4\text{H}_9)_2\text{NH} + (1-x)\text{c}-(\text{CH}_2)_5\text{O}$								
0.5848	22.16	2.0	0.4227	68.20	0.2	0.6376	47.96	-0.1
0.1082	41.19	1.1	0.4465	66.90	0.1	0.6590	46.05	0.7
0.1515	48.99	-1.4	0.4878	64.92	1.1	0.7328	36.92	1.4
0.2224	62.74	0.5	0.5229	60.75	-0.1	0.7968	26.42	-0.4
0.2806	69.08	1.5	0.5339	58.70	-1.0	0.7992	25.33	-1.2
0.3297	69.19	-0.3	0.6151	49.41	-1.3	0.9016	14.01	1.3
0.3690	68.51	-1.1	0.6176	50.67	0.2	0.9049	11.72	-0.5



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Table 2.10 - continued

$x$	$\overline{H_m^E}$ J·mol <sup>-1</sup>	$\overline{\delta H_m^E}$ J·mol <sup>-1</sup>	$x$	$\overline{H_m^E}$ J·mol <sup>-1</sup>	$\overline{\delta H_m^E}$ J·mol <sup>-1</sup>	$x$	$\overline{H_m^E}$ J·mol <sup>-1</sup>	$\overline{\delta H_m^E}$ J·mol <sup>-1</sup>
$x(\text{C}_4\text{H}_9)_2\text{NH} + (1-x)c\text{-(CH}_2)_2\text{O(CH}_2)_2\text{O}$								
0.0922	275.13	17.3	0.3789	1052.15	5.9	0.5594	846.17	10.6
0.1019	399.43	-0.2	0.4275	1038.99	-1.5	0.6517	754.97	8.3
0.1262	483.89	-11.8	0.4337	1022.17	-15.4	0.7139	659.94	19.6
0.1777	670.46	-12.3	0.4551	1010.50	-13.5	0.7431	581.84	-9.5
0.1932	726.70	-6.4	0.4766	984.04	-21.5	0.7588	571.85	6.5
0.1961	739.80	-2.3	0.5008	965.67	-14.0	0.7951	504.88	-0.3
0.2268	840.25	9.7	0.5412	925.12	-1.5	0.8659	378.45	-2.0
0.2692	840.95	12.4	0.5719	886.59	6.4	0.8746	357.71	-5.7
0.3051	1005.17	16.7	0.5916	845.47	-3.0	0.9234	227.15	-27.1
0.3372	1046.94	22.8						

## Chapter 2: Excess Molar Functions.....

TABLE 2.11 Parameters  $A_r$  from eqn.2.22 for  $\{ (x1-C_kH_{2k}) \text{ or } (x1-C_kH_{2k-2}) + (1-x)1-C_3H_7OH \}$  at the temperature 298.15 K.

Compound	$A_0$	$A_1$	$A_2$	$A_3$
$x C_6H_{12}$	2323	-1575	993	-242
$x C_7H_{14}$	2549	-1636	1057	-362
$x C_8H_{16}$	2737	-1603	1191	-428
$x C_6H_{10}$	3222	511	-242	-
$x C_7H_{12}$	3342	702	-845	-
$x C_8H_{14}$	3438	647	-347	-

## Chapter 2: Excess Molar Functions.....

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**TABLE 2.12** Parameters  $A_r$  from eqn.2.22 for  $\{ (x_1-C_kH_{2k}) \text{ or } (x_1-C_kH_{2k-2}) + (1-x)2-C_3H_7OH \}$  at the temperature 298.15 K

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Compound	$A_0$	$A_1$	$A_2$	$A_3$
$x C_6H_{12}$	3268	-1403	1221	-1178
$x C_7H_{14}$	3465	-1200	1360	-1411
$x C_8H_{16}$	3663	-1169	1451	-1129
$x C_6H_{10}$	4388	1682	-82	—
$x C_7H_{12}$	4503	1254	497	—
$x C_8H_{14}$	4617	1488	698	—

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## Chapter 2: Excess Molar Functions.....

**TABLE 2.13** Parameters  $A_r$  and standard deviations  $\sigma$  from equation 2.22 for  $\{x(\text{C}_4\text{H}_9)_2\text{NH} + (1-x)\text{ROR}'\}$  at the temperature 298.15 K

ROR'	$A_0$	$A_1$	$A_2$	$A_3$	$\sigma^a$
					$\text{J}\cdot\text{mol}^{-1}$
$\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$	209.0	56.71	-38.52	-	1.8
$\text{CH}_3(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{CH}_3$	275.1	0.499	-48.13	-	1.5
$\text{CH}_3\text{CH}(\text{CH}_3)\text{OCH}(\text{CH}_3)\text{CH}_3$	127.7	-20.52	29.40	-	1.3
$\text{CH}_3(\text{CH}_2)_3\text{O}(\text{CH}_2)_3\text{CH}_3$	291.5	40.64	-105.3	-	1.9
$\text{CH}_3\text{C}(\text{CH}_3)_2\text{OCH}_3$	321.5	100.5	-104.4	-	6.8
$\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)_2\text{OCH}_3$	180.7	37.23	-21.84	-	1.8
$c\text{-(CH}_2)_4\text{O}$	416.3	247.7	47.45	-	1.8
$c\text{-(CH}_2)_5\text{O}$	251.3	170.6	44.24	-	1.1
$c\text{-(CH}_2)_2\text{O}(\text{CH}_2)_2\text{O}$	3922.6	2329.4	-35.69	-2750.1	13.4

<sup>a</sup> given by eqn.  $\sigma = [\sum (\text{H}_{\text{m}(\text{exp})}^{\text{E}} - \text{H}_{\text{m}(\text{calc})}^{\text{E}})^2 / (n-k)]^{1/2}$  where  $n$  is the number of experimental points and  $k$  is the order of the polynomial in eqn.2.22

## 2.5 DISCUSSIONS

### 2.5.1 Mixtures of 1-alkenes + (1-propanol or 2-propanol)

It has been reported<sup>(76-78)</sup> that because the n-alkenes and n-alkynes are soluble in all proportions with methanol at 298.15 K and in comparison the n-alkanes<sup>(78)</sup> have only a limited solubility, that there are specific interactions between the unsaturated hydrocarbon (double bond of the alkene or triple bond of the alkyne) and the hydroxyl group of the alkanol. This interaction is representative by an increase in the solubility of the respective mixtures. For all the (1-alkene + alkanol) mixtures reported, including this work, the overall magnitude of the volume change is due basically to three effects. The positive effect due to the dissociation of the alkanol, the positive effect due to the dissociation of the 1-alkene molecules and the negative effect due to the association of the 1-alkene with the alkanol molecule.

The  $V_m^E$  results, at 298.15 K, for the (1-alkene + 1-propanol or 2-propanol) are reported in table 2.2 and in fig. 2.17. The  $V_m^E$  values for the (1-alkene + 1-propanol) become more positive with an increase in the 1-alkene chain length, while the  $V_m^E$  results for the (1-alkene + 2-propanol) mixtures are all positive for all the 1-alkenes investigated in this work. In particular, the  $V_m^E$  curves for the (1-hexene + 1-propanol) system is sine shaped, being negative at low  $x$  values and positive at high  $x$  values (see fig. 2.17). This is probably due to the contributions being relatively important at high values of  $x$  where the dissociation effect of the alkanol or the alkene is proportionally large. This observation is confirmed by the results of the (1-heptene or 1-octene + 1-propanol) mixtures where the volume changes are largely positive. In addition the  $V_{m,max}^E$  results for the (1-alkenes + 2-propanol) (see Table 2.14) are significantly larger than the 1-propanol results- this could be due to the steric effects of the methyl group adjacent to the C-OH bond on the 2-propanol.

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Comparing these results with those published previously<sup>(79)</sup> on related mixtures of 1-alkene with methanol or ethanol, (Table 2.14), it can be seen that  $V_{m,\max}^E$  decreases slightly (becomes less positive) with an increasing alcohol carbon number. This fact holds true for the methanol, ethanol and 1-propanol systems indicating that as the alkanol chain length increases, at low  $x$  values the double bond - OH interactions (i.e. the association between the 1-alkene and the alkanol) becomes more significant. The lower  $V_m^E$ s for an 1-alkenes + 1-propanol reflects a stronger association between the 1-alkene and the alkanol than the contribution from the dissociation of the OH-OH interaction in the alkanol or the dissociation of the interactions in the 1-alkene molecule.

The 2-propanol results are significantly larger, (more positive), than any of the reported alkanol + 1-alkene mixtures. This could well be due to the larger positive contribution from the breakdown of the hydrogen bonds between the alcohol molecules (rupture of the OH-OH interaction) enhanced by the steric effect of the methyl group adjacent to the C-OH.

**TABLE 2.14**  $V_{m,\max}^E$  for  $x\text{C}_y\text{H}_{2y} + (1-x)\text{C}_z\text{H}_{2z+1}\text{OH}$  at 298.15 K

Compound	$V_{m,\max}^E$ <sup>a</sup>			
	MeOH <sup>b</sup>	EtOH <sup>b</sup>	1-PrOH <sup>c</sup>	2-PrOH <sup>c</sup>
1-C <sub>6</sub> H <sub>12</sub>	0.280	0.236	0.116	0.427
1-C <sub>7</sub> H <sub>14</sub>	0.368	0.305	0.214	0.525
1-C <sub>8</sub> H <sub>16</sub>	0.395	0.354	0.278	0.555

<sup>a</sup> Units:  $\text{cm}^3 \cdot \text{mol}^{-1}$

<sup>b</sup> data taken from reference 79

<sup>c</sup> this work

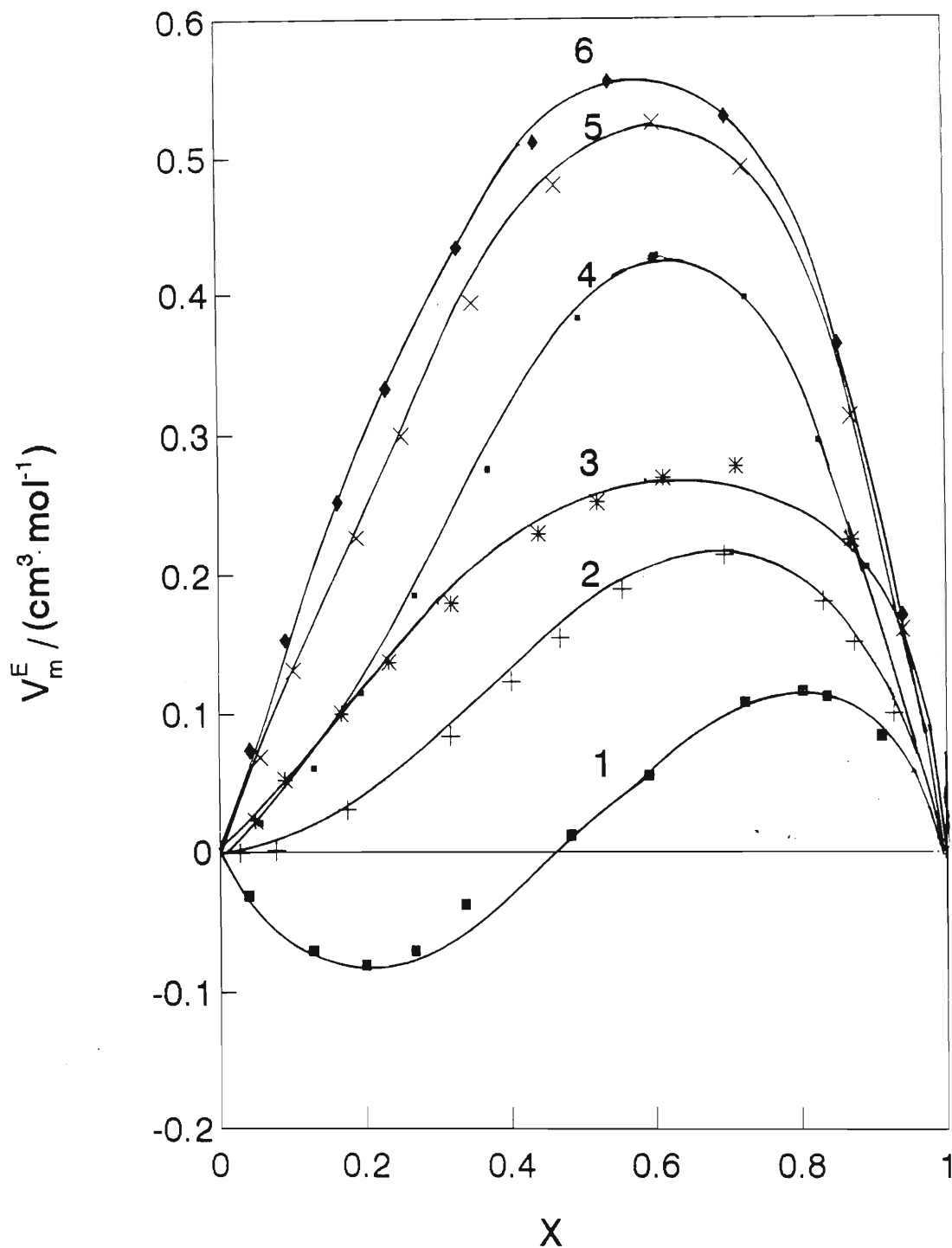


Figure 2.17. Excess molar volumes,  $V_m^E$  at the temperature 298.15 K for 1-propanol + (1), 1-hexene; or + (2), 1-heptene; or + (3), 1-octene and for 2-propanol + (4), 1-hexene; or + (5), 1-heptene; or + (6), 1-octene

## Chapter 2: Excess Molar Functions.....

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The  $H_m^E$  values for the 1-alkene + 1-propanol or 2-propanol are given in Table 2.8 and plotted in figs. 2.18. The enthalpy changes on mixing are all positive with a maximum at a composition between 0.6 and 0.7 mole fraction of the 1-alkene. This is most likely a reflection of the breaking of the hydrogen bonds between the alkanol molecules as a result of the mixing process.

Comparing these results with those published previously on related mixtures of 1-alkene with methanol or ethanol, it can be seen that  $H_{m,max}^E$  increases slightly with increasing alcohol carbon number.<sup>(79)</sup> For example  $H_{m,max}^E$  for mixtures of 1-hexene with methanol, ethanol and 1-propanol are 570, 620, 660 J·mol<sup>-1</sup>, respectively (see Table 2.15)

For each 1-alkene,  $H_{m,max}^E$  for mixtures containing 2-propanol are greater than  $H_{m,max}^E$  for mixtures containing 1-propanol. For example,  $H_{m,max}^E$  for 1-heptene with 2-propanol and 1-propanol are 910 and 710 J·mol<sup>-1</sup>, respectively (Table 2.15). The results for  $H_m^E \{x\text{C}_y\text{H}_{2y} + (1-x) \text{1-PrOH}\}$  and  $H_m^E \{x\text{C}_y\text{H}_{2y} + (1-x) \text{2-PrOH}\}$  show that for each 1-alkene the 2-PrOH isomers behave significantly different. In all cases  $H_m^E\{2\text{-PrOH}\} > H_m^E\{1\text{-PrOH}\}$ . This could be due to a weaker interaction of the double bond of the 1-alkene with the secondary alkanol than with the primary alkanol as a result of the steric effect of the methyl groups in the secondary alkanol which tend to hide the OH group from the double bond system of the 1-alkene. This would have the effect of a smaller negative contribution to the resulting overall  $H_m^E$  and hence a larger positive  $H_m^E$ .

For each alkanol, the  $H_{m,max}^E$  value increases slightly with the increasing 1-alkene carbon number. For example,  $H_{m,max}^E$  for mixtures containing methanol with 1-hexene, 1-heptene and 1-octene are 570, 600 and 630 J·mol<sup>-1</sup>, respectively. This indicates that on increasing carbon number of the 1-alkene, there is a slight positive increase in the enthalpy effect resulting from the dissociation of the 1-alkene molecules. This point is reinforced by the fact that the self association between 1-alkene molecules is relatively weak as judged by the small positive  $H_{m,max}^E$  for (1-C<sub>6</sub>H<sub>12</sub> + n-C<sub>6</sub>H<sub>14</sub>), (1-C<sub>7</sub>H<sub>14</sub> + n-C<sub>7</sub>H<sub>16</sub>) and (1-C<sub>8</sub>H<sub>16</sub> + n-C<sub>7</sub>H<sub>16</sub>) of between 40 and 55 J·mol<sup>-1</sup>.<sup>(80,81)</sup> In addition comparison of  $H_{m,max}^E$  literature values<sup>(79)</sup> for the system (1-hexene + ethanol), 620 J·mol<sup>-1</sup> with the value of (hexane + ethanol),<sup>(77,78)</sup> 580 J·mol<sup>-1</sup> shows



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that in going from a single to a double bond system there is only a very slight effect on the  $H_{m,max}^E$  value. The fact that the  $H_{m,max}^E$  results for the (1-alkene + ethanol) mixtures are only slightly more positive than the  $H_{m,max}^E$  results for the respective (n-alkane + ethanol) and that the association between the 1-alkene and the alkanol is not strong, indicate that dissociation of the alkanol molecules is the dominant factor in the relatively large positive  $H_{m,max}^E$  values. This dissociation seems to be enhanced in the 2-propanol possibly due to the presence of the methyl group next to the alcohol functional group.

**TABLE 2.15**  $H_{m,max}^E$  for  $xC_yH_{2y} + (1-x)C_zH_{2z+1}OH$  at 298.15 K

Compound	$H_{m,max}^E$ <sup>a</sup>			
	MeOH <sup>b</sup>	EtOH <sup>b</sup>	1-PrOH <sup>c</sup>	2-PrOH <sup>c</sup>
1-C <sub>6</sub> H <sub>12</sub>	570.0	620.0	658.2	863.5
1-C <sub>7</sub> H <sub>14</sub>	600.0	660.0	713.5	904.3
1-C <sub>8</sub> H <sub>16</sub>	630.0	690.0	759.0	952.5

<sup>a</sup> Units: J·mol<sup>-1</sup>

<sup>b</sup> data taken from reference 79

<sup>c</sup> this work

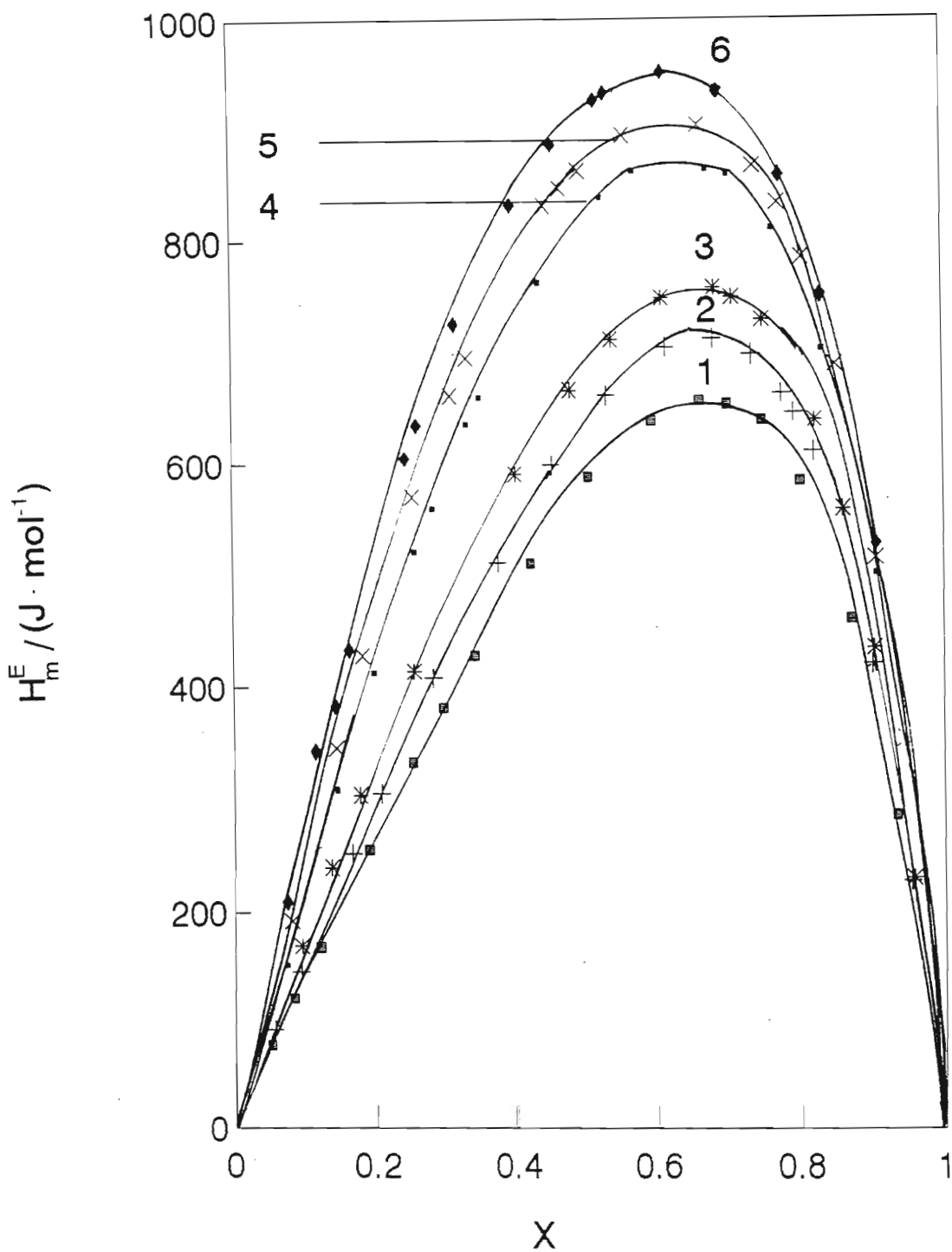


Figure 2.18. Excess molar enthalpies,  $H_m^E$  at the temperature 298.15 K for 1-propanol + (1), 1-hexene; or + (2), 1-heptene; or + (3), 1-octene and for 2-propanol + (4), 1-hexene; or + (5), 1-heptene; or + (6), 1-octene

### 2.5.2 Mixtures of 1-alkynes + (1-propanol or 2-propanol)

The results of the volume changes on mixing,  $V_m^E$  a 1-alkyne with an alkanol are presented in Table 2.3 and depicted in fig 2.19. The presence of the triple bond in the mixture seems to complicate the results somewhat, in that some of the results are negative while some show a positive excess molar volume. The  $V_m^E$  curves for most of the mixtures reported here, are sine shaped, being negative at low  $x$  values and positive at high  $x$  values. This is probably due to the fact that at low concentrations of the 1-alkyne ( $x$ ) the dissociation of the alkanol is of less importance than at high values of  $x$  where the effect of the breakdown of the hydrogen bonds between the alkanol is proportionally large. In effect, the  $V_m^E$  results of the (1-alkyne + 1-propanol or 2-propanol) system reflects three dominant contributory interactions: (a) a positive effect of the breakdown of the hydrogen bonds between the alkanol molecules on mixing, (b) a positive effect of the breakdown of the  $\pi \dots \pi$  interactions between the 1-alkyne molecules and (c) a negative effect of the association between an alkanol and a 1-alkyne molecule. A smaller unpredictable effect due to molecular packing can also be considered contributory to  $V_m^E$ .

Comparing these results to those published previously for a 1-alkyne<sup>(82)</sup> with methanol or ethanol, it can be seen that  $V_{m,\max}^E$  increases slightly with increasing carbon number (Table 2.16). In particular the (1-alkyne + ethanol) system exhibits sine curves for all the 1-alkynes investigated. Furthermore, the  $V_m^E$  for (1-alkyne + ethanol) is less positive than the  $V_m^E$  for (n-alkane + ethanol)<sup>(77,78)</sup> and (1-alkene + ethanol)<sup>(79)</sup> systems; this decrease is attributed to the packing effect induced by the specific interactions of the triple bonds of the 1-alkyne and the OH group of the alkanol. The results reported here exhibit similar behaviour to the (1-alkyne + methanol or ethanol)<sup>(82)</sup> systems whereby the  $V_m^E$  values are dependant on the carbon number of the 1-alkyne. These results are, however, significantly more positive than those for (1-alkyne + methanol or ethanol) indicating that as the chain length of the alkanol increases so does the  $V_m^E$  and  $V_{m,\max}^E$  (Table 2.16).

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For each 1-alkyne, the  $V_{m,\max}^E$  for mixtures containing 2-propanol are greater than  $V_{m,\max}^E$  for mixtures containing 1-propanol. For example,  $V_{m,\max}^E$  for 1-octene with 2-propanol and 1-propanol are  $+0.065$  and  $+0.282 \text{ cm}^3 \cdot \text{mol}^{-1}$ , respectively. This large difference could be due to a larger positive contribution arising from the enhanced dissociation of the hydrogen-hydrogen bonds between alkanol molecules.

**TABLE 2.16**  $V_{m,\max}^E$  for  $x\text{C}_y\text{H}_{2y-2} + (1-x)\text{C}_z\text{H}_{2z+1}\text{OH}$  at 298.15 K

Compound	$V_{m,\max}^E$ <sup>a</sup>			
	MeOH <sup>b</sup>	EtOH <sup>b</sup>	1-PrOH <sup>c</sup>	2-PrOH <sup>c</sup>
1-C <sub>6</sub> H <sub>10</sub>	-0.1350	-0.146	-0.094	-0.012
	-	0.004	-	0.226
1-C <sub>7</sub> H <sub>12</sub>	-0.0334	-0.066	-0.055	0.282
	-	0.050	0.065	-
1-C <sub>8</sub> H <sub>14</sub>	0.0280	-0.014	-0.026	0.296
	-	0.099	0.096	-

<sup>a</sup> Units:  $\text{cm}^3 \cdot \text{mol}^{-1}$

<sup>b</sup> data taken from reference 82

<sup>c</sup> this work

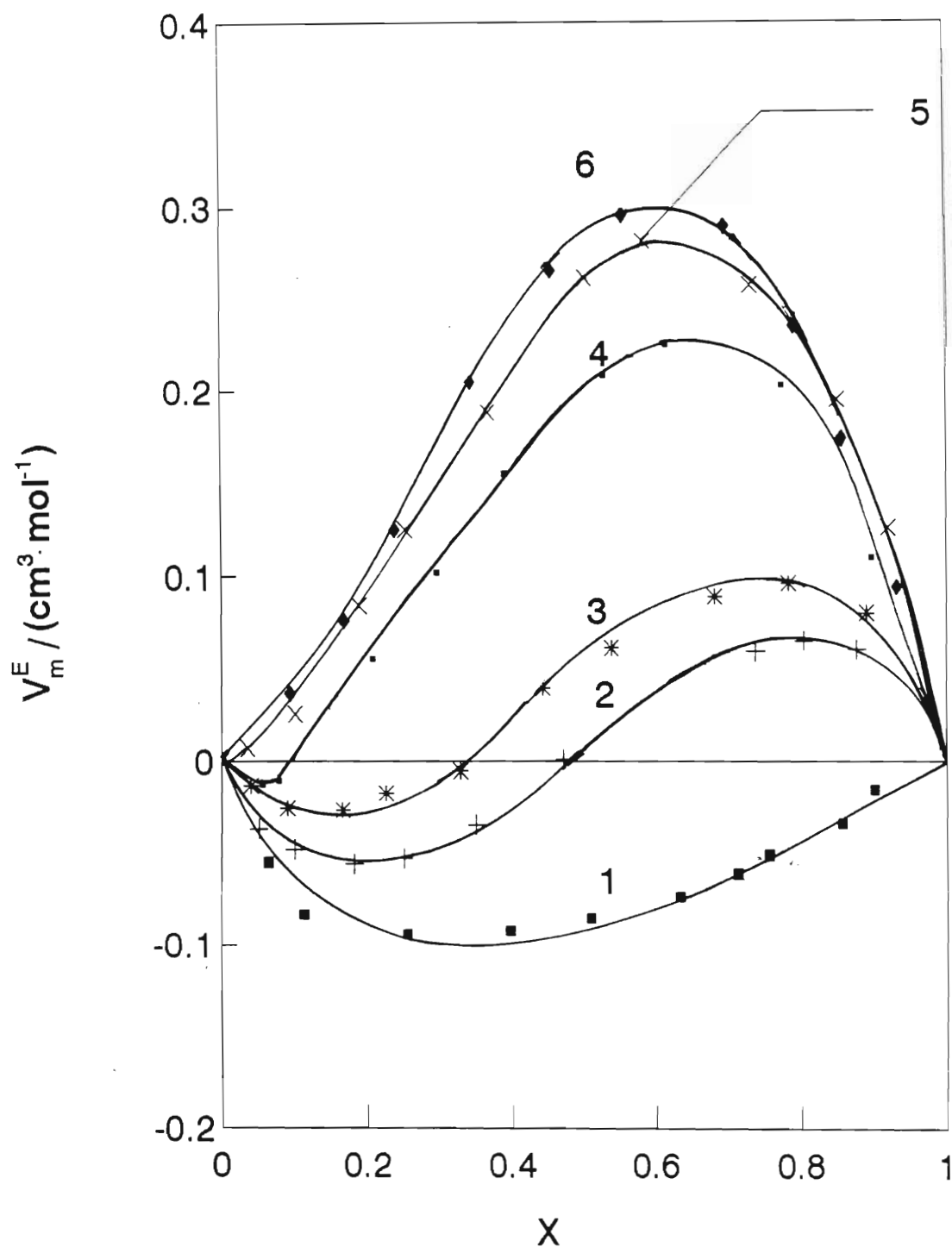


Figure 2.19. Excess molar volumes,  $V_m^E$  at the temperature 298.15 K for 1-propanol + (1), 1-hexyne; or + (2), 1-heptyne; or + (3), 1-octyne and for 2-propanol + (4), 1-hexyne; or + (5), 1-heptyne; or + (6), 1-octyne

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The  $H_m^E$  for a 1-alkyne + 1-propanol or 2-propanol are all positive with a maximum of about 0.7 mole fraction of 1-alkyne and are presented in Table 2.9 and figure 2.20. The large positive value is most likely a reflection of the breaking of the hydrogen bonds between the alkanol molecules as a result of the mixing process.

Comparing these results with those reported previously for a 1-alkyne with methanol or ethanol,<sup>(82)</sup> it can be seen that  $H_{m,max}^E$  increases with increasing carbon number (Table 2.17).

For example  $H_{m,max}^E$  for mixtures of 1-hexyne with methanol, ethanol, 1-propanol and 2-propanol are 642, 775, 922 and 1142 J·mol<sup>-1</sup>, respectively. The  $H_m^E$  results for 1-C<sub>6</sub>H<sub>10</sub> or 1-C<sub>7</sub>H<sub>12</sub> or 1-C<sub>8</sub>H<sub>14</sub> + ethanol<sup>(82)</sup> show markedly skew curves with maxima at about 0.7 mole fraction 1-alkyne. The  $H_{m,max}^E$  for these systems are between 150 and 300 J·mol<sup>-1</sup> less positive than the results for (1-alkyne + 1-propanol or 2-propanol) reported in this work.

For each 1-alkyne,  $H_{m,max}^E$  for mixtures containing 1-propanol are less positive than  $H_{m,max}^E$  for mixtures containing 2-propanol. This is due both to the enhanced dissociation between the alkanol molecules and the effect of the triple bond of the alkyne.

The self association between alkyne molecules is relatively strong as judged by the positive  $H_m^E$  results reported by Woycicki and Rhensius<sup>(83)</sup> and by Otsa *et al*<sup>(84)</sup> for (1-alkyne + n-alkane) mixtures. Woycicki *et al*<sup>(83)</sup> reported  $H_m^E$  and  $H_{m,max}^E$  for the mixtures (1-C<sub>6</sub>H<sub>10</sub> + C<sub>6</sub>H<sub>14</sub>)(592 J·mol<sup>-1</sup>) and (1-C<sub>7</sub>H<sub>12</sub> + C<sub>7</sub>H<sub>16</sub>)(567 J·mol<sup>-1</sup>). Otsa *et al*<sup>(84)</sup> reported  $H_m^E$  and  $H_{m,max}^E$  for the mixtures (1-C<sub>7</sub>H<sub>12</sub> + C<sub>7</sub>H<sub>16</sub>)(557 J·mol<sup>-1</sup>) and (1-C<sub>8</sub>H<sub>14</sub> + C<sub>8</sub>H<sub>18</sub>)(523 J·mol<sup>-1</sup>). This largely endothermic enthalpy contribution could possibly be the major contributory factor to the  $H_m^E$  results reported here.

For each alkanol, the  $H_{m,max}^E$  value increases only slightly with increasing alkyne carbon number. For example,  $H_{m,max}^E$  for mixtures containing 1-propanol with 1-hexyne, 1-heptyne and 1-octyne are 922, 941, 980 J·mol<sup>-1</sup>, respectively.

The effect of the triple bond in the 1-alkyne has a major effect on the  $H_{m,max}^E$  value. This can be seen by comparing  $H_{m,max}^E$  for (1-heptyne + 1-propanol)(945 J·mol<sup>-1</sup>) to (heptane + 1-propanol) (640 J·mol<sup>-1</sup>).<sup>(85)</sup> This endothermic enthalpy increase when replacing the single bond with a triple bond is probably due to the combined positive effects of the dissociation of alkanols (breakdown of H.....O bonding) and the dissociation of 1-alkynes (breakdown

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of  $\pi$ ..... $\pi$  interactions). There is no evidence, from the  $H_m^E$  results, to support the presence of interactions between the 1-alkyne molecules and the alkanols investigated( $\pi$ .....H or OH interactions).

**TABLE 2.17**  $H_{m,\max}^E$  for  $x1-C_yH_{2y-2} + (1-x)C_zH_{2z+1}OH$  at 298.15 K

Compound	$H_{m,\max}^E$ <sup>a</sup>			
	MeOH <sup>b</sup>	EtOH <sup>b</sup>	1-PrOH <sup>c</sup>	2-PrOH <sup>c</sup>
1-C <sub>6</sub> H <sub>12</sub>	650.0	770.0	922.0	1142
1-C <sub>7</sub> H <sub>14</sub>	755.0	860.0	941.0	1163
1-C <sub>8</sub> H <sub>16</sub>	682.0	810.0	976.0	1189

<sup>a</sup> Units: J·mol<sup>-1</sup>

<sup>b</sup> data taken from reference 82

<sup>c</sup> this work

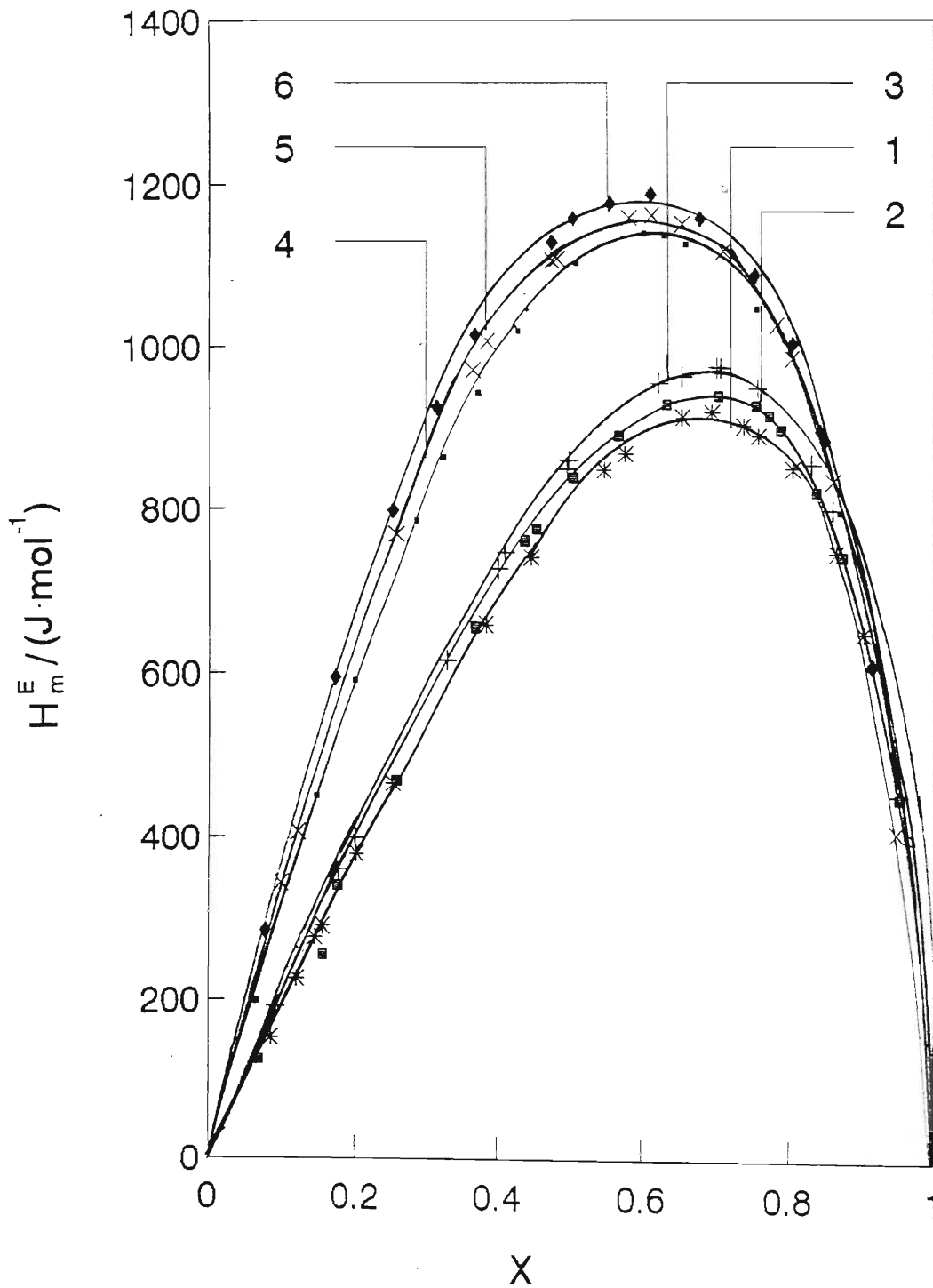


Figure 2.20. Excess molar enthalpies,  $H_m^E$  at the temperature 298.15 K for 1-propanol + (1), 1-hexyne; or + (2), 1-heptyne; or + (3), 1-octyne and for 2-propanol + (4), 1-hexyne; or + (5), 1-heptyne; or + (6), 1-octyne



### 2.5.3 Mixtures of di-n-butylamine(DBA) + ethers

It has been established that secondary amines interact with aromatic substances in the liquid phase.<sup>(86,87)</sup> Volume changes on mixing are reported in the literature for (di-n-butylamine + hexane or heptane or cyclohexane),<sup>(87)</sup> and for (di-n-butylamine + benzene or chlorobenzene or nitrobenzene or toluene).<sup>(87)</sup>  $V_m^E$  values of mixtures of (di-n-butylamine + hexane or chlorobenzene or nitrobenzene)<sup>(87)</sup> are negative over the whole concentration range. Negative  $V_m^E$  values were observed also for (di-n-butylamine + propan-1-ol)<sup>(88)</sup> at 298.15 K and 313.15 K.  $V_m^E$  values have been reported for many binary mixtures containing ethers. Negative  $V_m^E$  values were observed for the mixtures of chloroform<sup>(89)</sup> or tetrachloromethane<sup>(90)</sup> with ethers. Positive  $V_m^E$  values were reported for the mixtures of cyclohexane with ethers<sup>(91,92)</sup> or for {n-alkanes ( $C_6, C_8, C_{10}, C_{12}, C_{16}$ ) + dipropyl ether}<sup>(93)</sup> or for {an n-alkanes ( $C_6 - C_9$ ) + tetrahydrofuran or tetrahydropyran}<sup>(94)</sup> and for (cyclohexane + tetrahydrofuran) system.<sup>(95)</sup> The excess volumes of (a polar substance + a cyclic ether) were observed to be negative, i.e. (pyridine + tetrahydrofuran)<sup>(95)</sup> or (thiazole + tetrahydrofuran)<sup>(95)</sup> or (benzene + tetrahydrofuran)<sup>(95)</sup> or (dimethyl sulphoxide + 1,4-dioxane).<sup>(96)</sup>

The excess volumes  $V_m^E$  at the temperature 298.15 K are listed in Table 2.4 and the experimental data points are presented in figs 2.21 for each of the nine mixtures over the complete range of the mole fraction  $x$ .

Some of  $V_m^E$ 's are negative and some are positive but all the mixtures exhibit curves which are slightly asymmetrical with their minima or maxima at  $0.3 < x < 0.5$ . The  $V_m^E$  values are positive for (di-n-butylamine + dibutyl ether or tetrahydrofuran or tetrahydropyran or 1,4-dioxane). For n-chain ether, the branched ether and for the cyclic ether molecules  $V_m^E$  becomes less negative with increasing molecular weight.

