Ionic Liquids as Solvents in Separation Processes

Warren David

[BSc.Eng]

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Declaration

The work presented in this thesis was performed at the University of Natal, Durban from January 2002 to December 2003. The work was supervised by Professor D. Ramjugernath, Professor T. M. Letcher and Professor J. D. Raal.

This thesis is presented as the full requirement for the degree of MSc.Eng in Chemical Engineering. All the work presented in this thesis is original unless otherwise stated and has not (in whole or part) been submitted previously to any tertiary institute as part of a degree.

W. David

I hereby certify that I find this work to be suitable for submission for the degree of MSc.Eng in Chemical Engineering.

D. Ramjugernath

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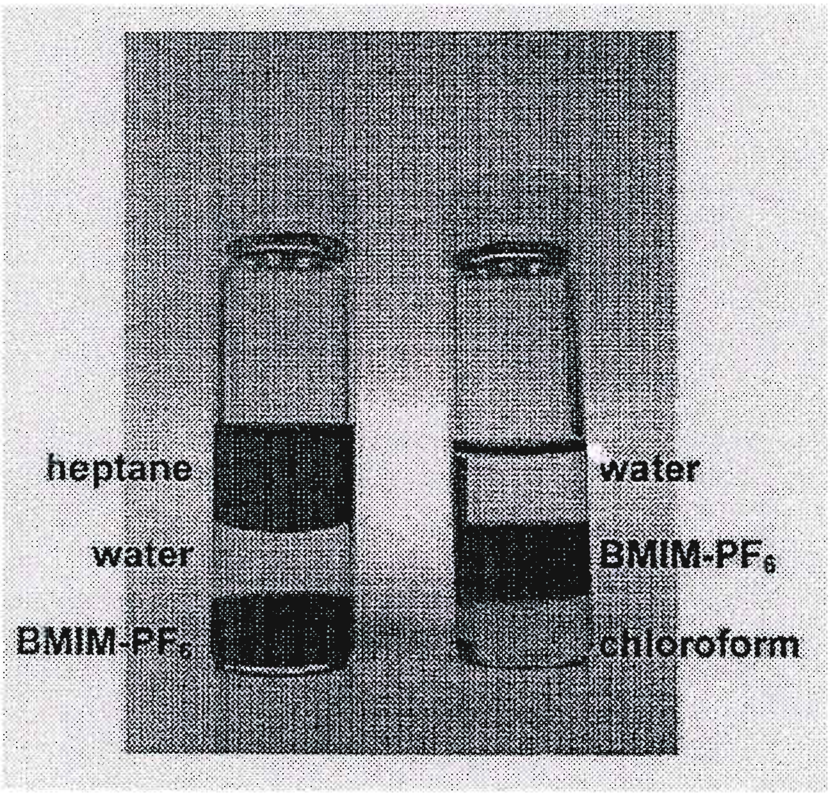

(Carda-Broch et al. 2003)

Abstract

Due to the ever increasing need for sustainable development, the chemical and allied industries have been at the focus of much change. Decreasing tolerances on pollution via waste streams has resulted in a re-examination of many chemical processes. This has ushered in the era of `green chemistry' which incorporates the synthesis of a process in both a sustainable and economically viable manner. In the petroleum and chemical industries, this has led to the search for alternatives to volatile organic compounds. Ionic liquids provide one such alternative.

With a wide liquid phase and no measurable vapour pressure, ionic liquids have been found to be successful as a medium for reactions. Ionic liquids differ from high-temperature molten salts in that they have a significantly lower melting point. This work investigates the use of ionic liquids as solvents in separations. The work focuses on the separation of alpha-olefins from complex mixtures.

The ionic liquids used in this study were:

- 1-methyl-3-octyl-imidazolium chloride
- 4-methyl-*N*-butyl-pyridinium tetrafluoroborate
- trihexyl-tetradecyl-phosphonium chloride

Three experimental techniques used to evaluate ionic liquids were:

- gas-liquid chromatography
- liquid-liquid equilibria measurements
- vapour-liquid equilibria measurements

1-Methyl-3-octyl-imidazolium chloride ([MOIM]Cl) was used as a stationary phase in gas-liquid chromatography. The solutes used were:

- Alkanes: *n*-Pentane; *n*-Hexane; *n*-Heptane; *n*-Octane
- Alkenes: 1-Hexene; 1-Heptene; 1-Octene
- Alkynes: 1-Hexyne; 1-Heptyne; 1-Octyne
- Cycloalkanes: Cyclopentane; Cyclohexane; Cycloheptane
- Aromatics: Benzene; Toluene

Activity coefficients at infinite dilution were measured at temperatures (298.15, 308.15 and 318.15) K. Values at 298.15 K ranged from 1.99 for benzene to 26.1 for *n*-octane. From the temperature dependence of the activity coefficients, the partial excess molar enthalpies at infinite dilution were calculated. These range from 2.0 $kJ.mol^{-1}$ for 1-octyne to 7.3 $kJ.mol^{-1}$ for *n*-pentane. [MOIM]Cl shows reasonable ability to separate 1-hexene from the longer *n*-alkanes and aromatics.

4-Methyl-*N*-butyl-pyridinium tetrafluoroborate ($BuMePyBF_4$) was used as a solvent in liquid-liquid equilibria measurements. The following systems were measured at 298.2 K:

- LLE System 1: $BuMePyBF_4$ + 1-Hexene + Toluene
- LLE System 2: $BuMePyBF_4$ + 1-Hexene + Ethanol
- LLE System 3: $BuMePyBF_4$ + 1-Hexene + 2-Butanone
- LLE System 4: $BuMePyBF_4$ + 1-Octene + Ethanol

LLE System 1 is a type II system and the other systems being type I. All systems exhibit a large two-phase region. LLE System 1 shows low distribution. LLE System 3 show almost equal distribution between phases resulting in a distribution ratio of close to 1. LLE Systems 2 and 4 show high distribution ratios at low concentrations of solute. LLE Systems 1 and 3 show low to moderate selectivity of the solvent towards the solute. LLE Systems 2 and 4 show high to moderate selectivity, but decrease exponentially with increasing solute concentration in the organic phase. For all systems investigated, the solvent shows no miscibility with feed solutions of low to medium solute concentration. The binodial curves were correlated to the Hlavaty equation, the beta function and the log gamma function. The correlations yielded acceptable results for

LLE Systems 2, 3 and 4. The tie-lines were correlated to the NRTL model, with LLE systems 2 and 4 giving acceptable results and LLE systems 1 and 3 give excellent results.

The following binary vapour-liquid equilibrium systems were measured:

- Acetone + Methanol at 99.4 kPa
- 1-Hexene + 2-Butanone at 74.8 kPa

The acetone + methanol system exhibits a minimum boiling azeotrope at 0.78 mole fraction acetone. The 1-hexene + 2-butanone system exhibits a minimum boiling azeotrope at 0.83 mole fraction 1-hexene.

Trihexyl-tetradecyl-phosphonium chloride $(C_6)_3C_{14}PhCl$ was then added to the above systems in order to evaluate it as a solvent in extractive distillation. $(C_6)_3C_{14}PhCl$ shifts the azeotrope of the acetone + methanol system to a higher acetone concentration, but does not remove it altogether. $(C_6)_3C_{14}PhCl$ has a negative effect on the relative volatility of the 1-hexene + 2-butanone, thus rendering it ineffective as an extractive distillation solvent for this system.

Another aspect that was considered in this work was the production of an ionic liquid. Synthesis steps and experimental considerations were discussed. A major factor in the use of ionic liquids is the cost of the ionic liquid itself. The major problem associated with ionic liquids is the general lack of available information that is necessary for them to be implemented in a process.

Ionic liquids show potential as solvents in liquid-liquid extraction for a number of systems. Their potential as solvents in extractive distillation is probably limited, due to their miscibility/immiscibility properties, to systems involving slightly polar to highly polar compounds.

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Nomenclature

List of Symbols

a	activity
B	viral coefficient
f	fugacity
G	Gibbs energy
g	interaction parameters
H	molar enthalpy
K	equilibrium ratio
k	Henry's constant
P	pressure
t	retention time
V	volumetric flowrate/ molar volume
x	liquid mole fraction
y	vapour mole fraction

Greek Letters

α	NRTL non-randomness parameter / relative volatility
β	selectivity
ε	dielectric constant
ϕ	fugacity coefficient
γ	activity coefficient
μ	dipole moment/ chemical potential/ viscosity
σ	standard deviation

Superscripts

∞	infinite dilution
E	excess
id	ideal
L	Liquid phase
sat	saturated
V	Vapour phase

Subscripts

a	component a
b	component b
i	component i
j	component j

Abbreviations

$(C_6)_3C_{14}$PhCl	trihexyl-tetradecyl-phosphonium chloride
(MOIM)Cl	1-methyl-3-octyl-imidazolium chloride
BuMePyBF$_4$	1-butyl-4-methylpyridinium tetrafluoroborate
GLC	Gas-Liquid Chromatography
ICCT	IUPAC Conference on Chemical Thermodynamics
LLE	Liquid-Liquid Equilibrium
NRTL	Non-random two liquid
QUILL	Queen's University Ionic Liquid Laboratories
VLE	Vapour-Liquid Equilibrium
VOC	Volatile organic compounds

Chapter One

Introduction

1.1 Background

The economic value of a chemical is exponentially proportional to its purity. Most chemicals are either produced from a reaction of other chemicals eg. ammonia from hydrogen and nitrogen, or sourced from natural resources eg. *n*-heptane from petroleum. Most reactions are not 100 per cent selective and may not run to completion, which results in by-products and unreacted reagents. Natural resources are generally mixtures of various chemicals. In order to produce a chemical of high purity, an effective separation process has to be employed.

1.2 Separation Techniques

Distillation is the common method used to separate liquids. This method uses the difference in relative volatility between the components in the mixture to separate the components. There are systems which may contain an azeotrope. This is the maximum composition point to which separation can occur using normal distillation. In order to produce high purity chemicals, this azeotrope needs to be shifted to a higher composition or removed altogether. Changing the operating pressure is usually useful only for pressure sensitive azeotropes. One of the ways to remove an azeotrope is to use extractive distillation. In extractive distillation, a solvent is added to selectively alter the activity coefficients in order to increase the relative volatility of the components to be separated. The solvent is generally a high-boiling polar chemical. Extractive distillation can also be used to reduce the number of equilibrium stages required to separate mixtures. Liquid-liquid extraction, where a solvent is added in order to create a second liquid phase, can be used as an alternative to or in conjunction with distillation. The solvent selectively dissolves components, which then have to be separated from the solvent. The economic viability of both extractive distillation and liquid-liquid extraction is dependent on the effectiveness of the solvent. Thus, research involving new solvents is important.

1.3 Ionic Liquids

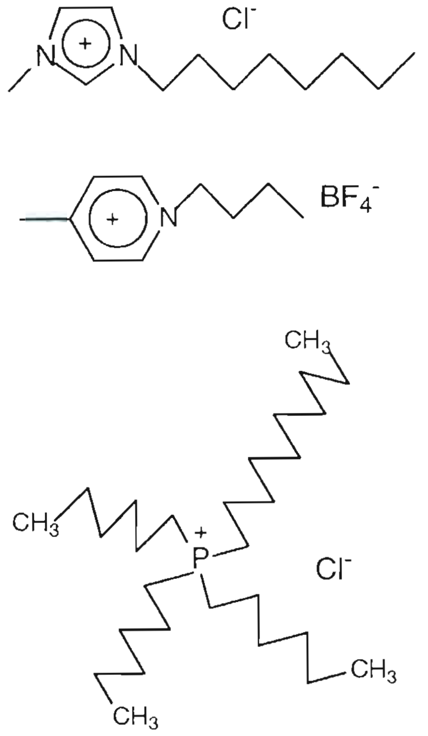
Ionic liquids are a relatively recent development. They are liquids that are comprised entirely of ions, i.e. they contain a mixture of only cations and anions. A number of ionic liquids freeze below room temperature, making them interesting candidates as solvents for applications at ambient conditions. Some of the interesting properties of ionic liquids are:

- Wide liquid-phase range
- No measurable vapour pressure
- Miscibility/immiscibility with organic compounds

Ionic liquids have proven to be effective solvents in reaction chemistry and this work looks at their suitability as solvents in separation science. Ever increasing environmental concerns in the chemical industry have brought about a need to find alternatives to volatile organic compounds (VOC's), since these may be released in to the atmosphere. Currently ionic liquids appear as a promising alternative. A review of the properties and applications of ionic liquids follows in Chapter 2.1.

1.4 Experimental Work

This work focuses on the use of ionic liquids to separate alpha-olefins from mixtures. The ionic liquids used in this study are given in Figure 1-1. A more detailed explanation of the nomenclature is given in Chapter 2.1.1.



(a) 1-methyl-3-octyl-imidazolium chloride, (MOIM)Cl

(b) 1-butyl-4-methylpyridinium tetrafluoroborate, $BuMePyBF_4$

(c) Trihexyl-tetradecyl-phosphonium chloride, $(C_6)_3C_{14}PhCl$

Figure 1-1: Structures and names of the ionic liquids used in this work

Activity coefficient measurements and both liquid-liquid and vapour-liquid equilibrium measurements were undertaken in order to evaluate the suitability of the above ionic liquids as solvents in separation processes.

1.4.1 Gas-Liquid Chromatography

(MOIM)Cl was, in this study, used as a stationary phase in gas-liquid chromatography in order to measure the activity coefficients of various hydrocarbons at infinite dilution. The following solutes were used:

- Alkanes: *n*-Pentane; *n*-Hexane; *n*-Heptane; *n*-Octane
- Alkenes: 1-Hexene; 1-Heptene; 1-Octene
- Alkynes: 1-Hexyne; 1-Heptyne; 1-Octyne
- Cycloalkanes: Cyclopentane; Cyclohexane; Cycloheptane
- Aromatics: Benzene; Toluene

Measurements were undertaken on a medium pressure apparatus at three different temperatures. The activity coefficients and infinite dilution were used to calculate selectivities and partial excess molar enthalpies at infinite dilution.

1.4.2 Liquid-liquid equilibria

$BuMePyBF_4$ was used in ternary LLE measurements in order to evaluate its suitability as a solvent in liquid-liquid extraction. Measurements were undertaken using the method of titration. The following systems were measured:

- LLE System 1: $BuMePyBF_4$ + 1-Hexene + Toluene
- LLE System 2: $BuMePyBF_4$ + 1-Hexene + Ethanol
- LLE System 3: $BuMePyBF_4$ + 1-Hexene + 2-Butanone
- LLE System 4: $BuMePyBF_4$ + 1-Octene + Ethanol

Compositions obtained from measurements allowed for the construction of binodial curves and tie lines on ternary phase diagrams. Further calculations yielded selectivities and equilibrium ratios. The binodial curve was correlated to the Hlavaty equation, the beta function and the log gamma function. The tie-lines were correlated to the NRTL model.

1.4.3 Vapour-liquid equilibria

Isobaric vapour-liquid equilibrium measurements were undertaken using a vapour-liquid recirculating still. The following binary VLE systems were measured:

- Acetone + Methanol
- 1-Hexene + 2-Butanone

The data were plotted on temperature verses composition (T-x-y) diagrams and regressed to the Wilson and NRTL models. $(C_6)_3C_{14}PhCl$ was then added to the above systems in order to evaluate its suitability as a solvent in extractive distillation. Compositions were represented on a solvent-free basis and relative volatility plots were used to compare the effect of solvent addition to the pure binary systems.

Chapter Two

Literature Review

Chapter overview

This chapter reviews ionic liquids in general and includes, but is not limited to, the following:

- The general naming of ionic liquids
- A brief history detailing the development of ionic liquids
- Some interesting properties of ionic liquids
- Ionic liquids in catalytic reactions
- Ionic liquids and their role in clean technology

The various methods used to measure activity coefficients at infinite dilution are listed. A closer look is taken at gas-liquid chromatography, which is the technique used in this work. Work involving ionic liquids in this area is also reviewed.

The separation techniques of distillation and liquid-liquid extraction are also discussed. The necessary phase equilibrium data and their measurement is also presented. Work involving ionic liquids in this area is also reviewed.

2.1 Ionic Liquids

2.1.1 Nomenclature of Ionic Liquids

Before anything on ionic liquids is to be discussed, a few examples of nomenclature will be given. While initial encounters with the names of ionic liquids might seem intimidating, a closer inspection will reveal similarities to nomenclature of organic compounds from which structures can be determined.

Ionic liquids are named in the same way as common salts. They follow the format of (cation)(anion). The cation is usually a large organic, while the anion usually consists of halides (i.e. F, Cl, Br, I) and/or other non-metals (i.e. P, B, etc). An example is the ionic liquid *1-Butylpyridinium nitrate* (Figure 2-1). From the figure below, the constituents can be easily seen. The cation consists of a pyridine ring which has a butyl group bonded to the nitrogen. The associated anion is a nitrate.

Figure 2-1: Structure of 1-Butylpyridinium nitrate

The above ionic liquid is produced by reaction *Step IIb* in Figure 6-1. The figure depicts the cation and anion that is present when the reagents used to produce the ionic liquid are combined in an equimolar ratio. Ionic liquids produced by reaction *Step IIa* in Figure 6-1 result in possibly more than one principal anion. An example is the ionic liquid *1-Ethyl-3-methylimidazolium tetrachloroaluminate* (Figure 2-2). However, ionic liquids formed when reagents are combined in other ratios can have more than one principal anion (see Chapter 6). In cases like this it may not be possible to state exactly which anions are present, however, it is sufficient to determine the neutral structure of the compound from the name.

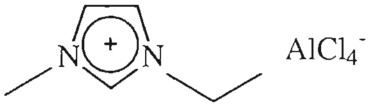
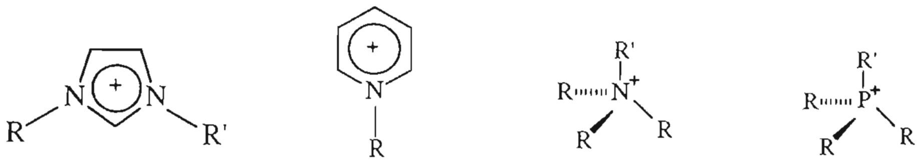


Figure 2-2: Structure of 1-ethyl-3-methyl-imidazolium tetrachloroaluminate

Seddon (1997) points out that the full name for the cation is 1-ethyl-3-methyl-1H-imidazolium cation. Whether out of convenience or ignorance, the *1H* has been omitted in most published literature and will also be followed here for uniformity. Ionic liquids usually have rather long names and abbreviating the name is fairly common. While not a strict rule, most authors use the following abbreviation for the imidazolium-type ionic liquids: The ionic liquid 1-**e**thyl-3-**m**ethyl-**im**idazolium bromide is abbreviated as (EMIM)Br.

Some common cation types are listed below as a reference.



a) Imidazolium ion b) Pyridinium ion c) Ammonium ion d) Phosphonium ion

Figure 2-3: Common cation types

2.1.2 History of Ionic Liquids

The following history of ionic liquids is quoted from a review by John Wilkes, 2002, detailing the development of ionic liquids. Wilkes is regarded as one of the 'grandfathers' of ionic liquids and his perspective is of interest.

2.1.2.1 Introduction

Depending on your definition of 'ionic liquid', the history of ionic liquids may be viewed as a relatively recent one, or one extending back to the 19th century. Consequently, this could be seen as a change in molten salt chemistry, or the discovery of new and important industrial materials.

A working definition of an ionic liquid is a salt with a melting point below the normal boiling point of water. A general feature of ionic liquids that is not included in the definition, is that most have organic cations and inorganic anions. 'Molten salts' is the most common term used to describe ionic compounds in the liquid state. However, the term 'ionic liquids' was also used to describe high temperature molten salts long before there was much literature on low-melting salts. The differences between ionic liquids and high temperature molten salts are significant enough to regard ionic liquids as a separate class of solvents. One of the main differences is the melting point. High temperature molten salts have a significantly higher melting point than that of ionic liquids.

Ionic liquids have been described using synonyms such as 'room temperature molten salt', 'low temperature molten salt', 'ambient temperature molten salt', 'ionic fluid' and 'liquid organic salt'. The term 'neoteric solvent' has been used in recent years, and is used to describe a new class of solvents or older materials that are finding new applications as solvents.

Much of the research involving ionic liquids has been linked to 'green' chemistry. The most valuable property from the perspective of 'green' chemistry is the extremely low vapour pressure. This allows more effective containment of the solvent.

2.1.2.2 Beginnings

Like many other discoveries of science, ionic liquids were brought about partly by a logical scientific path and partly by chance.

The development of ionic liquids, themselves being salts, can be traced back to the more traditional high temperature molten salts. To begin development in any field of research would require some motivation for its possible benefits. It is the same with molten salt chemistry. The motivation in this case is the different properties of molten salts over molecular solvents. Molten salts have great thermal, chemical and electrochemical stability. The electrochemical reduction of aluminium(III) is possible in molten cryolite ($NaAlF_6$), but is not practical in a molecular medium. In addition inorganic salts are cheap and easily available.

The problems associated with these salts are directly related to the melting point. Sodium chloride has a melting point of 800 °C and the popular 'low-melting' alkali halide eutectic mixture LiCl-KCl has a melting point of 355 °C. The energy and construction material requirements at elevated temperatures make such a process difficult to maintain. It will be seen that ionic liquids bring the advantages of molten salts and at the same time avoiding the disadvantages.

In the mid-19th century the first observation of an ionic liquid was during Friedel-Crafts reactions. The reaction of benzene with chloromethane to produce toluene was catalyzed by $AlCl_3$, a Lewis acid. A separate red-coloured phase formed during the reaction. The composition was not known and it was termed 'red oil'. With the development of NMR spectroscopy, much later, the composition was found to have the structure in Figure 2-4.

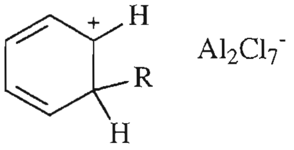


Figure 2-4: Structure of 'red oil' (Wilkes, 2002)

Simple alkylammonium nitrates were found to be liquids at room temperature in the early 20th century. Ethylammonium nitrate ($CH_3CH_2NH_3^+NO_3^-$) has a melting point of 12 °C. These were not specifically termed as ionic liquids at the time, but would today fall into the definition of ionic liquids. This class of ionic liquids was developed by the military as liquid propellants.

The work of Prof. John Yoke in the 1960's at Oregon State University could be regarded as a pioneering work in the field of ionic liquids. He discovered that mixtures of copper(I) chloride and alkylammonium chlorides were liquid near room temperature. CuCl and triethylammonium chloride (Et_3NHCl) which are both solids, produce a liquid when mixed as in Eq. (2-1).

$$CuCl\,(s) + Et_3NHCl\,(s) \rightarrow Et_3NHCuCl_2\,(l) \qquad (2\text{-}1)$$

Another class of compounds discovered in the 1970's which would now be regarded as ionic liquids, is liquid clathrates. These were discovered and characterized by Prof. Jerry Atwood and his group at the University of Alabama. Theses are formed by combining a salt with an aluminium alkyl, which then forms a compound with one or more aromatic molecules as the temperature is raised (Eq. (2-2); Wilkes, 2002).

$$M[Al_2(CH_3)_6X] + nAromatic \underset{low.temp}{\overset{high.temp}{\Leftrightarrow}} \underbrace{M[Al_2(CH_3)_6X].nAromatic}_{liquid.clathrate} \qquad (1\text{-}2)$$

They have found application in petroleum recovery from tar sands.

2.1.2.3 The chloroaluminates - high temperature

The progression from high temperature molten salts to ionic liquids through history can be viewed as a decrease in the melting point. The development involved a transition rather than a jump to the present day ionic liquids. The materials that occupy this transition are inorganic chloroaluminates. It is interesting to note that these were then described as 'low temperature molten salts.' The sodium chloride-aluminium chloride eutectic has a melting point of 107 °C.

Much of the work on chloroaluminates was undertaken at the U.S. Air Force Academy. It was started by Dr. L. A. King in the 1960's and centered around thermal batteries. Thermal batteries use a molten salt electrolyte and commonly use LiCl-KCl which results in temperatures of about 375-550 °C. The associated problems with these operating temperatures created the need to find electrolytes with much lower melting points. They chose the alkali chloride-aluminium chloride system and attempted to characterize these systems. Difficulties arose as these systems were somewhat complex and collaborations were established with other groups around the world in an attempt to understand these systems more completely. The work of Charles Hussey at the

Air Force Academy resulted in a patent for a thermal battery using a NaCl-$AlCl_3$ electrolyte.

2.1.2.4 The chloroaluminates – low temperature

Wilkes regards the start of the modern era of ionic liquids as 'the simultaneous collaborative discovery and development of the 1-butylpyridinium chloride-aluminium chloride mixture (BPC-$AlCl_3$), by groups at Colorado State University and the Air Force Academy.' Physical characterization was done at the Air Force Academy and electrochemical experiments were done at both institutions.

While this was a step forward in general, the particular system (BPC-$AlCl_3$) presented a few problems. It was not liquid at room temperature at the composition which gave the highest conductivity. It also had a smaller electrochemical window than the NaCl-$AlCl_3$ which resulted in electrode incompatibility.

This prompted the need to find systems with much lower melting points and cations which were more difficult to reduce. Depending on the composition, the anions present in a chloroaluminate binary salt are $AlCl_4^-$, $Al_2Cl_7^-$ and $Al_3Cl_{10}^-$. Researchers combined these large anions with large asymmetrical cations in an attempt to lower the melting point. This worked as crystal formation was inhibited. In order to find cations that were less easily reduced researchers used software developed at the University of Texas. Some of the outputs were the energies of all orbitals, which they correlated to the electrochemical potential.

In 1979 Charles Hussey (at the University of Mississippi) and John Wilkes concentrated their efforts on predominantly hetrocyclic cations which contained quaternary-N. Chloroaluminate salts containing these cations were synthesized and electrochemical measurements were performed. Of the many cations investigated, the class that proved to be the most promising was the dialkylimidazolium cation class (Figure 2-5). These had a larger electrochemical window and were less prone to reduction than the alkylpyridinium cations.

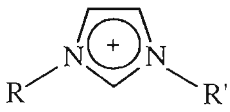


Figure 2-5: Structure of the dialkylimidazolium cation

In this class, a series of chloroaluminate systems were synthesized by varying the length of the alkyl substituents. Physical, chemical and electrochemical properties of these systems were measured. The system that proved to be the best balance of these properties was the 1-ethyl-3-methylimidazolium chloride-aluminium chloride (emimCl-$AlCl_3$) which has a freezing point below room temperature for compositions between 0,33 and 0,67 $AlCl_3$ mole fraction.

The publication of the work on emimCl-$AlCl_3$ by the Air Force Academy drew the attention of other researchers. Collaboration was setup between Charles Hussey and Kenneth Seddon (Sussex, England). It was out of this interest from Kenneth Seddon that the Queen's University Ionic Liquid Laboratories (QUILL) at Belfast was started.

2.1.2.5 Water stable ionic liquids

The problem with the previously discussed ionic liquids of the chloroaluminate type anion was that it reacted with water. A product of the reaction is HCl. While this was not a problem in the sealed electrolytes of batteries, it limited the application of ionic liquids. In 1990 Michael Zaworotko spent a year at the Air Force Academy and investigated the preparation and characterization of ionic liquids with water-stable anions. He prepared them by metathesis reaction of the dialkylimidazolium halide with the appropriate silver salt. The anions investigated were the tetrafluoroborate (BF_4^-), hexafluorophosphate (PF_6^-), nitrate (NO_3^-), sulfate (SO_4^{2-}) and acetate (CH_3COO^-). These were found to be stable towards hydrolysis at room temperature.

Joan Fuller continued the work of Michael Zaworotko. She spent a considerable amount of time extending the list of water stable ionic liquids. This included finding better preparation methods and testing of solids for nonlinear optical properties. She extended the range of cations to mono- and trialkylimidazoliums, and the range of anions to much larger anions. This resulted in an extensive number of ionic liquids.

In 1992 Richard Carlin took over the leadership of the Air Force Academy. He and his coworkers worked on the use of ionic liquids in battery cells similar to that of lithium-ion rechargeable batteries. They were able to develop a concept that uses ionic liquid as both the electrolyte and energy-storing electrode material.

This brings us to the current decade of research involving ionic liquids, some of which will be discussed in further detail. The area of research involving ionic liquids has developed to an extent where workshops at conferences have been dedicated entirely to the discussion of ionic liquid research e.g. *Workshop on Ionic Liquids*, 17th IUPAC Conference on Chemical Thermodynamics, Rostock, Germany (2002). In some cases, collaborations have been so extensive that whole conferences were dedicated to their discussion e.g. *Green Industrial Applications of Ionic Liquids*, A NATO advanced Research Workshop, Crete, Greece (2000).

2.1.3 Properties of ionic liquids

The physical and chemical properties of substances are important as they help characterize a substance and also help identify its limitations in applications. As ionic liquids are a relatively recent development, and realizing the need for properties, there has been an effort by many researchers to characterize them. This review looks at some of the physical and chemical properties of ionic liquids in order to give a picture of their potential and also some of their limitations as solvents.

2.1.3.1 Melting point

Perhaps the most interesting and arguably the most important property of ionic liquids is their melting point. The relationship between the structure of an ionic liquid and its melting point are of great value, especially if a predictive method for the melting point is to be developed.

Table 2-16: Influence of the cation on the melting points of various chlorides

Chloride Salt	Melting Point (°C)
NaCl	803
KCl	772
(MMIM)Cl	125
(EMIM)Cl	87
(BMIM)Cl	65

(Wasserscheid and Keim (2000))

The above table shows the influence of the cation on the melting point. The metal salts exhibit high melting points, whereas the organic salts have far lower melting points.

Wassercheid and Keim (2000) list some of the reasons for this effect:

- Low symmetry
- Weak intermolecular interactions
- A good distribution of charge in the cation

Taking a closer look at the organic salts, it can be seen that by increasing the chain length on the cation from methyl to butyl in the above table, the melting point decreases quite significantly. The more unsymmetrical it is, the more difficult for the ions to pack together as a solid. This effect does have a limit though, to about a chain length of 10 carbons. Longer chain lengths begin to interact with one another and increase the melting point. A longer chain on the aromatic ring allows for greater distribution of charge on the cation (Wasserscheid and Keim, (2000)). Weak intermolecular interactions are important for low melting points to occur. A quick survey of the available ionic liquids indicates only cations and anions with a singular charge. Having a larger charge would make the ions more coordinated and would raise the melting point.

Table 2-2: Influence of different anions on the melting point of imidazolium salts

Imidazolium Salt	Melting Point (°C)
(EMIM)Cl	87
(EMIM)NO_2	55
(EMIM)NO_3	38
(EMIM)$AlCl_4$	7
(EMIM)BF_4	6^a
(EMIM)CF_3SO_3	-9
(EMIM)CF_3CO_2	-14

a – Glass transition

(Wasserscheid and Keim (2000))

The table above indicates that larger univalent anions decrease the melting point. Comparing the melting points of the salts formed with the Cl^- , which is comprised of a single atom, and with $CF_3CO_2^-$, which is comprised of seven atoms, one can see a fairly large difference (>100°C). This gives added possibilities when finding salts with low melting points. While the greatest reduction in melting point is achieved by choice of the cation, a further decrease can be obtained by careful selection of the anion.

For ionic liquids prepared by *Step IIa* (Figure 6-1), the melting point is affected by the molar ratio in which the two reactants are mixed. These type of systems are not necessarily composed of a single anion type. Mixtures, other than a 1:1 ratio of reactants, usually contain multiple anion types. An example is the (EMIM)Cl/$AlCl_3$ system shown in Figure 2-6. It is interesting to note that a local maximum exists at an exactly equimolar ratio of reactants. This indicates that the presence of several anions in the ionic liquid has the effect of decreasing the melting point.

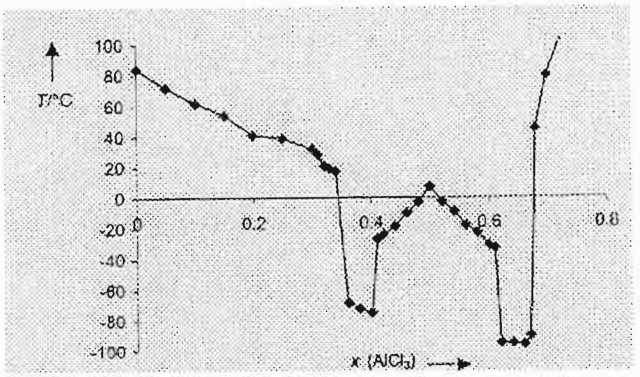


Figure 2-6: Experimental phase diagram for the system (EMIM)Cl/AlCl$_3$ (Wasserscheid and Keim (2000))

2.1.3.2 Vapour Pressure and Thermal Stability

Another interesting property of ionic liquids is that they have no measurable vapour pressure. This is reported by many authors including Wasserscheid and Keim (2000), Welton (1999) and Seddon (1997). This has a great advantage in that separation of the product from the reaction mixture by distillation is highly effective.

For an ionic liquid to exist in the vapour phase, it would have to exist in its principal ions and not change form. A great amount of energy would be required for these large ions to exist at these high temperatures, and more importantly great thermal stability of the bonds within the ion would be required. Wasserscheid and Keim (2000) indicate that the thermal stability of an ionic liquid is limited by the strength of their heteroatom-carbon and heteroatom-hydrogen bonds. Continual heating of an ionic liquid would sever these bonds rather than the ions going into the vapour phase. This gives us the upper limit of the liquid range of an ionic liquid: the decomposition temperature. This is important in that it gives the operating limit of temperature on a particular ionic liquid. Ionic liquids comprising alkylated amines or phophanes do not have very high thermal stability and Wasserscheid and Keim (2000) suggest a maximum working temperature of 150°C. Ionic liquids comprised of the imidazolium cation show much higher thermal stability.

Huddleston et al. (2001) gives a comprehensive list of ionic liquids and their decomposition temperatures, some of which are listed below in Table 1-3.

Table 2-3: Decomposition Temperatures of several ionic liquids

Ionic Liquid	Decomposition Temperature (°C)
(BMIM)Cl	254
(BMIM)I	265
(BMIM)BF_4	403
(EMIM)Cl	285
(HMIM)Cl	253
(HMIM)PF_6	417
(EMIM)Tf_2N	455
(EMIM)I	303

Tf_2N – Bis(triflylmethylsulfonyl)amide

It is quite evident that ionic liquids comprising the imidazolium-type cations have high thermal stability. This allows them to be applied to processes that require flexibility over a wide range of temperature conditions.

The thermal properties of ionic liquids were also studied by Ngo et al. (2000). They investigated over 30 ionic liquids using *differential scanning calorimetry* and *thermogravimetric analysis*. For many ionic liquids the thermal decomposition termperature was greater than 400 °C. They found that thermal decomposition is endothermic with inorganic anions and exothermic with the organic anions. Comparatively, halide anions drastically reduce the thermal stability of the ionic liquids.

2.1.3.3 Density

The density of an ionic liquid is dependent on both the cation and anion. The effect of the cation can be seen by comparing the densities of various chloroaluminate melts.

Table 2-4: Effect of cation size on density of ionic liquids

(Temperature = 60°C, Mole Fraction $AlCl_3$ = 0.5)

Ionic Liquid	Density (g/mL^{-1})
(MMIM) $AlCl_3$	1.305
(EMIM) $AlCl_3$	1.266
(PMIM) $AlCl_3$	1.235
(BMIM) $AlCl_3$	1.2113
(BBIM) $AlCl_3$	1.139

(Fannin et al., 1984)

(PMIM) = 1-propyl-3-methyl-imidazolium

Density decreases with an increasing chain length on the cation. By changing the bulkiness of the cation it is possible to fine-tune the density. The effect of the anion on the density is more pronounced.

Table 2-5: Effect of anion size on density of Ionic liquids

Ionic Liquid	Density (g.mL^{-1}) (25°C)
(BMIM)Cl	1.08
(BMIM)I	1.44
(BMIM)BF_4	1.12
(BMIM)PF_6	1.36
(BMIM)Tf_2N	1.43
(BMIM)CF_3CO_2	1.21
(BMIM)CF_3SO_3	1.29
(HMIM)Cl	1.03
(HMIM)PF_6	1.29

(Huddleston et al. 2001)

The simple halide salts have significantly lower densities than the more complex anions - compare (BMIM)Cl to (BMIM)Tf_2N and (HMIM)Cl to (HMIM)PF_6. The ionic liquids with chloride anions have densities which are comparable to water and dioxane. The larger anions have densities comparable to carbon disulfide and glycerol.

Table 2-6:17 Densities of various solvents (20°C)

Solvent	Density (g/mL^{-1})
Water	1.00
Dioxane	1.03
Carbon Disulfide	1.26
Glycerol	1.26

(C. R. C., Handbook of chemistry and physics)

Wasserscheid and Keim (2000) state, after comparison of other ions, that a certain density range is established by the choice of anion, within which a fine adjustment is possible by careful choice of the anion. The significance of having large densities is in the separation of immiscible liquid mixtures. This is, however, disadvantageous to the power requirements of mixing.

2.1.3.4 Surface Tension

Huddleston et al. (2001) have measured the liquid/air surface tension values for some ionic liquids listed below.

Table 2-7: Surface tension data (25 °C) for several Ionic Liquids

Ionic Liquid	Surface tension (dyn.cm^{-1})
(BMIM)Cl	54.7
(BMIM)BF_4	46.6
(BMIM)PF_6	48.8
(BMIM)Tf_2N	37.5
(HMIM)Cl	42.5
(HMIM)PF_6	43.4
(MOIM)Cl	33.8
(MOIM)PF_6	36.5

These values can be more easily understood by comparing them to surface tensions of other solvents.

Table 2-8: Surface tension data (25 °C) for various solvents

Solvent	Surface tension (dyn.cm^{-1})
Hexane	18
Toluene	32
Water	73

(C. R. C., Handbook of chemistry and physics)

The surface tensions of the ionic liquids listed in Table 2-7 are higher than solvents like hexane and toluene, but lower than water. These values are of importance in liquid-liquid extraction. High values lend more to rapid phase disengagement. Low values aid mass transfer between the two liquid phases. Since the surface tension values are somewhat in the middle, they suggest that ionic liquids are a compromise between these two objectives.

2.1.3.5 Viscosity

Bonhôte et al. (1996), state that the viscosity of ionic liquids is essentially determined by their tendency to form hydrogen bonds and by the strength of their van der Waals interactions. The hydrogen bonding effect can be seen when comparing chloroaluminate ionic liquids of different compositions.

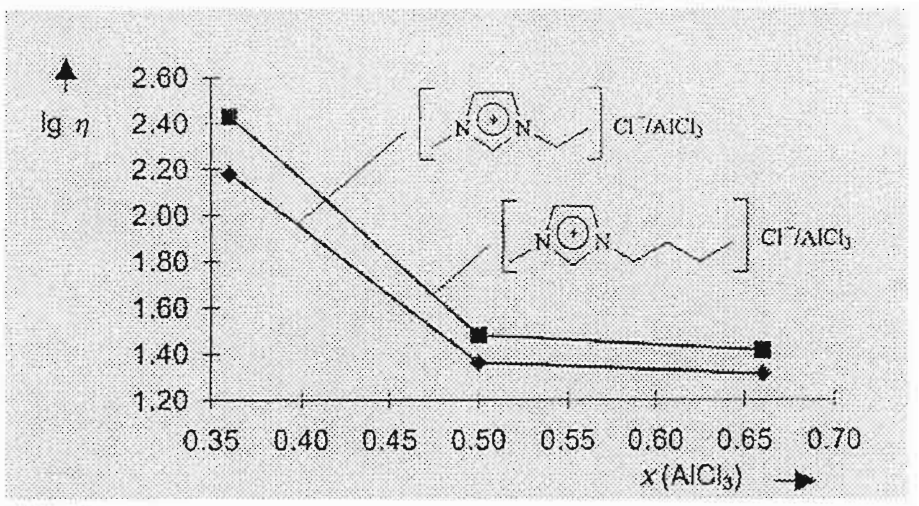


Figure 2-7: Dependence of the dynamic viscosity μ (cP) of two 1,3-dialkylimidazolium tetrachloroaluminate melts on the mole fraction of AlCl$_3$ at 25 °C (Wasserscheid and Keim, 2000)

According to Wasserscheid and Keim (2000), at low concentrations of AlCl$_3$, the Cl$^-$ ion predominates and there is hydrogen bonding between the hydrogen atoms of the imidazolium cation and the Cl$^-$ ion. The resulting viscosity at these concentrations is high (Figure 2-7). They refer to various analytical techniques which confirm this. In more acidic mixtures, the AlCl$_4^-$ and Al$_2$Cl$_7^-$ anions are present. These have a more distributed negative charge. The resultant hydrogen bonding is much weaker and therefore viscosity is lower. The van der Waals interactions can be seen by comparing a few (BMIM) ionic liquids.

Table 2-9: Dynamic viscosities η of various (BMIM) ionic liquids (20 °C)

Ionic Liquid	η (cP)
(BMIM)CF$_3$SO$_3^-$	90
(BMIM)n-C$_4$F$_9$SO$_3^-$	373
(BMIM)CF$_3$COO$^-$	73
(BMIM)n-C$_3$F$_7$COO$^-$	182
(BMIM)(CF$_3$SO$_2$)$_2$N$^-$	52

(Bonhôte et al. 1996)

Comparing the $CF_3SO_3^-$ and CF_3COO^- anions to the n-$C_4F_9SO_3^-$ and n-$C_3F_7COO^-$ anions reveals a significant increase in viscosity due to van der Waals interactions. However, the hydrogen bonding and van der Waals interactions are contrasting effects on the size of the anion. This can be seen by comparing the $CF_3SO_3^-$ and $(CF_3SO_2)_2N^-$ anions. Here, the almost complete suppression of hydrogen bonding overcompensates for the expected increase in viscosity.

Cation structure also affects the viscosity. Bonhôte et al. (1996), report that the lowest viscosities are obtained for ionic liquids incorporating the (EMIM) cation which combine sufficient side chain mobility and low molecular weight. Longer fluorinated alkyl chains result in higher viscosities because of stronger van der Waals interactions.

Huddleston et al. (2001), have also studied the viscosity of ionic liquids, which incorporate the cations (BMIM), (HMIM) and (MOIM) combined with the anions I^-, BF_4^-, PF_6^-, Tf_2N^-, Cl^-. They found that the viscosities of the ionic liquids (200 to >1000 cP) investigated were two or more orders of magnitude greater than traditional organics solvents and more comparable with typical oil. Their investigations also included temperature dependence of viscosity. For the ionic liquids containing the PF_6^- anion, the viscosity showed a non-Arrhenius type temperature dependence.

They also describe the relationship of viscosity to shear rate. The ionic liquids investigated fall into two classifications. As a Newtonian fluid whose viscosity remains constant with increasing shear rates (eg. (BMIM)BF_4), or a thixotropic fluid whose viscosity decreases as the shear rate increases (eg. 1-Dodecyl-3-methyl-imidazolium tetrafluoroborate).

