



**USE OF 1-ETHYL-3-METHYLIMIDAZOLIUM ETHYL  
SULFATE FOR LIQUID –LIQUID EQUILIBRIA FOR  
TERNARY MIXTURES**

Thesis submitted in fulfilment of the academic requirements of

**Masters in Applied Sciences (Chemistry)**

**By**

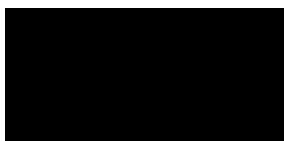
**MOHALE TSHEPANG**

**(2017)**

Department of Chemistry, Faculty of Applied Sciences,  
Durban University of Technology, Durban South-Africa, 4000

# PREFACE

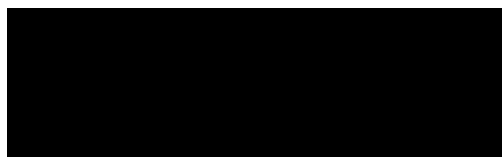
This work was conducted in the Department of Chemistry,  
Durban University of Technology, ML Sultan Campus, Durban,  
South-Africa.



T. Mohale (Signature)

9 May 2017

Date



Professor N. Deenadayalu (Signature)

9 May 2017

Date

# ABSTRACT

This thesis forms part of the Durban University of Technology Thermodynamics Research Unit's project which is aimed at developing a method for determination of the liquid-liquid equilibria (LLE) data for the azeotrope {methanol + water} with an ionic-liquid (IL) using DSA5000M to assess the efficiency of the ionic liquid to be used in liquid-liquid extractions for the recovery and recycling of methanol from petroleum refinery.

The objective of this study was to determine the liquid-liquid equilibria data of the azeotrope {methanol + water} using 1-ethyl-3-methylimidazolium ethyl sulfate ionic liquid with the intention to recycle methanol from the Fischer-Tropsch (FT) process by-products in petroleum industries and to utilize it in gasoline additives in a new methanol to gasoline (MTG) petroleum process.

LLE studies of systems containing alcohols and water are important due to the increasing demands of oxygenated compounds to produce lead free gasoline.

Light alkanols such as methanol and ethanol are reported to be suitable compounds in order to produce lead free gasoline, but the use of methanol in gasoline blends can cause phase separation problems in:

1. dry conditions, these are due to its partial solubility in saturated hydrocarbons.
2. the presence of water from ambient humidity or in storage tanks, this depend on unfavourable distribution factor between aqueous and the hydrocarbon phase.

To determine the possibility of separating methanol from water using ionic liquid, the liquid-liquid equilibria data was determined at room temperature,  $T = 298.15$  K and atmospheric pressure to investigate whether it separate from water and/or a non-phase separation if it is used as an additive.

The experimental data generated was compared to that of the literature for the system {methanol (1) +toluene (2) + dodecane (3)} and showed good agreement with the literature data with only maximum deviation of  $\pm 0.0015$  in the mole fraction using density calculations and  $\pm 0.0092$  in the mole fraction when using refractive index calculations. The selectivities and distribution coefficients for this system were also calculated and the maximum deviation between the two methods ( $n_D$  and  $\rho$ ) was  $\pm 1.33$  in selectivities and found to be  $\pm 0.001$  for distribution coefficients. The maximum deviation in distribution coefficients from literature when using  $n_D$  calculations for system 1 was  $\pm 0.04$  and  $\pm 0.01$  for  $\rho$ . For the selectivity values the deviation from that of literature of  $n_D$  when compared was found to be  $\pm 1.28$  and  $0.29$  for  $\rho$  respectively.

The selectivity values from the density calculations were found to be in the range 2.82 – 7.66 for this system with the distribution coefficient values reported in the range 0.17 – 0.23.

In the second system (system 2) the generated experimental data was also compared to that of the literature for the system {water (1) + methanol (2) + cyclohexane (3)} and in good agreement with literature values with only maximum deviation of  $\pm 0.0091$  in the weight fraction based on density calculations. The selectivities and distribution coefficients were also calculated and the maximum deviation between the literature and the experimental data was computed to be at  $\pm 0.0003$  for selectivity and  $\pm 0.09$  in distribution coefficient.

The selectivity values were found to be in a range 0.00 - 0.04 for this system and were constant throughout the phases but significantly less than one; with the distribution coefficient values in the range 0.00 – 0.008.

For 1-ethyl-3-methylimidazolium ethyl sulfate system (Ionic liquid system) the selectivity values were not constant throughout the two-phase region and the values were found to be in the range 0.63 -0.99 still below one which indicates that the ionic liquid used in this study could not be considered as a potential solvent for the separation of the investigated azeotrope.

The distribution coefficients for this system were determined and found to be in the range 0.23 – 0.74.

The certainty and reliability of experimentally measured tie-line data was ascertained by applying Othmer-Tobias (OT) correlations and the Non-Random, Two Liquid (NRTL) parameters.

The OT correlations for system 1 was linear and indicated the certainty of the five tie-lines prepared for this system.

In system 2 the OT correlation was not linear and indicated extensively high errors as well as high systematic multiplicative and additive errors in calculations of mole fractions.

For the IL system the OT correlation was linear throughout the whole tie-line range and indicated the adequate precision, which denotes that the investigation was carried out with minimal random and systematic errors and indicated the efficiency of the DSA 5000 M to generate the liquid-liquid equilibria data.

All the ternary systems were well correlated and in good agreement with the estimated NRTL data.

It was only system 1 {methanol (1) + toluene (2) + dodecane (3)} that gave a high maximum deviation ( %RSMD) of 1.288 when using the RI measurements with the minimum error margin of 0.6320, this account as to why RI measurements were not applied in other systems (system 2 and ionic liquid system).

Similarly for the same system; system 1 {methanol (1) + toluene (2) + dodecane (3)} when using the density measurements; the NRTL model gave a maximum deviation of 0.5620 and minimum error margin of 0.2590.

The NRTL obtained for system 2 {water (1) + methanol (2) + cyclohexane (3)} gave the maximum deviation of 0.5752 and minimum error margin of 0.0127.

The NRTL for the ionic liquid ternary system {[EMIM][EtSO<sub>4</sub>](1) + methanol (2) + water (3)} showed a good agreement between the experimental data and the NRTL model tie-line data with the %RSMD of 1.0201 on the upper limit and 0.1620 as a lower deviation.

# **DECLARATION-PLAGIARISIM**

I, Tshepang Mohale declare that this research is the result of my own investigation and study and the information presented and discussed within is true and original to the best of my knowledge and it has not been accepted in substance or as a requirement for other degree neither was it submitted concurrently for any other degree. Where use or quotes were made of the work of others, it was duly acknowledge in the text.

T.Mohale (Signature)

Date

# DEDICATION

This work was done in honour of my late father Mothonyana Andrew Mohale, whom I wish found the Perfect Peace.

It is also presented as a token of appreciation to my dearest, loving, caring and supporting mother Mofokeng Matshediso Linah “Madea” for being an understanding Mother.

*“The only way to get smarter is by playing a smarter opponent”*

Fundamentals of Chess 1883

# **CONFERENCE ATTENDANCE AND AWARDS**

## **CONFERENCES**

- **Oral presentation:** 42<sup>nd</sup> National Convention of the South African Chemical Institute, 29 – 4<sup>th</sup> December 2015, Southern Sun Elangeni Hotel, Durban.
- **Oral presentation:** 2015 Johannesburg Falling Walls Lab Conference, 18<sup>th</sup> September 2015, Witwatersrand University, Origin Centre, Johannesburg.
- **Oral presentation:** 2nd Annual Global Change Conference, 1<sup>st</sup> -6<sup>th</sup> December 2014, Nelson Mandela Metropolitan University, Port Elizabeth.
- **Oral Presentation:** Workshop: Thermodynamics Research Focus Area, 18<sup>th</sup> October 2014, Riverside Hotel, Durban.
- **Oral Presentation:** Durban University of Technology Institutional Research Day, 13<sup>th</sup> November 2012, Steve Biko Campus, Durban.

## **AWARDS**

- Awarded best overall oral presentation for the faculty of Applied Sciences from Durban University of Technology Institutional Research Day held on the 13<sup>th</sup> November 2012, Steve Biko campus, Durban

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# LIST OF ABBREVIATIONS AND SYMBOLS

LLE	Liquid-liquid equilibria.
MTBE	Methyl-t-butyl-ether.
FT	Fischer-Tropsch.
MTG	Methanol to gasoline.
ILs	Ionic liquids.
VOCs	Volatile Organic Compounds.
RI	Refractive index/indice.
F	Variance of the system.
C	Number of components in the system.
P	Number of phases.
PP	Plait points.
$\alpha$	Non-randomness parameter in NRTL model.
NRTL	Non-Random, Two Liquids.
UNIQUAC	Universal Quasi-Chemical.
W	Combinational factor (number of ways that molecule can be arranged in space)

$U_0$	potential energy of the lattice, closely related to the energy of isothermal vaporization from liquid to ideal gas state.
$\Theta$	molecular configuration of the mixture.
$\Phi$	average segment fraction.
$\alpha_{12}$	Constant characteristic of non-randomness of the mixture.
$g^{(1)}$	The residual energy for a cell containing molecule at its centre.
$G^{(E)}$	the molar Gibbs energy for binary solutions in the sum of the two changes in residual energy.
$\rho$	Density .
M	Mass.
V	Volume.
$n_D$	Refractive index/indice.
$\int_v$	Speed of the light in the vacuum.
$\int_S$	Speed of light in another substance.
Lit	Literature data.
Exp	Experimental data.

$S$	Selectivity value.
$k$	Distribution coefficient.
$x_1$	Mole fraction of component 1.
$x_2$	Mole fraction of component 2.
$x_3$	Mole fraction of component 3.
$x_1^s$	Mole fraction of component 1 in alkane rich region.
$x_2^s$	Mole fraction of component 2 in alkane rich region.
$x_3^s$	Mole fraction of component 3 in alkane rich region.
$x_1^a$	Mole fraction of component 1 in alcohol rich region.
$x_2^a$	Mole fraction of component 2 in alcohol rich region.
$x_3^a$	Mole fraction of component 3 in alcohol rich region.
$x_1^{aq}$	Mole fraction of component 1 in aqueous rich region.
$x_2^{aq}$	Mole fraction of component 2 in aqueous rich region.
$x_3^{aq}$	Mole fraction of component 3 in aqueous rich region.
$x_1^{IL}$	Mole fraction of component 1 in ionic liquid rich phase.

$x_2^{II}$	Mole fraction of component 2 in ionic liquid rich phase.
$x_3^{II}$	Mole fraction of component 2 in ionic liquid rich phase.
$x_2^I$	Mole fraction of component 2 in the extract phase.
$x_2^{II}$	Mole fraction of component 2 in the raffanite.
$w_1^a$	Weight Fraction 1 in alkane rich phase.
$w_2^a$	Weight Fraction 2 in alkane rich phase.
$w_3^a$	Weight Fraction 3 in alkane rich phase.
$w_1^o$	Weight Fraction 1 in organic rich phase.
$w_2^o$	Weight Fraction 2 in organic rich phase.
$w_3^o$	Weight Fraction 3 in organic rich phase
RMSD	Root mean square deviation
$\sigma$	% RMSD
[EMIM][EtSO <sub>4</sub> ]	1-ethyl-3-methylimidazolium ethyl sulfate

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# CHAPTER 1: INTRODUCTION

## 1.1 RESEARCH BACKGROUND

The focus of this research is the study of the phase equilibria of systems containing an azeotropic mixture of an alcohol and water. Azeotropic mixtures are difficult to separate due to closeness of the boiling points of the compounds that are present in such mixture.

There is also a demand for oxygenated compounds to produce lead free gasoline. Most oxygenated compounds tend to absorb water. To produce higher purity alcohol the water needs to be removed and currently ethers and alcohols which are used as gasoline additives to improve the antiknock property and help to reduce harmful combustion emission tend to absorb water. Monica *et al.*, (2003). Methyl-t-butyl ether (MTBE) is currently the main oxygenated compound used to reformulate gasoline. However, MTBE is volatile and causes the contamination of ground water. Therefore it is important to have some less harmful oxygenates as alternative gasoline additives. Monica *et al.*, (2003)

Light alkanols for example: methanol and ethanol are some possible substitutes for production of lead free gasoline. However, the use of methanol in gasoline blends can increase the phase separation problems, due to the presence of high water content in the atmosphere during the summer months (higher temperatures). In order to investigate the possibility of using methanol as a gasoline additive, phase diagrams studies need to be conducted at room temperatures and atmospheric pressure to ensure that there is no phase separation of the absorbed water. Monica *et al.*, (2003). To remove the water present, a suitable extractant (solvent) need to be used.

Certain petrochemical streams still use dodecane as the potential solvent for solvent extraction. In such process it is clear that dodecane and water will necessarily come into physical contact, due to the fact that water and dodecane are highly immiscible it will result in the formation of two liquid phases: an aqueous (water-rich) phase and organic (dodecane-rich) phase.

To remove water from light alcohols in certain petrochemical industries, solvent extraction is used as a technique of separation; although the use of environmentally friendly and cost effective solvents is still a challenge a new class of solvents namely, ionic liquids (ILs) can serve as a potential solvent in solvent extractions. After removal of the water from light alkanols with the use of ILs, it would be fairly simple to separate the alcohols from the solvents (ILs) by distillation due to the large differences in boiling points between the two chemicals.

Ionic liquid is defined as material containing only ionic species and referred to as green solvents or designer solvents due to their unique physical and chemical properties such as thermal stability, high solubility for polar and non-polar organic and inorganic substances, Most of the ionic liquids are the combinations of a 1-butyl-3-methylimidazolium, 1-ethyl-3-methylimidazolium or n-butylpyridinium cation and a charge diffuse inorganic anion.

Deenadayalu *et al.*, (2007)

## 1.2 ALCOHOLS

Alcohol is any organic compound in which a hydroxyl group is bonded to a carbon atom of the alkyl or substituted alkyl group. An important group of alcohols is formed by the simple acyclic alcohols, the general formula for which is  $C_nH_{2n+2}O$ .

### 1.2.1 Properties of Alcohols

There are three major subset of alcohols, which are primary, secondary and tertiary alcohols, which are based upon the number of carbon, and how the C-OH group is bonded. Alcohols are polar and they can form hydrogen bonds to one another and other compounds. Alcohols can be used as protonic solvents; there are two opposing solubility trends in alcohols the:

- (i) tendency of the polar OH to promote hydrophilicity in water.
- (ii) carbon chain to resist it.

Thus methanol, ethanol and propanol are miscible in water because they have a shorter carbon chain. Butanol is moderately soluble in water, and alcohols that have five and more carbon chain are effectively insoluble in water. All simple alcohols are miscible in organic solvents. Alcohols have an odour that is often described as biting and as hanging in the nasal passage. Sithole *et al.*, (2012)

### 1.2.2 Applications of Alcohols

- Ethanol is the only alcohol that can be used as an alcoholic beverage and has been consumed by humans since pre-historic times.
- Methanol and ethanol can also be used as the **alcohol fuel**; the fuel performance can be increased in force induction and internal combustion by injecting alcohol into the air intake, after the turbocharger or supercharger has pressurized the air.
- Alcohols can also be used in chemical industries as reagents or solvents because of their low toxicity property and ability to dissolve non polar substances.
- In organic synthesis alcohols serves as versatile intermediates.

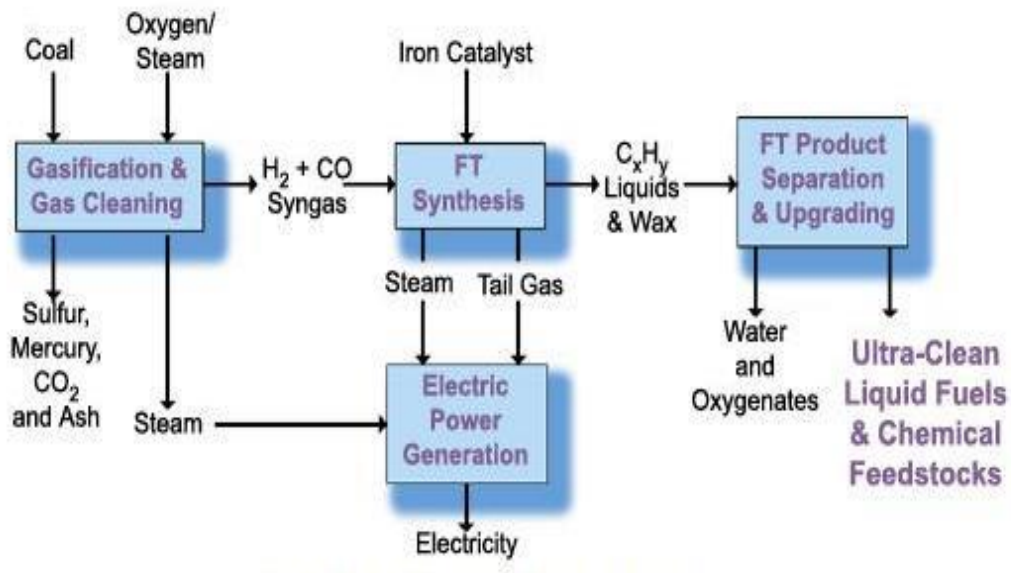
### 1.2.3 Significance of Methanol in the Petroleum Industry

Methanol is the major starting material for synthetic petrochemical production and is a promising alcohol to be used in blending of gasolines. Methanol is produced catalytically by the reaction of molecular hydrogen ( $H_2$ ) and Carbon monoxide (CO) at high pressure (300 psi) and temperature. Strelzoff *et al.*, (1970)

$H_2$  and CO are obtained from methane by reforming with steam to yield synthetic gas (syngas), the reforming step is generally carried out at 800 -1000  $^{\circ}C$  and 300 psi. The second step involves the water-gas shift reaction which is used to increase  $H_2/CO$  ratio and the reaction utilize a metal oxide catalyst at 400 – 500  $^{\circ}C$  and 300 psi. Shah *et al.*, (1970). These severe conditions result in high capital and operating costs and poor thermal efficiencies.

Catalytic conversion of coal to synthetic gas using the Fischer –Tropsch process have also been reported to produce methanol, higher alcohols and water with sustained catalytic activity. Thus simpler, more efficient processes for the water/methanol azeotrope separation are necessary. Klier *et al.*, (1986) and Dombek *et al.*, (1986). Fischer-Tropsch (FT) shown in Figure 1.1 overleaf is a catalyzed chemical reaction in which carbon monoxide and hydrogen are converted into liquid hydrocarbons of various forms. Typical catalysts used are based on iron and cobalt. The purpose of this process is to produce a synthetic petroleum substitute for use as synthetic lubrication oil or synthetic fuel. Broughton *et al.*, (1968)

Sasol is one of the petroleum industries using this kind of synthesis, to produce a synthetic petroleum substitute, typically from coal, natural gas or biomass, for use as synthetic lubrication oil or as synthetic fuel for motor vehicles and some air craft engines.

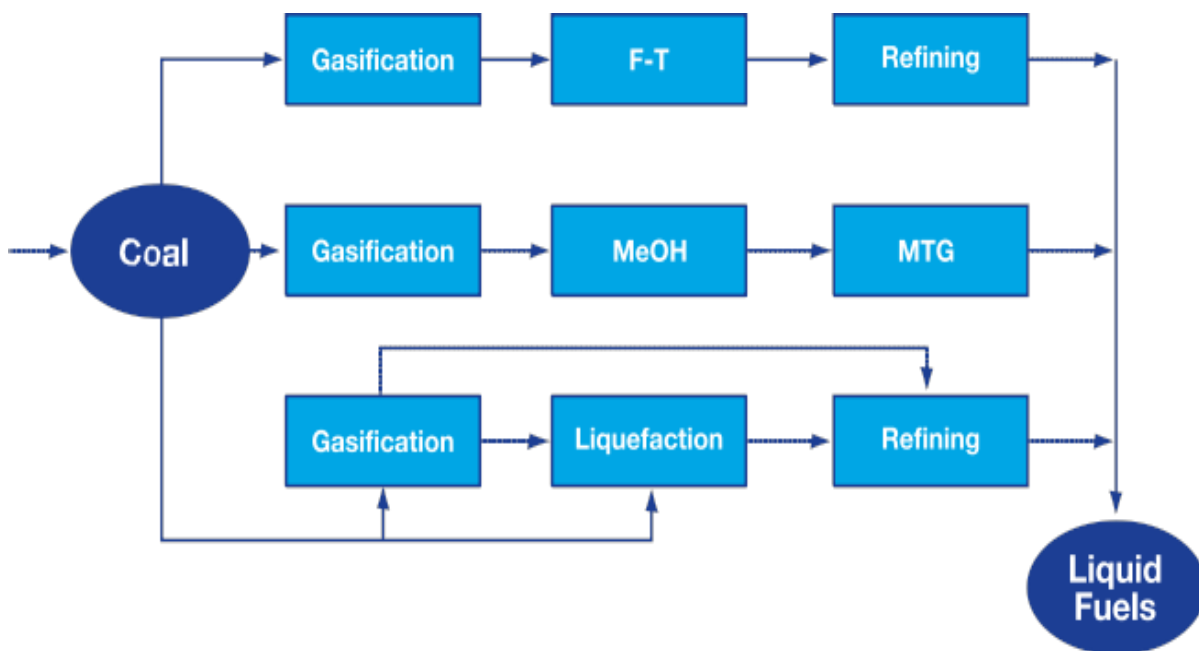


**Figure 1.1 Schematic diagram of Fischer-Tropsch process [Sithole and Reddy, (2012)]**

The by-products of the Fischer-Tropsch process also include the light hydrocarbon gases, mainly methane which is also a by-product of most gasification process. Mills, (1982)

The Mobil process also known as methanol to gasoline process (MTG) shown in Figure 1.2 overleaf was discovered by Exxon-Mobil scientists in 1970 shows the potential of using methanol as a gasoline in the near future.

An equilibrium mixture of methanol, di-methyl ether (DME) and water is converted to light olefins (C<sub>2</sub>-C<sub>4</sub>) and a final reaction step leads to the synthesis of higher olefins, n/isoparaffins, aromatics and naphthenes.



**Figure 1.2 Conversion of gas to liquid fuels by both FT and MTG**

Both the Fisher-Tropsch and MTG processes convert coal into synthesis gas before converting it to the final liquid products. However, their respective product slates are very different.

The Fisher-Tropsch process produces a broad spectrum of straight-chain paraffinic hydrocarbons that requires upgrading to produce commercial quality gasoline, jet fuel and diesel.

In contrast, MTG selectively converts methanol to one liquid product: a very low sulfur, low benzene regular octane gasoline. Due to the unique low sulfur and low benzene characteristics of the MTG gasoline product, it is a valuable blending component for meeting environmental regulations specific to sulfur and benzene.

### **1.3 WATER**

Water is a good solvent and is often referred to as the universal solvent. Substances that dissolve in water, e.g., salts, sugars, acids, alkalis, and some gases – especially oxygen, carbon dioxide (carbonation) are known as hydrophilic substances, while those that are immiscible with water (e.g., fats and oils), are known as hydrophobic substances.

A water molecule contains one oxygen and two hydrogen atoms ( $H_2O$ ) connected by covalent bonds. Water is a liquid at ambient conditions but often co-exists on earth with its solid state and gaseous state (water vapor or steam). It also exists in liquid crystal state near hydrophilic surfaces. Water covers 70.9% of the earth's surface and is vital for all known forms of life. On earth 96.5% of the planet's water is found in oceans, 1.7% in ground water, 1.7% in glaciers and the Ice caps of Antarctica and Greenland, a small fraction in other large bodies and 0.001%

in the air as vapor. Only 2.5% of earth's water is fresh water. 98.8% of that fresh water is contained with biological bodies and manufactured products. Upadhay, (2014)

### **1.3.1 Properties of Water**

- Pure water has a low electrical conductivity, but this increases significantly with the dissolution of a small amount of ionic material such as sodium chloride.
- The boiling point of water (and all other liquids) is dependent on the barometric pressure. For example, on the top of Mt. Everest water boils at 68 °C, compared to 100°C at sea level. Conversely, water deep in the ocean near geothermal vents can reach temperatures of hundreds of degrees and remain liquid.
- The maximum density of water occurs at 3.98 °C. It has the anomalous property of becoming less dense, not more, when it is cooled down to its solid form, ice. It expands to occupy 9% greater volume in this solid state, which accounts for the fact of ice floating on liquid water, as in icebergs.
- Water is miscible with many liquids, such as ethanol, in all proportions, forming a single homogeneous liquid. On the other hand, water and most oils are immiscible, usually forming layers according to increasing density from the top.
- Water forms an azeotrope with many other solvents.
- Water can be split by electrolysis into hydrogen and oxygen.
- As an oxide of hydrogen, water is formed when hydrogen or hydrogen-containing compounds burn or react with oxygen or oxygen-containing compounds. Water is not a fuel, it is an end-product of the combustion of hydrogen. The energy required to split water into hydrogen and oxygen by

electrolysis or any other means is greater than the energy that can be collected when the hydrogen and oxygen recombine.

### **1.3.2 Significance of Separating Water in Petroleum Industry**

Each industrial sector (e.g., chemicals, food processing, petroleum, etc.) depends on water for unique reasons. This demand is primarily divided among the three major industrial uses for water: process water, cooling, and heating; with a shifting emphasis for each industry.

A major environmental concern in the petroleum industry is the disposal of large amounts of water that is generally extracted together with the oil and the stated by-products during its production by Fischer-Tropsch process; thus more efficient ways for separation of such products is required in the new green approach to recycle and reuse those products instead of polluting the environment.

When the oil field begins to be depleted towards the end of its production lifetime, gas or seawater is pumped into these deposits, increasing the internal pressure at the well in order to enhance oil recovery however this technique is not efficient to recover all the hydrocarbons that are released as the by-products, especially light hydrocarbons and alcohols. This operation results in large recoveries of saline water along with the oil. This water is known in petroleum industry as produced water, which may have very high salinity, as well as a complex composition including mostly organic salts, toxic metals and many other substances. The volume of produced water generated in offshore platforms is very high and its discharge in surface water bodies is a great problem for the petroleum industry because the produced water waste or an effluent must be characterized and treated before disposal to meet or adhere to

environment and regulatory controls. Marcos, (2007). So the need for efficient separation processes is of high significance for separation and recycling of water and eluted by-products in petroleum industries.

## **1.4 SELECTION OF POTENTIAL SOLVENT FOR SOLVENT EXTRACTION**

Solvent extraction depends on the physical and chemical properties of a solvent when used for separation of complex liquid mixtures such as the recovery of valuable products and removal of contaminants in effluent streams. The separation potential and feasibility of solvents for commercial applicability are dependent on the physical properties such as boiling point, thermal stability, density and viscosity, ease of recovery, toxicity and corrosive nature of the solvent.

Selectivity of the solvent is the important component in characterizing a solvent. Letcher and Reddy , (2004).

With methanol and water being totally miscible to each other careful criteria is needed in separation of these two valuable solvents.

The choice of solvents for solvent extraction processes involves a systematic approach, which is influenced by the certain factors that affect the solubility of the solvent in solvent extraction.

## **1.4.1 Factors Affecting the Solubility of a Solvent in Solvent Extraction**

### **1.4.1.1 Density and Viscosity**

A large density difference between the equilibrium conjugate phases in the mixture is ideal to favor phase separation, as this facilitates rapid phase separation. The density difference between the two phases should be large and the interfacial tension of the solvent must be large. Both properties ensure rapid separation of the two phases. A low viscosity solvent is preferred from a theoretical and practical point of view.

### **1.4.1.2 Selectivity**

The selectivity,  $S$ , is the ratio of the mole fractions of two components that are to be separated in the one phase to the ratio of the same two components in the other phase as shown by equation 1.1 below :

$$S = (x_2 / x_3)^I \div (x_2 / x_3)^{II} \quad (1.1)$$

where  $x_2$  and  $x_3$  are the mole fractions of the components to be separated. For an efficient separation the value of selectivity,  $S$ , must not be 1, as this means that the overall composition of the two phases in equilibrium with each other is the same. Reddy, (2003).

### 1.4.1.3 Distribution Coefficient

The capacity is described by distribution coefficient,  $k$ , which is the ratio of the concentration of component to be separated in the solvent rich (extract) phase to the ratio of the same component in the solvent depleted (raffinate) phase as shown by equation 1.2 below:

$$k = x_2^{\text{II}}/x_2^{\text{I}} \quad (1.2)$$

$k$  should be large for a chosen solvent if it's a good solvent.

