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Application of selected ionic liquids for different separation problems: Liquid-liquid equilibria and activity coefficients at infinite dilution

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Submitted in the fulfilment of the academic requirements for the degree of Doctor of Philosophy in Chemistry, Faculty of Applied Sciences, Department of Chemistry, Durban University of Technology

March 2021

Preface

I, Kabane Bakusele, declare that:

1. The research work reported in this thesis, besides where indicated, is my original work.
2. This work has not been submitted for any examination or degree at any other university.
3. This work does not contain other person’s data, graphs, or information, unless specifically stated.
4. The work described in this thesis was performed by the author (Kabane Bakusele) under the supervision of Professor G. G. Redhi at Durban University of Technology, Durban, South Africa.

Dedication

To my Family

Especially to my mother Mrs Ntombosapho Educia Sanda, Ngcali, Kamvelihle and Zukhanye

To the late Mthetheleli Malcomes Sanda (father) and Khanyisa Kabane (brother)

Acknowledgements

I would like to express my sincere gratitude to God, who always gives me strength and power through good and hard times to complete every task I do in life. I also convey my greatest appreciation to **Prof. G. G. Redhi** for his dedicated supervision throughout this research work. This research work has been supported by Durban University of Technology (DUT), Ada and Bertie Levenstien, National Research Foundation (NRF), FoodBev SETA, and their financial support is gratefully acknowledged.

I express my profound respect and deep sense of gratitude to **Mr. S. R. Chetty** (Department of Chemistry, Durban University of Technology), **Miss. Ncomeka Mgxadeni** (Chemistry Department, North-West University, Mahikeng), **Dr. Thokozani Peterson Ngema** (Department of Chemical Engineering, Durban University of Technology) and **Dr. Marcin Durski** (School of Chemical Engineering, University of KwaZulu Natal) for the experimental and discussion insight.

Many thanks to my research group members: **Dr. Rajasekhar Chokkareddy, Dr. Vasanthakumar Arumugam, Mrs. N. M. Xhakaza, Mrs. Pelumi Oriyom**.

I would be neglectful if I do not extend my gratitude to the following:

- My very loving mother **Ntombosapho Eudocia Sanda** and **Nelisiwe Vannassa Khuluse** for their unlimited support;
- My brother **Maphelo Kabane** and sisters **Nontsikelelo** and **Nkosazana Kabane** for their encouragements;
- My heartfelt thanks to **Athenkosi Gogo**, **Zimkhitha Sanda** and **Ngcali Kabane** who always supported me.

Abstract

This work focusses on the application and pre-screening of selected ILs for different industrial separation problems based on limiting activity coefficients at infinite dilution (γ_{13}^{∞}), and liquid-liquid equilibrium data at different temperatures. The selected ionic liquids for pre-screening based on activity coefficients at infinite dilution data include (1,3-dimethyimidazolium dimethylphosphate, trioctylmethylammonium chloride, trihexyltetradecylphosphonium dicyanamide, 2,3-dihydroxypropyl-*N*-methyl-2-oxopyrrolidinium chloride, 2,3-epoxypropyl methyl-2-oxopyrrolidinium chloride) and deep eutectic solvent (1-butyl-3-methylimidazolium chloride + glycerol) at 1:2 molar ratio. These ionic liquids were tested in 33 solutes (alkanes, alkenes, alkynes, alcohols, tetrahydrofuran, ketones, aromatic hydrocarbons, thiophene, acetonitrile) and water at T = (313 – 343) K and at p = 101 kPa. The use of ionic liquid as a stationary phase on the column loading ranged between (30 – 36) % by mass.

Thermodynamic functions at infinite dilution such as (Gibbs free energy, $\Delta G_1^{\mathrm{E},\infty}$, entropy term, $T_{\mathrm{ref}}\Delta S_1^{E,\infty}$ and partial molar enthalpy, $\Delta H_1^{\mathrm{E},\infty}$) were also computed to further elucidate the types of intermolecular interactions existing between solutes and the investigated ionic liquids. The separation potential of the ionic liquids was determined from the selectivity (S_{ij}^{∞}), and capacity (k_j^{∞}), values. Different ionic liquids (1-ethyl-3-methylimidazolium tetrafluoroborate, 1-ethyl-3-methylimidazolim dicyanamide, 1,3-dimethylimidazolium dimethylphosphate) were also tested in the separation of azeotropic mixture (ethyl acetate/hexane) and in the desulfurization (thiophene/hexadecane or octane) process.

The extraction process was conducted at varying temperatures, T = (308 and 298) K and at p = 101 kPa. The results were compared to previously published ionic liquids involving thermodynamic data found in the literature. The separation capacity was based on the calculated values of selectivities (*S*) and distribution ratio (β). The data was successfully correlated using the thermodynamic non-random two liquids (NRTL). From this study, it was found that the investigated ionic liquids showed some possible application for selected industrial separation problems.

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Abbreviations

THF = Tetrahydrofuran

IDAC = infinite dilution activity coefficient

SLE = solid-liquid extraction

LLE = Liquid-liquid equilibria

GLC = gas liquid chromatography

ILs = ionic liquids

VOCs = volatile organic solvent

HPLC = high pressure liquid chromatography

NMR = nuclear magnetic resonance

TCD = thermal conductivity detector

FID = flame ionization detector

DES = deep eutectic solvent

FTIR = fourier transform infrared

He = helium gas

NRTL = non-random two liquids

EA = ethyl acetate

CAS NO = chemical abstracts service registry number

Ionic liquids

[BMIM]$^+$ [BF$_4$]$^-$ = 1-butyl-3-methylimidazolium tetrafluoroborate

[BMIM]$^+$ [Br]$^-$ = 1-butyl-3-methylimidazolium bromide

[BMIM]$^+$ [CF$_3$SO$_3$]$^-$ = 1-butyl-3-methylimidazolium trifluoromethanesulfonate

[BMIM]$^+$ [Cl]$^-$ = 1-butyl-3-methylimidazolium chloride

[BMIM]$^+$ [MeSO$_4$]$^-$ = 1-butyl-3-methylimidazolium methyl sulfate

[BMIM]$^+$ [OcSO$_4$]$^-$ = 1-butyl-3-methylimidazolium octyl sulphate

[BMIM]$^+$ [PF$_6$]$^-$ = 1-butyl-3-methylimidazolium hexafluorophosphate

[BMIM]$^+$ [Tf$_2$N]$^-$ = 1-butyl-3-methylimidazolium bis-(trifluoromethylsulfonyl) imide

[BDMIM]$^+$ [BF$_4$]$^-$ = 1-Butyl-2, 3-dimethyl tetrafluoroborate

[BDMIM]$^+$ [PF$_6$]$^-$ = 1-Butyl-2, 3-dimethyl hexafluorophosphate

[BMPy]$^+$ [BF$_4$]$^-$ = 4-Butyl-4-methylpyridinium tetrafluoroborate

[EMIM]$^+$ [Br]$^-$ = 1-ethyl-3-methylimidazolium bromide

[EMIM]$^+$ [BETI]$^-$ = 1-ethyl-3-methylimidazolium bis-(perfluoroethylsulphonyl) imide

[EMIM]$^+$ [Cl]$^-$ = 1-ethyl-3-methylimidazolium chloride

[EMIM]$^+$ [EtSO$_4$]$^-$ = 1-ethyl-3-methylimidazolium ethylsulfate

[EMMIM]$^+$ [Tf$_2$N]$^-$ = 2, 3-Dimethyl-1-ethylimidazolium bis-(trifluoromethylsulfonyl) imide

$[HMIM]^+ [Cl]^-$ = 1-hexyl-3-methylimidazolium chloride

$[HMIM]^+ [PF_6]^-$ = 1-hexyl-3-methylimidazolium hexafluorophosphate

$[HMIM]^+ [Tf_2N]^-$ = 1-hexyl-3-methylimidazolium bis-(trifluoromethylsulfonyl) imide

$[MMIM]^+ [MeSO_4]^-$ = 1,3-dimethylimidazolium methyl sulphate

$[MOA]^+ [Tf_2N]^-$ = methyl trioctylammonium bis-(trifluoromethylsulfonyl) imide

$[MOIM]^+ [BF_4]^-$ = 1-methyl-3-octylimidazolium tetrafluoroborate

$[MOIM]^+ [Cl]^-$ = 1- methyl-3-octylimidazolium chloride

$[MOIM]^+ [PF_6]^-$ = 1-methyl-3-octylimidazolium hexafluorophosphate

$[MOIM]^+ [Tf_2N]^-$ = 1-methyl-3-octylimidazolium bis-(trifluoromethylsulfonyl) imide

$[PMMIM]^+ [Tf_2N]^-$ = 2,3-Dimethyl-1-propylimidazolium bis(trifluoromethylsulfonyl) imide

$[PMIM]^+ [BF_4]^-$ = 1-methyl-3-pentylimidazolium tetrafluoroborate

$[RMIM]^+ [Br]^-$ = 1-alkyl-3-methylimidazolium bromide

$[P_{666\ 14}]^+ [DCA]^-$ = Trihexyltetradecylphosphonium dicyanamide

$[MMIM]^+ [DMP]^-$ = 1,3-dimethylimidazolium dimethylphosphate

$[PYR\text{-}PDO]^+ [Cl]^-$ = 2,3-dihydroxypropyl-*N*-methyl-2-oxopyrrolidinium chloride

$[Epmpyr]^+ [Cl]^-$ = 2′,3′-epoxypropyl methyl-2-oxopyrrolidinium chloride

$[M(C_8)_3N]^+ [Cl]^-$ = Methyltrioctylammonium Chloride

$[MMIM]^+ [DMP]^-$ = 1,3-dimethylimidazolium dimethylphosphate

List of symbols

T = temperature (K)

K = Kelvin

X_1 = mole fraction of the 1st component

X_2 = mole fraction of the 2nd component

X_3 = mole fraction of the 3rd component

σ = standard deviation

p = atmospheric pressure (MPa)

γ_{13}^{∞} = activity coefficients at infinite dilution

$\Delta H_1^{E,\infty}$ = partial molar excess enthalpies at infinite dilution (kJ · mol-1)

k_j^{∞} = capacity at infinite dilution

S_{ij}^{∞} = selectivity at infinite dilution

R = gas constant (J.mol-1 · K^{-1})

V_N = net retention volume of the solute (cm3 min)

P_o = outlet pressure (kPa)

$P_1{}^*$ = saturated vapour pressure of the solute

B_{11} = second virial coefficient of pure solute (cm3 · mol^{-1})

$P_0 J_2^3$ = mean column pressure (kPa)

$V1*$ = molar volume of the solute (cm3 · mol^{-1})

V_1^{∞} = partial molar volume of solute at infinite dilution in the solvent (cm3 · mol^{-1})

A = solute peak area detected by gas chromatography (mV · min^{-1})

a = slope (min^{-1})

D = pure carrier gas flow rate (cm3 · min^{-1})

R_b = radius of bubbles (cm)

T_b = boiling point temperature (K)

Z = compressibility factor

ω = acentric factor

ϕ = volume fraction

$\Delta S_1^{E,\infty}$ = entropy term (kJ · mol^{-1})

$\Delta G_1^{E,\infty}$ = Gibbs free energy (kJ · mol^{-1})

P_c = critical pressure

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2. **B. Kabane**, V. Arumugam, R. Chokkareddy, G.G Redhi* "Assessment of Pyrrolidinium-Based Ionic Liquid for the Separation of Binary Mixtures Based on Activity Coefficients at Infinite Dilution". **Journal of Chemical and Engineering Data** (**64, 2019, 5105 - 5112**) (https://doi.org/10.1021/acs.jced.9b00341)
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5. **Bakusele Kabane**, Gan G. Redhi* "Methyltrioctylammonium chloride as a separation solvent for binary mixtures: Evaluation based on experimental activity coefficients". **Journal of Chemical and Molecular Engineering** (**14, 2020, 101 - 106**) (https://publications.waste.org/chemical-and-molecular engineering)
6. **Bakusele Kabane**, Gan G. Redhi* "Thermodynamic properties and activity coefficients at infinite dilution for different solutes in deep eutectic solvent: 1-butyl-3-

methylimidazolium chloride + glycerol". **Journal of Molecular Liquids** (**311, 2020, 113216**) (https://doi.org/10.1016/j.molliq.2020.113216)

7. **Bakusele Kabane**, Marcin Durski, Thokozani Ngema, Gan G Redhi* "Liquid-liquid separation of azeotropic mixture (hexane/ethyl acetate) with imidazolium-based ionic liquids". **Journal of Chemical and Engineering Data (66, 2021, 94 - 100)** (https://doi.org/10.1021/acs.jced.0c00401)
8. **Bakusele Kabane** [a], Marcin Durski [b], Gan G Redhi [a,] * "Ternary phase equilibrium data for desulfurization utilizing imidazolium-based ionic liquids". **Journal of Chemical Engineering and Data** (**Under Revision**)

Chapter 1

Introduction

1.1. Introduction

The capability for the extraction of binary mixtures as efficiently as possible is related to a production of a possible use of the driving force. To understand the driving forces in separation processes, the study of thermodynamic equilibria of systems is an important and indispensable tool. Research studies and information based on thermodynamics of phase equilibrium data is extensively available in the literature. Besides, the data regarding phase equilibrium using ionic liquids is limited to an extent that some extraction processes cannot be efficiently designed. In addition, lack of optimal separation processes results to high investment costs, excessive energy usage and multiple stages for extraction or recovery.

Most of current research work have been addressing the importance of thermodynamic data for industrial applications. However, an understanding of activity coefficients at infinite dilution and ternary mixtures comprising ionic liquids and volatile organic solvents is important (Dupont et al, 2002; Singh, 2017). Furthermore, thermodynamic properties provide a better understanding and knowledge of intermolecular interactions between component molecules of liquid mixtures in a solution. Measurements for separation based on thermodynamics are important (Plechkova and Seddon, 2008), and these are functional in solvent extraction or distillation (Holbrey, 2004).

1.2. The need for separation processes

The processes that utilize chemicals, physical or electrical forces to concentrate or eliminate the specific constituents of a mixture are important and essential in the material processing, chemical and petroleum refining industries. Furthermore, to the essential point of these processes, the role of separation technologies is important as it presents opportunities and ways for waste reduction and the use of raw material as well as energy efficiency. Innovation in separation technologies is crucial for the global and local South African industries.

The process applied by SASOL (proprietary SASOL Advanced Synthol process) can successfully covert coal to synthetic oil which contains a number of different oxygenates and hydrocarbons, while the natural gas can be converted into high quality low emission diesel utilizing SASOL slurry phase distillation reactor. In this, the sulphur content is less than 5 parts per million (5 ppm) or 0.0005 %, thereby appeasing the mounting international and local environmental demand for green liquid fuels. Many of the compounds which includes alcohol, alkanes, aromatic hydrocarbons are useful in the production of plastic and other materials. Extraction of these high valued lucrative components would add synergistic value to the overall processes.

1.3. Separation process for chemical and petroleum refining

In the petroleum and chemical industries, several common separation issues are encountered. Two potential separation improvements for process efficiency were identified with the hope to meet several needs in these industries:

1.3.1. Separation techniques using multiple driving forces

This process includes the naturally occurring driving force for a selective operation (Humphrey et al., 1991; Bravo et al., 1986). The process is enhanced by an intervention that changes the thermodynamic systems, or where two or more separation methods are merged, and this involves separation and distillation, electrically aided separation, membrane and affinity-based adsorbent separation.

1.3.2. Separation associated with chemical reaction

This is achieved by combining separation and reaction in one process step. The process technique may include membrane reactors; merged separation process and chemical synthesis; electrochemical techniques of separation; and chemically facilitated transport membranes and reactive metal complex sorbents (Humphrey and Keller, 1977, Ho et al., 1988, Davis et al., 1993). This is a traditional technique in chemical engineering, this separation method mostly relies on the changes in physical properties (size, solubility, boiling point, etc) between the components of the mixture. If high selectivity or similar physical properties are required, extraction technique based on chemical changes, rather than physical differences may be functional.

1.4. Traditional chemical separation processes

Solvents are produced by a combination of processes that include purification, separation and synthesis. Distillation, solvent extraction, crystallization, absorption and stripping, adsorption and membrane processes are the traditional chemical techniques of purification and separation.