Liao and Hussey, (1996) and Perry et al. (1995) studied the effects of co-solvents on the (EMIM)$AlCl_4$ system. The addition of benzene to the system decreased the viscosity considerably. Huddleston et al. (2001), however, discuss the effect of chloride contamination on the viscosity. The ionic liquid (BMIM)BF_4 with a 0.01 molal Cl^- has a viscosity of 154 ($mPa.s^{-1}$). Increasing the chloride content to 0.5 molal, increases the viscosity to 201 ($mPa.s^{-1}$). This brings an important point for consideration. Ionic liquids in operation, whether in separation or in reactions, are likely to become cross-contaminated by other chemicals. Knowing what and how much an ionic liquid is being contaminated and its effects on the physical properties of the ionic liquid, will be necessary in order to design system tolerances.

2.1.3.6 Solubility characteristics and Solvent properties

Considering that most substances are in mixtures rather than solely in a pure state, it is necessary to know something of the solubility characteristics. Ionic liquids exhibit interesting miscibility/immiscibility characteristics with other organic liquids. These characteristics are related to the solvent properties or parameters that are used to characterize a solvent. This section will give an overview of these parameters rather than looking at specific mixtures that include ionic liquids (see Chapter 2.3.1.3).

The general rule for solubility is 'like dissolves like.' However, not all liquids fall into the extremes of polar and non-polar. Most are somewhere in-between, and various parameters are used to determine where they lie on this scale. For the case of ionic liquids, Aki et al. (2001), ask the appropriate question as the title of the paper 'How polar are room-temperature ionic liquids?' Welton (1999) suggests that a polar solvent is one that will dissolve and stabilize dipolar or charged solutes. Pagni (2000), suggests that a useful way of categorizing solvents is based on their polarity as judged qualitatively by dielectric constant (ε), dipole moment (μ), and E_T^N, an empirical parameter based on the energy of an electronic transition of a dipolar dye, and their ability to donate a proton or hydrogen bond to an acceptor. Solvents can be classified by four categories, listed below:

Table 2-10: Solvent Types

Type	ε	μ	E_T^N	Examples
Apolar aprotic	small	small	small	cyclohexane
Weakly polar aprotic	small	small	larger	ethyl ether
Dipolar aprotic	large	large	large	DMF, DMSO
Protic	-	-	large	HF, H_2O

(Pagni, 2000)

However, he does point out that when it comes to ionic liquids, ε and μ are difficult to quantify. A number of other parameters can be used to measure solvent properties, but for many of these parameters there is no data available for ionic liquids. A parameter which can be calculated is Ω, which is the product ratio formed in the Diels-Alder reaction of cyclopentadiene with methyl acrylate. This is available for some ionic liquids in Table 2-11. Larger values imply greater polarity.

Table 2-11: Solvent properties of Ionic and other liquids

Solvent	E_T^N	Ω
$EtNH_3Cl$	0.98	-
$EtNH_3NO_3$	0.95	0.83
$NH_4CF_3CO_2$	0.40	-
$(n\text{-Butyl})_4NBr$	0.39	-
$(n\text{-Butyl})_4PBr$	0.40	-
$(n\text{-Hexyl})_4NClO_4$	0.56	-
$(n\text{-Hexyl})_4NPhCO_2$	-	0.42
$(n\text{-Dodecyl})_4NClO_4$	0.22	-
$(EMIM)AlCl_4$ (basic)	-	0.70
$(EMIM)PF_6$	-	0.51
$(BMIM)ClO_4$	-	0.72
H_2O	1.00	0.87
$HCONH_2$	0.80	0.83
Ethyl ether	0.12	0.47
Cyclohexane	<0.01	0.60

(Pagni, 2000)

Pagni (2000), classifies $EtNH_3Cl$ and $EtNH_3NO_3$ into the protic category. The tetraalkylammonium and phosphonium ionic liquids have moderately high E_T^N values which lie between formamide and ethyl ether. Comparing $(n\text{-Hexyl})_4NClO_4$ to $(n\text{-Dodecyl})_4NClO_4$ indicates that the size of the constituents on the cation also have a large influence on the E_T^N. The influence of the anion can be seen by comparing the Ω values of $(EMIM)AlCl_4$ and $(EMIM)PF_6$. Pagni (2000), concludes that with proper selection of cation and anion one can create an ionic liquid that will fit into any of the categories (Table 2-10) except the apolar group. The majority of ionic liquids are likely to fit into the protic or aprotic dipolar categories.

Aki et al. (2001) studied the solvent strength and polarity of imidazolium and pyridinium based ionic liquds with a fluoroscent probe. The ionic liquids studied were $(BMIM)PF_6$, $(MOIM)PF_6$, $(BMIM)NO_3$ and $(BPy)BF_4$ and were found to be more polar than acetronitrile but less polar than methanol.

Muldoon et al. (2001) have also studied ionic liquids using solvatochromic probes. They investigated a series of imidazolium based ionic liquids containing PF_6^-, BF_4^- and Tf_2N^- anions. The E_T^N values ranged from 0.54 to 0.67 which is comparable to Propan-2-ol (0.55) and Ethanol (0.65). They also found that polarity appears to be largely cation controlled, while the donor strength is entirely anion dependent.

Determining properties and the influences of cations and anions on these properties will be key to engineering ionic liquid technologies on a production scale.

2.1.4 Reactions in Ionic Liquids

While reactions in ionic liquids are not the focus of this experimental work, any review on ionic liquids that omits their role in organic synthesis would be incomplete. While the field of electrochemistry was responsible for development of molten salts to ionic liquids, it is the field of organic synthesis that has drawn the attention of a large number of research groups. Excellent reviews by Welton(1999), Wasserheid and Keim (2000) and Pagni (2000) detail the use of ionic liquids in synthetic and catalytic applications. In order to fully grasp the extent of the potential of ionic liquids in organic synthesis, a brief description of the type of reactions possible using ionic liquids is given. For brevity, certain details are omitted and the reader is referred to the above reviews for further information.

Sheldon (2001) lists the following reasons that make ionic liquids potentially attractive media for homogenous catalysis:

- They have no vapour pressure
- They generally have reasonable thermal stability
- They are able to dissolve a wide range of organic, inorganic and organometallic compounds
- Solubility of gases, that are reactants, is generally good
- Polarity and hydrophilicity can be adjusted
- Have the potential to be highly polar yet non-coordinating solvents

- Some ionic liquids are strong Lewis, Franklin and Brønsted acids.

One of the main successes of ionic liquids as reaction solvents has been in transition-metal catalyzed reactions. Ionic liquids are able to dissolve organometallic compounds and therefore provide a medium for transition metal catalysts. Depending on the co-ordinating properties of the anion, the ionic liquid can be an inert solvent or a co-catalyst. Ionic liquids containing the tetrafluoroborate of hexafluorophosphate anions appear to act as an inert solvent. In the case of chloroaluminate type ionic liquids, the solvent acts as a co-catalyst. The reason being that the resulting Lewis acidity or basicity activates the transition metal catalyst. Biphasic reactions with an ionic catalyst phase has been the subject of much of the research involving reactions in ionic liquids. Here the aim is to use an ionic liquid which preferentially solubilizes a reactant while being quite immiscible with the product which forms a separate phase. According to Olivier (Freemantle, 1998), the biphasic catalysis processes offer the benefits of both homogeneous and heterogeneous catalysis. They combine the mild conditions and high efficiency and selectivity of homogeneous catalysis with the easy separation of catalyst from the reaction products and optimal use of catalysts that are possible with heterogeneous catalysis.

2.1.4.1 Hydrogenation reactions

Hydrogenation involves the addition of hydrogen to a compound with unsaturated bonds. An example is the hydrogenation of 1-pentene to pentane (Wasserscheid and Keim, (2000)). The reaction is a biphasic reaction with the catalyst phase comprising a rhodium-type catalyst dissolved in an ionic liquid. Even with limited solubility of the reactants in the catalyst phase, the rate of reaction was almost five times faster than for the comparable reaction in acetone. An important part of this investigation was that there was no detectable leaching of the catalyst into the organic phase. The catalyst phase could be repeatedly used. This showed that a rhodium catalyst could be "immobilized" in a polar solution without the use of specially designed ligands.

2.1.4.2 Oxidation reactions

Oxidation reactions involve the loss of electrons and are coupled with a reduction reaction. The reactions take place in the presence of an oxidizing agent, which itself is reduced. An example is the epoxidation of 2,2-dimethylchromene with a Mn^{III} catalyst complex in a mixture of $(BMIM)PF_6$ and CH_2Cl_2 (1:4 v/v) (Song and Roh (2000)). The presence of the ionic liquid greatly enhances the reaction. For a target yield of 86%, the reaction takes 2 hrs in the presence of the ionic liquid, but 6 hrs in the absence of the ionic liquid. Wasserscheid and Keim (2000), point out that some ionic liquids show high oxidation stability. Re-using the catalyst phase would not affect the ionic liquid although recycling the phase may cause the catalyst complex to degrade.

2.1.4.3 Hydroformylations

A hydroformylation reaction involves the combination of an olefin, CO and H_2 to form an aldehyde. An example is the hydroformylation of 1-octene. The catalyst phase comprises a platinum-type catalyst in the ionic liquid BMIM trichlorostannate. The reaction is performed at 120°C and 90 bar. Wasserscheid and Keim (2000) report a remarkable platinum activity. What also makes the reaction so successful is the selectivity of the products. Both the *n* and the *iso* products are formed but in the ratio of *n*:*iso* = 19:1 . The reaction is biphasic and thus the product is isolated fairly simply. The authors report no leaching of the catalyst into the product phase.

2.1.4.4 Heck Reactions

A Heck reaction consists of a palladium catalyzed carbon-carbon bond coupling of an alkyl, aryl or vinyl to form an alkene. An example is the reaction of bromobenzene with styrene (Wasserscheid and Keim, (2000)). A palladium-type catalyst is used. A yield of 20% is obtained when the reaction is carried out in DMF. A yield of over 99% is obtained when the reaction is carried out in

$(NBu_4)Br$. In this case the product can be separated from the reaction medium by distillation. Repeated use of the catalyst showed no significant drop in activity.

2.1.4.5 Oligomerizations

Oligomerization is the process of converting monomers into an oligomer. When preparing a catalyst for oligomerization, there is usually a trade-off between the solubility of the metal complex and the solvent. A more polar solvent will hold more of the metal complex, but may compete with the substrate for co-ordination sites. Ionic liquids are more suited as they are polar but weakly co-ordinated. An example is the oligomerization of ethylene (Wasserscheid and Keim, (2000)). A nickel complex is used. The activity of the nickel complex increases by a factor of seven when the reaction is carried out in the ionic liquid $(BMIM)PF_6$ as compared to CH_2Cl_2. The overall selectivity of the biphasic reaction to linear α-olefins is as high as 88%.

2.1.4.6 Fisher-Tropsch reactions

Demitras and Muetterties (1977) investigated the Fisher-Tropsch Synthesis in which hydrogen and carbon monoxide were reacted to produce a set of aliphatic hydrocarbons with ethane being the primary product. The catalyst was an iridium complex in the solvent $NaCl\text{-}2AlCl_3$. The authors report relatively high reaction rates at 180°C and 1-2 atm. What is interesting is that when the solvent was changed to $NaBr\text{-}2AlBr_3$, the major reaction product was propane. It may therefore be quite possible with other types of reactions to selectively produce a particular product by merely changing the ionic liquid.

2.1.4.7 Friedel-Crafts Reactions

The Friedel-Crafts reactions are the alkylation and acylation reactions. The alkylation involves an electrophilic substitution reaction that puts an alkyl group on a benzene ring. The acylation involves an electrophilic substitution reaction that puts an acyl group on a benzene molecule. Wilkes and co-workers (Boon,1986) investigated alkylation and acylation reactions in (EMIM)Cl-$AlCl_3$. What is interesting in these reactions is that the ionic liquid was used both as a solvent and as a catalyst. Only acid melts proved to be effective. The alkylation reactions involved reacting an alkyl chloride with benzene. The products included polyalkylated benzenes and at temperatures as low as -25°C. The acylation reactions involved reacting acetyl chloride with benzene to produce acetophenone. Complete conversion was attained in a few minutes compared to conventional reactions which take many hours. These reaction types were also investigated by Seddon's group (Freemantle, (1998)).

2.1.4.8 Biocatalysis

Sheldon (2001) describes reactions investigated by his group involving the *Candida antarctica* lipase. The reaction of octanoic acid with ammonia, in (BMIM)PF_6 at 40°C, gave complete conversion to octanamide in 4 days compared to 17 days for the same conversion using ammonium carbamate in methyl isobutyl ketone.

Other reactions that have been successfully investigated in ionic liquids include:

- Alkoxycarbonylations
- Hydrodimerizations/Telomerizations
- Trost-Tsuji Couplings
- Diels-Alders Reactions

- Olefin Dimerization
- Olefin Polymerization
- Electrophilic Substitutions
- Reactions with protons
- Olefin metathesis

From this rather brief description of the role of ionic liquids in organic synthesis it is possible to see that ionic liquids hold great potential. Their ability in transition metal catalysis is remarkable even to the extent where they act as a co-catalyst. In some cases there is no need for a metal catalyst as the ionic liquid is both catalyst and solvent. The variety of the successful reactions possible in ionic liquids shows that they are serious contenders to current organic solvents. The remark by Seddon (1998), that ionic liquids could revolutionise the methodology of synthetic organic chemistry, might just prove to be true.

2.1.5 Designer Solvents

Freemantle (1998), entitled his article on ionic liquids `Designer solvents.' Seddon (2002) explains why ionic liquids are being described as designer solvents. For this term to be truly appropriate, it should be possible to design a solvent to optimize every chemical reaction of interest. The current chemical industry uses about 600 molecular solvents. For a class of solvents to be labeled `designer', they should be synthesizable many orders of magnitude greater than those already being used. So the obvious question is: ` How many ionic liquid systems could there be?' Seddon (2002), starts to answer this question by considering a matrix of anions and various cations, with *n* being the alkyl chain length on the cation.

Table 2-12: Possible ionic liquid combinations that can be generated for a particular cation type

n	Cl	(Al_2Cl_7)	(BF_4)	(PF_6)	(CH_3CO_2)	(NO_3)	(H_2PO_4)	$(CoCl_4)$	(Ni_2Cl)
2									
4									
6									
8									
10									
12									
14									
16									
18									

(Seddon, 2002)

From the above matrix, 81 possible ionic liquids can be generated for each cation type. Using the basic imidazolium structure (i.e. ignoring methyl substituents on the 2,4 and 5 carbons) and including pyridinium, 3-methylpyridinium and 4-methylpyridium, it is possible to generate 324 ionic liquids. Seddon (2002), goes on to describe, with the addition of more simple cation and anion series, that it is possible to generate at least 10^6 simple ionic liquids. From this, he points out, it is possible to have 10^{12} binary systems and 10^{18} ternary systems. Binary and ternary systems of ionic liquids may be necessary to generate the required combination of properties. He concludes that an optimum solvent for any given reaction will exist and the only problem will be to find it.

The interest in ionic liquid research has grown in the last few years, and as a result a number of research groups around the world have begun their own experimentation using ionic liquids. The bulk of the research has previously focused on imidazolium-based ionic liquids. Due to the number of potential combinations of ionic liquids mentioned above, researchers are producing and characterizing new classes of ionic liquids.

Visser et al. (2001) developed ionic liquids with a polycyclic *N*-alkylisoquinolinium cation ($[C_n isoq]^+$) in combination with the bis(perfluoroethylsulfonyl)imide anion ([BETI]⁻). The alkyl chain lengths were even-numbered ranging from 4 to 18 with their melting points ranged from -77°C to -47°C. The ionic liquids were stable to about 400°C.

Hagiwara et al. (1999) developed acidic 1-ethyl-3-methylimidazolium fluoride. They produced this by reacting (EMIM)Cl with HF. The melting point was found to be -90°C.

MacFarlane et al. (2001) have developed ionic liquids based on the dicyanamide anion. They combined this with quaternary ammonium, *N*-alkyl-*N*-methylpyrrolidinium or 1-alkly-3-methylimidazolium cations. Their aim was to produce low viscosity ionic liquids and the resulting combinations yielded viscosities in the range of 21 to 50 cP at 25 °C. 7 out of the 8 ionic liquids investigated had melting points below 0 °C.

Dzyuba and Bartsch (2001), produced a series of C_2-symmetrical imidazolium cations in combination with the hexafluorophosphate anion. Both the alkyl constituents on the nitrogen atoms were of the same length, and ranged from methyl to decyl. The ionic liquids ranging from dibutyl through to didecyl were found to be liquid at room temperature.

Yoshizawa et al. (2001), prepared a number of imidazolium based ionic liquids. What is interesting is that they alkylated only one of the nitrogen atoms and the adjacent C_2 in the ring. They also used a benzyl group on one of the ionic liquids. These were analyzed for electrochemical properties.

Yang et al. (2003), investigated the EMIMCl/$InCl_3$ system. It is similar to the EMIMCl/$AlCl_3$ system in that the ionic liquid properties vary with composition of the reactants. The system was liquid at room temperature between the compositions of 0.40 and 0.75 $InCl_3$ mole fraction.

Merrigan et al. (2000), prepared a number of fluorous ionic liquids. It differs from those investigated by Hagiwara et al. (1999) in that the cation contains perfluorinated carbon chains. The aim was to solubilize perfluorinated hydrocarbons and this was successfully demonstrated.

Other investigations have resulted in ionic liquids with chiral cations (Wasserscheid et al. 2002), inert carborane anions (Larsen et al. 2000) and even gold containing anions (Hasan et al. 1999).

These ionic liquids investigated are only the tip of the iceberg in terms of possible ionic liquids. Certainly many more systems will be discovered in the near future. The only limitation, it seems, will be the imagination of the researcher and whether there is a use for the particular ionic liquid.

2.1.6 Ionic liquids for Clean Technology

The Montreal Protocol has highlighted the need to reduce the emission of volatile organic chemicals (VOC's) (Seddon, 1997). Chemical companies using VOC's in their processes have also realized that being environmentally responsible is important to find favour with an environmentally informed consumer base. The need for clean technology, or 'green chemistry' as it is also referred to, is necessary if this aim is to be achieved, and not only from an environmental perspective but also from a financial perspective. Sheldon (1993), uses the *E*-factor to describe general efficiency of some common industrial processes. The *E*-factor is the mass ratio of the by-products to the desired products.

Table 2-13: By-products as a factor of products for the chemical industry

Industry	Production (tpa)	*E*-factor
Oil refining	10^6-10^8	0.1
Bulk chemicals	10^4-10^6	1-5
Fine chemicals	10^2-10^4	5-50
Pharmaceuticals	10^1-10^3	25-100

(Sheldon, 1993)

This table gives a different view to popular perception that oil refining is the most inefficient industry. Comparing industries on net waste output is not a fair comparison as different industries process vastly different volumes of chemicals. Considering the throughputs of different industrial sectors, it is the oil refining that is the most waste conscious and the pharmaceuticals that are the least. Even though the net waste outputs of the fine chemicals and pharmaceutical industry are small, there will be increasing pressure on industries that operate 'dirty', inefficient processes. It consequently makes more sense for these industries to pursue clean technologies, as a reduction in the *E*-factor would bring about significant financial benefits in the high value end of the market.

One of the primary sources of waste in organic industrial processes are the VOC's used to synthesize organic chemicals. Seddon (1997), estimates the annual worldwide usage at £4 000 000 000. This is clearly a large market and alternatives to VOC's have to prove competitive. Seddon suggests four alternatives:

1. solvent-free synthesis
2. the use of water as a solvent
3. the use of supercritical fluids as solvents
4. the use of ionic liquids as solvents

The first option is to carry out synthesis in a solvent-free environment. Modifying current synthesis processes to work in a solvent-free environment may take too long and prove unfeasible. The second option of using water as a solvent may be limited as immiscibility between water and organics is generally great. The third and forth options are the most likely, as they can be used as substitutes to

VOC's. This would allow current processes to operate with little or no modification to the existing unit operations and accompanying equipment.

Ionic liquids and supercritical fluids have been described as the two most promising solvent systems for cleaning up the modern chemical industry. The reason ionic liquids have been thrust into the limelight of green chemistry is their lack of vapour pressure. VOC's, are difficult to contain. When considering the number of chemical processes that use VOC's and the quantities that are consumed annually, it can be seen that a more environmentally friendly substitute would prove greatly beneficial. While ionic liquids overcome the problem of containment, not much is known of their toxicity. This will have to be investigated if the use of ionic liquids in chemical process development is to be fully realised.

In addition to environmental considerations, 'green chemistry' favours the need for process intensification. This is done with the aim of using less solvent. This can be achieved by doing some of the following:

1. Choosing a solvent that dissolves a greater volume of reactant (in the case of a reaction) or component (in the case of a separation)
2. Increasing conversion of reactants to products
3. Improving selectivity in catalytic reactions and therefore reducing by-products

Research into ionic liquids in these fields will help determine the potential of ionic liquids to help achieve one or more of the above objectives.

2.1.7 Industrial potential of ionic liquids

For any research field to grow, it has to have a direction or an objective. In the case of ionic liquids it is to develop processes on an industrial scale in order for the potential benefits to be fully realized. This review will look at the various research groups and applications they have developed thus far.

Perhaps the most well-known hub of ionic liquid research is the Queen's University Ionic Liquid Laboratories (QUILL) based in Belfast and headed by Ken Seddon and Jim Swindall. This is the first and only institution dedicated to ionic liquid related research (Seddon, 2002). Founded in 1999 as an industrial consortium, it currently has 19 members some of which include BP, Chevron, DuPont, GlaxoSmithKline, Merck, and Sasol. The centre has generated about 20 patent applications in a diverse range of fields. One of the spin-offs of the centre is that there is now a commercial source of ionic liquids. The fact that there is such support from large chemical-related companies clearly shows the interest in developing ionic liquid applications.

Winterton of ICI Chemicals & Polymers (Freemantle, 1998) regards industrial exploitation of ionic liquids as somewhat in its early days. He gives 3 important economic drivers for the development of chemical processes using ionic liquids:

1. Greater reaction selectivity which results in less by-product or waste formation
2. Enhanced reaction rates in ionic liquid media can result in reduced plant size and cost.
3. A process with fewer steps and milder operating conditions will reduce energy requirements and improve safety

He does, however, point out some key questions that need to be addressed before ionic liquids can be used on a large scale. Some of these include:

1. Cost of ionic liquids
2. Robustness in use
3. Heat- and mass-transfer questions
4. Degree to which ionic liquids can be recycled and re-used
5. Ease of manipulation on the industrial scale
6. Materials compatibility
7. Safety issues

Possibly the first process involving an ionic liquid to be licensed is the Difasol process developed by the French Petroleum Institute (IFP). Chodorge (Freemantle, 1998), compares it to IFP's existing Dimersol X process which is a homogeneous catalytic process that converts n-butenes to isooctenes. The Dimersol X process is currently used in five industrial plants to produce 200 000 tons of isooctene per year. The new Difasol process, in addition to using less catalyst, has a conversion of between 70 and 80% and a dimer selectivity of 90 to 95% as the isooctene is poorly miscible in the ionic liquid. Chodorge regards this as very high. What is important is that the current Dimersol units can be modified to operate the Difasol process and the scale is likely to be between 20 000 to 90 000 tons per unit per year.

This modification of existing equipment is possibly key to implementing ionic liquid technologies. As Brennecke and Maginn (2001) point out, even if all of the technical challenges are overcome, the barriers inhibiting the adoption of ionic liquids by the chemical industry are still huge. The current economic structure of the chemical industry is such that return on investments is low and therefore technologies requiring large capital expenditures are unlikely to be adopted (Harold and Ogunnaike, 2000). While this has restricted many other promising technologies from being implemented, it may be different for ionic liquids. By modifying existing equipment, the bulk of the cost is associated with the ionic liquid itself.

BP chemicals have been collaborating with Seddon and his group since 1980 and have developed a number of applications since. In one application, an ionic liquid was used to replace hydrofluoric acid which was previously the only reagent that could work successfully for a particular application (Freemantle, 1998). The collaboration has in recent years, focused on the use of ionic liquids in refinery processes. According to Atkins of BP Chemicals (Freemantle, 1998), they are looking to replace the volatile and corrosive mineral acids. The mineral acids usually go out with the product and recovery usually involves many energy-intensive steps. Biphasic reactions in ionic liquids offer a better alternative. One possible reaction is the manufacturing of ethylbenzene. The aim is to use the ionic liquid as both solvent and catalyst and to produce ethylbenzene by the direct alkylation of benzene with ethylene without using ethyl chloride as an alkylating agent. Atkins does, however, stress that it is not a foregone conclusion that the technologies will be adopted as they first have to be compared economically to other new technologies. According to Atkins, there are two things that have to be in place before any technology can be developed further:

1. The final product has to meet the perfomance required in the marketplace.
2. The cost of production has to be in the right ballpark.

He sums up the current position on ionic liquid technology by stating that the 'engineering is lagging behind the chemistry.'

Another area which has found applications for ionic liquids is the nuclear processing industry. This has risen out of the collaboration between British Nuclear Fuels (BNFL) and QUILL. The application is in the processing of spent nuclear fuel. The spent fuel is first converted to a higher oxidation state which makes it soluble in an ionic liquid. The spent fuel is dissolved and the unreacted uranium and plutonium is recycled. The need for research was to develop a process that could handle more complex and highly irradiated fuels.

Another application in separation is a patented process by Chevron. The method separates olefins from mixtures of olefins and non-olefins. This involves complexing the olefin with an olefin-complexing metal salt in an ionic liquid. The method is enhanced by the poor solubility of the paraffins and other non-olefins in the ionic liquid. As a thorough review of patents has not been undertaken, it is possible that there are many other patented applications involving ionic liquids.

Brennecke and Maginn (2001) suggest other applications of ionic liquid technology.

- Gas separations
- Liquid separations
- Solvents for cleaning operations
- Electrolytes/Fuel Cells
- Lubricants
- Heat-Transfer Fluids

Some of the above applications that involve separation will be discussed further.

What is interesting is a project funded by the European Community to develop three pilot plants using ionic liquid technology (Freemantle, 1998). Managed by BP Chemicals and including groups such as QUILL, with the objective to examine the technical and the economic feasibility of using ionic liquids in comparison with other acid systems. The project has three specific aims:

1. To manufacture ionic liquids and make them commercially available
2. To explore the use of ionic liquids as catalysts for aromatic alkylation reactions
3. The use of ionic liquids as catalysts for producing fine chemical intermediates

From this brief description of the industrial potential of ionic liquids it is possible to see that the technology is not limited to the laboratory scale. It can work on a pilot-scale and should in the near future prove possible on an industrial scale. All that remains, is to prove the economic viability of these technologies.

2.1.8 Predicting the properties of ionic liquids

Ionic liquids have been shown to be appropriately called 'designer solvents'. While this has its obvious advantages, the sheer number of possible ionic liquid brings about the question: How do we find the right ionic liquid for the right task? This will have to be selected by properties required by the specific task. To determine the properties experimentally of all the possible ionic liquids is much like trying to measure the binary VLE of all the known chemicals - the task is just too enormous. If we cannot measure all the properties, then we have to try and predict them. With the computing power available today, even calculations involving complex species like ionic liquids are quite possible. Current group contribution methods do not work as they are limited to non-electrolyte compounds. Experimental measurements serve as an important source for determining trends and for use as a comparison to predictive methods. Currently there is a reasonable foundation of experimental work on which predictive methods can build. Some of the methods currently being developed are discussed below.

Brennecke and Maginn (2001) describe two distinct types of simulation that will be useful in the development of ionic liquids. The first are detailed atomistic simulations that require a molecular mechanics forcefield. These calculations are able to generate transport property data which is essential in engineering design. The simulations are, however, limited by the accuracy of the forcefields for the ionic liquid and are more useful when a maximum amount of information on a relatively small number of compounds is required.

The second is quantitative structure-property relationship (QSPR) modeling. This technique has been used in the pharmaceutical industry and is likely to be useful for ionic liquids. QSPR modeling works by making a statistical link between the physicochemical properties of a compound and a set of molecular descriptors. Given experimental data for a small number of representative compounds, the method can provide pseudo-quantitative property prediction for related compounds. This is where experiments and simulations need to work side by side in order to generate large quantities of data in a short time span. The simulation is also able to correlate properties such as toxicity and corrosivity which are not easily available from the first method described. QSPR methods are most useful when the goal is to obtain a qualitative ranking of properties for a large number of compounds.

Another technique is the 'Conductor-like Screening Model for Real Solvents' (COSMO-RS) developed by Klamt and coworkers (Klamt and Eckert, 2000). The method yields the necessary information about the molecular interactions in solution from quantum chemical interactions on the chemical compounds. One advantage over group contribution methods is that it can be used for calculations involving ionic liquids. Diedenhofen et al. (2003), used COSMO-RS to predict values for the systems measured experimentally by Heintz et al. (2001,2002a, 2002b). Comparisons were made for activity coefficients at infinite dilution for various organics solutes in ionic liquids for experimental and calculated values. Calculated values for the pyridinium-based ionic liquid showed a negative deviation from experimental values while the imidazolium-based ionic liquids showed both positive and negative deviations from experimental values. The absolute values of the deviations are quite significant and further work on the method should yield more accurate results.

Predictive methods have been investigated and are likely to improve in the future. While these methods may not always generate very accurate data, they can at least be used as a screening tool for further experimental work.

2.2 Activity coefficients at infinite dilution and Gas-Liquid chromatography

2.2.1 Activity coefficients at infinite dilution

Activity coefficients account for the deviation in behaviour of real solutions from ideal solutions. It is in dilute regions that some of the greatest departures from ideality are frequently observed, and consequently activity coefficients at infinite dilution are of significant importance. This can be summed up in a statement by Raal and Mühlbauer (1998), that 'infinite dilution activity coefficients almost always represent the most accurate characterization of system behaviour in the dilute regions.' Additional uses of activity coefficients at infinite dilution include:

- Screening for potential azeotropes (Palmer, 1987)
- Screening of solvents for solvent extraction (Palmer, 1987) and extractive distillation (Perry and Green, 1998)
- Prediction of binary VLE data, which in turn are used to predict multi-component VLE data (Howell et al., 1989)

These activity coefficients at infinite dilution can be determined experimentally by various techniques, each having their own benefits and drawbacks. Raal and Mühlbauer (1998), list the following principal techniques:

- Differential ebulliometry
- Use of a differential static apparatus
- Gas chromatographic methods
- Inert gas stripping

It is the gas-liquid chromatographic method that will be discussed further as it is the technique used in this work. The reader is referred to the above text for a review of the other methods.

The prediction of activity coefficients at infinite dilution are usually performed with group contribution models such as UNIFAC and ASOG. However, these models do not account for the long-range interactions in ions present in ionic liquids, and thus will not be discussed.

2.2.2 Gas-Liquid Chromatography

According to Letcher (1978), gas-liquid chromatography (GLC) may be used to measure, in addition to activity coefficients, second virial coefficients of gas mixtures, partition coefficients, adsorption and partition isotherms, and complex formation constants. Other temperature-dependent properties such as excess enthalpies may also be measured, but with less accuracy.

The mechanism of GLC is described by Moollan (1996): *'When the solute reaches the column, an equilibrium is set up between the liquid phase and the carrier gas phase so that a portion of the sample always remains in the gas phase. This portion moves a little further along the column in the carrier gas stream, where it again equilibrates with the stationary phase. At the same time, material already dissolved in the stationary phase re-enters the gas phase so as to restore equilibrium with the clean carrier gas, which follows the zone of vapour.'*

This technique allows for the measurement of activity coefficients at both finite and infinite solute concentrations. As the basic process involves the partitioning of a solute between two immiscible phases, limitations do arise on the type of systems measurable by this technique. Letcher (1978) describes a few of these limitations:

- The solute must be volatile if retention times are to be reasonable
- The solvent must be liquid at the experimental temperature and the corresponding vapour pressure must be sufficiently low to prevent evaporation off the column
- The carrier gas must be nearly insoluble in the stationary phase (solvent)
- Mixtures in which adsorption effects are negligible

Letcher (1978) does remark, however, that accurate activity coefficients at infinite dilution can be obtained for systems that meet these criteria.

Although somewhat dated, the data bank by Bastos et al. (1985) for activity coefficients at infinite dilution gives a good indication of the popularity of the technique among researchers. From a total of 2097 experimental values in the data bank, 1849 (>88%) were measured using the GLC technique.

2.2.3 Gas-Liquid chromatography involving Ionic Liquids

Ionic liquids are ideally suitable stationary phases when used in GLC. They are non-volatile and thus there is no possibility of them evaporating from the column. In most cases they are sufficiently viscous to coat the solid support, thus preventing adsorption of the solute onto the solid support surface.

The use of liquid salts in GLC has been investigated even before the term 'ionic liquid' was coined. Poole and co-workers evaluated liquid salts as stationary phases in GLC and much of their work focused on tetraalkylammonium (TAA) salts (Poole et al. 1984). A number of TAA thiocyanate salts were prepared and evaluated (Coddens et al. 1986). Solute-solvent interactions were investigated for a number of TAA salts and activity coefficients at infinite dilution were obtained (Furton and Poole, 1987). Butanol, nitropropane and pyridine exhibited negative deviations from Raoult's law as a result of strong interactions with the liquid salt. Benzene and 2-pentanone exhibited small positive deviations from Raoult's law due to dissimilarity in polarity between the solutes and the liquid salt. Attention was also given to tetraalkylphosphonium salts (Pomaville et al. 1988). Kersten et al. (1989) proposed a new method for the determination of solvent strength and solvent selectivity in GLC. They defined these in terms of the partial molar Gibbs free energy of solution. Comparisons were made between TEA alkanesulfonate and perfluoroalkanesulfonate liquid salts (Pomaville and Poole, 1989, 1990). Furton and Morales (1991) studied the effect of anion chain length on the solvent properties of liquid tetrabutylammonium alkylsulfonate salts. They found a net increase in solute-solvent interactions for non-polar solutes as the anion chain length increased.

In more recent years, ionic liquids have been used as stationary phases in GLC by Armstrong et al (1999) and Heintz et al. (2001, 2002a, 2002b). More attention has been given to the imidazolium-type ionic liquids in reaction chemistry and this has also been the case in GLC. Armstrong et al. (1999) used

(BMIM)Cl and (BMIM)PF_6 as stationary phases with benzene, butanol, 2-pentanone, nitropropane and pyridine as solutes. The ionic liquids were compared to commercial polysiloxane columns by determining the Rohrschneider-McReynolds constants for the systems. The ionic liquids show much larger variation in the constants compared to the polysiloxane stationary phases. These constants are thought to indicate various proton donor/acceptor capabilities and dipolar interactions and the effects of the different anions (i.e. Cl and PF_6) are discussed in terms of this.

Heintz and co-workers (2001, 2002a, 2002b) have investigated a wide range of solutes in three ionic liquids. The ionic liquids investigated were 4-methyl-*N*-butyl-pyridinium tetrafluoroborate ((MBPy)BF_4), 1-methyl-3-ethyl-imidazolium bis(trifluoromethyl-sulfonyl) amide ((EMIM)Tf_2N) and 1,2-dimethyl-3-ethyl-imidazolium bis(trifluoromethyl-sulfonyl) amide ((EM_2IM)Tf_2N). The solutes were alkanes, alkenes, aromatics, alcohols, carbonyls and chlorinated organics. Experiments were conducted in the temperature range 313 – 363 K, which explains the elution of alcohols and other polar solutes. Activity coefficients at infinite dilution were measured at a number of temperatures for each solute and the partial molar excess enthalpy at infinite dilution was subsequently calculated.

The use of the GLC method is an efficient method to determine activity coefficients at infinite dilution especially for ionic liquids used as a stationary phase. In addition, it should be quite possible to investigate solute-solvent interactions in a large number of ionic liquids systems.

2.3 Separation Techniques

Separation techniques have been used even before the field of chemical engineering was formally defined. The mixing of chemicals to form a mixture is spontaneous, and is accompanied by an increase in entropy. To reverse this process (i.e. separate a mixture into its pure components), energy is required as separation is non-spontaneous. The separation is brought about by the creation of a second phase, which involves an *energy-separating agent* (ESA) and/or a *mass-separating agent* (MSA). There are various separation processes available to the process engineer and a comprehensive discussion is given by Seader and Henley (1998). Only the separation processes of liquid-liquid extraction and distillation and the associated equilibrium data will be discussed further.

2.3.1 Liquid-liquid extraction and equilibrium data

2.3.1.1 Ternary liquid-liquid extraction

Liquid-liquid extraction (also referred to as solvent extraction) is used as an alternative or in conjunction with distillation. It is most often discussed, but not limited in practice, to ternary systems. The process is illustrated in Figure 2-8.

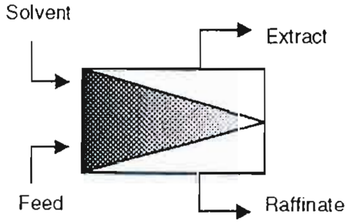


Figure 2-8: Phase splitting of ternary mixtures

A solvent is added to a mixture in order to create a second phase. The resulting mixture has an equilibrium composition which comprises two immiscible liquid phases. The composition of these two phases depends on the mutual solubility of the components. For a ternary system the feed comprises two components while the solvent is pure. The component to be extracted is the solute, while the other feed component is the carrier. While the compositions of the phases may vary, one phase is rich in the solvent and is called the extract and the other phase is rich in the carrier and is called the raffinate.

The extraction process is usually achieved in a number of steps or stages. The stages can be arranged in one of three ways:

1. Co-current
2. Cross-current
3. Counter-current

The co-current arrangement is usually not used as all it does is increase the residence time. The counter-current arrangement is generally used as it is the most efficient of the three arrangements.

Madhavan (2002) suggests that the following points be considered when optimizing an extraction process:

- Solvent selection
- Operating conditions
- Mode of operation
- Extractor type
- Design criteria

A closer look will be taken at solvent selection.

Madhavan (2002) proposes that for a particular system, the distribution/partition coefficient and the selectivity are the most important parameters that govern solvent selection. Selectivity is important when there are number of components in the feed. The solvent has to have a good affinity for the particular solute over other components in the feed. Therefore, the desired properties of a solvent are:

- A high distribution coefficient
- Good selectivity towards solute
- Little or no miscibility with feed solution
- Easy recovery for recycle

These are by no means the only factors, and other factors considered by Madhavan (2002) that affect solvent selection are:

- Boiling point
- Density
- Interfacial tension
- Viscosity
- Corrosiveness
- Flammability
- Toxicity
- Stability
- Compatibility with product
- Availability
- Cost

2.3.1.2 Liquid-liquid equilibrium data

There are usually two types of liquid-liquid equilibria reported in literature. The first type is the LLE of binary mixtures as a function of temperature. The second is the LLE of ternary mixtures at a fixed temperature. The first type finds its use in azeotropic distillation where the distillate forms two phases upon condensation. The second is more applicable to liquid-liquid extraction. Ternary LLE is usually represented on an equilateral triangle graph known as a ternary phase diagram. The apexes of the phase diagram represent the pure components. The binodal or co-existence curve separates the one-phase region from the two-phase region, and a tie-line connects two points corresponding to the compositions of the two liquid phases in equilibrium. Ternary phase diagrams are classified into two major types: type 1 in which the solvent and carrier show immiscibility (Figure 2-9a), and type 2 in which the solvent shows immiscibility with both the carrier and solute (Figure 2-9b).

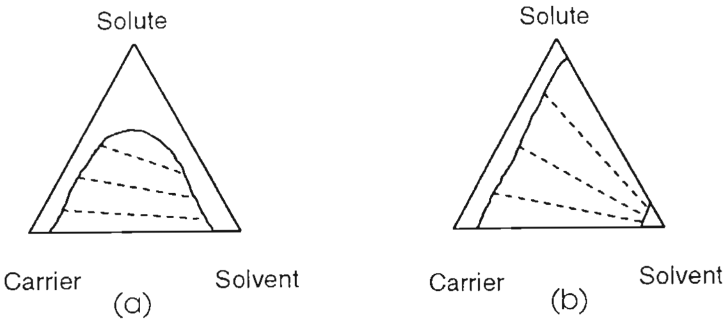


Figure 2-9: Two types of ternary phase diagrams

Sørensen et al. (1979a, 1979b) and Magnussen et al. (1980) compiled a data bank of LLE data and evaluated various aspects of the data. Out of a total of 405 ternary LLE systems, 75 % were of type 1 shown in Figure 2-9a and 20 % were of type 2 shown in Figure 2-9b. The remaining 5 % comprised variations that were not classified as above.

Sørensen et al. (1979a) mention that the effect of pressure on the liquid solubility is negligible for pressures ranging up to 20 atm and as a consequence, it is common that authors omit the pressure for LLE data.

There are two methods by which ternary LLE data are obtained. The first is the *method of analysis*. This consists of letting a ternary mixture separate into two liquid phases and then determining the compositions of the two phases by analyzing for each component. This method gives the tie-lines directly. The second is the *method of titration*. This involves adding the third component to a single-phase known mixture of the other two components until the onset of turbidity. This generates the binodial curve. Tie-lines are analyzed by determining the concentration of only a single component in each of the phases. A variation of this method has been used in this work and is described in Chapter 4.2.

Briggs and Comings (1943) took ternary LLE measurement a step further. They studied the effects of temperature on ternary LLE systems. Two systems were measured and the resulting effects were different. For the benzene-acetone-water system, an increase in temperature altered the slopes of the tie lines markedly but reduced the two-phase region only slightly. For the docosanediphenylhexane-furfural system, an increase in temperature hardly affected the slope of the tie lines, but reduced the two-phase region considerably.

2.3.1.3 Liquid-liquid equilibria/extraction involving Ionic Liquids

Ionic liquids have interesting miscibility/immiscibility properties with other liquids. LLE measurements involving ionic liquids have begun and the task is to develop these to the industrial scale. As discussed in Chapter 2.1.7, the ideal means would be to substitute ionic liquids for currently used solvents in existing processes. This may be quite possible in the case of liquid-liquid extraction. Madhavan (2002) mentions that for an existing process, replacing the solvent is usually a last resort as this requires re-optimization. He does, however, note that environmental and economic considerations often bring about the need to improve solute recovery. This is where ionic liquids have an opportunity to be developed. Currently, a number of possible applications for ionic liquids in liquid-liquid extraction have been investigated.

Huddleston et al. (1998) were the first to undertake LLE related investigations of ionic liquids. The partitioning of simple, substituted-benzene derivatives between water and (BMIM)PF_6 were investigated and related to the solute's charged state or relative hydrophobicity. The dependence of the distribution ratio on pH was also determined for the ionizable solutes. The distribution ratio varied significantly with pH, indicating that pH could be used to achieve the desired results even in a multicomponent system.

The first thorough LLE study was undertaken by Selvan et al. (2000). They studied the ternary LLE of toluene + heptane, in the ionic liquids (EMIM)I_3 and (BMIM)I_3 . They employed the method of analysis and thus generated a series of tie lines. The NRTL model was used to correlate the data and was shown to work satisfactorily. Analysis of the systems showed that the ionic liquids are effective solvents for removing toluene from heptane that contains only a small amount of toluene.