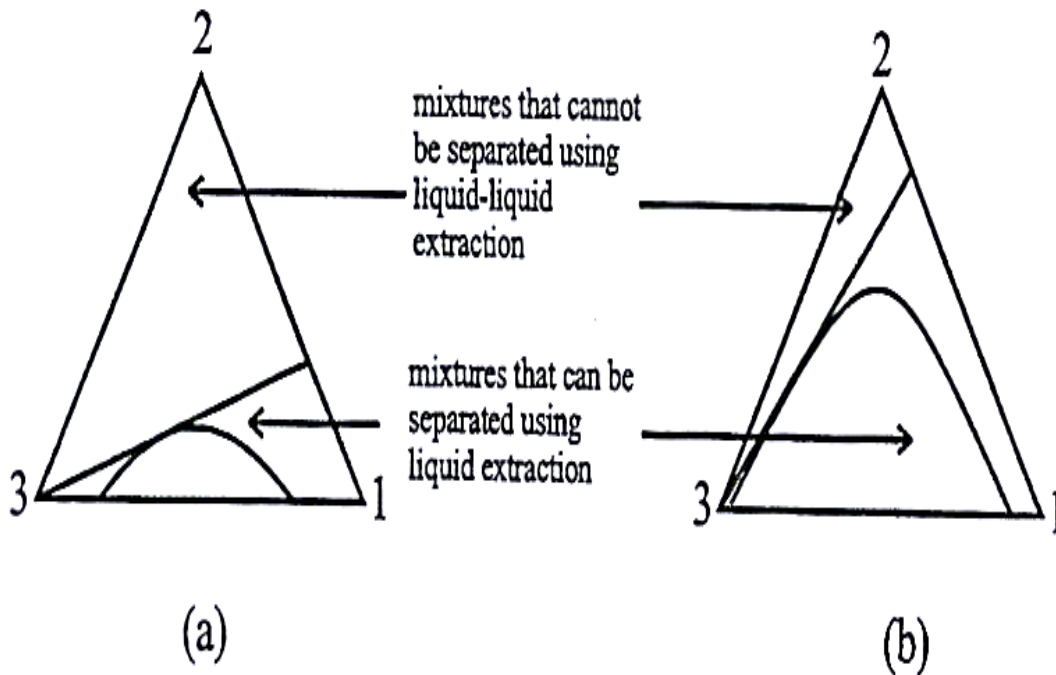
### 1.4.1.4 Ease of Recovery

A solvent need to be easily separated from the mixture and purified so that it can be recycled and be re-used. For effective separation, there should be a large difference in volatilities of the components in relation to the solvent. There should be a high boiling point difference between the solvent and the extracted components to ensure that the solvent can easily be recovered by distillation.

### 1.4.1.5 Solvent Solubility

The solvent should have low solubility in one of the components, and separation in the two phase region should be large. These denote a larger composition range in which the solvent can be used.

A ternary phase diagram with the large two phase region implies a relatively high mutual insolubility of the components in the ternary mixture. This is an advantage as the useful composition range over which the extraction solvent (entrainer) can be utilized as shown in Figure 1.3 below:



**Figure 1.3 (a) Ternary liquid-liquid phase diagram with a small two phase region. (b) Ternary liquid-liquid phase diagram with a large two-phase region [Reddy, (2003)]**

The solubility of different species in imidazolium ionic liquids (discussed in section 1.5) depends mainly on polarity and hydrogen bonding ability. Saturated aliphatic compounds are generally only sparingly soluble in ionic liquids, whereas olefins show somewhat greater solubility, and aldehydes can be completely miscible. Gas solubility follows the same trend, with carbon dioxide gas showing exceptional solubility in many ionic liquids, carbon monoxide being less soluble in ionic liquids than in many popular organic solvents, and hydrogen being only slightly soluble (similar to the solubility in water) and may vary relatively little between the more commonly used ionic liquids. Bahadur, (2010).

#### **1.4.1.6 Toxicity and Availability**

The solvent should have low toxicity from vapour inhalation or skin contact. When extraction is used as a pre-treatment for waste water before being finally discharged to a stream, low toxicity to aquatic life is vital. Another important factor which determines the economic viability of solvent extraction potential of prospective solvent is its ease of availability and unit cost.

#### **1.4.1.7 Cost Effective Disposals**

A potential solvent used in extractions should have no significant effect or impact associated with its disposal when a need for its disposal arises. It should adhere to the environmental stewardship standards of chemical disposal.

## 1.5 IONIC LIQUIDS

Room-temperature ionic liquids (RTILs) have recently shown an elevated interest from both industrial and academic communities due to their distinct properties. Vesna *et al.*, (2002)

Even though the first RTILs (Ethyl-ammonium-nitrate) was discovered in 1914, the huge interest in their application emerged rapidly in 1980 and since then their rapid significant growing interest have not yet been exhausted. Martyn *et.al*, (2000) and Suojiang *et al.*, (2006)

Their unique character to possess enormous potential interesting properties, both physical and chemical make them of fundamental significance to researchers, especially those that follow the principles of green chemistry.

Ionic liquid (ILs) are group of organic salts which contain organic cations and inorganic anions. In many cases they are defined as solvents that are liquid at ambient temperature and consist entirely of ions. One or both of the ions incorporated in the ionic liquids are large, and usually the cation has a low degree of symmetry.

As discussed by Martyn *et al.*, (2000); these factors tend to reduce the lattice energy (*measure of the strength of bonds*) of the crystalline form of the salt and thus contribute to the low melting point property of these solvents.

Ionic liquids are made up of at least two components (the anion and the cation) which can be adjusted or varied to fine tune a specific or particular need, thus the term “designer solvent”

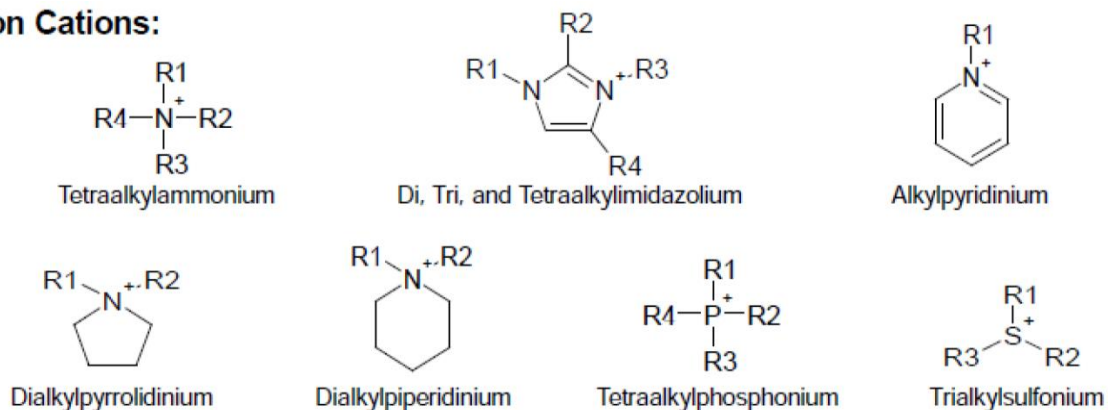
best fit their description. They can also be designed to possess or achieve a particular set of properties which may be desired for particular use or certain industrial processes/applications.

Martyn *et al.*, (2000)

### 1.5.1 Typical Structures of Cation and Anions of ILs

Figure 1.4 below represents typical cations and anions of ILs. Different cations and anions can be combined to give a very large possible number of ILs and can be used to fine tune the chemical or physical properties of ILs to allow them to be suitable for a particular application.

#### Common Cations:



#### Common Anions:

$\text{BF}_4^-$ ,  $\text{B}(\text{CN})_4^-$ ,  $\text{CH}_3\text{BF}_3^-$ ,  $\text{CH}_2\text{CHBF}_3^-$ ,  $\text{CF}_3\text{BF}_3^-$ ,  $\text{C}_2\text{F}_5\text{BF}_3^-$ ,  $n\text{-C}_3\text{F}_7\text{BF}_3^-$ ,  $n\text{-C}_4\text{F}_9\text{BF}_3^-$ ,  $\text{PF}_6^-$ ,  $\text{CF}_3\text{SO}_3^-$ ,  $\text{CF}_3\text{SO}_2^-$ ,  $\text{N}(\text{SO}_2\text{CF}_3)_2^-$ ,  $\text{N}(\text{COCF}_3)(\text{SO}_2\text{CF}_3)^-$ ,  $\text{N}(\text{SO}_2\text{F})_2^-$ ,  $\text{N}(\text{CN})_2^-$ ,  $\text{C}(\text{CN})_3^-$ ,  $\text{SCN}^-$ ,  $\text{SeCN}^-$ ,  $\text{CuCl}_2^-$ ,  $\text{AlCl}_4^-$ ,  $\text{F}(\text{HF})_{2.3}^-$  etc.

**Figure 1.4** Typical cations and anions of ILs

Many authors used in this study; Reiji *et al.*, (1997), George *et al.*, (1997), Martyn *et al.*, (2000), Andreas *et al.*, (2002), Zhang *et al.*, (2005), Vesna *et al.*, (2002), Yang *et al.*, (2005) and John (2005); have reported that both the thermodynamics, kinetics and synthetic reactions carried out with ILs to be of different nature to those of conventional molecular solvent, thus their chemistry is also different and unpredictable.

### **1.5.2 Properties of ILs**

- Low melting points.
- High solubility for polar and non-polar substances.
- Relatively wide electrochemical stability.
- Good electrical conductivity.
- High ionic mobility.
- Negligible vapour pressure.
- Excellent chemical and thermal stabilities.
- Some possess liquid crystal or lubricant properties.
- Non-flammable

These properties have been initially explored for applications in electrochemical technology and as solvents in electronic absorption spectroscopy of highly charged complex ions with high-or low oxidation state. Jia-Zheng *et al.*, (2005)

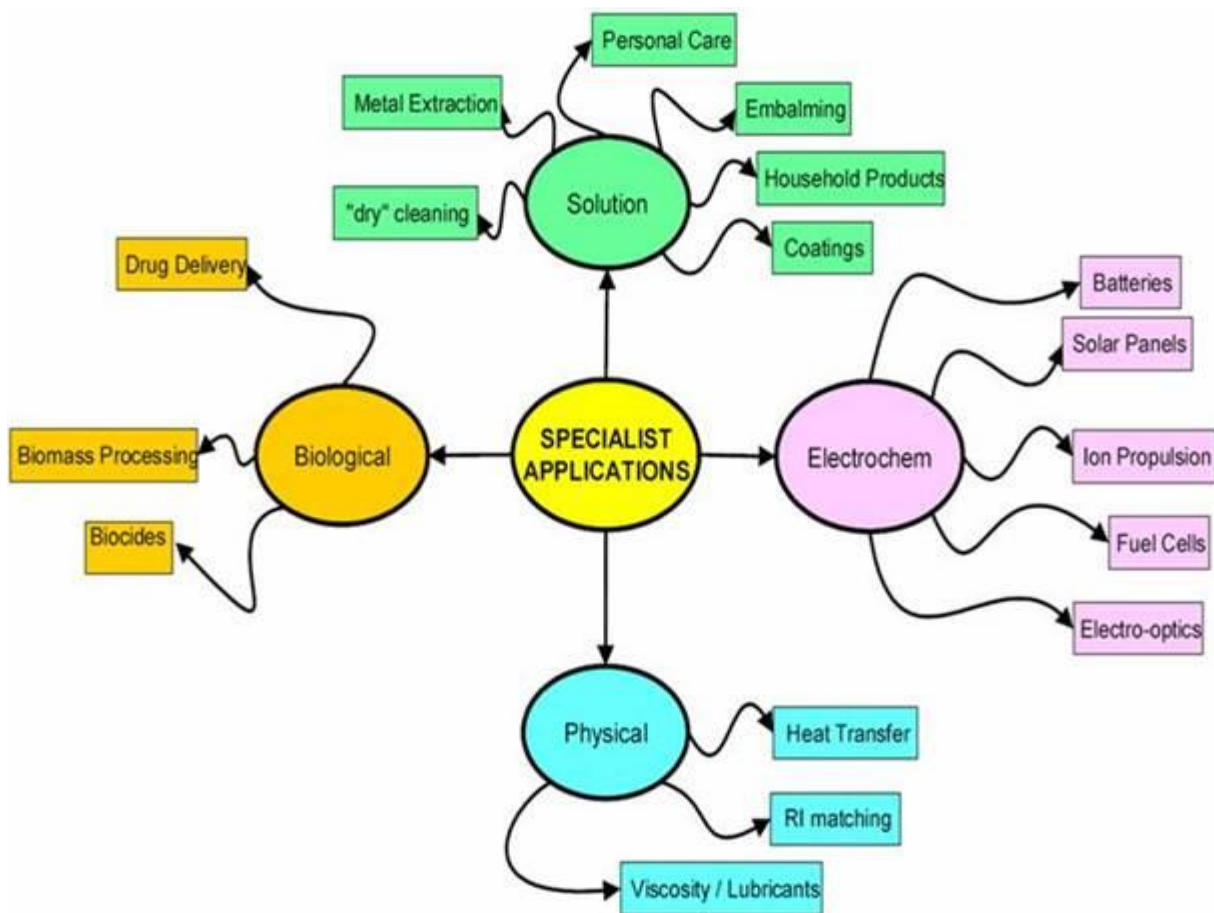
Ionic liquids have since been used in the broad contexts below:

### **1.5.3 Applications of ILs**

- In clean Liquid-Liquid Extraction process.
- Recyclable alternatives to aprotic solvents.
- In catalytic cracking.
- Catalysis for synthetic organic chemistry.
- In radical polymerization.

- As a medium in both analytical and physical chemistry applications
- They are better biocatalysts over conventional organic solvents.
- Currently used in biomass processing.

Figure 1.5 below shows many other uses of ionic liquids in different disciplines.



**Figure 1.5 Detailed schematic diagram of ILs applications [Brennecke and Maginn, (2001)]**

Ionic liquids are characterized into two classes:

- (i) Air-and water stable ionic liquid or simple salts. i.e [EtNH<sub>3</sub>][NO<sub>3</sub>]
- (ii) Organoaluminates (*versatile*) or binary ionic liquids. i.e aluminium(III)chloride and 1-ethyl-3-methylimidazoliumchloride [EMIM][Cl]

The simple salts ionic liquids are made of single anion and cation, whereas in the latter type the equilibrium is involved and thus contain several different ionic species. Martyn *et al.*, (2000) and Jia-Zheng *et al.*, (2005)

However, to optimize the use of ILs and design the desirable ILs, knowledge of their physical and chemical properties is of vital information. Zhang *et al.*, (2006)

It is imperative for any industry to understand the properties of ILs prior to their application in any of their processes. Physical properties such as density, viscosity and the melting point are associated with the engineering and mechanical components of the process. The properties of the ILs are also Important to validate theoretical models or for selection of suitable ILs to use for specific chemical process. Zhang *et al.*, (2006)

## 1.6 LIQUID-LIQUID EXTRACTION

An important step within the processes in the petrochemical industry is the recovery of high-purity hydrocarbons from naphtha. Aromatic compounds are separated from the aliphatic hydrocarbons present in naphtha through solvent extraction since distillation is not suitable due to close boiling points of these compounds. Santiago and Aznar, (2007)

Solvent extraction is one of the most significant methods to produce high-purity aromatic extracts from catalytic reformates .Yang-Xin *et al.*, (2001).

As an effective method, extraction and extractive distillation, with the separating agent especially a polar solvent have been used to separate the slightly polar compound from the non-polar compound. Sithole *et al.*, (2006)

The separation is based entirely on limited liquid miscibility and the distribution of solutes between two liquid phases. The separation of two components in solution is achieved by addition of the third component.

The liquid, third component (extractant) which is added to the solution to bring about the extract is known as the solvent or entrainer. This solvent takes up part of the components of the original solution and forms an immiscible layer composed of the remainder of the original solution plus some of the solvent, termed raffinate.

Phase equilibrium involves the transfer of substance from one phase to another. When two phases are brought into contact they exchange their constituents until the composition of each phase attains a constant value and equilibrium has been attained as shown in Figure 1.6 below.

The equilibrium composition of the two phases can be very different from one another and it is this difference which enables mixtures to be separated by distillation, extraction and other phase contacting operations. Reddy, (2003)

### 1.6.1 Principle of liquid-liquid extraction

In the design of such processes, it is necessary to know the data that can be used to calculate the composition of the two phases in equilibrium.

It is essential that liquid mixture and the solvent are at least partially or completely immiscible, generally, three stages are involved as shown by Figure 1.6 below:

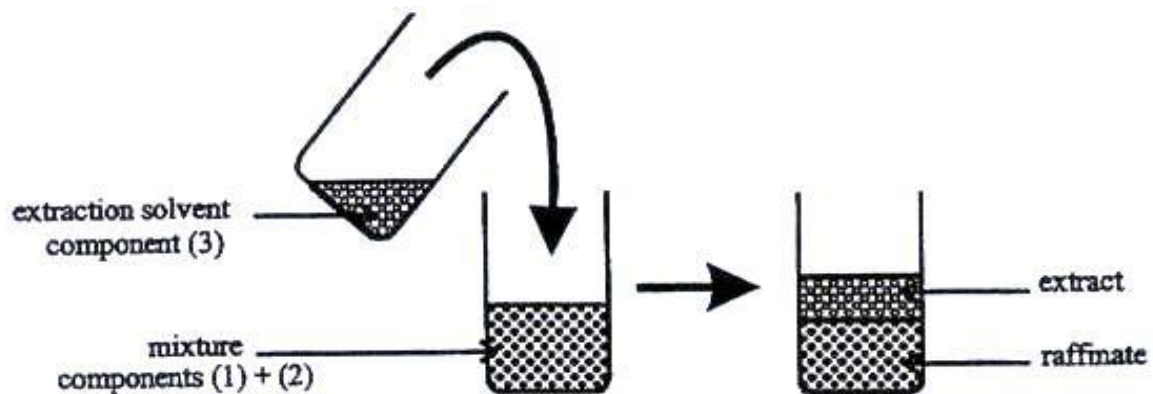


Figure 1.6 Principle of liquid -liquid extraction

From Figure 1.6 it is clear that the basic principle of LLE involves the following three simple steps:

- (i) Bringing the mixture and the solvent into intimate contact
- (ii) Separation of the resulting two phases,
- (iii) Removal and recovery of the solvent from each phase.

The equilibrium phase depends on variables such as temperature, pressure, chemical nature and concentration of the various substances involved.

Phase equilibrium thermodynamics seeks to establish the relationship between the various properties when the system is at equilibrium and it is related quantitatively to the intensive properties, that is, temperature and pressure which describe the equilibrium state of two or more homogenous phases. Naicker, (2000).

### **1.6.2 Phase Diagrams**

A phase diagram is defined as a map of a substance that shows the conditions of the temperature and pressure at which its physical state (solid, vapour or liquid) phases are thermodynamically stable. The phase boundaries are the boundaries between the regions and they show the values of temperature and pressure at which the two neighboring phases demonstrate or show equilibrium.

The condition of phase equilibrium involves the transfer of the solute particles from one phase to another phase in a dynamic fashion. It is achieved when the composition of the phases in contact with one another becomes constant, that is, there is no net transfer of solute particles between the phases. Sithole, (2012)

### **1.6.2.1 Phase rule**

In one of the most elegant calculations in the field of chemical thermodynamics, J.W. Gibbs deduced the phase rule: Barrow, (1996) and Atkins, (2002)

$$F = C - P + 2 \tag{1.3}$$

Where  $F$  is the variance of the system, which the number of intensive variables that can be changed, without changing the number of phases in equilibrium.  $C$  refers to the number of the components in the system and  $P$  is the number of phases.

Therefore for a three component system or in the ternary system:  $F = 5 - P$

Holding the temperature and pressure constant leaves two degrees of freedom, that is, the mole fraction of two of the components, mole composition of the third component is obtained by subtraction of the known two mole fractions.

### 1.6.2.2 Triangular Phase Diagrams

Phase diagrams show the region of thermodynamic stability and in particular are appropriate visual aids in observing the miscibility of the components in ternary liquid systems.

The data in this project for ternary liquid-liquid equilibria will be presented as shown in Figure 1.7 below:

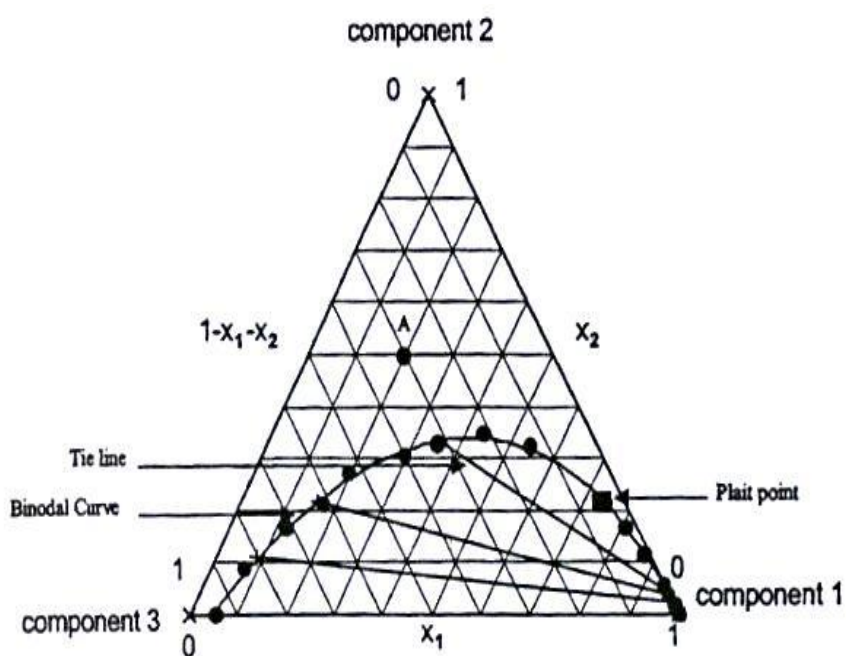


Figure 1.7 Representation of ternary liquid- liquid equilibria using a triangular phase diagram

In Figure 1.7 above; the curve separating the two-phase region (below the curve) from the single-phase (above the curve) is called a binodal curve.

The two-phase region is formed as a result of the system not being able to maintain homogeneity across the composition range and shows immiscibility by separating into two phases in equilibrium with each other at a particular composition range.

The tie-line is the line that intersects the binodal curve at two points and it serves to give the compositions of the two liquid phases (conjugate) in equilibrium at the experimental temperature and pressure of the system.

The plait point (PP) or critical point is approached as tie-lines become shorter and shorter, until the plait point is reached where only one phase exists. It is the point where the composition of the two phases in equilibrium is identical. Naicker, (1997)

$x_1$  and  $x_2$  represent the mole fraction of component 1 and 2 in a ternary mixture respectively.

The third component is given by the subtraction of the above mole fractions from one.

# CHAPTER 2: LITERATURE REVIEW

## 2.1 CONVENTIONAL SOLVENTS USED IN LLE

Ghanadzadeh, Moein *et al.*, (2012) presented liquid liquid equilibrium data for the system {water + propionic acid + isobutyl acetate} at  $T = (298.2, 303.2, 308.2 \text{ and } 313.2)$  K and atmospheric pressure. It was reported that the studied ternary system exhibit the type-1 behavior of LLE. For the investigated temperature range, it was noted that the separation factor changed little with temperature. Their findings confirmed that organic solvents has relatively high separation factor, indicating the ability of solvent to extract acid from water. The experimental LLE data was correlated using the universal-quasi-chemical (UNIQUAC) method of Abrams and Prausnitz and the Non-Random, Two Liquid (NRTL) model of Renon and Prausnitz at each temperature. The reliability of experimental tie-line data was determined by applying Othmer-Tobias and hand correlations.

Ebrahim, Hermayat and Safar (2012) presented the aqueous two phase system for {1-propanol,2-propanol,2-methyl-2-propanol,2- butanol or ethanol + sodium sulfate + water} ternary system at  $T = 298.15$  K and the experimental binodal and tie-line data for the ternary systems were reported and it was found that the phase- separation ability of studied alcohols is in order of 2- butanol>2-methyl-2-propanol>1-propanol>2-propanol>ethanol . Their results confirmed that the two-phase forming ability of the slightly soluble alcohols is more than the

completely miscible alcohols due to the weak intermolecular interactions with water molecules. Their boiling-points data demonstrated that the alcohol with higher boiling-points, in both completely miscible and slightly soluble cases, has more self-interaction forces between alcohol molecules and have more affinity to form an aqueous two phase system (ATPS). The cloud-point data showed the phase-separation ability of the system composed of {1-propanol or 2-methyl-2-propanol + sodium thiosulfate + water} to have an increasing effect with the increasing temperatures whereas in the case of {ethanol + sodium thiosulfate + water} system phase-separation ability was decreased. Furthermore, the temperature had no significant effect on the LLE of {2-propanol or 2-butanol + sodium thiosulfate + water} ATPS. The segment based Willison equation was generalized to represent the mixed organic-aqueous solvent electrolyte systems and successfully used for correlation of binary and ternary data and the restricted binary interactions were also reported. The tie-line composition were also correlated using the e-NRTL model and their comparison between the experimental and calculated values showed that the performance of generalized Willison model in the correlation of the binary and ternary data is very good and better as compared to the e-NRTL.

Trivesh *et al.*, (2011) presented liquid-liquid equilibria data for the system {dodecane + methanol + water} at  $T = 298.14$  K and  $T = 313.14$  K under atmospheric pressure. It was reported by the authors that the two liquid phases were almost entirely immiscible at low alcohol concentrations as evidenced by the data for all systems they studied. They also found out that the increase in temperature resulted in an increase in the mutual miscibility of the two liquid phases. They noted that water was totally immiscible in dodecane in almost all cases

presented, but the increase in carbon chain of the alcohol from C<sub>1</sub> (methanol) to C<sub>2</sub> and C<sub>3</sub> (ethanol and propan-2-ol), greatly increased the miscibility of the system. They reported the methanol system as their only case where plait point (PP) was not observed at temperatures investigated. The binodal curves were correlated using three equations with the best fit in all their cases being obtained with logY equation. Their greatest deviation from their experimental data was obtained with the Hlavaty equation in all their cases. Their tie-lines were correlated using NRTL and UNIQUAC equation and it was reported that the NRTL model provided an equivalent or better fit to the experimental data than the UNIQUAC equations even though there was not much deviations between the two models.

Gholam, Hassan and Nasser (2009) studied the liquid –liquid equilibrium data for the ternary system {water + 2, 3-butanediol + oleyl alcohol} at  $T = (300.2, 307.2 \text{ and } 314.2)$  K. The complete phase diagrams were obtained by determining solubility and tie-line data. The tie-line composition was correlated by Othmer-Tobias and Bancman methods. The NRTL was used to correlate the phase equilibrium in the system using the interaction parameters determined from their experimental data. It was reported that the NRTL could give good correlation for the LLE data. Distribution coefficients and selectivity factors were evaluated for the immiscibility region. It was noted that oleyl alcohol was very little soluble in water but miscible with 2, 3-butanediol. From their phase diagrams they deduced that the system exhibit type-1 phase behavior, having only one liquid pairs partially miscible {oleyl alcohol + water} and two pairs completely miscible {oleyl alcohol+ 2, 3-butanediol} and {water + 2, 3-butanediol}. It was also observed that oleyl alcohol has the advantage of very low mutual solubility and may be considered as a good solvent for liquid –liquid extraction process. Their experimental data also

indicated oleyl alcohol to have high separation factor, which shows its ability to extract 2, 3-butanediol from water

In-Chang, So-jin and Jong-Sup (2008) studied the liquid-liquid equilibria for the binary system of {di-isopropyl ether (DIPE) + water + C<sub>1</sub>- C<sub>4</sub> alcohol} at  $T = 298.15$  K. The ternary LLE for systems of {DIPE + water + C<sub>1</sub>- C<sub>4</sub> alcohols (methanol, ethanol, 1-propanol, 1-butanol and 2-butanol)} were determined at  $T = 298.15$  K and atmospheric pressure, both their binary and ternary LLE data were correlated with NRTL and UNIQUAC models. The lower alcohols (methanol, ethanol, 1-propanol and 2-propanol) were found to be totally miscible with water and DIPE, while 1-and 2-butanol showed partial solubility with water, therefore it was concluded that the latter alcohols show type 2 LLE behavior and showed no plait point, while the lower alcohols exhibit type 1 LLE behavior. It was again reported that methanol is more soluble in water than in DIPE, while ethanol, 1-propanol, 2-propanol, 1-butanol and 2-butanol are more soluble in DIPE than in water. It was stated that the hydrophobic effects depends roughly on the surface area of hydrocarbon group. Their experimental, NRTL and UNIQUAC calculated data showed good correlation.

Ghanadzadeh, Ganadadzadeh and Bahrpaima (2009) presented the measurement and prediction of tie-line data mixture of {water + 1-propanol + diisopropyl ether (DIPE)} as a function of temperature. The tie-line data for ternary systems of {water + 1-propanol + (DIPE)} were determined at  $T = (298.2, 308.2$  and  $313.2)$  K under atmospheric conditions. The ternary system exhibit type 1-LLE behavior as the {DIPE + water} was the only liquid pair partially miscible.

Their experimental data for the investigated system was predicted with the UNIQUAC model with their root mean square deviation at 2.64%. The reliability of their data (experimental tie-lines) was determined through the Othmer-Tobias and hand plots. The distribution coefficients ( $k$ ) and separation factors ( $S$ ) were measured to evaluate the extracting capability of the solvent. It was reported by authors that temperature influenced the equilibrium characteristics and separation factor. It was also stated that the area of two phase region depends on the solubility of water in organic phase. DIPE, due to its high boiling point and low solubility in water, was found to be good solvent for liquid-liquid extraction process.