1.4.1. Distillation

For azeotropic mixtures and mixtures that can be easily vaporized, extractive distillation is the most widely used techniques. Distillation is a technique employed for separating components from a solution according to the differences in their boiling points. In this, vapours are formed by heating solids or liquids which are then condensed into liquids. Azeotropic distillation is achieved by adding a compound to the mixture that can at least form an azeotrope with one component of the system (Widagdo and Seider, 1996, Ewell et al., 1944, Laroche et al., 1991). This step assists in an increase of volatility of the components which give rise to an easy separation of the components from the mixture. Extractive distillation is a combination of adsorption and continuous fractional distillation. This involves the use of high boiling point solvents that dissolves one of the components in the mixture. Organic solvents and gases are mostly separated by distillation technique (Lei et al., 2003, Luyben, 2013).

1.4.2. Crystallization

This procedure is applied to complete several functions which includes solidification, purification, separation, concentration, and the production of crystal that can be used to obtain a molecular structure (Myerson, 2002, Mersmann, 2001). This method is economical since heat of crystallization is lower as compared to heat of vaporization. The recovery of solutes can be obtained from the mixtures by decreasing the solubility, either through evaporation, heating, addition of non-solvent to the mixture or chemical reaction (Hu et al., 2003, Liu and Nagahama, 1996, Muschol and Rosenberger, 1997).

1.4.3. Solvent Extraction

In the research field of thermodynamics of solutions, most of research work has been focussing on separation of binary mixtures based on liquid-liquid extraction. This appears to be:

- More economically favourable as compared to distillation which is more energy intensive
- Operated at low temperature and pressure compared to high pressure and temperatures employed in distillation technique.
- Advancement and improved equipment for equilibration of liquid phases.
- Better knowledge of the technique behind design, scale-up and development of separation processes.

Liquid-liquid extraction is a method for isolating two partially miscible liquid phases. In this process, the extracting solvent separates the solutes from the mixture or other liquid phase. The raffinate clean-up and solvent recovery follow the extraction. The process design is important and essential since there is a multiple possible technique for purifying the raffinate and solvent phases. Liquid-liquid interfacial tension can be used for the pre-selection of extracting solvents.

When separating heterocyclic hydrocarbons from aliphatic hydrocarbons, distillations is not a suitable and economical technique (Redhi, 2003, Hauschild and Knapp, 1994). Such components can be preferable separated by a solvent extraction procedure. This is achieved by the addition of an extracting or polar solvent. By adding a polar solvent or ionic liquid to the mixture (aromatic hydrocarbon + aliphatic hydrocarbon), this mixture will split into two phases (like dissolves like) hydrocarbon-rich phase (raffinate) and ionic liquid-rich phase (extract). The liquid-liquid equilibrium (LLE) data comprising ionic liquids for optimising solvent extraction methods is important for a proper pre-selection of suitable solvents.

1.4.4. Absorption and stripping technique

The process in which one or more materials of gas phase is transferred to a liquid in which the gas phase is soluble, is known as absorption. Stripping involves the opposite of absorption. In this technique, the liquid phase component is transferred to the gas phase such that it dissolves to the gas phase. In addition, the gas phase should be in contact in the generation of extensive areas of liquid surface (Bahadori and Vuthaluru, 2010, Kianfar et al., 2017, Khudenko and Garcia-Pastrana, 1987).

1.4.5. Membrane processes

This process involves two bulk phases that are physically separated by a third phase. For all processes that comprises membrane technique, the feed is separated into two components. i.e retentate (components retained by the membrane) and the permeate (materials go through the membrane) (Rautenbach and Albrecht, 1989, Staverman, 1952, Ravanchi et al., 2009). The separation is conducted by passing the feed mixture through the membrane, the membrane is selective only towards these species. In these components, permeate phase contain more species, while the retentate phase is depleted (Porter, 1989, Ho and Sirkar, 2012).

1.5. Ionic liquids

It is important to find alternative ways to improve industrial and chemical separation processes, this is due to the currently used chemicals (volatile organic solvents, VOCs) that posses' hazardous properties which can potentially damage the ecosystem and are not environmentally friendly. The industrial emission for these volatile organic solvents is estimated to be 67 % (Maese et al., 1998). Some of the alternatives in addressing these issues is to introduce ideal replacement solvents characterized by special properties (high physical and chemical stability, low vapor pressure and easy recyclability). Most of research groups have been characterizing thermophysical properties of these potential solvents know as ionic liquids (ILs) (De Azevedo et al., 2005, Dong et al, 2007, Rebelo et al., 2005). The easy synthesis of ionic liquids (change of alkyl chain and anion) makes them difficult and almost impossible to characterize their properties for each ionic liquid. Ionic liquids are known to consist of ions, fused and molten salts (Fraser and MacFarlane, 2009, Fredlake et al., 2005). These promising liquids are characterized by low melting point (< 100 ^{o}C), but high melting ionic compounds regarded as molten salts (Keskin et al., 2007, Wasserscheid and Keim, 2000).

Ionic liquids were first noted without further investigation in the 9th, century during Friedel-Crafts reactions (Fredlake et al., 2005), and in 1914, a successful synthesis of ionic liquid was developed (Wasserscheid and Keim, 2000). This was noted when ethylammonium nitrate salt $[EtNH_3]$ $[NO_3]$ appeared as a liquid at room temperature. Moreover, the interest in ionic liquids started in the last three decades.

1.5.1. Structure and chemical composition of ILs

Ionic liquids are composed by the combination of either a bulk anion or cation, and the two ions are electrostatically bonded. Ionic liquids are tunable solvents due to possible multiple combinations of cations and anions (Chaippe et al., 2003). The possible combination of commonly used anions and cations are shown in figure 1.1.

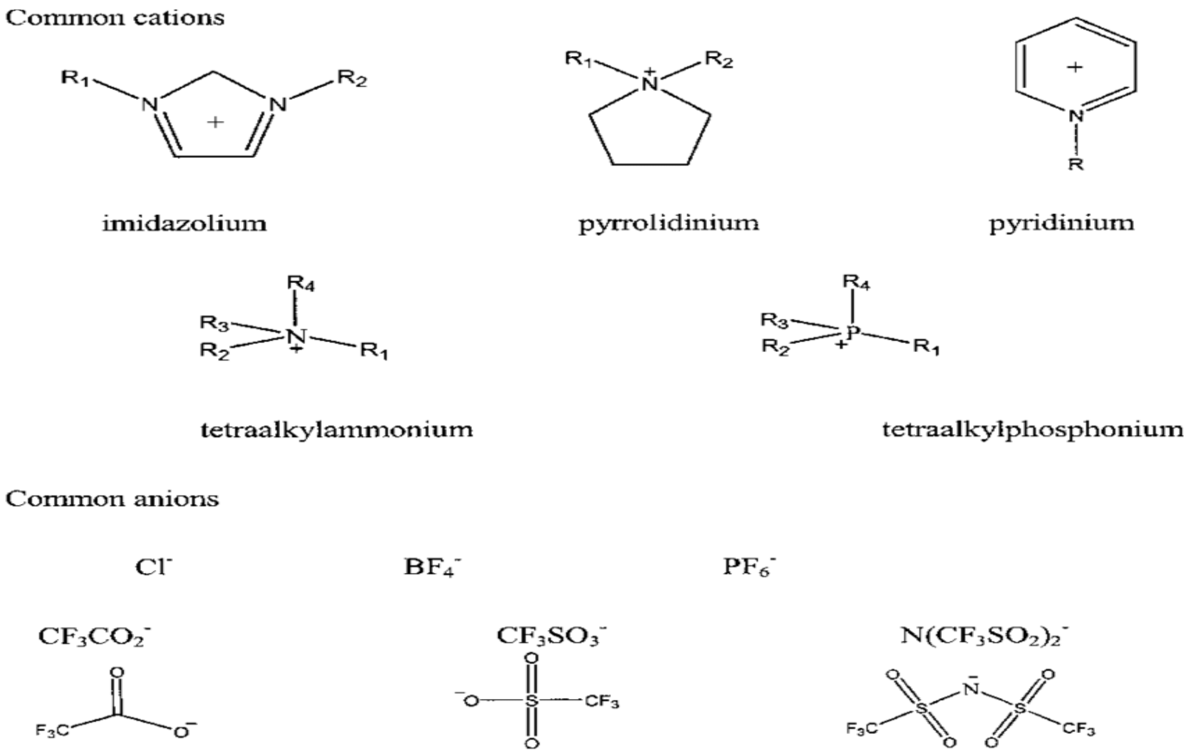


Figure 1.1: Structure of commonly used ions in synthesizing ionic liquid.

1.5.2. Properties of ionic liquids

Thermal stability and a wide liquidous rage are well known properties of ionic liquids. A range of ionic liquid between (- 96 to 400) ^{o}C was stated by (Carmichael and Seddon, 2000). This range is far less as compared to normal salt (NaCl), which melt at temperatures of up to 800 ^{o}C. Low vapour pressure is an important property of ionic liquids, and that attracts most researchers, and is one of the reasons why ionic liquids are referred as ‘‘greener’’ solvents. The ionic liquid vapour pressure can be detected at temperature, T = (100 – 120) ^{o}C, even though the vapour pressure is still negligible. This was observed for imidazolium based ionic liquid (1-ethyl-3-methylimidazolium ethylsulphate) with vapour pressure of 2.0 Pa at T = 120 °C (Singh, 2017).

Some of the ionic liquid properties including non-flammability, high ionic mobility, good solubility, or ability to dissolve inorganic or organic solvents and chemical stability (Deetlefs et al., 2006, Seddon et al., 2000, Zhang et al., 2006). Density of ionic liquids is always found to be higher as compared to molecular solvents, whilst the viscosity is always multiplied depending on the operational temperature. High solvating power is another property shared by the ILs (Khupse and Kumar, 2010), high electrochemical and thermal stability (Ignat'ev et al., 2005). Recyclability is a key characteristic for ionic liquids (Wu et al., 2009).

1.5.3. Solvating capacity

Generally solvating capacity of a liquid is always determined from the polarity, but in ion ionic liquids, it is always governed by the ionic combination. Hayes (2010) observed that the hydrophobicity is determined by the coordinating capacity of the anion, to give an example, [BMIM [BF_4] is miscible in water, while [BMIM] [PF_6] is 1.88 g/100 ml soluble in water. In ionic liquids containing the tosylate anion, it was observed that the solubility of octane is inversely proportional to the polarity of cation (Wasserscheid and Welton, 2008).

1.5.4. Limitations of ionic liquids

Ionic liquids are also faced with some limitations, and their synthesis is not always ''green'', these emerging solvents are characterized by high production costs and the degree of biodegradability or recyclability is limited (Swatloski et al., 2003, Freemantle, 2010).

The lack of comprehensive information is most probably due to the following:

- Few groups of ionic liquids are being investigated.
- The full description of ILs will be enforced once it is known what to design and how flexible the various combinations are (Crowhurst et al., 2003).

Insufficient details regarding to toxicology and safety result from:

- Toxicological information of ionic liquids has not been sufficiently dealt with or have not been well addressed.
- The solubility of ionic liquids with water can potentially contaminate the marine environment.
- Weak stability of hydrolysis from halogens contained in ([CF_3SO_3], [Tf_2N], [BF_4], [PF_6] or [$AlCl_4$]) (Wasserscheid et al., 2002, Gusain and Khatri, 2015), have potential to release hydrogen halides (HCl or HF) into aquatic system.

High costs and availability are also a huge problem:

- High cost is the major barrier in the implementation of ionic liquids for the industrial applications (Shamsuri and Abdullah, 2010, Aschenbrenner et al., 2009).
- Most of ILs are hygroscopic, and this influence their physical properties.
- As much as it is easy to synthesize, purification of ionic liquids is difficult due to low volatility (Rogers et al., 2003).

1.5.5. Possible industrial application of ILs

The characterization of ionic liquid properties has been the topic of interest (Clare et al., 2009), some possible industrial applications of ionic liquids were stated by (Keskin et al., 2007).

These includes:

- Extraction solvents.
- Lubricants.
- Electrolyte in batteries.
- Matrices for mass spectroscopy.
- Plasticizers.

- Gas absorption agents.
- Solvents to manufacture nanomaterials.

Some commercial applications of ionic liquids were reviewed by (Freemantle, 2010):

- The storage of hydrogen gas for usage in fuel cells was experimented with the use of IL-compressor by the Linde company.
- The separation of binary mixtures by ionic liquids (methanol/aliphatic hydrocarbons; thiophene/aliphatic hydrocarbons; water/alcohol) have been tested on a laboratory scale by extractive distillation (Revelli et al., 2009).
- Ionic liquids were used during the production of iso-octenes from butenes by DIFASOL.
- Pharmaceutical industry has used ionic liquids for the recovery of active ingredients. This was obtained by utilizing aqueous biphasic system base of ionic liquid, and the ionic liquids as an extracting solvent through solid-liquid process.
- In nuclear industries, ionic liquids are highly used for innovative applications, in this case, ILs are used as entrainer in solvent separation systems (Giridhar et al., 2007).

In addition, ionic liquids chosen in this work are reported to have various applications which include in extraction processes, electrochemically technology, chemical synthesis, and bio-catalysis (Maxim et al., 2010, Deng et al., 2012, Sun et al., 2014, Bailey et al., 2010). Furthermore, these have been utilized in liquid crystals, mass spectroscopy, materials for embalming, nanomaterials including those related to protein-DNA (Dupont and Suarez, 2006, Svintradze et al., 2008, Zhao et al., 2009).

1.6. Essence of thermodynamic functions

Volatile organic solvents are widely used in an extensive range of applications including medicine processing, plastic industries, food processing, separation and extraction (Carrea and Riva, 2000). These solvents are characterized by numerous setbacks related to environmental or safety issues.

The thermodynamic functions of solutions are not only essential for investigating the feasibility of reactions in a solution, but also give more desirable techniques to implement systematic theoretical aspects of solution structure. Some of the major goals for separation chemistry is to understand and study the behaviour and properties of liquid systems and apply the knowledge in an appropriate manner. The volume of a liquid can be changed by a small shift of pressure or temperature. The importance is within the dynamic process, chemical and phase equilibrium, and this comprises the charge transfer, reaction kinetics, phase transition as well as energy exchange between surroundings and systems. The study of physical analysis depends on a small number of fundamental quantities (Rodriguez et al., 2001).

1.7. Scope of the present study

1.7.1. Research problems

The research problems raised in this study are related to the problems associated with the conventional techniques that are currently used in the separation of useful solvents from industrial multicomponent systems.

These challenges and concerns include:

- Organic compounds used as extractants are generally toxic and flammable.
- High energy input and financial cost is needed for separating aromatic hydrocarbons by distillation techniques.
- The inability of convention solvents which include sulfolane as well as tetraethylglycol to extract low concentration aromatic hydrocarbons (less than 20%) (Gonzalez et al., 2013).

1.7.2. Aim of this research work

To examine the influence and effectiveness of various ILs for the separation of industrial mixtures, azeotropic mixtures and correlation of the experimental data.

1.7.3. Objectives of the research

- To measure activity coefficients at infinite dilution for different solutes in the ionic liquids using gas liquid chromatography.
- To determine the effect of temperature on activity coefficients at infinite dilution.
- To predict the separation potential of ionic liquids for the separation of solutes under investigation, by calculating selectivity and capacity.
- To determine the consistency of tie-line composition.
- To correlate the experimental data for ternary mixtures by using the non-random two-liquid model (NRTL).
- To determine the effectiveness of each ionic liquid for the separation of azeotropic mixtures and desulfurization by comparing the selectivity and distribution coefficient values.
- To determine the ternary data for the 3 component systems involving selected ionic liquids.