Letcher et al. (2003a, 2003b) have measured LLE of ternary mixtures which include the ionic liquid (MOIM)Cl. Measurements were undertaken with the aim of evaluating (MOIM)Cl as a solvent to extract alkanols and aromatics from alkanes. The systems exhibited large two-phase regions and high selectivities which make it a possible alternative to other solvents used for separation of these systems.

Ternary LLE were also measured by Swatloski et al. (2001), but for different reasons. With the possibility of using ionic liquids in industrial processes, the need for cleaning reaction vessels of residual ionic liquid without using VOC's becomes necessary. Hydrophobic ionic liquids are insoluble in water and supercritical CO_2. Swatloski et al. (2001), therefore, suggest the use of a mixture of ethanol and water (aqueous ethanol) to dissolve hydrophobic ionic liquids. The ionic liquid investigated was $(BMIM)PF_6$ and was found to be totally miscible in aqueous ethanol between 0.5 and 0.9 mol fraction ethanol.

Most of the measured LLE of mixtures containing ionic liquids are binary and are measured at various temperatures. Domańska and Marciniak (2003) studied the solubility of $(EMIM)PF_6$ and $(BMIM)PF_6$ in various aromatic hydrocarbons. The systems exhibit upper critical solution temperatures (UCST). The two-phase area was found to decrease with increasing alkyl chain length on the ionic liquid.

Heintz et al. (2003) and Wu et al. (2003) studied binary LLE of ionic liquids and alcohols. Heintz et al. (2003) studied the LLE of $(EMIM)NTf_2$ + 1-propanol, 1-butanol, 1-pentanol. All systems exhibited a UCST which increased with increasing chain length of the alcohol. Wu et al. (2003) studied the LLE of 1-butanol + $(R_nMIM)PF_6$ where R_n= butyl, pentyl, hexyl, heptyl, octyl. The systems exhibited UCST's which decreased with increasing alkyl chain length on the ionic liquid. COSMO-RS is used to predict the LLE and a comparison is made with the experimental data. The predicted UCST's are in good agreement with the experimental, however the compositions at which they predict are less by about 0.12 mol fraction. For a specific composition there is an over-prediction of the corresponding temperature.

Anthony et al. (2001) and Wong et al. (2002) studied binary LLE of ionic liquids and water. Anthony et al. (2001) investigated the ionic liquids (BMIM)PF_6, (MOIM)PF_6 and (MOIM)BF_4. The solubility of water at 22°C was 0.7 wt. % in (MOIM)PF_6, 2 wt. % in (BMIM)PF_6 and 1.8 wt. % in (MOIM)BF_4. The difference in water solubility in the ionic liquid containing the PF_6^- and BF_4^- anions is quite significant. A comparison of water solubility in organics shows that the three ionic liquids are similar to longer chain alcohols in this characteristic. Wong et al. (2002) measured the solubility between water and (EMIM)PF_6 or (BMIM)PF_6. Measurements were studied in the temperature range 308 – 323 K. The maximum solubility of water was 5 wt. % in (EMIM)PF_6 and 3.7 wt. % in (BMIM)PF_6. This is expected as the PF_6^- anion is hydrophobic.

A number of other investigations of ionic liquids as solvents for extraction have been undertaken. Visser et al. (2001) investigated ionic liquids as replacements for the hydrophobic phase in the extraction of metal ions from aqueous solutions. The ionic liquids used were (BMIM)PF_6 and (HMIM)PF_6 and the ions included Na^+, Hg^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}, Fe^{3+}, Cl^- and I^-. Without the use of additional extractants, the distribution ratios of the ions in the ionic liquid/water systems is relatively low. The increase of pH and the addition of extractants PAN (1-(pyridylazo)-2-napthol), and TAN (1-(thiazolylazo)-2-napthol) to the ionic liquid improved the distribution ratios significantly. Dia et al. (1999) combined dicyclohexano-18-crown-6, which is a crown ether, with a number of ionic liquids. This was used to extract strontium ions from acidic nitrate media and resulted in high distribution ratios (> 10^4). However, Dietz and Dzielawa (2001) performed further investigations and found that the transfer occurred by cation-exchange, which could place limitations on the benefits in metal ion extraction applications.

Ionic liquids also have potential in biochemical liquid-liquid processes. Cull et al. (2000) investigated the extraction of Erythromycin-A, an antibiotic, from an aqueous solution. They compared the partition coefficient of the ionic liquid (BMIM)PF_6/aqueous system with the butyl acetate/aqueous system as a function of pH. Except at high pH conditions, the ionic liquid compared favourably and can be considered as a direct replacement for solvents in this type of application.

Fadeev and Meagher (2001) studied the ability of (BMIM)PF$_6$ and (MOIM)PF$_6$ to extract n-butanol from an aqueous fermentation broth. The distribution coefficients at 23°C were 0.85 for (BMIM)PF$_6$ and 0.92 for (MOIM)PF$_6$. These values increase with an increase in temperature.

Carda-Broch et al. (2003) investigated the ability of (BMIM)PF$_6$ to extract phenol derivatives from aqueous solutions. Phenol derivatives are commonly used as antioxidants in food and as free radical scavengers. They also investigated the extraction of amino acids from aqueous solutions. Amino acids are not soluble in (BMIM)PF$_6$, but the extraction was made possible by the addition of a crown ether to the ionic liquid.

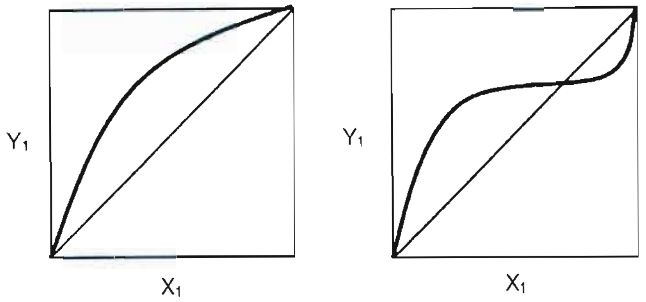
2.3.2 Distillation and Vapour-liquid equilibrium data

2.3.2.1 Distillation

Distillation is the most commonly used separation technique used in the chemical industry. Much of the design of the apparatus centers around the chemicals which are to be separated and more specifically the vapour-liquid equilibria which they form. In practice, few process streams are pure binaries. However, in certain cases, two components are in significant quantities and the system can be treated as a pseudo-binary. The review below is based on binary systems, unless otherwise stated.

Separation of components by distillation is based on the relative volatility of the components. The greater the relative volatility, the easier the separation. Not all chemical systems are easily separated by distillation. Some systems have components which have low relative volatilities ($\alpha < 1.05$). Separating a component to significant purity becomes uneconomical as high reflux ratios and a large number of trays are needed.

Some systems exhibit an azeotrope and cannot be separated into each of the pure components in the conventional manner. For a binary mixture, an azeotrope can be observed as the intersection of the equilibrium composition line with the 45° line on an x-y diagram (Figure 2-10(b)). These azeotropes result from liquid phase non-idealities, represented by activity coefficients. There are two types of azeotropes namely, maximum boiling azeotropes and minimum boiling azeotropes. Yee (2002) states that 90 % of known azeotropes are of the minimum variety. Depending on the feed composition, conventional distillation products result in the azeotrope composition and one of the pure components. In order to separate a binary mixture which is limited by an azeotrope, an enhanced distillation technique, described by Stichlmair et al. (1989), has to be employed.



(a) (b)

Figure 2-10: Equilibrium x-y diagrams of (a) a zeotropic mixture and (b) an azeotropic mixture, with x_1 and y_1 the liquid and vapour compositions of component 1 respectively.

1. Extractive distillation: a high boiling solvent is added near the top of the column to favourably alter the relative volatility in order to separate the components. A second column separates the bottoms in order to recycle the solvent.
2. Salt distillation: a salt is added to the top reflux in which it dissociates ionicly. Similar in principle to extractive distillation.
3. Pressure-Swing distillation: a method for separating a pressure-sensitive azeotrope that utilizes two columns operated in sequence at two different pressures.

4. Homogeneous azeotropic distillation: separation by addition of an entrainer that forms an azeotrope with one of the components.
5. Heterogeneous azeotropic distillation: the addition of an entrainer results in a minimum-boiling heterogeneous azeotrope. The azeotrope splits into two liquid phases in the condenser, one of which is recycled and the other sent to another separation step.
6. Reactive distillation : the separating agent reacts preferentially and reversibly with one of the azeotropic components. The reaction product is then distilled from the non-reacting component and the reaction is reversed to recover the initial component.

These techniques can possibly be compared as below:

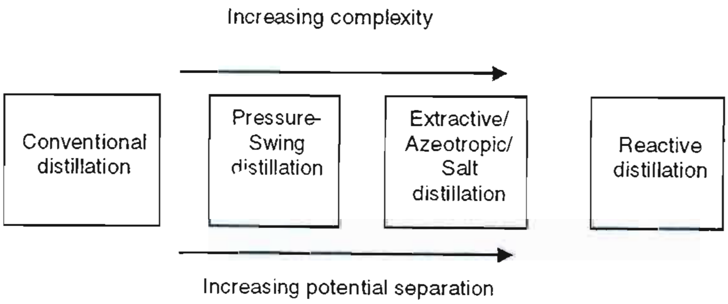


Figure 2-11: A comparison of distillation techniques

A further look will be taken at extractive distillation. In developing an extractive distillation process, Yee (2002) suggests the following steps:

1. Choosing the solvent
2. Developing or finding necessary data
3. Preliminary screening
4. Computer simulation
5. Small scale testing

Yee (2002) considers the selection of the solvent as one of the most important steps in developing a viable extractive distillation process. The following criteria are suggested in selecting a solvent:

- Solvent should enhance significantly the natural relative volatility of the key component.
- Solvent should not be required in high solvent/feed ratios
- Solvent should remain stable in the feed components and should not lead to formation of two liquid phases
- Solvent should be easily separable from the bottom product
- Solvent should be inexpensive and readily available
- Solvent should be stable at the temperature of distillation and solvent separation
- Solvent be non-reactive with the components of the feed mixture
- Solvent should have a low latent heat
- Solvent should be non-corrosive and non-toxic

However, no single solvent or solvent mixture satisfies all the criteria, and compromises must be reached.

Perry's handbook (Perry and Green, 1997) suggests a two-step procedure for the selection of solvents.

1. First level: Broad screening by functional group or chemical family. Selection is based on hydrogen and polarity characteristics. Solvents are also classed in groups according to their tendency to give positive or negative deviations from Raoult's law.
2. Second level : Identification of individual candidate solvents

- Boiling point characteristics: A solvent with a boiling point of at least 40 °C above the heaviest component ensures that it remains primarily in the liquid and is unlikely to form any additional azeotropes.
- Selectivity at infinite dilution : Rank the candidate solvents according to their selectivity at infinite dilution
- Experimental measurement of relative volatility: Rank the candidate solvents by the increase in relative volatility caused by the addition of the solvent.

The applicability of these criteria to ionic liquids will be discussed in Chapter 7.

2.3.2.2 Vapour-liquid equilibrium data

Accurate vapour-liquid equilibrium (VLE) data are essential to the design of any distillation process. Distillation processes usually, but not necessarily, operate at atmospheric and sub-atmospheric pressures. Thus the necessary data are usually obtained by low pressure VLE measurements. A brief description of the different types of apparatus and their development, as given by Raal and Mühlbauer (1998) and Ramjugernath and Raal (2001), is shown in Figure 2-12.

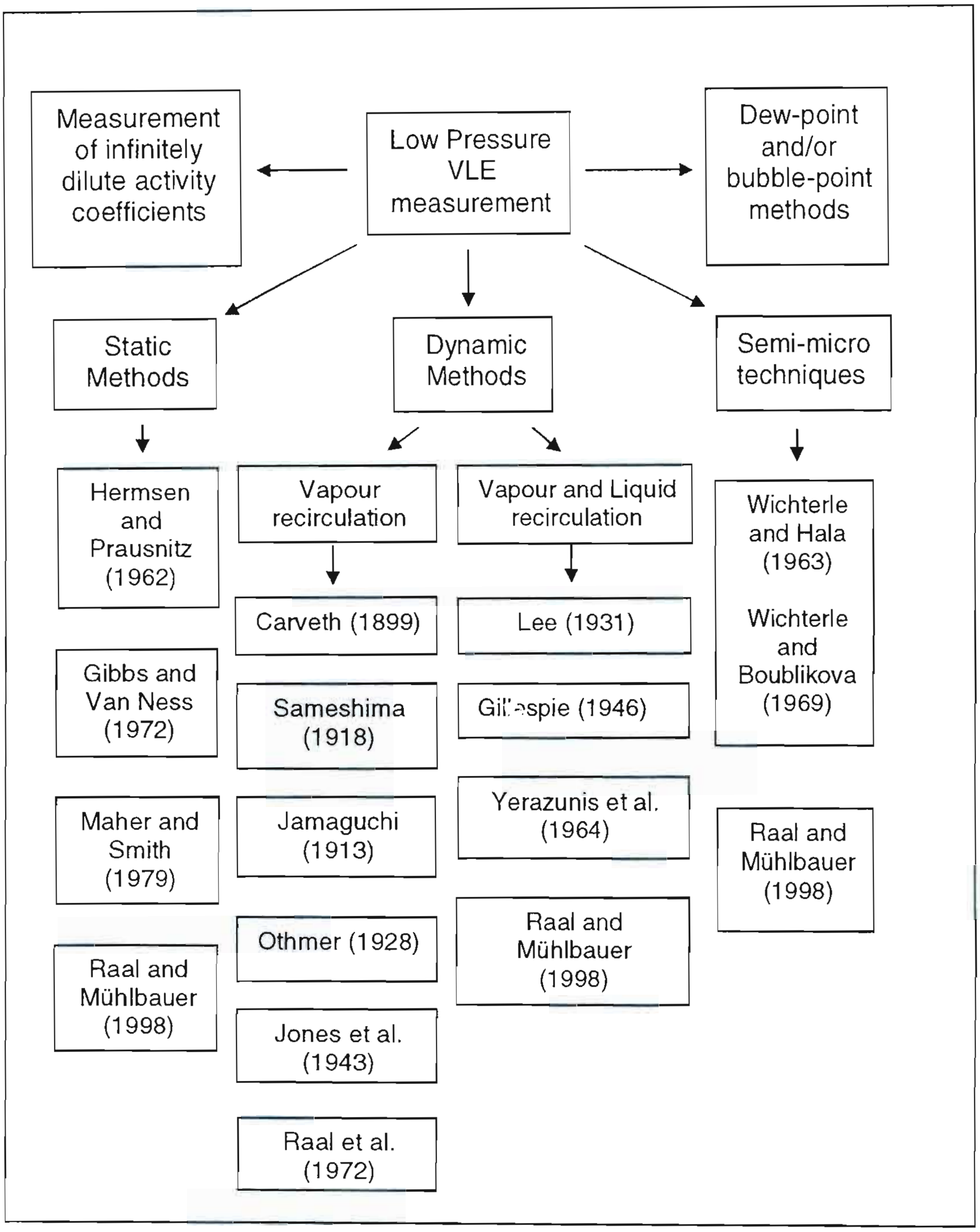


Figure 2-12: Methods and developments in low pressure VLE measurement

2.3.2.2.a) Dynamic Equilibrium Stills

Equilibrium stills that operate by vapour or vapour and liquid recirculation are classified as dynamic. Early designs allowed for recirculation of the vapour phase only such as stills developed by Carveth (1899), Jamaguchi (1913), Sameshima (1918), and Othmer (1928). Raal and Mühlbauer (1998) discuss some of the sources of error in the Othmer (1928) design which are:

- Incorrect equilibrium temperature measurement
- Likelihood of partial condensation of saturated vapour
- Preferential flashing of vapours rich in the more volatile component
- Entrainment of liquid droplets in the vapour stream

An improvement in the design was achieved by recirculation of both the vapour and liquid phases with the use of a Cottrell pump. This type of design was pioneered by Lee (1931) and Gillespie (1946). The design still had flaws especially with sampling of the liquid phase. This and other faults were rectified by the design of Yerazunis et al. (1964). It is on this design that the still of Raal and Mühlbauer (1998) is based, as is a further modification by Joseph (2001).

2.3.2.2.b) Static VLE Apparatus

These apparatus consist of a cell that contains a liquid which is stirred mechanically. This agitation allows the liquid to equilibrate with the vapour during isothermal operation. The apparatus of Hermsen and Prausnitz (1962) and Gibbs and Van Ness (1972) produced accurate data but in a time-consuming manner. Maher and Smith (1979) developed a 15 cell cluster in order to rapidly measure a complete isotherm. This, however, did require a lengthy degassing technique. Improvements were made to this in the design of Raal and Mühlbauer (1998).

2.3.2.2.c) Semi-micro Techniques

These techniques are used where there is only a very small quantity of sufficiently pure material available. The size of the apparatus reduces the required quantity of chemicals to a minimum. Wichterle and Hala (1963) designed a simple semi-micro static cell which allowed rapid measurement of VLE. Even with minor adjustments by Wicherle and Boublikova (1969), the apparatus had shortcomings. Improvements were made to the design in the apparatus of Raal and Mühlbauer (1998).

2.3.2.3 Vapour-liquid equilibrium involving Ionic Liquids

VLE data involving ionic liquids is rather limited at present. In terms of binaries with other liquids, it is assumed that the large relatively volatilities would pose no problem in separation and thus not much data is available. This is not to suggest that VLE measurements involving ionic liquids are not being undertaken. On the contrary, one of the suggested uses is in extractive distillation. Ionic liquids that work effectively for particular systems of interest, may culminate in patents as is in the case of Arlt et al. (2002). The patent title is '*Ionic liquids as selective additives for the separation of close-boiling or azeotropic mixtures.*' In this case, as may be found with other researchers, related information may be published at a later date (Jork, 2003).

Anthony et al. (2001) studied the VLE of water with (BMIM)PF_6, (MOIM)PF_6 and (MOIM)BF_4. Absorption/desorption isotherms were measured. In each of the ionic liquids, water solubility was found to increase with increasing temperature. (MOIM)BF_4 had the greatest solubility of water as it is completely water miscible compared with the hydrophobic ionic liquids containing the PF_6^- anion.

An area of active research is gas solubilities in ionic liquids. Although more applicable to scrubbers, absorbers and super-critical extraction, this information is of interest and will be discussed further. A number of investigations have been undertaken by Brennecke and co-workers (2001) involving ionic liquids and supercritical carbon dioxide ($scCO_2$), which is a promising 'green' solvent. The high pressure phase behavior of CO_2 with six ionic liquids was studied by Blanchard et al. (2001a). The ionic liquid-$scCO_2$ system forms two liquid phases even at pressures up to 400 bar. What is interesting is that while large amounts of CO_2 dissolve in the ionic liquid, no ionic liquid dissolves in the CO_2 phase. For each ionic liquid, the solubility of CO_2 in the ionic liquid increases significantly with increasing pressure and increases slightly with decreasing temperature. A comparison of the ionic liquids under investigation showed that (MOIM)PF_6 contained the most CO_2. An interesting feature of these systems is that volume of the ionic liquid barely increased even when the CO_2 solubility reached 75.5 mol %.

Further work was done to evaluate this system for the potential recovery of organic products (Blanchard and Brennecke, 2001b). The application is in the recovery of products which have been formed by an reaction in the ionic liquid phase. A number of compounds have been investigated including alcohols, amides and ketones, in the (BMIM)PF_6/$scCO_2$ system. All the organic solutes investigated exhibited a greater than 95 % recovery. However, solutes with a high volatility and low polarity required the least amount of CO_2 for extraction.

Brennecke and Maginn (2001) motivate the potential of ionic liquids in gas separations. A comparison is made of the Henry's Law constants for water, carbon dioxide, methane and ethane in (BMIM)PF_6. Since Henry's Law constants are inversely proportional to solubility, a small Henry's Law constant indicates high gas solubility. Large differences in the solubilities indicate that (BMIM)PF_6 could be used to separate water and carbon dioxide from methane and ethane in natural gas.

Husson-Borg et al. (2003) studied the solubilities of O_2 and CO_2 in (BMIM)BF_4 at atmospheric pressure and in the temperature range 303 - 343 K. They found that the solubility of CO_2 in (BMIM)BF_4 is an order of magnitude greater than O_2 in (BMIM)BF_4. This can be seen from the Henry's Law constants which range from 6 to 9 Mpa for CO_2 and 23 to 37 MPa for O_2. CO_2 solubility was found to decrease with increasing temperature while O_2 solubility was found to increase slightly with increasing temperature.

2.4 Concluding Remarks

This review covers much of the scope of ionic liquids. Their development from high temperature molten salts has brought the associated benefits without the drawbacks. Properties of ionic liquids show interesting trends with cation and anion variation. Development of prediction methods for properties may prove useful in the future. Ionic liquids show promise in biphasic reactions. The interesting miscibility/immiscibility properties make them a useful solvent in solvent extraction. According to Brennecke and Maginn (2001), the number of publications on ionic liquids has increased from 25-30 per year in the period 1991-1998 to about 250 in the period January - September of 2001. This clearly indicates the increased interest in the potential of ionic liquids. Their use as solvents in extractive distillation may be proven in the near future.

Chapter Three

Theoretical Considerations

Chapter Overview

An understanding of the theory and of the development of the resulting mathematical relationships is necessary in any area of science. This allows for shortcomings and possible limitations to be considered when using various equations in calculations. This chapter assumes an understanding of the fundamentals laws of thermodynamics and focuses on the theory of phase equilibria.

The criteria for phase equilibrium are considered and definitions are given of the fugacity, fugacity coefficient, activity and activity coefficient.

The representation of vapour-liquid and liquid-liquid equilibria is given. The development of gas-liquid chromatography is detailed along with the equations for the activity coefficient, partial excess molar enthalpy and selectivity.

Data are commonly reduced by correlation to models. The models used are discussed along with their necessary equations.

3.1 Criteria for Phase Equilibrium

The criteria for phase equilibrium are that the chemical potential (μ) of a particular species (i) in a multicomponent system, consisting of *N* phases, is identical in all phases and that the system is at uniform temperature and pressure.

$$\mu_i^{(1)} = \mu_i^{(2)} = \mu_i^{(3)} = \ldots = \mu_i^{(N)} \qquad (3\text{-}1)$$

The above criterion is proved by minimizing the Gibbs free energy of a multiphase, multicomponent closed system at constant temperature and pressure. The complete derivation can be found in many popular texts including Smith et al. (1996) and thus will not be covered here.

3.2 Fugacity and Fugacity Coefficient

Chemical potential values are difficult to relate to more easily understood physical quantities. Seader and Henly (1998) also state that '*the chemical potential approaches an infinite negative value as pressure approaches zero*'. Phase equilibrium calculations therefore incorporate fugacity. This was introduced by G. N. Lewis in 1901. Fugacity has the same units as pressure. The fugacity of a species (i) in a mixture is defined in terms of the chemical potential by:

$$\hat{f}_i = C\exp\left(\frac{\mu_i}{RT}\right) \qquad (3\text{-}2)$$

where C is a temperature dependent constant. Irrespective of the value of C, Eq. (3-1) can be written as:

$$\hat{f}_i^{(1)} = \hat{f}_i^{(2)} = \hat{f}_i^{(3)} = \ldots. = \hat{f}_i^{(N)} \qquad (3\text{-}3)$$

In the case of a pure substance, this becomes the pure-component fugacity f_i. Since pressure and fugacity are closely related, they are usually represented in the dimensionless form as:

$$\Phi_i = \frac{f_i}{P} \tag{3-4}$$

where Φ_i is the pure-component fugacity coefficient; and for mixtures as:

$$\hat{\Phi}_i^V = \frac{\hat{f}_i^V}{y_i P} \tag{3-5}$$

$$\hat{\Phi}_i^L = \frac{\hat{f}_i^L}{x_i P} \tag{3-6}$$

where $\hat{\Phi}_i^V$ and $\hat{\Phi}_i^L$ represent vapour and liquid phase fugacity coefficients respectively, and y_i and x_i are vapour and liquid mole fractions respectively. When ideal gas behavior is approached, then

$$\hat{\Phi}_i^V \longrightarrow 1 \text{ and}$$

$$\hat{\Phi}_i^L \longrightarrow \frac{P_i^{sat}}{P}$$

where P_i^{sat} is the saturated vapour pressure.

3.3 Activity and Activity Coefficient

Activity (a) at a given temperature is defined as the ratio of the fugacity of a component to its fugacity in some defined standard-state. The fugacity at standard-state can be defined as the pure-component fugacity at the same conditions of the mixture, resulting in

$$a_i \equiv \frac{\hat{f}_i}{f_i^o} \tag{3-7}$$

For an ideal solution $a_i = x_i$. Departure from ideal solution behavior is represented by activity coefficients defined as:

$$\gamma_i = \frac{a_i}{x_i} = \frac{\hat{f}_i}{x_i f_i^o} \tag{3-8}$$

Thus for an ideal solution $\gamma_i=1$.

Ideal solution behavior can be represented by the Lewis/Randall rule. The Lewis/Randall rule is defined as

$$\hat{f}_i^{id} = x_i f_i \tag{3-9}$$

It shows that the fugacity of a species in an ideal solution is proportional to its mole fraction. As $x_i \rightarrow 1$, the fugacity of a real solution becomes equal to the ideal fugacity, as defined by the Lewis/Randall rule. Henry's Law is defined as

$$\hat{f}_i = x_i k_i \tag{3-10}$$

where k_i is the *Henry's constant*. It defines the limiting slope of the $\hat{f}_i$ verses x_i curve as $x_i = 0$.

3.4 Equilibrium Ratios

The ratio of the concentrations of a component in each of two phases at equilibrium is referred to as an equilibrium ratio. For the vapour-liquid case, this is called the K-value and defined as:

$$K_i = \frac{y_i}{x_i} \tag{3-11}$$

For the liquid-liquid case, this is called the distribution ratio and defined as:

$$K_{D_i} = \frac{x'_i}{x''_i} \tag{3-12}$$

3.5 Vapour-liquid Equilibrium (VLE)

For a single vapour phase and a single liquid phase in equilibrium Eq. (3-3) reduces to:

$$\hat{f}_i^V = \hat{f}_i^L \tag{3-13}$$

In order to be useful in VLE calculations, these partial fugacities in solution are replaced by expressions relating them to compositions. The liquid phase fugacity is represented by:

$$\hat{f}_i^L = \hat{\Phi}_i^L x_i P \tag{3-14}$$

$$\text{or } \hat{f}_i^L = \gamma_i x_i f_i^{o,L} \tag{3-15}$$

The vapour phase fugacity is represented by:

$$\hat{f}_i^V = \hat{\Phi}_i^V y_i P \tag{3-16}$$

Substituting Eq. (3-14) and Eq. (3-16) in Eq. (3-13) gives:

$$\hat{\Phi}_i^V y_i = \Phi_i^L x_i \tag{3-17}$$

This representation of VLE known as the direct method uses equations of state to represent both phases. The other representation is formed by combining Eq. (3-15) with Eq.(3-16), resulting in

$$\hat{\Phi}_i^V y_i P = \gamma_i x_i f_i^{o,L} \tag{3-18}$$

This is the combined method and uses an equation of state for the vapour phase and an activity coefficient model for the liquid phase. The fugacity of the pure liquid $f_i^{o,L}$ at the same conditions as the mixture, is given by

$$f_i^{o,L} = p_i^{sat}\Phi_i^{sat}\exp\int_{P_i^{sat}}^{P}\frac{v_i^L}{RT}dP \qquad (3\text{-}19)$$

where v_i^L is the liquid molar volume. Substituting into Eq. (3-18) results in

$$y_i P = \gamma_i x_i p_i^{sat}\Gamma_i \qquad (3\text{-}20)$$

where

$$\Gamma_i = \frac{\Phi_i^{sat}}{\Phi_i^V}\exp\int_{P_i^{sat}}^{P}\frac{v_i^L}{RT}dP$$

For most systems at pressures below 1 bar, Γ_i is essentially equal to 1 which reduces Eq. (3-20) to the modified Raoult's Law:

$$y_i P = x_i\gamma_i p_i^{sat} \qquad (3\text{-}21)$$

Of interest in any separation is the degree of separation, or separation factor. For VLE this is the relative volatility α_{ij} and is a ratio of the K-values of components i and j:

$$\alpha_{ij} = \frac{K_i}{K_j} \qquad (3\text{-}22)$$

Values of α_{ij} >> 1 or << 1 indicate that components are easily separable by distillation. Values of $1<\alpha_{ij}<1.05$ indicate difficult and possibly uneconomical separation.

3.6 Liquid-liquid equilibrium

For two immiscible liquid phases in equilibrium Eq. (3-3) reduces to:

$$\hat{f}'_i = \hat{f}''_i \tag{3-23}$$

Using Eq. (3-15) to represent the fugacities

$$x'_i \gamma'_i = x''_i \gamma''_i \tag{3-24}$$

Thus the distribution ratio Eq. (3-12) can also be described in terms of activity coefficients

$$K_{D_i} = \frac{x'_i}{x''_i} = \frac{\gamma''_i}{\gamma'_i} \tag{3-25}$$

The separation factor for LLE is the relative selectivity β_{ij}. Liquid-liquid extraction involves a minimum of three components ((i)-solute, (j)-carrier and (k)-solvent). For the simplest case the selectivity is defined as:

$$\beta_{ij} = \frac{K_i}{K_j} = \frac{x_i'/x_i''}{x_j'/x_j''} = \frac{\left(x_i/x_j\right)'}{\left(x_i/x_j\right)''} \tag{3-26}$$

where (') represents the solvent phase and (") represents the carrier phase.

3.7 Gas-liquid Chromatography (GLC)

The development of the technique and theory of GLC is well-detailed by Letcher (1978). The idea of using a gas as a mobile phase and a liquid as a stationary phase in chromatography was mentioned by Martin and Synge (1941). James and Martin (1952) then demonstrated the use of the technique in separation. Martin (1956) indicated the usefulness of GLC in studying solution thermodynamics of gas and liquid phases. Porter et al. (1956) then related the net retention volume to the activity coefficient of the solute (1) at infinite dilution in the solvent (3) γ_{13}^{∞}. The mechanism of solute movement through the column is given in Chapter 2.2.2.

Conder and Young (1979) define the partition coefficient K_L by the equation

$$K_L = \frac{q}{c} \tag{3-27}$$

where c is the concentration of solute in the gas phase and q is the concentration of solute in the liquid phase when solute is distributed between a gas and a liquid at equilibrium. The net retention volume V_N is related to K_L and the volume of stationary phase V_L by

$$V_N = K_L V_L \tag{3-28}$$

Re-writing Eq. (3-27) in terms of mole fractions and numbers of moles gives

$$K_L = \frac{x n_3 V_g}{y n_2 V_L} \tag{3-29}$$

where n_3 is the number of moles of solvent in the liquid phase and n_2 is the number of moles of carrier gas component in the gas phase, V_g is the volume of the gas phase, V_L is the volume of the liquid phase and x and y are the mole fraction of solute in the liquid and gas phases respectively. Substituting pressures for fugacities in Eq. (3-8) gives

$$\gamma = \frac{p_1}{x_1 p_1^{sat}} \tag{3-30}$$

where p_1 and p_1^{sat} are the partial pressure and saturated vapour pressure of the solute. The partial pressure may also be expressed in terms of the total pressure P above the solution

$$p_1 = yP \tag{3-31}$$

Combining Eqs. (3-29), (3-30) and (3-31) gives

$$K_L = \frac{P}{\gamma p_1^{sat}} \frac{n_3}{n_2} \frac{V_g}{V_L} \tag{3-32}$$

Assuming the ideal gas law, $PV_g = n_2RT$ results in

$$K_L = \frac{n_3 RT}{\gamma p_1^{sat} V_L} \tag{3-33}$$

Substitution into Eq. (3-28) and re-arranging gives

$$\gamma = \frac{n_3 RT}{V_N p_1^{sat}} \tag{3-34}$$

Eq. (3-34) gives only a rough value for the activity coefficient. More accurate values are obtained by accounting for gas-phase imperfections and compressibility which gives the following equation developed by Cruikshank et al. (1966) and used by Letcher (1978)

$$\ln \gamma_{13}^{\infty} = \ln \frac{n_3 RT}{V_N p_1^{o}} - \frac{\left(B_{11} - \upsilon_1^{o}\right) p_1^{sat}}{RT} + \frac{\left(2B_{12} - \upsilon_1^{\infty}\right) J_2^3 P_o}{RT} \tag{3-35}$$

where P_o is the outlet pressure and is equal to atmospheric pressure, $J_2^3 P_o$ is the mean column pressure, B_{11} the second virial coefficient of the pure solute, υ_1^o the molar volume of the solute determined by the Rackett equation (Smith et al. 1996), υ_1^∞ the partial molar volume of the solute at infinite dilution in the solvent (here equated to υ_1^o), and B_{12} the mixed second virial coefficient of the solute (1) in the carrier gas (2). The saturated vapour pressure of the solute p_1^{sat} is conveniently determined by the Antoine equation (Reid et al. 1988). The net retention volume, V_N is given by:

$$V_N = \left(J_2^3\right)^{-1} q_v \left(t_R - t_G\right)\left(1 - p_w / P_o\right) T / T_f \tag{3-36}$$

where t_R and t_G are the retention times for the solute and non-retainable gas, respectively, T_f is the temperature of the flow meter, p_w is the vapor pressure of water at T_f and q_v is the outlet flow measured using a soap bubble flow meter.

$$J_2^3 = \tfrac{2}{3}\left[\frac{\left(P_i / P_o\right)^3 - 1}{\left(P_i / P_o\right)^2 - 1}\right] \tag{3-37}$$

where P_i is the column inlet pressure. The virial coefficients B_{11} were determined by McGlashan and Potter's (1962) equation:

$$B / V_c = 0.43 - 0.886\left(T_c / T\right) - 0.694\left(T_c / T\right)^2 - 0.0375\left(n - 1\right)\left(T_c / T\right)^{4.5} \tag{3-38}$$

where T_c is the critical temperature, n is the number of carbon atoms and V_c is the critical volume. The mixed virial coefficients B_{12} were also determined using Eq. (3-38) together with Hudson and McCoubrey's (1960) mixing rules and the Lorentz (Conder and Young, 1979) mixing rule Eq. (3-41)

$$T_{c12} = 128\left(T_{c11}.T_{c22}\right)^{1/2}\left(I_{c11}.I_{c22}\right).V_{c11}.V_{c22} / I_{c12} \tag{3-39}$$

where

$$I_{c12} = \left(I_{c11} + I_{c22}\right).\left(V_{c11}^{1/3} + V_{c22}^{1/3}\right)^6 \tag{3-40}$$

and

$$V_{c12} = \left(V_{c11}^{1/3} + V_{c22}^{1/3}\right)^3 / 8 \qquad (3\text{-}41)$$

and

$$n_{12} = (n_1 + n_2)/2 \qquad (3\text{-}42)$$

where I is the ionization potential and n is the number of carbon atoms in the molecule (equal to 1 for helium).

The temperature dependence of the activity coefficients can be used to calculate the partial molar excess enthalpies at infinite dilution $\overline{H}_1^{E,\infty}$. $\overline{H}_1^{E,\infty}$ can be calculated using the Gibbs-Helmholtz equation:

$$\left(\frac{\partial \ln \gamma_1}{\partial T}\right) = \frac{\overline{H}_1^E}{RT^2} \qquad (3\text{-}43)$$

which, at infinite dilution, gives:

$$\frac{\overline{H}_1^{E,\infty}}{R} = \frac{\Delta\left(\ln \gamma_1^\infty\right)}{\Delta\left(T^{-1}\right)} \qquad (3\text{-}44)$$

where subscript 1 refers to the solute. $\overline{H}_1^{E,\infty}$ values are obtained from the gradient of the plot $\ln \gamma_1^\infty$ vs $\frac{1}{T}$. These $\overline{H}_1^{E,\infty}$ are useful in obtaining activity coefficients at temperatures other than experimental, by interpolation and limited extrapolation using:

$$\ln \gamma_1^\infty = \ln \gamma_{1,ref}^\infty - \frac{\overline{H}_1^{E,\infty}}{R}\left(T_{ref} - T\right) \qquad (3\text{-}45)$$

The selectivity at infinite dilution β_{ab}^∞ is defined as:

$$\beta_{ab}^{\infty}=\frac{\gamma_a^{\infty}}{\gamma_b^{\infty}} \tag{3-46}$$

It gives the solvent selectivity of *solute a* over *solute b* at infinite dilution. It is a preliminary tool for assessing possible solvents (Tiegs et al. 1986), and the larger the value the more selective the solvent. The usefulness of this definition can be seen in the simplification below. By removing the correction terms and therefore using Eq. (3-34), Eq. (3-46) gives

$$\beta_{ab}^{\infty}=\frac{\dfrac{n_3RT}{V_{Na}p_a^{sat}}}{\dfrac{n_3RT}{V_{Nb}p_b^{sat}}}$$

using the same column at the same temperature

$$\beta_{ab}^{\infty}=\frac{V_{Nb}p_b^{sat}}{V_{Na}p_a^{sat}}$$

truncating the expression for the net retention volume results in

$$\beta_{ab}^{\infty}=\frac{(t_{Rb}-t_G)p_b^{sat}}{(t_{Ra}-t_G)p_a^{sat}} \tag{3-47}$$

These rough selectivity values can be obtained quite rapidly from the saturated vapour pressures and the experimental hold-up and retention times.

3.8 Correlation

Equilibrium data are commonly correlated to models. This usually allows a large set of data to be reduced to a set of parameters. The usefulness of this is that

1. the quality of the data can be evaluated, and

2. it may be possible to predict equilibrium data at conditions other than the experimental conditions

3.8.1 VLE Correlation

The data reduction for VLE was based on the method of Barker (1953) and is detailed by Raal and Mühlbauer (1998) as follows:

This method uses models based on the excess Gibbs energy.

1. A suitable expression is assumed for G^E as a function of composition.
2. The system total pressure is given by

$$P = \frac{x_1 \gamma_1 P_1^{sat}}{\Phi_1} + \frac{x_2 \gamma_2 P_2^{sat}}{\Phi_2} \tag{3-48}$$

3. The required activity coefficient expressions are obtained by differentiating the G^E equation as follows

$$\ln \gamma_i = \left(\frac{\partial \left(nG^E / RT \right)}{\partial n_i} \right)_{P,T,n_j} \tag{3-49}$$

4. Combination of Eq. (3-48) with the activity coefficient expressions gives an expression that does not involve the vapour composition (y_i) except in Φ_i, which are initially neglected. The only unknowns are the parameters for the G^E model. A regression technique is used to obtain the G^E model parameters that produce the best fit for the experimental *P-x* data for the whole composition range. The correction factor Φ_i, assumed = 1 in the first iteration, are recalculated when the vapor compositions have been found (step 5).
5. Once suitable values for the G^E model parameters have been found, the problem is solved and either vapour compositions Eq. (3-50) or activity coefficients Eq. (3-49) can be calculated.

$$y_i = \frac{x_i \gamma_i P_i^{sat}}{P\Phi_i} \tag{3-50}$$

The above procedure is modified to evaluate isobaric T-x data and the Φ_i correction factor is set = 1 for low pressures. Most of the G^E models require only binary parameters for the prediction of multicomponent VLE.

3.8.1.1 The Wilson Model

The concept of local composition was introduced by Wilson (1964). It described the local compositions, which were different from liquid overall compositions, for mixtures of components differing in size and in intermolecular forces. The excess Gibbs energy is expressed in binary form as:

$$\frac{G^E}{RT} = -x_1 \ln(x_1 - x_2\Lambda_{12}) - x_2 \ln(x_2 + x_1\Lambda_{21}) \tag{3-51}$$

The expressions for the activity coefficients, obtained using Eq. (3-48), are

$$\ln \gamma_1 = -\ln(x_1 + x_2\Lambda_{12}) + x_2\left(\frac{\Lambda_{12}}{x_1 + x_2\Lambda_{12}} - \frac{\Lambda_{21}}{x_2 + x_1\Lambda_{21}}\right) \tag{3-52}$$

$$\ln \gamma_2 = -\ln(x_2 + x_1\Lambda_{21}) + x_1\left(\frac{\Lambda_{21}}{x_2 + x_1\Lambda_{21}} - \frac{\Lambda_{12}}{x_1 + x_2\Lambda_{12}}\right) \tag{3-53}$$

with

$$\Lambda_{12} = \frac{V_2}{V_1}\exp\left(-\frac{\lambda_{12} - \lambda_{11}}{RT}\right) \tag{3-54}$$

$$\Lambda_{21} = \frac{V_1}{V_2}\exp\left(-\frac{\lambda_{21} - \lambda_{22}}{RT}\right) \tag{3-55}$$

where V_1 and V_2 are liquid molar volumes. The benefit of this model is that there are only two adjustable parameters ($\lambda_{12}-\lambda_{11}$) and ($\lambda_{21}-\lambda_{22}$). The limitation of this model is that it is not useful for partial miscibility. It is satisfactory for multicomponent systems.

3.8.1.2 The NRTL Model

The NRTL (Non-random two liquid) model was developed by Renon and Prausnitz (1968). This improved on the local composition concept of the Wilson model in that it could be used to predict liquid immiscibility and is effective for highly non-ideal systems. The excess Gibbs energy is expressed in binary form as:

$$\frac{G^E}{RT} = x_1 x_2 \left(\frac{\tau_{21} G_{21}}{x_1 + x_2 G_{21}} + \frac{\tau_{12} G_{12}}{x_2 + x_1 G_{12}} \right) \tag{3-56}$$

with

$$G_{12} = \exp(-\alpha_{12}\tau_{12}) \tag{3-57}$$

$$G_{21} = \exp(-\alpha_{12}\tau_{21}) \tag{3-58}$$

and

$$\tau_{12} = \frac{g_{12} - g_{22}}{RT} \tag{3-59}$$

$$\tau_{21} = \frac{g_{21} - g_{11}}{RT} \tag{3-60}$$

with the corresponding activity coefficient expressions being

$$\ln \gamma_1 = x_2^2 \left[\tau_{21} \left(\frac{G_{21}}{x_1 + x_2 G_{21}} \right)^2 + \left(\frac{\tau_{12} G_{12}}{(x_2 + x_1 G_{12})^2} \right) \right] \tag{3-61}$$

$$\ln \gamma_2 = x_1^2 \left[\tau_{12} \left(\frac{G_{12}}{x_2 + x_1 G_{12}} \right)^2 + \left(\frac{\tau_{21} G_{21}}{(x_1 + x_2 G_{21})^2} \right) \right] \tag{3-62}$$

This model consists of three adjustable parameters viz. $(g_{12}-g_{22})$, $(g_{21}-g_{11})$ and α_{12}. Values of α_{12} usually range from -1 to 0.5. It is common for the value of α_{12} to be fixed, and has thus been set to 0.3 as suggested by Walas (1985).

3.8.2 LLE Correlation

For ternary LLE, it is necessary to correlate two sets of data viz. the binodial curves and tie-line data.

The binodial curves were correlated using the Hlavaty equation, the β function and the log-γ function. These three models have no thermodynamic basis and are based purely on mathematical models.