Cháfer, de la Torre, Monton and Lladosa (2008) presented the liquid-liquid equilibria of the systems {isobutyl acetate + isobutyl alcohol + water} and {isobutyl acetate + isobutyl alcohol + glycerol} at different temperatures. The NRTL and UNIQUAC models were applied to both binary systems and successfully correlated the equilibrium compositions. For the studied systems measured at  $T = 283.15$  K and  $T = 323.15$  K, it was reported that temperature had no effect on the size of immiscibility region in the mentioned temperature range. The correlation with the NRTL equations gave better results for the system {isobutyl acetate + isobutyl alcohol + water} and the UNIQUAC equation fits the experimental data for the system {isobutyl acetate + isobutyl alcohol + glycerol} better. Their simultaneous correlation in all LLE experimental data for the two temperatures gave a unique set of parameters in the range of temperature considered, which allowed for the description of the phase equilibrium behavior appropriately. It was found that the UNIQUAC group contribution method gave relatively good prediction of the (liquid-liquid) equilibrium for {isobutyl acetate + isobutyl alcohol + water}

but very different for {isobutyl acetate + isobutyl alcohol + glycerol} system. The distribution coefficients of isobutyl alcohol in both liquid phases showed that water and glycerol could not be good solvents in separation of the studied azeotropic mixture, {isobutyl acetate + isobutyl alcohol}.

Mehmet and Arisoy (2006) presented liquid phase equilibria of {water + propionic acid + oleyl alcohol} ternary system at several temperatures and atmospheric pressure. The solubility curves and the tie-line compositions of liquid phases at equilibrium were determined and the tie line results were compared with the data predicted by the UNIFAC method. The distribution coefficients and selectivity factors for the immiscibility region were calculated to evaluate the effect of temperature change. The reliability of their experimental tie-lines was confirmed by using Othmer-Tobias correlation. It was found that oleyl alcohol showed little solubility in water but miscible with propionic acid. The effectiveness of the propionic acid extraction by oleyl alcohol was indicated by the high separation factor, which is a measure of the ability of the oleyl alcohol to separate the propionic acid from water. Although they observed the UNIFAC prediction not to fit the experimental data quantitatively, it agreed for the qualitative predictions. It was also deduced that temperature had no effect on the size of immiscibility region at the temperature studied. It was concluded that oleyl alcohol may serve as an adequate solvent to extract propionic acid from its dilute aqueous solution.

Monica, Gramajo *et al.*, (2003) reported the liquid-liquid equilibria data for the systems {cyclohexane + methanol + water} and {benzene + methanol + water} at  $T = 303.15$  K. The authors stated that when a phase separation occurs, a large fraction of methanol is drawn in to

the aqueous phase, and there is greater solubility of benzene compared to cyclohexane. The LLE data was fitted with UNIQUAC equation and UNIFAC model. The latter fit was poor in terms of solute distribution ratio due to large relative errors associated with very low concentrations of some compounds in both phases.

Deenadayalu and Letcher (1999) presented the liquid-liquid equilibria of the system {quinoline + methanol + water} at  $T= 298.2$  K and 1 atmosphere. It was reported that the shape of binodal curve is very much dependent on the type of alcohol. The minimum concentration (in mole fraction) for the alcohol solubility in the quinolone-water system was found to be 0.25; 0.26; 0.35; and 0.43; for 2-propanol, 1-propanol, ethanol, methanol and 1-butanol respectively. The tie-line slope indicated that in all cases the alkanols are more soluble in the quinolone-rich phase than the water –rich phase with a large skewing toward the water axis. The data fitting of binodal curves show good correlation with Hlavatý equation, the  $\beta$  density function and the logarithmic gamma functions. The authors concluded that the area of two phase region increases in the order 2-propanol < 2-methylpropan-2-ol < methanol < 1-propanol < ethanol < 2-butanol < 1-butanol < 2-methyl propan-1-ol.

Table 2.1 is a summary liquid-liquid equilibria literature data for azeotropic mixtures for conventional solvents together with the selectivity values and authors cited.

**Table 2.1 Literature data of conventional solvents, their azeotropic mixture, selectivity values and authors cited.**

Conventional solvent	Azeotropic Mixture	Selectivity values	Authors Cited
Acrylic acid	Butan-1-ol or Butan-2ol or pentan-1-ol + water	<b>4.8 -21.1</b>	Melissa <i>et al.</i> ; <i>J.Chem thermodyn.</i> 43(2011)1381-1388
n-amyl acetate	Ethanol or Methanol + water	<b>5.5 -788.7</b>	Alberto <i>et al.</i> ; <i>Fluid Phase Equilibria.</i> 109(1995)291-297
Diethyl ether and dichloromethane	Ethanol, Methanol and 1-Propanol + water	<b>2.03 -132.9</b>	Merzogui <i>et al.</i> ; <i>Fluid Phase Equilibria.</i> 309(2011) 161- 167
Diisopropyl ether(DIPE)	1-Propanol + water	<b>2.82 -258.0</b>	Ghanadzadeh <i>et al.</i> ; <i>Fluid Phase Equilibria.</i> 277(2009) 126-130
Ammonium Sulphate	Isopropanol,n-butanol + water	<b>2.82 -22.56</b>	Ziyan <i>et al.</i> ; <i>Fluid Phase Equilibria.</i> 317(2012) 1-8
<ul style="list-style-type: none"> <li>▪ 2-methylbutylethanoate</li> <li>▪ 1,2 dichloroethane,</li> <li>▪ 1-octanol,</li> <li>▪ Cyclohexane</li> <li>▪ ethyl acetate</li> </ul>	Tetrahydrofurfural alcohols + water	<b>0 - 114.70</b> <b>0 - 25.03</b> <b>0 - 91.23</b> <b>0 - 64.06</b> <b>0 - 12.23</b>	Senol <i>et al.</i> ; <i>Fluid Phase equilibria.</i> 106(1995) 169-183

**Table 2.1 Continued**

<b>Conventional solvent</b>	<b>Azeotropic Mixture</b>	<b>Selectivity values</b>	<b>Authors Cited</b>
Diisopropyl ether(DIPE)	C1-C4 alcohols + water	<b>0.13 -432.9</b>	In-Chang <i>et al.</i> ; <i>Fluid Phase Equilibria.</i> 269(2008) 1-5
Isobutyl acetate	Isobutyl alcohol + water	<b>79.02 -307.53</b>	Cháfer <i>et al.</i> ; <i>Fluid Phase Equilibria.</i> 265(2008) 1-5
Diisopropyl ether(DIPE)	Propargyl alcohol + water	<b>0.0 -0.54</b>	Kongmeng <i>et al.</i> ; <i>Fluid Phase Equilibria.</i> 260(2007)262 -265
Acetic acid	Isobutyl alcohol + water	<b>0.0- 49.58</b>	Cháfer <i>et al.</i> ; <i>Fluid Phase Equilibria.</i> 271(2008) 76-81
Acetone	C <sub>1</sub> -C <sub>5</sub> alcohols + water	<b>2.77- 38.0</b>	Tiryaki <i>et al.</i> ; <i>Fluid Phase Equilibria.</i> 94(1994) 267-280

**Table 2.1 Continued**

<b>Conventional solvent</b>	<b>Azeotropic Mixture</b>	<b>Selectivity values</b>	<b>Authors Cited</b>
Butyric Acid	Isobutyl alcohol + water	<b>38.0 -159.0</b>	Mehemet <i>et al.</i> ; <i>J. Chem. Thermodyn.</i> 37(2005) 297 – 303
Heavy alcohols :			
▪ 1-hexanol	2-Butanol + water	<b>4.35 -6.27</b>	Ghanadzadeh <i>et al.</i> ; <i>J. Chem. Thermodyn.</i> 49(2012) 39-45
▪ 1-Heptanol		<b>5.44 -8.17</b>	
▪ 1-Octanol		<b>4.68 -9.33</b>	
▪ 1-decanol		<b>5.14 -11.50</b>	
Propanoic Acid	Oleyl alcohol + water	<b>4.14 -411.37</b>	Mehemet <i>et al.</i> ; <i>Fluid Phase Equilibria.</i> 250(2006)59 –63
Cyclohexane/Benzene	Methanol + water	<b>3.20 – 475.0</b>	Monica <i>et al.</i> ; <i>J. Chem. Thermodyn.</i> 35(2003) 825 837
Carboxylic acid/alcohol	1-hexanol + water	<b>1.18 – 16.96</b>	Senol <i>et al.</i> ; <i>J. Chem Thermodyn.</i> 36(2004) 1007-1014
Tetrahydrofuran	Nonprotic Solvent + water	<b>3.20- 320.10</b>	Senol <i>et al.</i> ; <i>J. Chem Thermodyn.</i> 38(2006) 578-584
Propanoic Acid	Octanol or decanol or dodecanol + water	<b>1.12 -1.19</b>	Ismail <i>et al.</i> ; <i>Fluid Phase Equilibria.</i> 38 (2006) 1503 -1509
Phosphoric Acid	1-butanol or butyl acetate + water	<b>1.19 – 5.88</b>	Ghanadzadeh <i>et al.</i> ; <i>J.chem Thermodyn.</i> 40(2008)1666-1670

**Table 2.1 Continued**

<b>Conventional solvent</b>	<b>Azeotropic Mixture</b>	<b>Selectivity values</b>	<b>Authors Cited</b>
4-Methyl-pentanone	Ethanol/n-butanol + water	<b>20.61 -41.8</b>	Cháfer <i>et al.</i> ; <i>Fluid Phase Equilibria</i> . 317(2012) 89-95
Ethanol	Sodium thiosulfate + water	<b>13.87 -26.0</b>	Ebrahim <i>et al.</i> ; <i>Fluid Phase Equilibria</i> . 321(2012) 64-72
1-Propanol		<b>18.22 -26.35</b>	
2-Propanol		<b>8.25 - 10.51</b>	
2-Methyl-2-Propanol		<b>6.68 - 9.24</b>	
2-Butanol			

In summary, from Table 2.1 above, the highest selectivity (788.7) is observed with the use of the ester, *n*-amyl acetate, as an extractant in the separation of the azeotropic mixture {methanol or ethanol + water}. Alberto *et al.*, (1995). This separation for the alkanols is of interest but *n*-amyl acetate is more toxic than the aliphatic esters with a threshold limit (TLV) (human exposure limit) value of 100 ppm. John *et al.*; (2007). At higher concentrations it is not user and environmentally friendly.

The ether di-isopropyl ether (DIPE) gave the highest selectivity of 432.0, but ethers are also hazardous organic compounds which are not user and environmentally friendly at higher concentrations, with the reported ether (DIPE) having a TLV of 400 ppm. John *et al.*; (2007).

Ketones had low selectivity values (below 50), as much as the reported values are greater than one, the ketones reported (acetone and 2-methyl-pentanone) are still known to be volatile organic compounds which are also not user nor environmentally friendly.

Phosphoric acid is also not user friendly and had low selectivities (<5.58) as reflected in Table 2.1.

Volatile Organic Compounds (VOCs) which mostly are the conventional solvents discussed above are among the most common air pollutants emitted from chemical, petrochemical, and allied industries. VOCs are one of the main sources of photochemical reaction in the atmosphere leading to various environmental hazards and a depletion of ozone layer thus create more problems associated with global warming phenomena. Heavy reliance in organic solvent in any chemical processes requires new developed technologies which will enable the reduction of their emission and prevent the atmospheric pollution thereof due to a growing environmental awareness that has put up stringent regulations to control the emissions of VOCs. Khan and Goshal, (2000).

Most VOC's as discussed based on their TLV are again:

- Toxic and hazardous.
- Not environmentally friendly.
- Not user friendly.

- Major atmospheric pollutants.
- And not good to aquatic life.

Therefore there is a serious need to search for both user and environmentally friendly solvents for effective and efficient separation methods such as LLE.

## 2.2 GREEN SOLVENTS/“DESIGNER SOLVENTS” USED IN LLE

Marcinak and Krolkowski (2012) reported the ternary liquid –liquid equilibria of {bis (trifluoromethylsulfonyl)-amide based ionic liquids + methanol + heptane}. The ternary liquid-liquid equilibria for their three systems containing ionic liquids {(4-(2-methoxyethyl)-1-methylpyrrolidinium bis (trifluoromethylsulfonyl)-amide) + methanol + heptane} were determined at  $T = 298.15$  K. All systems showed total miscibility of methanol in the ionic liquids and low solubility of heptane. The solute distribution ratio and the selectivity were calculated for all systems and high selectivity and solute distribution ratios were obtained for all systems. Their experimental data have been correlated using NRTL model. They reported highest values of selectivity to be that of [COC<sub>2</sub>mMOR][NTF<sub>2</sub>] systems which were three times higher than for ionic liquids based on piperidinium and pyrrolidinium cations. They justified this as to due to a small difference in the structures of [COC<sub>2</sub>PIP][NTF<sub>2</sub>] and [COC<sub>2</sub>mPYR][NTF<sub>2</sub>] which revealed selectivities on the same level, it was also reported that in each case the selectivity increases with an increase of the solute concentration. The result obtained suggest that the investigated ionic liquids could efficiently perform the separation of methanol/heptane mixture, especially the use of [COC<sub>2</sub>mMOR][NTF<sub>2</sub>] IL.

Domańska, Krolikowski *et al.*, (2012) presented the study on solubility of ionic liquids in water and octan-1-ol/water or 2-phenylethanol/water partition coefficients. The solubility of ionic liquids [1-ethyl-3-methylimidazolium]-tris-(pentafluoroethyl)-tri-fluorophosphates, [EMIM][FAP] and [1-hexyl-3-methylpyridinium-triflate], [HM<sub>3</sub>Py][CF<sub>3</sub>SO<sub>3</sub>] in 1-octanol, water and 2-phenylethanol were investigated at  $T = 270$  K and  $T = 360$  K under ambient pressure, the immiscibility in the liquid phase with an upper critical solution temperature (UCST) was observed in the system of {[EMIM][FAP] + 1-octanol + water} and the complete miscibility in the liquid phase were observed for binary system {[EMIM][FAP] + 2-phenylethanol} and they also observed for binary {[HM<sub>3</sub>Py][CF<sub>3</sub>SO<sub>3</sub>] + 1-octanol or 2-phenylethanol} with miscibility gap in water. Their binary phase diagrams for [EMIM][FAP] reveal the liquid –liquid immiscibility windows with upper critical solution temperature (UCST), it was reported that the solubility of 1-octanol in [EMIM][FAP] is higher than that of water. They observed the complete miscibility in liquid phase at  $T = 298.15$  K. The phase diagrams for {[HM<sub>3</sub>Py][CF<sub>3</sub>SO<sub>3</sub>] + 1-octanol or 2-phenylethanol or water} showed simple liquidus curves with complete miscibility in the liquid phase for alcohols and the liquid-liquid immiscibility window with UCST for water.

The solubility of [HM<sub>3</sub>Py][CF<sub>3</sub>SO<sub>3</sub>] was reported to be lower in 1-octanol than it is in 2-phenylethanol and miscibility gap observed in the water-rich liquid mixture.

Domańska, Zawadziki, Krolikowski and Lewandrowska (2012) presented a paper on phase equilibria study of binary and ternary mixtures of {N-octylisoquinoliniumbis [(trifluoromethyl) sulfonyl] imide + hydrocarbon, or an alcohol or water}. They studied the isoquinolinium ionic liquids with the temperature composition phase diagrams of 13 binary mixtures composed of the ionic liquid {N-octylisoquinoliniumbis [(trifluoromethyl) sulfonyl] imide}, {[C<sub>8</sub>iQuin][NTF<sub>2</sub>]} and an aliphatic hydrocarbon (n-hexane or n-heptane) or cyclic hydrocarbons (cyclohexane or cycloheptane) or an aromatic hydrocarbon (toluene, or ethyl benzene, or n-propylbenzene, or thiophene) or an alcohol which was (1-butanol, or 1-hexanol, or 1-octanol, or 1 decanol, or 1-dodecanol or 2-phenyl ethanol) or water determined from ambient temperature to the boiling point temperature of the solvent at ambient pressure. A dynamic method was used over broad range of mole fractions and temperature from  $T = 260$  K to  $T = 360$  K.

For the binary systems authors observed the immiscibility in the liquid –phase with UCSTs in all mixtures. It was only in the binary system {IL + alkylbenzene} where they detected one experimental point of immiscibility due to high UCSTs and complete solubility was only observed for 1-butanol and 2-phenylethanol. The ternary systems of {[C<sub>8</sub>iQuin][NTF<sub>2</sub>] + 2-phenylethanol + water} was also investigated at  $T = 298.15$  K in order to analyze the the potential of the IL for extraction of 2-phenylethanol from the reaction medium in biosynthesis. The selectivities and the distribution co-efficient of the 2-phenylethanol were found to be high (1539 and 1214). All their experimental data was correlated using the NRTL model.

Urszula and Merék (2010) presented the phase equilibria study of the binary systems {1-butyl-3-methylimidazolium tosylate ionic liquid +water or organic solvent}. The liquid –liquid phase equilibria together with the solid-liquid phase equilibria were determined at ambient pressure and temperature range of  $T = 230$  K to  $T = 240$  K for the binary systems ionic liquid {1-butyl-3-methylimidazolium tosylate (*p*-toluenesulfonate)}([Bmim][TOS]) + water} an alcohol (ethanol, or 1-butanol, or 1-hexanol, or 1-octanol or 1-decanol)}, or n-hexane or an aromatic hydrocarbons (benzene, or toluene or ethyl benzene or propyl benzene, or thiophene).

They observed simple eutectic diagrams for binary systems containing water or an alcohol with complete miscibility in the liquid phase. But in the case of {IL + n-hexane, or benzene, or alkyl benzene or thiophene} the eutectic systems with mutual immiscibility in the liquid phase with an upper critical solution temperature were detected. They've also determined the basic thermal properties for the IL used for the investigation. The well-known UNIQUAC, Wilson and the NRTL models were used to correlate experimental SLE data sets for alcohols and water. For the systems containing immiscibility gaps {IL + n-hexane, or benzene or alkylbenzene or thiophene} the LLE correlation was derived using NRTL equation.

Table 2.2 list the literature data for the separation of azeotropic mixtures using ionic liquids for the separation: the azeotropic mixture, selectivity values and authors cited.

**Table 2.2 Literature data of ionic liquids, azeotropic mixture, selectivity values and the authors cited.**

<b>Ionic Liquid</b>	<b>Azeotropic Mixture</b>	<b>Selectivity values</b>	<b>Authors Cited</b>
1-hexyl-3-methylimidazolium tetracyanoborate	Butan-1-ol + water	<b>45.9 -66.5</b>	
1-decyl-3-methylimidazolium tetracyanoborate	Butan-1-ol + water	<b>45.2-124.8</b>	Domańska <i>et al.</i> , <i>J. Chem. Thermodyn.</i> 53 (2012) 108-113
Trihexyltetradecylphosphonium tetracyanoborate	Butan-1-ol + water	<b>50-903</b>	
N-octylisoquinolinium bis{(trifluoromethyl)sulphonyl}imide	1-butanol,1-hexanol,1-octanol,1-decanol,1-dodecanol,2-phenylethanol + water	<b>306.1-1214.2</b>	Domańska <i>et al.</i> , <i>J. Chem. Eng. Data.</i> 181-182 (2012) 63-71
1-Hexyl-3-methylimidazolium hexafluorophosphate	Cyclohexane + 2-butanone	<b>4.36-114.85</b>	Pereiro and Rodriguez. <i>J. Chem. Thermodyn.</i> 40(2008)1282-1289
1-methyl-3-octylimidazolium hexafluorophosphate		<b>2.71-55.30</b>	

**Table 2.2 Continued**

<b>Ionic Liquid</b>	<b>Azeotropic Mixture</b>	<b>Selectivity values</b>	<b>Authors Cited</b>
4-methyl-N-butylpyridinium tetrafluoroborate	Toluene + n-heptane	<b>12.14-53.09</b>	Andre B.de Haan <i>et al.</i> , <i>Fluid Phase Equilibria</i> , 247(2006)158 -168
1-ethyl-3-methylimidazolium ethylsulfate	Toluene + n-heptane	<b>5.61-55.29</b>	
1.3-dimethylimidazolium methylsulfate	Toluene + n-heptane	<b>6.34-61.35</b>	Garcia <i>et al.</i> , <i>J.Chem Thermodyn.</i> 42(2010)1004-1008
1-butyl-3-methylimidazolium methylsulfate	Toluene + n-heptane	<b>9.21-35.02</b>	
2-methyl-N-butylpyrididinium tetrafluoroborate	Toluene + Heptane	<b>23.1-60.0</b>	
3-methyl-N-butylpyrididinium tetrafluoroborate	Toluene + Heptane	<b>16.6 -55.0</b>	
4-methyl-N-butylpyrididinium tetrafluoroborate	Benzene + Cyclohexane	<b>16.8 -57.9</b>	Yang <i>et al.</i> , <i>J.Chem.Eng.Data</i> 55(2010)510-512
1-Butyl-3-Methylimidazolium Hexafluorophosphate.		<b>20.9-58.4</b>	
Hexyl(2-hydroxyethyl) dimethylammonium tetrafluoroborate	Ethanol + Hexane	<b>18.9-1584</b>	Domańska <i>et al.</i> , <i>J. Chem. Eng. Data</i> 54(2009)972-976

**Table 2.2 Continued**

Ionic Liquid	Azeotropic Mixture	Selectivity values	Authors Cited
Ethyl(2-hydroxyethyl)dimethylammonium bis(9trfluoromethyl)sulfonyl}imide	Alkane + Aromatic Hydrocarbons	<b>2.0-56.0</b>	Domańska <i>et al.</i> , <i>Fluid Phase Equilibria</i> . 259 (2007)173-179
4-methyl-N-butylpyridinium tetrafluoroborate	Aromatic + Aliphatic hydrocarbon	<b>22.9 -103.8</b>	Andre B.de Haan <i>et al.</i> , <i>J. Chem.Eng.Data</i> . 51(2006)1814-1819
1-Butyl-3-methylimidazolium methylsulfate	Hexane + Benzene	<b>21.0-64.7</b>	Garcia <i>et al.</i> , <i>J. Chem.Eng.Data</i> . 55(2010)258-261
1.3-dimethyl-2-imidazolidinone	an alkane + an aromatic compound	<b>3.0-59.0</b>	Deenadayalu <i>et al.</i> , <i>J. Chem.Eng.Data</i> . 46(2001)177-183
1-ethyl-3-methylpyridinium ethylsulfate	Benzene + alkanes	<b>42.27-160.03</b>	Gonzalez <i>et al.</i> , <i>J.Chem Thermodyn</i> . 42(2010)104-109

**Table 2.2 Continued**

Ionic Liquid	Azeotropic Mixture	Selectivity values	Authors Cited
1-ethyl-3-methylpyridinium ethylsulphate	Alkane + Benzene	<b>16.17-103.17</b>	<i>Calvar et al., J. Chem Thermodyn. 41(2009)1215-1221</i>
1-butyl-3-methylimidazolium Hexafluorophosphate	Aromatic + Aliphatic	<b>0.41-5.85</b>	<i>Aznar et al., Fluid Phase Equilibria. 265(2008)129-138</i>
1-ethylpyridinium ethyl sulfate	Alkane + Benzene	<b>24.88-94.20</b>	<i>Calvar et al., J. Chem Thermodyn. 42(2010)1234-1239</i>
1-ethyl-3-methylimidazolium ethylsulfate	Hexane/Heptane + Ethanol	<b>2.96-3631.0</b>	<i>Pereiro et al., Fluid Phase Equilibria. 291(2010)13-17</i>
1-butyl-3-methylimidazolium hexafluorophosphate.	Benzene + cyclohexane	<b>20.9-58.4</b>	<i>Lu et al.; J. Chem. Eng. Data. 55(2010)510 - 512</i>
1-hydroxyethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	Alcohols + water	<b>4.0 -300</b>	<i>Chapeaux. Dissertation, Notre Dame, Indiana.(2009)</i>
1-hexyl-3-methylimidazoliumbis(trifluoromethylsulfonyl)imide			

It is evident from Table 2.2 above that the imidazolium based ILs for separation of C<sub>4</sub> alcohol and water azeotrope gave selectivity values that are in the range (4-300) and they increase with an increase in the alkyl chain length of the imidazolium cation. The phosphonium based ILs gave a higher selectivity value of (903) for the same separation. Domańska, (2012).

The quinolinium based ILs show high selectivity (1214.2) for higher alcohols from water. Domańska, (2012).

Pyridinium based ILs were investigated for the separation of aromatic compounds and aliphatic compounds with the highest selectivity value of (160) reported by Gonzales (2010), for all outlined aliphatic compounds and aromatic compounds on table 2.2 above. In comparison the imidazolium based ILs for separation of latter azeotrope has the highest selectivity value (64.7). Garcia, (2010).

For the ammonium based ILs only two systems have been reported: the azeotrope of alcohol and an alkane with a selectivity value of 1584 Domańska, (2009) and the other for aliphatic compounds and aromatic compounds with the selectivity value of (57) Domańska, (2007).

The ionic liquid of interest (1-ethyl-3-methylimidazolium ethylsulfate) which showed the maximum selectivity of (3631.0) for the azeotrope (ethanol and aliphatic compounds) Pereiro, (2010) and was chosen as the best ILs to be used for the azeotrope of this investigation. There is no literature data on LLE for the alcohol and water azeotrope using the IL 1-ethyl-3-methylimidazolium ethylsulfate.

## **2.3 THEORETICAL FRAMEWORK**

### **2.3.1 CORRELATION OF TERNARY LIQUID-LIQUID EQUILIBRIA**

A significant fraction of chemical process design is concerned with separation of fluid mixtures by diffusional operations. All design methods for such separations require quantitative estimates of fluid-phase equilibria, and liquid phase activity coefficients must be known, Sithole, (2012).

Two models will be discussed, namely Non-Random, Two Liquid (NRTL) equation, and Universal Quasi-Chemical (UNIQUAC) equation.

In the NRTL equation, the consideration is given to the prediction of ternary vapour and ternary liquid-liquid equilibria based on the binary data and UNIQUAC is applicable to multicomponent mixtures of non-polar and polar liquids and encountered in typical chemical and petrochemicals systems. Reddy, (2003).

With the local composition equations, prediction of the properties of multicomponent systems is possible without additional ternary or higher order parameters. For the NRTL equation, the excess Gibbs energy is derived from the liquid theory by taking into account only two-body interactions, and there is no need to introduce higher order interactions in the treatment of multicomponent systems when they were neglected for binary mixtures. The NRTL equation is a good and general equation for the prediction of ternary vapour-liquid as well ternary liquid-

liquid equilibria using only data for binary mixtures, but no ternary constant, if the optimum value of  $x_{12}$  for each binary chosen.

### 2.3.1.1 UNIQUAC Equation

Abrams *et al.*, (1995); derived an equation which in a sense extends the quasi-chemical theory of Guggenheim for non-random mixtures to solutions containing molecules of different size. This extension was therefore called 53 theory (UNIQUAC). The UNIQUAC model allows the satisfactory correlation of liquid–liquid equilibrium (LLE) data and excellent correlation of vapour–liquid equilibrium (VLE) data making simultaneous correlation of LLE and VLE data for ternary mixtures. Alberto, (1995).

Lattice partition is given by:

$$Z_{\text{lattice}} = \sum_{\text{all}} \Phi^W(\theta) \exp[-U_o(\theta)/KT] \quad (2.1)$$

where the  $W$  = the combinatorial factor (number of ways that the molecule can be arranged in space)

$U_o$  = potential energy of the lattice, it is closely related to the energy of isothermal vaporization from liquid to ideal gas state.

Both  $W$  and  $U_o$  depend on the molecular configuration of the mixture, designated by variable  $\theta$ :

$$\Phi_1 = \frac{x_1 r_1}{x_1 r_1 + x_2 r_2} \quad (2.2)$$

$\Phi$  is the average segment fraction:

$$\Phi_2 = \frac{x_1 r_1}{x_1 r_1 + x_2 r_2} \quad (2.3)$$

The activity coefficient for component 1 is given by the following equation:

$$\ln \gamma^i = \ln \frac{\Phi_i}{x_i} + \frac{(z)}{(2)} q_i \ln \frac{(\theta_i)}{(\Phi_i)} q_i l_i - \frac{\Phi_i}{x_i} \sum_j x_j l_j \quad (2.4)$$

$$- q_i \ln \sum \theta_i T_{ij} + q_i - q_i \sum \frac{\sum_j \theta_j T_{ij}}{\sum_k \theta_k T_{kj}} \quad (2.5)$$

where  $l_j = (z/2) (r_j - q_j) - (r_j - 1)$  and the average area function  $\Theta$  and average segment fraction  $\phi$  are defined by  $\Theta$  is and :

$$\theta_i = \frac{q_i N_i}{\sum_j q_j N_j} = \frac{q_i x_i}{\sum_j J q_j X_j} \quad (2.6)$$

and

$$\varphi_i = \frac{r_i N_i}{\sum_j r_j N_j} = \frac{r_i x_i}{\sum_j J r_j X_j} \quad (2.7)$$

Since the derived equation is based on the generalization or extension of Guggenheim's quasi-chemical model, the equation is referred to as the UNIQUAC.

The UNIQUAC model results in two contributions, the combinatorial term which is evaluated using group contributions to compute size parameters and the residual term which has two adjustable parameters for each binary system that is to be fitted to experimental data.

### 2.3.1.2 Non-Random, Two Liquid (NRTL) Equation

To take into account the non-randomness mixing, it is assumed that the relation between the local fractions,  $x_{21}$  and  $x_{11}$  is given by a modification of the equation:

$$\frac{x_{21}}{x_{11}} = \frac{x_2 \exp\left(-\frac{g_{21}}{RT}\right)}{x_1 \exp\left(-\frac{g_{11}}{RT}\right)} \quad (2.8)$$

To the following equation:

$$\frac{x_{21}}{x_{11}} = \frac{x_2 \exp\left[\alpha_{12} - \frac{g_{21}}{RT}\right]}{x_1 \exp\left[\alpha_{12} - \frac{g_{11}}{RT}\right]} \quad (2.9)$$

Where  $\alpha_{12}$  is a constant characteristic of non-randomness of the mixture.