This thesis contains two parts:

1.7.4. Limiting activity coefficient measurements of ionic liquids

This work focusses on the application of selected ILs for various separation problems based on activity coefficients at infinite dilution, (γ_{13}^{∞}). The selected ionic liquids for activity coefficients data include (1,3-dimethyimidazolium dimethylphosphate, trioctylmethylammonium chloride, 2,3-dihydroxypropyl-*N*-methyl-2-oxopyrrolidinium chloride, 2,3-epoxypropyl methyl-2-oxopyrrolidinium chloride), deep eutectic solvent (1-butyl-3-methylimidazolium chloride + glycerol) and trihexyltetradecylphosphonium dicynamide. These were tested in 33 solutes (alkanes, alkenes, alkynes, alcohols, tetrahydrofuran, ketones, aromatic hydrocarbons, thiophene, acetonitrile) and water at T = (313 – 343) K and at p = 101 kPa. The ionic liquid as a stationary phase on the column loading range between (30 – 36) % by mass. Thermodynamic functions at infinite dilution such as (Gibbs free energy, $\Delta G_1^{\mathrm{E},\infty}$, entropy term, $T_{\mathrm{ref}}\Delta S_1^{E,\infty}$ and partial molar enthalpy, $\Delta H_1^{\mathrm{E},\infty}$) were also computed to further elucidate types of intermolecular interactions between solutes and investigated ionic liquids. The separation potential of the ionic liquids was determined from the selectivity, (S_{ij}^{∞}) and capacity, (k_j^{∞}) values.

1.7.5. Liquid-liquid equilibria

Different ionic liquids (1-ethyl-3-methylimidazolium tetrafluoroborate, 1-ethyl-3-methylimidazolim dicyanamide, 1,3-dimethylimidazolium dimethylphosphate) were tested in separation of azeotropic mixtures or in desulfurization. The extraction process was conducted at varying temperatures (308 and 298) K and at p = 101 kPa. The results were compared to previously published ionic liquids found in the literature. The separation capacity was based on the calculated values of selectivity (S) and distribution ratio (β). The data was successfully correlated using the thermodynamic non-random two liquids equation (NRTL).

1.7.6. Thesis outline

- Chapter 1: Content of research.
- Chapter 2: Literature review (showing the relevant topics on thermodynamics).
- Chapter 3: Theoretical framework.
- Chapter 4: Detailed experimental work.
- Chapter 5: Results (Tables and diagrams) are presented.
- Chapter 6: Discussion of the experimental results.
- Chapter 7: Conclusions (recommendations and main points based on the results presented).

Chapter 2

Literature Review

2.1 Description of ionic liquids:

Ionic liquids are classified as molten salts at room temperature and therefore are sometimes referred to as room temperature ionic liquids. Typically, an ionic liquid is composed of a small inorganic, weakly coordinating anion and an asymmetrically substituted bulky organic cation. Examples of bulky cations are tetraalkylphosphonium, dialkylimidazolium, N, N-pyrrolidinium, dialkylpyridinium, tetraalkylammonium and dialkylpyrrolidonium. Common anions used in ionic liquids are halides, alkylsulphates, hexafluorophosphate, tetrafluoroborate and bis-(perfluoroalkylsulphonyl) imades.

2.2 Systems using ionic liquids as solvents for extraction:

Many authors have highlighted the importance of studying thermodynamics of ionic liquids for chemical and connected industries. An analysis by several authors reveals a significant increase in use of ionic liquids in the chemical industries (Zhao et al., 2006, Plechkov and Seldon, 2008). However, some of the obstacles in the growth of ionic liquids for industrial use are the scarcity of their thermophysical properties (Rao, 2016), for both mixed and pure liquids in a broad range of temperature and pressure.

Separation of water/butan-1-ol mixtures based on limiting activity coefficients with phosphonium-based ionic liquid for 64 solutes was studied by (Wlazło et al., 2017). The gas-liquid partition coefficients K_L, at infinite dilution and the fundamental thermodynamic functions, the limiting partial molar excess Gibbs energy, enthalpy, and entropy were calculated. The values of selectivity and capacity for water/butan-1-ol separation problem was calculated from activity coefficients at infinite dilution. The tributyltetradecylphosphonium dodecylbenzenesulfonate ionic liquid revealed the best measured selectivity and capacity for the for water/butan-1-ol separation (Wlazło et al., 2017).

Activity coefficients at infinite dilution and thermodynamic data for diols, water, and organic solutes in the ionic liquid choline bis(trifluoromethylsulfonyl) imide was conducted by (Domanska et al., 2014). The results obtained revealed strong chemical interactions of pyridine and [N_{1112}OH] [NTf_2] and this might be responsible for the related high pyridine/heptane selectivity value (Domanska et al., 2014).

Interaction studies of organic compounds in the ionic liquid [1-ethyl-3-methylimidazolium 2-(2-methoxyethoxy)] ethylsulfate were examined by (Bahadur et al., 2014). The 28 volatile organic compounds include (alcohol, ketones, aromatic compounds, alkynes, alkenes, cycloalkanes, and alkanes). The calculated selectivity values obtained were higher when compared to the literature values containing the cation (1-ethyl-3-methylimidazolium). The obtained data propose that the ionic liquid used has a good potential for industrial separation processes (Bahadur et al., 2014).

Liquid-liquid equilibrium data for the system containing toluene, n-heptane and Aliquat 336 ionic liquid was reported by (Kulkarni et al., 2017). The data was obtained at T = 303.15 K and atmospheric pressure. Mathematical modelling related to the distribution coefficient and dispersion, dipolar interactions and hydrogen bonding was developed. The parameters were determined from the Hansen’s solubility parameters. This technique showed great potential to act as a knowledge-based framework to aid development of new tailor-made solvents. In addition, this could considerably save cost and time in experimental analysis (Kulkarni et al., 2017).

Nunez-Rojas et al., (2018) reported molecular dynamics simulations to separate benzene from hydrocarbons using polar and ionic solvents. This was performed to study benzene extraction from dodecane using polar and ionic solvents in liquid-liquid equilibria. In this work, results based on density profile analysis shows that all polar solvents can extract benzene. It was also observed that 1-butyl-1-methylpirrolidonium dicynamide can extract more benzene from the non-polar phase as compared to 1-butyl-3-methyimidazolium hexafluorophosphate and 1-ethyl-3-methylimidazolium hexafluorophosphate (Nunez-Rojas et al., 2018).

Deep eutectic solvent (tetramethylammonium chloride + glycerol) was utilized by (Nkosi et al., 2018) as a separation agent for organic liquid mixtures. The assessment was based on activity coefficients at infinite dilution. It was observed that tetramethylammonium chloride + glycerol can potentially be used as an alternative solvent for nitrogen and sulphur removal from transportation fuels as well as the separation of cycloalkanes, aromatics, and esters from ethanol (Nkosi et al., 2018).

Recovery of biobutanol and n-propanol utilizing a low density phosphonium based ionic liquid at $T = 298.15$ K at $p = 1$ atm was studied by (Rabari et al., 2013). In this work, a low density (0.895 gm/cm^3) ionic liquid was used to recover butanol and n-propanol from water. It was observed that the distribution coefficient is greater than unity which indicates easier diffusion of solute from aqueous phase to extract phase. This effect shows that a reduced amount of solvent (IL) is required for separation of specific amount of alcohol from water.

The NMR spectra also pointed out to the fact that the aqueous rich phase was relatively free of IL and contained high percentage (92 %) of water (Rabari et al., 2013).

Domanska et al., (2018) investigated thermodynamic properties of quaternary ionic liquid (N-dimethyl-N-tetradecylammonium cinnamate) by inverse chromatography with 65 different solutes at five temperatures ranging from (328.15 – 368.15) K. In this work, it was observed that the investigated ionic liquid revealed very large selectivity for hexane/ethanol and heptane/ethanol separation. Based on results obtained in this work, it was concluded that the investigated ionic liquid was not a suitable entrainer for petrochemical processes (Domanska et al., 2018).

The activity coefficients at infinite dilution data for 46 solutes in the ionic liquid 1-butyl-1-methylpyrrolidinium dycinamide was presented by (Durski et al., 2018). The solute retention data was acquired using gas liquid chromatography at five temperatures (313.15 to 373.15) K at p = 101 kPa. It was observed that the dicynamide ionic liquid presents high selectivities for the separation of aromatic hydrocarbons from aliphatic hydrocarbons, and especially for the extraction of thiophene or, or pyridine from heptanes with slightly lower capacity as compared to [TCM] and [SCN] anions (Durski et al., 2018).

The ionic liquid 1-ethyl-3-methylimidazolium tricyanomethanide was tested by (Krolikowski et al., 2013) as a solvent for the separation of sulphur compounds from aliphatic hydrocarbon. The liquid-liquid phase equilibrium data was determined for ternary systems containing the ionic liquid, thiophene or benzothiophene and heptanes. In this work, high values of selectivity were obtained. They also observed high solubility of sulphur compounds and practical immiscibility of aliphatic hydrocarbon in ionic liquid. The NRTL equation was used as to correlate the experimental data (Krolikowski et al., 2013).

Krolikowski et al., (2016) reported data of liquid-liquid extraction of p-xylene from their mixtures with alkanes (p-xylene + octane, or decane) utilizing 1-butyl-1-methylmorpholinium tricyanomethanide and 1-butyl-3methylimidazolium tricyanomethanide ionic liquid at T = 298.15 K and atmospheric pressure. It was observed that with an increase of the alkyl chain length in the aliphatic hydrocarbons, the value of selectivity increases (Krolikowski et al., 2016).

Application of 1-hexyl-3-methylimidazolium trifluoromethanesulfonate to the removal of alcohol from mixtures with heptanes was studied by (Liu et al., 2017). This was conducted to investigate the ionic liquid as a possible extraction solvent in petrochemical processes for removal of alcohol from an azeotropic mixture with heptane. The experimental work was conducted at atmospheric pressure and at T = 298.15 K. In this work, the experimental data were compared with the LLE data predicted by the UNIFAC group contribution method. It was observed that the prediction method was in good agreement with the LLE data of the heptanes-(1-propanol or 2-propanol) systems. It was also observed that in general the UNIFAC prediction of the LLE in behaviour is not always positive universal and that the LLE experimental work is essential for further study (Liu et al., 2017).

The experimental results of cadmium extraction from sulphate medium using two ionic liquid trihexyltetradecylphosphonium chloride and trioctylmethylammonium chloride diluted in kerosene were reported by (Swain et al., 2016). It was observed that the percentage extraction of cadmium increased with increase in aqueous phase pH with trioctylmethylammonium chloride whilst it does not vary much with trihexyltetradecylphosphonium chloride. Fast extraction equilibration was achieved for both ionic liquids (Swain et al., 2016).

Marciniak et al., (2018) reported activity coefficients at infinite dilution data and physicochemical properties for organic solutes and water in the ionic liquid trihexyltetradecylphosphonium tricyanomethanide at T = (328.15 to 368.15) K. the experimental activity coefficients at infinite data was used to calculate thermodynamic properties including partial molar excess Gibbs energies, enthalpies and entropies. High selectivity for (water/butanol) was obtained as compared to other ionic liquids (Marciniak et al., 2018).

Evaluation and correlation of separating heptane/ethanol with ionic liquids was investigated by (Domanska et al., 2018). This was based on ternary liquid-liquid phase equilibrium data for four ternary mixtures (IL + ethanol + heptane) at atmospheric pressure and T = 313.15 K. In this work, it was observed that the investigated ionic liquid (N-benzyl-N-dimethyl-N-tetradecylammonium vannilliate) revealed lower selectivity for the heptanes/ethanol separation than the other used ionic liquids (1-ethyl-3-methylimidazolium trifluoromethyl and 1-hexyloxymethyl-3-methylimidazolium bis{(trifluoromethyl) sulfonyl}imide. All experimental data were well correlated with the NRTL model (Domanska et al., 2018).

Extraction of organic compounds involved in the kinetic resolution of rac-2-pentanol from n-hexane by imidazolium ionic liquids based on liquid-liquid equilibrium was studied by (Montalban et al., 2018). The results obtained in this work showed that the studied ionic liquids could be successfully used as solvent for the selective extraction of rac-2-pentanol and butyric acid (Montalban et al., 2018).

Liquid-liquid equilibrium data for the two ternary systems of methyl tert-butyl ether (MTBE) + methanol + N-methylimidazolium hydrosulfate ([MIM][HSO_4]) and MTBE + methanol + 1-butyl-3-methylimidazolium hydrosulfate ([BMIM][HSO_4]) were measured at 278.15 K, 298.15 K and 318.15 K at 101.325 kPa and reported by (Bai et al., 2019). In this work it was observed that [BMIM][HSO_4] was a better choice than [MIM][HSO_4] when a high product purity was required. However, [MIM][HSO_4] was a better choice than [BMIM][HSO_4] when the production requirements for the product were large (Bai et al., 2019).

The separation of thiophene, or benzithiophene from model fuel using glycols was reported by (Krolikowski and Lipinska, 2019). The feasibility of the investigated glycols to separate sulphur compounds was based on experimental liquid-liquid phase equilibria and oxidative desulfurization study. The investigated glycols include polyethylene glycol, triethyl glycol and diethylene glycol. Different oxidative agents were used for the oxidative extractions: the mixture of hydrogen peroxide with benzoic acid or formic acid or acetic acid or vanadium (V) oxide and iron (III) chloride and the mixture of oxygen with N-hydroxyphthalamide (NHPI). In this work, high high selectivities were obtained in separation of benzothiophene as compared to thiophene. The performance of separating solvents was in the following order: polyethylene glycol < triethylene glycol < diethylene glycol (Krolikowski and Lipinska, 2019).

The applicability of two selected ionic liquids for the extraction of thiophene from hexadecane or octane as a model of diesel stream was reported by (Durski et al., 2019). This was based on the experimental liquid-liquid phase equilibrium data measured at temperature, T = 308.15 K and at atmospheric pressure. The two selected ionic liquids include 1,3-dihydroxyimidazolium bis [(trifluoromethyl) sulfonyl] imide and 1-butyl-3-methylimidazolium trifluoromethanesulfonate. For both ternary systems (IL + thiophene + hexadecane or octane), 1-butyl-3-methylimidazolium trifluoromethanesulfonate showed better separation parameters as compared to ionic liquid 1,3-dihydroxyimidazolium bis [(trifluoromethyl) sulfonyl] imide. The investigated ionic liquids by Durski et al., 2019 presented interesting results specifically for 1-butyl-3-methylimidazolium trifluoromethanesulfonate compared to those found in the literature involving the systems of (IL + thiophene + octane or hexadecane) (Durski et al., 2019).

Krolikowski, 2019 conducted a study for the separation thiophene or benzothiophene from heptane. This study involves different ionic liquids for the separation: 1-butyl-1-methylmorpholinium tricyanomethanide [EMIM] [TCM], 1-hexyl-1-methylmorpholinium tricyanomethanide [HMMOR] [TCM], and 1-butyl-1-methylpyrrolidinium tricyanomethanide [BMPYR] [TCM]. The feasibility of the selected ionic liquids was based on the experimental liquid-liquid equilibria measured at $T = 308.15$ K and at atmospheric pressure. A practically complete immiscibility of heptane and solubility of thiophene or benzothiophene was observed. High selectivity values were observed for (benzothiophene/heptane) compared to (thiophene/heptane) systems. This is due to a better solubility of benzothiophene in the investigated ionic liquid rich phase. In morpholinium based ionic liquids, the selectivity values increase with an increase in alkyl chain of a cation. The separation hierarchy of the studied ionic liquids systems are as follows: [EMIM] [TCM] > [BMPYR] [TCM] > [HMMOR] [TCM] > [BMMOR] [TCM] (Krolikowski, 2019).

Karpinska et al., (2018) investigated the possible separation of (hexane/hexene and cyclohexane/cyclohexene) with dicyanamide ionic liquids based on liquid-liquid equilibria. The six cations with dicyanamide anion include: N-ethyl-N-methylmorpholinium, (3-hydroxypropyl)-1-methylmorpholinium, 1-(3-hydroxypropyl)-3-methylimidazolium, 1-(3-hydroxypropyl) pyridinium, (3-cyanopropyl) pyridinium and (3-cyanopropyl) methylpyrrolidinium. In this study, the experimental work was conducted at temperature, $T = 298.15$ K and at $p = 0.1$ MPa. The effect of cation was examined based on the selectivities and distribution coefficients. Ionic liquid [N-C_3CNMPyr] [DCA] gave better separation as compared to 1-ethyl-3-methylimidazolium dicyanamide reported earlier, but with low distribution ratios (Karpinska et al., 2018).