The Hlavaty equation (Hlavaty, 1972):

$$x_2 = A_1 x_A \ln x_A + A_2 x_B \ln x_B + A_3 x_A x_B \tag{3-63}$$

The β function (Shultz et al., 1973):

$$x_2 = B_1 (1 - x_A)^{B_2} x_A{}^{B_3} \tag{3-64}$$

The log-γ function (Letcher et al., 1989)

$$x_2 = C_1 (-\ln x_A)^{C_2} x_A{}^{C_3} \tag{3-65}$$

where

$$x_A = \frac{\left(x_1 + \frac{1}{2} x_2 - x_1^0\right)}{\left(x_{11}^0 - x_1^0\right)} \tag{3-66}$$

and

$$x_B = \frac{\left(x_{11}^0 - x_1 - \frac{1}{2} x_2\right)}{\left(x_{11}^0 - x_1^0\right)} \tag{3-67}$$

where x_1 refers to the mole fraction of the solute, x_2 refers to the mole fraction of the carrier and x_{11}^0 and x_1^0 are the values of x_1 on the binodial curve which cuts the x_2=0 axis.

The standard deviation is defined as follows:

$$\sigma = \left[\frac{\Sigma\left(x_{2calc} - x_{2\exp}\right)^2}{n-3}\right]^{0.5} \tag{3-68}$$

where n is the number of data points and 3 is the number of coefficients.

The tie-lines were correlated using the NRTL model, described previously. The ternary form was used and the parameters obtained were α, $(g_{12}-g_{11})$, $(g_{21}-g_{22})$, $(g_{13}-g_{11})$, $(g_{31}-g_{33})$, $(g_{23}-g_{22})$, $(g_{32}-g_{33})$. The equations and algorithms used in the calculation of the composition of the liquid phases follow the method used by Walas (1985). The objective function F(P), used to minimize the difference between the experimental and calculated concentrations is defined as:

$$F(P) = \sum_{i=1}^{n} \left\{ \begin{array}{l} \left[x_{1i}'(\exp) - x_{1i}'(cal)(P)\right]^2 + \left[x_{2i}'(\exp) - x_{2i}'(cal)(P)\right]^2 \\ + \left[x_{1i}''(\exp) - x_{1i}''(cal)(P)\right]^2 + \left[x_{2i}''(\exp) - x_{2i}''(cal)(P)\right]^2 \end{array} \right\} \tag{3-69}$$

where P is the set of parameters vector, n is the number of experimental tie-lines, x_{1i}'(exp), x_{2i}'(exp) and x_{1i}'(cal),x_{21}'(cal) are the experimental and calculated mole fractions respectively of the solvent-rich phase and x_{1i}''(exp), x_{2i}''(exp) and x_{1i}''(cal),x_{21}''(cal) are the experimental and calculated mole fractions respectively of the carrier-rich phase.

Chapter Four

Experimental Apparatus and Procedure

Chapter Overview

Phase equilibrium data are usually determined experimentally and such was the case in thi' work. A review of published literature will reveal numerous experimental apparatus used in phase equilibria measurement, each with its strengths and weaknesses. An apparatus which works satisfactorily for one system may not necessarily work as well for another system. This chapter considers the experimental apparatus and procedures used for measurement of phase equilibria in this work and the applicability to systems involving ionic liquids. The primary areas under consideration are:

- Activity coefficients at infinite dilution from gas-liquid chromatography
- Ternary liquid-liquid equilibrium measurements
- Vapour-liquid equilibrium measurements

Chemical purity and additional purification steps are also discussed.

4.1 Chemical Purity

4.1.1 Ionic Liquids

The suppliers and purities of the ionic liquids used in this work are listed in Table A-1. Densities of the ionic liquids have been measured and compared to literature values where available. There is good agreement between the measured and literature values. Ionic liquids were purified by subjecting them to a vacuum of between 2 to 8 x 10^{-4} mbar and a temperature of between 40 to 45 °C for 30 minutes in order to remove volatiles, including water. Ionic liquids were then stored in a desiccator.

4.1.2 GLC

The suppliers and quoted purities of the solutes used in GLC are listed in Table A-2. Since the GLC process separates the solutes from any impurities, the solutes were not purified further.

4.1.3 LLE

The suppliers and purities of the chemicals used in LLE measurements are listed in Table A-3. A comparison between measured and literature density values showed good agreement. Hygroscopic chemicals were stored under 4°A molecular sieves. Ethanol is purified by the method of Lund and Bjerrum (Furniss et al. 1978). A small amount of ethanol is reacted with magnesium in the presence of iodine to form a Grignard reagent. This is reacted with a larger quantity of ethanol. The water present reacts to produce insoluble magnesium hydroxide. The ethanol is distilled off.

4.1.2 VLE

The suppliers and purities of the chemicals used in VLE measurements are listed in Table A-4. Hygroscopic chemicals were stored under 4°A molecular sieves. The vapour pressures of the chemicals are compared to the Antoine equation (Reid et al. 1988) and good agreement is observed.

4.2 Activity Coefficients at Infinite Dilution from Gas-Liquid Chromatography

4.2.1 Experimental setup

The experimental setup consists of the atmospheric pressure apparatus described by Letcher (1978) and used by Harris (2001) as shown in Figure 4-1. Helium is used as the carrier gas. Helium flows from the cylinder regulator through a needle valve and into a coiled copper column used to pre-heat/pre-cool the gas. This is connected in parallel to a mercury manometer, used to measure the inlet pressure, and to the sample injection port. The solute is injected into the carrier gas with a micro-syringe. The solute-carrier gas mixture flows over the celite-supported solvent in a stainless-steel column and then to the thermal conductivity detector which detects the concentration of solute in the carrier gas. The solute-carrier gas mixture then flows to a soap bubble flow-meter where the flow rate is measured. The stirred water bath provides an isothermal environment by incorporating a thermometer and a temperature controller. The signal from the detector is amplified by a power supply unit and then printed by a chart recorder.

4.2.2 Determination of experimental parameters

The following parameters are used to calculate activity coefficients at infinite dilution from Eq. 3-33:

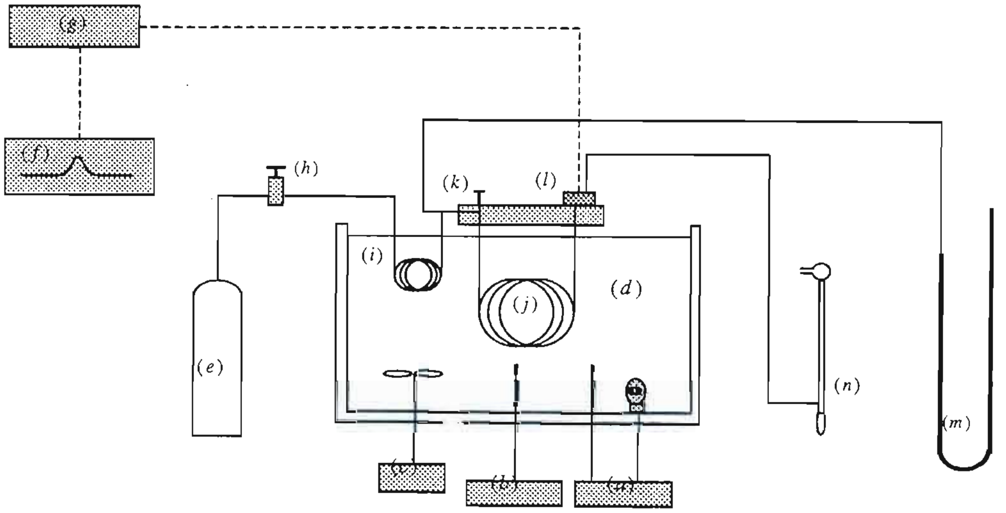
- The outlet pressure (P_o), which is equal to atmospheric pressure
- The inlet pressure (P_i)
- The flow rate (U)
- The number of moles of solvent (n_3)
- The solute retention time (t_r) and non-retainable gas retention time (t_G)
- The column temperature (T)

4.2.2.1 Determination of outlet pressure (P_o) and inlet pressure (P_i)

The end of the column was open to atmosphere. This was measured with a calibrated barometer in mm Hg. The inlet pressure was determined with a mercury manometer. The difference in the height of mercury between each leg of the manometer, determined with a cathetometer, was added to the atmospheric pressure in order to give the inlet pressure. These pressures were converted to units of kPa. The measurements are accurate to within 7 Pa.

4.2.2.2 Determination of flow rate (U)

The flow rate was measured using a calibrated soap bubble flow meter. The flow rate was maintained between 0.65 $cm^3.s^{-1}$ and 1.00 $cm^3.s^{-1}$ and was adjusted according to the solute injected to give suitable retention times. The estimated error is less than 1 per cent.



(a)	Tronac Model PTC-41 Temperature Controller
(b)	Hewlett Packard Model 2804A Quartz thermometer
(c)	Mechanical Stirrer
(d)	Water Bath
(e)	Helium Cylinder
(f)	Kipp and Zonoen Chart Recorder
(g)	Gow-Mac Instrument Co. Series 350 Power Supply Unit
(h)	Negretti Zambra Needle Valve
(i)	Pre-column (Copper)
(j)	Column (Stainless Steel)
(k)	Sample Injection Port
(l)	Thermal Conductivity Detector
(m)	Mercury Manometer
(n)	Soap Bubble Flow Meter

Figure 4-1: Schematic diagram of the G.L.C experimental setup

(Harris, 2001)

4.2.2.3 Determination of number of moles of solvent (n_3)

The celite (Chromosorb W HP 80/100 mesh) was weighed. An amount of purified ionic liquid was added to give a loading of approximately 30 % by mass of ionic liquid. This value was also used by Heintz et al. (2001, 2002a and 2002b). Dichloromethane was used to aid uniform coating of the ionic liquid on the celite, and then removed by evaporation using a rotating evaporator. The ionic liquid-coated celite was re-weighed to ensure that all the dichloromethane has been removed. A stainless-steel column (bore 4.2 mm and length 0.5 m) was then carefully packed. The mass of the packing, and therefore n_3, is obtained by difference. The estimated error of n_3 is 1 per cent. The column was coiled and then placed in an ultrasonic water bath to ensure that the packing distributed evenly.

4.2.2.4 Determination of retention times (t_r and t_G)

The retention times were determined from the chromatograms, which plot detector response with time. The base line was the thermal conductivity of the dry helium gas. When the solute or air carried in the helium gas passed through the detector, a peak was registered on the chromatogram. The retention time was determined from the chart speed and the distance from the point of injection to the intersection of the tangents to the peak, as described by Letcher (1978) and illustrated by Harris (2001) in Figure 4-2. The estimated error in t_r and t_G was 1 per cent or 0.2 s whichever is greater.

4.2.2.5 Temperature Measurement and Control

The column was immersed into a water bath to ensure isothermal conditions. The temperature was controlled to within ±0.005 K with a Tronac temperature controller and was measured with a calibrated Hewlett-Packard quartz thermometer which is accurate to 0.001 K.

4.2.4 Applicability to mixtures with Ionic liquids

As discussed in Chapter 2.2.3 the G.L.C. technique is highly suitable for the use of ionic liquids as stationary phases. The non-volatile nature of the ionic liquid prevents losses of the stationary phase by evaporation. This non-volatile nature has allowed authors to measure activity coefficients at relatively high temperatures such as 90 °C (Heintz, 2001). From the literature review it is possible to note the extent of information, not limited to activity coefficients, which can be gained from using ionic liquids in this technique.

4.3 Ternary liquid-liquid equilibria

Ternary liquid-liquid equilibrium data were obtained by the method of titration. The measurements were done isothermally. The data obtained from these measurements were:

- Cloud point compositions
- Tie-line compositions

4.3.1 Experimental setup

The experimental setup is shown in Figure 4-3.

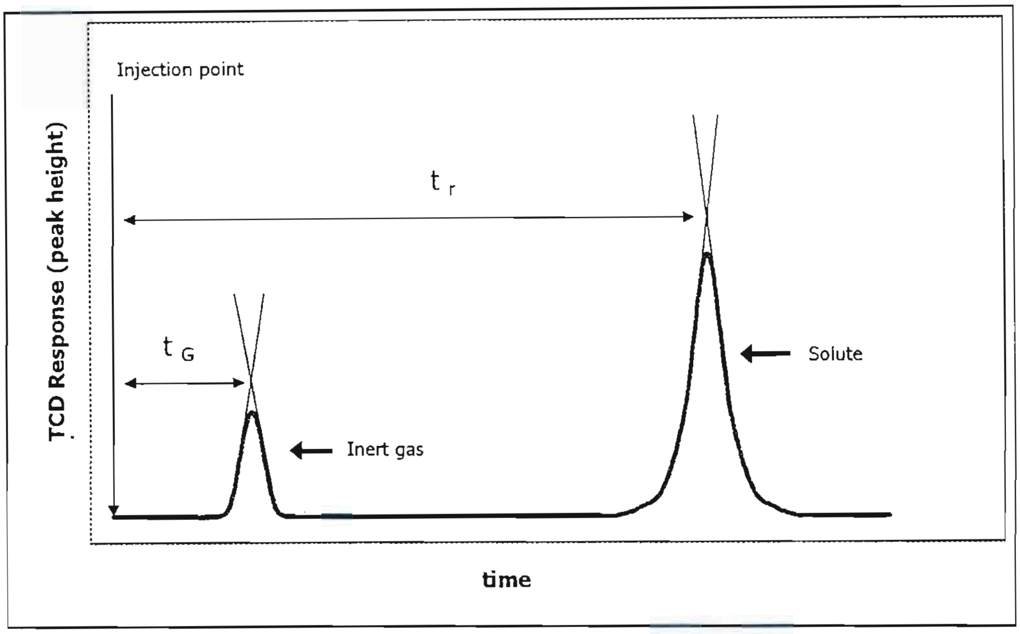


Figure 4-2: Typical chromatogram showing detector response with time

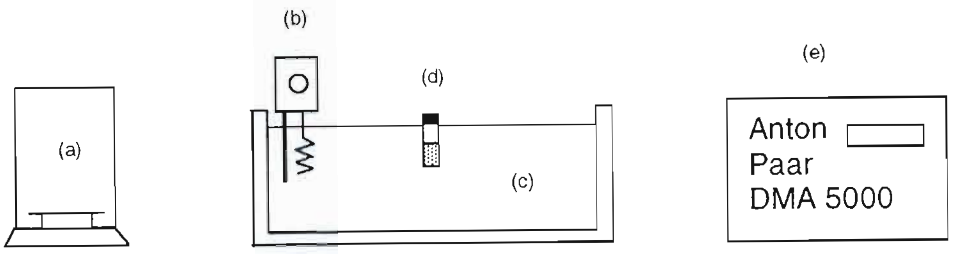
Harris (2001)

4.2.3 Systems measured

(MOIM)Cl was, in this study, used as a stationary phase in gas-liquid chromatography in order to measure the activity coefficients of various hydrocarbons at infinite dilution. The following solutes were used:

- Alkanes: *n*-Pentane; *n*-Hexane; *n*-Heptane; *n*-Octane
- Alkenes: 1-Hexene; 1-Heptene; 1-Octene
- Alkynes: 1-Hexyne; 1-Heptyne; 1-Octyne
- Cycloalkanes: Cyclopentane; Cyclohexane; Cycloheptane
- Aromatics: Benzene; Toluene

Measurements were undertaken at temperatures of 298.15, 308.15 and 318.15 K.



(a) Mettler Mass balance
(b) Temperature controller
(c) Water bath
(d) Glass flask
(e) Anton Paar DMA 5000 density meter

Figure 4-3: Experimental setup for LLE measurements

The primary equipment consisted of a water bath with a temperature controller. The temperature controller circulated the water to maintain bath temperature to within 0.05 K of the set point. Masses of the components were determined on a Mettler mass balance which had a precision of 0.0001 g. The densities of the samples were analyzed with an Anton Paar DMA 5000 density meter. It is capable of a precision of 0.00001 g.cm^{-3}. Chemicals were titrated using syringes with needles capable of dispensing 0.05 g quantities at a time.

4.3.2 Experimental Procedure

The method used was that of Letcher and Siswana (1992), which was developed from Briggs and Comings (1943). The first task is to determine the cloud points and thus the binodial curve. A miscible mixture of two of the three components is accurately weighed. The flask is agitated to ensure a homogenous mixture and then placed in the water bath. To this mixture the third component is titrated until the mixture turns cloudy. The total mixture mass is recorded, from which the third component mass is able to be calculated, and then converted to mole fractions in order to plot a point on the binodial curve. This density of this mixture is then measured at 25 °C with the density meter. This density, along with the vertical intercept of the cloud point on the x-axis, is plotted to form a calibration curve. This process is repeated to give the complete binodial curve and a calibration curve of density vs x-intercept as shown in Figure 4-4.

Tie-lines were determined from mixtures whose compositions lie in the two-phase region. These mixtures were agitated and then allowed to separate into two phases. A time of at least six hours was allowed in order for the phases to reach equilibrium as the ionic liquids are slightly more viscous than organic solvents. The density of each phase was then analyzed. This density is related to an x-intercept using the calibration graph. The x-intercept value of each phase then intersects with the binodial curve, giving each end of the tie-line.

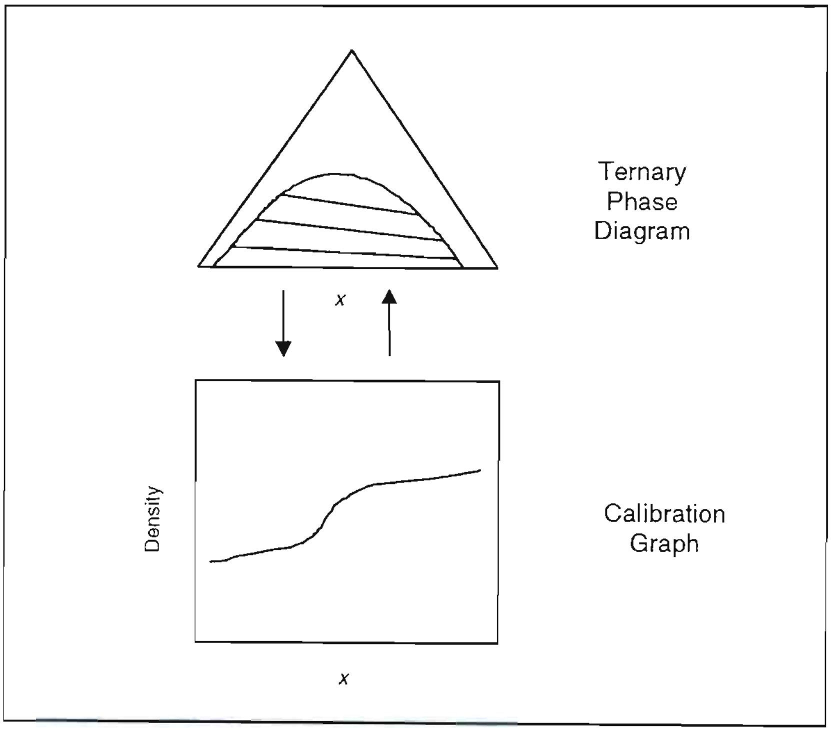


Figure 4-4: Procedure for determination of tie lines

4.3.3 Systems measured

BuMePyBF$_4$ was used as a solvent in ternary LLE measurements at 298.2 K. The following systems were measured:

- LLE System 1: BuMePyBF$_4$ + 1-Hexene + Toluene
- LLE System 2: BuMePyBF$_4$ + 1-Hexene + Ethanol
- LLE System 3: BuMePyBF$_4$ + 1-Hexene + 2-Butanone
- LLE System 4: BuMePyBF$_4$ + 1-Octene + Ethanol

4.3.4 Applicability to mixtures with Ionic liquids

As an ionic liquid cannot be analyzed by a GC, this procedure is suitable. The procedure allows for small quantities to be used thus there is a significant benefit when using expensive ionic liquids. The small quantities also allow for reasonable equilibrium times even though the ionic liquid is more viscous than most organic solvents. Although working with small quantities can result in greater risk of error, the small dispensing quantity for titration produces results within acceptable error limits. While this technique is applicable to clear and slightly coloured ionic liquids, much stronger coloured ionic liquids may prove more difficult to work with. Cloud points in this work are determined purely from observation and cloud points in stronger coloured ionic liquids may be difficult to determine with sufficient accuracy. In order to overcome this problem, an apparatus similar to that of Heintz et al. (2003) may be used. Here a laser and a detector are used to measure the intensity of the scattered light which is an indication of phase separation.

4.4 Vapour-liquid equilibria

The VLE measurements were carried out isobarically using a recirculating still. The following information is obtained from the experiments:

- Equilibrium temperatures
- Equilibrium liquid mole fractions
- Equilibrium vapour mole fractions

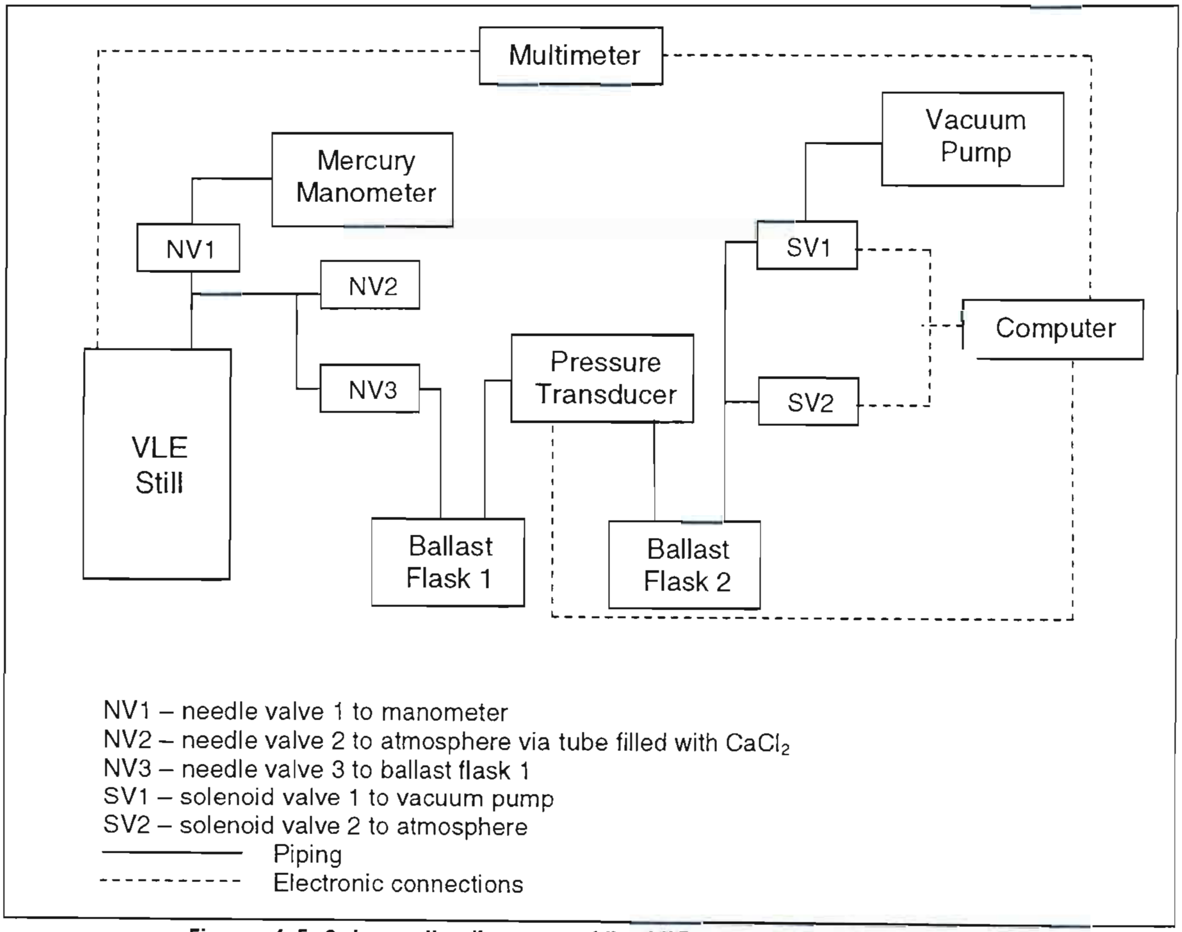


Figure 4-5: Schematic diagram of the VLE apparatus setup

Joseph (2001)

4.4.1 Experimental Setup

The experimental setup is shown in Figure 4.5. The condenser of the VLE still was connected to three needle valves in parallel. The first was to a mercury manometer and the second to atmosphere. The third was on the line used to control pressure, which included a ballast flask, a pressure transducer, a second ballast flask and two solenoid valves connected in parallel. A computer was used to open and close the solenoid valves, one open to a vacuum pump and the other to atmosphere.

4.4.1.1 Control

The pressure was controlled by the computer by interfacing with the pressure transducer and solenoid valves. The valves were initially in a closed position. Isobaric control was selected on the computer and the set point entered. The computer then compared the value from the pressure transducer and set point. A set point lower than the measured pressure caused the valve to the vacuum pump to open. A set point higher than the measured pressure caused the valve to atmosphere to open.

4.4.1.2 Measurement of equilibrium temperature

A PT-100 temperature sensor was used to measure the equilibrium temperature and was positioned as shown in Figure 4-6. The temperature sensor was, however, not in direct contact with the chemicals but rather housed in a glass well where it was encased in thermal paste. This allowed a larger area of contact between the Pt-100 bulb and glass well, and tended to smooth out short-term temperature fluctuations. The absolute accuracy of the temperature measurement was estimated to be within 0.02 K.

4.4.1.3 Heating

Heating of the mixture was achieved by both external and internal heaters. Each was controlled by a variac. The internal element heater was used to boil the mixture. The external heater was used to maintain the mixture at the boiling temperature. The power input to the still was adjusted until the 'plateau' region was reached. Kneisl et al. (1989) indicated that this was the region where the boiling temperature remains constant for a small change in input power. Operating outside this region would result in incorrect boiling points.

4.4.2 The Equilibrium Still

Central to the setup is the equilibrium still and this will be discussed further.

The Raal dynamic still (Raal and Mühlbauer, 1998), shown in Figure 4-6, incorporates some of the features of the Yerazunis et al. (1964) design. It is made of glass and is suitable to low pressure measurements. Both the liquid and vapour phases are recirculated. The design features a Cottrell tube which begins at the reboiler and ends in a concentrically aligned packed equilibrium chamber. The Cottrell pump is vacuum-insulated thereby minimizing heat loss to the surrounding.

The heating element in the reboiler ensures sufficient heating to boil the liquid. The vapour bubbles formed then move up the insulated Cottrell tube while at the same time entraining pockets of liquid. The mixture discharges onto the equilibrium chamber packing which consists of stainless steel wire mesh cylinders (3 mm diameter). The large surface area allows the phases to equilibrate. The mixture then flows onto a Pt-100 temperature sensor at the bottom of the packing.

The liquid moves through drain holes in the chamber to a small liquid trap and is then returned to the reboiler. The vapour flows up and around the chamber thus providing additional insulation. It then flows to the condenser where it is condensed into a small liquid trap and returned to the reboiler.

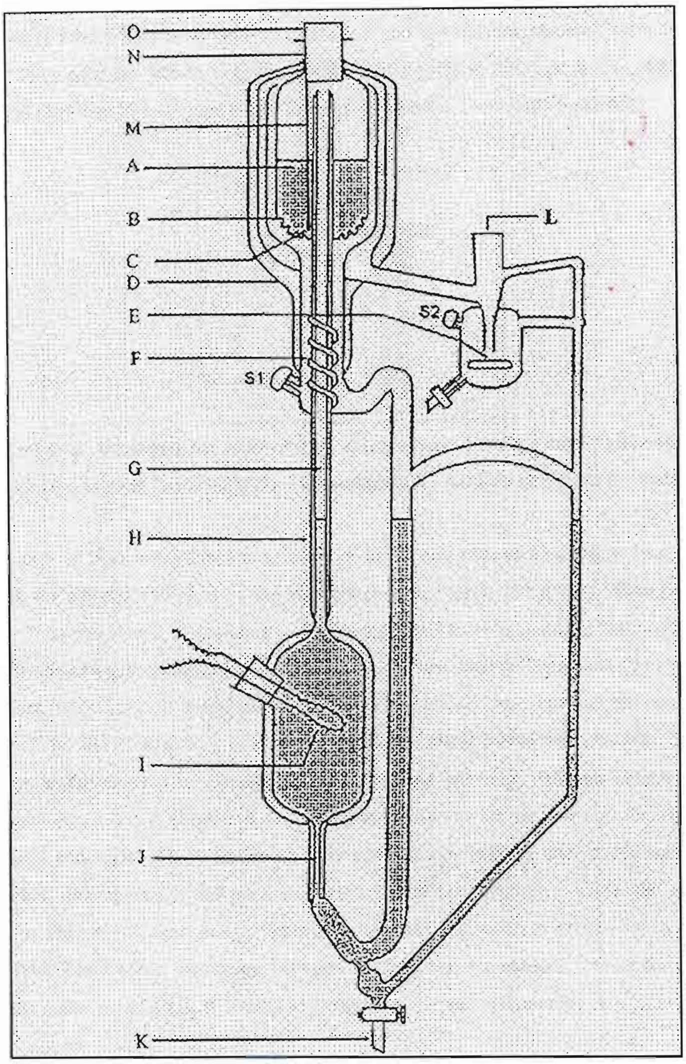


Figure 4-6: Schematic diagram of the dynamic VLE still (Joseph 2001)

A – stainless steel wire mesh packing; B – drain holes; C – Pt-100 bulb; D – vacuum jacket; E – magnetic stirrer; F – stainless steel mixing spiral; G – insulated Cottrell pump; H – vacuum jacket; I – internal heater; J – capillary; K – drain valve; S1 – liquid sampling point; S2 – vapour sampling point; L – condenser is attached here; M – glass tube housing Pt-100; N – standard taper opening at the top of the equilibrium chamber; O – glass stopper.

4.4.3 Pressure Calibration

It was necessary to calibrate the pressure sensor as it was not completely accurate. This was done by connecting a mercury manometer in parallel with the pressure sensor. A pressure was set on the controller and allowed to stabilize. The pressure reading displayed by the sensor was recorded. The corresponding manometer reading, determined with the aid of a cathetometer, was recorded and the actual pressure calculated by adding to the atmospheric pressure. This process was repeated for various pressures ranging from vacuum to atmospheric. A plot of the display pressure versus actual pressure gave a linear relationship (Appendix B). The absolute accuracy of the pressure measurement was estimated to be within 0.03 kPa.

4.4.4 Temperature Calibration

The PT-100 was connected through an RS 232 port to a multimeter (HP 34401A 6 digits) which displays its resistance. The calibration was undertaken with a very pure ethanol (> 99.5 % purity) in the VLE still. The still was operated isobarically at a number of different pressures. For each pressure reading, the corresponding resistance of the PT-100 (displayed on the multimeter) was recorded. Antoine's equation (Reid et al. 1988) was then used to determine the actual temperatures at these pressures. A plot of the actual temperature as a function of resistance gives a straight line (Appendix B). The equation of this straight line was then used in the computer program, which receives the resistance value from the multimeter via the serial port, to continually display the actual temperature.

4.4.5 Equilibrium time

Attainment of equilibrium (or as near as possible to equilibrium) is usually indicated by a constant equilibrium temperature, measured by the PT-100. This is not always the case, especially with highly non-ideal azeotropic systems, as measured in this work. Near the azeotropic region, a change in composition results in a very small change in temperature. Thus it is necessary to periodically analyze composition samples from the still to ensure the attainment of equilibrium. The time required to reach equilibrium depends on the concentration region. Equilibrium times of between sixty to ninety minutes were found to be sufficient.

4.4.6 Determination of the vapour and liquid sample compositions

Standard samples of the relevant binary mixtures were made up gravimetrically and then analyzed using a GC. The samples were cooled in the water-glycol mixture feeding the condenser, in order to minimize errors associated with the volatility of the chemicals. The ternary systems were analyzed on a solvent-free basis and therefore only binary calibrations were necessary. The mole fraction and peak areas (A_1 and A_2) of the components (x_1 and x_2) are related by Eq. 4-1.

$$\frac{A_1}{A_2} = G\frac{x_1}{x_2} \qquad (4\text{-}1)$$

Samples cover the entire composition range. The calibration graphs are plotted as x_1/x_2 *vs* A_1/A_2 and x_2/x_1 *vs* A_2/A_1 (i.e. area ratio method of Raal and Mühlbauer, 1998). If a comparison of the gradients shows that the gradient of figure 1 $\simeq$ the inverse of the gradient of figure 2 then the relationship is linear across the entire composition range and is equated to the response factor G (i.e. $G_1 \simeq G_2 \simeq G$). Analysis of the samples from the still gives values for A_1 and A_2. Using the response factor G from the calibration graphs in Eq. (4-1) and the relationship for a binary mixture (Eq. 4-2), x_1 and x_2 can be calculated. The same applies for vapour compositions y_1 and y_2.

$$x_1 + x_2 = 1 \tag{4-2}$$

Samples were taken in triplicate and are accurate to 0.001 mole fraction. GC information and settings are given in Table 4-1.

Table 4-1: GC information and settings

GC	Varian model 3000
Column	30 m megabore capillary column with 007-FFAP on fused silica
Detector	FID
Injector Temperature	100 °C
Column Temperature	40 °C
Detector Temperature	120 °C

4.4.7 Systems measured

Isobaric VLE data were measured for the following binary systems:

- Acetone + Methanol at 99.4 kPa
- 1-Hexene + 2-Butanone at 74.8 kPa

Isobaric VLE data were measured for the following ternary systems:

- $(C_6)_3C_{14}PhCl$ + Acetone + Methanol at 99.4 kPa
- $(C_6)_3C_{14}PhCl$ + 1-Hexene + 2-Butanone at 74.8 kPa

4.4.8 Applicability to mixtures with ionic liquids

The apparatus was found to be adequate to analyze mixtures on a solvent-free basis. Introducing the feed into the still via the liquid sample septum prevents any solvent from accumulating in the vapour condensate septum. Analyzing samples with a GC gives results on a solvent-free basis immediately. It is not possible to determine the solvent concentration by the same method as determined for LLE, which uses the binodial curve to reduce a degree of freedom. The concentration of the solvent in the feed must be well within the limit of miscibility, if there is any. The reason for this is that upon separation of liquid and vapour phases all the solvent, as in the case of an ionic liquid, is then present in the liquid phase at a higher concentration than in the original feed. As the apparatus is not designed to measure VLLE, it is a good precaution to determine, if any, limits of miscibility.

Chapter Five

Results

Overview

Results obtained from Gas-Liquid chromatography

- Activity coefficients at infinite dilution, calculated from Eq. (3-33)
- Selectivities at infinite dilution of various solutes with benzene, calculated from Eq. (3-44)
- Partial excess molar enthalpies at infinite dilution, calculated from Eq. (3-42)

Results obtained from liquid-liquid equilibria measurements

- Cloud point compositions, and
- Tie-line compositions
- Ternary phase diagrams
- Distribution and selectivity diagrams

Results obtained from isobaric vapour-liquid equilibria measurements

- Liquid and vapour phase compositions
- T-x-y and x-y diagrams
- Relative volatility diagrams

5.1 Results from Gas-liquid chromatography

5.1.1 Activity coefficients at infinite dilution

The results of the test system benzene in hexadecane are given in Table 5-1, and the results of various hydrocarbons in (MOIM)Cl are given in Table 5-2. Values of γ_{13}^{∞} are accurate to within 3 %.

Table 5-1: Activity coefficients at infinite dilution γ_{13}^{∞} for the test system benzene in hexadecane at 298.15 K

Solute	γ_{13}^{∞}	
	Experimental	Literature [a]
Benzene	1.004	1.00
	1.006	1.06

[a] - DECHEMA, Chemistry Data Series (Tiegs et al., 1986)

Table 5-2: Activity coefficients at infinite dilution γ_{13}^{∞} for hydrocarbon solutes in 1-methyl-3-octyl-imidazolium chloride

Solute	γ_{13}^{∞}		
	$T = 298.15$ K	$T = 308.15$ K	$T = 318.15$ K
n-Pentane	15.3	13.0	12.7
n-Hexane	17.2	15.8	15.6
n-Heptane	21.3	20.8	19.6
n-Octane	26.1	24.7	23.1
1-Hexene	11.1	10.5	9.78
1-Heptene	13.8	12.8	12.4
1-Octene	17.2	16.3	15.3
1-Hexyne	2.47	2.32	2.26
1-Heptyne	3.07	2.91	2.82
1-Octyne	3.78	3.65	3.59
Cyclopentane	8.06	7.50	7.04
Cyclohexane	10.5	9.71	9.56
Cycloheptane	12.1	11.0	10.4
Benzene	1.99	1.82	1.75
Toluene	2.79	2.60	2.55

5.1.2 Selectivities

Selectivities at infinite dilution for various hydrocarbon solutes with benzene in the ionic liquid (MOIM)Cl are given in Table 5-3. The estimated error is less than 5 %.

Table 5-3: Selectivities at infinite dilution β_{ab}^{∞} for various solutes (a) mixed with 1-Hexene (b) at temperature *T*

Solute	β_{ab}^{∞}		
	T = 298.15 K	*T* = 308.15 K	*T* = 318.15 K
n-Pentane	1.4	1.2	1.3
n-Hexane	1.5	1.5	1.5
n-Heptane	1.9	1.9	1.9
n-Octane	2.4	2.2	2.2
1-Heptene	1.2	1.2	1.3
1-Octene	1.5	1.6	1.5
1-Hexyne	0.22	0.22	0.23
1-Heptyne	0.28	0.28	0.29
1-Octyne	0.34	0.35	0.37
Cyclopentane	0.73	0.71	0.72
Cyclohexane	0.95	0.92	0.98
Cycloheptane	1.1	1.0	1.1
Benzene	0.18	0.17	0.18
Toluene	0.25	0.25	0.26

5.1.3 Partial excess molar enthalpies

Partial excess molar enthalpies at infinite dilution are given in Table 5-4. Values are accurate to within 10 %.

Table 5-4 : Partial excess molar enthalpies at infinite dilution $\overline{H}_1^{E,\infty}$

Solute	$\overline{H}_1^{E,\infty}$ /kJ.mol^{-1}
n-Pentane	7.3
n-Hexane	3.9
n-Heptane	3.3
n-Octane	4.9
1-Hexene	5.0
1-Heptene	4.3
1-Octene	4.6
1-Hexyne	3.5
1-Heptyne	3.4
1-Octyne	2.0
Cyclopentane	2.8
Cyclohexane	3.6
Cycloheptane	6.1
Benzene	5.1
Toluene	3.5

5.2 Results from LLE measurements

All compositions are estimated to be accurate to within 0.006 mole fraction.