Interchanging subscripts 1 and 2, Yield:

$$\frac{x_{21}}{x_{11}} = \frac{x_2 \exp\left[\alpha_{12} - \frac{g_{12}}{RT}\right]}{x_1 \exp\left[\alpha_{12} - \frac{g_{22}}{RT}\right]} \quad (2.10)$$

The local mole fractions are related by:

$$x_{21} + x_{11} = 1 \quad (2.11)$$

$$x_{12} + x_{22} = 1 \quad (2.12)$$

From equation (2.8) and (2.11) above we obtain for local fractions:

$$x_{21} = \frac{x_2 \exp\left[-\alpha_{12} - \frac{g_{12}}{RT}\right]}{x_1 + x_2 \exp\left[-\alpha_{12} - \frac{g_{22}}{RT}\right]} \quad (2.13)$$

Similarly from equation (2.11) and (2.14):

$$\alpha_{12} = \frac{x_1 \exp\left[-x_{12} \frac{(g_{12} - g_{22})}{RT}\right]}{x_2 + x_1 \exp\left[-g_{12} \frac{(g_{12} - g_{22})}{RT}\right]} \quad (2.14)$$

The residual energy for a cell containing molecule at its Centre is  $g^{(1)}$  and is given by:

$$g^{(1)} = x_{11}g_{11} + x_{21}g_{21} \quad (2.15)$$

If we consider pure liquid, 1,  $x_{11} = 1$  and  $x_{21} = 0$ .

In this case residual Gibbs energy for a cell containing a molecule 1 at its Centre:

$$g_{\text{pure}}^{(1)}, \text{ is } g_{\text{pure}}^{(1)} = g_{11} \quad (2.16)$$

and

$$g_{\text{pure}}^{(2)} = g_{22} \quad (2.17)$$

Thus the molar Gibbs energy for binary solutions is the sum of the two changes in residual energy, therefore:

$$G^E = x_1 (g^{(1)} - g_{\text{pure}}^{(1)}) + x_2 (g^{(2)} - g_{\text{pure}}^{(2)}) \quad (2.18)$$

Substituting equations from (2.8, up to 2.13 into 2.14) gives:

$$G^E = x_1 x_{22} (g_{21} - g_{11}) + x_2 x_{12} (g_{12} - g_{22}) \quad (2.19)$$

Where  $x_1$  and  $x_{12}$  are given by equation (2.1.7) and (2.1.8).

Equation (2.6) coupled with equation (2.10) and (2.11) is referred to as the NRTL equation.

With the local composition equations, prediction of the properties of multicomponent systems is possible without additional ternary or higher order parameters. For the NRTL equation, the excess Gibbs energy is derived from the liquid theory by taking into account only two -body interactions, and there is no need to introduce higher order interaction in the treatment of multicomponent systems when they are neglected for binary mixtures. The NRTL equation is a good and general equation for the prediction of ternary liquid-liquid equilibria (LLE) as well as ternary vapour-liquid equilibria(VLE) using only data for binary mixtures with no ternary constant if the optimum value of  $x_{12}$  for each binary is chosen.

The Root mean square deviation (RMSD) in NRTL parameter is given by the following equation:

$$\text{RMSD} = [\sum_i \sum_j \sum_k (\chi_{ijk}^{\text{exp}} - \chi_{ijk}^{\text{calc}})^2 / 6M]^{1/2} \quad (2.20)$$

# **CHAPTER 3: EXPERIMENTAL**

## **3.1 INTRODUCTION**

The measurement of the phase equilibrium involves the experimental determination or principally it is a measurement of pressure, temperature, phase composition and phase amounts. However experimentally it is not easy to obtain data of high and sufficient accuracy, great care must be taken to ensure and assure that equilibrium has been attained. The temperature and pressure measured at the point where equilibrium really exist need to be accurate. Also, sampling and conducting of analysis should not disturb the equilibrium and affect the composition. Reddy, (2003)

## **3.2 DETERMINATION OF THE BINODAL CURVES AND TIE-LINES IN A TERNARY SYSTEM**

### **3.2.1 Titration Method**

In this study the titration method adapted from that of Briggs and Comings, (1943) and modified by Letcher, (1989) was applied. The initial objective for development of titration method was for its application in situations where one component of the system is a non-volatile hence difficult to analyse by Gas-liquid Chromatography (GLC). Xhakaza, (2012); Sithole, (2012).

It is ideal to determine the binodal curves before the determination of the tie-lines which are easily determined by measuring the physical property of the thermodynamically stable sample. Binodal curves does not yield complete information on phase equilibria. It only defines the heterogeneous region, it is or can then be used to determine the composition of the conjugate phases when the properties of the system are known. Reddy, (2003). The basic technique of the titration method involves the addition of the third compound/component to the homogeneous binary mixture of the component 1 and 2 until the solution appears to be turbid or the “cloud-point” is attained. Reddy, (2003); Sithole, (2012). The mixture is then well agitated, maintained and kept at a constant temperature.

The determination of the tie-line composition is only to develop the standard curve that relates the composition of points, through the concentration of one of the components of the binodal curve, to simply allow the determination of physical or chemical properties such as density, refractive index or/and speed of sound.

The two-phase mixtures across the entire mole fraction range were prepared and left to reach equilibrium at constant temperature. This was achieved by vigorously mixing the components and allowing them to separate completely from one another. The conjugate phase composition was then determined by analyzing for the same property in both phases upon which standard curve is implemented. The measured physical property was then correlated by means of the standard curve to obtain the composition or stoichiometric reaction between components in the conjugate phases, hence establish the tie-line.

### **3.3 MEASURED PHYSICAL PROPERTIES IN THIS STUDY FOR DETERMINATION OF TIE-LINES**

#### **3.3.1 Density**

##### **3.3.1.1 Introduction**

The density ( $\rho$ ) of the sample is defined as the relationship between the mass (M) of the sample and its volume (V):

$$\rho = \frac{M}{V} \quad (3.1)$$

Density together with specific gravity values are highly temperature dependent.

#### **3.3.2 Refractive Index**

##### **3.3.2.1 Introduction**

The refractive index/indice ( $n_D$ ) of the sample is expressed as the ratio of the speed of the light in the vacuum ( $\int V$ ) to the speed of light in another substance or sample ( $\int S$ ):

$$n_D = \frac{\int V}{\int S} \quad (3.2)$$

The speed of light in the vacuum is always the same, but when the light travels through any other medium its speed is reduced since it is continuously absorbed and emitted by the atoms that are in substance or constitute the sample.

## 3.4 INSTRUMENTATION USED FOR ANALYSIS - DSA

### 5000 M

Figure 3.1 below is the front view photograph of the DSA 5000M instrument, The DSA 5000 M denoting the Density and Speed of Sound Analyzer 5000 M lab instrument has a robust design and precision and is both the density and sound velocity analyser/meter developed to combine the highest precision with ease of operation.



**Figure 3.1 Photograph of density and speed of sound analyzer (DSA 5000M)**

(Taken from the Anton Paar User Manual)

The DSA 5000M similar to the conventional DMA 38 densitometer also uses the oscillating U- tube method, the principle of operation for density determination outline the introductory of a sample into a U-shaped borosilicate glass tube that is being excited to vibrate at the

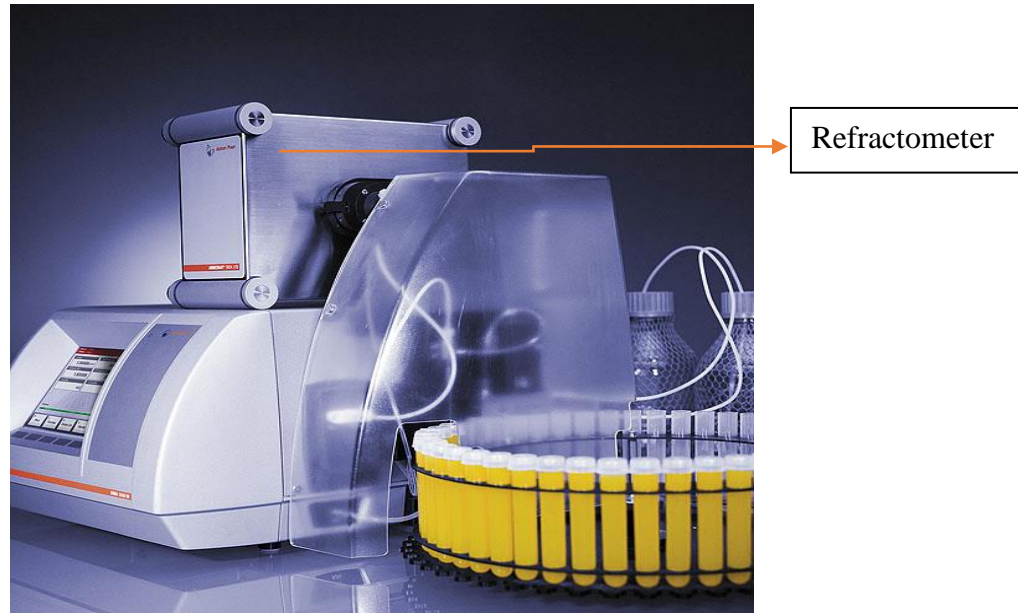
sample characteristics frequency electronically. The characteristic frequency changes depending on the density of the sample.

Through the precise determination of the characteristic frequency and the mathematical conversion, the density of the sample can be measured. The density is calculated from the quotient of the period of oscillations of the U-tube and the reference oscillator. Thus density ( $\rho$ ) is given by the apparatus constants ( $KA$ ,  $KB$ ) into correlation terms of temperature, viscosity and nonlinearity ( $f_1$ ,  $f_2$ ) where the first apparatus constant is into the quotient ( $Q$ ) of the period of oscillation of the U-tube divided by the period of the reference oscillator.

Therefore density can also be given by:

$$\rho = (KA)(Q^2) \times f_1 - (KB)(f_2) \quad (3.3)$$

DSA 5000 M simultaneously determines the two physical independent properties within one sample. The instrument is equipped with the density cell and the sound velocity cell on origin thus combining the “traditional” Anton Paar oscillating U-tube method with highly accurate measurement of sound velocity. However the instrument can alternately be incorporated with the refractometer and give the third independent physical property of the sample, thus with the refractometer incorporated into DSA5000 M as shown by figure 4.2 below, three physical properties within one sample can simultaneously be attained with the accuracy and reproducibility of ( $\pm 0.001$  K) for Temperature, ( $\pm 5 \times 10^{-6}$  and  $\pm 10^{-6}$ ) g.cm<sup>-3</sup> for density and ( $\pm 0.01$  and  $0.1$ ) m.s<sup>-1</sup> for speed of sound and (RI) as indicated by table 4.1 below.



**Figure 3.2 Side view photograph of DSA 5000M incorporated with the refractometer and showing the X.module 452 automatic sampler**

(Taken from the Anton Paar User Manual)

The specifications of the DSA 5000M are given in the Table 3.1 overleaf:

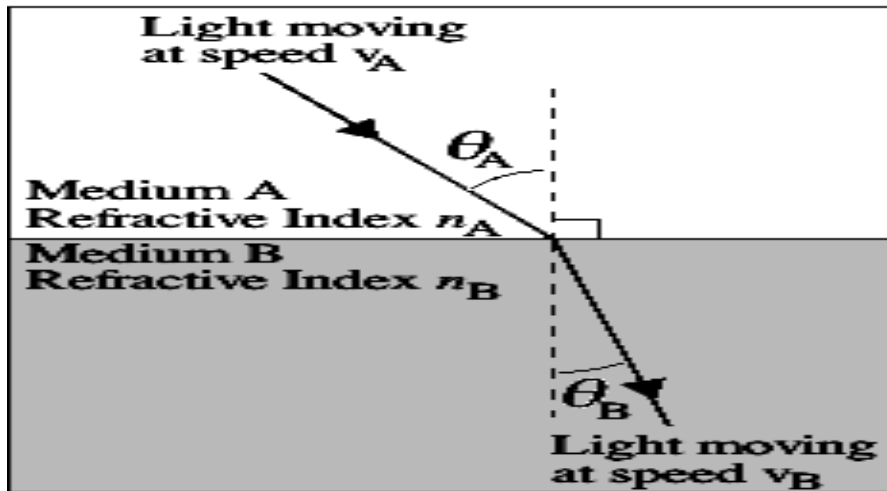
**Table 3.1 DSA 5000M specifications.**

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Measuring range density	0 to 3 g.cm <sup>-3</sup>
Measuring range velocity	1000 to 2000 m.s <sup>-1</sup>
Measuring range temperature	273.15 to 343.15 K (32 to 158 F)
Pressure range	0 to 3 bar (0 to 44 psi)
Repeatability density	
Repeatability sound velocity	0.000001 g.cm <sup>-3</sup>
Repeatability temperatures	0.1 m.s <sup>-1</sup>
Measuring time per sample	273.151 K (0.002 F)
Sample volume	1 to 4 minutes
Ambient air pressure sensor	
Reference oscillator	approx. 3 ml
Automatic bubble detection	yes
Visual check of the density measuring cell	yes
	yes
	camera

---

The measurement for refractive index is obtained when there is a change in the speed of light as it crosses the boundary from one medium into another causing change in its direction of travel that is refraction.



**Figure 3.3 Refraction of light passing from medium A to medium B**

The relationship between the speed of the light in two mediums, that is medium A and B is the angles of incidence ( $\theta_A$ ) over refraction ( $\theta_B$ ) and the refractive indices of the two mediums ( $n_A$  and  $n_B$ ), Thus:

$$\frac{A}{B} = \frac{\sin\theta_A}{\sin\theta_B} = \frac{n_A}{n_B} \quad (3.4)$$

Therefore it is not necessary to measure the speed of light in the sample in order to determine its index of refraction. Rather by measuring the angle of refraction, and knowing the index of refraction of the layer that is in contact with the sample, it is possible to determine the refractive index of the sample with high accuracy. Sithole, (2012).

The principle of operation of the refractometer outline the liquid sample been sandwiched into a thin layer between the illuminating prism and the refracting prism.

Figure 3.4 below is the cross section diagram illustrating the principle of the refractometer.

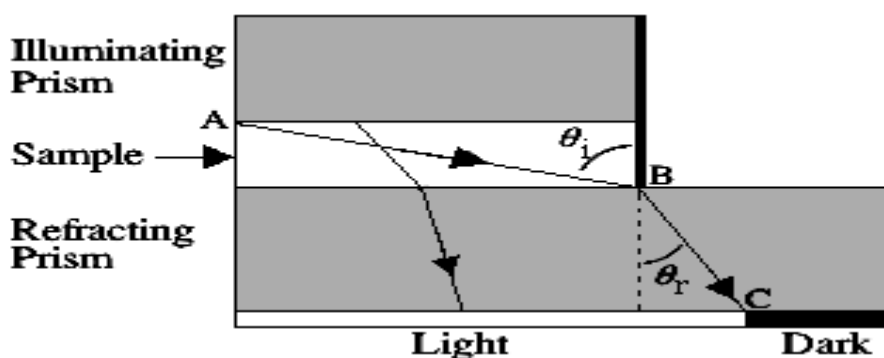


Figure 3.4 The cross section of the refractometer

## 3.5 EXPERIMENTAL SECTION

### 3.5.1 Treatment of Materials

The solvents were kept in the dry box before use. The water used in this work was prepared in the laboratory by further boiling the double deionized mill-Q water obtained from Durban University of Technology (DUT) and it was allowed to cool at room temperature before use. Molecular sieves (4 nm) were used to extract traces amount of moisture before any experimental run, the moisture content of the IL was predetermined using the Karl Fischer 831 coulometer titration instrument supplied by Metrohm.

A summary of the materials used in this work, their suppliers and mass %purity is given in Table 3.2 below.

**Table 3.2 Compound, their suppliers and mass% purity.**

---

<b>COMOPUND</b>	<b>SUPPLIER</b>	<b>MASS% PURITY</b>
Methanol	Sigma Aldrich	99.99
Toluene	Sigma Aldrich	99.99
Dodecane	Sigma Aldrich	99.99
Cyclohexane	Sigma Aldrich	99.99
Deionized Water	DUT	≥99.99
[EMIM][ EtSO <sub>4</sub> ]	Sigma Aldrich	≥95

---

The densities and refractive indices of pure components were initially measured before determination of neither binodal curves nor tie-lines and compared to known literature values.

The data is presented in the Table 3.3 overleaf:

**Table 3.3 Refractive index ( $n_D$ ) and Densities ( $\rho$ ) of pure Components at 298.15 K.**

COMPONENT	$n_D$ Exp	$n_D$ Lit	$\rho$ Exp	$\rho$ Lit
Methanol	1.3271	1.3265 <sup>k</sup>	0.787148	0.78657 <sup>a</sup>
		1.3288		0.78688 <sup>k</sup>
Toluene	1.41939	1.4194 <sup>e</sup>	0.862019	0.862100 <sup>e</sup>
		1.4941 <sup>i</sup>		0.862220 <sup>f</sup>
		1.4968 <sup>k</sup>		0.864989 <sup>j</sup>
				0.861440 <sup>k</sup>
Dodecane	1.4199	1.41992 <sup>n</sup>	0.745359	0.745200 <sup>n</sup>
Cyclohexane	1.4240	1.42354 <sup>g</sup>	0.773991	0.77380 <sup>g</sup>
Water	1.3325	1.3326 <sup>a</sup>	0.997188	0.99734 <sup>a</sup>
		1.3325 <sup>b</sup>		0.99706 <sup>b</sup>
		1.3324 <sup>c</sup>		0.99990 <sup>c</sup>
		1.3326 <sup>d</sup>		0.99705 <sup>d</sup>
		1.3325 <sup>m</sup>		0.99704 <sup>m</sup>

**Table 3.3 Continued**

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[EMIM][EtSO <sub>4</sub> ]	1.4776	1.47889 <sup>h</sup>	1.237534	1.23882 <sup>h</sup>
		1.47940 <sup>l</sup>		1.23750 <sup>l</sup>
		1.47940 <sup>n</sup>		1.23763 <sup>n</sup>
		1.47940 <sup>o</sup>		1.23750 <sup>o</sup>

---

<sup>a</sup> (Hwang *et al.*, 2008), <sup>b</sup> (Cháfer *et al.*, 2008), <sup>c</sup> (Mehmet *et al.*, 2006), <sup>d</sup> (Ghanadzadeh *et al.*, 2009), <sup>e</sup> (Ritzoulis *et al.*, 1997), <sup>f</sup> (Tanaka *et al.*, 1997), <sup>g</sup> (Pereiro *et al.*, 2008), <sup>h</sup> (Alberto *et al.*, 2006), <sup>i</sup> (Pereiro *et al.*, 2010), <sup>j</sup> (Aznar *et al.*, 2008), <sup>k</sup> (Letcher *et al.*, 1992), <sup>l</sup> (Calvar *et al.*, 2009), <sup>m</sup> (Alberto *et al.*, 2000), <sup>n</sup> (Rodriguez *et al.*, 2010) and <sup>o</sup> (Letcher *et al.*, 2015)

## **3.6 VALIDATION AND VERIFICATION OF EXPERIMENTAL TECHNIQUE**

### **3.6.1 System 1: {methanol (1) + toluene (2) + dodecane (3)} at $T = 298.15$ K**

The validation and verification of the technique was implemented by measuring the stable thermodynamic properties of the first system (system 1) studied by Mohsen-Nia *et al.*, (2006) at  $T = 298.15$  K using the DSA5000 M. The experimental results obtained were compared with the literature data for the mixtures (methanol, toluene and dodecane) at  $T = 298.15$  K.

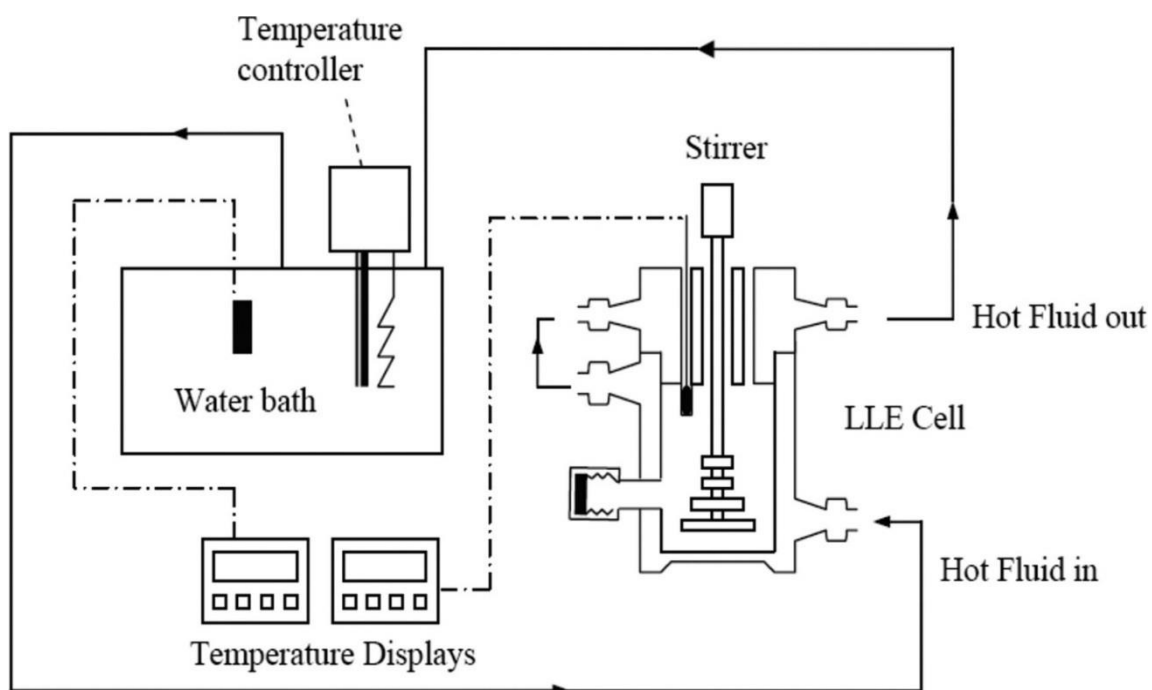
### **3.6.2 System 2: {methanol (1) + water (2) + cyclohexane (3)} at $T = 303.15$ K**

The method was further validated by performing analysis on a different system with slightly different temperature range to ensure that robust data is obtained. The analysis of the second system (system 2) studied were compared with the data of Monica *et al.*, (2003) at  $T = 303.15$  K for the mixtures (methanol, water and cyclohexane) at  $T = 303.15$  K.

### 3.7 EXPERIMENTAL PROCEDURE/ METHODOLOGY

As stated prior, in this investigation the “method of titration” or the ‘cloud-point’ technique was used, which is the method adapted from Briggs and Comings (1943) and modified by Letcher and Siswana (1992). The binodal curves were first obtained prior to determination of the tie-lines.

A double wall LLE glass cell was used to carry out binodal curve measurements on a magnetic stirrer plate. The cell temperature was controlled at a constant temperature with circulation of water using GD120 Grant water bath incorporated with two GD120 thermostat supplied by Polychem Supplies (cc). The binodal curves were determined by cloud-point technique. As shown in Figure 3.5 below:



**Figure 3.5 Schematic diagram of the experimental setup.** [Matthew *et al.*, (2011)]

For the first system (system 1); {methanol (1) + toluene (2) + dodecane (3)}, the LLE data for stated aromatic hydrocarbon, alkane and alcohols reported by Mohnsen-Nia and Modarress (2006) was studied to validate the method. The binary solubilities for three solvents in each case were determined and the % solubility was calculated.

The points on the phase diagram were obtained using the following procedure: The mixture of two miscible solvents; methanol and toluene were prepared and weighed accurately by mass difference, the mixtures were then left to equilibrate in a water bath maintained at  $T = 298.15 \pm 0.1$  K for approximately two hours. The third component, the hydrocarbon (dodecane) was then added drop wise from a gas tight Hamilton syringe until the mixture turned turbid/cloudy. The syringe was then weighed to determine the exact mass of hydrocarbon transferred into the mixture to bring the cloudiness.

To obtain the miscible/clear solution, alcohol was added dropwise to the cloudy solution. At the hydrocarbon-rich phase end of the binodal curve the dual/binary mixture was made up of methanol and toluene, and the third component, dodecane, was introduced gradually by titrating the mixture. The mass of the components were accurately weighed using the (OHAUS, Pine Brook (U.S.A.)) analytical balance with the precision of ( $\pm 0.0001$  g) to get exact masses of the compositions. The mixtures were then left to equilibrate in a water bath maintained at  $T = 298.15 \pm 0.1$  K for at least two hours.

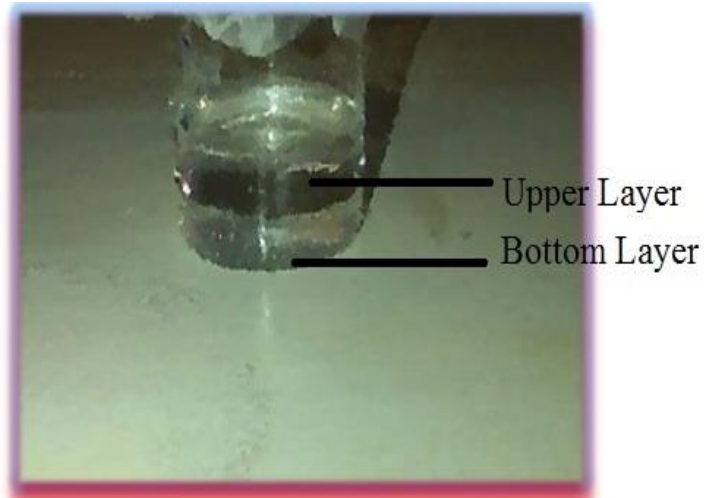
The physical properties of the clear mixtures at equilibrium, namely: density ( $\rho$ ) and refractive index ( $n_D$ ) were measured by injection of the mixture in a DSA5000 M instrument set at  $T = 298.15$  K.

Prior to each experimental run, the sample cells were first flushed with ethanol, followed by a thorough rinsing with acetone. The double deionized water was further used to clean the cells and to ensure thorough drying; the cells were allowed to dry in an oven set at  $T = 423.15$  K for approximately an hour.

For verification or basic calibration of the instrument the water and air checks with known  $n_D$  and  $\rho$  values at different temperatures were monitored to ensure true integrity of results.

For the determination of the tie-lines, five feed samples ( $\pm 50$ ml) were prepared by mixing appropriate amount of solvents - aromatic hydrocarbon (toluene), alkane (dodecane) and alcohol (methanol), determined graphically from the binodal curves, into the glass cells. Once the samples were mixed vigorously by shaking and stirring for about 10 minutes, the glass cells were placed in the water bath set at  $T = 298.15$  K for at least 12 hours.

The samples were once again shaken and allowed to rest for an hour, after the rest time the mixtures were split into a clear and transparent liquid phases as demonstrated by Figure 3.6 overleaf, with a well-defined interface and the equilibrium state was achieved. The samples (two-liquid phases) as in Figure 3.6, were carefully withdrawn using long needle Hamilton syringe maintained at  $T = 298.15$  K. After the separation of the two phases, the concentration of both phases - top (alkane-rich) and bottom (alcohol-rich) were determined by DSA5000 M instrument which measures simultaneously the density ( $\rho$ ), speed of sound ( $u$ ) and refractive index ( $n_D$ ) property of the sample.



**Figure 3.6 Photograph of a sample showing the two- phase at equilibrium**

A calibration curve of density and/or refractive index versus mole fractions was constructed for each system as shown in appendices A to D to calculate the tie-line compositions. Calibration curves were constructed for density and refractive index parameters only for (system 1) to assess which property gave better accuracy for the mole-fractions of tie-line compositions.

In this work one parameter, ( $\rho$ ) was taken into consideration for determination of the LLE data for (system 2) and (IL system) due to nonlinearity in ( $n_D$ ) values observed and demonstrated in the generated data of (system 1). Thus the generated LLE results for (system 2) and the ionic liquid system investigated were measured and obtained using only the ( $\rho$ ) parameter as outlined in the following chapter.

# CHAPTER 4: RESULTS AND DISCUSSION

The results for the experimental tie-line and global composition LLE data for the ternary mixture {methanol (1) + toluene (2) + dodecane (3)} (system 1) using the refractive index and density properties at  $T = 298.15$  K are given in Tables 4.1 and 4.2 respectively, and plotted in Figures 4.1 and 4.2, where  $x^s$  is the mole fraction composition in the alkane rich region and  $x^a$  is the mole fraction composition in the alcohol rich region respectively.