$V_m^E$ s for the systems (di-n-butylamine + an ether) show increased values in the order: di-1-methylethyl ether < diethyl ether < 1,1-dimethylethyl methyl ether < dipropyl ether < 1,1-dimethylpropyl methyl ether < dibutyl ether < tetrahydrofuran < tetrahydropyran < 1,4-dioxane.

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The results are similar to those, recently reported<sup>(97)</sup> for the (tri-n-butylamine + an ether). The shape of the experimental curves is the same, but the values of  $V_m^E$  maximum are lower {e.g.  $V_{m,max}^E$  for (tri-n-butylamine + 1,4-dioxane) is  $0.905 \text{ cm}^3 \cdot \text{mol}^{-1}$  and  $V_{m,max}^E$  for (di-n-butylamine + 1,4-dioxane) is  $0.488 \text{ cm}^3 \cdot \text{mol}^{-1}$ }. This is also true for the systems displaying negative  $V_m^E$ , e.g.  $V_{m,max}^E$  for (tri-n-butylamine + di-1-methylethyl ether) is  $-0.328 \text{ cm}^3 \cdot \text{mol}^{-1}$  and for (di-n-butylamine + di-1-methylethyl ether) it is  $-0.405 \text{ cm}^3 \cdot \text{mol}^{-1}$ .

Assuming that negative  $V_m^E$  values correspond to intermolecular associations, then the  $V_m^E$  results obtained in this work, show for most of the mixtures discussed here some degree of association between di-n-butylamine and an ether. This can be judged by comparing  $V_{m,max}^E$  of (di-n-butylamine + an ether) to  $V_{m,max}^E$  of (di-n-butylamine + an n-alkane or a cycloalkane of comparable carbon number). For example  $V_{m,max}^E$  for (di-n-butylamine + dipropyl ether) is  $-0.10 \text{ cm}^3 \cdot \text{mol}^{-1}$  and for (di-n-butylamine + n-heptane) is  $0.06 \text{ cm}^3 \cdot \text{mol}^{-1}$ .<sup>(87)</sup> Unfortunately these associations are complicated by the effects of molecular packing which can be significant as can be judged from the  $V_{m,max}^E$  for (di-n-butylamine + heptane) and (di-n-butylamine + cycloalkane) which are  $0.06$  and  $0.56 \text{ cm}^3 \cdot \text{mol}^{-1}$  respectively.<sup>(87)</sup>

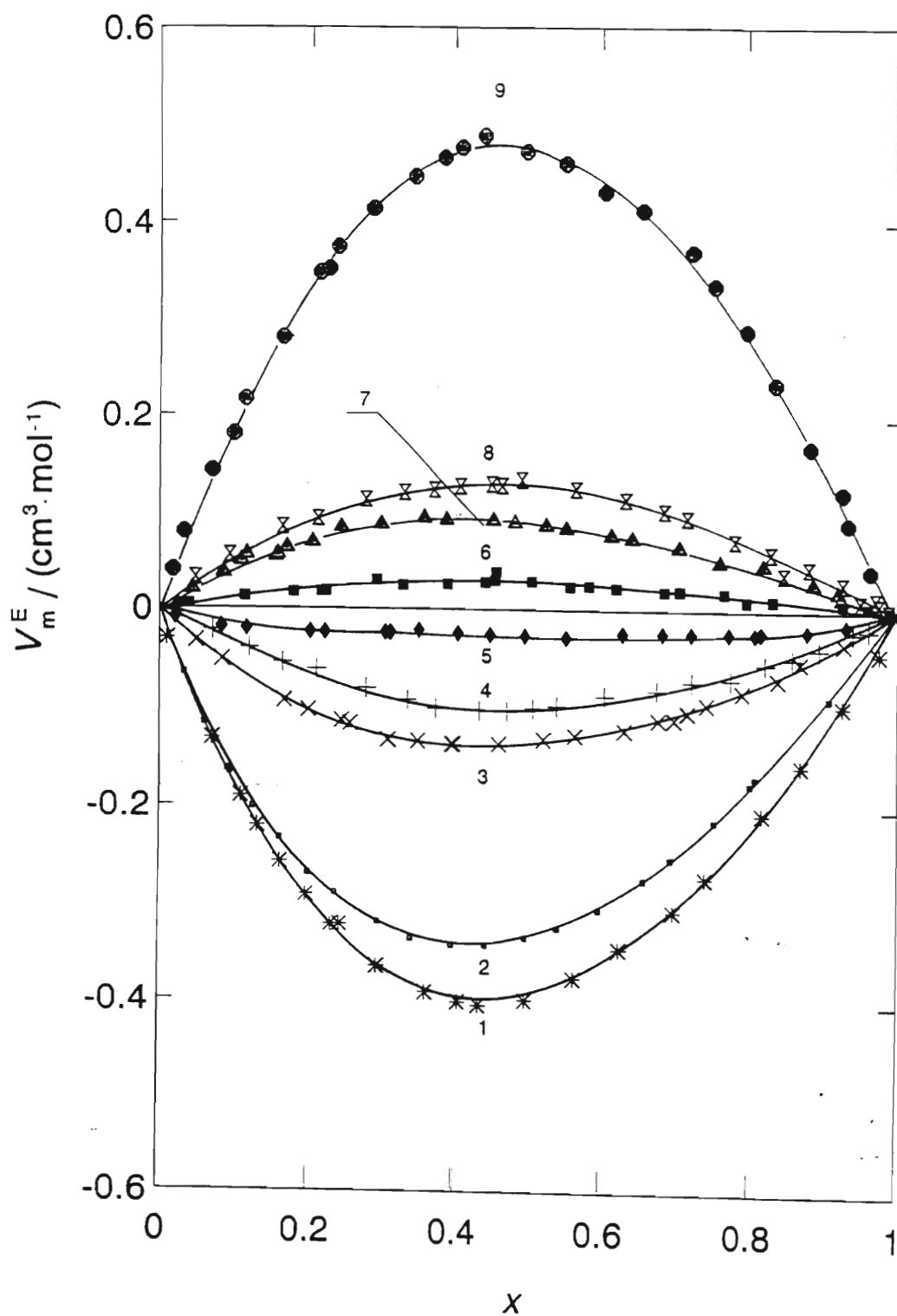


Figure 2.21. Excess molar volumes  $V_m^E$  at the temperature 298.15 K as a function of  $x$  for  $[x\text{C}_{12}\text{H}_{27}\text{N} + (1-x)\{1, \text{CH}_3\text{CH}(\text{CH}_3)\text{OCH}(\text{CH}_3)\text{CH}_3; 2, \text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3; 3, \text{CH}_3\text{C}(\text{CH}_3)_2\text{OCH}_3; 4, \text{CH}_3(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{CH}_3; 5, \text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)_2\text{OCH}_3; 6, \text{CH}_3(\text{CH}_2)_3\text{O}(\text{CH}_2)_3\text{CH}_3; 7, \text{c}-(\text{CH}_2)_4\text{O}; 8, \text{c}-(\text{CH}_2)_5\text{O}; 9, \text{c}-(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{O}\}]$ .

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$H_m^E$  values have been reported for many binary mixtures containing di-n-butylamine. Negative  $H_m^E$  values, which were symmetrical about mole fraction  $x = 0.4$  were observed for (di-n-butylamine + an alkanol) mixtures<sup>(89,90)</sup> with minimum value ranging from  $3910 \text{ J}\cdot\text{mol}^{-1}$  for methanol to  $-2851 \text{ J}\cdot\text{mol}^{-1}$  for heptan-1-ol at the temperature  $293.15 \text{ K}$ . Negative  $H_m^E$ s, with minimum value of  $-3390 \text{ J}\cdot\text{mol}^{-1}$  was reported for (di-n-butylamine + tetrachloromethane) at the temperature  $298.15 \text{ K}$ .<sup>(89)</sup> Endothermic effects were observed for (di-n-butylamine + n-alkanes) with maximum values of  $281 \text{ J}\cdot\text{mol}^{-1}$  (at  $303.15 \text{ K}$ ) and of  $1050 \text{ J}\cdot\text{mol}^{-1}$  (at  $293.15 \text{ K}$ ) for n-hexane and n-hexadecane, respectively. Endothermic effects were also observed for (di-n-butylamine + ethyl acetate or ethyl propionate) with maximum values of  $701 \text{ J}\cdot\text{mol}^{-1}$  and  $397 \text{ J}\cdot\text{mol}^{-1}$  at  $298.15 \text{ K}$ .<sup>(91)</sup>

The  $H_m^E$  results reported here are tabulated in Table 2.10 and figs 2.22-2.24 show the curves calculated from eqn. 2.22 and the experimental results for the mixtures discussed in the section.

Excess enthalpies measured on mixtures of (an amine + an alkanol) show some of the strongest negative values, found for organic mixtures in the literature.<sup>(89,90,93)</sup> The reason is the existence of strong intermolecular interactions between the NH-group of the amine molecule (A) and the OH-group of the alcohol molecule. In contrast to that,  $H_m^E$  for (an amine + an ester or an ether)<sup>(91)</sup> were found to be positive. A measure of the self association between the molecules of a species (A), can be obtained from  $H_{m,\text{max}}^E$  for (A + a hydrocarbon). Similarly a measure of A—B interactions, can be given by a comparison of  $H_{m,\text{max}}^E$  for (A + a hydrocarbon) and  $H_{m,\text{max}}^E$  for (B + a hydrocarbon) with  $H_{m,\text{max}}^E$  for (A + B). If  $H_{m,\text{max}}^E$  for (A + B)  $\ll$   $\{H_{m,\text{max}}^E$  for (A + a hydrocarbon) +  $H_{m,\text{max}}^E$  for (B + a hydrocarbon) $\}$  then it can be assumed that the species A interact with species B.<sup>(94)</sup> In this work  $H_{m,\text{max}}^E$  for (di-n-butylamine + an ether) is compared with  $H_{m,\text{max}}^E$  for (di-n-butylamine + a hydrocarbon) and  $H_{m,\text{max}}^E$  for (an ether + a hydrocarbon). The results are given in Table 2.18. The overall magnitude of  $H_{m,\text{max}}^E$  for (di-n-butylamine + an ether) is due to three effects. The positive effect due to the breakdown of the di-n-butylamine self-association, the positive effect due to the breakdown of the ether self-association, and the negative effect of the (di-n-butylamine + an ether) association.

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A comparison of the enthalpies given in Table 2.10 reported in this work indicate a strong interaction between di-n-butylamine and an ether, which increases in the following order: diethyl ether > dipropyl ether > dibutyl ether for the n-chain ethers and di-1-methylethyl ether > 1,1-dimethylpropyl methyl ether > 1,1-dimethylethyl methyl ether for the branched ethers and tetrahydropyran > tetrahydrofuran > 1,4 dioxane for the cyclic ethers. In general the longer the alkyl groups of the ether, the weaker is the interaction with di-n-butylamine. For the branched ethers the inductive effect of the methyl groups in the branched ethers appears to increase the electron density in the oxygen atom, resulting in an enhanced self-association effect. The fact that the  $H_{m,max}^E$ s for (di-n-butylamine + tetrahydrofuran or 1,4 dioxane) are much more positive than those for (di-n-butylamine + an aliphatic ether) indicates that the effect of the breakdown of the ring ether molecules self-association is much stronger due to the large dipole or quadropole moment of these ethers.<sup>(95)</sup>

The excess enthalpies for the mixtures (tri-n-butylamine + an ether)<sup>(98)</sup> at the temperature 298.15 K, have been recently reported and the  $H_m^E$  values were very much more positive indicating a dominance of the breakdown of self-association effects.

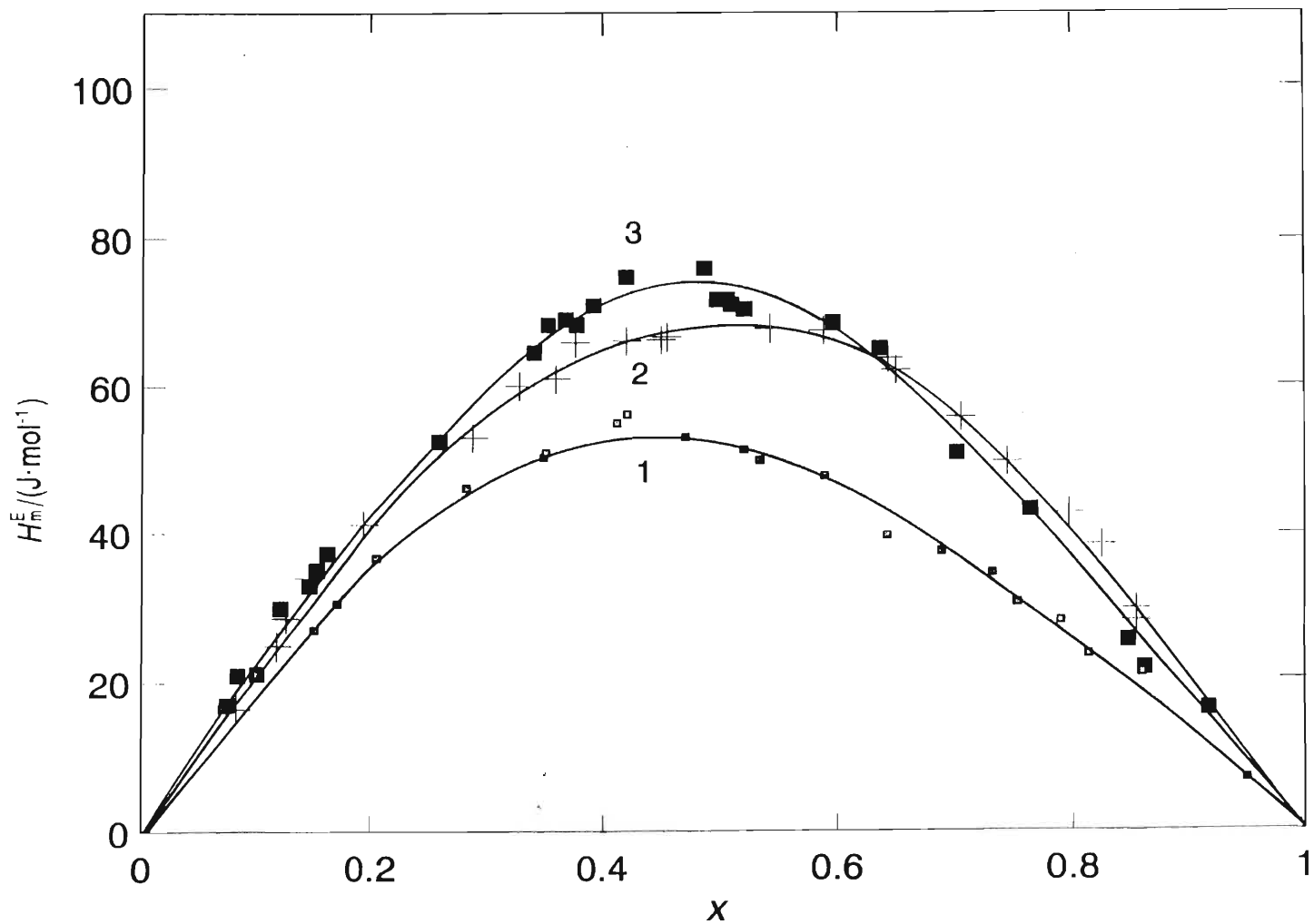


Figure 2.22 Excess molar enthalpies  $H_m^E$  at the temperature 298.15 K as a function of  $x$  for  $[x(\text{C}_4\text{H}_9)_2\text{NH} + (1-x)\{1, \text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3; 2, \text{CH}_3(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{CH}_3; 3, \text{CH}_3(\text{CH}_2)_3\text{O}(\text{CH}_2)_3\text{CH}_3\}]$

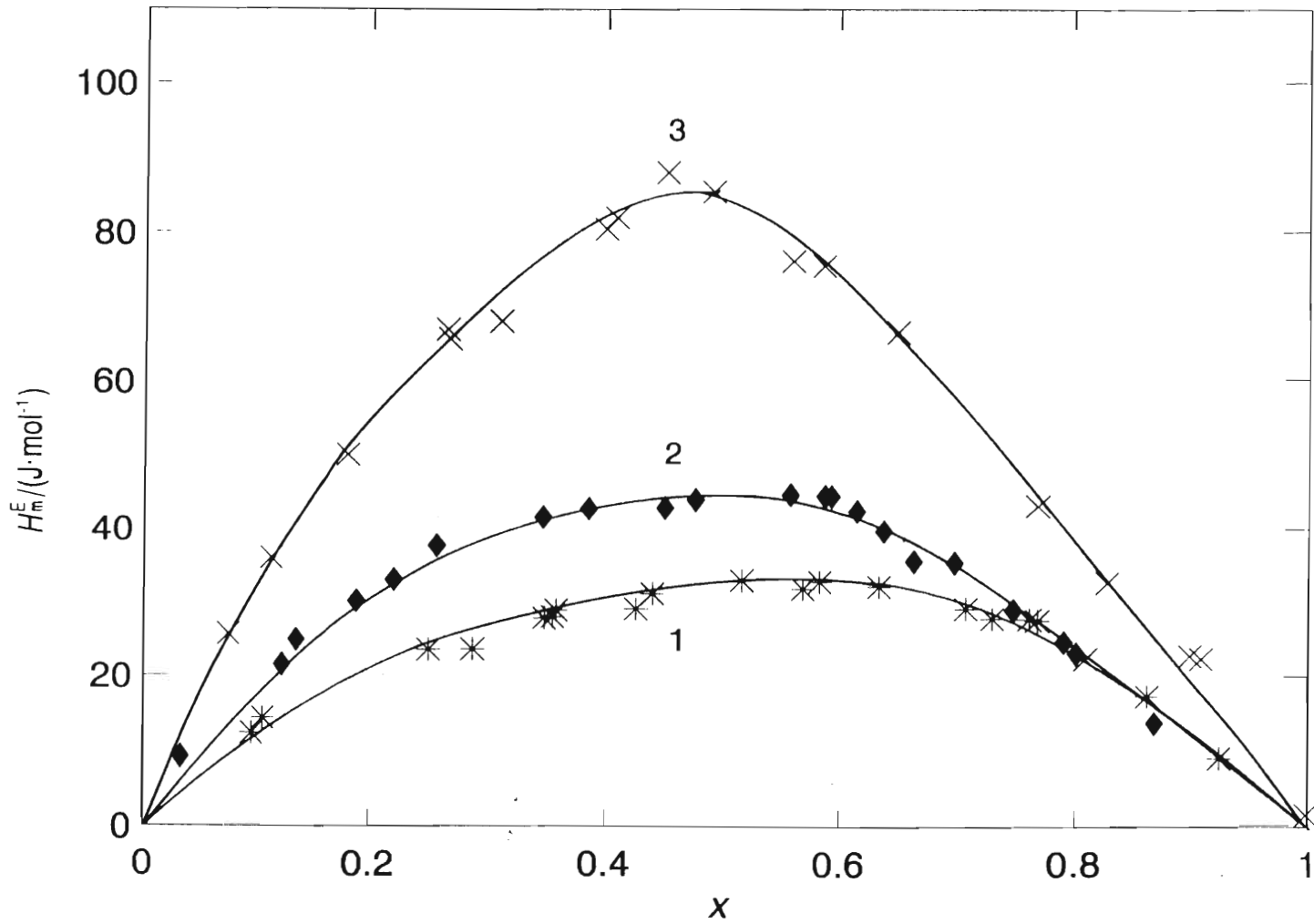


Figure 2.23 Excess molar enthalpies  $H_m^E$  at the temperature 298.15 K as a function of  $x$  for  $[x(\text{C}_4\text{H}_9)_2\text{NH} + (1-x)\{1, \text{CH}_3\text{CH}(\text{CH}_3)\text{OCH}(\text{CH}_3)\text{CH}_3; 2, \text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)_2\text{OCH}_3; 3, \text{CH}_3\text{C}(\text{CH}_3)_2\text{OCH}_3\}]$

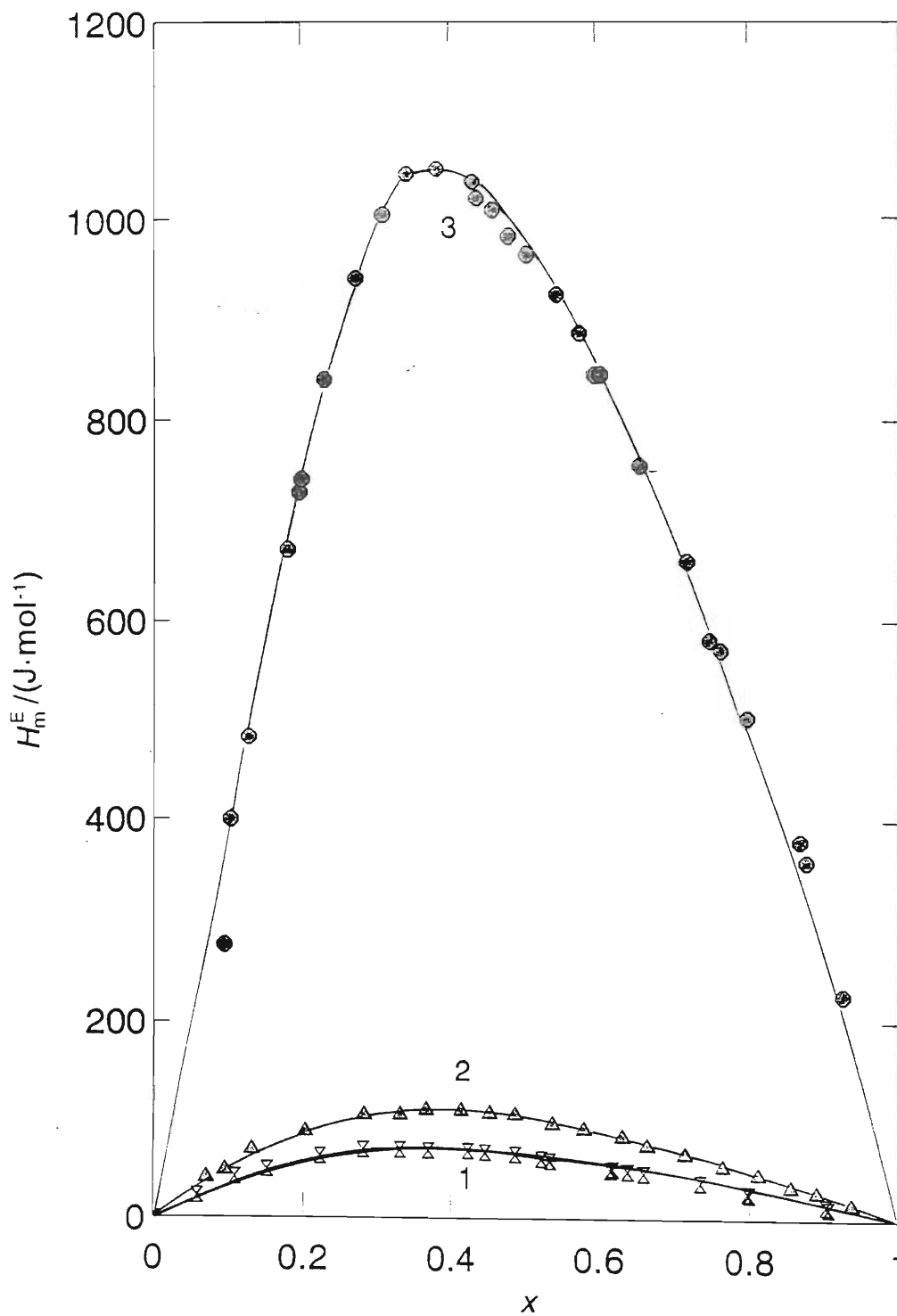


Figure 2.24 Excess molar enthalpies  $H_m^E$  at the temperature 298.15 K as a function of  $x$  for  $[x(\text{C}_2\text{H}_5)_2\text{NH} + (1-x)\{1, c\text{-(CH}_2)_3\text{O}; 2, c\text{-(CH}_2)_4\text{O}; 3, c\text{-(CH}_2)_2\text{O(CH}_2)_2\text{O}\}]$



## Chapter 2: Excess Molar Functions.....

TABLE 2.18  $H_{m,\max}^E \{ x(C_4H_9)_2 NH + (1-x)ROR' \} = A$  together with  $H_{m,\max}^E \{ x ROR' + (1-x) C_kH_l \} = B$  where  $C_kH_l$  refers to a hydrocarbon.  $H_{m,\max}^E \{ x (C_4H_9)_2 NH + (1-x) C_6H_{14} \}$  is  $281 \text{ J}\cdot\text{mol}^{-1}$  at  $303.15 \text{ K}$ .<sup>(5)</sup> All measurements refer to the temperature  $298.15 \text{ K}$

ROR'	A	B <sup>a</sup>	C <sub>k</sub> H <sub>l</sub>
	J·mol <sup>-1</sup>	J·mol <sup>-1</sup>	
CH <sub>3</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>3</sub>	56	439	<i>c</i> -(CH <sub>2</sub> ) <sub>6</sub>
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> O(CH <sub>2</sub> ) <sub>2</sub> CH <sub>3</sub>	68	305	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub> CH <sub>3</sub>
CH <sub>3</sub> CH(CH <sub>3</sub> )OCH(CH <sub>3</sub> )CH <sub>3</sub>	33	240	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub> CH <sub>3</sub>
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> O(CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>	75	93	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> CH <sub>3</sub>
CH <sub>3</sub> C(CH <sub>3</sub> ) <sub>2</sub> OCH <sub>3</sub>	88	383 <sup>b</sup>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub> CH <sub>3</sub>
CH <sub>3</sub> CH <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub> OCH <sub>3</sub>	45	-	-
<i>c</i> -(CH <sub>2</sub> ) <sub>4</sub> O	111	780	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> CH <sub>3</sub>
<i>c</i> -(CH <sub>2</sub> ) <sub>5</sub> O	69	607 <sup>c</sup>	<i>c</i> -(CH <sub>2</sub> ) <sub>5</sub>
<i>c</i> -(CH <sub>2</sub> ) <sub>2</sub> O(CH <sub>2</sub> ) <sub>2</sub> O	1052	1639	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub> CH <sub>3</sub>

<sup>a</sup> data from reference 99

<sup>b</sup> data from reference 102

<sup>c</sup> data from reference 100

The experimental results have been correlated using the NRTL equation,<sup>(104)</sup> the simple UNIQUAC equation<sup>(105)</sup> and UNIQUAC ASM model.<sup>(106)</sup> The exact mathematical forms of the pure components structural parameter  $r$  (volume parameter) and  $q$  (surface parameter) have been presented in a paper authored by Domanska *et al.*<sup>(107)</sup> The results are shown in table 2.19, where the binary parameters and absolute arithmetic-mean deviations obtained by

## Chapter 2: Excess Molar Functions.....

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minimizing the sum of the deviations between the experimental and calculated  $H_m^E$  values using the Marquardt's maximum neighbourhood method for minimization are presented.<sup>(108)</sup> The calculations with the UNIQUAC ASM (Kretshmer and Wiebe model of association) were carried out by the use of the association equilibrium constant for the pure di-n-butylamine:  $K_A = 0.16$  at the temperature 298.15 K, taken from the values of Reimann and Heintz.<sup>(88)</sup> The molar enthalpy of formation for the cyclic dimer of di-n-butylamine was taken as  $h_A = -13.2 \text{ kJ}\cdot\text{mol}^{-1}$  at the temperature 298.15 K.<sup>(109)</sup> The enthalpy was assumed to be independent of temperature and the temperature dependence of the equilibrium constant was calculated by the van't Hoff relation. The molar volume for di-n-butylamine used was  $171.066 \text{ cm}^3\cdot\text{mol}^{-1}$  at the temperature 298.15 K. The molar volumes of ethers were taken from previously reported work.<sup>(98,110)</sup>

Figure 2.25 shows the comparison of the experimental and calculated  $H_m^E$  values using the NRTL equation for (di-n-butylamine + tetrahydrofuran) as an example. The results of the correlation of experimental points with the two parameters NRTL and UNIQUAC equations are in the same range as the three or four parameters Redlich-Kister equation. For the nine systems presented in table 2.19, the description of excess molar enthalpy were given by the NRTL and UNIQUAC models with average standard deviations  $\langle \sigma \rangle = 2.3 \text{ J}\cdot\text{mol}^{-1}$  and  $\langle \sigma \rangle = 2.7 \text{ J}\cdot\text{mol}^{-1}$  (with the exception of 1,4-dioxane), respectively.

The correlation of experimental points in binary mixtures with the results, obtained by means of the UNIQUAC ASM model are the same as those obtained by simple NRTL and UNIQUAC models ( $\langle \sigma \rangle = 2.8 \text{ J}\cdot\text{mol}^{-1}$ ). The description obtained by means of the UNIQUAC ASM model with the association constant as the third adjustable parameter is also in the same range.

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**TABLE 2.19** Correlation of the excess molar enthalpies data for  $\{x(\text{C}_4\text{H}_9)_2\text{NH} + (1-x)\text{ROR}'\}$  by means of the NRTL, UNIQUAC and UNIQUAC ASM equations: values of parameters and measures of deviations

Ether	Parameters			Deviations		
	NRTL <sup>a</sup>	UNIQUAC	UNIQUAC ASM	NRTL	UNIQUAC	UNIQUAC ASM
	$g_{12}-g_{11}$	$\Delta u_{12}$	$\Delta u_{12}$	$\sigma(\text{J}\cdot\text{mol}^{-1})$		$\sigma(\text{J}\cdot\text{mol}^{-1})^b$
	$g_{12}-g_{22}$	$\Delta u_{21}$	$\Delta u_{12}$	$\sigma(\delta H_m^E/H_m^E)$		$\sigma_r^c$
	J·mol <sup>-1</sup>					
CH <sub>3</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>3</sub>	171.07	-23.39	-624.89	2.3	2.5	2.6
	104.75	87.46	457.50	6.8	7.5	7.9
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> O(CH <sub>2</sub> ) <sub>2</sub> CH <sub>3</sub>	127.19	266.54	-732.40	2.2	2.2	2.5
	145.60	-175.38	640.13	8.0	7.9	8.2
CH <sub>3</sub> CH(CH <sub>3</sub> )OCH(CH <sub>3</sub> )CH <sub>3</sub>	630.37	401.54	-615.16	1.5	1.5	1.6
	-427.94	-314.80	403.33	9.5	9.6	9.4
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> O(CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>	-212.75	-162.49	-504.42	4.1	4.1	4.4
	533.19	247.07	281.21	14.1	14.1	15.4
CH <sub>3</sub> C(CH <sub>3</sub> ) <sub>2</sub> OCH <sub>3</sub>	-529.45	-92.46	-773.89	4.1	4.3	4.3
	1000.95	191.97	774.84	20.0	20.0	20.0
CH <sub>3</sub> CH <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub> OCH <sub>3</sub>	-473.96	-137.17	-519.48	1.9	2.0	2.1
	747.60	197.01	283.49	10.0	10.2	10.5
<i>c</i> -(CH <sub>2</sub> ) <sub>4</sub> O	-869.45	-153.25	-359.34	1.8	2.9	3.1
	1755.30	344.69	187.06	3.8	5.0	5.4
<i>c</i> -(CH <sub>2</sub> ) <sub>5</sub> O	-974.87	-419.27	-199.73	1.1	2.1	2.0
	1694.84	627.11	-67.14	4.1	7.9	7.7
<i>c</i> -(CH <sub>2</sub> ) <sub>2</sub> O(CH <sub>2</sub> ) <sub>2</sub> O	2280.62	953.08	833.54	65.0	56.0	55.0
	4763.12	731.16	361.82	14.7	13.6	13.5

<sup>a</sup>: calculated for  $\alpha_{12} = 0.3$

<sup>b</sup>: given by eqn.  $\sigma = [\Sigma(H_{m(\text{exp})}^E - H_{m(\text{calc})}^E)^2 / (n - k)]^{1/2}$

and <sup>c</sup>: given by eqn.  $\sigma_r = 100 [\Sigma(H_{m(\text{exp})}^E - H_{m(\text{calc})}^E)^2 / (H_{m(\text{exp})}^E)^2 (n - k)]^{1/2}$ .

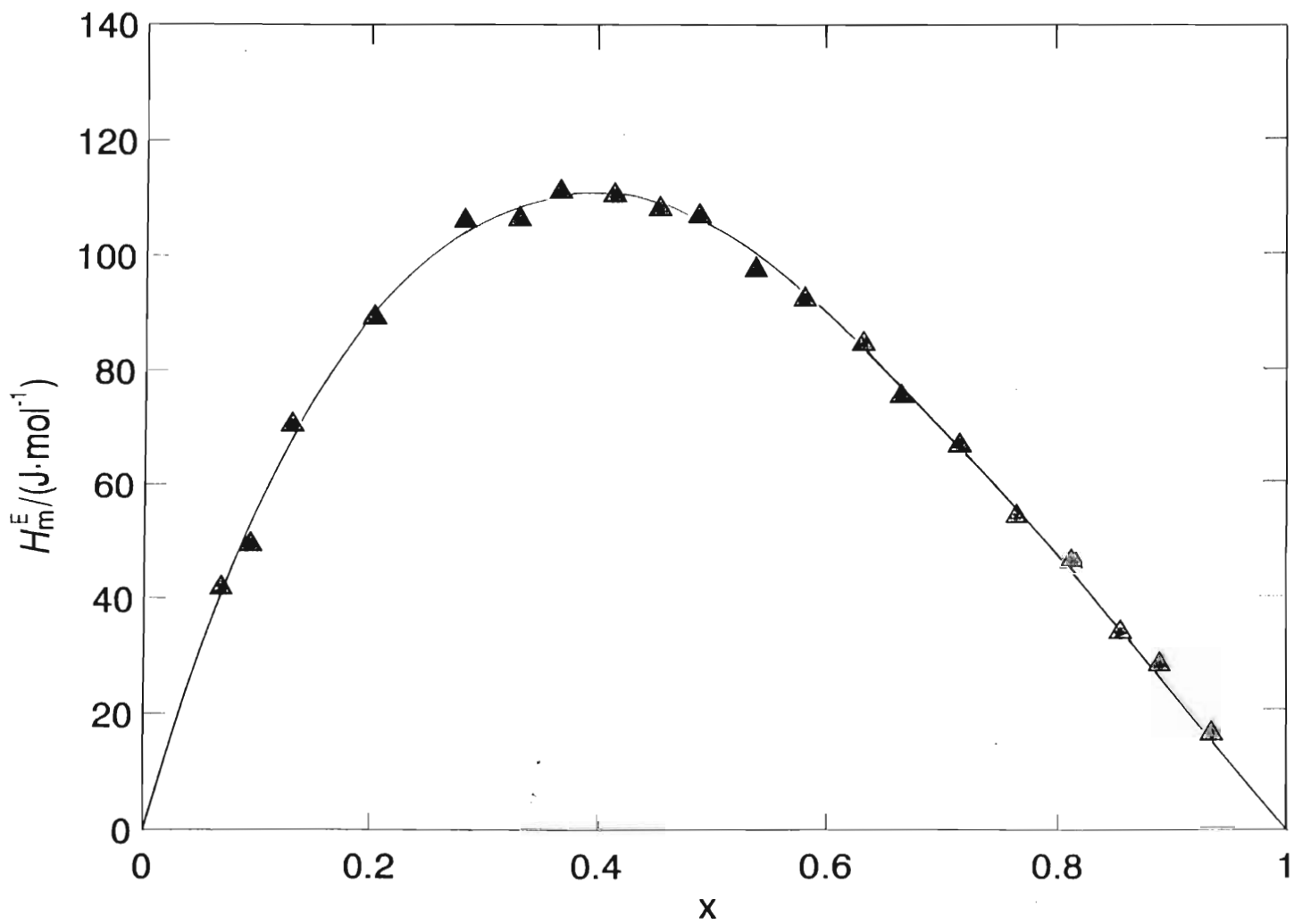


Figure 2.25. Excess enthalpy  $H_m^E$  for  $\{x(\text{C}_4\text{H}_9)_2\text{NH} + (1-x)c\text{-(CH}_2)_4\text{O}\}$  at  $T = 298.15$  K. Experimental points are matched by the curve calculated by the NRTL equation.

## Chapter 3

### The Principle of Congruence

#### 3.1 Introduction

The principle of congruence in its most general form<sup>(111)</sup> asserts that the configurational properties of members of a homologous series and of mixtures of members of such a series at a given temperature and pressure are a function only of the number average chain length. Thus for an excess property,  $X_m^E$ , such as volume or enthalpy, we may write

$$X_m^E(T, p, x_1, x_2, \dots, n_1, n_2, \dots) = X_m^E(T, p, \sum x_i n_i) \quad 3.1$$

The principle has been applied to many binary systems<sup>(112)</sup> and to some special cases of multicomponent mixtures. The simplest kinds of multicomponent systems to which one might expect to apply are ternary mixtures of members of a homologous series.<sup>(113)</sup> For such systems, several possible experimental tests of the principle of congruence suggest themselves, some of which are outlined as follows<sup>(112)</sup>: (a) null experiments involving mixing of a binary mixture with its congruent pure homologue and (b) experiments in which a binary pseudo- $n$ -alkane (**A**) of integral average chain length  $n_1$  is mixed with a number of other  $n$ -alkanes (**B**, **C**, ..... ) of various chain lengths  $n_2, n_3, \dots$ . The excess functions for such experiments would be expected to be the same as those for binary mixtures of pure component of chain length  $n_1$  in the same proportions with the alkanes of chain length ( $n_2, n_3, n_4, \dots$ )<sup>(112)</sup>

The work reported here is an extension of the principle of class (b) above and involves ternary mixtures obtained by mixing a single component with a equimolar binary mixture. A novel set of mixtures involving accurately made up pseudo-cycloalkanes has been used to test the principle which implies that a pseudo-cycloalkane  $[0.5c\text{-C}_k\text{H}_{2k} + 0.5c\text{-C}_l\text{H}_{2l}]$  will behave like  $c\text{-C}_m\text{H}_{2m}$  where  $m = (k + l)/2$ . The  $V_m^E$ 's and  $H_m^E$ 's values for  $m = 7$  and 8 are reported in this work over the whole composition range and the results were used to test the

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principle of congruence. The  $H_m^E$  values for (pseudo-c-C<sub>6</sub>H<sub>12</sub>[0.5c-C<sub>5</sub>H<sub>10</sub> + 0.5c-C<sub>7</sub>H<sub>14</sub>] + c-C<sub>6</sub>H<sub>12</sub>) and ([0.6c-C<sub>5</sub>H<sub>10</sub> + 0.4c-C<sub>10</sub>H<sub>20</sub>] + c-C<sub>7</sub>H<sub>14</sub>) over the whole composition range are also reported.