5.2.1 LLE System 1: BuMePyBF$_4$(1) + 1-Hexene(2) + Toluene(3) at 298.2 K

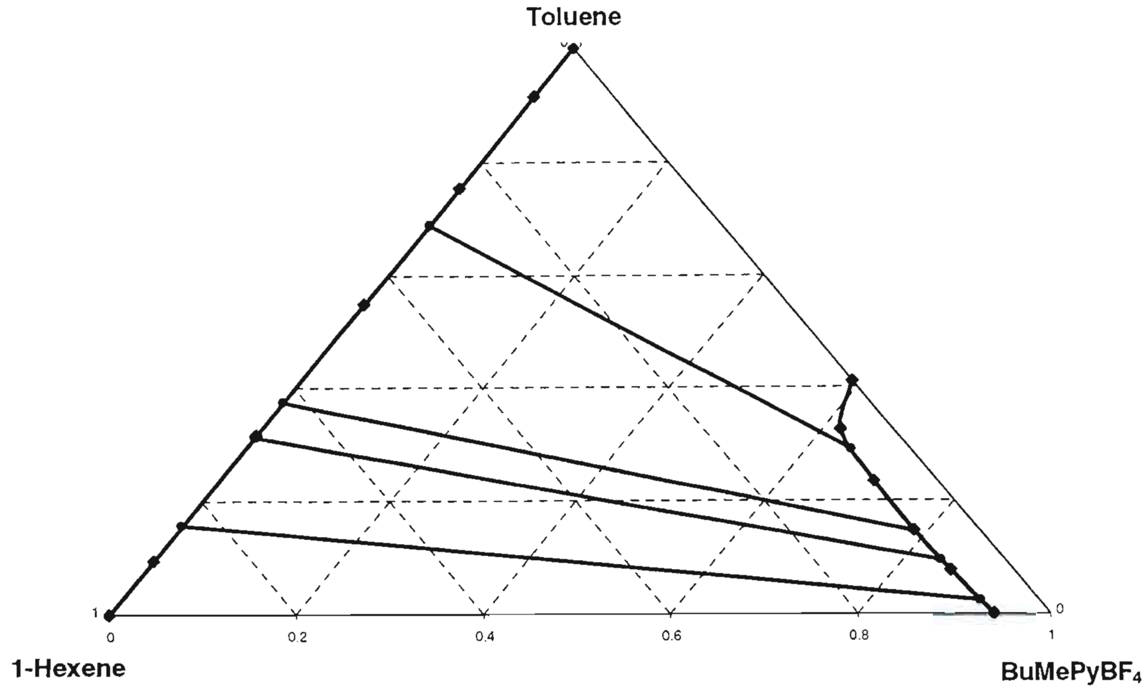


Figure 5-1: Ternary phase diagram for LLE System 1

Table 5-518: Cloud point compositions for the LLE System 1

x_1	x_2	x_3	x_1	x_2	x_3
0.941	0.059	0.000	0.000	0.085	0.915
0.858	0.065	0.077	0.000	0.245	0.755
0.785	0.069	0.146	0.000	0.450	0.550
0.700	0.065	0.235	0.000	0.682	0.318
0.619	0.055	0.326	0.000	0.904	0.096
0.588	0.000	0.412	0.000	1.000	0.000
0.000	0.000	1.000			

Table 5-6: Tie Line compositions and Selectivities for LLE System 1

Ionic Liquid Phase			Organic Liquid Phase			Selectivity
x_1	x_2	x_3	x_1	x_2	x_3	
0.915	0.061	0.024	0.000	0.843	0.157	2.1
0.839	0.066	0.095	0.000	0.686	0.314	3.1
0.783	0.069	0.148	0.000	0.624	0.376	3.6
0.648	0.062	0.290	0.000	0.311	0.689	2.1

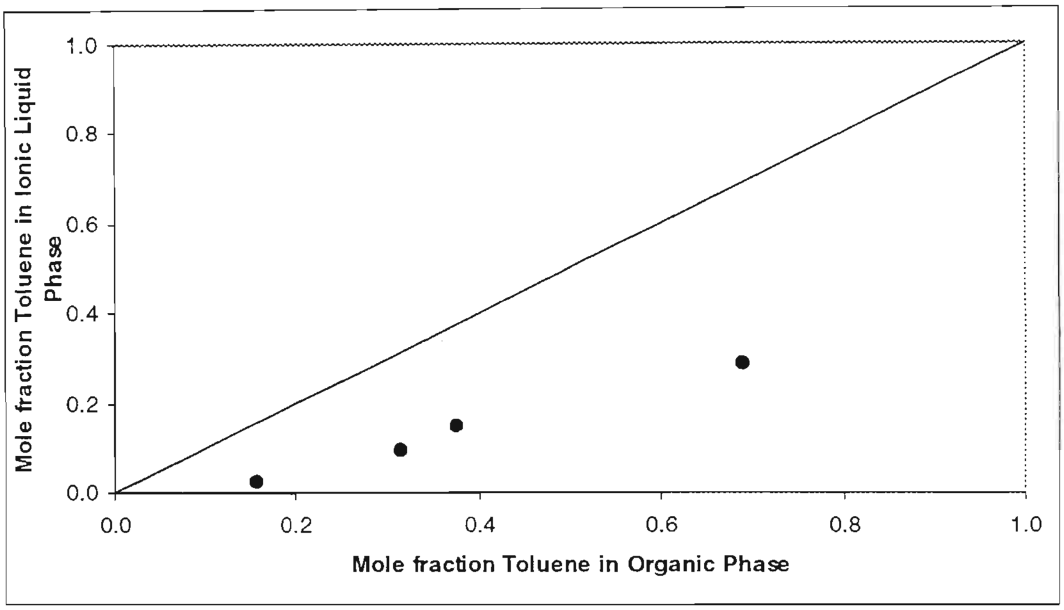


Figure 5-2: Distribution diagram for LLE System 1

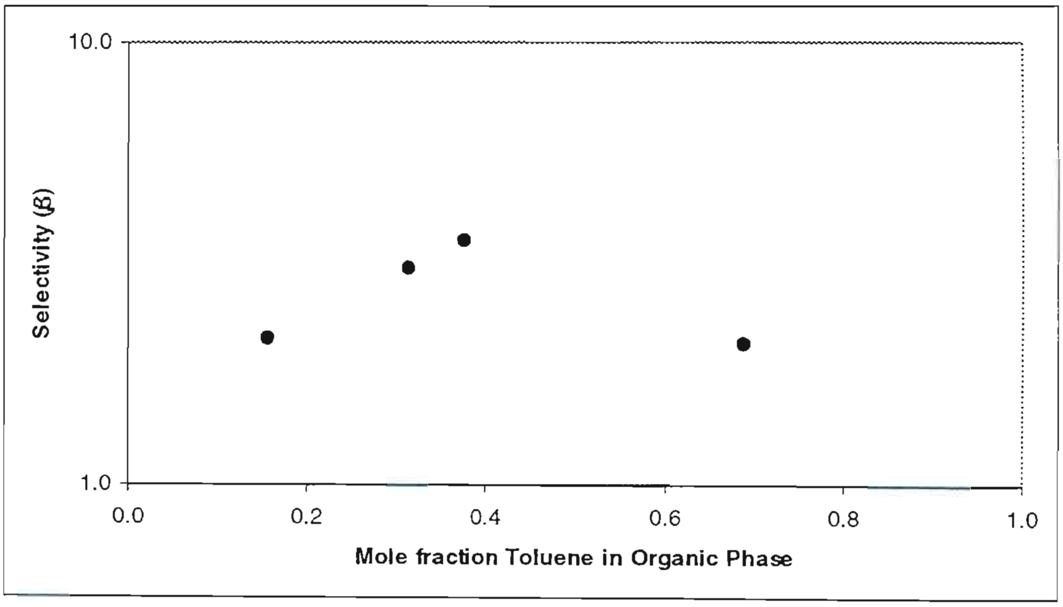


Figure 5-3: Selectivity diagram for LLE System 2

5.2.2 LLE System 2 : $BuMePyBF_4$(1) + 1-Hexene(2) + Ethanol(3) at 298.2 K

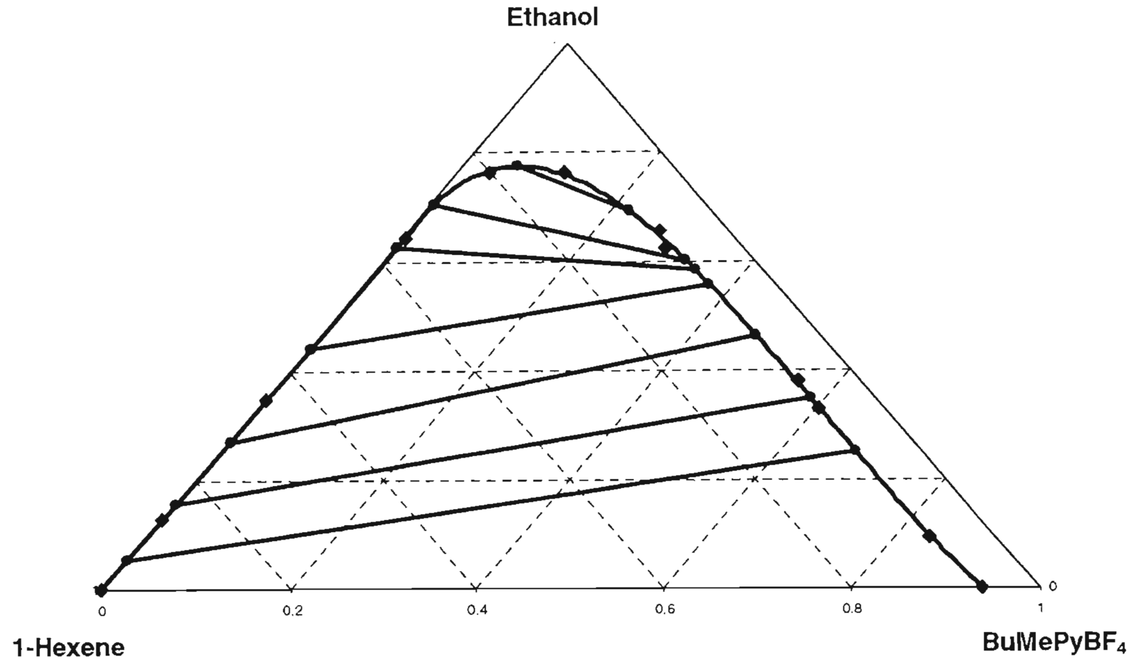


Figure 5-4: Ternary phase diagram for LLE System 2

Table 5-7: Cloud point compositions for System 2

x_1	x_2	x_3	x_1	x_2	x_3
0.941	0.059	0.000	0.114	0.122	0.764
0.837	0.069	0.094	0.034	0.201	0.765
0.601	0.069	0.330	0.005	0.352	0.643
0.555	0.064	0.381	0.000	0.651	0.349
0.293	0.083	0.624	0.000	0.871	0.129
0.270	0.073	0.657	0.000	1.000	0.000

Table 5-8: Tie Line compositions and Selectivities for System 2

Ionic Liquid Phase			Organic Liquid Phase			Selectivity
x_1	x_2	x_3	x_1	x_2	x_3	
0.679	0.069	0.252	0.000	0.946	0.054	64
0.584	0.067	0.349	0.000	0.844	0.156	28
0.469	0.066	0.465	0.001	0.729	0.270	19
0.373	0.069	0.558	0.002	0.556	0.442	10
0.345	0.071	0.584	0.004	0.371	0.625	4.9
0.325	0.072	0.603	0.004	0.290	0.706	3.4
0.219	0.088	0.693	0.059	0.165	0.776	1.7

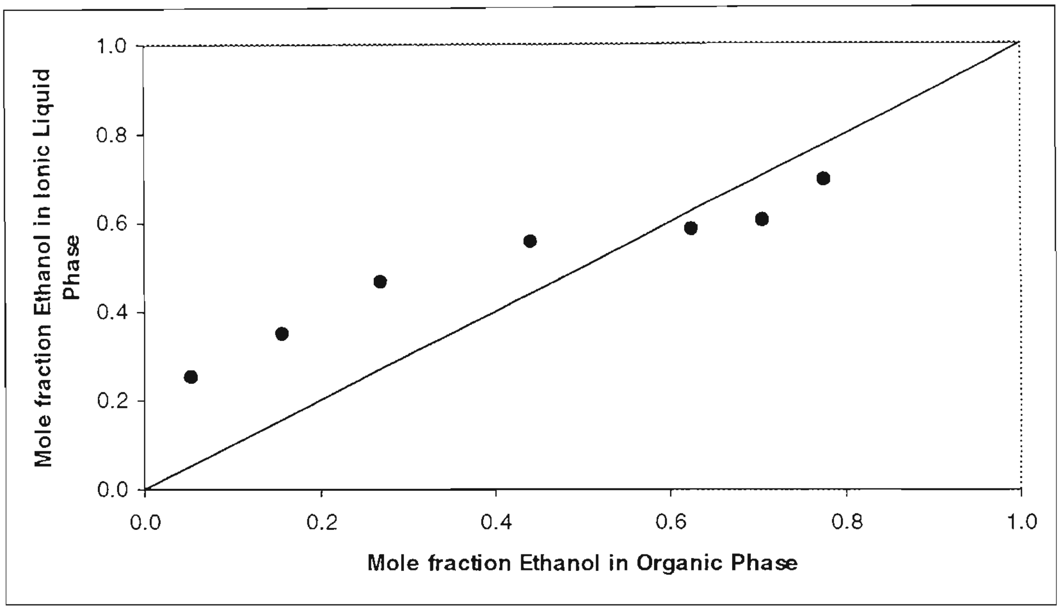


Figure 5-5: Distribution diagram for LLE System 2

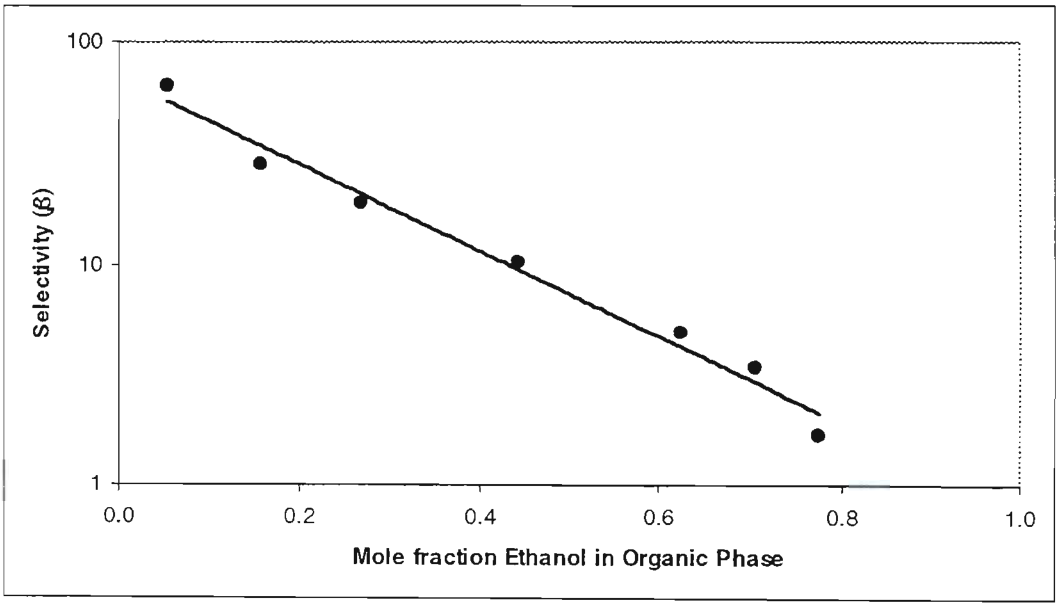


Figure 5-6: Selectivity diagram for LLE System 2

5.2.3 LLE System 3: BuMePyBF$_4$(1) + 1-Hexene(2) + 2-Butanone(3) at 298.2 K

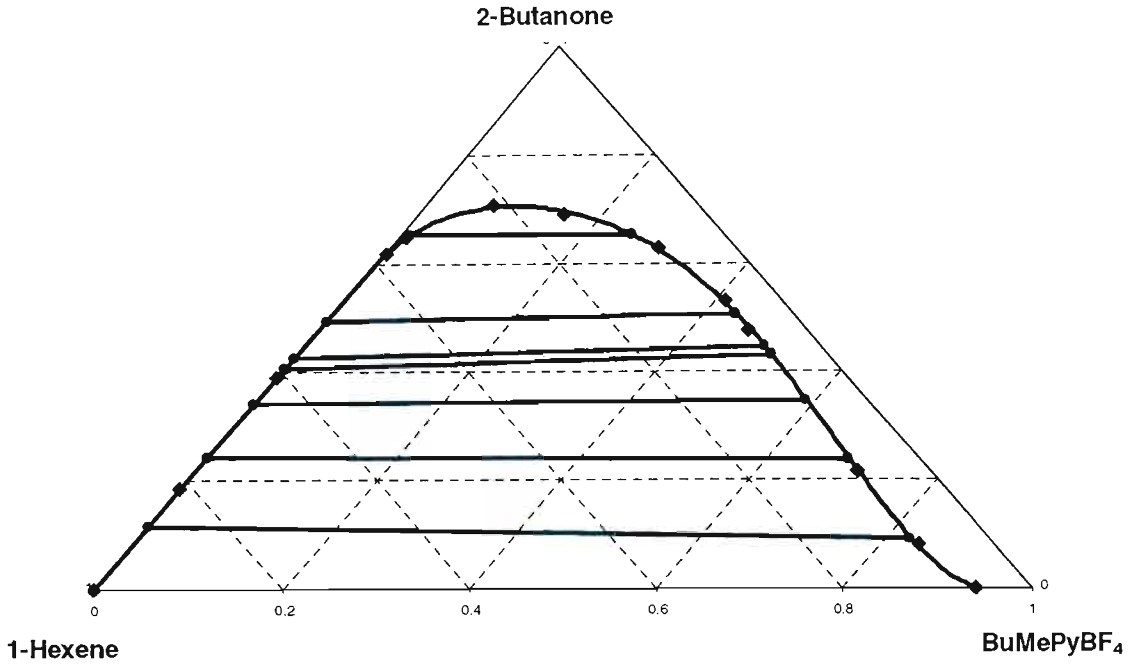


Figure 5-7: Ternary phase diagram for LLE System 3

Table 5-9: Cloud point compositions for System 3

x_1	x_2	x_3	x_1	x_2	x_3
0.941	0.059	0.000	0.074	0.218	0.708
0.839	0.080	0.081	0.009	0.342	0.649
0.710	0.076	0.214	0.002	0.378	0.620
0.462	0.062	0.476	0.000	0.610	0.390
0.410	0.059	0.531	0.000	0.814	0.186
0.290	0.081	0.629	0.000	1.000	0.000
0.160	0.150	0.690			

Table 5-10: Tie Line compositions and Selectivities for System 3

Ionic Liquid Phase			Organic Liquid Phase			Selectivity
x_1	x_2	x_3	x_1	x_2	x_3	
0.824	0.083	0.092	0.000	0.883	0.117	8.4
0.689	0.074	0.237	0.000	0.757	0.243	10
0.588	0.065	0.347	0.000	0.658	0.342	10
0.509	0.061	0.430	0.000	0.594	0.406	10
0.494	0.061	0.445	0.001	0.573	0.426	9.9
0.433	0.062	0.505	0.001	0.506	0.493	8.4
0.250	0.098	0.652	0.011	0.336	0.653	3.4

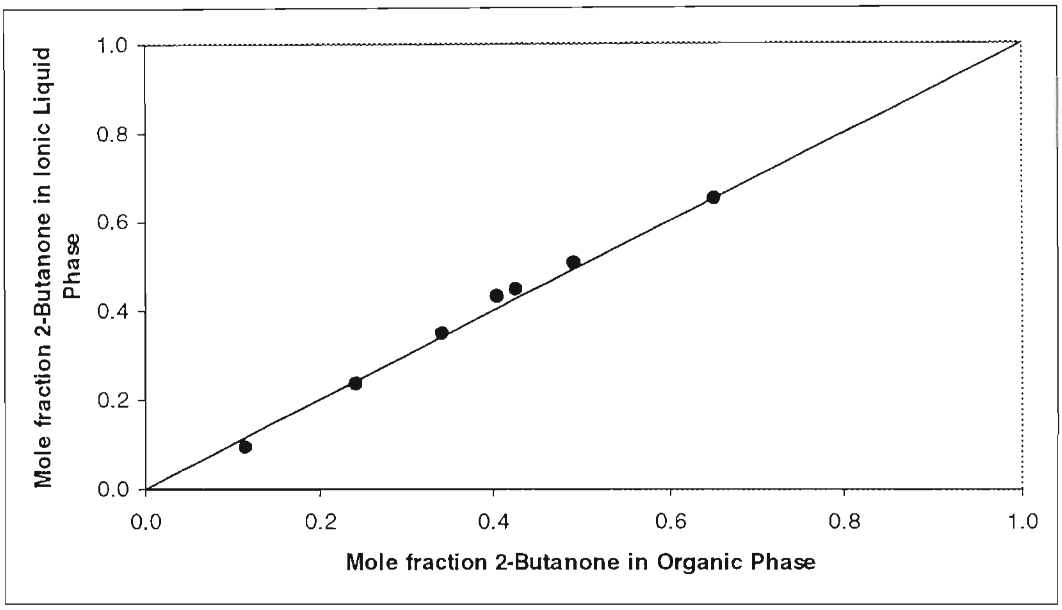


Figure 5-8: Distribution diagram for LLE System 3

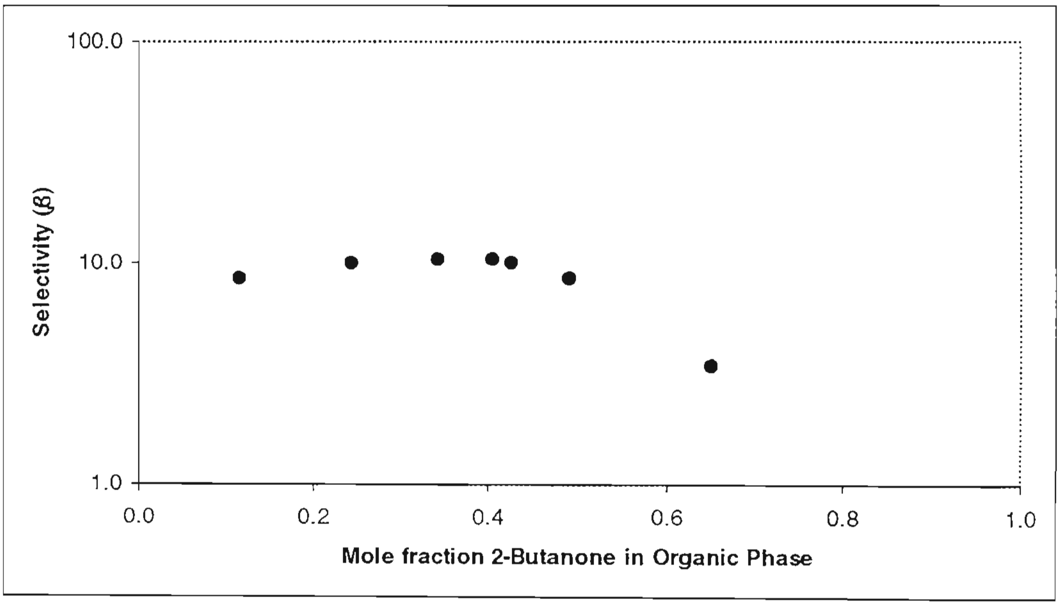


Figure 5-9: Selectivity diagram for LLE System 3

5.2.4 LLE System 4: BuMePyBF$_4$(1) + 1-Octene(2) + Ethanol (3) at 298.2 K

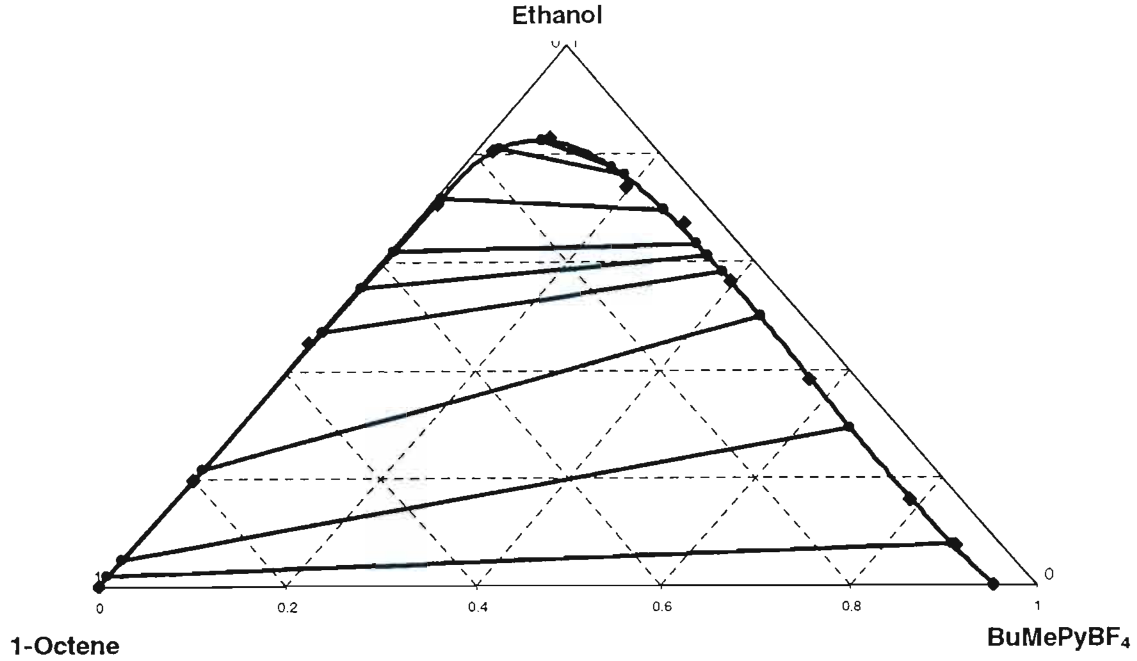


Figure 5-10: Ternary phase diagram for LLE System 4

Table 5-11: Cloud point compositions for System 4

x_1	x_2	x_3	x_1	x_2	x_3
0.954	0.046	0.000	0.066	0.104	0.830
0.877	0.049	0.074	0.019	0.179	0.802
0.784	0.056	0.160	0.008	0.286	0.706
0.567	0.051	0.382	0.000	0.549	0.451
0.393	0.043	0.564	0.000	0.802	0.198
0.292	0.038	0.670	0.000	1.000	0.000
0.195	0.067	0.738			

Table 5-12: Tie Line compositions and Selectivities for System 4

Ionic Liquid Phase			Organic Liquid Phase			Selectivity
x_1	x_2	x_3	x_1	x_2	x_3	
0.871	0.052	0.077	0.000	0.979	0.021	70
0.655	0.052	0.293	0.000	0.950	0.050	110
0.457	0.045	0.498	0.001	0.781	0.218	40
0.376	0.043	0.581	0.003	0.526	0.471	15
0.346	0.043	0.611	0.004	0.442	0.554	11
0.323	0.044	0.633	0.005	0.374	0.621	8.7
0.258	0.048	0.694	0.007	0.276	0.717	5.6
0.183	0.059	0.758	0.023	0.168	0.809	2.7
0.161	0.064	0.775	0.061	0.115	0.824	1.7

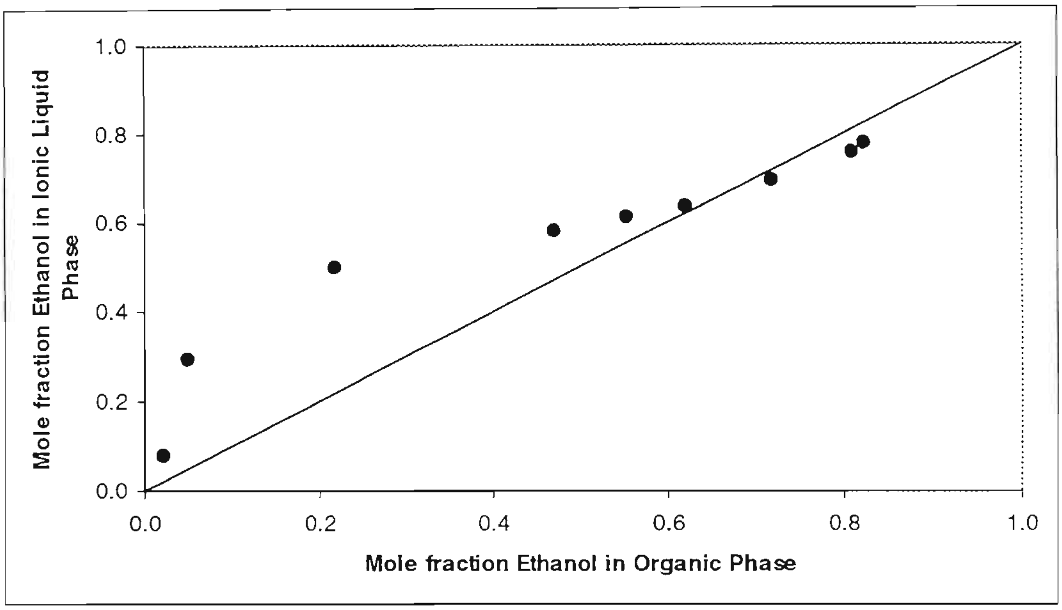


Figure 5-11: Distribution diagram for LLE System 4

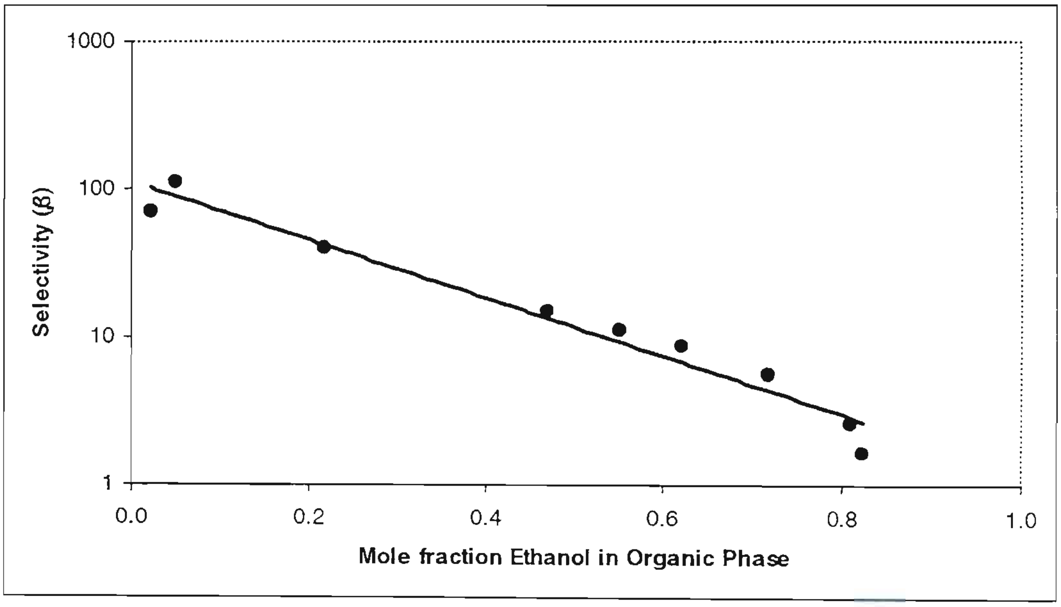


Figure 5-12: Selectivity diagram for LLE System 4

5.3 Results from VLE measurements

Temperatures and pressures are accurate to within 0.02 K and 0.03 kPa respectively. Vapour and liquid compositions are accurate to within 0.001 mole fraction

5.3.1 Binary VLE

5.3.1.1 VLE System 1: Acetone(1) + Methanol (2)

Isobaric data was measured at 99.4 kPa and compared with data measured by Verhoeye and Schepper (1973) at 101.3 kPa. Measurements are listed in Table 5-13 and presented in Figures 5-1 and 5-2.

Table 5-13: VLE data for Acetone(1) + Methanol(2) at 99.4 kPa

	99.4 kPa	
T/[°C]	x_1	y_1
64.42	0.000	0.000
63.46	0.028	0.062
62.53	0.059	0.124
60.59	0.135	0.244
59.28	0.207	0.339
57.78	0.304	0.436
56.82	0.401	0.508
56.00	0.508	0.577
55.47	0.582	0.634
55.05	0.696	0.716
55.05	0.781	0.777
55.20	0.870	0.855
55.57	0.950	0.942
55.94	1.000	1.000

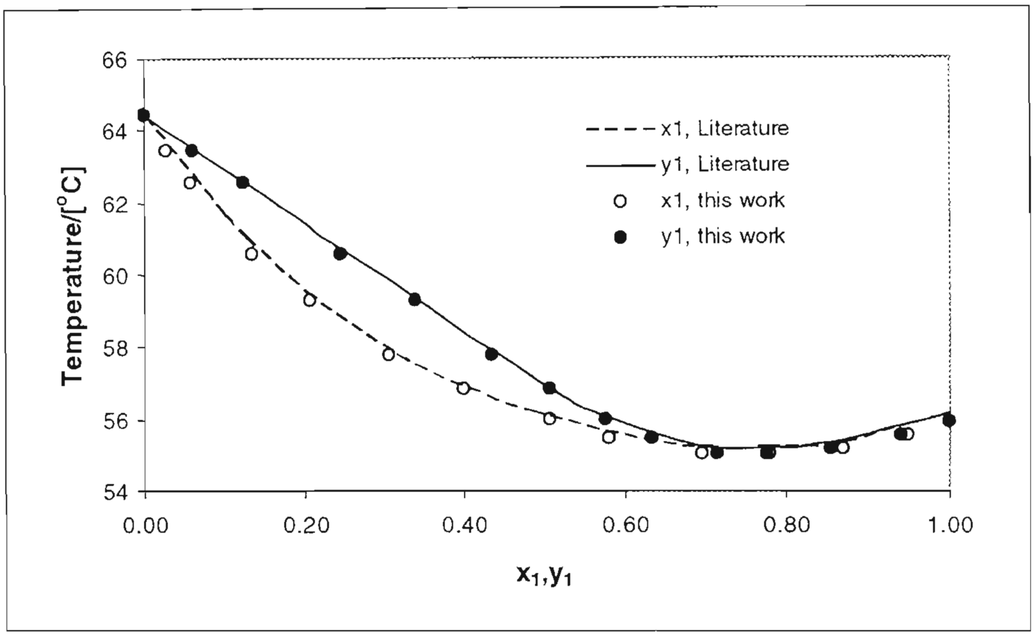


Figure 5-13: T-x-y diagram for Acetone(1) + Methanol(2) at 99.4 kPa

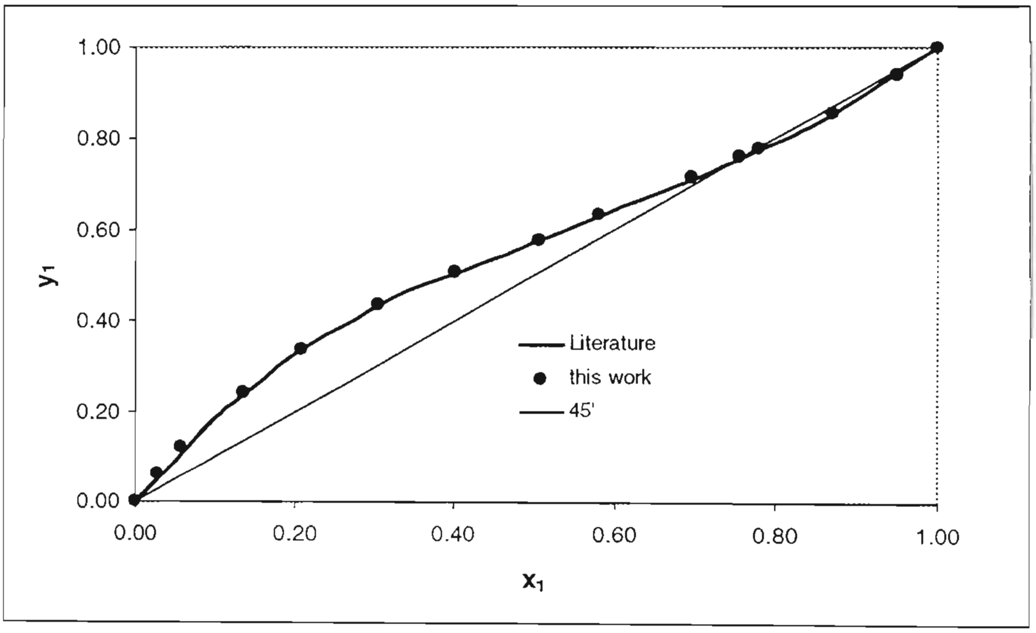


Figure 5-14: x-y diagram for Acetone(1) + Methanol(2) at 99.4 kPa

5.3.1.2 VLE System 2 : 1-Hexene(1) + 2-Butanone(2)

Isobaric data was measured at 74.8 kPa. Measurements are listed in Table 5-14 and presented in Figures 5-3 and 5-4.

Table 5-14: VLE for 1-Hexene(1) + 2-Butanone(2) at 74.8 kPa

74.8 kPa		
T/(°C)	**x_1**	**y_1**
70.53	0.000	0.000
68.10	0.031	0.113
65.96	0.068	0.212
64.08	0.109	0.286
61.10	0.189	0.397
59.60	0.236	0.441
57.11	0.312	0.503
55.14	0.435	0.590
53.93	0.619	0.720
53.30	0.759	0.787
53.22	0.834	0.834
53.43	0.901	0.882
54.11	0.974	0.966
54.44	1.000	1.000

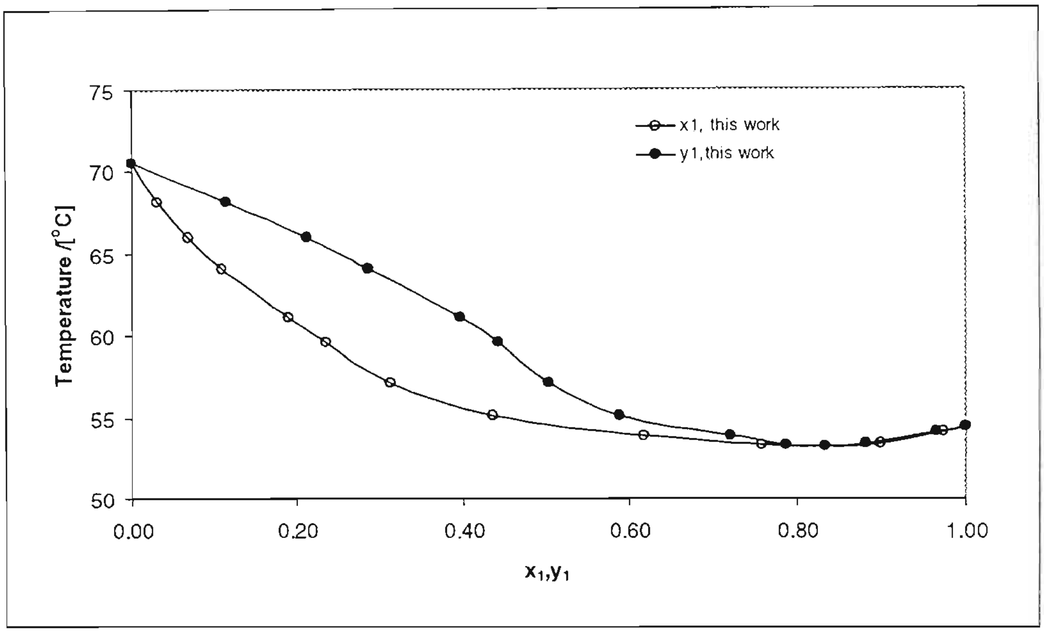


Figure 5-15: T-x-y diagram for 1-Hexene(1) + 2-Butanone(2) at 74.8 kPa

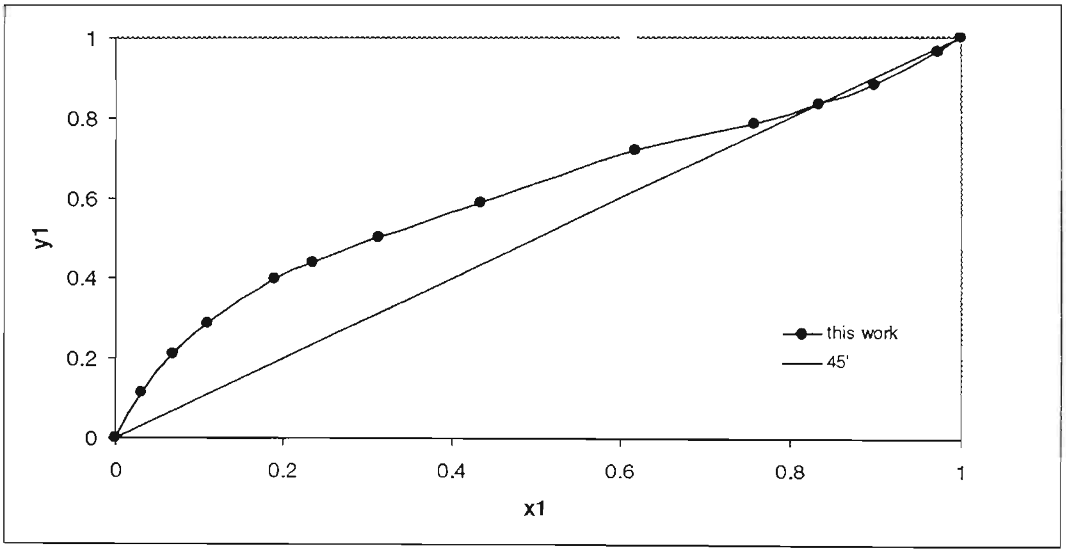


Figure 5-16: x-y diagram for 1-Hexene(1) + 2-Butanone(2) at 74.8 kPa

5.3.2 Ternary VLE

5.3.2.1 VLE System 3: Acetone(1) + Methanol(2) + $(C_6)_3C_{14}PhCl$

Isobaric data was measured at 99.4 kPa and constant $(C_6)_3C_{14}PhCl$ mol % (solvent). The data is listed in Table 5-15 and presented on a solvent-free basis in Figure 5-5.

Table 5-15: VLE data for Acetone(1) + Methanol(2) + $(C_6)_3C_{14}PhCl(3)$

99.4 kPa		
0.5 mol % $(C_6)_3C_{14}PhCl$		
$m_{3,feed}$ (%)	x_1^*	y_1
6.54	0.197	0.334
5.18	0.607	0.692
4.69	0.814	0.830
4.48	0.911	0.917
0.8 mol % $(C_6)_3C_{14}PhCl$		
$m_{3,feed}$ (%)	x_1^*	y_1
8.06	0.647	0.712
7.32	0.816	0.836
7.00	0.919	0.924

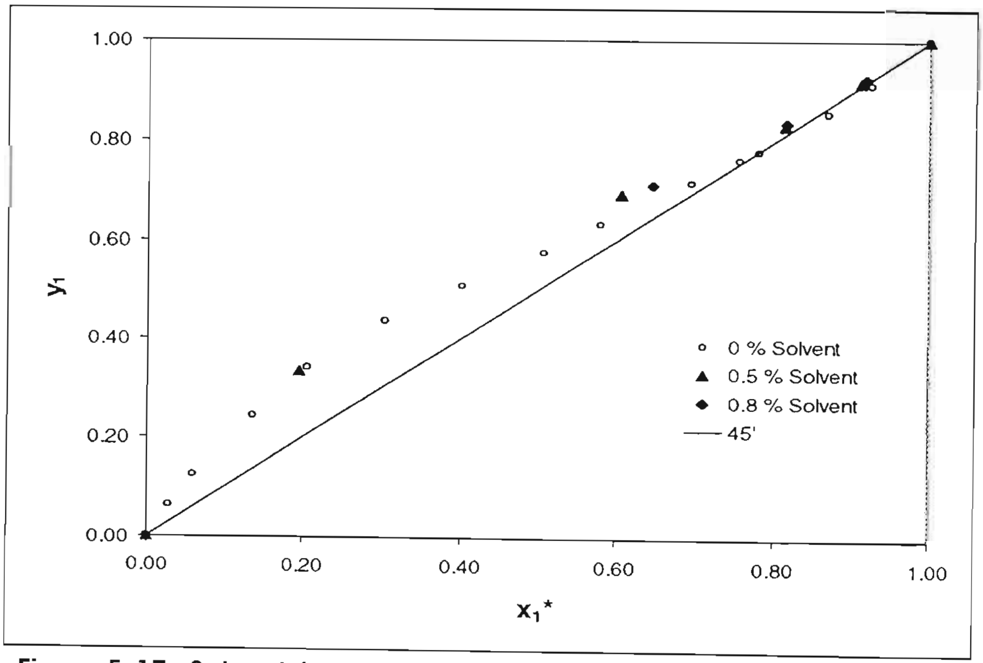


Figure 5-17: Solvent-free x-y diagram for Acetone(1) + Methanol(2) at 99.4 kPa

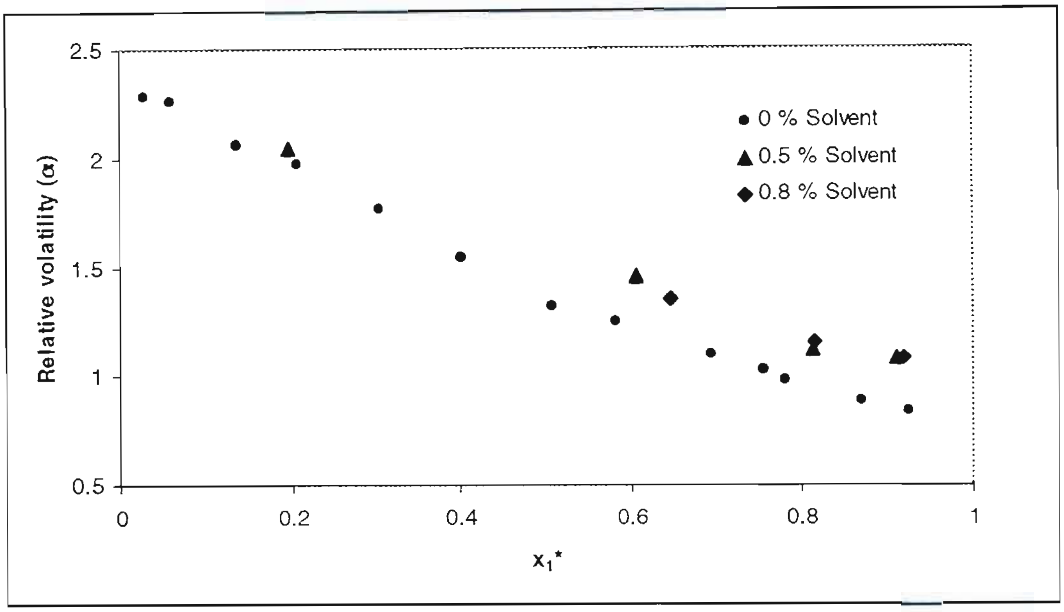


Figure 5-18: Relative volatility diagram for Acetone(1) + Methanol(2) at 99.4 kPa

5.3.2.2 VLE System 4: 1-Hexene(1) + 2-Butanone(2) + $(C_6)_3C_{14}$PhCl

Isobaric data was measured at 74.8 kPa and constant $(C_6)_3C_{14}$PhCl mol % (solvent). The data is listed in Table 5-16 and presented on a solvent-free basis in Figure 5-6.