**Table 4.1 Experimental tie-line and global composition LLE data for ternary mixture {methanol (1) + toluene (2) + dodecane (3)} (system 1) using Refractive Index measurement at  $T = 298.15$  K.**

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### LLE Tie-line Data

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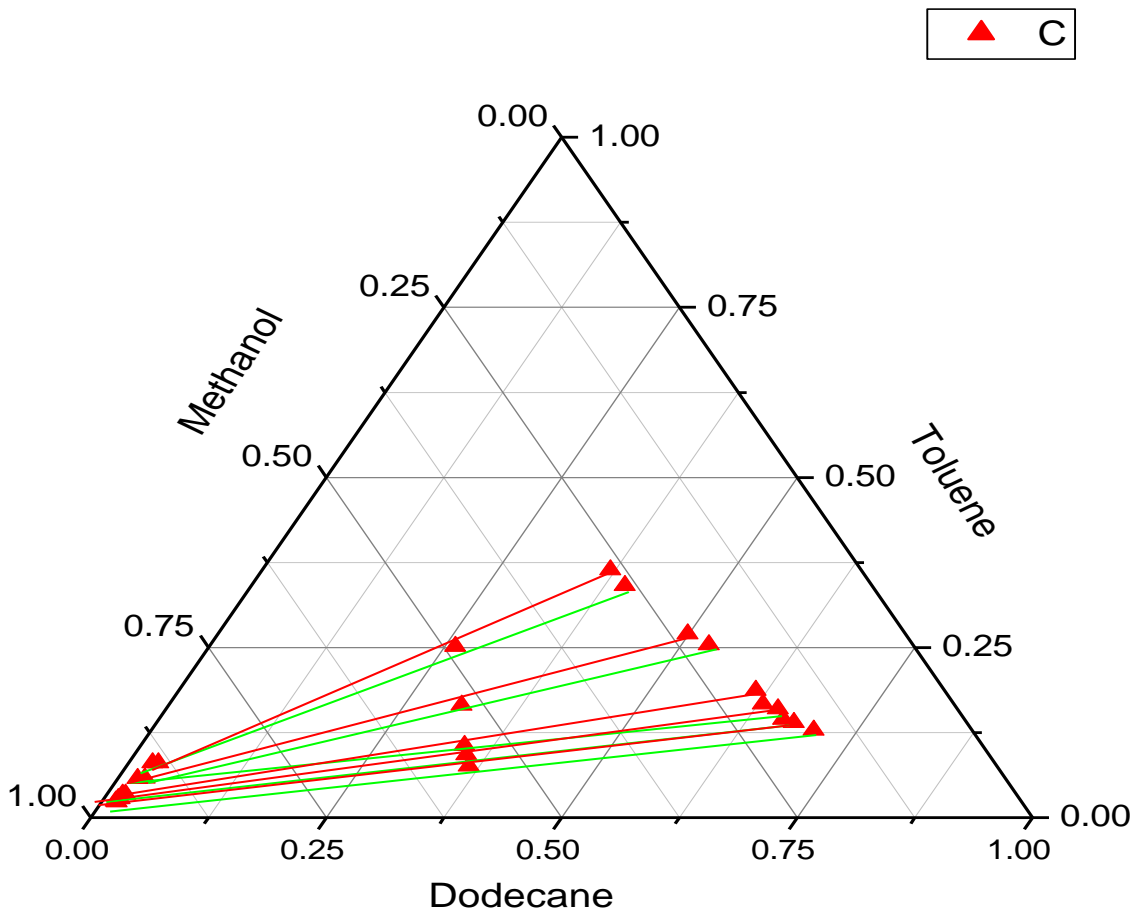
Global Composition			Alkane-Rich Phase			Alcohol-Rich Phase			$S$	$k$
$x_1$	$x_2$	$x_3$	$x_1^s$	$x_2^s$	$x_3^s$	$x_1^a$	$x_2^a$	$x_3^a$		
0.8907	0.0837	0.0256	0.2661	0.3699	0.3640	0.8943	0.0774	0.0252	3.24	0.22
0.9130	0.0580	0.0290	0.2312	0.4989	0.2699	0.9218	0.0544	0.0209	5.06	0.21
0.9455	0.0346	0.0199	0.2006	0.6125	0.1869	0.9491	0.0315	0.0167	6.71	0.18
0.9553	0.0278	0.0169	0.1905	0.6496	0.1599	0.9569	0.0250	0.0154	7.31	0.17
0.9602	0.0236	0.0162	0.1832	0.6768	0.1400	0.9612	0.0214	0.0147	7.89	0.17

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**Table 4.2 Experimental tie-line and global composition LLE data for ternary mixture {methanol (1) + toluene (2) + dodecane (3)} (system 1) from density measurements at  $T = 298.15$  K.**

LLE Tie-line Data

Global Compositions			Alkane-Rich Phase			Alcohol-Rich Phase			$S$	$k$
$x_1$	$x_2$	$x_3$	$x_1^s$	$x_2^s$	$x_3^s$	$x_1^a$	$x_2^a$	$x_3^a$		
0.8907	0.0837	0.2615	0.2718	0.3875	0.3407	0.8823	0.0897	0.0280	2.82	0.23
0.9130	0.0580	0.3112	0.2292	0.2715	0.4993	0.9197	0.0579	0.0224	4.75	0.21
0.9455	0.0346	0.3439	0.2061	0.2083	0.5856	0.9461	0.0354	0.0185	5.38	0.17
0.9553	0.0278	0.3526	0.1911	0.1674	0.6415	0.9522	0.0303	0.0175	6.64	0.18
0.9602	0.0236	0.3635	0.1762	0.1267	0.6971	0.9610	0.0227	0.0163	7.66	0.18



**Figure 4.1.** Ternary phase diagram for {methanol (1) + toluene (2) + dodecane (3)} (system 1) at  $T = 298.15$  K, — experimental data and — literature data using refractive index parameter

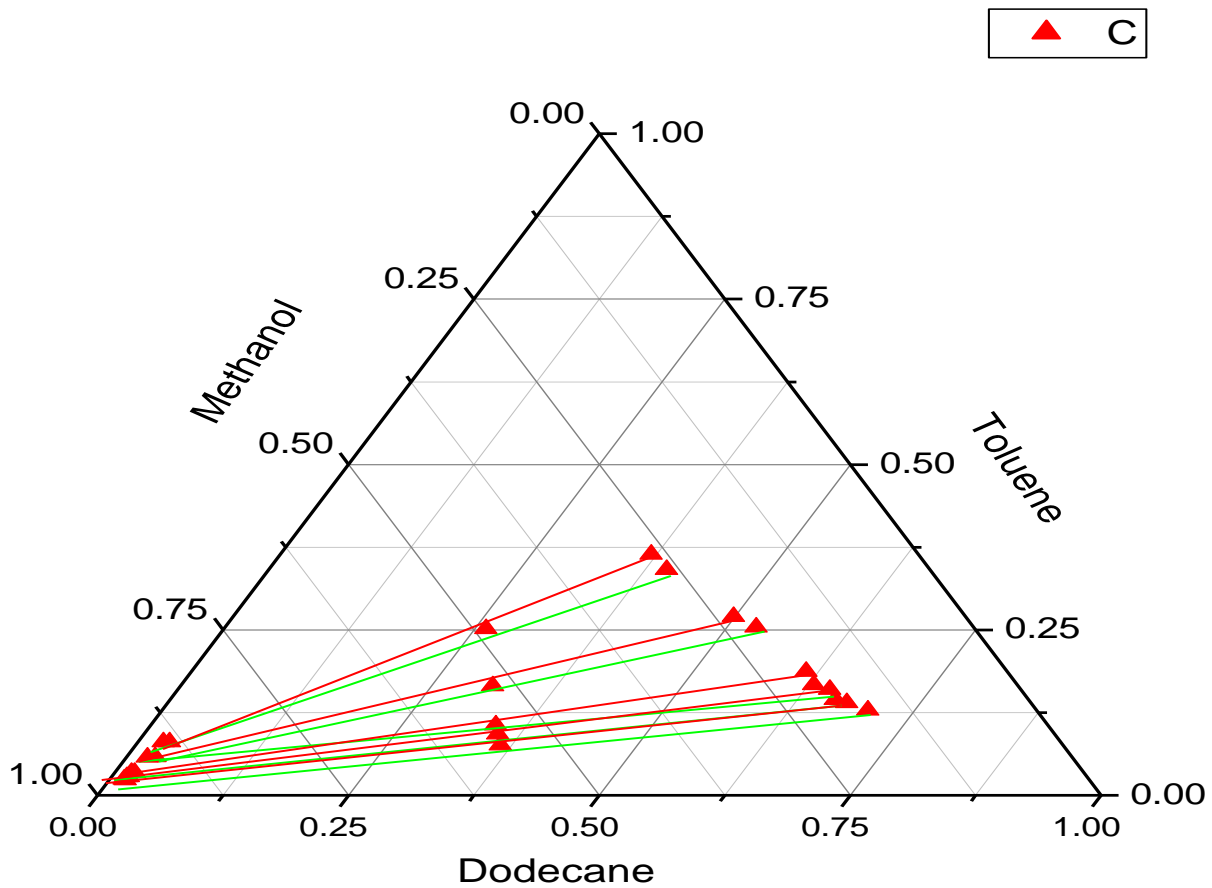


Figure 4.2 Ternary phase diagram for {methanol (1) + toluene (2) + dodecane (3)} (system 1) at  $T = 298.15$  K, — experimental data and — literature data using density parameter.

Table 4.3 is the literature data for the ternary mixture {methanol (1) + toluene (2) + dodecane (3)} (system 1).

**Table 4.3 Literature LLE data for ternary mixture {methanol (1) + toluene (2) + dodecane (3)} (system 1) at  $T = 298.15$  K.**

$x_1^s$	$x_2^s$	$x_3^s$	$x_1^a$	$x_2^a$	$x_3^a$	$S$	$k$
0.2622	0.3406	0.3966	0.8878	0.0805	0.0312	2.96	0.24
0.2165	0.2542	0.5293	0.9135	0.0579	0.0286	4.22	0.23
0.2023	0.1672	0.6305	0.945	0.0346	0.0196	6.66	0.21
0.1922	0.1446	0.6635	0.9547	0.0278	0.017	7.50	0.19
0.1680	0.1283	0.7036	0.9607	0.0232	0.0161	7.90	0.18

A similar experimental procedure was used for both the second system (system 2) and the ionic liquid system (IL system) investigated and only the density parameter was measured and monitored in all phases at equilibrium.

A comparison between this work and the literature data for ternary mixture {water (1) + methanol (2) + cyclohexane (3)} (system 2) at  $T = 303.15$  K is shown on Tables 4.4 (a) for mole fraction compositions, 4.4 (b) for weight fraction compositions and literature values are given on Table 4.5.

The data is graphically represented on Figures 4.3 and 4.4 for both the literature data and generated experimental data respectively where again  $x^s$  is the mole fraction composition in alkane rich region and  $x^{aq}$  is the mole fraction composition in aqueous rich region and  $w^s$  is the weight fraction composition in alkane rich region and  $w^{aq}$  is the weight fraction composition in aqueous rich region.

**Table 4.4 (a) Experimental tie-line and global composition LLE data for ternary mixture {water (1) + methanol (2) + cyclohexane (3)} (system 2) from density measurements at  $T= 303.15$  K in mole fractions.**

LLE Tie-line Data										
Global Composition			Aqueous-Rich Phase			Alkane-Rich Phase				
$x_1$	$x_2$	$x_3$	$x_1^{\text{aq}}$	$x_2^{\text{aq}}$	$x_3^{\text{aq}}$	$x_1^{\text{s}}$	$x_2^{\text{s}}$	$x_3^{\text{s}}$	$S$	$k$
0.8294	0.0000	0.1706	1.0000	0.0000	0.0000	0.0000	0.0000	1.0000	0.000	1.00
0.7755	0.0515	0.1730	0.9399	0.0601	0.0000	0.0000	0.0000	1.0000	0.000	0.00
0.6817	0.1345	0.1838	0.8316	0.1682	0.0002	0.0000	0.0345	0.9655	0.000	0.00
0.6145	0.1984	0.1870	0.7586	0.2404	0.0010	0.0000	0.0555	0.9445	0.000	0.05
0.5574	0.2480	0.1945	0.6939	0.3044	0.0017	0.0000	0.0736	0.9264	0.000	0.01
0.4621	0.3270	0.2109	0.5917	0.4054	0.0029	0.0000	0.1382	0.8618	0.000	0.01
0.3095	0.4293	0.2612	0.4510	0.5445	0.0045	0.0000	0.2027	0.7973	0.000	0.10

**Table 4.4 (b) Experimental tie-line and global composition LLE data for ternary mixture {water (1) + methanol (2) + cyclohexane (3)} (system 2) from density measurements at  $T= 303.15$  K in weight fractions.**

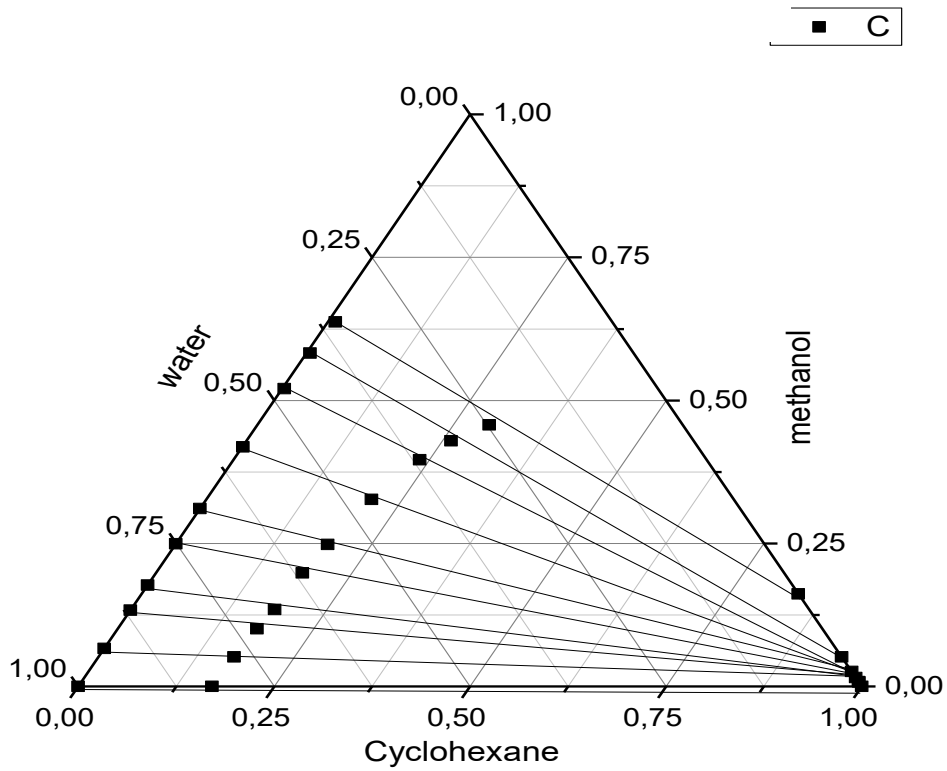
LLE Tie-line Data

Global Composition			Aqueous-Rich Phase			Alkane-Rich Phase			$S$	$k$
$w_1$	$w_2$	$w_3$	$w_1^{\text{aq}}$	$w_2^{\text{aq}}$	$w_3^{\text{aq}}$	$w_1^{\text{s}}$	$w_2^{\text{s}}$	$w_3^{\text{s}}$		
0.5099	0.0000	0.4901	0.9673	0.0327	0.0000	0.0000	0.0000	1.0000	0.00	1.00
0.4629	0.0547	0.4825	0.8833	0.1170	0.0000	0.0000	0.0000	1.0000	0.00	0.00
0.3831	0.1344	0.4825	0.7638	0.2362	0.0000	0.0000	0.0005	0.9995	0.00	0.00
0.3337	0.1916	0.4747	0.5985	0.4015	0.0000	0.0000	0.0190	0.9981	0.00	0.05
0.2923	0.2313	0.4764	0.5967	0.4033	0.0000	0.0000	0.0017	0.9983	0.00	0.01
0.2278	0.2867	0.4855	0.5507	0.4493	0.0022	0.0000	0.0000	1.0000	0.00	0.01
0.1350	0.3330	0.5320	0.3354	0.6646	0.0045	0.0000	0.0000	1.0000	0.00	0.10

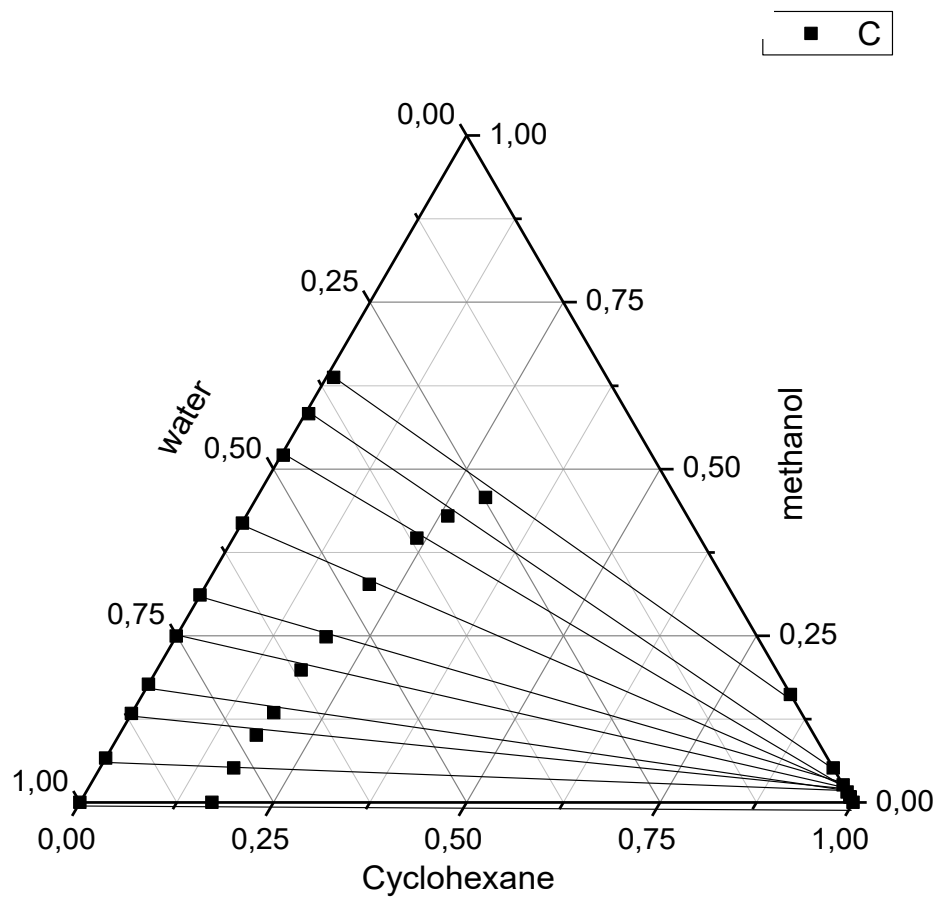
**Table 4.5 Literature tie-line and global composition LLE data for ternary mixture {water (1) + methanol (2) + cyclohexane (3)} (system 2) at  $T = 303.15$  K.**

LLE Tie-line Data

Global Composition			Aqueous-Rich Phase			Alkane-Rich Phase			$S$	$k$
$w_1$	$w_2$	$w_3$	$w_1^s$	$w_2^s$	$w_3^s$	$w_1^a$	$w_2^a$	$w_3^a$		
0.5098	0.0000	0.4902	1.0000	0.0000	-	-	0.0000	1.0000	0.00	0.00
0.4629	0.0547	0.4824	0.8840	0.1160	-	-	-	1.0000	0.00	0.00
0.4160	0.1053	0.4787	0.7850	0.2150	-	-	-	1.0000	0.00	0.00
0.3831	0.1344	0.4825	0.7220	0.2780	-	-	-	0.9980	0.00	0.00
0.3338	0.1916	0.4747	0.6300	0.3700	-	-	0.0210	0.9980	0.00	0.01
0.2917	0.2315	0.4768	0.5440	0.4460	-	-	0.0029	0.9970	0.00	0.01
0.2278	0.2867	0.4856	0.4370	0.5610	0.0019	-	0.0038	0.9960	0.00	0.01
0.1680	0.3226	0.5095	0.3380	0.6540	0.0086	-	0.0060	0.9940	0.00	0.01
0.1347	0.3331	0.5322	0.2810	0.7040	0.0153	-	0.0073	0.9930	0.00	0.01
0.1009	0.3331	0.5660	0.2310	0.7400	0.0298	-	0.0101	0.9900	0.00	0.01



**Figure 4.3 Ternary phase diagram for {water (1) + methanol (2) + cyclohexane (3)} (system 2) at  $T = 303.15 \text{ K}$**

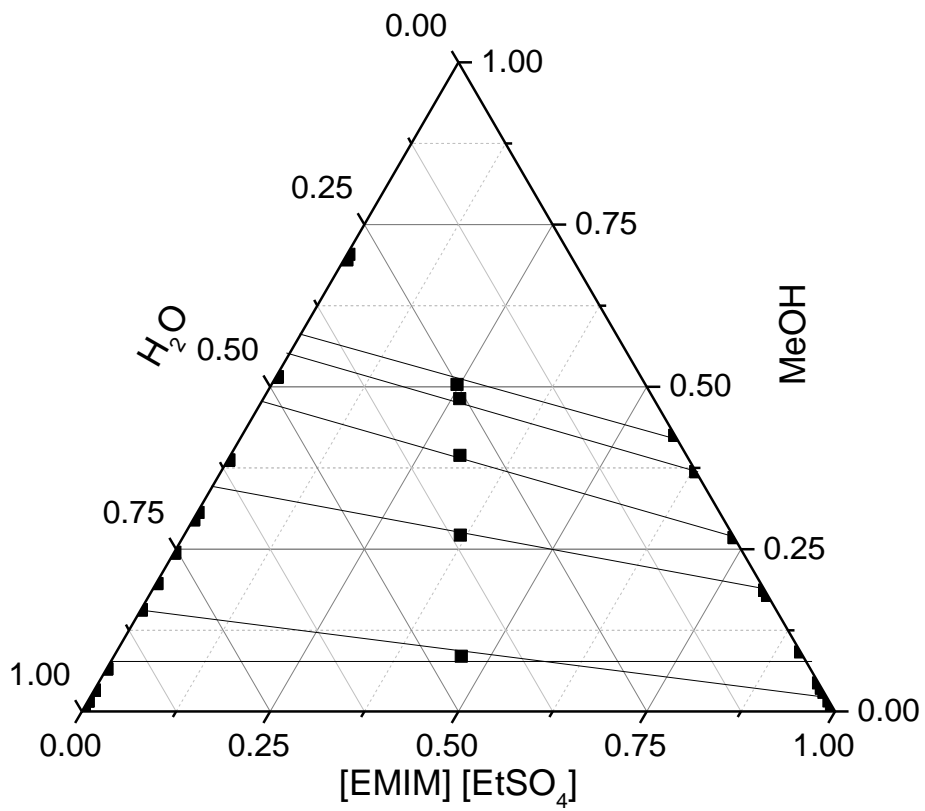


**Figure 4.4 Ternary phase diagram for {water (1) + methanol (2) + cyclohexane (3)} (system 2) at  $T = 303.15$  K using literature data**

Table 4.6 below represents the LLE data for the ternary mixture of an ionic liquid 1-ethyl-3-methylimidazolium ethyl sulfate with the azeotrope; {[EMIM][EtSO<sub>4</sub>] (1) + methanol (2) + water (3)} at  $T = 298.15$  K respectively, where  $x^{\text{aq}}$  is the mole fraction composition in aqueous rich region and  $x^{\text{IL}}$  is the mole fraction composition in ionic liquid rich region. The results are also graphically presented in Figure 4.5 overleaf.

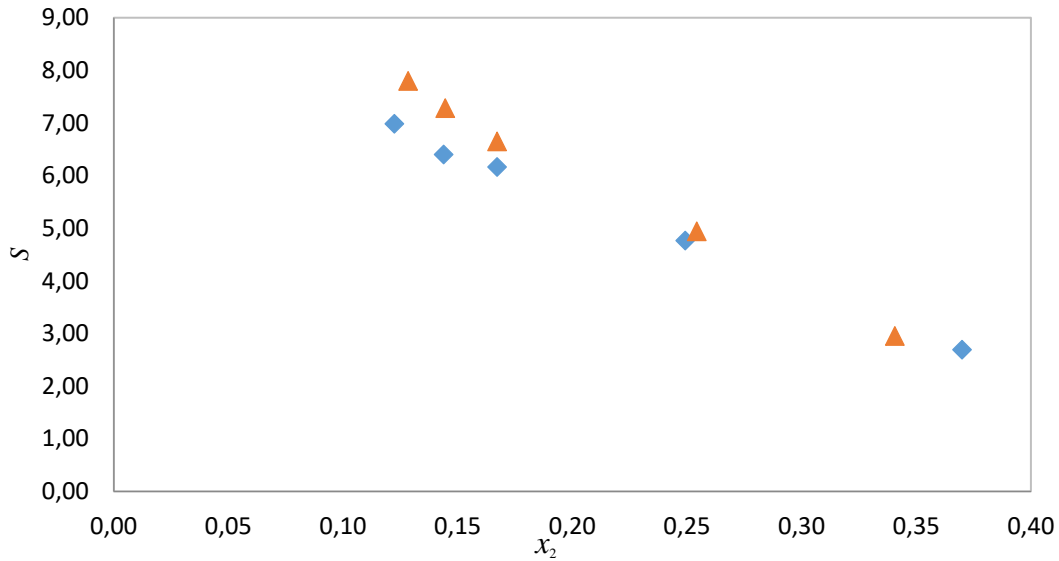
**Table 4.6 Experimental tie-line and global composition LLE data tie-line for ternary mixture {[EMIM][EtSO<sub>4</sub>] (1) + methanol (2) + water (3)} (IL System)**

LLE Tie-line Data										
Global Composition			Aqueous-Rich Phase			Ionic Liquid-Rich Phase			$S$	$k$
$x_1$	$x_2$	$x_3$	$x_1^{\text{s}}$	$x_2^{\text{s}}$	$x_3^{\text{s}}$	$x_1^{\text{a}}$	$x_2^{\text{a}}$	$x_3^{\text{a}}$		
0.4612	0.0850	0.4537	0.000	0.1571	0.8429	0.9641	0.0359	0.000	0.99	0.23
0.3668	0.2715	0.3617	0.000	0.3485	0.6515	0.8211	0.1789	0.000	0.71	0.51
0.3050	0.3943	0.3007	0.000	0.4524	0.5476	0.7323	0.2677	0.000	0.63	0.59
0.2610	0.4817	0.2572	0.000	0.5476	0.4524	0.6307	0.3693	0.000	0.65	0.67
0.2464	0.5035	0.2501	0.000	0.5771	0.4225	0.5748	0.4252	0.000	0.68	0.74



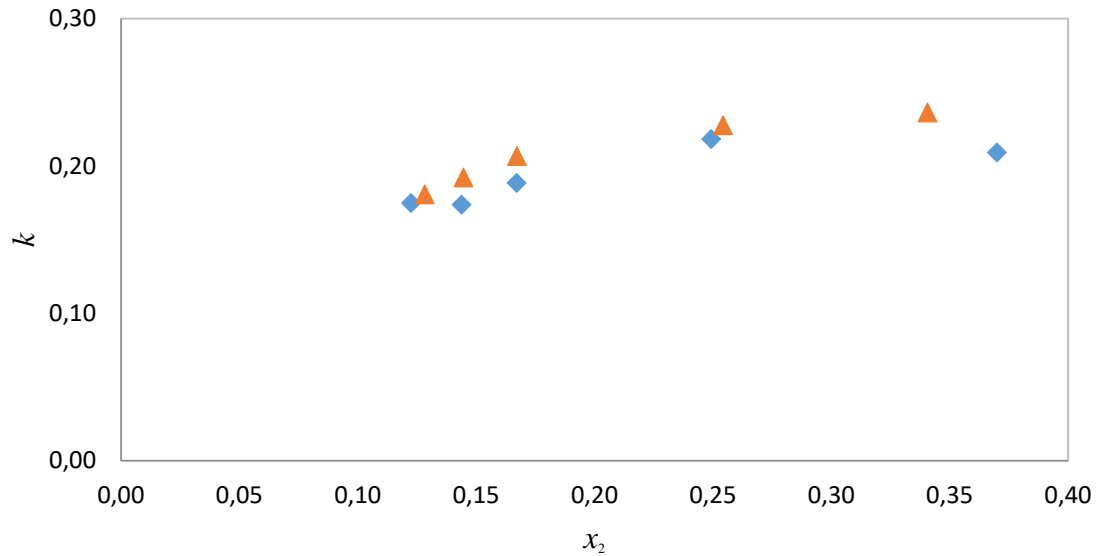
**Figure 4.5 Ternary phase diagram for {[EMIM][EtSO<sub>4</sub>](1) + methanol (2) + water (3)} at  $T = 298.15$  K**

Figure 4.6 below represent the comparison between the selectivity values of the experimental data and the literature values of (system 1) {methanol (1) + toluene (2) + dodecane (3)} at  $T = 298.15$  K.