Desulfurization utilizing ionic liquids is a process which can be operated at low pressure and temperature. Mafi et al., (2018) used low pressure (101 kPa) and low temperature (25 $^\circ$C) to separate thiophene from hexane, octane or decane using ionic liquid (1-butyl-3-methylimidazolium thiocyanate). The experimental data was based on liquid-liquid equilibrium data. It has been found that the solubility is directly proportional to the cation chain. In addition, the selectivity values decrease as the chain length alkanes decreases, while the solubility of alkanes in ionic liquid increases. This demonstrated the inherent high cost for the removal of sulphur compounds. As it was expected, the investigated ionic liquid revealed the lowest solubility of alkanes and highest selectivity coefficients in the ternary systems containing (IL + thiophene + decane). The experimental data was correlated using non-random two liquid equation (Mafi et al., 2018).

The experimental and modelling study for the gas solubility of hydrocarbons in phosphonium based ionic liquids was reported by (Sousa et al., 2014). This was conducted in three ionic liquids [trihexyltetradecylphosphonium chloride, tributyl (methyl) phosphonium methylsulfate and tributyl (ethyl) phosphonium diethylphosphate] at a broad range of temperature, T = (288.15 – 308.15) K and at atmospheric pressure. Two modelling systems were used [regular-solution theory (RST) and Cubic Plus Associated Equation of state (CPAEoS)]. The values of solubility were greater in tributyl (ethyl) phosphonium diethylphosphate. These values were 2 to 10 times better as compared to the ammonium based ionic liquid. Furthermore, the values of entropy and enthalpy computed by the solubility dependence on temperature agree with the thermodynamic prediction from the theory of regular solutions for highly soluble gases, the solubility is proportional to the temperature since enthalpy or entropy of condensation exceeds partial molar enthalpy of mixing (Sousa et al., 2014).

In the chemical industry, the design of an extraction process regarding liquid mixtures containing alcohols (tertbutanol, butan-2-ol, butan-1-ol, ethanol) and water is increasing in importance. The separation of water/butan-1ol with ionic liquids was described by

(Domanska et al., 2019). This was based on the experimental liquid-liquid phase equilibrium data. The investigated ionic liquids with long alkyl chain include: tetrabutylphosphonium bis (trifluoromethyl sulfonyl) imide, 1,3-didecyl-2-methylimidazolium dicyanamide and hexadecyltrimethylammonium bis-[(trifluoromethyl) sulfonyl] imide. The experimental data was conducted at temperature, T = 328.15 K and at atmospheric pressure. Complete immiscibility was observed for the binary systems of water and three ionic liquids. Lower distribution coefficients and selectivity values were observed in the ammonium based ionic liquids. The experimental tie-lines were correlated by the NRTL equation (Domanska et al., 2019).

The close boiling points of mixtures make it more difficult to separate from an industrial point of view. Wen et al., (2018) reported the separation of azeotropic mixture involving (ethylacetate + hexane) at temperature, T = 298.15 K and at atmospheric pressure. The measurements were based on the ternary phase equilibrium data using different ionic liquids (1-octyl-3-methylimidazolium trifluoromethanesulfonate, 1-octyl-3-methylimidazolium tetrafluoroborate, 1-octyl-3-methylimidazolium trifluoromethanesulfonate) and 1-hexyl-3-methylimidazolium tetrafluoroborate. A treybal type I behaviour was seen for all the investigated systems. These results revealed the impact of the alkyl chain on the cation and the use of different anions in the formation of ionic liquids. A better separation was shown by the ionic liquids containing trifluoronethanesulfonate compared to tetrafluoroborate and ionic liquid with short alkyl chain gave better separation (Wen et al., 2018).

The measurements of liquid-liquid equilibrium data for the systems containing (deep eutectic solvents + benzene + hexane) and (deep eutectic solvents + ethyl acetate + hexane) at different temperatures (25, 35 and 45) °C and at atmospheric pressure was reported by (Gonzalez et al., 2013). The deep eutectic solvents were made of (choline chloride + lactic acid or glycerol), both formed at 2 lactic acid or glycerol : 1 choline chloride, molar ratio.

The results obtained showed that glycerol based deep eutectic solvent have high distribution coefficients, however, these prepared low transition temperature mixtures are less as compared to sulfolane regarding the distribution ratio. High selectivity values were obtained for both of prepared sepataing agents. The experimental tie-lines were correlated by the non-random two liquid equation (Gonzalez et al., 2013).

Durski et al., (2020) showed the possible separation of thiophene from octane or hexadecane with ionic liquids based on phase equilibrium data at T = 308.15 K and at atmospheric pressure. The ionic liquids for desulfurization include 1-butyl-1-methylpiperidinium dicyanamide and triisobutylphosphonium tosylate. The systems were used as a model substances of fuel stream. A better separation was observed in ionic liquid containing dicyanamide anion, but with much lower distribution ratios as compared to the tosylate based ionic liquid. The selectivities shown by both investigated ionic liquids are acceptable when compared to other published systems comprising ionic liquids in the literature. The NRTL equation revealed satisfactory correlation of the measured phase data (Durski et al., 2020).

Separation based on liquid-liquid extraction is not only cheap; but simplifies the problem of separating azeotropic mixtures. Pereiro and Rogriguez, (2008) used a technique of liquid-liquid extraction to separate close boiling mixture formed by (hexane + ethyl acetate) with two imidazolium based ionic liquids at temperature, T = 298.15 K and at atmospheric pressure. Thermophysical properties such as densities, speed of sound and refractive index was also measured for these systems. Excess thermodynamic properties such as isentropic compressibility, change in refractive index and excess molar volume were calculated. The ionic liquid 1-hexyl-3-methylimidazolium hexafluorophosphate showed strong intermolecular interactions with ethyl acetate and weak interactions were observed in hexane and ethyl acetate (positive excess molar volumes). Higher selectivity values were obtained for ionic liquid [HMIM] [PF_6] when compared with ionic liquid containing long alkyl chain [OMIM] [PF_6] (Pereiro and Rogriguez, 2008).

The measurements and correlation of liquid-liquid equilibrium data for three imidazolium based ionic liquids with (acetone + cyclohexane) was reported by (Zhu et al., 2020). The three ionic liquids (1-butyl-3-methylimidaolium bis(trifluoromethylsulfonyl) imide, 1-butyl-3-methylimidaolium dicyanamide and 1-butyl-3-methylimidaolium trifluoromethanesulfonate) were tested in the separation of azeotropic mixture (acetone/cyclohexane) at temperature, T = 298.15 K and at atmospheric pressure. The order of interaction energy and extraction capacity for the investigated ionic liquids were as follows: [BMIM] [NTf_2] > [BMIM] [OTF] > [BMIM] [DCA]. The data was successfully correlated by the NRTL and UNIQUAC models. All the investigated ionic liquids were found suitable for the separation of acetone from cyclohexane (Zhu et al., 2020).

Gilani et al., (2020) reported a comparative study of liquid-liquid extraction of (water + butyric or 3-methylbutyric acid + methyl isobutyl carbinol) measured at T = (298.15, 303.15 and 308.15) K, and at atmospheric pressure. It was observed that the ternary system containing straight chain carboxylic acid (butyric acid) presents type 1 phase diagram as the water-butyric acid and alcohol-butyric acid are soluble in each other, while water-alcohol is partially miscible. The branched chain acid showed a tribal type 2 phase diagram (Gilani et al., 2020).

Li et al., (2020) reported the thermodynamic solubility, solvent effect and preferential solvation analysis involving rebamipide in aqueous co-solvent mixtures composed of ethanol, isopropanol, n-propanol and propylene glycol at temperature, T = (273.15 – 318.15) K and at atmospheric pressure. The experimental work was conducted using isothermal saturation methods at the same mass fraction for all the compounds. Negative solvation parameters for water rich-phase were observed while positive solvation parameters were observed at the co-solvent composition ranging from (0 – 0.20) in the mole of fraction n-propanol, and (0 – 0.25) at the mole fraction of ethanol/isopropanol. In addition, it was also found that the rebamipide solubility changes due to hydrogen bond acidity and cavity term for the ethanol (isopropanol, n-propanol) systems as well as the cavity term for the propylene glycol + water mixtures (Li et al., 2020).

The measurements and correlation of liquid-liquid equilibrium data for three imidazolium based ionic liquids with acetone and cyclohexane were reported by (Zhu et al., 2020). The three ionic liquids (1-butyl-2-methylimidazolium bis (trifluoromethylsulfonyl) amide, 1-butyl-2-methylimidazolium dicynamide and 1-butyl-2methylimidazolim trifluoromethanesulfonate) were tested in the separation of this azeotropic mixture at temperature, T = 298.15 K and at atmospheric pressure. The order of interaction energy and extraction capacity for the investigated ionic liquids was as follows: [BMIM] [NTf_2] > [BMIM] [OTF] > [BMIM] [DCA]. The data was successfully correlated by the NRTL and UNIQUAC models. All the investigated ionic liquids were found suitable for the separation of acetone from cyclohexane (Zhu et al., 2020).

Solvent extraction plays a vital role in industrial separation processes as an energy efficient separation technique. The recovery of phenols from wastewater through liquid-liquid extraction was reported by (Yuan and Chen, 2020). In this study, dibutyl ether was used as an extraction solvent for the separation of phenols from the aqueous phase. The experimental work was conducted at varying temperatures, T = (298.15 – 315.15) K at 15 K interval and at atmospheric pressure. Better separation of phenols was observed at lower temperature (298.15 K) with selectivity and capacity of 1182.29 and 16.63, respectively. The data was satisfactorily correlated with non-random two liquid equation (Yuan and Chen, 2020).

Thermodynamic modelling and liquid-liquid equilibria data for quaternary mixtures of toluene, dimethyl carbonate, methanol + water at temperature, T = (298.15 – 318.15) K and at atmospheric pressure were reported by (Fakhri et al., 2020). The Othmer-Tobias and Bachman correlation technique were used to validate the reliability and experimental tie-lines of the quaternary systems. The results obtained showed that lower temperature results in better extractions as compared to higher temperatures. The UNIQUAC and NRTL models were again used to correlate the experimental data (Fakhri et al., 2020).

Development of Abraham correlations for short chain glycol-grafted pyridinium and imidazolium based ionic liquids from inverse gas chromatographic measurements were reported by (Mutelet et al., 2020). The gas partition coefficients and infinite dilution activity coefficients were determined for 45 organic solutes in ether crafted ionic liquids (1-ethyl-3-(2-methoxyethyl) imidazolium bis-(trifluoromethylsulfonyl) imide and N-(2-methoxyethyl) pyridinium bis-(trifluoromethylsulfonyl) imide. The experimental data was conducted between the temperature range, T = (323.15 – 373.15) K in 10 K intervals and at atmospheric pressure. The intermolecular interactions were further expressed by calculating the excess thermodynamic properties (Gibbs free energy, enthalpies and entropies) at infinite dilution. Good separation potential based on selectivities and capacity values was observed in the pyridinium based ionic liquid (Mutelet et al., 2020).

A short communication regarding the corrections of the published data by (Shekaari et al., 2017) was reported by (Acree Jr, 2020). This includes the data of deep eutectic solvent (choline chloride/urea) in a full range of concentration at temperature, T = 298.15 – 323.15) K. The problem was the incorrect partial molar volumes that the author reported in their published work. Acree Jr, (2020) argues that the tabulated values do not conform to many standard thermodynamic relations and the given values of partial molar volumes are positive. The difference was found when Acree Jr, (2020) computed the numerical value of V^E = -

41.689 $cm^3 \cdot mol^{-1}$ which he compared from one found in the literature $V^E = 0.131$ $cm^3 \cdot mol^{-1}$. It was also suggested that the author should have used the Equation 2.1 below to check for internal consistency between partial molar volume and excess molar volume (Acree Jr, 2020).

$$V^{\mathrm{E}} = x_1 \left(\tilde{\mathrm{V}}_{m,1}^{*} - V_1^{*}\right) + x_2 \left(\tilde{\mathrm{V}}_{m,2}^{*} - V_2^{*}\right)$$

(2.1)

Where x_1, x_2 and V_1^*, V_2^* are the mole fraction composition and pure state molar volume of the components.

Shekaari et al., (2020) reported the liquid-liquid equilibria and thermophysical properties of ternary systems comprising (deep eutectic solvent + hexane + benzene or thiophene) measured at atmospheric pressure and temperature, T = (303.15 – 313.15) K. The thermophysical properties (partial molar isentropic compressibility, standard partial molar volume and viscosity *B*-coefficient were computed for the systems at dilution region of aromatic compounds. The liquid-liquid equilibria for the ternary systems of (deep eutectic solvent or glycolamine or sulfolane or N-formylmorpholine + hexane + benzene or thiophene) were measured at T = (303.15 – 313.15) K. The experimental results revealed good separation of glycolamine with the use of deep eutectic solvent compared to other investigated extracting solvents in this work. The data was also correlated using NRTL model (Shekaari et al., 2020).

Table 2.1 Ionic liquid properties in contrast with volatile organic solvents (VOSs)

Property	Volatile organic solvents (VOSs)	Ionic liquids
Density	(0.6 – 1.7) g · cm^{-1}	(0.8 – 3.3) g · cm^{-1}
Vapour Pressure	Obeys the Cluasius-Clapeyron equation	Negligible vapour pressure under normal conditions
Viscosity	(0.2 – 100) c/p	(22 – 40 000) c/p
Cost	Relatively cheap	2 to 100 times compared to organic solvents
Polarity	Traditionally polarity cocept	Polarity concept doubtable
Refractive index	(1.3 – 1.6)	(1.5 – 2.2)
Solvation	Weakly solvating	Strongly solvating
Recyclability	Green imperative	Economic imperative

Chirality	Rare	Tuneable and common
Applicability	Single function	Multifunction
Tuneability	Little number of solvents accessible	Inexhaustible range of solvents
Catalytic capacity	Rare	Tuneable and common
Flammability	Highly flammable	Non-flammable

Thermophysical properties of volatile organic solvents compared to the ionic liquids. The ionic liquids revealed good and exceptional properties as compared to the VOCs as seen in table 2.1.

Chapter 3

Theoretical framework

3.1. Introduction of thermodynamics

Thermodynamics was introduced in the 19th century driven by the dawn of the industrial revolution (Carnot et al., 1960). This was developed to understand and attain knowledge that will help in optimising the separation of useful work from engines. These engines were powered by the flow of heat, an important source of the work was the chemical fuel, typically from coal. Gibbs (1960) incorporated the chemical process into the framework of thermodynamics. Thermodynamics was a theory based on interrelation of microscopic observables including energy, volume, pressure, and temperature.

In many chemical processes, the investigation of thermodynamic properties of liquid mixtures is very essential. These thermodynamic properties are used for designing process equipment in industries. Besides, the chemistry of liquids is complicated. Direct measurements are not always conducted, important properties are always derived from the direct measured properties. Branches of thermodynamics such as hydrodynamics, mechanics and electrostatistics are always useful in interpreting the results. The organised experimental and theoretical examination of solutions begun in 1887. This was first conducted by Van't Hoff (1957). Here, it was shown that properties such as boiling point, freezing point and vapour pressure are features of a system. The important theory of electrolytic dissociation by Arrhenius (1903) was also observed. The theory includes the important concept of ions and charged particles in a system.

The powerful technique of thermodynamics in a systematic manner to liquid mixtures was first applied by Van't Hoff (1957). A clear understanding to thermodynamics of solutions was then clarified by Gibbs (1961) experiments. All the basic principles that are applied in thermodynamics of liquid mixtures were provided by Gibbs (1906). One of the fundamental contribution of thermodynamics is to reduce measurements of mixtures in equilibrium. Now, thermodynamics consists of large part of industrial application of thermodynamics in chemistry. Theories of solutions are based on two aspects of liquid systems, and these include:

- One is that the entropy is associated with dispersion of the two molecular species.
- Second aspect is related to the molecular interactions among neighbouring molecules, and particularly the interactions occurring between like and unlike species in a system.

The studies based on thermodynamics has progressed beyond the two aspects of interpretation. The scope of thermodynamics began to widen in the late 19th century. This became the same concept to interpret and predict the efficiency of heat engines applied to other energy transformation including innovations in geological, biological and chemical systems if any energy change is not obvious. From this period, the interest in investigating properties of binary mixtures became significant.

There are two fundamental reasons in examining properties of binary mixtures:

- They provide ways of examining physical forces acting among two molecules of different species.
- Is the appearance of new phenomenon that are not present in the pure substance.