Table 5-16: VLE for 1-Hexene(1) + 2-Butanone(2) + $(C_6)_3C_{14}$PhCl(3)

74.8 kPa		
0.5 mol % $(C_6)_3C_{14}$PhCl		
$m_{3,feed}$ (%)	x_1*	y_1
3.09	0.798	0.811
1 mol % $(C_6)_3C_{14}$PhCl		
$m_{3,feed}$ (%)	x_1*	y_1
6.20	0.552	0.645
6.02	0.763	0.779
5.94	0.884	0.874

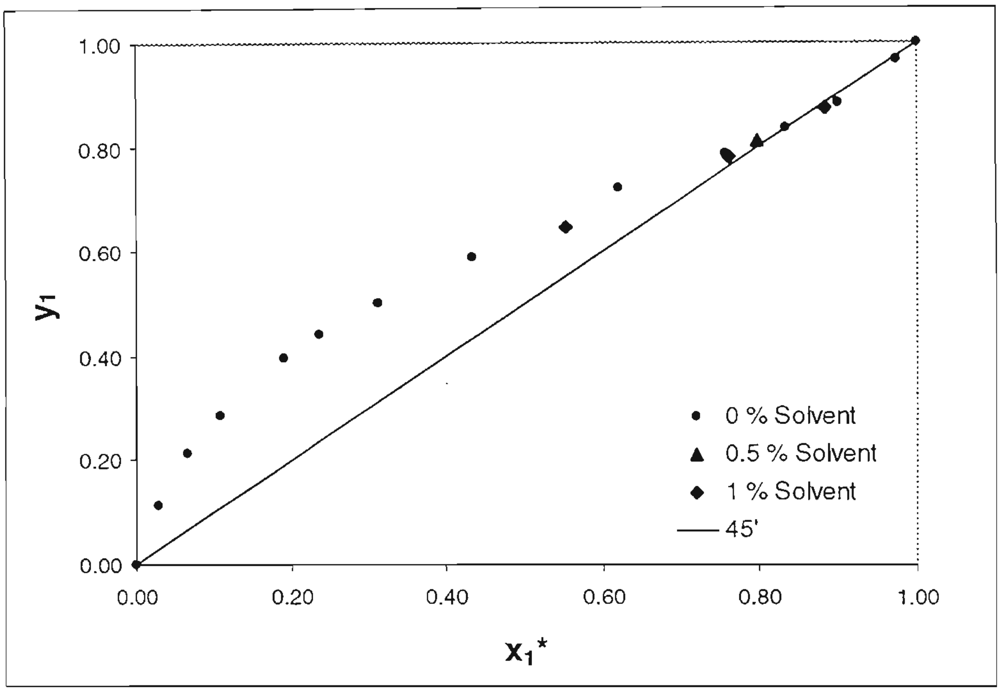


Figure 5-19: Solvent-free x-y diagram for 1-Hexene(1) + 2-Butanone(2) at 74.8 kPa

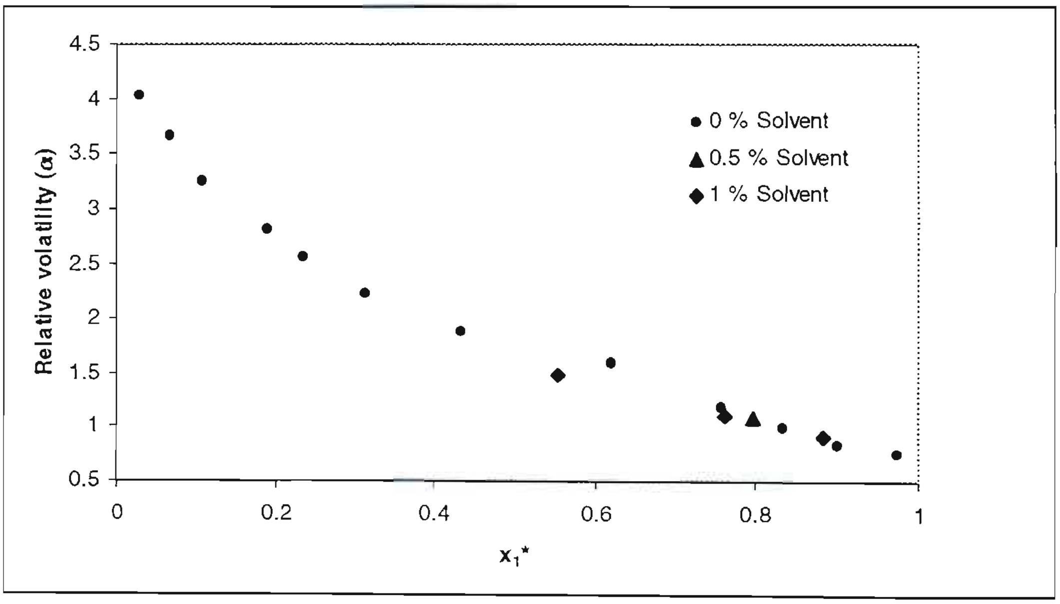


Figure 5-20: Relative volatility diagram for 1-Hexene(1) + 2-Butanone(2) at 74.8 kPa

Chapter Six

Producing an Ionic Liquid

Chapter overview

It is necessary to know how ionic liquids are made in order for a satisfactory assessment to be made of their ability to replace volatile organic compounds. This chapter looks at the various aspects of producing an ionic liquid, some of which include:

- Synthesis steps
- Experimental work
- Associated costs

6.1 Ionic liquid Synthesis

The necessary reaction steps are discussed from excellent reviews by Wasserscheid and Keim (2000) and Welton (1999). While only discussed in a somewhat qualitative manner, it is sufficient to give the reader an understanding of the factors involved.

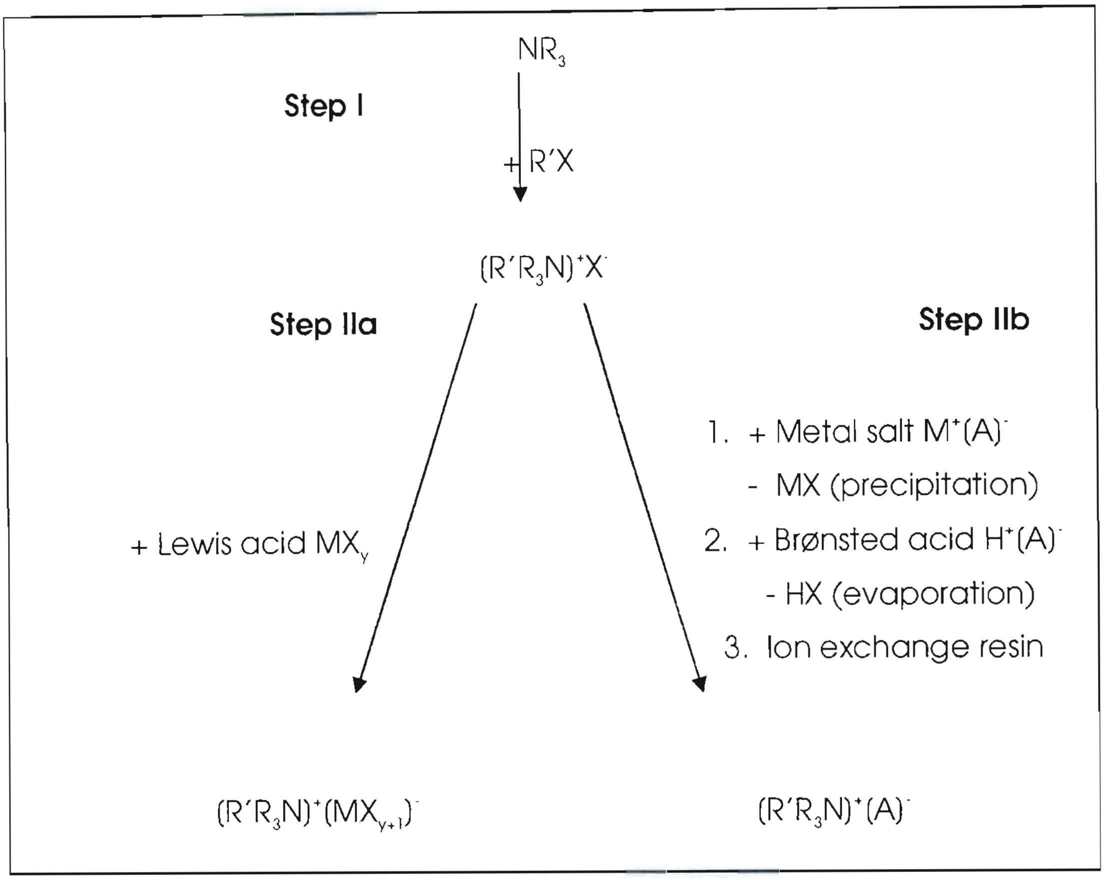


Figure 6-1: Synthesis paths for the preparation of ionic liquids examplified for an ammonium salt (Wasserscheid and Keim (2000))

The synthesis of an ionic liquid is shown in Figure 6-1, using an ammonium salt as the example. *Step I*, involves the quaternization of an amine or phosphane group to form the desired cation. The associated anion at the end of *Step I* will depend on the alkylating reagent used. If the desired cation and anion are formed then no further synthesis is required. There are many ionic liquids that can be synthesized by *Step I* alone, two of which are (EMIM)CF_3SO_3 are (BMIM)Cl.

If a different anion is required which cannot be formed directly by *Step I*, then a further step is required. There are two options to synthesize a different cation. The first (*Step IIa*) is the reaction of the ammonium halide product of *Step I* $(R'R_3N)^+X^-$, with a Lewis acid MX_y. This produces an ionic liquid of the type $(R'R_3N)^+(MX_{y+1})^-$. The second (*Step IIb*) is an exchange of the halide anion X^- for the desired anion. This can be achieved by addition of a metal salt $M^+(A)^-$, displacement of the halide anion by a strong acid $H^+(A)^-$ or over an ion exchanger.

Synthesis by *Step IIa* can result in more than one anion being present in the ionic liquid depending on the ratio of the two components $(R'R_3N)^+X^-$ and MX_y. Examples of this are the chloroaluminate melts. The formation of additional anion species is a result of further acid-base reactions of the Lewis acid with anions already present in the melt.

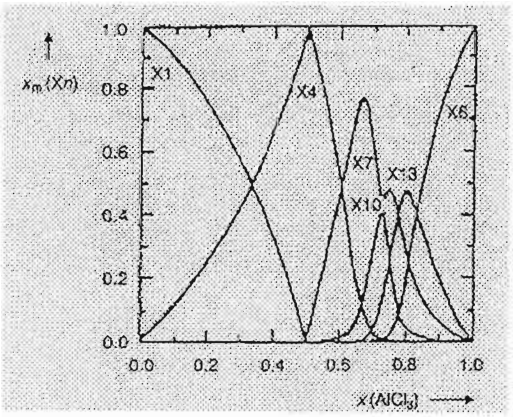


Figure 6-2: Mole fraction x_m of different anion species *Xn* in chloroaluminate melts (X1=Cl^-; X4=$AlCl_4^-$; X7=$AlCl_7^-$; X10=$Al_3Cl_{10}^-$; X13=$Al_4Cl_{13}^-$; X6=Al_2Cl_6) (Wasserscheid and Keim (2000))

From Figure 6-2 it can be seen that the addition of $AlCl_3$ to the chloride results in the formation of $AlCl_4^-$ anion. At an equimolar concentration only this anion is present. Further addition of $AlCl_3$ results in more complex chloroaluminate anions, with $Al_2Cl_6^-$ at very high concentrations. Other ionic liquids that can be formed by this route are the (EMIM)Cl/CuCl and (EMIM)Cl/$SnCl_2$ melts.

Ionic liquids formed by *Step IIb* contain only one anion species when the reaction has reached completion. Examples of ionic liquids prepared by this route are (BMIM)PF_6 and (EMIM)BF_4.

The preparation of high purity ionic liquids requires great care. As ionic liquids cannot be purified by distillation, it is in the synthesis itself that the purity must be attained. Two main sources of impurities are:

- Water
- Halide impurities

Many ionic liquids are hygroscopic and water is usually found in small amounts. This is less of a problem in hydrophobic ionic liquids. The alkylating reagent is sometimes used in slight excess in order to drive the reaction to completion. In the anion exchange, incomplete exchange will result in the ionic liquid containing some halide impurities.

6.2 Experimental Considerations

6.2.1 Review of Synthesis Techniques

Some early reviews (Welton, 1999) have indicated the preparation of ionic liquids as being quite easy and cheap. However, this has not proven to be quite the case. The synthesis, while not complicated, can be fairly lengthy and the purification technique is not necessarily the same for all ionic liquids. The cost of most ionic liquids, when compared to other chemicals, is still fairly high.

While many researchers (including this work) purchase ionic liquids from commercial sources, there are some who synthesize their ionic liquids in-house. This is especially the case where a new class of ionic liquids is to be synthesized. Preparation of the chloroaluminates involved combining the reagents in an inert atmosphere. With the air- and water-stable imidazolium-type ionic liquids, most authors use conventional heating under reflux to achieve *Step I*, Figure 6-1. This is usually the most time-consuming step in the synthesis and depends on the reactivity of the reagents. Huddleston et al. (2001), report 24-72 hours of refluxing at 70 °C for the synthesis of (BMIM)Cl from chlorobutane and 1-methylimidazole. However, the reaction is not complete even after such a long duration. The ionic liquid forms a separate liquid phase from the reagents. In this particular synthesis, the unreacted reagents were decanted. Any remaining reagents in the ionic liquid phase were extracted with ethyl acetate. The residual ethyl acetate is driven off by heating under vacuum. This final step usually also removes water from the ionic liquid.

Ionic liquids comprising the BF_4^- and PF_6^- anions are usually formed by *Step IIb*, Figure 6-1. Huddleston et al. (2001) produce $(BMIM)PF_6$ from (BMIM)Cl by using a strong acid HPF_6. The PF_6^- displaces the Cl^- resulting in a second liquid phase of HCl above the $(BMIM)PF_6$. Residual HCl was removed by extraction with deionised water. This is possible as the $(BMIM)PF_6$ is immiscible with water. For the synthesis of $(BMIM)BF_4$, methylene chloride was used to extract the HCl. The resulting ionic liquid is purified by heating under vacuum. Using strong acids appears to yield rapid reactions as the authors give no indication of reaction times.

A more common approach in literature is the use of metal salts in *Step IIb*, Figure 6-1. This method usually involves dissolving the product of *Step I*, Figure 6-1, in a solvent and then introducing the metal salt. The resulting reaction is carried out at room temperature under constant agitation. Yoshizawa et al. (2001) synthesized ionic liquids using lithium salts and report an agitation period of 1 day. Larsen et al. (2000) synthesized ionic liquids using silver salts and report an agitation period of 10 hours. The use of silver reduces the reaction time, but it is significantly more expensive than the lithium salts. Using an appropriate solvent, the resulting metal halide will precipitate and can filtered from the solution. Suarez et al. (1996), filtered their reaction mixture through a plug of celite. The remaining volatiles are removed by heating under vacuum.

Ionic liquids produced by Step IIa, Figure 6-1, can be formed by various anion and cation reagent mole ratios. In the case of chloroaluminate melts, it is necessary to undertake the reaction in dry atmosphere as the $AlCl_3$ reacts with moisture. It is interesting, as the reactants which are usually powders, collapse into a clear liquid when mixed together and without additional heating.

A significant improvement in the synthesis of ionic liquids was contributed by Varma and Namboodiri (2001). They used a household microwave oven to synthesize a number of ionic liquids. What is significant is that *Step I*, Figure 6-1 which is the most time-consuming, can be completed in a few minutes. It is also important from an environmental perspective in that it is solvent-free thus making no additional use of volatile organics and further promoting ionic liquids as 'green' solvents. They found that a power level of 240 W was an optimum. As the ionic liquid forms, it increases the polarity of the reaction medium and thereby increasing the rate of microwave absorption. The problem at higher power levels is that there is significant alkyl halide evaporation and localized overheating causes the ionic liquid to degrade. This is because there is no means to continually agitate or stir the mixture. To overcome this, the reaction is heated and then mixed intermittently to obtain better results. For the mixtures investigated, heating for 30 s at 240 W results in a bulk temperature of between 70 to 100 °C.

A comparison is made of heating by microwave and by oil bath for the various 1-methylimidazole + alkyl halide mixtures in Table 6-1. The microwave heating was applied for 30 s with 10 s for mixing, and thereafter further 15 s heating time and 10 s mixing until the mixture was completely reacted. The time is the sum of the heating and mixing times. What is evident is the significant difference in the time to reaction completion by each of the methods. The heating by microwave is many orders of magnitude smaller than the oil bath heating. In all cases the yield was improved, showing the improved efficiency of the process. The method is, however, suited to higher boiling alkyl halides as these are less likely to evaporate. The use of lower boiling alkyl halides requires them to be in excess, as some evaporates.

Table 6-1: A comparison of microwave and oil bath heating for preparing ionic liquids

Alkyl Halide	Microwave Heating at 240 W		Oil bath heating at 80 °C	
	Yield (%)	Time (s)	Yield (%)	Time (h)
1-bromobutane	86	105	76	5
1-chlorohexane	81	130	53	5
1-bromohexane	89	105	78	5
1-iodohexane	93	90	89	3
1-iodoheptane	94	90	95	3
1-bromooctane	91	105	73	5

(Varma and Namboodiri, 2001)

In addition the authors report a superior purity by microwave heating over other conventional methods. Additional work (Namboodiri and Varma, 2002) has been done involving *Step IIa*, Figure 6-1. The preparation of a number of chloroaluminate ionic liquids was achieved with 100 % yield in each case and total heating times of a few minutes.

6.2.2 Synthesis of an Ionic Liquid

While not of core importance to the experimental scope of this work, the synthesis of an ionic liquid provides an interesting addition to the phase equilibria measurements. Thus, an ionic liquid was produced purely for the purpose of observing the reaction. As such, reagents which were available in the laboratory were used.

The following reaction was investigated:

Pyridine + Cyclohexyl Chloride → *N*-Cyclohexyl Pyridinium chloride (6-1)

The reaction is a substitution reaction and proceeds by the S_{N2} mechanism as follows:

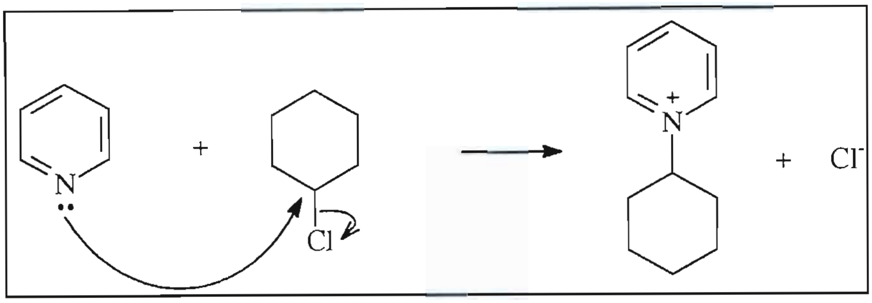


Figure 6-3: The SN2 mechanism for the reaction of pyridine with cyclohexyl chloride

The pyridine and cyclohexyl chloride were mixed together with the cyclohexyl chloride in a slight molar excess. The mixture, approximately 100 g, was stirred and heated under reflux in a conventional manner. The heating plate was set to 120 °C for 3 days and then to 150 °C for 4 days in an attempt to increase the reaction rate. The product formed a slightly orange immiscible phase compared to the clear reagents. After a reaction time of 7 days, the ionic liquid product was observed to be approximately 20 % v/v. As this was qualitative, no measurements were made to obtain an exact yield. Consequently, the structure was determined purely from the mechanism and is not confirmed by NMR or other spectroscopy methods.

The reason for the reaction rate being so low can be explained by the classification of the alkyl halide. A comparison of the reaction rates of various alkyl halide classes is made by Bruice (1998). The reaction rate of Cl^- with 1-bromopropane, a primary halide, is 16 times faster than the reaction of Cl^- with 2-bromopropane, a secondary halide. The reaction of Cl^- with 2-bromo-2-methyl-propane, a tertiary halide, is too slow to measure. Applying this to the above reaction in Figure 6-3, we see that cyclohexyl chloride is a tertiary halide. The lone pair of electrons on the nitrogen in the pyridine has to attack the tertiary carbon from the side opposite to the chloride. This side is occupied by the carbon ring and thus the probability of attack, and hence the reaction rate, is very low.

Since the melting point was between 60 and 70 °C, no further use could be made of the ionic liquid as a solvent at room temperature. The high melting point can be attributed to the structure of the ionic liquid. The cation is rather symmetrical about the nitrogen-carbon bond, although one side is cyclic and the other aromatic. There are no side chains on either of the rings and thus very little inhibition to crystal packing. The anion is also mono-atomic and thus comparatively small in size.

An attempt was made to produce the ionic liquid via microwave heating. A Samsung M160N microwave oven was operated at 300 W. The mixture was heated in a flat bottom conical flask for 30 s intervals with intermittent agitation. After a heating time of 4 min the reaction proved inconclusive. The mixture was found to heat up quite quickly, but on further heating evaporation of the reagents became significantly noticeable. It was not possible to seal the flask with a stopper due to the increase in pressure within the flask. The ionic liquid did not form for possibly two reasons:

1. Quantity. In order for a comparison of the different methods to be made, similar quantities of reagents have to be used. Quantities used by Varma and Namboodiri (2001) were in the order of 3-4 mmol. The quantities used in this experiment were in the order of 1 mol. Such a significant order of magnitude increase in the heat capacity would probably increase the reaction time significantly. Another difficulty is achieving uniform mixing and heating in such a large quantity of reagent.
2. Reaction rate. As explained above, the reaction rate involving a tertiary halide is very slow. Varma and Namboodiri, on the other hand, used primary halides which are far more reactive than tertiary halides. No continuous mixing also reduces the number of possible desired collisions between the lone pair of electrons on the nitrogen and the tertiary carbon on the halide.

6.3 Associated Costs

For researchers wishing to focus primarily on using ionic liquids in various experiments, it is necessary to purchase the required ionic liquid. Initially ionic liquids were produced only in research laboratories as the required quantities were small. With increasing interest in the last few years, commercial sources of ionic liquids have been developed from some of these laboratories as they have the necessary expertise in ionic liquid synthesis. This has also drawn the attention of commercial specialty chemical companies who have begun to offer their own range of ionic liquids. Some of these companies are listed below, with websites in the reference section.

- Acros Organics
- Ozark Fluorine Specialities
- Sachem Inc.
- Solvent Innovation GmBH
- Merck Chemicals

From a market perspective it is important to have a number of companies manufacturing ionic liquids as it creates some competition and offers choice to researchers.

The cost of an ionic liquid is significantly dependent upon the particular ionic liquid being produced. This can be seen by comparing prices of various ionic liquids in Table 6-2 available from Solvent Innovation GmBH, Germany.

Table 6-2: Prices of various ionic liquids available from Solvent Innovation GmBH

Ionic Liquid	Price (€) (2003)		
	100 g	500 g	1000 g

(BMIM)Br	98.80	290.70	415.30
(BMIM)Cl	91.00	276.70	382.40
(HMIM)Cl	125.20	368.10	525.90
(MOIM)Cl	107.90	317.30	453.30
(BMIM)BF_4	194.70	572.70	954.50
(HMIM)BF_4	312.90	920.40	1534.00
(MOIM)BF_4	223.90	658.60	1097.60
(BMIM)PF_6	253.80	746.50	1244.20

(N.B. Prices do not include any delivery charges, etc.)

Using the pricing as a comparison it can be seen that the ionic liquids containing simple halides are much cheaper than those containing more complex fluorinated anions. This is because the halides are formed by a single synthesis step (Step I, Figure 6-1) while the fluorinated anions require a further step (Step IIb, Figure 6-1). This step usually involves strong acids or metal salts, which can be expensive. A variation in the alkyl chain length on the cation does not seem to change the price significantly. However this is within the same cation type and may vary considerably with other cation types. The purification steps required for each ionic liquid may vary somewhat, thus varying the cost. A look at the scale-up shows that a 10 fold scale up brings about a 4 to 5 fold increase in price resulting in the price/kg being halved.

A useful discussion from a manufacturing perspective is given by Oude Nijeweme (2003) of Merck Chemicals. He regards the setup and mixing of reagents as simple and not that time-consuming. It is the chemical reaction, however, that can take several weeks and thus cause high costs. At the end of the reaction period the ionic liquid is likely to have impurities such as water and chloride. It is the cleaning and subsequent drying of the ionic liquid that can be time-consuming and can add significantly to costs. The final step is measuring, filling and packaging which is done under a protective atmosphere. This is the conventional method.

Some improvements Oude Nijeweme (2003) suggests are:

- The use of high purity reagents to avoid costly treatment afterwards
- Use of microwaves to reduce reaction times

It seems to be somewhat of a tradeoff as he regards both the high purity chemicals (which are difficult to find) and purification process to be very expensive at this stage.

Another process consideration is scaling up of the reactions. Some of the ionic liquids induce exothermic reactions and this does impose some limitations.

The price of ionic liquids that Merck Chemicals produces ranges from a few $ to 10 000 $ per kg. Prices are still high as the market is in its early stage with low demand. This is mainly due to demand only from R&D institutes which require small, high purity quantities.

Oude Nijeweme (2003) points out that large scale development of applications for particular ionic liquids will bring about scale benefits of ionic liquid production. This benefit is particularly effective if the demand increases about ten fold. He does mention, however, that the reduction in cost of a particular ionic liquid varies and is dependent on:

- Ingredients
- License fees
- Fabrication processes

As a final point he mentions a point which has been motivated by a number of researchers and discussed in Chapter 2.1.4. The ability of ionic liquids to be recycled in chemical processes is an important factor. No one would substitute a 3 $/litre chemical for a 300 $/litre ionic liquid. However if the efficiency is increased and/or you can use the ionic liquids more than 100 times, then the ionic liquid is the more cost-effective solution even though it is 100 times more expensive.

Chapter Seven

Discussion

Chapter Overview

This chapter looks at the factors to consider when choosing an ionic liquid as a solvent for research purposes.

Much of the discussion is of the experimental results. The following results are discussed:

- GLC
- LLE
- VLE

The LLE and VLE data have been regressed to obtain the parameters for various models. The accuracy to which these models correlate the experimental data is discussed.

Possible problems associated with ionic liquids concerning their use in industrial separation processes are discussed. Solutions are suggested for some of these problems.

A possible process design is considered for the separation of 1-hexene and 2-butanone.

7.1 Choice of Ionic Liquids

While it is quite possible to produce ionic liquids in a standard laboratory (Welton, 1999), it is easier to purchase them from manufacturers who have vast experience in synthesis and purification. Many of these companies are working in conjunction with leading synthetic chemists involved in ionic liquid research. The choice of ionic liquids was based on:

- Availability of ionic liquids
- Physical properties and solubility data supplied by manufacturers
- Price
- Work done by other researchers

7.1.1 Availability of ionic liquids

While many combinations are possible, only certain ionic liquids are produced by manufacturers. The choice, it seems, is usually based upon ionic liquids used in previous research, as references are given alongside many ionic liquids. Smaller manufacturers usually concentrate on four or five anions and combine these with cations. By varying the length of the alkyl chain on the cation, a number of different ionic liquids can be produced with little or no variation in the manufacturing process. With larger manufacturers entering the market, a significant number of ionic liquids, including new cation and anion types, are available to researchers.

7.1.2 Physical properties and solubility data

While physical properties are necessary in selecting an ionic liquid, not all manufacturers give comprehensive information. However, most of the time the single most important property, the melting point, is given. This will determine the state of the ionic liquid at the desired conditions. As can be seen from Chapter 2.1.3, not all ionic liquids are liquid at room temperature. In fact, a search of the Merck ionic liquid catalogue shows that relatively few are liquid at room temperature. Care must be taken to ensure that it is a liquid at the desired conditions in order for costly mistakes to be avoided. It is probably left to the researchers to fully characterise ionic liquids. In phase equilibria measurements it is necessary to know, to some extent, the miscibility/immiscibility properties. In LLE there has to be some immiscibility region in the mixture of interest. Conversely, in VLE a homogenous mixture is preferred. While exact limits of miscibility are not required, approximate miscibility characteristics should be known.

7.1.3 Price

The price of an ionic liquid is a significant factor especially in research. As can be seen from Chapter 6.3, costs of ionic liquids vary with structure. With the current small quantities and high purities required for research, manufacturers are unlikely to reduce prices too soon. Therefore it is necessary to make an informed decision in order to get the most value for money, as random selection may prove wasteful. The necessary physical properties required by the task and the impurity tolerances must first be established. A search of ionic liquids available from various manufacturers against these criteria should yield a handful of possible candidates. Prices for ionic liquids containing various anions can differ significantly. Thus if the process can accept a halide containing ionic liquid than a more complex anion, it may be more cost effective to begin with a chloride or a bromide.

7.1.4 Work done by other researchers

Choosing ionic liquids investigated by other researchers should be quite applicable to reaction chemistry, but is also be applicable to separations. In reaction chemistry, an ionic liquid that enhances or catalyzes a particular reaction may be a good starting point for a similar type of reaction. The ionic liquid BMIM(PF_6) has been investigated extensively and has shown to be quite effective as a catalyst medium for a number of reactions. Consequently, it is comparatively cheaper than other (PF_6) ionic liquids. In separations, solvents are usually effective for separating classes of compounds. Therefore if an ionic liquid separates two compounds from two different classes effectively, it may work suitably for two other compounds also from the respective classes.

7.2 Results from GLC

The primary results obtained from GLC were activity coefficients at infinite dilution. From these values, selectivities at infinite dilution have been calculated. From the temperature dependence, partial excess molar enthalpies have been calculated. These results have been presented at the *17th International Conference on Chemical Thermodynamics,* Rostock, Germany (David et al., 2002), and have recently been published (David et al., 2003a).

As a test of the experimental technique, activity coefficients of the solute benzene at infinite dilution in the solvent hexadecane were determined at 298.15 K. The results obtained, shown in Table 5-1, are comparable with literature values.

Since the focus of this work is to separate alpha olefins from mixtures, it is beneficial to investigate a variety of hydrocarbons as solutes. This allows possible trends to be established with regard to the different classes of solutes. The solvent used is the ionic liquid (MOIM)Cl (Figure 1-1a). The data presented are new as no activity coefficient data has previously been reported on work involving this ionic liquid.

One method of analyzing solute trends is to plot the activity coefficient at infinite dilution as a function of the number of carbons in the solute. Using the values in Table 5-2 at 298.15 K, a plot can be generated as shown in Figure 7-1. The trends in Figure 7-1 indicate the following hierarchy in activity coefficients at infinite diliution: alkanes > alkenes ≥ cycloalkanes > alkynes ≥ aromatics. The magnitude of these values can be explained by the polar nature of the solvent. The positive aromatic ring of the ionic liquid and the chlorine anion are more likely to interact with polarizable aromatic compounds and polar (including acid proton) alkyne compounds, than with linear non-polar alkanes.

The linear alkanes, due to their completely saturated bonds, interact very little with (MOIM)Cl. This is can be seen by the larger activity coefficients, indicating a fairly non-ideal mixture. The alkenes are slightly more polar than the alkanes due to the double bond which comprises of a sigma and a pi bond. This results in a slightly more ideal mixture as shown by the activity coefficient values. Although completely saturated, the cycloalkanes are ring structures. This similarity to the imidazolium ring results in lower activity coefficients than for linear alkanes. The alkynes contain a triple bond which comprises a sigma bond and two pi bonds resulting in the terminal hydrogen being acidic. This significantly increases the interaction between the alkyne and the ionic liquid and results in quite ideal mixtures. The aromatics, in addition to being ring structures, have delocalised electrons and therefore a significant electron density above and below the ring. The resulting interactions produce almost completely ideal mixtures shown by the small activity coefficients.

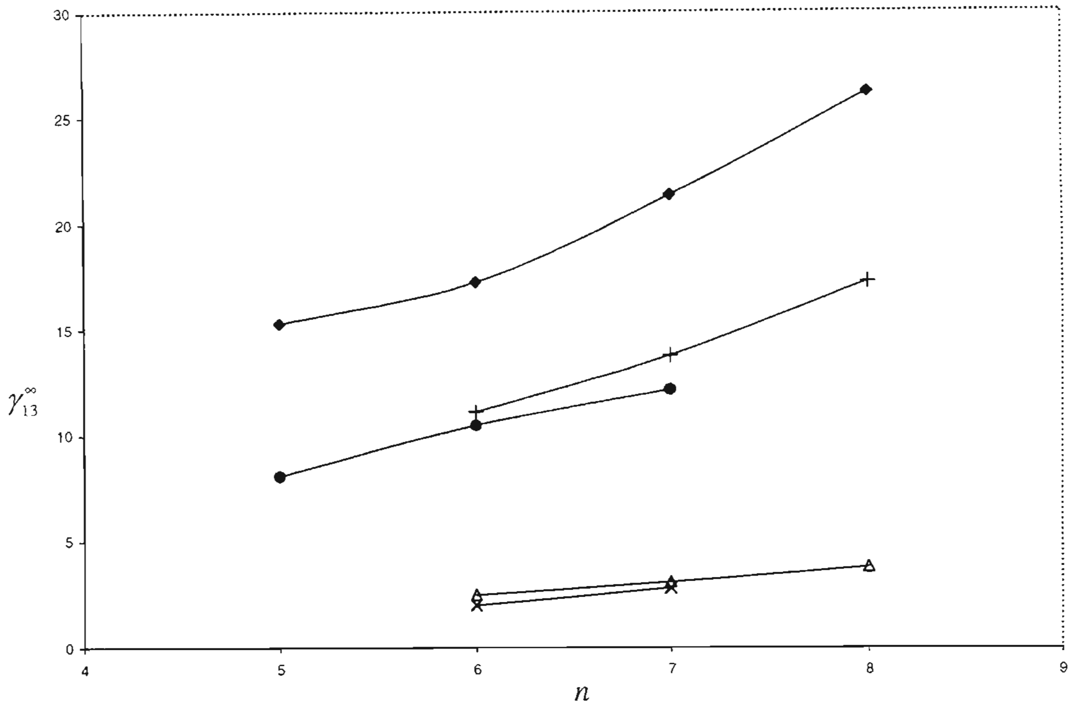


Figure 7-1: γ_{13}^{∞} for ((MOIM)Cl + hydrocarbon solutes) at T = 298.15 K against the number of carbon atoms in the solute n; ♦,alkanes; +,alkenes; •,cycloalkanes; Δ,alkynes; x,aromatics.

Overall, the activity coefficient values of the hydrocarbons solutes are much lower than for smaller polar solvents such as monoethanolamine (Harris, 2001). For alkanes, pentane through nonane, values range from 383 to 1608 (Harris, 2001). The much smaller values for the alkanes in (MOIM)Cl are probably due to the octyl side chain on the imidazolium ring. This produces a greater interaction with linear alkanes than a small polar solvent.

Measurements were made at three convenient temperatures in order to be able to calculate molar enthalpies of mixing at infinite dilution. Three, rather than two temperatures were chosen in order to improve the reliability of the enthalpy values. The partial molar excess enthalpies at infinite dilution are reported in Table 5-4. The values for all solutes are positive, indicating that dissociation effects outweigh association effects in mixtures involving very low hydrocarbon concentrations.

A benefit of using a range of solutes is that the solvent selectivity of the desired solute over other solutes can be determined. Choosing 1-hexene as the desired solute, the solvent selectivities have been calculated at 298.15 K and are listed in Table 5-3. Possible effective separations are indicated by β_{ab}^{∞} >> 1 and $0 < \beta_{ab}^{\infty} << 1$. These values are at infinite solute diliution and represent the upper limit of separation. They are therefore used as an indication of selectivity since finite concentrations are dealt with in practice. (MOIM)Cl will select 1-hexene over heptane and octane reasonably. (MOIM)Cl does not show considerable selectivity of 1-Hexene over Pentane, Hexane, 1-Heptene, 1-Octene and the cycloalkanes. The alkynes and aromatics have selectivities <<1 indicating that (MOIM)Cl has significant affinity for them as compared to 1-Hexene, thus indicating a possible separation. The selectivity values show very little variation with temperature. This indicates that it may not be possible to use to temperature to manipulate separation of a multicomponent mixture.

Table 7-1: A comparison of the selectivity β_{ab}^{∞} of solvents for various mixtures which include 1-Hexene at 298 K

Solute (a)	Benzene	*n*-Hexane	1-Octene	Cyclohexane	Ref.
Solute (b)	1-Hexene	1-Hexene	1-Hexene	1-Hexene	
Solvent					
Acetonitrile	0.22	2.1	-	1.7	1
Sulfolane	0.08	2.8	-	1.3	1
N-methyl-2-pyrrolidinone	0.15	1.9	-	1.6	1
1-Ethylpyrrolidin-2-one	0.18	1.8	1.3	1.1	2
1,5 Dimethylpyrrolidin-2-one	0.19	1.9	1.3	1.1	2
1,4 Dicyanobutane	0.11	2.3	1.9	1.2	3
(MOIM)Cl	0.18	1.5	1.5	0.95	
(HMIM)PF_6	0.10	2.2	2.1	1.2	4
(HMIM)BF_4	0.09	2.0	2.0	1.2	5
(EMIM)$((CF_3SO_2)_2N)^{a,c}$	0.09	2.3	-	1.3	6
(EMIM)$(C_2H_5OSO_3)^{b,c}$	0.06	2.2	-	1.2	6

[a] 1-ethyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide
[b] 1-ethyl-3-methylimidazolium Ethylsulfate
[c] values at 303.15 K
1) Tiegs et al., 1986
2) Krummen et al., 2002
3) Letcher and Naicker, 2000
4) Letcher et al. 2003c
5) Letcher et al. 2003d
6) Krummen et al. 2002

Table 7-1 shows the selectivities at infinite dilution of a number of solvents for mixtures which include 1-hexene at 298 K. While the list is not comprehensive and is somewhat subjective, it is nevertheless useful. Above (MOIM)Cl are listed some molecular solvents, and below are other ionic liquids. For the benzene + 1-hexene system, (EMIM)$(C_2H_5OSO_3)$ shows the best separation. (MOIM)Cl has selectivity comparable with the pyrrolidinones. For the *n*-hexane + 1-hexene system, most selectivities are in the order of 2 with (MOIM)Cl showing the least selectivity. For the 1-Octene system, (MOIM)Cl has a greater selectivity than the pyrrolidinones, but not as large as 1,4 Dicyanobutane and the ionic liquids (HMIM)PF_6 and (HMIM)BF_4. For the cyclohexane + 1-hexene system, the only solvents showing any potential are acetonitrile and N-methyl-2-pyrrolidinone. Overall (MOIM)Cl can be regarded as a reasonable solvent to separate mixtures involving 1-hexene. Other ionic liquids listed, show similar and greater selectivities and these could prove to be effective solvents in the near future.

Further work on (MOIM)Cl has been done by Letcher et al. (2003a, 2003b) as a solvent in LLE. They showed (MOIM)Cl to be effective for separating alkanes from benzene and linear alcohols.

7.3 Results from LLE

These results have been presented at the *2003 South African Chemical Engineering Congress*, Sun City, South Africa (David et al., 2003b).

As mentioned in Chapter 2.2.2, ionic liquids have been found to be promising solvents in liquid-liquid separations due to their interesting miscibility/immiscibility properties. The ionic liquid used in LLE measurements in this work is $BuMePyBF_4$ (Figure 1-1b). The primary information obtained from these experiments are cloud points compositions (which form the binodial curve) and tie lines. From this information, selectivities and distribution curves have been generated.

The simplest liquid-liquid extraction system comprises of only three components, viz. solute, solvent and carrier. Usually the solute and carrier are significantly or completely miscible over the binary composition range. A effect solvent is completely immiscible with the carrier and completely miscible with the solvent. This usually gives good selectivities, which results in only the need for solute and solvent to be separated, and high distribution ratios which reduce the number of equilibrium stages. However, most of the time there is limited miscibility between the solvent and carrier. This would require separation of the carrier from the solvent-rich phase and of the solvent from the carrier-rich phase.

The systems investigated will be discussed by:

1. The area of the two phase region. This indicates the range of compositions which can be separated.
2. Selectivity and distribution ratios. This indicates the extent of separation.

The systems were measured at 298.2 K. The mixtures are labelled in order {solvent + carrier + solute}.

LLE System 1 {BuMePyBF$_4$ + 1-Hexene + Toluene} (Figure 5-1) has a large two phase region, the largest of systems investigated. It is a type II system. The BuMePyBF$_4$ is immiscible in 1-hexene and toluene and mixtures thereof. 1-Hexene is miscible to only 0.059 mole fraction in BuMePyBF$_4$, a desirable characteristic of the system. Toluene is miscible to 0.41 mole fraction in BuMePyBF$_4$ and this lack of complete miscibility has an effect on the selectivity and distribution ratios. Figure 5-2 shows that the toluene distributes more to the organic phase throughout the concentration range. The selectivity exhibits a maximum of 3.6 at approximately 0.4 mole fraction toluene in the organic phase. In this case, separation is possible using a large number of equilibrium stages and possibly refluxing the extract.

LLE System 2 {BuMePyBF$_4$ + 1-Hexene + Ethanol} (Figure 5-4) is a type I system and has a large two phase area. This allows the feed to have a composition ranging from 0 to 0.8 mole fraction ethanol. BuMePyBF$_4$ is effectively completely immiscible in feed mixtures up to 0.7 mole fraction ethanol. The ethanol, being polar, is completely miscible in BuMePyBF$_4$. The tie lines indicate that this is a solutropic system. These systems contain tie lines (solutropes) which are parallel to the base line. The LLE data bank compiled by Sørensen et al. (1979), indicate that these comprise < 1 % of 405 systems documented. Another example of this system is water + 1-propanol + heptane. This can also be seen from the intersection of the distribution curve with the 45° line in Figure 5-5. At low to medium concentrations of ethanol in the organic phase, there is a greater affinity for the BuMePyBF$_4$-rich phase. At higher concentrations, the ethanol distributes more to the organic phase. However, the curve does not deviate significantly below the 45° line and therefore does not require a large number of stages to effect a separation. Figure 5-6 shows that selectivity exponentially decreases with increasing mole fraction of ethanol in the organic phase. At low to medium ethanol concentrations, separation is most effective. At high concentrations of ethanol a reasonable amount of 1-hexene will be present in the BuMePyBF$_4$ phase, requiring further unit operations to affect good separation.

LLE System 3 {BuMePyBF$_4$ + 1-Hexene + 2-Butanone} (Figure 5-7) is a type I system. A comparison can be made with LLE System 2 as only the solutes differ, viz. 2-butanone and ethanol. The two phase region is large but slightly smaller than LLE System 2. Feed compositions ranging from 0 to 0.8 mole fraction 2-butanone can be used, which is the same for ethanol. $BuMePyBF_4$ is effectively completely immiscible in feed mixtures up to 0.6 mole fraction 2-butanone, which is less than for ethanol. 2-Butanone, as with ethanol, is completely miscible in $BuMePyBF_4$. This is also a solutropic system as shown by the slopes of the tie lines. While many seem parallel to the base line, Figure 5-8 indicates a single solutrope. As this is a type I system, it contains a plait point indicated by the termination of the distribution curve with the 45° line (Figure 5-8). This is the pinch point, at which each phase has the same composition – analogous to an azeotrope in VLE. 2-Butanone distributes quite evenly between the two phases through the whole composition range. The selectivity, shown in Figure 5-9, is approximately 10 from 0 to 0.4 mole fraction 2-butanone in the organic phase, and decreases with increasing concentration. As ethanol is more polar than 2-butanone, the solvent selectivity of ethanol over 1-hexene is much greater than for 2-butanone over 1-hexene.