#### 3.2 Short description of the application of the congruency principle to ternary mixtures

First proposed by Bronsted and Koefoed in 1946<sup>(111)</sup>, the principle of congruence asserts that a mixture of chain molecules from a given homologous series may be characterized by an index  $\vartheta$  and that, at a given temperature and pressure, mixtures with the same index have the same values for certain of their properties. For n-alkanes,<sup>(114)</sup> n-alcohols,<sup>(115)</sup> perfluoro-n-alkanes,<sup>(116)</sup> 1-alkenes,<sup>(117)</sup> 1-chloroalkenes<sup>(118)</sup> and methylalkanoates,<sup>(119)</sup> the index,  $\vartheta$  has usually been identified with  $n$ , the average number of carbon atoms per molecule, defined by

$$n = \sum x_i n_i \quad 3.2$$

where  $x_i$  is the mole fraction of the member of the series containing  $n_i$  carbon atoms. Mixtures of the same average chain length are said to be congruent.<sup>(112)</sup>

Various experimental studies have been made of the applicability of this principle to binary systems.<sup>(114-118)</sup> The most widely referenced application of the congruency theory for a binary mixture is that reported by McGlashan<sup>(120,125)</sup> for (n-hexane + n-hexadecane). McGlashan<sup>(120)</sup> reported an equation in which the principle of congruence was applicable to mixtures which have asymmetric excess property versus mole fraction curves. (cf. equation 3.3)

$$X_m^E(n; 1, 2) = -(n_2 - n_1)^2 x_1 x_2 \sum_{r=0}^s A_r / x [\sum_{i=0}^r (x_1 n_1 + x_2 n_2)^i] x \{n_2^{r-t+1} - n_1^{r-t+1}\} / n_2 - n_1 \quad 3.3$$

A fit to the data for (n-hexane + n-hexadecane) at 20 °C gave the following equation for the excess enthalpy:

$$H_m^E = (n_1 - n_2)^2 x_1 x_2 \{8.08 - 0.088 [(1 + x_1)n_1 + (1 + x_2)n_2]\} \quad 3.4$$

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In the application of the congruency principle to ternary mixtures for the n-alkanes, the above system has been extensively examined as a reference for other mixtures.<sup>(113,121)</sup>

Ternary mixtures may be most simply tested for conformity with the principle of congruence by considering them as being constituted from two components, one of which is a binary mixture and the other may be a single component or a binary mixture.. Two kinds of experimental tests may be used, a *null test* or a *comparative test*. Various versions<sup>(112)</sup> of these two tests are listed in Table 3.1 where components A., B, C, D, E and F are homologues. In a null test, components 1 and 2 (from the table) are congruent and should yield no observable change on mixing for properties such as volume or enthalpy. In a comparative test, components 1 and 2 are not congruent, and a change observed on mixing is compared against a binary mixture with which it is congruent. These changes observed on mixing should be the same if the principle of congruence is valid.<sup>(112)</sup>

**Table 3.1** Summary of the various tests for ternary mixtures.

Component 1	Component 2	Test Type
(A + B), n = n <sub>c</sub>	C	Null Test
(A + B), n = n <sub>c</sub>	(D + E), n = n <sub>c</sub>	Null Test
(A + B), n = n <sub>c</sub>	D	⎛ Comparative ⎞ ⎝ Test ⎝
i.e. C	D	
(A + B), n = n <sub>c</sub>	(D + E), n = n <sub>F</sub>	⎛ Comparative ⎞ ⎝ Test ⎝
i.e. C	F	

Looi *et al*<sup>(113)</sup> initiated the application of the congruence principle to ternary mixtures in which the comparative test [(A + B) + C] was conducted on a ternary mixture comprising of a [(0.5C<sub>13</sub>H<sub>28</sub> + 0.5C<sub>19</sub>H<sub>40</sub>) + C<sub>6</sub>H<sub>14</sub>] mixture. They called the binary mixture (0.5C<sub>13</sub>H<sub>28</sub>

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+ 0.5C<sub>19</sub>H<sub>40</sub>) a "pseudo-*n*-hexadecane". The V<sub>m</sub><sup>E</sup> and H<sub>m</sub><sup>E</sup> results were compared with that of system *n*-hexadecane with *n*-hexane. The excess volumes are in good agreement with the results of Diaz Peña *et al*<sup>(122)</sup> and also with those of Gomaz-Ibanez and Liu.<sup>(123)</sup> A slightly poorer correlation was obtained between the excess enthalpies and those of Larkin *et al*<sup>(124)</sup> and those interpolated from the data of McGlashan and Morcom,<sup>(125)</sup> as shown in fig. 3.1.

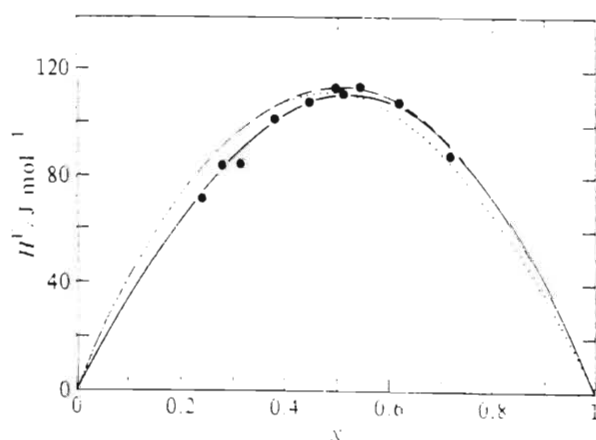


Fig 3.1 Excess enthalpies. •, (1-x)C<sub>6</sub>H<sub>14</sub> + x(0.5C<sub>13</sub>H<sub>28</sub> + 0.5C<sub>19</sub>H<sub>40</sub>) at 298.15K; —, (1-x)C<sub>6</sub>H<sub>14</sub> + xC<sub>16</sub>H<sub>34</sub>; results of Larkin *et al*; ····, (1-x)C<sub>6</sub>H<sub>14</sub> + xC<sub>16</sub>H<sub>34</sub>; results of McGlashan *et al* copied from reference 113

In a later paper, Lim and Williamson<sup>(121)</sup> reported V<sub>m</sub><sup>E</sup> data at 303.15 K on quaternary mixtures of pseudo-*n*-hexadecane + pseudo-*n*-hexane which were in excellent agreement with



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the data for pure n-hexane + pure n-hexadecane and the principle of congruence. The pseudo-n-hexane and the pseudo-n-hexadecane was composed of a binary mixture of  $(0.6667\text{C}_5\text{H}_{12} + 0.3333\text{C}_8\text{H}_{18})$  and  $(0.2\text{C}_8\text{H}_{18} + 0.8\text{C}_{18}\text{H}_{38})$ , respectively. These workers<sup>(121)</sup> concluded that the excellent agreement between their work and those reported for the pure n-alkane mixtures confirms the applicability of the principle of congruence to the volumetric behaviour of mixtures containing a wide range of components of very different chain lengths.<sup>(121)</sup>

This work extends the work done by Letcher *et al*<sup>(126)</sup> for the (*n*-alkane + pseudo-*n*-alkane) system to include the cycloalkanes. These workers reported studies done on the application of the congruency null test to a ternary mixture obtained by mixing a pseudo-*n*-alkane of carbon number *m* with the *n*-alkane of carbon number *m* over the whole composition range. The excess molar volumes and excess molar enthalpies for  $\{x(0.5\text{C}_k\text{H}_{2k+2} + 0.5\text{C}_l\text{H}_{2l+2}) + (1-x)\text{C}_m\text{H}_{2m+2}\}$  where  $m = (k + l)/2$  were reported to be within zero to  $\pm 0.005 \text{ cm}^3 \cdot \text{mol}^{-1}$  and zero to  $\pm 1.1 \text{ J} \cdot \text{mol}^{-1}$ , respectively.<sup>(126)</sup> The results show that  $V_m^E$  and  $H_m^E$  for (an *n*-alkane of carbon number *m* + a pseudo-*n*-alkane of the same carbon number) are relatively small and can be interpreted as confirmation of the application of the principle of congruence to homologous mixtures of widely differing chain length.<sup>(126)</sup>

In this work, a pseudo-cycloalkane of carbon number *m* was mixed with a cycloalkane of carbon number *m* over the whole composition range. The results of this null method was used to test the principle of congruence.

The experimental  $V_m^E$  and  $H_m^E$  values for (pseudo-c-C<sub>8</sub>H<sub>16</sub> [0.5c-C<sub>6</sub>H<sub>12</sub> + 0.5c-C<sub>10</sub>H<sub>20</sub>] + c-C<sub>8</sub>H<sub>16</sub>) and (pseudo-c-C<sub>7</sub>H<sub>14</sub> [0.5c-C<sub>8</sub>H<sub>16</sub> + 0.5c-C<sub>6</sub>H<sub>12</sub>] + c-C<sub>7</sub>H<sub>14</sub>) and  $H_m^E$  values for (pseudo-c-C<sub>6</sub>H<sub>12</sub> [0.5c-C<sub>5</sub>H<sub>10</sub> + 0.5c-C<sub>7</sub>H<sub>14</sub>] + c-C<sub>6</sub>H<sub>12</sub>) and ([0.6c-C<sub>5</sub>H<sub>10</sub> + 0.4c-C<sub>10</sub>H<sub>20</sub>] + c-C<sub>7</sub>H<sub>14</sub>) are determined and the principle of congruence tested.

### 3.3 Experimental

#### 3.3.1 Materials and Apparatus

The cyclopentane was obtained from Fluka (>99 % GC), the cyclohexane from SARchem (99 % GC), the cycloheptane from Aldrich (>99 % GC), the cyclooctane from Janssen Chemicals (>99 % GC), and the cyclodecane from Fluka (99 % GC). All the liquids were analyzed by g.l.c after being fractionally distilled. The  $V_m^E$  and  $H_m^E$  values were measured using an Anton Paar DMA 601 vibrating-tube densimeter and the Thermometric 2277 Thermal Activity Monitor, respectively. The methods have been described in Section 2.3.2.1.

#### 3.3.2 Preparation of mixtures

The pseudo-cycloalkane mixtures were made up to within  $1 \times 10^{-4}$  of  $x = 0.5$ , in each case. The bottles were weighed on a Mettler AT 250 (accurate to  $\pm 0.001$  mg). The liquids were degassed just before use by immersing the flask in a sonic bath for 10 to 15 minutes. All the mixtures were made up in 5 cm<sup>3</sup> bottles, and care was taken to keep the vapour space to a minimum. In all cases the least volatile component was added to the bottle first. The experimental error in  $V_m^E$  is of the order  $0.002 \text{ cm}^3 \cdot \text{mol}^{-1}$  and in  $H_m^E$  they are of the order  $1 \text{ J} \cdot \text{mol}^{-1}$  or 1 %.

### 3.4 Results

The  $V_m^E$  results are given in Table 3.2 and the  $H_m^E$  results in Table 3.3. Each of the measured properties are given together with their deviations,  $\delta$ , calculated from the Redlich-Kister polynomial (eqn. 2.22). The co-efficients  $B_r$  and  $A_r$  are given in Table 3.4.

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**TABLE 3.2.** Excess molar volumes,  $V_m^E$ , for  $x(0.5c-C_kH_{2k} + 0.5c-C_lH_{2l}) + (1-x)c-C_mH_{2m}$  where  $m = (k + l)/2$  and the deviations,  $\delta V_m^E$ , calculated from equation (2.22) and Table 3.4 at the temperature 298.15 K

$x$	$V_m^E$	$\delta V_m^E$	$x$	$V_m^E$	$\delta V_m^E$	$x$	$V_m^E$	$\delta V_m^E$
	$\text{cm}^3 \cdot \text{mol}^{-1}$	$\text{cm}^3 \cdot \text{mol}^{-1}$		$\text{cm}^3 \cdot \text{mol}^{-1}$	$\text{cm}^3 \cdot \text{mol}^{-1}$		$\text{cm}^3 \cdot \text{mol}^{-1}$	$\text{cm}^3 \cdot \text{mol}^{-1}$
$x(0.5c-C_8H_{16} + 0.5c-C_6H_{12}) + (1-x)c-C_7H_{14}$								
0.2191	-0.00203	0.0020	0.4706	-0.0034	0.002	0.7337	-0.00237	0.002
0.3631	-0.00300	-0.0010	0.6263	-0.00562	-0.002	0.8569	-0.00488	-0.0006
$x(0.5c-C_6H_{12} + 0.5c-C_{10}H_{20}) + (1-x)c-C_8H_{16}$								
0.0505	-0.00181	-0.003	0.5015	-0.02492	-0.002	0.8135	-0.01438	-0.0004
0.2134	-0.00736	0.003	0.6416	-0.01756	0.002	0.8910	-0.01073	-0.0005
0.3999	-0.02237	-0.0007						

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**Table 3.3** Excess molar enthalpies,  $H_m^E$ , for  $x(0.5c-C_kH_{2k} + 0.5c-C_lH_{2l}) + (1-x)c-C_mH_{2m}$  where  $m = (k + l)/2$  and for  $x(0.6c-C_5H_{10} + 0.4c-C_{10}H_{20}) + (1-x)c-C_7H_{14}$  and the deviations,  $\delta V_m^E$ , calculated from equation (2.22) and Table 3.4 at the temperature 298.15 K.

			$x(0.5c-C_5H_{10} + 0.5c-C_7H_{14}) + (1-x)c-C_6H_{12}$					
$x$	$H_m^E$	$\delta H_m^E$	$x$	$H_m^E$	$\delta H_m^E$	$x$	$H_m^E$	$\delta H_m^E$
	J·mol <sup>-1</sup>	J·mol <sup>-1</sup>		J·mol <sup>-1</sup>	J·mol <sup>-1</sup>		J·mol <sup>-1</sup>	J·mol <sup>-1</sup>
0.1120	9.2	-0.1	0.5609	21.6	0.6	0.8466	10.8	-0.1
0.1638	12.7	0.1	0.6038	20.2	-0.3	0.8787	8.6	-0.2
0.3524	19.6	-0.1	0.7204	17.5	0.1	0.9045	7.3	0.3
0.5408	20.7	-0.4						
$x(0.5c-C_8H_{16} + 0.5c-C_6H_{12}) + (1-x)c-C_7H_{14}$								
0.0648	0.6	-0.03	0.4833	2.2	0.04	0.7482	1.6	-0.3
0.1526	1.3	-0.04	0.6222	2.2	-0.4	0.8191	1.3	-0.09
0.1807	1.6	0.03	0.6605	2.9	0.5	0.8287	1.5	0.2
0.2708	2.2	-0.02						
$x(0.5c-C_{10}H_{20} + 0.5c-C_6H_{12}) + (1-x)c-C_8H_{16}$								
0.1676	4.5	-0.4	0.4881	8.6	0.03	0.8168	5.5	-0.04
0.1984	6.1	0.4	0.5638	8.9	-0.2	0.8758	4.2	-0.2
0.3642	8.6	0.0	0.7796	8.3	0.3			

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Table 3.3- continued

$x$	$H_m^E$	$\delta H_m^E$	$x$	$H_m^E$	$\delta H_m^E$	$x$	$H_m^E$	$\delta H_m^E$
	J·mol <sup>-1</sup>	J·mol <sup>-1</sup>		J·mol <sup>-1</sup>	J·mol <sup>-1</sup>		J·mol <sup>-1</sup>	J·mol <sup>-1</sup>
$x(0.6c-C_5H_{10} + 0.4c-C_{10}H_{20}) + (1-x)c-C_7H_{14}$								
0.1625	26.3	0.04	0.4306	47.8	1.5	0.8395	23.1	-0.3
0.2799	39.2	-0.1	0.5307	44.2	-0.9	0.8712	19.8	0.1
0.3991	44.9	-0.8	0.6805	37.8	0.4			

**Chapter 3: The Principle of Congruence.....**

**TABLE 3.4** Coefficients  $B_r$  and  $A_r$  for  $V_m^E$  or  $H_m^E$  [ $x(0.5c-C_kH_{2k} + 0.5c-C_lH_{2l}) + (1-x)c-C_mH_{2m}$  where  $m = (k + l)/2$  and for [ $x(0.6c-C_5H_{10} + 0.4c-C_{10}H_{20}) + (1-x)c-C_7H_{14}$ ]} at the temperature 298.15 K by equation (2.22)

Mixture	$B_0$	$B_1$	$B_2$
$x(0.5c-C_8H_{16} + 0.5c-C_6H_{12}) + (1-x)c-C_7H_{14}$	-0.0092	0.0109	-0.0326
$x(0.5c-C_6H_{12} + 0.5c-C_{10}H_{20}) + (1-x)c-C_8H_{16}$	-0.0913	-0.0099	0.0529
	$A_0$	$A_1$	$A_3$
$x(0.5c-C_5H_{10} + 0.5c-C_7H_{14}) + (1-x)c-C_6H_{12}$	85.2145	-0.9939	5.7348
$x(0.5c-C_8H_{16} + 0.5c-C_6H_{12}) + (1-x)c-C_7H_{14}$	11.4067	1.3863	-3.4867
$x(0.5c-C_{10}H_{20} + 0.5c-C_6H_{12}) + (1-x)c-C_8H_{16}$	35.3082	7.7945	2.3380
$x(0.6c-C_5H_{10} + 0.4c-C_{10}H_{20}) + (1-x)c-C_7H_{14}$	183.5826	37.7464	-2.1561

### 3.5 DISCUSSION

The  $V_m^E$  and  $H_m^E$  results for all the systems investigated are represented in Figs. 3.2 and 3.3 respectively, where the mole fraction of the pseudo-cycloalkane is calculated by using its mean molar mass and regarding it as a single pure substance.

The results show a small positive excess enthalpy and a small negative excess volume of mixing for all the mixtures. Mixtures containing the  $c\text{-C}_5\text{H}_{10}$  appear to produce the greatest divergence from the congruence principle. This shows that the effect of adding a  $-\text{CH}_2-$  group to  $c\text{-C}_5\text{H}_{10}$  is not the same as the addition of a  $-\text{CH}_2-$  group to  $c\text{-C}_8\text{H}_{16}$  or  $c\text{-C}_{10}\text{H}_{20}$ . In general, the greater the disparity in the carbon number, the greater the divergence from the congruence principle. The cycloalkane mixtures do not satisfy null test of the congruence principle as well as the  $n$ -alkanes have shown to do.

#### *Future work*

In continuation of this congruency work, it is thought that the null method could perhaps be applied to mixtures containing alkanols, or alkenes, or alkynes.

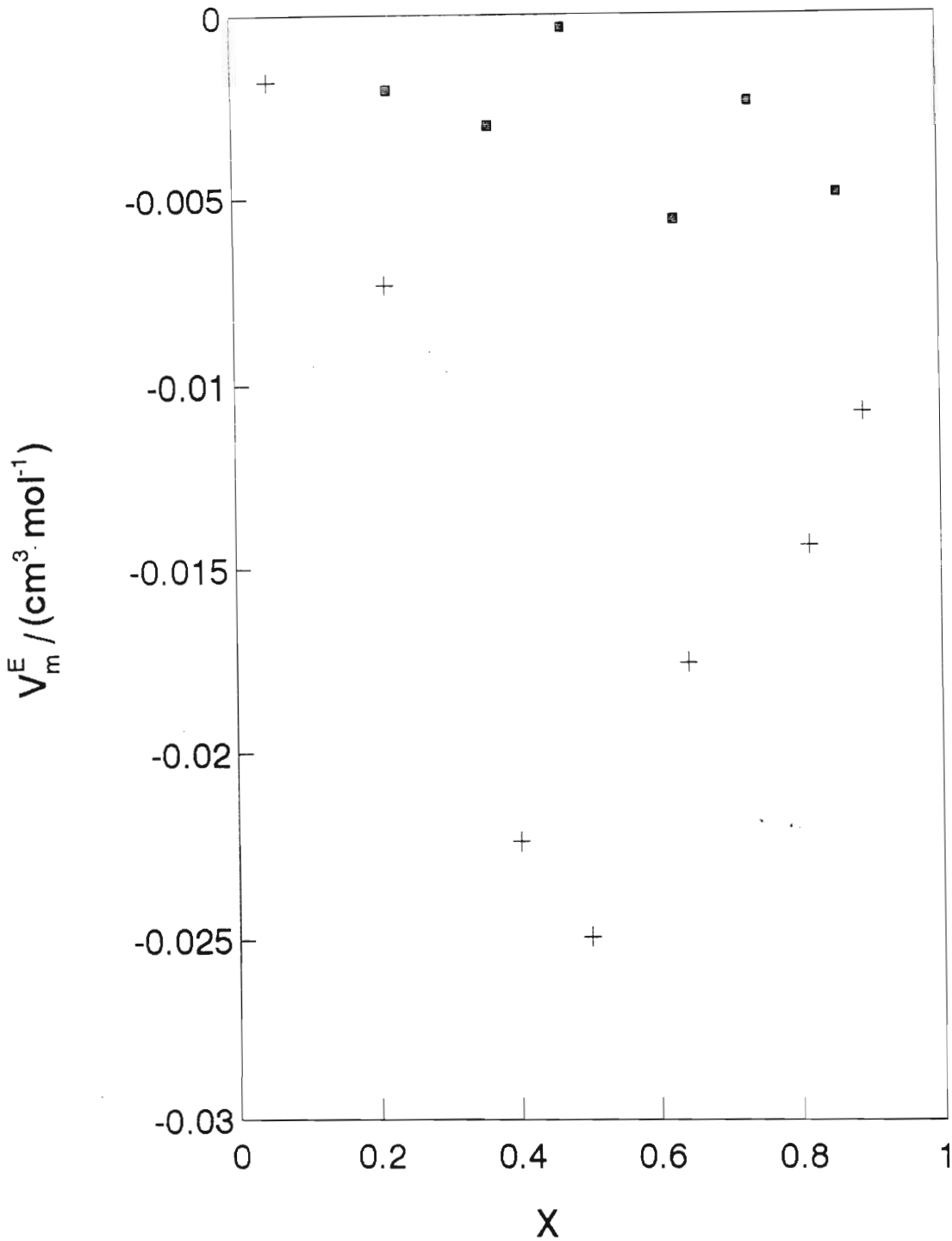


Figure 3.2. Excess molar volume  $V_m^E$  for: (1)  $\{x \text{ c-C}_8\text{H}_{16} + (1-x) \text{ pseudo-c-C}_8\text{H}_{16} [0.5\text{c-C}_8\text{H}_{12} + 0.5\text{c-C}_{10}\text{H}_{20}]\}$  and (2)  $\{x \text{ c-C}_7\text{H}_{14} + (1-x) \text{ pseudo-c-C}_7\text{H}_{14} [0.5\text{c-C}_8\text{H}_{16} + 0.5\text{c-C}_8\text{H}_{12}]\}$



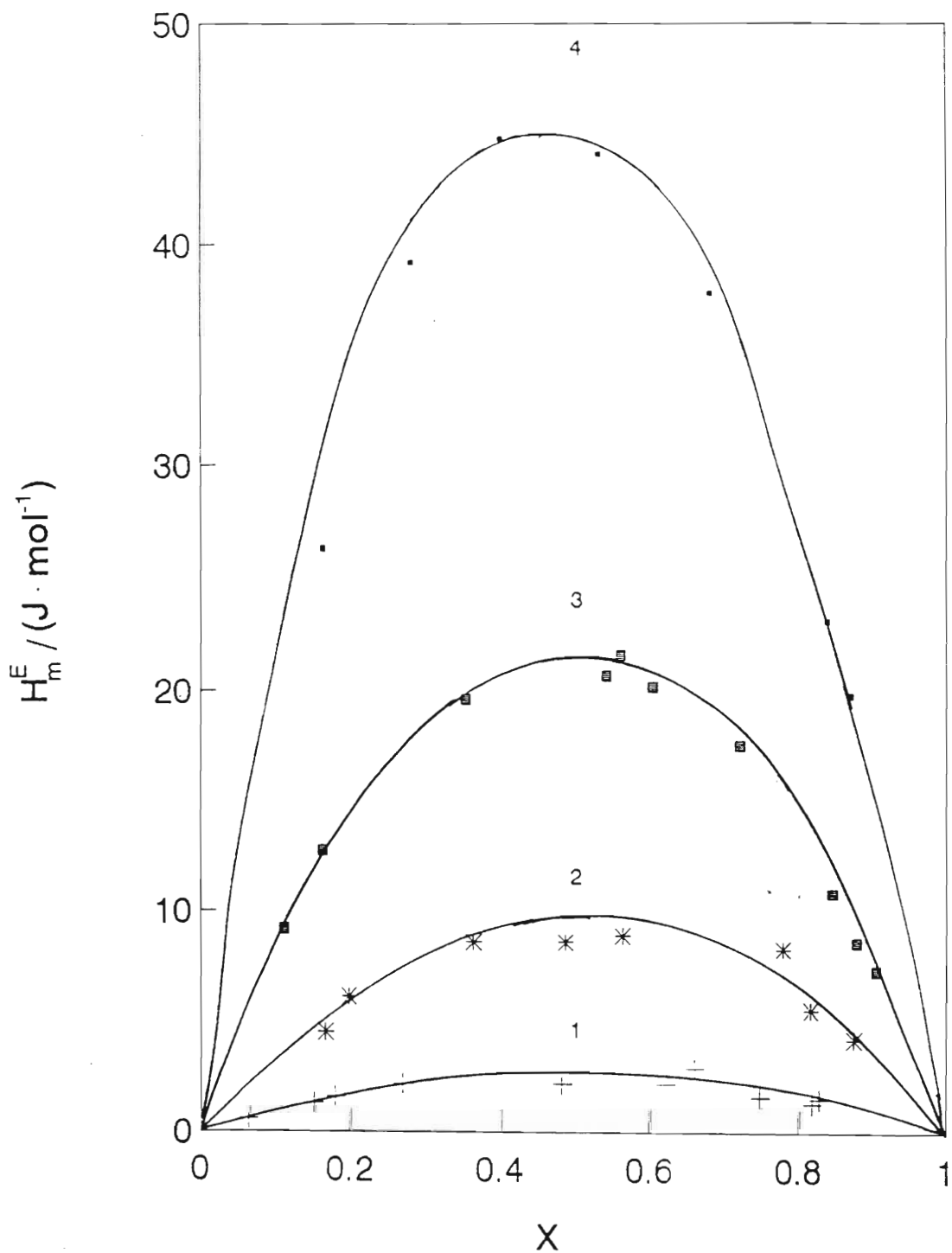


Figure 3.3. Excess molar enthalpies  $H_m^E$  for: (1)  $\{x \text{ } c\text{-}C_8H_{16} + (1-x) \text{ pseudo-}c\text{-}C_8H_{16} [0.5c\text{-}C_8H_{12} + 0.5c\text{-}C_{10}H_{20}]\}$ ; (2)  $\{x \text{ } c\text{-}C_7H_{14} + (1-x) \text{ pseudo-}c\text{-}C_7H_{14} [0.5c\text{-}C_8H_{16} + 0.5c\text{-}C_8H_{12}]\}$ ; (3)  $\{x \text{ } c\text{-}C_8H_{12} + (1-x) \text{ pseudo-}c\text{-}C_8H_{12} [0.5c\text{-}C_5H_{10} + 0.5c\text{-}C_7H_{14}]\}$  and (4)  $\{x \text{ } c\text{-}C_7H_{14} + [0.6c\text{-}C_5H_{10} + 0.4c\text{-}C_{10}H_{20}]\}$ .

### CONCLUSIONS

1.

**a) (1-alkenes + 1 or 2-propanol)**

For each alkanol, the  $H_{m,max}^E$  and  $V_{m,max}^E$  value increases (becomes more positive) slightly with increasing 1-alkene carbon number. This indicates that on increasing the carbon number of the 1-alkene, the dissociation effect of the 1-alkene becomes more contributory. In addition, the  $H_{m,max}^E$  and  $V_{m,max}^E$  results for the (1-alkenes + 2-propanol) are significantly larger than the 1-propanol results. This could be due to a weaker interaction of the double bond of the 1-alkene with the secondary alkanol as a result of the steric effects of the methyl groups in the secondary alkanol which tend to hide the OH group from the double bond system of the 1-alkene.

**(b) (1-alkynes + 1 or 2-propanol)**

For each alkanol, the  $H_m^E$  and  $V_m^E$  results reflects three dominant contributory interactions : (i) a positive effect due to the breakdown of the hydrogen bonds between the alkanol molecules on mixing, (ii) a positive effect due to the breakdown of the  $\pi\dots\pi$  interactions between the 1-alkyne molecules and (iii) a negative effect of the association between an alkanol and a 1-alkyne molecule.

For each 1-alkyne, the  $H_m^E$  and  $V_m^E$  for mixtures containing 2-propanol are greater than  $H_m^E$  and  $V_m^E$  for mixtures containing 1-propanol. This was attributed to the enhanced dissociation between the hydrogen-hydrogen bonds of the 2-propanol.

**c) Future Work**

Further work could be done on mixtures of (a ketone + an alkanol) or (an aldehyde + an alkanol) to determine the effect of the interaction of the double bond of the carbonyl group with the alkanol functional group.

## Conclusions and Future Work

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### 2. (di-n-butylamine + an ether)

The overall magnitude of the  $H_m^E$  and  $V_m^E$  results presented here are due to three effects: (i) the positive effect due to the breakdown of the di-n-butylamine self association, (ii) the positive effect due to the breakdown of the ether self association and (iii) the negative effect of the (di-n-butylamine + an ether) association.

Further work could be done on (n-butylamine + an ether) to compare it to this work and the recently reported (tri-n-butylamine or acetonitrile + an ether) results.

In addition, the results presented here have been sent to Dr. A. Heintz of the *Physikalisch-Chemisches Institut, Universitat Heidelberg*, for correlation with the recently reported DISQUAC theory.

### 3. Congruency

The cycloalkane mixtures reported in this work did not satisfy the null test of the congruence principle. Further null tests could be done on mixtures of (1-alkene + a pseudo-1-alkene) or (an alkanol + a pseudo-alkanol).

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## **PART 2**

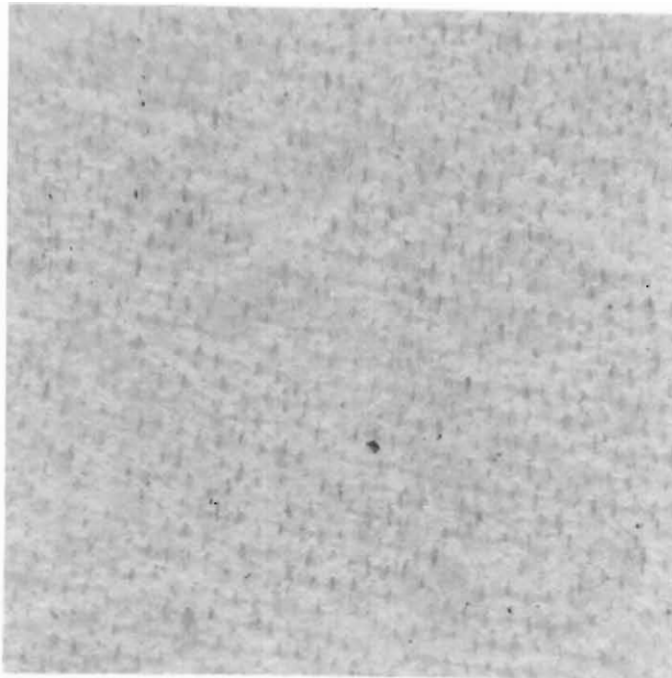
### **AN INVESTIGATION INTO THE LOW TEMPERATURE BLEACHING OF A COTTON NON-WOVEN FABRIC USING HYDROGEN PEROXIDE**

## CHAPTER 4

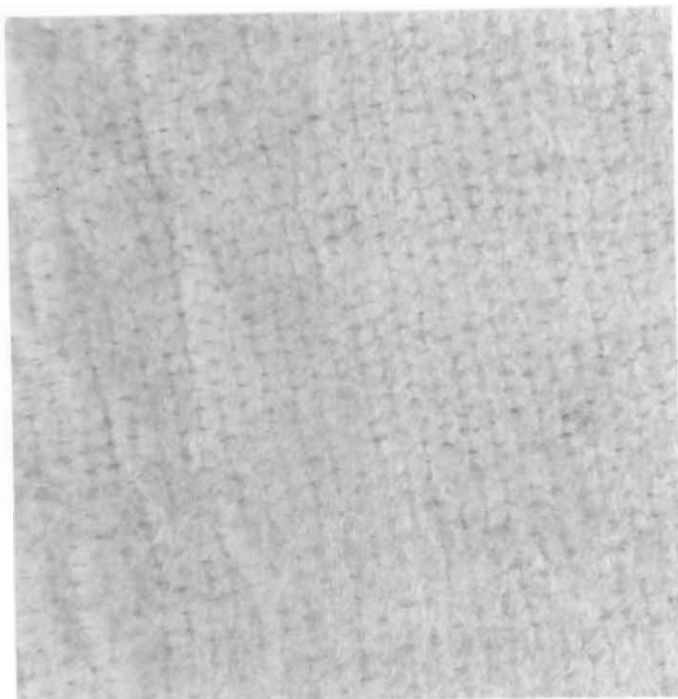
### Introduction and literature review

#### 4.1 Introduction

Non-woven cotton fabrics have been defined by EDANA<sup>(1)</sup> (European Disposables and Non-woven Association) as " a manufactured sheet web or batt of directionally or randomly orientated fibres, bonded by friction, and/or cohesion and/or adhesion, excluding paper and products which are woven, knitted, tufted, stitch - bonded incorporating binding yarns or filaments, or felted by milling whether additionally needled or not". The non-woven fabric used in this research is a cellulosic fabric made from using a series of high pressure water jets which impinge on the greige (raw) fibre webs from above.<sup>(2)</sup> This process entangles the web and produces a pattern in the fabric with the following construction : 47 holes/0.01 m in the warp and 63 holes/0.01 m in the weft. Greige cotton fibres are used and the resultant non-woven fabric is bleached and dried to produce a coherent patterned non-woven fabric (CPNF). Figures 4.1. and 4.2. show a typical unbleached and bleached CPNF, respectively. These fabrics can also be seen in Appendices 2.1. (a) and (b), respectively.



*Figure 4.1. Unbleached coherent patterned non-woven fabric*



*Figure 4.2. Bleached coherent patterned non-woven fabric*

Non-wovens differ from woven fabrics primarily in their manner of construction and the structural arrangement of the fibres. This difference manifests itself in a lower mechanical strength property for the non-woven fabric.<sup>(3)</sup> These differences can be seen in Table 4.1 where the tensile strength properties of the CPNF and a standard woven fabric (60s weft count and 60s warp count) are given.<sup>(5)</sup> In the application of any preparation process, designed for woven fabrics, to non-woven fabrics, it is important to take into account the inherent differences in the forces holding the fibres of the fabric together and the effect of the processing chemicals on these forces. In woven fabrics, the very nature of the spinning and weaving process, i.e the extensive intertangling and interweaving of cotton yarns, produces a fabric of exceptionally strong physical properties (cf. Table 4.1), which can withstand chemical treatment without integral fibre degradation and damage. In addition cross linking agents can be utilized in woven fabrics to hold the fibres together.<sup>(6)</sup> In the CPNF used in this work, the fibres are held together solely by the interfibre cohesion forces of the web.<sup>(4)</sup> The good frictional property of the greige cotton fibre are responsible for these forces.<sup>(4)</sup> The tensile property of this type of fabric is substantially lower than that of a woven fabric and the preparation process should not decrease this any further.

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**Table 4.1** Comparison of tensile strength values

Fabric	Tensile strength (kg/g)
CPNF (unbleached), dry	3.0
CPNF (conventionally bleached), dry	7.5
bleached woven, dry <sup>(5)</sup>	34.03

The only preparation process that the CPNF is presently subjected to is bleaching. Conventional bleaching methods for cellulosic woven fabrics have been utilized to brighten, remove husks and bleach the CPNF.<sup>(7)</sup> This conventional bleaching sequence involves a single stage high temperature, high pressure alkaline peroxide bleach in a kier. No work has been reported in the literature on the effect of a low temperature bleaching treatment on the surface or inherent fibre properties of cellulosic CPNF. The study of the effect of these treatments on the physical and inherent fibre properties of the CPNF forms the basis of this thesis. The fabric properties which are of interest in this study, are those that appear likely to undergo change during the combined scouring and bleaching step. The fibre characteristics chosen for this study were:

- a) a Scanning Electrom Microscope (SEM) evaluation of the cotton fibre surface of the bleached and unbleached CPNF,
- b) the degree of degradation of the cotton fibres of the CPNF as a result of the various bleaching steps i.e the fluidity values,
- c) the degree of whiteness of the bleached CPNF,
- d) the absorbency of the bleached fabric,

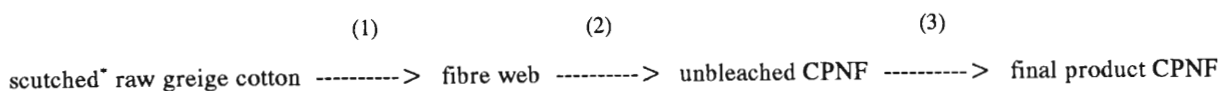
## Chapter 4: Introduction and literature.....

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These criteria are based on the anticipated end uses of the CPNF, such as in medicinal dressings, as well as on the criteria used by institutions involved in the development of methods for the evaluation of non-woven fabrics.<sup>(1,8)</sup>

### 4.2 The stages in the production of the coherent patterned non-woven fabric (CPNF)

There are three stages in the production for the CPNF used in this research.<sup>(4)</sup> These stages are shown in Figure 4.3.



*Figure 4.3 A flow diagram of the processes involved in the manufacture of the coherent patterned non-woven fabric<sup>(4)</sup>*

where (1) is the carding<sup>†</sup> stage

(2) is the entangling and patterning by water jets

(3) is the scouring and bleaching stage

At present the final stage in the CPNF process (bleaching and scouring) is carried out in a single step alkaline hydrogen peroxide batch process. It serves to clean and remove the greasiness of the unbleached CPNF.<sup>(4)</sup> In this treatment, the unbleached CPNF is placed in a kier, on a rolling spindle, containing an aqueous solution of hydrogen peroxide, sodium hydroxide, sodium carbonate and a commercially available wetting agent, at a temperature of 250 °C<sup>#</sup>.<sup>(4,7)</sup> One of the primary aims of this investigation was to establish a low temperature (25-45 °C) combined scouring and bleaching method to replace this high

\* mechanically opened, cleaned and formed into a continuous lap

† the disentanglement, cleaning and intermixing of fibres to produce a continuous web suitable for subsequent processing.

# This information was obtained from the confidential, restricted data supplied to the author by the company producing the CPNF



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temperature bleaching process for the CPNF and to optimise this method with respect to the CPNF property of whiteness and in addition to determine suitable conditions for the bleaching variables. The variables that were considered important in this work were hydrogen peroxide concentration, time and temperature.<sup>(9)</sup> The optimisation investigation with respect to whiteness is done in chapter 8.

### 4.3 Preparation processes for cellulosic fibres

Butcher <sup>(10)</sup> in his review has defined preparation as the cleansing, whitening and stabilising process for cotton. All preparation processes should produce a fabric that is evenly treated with excellent absorbency, free of husks, seeds or impurities, whiteness appropriate to the end use specifications and minimal fibre degradation.<sup>(11)</sup>

The traditional sequence for preparation and finishing of cotton wovens is shown in Figure. 4.4.

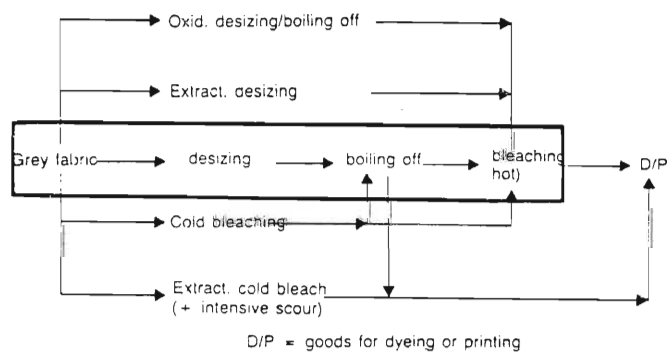


Figure 4.4. Preparation processes for woven fabrics<sup>27</sup>

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The requirements for preparing and finishing non-woven fabrics are very similar to woven fabrics, however woven fabrics have a particular requirement, desizing,<sup>(11)</sup> which is excluded in the preparation process for non-woven fabric.

### *a) Desizing*

Yarns for woven fabrics are sized to enable the yarn to withstand mechanical actions of the machinery when weaving.<sup>(11,12)</sup> Most sizes are applied as a solution in water and dried onto the yarn to provide a protective film.<sup>(11,13)</sup> This film-forming material provides fibre cohesion by combining with fats and waxes found on the surface of the cotton. The desizing operation, as part of the preparation sequence is designed to remove size film.<sup>(13)</sup> Desizing processes use either water or organic solvents. Hot caustic soda treatments have been known to be used in size removal.<sup>(13)</sup> Here again this process is not necessary for the CPNF as the fibre is not chemically treated in any way prior to bleaching.

### *c) Mercerising and scouring*

Mercerization is based on the treatment of cotton fabrics with a strong sodium hydroxide solution to improve strength and bleaching substantivity with improved lustre.<sup>(11,14,15)</sup> Typically the caustic soda is a 25-26 % wt/wt solution.<sup>(14)</sup> At this concentration considerable swelling of the cellulosic fibre is obtained, accompanied by shrinkage if the fabric is not held under tension.<sup>(14)</sup>

The benefits sought in this process are improved lustre, tensile strength, coverage of dead cotton and dimensional stability.<sup>(16)</sup> All these properties are influenced by alkali concentration, temperature and dwell time in alkali prior to washing-off.<sup>(16)</sup>

The effects tend to be confined to the surface since full penetration into the fabrics by concentrated caustic soda at low temperature is not obtained, even with the aid of wetting agents.<sup>(11)</sup> Hot mercerising has been used where saturation of the fabric with concentrated caustic soda solution near its boiling point is performed.<sup>(17,18)</sup> The advantages indicated for this process are:<sup>(17,18)</sup>

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- a) increased efficiency and uniformity,
- b) improved lustre, tensile strength and dimensional stability since greater fabric stability is possible,
- c) good desizing,
- d) better fabric penetration by a hot caustic liquor than with normal mercerisation,

Scouring is applied to the fabric to remove oils, fats, waxes, soluble impurities and particulate dirt which adheres to the cotton fibres.<sup>(11)</sup> Natural and other fats and waxes may be removed prior to dyeing or bleaching by the use of organic solvents, but most preparation routes use alkali scouring.<sup>(11)</sup> This may be a single process or be combined with the desizing or/and bleaching.<sup>(11,19)</sup> Apart from the fats and waxes, other non-cellulosic constituents can be removed, particularly nitrogenous matter and pectate. Most importantly cotton seed can be softened or burst for subsequent removal. Modern scouring practice consists of treatment with a detergent, with or without the addition of an alkali.<sup>(19,20)</sup>

Scouring can be carried out in a kier.<sup>(20,21)</sup> Conventionally the fabric is loaded into the kier and hot alkaline liquor is circulated for several hours.<sup>(20)</sup> The process may be carried out at 100 °C, but pressure boiling is also practised with temperatures of 120 °C being reached.<sup>(11)</sup>

\* Methods of treatment are described in the literature.<sup>(22)</sup>

Currently sodium hydroxide is the most generally used reagent. In kier boiling care must be taken to ensure that air is not entrapped in the fabric since its presence can lead to the formation of oxycellulose.<sup>(11)</sup> Provided that there is control of alkali and temperature, good scouring removal and some fabric whitening can be obtained during this process with little fibre damage.<sup>(11,19,23)</sup>

In the non-woven fabric under investigation in this work, the mercerization process is not considered necessary as the fabric is been subjected to alkali in the combined scouring and bleaching stage. The CPNF is subjected to a short single stage combined scouring and bleaching stage.