New phase equilibrium measurements are the most interesting part in studying liquid mixtures which arise from the extra degrees of freedom coming from different proportion of components. Three degrees of freedom are involved in a two-component mixture of one phase. These include temperature and pressure; composition may also be varied.

3.1.1. Importance of thermodynamics

The importance in studying thermodynamics liquid properties are listed below.

- To gain knowledge and understanding of energy transfer inside a mixture utilizing mathematical framework. This helps to calculate, predict and design the efficiency of chemical process.
- It gives a framework to predict the behaviour of matter in different situations.
- The occurrence of a reaction can be predicted from thermodynamic functions.

- It gives us the second law which assist us in understanding the spontaneity of some processes. Thermodynamics is one of the few basic branches of science which gives us some notation of time.

3.2. Activity coefficients at infinite dilution

In a binary system, the concept of infinite dilution can be expressed mathematically as the composition of the solvent approaches one or that of the solute approaches zero.

The activity coefficients (γ_i) of a substance (i) in a mixture is represented by:

$$\gamma_i = \frac{\hat{f}_i}{x_i f_i}$$

(3.2.1)

In equation (3.2.1) above, the fugacity of components i in a solution is represented by $\hat{f}_i$, fugacity for pure substance is given by f_i and the mole fraction of liquid phase is shown by x_i. In the case of interest for readers, the equation is further described by Smith (1950). The maximum non-ideality of mixtures is described by activity coefficients at infinite dilution (γ_{13}^{∞}). This measure helps with interpreting the intermolecular interactions between solvent and solute (McMillan and Mayer, 1945).

Based on the stated definition of infinite dilution, from the practical perspective, it will be nearly impossible to obtain true infinite dilution. Kojima et al., (1997) stated that for a valid measurement of infinite dilution, a range for the volume of x_i is required. To give an example, for hexane in ionic liquid or hexadecane system, a concentration of 1 % would adequately approximate infinite dilution. For the highly associated components, this region may be low as 10^{-7}. This can require one to consider measuring these systems over the simulated phase equilibria or extrapolation of modelled data (Kojima et al., 1997).

3.3. Techniques of obtaining activity coefficients at infinite dilution (γ^{∞})

3.3.1. Predictive techniques of determining limiting activity coefficients

The relatively easy syntheses of ionic liquids make it nearly impossible to characterise every combination (cations + anions) of these liquids. Prediction and correlation models are supposed to characterise their properties and molecular structure. UNIFAC and COSMO are commonly used models and are briefly discussed.

3.3.2. COSMO

This model is called the conductor-like screening model for real solvents (COSMO-RS) and the variation known as segment activity coefficient model (COSMO-SAC) which predict thermodynamic information by utilizing intermolecular quantum mechanics (Constantinescu et al., 2005). This model is still in the early stages in predicting ionic liquids and does not rely on heavily experimental data. Besides, the profiles required by the model have not been tested yet.

3.3.3. UNIFAC

This model is mostly utilized for determining phase equilibria, mostly in the study of vapour liquid equilibria (VLE). The Universal Functional Group Activity Coefficients (UNIFAC) was first developed for molecular mixtures, but this was later improved by some of the research groups including Wang et al., (2008) for specific ionic groups such as ionic liquids. This model technique is also applied in determining activity coefficients at infinite dilution.

3.3.4. Determination of excess thermodynamic parameters

The excess thermodynamic parameters such as partial molar enthalpies ($\Delta H_1^{\mathrm{E},\infty}$), Gibbs free energy ($\Delta G_1^{\mathrm{E},\infty}$), and entropy term ($\mathrm{T_{ref}}\Delta S_1^{E,\infty}$), at infinite dilution were computed from the experimental activity coefficients data. These parameters were used to explain the types of molecular interactions occurring between solvent and the solutes. The Van’t Hoff relation was used to compute the values of entropies and enthalpies at infinite dilution.

$$\ln(\gamma_{13}^{\infty}) = \frac{\Delta H_1^{E,\infty}}{RT} - \frac{\Delta S_1^{E,\infty}}{R}$$

(3.3.1)

The fitting of the natural logarithm of the experimental activity coefficients was used to obtain the two thermodynamic functions.

$$\ln(\gamma_{13}^{\infty}) = \frac{a}{T} + b$$

(3.3.2)

In the equation (3.3.2) above, “a” denotes the slope and “b” represents the intercept in a way that

$\Delta H_1^{\mathrm{E}\infty}$ = aR and $\Delta S_1^{\mathrm{E},\infty}$ = −bR.

(3.3.3)

Equation (3.3.4) below was used to obtain the values of Gibbs free energies.

$$\Delta G_1^{\mathrm{E},\infty} = RT\ln(\gamma_{13}^{\infty}) = \Delta H_1^{\mathrm{E},\infty} - T\Delta S_1^{\mathrm{E},\infty}$$

(3.3.4)

3.3.5. Activity coefficients by gas liquid chromatography

The gas liquid chromatography (g.l.c) was used to measure the retention data of solutes in the investigated ionic liquids. Three assumption to consider when using g.l.c for γ_{13}^{∞} measurements were discussed by Tumba (2010), and these includes:

- An ideal mixture is formed by the gas phase which is composed of a solute (1) in a carrier gas (2).
- A real liquid system with the solute (1) and solvent (3) is formed by the stationary phase.

- The liquid and gas phase are in thermodynamic equilibrium.

The equation (3.3.5) below which was proposed by Cruickshank et al., (1969) and Everett (1965) was utilized to compute γ_{13}^{∞} of solute in the ionic liquids used.

$$\ln \gamma_{13}^{\infty} = \ln \left(\frac{n_3 RT}{V_N P_1^*}\right) - \frac{P_1^* \ (B_{11} - V_1^*)}{RT} + \frac{P_0 J_2^3 \ (2B_{12} - V_1^{\infty})}{RT}$$

(3.3.5)

From the equation above, number of moles of ionic liquid in the column packing is represented by n_3, R denotes molar gas constant; temperature of the column denoted by T, V_N is the net retention volume of the solute, P_o the outlet pressure, saturated vapour pressure of the solute at temperature T is represented by P_1^*, the second virial coefficient of pure solute denoted by B_{11}, $P_o J_2^3$ represent the mean column pressure, molar volume of the solute is denoted by V_1^*, V_1^{∞} denotes partial molar volume of the solute at infinite dilution in the solvent and B_{12}(where 2 denotes the inert gas used), the mixed second virial coefficient of the carrier gas and the solute.

Equation (3.3.6) was used to determine the net retention volume of solute (V_N).

$$V_N = J_2^3 (t_R - t_G) q_{ov,}$$

(3.3.6)

In the above equation, t_R denotes to the retention time of a specified solute, q_{ov} represents the carrier gas flow at the column outlet pressure and column temperature, and t_G is the gas retention time of the non-retainable constituents. The equation (3.3.7) below was used to correct the carrier gas flow for the impact of water vapour.

$$q_{ov} = q_o \left(\frac{T}{T_f}\right) \left[1 - \left(\frac{P_w^*}{P_o}\right)\right]$$

(3.3.7)

Where q_o denotes the flow rate measured at the column outlet pressure with the bubble flow meter, P_w^* represents saturated vapour pressure of water at temperature, and T_f is the flow meter temperature, obtained by using a thermometer. The expression J_2^3 which appears in equation (3.3.6 and 3.3.8) is used to correct the impact of pressure drop through the column and is displayed in equation (3.3.8):

$$J_2^3 = \frac{2}{3}\frac{\left(\frac{P_i}{P_O}\right)^3 - 1}{\left(\frac{P_i}{P_O}\right)^2 - 1}$$

(3.3.8)

In the equation above, P_i represents column inlet pressure.

The second virial coefficients of pure solute, B_{11}, was given by Tsonopoulos (1974):

$$\frac{BP_c}{RT_c} = \frac{B}{V^*} \quad f^{(0)} + \omega f^{(1)} + af^{(1)} + bf^{(2)}$$

(3.3.9)

Where $f^{(0)} = 0.1445 - \frac{0.330}{T_r} - \frac{0.1385}{T_r^2} - \frac{0.0121}{T_r^3} - \frac{0.000607}{T_r^8}$ (3.3.10)

$$f^{(1)} = 0.0637 + \frac{0.331}{T_r^2} - \frac{0.423}{T_r^3} - \frac{0.008}{T_r^8}$$

(3.3.11)

$$f^{(2)} = \frac{1}{T_r^6}$$

(3.3.12)

$$f^{(3)} = \frac{1}{T_r^8}$$

(3.3.13)

$$T_r = \frac{T}{T_c}$$

(3.3.14)

From equations above, the virial coefficient is given by B, the critical temperature is presented by T_c, the acentric factor is denoted by ω, P_c is the critical pressure, T_r is the reduced temperature and V^* is the characteristic volume. For the variables of a and b, correlations were utilized from the work of Tsonopoulos and Dymond (1997) and Tsonopoulos and Heidman (1990).

The values for B_{12} (cross virial coefficient) are computed from equation (3.3.9) with the mixing rule of Tsonopoulos (1974):

$$T_{cij} = (T_{cij}T_{cjj})^{½}(1 - k_{ij})$$

(3.3.15)

$$V_{ij}^{*} = \frac{(V_{cii}^{1/3} + V_{cjj}^{1/3})}{4(Z_{cii} + Z_{cjj})}$$

(3.3.16)

$$\omega_{ij} = \frac{(\omega_{ii} + \omega_{jj})}{2}$$

(3.3.17)

$$a_{ij} = \frac{(a_{ii} + a_{jj})}{2} \qquad (3.3.18)$$

$$b_{ij} = \frac{(b_{ii} + b_{jj})}{2} \qquad (3.3.19)$$

In the above equations, the critical volume is denoted by V_c, and the binary interaction parameter represented by k_{ij}. Chueh and Prausnitz (1967) proposed an equation for the estimation of binary interaction parameters for a reduced dipole moment (μ_r) that is close to zero.

$$k_{ij} = \left[\frac{2\left(V_{cii}\,V_{cjj}\right)}{(V_{cii}^{1/3} + V_{cjj}^{1/3})}\right]^3$$

(3.3.20)

Yamada and Gunn (1973) modified an equation of the Rackett model (1970) for the estimation of molar volume.

$$V_s = V_c\,(0.29056 - 0.08775\,\omega)^{(1 - T_r)^{2/7}}$$

(3.3.21)

The saturated liquid molar volume is denoted by V_s.

The Antoine's equation was used to estimate the saturated vapour pressure. The critical properties of solutes (V_c, T_c, P_c) Antoine's coefficients and the acentric factor (ω) were taken from various literature sources.

3.3.6. Calculation of uncertainty

The law of propagation of uncertainties was used to calculate the uncertainties for all calculated values in this research study. Repeatability, accuracy, and other contributions in conducting the experimental work were taken into consideration when calculating uncertainties. Further enlightenment is briefly described by Taylor and Kuyatt (1994). The equation in calculating uncertainties is given below.

$$\mathrm{u}(\theta) = \sqrt{\sum_{i=1}^{y}\left[\frac{\partial\theta}{\partial x_i}\,u(x_i)\right]^2}$$

(3.3.22)

Where θ is the computed variable (in this work, γ_{13}^{∞}), *y* represents the number of independent variables and the independent variable in calculating θ is denoted by x_i. In consideration of repeatability of type, *A* distributions of q repetitions, the error (u_r) is given by the standard deviation:

$$\mathrm{u}_r\ (\theta) = \sigma = \sqrt{\frac{1}{n-1}\sum_{j=1}^{q}(\theta_j - \theta^{-})}^2$$

(3.3.23)

Where θ^{-} is the mean value of θ and θ_j is the j^{th} repetition.

3.4. Phase equilibrium problem

Phase separation is a common industrial, physiological phenomenon and comprises exchange of a constituent from one phase to another phase. This normally takes place when two liquid phases are brought into contact, and they transfer their constituents until the concentration of each phase reaches a constant value. When this occurs, the system is said to be in equilibrium. Furthermore, the concentration of the two phases that are in equilibrium are very different from each other, and this variation enables one to separate mixtures by either extraction, distillation, or any phase contacting techniques (Cotterman et al., 1986).

The composition of the two phases in a mixture mostly depends on pressure and temperature, including the concentration and chemical nature of substances in a system. Phase equilibrium thermodynamics is of interest in chemical engineering and chemistry, due to industrial manufacturing processes that involves phase contact. The science of phase equilibrium involves absorption, leaching, distillation, adsorption, and extraction which forms an important unit in chemical industry. A typical industrial process and a full view is shown in figure 3.1 and 3.2.

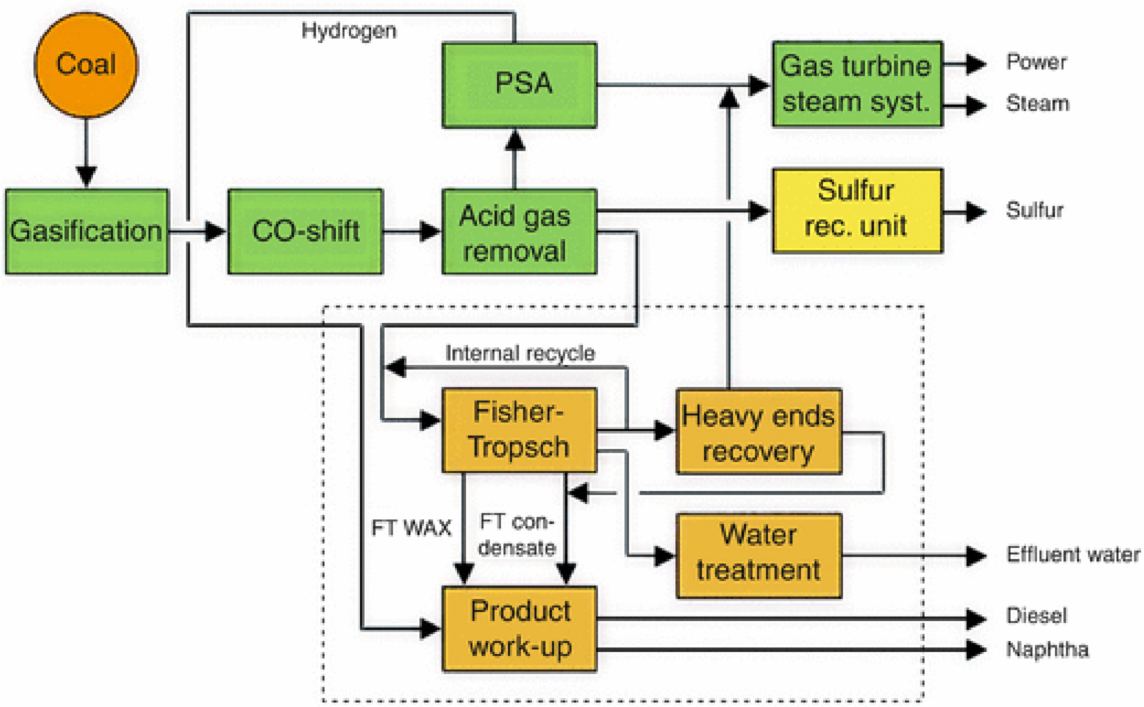


Figure 3.1: Chemical plant (combustion of coal) (SASOL).

Figure 3.2: Full view of a chemical plant (SASOL).

3.5. Liquid-liquid equilibrium

A process in which two components in a solution are separated by their distribution between two immiscible liquid phases by means of adding a separating entrainer (third component), is known as liquid-liquid extraction. The role of an entrainer in a solution is to form an immiscible layer with the mixture. In this, the layer composed of the remainder of original solution with entrainer is known as raffinate, and the solvent layer is termed as the extract (Peters, 1984).

Extraction technique based on liquid-liquid extraction has been widely used as it is the cheapest process for industrial application and has been applied in the production of fuels in the nuclear industry and in the processing of coal tar liquids. These techniques have been extensively used in the separation of sulphur compounds and hydrocarbons in fuel industries. In any separation process, it is important and essential that the solvent and liquid mixture feed are completely immiscible or at least partially immiscible. In this separation, essentially three steps are involved:

- Bringing the entrainer and the feed mixture into contact,
- Extraction of the resulting two-phase region,
- Recovery and removal of the entrainer from each phase.