LLE System 4 {$BuMePyBF_4$ + 1-Octene + Ethanol} (Figure 5-10) is a type I system. A comparison can be made with LLE System 2 as only the carriers differ, viz. 1-octene and 1-hexene. The two phase region is the largest of the type I systems. Feed compositions ranging from 0 to 0.85 mole fraction ethanol can be used, slightly more than for 1-hexene. $BuMePyBF_4$ is effectively completely immiscible in feed mixtures up to 0.7 mole fraction ethanol, which is the same as for 1-hexene. 1-Octene is miscible in $BuMePyBF_4$ up to 0.046 mole fraction, which is less than for 1-hexene. This is due to 1-octene being longer in length and more non-polar resulting in less miscibility in the polar $BuMePyBF_4$. This trend would probably be seen for longer alpha-olefins. This system is also a solutropic system as seen by the tie-lines (Figure 5-10) and the distribution curve (Figure 5-11). As with 1-hexene, ethanol in this system exhibits greater affinity for the $BuMePyBF_4$-rich phase at low to medium concentrations. The distribution ratios are, however, higher for this system than for 1-hexene. This is again due to the more non-polar nature of 1-octene than 1-hexene. At higher concentrations of ethanol, the distribution is slightly more to the organic phase. As for 1-hexene, the selectivity exponentially decreases with increasing mole fraction ethanol in the organic phase. The selectivities are much higher at the same mole fraction of ethanol in the organic phase due to 1-octene being more non-polar.

The LLE binodial curves were correlated to the Hlavaty equation, beta function and log gamma function. Parameters were obtained using the Solver tool in MS-Excel. The coefficients are listed in Table 7-2, along with the standard deviations calculated by Eq. (3-64). Standard deviations in the order of 0.15 and less, indicate a good correlation. System 1 is a type II system. The correlations are not intended to represent this type of system, but it was correlated nevertheless to prove this, which can be seen from the range of the standard deviations (0.68 to 0.52). Systems 2 and 4 give similar standard deviations ranging from 0.34 to 0.18. The Hlavaty equation gives higher standard deviations than the other two correlations. The reason for this is that the Hlavaty equation was developed with the shape of the Gibbs excess energy vs composition plot in mind, which has a gradual maximum. Systems 2 and 4 have rather sharp maxima and are represented better by the other two correlations which contain the coefficients as indices. System 3 is represented the best from the four systems having standard deviations ranging from 0.13 to 0.11. This is due to the binodial curve having a gradual maximum.

The LLE tie-lines were regressed to obtain parameters for the NRTL model. Parameters were obtained using a program incorporating the Rosenbrock regression technique. The regression was designed to obtain the interaction parameters from a selected value of α the non-randomness parameter. This was repeated for α ranging from 0.2 to 0.4 with the α and $(g_{ji}-g_{ii})$ for the smallest standard deviation σ being chosen. These values are presented in Table 7-3. A comparison of α shows that a slightly lower value represents type II systems much better i.e. 0.2 for system 1 compared to 0.35 for systems 2, 3 and 4. The standard deviation σ indicates that the NRTL model represents systems 1 and 3 better than systems 2 and 4. Systems 2 and 4 have a significant change in the slope of the tie lines and the NRTL model gives a slightly worst but acceptable representation of the tie lines.

Table 7-2: Coefficients and standard deviations from the correlation of the ternary LLE binodial curve

Correlation		Ternary LLE			
		System 1	System 2	System 3	System 4
Hlavaty	A_1	2.373	1.244	1.123	1.492
	A_2	1.886	1.494	1.315	1.556
	A_3	9.442	6.757	6.218	7.347
	σ	0.068	0.025	0.011	0.034
β	B_1	11.894	6.211	5.195	7.189
	B_2	1.724	1.555	1.455	1.600
	B_3	1.965	1.491	1.404	1.576
	σ	0.052	0.018	0.011	0.024
$\log \gamma$	C_1	10.520	5.400	4.565	6.257
	C_2	1.672	1.488	1.394	1.533
	C_3	2.629	2.059	1.939	2.166
	σ	0.054	0.019	0.013	0.025

Table 7-3: Parameters and standard deviations for the NRTL model for the ternary LLE tie-lines

NRTL Parameters	Ternary LLE			
	System 1	System 2	System 3	System 4
α	0.2	0.35	0.35	0.35
$g_{12}-g_{11}$	-330	-315	5471	275
$g_{21}-g_{22}$	33922	15646	40267	15472
$g_{13}-g_{11}$	7369	4004	7373	3311
$g_{31}-g_{33}$	44648	8762	23141	14726
$g_{23}-g_{22}$	-4283	6267	535	7909
$g_{32}-g_{33}$	561	2009	2755	1872
σ	0.0036	0.0123	0.0027	0.0205

Chapter 2.3.1 lists criteria by Madhavan (2002) for an effective liquid-liquid extraction solvent in a specific system. These can be applied to $BuMePyBF_4$ in the systems measured.

- *A high distribution ratio.* A high distribution ratio indicates higher affinity for the solvent phase over the organic phase. LLE System 1 shows low distribution. LLE System 3 show almost equal distribution between phases resulting in a distribution ratio of close to 1. LLE Systems 2 and 4 show high distribution ratios at low concentrations of solute.

- *Good selectivity towards solute.* LLE Systems 1 and 3 show low to moderate selectivity of the solvent towards the solute. LLE Systems 2 and 4 show high to moderate selectivity, but decrease exponentially with increasing solute concentration in the organic phase.
- *Little or no miscibility with feed solution.* For all systems investigated, the solvent shows no miscibility with feed solutions of low to medium solute concentration. At high solute concentrations of feed, LLE Systems 2, 3 and 4 show minimal miscibility of solvent in the feed.
- *Easy recovery for recycle.* The ionic liquid, having no measurable vapour pressure, is easily recovered using distillation.

BuMePyBF$_4$ can be analyzed more generally by further criteria given by Madhavan (2002).

- *Boiling point.* As ionic liquids have no measurable vapour pressure, there is no risk of loss through evaporation.
- *Density.* The density of BuMePyBF$_4$ is 1.18 g/cm^3. The density of most liquid hydrocarbons range from 0.6 to 0.8 g/cm^3. This significant difference in density aids separation of the two phases after mixing.
- *Interfacial tension.* No literature data is available. These values are difficult to predict as the characteristics of the interface is usually quite different to that of the bulk phase.
- *Viscosity.* No literature data is available. From experimental observation, the viscosity appears to be much lower than that of chloride containing ionic liquids.
- *Corrosiveness.* In general, not much, if any, investigations have been undertaken involving the effects of ionic liquids on metals. They are, however, expected to be much less corrosive than salt solutions or high temperature molten salts.
- *Flammability.* No literature data is available. It is likely that they may be flammable, but only upon decomposition.
- *Toxicity.* No literature data is available. In general, this information has come to be a necessity as lack of this information may limit use of ionic liquids.

- *Stability.* $BuMePyBF_4$ appears to be stable at room temperature. Significant water absorption may cause halide containing ionic liquids to hydrolyze at elevated temperatures. This should not effect liquid-liquid extraction.
- *Compatibility with product.* $BuMePyBF_4$ does not alter organics and can be separated from them readily.
- *Availability.* Currently $BuMePyBF_4$ is available in laboratory scale and small pilot plant quantities.
- *Cost.* The cost of $BuMePyBF_4$ is in the order of R 2500 for a 50 g quantity. This currently makes it viable for only laboratory scale use.

7.4 Results from VLE

7.4.1 Binary systems

Two isobaric binary systems were measured viz. acetone + methanol at 99.4 kPa and 1-hexene + 2-butanone at 74.8 kPa. Measurements were undertaken somewhat below atmospheric pressure due to daily fluctuations in the atmospheric pressure and to allow the pressure controller to work effectively. The acetone + methanol system (Figure 5-13) exhibits a minimum boiling azeotrope at 0.78 mole fraction acetone. This system was measured as a test system. Due to the non-ideality of the liquid phase, the measurement of this system is sufficient to evaluate the suitability of the experimental procedure and apparatus. Measurements are compared to data by Verhoeye and Schepper (1973) at 101.3 kPa. Figure 5-13 shows good agreement between the two sets of data, considering that the literature values are at a pressure 1.9 kPa higher. Figure 5-14 shows a very narrow distance between the equilibrium line and the 45° line for acetone mole fractions 0.6 to 0.78, indicating that a large number of stages would be required for separation. Clearly a solvent is required to shift or break the azeotrope if distillation is to be used to produce high purity acetone.

Figure 5-15 shows a T-x-y plot of the 1-hexene + 2-butanone system. This system also exhibits a minimum boiling azeotrope at 0.83 mole fraction 1-hexene. No isobaric data is available on this system. Separation of a mixture from 0.7 to

0.83 mole fraction 1-hexene would require a large number of stages due to the low relative volatility as shown in Figure 5-16. To produce a distillate of purity greater than 0.83 mole fraction 1-hexene would require a solvent to shift or break the azeotrope.

Table 7-4: Model parameters from the regression of the binary VLE

	Acetone (1) + Methanol (2)	**1-Hexene (1) + 2-Butanone (2)**
Activity coefficient model	99.4 kPa	74.8 kPa
Wilson		
λ_{12}-λ_{11} (J/mol)	-948	-1121
λ_{12}-λ_{22} (J/mol)	2569	4018
δT % (average)	0.28	0.36
δy (average)	0.006	0.009
NRTL		
g_{12}-g_{11} (J/mol)	951	2727
g_{12}-g_{22} (J/mol)	622	69
α	0.3	0.3
δT % (average)	0.27	0.35
δy (average)	0.006	0.01

The model parameters, shown in Table 7-4, were obtained using a Matlab program written by M. Soni which incorporated the Maquard non-linear regression technique. The regression was performed by minimizing an objective function of pressure only as suggested by Van Ness (1964). The experimental values for the acetone + methanol system are compared to the Wilson model in Figures 7-2 and 7-3, and to the NRTL model in Figures 7-4 and 7-5. Both models correlate the experimental data in much the same manner as noted by the •T %. The experimental pure component temperatures are higher than the correlated temperatures. Both models correlate the azeotropic composition accurately. The experimental values for the 1-hexene + 2-butanone are compared to the Wilson model in Figures 7-6 and 7-7, and to the NRTL model in Figures 7-8 and 7-9. Except for two pairs of data points, both models correlate the experimental values with good accuracy.

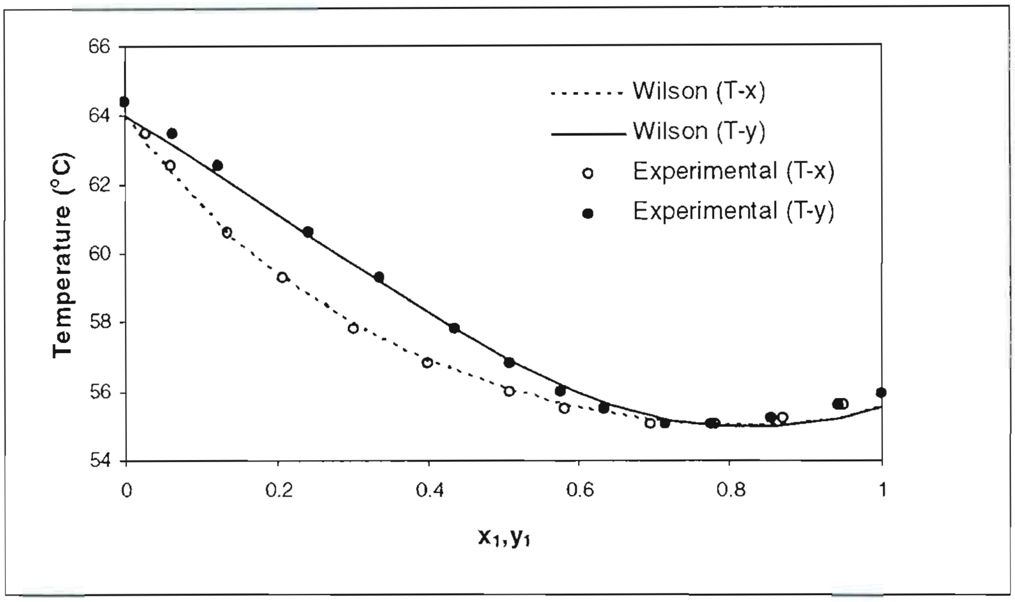


Figure 7-2: A T-x-y comparison between the Wilson model and experimental data for the Acetone (1) + Methanol system at 99.4 kPa

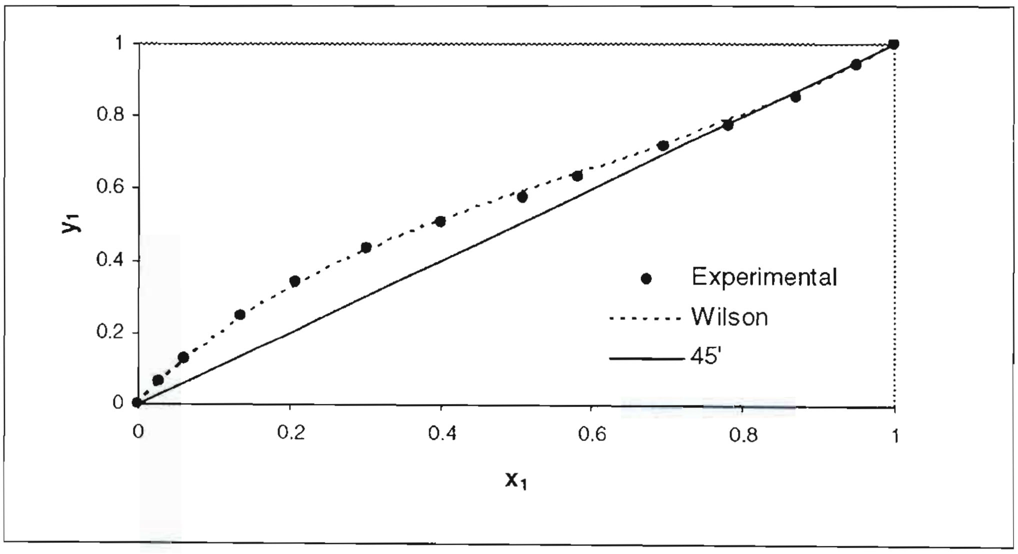


Figure 7-3: An x-y comparison between the Wilson model and experimental data for the Acetone (1) + Methanol system at 99.4 kPa

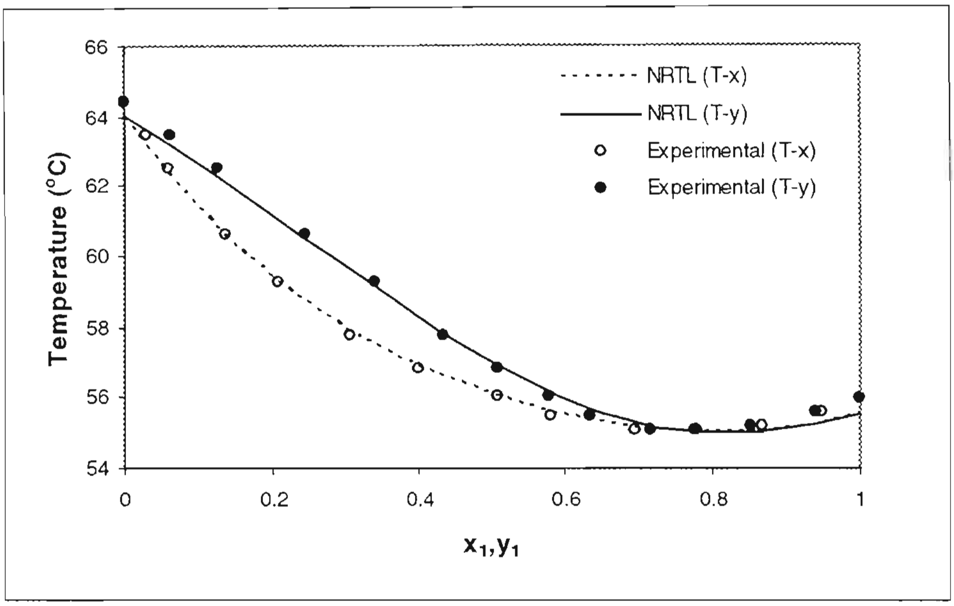


Figure 7-4: A T-x-y comparison between the NRTL model and experimental data for the Acetone (1) + Methanol system at 99.4 kPa

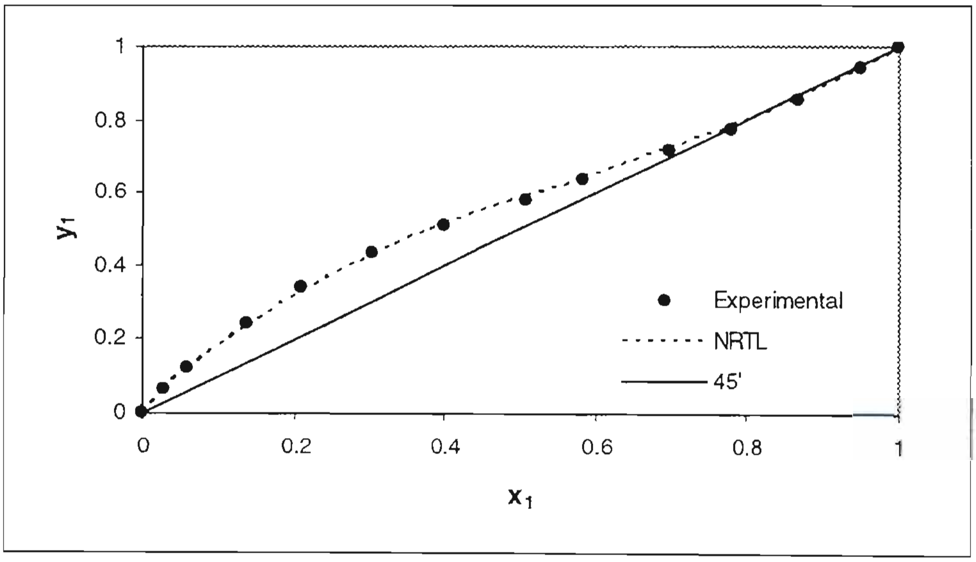


Figure 7-5: An x-y comparison between the NRTL model and experimental data for the Acetone (1) + Methanol system at 99.4 kPa

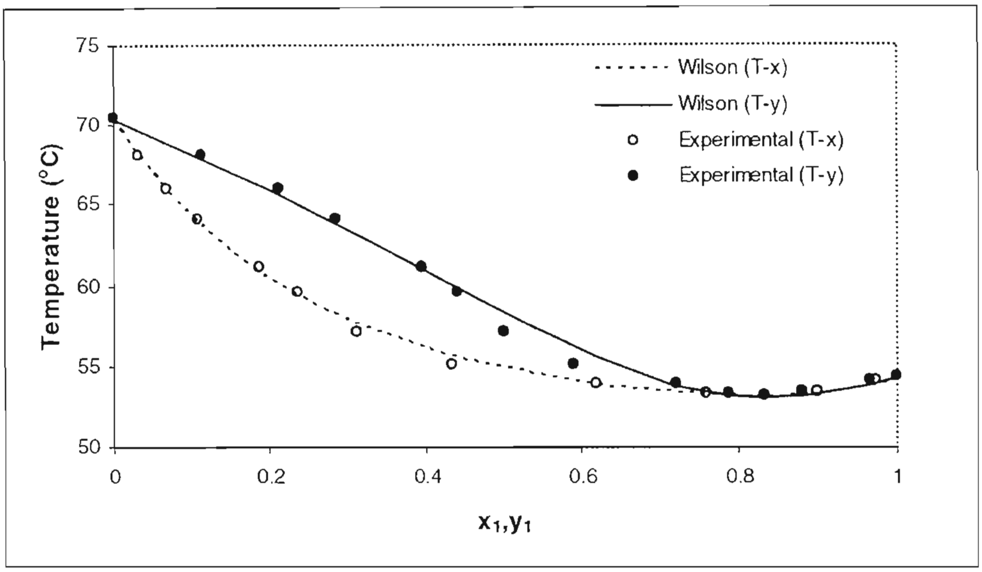


Figure 7-6: A T-x-y comparison between the Wilson model and experimental data for the 1-Hexene (1) + 2-Butanone (2) at 74.8 kPa

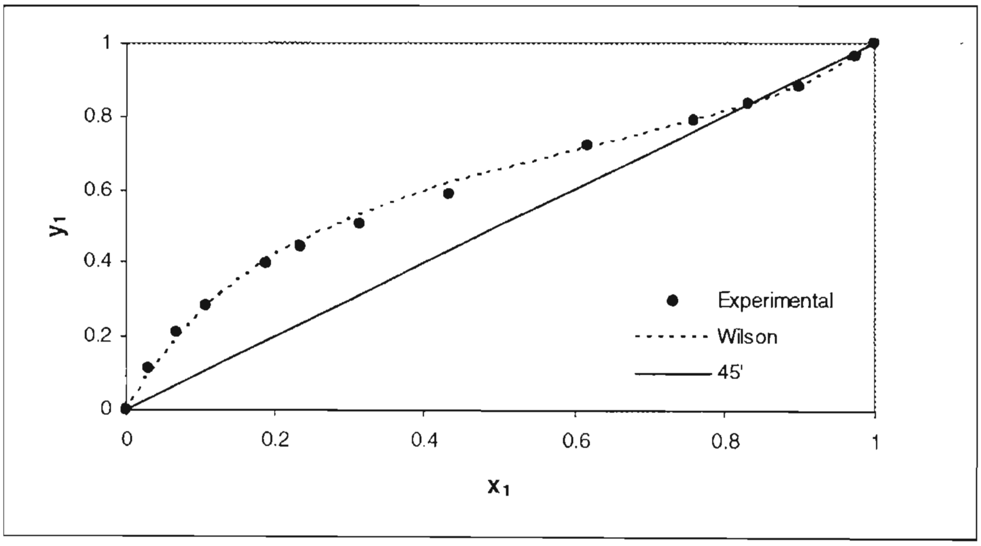


Figure 7-7: An x-y comparison between the Wilson model and experimental data for the 1-Hexene (1) + 2-Butanone (2) at 74.8 kPa

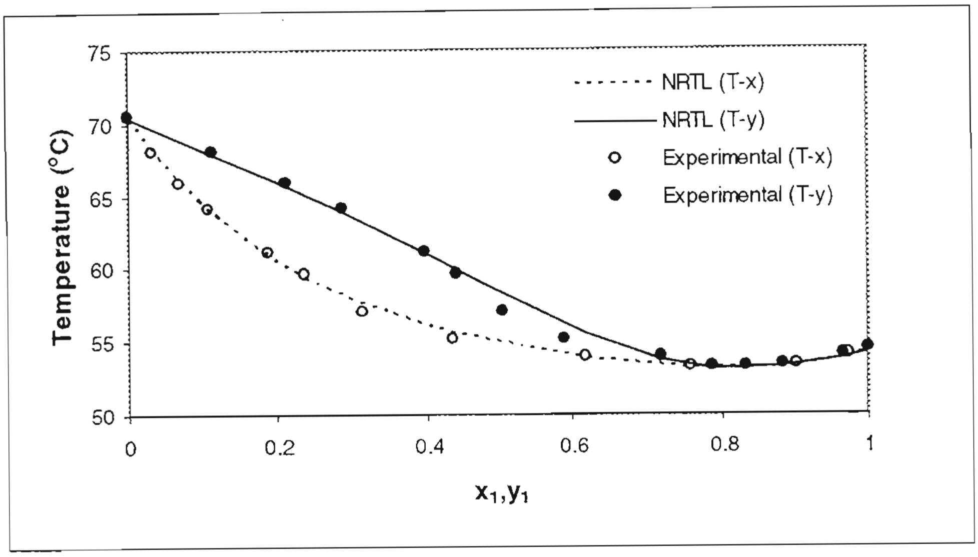


Figure 7-8: A T-x-y comparison between the NRTL model and experimental data for the 1-Hexene (1) + 2-Butanone (2) at 74.8 kPa

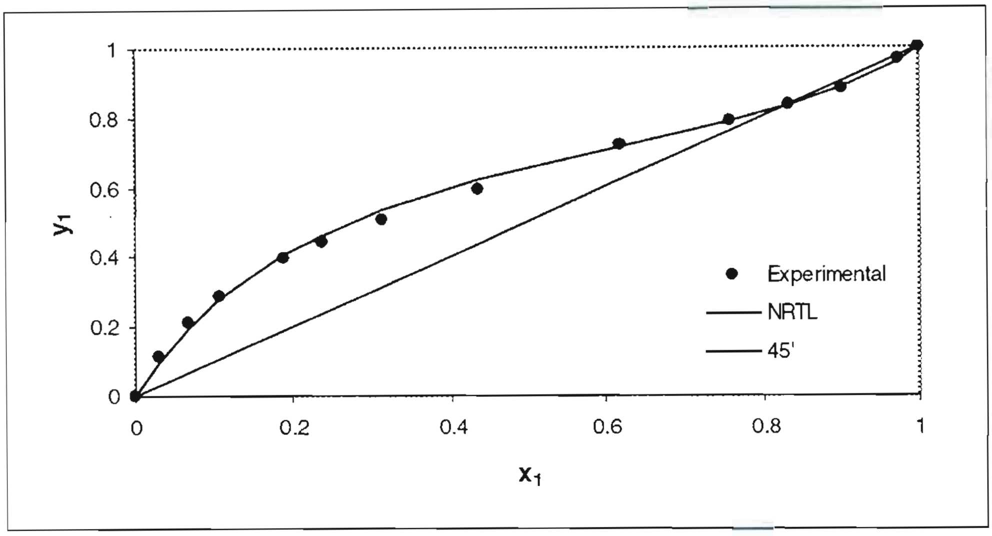


Figure 7-9: An x-y comparison between the NRTL model and experimental data for the 1-Hexene (1) + 2-Butanone (2) at 74.8 kPa

It is necessary to test experimental VLE data for thermodynamic consistency. Here, the point test by Van Ness et al. (1973) has been employed. This test is intended primarily for isothermal data, but may be applied to isobaric data. The regression makes use of only the T-x data, and this consistency test uses the y values, thus using making use of the full T-x-y data. For each measured value of x, the difference between the experimental and calculated y values (δy), is plotted. The consistency requirement given by Van Ness (1973), is that he δy values must scatter randomly about zero. An addition requirement given by Danner and Gess (1990) is that the average δy must be less than 0.01. The δy for acetone + methanol is shown in Figures 7-10 and 7-11. The plots show positive bias for $x_1 < 0.4$ and negative bias for $x_1 > 0.4$. The average δy is 0.006 for both models. Danner and Gess (1990) do mention that for systems that have a very small average δy, even with the presence of bias the system can be regarded as consistent. However, no values are given to apply this condition to this data. The δy for 1-hexene + 2-butanone is shown in Figures 7-12 and 7-13. For models there is systematic error for $x_1 < 0.6$ but the data is quite consistent for $x_1 > 0.6$. The average δy is 0.009 and 0.01 for the Wilson and NRTL models respectively, which is quite satisfactory.

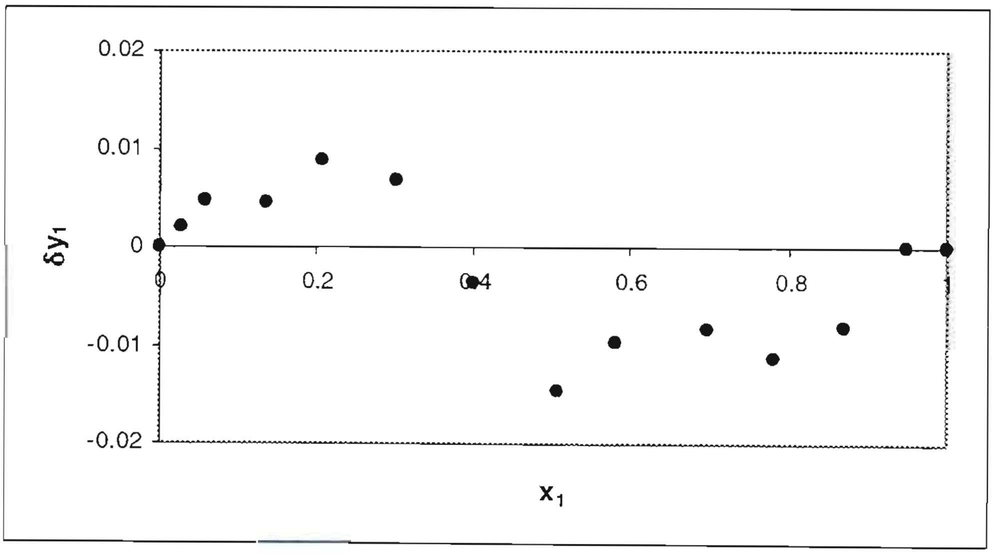


Figure 7-10: Plot used for point test of acetone (1) + methanol (2) for the Wilson model

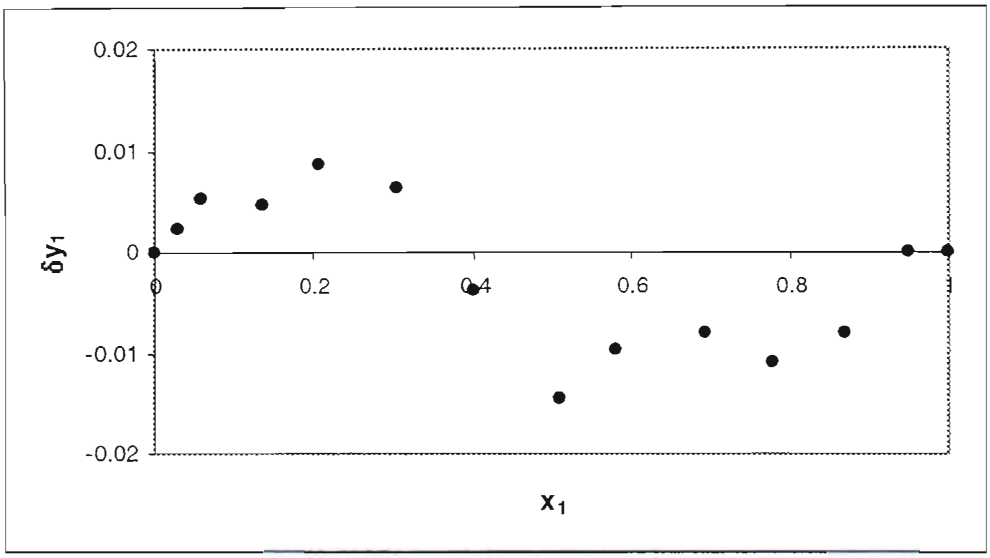


Figure 7-11: Plot used for point test of acetone (1) + methanol (2) for the NRTL model

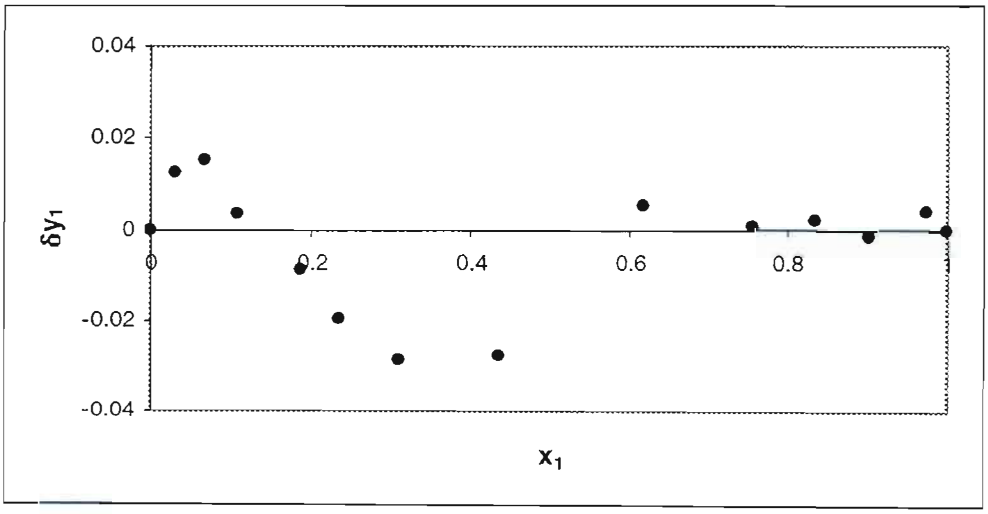


Figure 7-12: Plot used for point test of 1-hexene (1) + 2-butanone (2) for the Wilson model

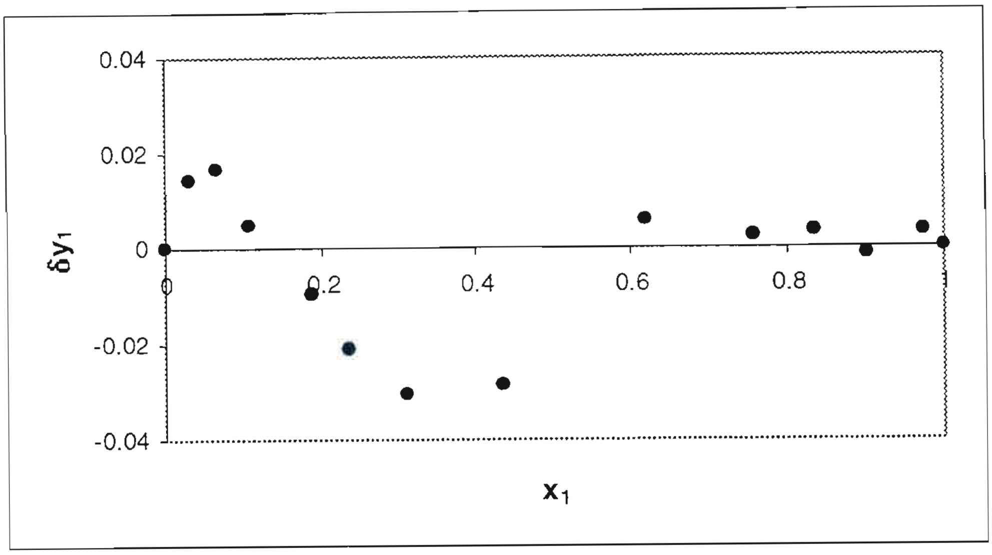


Figure 7-13: Plot used for the point test of 1-hexene (1) + 2-butanone (2) for the NRTL model

7.4.2 Ternary systems

One of the methods of evaluating the effects of a solvent on a binary system in VLE, is to measure the VLE of the solvent with each of the components of binary system. Examples of these are the effect of trichloropropane on the n-Hexane – 1-Hexene system (Suryanarayana and van Winkle, 1966) and of NMP on a variety of C_5 and C_6 hydrocarbon mixtures (Fisher and Gmehling, 1996). This is beneficial in that the data for the binary VLE is reduced using excess Gibbs energy models. This allows for the prediction of the ternary compositions from which distillation curves can be constructed.

Ionic liquids, on the other hand, have no measurable vapour pressure. Measurement of the ionic liquid in a binary mixture would produce limited usefulness. In addition, the higher viscosity would result in circulation problems in the ionic liquid-rich region. As it is essentially a salt, the ionic liquids were evaluated in a similar manner to that of Linberg and Tassios (1971), and Iliuta and Thyrion (1995). Iliuta and Thyrion (1995), studied the effects of potassium iodide and sodium iodide on the VLE of the acetone-methanol system. As the azeotrope is in the acetone-rich region, the solubility limits of the salts in the acetone are important. Sodium iodide is soluble to 27.5 g/100 g acetone, while potassium iodide is soluble only to 0.91 g/100 g acetone. The sodium iodide has a significant positive effect on the relative volatility, while the limited solubility of potassium iodide results in little increase in the relative volatility. Linberg and Tassios (1971) studied the effects of potassium acetate and lithium bromide on the n-Hexane – 1-Hexene system. Owing to the limited solubility of these salts in hydrocarbons, it was necessary to use each of them in a mixture with ethanol. As was expected, the salt associated more with the ethanol molecules than with the hydrocarbon molecules. The resulting relative volatility plot showed a decrease to almost 1.0 with increasing salt concentration. Thus, finding salts that show reasonable solubility in hydrocarbons and have a positive effect on the relative volatility, is difficult.

It is expected that ionic liquids may prove effective as solvents in extractive distillation for highly polar systems as there is unlikely to be any partial miscibility. What is challenging is to find ionic liquids that may be useful in slightly polar systems such as hydrocarbons. The ionic liquid trihexyl-tetradecyl-phosphonium chloride (Figure 1-1c) is a relatively new ionic liquid. It is of the phosphonium class, and has not been the subject of any experimental investigations. What makes this ionic liquid interesting, is its miscibility properties. In n-hexane, it shows a miscibility of 0.5 mol %. In 1-hexene, it shows no miscibility limit even up to 20 mol %. This can be explained from the structure of the ionic liquid. The cation consists of four long alky chains which terminate in a phosphonium ion in the centre, while the anion is a chloride. These alkyl chains mask the charge on the cation to an extent. This allows for limited miscibility in the non-polar n-hexane, which would normally be totally immiscible with other ionic liquids. But being a charged species, the miscibility is highly limited. When compared to a slightly polar compound like 1-hexene, the similarities are significant. 1-Hexene is an alpha-olefin having a terminal double bond and a long alkyl chain. It is quite possible that multiple 1-hexene molecules are able to associate with a single cation by aligning the electron-dense terminal double bonds to the positive phosphonium ion and the rest of the molecule with one of the four alkyl chains. These strong similarities result in high solubilities.

$(C_6)_3C_{14}PhCl$ was added to both the binary systems, thus forming ternary systems. The systems were measured on a solvent-free basis. The data, listed in

Tables 5-15 and 5-16, was analyzed using x-y and relative volatility plots. The measurements were done at constant mole fraction solvent in feed, with the equivalent mass % for each point listed along side. VLE System 3 (Acetone(1) + Methanol(2) + $(C_6)_3C_{14}PhCl(3)$) was measured at two concentrations of solvent viz. 0.5 and 0.8 mole %. For 0.5 mole % solvent, the equivalent mass % ranged from 4.5 to 6.5. For 0.8 mole % solvent, the equivalent mass % ranged from 7 to 8. From Figure 5-17, it can be seen that at a solvent concentration of 0.5 mole %, the azeotrope, although not broken, is shifted up to 0.9 mole fraction. The relative volatility plot, Figure 5-18, shows an increased relative volatility over the pure binary at higher concentrations of acetone. An increase in the solvent concentrations shows no improvement in the relative volatility and thus does not shift the azeotrope any further.

VLE System 4 1-Hexene(1) + 2-Butanone(2) + $(C_6)_3C_{14}PhCl$ was measured at two solvent concentrations viz. 0.5 and 1 mole %. For 0.5 mole % solvent, the equivalent mass % was 3.1. For 1 mole % solvent, the equivalent mass % ranged from 5.9 to 6.2. Figure 5-19 shows that at 0.5 mole % solvent there is no visible difference to the VLE when compared to the pure binary. At a solvent concentration of 1 mole %, there appears to be a slight negative effect on the relative volatility. However, due to experimental uncertainties no conclusions can be made from this data.

An interesting comparison can be made between $(C_6)_3C_{14}PhCl$ and inorganic salts on the relative volatility of the acetone + methanol system. The data of Iliuta and Thyrion (1995) is measured at 101.32 kPa. Figure 7-14 shows selected data points of KI and NaI but it is not possible to make exact conclusions as the concentrations are not equal. At a NaI mole fraction of 0.15, the azeotrope is shifted to about 0.98 mole fraction acetone (solvent-free basis). Above this KI concentration, the azeotrope is removed. KI is soluble to not much more than 0.003 mole fraction. This limits the effectiveness on the relative volatility. The $(C_6)_3C_{14}PhCl$ appears to lie somewhere in-between the two salts. A positive effect of a salt on the relative volatility of a particular system is called the 'salted out' effect. This describes the enhanced volatility of one of the components due to the salt forming an association complex with the other component. Linberg and Tassios (1971) comment that the salting out effect increases with increasing charge and decreasing radius of the ion. These trends can be applied to the above salts. NaI has the smallest cation radius, with KI having a larger radius. $(C_6)_3C_{14}PhCl$ has a significantly large radius due to the four alkly chains. All the above salts are univalent. Thus, NaI has the greatest salting out effect. However, a comparison of KI and $(C_6)_3C_{14}PhCl$ shows that $(C_6)_3C_{14}PhCl$ is more effective. This is probably due to the greater solubility of $(C_6)_3C_{14}PhCl$ in the acetone + methanol mixture.

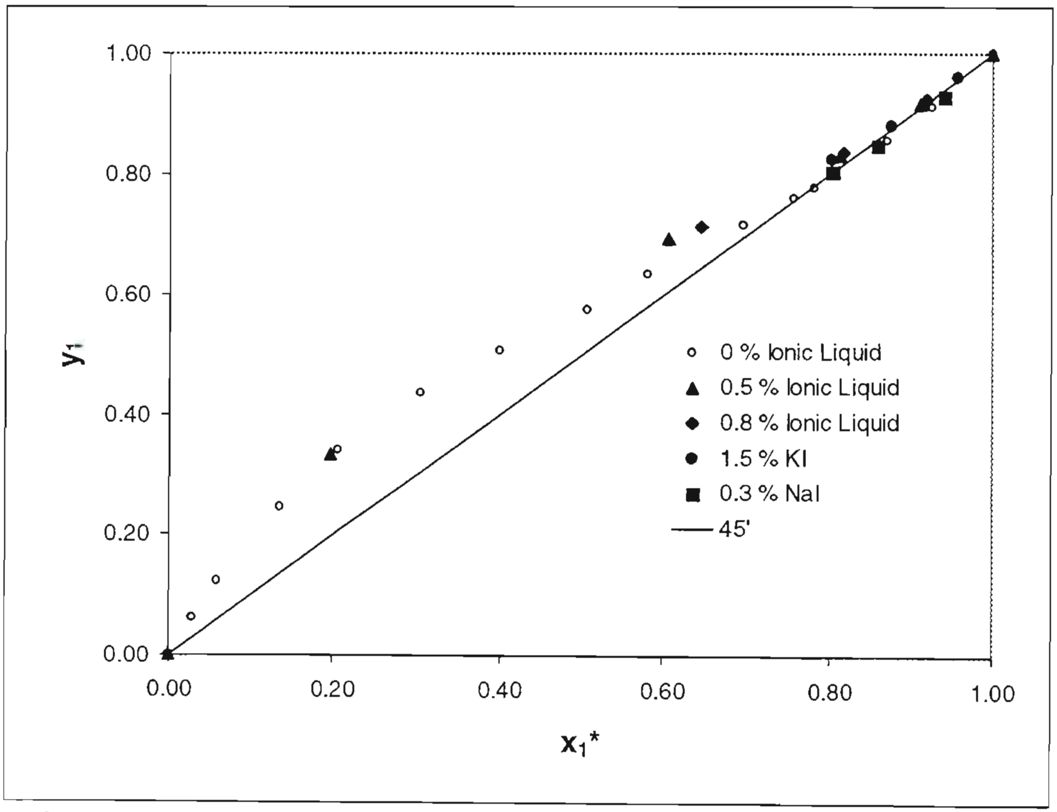


Figure 7-14 Effect of $(C_6)_3C_{14}PhCl$ as compared to other salts on the solvent-free VLE of the acetone (1) + methanol (2) system

$(C_6)_3C_{14}PhCl$ can be evaluated as a solvent for extractive distillation against the criteria suggest by Yee (2002).