### *d) Bleaching*

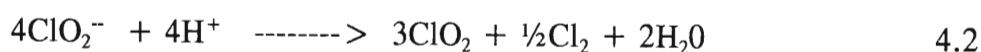
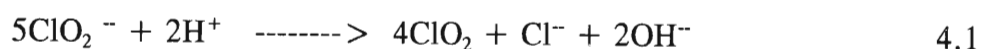
The three chemicals that can be used for bleaching are sodium hypochlorite, sodium chlorite and hydrogen peroxide.

#### *i) Hypochlorite*

Prior to bleaching with hypochlorite it is essential that the cellulose be cleared of natural impurities by a thorough scouring.<sup>(11)</sup> This alone implies complexity in the process with one or two alkaline boils being required with intermediate washing. These will be followed by scouring and further washing prior to bleaching.<sup>(11,24)</sup> Bleaching must be followed by washing and an antichlor treatment, the latter being performed to remove the products of the bleaching reaction. The end result is, therefore, a process with high labour content, lengthy processing time and high water demand.<sup>(11,25)</sup> In the last decade hypochlorite bleaching has been replaced very widely by formulations and processes based on hydrogen peroxide, sodium chlorite or combinations of the two.<sup>(26,27)</sup>

#### *ii) Sodium chlorite*

Sodium chlorite bleaching, in contrast to hypochlorite or hydrogen peroxide bleaching, is carried out under acidic conditions.<sup>(11,25)</sup> Under the acid bleaching conditions, a relatively small amount of natural fats and waxes is removed.<sup>(11,22)</sup> Chlorite bleaching is also relatively unaffected by low levels of iron and copper contamination,<sup>(10)</sup> however, there are several disadvantages in chlorite bleaching.<sup>(11,25)</sup> It is difficult to control chlorine dioxide release and the products of the bleaching reaction (scheme 4.1) are known to be environmentally unfriendly.



*Scheme 4.1*

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Also in contrast to hydrogen peroxide bleaching the temperature, pH etc. cannot be selected to provide very rapid bleaching.<sup>(11)</sup>

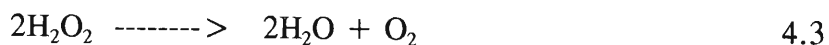
### *iii) Hydrogen peroxide*

Hydrogen peroxide bleaching for cellulosic textiles is carried out under alkaline conditions. Consequently scouring and bleaching can frequently be combined.<sup>(11,27,28)</sup> Hydrogen peroxide is adaptable to a wide range of bleaching conditions: a temperature range from ambient to 250 °C and a time range from a few minutes to several hours.<sup>(11,27)</sup> Cotton oxidised by hydrogen peroxide is characterised by a high content of ketone groups but a very low aldehyde and carboxyl content. The ketones formed are inactive carbonyls i.e. they cause no yellowing on ageing.<sup>(11)</sup> This research is based on the utilization of hydrogen peroxide as the bleaching agent.

## 4.4 Hydrogen Peroxide Bleaching

A prime advantage of hydrogen peroxide bleaching is the wide range of conditions over which it can be used for bleaching cellulosic textiles.<sup>(11,27)</sup> However, with all bleaching processes correct process control is essential.<sup>(11)</sup>

Although considerable progress has been made in the optimisation of bleaching conditions, the bleaching mechanism is not yet fully understood.<sup>(11,24,29)</sup> The reason for this is the heterogeneous nature of the process and the lack of absolute knowledge about the coloured material that is destroyed.<sup>(11)</sup> It is well known that hydrogen peroxide can breakdown into water and oxygen (Scheme 4.2).<sup>(24)</sup>



*Scheme 4.2*

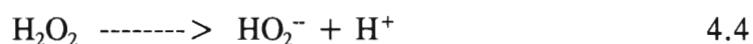
However, it is most unlikely that bleaching can be attributed to such a simple mechanism.

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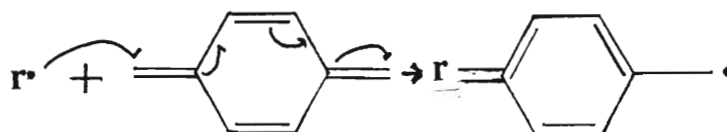
This direct decomposition equation is undesirable for bleaching because the liberated oxygen has little bleaching effect but rather a fibre damaging effect.

On the basis that the rate of bleaching with hydrogen peroxide increases with a rise in pH, it was proposed that the bleaching action is due to the perhydroxyl anion formed by ionisation (Scheme 4.3)<sup>(11,27)</sup>



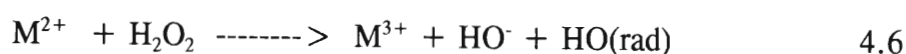
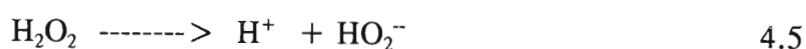
*Scheme 4.3*

It is probable that the pigments responsible for the natural colour of the cotton contain a chromophoric system of conjugated double bonds. These will be attacked by a free radical system and it has been proposed by Cates and Taher<sup>(30,31)</sup> that peroxide bleaching takes place by such a mechanism (Scheme 4.4).



*Scheme 4.4*

Such free radicals might be produced by reaction of hydrogen peroxide with an electron donor, possibly derived from a metal cation or perhydroxyl anion.<sup>(30)</sup> The reaction mechanism proposed is shown in Scheme 4.5<sup>(30,31)</sup>



*Scheme 4.5*

where  $\text{M}^{2+}$  is the metal cation. The free radicals are considered to induce decomposition

through a chain mechanism. The decomposition within a given time interval is limited by the level of colour bearing impurities or by inhibiting metal cations.<sup>(30)</sup> The latter appears to protect the cellulose from chemical damage by minimising the production of molecular oxygen in the alkaline medium.<sup>(31)</sup>

While absolute mechanisms are not yet fully understood, control systems for the decomposition reaction have been developed.<sup>(10,11)</sup> This control is termed stabilisation.<sup>(11,24)</sup> Correct process stabilisation conditions control the rate of bleaching and ensure a residual peroxide content prior to washing off. In this way the required standards of whiteness with minimum chemical damage are obtained. In effect, for peroxide bleaching four parameters are to be balanced for efficient and successful bleaching: time, temperature, alkalinity and hydrogen peroxide concentration.<sup>(10,11,19)</sup>

In this work time, temperature and hydrogen peroxide concentration are optimised with respect to a low temperature bleaching process for the CPNF.

### 4.4.1 The role of chemicals in hydrogen peroxide bleaching

In modern preparation technology, the bleaching process is not only concerned with the brightening of the fibre by the destruction of the natural colouring matter but it must frequently make a significant contribution towards preparation for subsequent dyeing, printing or chemical finishing.<sup>(27)</sup> The bleaching process may be the only preparation process or more often it is used in conjunction with other treatments i.e scouring or desizing.<sup>(27)</sup> In this study a low temperature single stage combined scouring and bleaching process was investigated and optimised with respect to the CPNF property of whiteness.

Besides the bleaching agent itself, other chemicals are used which have various functions. These chemicals serve to activate the bleaching agent,<sup>(11)</sup> stabilise or control the degree of bleaching agent activation,<sup>(9)</sup> to give good wetting, surfactant and detergent action in order to assist in the removal of impurities and to sequester metallic impurities found in the fibre.<sup>(11,25)</sup> Extensive research<sup>(9,11,25,27,32)</sup> has been conducted on the considerations that have to be given as to the role of each individual chemical used in conjunction with the peroxide

bleaching agent.

### *a) Alkaline activators*

When peroxide bleaching cotton, the alkali added activates the peroxide bleaching and provides a scouring action.<sup>(11)</sup> Bleaching processes are most effective when carried out within the pH range 10.5 to 11. Above this level peroxide bleach liquors are overactivated, giving excessive wasteful breakdown to oxygen and water.<sup>(11,24)</sup> If the pH is lower than 10 the bleaching activity is very low.<sup>(11)</sup> Alkalinity is normally provided by sodium hydroxide, sodium carbonate or phosphate. Sodium silicate, when used as a stabiliser, adds to the total alkalinity.<sup>(10)</sup>

Sodium hydroxide however, if used alone induces too rapid a decomposition of hydrogen peroxide (equation 4.3) so that significant amounts of peroxide are lost for bleaching.<sup>(11)</sup> As a result stabilisers have to be introduced into the bleaching liquor.

Amides have recently shown<sup>(33)</sup> to facilitate faster but controlled bleaching action in alkaline (sodium hydroxide) bleach baths. When the bleach liquor is peroxide based the amides have shown to inhibit the decomposition reaction of  $H_2O_2$  and accelerate the formation of the perhydroxyl ion (equation 4.4). The amides responsible for this increase in the bleaching activity of peroxide bleach bath include urea, benzamide, formamide and N,N dimethyl formamide (DMF).<sup>(33)</sup>

### *b) Stabilisers*

The activity of the peroxide bleaching liquor brought about by addition of alkali is controlled by the action of stabiliser additives. Stabilisation is described as a process of regulation and control. The function of these chemicals is to inactivate impurities particularly metallic impurities, which tend to cause catalytic decomposition of the hydrogen peroxide.<sup>(10,11)</sup> These impurities can be introduced into the bleaching system from the fabric, water or the chemicals used.<sup>(11)</sup>

The stabilisers first used in bleaching cellulosic fibres were the colloidal sodium silicates.<sup>(32)</sup> These are highly effective and have an additional advantage of being comparatively low in cost. Metasilicate ( $Na_2SiO_3$ ) and orthosilicates have also been used and these have been found to wash out more readily than colloidal silicates.<sup>(11,34)</sup>



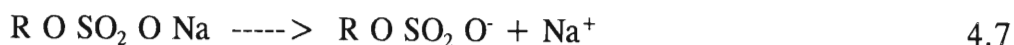
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The use of sodium silicate requires the provision of good washing off facilities after bleaching in order to prevent problems caused by residual silicates.<sup>(32)</sup> Consequently, although sodium silicate is both effective and economic and is the most widely utilised stabiliser both in high and low temperature cellulosic bleaching methods, there have been reviews on the use of alternative chemicals for peroxide stabilisation.<sup>(32,35)</sup> The commercial products available are basically organic sequestering agents which are designed to impart a combined stabilisation, detergency and softening effect.<sup>(35,36,37)</sup> The organic stabilisers include polyphosphates, ethylenediamine tetracetic acid (EDTA) and tetrasodium pyrophosphate.<sup>(36)</sup> Sodium silicate has been used in most of the low temperature peroxide bleaching treatments previously reported for cellulosic fibres<sup>(10)</sup> and as such this stabiliser was used in all the bleaching treatments investigated for the CPNF.

### c) *Wetting agents*

Good wetting of material is required to ensure penetration of preparation chemicals and evenness of treatment.<sup>(11)</sup> Commercial wetting agents are usually anionic or non-ionic surfactants or blends of the two.<sup>(12)</sup> In solution the compounds anionic ionise, with the surface active component carrying the negative charge (Scheme 4.6, in which R is the long chain hydrocarbon)



*Scheme 4.6*

Most commercial products used in the textile preparation processes are ethoxylated fatty alcohols with the general formula shown below<sup>(12)</sup>



An important factor affecting the use of wetting agents for the low temperature used batch bleaching in kiers is the degree to which the bleaching liquor foam.<sup>(12)</sup> Excessive foam in kiers can cause cavitation in pumps with resultant poor circulation.<sup>(11)</sup>

A commercially available wetting agent termed "Foryl B" was used in all the investigations

in this work.

### 4.5 Cold pad batch bleaching

The process of padding the grey fabric with a strong solution of alkali and hydrogen peroxide, and storing for several hours, usually overnight, at ambient temperature is called cold pad batch bleaching. In the last decade, an interest in cold bleaching has increased as it provides a low energy preparation route.<sup>(39,40)</sup> Fabric can be impregnated with the bleach solution in a kier or on open width washers and left batched up overnight. Cold pad batch bleaching requires:<sup>(11)</sup>

1. Control of pad liquor concentration and temperature, preferably 25°C
2. Fabric storage without surface drying
3. Washing-off at a minimum of 95 °C.

A good wetting agent is essential to ensure good penetration of the grey fabric by the bleaching liquor, with a detergent auxiliary to aid wax removal and development of good absorbency.<sup>(11)</sup>

Numerous recipes <sup>(33,35,39,40,41,42)</sup> have been described over the years for the single stage low temperature peroxide scouring and bleaching of cellulosic woven fabrics. Most of these differ greatly with respect to the treatment time, the range of low temperatures investigated and additional additives used. Some of the recipes that have been described are outlined here, with special emphasis on those that have been adapted to the CPNF.

Although the first ever bleaching of cotton with hydrogen peroxide was carried out at a low temperature as 1928 by Smolens<sup>(38)</sup>, it was not until approximately 15 years ago that it regained its popularity over the any of the high temperature shock bleach treatments (sodium chlorite and hypochlorite bleaching etc) because of its energy saving and cost effective advantages. In particular the single stage combined scouring and bleaching process at

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ambient temperature has recently superseded the single stage high temperature treatment.<sup>(63)</sup> Dalmas<sup>(35)</sup> in the early eighties patented a bleaching process for cellulosic fibres done at 60 °C. The invention was a process of bleaching cellulose materials with potassium based bleach liquors or the products of the reaction between sodium silicate and potassium hydroxide (equation 4.8).



*Scheme 4.7.*

The bleaching liquor employs potassium orthosilicate as the peroxide stabiliser and the sodium hydroxide as the alkaline medium. Greige cotton fabrics are immersed in a liquor in a kier at 60 °C, allowed to seep for an hour and then rinsed at 60 °C. The bleach liquor employs a formula of the following composition: potassium orthosilicate, a wetting agent, 50 % hydrogen peroxide and water. These workers have reported that the fabric produced was soft, absorbent, free of any seeds and husks and of a uniform white.<sup>(35)</sup>

Wani<sup>(39)</sup> investigated various bleaching methods including a cold bleaching process as used by the Ahmedabad Textile Industry Research Association in India (ATIRA) and concluded that in comparing the cold pad batch process to the conventional high temperature process a considerable saving in energy, steam and cost is afforded. The cold batch process used by ATIRA (a) and one of the high temperature treatments (b) is shown in scheme 4.8.

Desize ---> Scour\* ---> Wash (hot or cold) ---> Scour ---> Dry (a)

Desize ---> Wash ---> Open kier boiling† ---> 2 hot washes ---> 2 cold washes (b)

*Scheme 4.8.*

\* = 60 °C circulation for 12 h with (50 %) H<sub>2</sub>O<sub>2</sub> 0.22 %, sodium hydroxide 0.9 %, ATIRA catalyst 0.3 %, non-ionic wetting agent 0.22 %, and

† = 50 % H<sub>2</sub>O<sub>2</sub> 1 %, sodium hydroxide 0.3 %, sodium carbonate 0.5 %, SCOUREX 0.3 %, for 4 h at 90 °C.

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Wani reported that the fabrics produced from the cold pad batch process contain minimum damage with an acceptable degree of whiteness and absorbency.<sup>(39)</sup>

Hickman and Andrianjafy<sup>(9)</sup> evaluated the role of different stabilisers for the hydrogen peroxide bleaching treatments of cotton woven fabrics. Three organic stabilisers in addition to sodium silicate were investigated under short and long bleaching times on 100 % desized but unscoured cotton fabric at a temperature of 95 °C and the results were compared to those obtained when sodium silicate was used alone as the peroxide stabiliser. This temperature was a little high to be termed low temperature, however the results produced are of importance and can be applied to low temperature bleaching. The bleaching liquor contained sodium silicate, magnesium sulphate, a wetting agent, caustic soda and hydrogen peroxide. The bleached samples were analyzed for their whiteness and fluidity properties. Sodium silicate was shown to be the most effective stabiliser and that the order in which the organic stabilisers can be ranked depends on the bleaching system itself.<sup>(9)</sup>

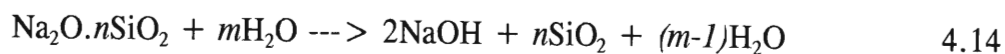
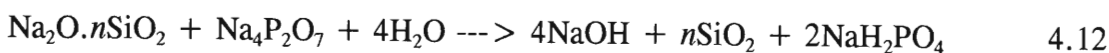
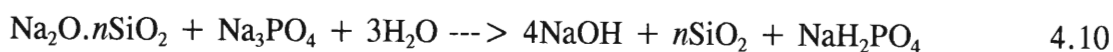
Das and coworkers<sup>(40)</sup> carried out extensive laboratory studies of the combined scouring and bleaching cold temperature bleaching processes. In their cold bleaching process, desized and chemicked\* fabrics were bleached at room temperature for time periods ranging from 2 to 24 h. Two bleaching recipes have been described: one containing sodium hydroxide, sodium metasilicate, hydrogen peroxide and a non-ionic wetting agent and the other containing sodium-metasilicate, tetra sodium pyrophosphate, hydrogen peroxide and the non ionic wetting agent in the bleaching bath. The wetting agent has been described as a 1:1 mixture of perchloro-ethylene and the product obtained from the condensation of one mole of nonyl phenol with 6 - 8 moles of ethylene oxide. These workers reported that for all the treatments investigated, the fabrics exhibited uniformity in treatment and comparatively lower damage when compared the traditional high temperature process.<sup>(40)</sup> The whiteness, absorbency and fluidity results are all satisfactory for the fabrics bleached by the low temperature method.<sup>(40)</sup>

\* immersion of the fabric in 2 - 3 g·l<sup>-1</sup> of sodium hypochlorite solution for 1 - 2 h.

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Sukumar and Gulrajani<sup>(41)</sup> assessed a low temperature single stage preparatory process for cotton wovens wherein five compounds, viz. trisodium phosphate, tetrasodium pyrophosphate, sodium hexametaphosphate, magnesium sulphate and a sodium salt of ethylenediamine tetracetic acid (EDTA), were investigated for the activation and stabilization of the peroxide in the bleach bath. The untreated fabrics were bleached with a solution containing 4 % scouring agent, 1 % hydrogen peroxide (100 %), 2 % sodium silicate and 2 % activator at room temperature for different time periods (12 - 24 hours). The fabrics were evaluated for their tensile strength, whiteness, wettability and ash content. These workers concluded that of the five compounds investigated, only two are suitable for the low temperature single stage process, viz. tri-sodium phosphate and tetrasodium pyrophosphate.<sup>(41)</sup> A mechanism for the activation process for all the activators investigated was reported and these are shown in equations 4.9 to 4.14.<sup>(41)</sup> In addition a stabilization mechanism of the peroxide by sodium silicate was also proposed whereby the silica gel ( $n\text{SiO}_2$ ) is responsible for physically trapping the perhydroxyl ions and thus controlling hydrogen peroxide decomposition.



*Scheme 4.9.*

## Chapter 4: Introduction and literature.....

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Dickenson and Hickman<sup>(42)</sup> investigated the cold pad bleaching with experiments based on a central rotatable plan with the following range of conditions: temperature - 20 to 60 °C, time - 7 to 75 hours, sodium persulphate - 0 to 10 g·l<sup>-1</sup>, caustic soda - 1 to 40 g·l<sup>-1</sup>, hydrogen peroxide (35 %) - 60 ml·l<sup>-1</sup>, sodium silicate - 40 g·l<sup>-1</sup> and a commercially available wetting agent. A recipe based on mixed organic and silicate stabiliser system was also described for cotton and cotton/polyester blends. These cold processes were compared to the pad steam processes. Analysis of results showed that the chemical damage increases as the alkalinity and/or temperature increases and that the use of persulphates can cause an increase in chemical damage but their influence is substantially less than that of alkali concentration or temperature.<sup>(42)</sup> For all the bleached fabrics, a satisfactory final whiteness was obtained over a wide range of conditions. On comparison with the multistage steam process (conventional bleaching), it was reported that cold pad bleaching was favourable from both an energy and cost point of view.<sup>(42)</sup>

Das *et al*<sup>(33)</sup> reported an amide activated bleaching process whereby the amides are incorporated into the bleaching bath to facilitate faster decomposition of the hydrogen peroxide. Desized and scoured cotton fabrics were padded through a bleaching bath containing one of the various amides (urea, benzamide, formamide, N,N-dimethyl formamide [DMF]), sodium hydroxide 10 g·l<sup>-1</sup>, sodium silicate 15 g·l<sup>-1</sup>, hydrogen peroxide 20 g·l<sup>-1</sup> and a wetting agent. The bleaching experiments were carried out at ambient temperature, 60 °C and 90 °C for 8 h. The bleached fabrics were evaluated on the basis of their final whiteness. At ambient temperature, the rate of peroxide decomposition decreases in the following sequence:<sup>(33)</sup>

formamide > DMF > benzamide > urea

Benzamide affords the maximum whiteness with the whiteness value increasing with time and temperature of bleaching. The benzamide bleaching process is quite useful in cold bleaching

## Chapter 4: Introduction and literature.....

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where the time of bleaching can be reduced without impairing the whiteness of the fabric.<sup>(33)</sup>

Sarma *et al*<sup>(43)</sup> recently investigated a combined scouring and bleaching process for chemicked cotton fabrics. The bleaching bath contained the following activators and/or stabilisers for peroxide: sodium hydroxide, sodium silicate, potassium persulphate, magnesium sulphate, a wetting agent. Fabrics were bleached at 25, 35 and 45 °C and analyzed with respect to the physical properties of whiteness, fluidity and absorbency. An optimum treatment for bleaching was established which produces a fabric of acceptable values of whiteness, absorbency and fluidity.<sup>(43)</sup>

Muresan *et al*<sup>(44)</sup> reported an alkaline cleaning treatment and conditions for cotton materials. Experiments were carried out at 25 °C on a 100 % cotton textile material in the raw state in a bleaching bath containing the following chemicals: hydrogen peroxide, sodium persulphate, sodium silicate and sodium hydroxide. The fabrics were assessed for their breaking strength, whiteness and hydrophilicity. A multiple regression analysis was used with four influencing parameters (sodium hydroxide concentration, hydrogen peroxide concentration, sodium persulphate concentration and time) to optimise the chemical concentrations and the treatment conditions. The following optimum conditions were obtained: 20 to 40 g·l<sup>-1</sup> sodium hydroxide, 60 g·l<sup>-1</sup> hydrogen peroxide, 12 g·l<sup>-1</sup> sodium persulphate and a treatment time of 5 h.<sup>(44)</sup> Under these conditions, the whiteness and hydrophilicity reach maximum values while the breaking strength is low.<sup>(44)</sup>

Five bleaching treatments based on the methods of Sarma *et al*,<sup>(43)</sup>(the most recent literature procedure obtainable) Muresan *et al*,<sup>(44)</sup> Dickenson *et al* <sup>(42)</sup> and Das *et al* <sup>(33)</sup> have been used in this work for the low temperature bleaching of the CPNF. The adaptation of these methods is discussed in chapter 5.

## Chapter 5

### Bleaching treatments used in this work

#### 5.1 Introduction

Numerous recipes have been described over the years for the low temperature bleaching of cotton woven fabrics.<sup>(33,39,40,41,42,43,44)</sup> Although most of these recipes differ greatly with respect to the treatment conditions and the additives used, all served to improve the process with respect to optimising the bleaching effect while minimising the extent of fibre damage of the woven cellulosic fabrics.

The treatment conditions employed throughout this investigation were based on those most recently optimised for the low temperature single stage bleaching process for cotton woven fabrics. Five combined scouring and bleaching procedures<sup>(33,42,43,44)</sup> were selected for this study with the aim of developing a low temperature bleaching process which maximised the property of whiteness and absorbency. In addition the extent of fibre damage for the CPNF should be kept minimal. In view of the differences between physical properties of the woven and non-woven fabrics, (cf Table 4.1) it was considered important to establish whether the chosen bleaching chemicals and their corresponding treatment conditions resulted in any CPNF fibre degradation. These effects are discussed in chapters 6 and 7.

This chapter describes the bleaching treatments utilized in this work together with the materials, laboratory apparatus and chemicals used throughout this study.

#### 5.2 Bleaching treatments investigated in this work

All of the bleaching treatments investigated in this work represent the most recent advances in low temperature peroxide bleaching research done over the past 10 years for woven fabrics. As a starting point, the low temperature amide activated bleaching process designed by Das and coworkers was investigated.<sup>(33)</sup> In their work amides are incorporated into the bleaching bath recipe to facilitate faster but controlled decomposition of hydrogen peroxide. Their formulations are based on the utilization of four amides i.e urea, benzamide, formamide and dimethyl-formamide. Scoured and desized cotton woven fabrics are



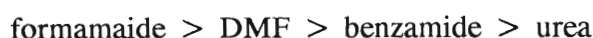
## Chapter 5: Bleaching treatments.....

immersed into a bleaching bath containing the bleaching chemicals listed in Table 5.1 and bleaching was carried out at 25, 60 and 90 °C for the time period ranging from 3.5 to 7 h.

**Table 5.1 Bleaching conditions at room temperature for 3.5 to 8 h of Das *et al*<sup>(33)</sup>.**

Chemical (g·l <sup>-1</sup> )	Experiment				
	1	2	3	4	5
NaOH	10	10	10	10	10
Na <sub>2</sub> Si <sub>2</sub> O <sub>3</sub>	15	15	15	15	15
H <sub>2</sub> O <sub>2</sub> (50 %)	20	20	20	20	20
Emul.Agent	5	5	5	5	5
Urea	-	30	-	-	-
Benzamide	-	-	30	-	-
Formamide	-	-	-	30	-
DMF	-	-	-	-	30

At 25 °C it was reported that the sequence in the rate of hydrogen peroxide decomposition is as follows :



Benzamide affords the maximum whiteness and in all cases there is practically no loss of strength of the bleached fabric. Similar trends are observed at the higher temperatures.<sup>(33)</sup>

Sarma *et al*<sup>(43, 63)</sup> reported two papers for the bleaching of woven fabrics at a low temperature using a persulphate salt as the hydrogen peroxide activator. These workers utilized a statistical plan similar to the one being used in this investigation. In both their papers they

## Chapter 5: Bleaching treatments.....

concluded that the optimum combined scouring and bleaching process for a desized cotton woven fabric was one carried out at 35 °C for a time period of 7 hs.<sup>(43)</sup> The optimum bleaching concentrations for the chemicals used in their research is listed in Table 5.2.

This treatment produced a fabric with excellent fabric properties of whiteness, absorbency, with their fluidity values showing minimum fibre damage.<sup>(43)</sup>

**Table 5.2 Bleaching conditions at 35°C for 7 hs of Sarma *et al*<sup>(43)</sup>.**

Chemical	% o.w.f.*
Sodium Hydroxide	2.5
Sodium Silicate	1.5
K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	0.4
MgSO <sub>4</sub>	0.32
Scouring Agent	0.9
Hydrogen Peroxide(50%)	1.3

\* refers to the percentage weight of fabric and related to g·l<sup>-1</sup> by the equation:

$$\text{conc. (g·l}^{-1}\text{)} = (\% \text{ o.w.f.} \times 10) / \text{liquor ratio (goods to liquor ratio} = 1:5)$$

More recently, Muresan *et al*<sup>(44)</sup> formulated a recipe for bleaching untreated cotton woven fabrics that involved sodium persulphate as the peroxide activator at room temperature for a time of 5 h. According to this method the extent of fibre damage incurred during the single stage scouring and bleaching process is equal to that obtained by the classical procedure i.e alkaline boiling, whitening with hypochlorite ( 1<sup>st</sup> stage ) and then with hydrogen peroxide ( 2<sup>nd</sup> stage).<sup>(44)</sup> The concentrations of the bleaching chemicals used by Muresan *et al* are listed in Table 5.3.

## Chapter 5: Bleaching treatments.....

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**Table 5.3** Bleaching conditions at room temperature for 5 hs of Muresan *et al*<sup>(44)</sup>.

Chemical	Conc. (g·l <sup>-1</sup> )
Sodium Hydroxide	20-40
Sodium Persulphate	12
Sodium Silicate	18
Hydrogen Peroxide(50%)	60

The treatment conditions recommended by Das and co-workers,<sup>(33)</sup> Sarma *et al*<sup>(43)</sup> and Muresan *et al*<sup>(44)</sup> were used for all the bleaching treatments investigated in his work. In addition the conventional bleaching process was carried out at ambient temperature to compare it with the other bleaching treatments. All these treatments are detailed in Table 5.4.

## Chapter 5: Bleaching treatments.....

**Table 5.4** Treatment conditions (T) for the various bleaching recipes investigated

Chemical	T <sub>0</sub> <sup>a</sup>	T <sub>1</sub> <sup>b</sup>	T <sub>2</sub> <sup>b</sup> conc.	T <sub>3</sub> <sup>b</sup> (g·l <sup>-1</sup> )	T <sub>4</sub> <sup>c</sup>	T <sub>5</sub> <sup>d</sup>
NaOH	23	30	30	30	30	30
Na <sub>2</sub> CO <sub>3</sub>	20	-	-	-	-	-
Na <sub>2</sub> Si <sub>2</sub> O <sub>3</sub>	-	18	18	18	18	18
H <sub>2</sub> O <sub>2</sub> (50 %)	75	65	65	65	65	65
Wetting Agent	10	10	10	10	10	10
NH <sub>2</sub> CONH <sub>2</sub>	-	15	-	-	-	-
C <sub>6</sub> H <sub>5</sub> CONH <sub>2</sub>	-	-	15	-	-	-
HCONH <sub>2</sub>	-	-	-	15	-	-
MgSO <sub>4</sub>	-	-	-	-	0.5	-
K <sub>2</sub> S <sub>2</sub> O <sub>4</sub>	-	-	-	-	0.5	-
Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	-	-	-	-	-	12

T<sub>0</sub>, T<sub>1</sub> etc. refers to treatment condition 0 and 1 etc., respectively

<sup>a</sup> conventional bleaching process done at 25 °C (normally done at 250 °C)

<sup>b</sup> based on reference 33

<sup>c</sup> based on reference 43

<sup>d</sup> based on reference 44

## Chapter 5: Bleaching treatments.....

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### 5.3 Apparatus and Experimental procedure

#### 5.3.1 Materials

The CPNF fabric samples used in this investigation has been described in chapter 4 and shown in appendix 2.1 and were obtained directly from the mill. These samples were not pretreated in any way prior to bleaching.

Reagent grade chemicals and deionised water was used in all the investigations. The bleaching chemicals used for each of the investigations together with their suppliers are listed in Table 5.5

**Table 5.5** List of chemicals and their suppliers

Chemical	Supplier
NaOH	Aldrich
Na <sub>2</sub> CO <sub>3</sub>	Saarchem
Na <sub>2</sub> Si <sub>2</sub> O <sub>3</sub>	Aldrich
H <sub>2</sub> O <sub>2</sub> (50 %)	Alliance Peroxide
Wetting Agent	"Foryl D"* Merck
NH <sub>2</sub> CONH <sub>2</sub>	Kleber Chemicals
C <sub>6</sub> H <sub>5</sub> CONH <sub>2</sub>	BDH
HCONH <sub>2</sub>	BDH
MgSO <sub>4</sub>	Saarchem
K <sub>2</sub> S <sub>2</sub> O <sub>4</sub>	Merck
Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	Aldrich

\* Foryl D is the patented name for a commercially available wetting agent.

### 5.3.2 Experimental methods

All bleaching recipes employed in this work were carried out in a thermally controlled reaction vessel as shown diagrammatically in Figure 5.1. This setup was carried out so as to emulate the kier bleaching system as close as possible. The samples were preweighed prior to being wrapped around the glass tripod, D, and totally immersed in a liquor containing all the relevant bleaching chemicals except hydrogen peroxide. Temperature control was achieved by water being pumped from a thermally controlled water bath, C, into a glass jacket insulating the reaction vessel. The entire assembly was placed on a magnetic stirrer thus ensuring good mixing and dispersability of the bleaching chemicals. The glass combination quickfit stopper and tripod, D, was made with two outlets, one for a thermometer, one to allow the introduction of chemicals and the other to allow the release of the products of decomposition (oxygen).

All investigations into the bleaching behaviour of the CPNF were performed as follows: 10 grams of unbleached CPNF was immersed in an alkaline bleach liquor (180 ml deionised water) containing all the relevant bleaching chemicals except hydrogen peroxide for 30 min under stirring. A known amount of hydrogen peroxide was added to the bleach liquor and bleaching was carried out under stirring for a fixed time. The CPNF was then removed from the liquor and washed with glacial acetic acid, followed by a thorough hot water rinse (80 to 85 °C) for five min. to ensure removal of residual chemicals. All the samples were dried in an oven at 100 °C for 60 min.

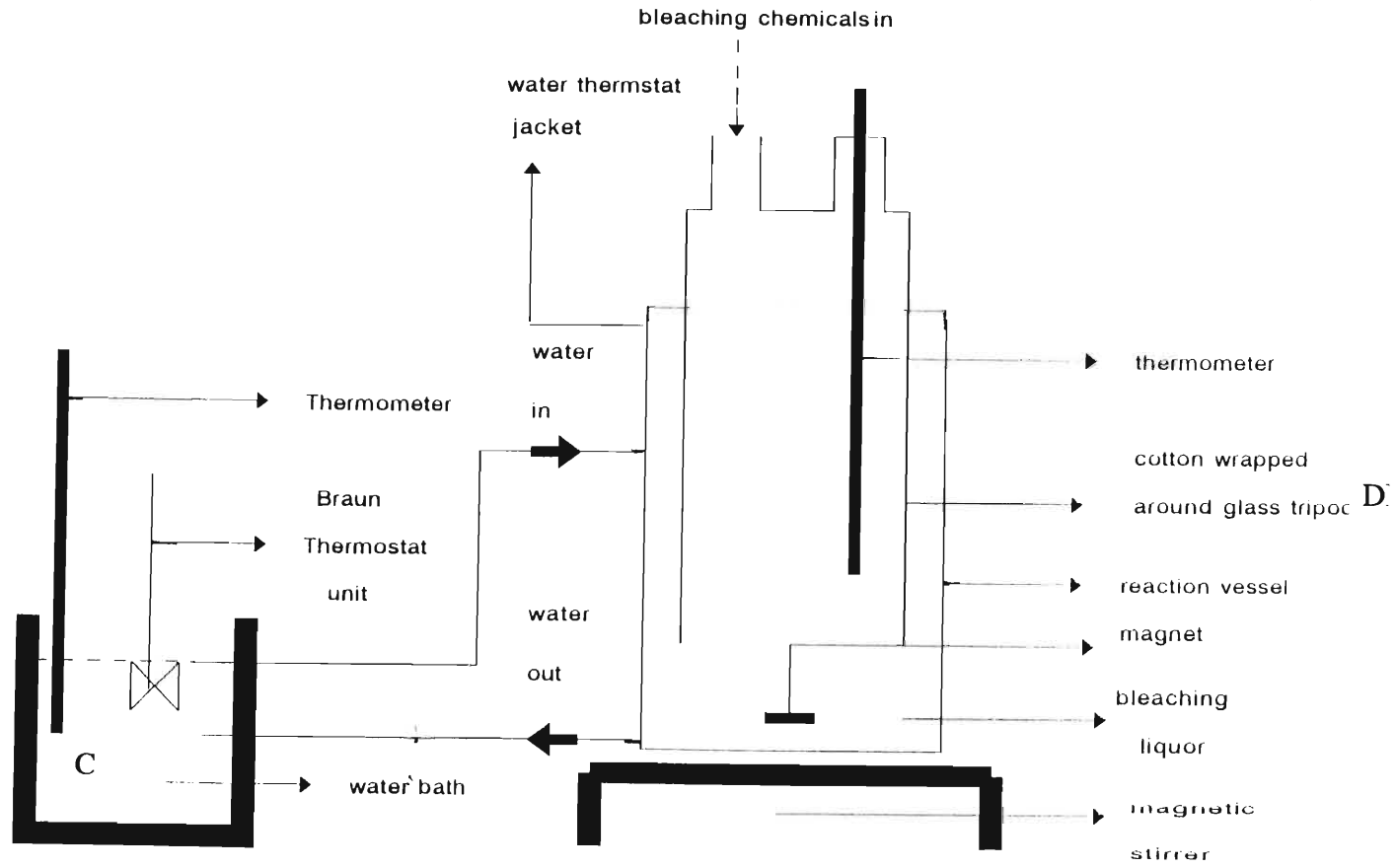


Figure 5.1 Diagrammatic representation of the laboratory apparatus used in all the bleaching treatments

## Chapter 6

### Evaluation of the bleached CPNF

#### 6.1 Introduction

In the development of any bleaching process and their corresponding optimisation technique, it is important to characterise the final fabric as thoroughly as possible.<sup>(46)</sup> This includes comparison of the critical fibre properties such as the extent of fibre damage incurred (fluidity tests, cf. section 6.2)<sup>(47)</sup>, whiteness,<sup>(11)</sup> absorbency,<sup>(11,48)</sup> change in the mechanical properties of the fibre<sup>(49)</sup>, and the complete removal of any impurities found in the cotton,<sup>(11)</sup> to the bleached fabric products made by the conventional bleaching process.

In this study the evaluation of effective bleaching for the CPNF, for the five bleaching treatments described in chapter 5, was performed with respect to the degree of fibre damage (fluidity), absorbency, and whiteness observations. A scanning electron microscope analysis was also performed and the results of these are detailed in chapter 7. These results are compared to those obtained for the high temperature, high pressure bleaching process i.e. the factory bleached fabric).

The fibre properties of all CPNF samples, both bleached and unbleached, were measured using standard procedures<sup>(50,51,52)</sup> (cf. appendix 2.2 and 2.3) and equipment and this information together with their results are detailed in the following subsections.

The CPNF samples were obtained directly from the mill (see appendix 2.1) and were not treated chemically in any way prior to bleaching/scouring. Combined scouring and Bleaching was carried out according to the methods detailed in Table 6.1.

Reagent grade chemicals were used in all the fibre property determinations and deionised water was used in all appropriate cases. All determinations were carried out at 25 °C and the bleaching time was kept constant at 1 hour.



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**Table 6.1** Chemicals and their concentrations for the bleaching treatments (T) investigated.