A principle of liquid-liquid extraction is shown below.

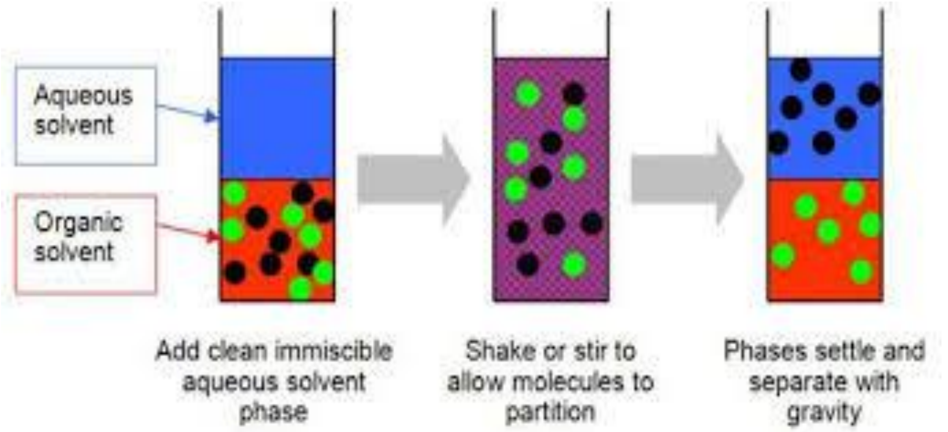


Figure 3.3: Principle of liquid-liquid extraction.

3.6. Uses of liquid-liquid extraction

Liquid-liquid extraction (LEE) is mostly used when it is not feasible to separate binary mixtures by simple distillation or to reduce the process costs. Liquid-liquid extraction is more practical in separating azeotropic mixtures (close boiling point mixtures), i.e. (heptane/ethanol; hexane/ethanol, THF/methanol, etc). Liquid-liquid extraction is more economical as compared other separation techniques. One of the advantages of liquid-liquid extraction is the operational costs, low temperature and pressure being used, and easy recovery of the entrainer.

An extraction process usually requires:

- Liquid-liquid extraction.
- Solvent recovery.
- Raffinate separation or desolventizing.

Conventional distillation is not a suitable technique to separate azeotropic mixtures due to the formation of minimum azeotropic mixtures, and it is not economically feasible. Azeotropic batch distillation was used to separate close boiling mixtures (Rodríguez-Donis et al., 2005) using different entrainers including water, acetonitrile, nitromethane, and methanol (Feng et al., 2015). This technique is characterised by some setbacks which include long exposure times of the mixture to high temperatures that can result in thermal degradation (Kabane et al., 2018). In addition, batch distillation is also disadvantaged by high energy input costs required for the process in comparison to liquid-liquid extraction or continuous distillation. The problem of separating azeotropic mixtures can be drastically simplified by liquid-liquid extraction, and this technique is relatively cheap and effective. This also require the knowledge of equilibrium behaviour that is required for the applied separation method. This requires an introduction of new solvents with special properties such as ILs that possess high selectivity, high distribution ratio with none or little solvent loss in LLE (Zhang et al., 2007, Ali et al., 2003, Holbrey and Seddon, 199, Kubisa, 2004). The special properties of ILs also include low vapour pressure (de Castro, 2010), thermal stability (Fraser and MacFarlane, 2009) and ability to dissolve organic compounds (Millero, 1971). In naphtha purification, ILs have been reported as promising solvents with satisfactory results (Meindersma et al., 2006, Selvan et al., 2000, Arlt et al., 2008). Even ionic liquids are reported to have some setbacks which limit their use in large scale applications, these disadvantages entail their degree of biodegradability or recyclability, and the high cost of production is also cause of concern (Swatloski et al., 2003, Abbott et al., 2004, Królikowski, 2017). Ionic liquids have been applied in liquid-liquid extraction of various separation problems (Domańska et al., 2018, Królikowski and Lipińska, 2019, Durski et al., 2019), and encouraging results were observed. Recently, different solvents including imidazolium based ionic liquids and low transition temperature mixtures (deep eutectic solvent) were tested in the separation of azeotropic mixtures (Pereiro and Rogriguez, 2008, Wen et al., 2018, Gonzalez et al., 2013, Kabane et al., 2020).

The flexibility of ionic liquids created by the combination of anion and cation permit them to have unique properties. In the desulfurization process, a suitable ionic liquid must be selective towards sulphur compounds and possess low solubility in fuels (Domańska et al., 2013). In ternary phase equilibrium, the separation is evaluated from selectivity and distribution coefficients. Ionic liquids for extractive HDS are promising solvents for future complementary innovations (Ibrahim et al., 2017, Kulkarni and Afonso, 2010). In various processes, ionic liquids are labelled as suitable entrainers. Some of the ionic liquids have been tested in petrol desulfurization processes and the data is also found in the literature (Domańska and Walczak, 2015, Gao et al, 2015, Ahmed et al., 2016, Rodríguez-Cabo et al., 2013). For liquid fuels oils, thiophene derivatives are considered as key substances to be extracted, and in this regard, alkanes (C_7 – C_{16}) are usually tested.

Although ionic liquids are still under intense investigation, these solvents are found to give satisfactory results based on separation parameters when compared to the currently used industrial separating solvents including dimethyl sulfoxide, quinoline, N-methyl-2-pyrrolidone and sulfolane.

3.7. Essential properties for solvent selection

3.7.1. Density

The variation in densities among two conjugate phases in equilibrium state influence the counter current rates that can be obtained in separation equipment and the coalescence rate (Perry et al., 1997). A notable difference in densities is preferred between the two liquid phases to ensure a fast disengagement of phases (Redhi, 2003).

3.7.2. Viscosity

In liquid extraction, solvent that possess the highest solvent power normally yields a solution of lowest viscosity. This implies that the viscosity of a solution is an indirect measure of the solvent power of the entrainer (Rewat and Thind, 1976).

Whilst, a eutectic solvent is preferred, however this might well change the properties of the solvent. Better dispensing media are always observed in liquids having small molecules and give mixtures of low viscosity, this is also observed in ionic liquids. The selective properties of a solvent always change after it is loaded in a mixture to be separated.

3.7.3. Toxicity

It is always preferred to work with solvents that give low levels of toxicity. Low solvent toxicity can be determined from low risks such as solvent vapour inhalation or skin contact, and solvents with good level of toxicity reveal high standards of the industrial plant. Ionic liquids are said to have good properties compared to currently used volatile organic solvents (VOCs), but these solvents are also characterized by few setbacks which limit them in large scale of industrial applications. These disadvantages include the level of biodegradability or recyclability. Solvent toxicity is low when water solubility is high.

3.7.4. Chemical characteristics

It was noted that the selectivity depends on the differences in molar volumes of species to be extracted and the polar energy density of the solvent (Prausnitz and Anderson, 1961). In the case of separating mixtures with slightly different molar volumes, the selectivity depends on the entrainer to act as an electron acceptor and hydrocarbon as an electron donor in forming acid-base complexes. Rewat and Thind, (1976) stated that a good extracting solvent should have low molecular volumes ($< 150\ \text{cm}^3 \cdot \text{mol}^{-1}$).

The following characteristics are always preferred in an extracting solvent:

- Low specific heat capacity and latent heat.
- Non-corrosive.
- High chemical and thermal stability.
- Density range (1.0 – 1.3) $\text{g} \cdot \text{cm}^{-3}$.

- Low melting point.
- High boiling point.

The reasons why ionic liquids are referred as good entrainers for industrial separation problems is that they meet the above-mentioned characteristics of preferred extracting solvents.

3.7.5. Interfacial tension

Chaar et al., (1986) highlighted that a good separating solvent should have high interfacial tension. This ensures the rapid disengagement and an increase of rapid coalescence.

3.7.6. Selectivity and distribution ratio

These are the most important and essential parameters in an extraction process. The essence of these parameters was previously discussed (Gruber et al, 1997, Krummen and Gmehling, 2004, Odele and Macchietto, 1993). Selectivity (S) is the measure of the solvent potentially to extract a solution system into its pure component (Perry et al., 1997). Selectivity is given by the equation (3.7.1) below.

$$S = \frac{x_2^{\mathrm{II}} \cdot x_3^{\mathrm{I}}}{x_2^{\mathrm{I}} \cdot x_3^{\mathrm{II}}}$$

(3.7.1)

In the equation (3.7.1) above, x_2 and x_3 represents the mole fractions and superscripts I and II and subscripts 2 and 3 denotes components in the upper phase and bottom phase, respectively. The separation power of a liquid-liquid mixture is determined by the deviation of selectivity from unity.

The mole fraction of a substance in the extract phase (organic stream) divided by the mole fraction of the same substance in the raffinate phase (aqueous stream) at phase equilibrium is defined as a distribution ratio or partition coefficients. Depending on the system, the distribution ratio can be a function of temperature, the concentration of chemical species in the system, and many other parameters. Note that distribution ratio is related to the Gibbs free energy of the extraction process. The amount of extracting solvent required for a specific extraction is determined from distribution ratio data. A good separating solvent should show a distribution ratio above the unity ($\beta > 1$). Distribution ratio (β) is given by the equation below:

$$\beta = \frac{x_2^{\mathrm{II}}}{x_2^{\mathrm{I}}}$$

(3.7.2)

Where x_2 represents the mole fractions and superscripts I and II denotes substance in the extract phase and aqueous phase. Sometimes, the distribution ratio is referred to as the partition coefficient, which is often expressed as the logarithm. In solvent extraction, two immiscible liquids are shaken together. The more polar solutes dissolve preferentially in the more polar solvent, and the less polar solutes in the less polar solvent. Although the distribution ratio and partition coefficient are often used synonymously, they are not necessarily so. Solutes may exist in more than one form in any phase, which would mean that the partition coefficient and distribution ratio will have different values. This is an important distinction to make as whilst the partition coefficient has a fixed value for the partitioning of a solute between two phases, the distribution ratio changes with differing conditions in the solvent.

3.7.7. Solvent recovery

For any extracting solvent, it should be easy and simple to recover the entrainer from the raffinate stream and extract stream, after the separation process. Most of industries are utilizing distillation techniques and this means that the volatility of non-solvent components to extraction-solvent should be significantly less or greater than the unity.

Tochigi et al., (1985) defined relative volatility (x_{13}) as follows:

$$x_{13} = \frac{\mathrm{P}_1 \, \gamma_1}{\mathrm{P}_3 \, \gamma_3}$$

(3.7.3)

In distillation technique, vapour pressures of the two components to be separated are represented by P_1 and P_3, and the activity coefficients of the two components is denoted by γ_1 and γ_3.

3.7.8. Cost and availability

The unit cost and availability of extracting solvents is an important factor when designing an extraction process. This determines the economic viability of liquid-liquid extraction. In addition, the most important factor is that high solvent loading should yield high efficiency.

Some of the typical extraction equipment used are shown in figure 3.4 below.

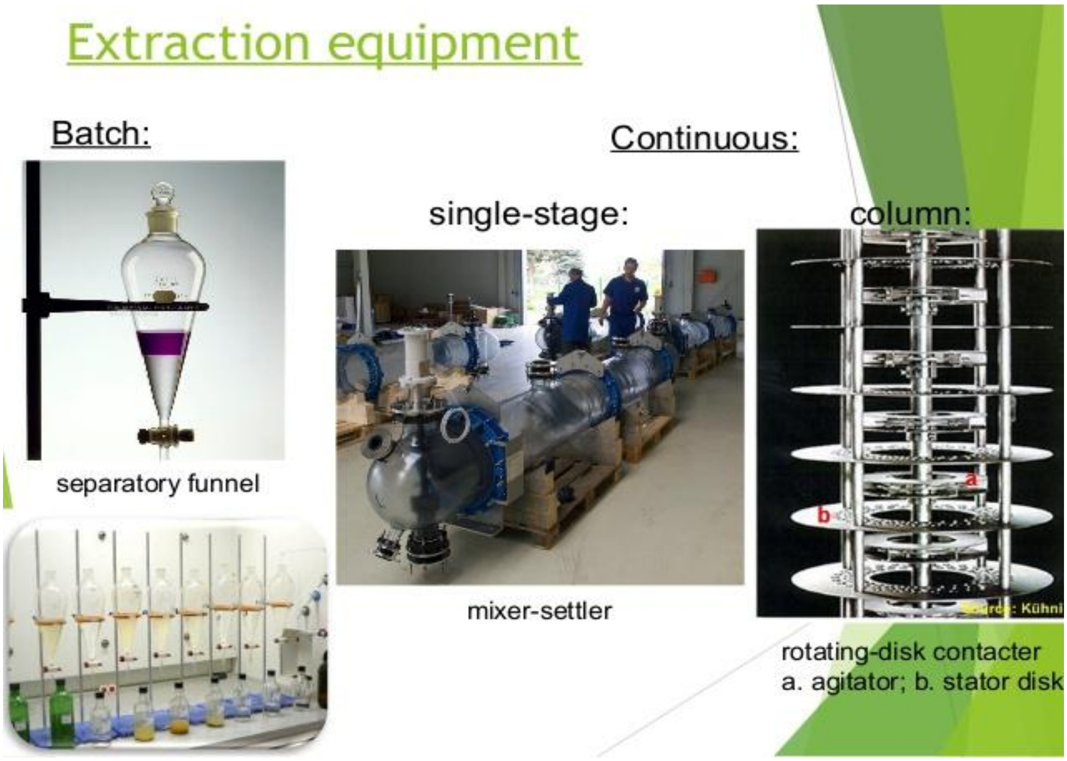
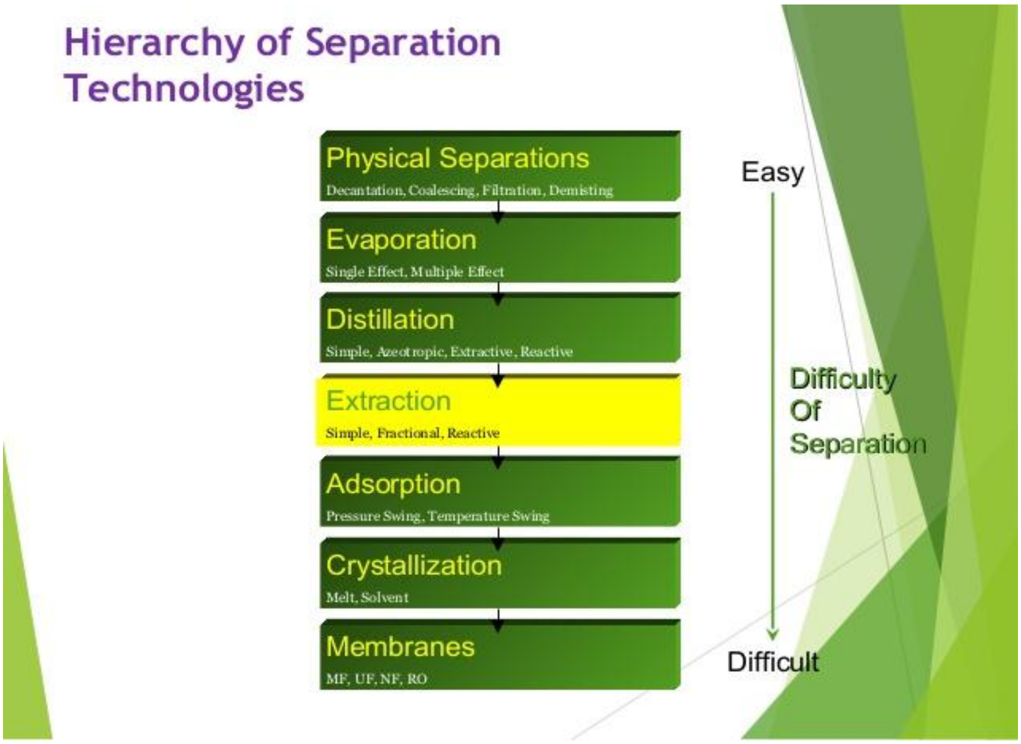


Figure 3.4: Solvent extraction equipment.

The hierarchy of separation technologies used in separation processes are shown in figure 3.5 from easy operation to difficult.