- *Solvent should enhance significantly the natural relative volatility of the key component.* For VLE System 3, the relative volatility is enhanced, although not significantly.

- *Solvent should not be required in high solvent/feed ratios.* For the systems investigated, the corresponding solvent/feed ratios are about 0.1. However, in order to get more effective separation, a higher ratio would be required.
- *Solvent should remain stable in the feed components and should not lead to formation of two liquid phases.* Solubility tests indicated an appreciable miscibility of the solvent in the feed components. In distillation, the higher temperatures should result in higher solubilities.
- *Solvent should be easily separable from the bottom product.* This is the benefit of ionic liquids, as they can easily be separated distillation or pervaporation.
- *Solvent should be inexpensive and readily available.* $(C_6)_3C_{14}PhCl$ is currently expensive (R 700/ 50 g) and is only feasible for laboratory scale work. Availability is limited as chemicals are produced on demand.
- *Solvent should be stable at the temperature of distillation and solvent separation.* $(C_6)_3C_{14}PhCl$ is stable up to 120 °C. Above this temperature degradation may occur.
- *Solvent be non-reactive with the components of the feed mixture.* $(C_6)_3C_{14}PhCl$ has a low coordination due to its low charge. It is thus stable in most feed mixtures.
- *Solvent should have a low latent heat.* No measurements have been undertaken to indicate the value of this property.
- *Solvent should be non-corrosive and non-toxic.* $(C_6)_3C_{14}PhCl$ is relatively new and no corrosion or toxicity data is available on it.

7.5 Problems associated with Ionic Liquids

In order to present a balanced view on the potential of ionic liquids, it is necessary to mention various problems or drawbacks that may be associated. Many of the problems mentioned in previous chapters will be summarized here. Possible solutions are given in some cases.

- *The effect of various impurities on ionic liquid solvent strength.* Over an operating period, it is likely that impurities may find their way into the ionic liquid. This may be water from the atmosphere or metal impurities from equipment. Impurities are likely to reduce the solvent strength of the ionic liquid as they will dilute and/or inhibit the ionic liquid from interacting with the intended component. Contamination is possible where an ionic liquid is recycled. Recycling of an ionic liquid in any process is vitally important. Where there is a significant change in properties due to impurities, an additional purification step, such as a filter, may be required.
- *The cost of ionic liquids.* This has been discussed in Chapter 6.3. As with many new processes, no matter how environmentally friendly they may be, if they cannot be shown to be economically viable then it is unlikely that it will be implemented. As mention previously, the cost of ionic liquids in general is quite high, while there is considerable variation in price between specific ionic liquids.
- *Viscosity.* The viscosity of most ionic liquids is generally higher than that of organic solvents. The easiest modification of a process would be to simply replace a solvent. This may not be the as easy if the viscosity of the new solvent is an order of magnitude greater. Viscosity has significant effect on the mass transfer, heat transfer and flow characteristics of a liquid, and is subsequently used to size pumps, pipes, heat exchangers and other pieces of equipment. One solution is heat tracing (Perry and Green, 1997). This involves heating of a pipe with a tracer, usually steam. This increases the temperature of the fluid in the pipe above ambient, thus reducing the viscosity and improving the ease of transportation. The use of ionic liquids in liquid-liquid extraction at ambient conditions may prove to be difficult if the ionic liquid is significantly viscous. A slightly viscous ionic liquid will have its viscosity reduced by the miscibility of the solute in it. For cases where this is still a concern, operating at 10-15 °C above ambient may given acceptable mass transfer rates. An increase in temperature is usually accompanied by a decrease in the two-phase region of the equilibrium curve, however this may allow the ionic liquid to be used in existing equipment. Extractive distillation is operated at temperatures significantly above

ambient. Considering that the ionic liquid is not intended to form its own phase, viscosity should not be a concern.

- *No corrosion information.* Currently there is no information on how metals and other materials behave in ionic liquids. This information is necessary to know possible limitations on the types of materials and the lifespan of the equipment they are used to build. Ionic liquids are quite different from high temperature molten salts. The equipment used to contain high temperature molten salts are able to contain high temperatures and a highly corrosive environment. Ionic liquids, on the other hand, are liquid at much lower temperatures and consist of weakly coordinating ions which make them less reactive. It should be sufficient to use stainless-steel for most applications.
- *No toxicity information.* Attention has only recently been given to toxicity data of ionic liquids (ICCT, 2002). As ionic liquids are non-volatile, there is no problem of air pollution. There is however a possibility of ionic liquids being part of effluent streams. Attention has to be given to removal of ionic liquids from effluent streams. It is impractical to evaporate the water and other volatiles in order to recover the ionic liquids. One technique investigated is the use of activated carbon to adsorb ionic liquids, and this has proven useful.
- *No satisfactory predictive method for ionic liquid property determination.* As discussed in Chapter 2.1, there is need for a reasonably accurate predictive method for ionic liquid properties. When determining what may work and what won't is currently a case of part art and part science. A screening procedure is clearly needed in order to allow more effective experimentation to be carried out.

7.6 Process Design

Using the information available from experimental results, it is possible to qualitatively suggest a process scheme. The 1-hexene + 2-butanone system was chosen as these components were measured in both VLE and LLE systems. In VLE this system was first measured as a binary which indicated an azeotrope at 0.83 mole fraction 1-hexene. The ionic liquid $(C_6)_3C_{14}PhCl$ was then used as a solvent. However this affected the relative volatility negatively and thus cannot be used as a solvent in extractive distillation for this system. In LLE this system was measured as a ternary system with $BuMePyBF_4$.

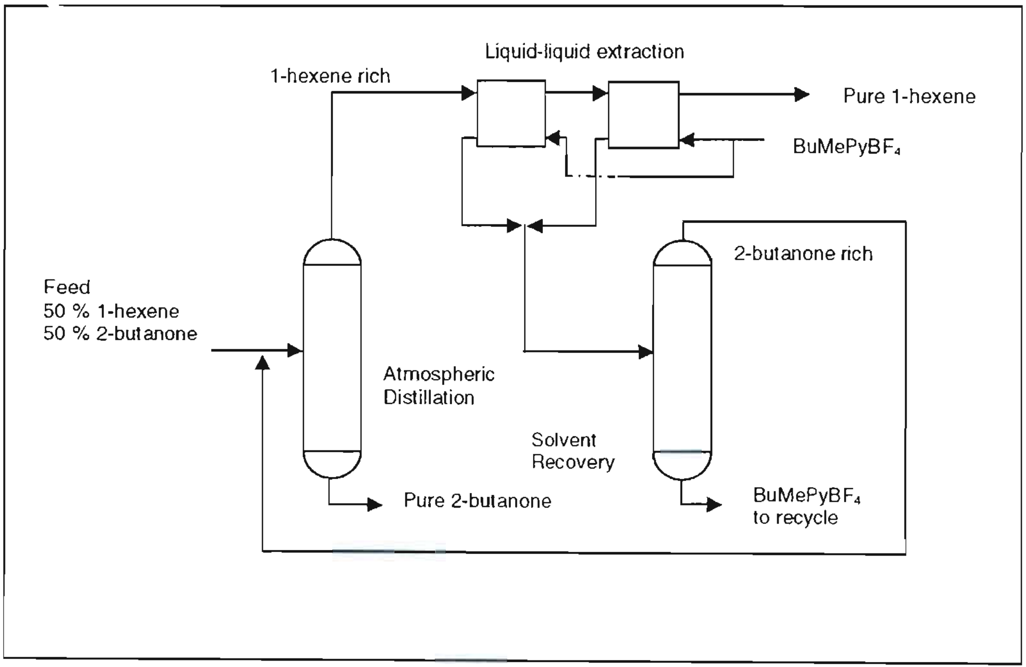


Figure 7-15: Process flow diagram for separating a mixture of 1-hexene + 2-butanone

The process design considered is shown above in Figure 7-15. Consider a feed which has equal quantities of 1-hexene and 2-butanone. The binary VLE (Figure 5-16) indicate that pure 2-butanone can be produced as a bottoms product. Although the distillate can be produced at an azeotrope composition of 0.83

mole fraction 1-hexene, producing a distillate slightly less rich in 1-hexene would reduce the number of separation stages significantly. Therefore a distillate of 0.7 to 0.75 mole fraction 1-hexene can be produced without much difficulty. The ternary LLE indicates that $BuMePyBF_4$ is most effective as a solvent at low to moderate concentrations of 2-butanone. Thus, the distillate composition is ideally suited as a feed to the liquid-liquid extraction process. It may be necessary to use a combination of counter-current and cross-current arrangements in order to extract all of the 2-butanone with reasonable mass transfer rates. This can be achieved by removing the extract after half the number of equilibrium stages, and then introducing pure solvent into the next stage. The ternary phase diagram shows that the raffinate does not contain any solvent for the range of concentrations considered. Therefore, the final raffinate does not require any additional solvent removal. The phase diagram also indicates that the extract would contain about 0.1 mole fraction 1-hexene. The two extract streams are directed to a distillation column were the solvent is recovered. As the $BuMePyBF_4$ has no measurable vapour pressure, it is easily recovered from the other components and recycled. The distillate, which is rich in 2-butanone, is recycled to the first distillation column.

Chapter Eight

Conclusions

Conclusions drawn are from three sources of information namely:

- Review of literature on ionic liquids
- Experiments involving ionic liquids
- Workshop on Ionic Liquids (ICCT, 2002)

Experimental work was done to evaluate specific ionic liquids as solvents in separation processes. Conclusions that are specifically related to the experimental work:

- (MOIM)Cl was used as a solvent in GLC and found to be a reasonable solvent for the separation of 1-hexene from mixtures which include alkanes, aromatics and alkynes. (MOIM)Cl is not as highly selective as some organic solvents, but has the advantage of being easily separable from the solute using distillation.
- $BuMePyBF_4$ was found to be an effective liquid-liquid extraction solvent for the separation of alkenes from alcohols, aromatics and ketones. This is indicated by the large two-phase regions and reasonable selectivities. Distillation or pervaporation can be used to easily separate solute and solvent.
- $(C_6)_3C_{14}PhCl$ had a limited positive effect on the relative volatility of the acetone + methanol system, and little effect on the 1-hexene + 2-butanone system. $(C_6)_3C_{14}PhCl$ cannot be recommended as a solvent for extractive distillation involving these systems, as its effectiveness is low.

A literature review was undertaken covering a wide scope of ionic liquid research. Information exchanged at the *Workshop on Ionic Liquids* (ICCT, 2002) was also useful. Conclusions that can be made concerning ionic liquid research in general:

- Ionic liquids are currently at the forefront of scientific research and involve many leading researchers in the areas of chemistry and chemical engineering. Through exposure at conferences and in journals, ionic liquids have become the subject of increasing attention.
- The possible number of ionic liquids (due to the various combinations of cations and anions) are likely to allow solvents to be tailored to specific processes. The uses of ionic liquids as more effective solvents will at the same time replace hazardous volatile organic compounds.
- Ionic liquids are interesting from a practical as well as a theoretical perspective. Most reaction mechanisms and solution theories have focused on molecular liquids. Ionic liquids provide a different environment for theories and experimental investigations.
- Genuine interest from a variety of industrial leaders has caused ionic liquids to succeed where other technologies have failed. Collaboration between industry and academic institutions eg. QUILL, has led to a distinct driving force in ionic liquid research. Research is done with industrial applications in mind.

Chapter Nine

Recommendations

The following recommendations may be considered for future work:

- Ionic liquids are very suitable as stationary phases in GLC. In addition to using single ionic liquids, mixtures of ionic liquids as a stationary phase in GLC are easily possible. This may yield greater selectivities than those possible with a single ionic liquid.
- Ionic liquids are more viscous that molecular solvents. The effect of elevated temperature on the size of the two-phase region in LLE ternary phase diagrams needs to be investigated. This will determine the extent to which the viscosity can be reduced without significantly affecting the range of feed compositions.
- Most ionic liquids are completely miscible with polar compounds, while very few are to any extent miscible in non-polar or slightly-polar compounds. Extractive distillation requires that the solvent be completely miscible in the key component in order to retain it in the liquid phase. Due to the solubility of $(C_6)_3C_{14}PhCl$ in slightly-polar hydrocarbons, it may proven an effective solvent in systems other than those investigated in this work
- The in-house production of an ionic liquid. This will allow for larger quantities to be produced which could be used for pilot plant scale testing. Most suppliers do not stock ionic liquids locally, therefore an order may take 6-8 weeks to arrive. In-house production would eliminate this most of this delay by ordering the reagents, which are supplied locally.

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Appendix A

Chemical Purity

Materials of sufficient chemical purity are required if meaningful results are to be obtained.

1. Ionic Liquids

The ionic liquids used in experiments are listed below along with the supplier and quoted purity.

Table A-1: Suppliers and purities of Ionic liquids used in this work

Ionic liquid*	Supplier	Quoted Purity (%)	Density (25 °C)	
			Exp. (g/cm^3)	Lit. (g/cm^3)
1-methyl-3-octyl-imidazolium chloride	Solvent Innovation	> 98	1.0104	1.00^a
1-Butyl-4-metylpyridinium tetrafluoroborate	Fluka	> 97	1.18472	1.18424^b
Trihexyl-tetradecyl-phosphonium chloride	Merck	n/a	0.89321	-

[a](Huddleston et al. 2001)

[b](Heintz et al. 2002a)

* Ionic liquids were purified by subjecting them to a vacuum of between 2 to 8 x 10^{-4} mbar and a temperature of between 40 to 45 °C for 30 minutes in order to remove volatiles, including water. Ionic liquids were then stored in a desiccator.

2. GLC

Table A-2: Suppliers and purities of solutes used in GLC

Solute	Supplier	Quoted Purity (%)
n-Pentane	Saarchem	> 98
n-Hexane	Sigma-Aldrich	> 98
n-Heptane	Saarchem	> 98
n-Octane	Saarchem	> 98
1-Hexene	Merck	> 98
1-Heptene	Merck	> 98
1-Octene	Sigma-Aldrich	> 98
1-Hexyne	Sigma-Aldrich	> 98
1-Heptyne	Sigma-Aldrich	> 98
1-Octyne	Sigma-Aldrich	> 98
Cyclopentane	Saarchem	> 98
Cyclohexane	Saarchem	> 98
Cycloheptane	Sigma-Aldrich	> 98
Benzene	Saarchem	> 98
Toluene	BDH	> 98

Since the GLC process separates the solutes from any impurities, the solutes were not purified further.

3. LLE

Table A-3: Suppliers and purities of chemicals used in LLE measurements

Chemical	Supplier	Purity by GC analysis (%)	Density		Special Storage
			Exp.[a] (g/cm^3)	Lit.[b] (g/cm^3)	
1-Hexene	Merck	99.6	0.669821	0.666	None
1-Octene	Merck	99.1	0.713064	0.709	None
Toluene	BDH	99.8	0.863749	0.866	4°A molecular sieves
Ethanol*	BDH	99.3	0.787823	0.783	4°A molecular sieves
2-Butanone	Saarchem	99.5	0.803336	0.795	4°A molecular sieves

[a] Measured with an Anton Paar DMA 5000 at 25 °C

[b] Physical Properties of Hydrocarbons (Gallant and Yaws, 1992) at 25 °C

* Ethanol is purified by the method of Lund and Bjerrum (Furniss et al. 1978). A small amount of ethanol is reacted with magnesium in the presence of iodine to form a Grignard reagent. This is reacted with a larger quantity of ethanol. The water present reacts to produce insoluble magnesium hydroxide. The ethanol is distilled off.

4. VLE

Table A-4: Suppliers and purities of chemicals used in VLE measurements

Chemical	Supplier	Purity by GC analysis (%)	Special Storage
1-Hexene	Merck	99.6	None
2-Butanone	Saarchem	99.5	4°A molecular sieves
Acetone	Merck	99.3	4°A molecular sieves
Methanol	Orion Chemicals	99.4	4°A molecular sieves

As a measure of the purity of the chemicals used for VLE, their experimental vapour pressures are compared with literature values (Reid et al. 1988).

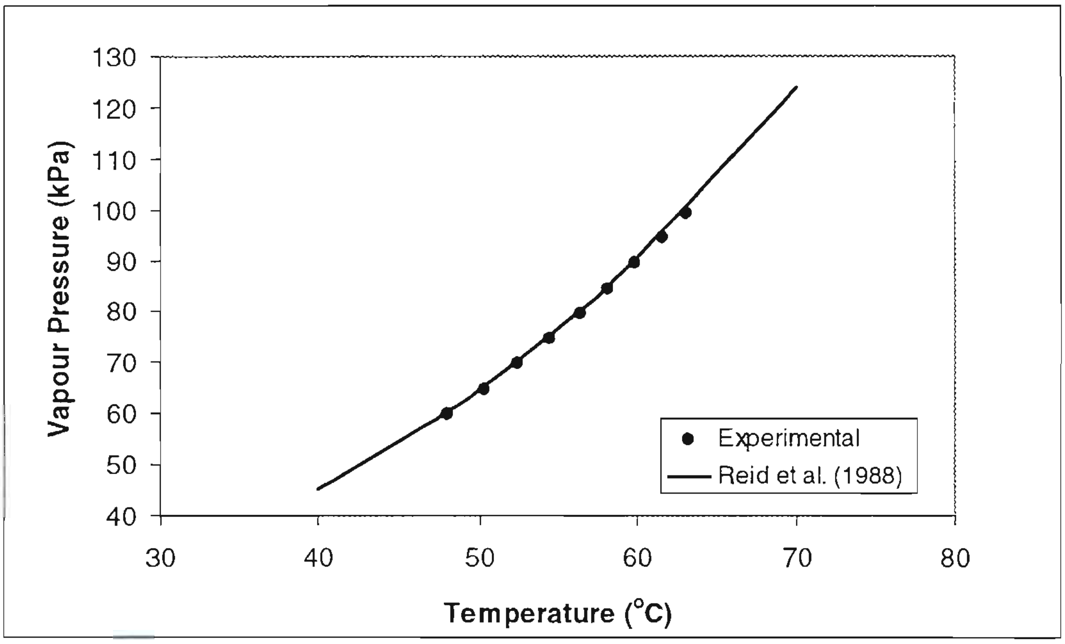

Figure A-1: Experimental and literature vapour pressures of 1-Hexene

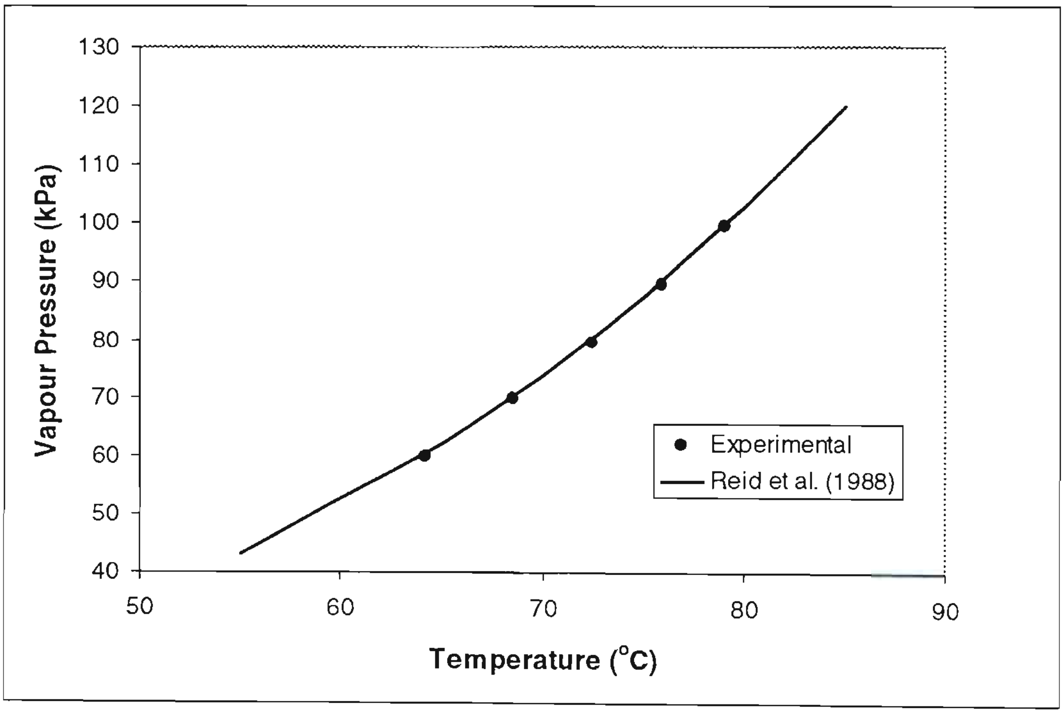

Figure A-2: Experimental and literature vapour pressures of 2-Butanone

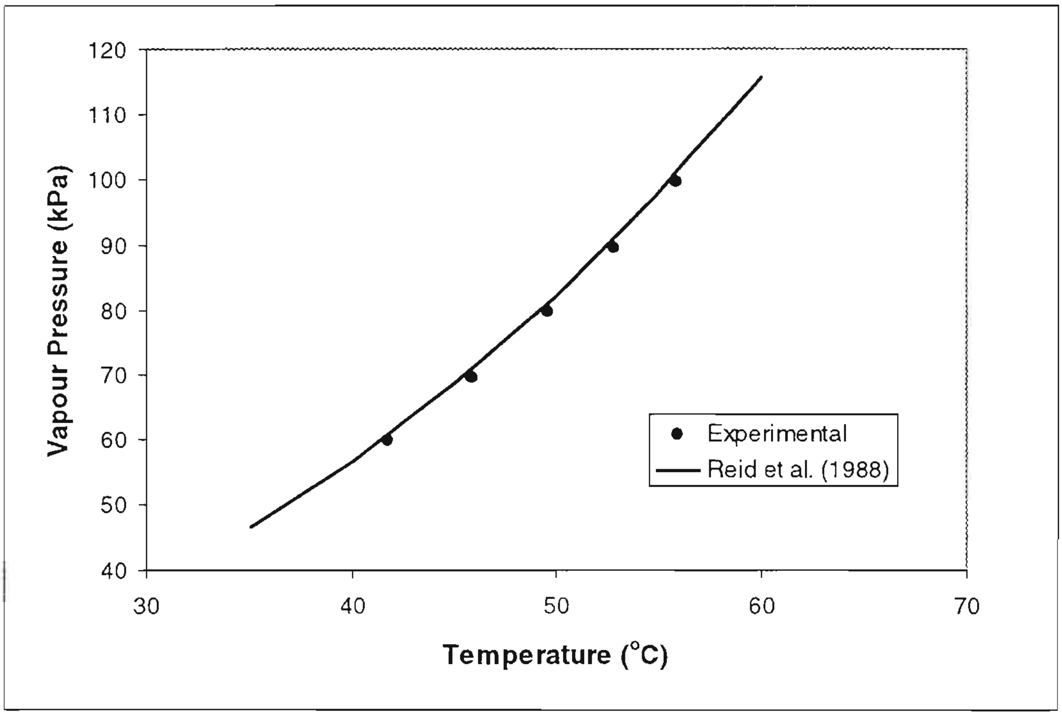

Figure A-3: Experimental and literature vapour pressures of Acetone

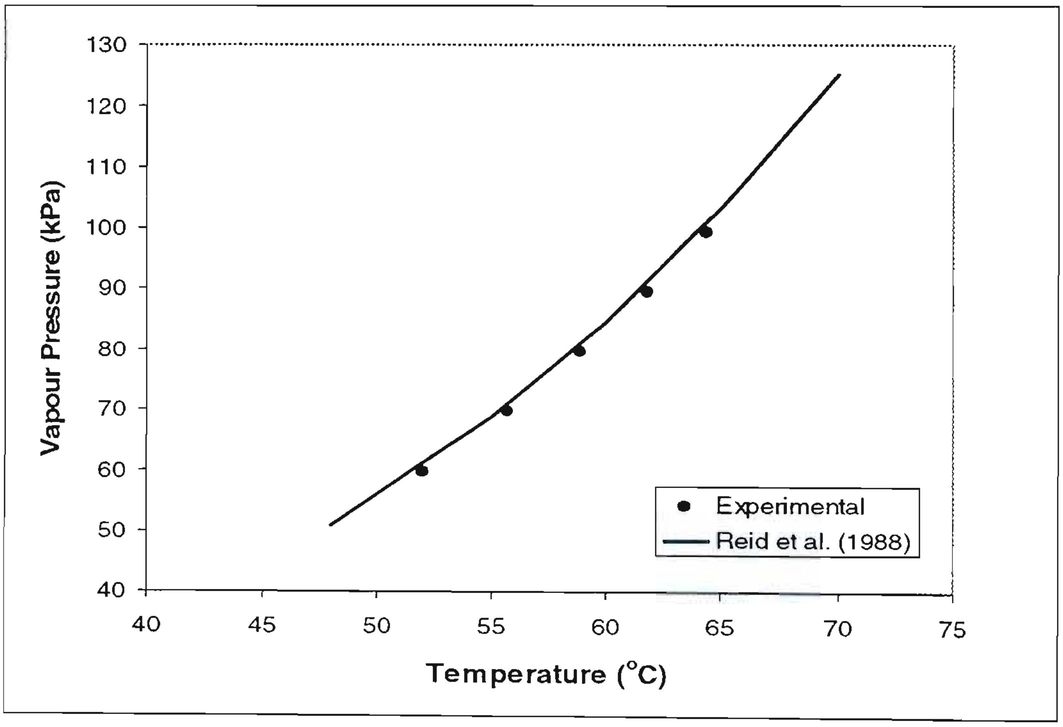

Figure A-4: Experimental and literature vapour pressures of Methanol

Appendix B

Calibration

1. Ternary LLE calibration

LLE calibrations are necessary to relate tie line density values to compositions. Best fit polynomials are used to interpolate values. LLE System 1 is a type II system and as a result the calibration curve is segmented due to a discontinuity in the binodial curve. Some of the other systems, even though type I systems, are also segmented as a more accurate representation of the calibration curve is produced using two lower order polynomials than a single higher order polynomial.

The LLE calibration curves are different to those for VLE. Here the density of the mixture on the binodial curve is not plotted against a specific component, rather it is plotted against the x intercept of a perpendicular dropped from the point on the binodial curve to the x axis. This x intercept is designated 'X' on the plot. This is repeated for points along the binodial curve and results in a plot of density vs X. Polynomials are used to represent the curve and to subsequently determine tie-line compositions from density measurements.

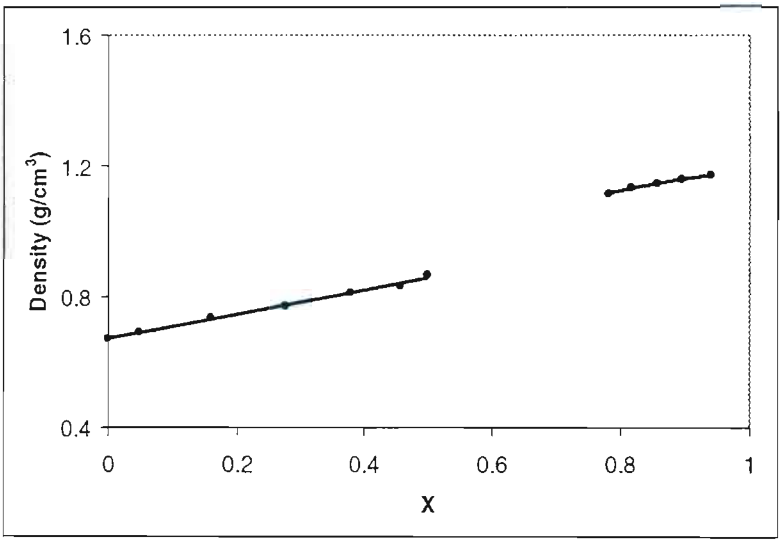

Figure B-1: Calibration curve for LLE System 1

For $0 > X > 0.5$
Density = $0.3727\ X + 0.6726$ $R^2 = 0.993$

For $0.79 > X > 0.94$
Density = $-0.4855\ X^2 + 1.1845\ X + 0.4883$ $R^2 = 0.995$

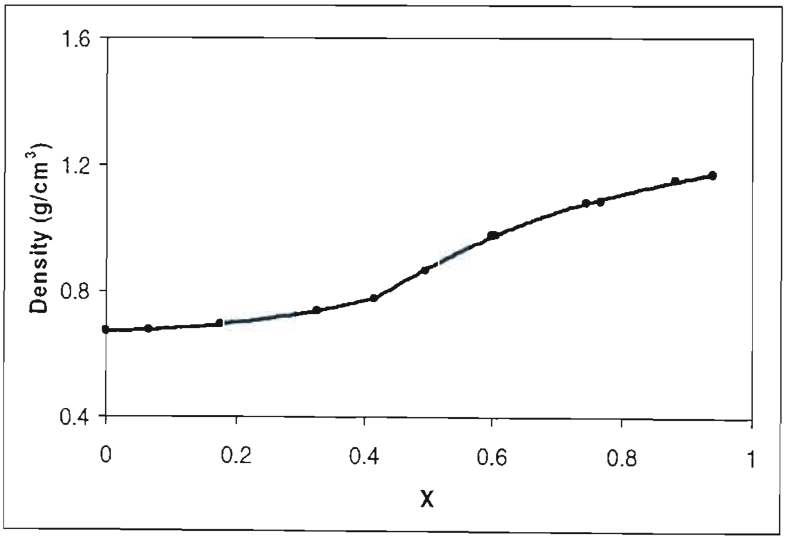

Figure B-2: Calibration curve for LLE System 2

For $0 > X > 0.42$
Density = $0.4729\ X^3 + 0.2701\ X^2 + 0.062\ X + 0.6719$ $R^2 = 0.999$

For $0.42 > X > 0.94$
Density = $2.9992\ X^4 - 7.6241\ X^3 + 6.1263\ X^2 - 0.8081\ X + 0.5122$ $R^2 = 1$

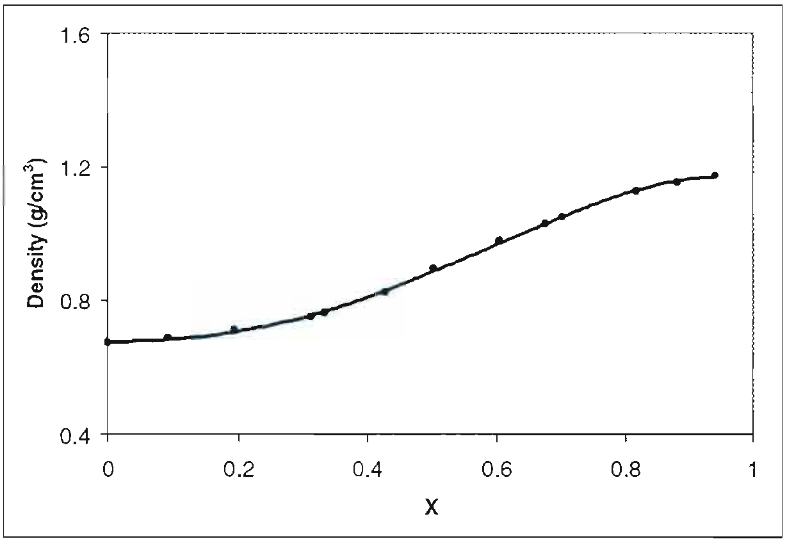

Figure B-3: Calibration curve for LLE System 3

For 0 > X > 0.94

Density = $-1.2312\ X^4 + 1.2015\ X^3 + 0.4936\ X^2 + 0.022\ X + 0.6755$ $R^2 = 0.999$

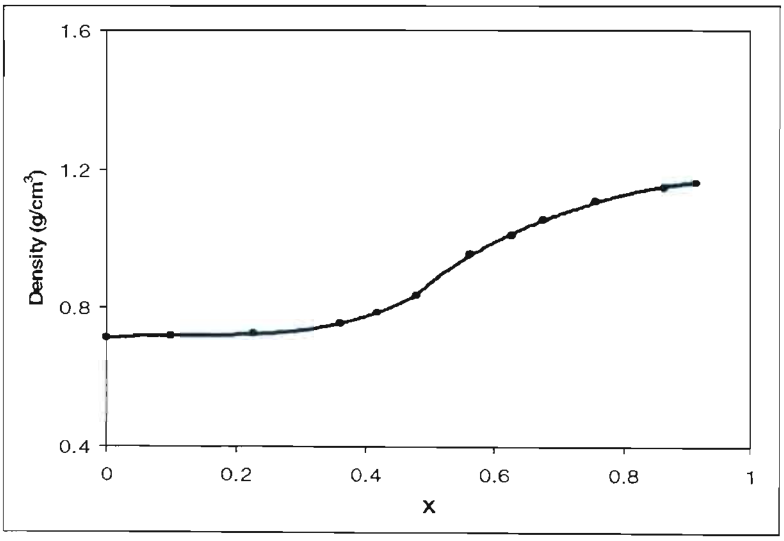

Figure B-4: Calibration curve for LLE System 4

For 0 > X > 0.48

Density = $2.6074\ X^3 - 1.0593\ X^2 + 0.1641\ X + 0.7122$ $R^2 = 0.998$

For 0.48 > X > 0.95

Density = $-6.8923\ X^4 + 20.807\ X^3 -24.577\ X^2 + 13.945\ X - 2.1301$ $R^2 = 0.999$

2. VLE Apparatus Pressure and Temperature Calibration

Pressure calibration is necessary to determine the actual pressure being measured by the pressure sensor. The actual pressure is read on the manometer using a cathetometer. The corresponding pressure on the pressure sensor display is recorded. This is repeated for a number of pressures to generate the plot below.

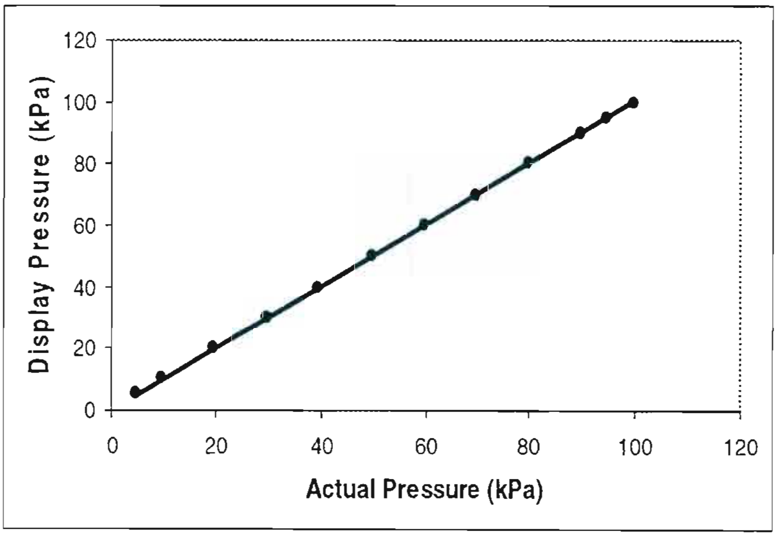

Figure B-5: Pressure calibration

A best fit straight line is used to represent the data. The relationship between the display pressure and the actual pressure is shown below.

Display pressure = 1.0059 x Actual pressure $R^2 = 0.999$

Temperature calibration is necessary to relate the resistance of the Pt 100 to the temperature measured in the equilibrium chamber. A multimeter (HP 34401A 6 digits) was used to measure the resistance. The actual temperature is determined using the vapour pressure and Antoine's equation (Reid et al. 1988)

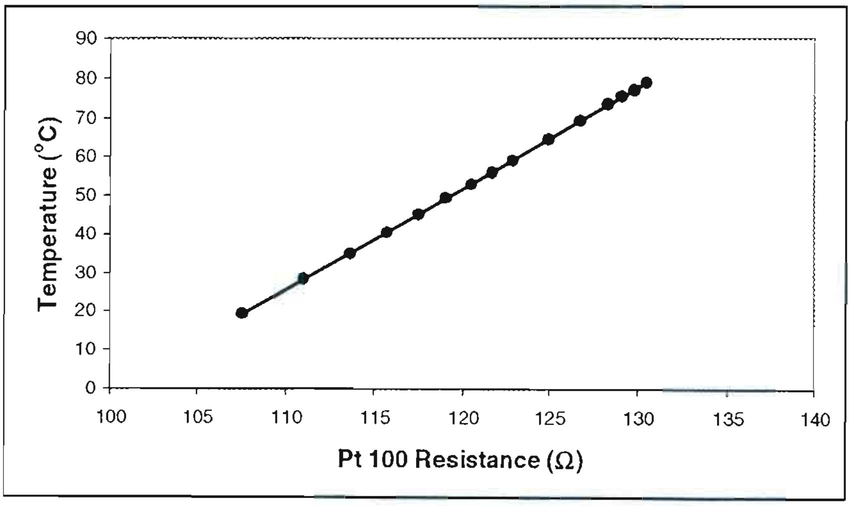

Figure B-6: Temperature Calibration

Temperature (°C) = 2.5954(Resistance(Ω)) - 260.04 $R^2 = 1$

3. GC calibrations for determining VLE compositions

GC calibrations are necessary to determine the detector response factors to various binary mixtures.

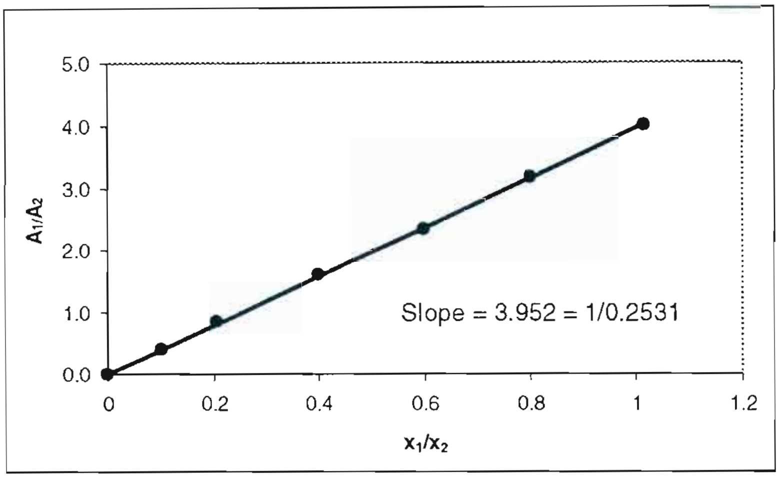

Figure B-7: GC calibration for Acetone(1) + Methanol(2) - Methanol rich region

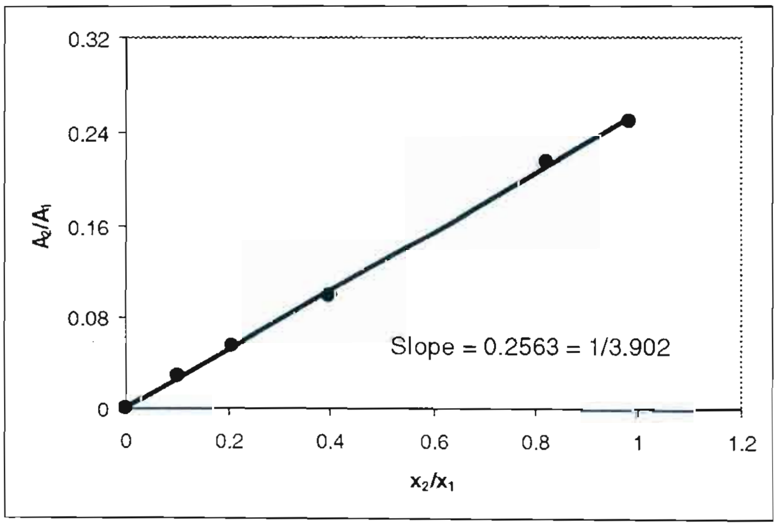

Figure B-8: GC calibration for Acetone(1) + Methanol(2) - Acetone rich region

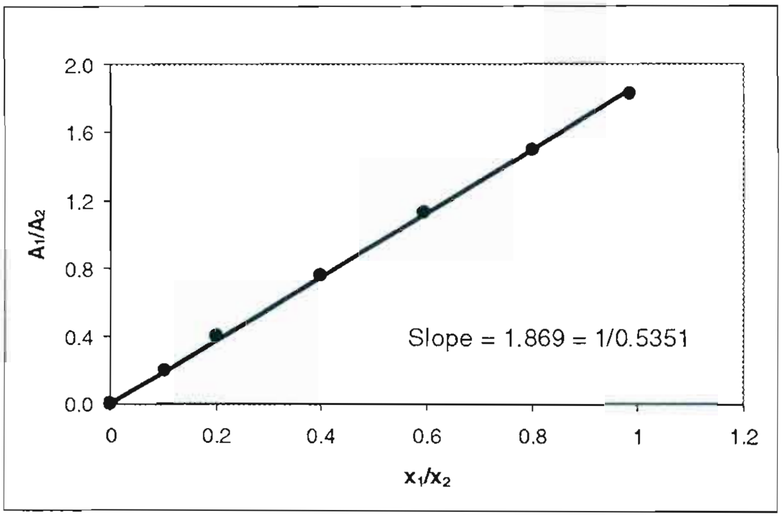

Figure B-9: GC calibration for 1-Hexene(1) + 2-Butanone(2) - 2-Butanone rich region

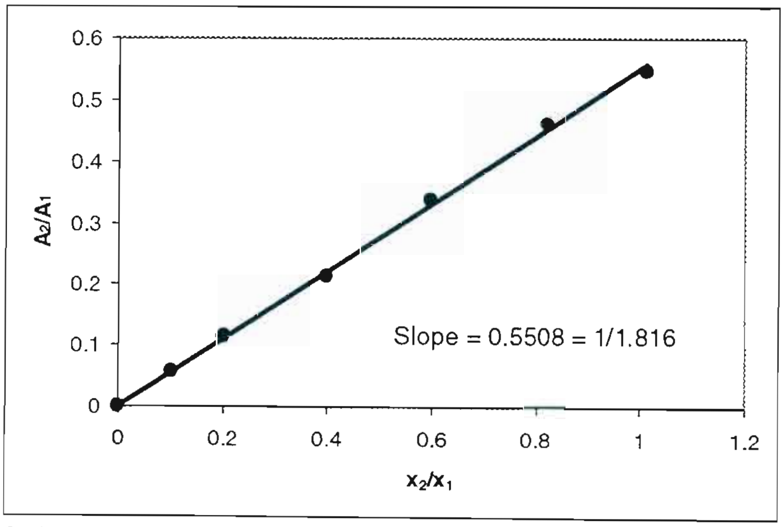

Figure B-10: GC calibration for 1-Hexene(1) + 2-Butanone(2) - 1-Hexene rich region