Chemical	T <sub>0</sub> <sup>a</sup>	T <sub>1</sub> <sup>b</sup>	T <sub>2</sub> <sup>b</sup> conc.	T <sub>3</sub> <sup>b</sup> (g · l <sup>-1</sup> )	T <sub>4</sub> <sup>c</sup>	T <sub>5</sub> <sup>d</sup>
NaOH	23	30	30	30	30	30
Na <sub>2</sub> CO <sub>3</sub>	20	-	-	-	-	-
Na <sub>2</sub> Si <sub>2</sub> O <sub>3</sub>	-	18	18	18	18	18
H <sub>2</sub> O <sub>2</sub>	75	65	65	65	65	65
Wetting Agent	10	10	10	10	10	10
NH <sub>2</sub> CONH <sub>2</sub>	-	15	-	-	-	-
C <sub>6</sub> H <sub>5</sub> CONH <sub>2</sub>	-	-	15	-	-	-
HCONH <sub>2</sub>	-	-	-	15	-	-
MgSO <sub>4</sub>	-	-	-	-	0.5	-
K <sub>2</sub> S <sub>2</sub> O <sub>4</sub>	-	-	-	-	0.5	-
Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	-	-	-	-	-	12

T<sub>0</sub>, T<sub>1</sub> etc. refers to treatment condition 0 and 1 etc., respectively

<sup>a</sup> conventional bleaching process done at 25 °C (normally done at 250 °C)

<sup>b</sup> based on reference 33

<sup>c</sup> based on reference 43

<sup>d</sup> based on reference 44

### 6.2 The degree of chemical degradation of the CPNF samples (fluidity determinations)

#### 6.2.1 Introduction

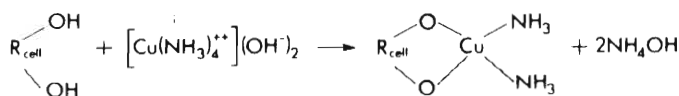
In many applications textile fibres require high tensile strength and resistance to chemical attack.<sup>(53)</sup> Even slight degradation of cellulose is invariably accompanied by a loss of strength and/or tendering.<sup>(46)</sup> The study of degradation mechanisms therefore has important implications for the production of satisfactory finished fabrics.<sup>(53)</sup>

From a chemical point of view the complete degradation of cellulose is its conversion into carbon dioxide and water.<sup>(53)</sup> Any intermediate stage in this process may be described as partial degradation and it is these early stages of degradation that has been determined by the prescribed methods. Quite small changes in chemical composition may profoundly affect the physical properties of cellulose.<sup>(53)</sup>

Although many reagents swell cellulose, very few are capable of dissolving it.<sup>(53)</sup> Much effort has been put into the search for cellulose solvents and for many years the only known solvents for cellulose were moderately concentrated acids (70 % sulphuric acid) and cuprammonium hydroxide.<sup>(11)</sup> Cuprammonium hydroxide dissolves cellulose without degradation provided that atmospheric oxygen and light are excluded.<sup>(11,42)</sup>

Ost in 1911,<sup>(54)</sup> first suggested that the viscosity of a solution of cellulose in ammoniacal copper hydroxide can be used as an indication as the average cellulose chain length. This suggestion was investigated critically by Farrow and Neale in 1924<sup>(55)</sup> and finally perfected by Clibbins and his collaborators at the Shirley Institute.<sup>(56,57,58)</sup>

It has been reported that cellulose dissolves in cuprammonium hydroxide because a 1:1 complex is formed between the cuprammonium ion and the 2,3 diol group of the anhydroglucose chain units.<sup>(59)</sup> A uncharged square planar complex, as shown in Scheme 6.1 is formed and the formation of this complex involves distortion of the pyranose ring.<sup>(53,60)</sup>



Scheme 6.1

## Chapter 6: Evaluation of the .....

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Kenner *et al*<sup>(61)</sup> have shown that cellulose degraded by alkali at temperatures above 170 °C results in scission of the glycosidic bonds randomly along the lengths of the fibres and the newly formed shorter chains can be degraded further.

Under unfavourable conditions the hydrogen peroxide can cause serious oxidative degradation causing extensive tendering to the fabric.<sup>(53)</sup> The nature of the degradation is not well understood.<sup>(53)</sup> This is due to the strong catalytic influence of metal ions, such as those of copper and iron, which may be found both in the cellulose and the sodium hydroxide used for the oxidising liquor.<sup>(53)</sup> Oxidation by alkaline peroxide has been found to almost certainly involve peroxy radicals which leads ultimately to chain scission.<sup>(53)</sup>

### 6.2.2 Fluidity test

The fluidity method of test is sensitive to the onset of chemical damage before such damage would become apparent through a loss in tensile strength.<sup>(11)</sup> The fluidity of cellulose in cuprammonium is determined in a viscometer as shown in Figure 6.1.

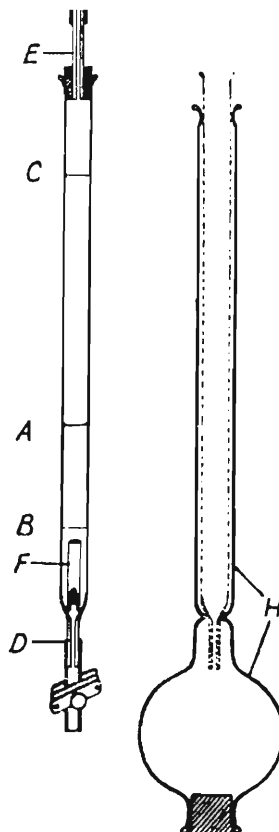


Fig 6.1 Viscometer taken from referance 63

## Chapter 6: Evaluation of the .....

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According to the British Standards test method,<sup>(62)</sup> the fluidity of a specimen of cotton is the fluidity of a solution in the standard cuprammonium solvent containing 0.5 g of cotton per 100 ml of solution at 2 °C. In this test a weighed sample of cellulose finely chopped to give fibres of 1 - 2 mm length is dissolved in standard cuprammonium hydroxide in a standard viscometer. The viscometer must be filled completely to exclude air and covered to prevent exposure to light, whilst controlled agitation is given over 16 hours. The viscometer and its contents are then brought to 20 °C in a thermostatically controlled bath and the rate of flow through the capillary measured i.e. the time taken for the meniscus to fall from one fixed mark to another( C to A in the Figure 6.1).<sup>(8,62,64)</sup> As each viscometer is precalibrated, from data provided with the instrument, fluidity is then calculated by dividing the viscometer constant by the time recorded. This gives a direct calculation of fluidity in terms of  $\text{Pa}^{-1}\cdot\text{s}^{-1}$  (reciprocal poise or rhe units).

The principle of the test is that during dissolution, no further breakdown of the cellulose chain structure will occur. Long chained fabrics i.e with low fibre damage, will provide a high viscosity solution, hence low fluidity. As a general rule, bleached cotton with a fluidity above  $10 \text{ Pa}^{-1}\cdot\text{s}^{-1}$ , is regarded as chemically damaged.

### 6.2.3 Experimental

Unbleached CPNF samples were obtained directly from the mill and bleached according to the specifications in Table 6.1. Both the bleached and unbleached samples were analyzed for fluidity using a viscometer of the type shown in Figure 6.2. Samples were selected at random and sent to Sybron Chemicals (George Naidoo) and The Frame Group (Ivan Veerasamy) for confirmative analysis. This served as a check for the technique employed in our laboratory. All the results reported here were within 2 % of those analyzed by Sybron Chemicals and The Frame Group. The viscometer and the cuprammonium solution were bought from the Shirley Institute and fluidity determinations were conducted according to the procedure outlined in the SABS method 115 (revised version, see appendix 2.2)

The fluidity was calculated from the following equations

## Chapter 6: Evaluation of the .....

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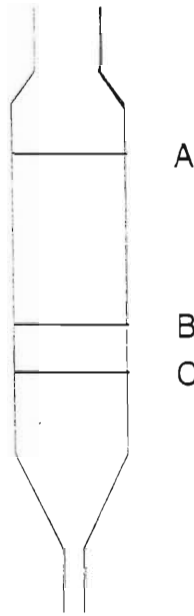
$$\text{if } t > 200 \text{ seconds, } F = C' / t \quad 6.1$$

and


$$\text{if } t < 200 \text{ seconds, } F = C' / t - (K/t) \quad 6.2$$

where  $F$  is the fluidity of the sample, ( $\text{Pa}^{-1}\cdot\text{s}^{-1}$ )  $t$  is the time for the solution to flow from one fixed mark to another (C to A in Figure 6.2),  $C'$  is the viscometer constant and is supplied with the viscometer certificate (see Figure 6.2) and  $K$  is the correction constant for the viscometer supplied with the viscometer certificate (see Figure 6.2).

Chapter 6: Evaluation of the .....



(a)

  
**Shirley Developments Ltd.**  
7 D. Box G, 898 Wotton Road  
 Manchester M30 8BA England  
 Telephone 061 - 456 7797  
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**CALIBRATION DATA FOR "SHIRLEY"  
 X-TYPE VISCOMETERS**  
 supplied by  
 SHIRLEY DEVELOPMENTS LTD.

Viscometer No. <u>3664</u>	Date: <u>20.3.91</u>
Viscometer Constant, C	<u>1931.5</u>
Correction Constant, K	<u>0.23 s</u>
Time of flow of "Standard" Glycerine Solution	<u>193.69</u> sec
Ratio of the times of flow in the two sections $t_1/t_2$	<u>1.03</u>
Volume of solution enclosed	<u>20.1</u> c.c.
Weight of Cotton with assumed 8 per cent moisture content, for 0.5 per cent solution	<u>0.1032</u> g
Weight of Rayon with assumed 10 per cent moisture content, for 2 per cent solution	<u>0.431</u> g

*Ed. Conroy*

for Lab-Plant Ltd.

The manufacturing and calibration procedure used by Lab-Plant Ltd. for the production of "SHIRLEY" X-Type Viscometers is in accordance with the standards set up by Shirley Institute.

*amman*

Managing Director  
Shirley Institute

(b)

Fig 6.2(a) Viscometer used in this investigation together with its calibration certificate(b)

### 6.2.4 Results

Bleaching was carried out at 25 °C on ca 10 g CPNF samples for a total time of 1 h and the concentrations of all chemicals as specified in Table 6.1. For each of the samples obtained from the various bleaching treatments, triplicate fluidity experiments were conducted and the results are detailed in Table 6.2.

Chapter 6: Evaluation of the .....

**Table 6.2** Fluidity Results

Treatment no.*	H <sub>2</sub> O <sub>2</sub> Activator	Fluidity, Pa <sup>-1</sup> ·s <sup>-1</sup>
Unbleached CPNF	-	3
Factory bleached CPNF	-	3
T <sub>0</sub>	conventional bleaching	5
		5
		5
T <sub>1</sub>	Urea	9
		9
		8
T <sub>2</sub>	Benzamide	7
		6
		6
T <sub>3</sub>	Formamide	9
		10
		10
T <sub>4</sub>	MgSO <sub>4</sub> and K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	14
		14
		15
T <sub>5</sub>	Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	4
		4



### 6.2.5 Discussion

In any bleaching process one of the primary objectives is to ensure preservation of inherent fibre quality - this property after subsequent processing can never be improved.<sup>(6)</sup>

Attempts at applying the amide activated bleaching treatments ( $T_1$  - $T_3$ ) to the CPNF<sup>(33)</sup> were mildly successful except for the benzamide activated treatment ( $T_2$ ). Relatively high fluidity results (between 8 - 9  $\text{Pa}^{-1}\cdot\text{s}^{-1}$ ) were obtained for the urea ( $T_1$ ) and formamide ( $T_3$ ) hydrogen peroxide bleaching treatments as compared to the fluidity value of the unbleached CPNF (2.60  $\text{Pa}^{-1}\cdot\text{s}^{-1}$ ). Bleaching with benzamide as the peroxide activator was, however, successful producing a fabric whose fluidity value ranged from 6 to 6.8  $\text{Pa}^{-1}\cdot\text{s}^{-1}$ .

Of the bleaching treatments studied, the sodium persulphate peroxide activated bleaching method ( $T_5$ ) yielded the best results with fluidity values ranging between 3.65 and 4.15  $\text{Pa}^{-1}\cdot\text{s}^{-1}$  and these results are comparable to the results of the factory produced bleached fabric. The double activation treatment with potassium persulphate and magnesium sulphate ( $T_4$ ) was highly unsuccessful causing extensive damage to the CPNF fibres.

The results of the sodium persulphate activated bleaching treatment ( $T_5$ ) is superior to the results obtained by Sarma *et al*<sup>(43)</sup> in their similar treatment of cotton woven fabrics (3.6 - 15.5  $\text{Pa}^{-1}\cdot\text{s}^{-1}$ ). This difference could probably be due to the longer treatment times studied in their research (7 h).

The finding that sodium persulphate ( $T_5$ ) produces the smallest amount of fibre damage is in agreement with the work conducted on woven fabrics.<sup>(43,44,66)</sup> This activator has been incorporated in some cold alkaline peroxide bleaching recipes done.<sup>(28)</sup>

The results obtained here are supported by the scanning electron microscope (SEM) results discussed in chapter 7 and the sodium persulphate activated bleaching recipe is utilised to optimise the treatment conditions of time, temperature and hydrogen peroxide concentration in chapter 8.

### 6.3 Determination of the wettability of the bleached CPNF

#### 6.3.1 Introduction

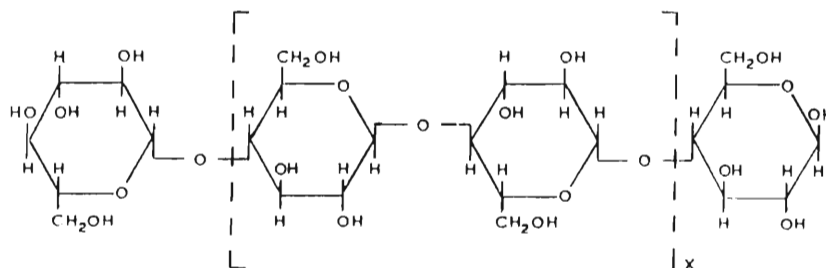
The absorbency or wettability of cotton CPNF is its most important fibre property as it is used as a wound dressing. One of the basic objectives of bleaching research is to ensure preservation or improvement of this property.

In this work the wettability of all the bleached CPNF fabrics described in Table 6.1 were determined with the aim of investigating the changes in water absorbency capacity before and after bleaching.

#### 6.3.2 General properties of water towards cellulose

The affinity of water to cellulose is not difficult to understand. From the chemical formula (cf scheme 6.2) it can be seen that cellulose possesses an abundance of hydroxyl groups that need to be solvated. Not all the hydroxyl groups are bound together in the crystalline region and a proportion of them exist in a sufficiently accessible state on the micellar surfaces in the fibres to attract water molecules. The moisture relations of cellulose have been studied<sup>(67,68)</sup> over many years pioneered by the early work of Urquhart and Williams<sup>(67)</sup> on scoured cotton.

On exposing the dry cellulose to a moist atmosphere, water is first absorbed on whatever free hydroxyl groups are present, and then by groups held together by weak hydrogen bonds. This imbibed water causes the chain molecules to be pushed apart, exposing more free hydroxyl groups.<sup>(69)</sup>



Scheme 6.2

## Chapter 6: Evaluation of the .....

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The cellulose fibres have been reported to absorb water into their interfibrillar spaces where the liquid is held by capillary action.<sup>(70)</sup> This type of process depends on physical properties such as fibre surface energy and fibre geometry.<sup>(70)</sup> The absorbency characteristics of a fibre are a function of<sup>(71)</sup>

a) the volume available to the fluid i.e. the volume available or created in the structure of the fibre before or during absorption

b) the speed with which the volume takes up fluid and retains it.

Cellulose fibres are extremely absorbent because their natural structure is porous which provides spaces between where liquids can be held by capillary action.<sup>(71,72)</sup> This property has been enhanced in cellulose processing treatments by the action of swelling agents.<sup>(53)</sup> Swelling of cotton may be regarded as the disruption of the fibre solid structure by the intrusion of the molecules of the swelling agent.<sup>(48)</sup> When the swelling agent is removed by washing or other means the cellulose structure contracts again and in all cases forms an accessible fine structure with increased absorbency properties.<sup>(53)</sup> In most cases the swelling agent used for cellulose is aqueous alkali which is incorporated into the preparation process or applied directly by a process known as mercerisation.<sup>(53)</sup>

### 6.3.3 Factors which determine the absorbency of the CPNF

CPNF is made from greige cotton fibres whose structural component is cellulose. Cellulose in its natural state, has a hydrophobic outermost surface because of wax and other non-cellulosic material found in the cuticle and the primary layer (see fig. 7.3). The removal of cotton wax from the cotton fibre during scouring and bleaching reduces the hydrophobic components and increases the wettability of the cotton making it hydrophilic.<sup>(48)</sup> This removal of waxes facilitates fibre swelling and hence greater volume available to the sorbing liquid.

The degree of wettability depends to some extent on the morphology of the CPNF.<sup>(48)</sup> CPNF has been reported to possess a fibrillar structure with a helical fibre orientation.<sup>(74)</sup> The fibre helix reverses in direction at intervals along the fibre length and these reversal regions coincide with the convolutions that are seen in the dried, collapsed fibre. A sorbing species such as water has been reported to open a network of channels or pores by acting as agents

for interfibrillar swelling thus increasing the volume available for absorption.<sup>(53)</sup> In addition it has been reported<sup>(48)</sup> that the phenomenon of hydrophilicity is mainly determined by the competitive effects of spreading amongst the fibers, absorption amongst the fibers and the influence of surface active agents.

### 6.3.4 Experimental

Several methods of testing fabric absorbency are available.<sup>(75,76,77,78)</sup> In practice, tests based on the timing of a water drop to wet out the fabric,<sup>(79)</sup> or for a sample of fabric to sink in water or dye liquor,<sup>(52)</sup> are frequently used. Well prepared fabrics should show a water absorbency of less than 5 seconds.<sup>(52)</sup>

For nonwoven fabrics, the absorbency properties are evaluated according to the EDANA<sup>(80)</sup> test method 10.1-72. These methods evaluate the liquid absorptive capacity (commonly known as absorbency capacity), the liquid absorbency time, and the liquid wicking rate.<sup>(80)</sup> In this work the absorbency of the CPNF were evaluated by the method detailed for absorbent cotton in the British Pharmaceutical Standard Handbook, A226 appendix XX L and on page 1094, surgical dressings.<sup>(52)</sup>(see appendix 2.3). In this method, a 1 g sample was folded four times and allowed to drop lightly on to the surface of water contained in a beaker. The beaker must be a least 0.012 m in diameter and filled with water to a depth of 0.010 m. The time taken for the sample to sink below the surface of the water is measured with a stopwatch. This procedure was repeated on two further samples and the average value was calculated. Distilled water at 20 °C was used as the test liquid.

According to the specifications in the British Pharmaceutical Handbook<sup>(51)</sup> for absorbent cotton gauze, the sinking time must not exceed 10 secs.

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### 6.3.5 Results

Bleaching was carried out at 25 °C on  $\pm$  10 g CPNF samples for a total time of 1 hour and concentrations of the chemicals according to the specifications in Table 6.1. For each of the samples obtained from the various bleaching treatments, triplicate absorbency experiments were conducted and the average results are summarised in Table 6.3.

**Table 6.3** Absorbency Results

Treatment no.*	H <sub>2</sub> O <sub>2</sub> Activator	Absorbency (s)
Unbleached CPNF	-	8
Factory bleached CPNF	-	1
T <sub>0</sub>	conventional bleaching	3
T <sub>1</sub>	Urea	4
T <sub>2</sub>	Benzamide	3
T <sub>3</sub>	Formamide	2
T <sub>4</sub>	MgSO <sub>4</sub> and K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	36
T <sub>5</sub>	Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	3

\* taken from table 6.1

### 6.3.6 Discussion

The results in Table 6.3 show that for the following bleaching processes, T<sub>0</sub>, T<sub>1</sub>, T<sub>2</sub>, T<sub>3</sub> and T<sub>5</sub>, the absorbency of the fabrics is not significantly different from that of both the conventionally bleached and the factory bleached CPNF. The slight improvement in the absorbency value when comparing these bleached fabrics with the unbleached CPNF could possibly be due to similar effects produced from the swelling agents present in the bleaching treatments. Sodium hydroxide and a commercially available wetting agent were used in all the combined scouring and bleaching treatments as the swelling agent. It has been reported that the degree of swelling depends on both the reagent used and on the morphology of the fibre.<sup>(6)</sup> In all the samples used in this work both these factors are constant and hence it is found that the degree of swelling should be the same. This is true for all the samples except for the sample undergoing treatment number 4. The results of all the other treatments except T<sub>4</sub> are in good agreement with the findings of other workers researching into the properties of the CPNF.<sup>(3,46)</sup>

The results in Table 6.3 are also in good agreement with the mechanism that has been suggested for the absorbency of cotton fabrics.<sup>(81)</sup> According to this mechanism, for a given fabric construction, cotton fabrics of the same weight end up with practically identical properties after laundering and subsequent bleaching processes.

It is clear that although the application of treatment 1, 2 and 4 in Table 6.3 results in a fabric whose fibres are damaged (see fluidity and SEM results), it does not alter the absorbency capacity of the fabric in any way. This suggests that the differing peroxide activators in treatments 1, 2 and 4 have little or no effect on the degree of swelling of the cellulose and hence on the property of absorption.

It is furthermore clear that, under the treatment conditions 4 in Table 6.1 used in this study, the bleached CPNF yielded a significantly higher absorbency value. This may be ascribed, at least in part, to the resistance of these chemicals to the rinsing treatments used in this work. This in turn could possibly result in these chemicals forming a layer on the fibre surface hence shielding the available volume on the fibre surface to water impregnation.

### 6.4. Whiteness of the bleached fabric

#### 6.4.1 Introduction

Whiteness of bleached fabric may be assessed visually or determined instrumentally by a spectrophotometer.<sup>(53)</sup> Greisser<sup>(82)</sup> investigated the correlation between the subjective evaluation and the objective (instrumental) measurement of the resultant bleached karakul fabrics and reported that for colour determinations there is excellent agreement between the visual and instrumental appraisals, but for whiteness determinations instrumental appraisals provided more consistent and accurate results. This is in keeping with the accepted view by many workers<sup>(24,46)</sup> that the instrumental analysis of whiteness of bleached fabrics is the simplest and most precise property to evaluate the process of bleaching.

All instrumental methods illuminate the sample and measure the amount of light reflected.<sup>(46)</sup> The assessment ranges from the measurement of reflectance at a single wavelength to a complete spectral scan which can be processed to give colour difference or a whiteness index. Dyer and Daul<sup>(83)</sup> have reviewed these whiteness indices, one of which is recommended in the American Association of Textile Color and Colorists test method 110.<sup>(79)</sup>

The most widely spectrophotometer is the Beckmann DK-2 spectrophotometer.<sup>(5)</sup> In this instrument comparison is made with a magnesium oxide reference. Estimates of the degree of whiteness are obtained by the index  $W$  as reported by Cegarra *et al*<sup>(84)</sup> :

$$W = (CF)^2 = (100 - AS)^2 \quad 6.1$$

where  $CF$  is the difference between the reflectance at 650 and 450 nm called the colouring factor and  $AS$  is the average of reflections at 450, 500, 550, 600 and 650 nm called the average colour. The higher the value of  $W$  the inferior the whiteness.

Another popular instrument, a Hunterlab Multipurpose Reflectometer measures light reflected at a single wavelength of 457 or 460 nm.<sup>(19,46)</sup> These wavelengths lie within the blue region of the spectrum and provide information on both the brightness and yellowness of the sample.

## Chapter 6: Evaluation of the .....

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The reflectance on this instrument is always related to an ideal white standard, the international basis now being magnesium oxide which is taken to have 100 % reflectance.<sup>(50)</sup> The reflectance of well bleached samples should be between 80 to 90 %.<sup>(24)</sup> Extensive reviews on whiteness and colour measurements are given by Ciba Geigy LTD<sup>(86)</sup> and Farbenfabriken Bayer A.G.<sup>(87)</sup>

More sophisticated and technologically advanced on-line colour spectrophotometers have just recently been introduced offering an advanced computerized colour and whiteness analysis system designed to record and report color and whiteness characteristics against predetermined reference whiteness.<sup>(88)</sup> These spectrophotometers are rapidly gaining popularity for their ease of measurement, their exceptionally high measuring accuracy and their extensive compatible reference software.

A Datacolor International computer driven spectrophotometer utilizing the Datacolor Uniflash program was used in this study.<sup>(82)</sup>

### 6.4.2 Experimental

The CPNF samples obtained from the bleaching treatments ( $T_0$  to  $T_5$ ) listed in Table 6.1 were analyzed for their whiteness property by Mr Ivan Veerasamy of The Frame Group. A Datacolor spectrophotometer programmed with magnesium oxide (100 % reflectance) as the reference whiteness material was used.

### 6.4.3 Results

For each of the bleached CPNF samples obtained from the various bleaching treatments listed in Table 6.1, triplicate whiteness tests was conducted and the results are detailed in Table 6.4.



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Table 6.4 Whiteness Results

Treatment no.*	H <sub>2</sub> O <sub>2</sub> Activator	Whiteness (%)
Unbleached CPNF	-	49.67
Factory bleached CPNF	-	75.73
T <sub>0</sub>	conventional bleaching	67.25
		70.10
		69.87
T <sub>1</sub>	Urea	73.27
		77.34
		77.88
T <sub>2</sub>	Benzamide	80.47
		78.27
		76.63
T <sub>3</sub>	Formamide	68.67
		69.87
		72.27
T <sub>4</sub>	MgSO <sub>4</sub> and K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	65.73
		60.54
		59.23
T <sub>5</sub>	Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	79.16
		80.21
		78.90

\*taken from Table 6.1

### 6.4.4 Discussion

Of the five bleaching treatments selected in this investigation, only the use of treatment 4 ( $T_4$ ) resulted in a bleached CPNF exhibiting poor whiteness. The remainder of the samples representing the range of bleaching treatment investigated showed equal and superior whiteness values to that of the factory bleached and conventionally bleached samples.

In particular, treatment 2 and 5 ( $T_2$  and  $T_5$ ) in table 6.4, yielded the best whiteness results indicating a well bleached sample. It was reported earlier in this work (section 6.2) that the treatment conditions incorporating urea, formamide or magnesium sulphate/potassium persulphate ( $T_1$ ,  $T_3$  and  $T_4$ , respectively) in the bleaching bath as the peroxide activator resulted in a highly damaged fibre. From Table 6.4 it can be seen that this damaged fibre was successfully bleached with an acceptable whiteness value although extensive damage was caused to the fibres. This indicates that the rate of activation of the hydrogen peroxide was too rapid resulting in overbleaching and degradation of the cotton fibres.

In view of the preceding discussion, the rates of hydrogen peroxide decomposition were determined for bleaching treatments  $T_1$  to  $T_5$  by withdrawing 1 ml aliquots at intervals and adding 100 ml of 10 % sulphuric acid solution and titrating with standard (0.1N) potassium permanganate.<sup>(24)</sup> These results are tabulated in Table 6.5 and plotted against the time of bleaching (1 h) in Figures 6.1 (a) and (b).

From Figure 6.1. (a) bleaching in the presence of sodium persulphate ( $T_5$ ) and benzamide ( $T_2$ ) resulted in a slow and constant rate of decomposition for the time period investigated. From Figure 6.1. (b) it is evident that the decomposition rate is much faster, indicating that the activators ( $T_1$ ,  $T_3$  and  $T_4$ ) employed enhance too fast a decomposition of the peroxide. Thus excessive oxygen is produced accompanied by fibre degradation.

These results are supported by both the fluidity results reported earlier and by the SEM investigation discussed in chapter 7.

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**Table 6.5** The decrease of hydrogen peroxide concentration with an increase in time using the various bleaching treatments

Time	[50 % H <sub>2</sub> O <sub>2</sub> ]	Time	[50 % H <sub>2</sub> O <sub>2</sub> ]
minutes	g·l <sup>-1</sup>	minutes	g·l <sup>-1</sup>
<i>Treatment No. 1 (T<sub>3</sub>) *</i>			
0.00	6.200	15.00	4.726
2.00	4.862	16.00	4.692
4.00	4.862	20.00	4.692
5.00	4.828	25.00	4.692
6.00	4.828	30.00	4.692
8.00	4.828	40.00	4.624
9.00	4.828	50.00	4.624
10.00	4.726	60.00	4.624
<i>Treatment No. 2 (T<sub>2</sub>) *</i>			
0.00	6.200	20.00	4.624
1.00	4.896	25.00	4.624
3.00	4.760	30.00	4.534
5.00	4.760	35.00	4.534
7.00	4.692	40.00	4.534
10.00	4.624	50.00	4.216
15.00	4.624	60.00	4.216

\* taken from Table 6.1

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Table 6.5 continued

Time	[50 % H <sub>2</sub> O <sub>2</sub> ]	Time	[50 % H <sub>2</sub> O <sub>2</sub> ]
minutes	g·l <sup>-1</sup>	minutes	g·l <sup>-1</sup>
<i>Treatment No. 3 (T<sub>3</sub>)*</i>			
0.00	8.800	20.00	5.318
1.00	7.344	25.00	5.008
3.00	7.140	30.00	4.997
5.00	5.832	35.00	4.930
8.00	5.644	40.00	4.260
10.00	5.372	50.00	4.080
15.00	5.348	60.00	3.910
<i>Treatment No. 4 (T<sub>1</sub>)*</i>			
0.00	8.800	20.00	4.930
3.00	6.800	25.00	4.760
6.00	6.460	30.00	4.760
8.00	5.780	35.00	4.760
10.00	5.610	40.00	4.420
12.00	5.440	50.00	3.916
15.00	5.440	60.00	3.230

\* taken from Table 6.1

## Chapter 6: Evaluation of the .....

Table 6.5 *continued*

Time	[50 % H <sub>2</sub> O <sub>2</sub> ]	Time	[50 % H <sub>2</sub> O <sub>2</sub> ]
minutes	g·l <sup>-1</sup>	minutes	g·l <sup>-1</sup>
<i>Treatment No. 5 (T<sub>4</sub>)*</i>			
0.00	8.800	25.00	4.624
2.00	6.052	30.00	4.352
5.00	5.780	35.00	4.012
10.00	5.508	40.00	3.740
15.00	5.236	50.00	3.320
20.00	5.100	60.00	3.080

\* taken from Table 6.1

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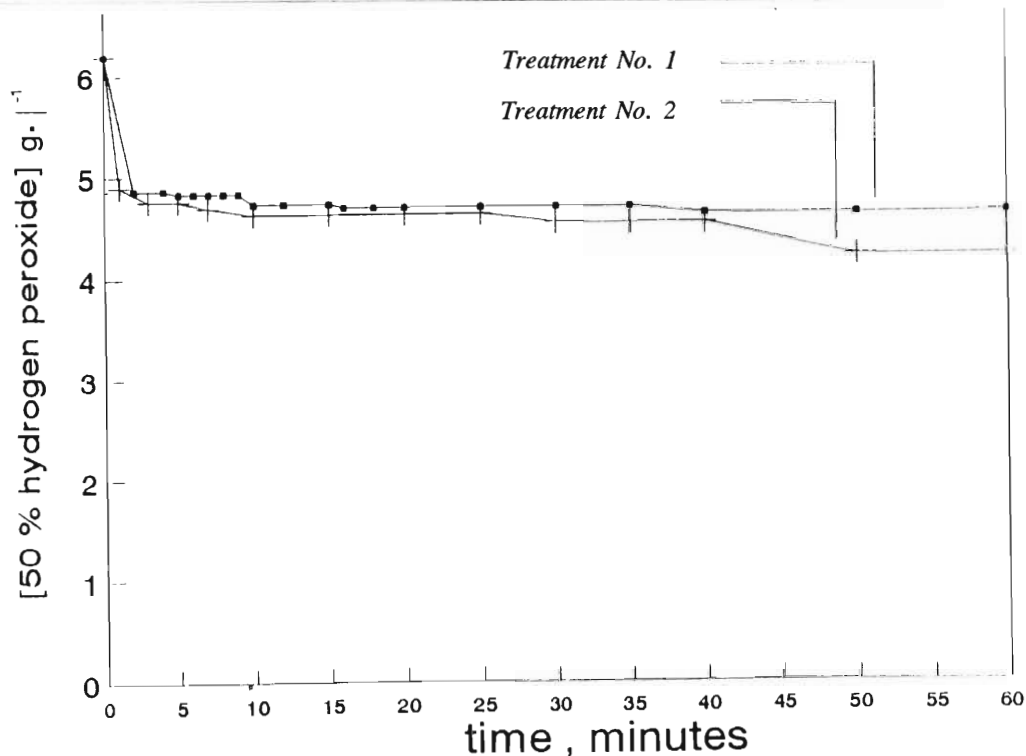


Figure 6.1 (a) The decrease of hydrogen peroxide composition plotted against the time of bleaching in the presence of (1)  $\text{Na}_2\text{S}_2\text{O}_8$  (T5) and (2)  $\text{C}_6\text{H}_5\text{CONH}_2$  (T2)

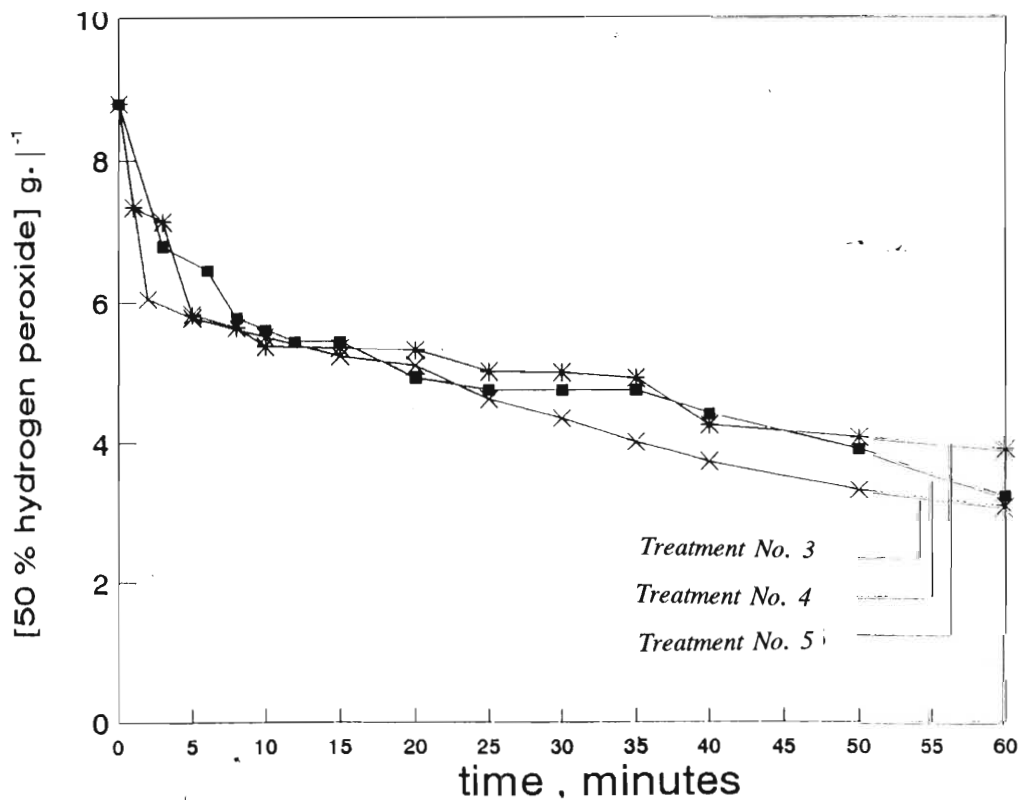


Figure 6.1 (b) The decrease of hydrogen peroxide composition plotted against the time of bleaching in the presence of (3)  $\text{HCONH}_2$  (T3), (4)  $\text{H}_2\text{NCONH}_2$  (T1) and (5)  $\text{K}_2\text{S}_2\text{O}_8 + \text{MgSO}_4$  (T4)

**6.5 Conclusions**

1. The sodium persulphate activated bleaching ( $T_5$ ) and to a lesser extent the benzamide activated bleaching ( $T_2$ ) method, produced a fabric with minimum fibre damage and hence low fluidity values.
2. All the bleaching treatments investigated, with the exception of  $T_4$  produced a fabric of acceptable absorbency properties.
3. All the bleaching treatments ( $T_0$  to  $T_5$ ) investigated in this study except the treatment incorporating  $MgSO_4$  and  $K_2S_2O_8$  ( $T_4$ ) as the peroxide activator produced a fabric of acceptable whiteness property.

## Chapter 7

### Scanning Electron Microscope (SEM) investigation of the unbleached and bleached Cotton Patterned Non-Woven Fabric

#### 7.1 Introduction

Electron microscopy has been shown<sup>(89)</sup> to provide valuable information on the essential elements of the fibre structure of cotton. Research by workers<sup>(90)</sup> has revealed that cellulose (the basic structural component of cotton) is organized in the form of relatively course fibrous structure and that these fibres are further subdivided into microfibrils as shown in Figures. 7.1. It has been established that the morphology of these fibres are altered considerably by the differing finishing treatments and their related chemicals.<sup>(6)</sup>



*Fig 7.1. Electron micrograph of the course fibrous structure of cotton*

In this work, the surface structures of the CPNF were observed before and after bleaching. This was done in order to investigate the modifications (if any) to the fibre surfaces of the final CPNF by the various bleaching treatments.



## 7.2 The surface structure of CPNF

Cotton has been regarded as composed of structural units termed fibrils.<sup>(49,91,92)</sup> These fibres are essentially a build up of a number of identical units of cellulose and chemical reactions have been proposed as taking place on the surfaces of these fibrils.<sup>(92)</sup> An essential aspect of all chemical finishing processes involving cotton is degree of access of the chemicals to the fibrillar surfaces. The way in which the fibrillar units are altered during chemical treatment can exert a profound effect on the final properties of the fabric.<sup>(6)</sup>

Cellulose is the basic structural component of the fibrils and the literature on the physical structure of these cellulose fibres is extensive.<sup>(25,93,94)</sup> In recent years, natural cellulose fibre structures have altered in minor detail as more powerful analytical techniques have been developed. Essentially, a mature fibre forms a flat ribbon containing approximately thirty cellulose chains and appear under the electron microscope to be 0.02 to 0.03  $\mu\text{m}$  thick and at least 10  $\mu\text{m}$  long. It has been postulated<sup>(53)</sup> that the fibrils consist of "bundles" of smaller microfibrils that are approximately 0.004 to 0.006  $\mu\text{m}$  in cross section. One of the main features of the structure of the cotton fibres is the spiral arrangement of the fibrils, which reverses in direction of rotation periodically along the length of the fibre. This causes the convolutions observed by many workers<sup>(74)</sup> and it has been reported that the number of convolutions varies between 4 and 6 per millimetre.<sup>(53,74)</sup> It is these convolutions that play a large part in determining the mechanical properties of the fabric (e.g. tensile strength, elasticity etc.) These unique characteristics of cotton fibres are represented lengthwise in fig. 7.2 at a fairly low magnification. In this study these convolutions were observed in all the fibre and fabric micrographs taken at magnifications of 1000 and lower (see figures 7.4 to 7.10).

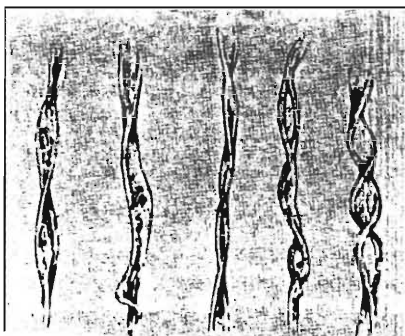


Fig. 7.2 Electron micrograph of greige cotton fibres showing the convolutions<sup>44</sup>

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Electron microscopy of the cross-section of the cotton fibres has been extensively researched.<sup>(95,96)</sup> It has been established that each fibre consists of three main parts: primary wall, secondary wall and lumen as shown in fig 7.3). The primary wall consists of a network of cellulose fibrils covered with an outer layer or cuticle of pectin, protein, mineral matter and wax. It is the wax that renders the fibre impermeable to water and aqueous solutions unless a wetting agent is present. The secondary wall constitutes the bulk of a mature fibre and consists entirely of fibrils of cellulose arranged spirally around the fibre axis. Thus the cotton fibre consists of an assembly of fibrils in which the cellulose is accessible to most chemical reagents only at fibrillar surfaces.