Hierarchy of Separation Technologies

Physical Separations
Decantation, Coalescing, Filtration, Demisting

Evaporation
Single Effect, Multiple Effect

Distillation
Simple, Azeotropic, Extractive, Reactive

Extraction
Simple, Fractional, Reactive

Adsorption
Pressure Swing, Temperature Swing

Crystallization
Melt, Solvent

Membranes
MF, UF, NF, RO

Easy

Difficulty Of Separation

Difficult

Figure 3.5: Hierarchy of separation technologies.

A basic type of ternary system with two phase region is shown in the figure below.

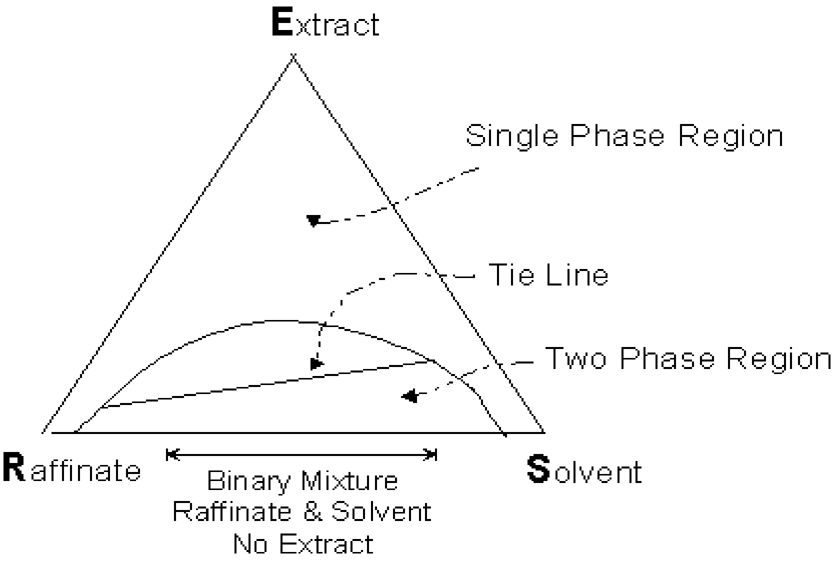


Figure 3.6: A basic type of ternary system with two phase regions.

Chapter 4

Experimental work

4.1. Techniques for determining activity coefficients at infinite dilution

4.1.1. Inert gas stripping technique

This technique occurs in a confined cell where a dilute compound is stripped from a solution by a flow of an inert gas at a specific isotherm. Within a set of intervals, the exiting concentration is always determined as the time advances. The activity coefficients at infinite dilution are then computed in this method. For volatile solutes in volatile or non-volatile solvents, this technique can be used with comparatively high volatilities (Tumba, 2010). This technique is also termed as continuous gas extraction or dilute cell procedure (Tumba, 2010, Kojima et al., 1997).

4.1.2. Differential ebulliometer technique

Activity coefficients at infinite dilution values can also be determined from the linear relationship between the solute concentration and bubble point temperature (Dallinga et al., 1993). This technique should be applied for substances with comparable volatilities; however, it is not suitable for non-ideal mixtures (Dallinga et al., 1993).

4.1.3. Gas liquid chromatography

Gas liquid chromatography (g.l.c) is the most prevalent technique currently used and was projected in 1956 (Kojima, 1997). This method is functional in examining thermophysical properties at infinite dilution. It is now being utilised in the measurements of retention data of volatile solutes in non-volatile solvents to calculate infinite dilution activity coefficients. For such measurements, the technique is reliable and rapid. Recent modification and improvements of the method have permitted measurements of medium volatility (Williams-

Wynn et al., 2013). However, the solvents tested for possible industrial separation processes are always coated inside the column and set to a controlled temperature. With the use of this method, relative uncertainties of (3 – 5) % have been noted by many researchers (Dalling et al., 1993, Letcher et al., 2005, Bahadur et al., 2014). Besides, the infinite dilution activity coefficients for non-volatile solvents cannot be determined in volatile solutes (Goerge, 2008). However, the g.l.c technique for determining activity coefficients remains comparable with small alterations that are observed in the literature. A pre-coiled stainless steel was utilised by (Letcher and Reddy, 2007) and pre-coiled glass column by (Domanska and Marciniak, 2008) to prevent any possible damages of the solid support material incorporated as the stationary phase. The column temperature is kept constant on the g.l.c oven.

4.2. Procedure and experimental apparatus

The experimental technique used in this work has been described in the literature (Letcher and Whitehead, 1996, Bayles et al., 2003). The method and any used modifications in this study is expansively described.

4.2.1. Materials

The investigated volatile organic solvents (referred to as, solutes) in non-volatile solvent (referred to as, entrainer) are listed in table 4.2.1 with their corresponding purities, CAS number, suppliers, and analysis method. There was no need to additionally purify the solutes as the gas liquid chromatography technique eliminates any unwanted species on the column.

Table 4.1

Purity of organic solutes used in this work.

Compounds [a]	Supplier	Purity (mass fraction)	CAS No.	Analysis method
2,2-dimethylbutane	Sigma-Aldrich	≥ 0.99	75-83-2	GC
Pentane	Sigma-Aldrich	≥ 0.99	109-66-0	GC
Hexane	Sigma-Aldrich	≥ 0.99	110-54-3	GC
Heptane	Sigma-Aldrich	≥ 0.99	142-82-5	GC
n-Nonane	Sigma-Aldrich	≥ 0.99	111-84-2	GC
n-Decane	Sigma-Aldrich	≥ 0.99	124-18-5	GC
1-Pentene	Merck	≥ 0.99	109-67-1	GC
1-Hexene	Merck	≥ 0.99	592-41-6	GC
1-Heptene	Merck	≥ 0.99	592-76-7	GC
1-Nonene	Sigma-Aldrich	≥ 0.99	124-11-8	GC
1-Decene	Sigma-Aldrich	≥ 0.99	872-05-9	GC
Cyclohexene	Sigma-Aldrich	≥ 0.99	110-83-8	GC
Cyclohexane	Sigma-Aldrich	≥ 0.99	110-82-7	GC
Cyclooctane	Sigma-Aldrich	≥ 0.99	292-64-8	GC
1-Pentyne	Fluka	≥ 0.99	627-19-0	GC
1-Hexyne	Sigma-Aldrich	≥ 0.99	693-02-7	GC
1-Heptyne	Sigma-Aldrich	≥ 0.99	628-71-7	GC
Benzene	Sigma-Aldrich	≥ 0.99	71-43-2	GC
Toluene	Sigma-Aldrich	≥ 0.99	108-88-3	GC
Ethylbenzene	Sigma-Aldrich	≥ 0.998	100-41-4	GC
m-Xylene	Sigma-Aldrich	≥ 0.99	108-38-3	GC
p-Xylene	Sigma-Aldrich	≥ 0.99	106-42-3	GC
o-Xylene	Sigma-Aldrich	≥ 0.99	95-47-6	GC
Methanol	Sigma-Aldrich	≥ 0.999	67-56-1	HPLC
Ethanol	Sigma-Aldrich	≥ 0.998	64-17-5	GC

Propan-1-ol	Sigma-Aldrich	≥ 0.997	71-23-8	GC
Butan-1-ol	Sigma-Aldrich	≥ 0.998	71-36-3	GC
(Tetrahydrofuran, THF)	Sigma-Aldrich	≥ 0.99	109-99-9	GC
Acetonitrile	Sigma-Aldrich	≥ 0.998	75-05-8	HPLC
Thiophene	Sigma-Aldrich	≥ 0.99	110-02-1	GC
(Acetone)	Sigma-Aldrich	≥ 0.999	67-64-1	HPLC
2-butanone	Sigma-Aldrich	≥ 0.99	78-93-3	GC
Water	Sigma-Aldrich	≥ 0.999	7732-18-5	HPLC

[a] Names in parentheses are common names used in text.

The list of solvents tested as a possible entrainers based on activity coefficients at infinite dilution are listed below:

Table 4.2

Properties of ionic liquids under investigation for activity coefficients measurements

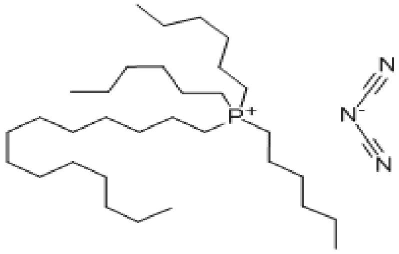
Compound	Supplier, CAS. No	Purification method	Analysis method	Purity (mass fraction)
Trihexyltetradecylphosphonium dicyanamide	Sigma-Aldrich, 701921-71-3	Vacuum heating, dried at 353.15 K for 9 hrs	Karl-Fischer auto titrator	≥ 0.95
1,3-dimethylimidazolium dimethylphosphate	Sigma-Aldrich, 654058-04-5	Vacuum heating, dried at 353.15 K for 9 hrs	Karl-Fischer auto titrator	≥ 0.98
2,3-dihydroxypropyl-*N*-methyl-2-oxopyrrolidinium chloride	Own synthesis	Vacuum heating, dried at 353.15 K for 20 hrs	NMR, Karl-Fischer auto titrator	≥ 0.98
2′,3′-epoxypropyl methyl-2-oxopyrrolidinium chloride	Own synthesis	Vacuum heating, dried at 353.15 K for 20 hrs	NMR, Karl-Fischer auto titrator	≥ 0.98
Methyltrioctylammonium Chloride	Sigma-Aldrich,	Vacuum heating, dried at 353.15 K for 9 hrs	Karl-Fischer auto titrator	≥ 0.97
Deep eutectic solvent (1-butyl-3-methylimidazolium chloride + glycerol)	Own preparation	Vacuum heating, dried at 353.15 K for 9 hrs	Karl-Fischer auto titrator	-----

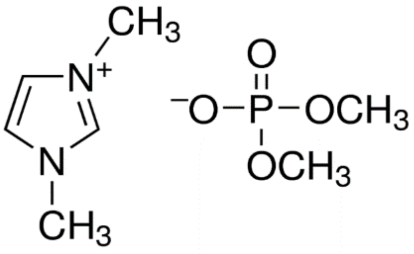
Water content for the purchased ionic liquids was less than $360 \cdot 10^{-6}$ %.

For the synthesised ionic liquids, water content was 0.0003 %.

The solid support material (chromosorb WHP 80/100 mesh) was supplied by SUPELCO.

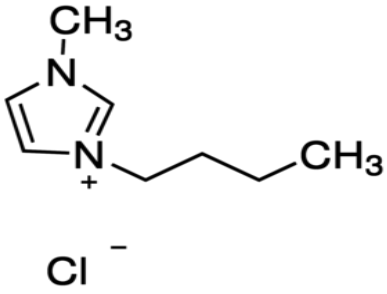
Structures of the ionic liquids used are listed below:

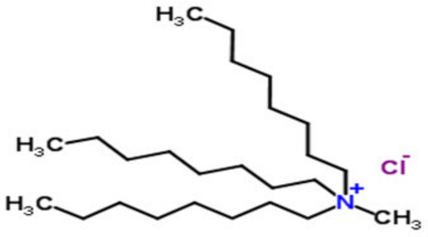




Trihexyltetradecylphosphonium Dicyanamide 1,3-dimethylimidazolium

Dimethylphosphate





1-butyl-3-methylimidazolium Chloride Methyltrioctylammonium Chloride

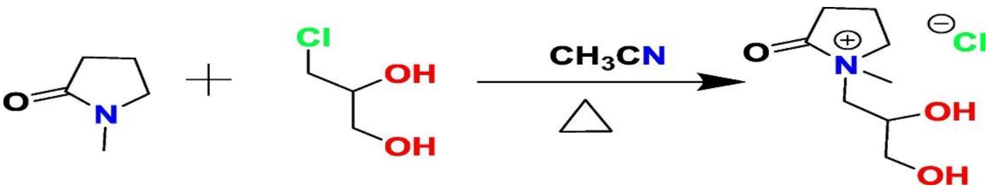
4.2.2. Synthesis of 2,3-dihydroxypropyl-N-methyl-2-oxopyrrolidinium chloride and 2′,3′-epoxypropyl methyl-2-oxopyrrolidinium chloride

4.2.2.1. Material

2-pyrrolidone (98.0%), epichlorohydrin (96.0%), acetonitrile (99.0%), acetone (98.0%), methanol (99.0%), dichloroethane (98.0%), chromosome (99.0%) and double distilled water were purchased from Sigma Aldrich.

4.2.2.2. Synthesis

2,3-dihydroxypropyl-N-methyl-2-oxopyrrolidinium chloride:

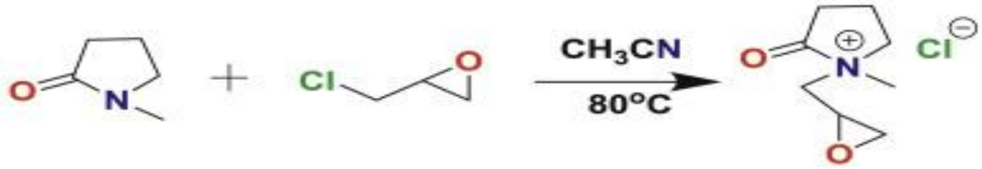


The ionic liquid was prepared into a 100 ml three-necked round bottom flask. This was fitted with a water condenser containing a thermometer. A 50 mmol (4.45 g) sample of 1-methyl-2-oxopyrrolidinine was added in 50 ml of ethanol and followed by slowly adding 55 mmol (6.0819 g) of 3-chloro-1,2-propanediol in an ice box setup at temperature, T = (8 – 10) °C, with constant stirring of the mixture. The prepared mixture was then brought to a moderate reflux, T = (90 – 100) °C for a period of 24 hrs. After 24 hrs, the flask was cooled and any unwanted species were completely removed in vacuo to give a yellow-coloured ionic liquid (N-2,3-dihydroxypropyl-1-methyl-2-oxopyrrolidinium chloride [PYR-PDO] [Cl] with 99% yield.

Characterization:

The synthesized ionic liquid was characterized using the following techniques: FTIR, ^{1}H NMR, ^{13}C NMR and elemental analyses. $[PYR\text{-}PDO]^+$ $[Cl]^-$. FTIR (υ=cm-1): 3309, 2940, 2871, 1644, 1505, 1407, 1304, 1262 and 1036. 1H NMR (400 MHz, $CDCl_3$): δ 4.3 (s, 2H), 3.8 (s, 1H), 3.7 (d, 2H), 3.4-3.6 (m, 2H), 3.3 (d, 2H), 2.7 (s, 3H), 2.2 (t, 2H), (1.9-2.0 (m, 2H). 13C NMR (100 MHz, $CDCl_3$): δ 158, 135, 132, 130, 125, 88, 25, 15. The elemental composition (%) calculated for $C_8H_{16}ClNO_3$ is: C, 45.83; H, 7.69; N, 6.68, which are close to the values found: C, 45.56; H, 7.10; N, 6.29.

2′,3′-epoxypropyl methyl-2-oxopyrrolidinium chloride:



This was prepared in a 200 ml three-necked round bottom flask. The reaction was kept in a heating oil bath with thermometer. Nitrogen gas was used to flush the flask and followed by adding 1 mol of freshly distilled N-methyl-2-oxopyrrolidine in 100 ml pf acetonitrile and 1.1 mol of epichlorohydrin. The mixture was then brought to reflux at temperature, T = (90 – 100) °C. The remainder solution was then heated under reflux for 48 hrs and cooled at room temperature. A vacuum was used to remove the volatile species contained in the mixture. The prepared ionic liquid was then purified by acetone and hexane to eliminate the unwanted starting material and distilled at T = 80 °C for 48 hrs. The IL was characterized by FTIR, ^{1}H NMR, ^{13}C NMR and elemental analysis.

Characterization:

The [Epmpyr]$^+$ [Cl]$^-$ was characterized by the following techniques: FTIR, ^{1}H NMR, ^{13}C NMR and elemental analysis. FTIR: (υ =cm^{-1}) 3442, 2995, 1621, 1501, 1403, 1332, 1256, 1113, 967, 856, 756, 679, 561, 479. ^{1}H NMR (400 MHz, DMSOd$_6$): δ 3.48-3.51 (m, 1H), 3.30-3.32 (t, 2H), 2.76- 3.29 (s, 1H), 2.61-2.62 (s, 3H). 2.26- 2.30 (d, 2H) 1.96-1.98 (t, 2H) 1.90-1.94 (m, 2H) ^{13}C NMR (100 MHz, DMSOd$_6$): δ 175.03, 51.22, 49.38, 45.72, 45.00, 30.62, 29.50, and 17.59. Elemental Analysis: theoretical calculation for (in %): $C_8H_{14}NO_2$: C, 50.14; H, 7.36; N, 7.31; the values found (in %): C, 50.45; H, 7.10; N, 7.17.