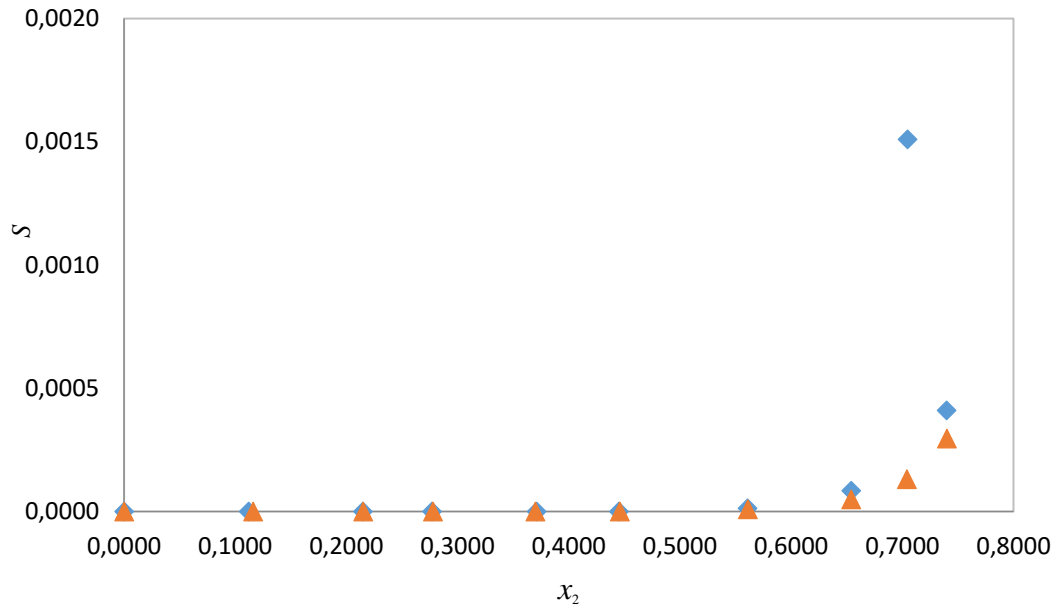
**Figure 4.6 Graph of selectivity ( $S$ ) versus mole fraction of component 2 ( $x_2$ ) for {methanol (1) + toluene (2) + dodecane (3)} at  $T = 298.15$  K.  $\blacklozenge$  Exp data  $\blacktriangle$  Lit data**

Figure 4.7 below is the chart showing the comparison between the distribution coefficients of the generated experimental data and the literature values of the (system 1) {methanol (1) + toluene (2) + dodecane (3)} at  $T = 298.15$  K.



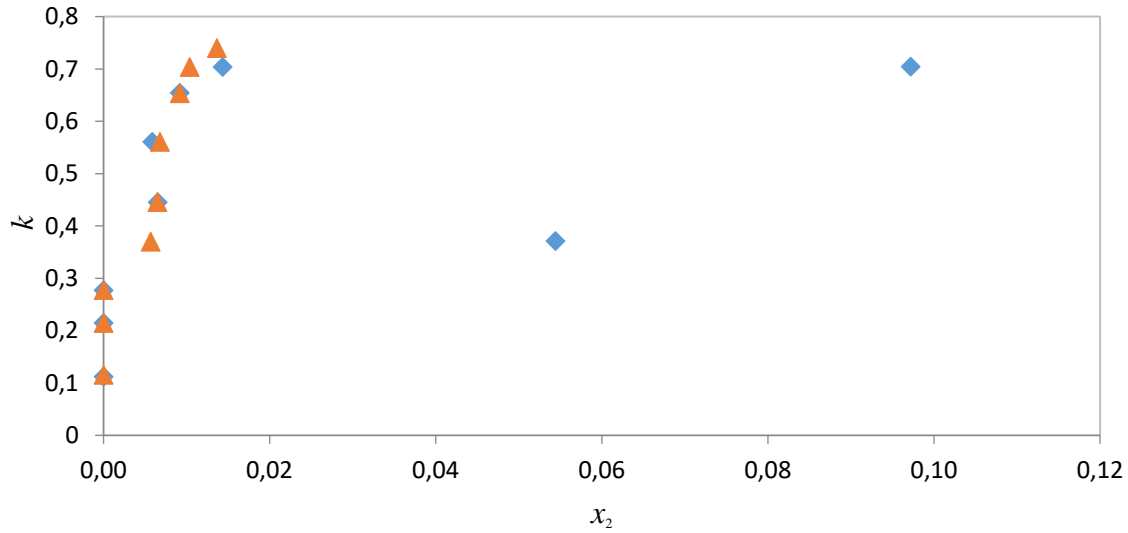
**Figure 4.7 Graph of distribution coefficient ( $k$ ) versus mole fraction of component 2 ( $x_2$ ) for {methanol (1) + toluene (2) + dodecane (3)} at  $T = 298.15$  K. ♦Exp data ▲ Lit data**

Figure 4.8 below is the chart outlining the comparison between the selectivity values of the generated experimental data and the literature values of the (system 2) {water (1) + methanol (2) + cyclohexane (3)} at  $T = 303.15$  K.



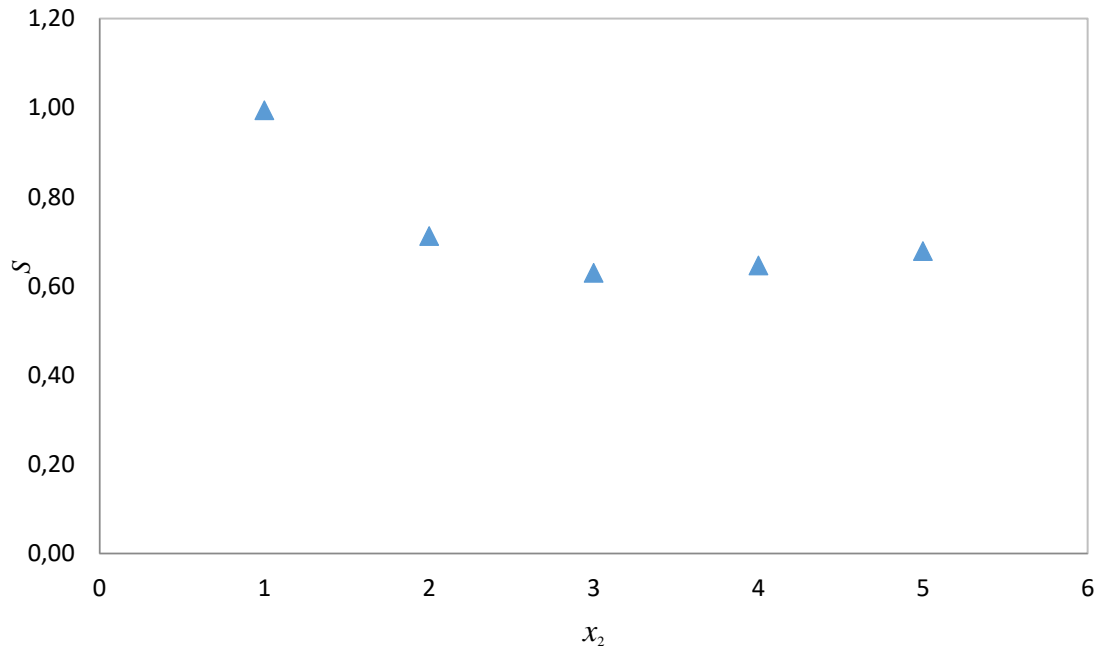
**Figure 4.8 Graph of selectivity ( $S$ ) versus mole fraction of component 2 ( $x_2$ ) for {water (1) + methanol (2) + cyclohexane (3)} at  $T = 303.15$  K.  $\blacklozenge$  Exp data and  $\blacktriangle$  Lit data**

Figure 4.9 below is the chart showing the comparison between the distribution coefficients of the generated experimental data and the literature values of the (system 2) {water (1) + methanol (2) + cyclohexane (3)} at  $T = 303.15$  K.



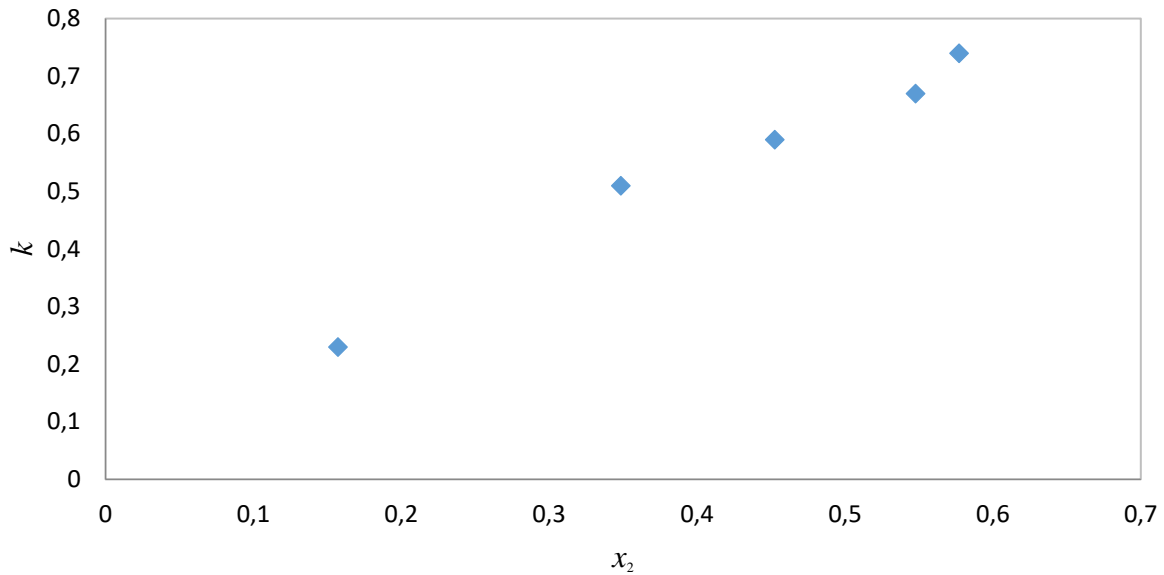
**Figure 4.9** Graph of distribution coefficient ( $k$ ) versus mole fraction of component 2 ( $x_2$ ) for {water (1) + methanol (2) + cyclohexane (3)} at  $T = 303.15$  K.  $\blacklozenge$  Exp data and  $\blacktriangle$  Lit data

Figure 4.10 below is the chart for selectivity values for the actual ionic liquid system  $\{[\text{EMIM}][\text{EtSO}_4] (1) + \text{methanol} (2) + \text{water}(3) \}$  at  $T = 298.15 \text{ K}$



**Figure 4.10 ▲ Graph of selectivity ( $S$ ) versus mole fraction of component 2 ( $x_2$ ) for  $\{[\text{EMIM}][\text{EtSO}_4] (1) + \text{methanol} (2) + \text{water}(3) \}$  at  $T = 298.15 \text{ K}$**

Figure 4.11 below is the chart for distribution coefficient values for the actual ionic liquid system {[EMIM][EtSO<sub>4</sub>] (1) + methanol (2) + water(3) } at  $T = 298.15$  K



**Figure 4.11** ♦ Graph of distribution coefficient ( $k$ ) versus mole fraction of component 2 ( $x_2$ ) for {[EMIM][EtSO<sub>4</sub>] (1) + methanol (2) + water(3)} at  $T = 298.15$  K

## 4.1 MOLE FRACTION, SELECTIVITY AND DISTRIBUTION COEFFICIENT

### (i) System 1

In the first system (system 1) the mole fraction error computed when using the density ( $\rho$ ) and the refractive index ( $n_D$ ) calibration curves gave the maximum deviation of  $\pm 0.007$ . This information is significant for selectivity calculations .Julia *et.al*, (2004)

The experimental data generated for this system {methanol (1) + toluene (2) + dodecane (3)} when compared to that of literature showed good agreement with a maximum deviation of  $\pm 0.015$  in the mole fraction using the density property for calculating the composition and  $\pm 0.0092$  in the mole fraction using refractive index (RI) property for calculating the composition.

The selectivity or separation factor and distribution coefficients were also calculated and the maximum experimental deviation between the two methods ( $n_D$  and  $\rho$ ) was  $\pm 1.33$  in selectivities and  $\pm 0.001$  for distribution coefficients. The maximum deviation in distribution coefficients between the experimental and literature data when using RI and  $\rho$  properties was  $\pm 0.04$  and  $\pm 0.01$ , respectively, and similarly for the selectivity values the maximum deviation between the experimental and literature data when using the RI property was  $\pm 1.28$  and  $0.29$  for  $\rho$  property. The maximum deviation between the experimental and the literature data

showed the effectiveness of the “cloud point” method used to generate liquid-liquid equilibria data. The better result when comparison of the two thermodynamic properties (density and refractive index) measured was obtained from the density measurements using calibration curve of system1 as explained previously, therefore only the density calibration curves were used for system 2 and the ionic liquid system.

**(ii) System 2**

For the second system (system 2) the experimental data was also compared to that of the literature for the system {water (1) +methanol (2) + cyclohexane (3)} which showed good agreement with only maximum deviation of  $\pm 0.0091$  in the weight fraction when using the density for calculation of the composition.

The selectivity and distribution coefficients were also calculated and the maximum deviation between the experimental and literature data was computed to be at  $\pm 0.0003$  for selectivity and  $\pm 0.09$  in distribution coefficients respectively.

For the IL system a comparison between experimental and literature data could not be done because there is no published data for this system.

## 4.2 SOLUTE DISTRIBUTION AND SELECTIVITY

The solute distribution or distribution coefficient ( $k$ ) and selectivity ( $S$ ) shown in Tables 4.1 and 4.2 for system 1, Tables 4.4 (a), 4.4 (b) and 4.5 for system 2 and Table 4.6 for the ionic liquid system were calculated using equation 1.1 for selectivity and equation 1.2 for solute distribution:

$$S = (x_2/x_3)^I \div (x_2/x_3)^{II} \quad (1.1)$$

$$k = x_2^{II}/x_2^I \quad (1.2)$$

Where  $(x_2/x_3)^I$  is the ratio of mole fraction 2 over mole fraction 3 of the extract phase or phase 1 (Upper layer) and  $(x_2/x_3)^{II}$  is the ratio of mole fraction 2 over mole fraction 3 of the raffinate phase or phase 2 (Bottom layer). Table 4.7 below shows a brief summary of the generated selectivity and distribution values in all measured systems.

**Table 4.7 Summary of  $S$  and  $k$  values for the systems measured**

System	$S$ values	$k$ values
{methanol (1) + toluene (2) + dodecane (3)} $n_D$	2.82 – 7.66	0.18 – 0.23
{methanol (1) + toluene (2) + dodecane (3)} $\rho$	3.24 – 7.89	0.17 – 0.22
{water(1) + methanol (2) cyclohexane(3)}	0.00 – 0.017	0.00 -1.00
{[EMIM][EtSO <sub>4</sub> ](1) + methanol (2) + water(3)}	0.63 – 0.99	0.23 – 0.74

The selectivity is an essential parameter in monitoring the efficiency of the solvent in separating the components of the azeotropic mixture. As discussed earlier and observed from the selectivity results presented by Figure 4.6 and summarized in Table 4.7, the selectivity values range between (2.82 – 7.66) for (system 1) using refractive index parameter and (3.24 - 7.89) respectively when using the density parameter. The values are not constant over the whole two-phase region and are greater than one in all cases which denotes that the solvent alcohol (methanol) used is suitable for extraction of aromatic hydrocarbon (toluene) from the alkane (dodecane).

For system 2 the selectivity values presented by Figure 4.8 and summarized in Table 4.7 range from (0.00 – 0.017) and were constant throughout the phases but significantly less than one

especially for smaller mole fractions which indicates that the aromatic hydrocarbon (cyclohexane) used for the separation of solvent alcohol (methanol) from the azeotrope is not efficient in extracting methanol from water, however it is observed that at higher mole fractions ( $\geq 0.0004$ ) the selectivity values tend to increase. This shows a true reflection that the selectivity values do increase with an increase in the solute concentration as discussed by In-Chang *et al.*, (2008) and Marcinak *et al.*, (2012).

For the ionic liquid system, the selectivity values presented by Figure 4.10 also summarized in Table 4.7, the selectivity values ranged from (0.63 – 0.99) and the values were not constant throughout the two-phase region and also below one which indicates that the ionic liquid {[EMIM][EtSO<sub>4</sub>]} used in this study cannot be considered as a potential or suitable solvent for separation of the studied azeotrope, the selectivity values were observed to decrease with an increase in the mole fraction range.

For an efficient separation the value of selectivity,  $S$ , must not be 1, since this indicate that the overall composition of the two phases in equilibrium is the same, but selectivity greater than one will mean that the entrainer used is suitable for separation of the respective azeotrope. Mohnsen-Nia *et al.*, (2006).

The solute distribution coefficient ( $k$ ) was also calculated for all the systems using equation 1.2 (given in page 12 and 92) where  $x_2^{\text{II}}$  refers to mole fraction 2 in the raffinate phase and  $x_2^{\text{I}}$  refers to mole fraction 2 in the extract phase. The distribution coefficient indicates the amount of solutes in each phase at equilibrium. Lower distribution coefficient values show high distribution and mobility of solutes in both phases.

The distribution coefficient for system 1 presented by Figure 4.7 are very low and not constant throughout the whole two-phase region. However the selectivity values are greater than one (Table 4.2,  $S$  ranged from 2.82 – 7.66) which denotes that methanol is a suitable solvent for separation of aromatic hydrocarbon from the alkane.

System 2 did not indicate any suitable mobility of solute in the two phases that are in equilibrium as it is observed from Figure 4.9 and that for a wide range of mole fractions  $k$  is constant at zero which shows that the entrainer solvent was not good for the azeotrope, the values tend to increase at higher mole fractions emphasizing the fact that cyclohexane is not a good solvent for the extraction of methanol in water using the LLE technique.

Similar observations from system 2 were noticed in calculating the  $k$  for the ionic liquid system as demonstrated by Figure 4.11, the values of  $k$  increase with an increasing concentration in mole fraction but the values obtained still indicate that [EMIM][EtSO<sub>4</sub>] is not a good solvent for separation of the azeotrope {methanol +water}.

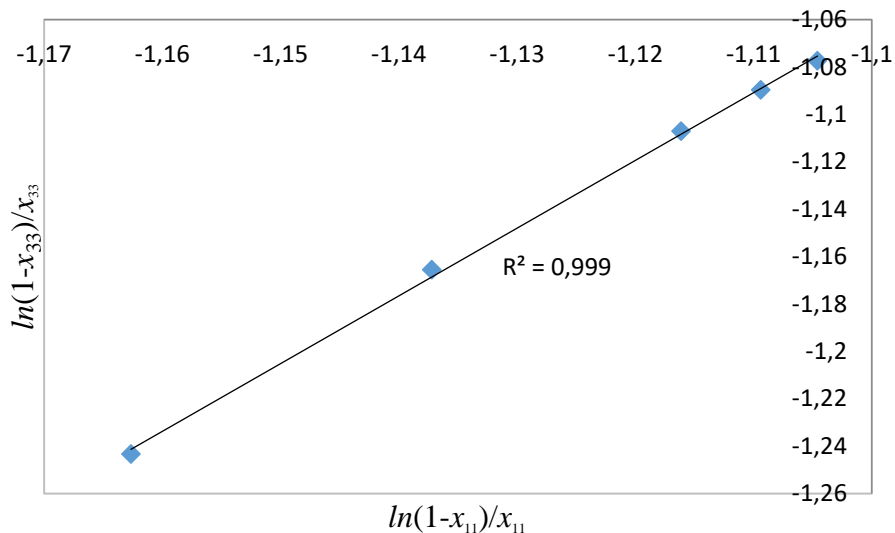
### 4.3 OTHMER-TOBIAS CORRELATIONS

The certainty and reliability of experimentally measured tie-line data was ascertained by applying the Othmer-Tobias (OT) correlations. The OT correlations for system 1 were linear as shown in Figure 4.12 below to indicate the robustness of the calculated mole fraction composition in each phase for the five tie-lines. This indicated that there was minimal systematic additive errors in both the experimental procedure and the use of the calibration curves for the calculation of the mole fraction in each phase.

The Othmer-Tobias is given by equation 4.1 below:

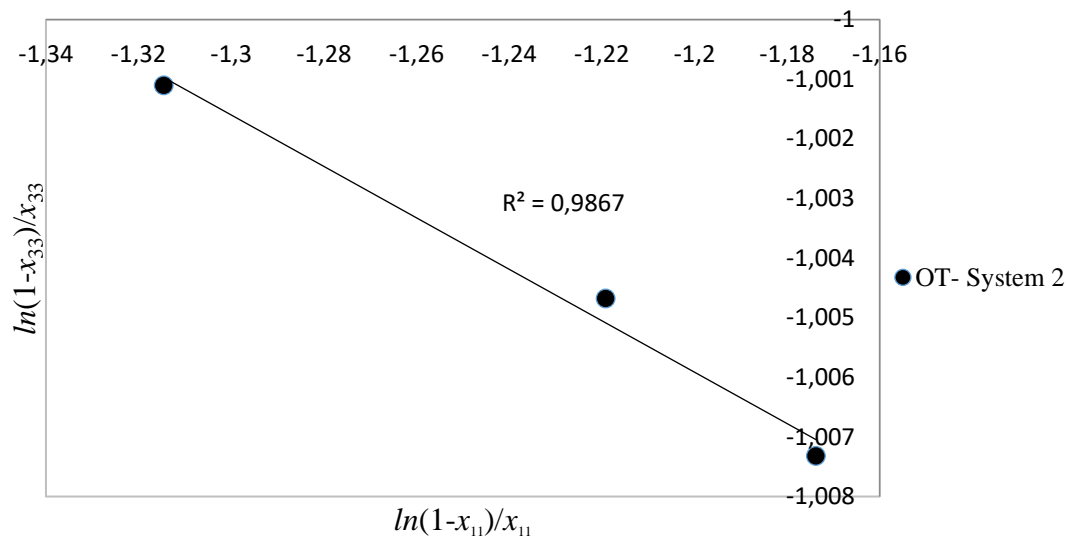
$$\ln\left(\frac{1-x_{33}^{\text{II}}}{x_{33}^{\text{II}}}\right) = A + B \ln\left(\frac{1-x_{11}^{\text{I}}}{x_{11}^{\text{I}}}\right) \quad (4.1)$$

Where  $x_{33}^{\text{II}}$  and  $x_{11}^{\text{I}}$  are the mass/mole fractions of the component 1 and 3 in the raffinate phase and the extract phase respectively.



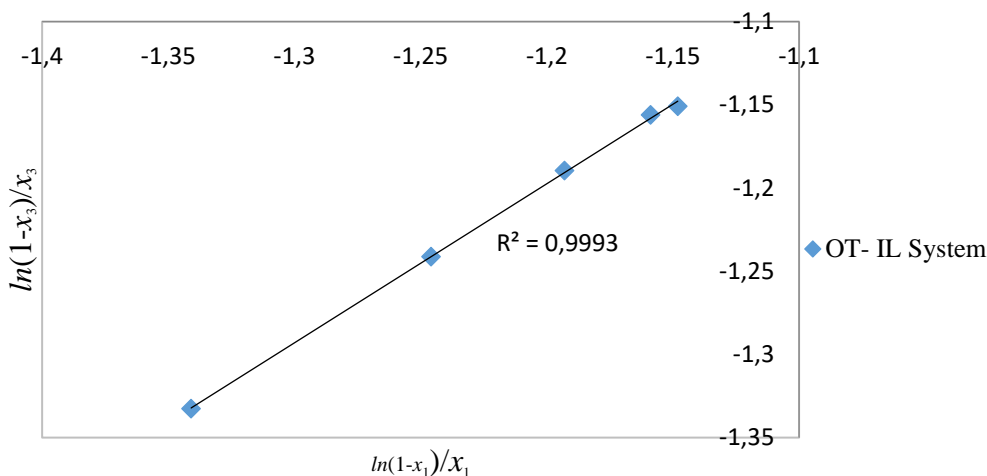
**Figure 4.12 Graph of the Othmer-Tobias (OT) correlation for {methanol (1) + toluene (2) + dodecane (3)} at  $T = 298.15$  K**

In the second system (system 2) which was performed at a slightly higher temperature ( $T = 303.15$  K) as opposed to the two other systems studied at ambient temperatures; the OT correlation was nonlinear indicating extensively high random errors and both the systematic multiplicative and additive errors resulted in large mole fractions errors. Of the eight tie-lines only three tie-lines mole fractions proved to be certain and reliable as demonstrated by Figure 4.13 below. Also five mole fractions were zero and gave undefined ratios.



**Figure 4.13 Graph of the Othmer-Tobias (OT) correlation for{water (1) + methanol (2) + cyclohexane (3)} at T = 303.15 K**

For the IL system the OT correlation was linear throughout the whole tie-line range and indicates the adequate accuracy in the tie-line mole fraction composition, which denotes that the investigation was carried out with minimal errors, both random and systematic errors indicating that when the last system was done i.e. the ionic liquid system greater skill was used in the experimental procedure. The OT correlation outlines the reliability of the five feed tie-line of the IL system. The poor separation of the azeotrope mixture can be attributed by the intermolecular interactions between all components in the system, namely [EMIM][EtSO<sub>4</sub>], methanol and water.



**Figure 4.14 Graph of the Othmer-Tobias (OT) correlation for {[EMIM][EtSO<sub>4</sub>](1)+ methanol (2) + water (3)} at T = 298.15 K**

Even though water was partially immiscible in the ionic liquid, the investigated ionic liquid proved to be a poor solvent for extraction of methanol from water. Ebrahim *et al.*, (2012) stated that two-phase region of slightly soluble alcohols in water is greater than that of a completely miscible alcohol with water due to weak intermolecular interactions in the former, however since the water was partially immiscible in the ionic liquid in this work a clear two-phase region with the studied IL was obtained at equilibrium.

It was however expected that the studied IL will give better results as a potential solvent for separation of water and methanol due to high differences in densities ( $> 0.24$ ) for IL and water, ( $> 0.45$ ) for IL and the alcohol and (0.21) for the alcohol and water. Reddy, (2003) stated that “the density difference between the two phases should be large and the interfacial tension of the solvent must be large and that both properties ensure rapid separation of the two phases” however from the IL system it is evident that it is not always the large difference

between the two phase's densities and the large interfacial tension of the solvents that ensures a rapid separation of two-phases but rather the mobility and distribution of solutes between two phases that are in equilibrium.

Although methanol is miscible in water and the studied IL, it is a primary alcohol with low boiling point and it thus have poor self-interaction forces within the alcohol molecules and have less affinity to produce aqueous two phase system (ATPs) as explained by Ebrahim *et al.*, (2012).

Ghanadzadeh *et al.*, (2009) emphasized that the area of the two phase region depends on the solubility of water in the organic phase. The studied IL was slightly immiscible in water and completely miscible in methanol hence a high distribution of solutes in both phases was observed which denotes the ineffectiveness of the used IL for the separation of the studied azeotrope, as indicated by low  $S$  values ( $< 1$ ) obtained.

Deenadayalu *et al.*, (1999) stated that the binodal curve usually depend on the nature of the alcohol used and the tie-line slope indicates the phase in which the alcohol is more soluble. In this work the studied alcohol is more soluble in aqueous-rich phase than the IL-rich phase.

The studied azeotrope (methanol + water) was not investigated under different temperatures because; as stated by Cháfer *et al.*, (2008) temperature has no effect on the size of immiscibility and the solvents studied were totally miscible in each other except water in ionic liquid which again was slightly immiscible, Matthew *et al.*, (2006) also stated that an increase in temperature only result in an increase in the mutual miscibility of the two liquid phases. Ghanadzadeh *et al.*, (2012) also stated that the selectivity values or the separation factor will only show a minimal change with temperature effect.

## 4.4 NRTL MODELING AND CORRELATION OF LLE DATA

In this study the NRTL equations as discussed in chapter two were used to correlate the experimental LLE data.

The root mean square deviation (RMSD) is a measure of the agreement between the experimental data and calculated values. The RMSD value is given by equation 2.20 below:

$$\text{RMSD} = \left[ \sum_i \sum_j \sum_k (x_{ijk}^{\text{exp}} - x_{ijk}^{\text{calc}})^2 / 6M \right]^{1/2} \quad (2.20)$$

Where  $M$  is the total number of tie-lines and or number of interactions components,  $x^{\text{exp}}$  and  $x^{\text{calc}}$  are the experimental and calculated mole fractions, and subscript  $i$ ,  $j$  and  $k$  designate, the component, phase and tie-line respectively. The experimental and the NRTL data are given in Tables 4.8 to 4.11 for all the studied systems together with the %RMSD values for each tie-line, the ternary diagrams were constructed to evaluate the agreement between the experimental data and the NRTL calculated data (estimated data) and are presented in Figures 4.15 to 4.18 below. The interaction energies and the fitting parameters of the NRTL are presented in Table 4.12.