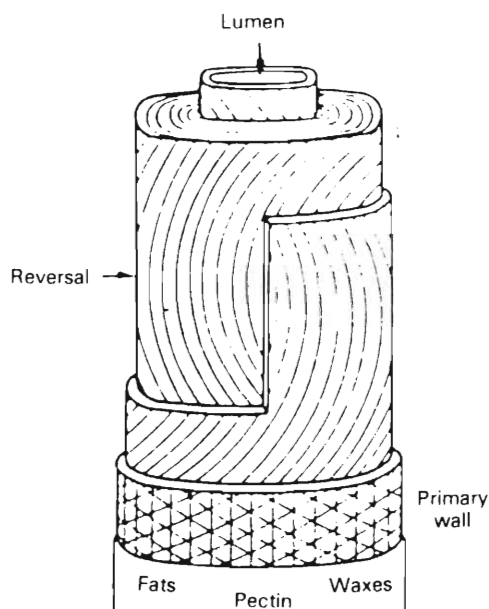
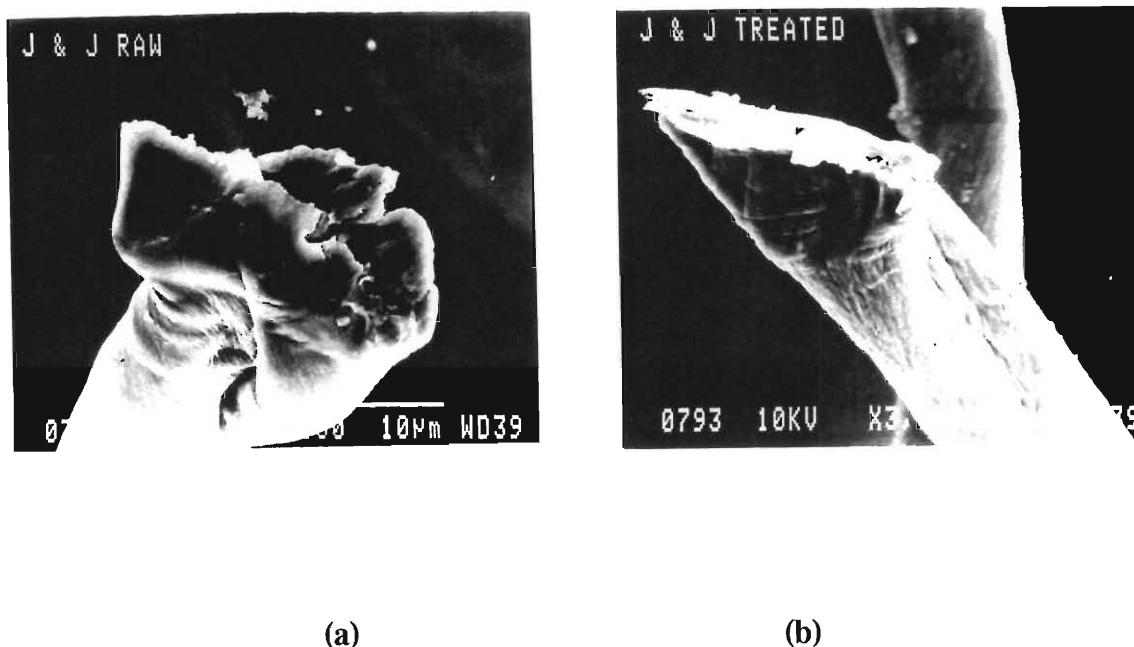


Fig 7.3. Idealised morphology of cotton fibre taken from ref 6

A cross-section of the CPNF before and after bleaching is shown in fig 7.4 (a) and 7.4 (b). The CPNF fibres for this micrograph were bleached using the conventional high temperature, high pressure peroxide bleach method described at the beginning of this study (Table 5.4). From these figures, it can be seen that the fibres were never stripped of their primary walls after bleaching because the combined scouring and bleaching process was reasonably mild. Electron microscopic examination of the bleached CPNF fibres prepared by various methods was performed in order to examine them for surface changes as compared to the unbleached cotton fibre.



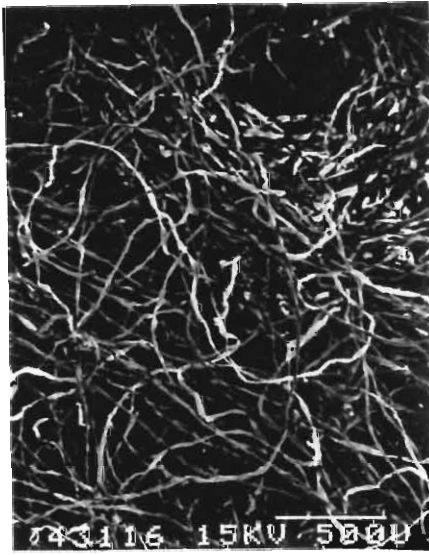
*Fig 7.4 Cross section of the surface fibres of the CPNF (a) before bleaching and (b) after bleaching at 250 °C.*

### 7.3 Experimental

All the micrographs were taken by Mrs Wendy Baier on a Hitachi S-430 scanning electron microscope. Instrument operating voltages are recorded on the individual micrographs. The samples were mounted horizontally on hollowed-out specimen stubs and coated with gold.

### 7.4 Results

Electron micrographs of fibres from five of the CPNF samples scoured and bleached as described in chapter 6 and table 6.1 were examined and are shown in figs. 7.5 to 7.9. Details of the treatments and the results obtained in terms of the bleaching effect and extent of fibre damage, have been given in Table 6.1. The electron micrographs of untreated CPNF fibres and fibres of the high temperature, high pressure bleaching process are also shown in Figures 7.10. and 7.11, respectively.



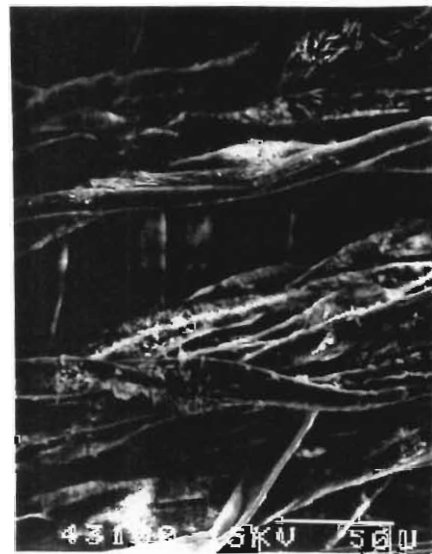
(a)



(b)

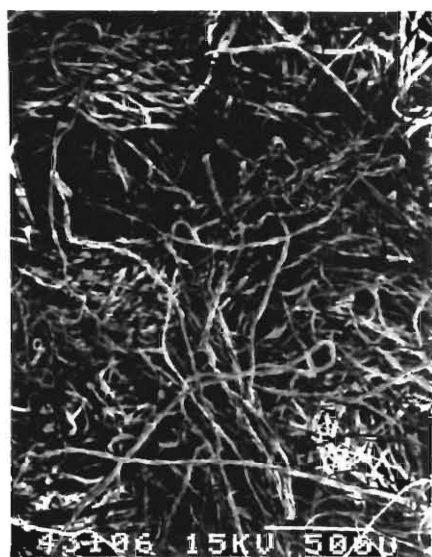


(c)



(d)

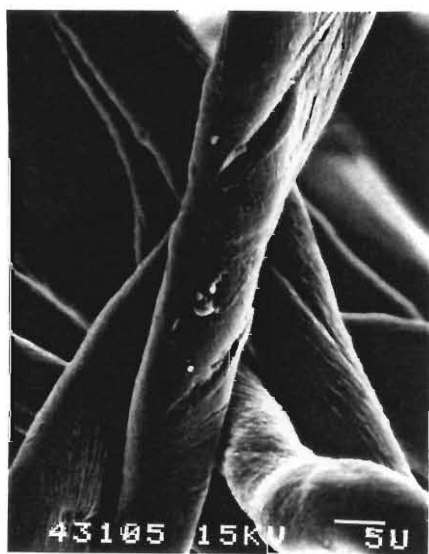
*Fig 7.5 SEM micrographs of bleached CPNF to show surface fibre morphology after application of treatment 1 in Table 6.1, (a) 45X, (b) 200X, (c) 500X and (d) 1500X*



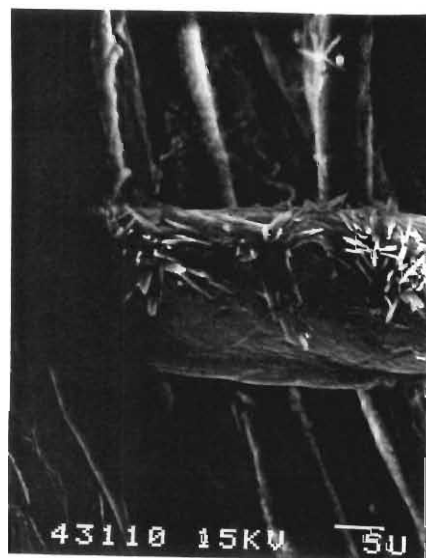
(a)



(b)

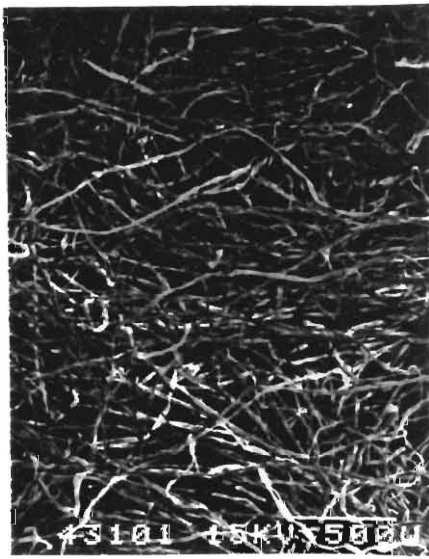


(c)



(d)

*Fig 7.6 SEM micrographs of bleached CPNF to show surface fibre morphology after application of treatment 2 in Table 6.1, (a) 45X , (b) 500X, (c) 2000X and (d) 2000X*



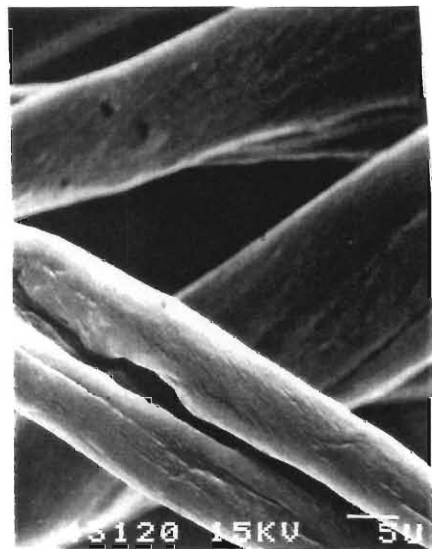
(a)



(b)

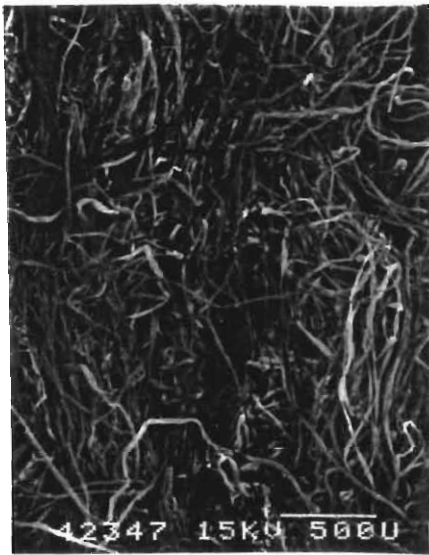


(c)

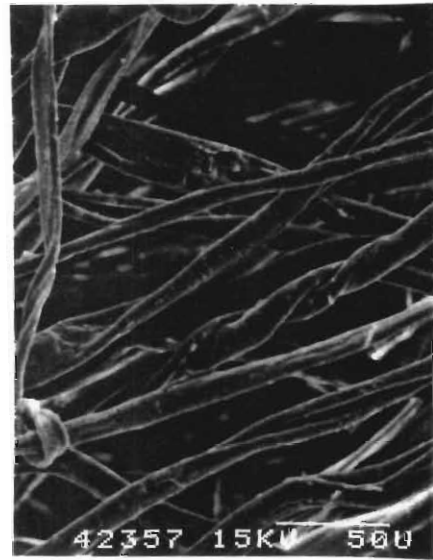


(d)

*Fig 7.7 SEM micrographs of bleached CPNF to show surface fibre morphology after application of treatment 3 in Table 6.1, (a) 45X, (b) 500X, (c) 1500X and (d) 2000X*



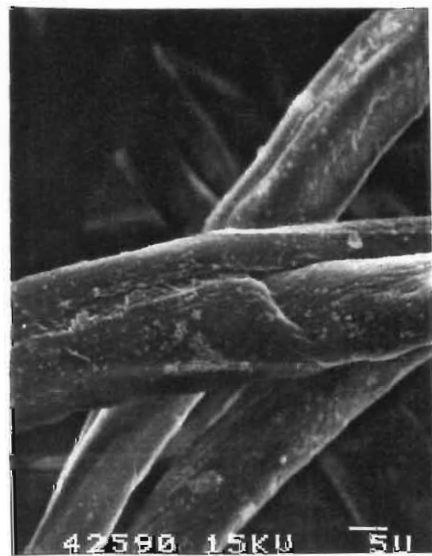
(a)



(b)

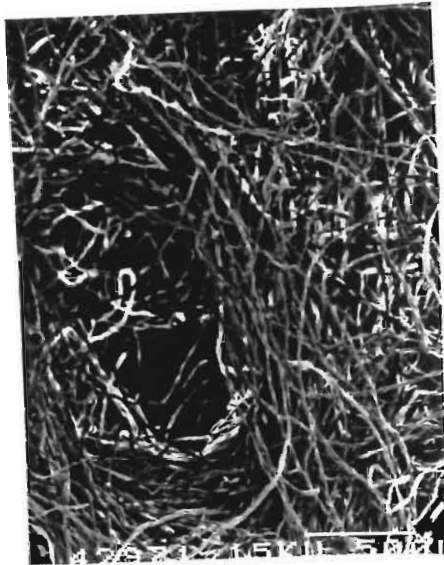


(c)



(d)

*Fig 7.8 SEM micrographs of bleached CPNF to show surface fibre morphology after application of treatment 4 in Table 6.1, (a) 42X, (b) 500X, (c) 1000X and (d) 1500X*



(a)



(b)



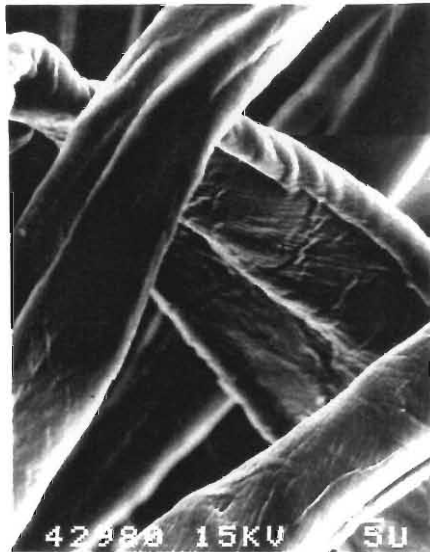
(c)



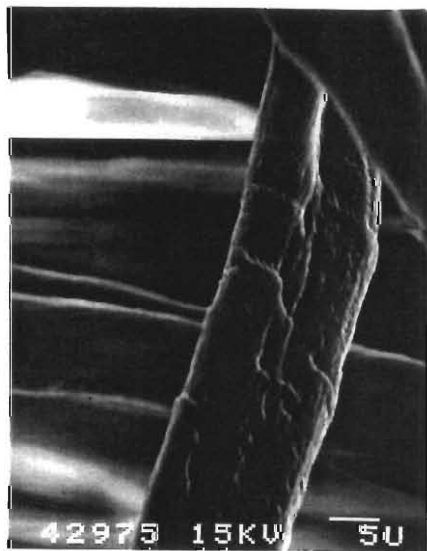
(d)

*Fig 7.9 SEM micrographs of bleached CPNF to shoe surface fibre morphology after application of treatment 5 in Table 6.1, (a) 45X, (b) 500X, (c) 1000X and (d)1500X*



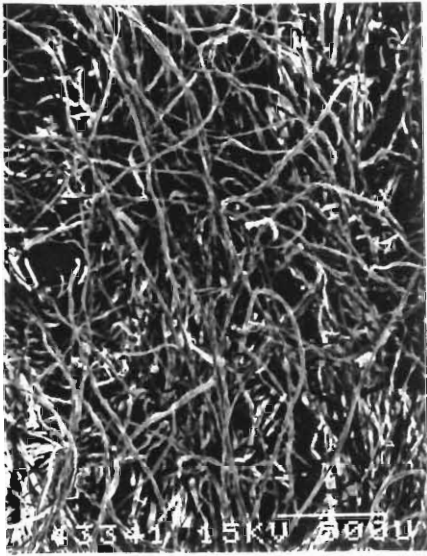


(e)



(f)

*Fig 7.9 continued, (e) 2000X (f) 2000X*



(a)



(b)

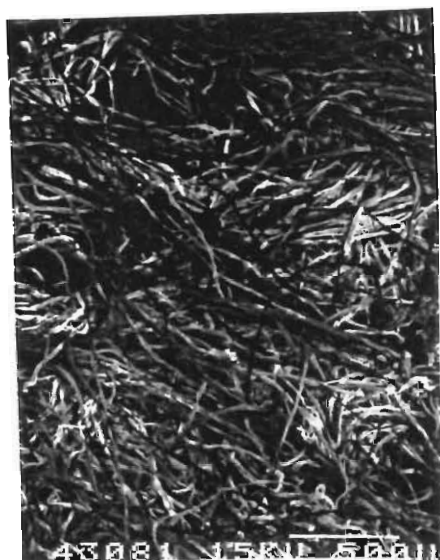


(c)

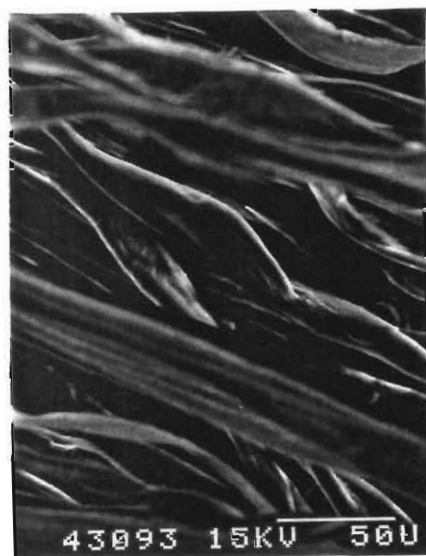


(d)

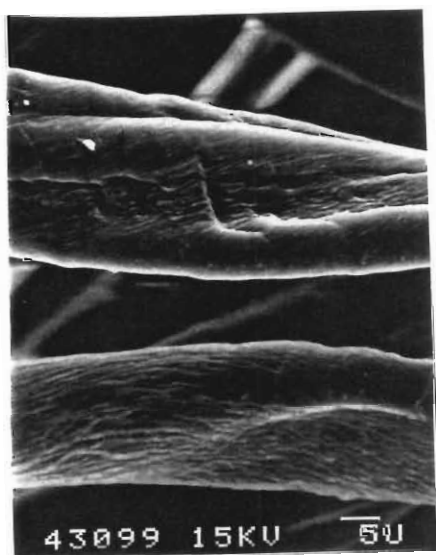
*Fig 7.10 SEM micrographs of unbleached CPNF to show surface fibre morphology, (a) 45X, (b) 200X, (c) 1500X and (d) 2000X*



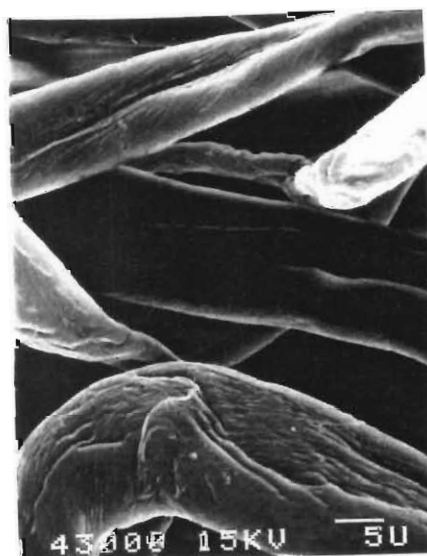
(a)



(b)



(c)



(d)

*Fig 7.11 SEM micrographs of bleached CPNF to show surface fibre morphology after high temperature and high pressure bleaching, (factory bleaced sample), (a) 45X, (b) 500X, (c) 1500X and (d) 2000X*

### 7.5 Discussions

The SEM micrographs obtained in this work confirm the flat ribbonlike structure of cotton as well as the convolutions observed by other workers.<sup>(53,94)</sup> These microscopic features are seen clearly at low magnifications (200X and below). The reversals in the directions of the twists of the convolutions could also be seen clearly (Figures 7.5. to 7.11.). More detailed examination of all the samples at higher magnifications (1500 and 2000X), (c) and (d) in Figures 7.5 to 7.11, showed a wrinkled, rough and corrugated surface. Workers<sup>(3)</sup> have shown that it is this property of the greige cotton fibre that is partially responsible for the success in patterning and forming the CPNF.

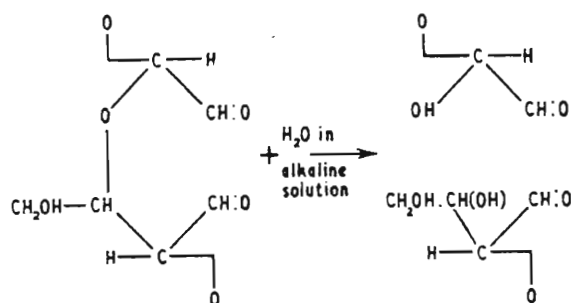
Lower magnification micrographs were taken to compare the spatial or geometric arrangement of the fibres of the webs in the unbleached and bleached samples. It has been reported<sup>(3)</sup> that the geometric pattern of unbleached, entangled fabric made with greige cotton shows a well defined hole that is typical of CPNF. In a successfully produced CPNF, the water jets will produce this hole. In both the unbleached and bleached fibre samples used in this work, this characteristic hole is clearly defined (see (a) in Figures 7.5 - 7.11).

Untreated CPNF fibres were generally found to have a well defined, undamaged surface morphology as shown in Figures 7.10. Some of the bleached fibres, on the other hand, showed signs of fibre damage and surface contamination which, not surprisingly, was found to increase with increasing fluidity (see chapter 8) ie. extent of fibre damage of the samples.

The extent of fibre damage was greatest when urea ( $T_1$ ) was used as the activator for hydrogen peroxide. As shown in Figure 7.5 the urea in conjunction with the other bleaching chemicals ( $Na_2Si_2O_8$ , NaOH and  $H_2O_2$ ) seems to have attacked the outer surface at intervals along the length of the fibre. In addition, the hot water washing and neutralization of the fabric after bleaching failed to remove all of the urea, and crystallites of the chemical can be seen on the surface.

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This fibre damage could possibly be attributed to urea inducing too fast an activation of the hydrogen peroxide resulting in extensive oxygen being produced (see eqn. 4.3). This suggestion is collaborated by the work reported by Das *et al.*<sup>(33)</sup> Oxygen has been shown to react with cellulose to produce oxycellulose (according to scheme 7.1), the formation of which is accompanied by cellulose chain scission and fibre degradation.<sup>(6)</sup>



Scheme 7.1.

The fibre produced with formamide (HCONH<sub>2</sub>) (T<sub>3</sub>) as the peroxide activator exhibits similar behaviour along the surface of the fibre as shown in Figures 7.6. Here again the extensive variations and damage to the surface of the fibre is noted as compared to that of the unbleached fibre. In particular, from Figure 7.6 (c), a rupture of the fibre surface is visibly distinguishable. This surface damage could possibly lead to breakage in the fibre and hence fibre degradation.

The SEM micrographs of the fibres produced with benzamide (T<sub>2</sub>) as the peroxide activator is shown in Figures 7.7. Comparison of these micrographs with the unbleached fibres (Figure 7.10) shows that there is no surface damage present after bleaching. In fact, the surface of bleached fibre is much "cleaner" than that of the unbleached fibre. This is understandable as the bleaching process serves to remove any impurities present in the raw unbleached state.<sup>(6)</sup> These slight impurities are visible in the unbleached fibre and absent in the benzamide bleached fibre. It is surprising that the benzamide activated bleaching method

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should produce differing results to those of the urea and formamide results discussed above. Das and co-workers<sup>(33)</sup> in their paper utilise all of the above amides as activators for the cold peroxide bleaching process of woven fabrics, with a certain degree of success. From this one can deduce that each of the amides behave in a similar manner during bleaching. Thus it was expected that the benzamide bleaching ( $T_2$ ) method would produce similar surface and extent of fibre damage results to the urea ( $T_1$ ) and formamide ( $T_3$ ) bleaching methods. For the bleaching of the CPNF this is not the case. Benzamide, in contrast to urea and formamide, produces a fabric whose fibres exhibit little or no surface degradation or damage. This behaviour could perhaps be attributed to the structural differences between the amides resulting in differing activation properties for the hydrogen peroxide.

The SEM micrographs of the bleaching methods adopted by Sarma *et al*<sup>(43)</sup> where magnesium sulphate and potassium persulphate ( $T_4$ ) are the peroxide activators is shown in Figure 7.8. All of the surfaces of the fibres seem to be penetrated and damaged by the bleaching chemicals used. In particular the micrograph in Figure 7.8(c) shows a distinct rupture of the surface of the fibre. However, what is noticeable is that the degree of damage to the fibre surface in this treatment is not as extensive as that of the urea ( $T_1$ ) and formamide ( $T_3$ ) bleaching methods.

The low temperature peroxide bleaching method by Dickenson and Hickman<sup>(42)</sup> and adapted to the CPNF ( $T_5$ ) seems to have produced the most successful results with regards to surface damage to the fibre. The SEM micrographs of these fibres are shown in Figure 7.9. Analysis of these micrographs shows that the fibres exhibit little or no damage after bleaching. Comparing these micrograph results with the micrographs of the high temperature, high pressure conventional bleaching process ( Figure 7.11) shows that there is little or no discrepancy in surface morphology. This indicates that a peroxide bleached CPNF with little or no fibre damage can be produced at a low temperature with sodium persulphate ( $T_5$ ) as the peroxide activator.

It is this method which has been chosen and rigorously optimised for CPNF bleaching in Chapter 8.

### 7.6 Conclusions

The SEM investigation showed very significant differences between the surfaces of the bleached fibres obtained using the various bleaching processes. The urea ( $T_1$ ) and formamide ( $T_3$ ) peroxide activated bleaching treatments produced a fabric with extensive fibre damage and degradation. The benzamide ( $T_2$ ) activated process, surprisingly, produced a fabric with little or no damage. The presence of the ring structure in the benzamide and its reactivity towards peroxide could probably offer an explanation to this behaviour. The potassium persulphate and magnesium sulphate ( $T_4$ ) peroxide activated bleaching methods also produce a fabric whose fibres show extensive surface damage.

The SEM study also elucidated a bleaching method with minimum fibre damage. The sodium persulphate ( $T_5$ ) activated bleaching process produced a fabric whose fibres undergo little or no change during bleaching. This method has thus been used to optimise the bleaching process for the CPNF in the following chapters.

## Chapter 8

### Optimisation of the single stage bleaching process using regression analysis

#### 8.1 Introduction

The treatment conditions employed and the results obtained in the previous chapters (6 and 7) suggests that bleaching in the presence of sodium persulphate produced a fabric with minimum fibre damage. In view of these results, it was considered important to investigate the influences of certain bleaching variables in a bleaching recipe containing sodium persulphate as the peroxide activator.

As many workers have shown,<sup>(5,9,42,43,98)</sup> when investigating aspects of bleaching, a mathematically designed evaluation is necessary to assess interactions between variables and the statistical significance of the experimental results. In this study, a technique similar to the one described by Sarma *et al*<sup>43</sup> was employed with the treatment conditions for the combined scouring and bleaching with hydrogen peroxide were varied according to a statistical plan for 3 variables. Hydrogen peroxide concentration, bleaching time and bleaching temperature were chosen as the bleaching variables. Whiteness was chosen as the criteria for assessing the quality of the bleaching as it was considered the simplest and most accurate (instrumental analysis) measure to describe the quality of bleaching.

#### 8.2 Basic theory of regression analysis

Regression is the study of the analysis of data aimed at discovering how one or more variables (called independent variables) affect other variables (called response variables).

For the sake of completeness, the basic equations and their inferences are demonstrated briefly here,<sup>(99,100)</sup> but using a computer is the only practical means of performing a multiple regression analysis on a data set.

For data with an underlying linear pattern i.e. one of the form

$$Y = \beta_0 + \beta_1x \quad 8.1$$



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a hypothesized straight line is used to explain the behaviour of the variables. For observations that do not fit this pattern of a straight line, a relationship of the form

$$Y_i = \beta_0 + \sum_{i=1}^n \beta_i x_i + \sum_{i=1}^n \beta_{ii} x_i^2 + \sum_{i < k} \beta_{ik} x_i x_k + c_j \quad 8.2$$

may be utilized where  $i = 1, 2, \dots, n$ ,  $n$  is the number of data points and  $(k+1)$  represents the number of independent variables. Equation 8.2 is called a regression model and since  $k > 1$ , it is called a *multiple quadratic regression model*.<sup>(99)</sup>

The  $\beta_i$ 's,  $i = 0, 1, \dots, k$ , represent the regression parameters and the  $c_j$ 's,  $j = 1, 2, \dots, n$ , the error terms or residuals.<sup>(100)</sup> The values of the  $\beta_i$ 's and  $c_j$ 's are estimated using the ordinary least squares (O.L.S.) procedure. In multiple regression the  $Y_i$ 's are called the observations or response variables and  $x_i^0, x_i^1, \dots, x_i^n$  is said to constitute the design point corresponding to  $Y_i$ .<sup>(99)</sup>

In multiple regression, the residuals are estimated as follows

$$\hat{c}_j = Y_i - Y_{i(\text{calc})} \quad 8.3$$

where  $Y_{i(\text{calc})}$  represents the predicted value of  $Y_i$

When there is a good fit to the predicted model, the residuals ( $c_j$ ) are small. When  $\beta_0$  i.e the constant term in equation 8.2 above, is not equal to zero, a measure of fit is also given by the equation

$$R^2 = 1 - \left\{ \sum_{i=1}^n c_j / \sum_{i=1}^n (Y_i - \bar{Y})^2 \right\} \quad 8.4$$

$\bar{Y} = \sum_{i=1}^n Y_i / n$  and  $R^2$  is called the multiple regression coefficient.  $R^2$  lies between 0 and 1 and the closer this value is to 1 the better the fit of the model. Another parameter  $R_{\text{adj}}^2$  gives the multiple regression coefficient adjusted for sample size,  $n$ . This parameter is obtained from the following equation

$$R_{adj}^2 = 1 - \left\{ \left[ \sum_{i=1}^n (Y_{obs} - Y_{calc})^2 / n - k - 1 \right] / \left[ \sum_{i=1}^n (\bar{Y}_{obs} - Y_i)^2 / n - 1 \right] \right\} \quad 8.5$$

in which  $n$  is the number of data points and  $k$  is the number of independent variables.<sup>(100)</sup>

Most computer packages provide all the above statistical values and the simple statistics of the mean, variance and standard deviation.<sup>(101)</sup> In addition the standard error of the estimate is obtained from the equation

$$\text{standard error} = s. \left\{ \sum_{i=1}^n (x_i - \bar{x})^2 \right\}^{1/2} \quad 8.6$$

and is also provided by a statistical computer package. The assumption that the independent variables are fixed and predetermined by the investigator is made in all multiple regression correlation procedures.<sup>(100)</sup>

Equation 8.2 can be represented as a regression or response surface of  $Y$  (response variable) on  $x_1, x_2, \dots, x_n$  (independent variables).<sup>(102)</sup> This plotted response surface enables the response variable,  $Y$ , to be optimised as a function of the independent variables. This fitted surface may attain (a) a maximum, or (b) a minimum, or (c) a saddle point in the region of interest or (d) it may do none of these things.<sup>(100)</sup> Analysis of the response surface can therefore provide a method of solving problems of determination of optimum conditions.<sup>(44,102)</sup>

In this work, the influence of three independent variables i.e time, temperature and concentration of hydrogen peroxide, on the response property of whiteness was determined. Detailed laboratory experiments were performed to investigate the effect of these three variables on the measured property of whiteness. The whiteness value of the bleached fabrics was compared to the values obtained for the same fabric prepared using the conventional high temperature (250 °C) high pressure bleach. Response surface diagrams were drawn and the optimum conditions for the low temperature bleaching with respect to hydrogen peroxide concentration, time and temperature were obtained.

### 8.3 Experimental

CPNF samples were bleached according to the treatment conditions established earlier (cf chapter 6 and 7) as the method producing the minimum fibre damage while achieving a good degree of whiteness and absorbency. For the sake of convenience this method is shown in Table 8.1.

Values for peroxide concentration, bleaching temperature and time were established according to a central rotatable plan for three variables. The treatment conditions for the bleaching process involves a range of hydrogen peroxide concentration, ( $34 \text{ g}\cdot\text{l}^{-1}$  to  $96 \text{ g}\cdot\text{l}^{-1}$ ), time (2 hours to 6 hours) and temperature ( $25 \text{ }^\circ\text{C}$  to  $45 \text{ }^\circ\text{C}$ ) and is presented in Table 8.2.

#### *Statgraphics*

The *Statgraphics* software is a PC software program integrating a variety of statistical functions with high resolution colour graphics. In this study *Statgraphics* was used in the multiple regression analysis and to plot the response surface diagrams. A computer output was obtained using the *Statgraphics* program for multiple regression as shown in appendix 2.4.

Further details of this program can be found in the *Statgraphics Users Guide*<sup>(101)</sup> manual.

**Table 8.1** Treatment conditions for the bleaching recipe chosen to be optimised

Chemical	T <sub>5</sub> conc (g·l <sup>-1</sup> )
NaOH	30
Na <sub>2</sub> Si <sub>2</sub> O <sub>3</sub>	18
H <sub>2</sub> O <sub>2</sub>	65
Wetting Agent	10
Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	12

#### 8.4 Results

The results of the response analysis for whiteness are listed in Table 8.2. The regression coefficients and the multiple correlation coefficient for the bleached CPNF are shown in Table 8.3.

The surface diagrams for the effects of two variables on the measured property of the bleached fabrics are shown in Figures 8.1 - 8.3.

The data were analyzed by fitting the variables in a quadratic polynomial of the type

$$Y = B_o + \sum_{i=1}^k B_i X_i + \sum_{i=1}^k B_{ii} X_i^2 + \sum_{i < j}^k B_{ij} X_i X_j$$

where Y is the experimentally measured whiteness response for each experiment and B is the regression coefficient. From the fitted regression equation 15 possible treatment combinations were obtained.

Table 8.2 Treatment conditions and whiteness property of prepared fabrics where  $x_1$  refers to hydrogen peroxide concentration,  $x_2$  to time,  $x_3$  to temperature and Y to the observed whiteness. The calculated whiteness is defined as  $Y_{calc}$ .

Expt.No.	$\frac{x_1}{g \cdot l^{-1}}$	$\frac{x_2}{hrs}$	$\frac{x_3}{^{\circ}C}$	$\frac{Y}{\%}$	$\frac{Y_{calc}}{\%}$
1	65	4	35	80.48	80.36
2	65	2	25	80.77	81.50
3	65	6	25	77.01	75.52
4	96	4	45	79.80	81.30
5	96	4	25	79.49	78.76
6	65	6	45	77.02	77.82
7	96	2	35	80.45	78.22
8	65	4	35	80.28	80.36
9	34	6	35	79.98	78.55
10	34	4	25	77.13	78.56
11	34	4	45	76.70	77.40
12	65	2	45	81.64	80.84
13	34	2	35	81.13	80.43
14	96	6	35	73.24	75.47
15	65	4	35	80.32	80.36
Conventionally prepared fabric		—	—	77.90	—

Table 8.3 Coefficients of the regression equations for whiteness

Reg.Coefficients	Full model
$B_0$	74.05
$B_1$	0.35
$B_2$	1.71
$B_3$	-0.65
$B_{11}$	-0.0016
$B_{22}$	-0.46
$B_{33}$	-0.0091
$B_{12}$	-0.0019
$B_{13}$	0.0027
$B_{23}$	-0.066
$R^2$	0.70

### 8.5 Discussion

From Table 8.2, close agreement between the observed and calculated values of the various parameters shows that the regression equation is applicable in this investigation. The multiple correlation coefficient ( $R$ )<sup>(99)</sup> is used to ascertain the validity of the regression equation.  $R^2$  was found to be 0.705 and showed fair correlation with respects to the observed and fitted values.

The regression equation for whiteness has the form

$$Y = 74.05 + 0.35x_1 + 1.71x_2 - 0.65x_3 - 0.0012x_1^2 - 0.46x_2^2 - 0.0091x_3^2 - 0.0019x_1x_2 + 0.0027x_1x_3 - 0.066x_2x_3 \quad 8.7$$

and  $Y$  has a positive contribution from two independent variables ( $x_1$  and  $x_2$ ). The largest positive contribution to whiteness (i.e. the regression coefficient for  $x_2$ , 1.71) is time. This value suggests that the longer the time of bleaching the higher the degree of whiteness. However an acceptable degree of whiteness was obtained after 3 hrs.

The regression coefficients for the other major parameters  $B_1$  (hydrogen peroxide concentration) and  $B_3$  (temperature) show a small but significant effect on the degree of whiteness in the ranges investigated in this work (Table 8.2). It is possible that outside the range, the effect of these parameters might be significant. Other workers<sup>(11,19,27)</sup> have found that this effect becomes significant and contributory at higher temperatures (180°C).

The regression equation (8.7) has been used to plot surface diagrams (Figures 8.1-8.3). The values used for plotting these figures are the smoothed values (equation 8.7) of the responses obtained from the 15 data points.

Figure 8.1 shows the effect of three levels of temperature on the whiteness. There is only a small difference between the whiteness at 25 °C (80 %) and 45 °C (84 %). This indicates that bleaching can effectively be carried out at ambient temperature. In addition, the curvature of both surfaces shows a maximum whiteness (which is of an acceptable whiteness\*) at approximately 3 hrs and 65 g·l<sup>-1</sup> hydrogen peroxide concentration. This

suggests that in the range investigated, 3 hrs was sufficient for efficient CPNF bleaching. Figure 8.2 shows the effect of bleaching on the whiteness of the fabrics after 2 hrs (surface c) and 6 hrs (surface d) of bleaching respectively. At both surfaces, the whiteness increases as the hydrogen peroxide concentration increases until approximately  $65 \text{ g}\cdot\text{l}^{-1}$ , where the surface begins to taper off and decrease as the concentration approaches  $96 \text{ g}\cdot\text{l}^{-1}$ . This suggests that a concentration of about  $65 \text{ g}\cdot\text{l}^{-1}$  is necessary to obtain a fabric that satisfies the whiteness control level\*.

The inference drawn from Figures 8.1 and 8.2 is that 3 hours and  $65 \text{ g}\cdot\text{l}^{-1}$  hydrogen peroxide concentration is sufficient for the effective bleaching of CPNF and this is supported by the analysis given in Figure 8.3.

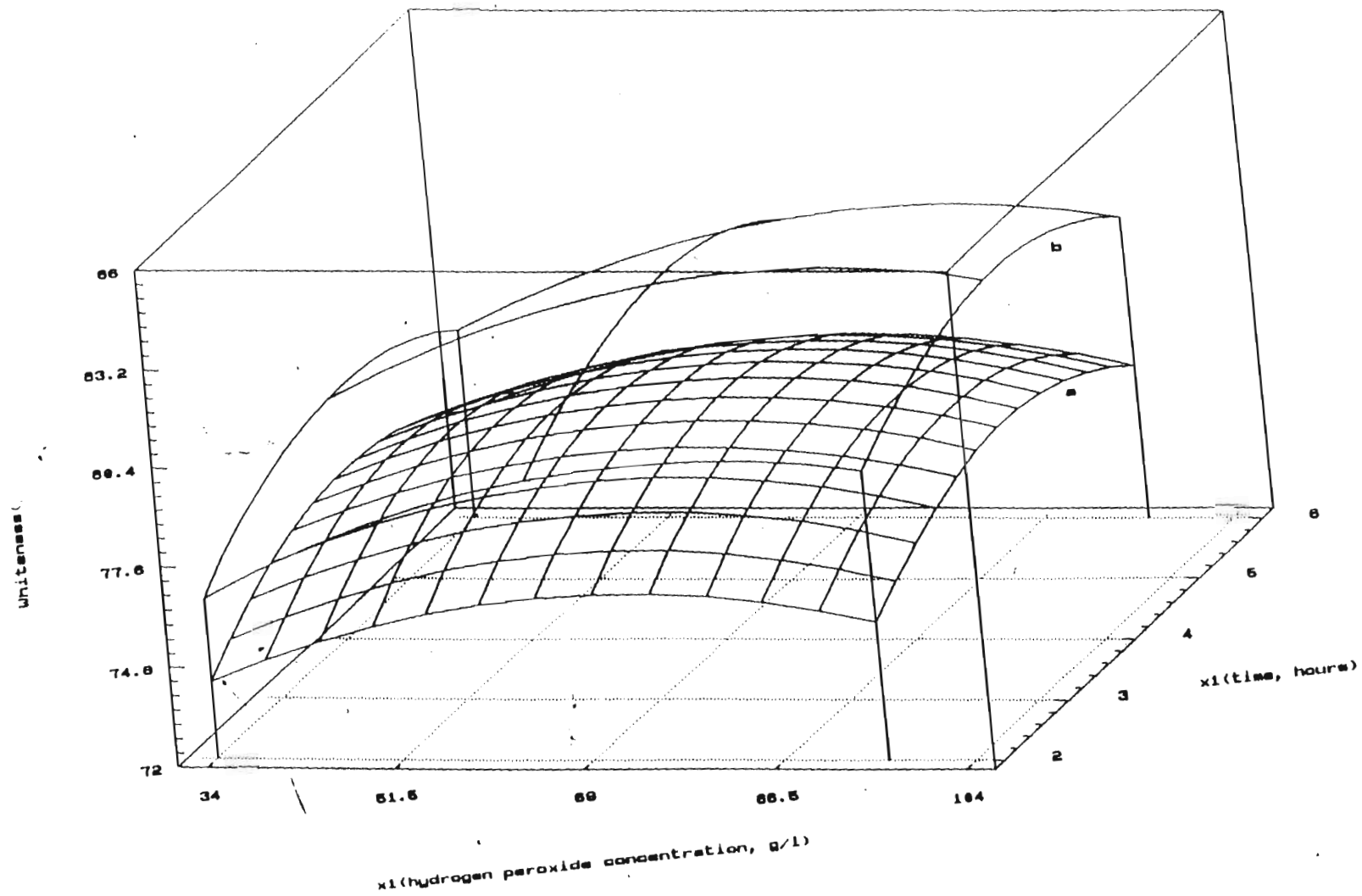
In Figure 8.3, the effect on whiteness obtained using a concentration of hydrogen peroxide of  $34 \text{ g}\cdot\text{l}^{-1}$  and  $96 \text{ g}\cdot\text{l}^{-1}$  are shown. Surface e shows that an increase in time has a marginal increase on the whiteness. For times greater than 3 hrs, the whiteness approaches a constant value. Surface f exhibits similar behaviour.