**Table 4.8 NRTL modelling, experimental and NRTL data for system {methanol (1) + toluene (2) + dodecane (3)} (system 1) and % RMSD using refractive index parameter at  $T = 298.15$  K.**

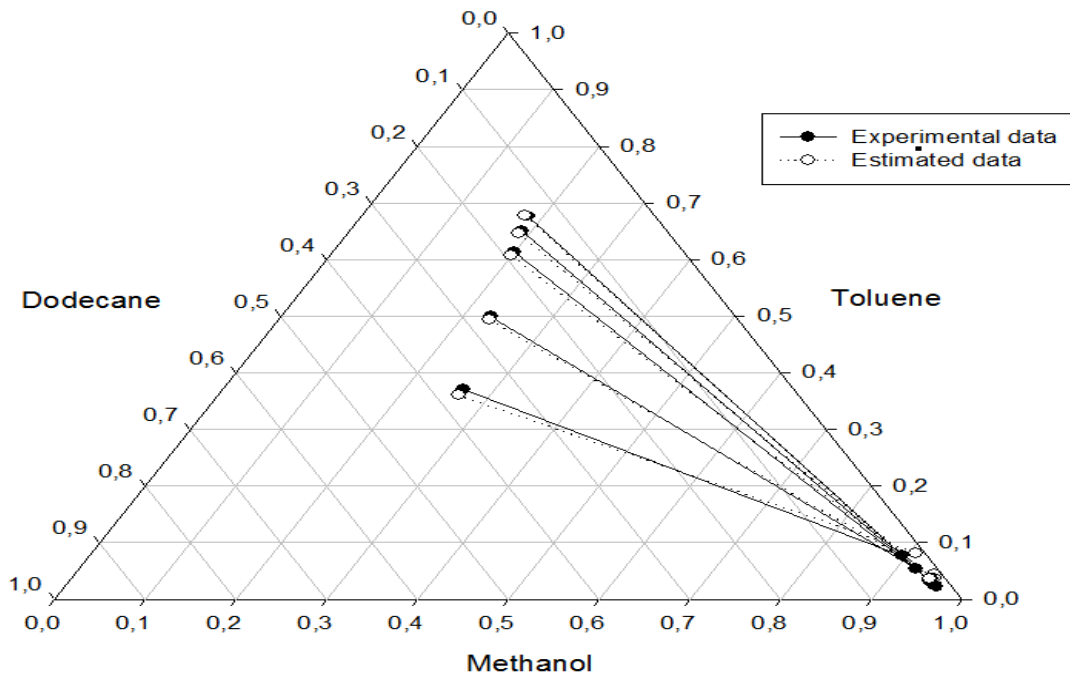
<b>Equilibrium</b>	<b>Experimental Data</b>			<b>NRTL Data</b>			
<b>Phase</b>	$x_1$	$x_2$	$x_3$	$x_1$	$x_2$	$x_3$	<b>%RMSD</b>
<b>Alkane -Rich</b>	0.2661	0.3699	0.3640	0.2649	0.3603	0.3749	
<b>Phase</b>							1.1440
<b>Alcohol-Rich</b>	0.8943	0.0774	0.0252	0.9090	0.0812	0.0098	
<b>Phase</b>							
<b>Alkane-Rich</b>	0.2312	0.4989	0.2699	0.2326	0.4931	0.2744	
<b>Phase</b>							1.288
<b>Alcohol-Rich</b>	0.9218	0.0544	0.0209	0.9468	0.0437	0.0096	
<b>Phase</b>							

**Table 4.8 Continued**

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<b>Alkane -Rich</b>	0.2006	0.6125	0.1869	0.2003	0.6066	0.1931	
<b>Phase</b>							0.4920
<b>Alcohol-Rich</b>	0.9491	0.0315	0.0167	0.9501	0.0370	0.0130	
<b>Phase</b>							
<b>Alkane -Rich</b>	0.1905	0.6496	0.1599	0.1889	0.6464	0.1647	
<b>Phase</b>							0.6320
<b>Alcohol-Rich</b>	0.9569	0.0250	0.0154	0.9485	0.0362	0.0153	
<b>Phase</b>							
<b>Alkane -Rich</b>	0.1832	0.6768	0.1400	0.1801	0.6774	0.1425	
<b>Phase</b>							0.8870
<b>Alcohol-Rich</b>	0.9612	0.0214	0.0147	0.9459	0.0363	0.0179	
<b>Phase</b>							

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**Figure 4.15** Graph of the ternary system {methanol (1) + toluene (2) + dodecane (3)} at  $T = 298.15$  K, (●) experimental tie-line data and (○) NRTL data compositions calculated from refractive index.

**Table 4.9 NRTL modelling, experimental and NRTL data for system {methanol (1) + toluene (2) + dodecane (3)} (system 1) and % RMSD using density parameter at  $T = 298.15$  K.**

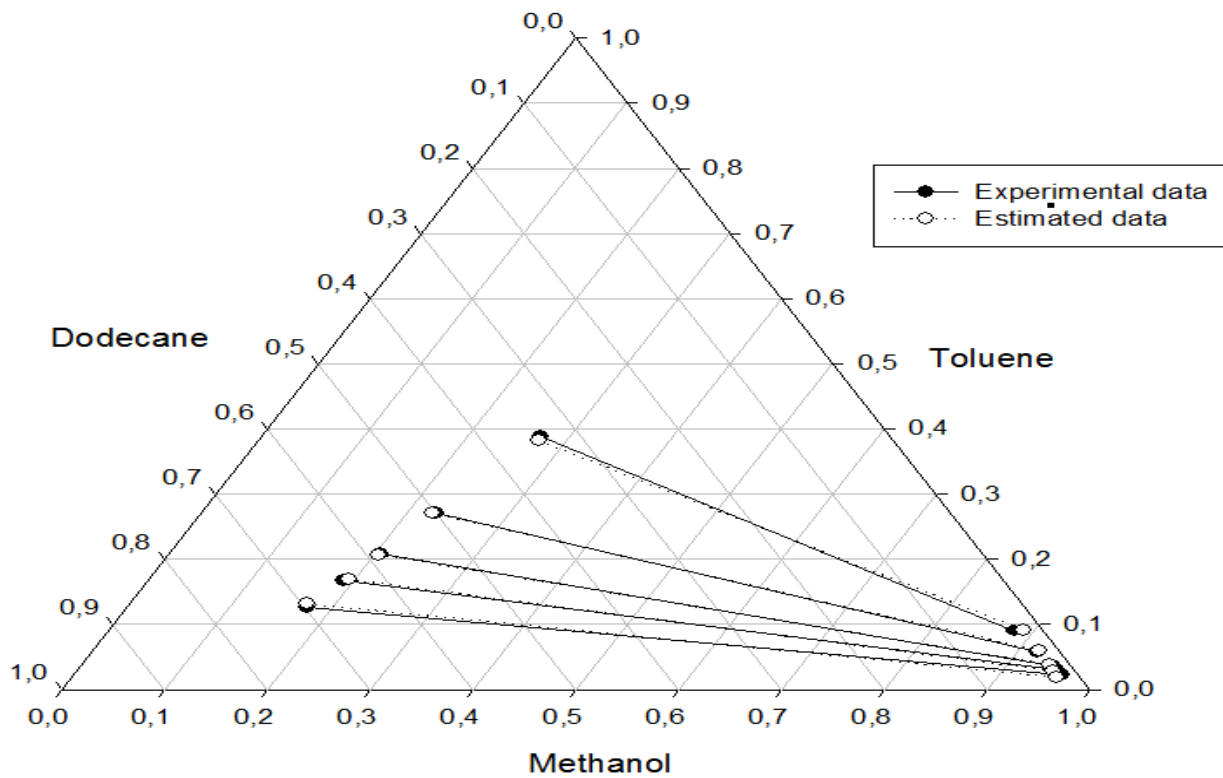
<b>Equilibrium</b>	<b>Experimental Data</b>			<b>NRTL Data</b>			
<b>Phase</b>	$x_1$	$x_2$	$x_3$	$x_1$	$x_2$	$x_3$	<b>%RMSD</b>
<b>Alkane -Rich</b>	0.2718	0.3875	0.3407	0.2740	0.3813	0.3447	
<b>Phase</b>							0.5620
<b>Alcohol-Rich</b>	0.8823	0.0897	0.0280	0.8893	0.0916	0.0192	
<b>Phase</b>							
<b>Alkane-Rich</b>	0.2292	0.2715	0.4993	0.2254	0.2704	0.5042	
<b>Phase</b>							0.3020
<b>Alcohol-Rich</b>	0.9197	0.0579	0.0224	0.9210	0.0597	0.0193	
<b>Phase</b>							
<b>Alkane -Rich</b>	0.2061	0.2083	0.5856	0.2060	0.2065	0.5876	
<b>Phase</b>							0.2590
<b>Alcohol-Rich</b>	0.9461	0.0354	0.0185	0.9415	0.0383	0.0203	
<b>Phase</b>							

**Table 4.9 Continued**

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<b>Alkane -Rich</b>	0.1911	0.1674	0.6415	0.1945	0.1693	0.6362
<b>Phase</b>						0.3290
<b>Alcohol-Rich</b>	0.9522	0.0303	0.0175	0.9508	0.0280	0.0212
<b>Phase</b>						
<b>Alkane -Rich</b>	0.1762	0.1267	0.6971	0.1740	0.1313	0.6948
<b>Phase</b>						0.3880
<b>Alcohol-Rich</b>	0.9610	0.0227	0.0163	0.9587	0.0188	0.0225
<b>Phase</b>						

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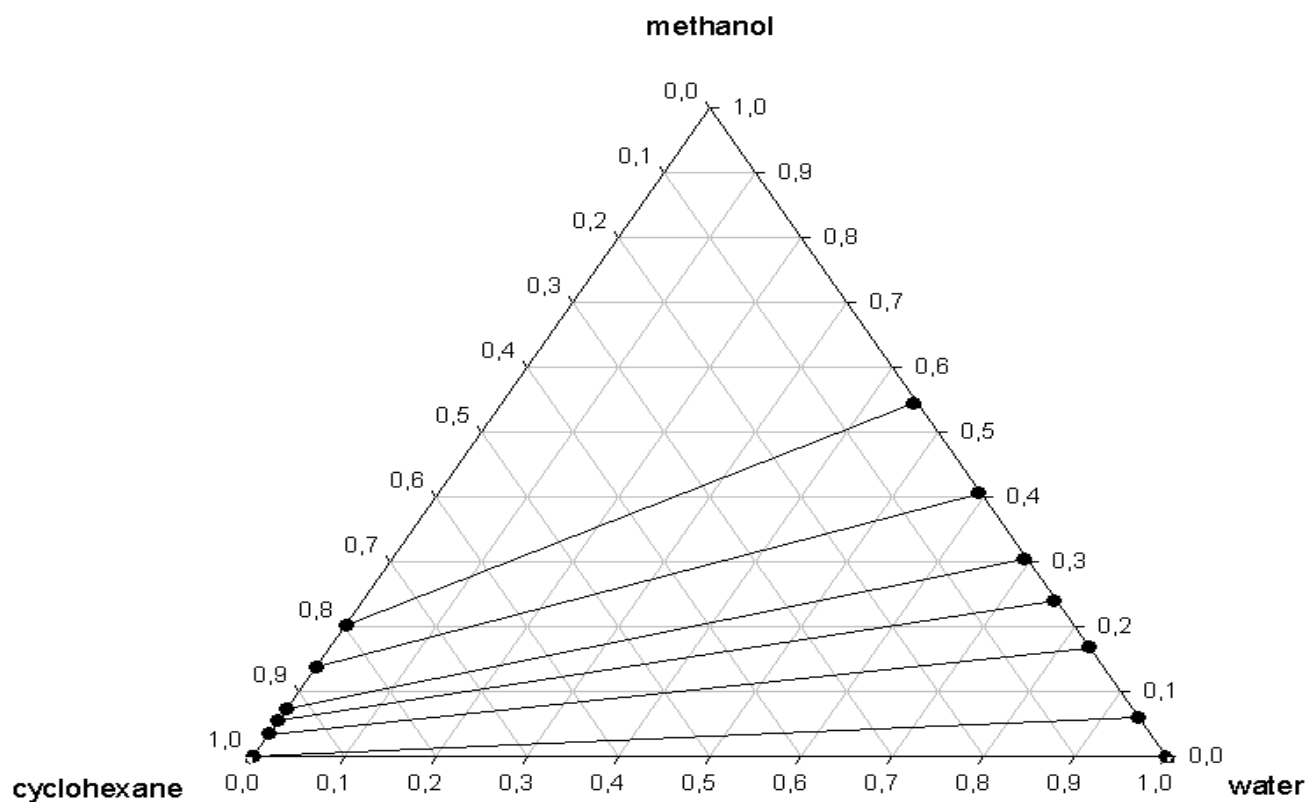
**Figure 4.16** Graph of the ternary system {methanol (1) + toluene (2) + dodecane (3)} at  $T = 298.15 \text{ K}$ , (●) experimental tie-line data and (○) NRTL data compositions calculated from density.

**Table 4.10 NRTL modelling, experimental and NRTL data for system {water (1) + methanol (2) + cyclohexane (3)} (system 2) and % RMSD using density parameter at  $T = 303.15$  K**

<b>Equilibrium</b>	<b>Experimenta Data</b>			<b>NRTL Data</b>			
<b>Phase</b>	$x_1$	$x_2$	$x_3$	$x_1$	$x_2$	$x_3$	<b>%RMSD</b>
<b>Aqueous- Rich Phase</b>	1.000	0.000	0.000	0.9999	0.9998	0.0002	0.0127
<b>Alkane-Rich Phase</b>	0.000	0.000	1.000	0.000	0.000	1.00	
<b>Aqueos- Rich Phase</b>	0.9399	0.0601	0.000	0.9396	0.0601	0.0003	0.0193
<b>Alkane- Rich Phase</b>	0.000	0.000	1.000	0.000	0.000	1.000	
<b>Aqueous- Rich Phase</b>	0.8316	0.1682	0.0002	0.8300	0.1693	0.0007	0.1164
<b>Alkane- Rich Phase</b>	0.000	0.0345	0.9655	0.000	0.0331	0.9669	

**Table 4.10 Cotinued**

<b>Aqueous -</b>	0.7586	0.2404	0.0010	0.7596	0.2393	0.0011	
<b>Rich Phase</b>							0.0959
<b>Alkane- Rich</b>	0.000	0.0555	0.9445	0.000	0.0568	0.9423	
<b>Phase</b>							
<b>Aqueous-</b>	0.6936	0.3044	0.0017	0.6987	0.2998	0.0015	
<b>Rich Phase</b>							0.4433
<b>Alkane- Rich</b>	0.000	0.0736	0.9264	0.000	0.0797	0.9203	
<b>Phase</b>							
<b>Aqueous-</b>	0.5917	0.4054	0.0029	0.5863	0.4111	0.0026	
<b>Rich Phase</b>							0.5752
<b>Alkane- Rich</b>	0.000	0.1382	0.8618	0.000	0.1299	0.8701	
<b>Phase</b>							
<b>Aqueous -</b>	0.4510	0.5445	0.0045	0.4526	0.5429	0.0045	
<b>Rich Phase</b>							0.1860
<b>Alkane-Rich</b>	0.000	0.2027	0.7973	0.000	0.02055	0.7945	
<b>Phase</b>							



**Figure 4.17** Graph of the ternary system {water (1) + methanol (2) + cyclohexane (3)} at  $T = 303.15 \text{ K}$ , (●) experimental tie-line data and (○) NRTL data compositions

**Table 4.11 NRTL modelling, experimental and NRTL data for system**

**{[EMIM][EtSO<sub>4</sub>](1) + methanol (2) + water(3)} (Ionic liquid system), and % RMSD at**

**$T = 298.15$  K**

<b>Equilibrium</b>	<b>Experimental Data</b>			<b>NRTL Data</b>			
<b>Phase</b>	$x_1$	$x_2$	$x_3$	$x_1$	$x_2$	$x_3$	<b>%RMSD</b>
<b>Aqueous -</b>	0.0001	0.1571	0.8429	0.0042	0.1444	0.8514	
<b>Rich Phase</b>							1.0201
<b>IL- Rich</b>	0.9641	0.0359	0.0001	0.9505	0.0495	0.0000	
<b>Phase</b>							
<b>Aqueous-</b>	0.0001	0.3485	0.6515	0.0035	0.3511	0.6455	
<b>Rich Phase</b>							0.3850
<b>IL -Rich</b>	0.8211	0.1789	0.0001	0.8253	0.1747	0.0000	
<b>Phase</b>							
<b>Aqueous-</b>	0.0001	0.4524	0.5476	0.0031	0.4519	0.5450	
<b>Rich Phase</b>							0.1620
<b>IL-Rich</b>	0.7323	0.2677	0.0001	0.7326	0.2673	0.0000	
<b>Phase</b>							

**Table 4.11 Continued**

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<b>Aqueos -</b>	0.0001	0.5476	0.4524	0.028	0.5434	0.4538	
<b>Rich Phase</b>							0.3470
<b>IL -Rich</b>	0.6307	0.3693	0.0001	0.6260	0.3741	0.0000	
<b>Phase</b>							
<b>Aqueous-</b>	0.0001	0.5771	0.4225	0.0027	0.5789	0.4185	
<b>Rich Phase</b>							0.2920
<b>IL-Rich</b>	0.5748	0.4252	0.0001	0.5782	0.4218	0.0001	
<b>Phase</b>							

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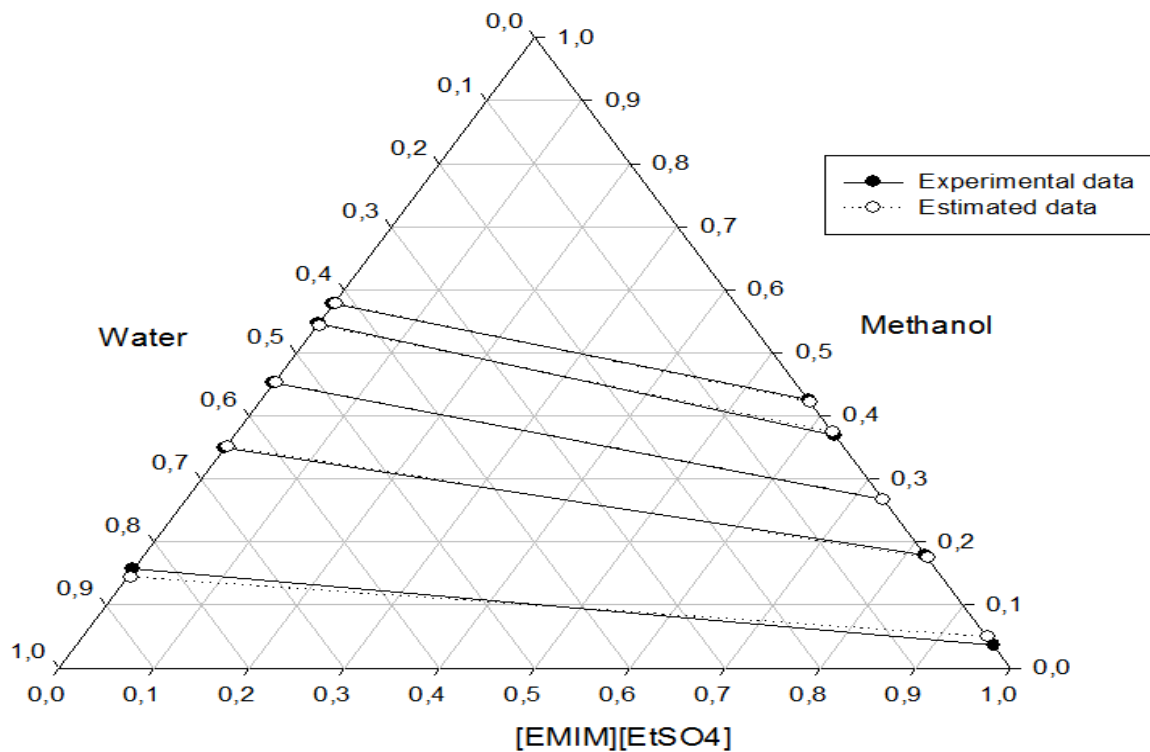


Figure 4.18 Graph of the ternary system {[EMIM][EtSO<sub>4</sub>](1) + methanol (2) + water(3)} at  $T = 298.15 \text{ K}$ , (●) experimental tie-line data and (○) NRTL data compositions

**Table 4.12 Fitting parameters of the NRTL equations determined from the ternary Liquid-Liquid Equilibrium of the studied systems.**

System	<u>NRTL</u> <u>Component</u>			
	<i>i - j</i>	$\Delta g_{ij}/(\text{J.mol}^{-1})$	$\Delta g_{ji}/(\text{J.mol}^{-1})$	$\alpha$
{methanol (1) + toluene (2) + dodecane (3)} $n_D$	1 - 2	1030.6	59.158	0.2
	1 - 3	1078.8	1991.7	0.3
	2 - 3	1922.1	66.45	0.2
{methanol (1) + toluene (2) + dodecane (3)} $\rho$	1 - 2	911.47	612.85	0.4
	1 - 3	1339.8	535.76	0.4
	2 - 3	905.54	366.55	0.2
{water(1) + methanol (2) cyclohexane(3)}	1 - 2	-292.11	14983.0	0.2
	1 - 3	2520.9	14432.0	0.3
	2 - 3	1219.5	4143.8	0.4
{[EMIM][EtSO <sub>4</sub> ](1) + methanol (2) + water(3)}	1 - 2	7.6203	1373.5	0.4
	1 - 3	861.3	1588.8	0.3
	2 - 3	2779.7	-417.47	0.3

Several authors used in this study, namely : In- Chang *et al.*, (2008); Domńska *et al.*,(2010); Domńska *et al.*, (2012); Krolikowski *et al.*, (2012) and others have used the NRTL model to describe their measurements of liquid- liquid equilibria, vapour –liquid equilibria and solid-liquid equilibria studies with ionic liquids. The NRTL model was also used for the correlations of conventional solvents in most studies, namely: Deenadayalu *et al.*, (1999); Trivesh *et al.*, (2011); Ghanadzadeh *et al.*, (2012); Ebrahim *et al.*, (2012). Binary interactions  $\Delta g_{ij}$  and  $\Delta g_{ji}$  were measured using the non-randomness  $\alpha$  and equations given in chapter two.

The objective function for the regression of the NRTL parameter is the equality of the activity for each component in both raffinate and extractant phase coupled with the assumption of equilibrium in the liquid phase as referred to in equation 2.15 in chapter two.

Even though all the results of the studied systems show good correlation and agreement with the NRTL parameters, The %RSDM was observed to be high in (system 1){ methanol (1) + toluene (2) + dodecane (3)} when using RI measurements, with the maximum %RSMD ( $\sigma$ ) of 1.1440 and minimum of 0.4920 and it showed a very small error margin with the density measurements where the maximum %RSMD ( $\sigma$ ) at 0.5628 and the minimum at 0.2590 indicating that density parameter when compared to the refractive index parameter gave better results for compositions as in method verification and validation.

The second system :{ water (1) + methanol (2) + cyclohexane (3)} showed better NRTL correlation with an exception to the two tie-lines which was also discussed with the OT correlation, the system gave the maximum %RSMD ( $\sigma$ ) of only 0.5752 with the minimum error margin of 0.0127.

The IL system :{ [EMIM][EtSO<sub>4</sub>] (1) + methanol (2) + water (3)} also showed a very good agreement with the maximum %RSMD ( $\sigma$ ) of 1.0201 and the minimum error of 0.1620 in tie-lines.

## CHAPTER 5: CONCLUSION AND RECOMMENDATIONS

Liquid-liquid equilibrium studies for the ternary mixtures {methanol (1) + toluene (2) + dodecane (3)}, {water (1) + methanol (2) + cyclohexane (3)} and {[EMIM][EtSO<sub>4</sub>] (1) + methanol (2) + water (3)} were successfully conducted and the generated LLE data presented at  $T = 298.15$  K for both {methanol (1) + toluene (2) + dodecane (3)} and {[EMIM][EtSO<sub>4</sub>] (1) + methanol (2) + water (3)} systems and at  $T = 303.15$  K for {water (1) + methanol (2) + cyclohexane (3)} system.

The generated experimental data was correlated using the Othmer-Tobias correlations and NRTL modelling and the latter model was also used to calculate the phase compositions and component interactions of the studied mixtures.

The selectivity and the distribution co-efficient were also presented for the three systems.

(System 1) selectivities were greater than one and selectivities for (system 2) and (IL system) were less than one. The distribution co-efficients for all the systems were below one.

A recommendation is to explore the use of ILs with low mutual solubility with water since methanol is highly miscible in water, these ILs were listed by Chapeaux (2009) contained the imidazolium cation and the following anions: tris(pentafluoroethyl) trifluorophosphate, tris(trifluoromethylsulfonyl) methide, bis(trifluoromethylsulfonyl) imide, hexafluorophosphate, tetracyanoborate, trifluoromethane sulfonate and tetrafluoroborate as

their mutual solubility increase in that order with diacynoamide anion having the largest mutual solubility with water.

If the mutual solubility of IL was to be decreased with methanol or any alcohol, it is recommended to add the hydroxyl group on the cation alkyl chain as this significantly decreases the mutual solubility of ILs with alcohols. Again we can explore the use of tris(pentafluoroethyl) trifluorophosphate anion based ILs which is reported to have low solubility with alcohols as opposed to bis(trifluoromethylsulfonyl)imide anion and the tetrafluoroborate anion.

Chapeaux (2009) reported that distillation of alcohol requires the energy between 100 -2000  $\text{kJ}\cdot\text{mol}^{-1}$  whereas the use of solvent extraction for the separation of alcohol requires 50  $\text{kJ}\cdot\text{mol}^{-1}$  or less.

It is also recommended that once the suitable IL/s is found, industrial samples be used to separate azeotropic mixtures common in the petrochemical industries.

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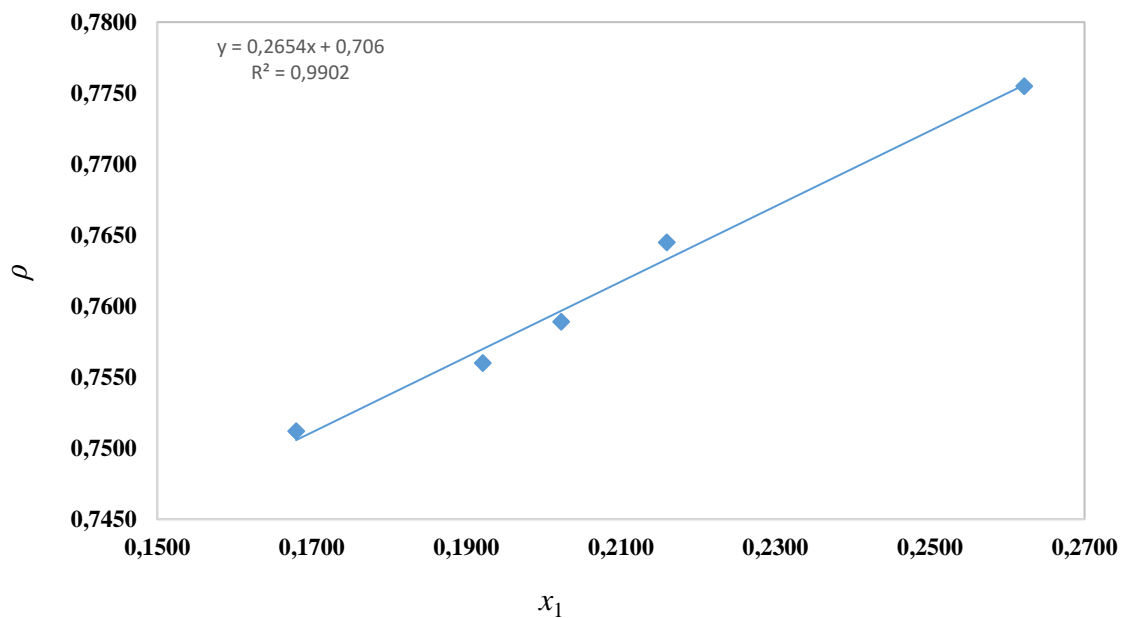
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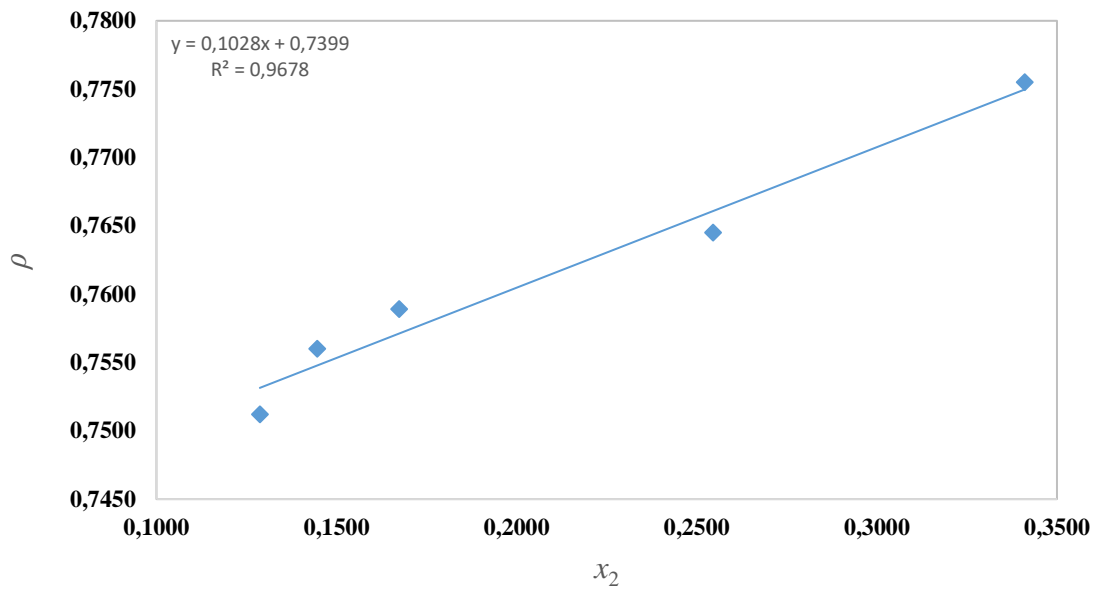
# APPENDICES

The appendices contains experimental calibrations curves used for the determination of the exact tie-line compositions for each system reported in chapter 5 and Glossary of terms used in context.