### 8.6 Conclusion

Based on the correlation of the regression equation analysis to the spatial diagrams, a bleaching formulation consisting of sodium hydroxide ( $30 \text{ g}\cdot\text{l}^{-1}$ ), sodium silicate ( $18 \text{ g}\cdot\text{l}^{-1}$ ), sodium persulphate ( $12 \text{ g}\cdot\text{l}^{-1}$ ), hydrogen peroxide ( $65 \text{ g}\cdot\text{l}^{-1}$ ) and a wetting agent ( $10 \text{ g}\cdot\text{l}^{-1}$ ) at  $25^\circ\text{C}$  for 3 hours using a laboratory scale pad-batch kier system provides a potential method for combined scouring and bleaching of the CPNF.

\* The whiteness control level is the value obtained for the conventionally bleached fabric i.e. 77.90 %





a refers to 26 C and b 48 C

Fig 8.1 Whiteness response function; Variables are hydrogen peroxide concentration and time

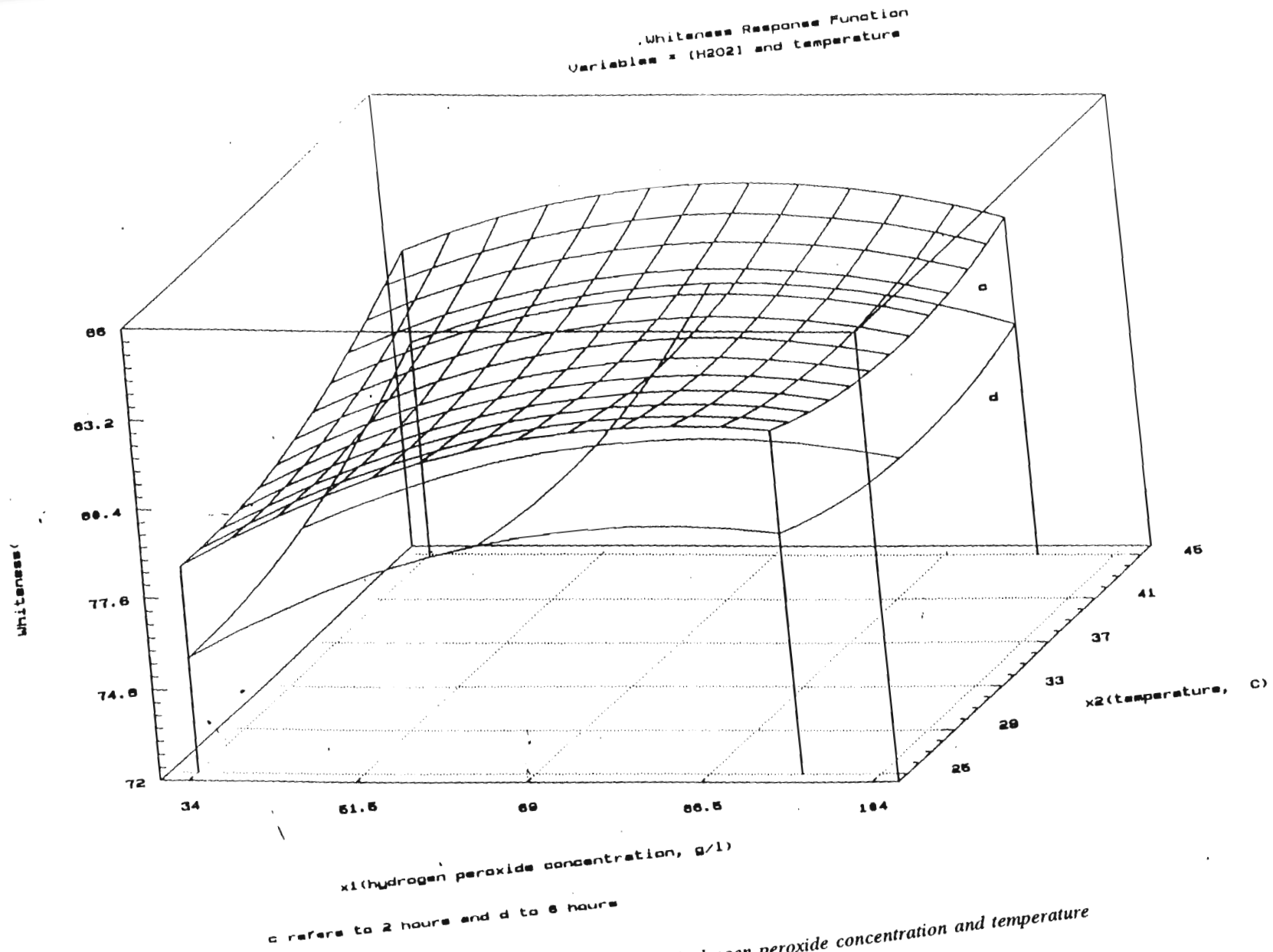
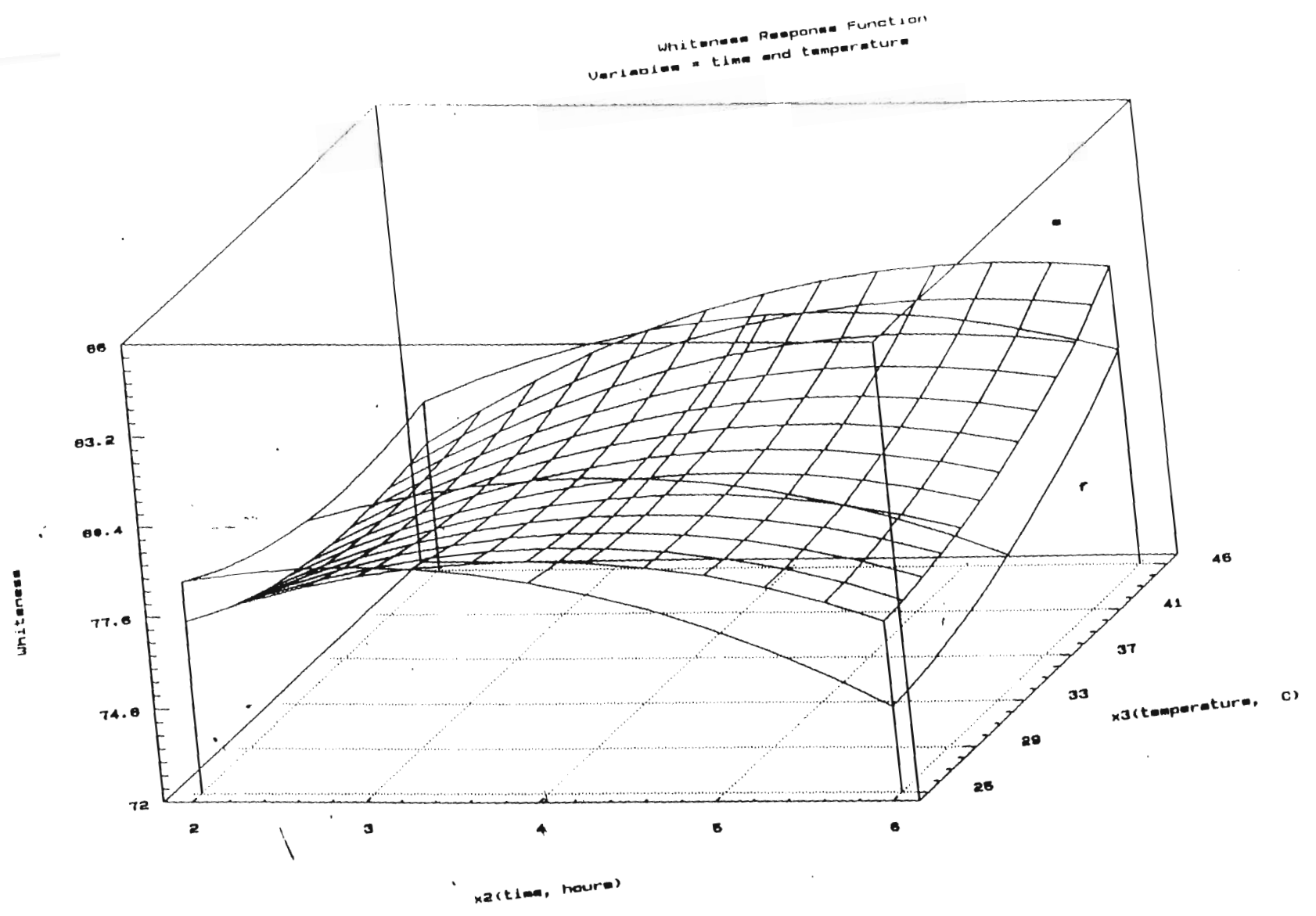


Fig 8.2 Whiteness response function; Variables are hydrogen peroxide concentration and temperature



■ refers to 34g/l and r to 98g/l  
Fig 8.3 Whiteness response function; Variables are time and temperature

### Chapter 9

#### Conclusions

Five bleaching treatments for the CPNF were investigated. Based on the results of the whiteness, fluidity, absorbency and regression analysis, a bleaching formulation consisting of sodium persulphate ( $12 \text{ g}\cdot\text{l}^{-1}$ ) as the hydrogen peroxide activator, sodium hydroxide ( $30 \text{ g}\cdot\text{l}^{-1}$ ) sodium silicate ( $18 \text{ g}\cdot\text{l}^{-1}$ ), hydrogen peroxide ( $65 \text{ g}\cdot\text{l}^{-1}$ ), and a wetting agent at  $25 \text{ }^\circ\text{C}$  for 3 hours using a laboratory scale pad batch kier system, provides a potential method for combined scouring and bleaching of the CPNF.

Further work could be done to investigate the conversion of the above process to a continuous on-flow process. In addition, silicate problems of precipitation on the machinery in continuous processes need to be accounted for and investigations into an alternate stabiliser should be done.

## List of Publications

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### List of publications

1. T.M. Letcher, J.D. Mercer Chalmers, U.P. Govender, R. Battino, *Thermochimica Acta*, **224**, 39 (1993).
2. T.M. Letcher, J.D. Mercer Chalmers, U.P. Govender, S. Radloff, *Thermochimica Acta*, **224**, 33 (1993).
3. T.M. Letcher, J.D. Mercer Chalmers, U.P. Govender, S. Radloff, *Fluid Phase Equilibria*, **79**, (1993) accepted for publication.
4. T.M. Letcher, U. Domanska, P. Govender, *J. Chem Thermodynamics*, **1993**, submitted for publication.
5. T.M. Letcher, U. Domanska, P. Govender, *J. Chem Thermodynamics*, **1993**, submitted for publication.
6. T.M. Letcher, U.P. Govender, S. N. Lutseke, *Textile Research J.*, 1993, submitted for publication.

## REFERENCES AND APPENDICES

## References

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## Appendix 1.1

### Error Analysis

Using the notation in the GWBASIC computer programme:

$$V^E = \{X_A \cdot M_A + (1-X_A)M_B\}/D_U - (X_A \cdot M_A)/D_A - \{(1-X_A)M_B\}/D_B$$

where  $V^E$  is the excess molar volume,  $X_A$  is the mole fraction of A,  $X_B$  is the mole fraction of B,  $M_A$  is the molar mass of A,  $M_B$  is the molar mass of B,  $D_U$  is the density of the mixture,  $D_A$  is the density of A, and  $D_B$  is the density of B.

$$X_A = \{(B_A - B_o)/M_A\} / \{(B_A - B_o)/M_A + (B_B - B_A)/M_B\}$$

where  $B_o$  is the mass of the weighing bottle,  $B_A$  is the mass of  $B_o + A$ , and  $B_B$  is the mass of  $B_o + B$ .

$$D_U = C(\tau_u^2 - \tau_w^2) + D_w$$

where  $C$  is the densimeter constant (0.542394),  $\tau_u$  is the periodicity value obtained from the densitometer for the mixture,  $\tau_w$  is the periodicity value for distilled and deionised water, and  $D_w$  is the density of the water.

$$D_A = C(\tau_A^2 - \tau_w^2) + D_w$$

where  $\tau_A$  is the periodicity value obtained for A.

$$D_B = C(\tau_B^2 - \tau_w^2) + D_w$$

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where  $\tau_B$  is the periodicity value for B.

$$V_\phi = \{1000(d - d_0)\}/(C_1 d_0) + M_1/d_0$$

where  $V_\phi$  is the apparent molar volume,  $d$  is the density of the solution,  $d_0$  is the density of the pure solvent,  $C_1$  is the concentration of the solution, and  $M_1$  is the molar mass of the solute.

### Calculation of errors

Here  $\Delta$  represents the error in the quantity, and an example of a typical (average value) calculation is given.

$$(\Delta X_A)^2 = (\partial X_A/\partial B_0)^2(\Delta B_0)^2 + (\partial X_A/\partial B_A)^2(\Delta B_A)^2 + (\partial X_A/\partial B_B)^2(\Delta B_B)^2$$

$$\begin{aligned}(\partial X_A/\partial B_0) &= -[M_A \cdot M_B(B_B - B_A)]/[M_B(B_A - B_0) + M_A(B_B - B_A)]^2 \\ &= -[100.40(1.0)]/[40(1.0) + 100(1.0) + 100(1.0)]^2 \\ &= -0.20408\end{aligned}$$

$$\begin{aligned}(\partial X_A/\partial B_A) &= [M_A \cdot M_B(B_B - B_0)]/[M_B(B_A - B_0) + M_A(B_B - B_A)]^2 \\ &= [100.40(1.0)]/[40(1.0) + 100(1.0)]^2 \\ &= 0.20408\end{aligned}$$

$$\begin{aligned}(\partial X_A/\partial B_B) &= -[M_A \cdot M_B(B_A - B_0)]/[M_B(B_A - B_0) + M_A(B_B - B_A)]^2 \\ &= -[100.40(0.1)]/[40(1.0) + 100(1.0)]^2 \\ &= -0.20408\end{aligned}$$

Thus,  $\Delta X_A = 0.000004$  moles

## Appendices

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$$(\Delta D_U)^2 = (\partial D_U / \partial \tau_u)^2 (\Delta \tau_u)^2 + (\partial D_U / \partial \tau_w)^2 (\Delta \tau_w)^2$$

$$(\partial D_U / \partial \tau_u) = 2\tau_u = 2(1.780000) = 3.56000$$

$$(\partial D_U / \partial \tau_w) = 2\tau_w = 2(1.739781) = 3.47956$$

$$(\Delta D_U)^2 = (3.56000)^2 (0.00002)^2 + (3.47956)^2 (0.00002)^2$$

$$\text{Thus, } \Delta D_U = 0.00001 \text{ g.cm}^{-3}$$

$$\text{Similarly, } \Delta D_A \text{ and } \Delta D_B \text{ are equal to } 0.00001 \text{ g.cm}^{-3}$$

$$(\Delta V^E)^2 = (\partial V^E / \partial X_A)^2 (\Delta X_A)^2 + (\partial V^E / \partial D_U)^2 (\Delta D_U)^2 + (\partial V^E / \partial D_A)^2 (\Delta D_A)^2 + (\partial V^E / \partial D_B)^2 (\Delta D_B)^2$$

$$(\partial V^E / \partial X_A) = (M_A - M_B) / D_U - M_A / D_A + M_B / D_B = 60 / 0.9 - 100 / 0.8 + 40 / 0.8 = -8.33333$$

$$(\partial V^E / \partial D_U) = -[X_A \cdot M_A - (1 - X_A) M_B \cdot D_U] / (D_U)^2 = -[0.5(100) - (0.5)40(0.9)] / (0.9)^2 = 39.50617$$

$$(\partial V^E / \partial D_A) = -M_A / (D_A)^2 \cdot (-D_A) = -[100 / (0.8)^2](-0.8) = 125$$

$$(\partial V^E / \partial D_B) = -\{(1 - X_A) M_B\} / (D_B)^2 \cdot (-D_B) = -[0.5 \cdot 40 \cdot (-0.8)] / (0.8)^2 = 25$$

$$\text{Thus, } \Delta V^E = 0.00132 \text{ cm}^3 \cdot \text{mol}^{-1}$$

$$(\Delta V_\phi)^2 = (\partial V_\phi / \partial d_o)^2 (\Delta d_o)^2 + (\partial V_\phi / \partial d)^2 (\Delta d)^2 + (\partial V_\phi / \partial C_1)^2 (\Delta C_1)^2$$

$$(\partial V_\phi / \partial d_o) = [-1000(d - d_o)(d_o)] / [C_1(d_o)^2] - (M_1 \cdot d_o) / (d_o)^2 = [-1000(0.9 - 0.8)(0.8)] / [(0.05 \cdot (0.8)^2)]$$

$$(\partial V_\phi / \partial d) = 1000 / (C_1 d_o) = 1000 / (0.05 \cdot 0.8)$$

$$(\partial V_\phi / \partial C_1) = -[1000(d - d_o)C_1] / (C_1^2 d_o) = [-1000(0.9 - 0.8)(0.05)] / [(0.05)^2 (0.8)]$$

$$\text{Thus, } \Delta V_\phi = 0.025 \text{ cm}^3 \cdot \text{mol}^{-1}$$

## Appendix 1.2.

### Calibration of the Hewlett-Packard 2804 $\Lambda$ Quartz Thermometer

The Hewlett Packard quartz thermometer was used for all the accurate temperature measurements in this work, and was calibrated against a Tinsley platinum resistance thermometer, which had been previously calibrated by the CSIR-South Africa. The resistance of the platinum thermometer at any temperature,  $T$ , was measured with an FE Smith difference bridge. This is a modification of a Kelvin double bridge. This and other Wheatstone bridge type assemblies have been discussed by Hall and Barber.<sup>(316)</sup> The off-balance current was amplified using a PYE Galvanometer Photocell preamplifier, and was fed to a PYE Scalamp galvanometer. A 2V emf source was used to drive the circuit.

The heating effects could not be neglected for accurate readings. To a first approximation the heating effect at different temperatures is constant if the current in the thermometer bulb is kept constant. This is only true if the conditions of heat transfer between the bulb and its surroundings remain approximately the same. For this reason calibration was carried out in an environment closely resembling that in which later measurements would be made. The calibration of the quartz thermometer was carried out at 5 K intervals over the temperature range 273 K to 323 K in a thermostatted bath similar to the one described in Chapter 2.

To eliminate any stray emf's it was necessary to take resistance readings of both the platinum resistance thermometer and of the standard resistance with the current flowing in both directions in turn; that is four readings,  $x_i$ , for each temperature. The resistance,  $R_T$ , of the thermometer at the temperature,  $T$ , is given to a good approximation by:

$$R_T = [(x_3 + x_4)/2] - [(x_1 + x_2)/2] \quad \text{B.1}$$

where the first term in equation B.1 corresponds to the average of the resistance of the

## Appendices

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standard resistance,  $R$ , with the current flowing in both directions, and the second term is with respect to the platinum resistance thermometer at the temperature,  $T$ .

Resistance readings were converted to temperature values using the iterative relationship:

$$T^* = [(R_T - R_0)/\alpha R_0] + \delta[(T/100) - 1](T/100) \quad \mathbf{B.2}$$

together with:

$$\dots\dots\dots t_{68} = T^* + 0.045(T^*/100)[(T^*/100) - 1][(T^*/630.74) - 1] \quad \mathbf{B.3}$$

where  $\alpha$ ,  $\delta$  and  $R_0$  are the constants for the platinum resistance thermometer. In this case:  $\alpha = 3.9214\text{E-}03$ ,  $\delta = 1.4962$  and  $R_0 = 24.9573\Omega$ .



### Appendix 1.3.

## GW Basic computer program. to determine excess molar volumes from density measurements

```

10  REM *****
20  REM THE FOLLOWING PROGRAM IS WRITTEN IN GWBASIC FOR ANY IBM PC 100%
30  REM COMPATIBLE WITH IBM PERSONAL COMPUTERS.
40  REM THIS PROGRAM CALCULATES EXCESS VOLUMES FOR BINARY LIQUID MIXTURES
50  REM FROM DENSITY MEASUREMENT, BY THE FOLLOWING SIMPLE RELATIONSHIP :
60  REM
70  REM   VE = ((XA*MA + XB MB) / P.UNKNOWN) - (CA + CB)
80  REM
90  REM
100 REM WHERE : P.UNKNOWN IS THE DENSITY OF THE MIXTURE
110 REM   C1 = ((XA*MA) / P.A)
120 REM   C2 = ((XB*MB) / P.B)
130 REM
140 REM
150 REM (AN ANTON PAAR VIBRATING TUBE DENSITOMETER WAS USED IN THIS STUDY)
160 REM

170 REM ORIGINALLY WRITTEN FOR APPLE BY : R C BAXTER, RHODES UNIVERSITY
180 REM CONVERTED TO GWBASIC FOR IBM BY : B BEAN , RHODES UNIVERSITY
185 REM ADAPTED FOR EXP USE BY           : J M-CHALMERS, RHODES UNIVERSITY
190 REM
200 CLS
210 PRINT "THE FOLLOWING PROGRAM CALCULATES EXCESS VOLUMES"
220 PRINT
230 PRINT "INPUT THE FOLLOWING CONSTANTS:"
240 PRINT "-----"
250 PRINT
260 REM *****
270 REM INPUT CONSTANTS
280 REM *****
290 PRINT"(MA AND MB - MOLAR MASSES, T-PERIODS FOR WATER(W), FOR STD(S),"
300 PRINT"AND FOR COMPOUNDS A AND B,"
310 PRINT"DW AND DS - THE DENSITIES OF WATER AND STD RESPECTIVELY,"
320 PRINT"B-MASSES OF SAMPLE CONTAINER(BO), CONTAINER+A(BA), CONTAINER+B(BB).
330 PRINT"T-PERIOD FOR UNKNOWN(U)"
340 PRINT
350 PRINT" NOTE :- SEPARATE VALUES BY COMMAS" : PRINT
360 PRINT" INPUT YOUR VALUES FOR: MA,MB,TW,TS,TA,TB,DW,DS"
370 INPUT MA,MB,TW,TS,TA,TB,DW,DS
380 PRINT : PRINT" INPUT YOUR VALUES FOR: BO,BA,BB,TU"
390 INPUT BO,BA,BB,TU
393 REM
394 REM
395 GOTO 1500 : REM *****          CALCULATE ANSWERS          *****
396 REM
397 REM
400 REM *****
401 REM
402 REM          PRODUCE OUTPUT
403 REM
404 REM *****
420 CLS
430 LPRINT"THE CONSTANTS ARE :"
440 LPRINT"-----"
450 LPRINT""
460 LPRINT"MA :",MA," MB :",MB,"
470 LPRINT"TW :",TW," TS :",TS,"
480 LPRINT"TA :",TA," TB :",TB,"
490 LPRINT"DW :",DW," DS :",DS,"
500 LPRINT"BO :",BO," BA :",BA,"
510 LPRINT"BB :",BB," TU :",TU,"
520 LPRINT""
530 LPRINT"THE RESULTS ARE :-"
540 LPRINT"-----"
550 LPRINT""
560 LPRINT"DENSITY OF MIXTURE = ",DU
570 LPRINT"-----"
580 LPRINT"MOLE FRACTION OF COMPONENT A = ",XA
590 LPRINT"-----"

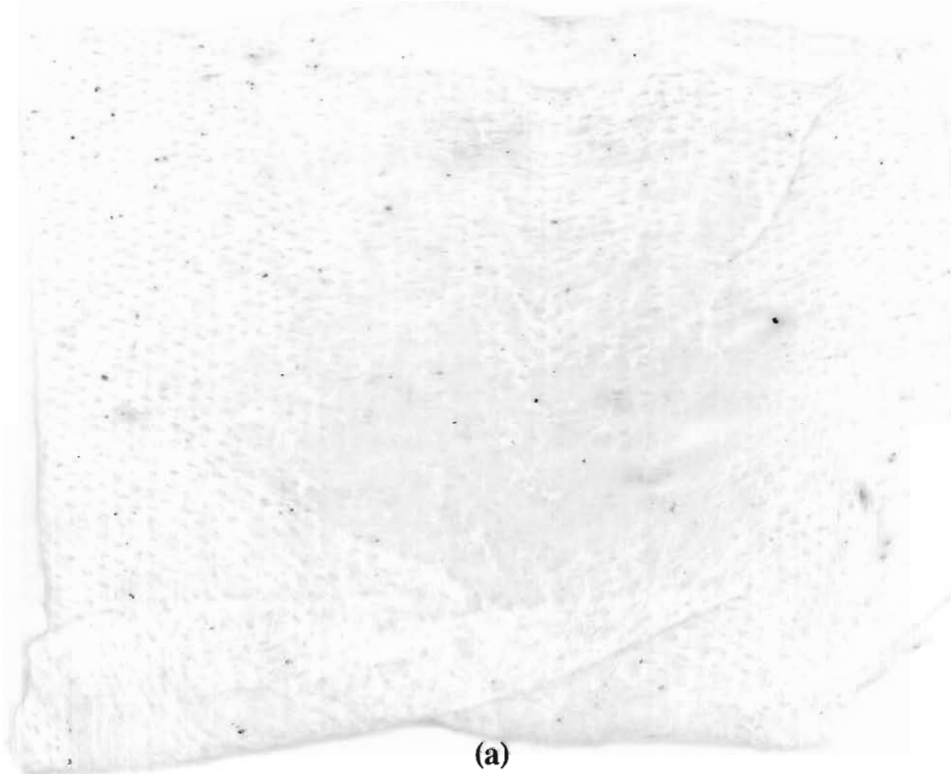
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```
600 LPRINT"EXCESS VOLUME = ",VE
1000 INPUT "ENTER OUTPUT DATA FILENAME.[<ENTER> TO SKIP]";FLNMS
1010 IF FLNMS = "" GOTO 2000
1020 OPEN "O",#1,FLNMS
1030 PRINT#1,"THE CONSTANTS ARE : "
1040 PRINT#1,"-----"
1050 PRINT#1," "
1060 PRINT#1,"MA : ",MA," MB : ",MB
1070 PRINT#1,"TW : ",TW," TS : ",TS
1080 PRINT#1,"TA : ",TA," TB : ",TB
1090 PRINT#1,"DW : ",DW," DS : ",DS
1100 PRINT#1,"BO : ",BO," BA : ",BA
1110 PRINT#1,"BB : ",BB," TU : ",TU
1120 PRINT#1," "
1130 PRINT#1,"THE RESULTS ARE :-"
1140 PRINT#1,"-----"
1150 PRINT#1," "
1160 PRINT#1,"DENSITY OF MIXTURE = ",DU
1170 PRINT#1,"-----"
1180 PRINT#1,"MOLE FRATION OF COMPONENT A = ",XA
1190 PRINT#1,"-----"
1200 PRINT#1,"EXCESS VOLUME = ",VE
1210 PRINT#1,"-----"
1220 CLOSE#1
1230 GOTO 2000
1400 REM
1410 REM
1420 REM
1500 REM *****
1510 REM
1520 REM                PERFORM CALCULATIONS
1530 REM
1540 REM
1550 REM *****
1560 REM CALCULATE MOLE FRACTIONS
1570 REM *****
1580 XA = ((BA - BO) / MA) / ((BA - BO) / MA + (BB - BA) / MB)
1590 XB = 1 - XA
1600 REM *****
1610 REM CALCULATE EXCESS VOLUME
1620 REM *****
1630 C = (DW - DS) / (TW^2 - TS^2)
1640 DU = C * (TU^2 - TW^2) + DW
1650 DA = C * (TA^2 - TW^2) + DW
1660 DB = C * (TB^2 - TW^2) + DW
1670 VE = (XA * MA + XB * MB) / DU - XA*MA/DA - XB*MB/DB
1680 REM *****
1690 REM END OF CALCULATIONS
1700 REM *****
1710 REM RETURN TO PRODUCE OUTPUT
1720 REM *****
1730 GOTO 400
2000 PRINT
2010 INPUT "DO YOU WANT TO USE THE PROGRAM AGAIN ?>";YNS
2020 IF (YNS="YES") OR (YNS="Y") OR (YNS="yes") OR (YNS="y") GOTO 2040
2030 IF (YNS="NO") OR (YNS="N") OR (YNS="no") OR (YNS="n") GOTO 2200
2035 GOTO 2010
2040 PRINT
2050 PRINT "DO YOU WANT TO EMPLOY THE SAME CONSTANTS IN YOUR NEXT CALCULATION?"
2060 INPUT ">";YNS
2070 IF (YNS="YES") OR (YNS="Y") OR (YNS="yes") OR (YNS="y") GOTO 380
2080 IF (YNS="NO") OR (YNS="N") OR (YNS="no") OR (YNS="n") GOTO 360
2090 GOTO 2050
2200 END
```

**Appendix 2.1.**



**(a)**

***Unbleached CPNF***

**(b)**

***Bleached CPNF***

## Appendix 2.2.

### SABS Method for Fluidity Determination

S A BUREAU OF STANDARDS

STANDARD METHODS

SABS Method 115

Second Revision

Fluidity of cotton and certain cellulosic man-made fibres  
in cuprammonium solution (Modified method)

#### SECTION 1. APPARATUS

1.1 A capillary viscometer<sup>1)</sup>, X-type

1.2 Bottles<sup>2)</sup>. Transparent polyethylene bottles of capacity  $35 \pm 5$  ml and fitted with an insert of one of the types shown in Fig. 1.

1.3 A camel-hair brush, artists' type

1.4 Steel balls. Stainless steel balls, 6 mm diameter.

1.5 Funnel. A short-stemmed glass funnel of nominal diameter 35 mm .

1.6 Oven. A drying oven maintained at  $105 \pm 5$  °C .

1.7 Revolving wheel. A wheel capable of being rotated at 4 r/min .

1.8 Water bath. A glass water bath maintained at  $20 \pm 2$  °C, of size such as to accommodate the bottle, and provided with a stirrer.

1.9 Stop-watches. Two stop-watches, each of accuracy 0,2 s (or better).

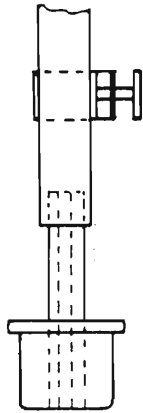
1.10 Balance. A balance having a sensitivity of 0,001 g (or better).

NOTE: In this method reference is made to the latest issues of BS Handbook 11, and SABS Methods 70, 114, and 1027.

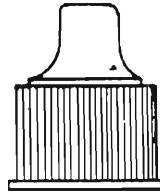
1) Calibrated viscometers are obtainable from the Shirley Institute, Didsbury, Manchester M20 8RX, United Kingdom. Uncalibrated viscometers can be manufactured locally to the dimensions prescribed in SABS Method 1027. The calibration of these viscometers is also given in SABS Method 1027.

2) Bottles with plug-type inserts that can be modified to the required shape and to carry the capillary tube(s) are obtainable locally.

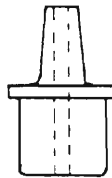
SABS Method 115



Alternative plug insert

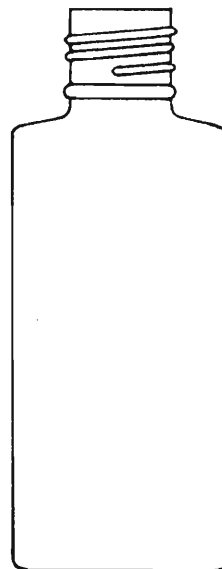


Cap



Modified plug insert

8425/1-1412/1



Polyethylene bottle

Fig. 1

SECTION 2. REAGENTS

2.1 Standard cuprammonium solvent<sup>3)</sup>. A solution, 1 ℓ of which contains  $15 \pm 0,1$  g of copper and  $200 \pm 5$  g of ammonia, and whose nitrous acid content is less than 0,5 g .

NOTE: It is essential that oxidation of this solvent be avoided by storing it in a blackened stoppered glass container at an ambient temperature of  $20 \pm 2$  °C .

SECTION 3. DETERMINATION OF THE TOTAL VOLUME ( $V_0$ ) ENCLOSED BY THE POLYETHYLENE BOTTLE

3.1 Place five stainless steel balls in the bottle. Push the insert into the neck of the bottle and determine the mass. Remove the insert and fill the bottle (still containing the steel balls) with distilled water at  $20 \pm 2$  °C, taking care to tap out any entrapped air bubbles. Push the insert fully home into the neck of the bottle so that the excess of water overflows and, without squeezing the bottle, carefully dry the outside of the bottle with blotting paper or a paper towel. Determine the mass. Record the difference between the initial and final masses of the bottle (containing the five steel balls) as the volume of liquid it will hold.

SECTION 4. PREPARATION OF TEST SPECIMEN

4.1 Desizing. From the test sample cut a portion of mass at least 5 g, desize it as described in SABS Method 114, dry it for 2 h in the oven, and condition it in accordance with SABS Method 70.

NOTE

- a) In the case of fabric, cut it first diagonally into narrow strips and then into short fragments.
- b) In the cases of fibres and yarns, cut them into very short lengths.

---

3) Instructions for the preparation of the solvent are contained in Section 5 of BS Handbook 11: 1974, but the solvent is also available commercially.

4.2 Determination of mass of specimen required for standard concentration

4.2.1 Cotton or cellulosic man-made fibres. Calculate, as follows, the mass of specimen needed to produce the required standard concentration of cellulose in the cuprammonium solvent:

$$M = \frac{V_o \times P}{100 - m}$$

where M = numerical value of the mass of the desized fibres required, g  
 V<sub>o</sub> = numerical value of the volume of the polyethylene bottle (see Section 3), cm<sup>3</sup>  
 P = standard percentage of cellulose required in the cuprammonium solution, i.e. 0,5 % in the case of cotton, and 2 % in the cases of rayon and cellulose acetate  
 m = assumed moisture content of the test specimen, i.e. 6 % for cotton, or 10 % for rayon and cellulose acetate

NOTE: The mass of acetate fibre required to give a 2 % solution of cellulose may be obtained from the following modification of the above formula:

$$M = 2V_o \left[ \frac{1}{90} \times \frac{142,9}{142,9 - A} \right]$$

where A = acetic acid yield of the desized fibres, i.e. 62,5 %, 48,8 %, and 29,4 % in the cases of triacetate, diacetate, and monoacetate respectively

4.2.2 Mixtures of cotton and cellulosic man-made fibres

a) Calculate, as follows, the mass of the desized and air-dry mixture needed to produce the standard concentration of cellulose in the cuprammonium solvent:

$$M = \frac{C_m V_o}{100}$$

where M = numerical value of the mass of desized and air-dry fibres required, g

C<sub>m</sub> = numerical value of the concentration of the air-dry mixture calculated in accordance with (b) below, g/100 ml

V<sub>o</sub> = numerical value of the volume of the polyethylene bottle, cm<sup>3</sup>

b) Calculate the required concentration C<sub>m</sub> as follows:

$$C_m = \frac{1}{1,5 R_c + 0,5}$$

where C<sub>m</sub> = the mass of air-dry mixture per 100 ml of solvent, g

R<sub>c</sub> = the mass of cotton per gram of air-dry mixture, g

NOTE: The above calculation gives a concentration which equals that which would have been obtained if the components had been separate, the whole of the cotton dissolved at a concentration of 0,5 %, the whole of the cellulosic man-made fibre dissolved at a concentration of 2 %, and the two solutions then mixed.

SECTION 5. PROCEDURE

NOTE: It is essential that in all operations the cuprammonium solvent and the solution of cellulose in cuprammonium are kept in subdued light and that the ambient temperature is between 18 and 22 °C during the outflow of the solution from the viscometer.

5.1 From the desized material (see 4.1) weigh out accurately a test specimen of the mass, determined in accordance with 4.2, that will provide a solution of standard concentration in the bottle. Using the funnel and brush, introduce the weighed specimen into the bottle and add five stainless steel balls.



SABS Method 115

Half fill the bottle with the cuprammonium solvent and shake it gently until the specimen is thoroughly wetted. Then, using the technique described for the determination of its volume, completely fill the bottle with the solvent.

5.2 Attach the bottle to the revolving wheel and rotate it for not less than 15 h and not more than 25 h. Place the bottle with its contents in the water bath, and cool until its contents reach a temperature of  $20 \pm 2$  °C. Then remove the bottle from the bath and dry it with blotting paper or a paper towel.

5.3 By holding the bottle against the light, check that the contents are free from undissolved cellulose. Then fill with the test solution the viscometer (clamped in an exactly vertical position) to above the top circumferential mark, by pouring the solution from the bottle into the open end of the viscometer, blocking the outlet as soon as the capillary is filled. Measure the times, in seconds, required for the meniscus to fall from the top mark to the intermediate mark, and from the top mark to the bottom mark and, by checking that the two periods are approximately equal, ensure that the capillary has not become partially choked during the outflow of the liquid.

SECTION 6. CALCULATIONS

6.1 Fluidity of cotton and cellulosic man-made fibres.

Calculate the fluidity as follows:

- a) If  $t > 200$  s,  $F = C'/t$
- b) If  $t \leq 200$  s,  $F = C'/(t - (K/t))$

where  $F$  = cuprammonium fluidity of the cellulose solution, rhe

\* $C'$  = viscometer constant

$t$  = total time for the meniscus of the liquid to travel from the top to the bottom circumferential mark, s

\* $K$  = kinetic energy constant of the viscometer

\*In the case of a viscometer supplied with a calibration certificate, these constants are supplied by the manufacturer of the viscometer.

6.2 Fluidity of mixtures of cotton and cellulosic man-made fibres. Calculate, as in 6.1, the fluidity of the mixture, and then use the following formula to calculate the cuprammonium fluidity of the cotton component:

$$F_c = 1,15 F_m - 2,2$$

where  $F_c$  = cuprammonium fluidity of the cotton component, rhe

$F_m$  = cuprammonium fluidity of the mixture, rhe

Record the cuprammonium fluidity to the nearest whole number.

NOTE

1) Owing to the variety of man-made cellulosic fibres that may be used and the variation in the percentage of man-made cellulosic fibres in the blend, the cotton fluidity may be in error by 1 or 2 units of cuprammonium fluidity.

2) Cuprammonium fluidity is the reciprocal of the dynamic viscosity of a solution of cellulose of prescribed concentration in a cuprammonium solvent of prescribed composition measured under precisely defined conditions. These solutions commonly exhibit non-Newtonian flow behaviour. Cuprammonium fluidity does not, therefore, have absolute physical significance as does the fluidity of a Newtonian liquid and, although it has been expressed in reciprocal poises, it is considered that it should be regarded as an empirical quantity and the results given in 'units of cuprammonium fluidity' and not in the SI unit  $\text{Pa}^{-1} \cdot \text{s}^{-1}$ .

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7 (7p.)

## Appendix 2.3.

### British Pharmaceuticals Test Method for Absorbency

A226 Appendix XX L

#### **A** Absorbency

##### Apparatus

A dry, cylindrical copper wire basket, 80 mm high and 50 mm in diameter, fabricated from wire of diameter 0.4 mm and having a mesh aperture of 15 to 20 mm; the basket weighs 2.4 to 3.0 g.

##### 1. Sinking time

**Method I** Weigh the basket to the nearest 10 mg. Take five samples, each of approximately 1 g, from different places in the material being examined, pack loosely in the basket and weigh the packed basket to the nearest 10 mg. Hold the basket with its long axis in the horizontal position and drop it from a height of about 10 mm into water at 20° contained in a beaker at least 12 cm in diameter and filled to a depth of 10 cm. Measure with a stopwatch the time taken by the basket to sink below the surface of the water. Repeat the procedure on two further samples and calculate the average value.

**Method II** Using forceps fold a sample of the material, weighing 1 g, four times (that is, into 16-ply) and smooth the surface. For narrow ribbon gauze, fold as many times as is necessary to obtain a length not greater than 8 cm. Allow the material to drop lightly on to the surface of water at 20° contained in a beaker at least 12 cm in diameter and filled to a depth of 10 cm. Measure with a stopwatch the time taken for the sample to sink below the surface of the water. Repeat the procedure on two further samples and calculate the average value.