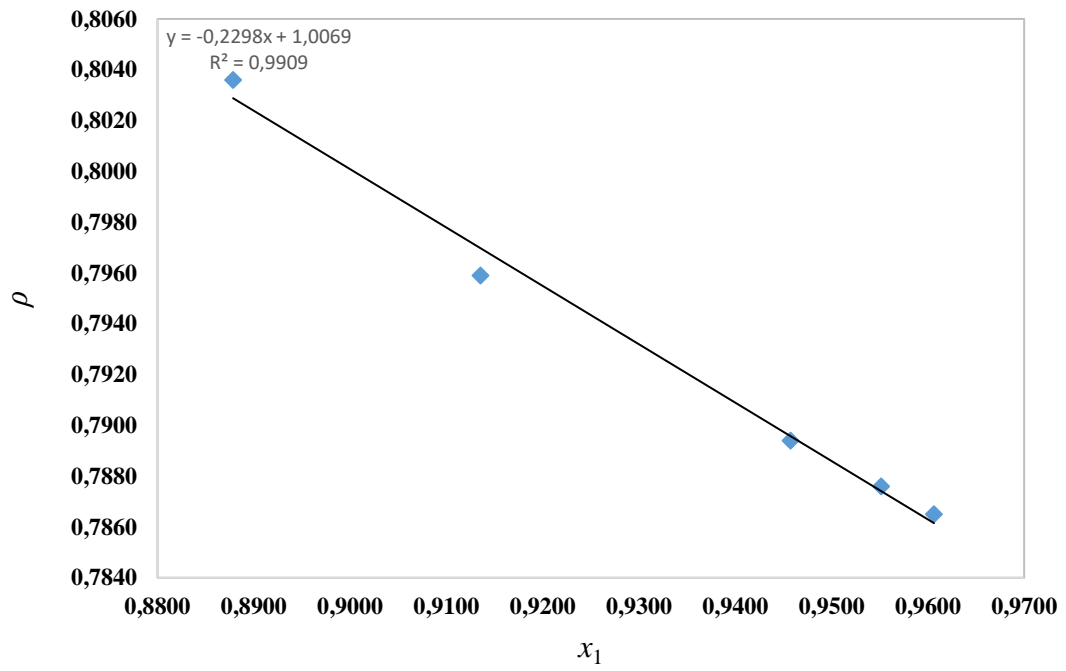
## 1. APPENDIX A System 1 {METHANOL (1) + TOLUENE (2) + DODECANE (3)}



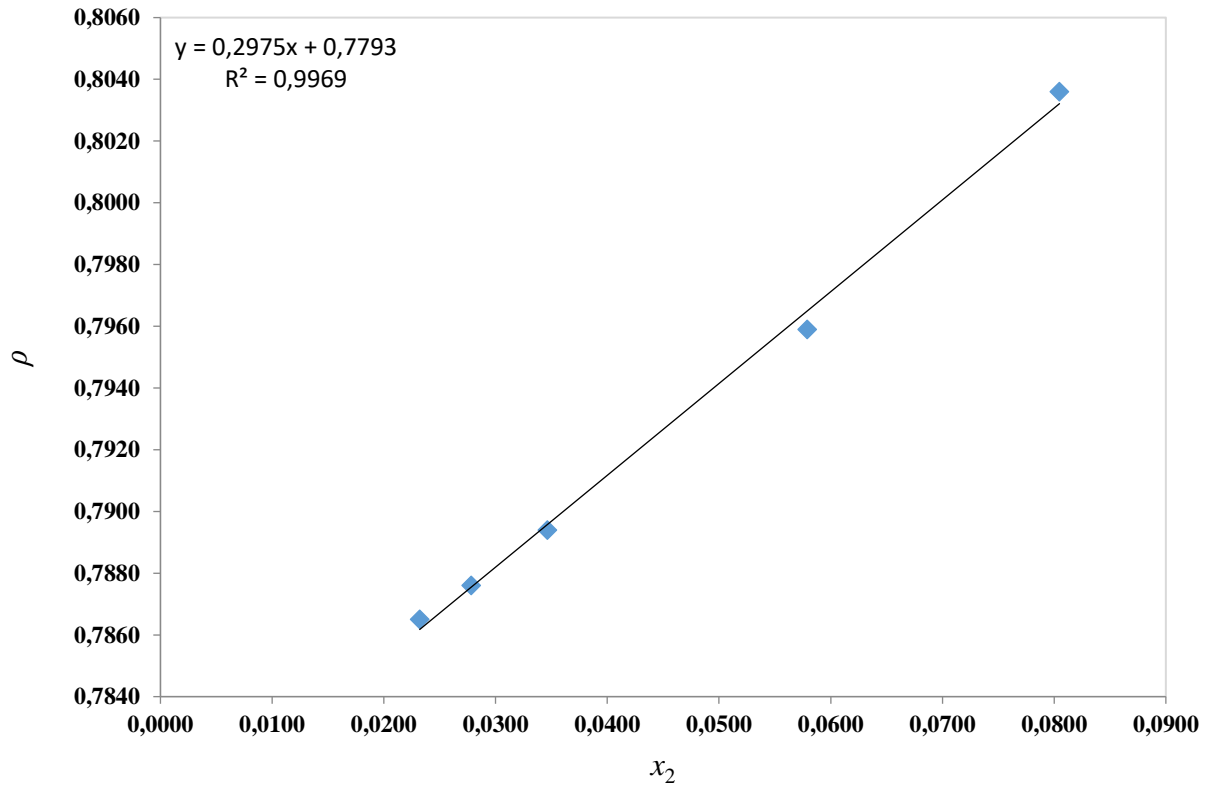
**Figure A.1 Calibration curve of ( $x_1$ ) versus ( $\rho$ ) in the alkane - rich region**



**Figure A.2 Calibration curve of ( $x_2$ ) versus ( $\rho$ ) in the alkane - rich region**



**Figure A.3 Calibration curve of ( $x_1$ ) versus ( $\rho$ ) in the alcohol - rich region**



**Figure A.4 Calibration curve of ( $x_2$ ) versus ( $\rho$ ) in the alcohol- rich region**

## 2. APPENDIX B System 2 { WATER (1) + METHANOL (2) + CYCLOHEXANE (3)}

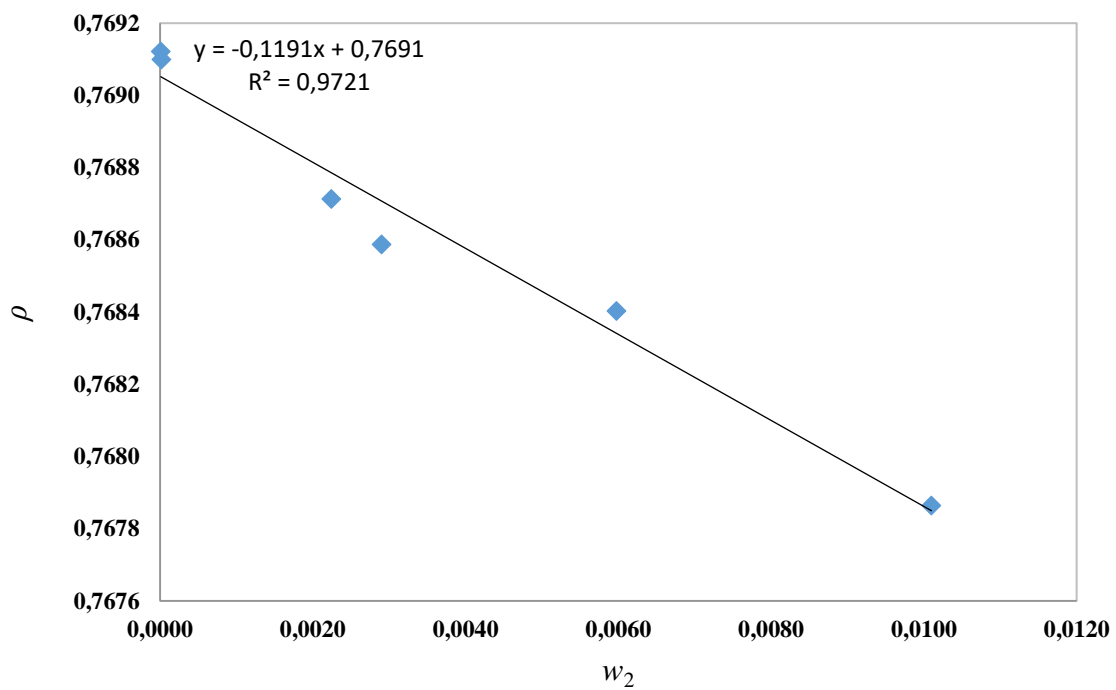
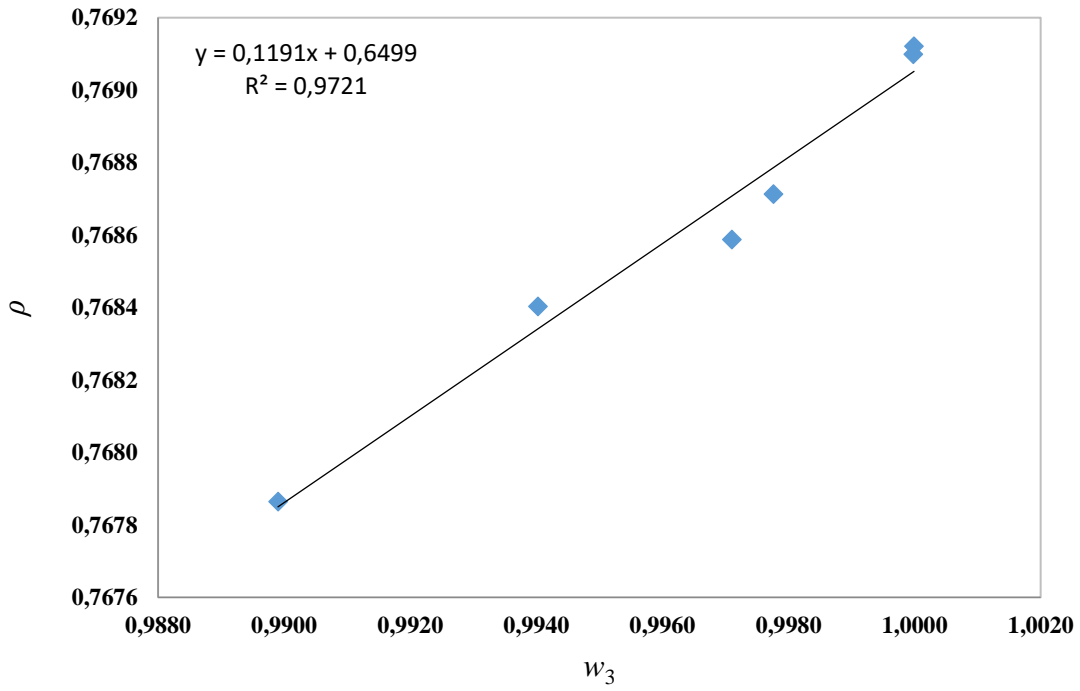
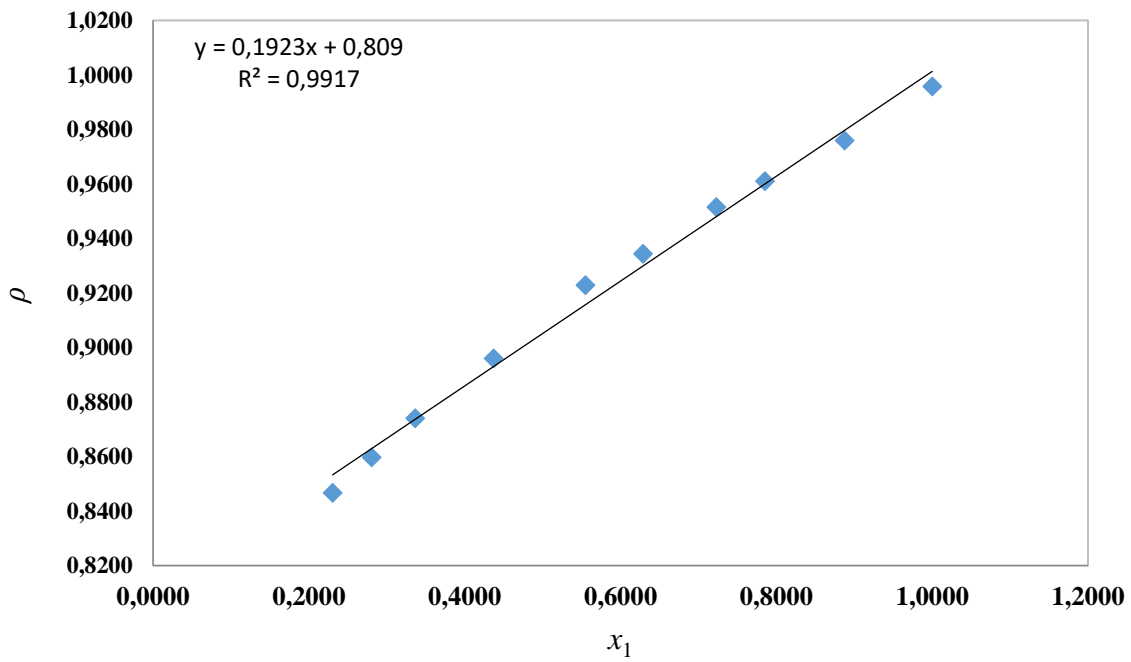


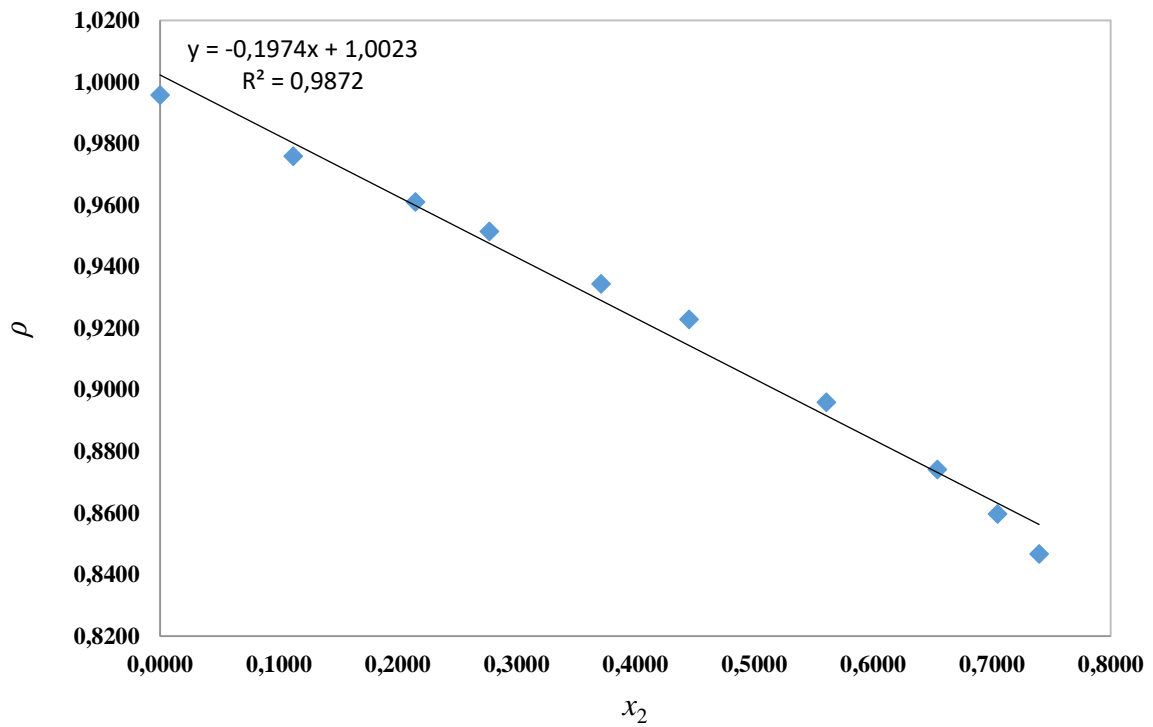
Figure B.1 Calibration curve of ( $w_2$ ) versus ( $\rho$ ) in the organic-rich region



**Figure B.2 Calibration curve of ( $w_3$ ) versus ( $\rho$ ) in the organic-rich region**

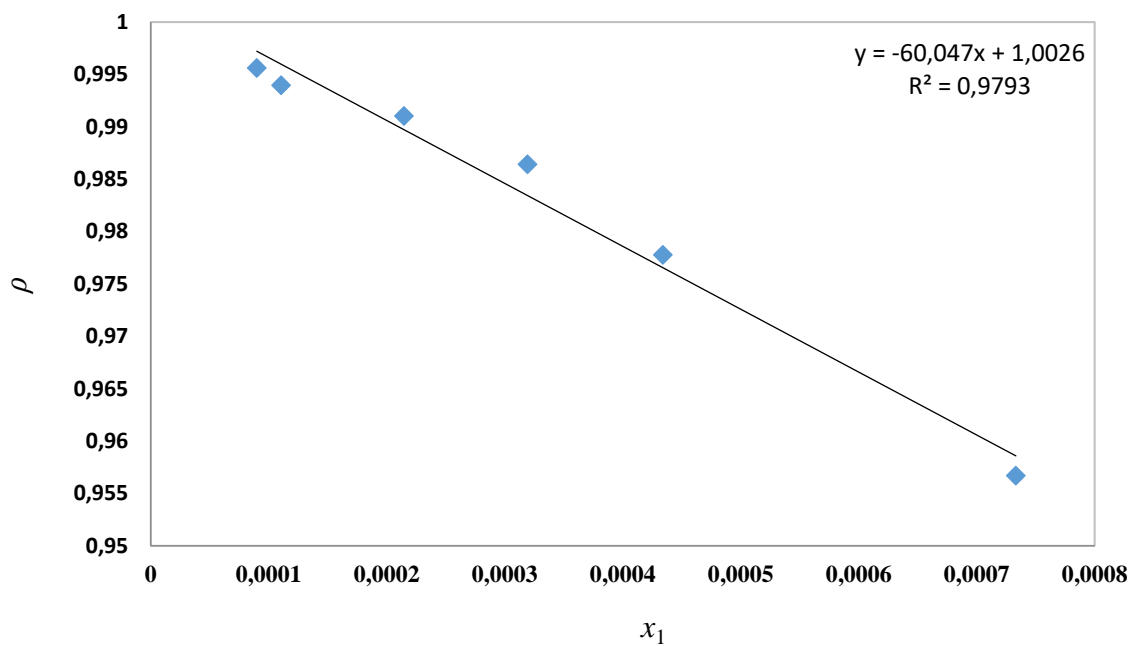


**Figure B.3 Calibration curve of ( $x_1$ ) versus ( $\rho$ ) in the aqueous- rich region**

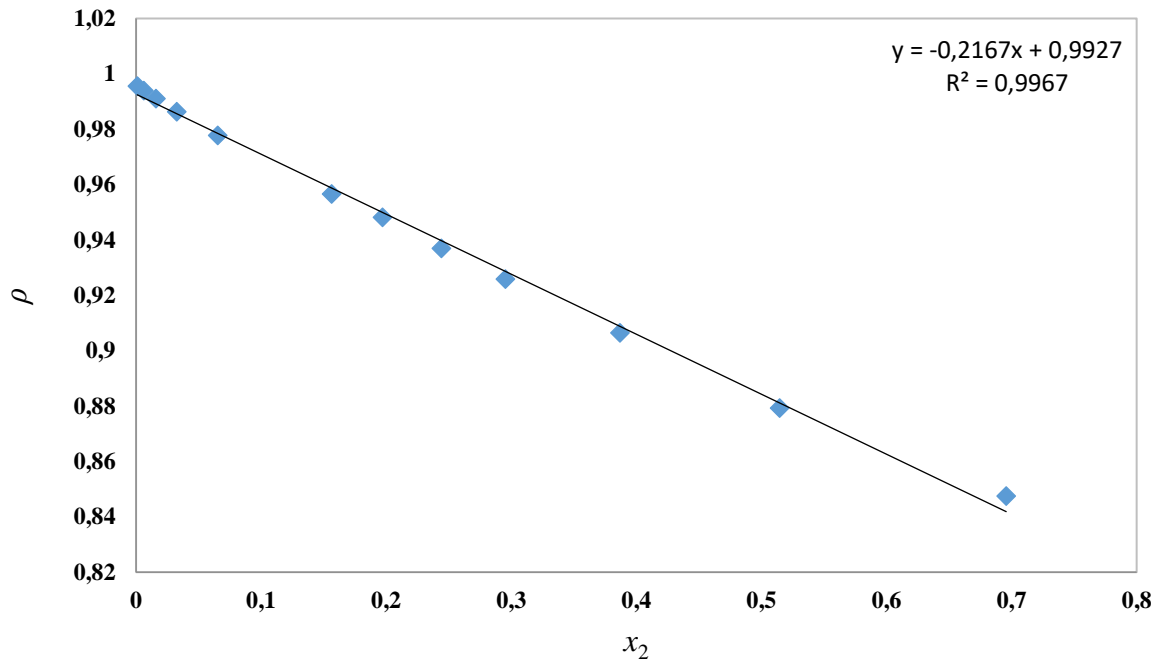


**Figure B.4 Calibration curve of ( $x_2$ ) versus ( $\rho$ ) in the aqueous-rich region**

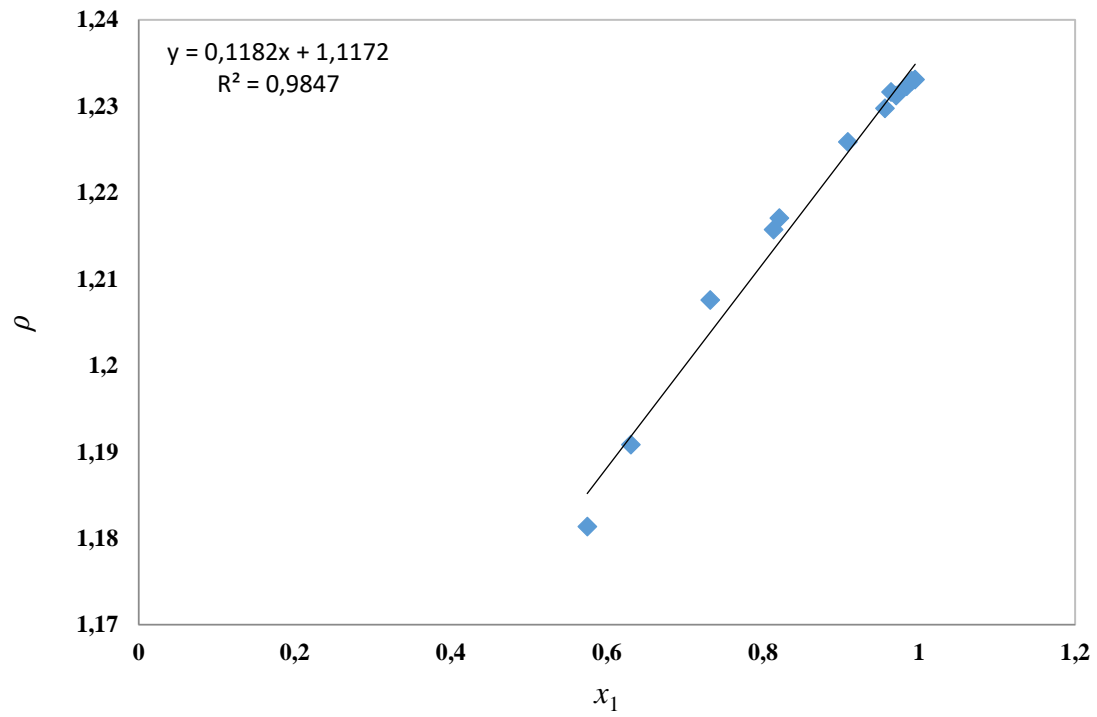
**3. APPENDIX C System 3 {[EMIM][ETSO<sub>4</sub>](1) + METHANOL (2) + WATER(3) }**



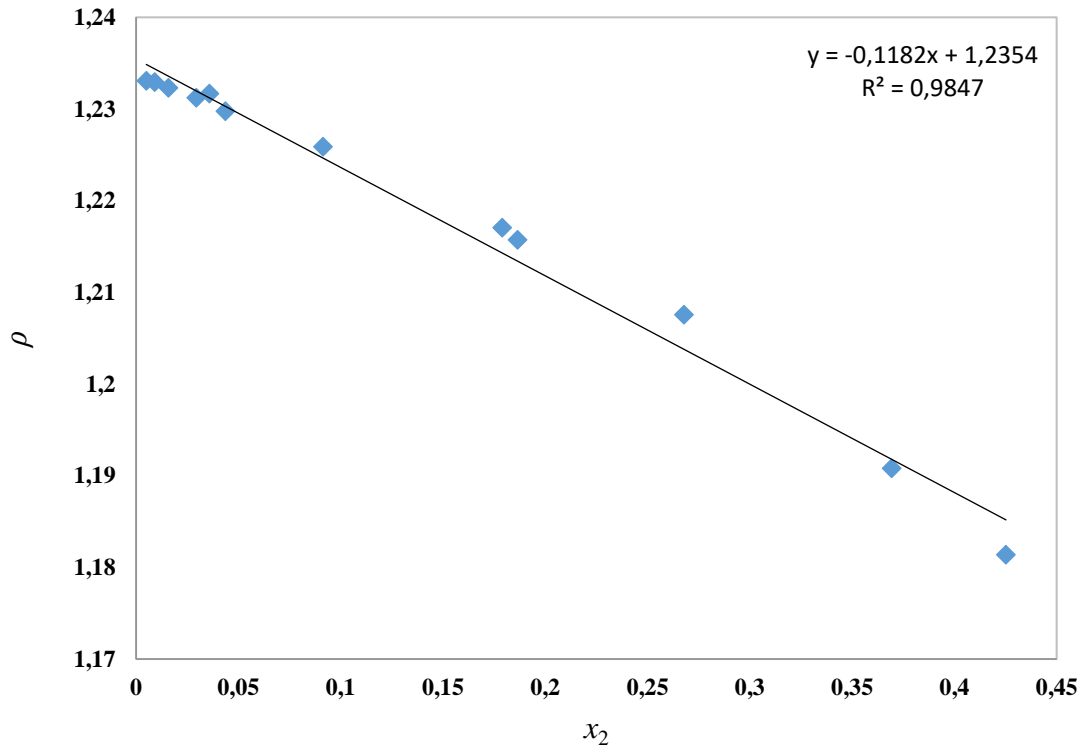
**Figure C.1 Calibration curve of ( $x_1$ ) versus ( $\rho$ ) in the aqueous-rich region**



**Figure C.2 Calibration curve of ( $x_2$ ) versus ( $\rho$ ) in the aqueous-rich region**



**Figure C.3 Calibration curve of ( $x_1$ ) versus ( $\rho$ ) in the IL-rich region**



**Figure C.4 Calibration curve of ( $x_2$ ) versus ( $\rho$ ) in the IL-rich region**

## **4. APPENDIX D**

### **GLOSSARY**

- 1. Alcohol:** Any organic compound in which a hydroxyl group is bonded to a carbon atom of the alkyl or substituted alkyl group.
- 2. Alkanol:** Any of a class of organic compounds containing the hydroxyl (-OH) functional group except those in which the (-OH) group is attached to an aromatic ring.
- 3. Binodal curve:** Coexistence curve. Curve defining the region of composition and temperature in a phase diagram for a binary mixture across which a transition occurs from miscibility of the components to conditions where single-phase mixtures are metastable or unstable resulting in two phases.
- 4. Distillation:** A method of separating mixtures based on differences in volatility of components in a boiling liquid mixture.
- 5. Distribution coefficient:** Is the ratio of the concentration of component to be separated in the solvent rich (extract) phase to the ratio of the same component in the solvent depleted (raffinate) phase.
- 6. Entrainer:** The solvent/component that is added in a binary solution to bring about the extract in liquid-liquid equilibrium.
- 7. Ether:** An organic compound having an oxygen atom bonded to two carbon atoms; R–O–R'.
- 8. Fischer-Tropsch (FT):** Is a catalyzed chemical reaction in which carbon monoxide and hydrogen are converted into liquid hydrocarbons of various forms.
- 9. Hydrophobic:** Repelling, tending not to combine with, or incapable of dissolving in water.

- 10. Hydrophilic:** Having an affinity for water; readily absorbing or dissolving in water.
- 11. Ionic liquid:** Compound that is composed of cations and anion pairs, but is not a molten salt
- 12. Liquid-liquid extraction/solvent extraction:** A method to separate compounds based on their relative solubilities in a solvent (extractant), usually water or an organic solvent. It is an extraction of a substance from one liquid into another liquid phase.
- 13. Oxygenated compounds:** Compounds that consist of oxygen as part of their chemical structure.
- 14. Raffinate:** Immiscible layer formed by the remainder of the original solution in liquid-liquid equilibrium.
- 15. Plait point:** It is the point where the composition of the two phases in equilibrium is identical.
- 16. Phase diagram:** A diagram of a substance that indicates the conditions of the temperature and pressure at which its physical state (solid, vapour or liquid) phases are thermodynamically stable.
- 17. Phase equilibrium:** The transfer of a substance from one phase to another for two phases in contact to exchange their constituents until the composition of each phase attains a constant or equilibrium.
- 18. Polar solvent:** A solvent that contains bonds between atoms which are polar.
- 19. Selectivity:** Is the ratio of the mole fractions of two components that are to be separated in the one phase to the ratio of the same two components in the other phase.
- 20. Synthetic gas:** A gas produced catalytically by the reaction of hydrogen ( $H_2$ ) and carbon monoxide (CO) at high pressure in reforming steam.

**21. Tie lines:** Are the lines that connect two phases which are in equilibrium on a ternary phase diagram.