##### 2. Water-holding capacity

After the sinking time has been recorded in Test 1, Method I remove the basket from the water, allow it to drain for 30 seconds with its long axis in the horizontal position, transfer it to a tared beaker and weigh to the nearest 10 mg. Calculate the weight of water retained by the sample. Repeat the procedure on two further samples and calculate the average value.

#### **M** Water-soluble Substances

Use Method I unless otherwise directed in the monograph.

##### Method I

Boil 7 g with 700 ml of water for 30 minutes, stirring frequently, and replace the water lost by evaporation. Decant the liquid into a beaker, squeeze the residual liquid from the material carefully with a glass rod, mix the liquids and filter the extract whilst hot. Evaporate 400 ml and dry the residue to constant weight at 100° to 105°.

##### Method II

Dry 5 g to constant weight at 105° and determine the loss of weight. Heat slowly with 400 ml of water and boil for 1 minute, cool by adding about the same quantity of water and decant the liquid through a sieve with a nominal mesh aperture of 106 µm, wringing the material by hand

to remove as much of the liquid as possible; return the material to the vessel and repeat the washing process with five 400-ml quantities of water. Place the washed material and any loose threads or fibres from the sieve in a beaker, cover with a 0.5% solution of diastase and maintain at 70°, or if the material being examined contains wool, 45° to 50°, until free from starch. Decant the liquid through the sieve, return any loose fibres or threads retained on the sieve to the bulk material in the vessel, repeat the washing process with boiling water and again return any loose fibres or threads retained on the sieve to the bulk material. Dry the material and determine the loss in weight.

For cotton crêpe, cotton stretch, cotton and rubber elastic, heavy cotton and rubber elastic and elastic net bandages, and unbleached calico that has not been dyed, subtract from the loss in weight 3% of the weight of the final dry sample; if the materials have been dyed, subtract 1%; with crêpe bandage and domette bandage, subtract 2%.

Calculate the percentage of water-soluble substances with reference to the material dried to constant weight at 105°.

#### **N** Ether-soluble Substances

Extract 5 g with ether in a Soxhlet apparatus for 4 hours, operating the apparatus in such a manner that the rate is at least four extractions per hour. Evaporate the ether extract and dry the residue to constant weight at 100° to 105°, unless otherwise specified in the monograph.

#### **O** Colour Fastness

Make two 8-ply pads, 5 cm × 5 cm, of the material being examined, place each pad between two pieces of standard undyed bleached cotton lawn and, for each set, sew the three pieces of material together along one edge to form a composite pad. Carry out Test A and Test B.

##### Test A

Saturate one of the composite pads with ethanol (70%), lay it smoothly in a suitable flat-bottomed dish, add sufficient ethanol (70%) to cover the pad completely, place a smooth, square glass plate, with sides of 5 cm and weighing about 50 g, centrally on top of the pad, press lightly on the glass plate to remove air bubbles and allow to stand at 36° to 38° for 15 minutes. Without removing the glass plate, pour off the ethanol and allow the pad to stand at 36° to 38° for 4 hours. Remove the glass plate, separate the three pieces of cloth forming the composite pad, allow them to dry separately at a temperature not exceeding 60° and examine the two outer pieces of undyed cloth for staining. They are virtually unstained.

##### Test B

Subject the other composite pad to steam at 134° to 138° for 3 minutes in an autoclave together with a separate piece of the standard undyed bleached cotton lawn. Separate the three pieces of cloth forming the composite pad and compare the two outer pieces of cloth with the separate

seed coat or other impurities. It offers appreciable resistance when pulled and does not shed a significant quantity of dust when shaken gently.

**Fibre identification** Complies with tests A, B and D for cotton, Appendix XX A.

**Absorbency:** The *sinking time* is not more than 10 seconds, Appendix XX L1, Method I, and the *water-holding capacity* is not less than 23.0 g g<sup>-1</sup>, Appendix XX L2.

**Acidity or alkalinity** To 15 g add 150 ml of water, macerate for 2 hours in a closed vessel, decant the liquid, carefully squeezing out the residual liquid with a glass rod and mix. Reserve 10 ml for the test for Surface-active substances and filter the remainder. To 25 ml of the filtered extract add 0.1 ml of *dilute phenolphthalein solution*; to another 25 ml add 0.05 ml of *methyl orange solution*. Neither solution shows a pink colour.

**Colouring matter** Slowly extract 10 g in a narrow percolator with *ethanol (96%)* until 50 ml of extract is obtained. The extract is not more intensely coloured than *reference solution Y*, or *GY*, Appendix IV B, Method I, or a solution prepared in the following manner. To 3.0 ml of *blue primary solution* add 7.0 ml of a solution of *hydrochloric acid* containing 1% w/v of HCl and dilute 0.5 ml of the resulting solution to 10 ml with the same solution of hydrochloric acid.

**Ether-soluble substances** Not more than 0.50%, Appendix XX N.

**Fluorescence** When examined under ultra-violet light (365 nm) a layer about 5 mm in thickness displays only a slight brownish-violet fluorescence and a few yellow particles. Not more than a few isolated fibres show an intense blue fluorescence.

**Foreign fibres** When examined under a microscope, it is seen to consist almost exclusively of typical cotton fibres. Only occasional isolated foreign fibres may also be present.

**Neps** When 1 g is spread evenly between two colourless, transparent plates, each 10 cm × 10 cm, and examined for neps by transmitted light, it is not more neppy than the *European Pharmacopœia Standard for neps*.

**Surface-active substances** Introduce into a 25-ml graduated, ground-glass stoppered cylinder with an external diameter of 18 to 22 mm, previously rinsed with *sulphuric acid* and then with *water*, the portion of the extract reserved in the test for Acidity or alkalinity, shake vigorously 30 times in 10 seconds, allow to stand for 1 minute and repeat the shaking. After 5 minutes the height of froth does not exceed 2 mm above the surface of the liquid.

**Water-soluble substances** Not more than 0.50%, Appendix XX M. Use 5 g and 500 ml of *water*.

**Loss on drying** When dried to constant weight at 100° to 105°, loses not more than 8.0% of its weight. Use 5 g.

**Sulphated ash** Not more than 0.40%, Appendix XX S.

## Absorbent Cotton and Viscose Gauze

Absorbent Cotton and Viscose Gauze consists of fabric of plain weave, in which the warp threads are of cotton and the weft threads are of viscose or of combined cotton and viscose yarn, or the warp threads are of combined cotton and viscose yarn and the weft threads are of cotton or of combined cotton and viscose yarn. It is bleached to a good white and purified. It is practically odourless, reasonably free from weaving defects and contains not more than traces of leaf residue, seed coat and other impurities.

**Fibre identification** Complies with the tests for cotton and viscose, Appendix XX A.

**Content of viscose** Not more than 45% when determined by Method 3 of British Standard 4407:1975 (Methods of test. Quantitative analysis of fibre mixtures).

**Absorbency** *Sinking time* Not more than 10 seconds, Appendix XX L1, Method I.

**Acidity or alkalinity** To 10 g add 100 ml of *water*, macerate for 2 hours in a closed vessel, decant the liquid, carefully squeezing out the residual liquid with a glass rod, mix, reserve 10 ml for the test for Surface-active substances and filter the remainder. To 25 ml of the filtered extract add 0.15 ml of *dilute phenolphthalein solution*; to another 25 ml add 0.05 ml of *methyl orange solution*. Neither solution shows a pink colour.

**Colouring matter** Slowly extract 10 g in a percolator about 30 mm in diameter with *ethanol (96%)* until 50 ml of extract is obtained, pour the liquid into a colourless glass cylinder and examine a 20-cm layer against a white background. A very faint yellowish tinge may be observed, but no bluish or greenish tinge is present.

**Threads per 10 cm** Type 1: warp, 69 to 77; weft, 53 to 61; Type 2: warp, 69 to 77; weft, 41 to 49; Appendix XX C1, Method I.

**Weight per unit area** Type 1: not less than 14.0 g m<sup>-2</sup>; Type 2: not less than 13.0 g m<sup>-2</sup>; Appendix XX D1, Method III.

**Ether-soluble substances** Not more than 0.50%, Appendix XX N.

**Fluorescence** When examined under ultra-violet light (365 nm) a two-ply layer may display only a slight brownish-violet fluorescence and a few yellow particles. Not more than a few isolated fibres show an intense blue fluorescence.

**Starch and dextrin** To the 200 ml of cooled extract reserved in the test for Water-soluble substances add 5 ml of 5M *acetic acid* and 0.15 ml of 0.05M *iodine*. No blue, violet, reddish or brownish colour is produced.

**Surface-active substances** Shake vigorously in a clean test-tube the portion of the aqueous extract reserved in the test for Acidity or alkalinity and examine after 10 minutes. Not more than a ring of froth, in contact with the walls of the tube, remains.

**Water-soluble substances** Not more than 0.50%, Appendix XX M. Reserve 200 ml for the test for Starch and dextrin before filtering the extract.

**Loss on drying** When dried to constant weight at 100° to 105°, loses not more than 11.0% of its weight. Use 5 g.

**Loss on drying** When dried to constant weight at 100° to 105°, loses not more than 11.0% of its weight. Use 5 g.

**Sulphated ash** For products containing bright viscose, not more than 0.45%; for products containing matt viscose, not more than 1.2%, Appendix XX S, Method III. Use 5 g.

**Labelling** The label on the package states the type, the length and the width.

Only Absorbent Cotton and Viscose Ribbon Gauze Type 22b is usually available in the United Kingdom. In the absence of instructions to the contrary in the prescription or order, Absorbent Cotton and Viscose Ribbon Gauze Type 22b shall be supplied.

### Absorbent Cotton and Viscose Wadding

Absorbent Cotton and Viscose Wadding consists of a well-carded blend of Absorbent Cotton and Absorbent Viscose Wadding in approximately equal amounts. It is white or slightly yellow and practically odourless. It contains not more than traces of leaf residue, pericarp, seed coat or other impurities. It is composed of fibres of average length not less than 10 mm. It offers appreciable resistance when pulled and does not shed a significant quantity of dust when shaken gently.

The viscose component consists of either Viscose or Matt Viscose, but not a mixture of the two.

**Fibre identification** Complies with the tests for cotton and viscose, Appendix XX A.

**Content of cotton** 40 to 60%, calculated with reference to the dried material, when determined by the following method.

Cut the wadding in a cross-section to obtain a sample weighing 0.5 to 0.7 g, dry it at 105° to 110° and reweigh. Place the sample in a wide-necked flask with a ground-glass stopper, add 50 ml of zinc chloride solution, previously heated to 40°, stopper the flask, shake vigorously, allow to stand for 2.5 hours, shaking twice during this period, and filter through sintered glass. Wash the residue, first with zinc chloride solution and then with water until the filtrate is neutral to litmus paper, dry the residue at 105° to 110° and weigh. Calculate the cotton content of the wadding assuming the residue to be cotton. Repeat the operation using a further three samples and calculate the average result.

**Absorbency** The *sinking time* is not more than 10 seconds, Appendix XX L1, Method I, and the *water-holding capacity* is not less than 20.0 g g<sup>-1</sup>, Appendix XX L2.

**Ether-soluble substances** Not more than 0.4%, Appendix XX N.

**Water-soluble substances** Not more than 0.6%, Appendix XX M.

**Loss on drying** When dried to constant weight at 100° to 105°, loses not more than 11.0% of its weight. Use 5 g.

**Sulphated ash** For wadding containing Viscose, not more than 0.45%; for wadding containing Matt Viscose, not more than 1.2%, Appendix IX A, Method II. Use 5 g.

### Absorbent Cotton Gauze ☆

Absorbent Gauze

Absorbent Cotton Gauze consists of cotton fabric of plain weave, bleached to a good white and purified. It is practically odourless, reasonably free from weaving defects and contains not more than traces of leaf residue, pericarp, seed coat or other impurities.

**Fibre identification** The warp and weft threads comply with tests A, B and D for cotton, Appendix XX A.

**Absorbency** *Sinking time*, not more than 10 seconds, Appendix XX L1, Method II.

**Acidity or alkalinity** To 15.0 g add 150 ml of water, allow to macerate for 2 hours in a closed vessel, decant the solution, carefully squeezing out the residual liquid with a glass rod, and mix. Reserve 10 ml for the test for Surface-active substances and filter the remainder. To 25 ml of the filtered aqueous extract add 0.10 ml of dilute phenolphthalein solution; to another 25 ml add 0.05 ml of methyl orange solution. Neither solution shows a pink colour.

**Colouring matter** Slowly extract 10.0 g in a narrow percolator with ethanol (96%) until 50 ml of extract is obtained. The liquid is not more intensely coloured than reference solution Y<sub>3</sub> or GY<sub>6</sub>, Appendix IV B, Method I, or a solution prepared in the following manner. To 3.0 ml of blue primary solution add 7.0 ml of a solution of hydrochloric acid containing 1% w/v of HCl and dilute 0.5 ml of the resulting solution to 10 ml with the same solution of hydrochloric acid.

**Minimum breaking load** Complies with the appropriate requirements given in the Table, Appendix XX E, Method IV.

**Threads per 10 cm** Complies with the appropriate requirements given in the Table when determined by the following method. Count the number of threads in the warp and in the weft in a square piece with sides of 10 cm, well away from the edges. Make three counts in each of the warp and the weft, not including the same threads in the different counts, and calculate the average count in each direction.

**Weight per unit area** Complies with the appropriate requirement given in the Table when determined by weighing a piece 100 cm long using the full width or, for smaller samples, pieces of not less than 250 cm<sup>2</sup>, giving a total surface of not less than 0.5 m<sup>2</sup> and calculating the weight per unit area.

Appendices

Appendix 2.4.

Statgraphics Computer Printout

Cursor at Row: 15      Data Editor      Maximum Rows: 15  
 Column: 1      File: STATC1      Number of Cols: 4

Run	x1	x2	x3	whiteness
2	12.	4.	45.	80.77
3	8.	2.	25.	77.01
4	8.	6.	45.	79.80
5	4.	4.	25.	79.49
6	12.	4.	25.	77.02
7	12.	6.	35.	80.45
8	8.	4.	35.	80.28
9	8.	2.	45.	79.98
10	8.	6.	25.	77.13
11	12.	2.	35.	76.70
12	4.	4.	45.	81.64
13	4.	6.	35.	81.13
14	4.	2.	35.	73.24
15	8.	4.	35.	80.32

Length	15	15	15	15
Typ/Wth	N/13	N/13	N/13	N/13

Model fitting results for: W.w

Independent variable	coefficient	std. error	t-value	sig.lev
CONSTANT	60.5875	18.530815	3.2696	0.02
W.x1	0.765	1.524622	0.5018	0.63
W.x2	5.62	3.049244	1.8431	0.12
W.x3	0.08975	0.819753	0.1095	0.91
(W.x1)*(W.x1)	-0.038437	0.067954	-0.5656	0.59
(W.x2)*(W.x2)	-0.46625	0.271814	-1.7153	0.14
(W.x3)*(W.x3)	-0.00015	0.010873	-0.0138	0.98
(W.x1)*(W.x2)	-0.129375	0.130575	-0.9908	0.36
(W.x1)*(W.x3)	0.01	0.026115	0.3829	0.71
(W.x2)*(W.x3)	-0.00375	0.05223	-0.0718	0.94

R-SQ. (ADJ.) = 0.1741    SE=      2.089206    MAE=      1.000000    DurbWat= 2.88  
 Previously: 0.0000      0.000000      0.000000      0.00  
 15 observations fitted, forecast(s) computed for 0 missing val. of dep. var.

## Appendices

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### Analysis of Variance for the Full Regression

Source	Sum of Squares	DF	Mean Square	F-Ratio	P-val
Model	52.1618	9	5.79575	1.32785	.39
Error	21.8239	5	4.36478		
Total (Corr.)	73.9857	14			

R-squared = 0.705025

R-squared (Adj. for d.f.) = 0.174071

Std. error of est. = 2.089

Durbin-Watson statistic = 2.886

### Regression results for W.w

Observation Number	Observed Values	Fitted Values
1	80.4800	80.3600
2	80.7700	81.5025
3	77.0100	75.5150
4	79.8000	81.2950
5	79.4900	78.7575
6	77.0200	77.8175
7	80.4500	78.2225
8	80.2800	80.3600
9	79.9800	78.5500
10	77.1300	78.5600
11	76.7000	77.3975
12	81.6400	80.8425
13	81.1300	80.4325
14	73.2400	75.4675
15	80.3200	80.3600

## Appendix 2.5.

### Published Papers

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39

### Excess molar enthalpies and excess molar volumes of mixtures of cycloalkanes and pseudo-cycloalkanes

T.M. Letcher<sup>a,\*</sup>, J.D. Mercer-Chalmers<sup>a</sup>, U.P. Govender<sup>a</sup> and R. Battino<sup>b</sup>

<sup>a</sup> *Department of Chemistry and Applied Chemistry, University of Natal, Durban (South Africa)*

<sup>b</sup> *Department of Chemistry, Wright State University, Dayton, OH (USA)*

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#### Abstract

Excess molar enthalpies and volumes were measured at atmospheric pressure and at 298.15 K for three-component systems. A pseudo-cycloalkane of carbon number  $m$  was mixed with a cycloalkane of carbon number  $m$  over the whole composition range. The values of  $m$  ranged from 6 to 8. The results were used to test the principle of congruence.

#### INTRODUCTION

In an earlier investigation [1], we tested the principle of congruence on a mixture of alkanes and pseudo-alkanes, by means of a novel null method. In this work, a novel set of mixtures involving accurately made up pseudo-cycloalkanes has been used to test the principle which implies that a pseudo-cycloalkane  $[0.5c-C_kH_{2k} + 0.5c-C_lH_{2l}]$  will behave like  $c-C_mH_{2m}$  where  $m = (k + l)/2$ . This paper reports  $H_m^E$  and  $V_m^E$  values for (pseudo- $c-C_8H_{16}$   $[0.5c-C_6H_{12} + 0.5c-C_{10}H_{20}] + c-C_8H_{16}$ ), and (pseudo- $c-C_7H_{14}$   $[0.5c-C_8H_{16} + 0.5c-C_6H_{12}] + c-C_7H_{14}$ ) and  $H_m^E$  values for (pseudo- $c-C_6H_{12}$   $[0.5c-C_5H_{10} + 0.5c-C_7H_{14}] + c-C_6H_{12}$ ) and ( $[0.6c-C_5H_{10} + 0.4c-C_{10}H_{20}] + c-C_7H_{14}$ ).

#### EXPERIMENTAL

The cyclopentane was obtained from Fluka (>99% GC), the cyclohexane from SARchem (99% GC), the cycloheptane from Aldrich (>99% GC), the cyclooctane from Janssen Chemicals (>99% GC), and the



cyclodecane from Fluka (>99% GC). The pseudo-cycloalkanes were made up as previously described [1]. The  $H_m^E$  values were measured using an LKB 2277 (Bioactivity Monitor) microflow calorimeter, and the  $V_m^E$  values were measured using an Anton Paar DMA 601 vibrating-tube densimeter. The methods have been previously described [2, 3].

RESULTS

The  $H_m^E$  results are given in Table 1, together with the deviations  $\Delta$ , where

$$\Delta = H_m^E/\text{J mol}^{-1} - x(1-x) \sum_{r=0}^n A_r(1-2x)^r$$

The  $V_m^E$  values are given in Table 2, together with the deviations  $\Delta'$ , where

$$\Delta' = V_m^E/\text{cm}^3 \text{ mol}^{-1} - x(1-x) \sum_{r=0}^n B_r(1-2x)^r$$

The experimental error in  $H_m^E$  is of the order of  $1 \text{ J mol}^{-1}$  or 1%, and in

TABLE 1

Excess molar enthalpies  $H_m^E$  for  $x(0.5\text{c-C}_k\text{H}_{2k} + 0.5\text{c-C}_l\text{H}_{2l}) + (1-x)\text{c-C}_m\text{H}_{2m}$ , where  $m = (k+l)/2$  and for  $x(0.6\text{c-C}_5\text{H}_{10} + 0.4\text{c-C}_{10}\text{H}_{20}) + (1-x)\text{c-C}_7\text{H}_{14}$  at 298.15 K

$x$	$H_m^E/\text{J mol}^{-1}$	$\Delta$	$x$	$H_m^E/\text{J mol}^{-1}$	$\Delta$	$x$	$H_m^E/\text{J mol}^{-1}$	$\Delta$
$x(0.5\text{c-C}_5\text{H}_{10} + 0.5\text{c-C}_7\text{H}_{14}) + (1-x)\text{c-C}_6\text{H}_{12}$								
0.1120	9.2	-0.1	0.5609	21.6	0.6	0.8466	10.8	-0.1
0.1638	12.7	0.1	0.6038	20.2	-0.3	0.8787	8.6	-0.2
0.3524	19.6	-0.1	0.7204	17.5	0.1	0.9045	7.3	0.3
0.5408	20.7	-0.4						
$x(0.5\text{c-C}_8\text{H}_{16} + 0.5\text{c-C}_6\text{H}_{12}) + (1-x)\text{c-C}_7\text{H}_{14}$								
0.0648	0.6	0.03	0.4833	2.2	0.04	0.7482	1.6	-0.3
0.1526	1.3	-0.04	0.6222	2.2	-0.4	0.8191	1.3	-0.09
0.1807	1.6	0.03	0.6605	2.9	0.5	0.8287	1.5	0.2
0.2708	2.2	-0.02						
$x(0.5\text{c-C}_{10}\text{H}_{20} + 0.5\text{c-C}_6\text{H}_{12}) + (1-x)\text{c-C}_8\text{H}_{16}$								
0.1676	4.5	-0.4	0.4881	8.6	0.03	0.8168	5.5	-0.04
0.1984	6.1	0.4	0.5638	8.9	-0.2	0.8758	4.2	-0.2
0.3642	8.6	0.0	0.7796	8.3	0.3			
$x(0.6\text{c-C}_5\text{H}_{10} + 0.4\text{c-C}_{10}\text{H}_{20}) + (1-x)\text{c-C}_7\text{H}_{14}$								
0.1625	26.3	0.04	0.4306	47.8	1.5	0.8395	23.1	-0.3
0.2799	39.2	-0.1	0.5307	44.2	-0.9	0.8712	19.8	0.1
0.3991	44.9	-0.8	0.6805	37.8	0.4			

TABLE 2

Excess molar volumes  $V_m^E$  for  $x(0.5c-C_kH_{2k} + 0.5c-C_lH_{2l}) + (1-x)c-C_mH_{2m}$  where  $m = (k + l)/2$  at 298.15 K

$x$	$V_m^E/$ $cm^3 mol^{-1}$	$\Delta$	$x$	$V_m^E/$ $cm^3 mol^{-1}$	$\Delta$	$x$	$V_m^E/$ $cm^3 mol^{-1}$	$\Delta$
$x(0.5c-C_8H_{16} + 0.5c-C_6H_{12}) + (1-x)c-C_7H_{14}$								
0.2191	-0.00203	0.0020	0.4706	-0.00034	0.002	0.7337	-0.00237	0.002
0.3631	-0.00300	-0.001	0.6263	-0.00562	-0.002	0.8569	-0.00488	-0.0006
$x(0.5c-C_6H_{12} + 0.5c-C_{10}H_{20}) + (1-x)c-C_8H_{16}$								
0.0505	-0.00181	-0.003	0.5015	-0.02492	-0.002	0.8135	-0.01438	-0.0004
0.2134	-0.00736	0.003	0.6416	-0.01756	0.002	0.8910	-0.01073	-0.0005
0.3999	-0.02237	-0.0007						

TABLE 3

Coefficients  $A$ , and  $B$ , for  $H_m^E$  or  $V_m^E$  [ $x(0.5c-C_kH_{2k} + 0.5c-C_lH_{2l}) + (1-x)c-C_mH_{2m}$ ] where  $m = (k + l)/2$  and [ $x(0.6c-C_5H_{10} + 0.4c-C_{10}H_{20}) + (1-x)c-C_7H_{14}$ ]

Mixture	$A_0$	$A_1$	$A_2$
$x(0.5c-C_5H_{10} + 0.5c-C_7H_{14}) + (1-x)c-C_6H_{12}$	85.2145	-0.9939	5.7348
$x(0.5c-C_8H_{16} + 0.5c-C_6H_{12}) + (1-x)c-C_7H_{14}$	11.4067	1.3863	-3.4867
$x(0.5c-C_{10}H_{20} + 0.5c-C_6H_{12}) + (1-x)c-C_8H_{16}$	35.3082	7.7945	2.3380
$x(0.6c-C_5H_{10} + 0.4c-C_{10}H_{20}) + (1-x)c-C_7H_{14}$	183.5826	37.7464	-2.1561
	$B_0$	$B_1$	$B_2$
$x(0.5c-C_8H_{16}) + 0.5c-C_6H_{12}) + (1-x)c-C_7H_{14}$	-0.0092	0.0109	-0.0326
$x(0.5c-C_6H_{12} + 0.5c-C_{10}H_{20}) + (1-x)c-C_8H_{16}$	-0.0913	-0.0099	0.0529

$V_m^E$  they are of the order of  $0.002 cm^3 mol^{-1}$ , and in  $x$  it is estimated to be less than  $1 \times 10^{-4}$ . The coefficients  $A$ , and  $B$ , are given in Table 3.

DISCUSSION

Our results show a small positive excess enthalpy and a small negative excess volume of mixing for all the mixtures. Mixtures containing the  $c-C_5H_{10}$  appear to produce the greatest divergence from the congruence principle. This shows that the effect of adding a  $-CH_2-$  group to  $c-C_5H_{10}$  is not the same as the addition of a  $-CH_2-$  group to  $c-C_8H_{16}$  or  $c-C_{10}H_{20}$ . In general, the greater the disparity in the carbon number the greater the divergence from the congruence principle. The cycloalkane mixtures do not satisfy the congruence principle as well as the  $n$ -alkane mixtures do.

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## Excess molar enthalpies and excess molar volumes of binary mixtures of 1-alkenes with 1-propanol and 2-propanol

T.M. Letcher <sup>a,\*</sup>, J. Mercer-Chalmers <sup>a</sup>, U.P. Govender <sup>a</sup> and S. Radloff <sup>b</sup>

<sup>a</sup> *Department of Chemistry, University of Natal, Durban (South Africa)*

<sup>b</sup> *Department of Mathematical Statistics, Rhodes University, Grahamstown (South Africa)*

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### Abstract

Molar excess enthalpies  $H_m^E$  and molar excess volumes  $V_m^E$  have been determined using a Thermometric flow calorimeter and a Paar DMA 601 density meter, respectively. The measurements were made over the whole composition range for mixtures of 1-hexene, 1-heptene and 1-octene with 1-propanol and 2-propanol at 298.15 K. The results were compared with  $H_m^E$  and  $V_m^E$  values for binary mixtures of a 1-alkene with methanol and ethanol, and of an *n*-alkane with an alkanol, in order to determine the effect of the double bond in the 1-alkene on the measured properties.

### INTRODUCTION

In a previous paper [1] the molar excess enthalpies  $H_m^E$  and molar excess volumes  $V_m^E$  at 298.15 K for binary mixtures of a 1-alkene with methanol and ethanol were reported and discussed. In this work, the above  $H_m^E$  and  $V_m^E$  measurements were extended to include the alkanols, 1-propanol and 2-propanol. The results are discussed in terms of specific interactions between the double bond in the 1-alkene and the hydroxyl group in the alkanol and the hydrogen bonds in the alkanol.

### EXPERIMENTAL

1-Hexene, 1-heptene and 1-octene were supplied by the Aldrich Chemical Co., and distilled before use. Analysis by GLC showed that total impurities were less than 0.2 mol% for 1-hexene and 1-heptene and less than 0.5 mol.% for 1-octene.

The propanols, supplied by Aldrich Chemical Company, were dried repeatedly using the method of Lund and Bjerrum [2]. The alcohols were analysed for water content before mixing using a Karl-Fischer titration

\* Corresponding author.

TABLE 1

Excess enthalpy  $H_m^E$  data in  $J\ mol^{-1}$  for binary mixtures of 1-hexene, 1-heptene and 1-octene with 1-propanol and 2-propanol at 298.15 K

$x$	$H_m^E$	$\Delta'$	$x$	$H_m^E$	$\Delta'$	$x$	$H_m^E$	$\Delta'$
$xC_6H_{12} + (1-x)CH_3CH_2CH_2OH$								
0.0518	75.6	0.2	0.3409	428.8	-1.5	0.7014	655.2	-1.4
0.0836	119.2	-0.3	0.4222	510.7	-1.9	0.7489	640.5	4.2
0.1202	168.5	0.0	0.5052	588.2	3.3	0.8016	585.3	-1.2
0.1895	255.6	-0.9	0.5956	639.8	-1.5	0.8722	461.4	-0.8
0.2518	332.3	1.4	0.6636	658.2	-1.1	0.9334	285.7	0.2
0.2944	380.8	1.3						
$xC_7H_{14} + (1-x)CH_3CH_2CH_2OH$								
0.0559	90.2	1.7	0.4533	598.9	2.9	0.7768	664.8	-1.0
0.0928	144.4	-0.6	0.5317	662.8	1.2	0.7932	647.4	0.3
0.1655	252.4	1.1	0.6157	705.8	-1.4	0.8206	611.5	3.8
0.2072	305.2	-3.7	0.6824	713.5	-2.6	0.9007	420.8	-1.8
0.2807	408.1	3.4	0.7352	699.8	0.9	0.9536	228.2	-0.7
0.3746	511.8	-3.5						
$xC_8H_{16} + (1-x)CH_3CH_2OH_2OH$								
0.0944	169.6	-0.7	0.4798	667.7	0.2	0.7504	730.6	1.6
0.1361	239.9	0.5	0.5387	712.8	0.0	0.8226	640.4	1.0
0.1773	303.8	-0.1	0.6116	749.8	-0.6	0.8612	560.2	1.1
0.2539	414.4	0.3	0.6848	759.0	0.6	0.9033	435.6	-3.7
0.4005	591.0	-0.1	0.7094	750.4	-1.7	0.9568	230.1	1.9
$xC_6H_{12} + (1-x)CH_3CH(OH)CH_3$								
0.0736	151.4	-0.5	0.3294	636.5	0.7	0.6756	863.5	-4.9
0.1446	308.5	3.7	0.3489	660.9	-3.1	0.7044	859.7	0.5
0.1975	412.8	-0.1	0.4357	763.5	0.1	0.7647	811.7	-3.1
0.2556	521.5	0.9	0.5265	838.2	4.1	0.8335	704.6	-2.8
0.2812	560.4	-3.3	0.5734	862.2	5.1	0.9066	502.2	6.8
$xC_7H_{14} + (1-x)CH_3CH(OH)CH_3$								
0.0808	192.4	0.5	0.4455	830.7	3.5	0.7736	833.8	0.1
0.1432	344.8	2.7	0.4677	846.2	1.6	0.8062	786.1	-0.4
0.1814	428.0	-0.7	0.4955	862.0	-1.5	0.8516	690.7	-0.9
0.2526	571.0	-1.6	0.5594	894.7	0.2	0.9055	516.2	-4.5
0.3066	662.7	-1.1	0.6655	904.3	0.0	0.9449	352.6	8.8
0.3304	696.9	-2.0	0.7405	866.7	-0.7			
$xC_8H_{16} + (1-x)CH_3CH(OH)CH_3$								
0.0736	209.4	3.4	0.3133	726.4	1.3	0.6142	952.5	0.1
0.1144	314.8	0.0	0.3970	831.3	-0.4	0.6926	935.5	0.1
0.1425	382.4	-3.3	0.4574	885.7	-1.2	0.7759	858.4	-0.6
0.1622	433.7	0.5	0.5188	926.9	0.9	0.8326	752.7	-2.1
0.2429	605.0	-0.4	0.5333	933.7	0.9	0.9059	528.9	2.7
0.2590	635.2	-0.1						

procedure. The water content was always found to be <0.02 mol.%. The densities of the 1-hexene, 1-heptene, 1-octene, 1-propanol and 2-propanol were found to be 0.6684, 0.6926, 0.7107, 0.7998 and 0.7815 g cm<sup>-3</sup>, respectively.

RESULTS

Results for  $H_m^E$  and  $V_m^E$  are given in Tables 1 and 2, respectively, together with the corresponding deviations  $\Delta'$  and  $\Delta''$ . The deviations were

TABLE 2

Excess volume  $V_m^E$  data in cm<sup>3</sup> mol<sup>-1</sup> for binary mixtures of 1-hexene, 1-heptene and 1-octene with 1-propanol and 2-propanol at 298.15 K

$x$	$V_m^E$	$\Delta'' \times 10^4 x$	$V_m^E$	$\Delta'' \times 10^4 x$	$V_m^E$	$\Delta'' \times 10^4$
$x\text{C}_6\text{H}_{12} + (1-x)\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$						
0.0394	-0.032	1	0.3773	-0.038	-5	0.8027
0.1273	-0.071	10	0.4837	0.012	28	0.8362
0.1995	-0.081	-15	0.5917	0.056	-35	0.9100
0.2673	-0.071	4	0.7237	0.108	15	0.084
$x\text{C}_7\text{H}_{14} + (1-x)\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$						
0.0276	-0.001	-7	0.4013	0.123	-6	0.8314
0.0779	0.001	-32	0.4706	0.154	-9	0.8736
0.1747	0.031	37	0.5563	0.189	10	0.9276
0.3181	0.084	-9	0.6964	0.214	2	0.100
$x\text{C}_8\text{H}_{16} + (1-x)\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$						
0.0492	0.023	-21	0.3195	0.179	-30	0.6133
0.0900	0.053	31	0.4401	0.230	25	0.7134
0.1673	0.100	9	0.5232	0.253	20	0.8703
0.2333	0.137	-15				0.225
$x\text{C}_6\text{H}_{12} + (1-x)\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$						
0.0557	0.021	1	0.3694	0.276	-28	0.7268
0.1294	0.061	-27	0.4987	0.382	-22	0.8254
0.1950	0.115	8	0.6039	0.427	18	0.8910
0.2680	0.185	44				0.205
$x\text{C}_7\text{H}_{14} + (1-x)\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$						
0.0566	0.069	-33	0.3505	0.393	-2	0.7241
0.1031	0.131	19	0.4667	0.480	-9	0.8704
0.1886	0.227	-13	0.6027	0.525	-14	0.9409
0.2516	0.299	23				0.160
$x\text{C}_8\text{H}_{16} + (1-x)\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$						
0.0419	0.074	-1	0.3305	0.434	15	0.7012
0.0916	0.153	-1	0.4383	0.511	-7	0.8534
0.1633	0.253	3	0.5435	0.555	2	0.9401
0.2304	0.332	-10				0.170

TABLE 3

Values at 298.15 K of coefficients  $A_r$  in  $\text{J mol}^{-1}$  for eqn. (1)

Mixture	$A_r$			
	$A_0$	$A_1$	$A_2$	$A_3$
$x1\text{-C}_6\text{H}_{12} + (1-x)\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	2323	-1575	993	-242
$x1\text{-C}_7\text{H}_{14} + (1-x)\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	2549	-1636	1057	-362
$x1\text{-C}_8\text{H}_{16} + (1-x)\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	2737	-1603	1191	-428
$x1\text{-C}_6\text{H}_{12} + (1-x)\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$	3268	-1403	1221	-1178
$x1\text{-C}_7\text{H}_{14} + (1-x)\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$	3465	-1200	1360	-1411
$x1\text{-C}_8\text{H}_{16} + (1-x)\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$	3663	-1169	1451	-1129

calculated from the smoothing equation

$$\Delta = X_m^E - x(1-x) \sum_{r=0}^{r=3} X_r(1-2x)^r \quad (1)$$

where  $\Delta$  may be either  $\Delta'$  or  $\Delta''$ ,  $X_m^E$  may be either  $H_m^E$  or  $V_m^E$  and  $X_r$  may be either  $A_r$  or  $B_r$ , respectively. The coefficients  $A_r$  and  $B_r$  are given in Tables 3 and 4.

DISCUSSION

The  $H_m^E$  values for 1-alkene + 1-propanol or 2-propanol are all positive with a maximum at a composition between 0.6 and 0.7 mole fraction of 1-alkene. This is most likely a reflection of the breaking of the hydrogen bonds between the alkanol molecules as a result of the mixing process.

TABLE 4

Values at 298.15 K of coefficients  $B_r$  in  $\text{cm}^3 \text{mol}^{-1}$  for eqn. (1)

Mixture	$B_r$			
	$B_0$	$B_1$	$B_2$	$B_3$
$x1\text{-C}_6\text{H}_{12} + (1-x)\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	0.068	-1.015	0.126	-
$x1\text{-C}_7\text{H}_{14} + (1-x)\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	0.670	-0.827	0.142	-
$x1\text{-C}_8\text{H}_{16} + (1-x)\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	0.980	-0.538	0.624	-0.633
$x1\text{-C}_6\text{H}_{12} + (1-x)\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$	1.540	-1.239	-0.383	0.378
$x1\text{-C}_7\text{H}_{14} + (1-x)\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$	1.994	-0.922	0.182	-
$x1\text{-C}_8\text{H}_{16} + (1-x)\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$	2.165	-0.736	0.389	-

Comparing these results with those published previously [1] on related mixtures of 1-alkene with methanol or ethanol, it can be seen that  $H_m^E(\text{maximum})$  increases slightly with increasing alcohol carbon number. For example  $H_m^E(\text{maximum})$  for mixtures of 1-hexene with methanol, ethanol and 1-propanol are 570, 620 and 660 J mol<sup>-1</sup>, respectively.

For each 1-alkene,  $H_m^E(\text{maximum})$  for mixtures containing 2-propanol are greater than  $H_m^E(\text{maximum})$  for mixtures containing 1-propanol. For example,  $H_m^E(\text{maximum})$  for 1-heptene with 2-propanol and 1-propanol are 920 and 710 J mol<sup>-1</sup>, respectively.

For each alkanol, the  $H_m^E(\text{maximum})$  value increases slightly with increasing 1-alkene carbon number. For example,  $H_m^E(\text{maximum})$  for mixtures containing methanol with 1-hexene, 1-heptene and 1-octene are 570, 590 and 630 J mol<sup>-1</sup>, respectively.

The double bond in the 1-alkene has only a slight effect on the  $H_m^E(\text{maximum})$  value. This can be seen by comparing  $H_m^E(\text{maximum})$  for 1-hexene + ethanol (620 J mol<sup>-1</sup>) with the value for hexane + ethanol (580 J mol<sup>-1</sup>) from the literature [3].

The magnitude of the partial molar excess enthalpies at infinite dilution gives some clue to the process taking place on mixing. For each mixture ( $x_1 1\text{-C}_n\text{H}_{2n} + x_2 \text{C}_n\text{H}_{2n-1}\text{OH}$ ),  $H_2^E(x_2 = 0) > H_1^E(x_1 = 0)$ , indicating a higher endothermic enthalpy for the complete dissociation of the alkanol molecules ( $x_2 = 0$ ) than for the dissociation of 1-alkene molecules and the association of a 1-alkene with an alkanol molecule ( $x_1 = 0$ ). The partial molar excess enthalpies at infinite dilution  $H_1^E(x_1 = 0)$  were calculated by the method described by Letcher and Jerman [4] and are given in Table 5.

The volume changes on mixing a 1-alkene with an alkanol are largely positive which again reflects the dissociation effect of the alkanol. This is reinforced by the magnitude of the partial molar excess volumes of the alkanols at infinite dilution,  $V_2^E(x_2 = 0)$  which are larger than  $V_1^E(x_1 = 0)$ . These values are given in Table 5.

TABLE 5

Values of the partial molar excess properties  $H_1^E(x_1 = 0)$ ,  $H_2^E(x_2 = 0)$ ,  $V_1^E(x_1 = 0)$  and  $V_2^E(x_2 = 0)$

Mixture	$H_1^E(x_1 = 0)/$ J mol <sup>-1</sup>	$H_2^E(x_2 = 0)/$ J mol <sup>-1</sup>	$V_1^E(x_1 = 0)/$ cm <sup>3</sup> mol <sup>-1</sup>	$V_2^E(x_2 = 0)/$ cm <sup>3</sup> mol <sup>-1</sup>
$x 1\text{-C}_6\text{H}_{12} + (1 - x)\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	1499	5133	-0.82	1.21
$x 1\text{-C}_7\text{H}_{14} + (1 - x)\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	1608	5604	-0.02	1.64
$x 1\text{-C}_8\text{H}_{16} + (1 - x)\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	1897	5959	0.43	2.78
$x 1\text{-C}_6\text{H}_{12} + (1 - x)\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$	1908	7070	-0.30	3.54
$x 1\text{-C}_7\text{H}_{14} + (1 - x)\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$	2214	7436	1.25	3.10
$x 1\text{-C}_8\text{H}_{16} + (1 - x)\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$	2816	7412	1.82	3.29



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