4.2.3. Preparation of deep eutectic solvent (DES)

A (2) [1-butyl-3-methylimidazolium chloride] : (1) [glycerol] molar ratio was prepared by adding glycerol to the ionic liquid. This was done by accurately weighing the two components using an analytical balance. The prepared mixture was vigorously mixed at 363.15 K. After a period of 8 hr, a clear homogeneous DES was obtained. A rotary evaporator was then used to eliminate any volatile components in the prepared deep eutectic solvent. An airtight cell was then used to store the DES, to prevent moisture from reaching the DES. The moisture content of the prepared DES determined by Karl-Fischer auto titrator was $330 \cdot 10^{-6}$ %.

4.2.4. Equipment description for activity coefficient measurements

Important equipment used in determining activity coefficients was as follows:

- Digital barometer
- Analytical balance (OHAUS)
- Soap bubble flow meter
- Karl-Fischer auto titrator
- Rotary evaporator with water bath
- Vacuum pump
- Ultrasonic water bath
- 1 m long, 4.1 mm diameter stainless steel column
- SHIMADZU GC-2014 Gas-chromatography coupled with thermal conductivity detector (TCD)

4.2.5. Gas liquid chromatography

The retention data of solutes under investigation in the ionic liquid were measured by the gas liquid chromatography. A 1 m long and 4.1 mm diameter column was used to pack the solvent and the stationary phase. The g.l.c is equipped with temperature-controlled oven.

During the analysis, a constant flow rate of inert gas is controlled. A typical schematic diagram of gas chromatography is shown below. A key disadvantage of the instrument used is the manual injections, and the injection volume was kept between (0.2 – 0.3) µL. The measured data was recorded in an output device (computer). The column was conditioned for 9 hours to dry the stationary phase and completely remove any volatile material on the column at temperature, T = 348.15 K and at p = 101 kPa. Soap bubble flow meter located at the outlet of the detector was used to ensure the flow rate of the instrument was controlled. The room pressure and temperature were measured by a digital barometer and thermometer, respectively.

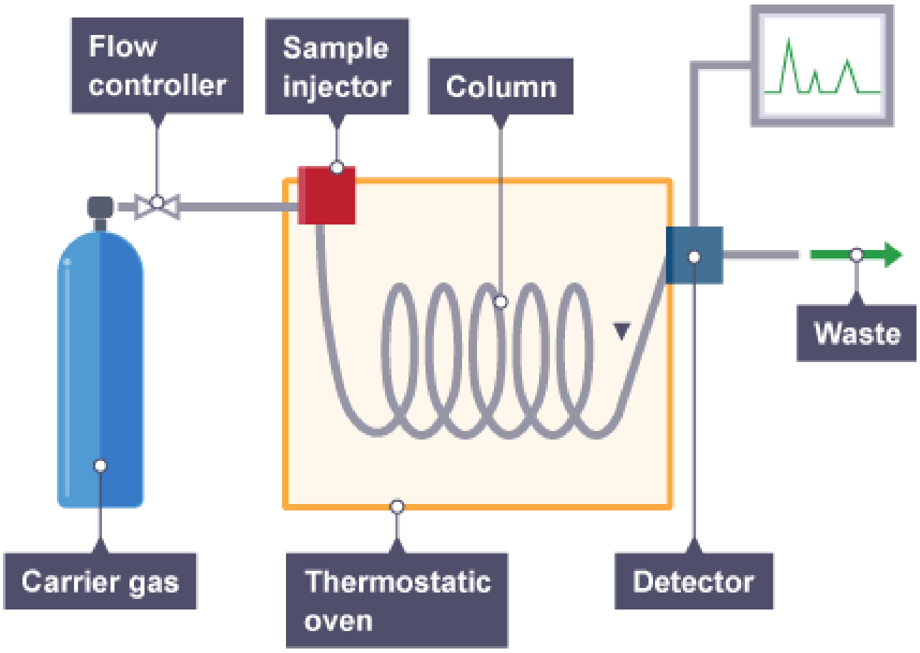


Figure 4.1: A typical schematic diagram of a gas liquid chromatography.

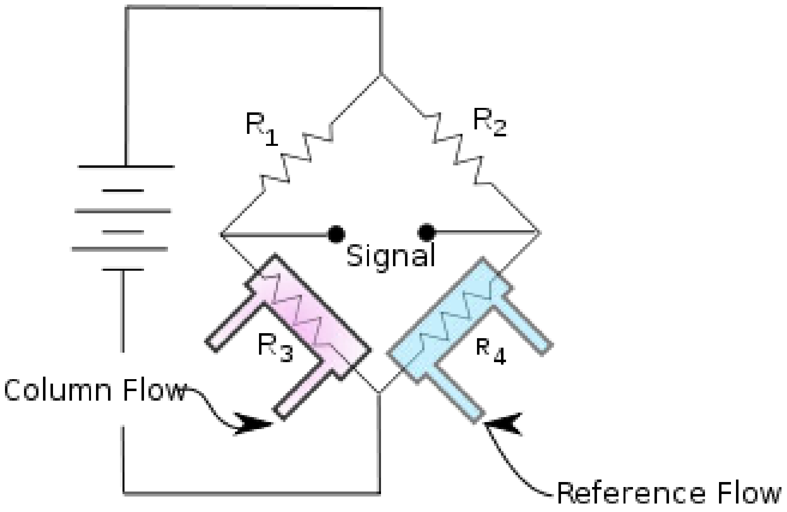


Figure 4.2: A Schematic diagram of thermal conductivity detector which is also known as a "Katharometer".

This is a chemical specific detector and bulk property detector mostly used in gas chromatography. Because most of the compounds used have lower thermal conductivities as compared to inert gases used in gas chromatography, when an analyte elutes the column, the effluent thermal conductivity is reduced, and an identified signal is produced. This type of detector is composed of an electrically heated filament in a temperature-controlled cell. For initial examination with unknown samples, this detector serves as good purpose. As much as the detector is not sensitive in comparison to the other detectors, but it is non-specific and non-destructive.

4.2.6. Method

4.2.6.1. Solvent purification

Before commencement of the experimental analysis, the tested ionic liquids were purified at low vapour pressure $6 \cdot 10^{-3}$ Pa at T = 343 K for 10 hrs. This was to ensure that the ionic liquids are free of contaminants. Immediately after the purification step, the flask was sealed with a parafilm, followed by insulation tape, and was stored in a covered beaker containing silica gel crystals. The beaker was kept in a desiccator. The water content was determined by using the Karl-Fischer auto titrator.

4.2.6.2. Preparation of stationary phase

The mass of a solid support material was weighed in a clean round bottom flask using an analytical mass balance with a precision of 0.0001 g. A calculated mass of ionic liquid was weighed in a flask containing a solid support material, this was done quickly to avoid moisture contamination. This was then followed by the addition of dichloromethane or methanol depending on the compatibility of the ionic liquid to ensure a uniform spread of the ionic liquid in chromosorb. The technique of rotary evaporation was applied to remove the added volatile solvent; the mass of the stationary phase was weighed to determine the corresponding mass before adding dichloromethane or methanol. The low boiling point of dichloromethane or methanol make it very easy to remove from the stationary phase. The prepared mass of ionic liquid (25 – 36) % was regarded as high enough to avoid adsorption of unwanted compounds on the column.

4.2.6.3. Preparation of the column

The stainless-steel column was manually straightened using a bench vice and uncurling by hand. No kinks were observed or allowed during the process. The material content previously used prior was removed from the column by applying ½ inch steel rod on the column until the entire material was dispersed, and the column was blown through with compressed air. The column was then cleaned with hot soapy water, rinsed by water, and dried by acetone. Compressed air was then blown through for 10 minutes.

4.2.6.4. Loading of the column

A glass wool was inserted in one end of the cleaned and empty column, followed by weighing the column. This prevented the stationary phase from passing through during the loading process. Before loading, the column was clamped vertically in a burette stand, a vacuum rubber tube connected to a flask was connected in the sealed bottom of the column to assist with a uniform and tight packing of the column. The prepared stationary phase was loaded in the column with gentle beating of the column with the ½ inch steel rod. After filling the material, the second opening of the column was sealed with a glass wool. The mass of the stationary phase loaded was calculated by taking the mass difference (fully packed column – empty column) both ends with glass wool.

4.2.6.5. Conditioning and installing of the column

The packed column was manually coiled. After coiling the column, it was inserted on the g.l.c oven and was conditioned by passing the carrier gas (helium) at a flow rate of 30 ml/min at T = 90 ^{o}C for a period of 14 hours.

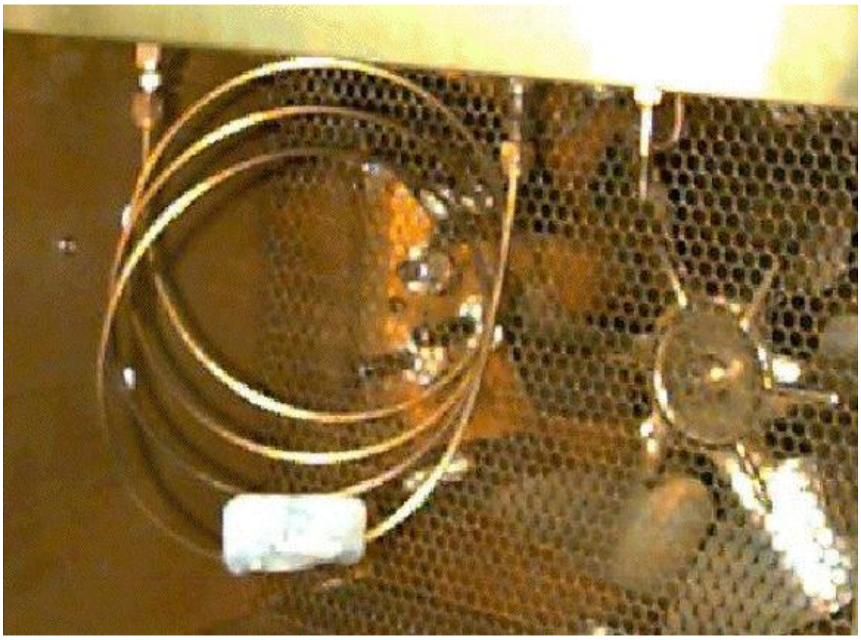


Figure 4.3: A diagram showing a packed column inserted in a gas liquid chromatography oven.

The column was fully packed with fine particles and not “Open”. Since the column is fully packed, the pressure drop in the column is high. These coated particles are the solid support for the liquid phase. The column has more compound capacity and is mostly used when working with the thermal conductivity detector.

4.2.6.6. Measurements

The measurements were conducted at temperature, T = (313.15 – 343.15) K, at 10 K intervals and p = 101 kPa. The injection volume of solutes was between (0.2 – 0.3) µL, injected manually. The pressure drop of the column, temperature and retention time of solutes were measured by the g.l.c internal sensors. The atmospheric pressure was measured by a digital barometer for pressure correction calculations.

The method was validated by the test system of hexane in hexadecane at T = 298.15 K and the results are presented below.

Table 4.3

Comparison of activity coefficient values of hexane in hexadecane measured at T = 298.15 K by Tiegs et al,1986

Chemical Name	Mass fraction Purity	CAS No	T/K	Experimental γ_{13}^{∞}	Literature γ_{13}^{∞}	RD/ %
Hexane	≥0.99	110-54-3	298.15	0.874	0.870	0.46
Hexadecane	≥0.98	544-76-3				

[a] Standard uncertainties u are u(γ_{13}^{∞}) = 5 %, u(T) = 0.02 K, u(p) = 1 kPa.

4.3. Representation of ternary liquid-liquid equilibrium

4.3.1. The phase rule

This is one of the greatest sophisticated calculations in the field of chemical thermodynamics. The phase rule was deduced by JW Gibbs et al., (1960) explaining the relation between the number of phases (P), the number of components (C), and the number of degrees of freedom (or variance) (F), at equilibrium for a mixture of any composition.

$$\mathrm{F} = \mathrm{C} - \mathrm{P} + 2$$

(4.3.1)

The number of intensive variables that can be changed without disturbing the number of phases is presented by the variance.

$$\mathrm{F} = 5 - \mathrm{P}$$

(4.3.2)

By keeping the pressure and temperature constant leaves two degrees of freedom, i.e. mole composition of the two components.

4.3.2. Triangular phase diagram

Triangular phase diagram is one of the methods of displaying how phase equilibria vary with composition of the system. The currently utilized triangular diagram (geometrical representation) was introduce in 1894 by Roozeboom and Schreinemakers.

The mole composition of the three components in a ternary mixture (C = 3) satisfy:

$$x_{\mathrm{A}} + x_{\mathrm{B}} + x_{\mathrm{C}} = 1$$

(4.3.3)

In case of non-volatile substances (ionic liquids) when using gas liquid chromatography, the ionic liquid mole fraction is calculated as follows:

$$x_{\mathrm{C}} = 1 - x_{\mathrm{A}} - x_{\mathrm{B}}$$

(4.3.4)

A phase diagram drawn as an equilateral triangle ensures that this property is satisfied automatically. An example of a three-component mixture in ternary systems is shown below.

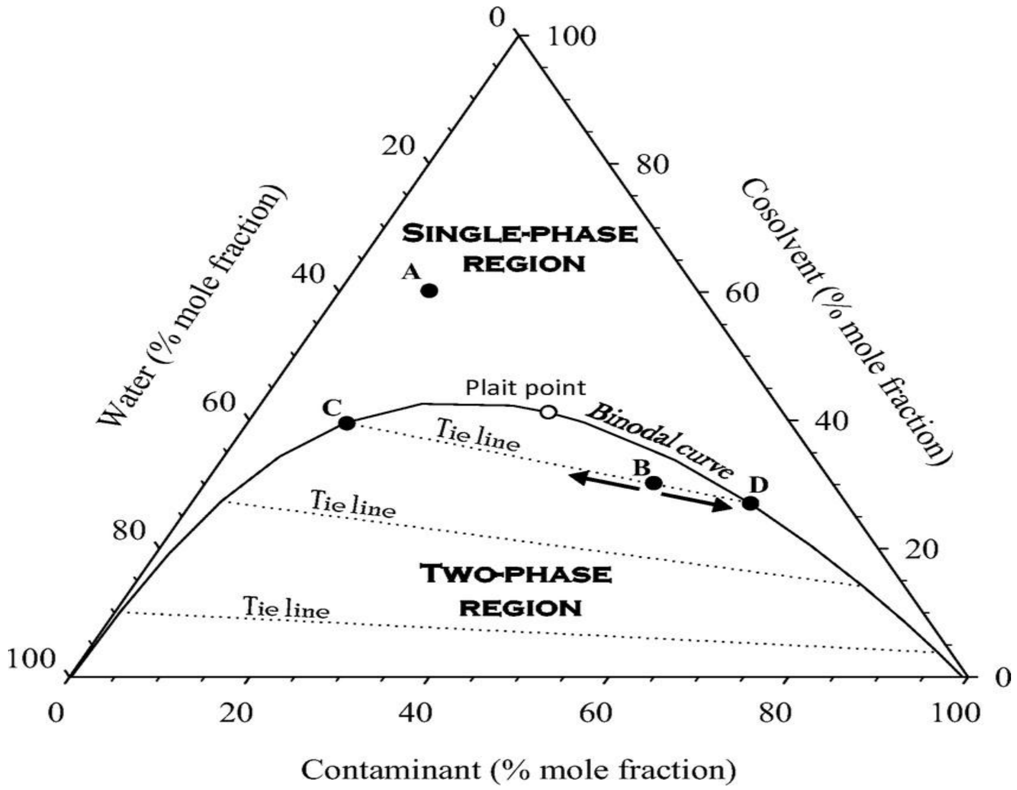


Figure 4.4: Three component mixture, in ternary phase system.

4.4. Liquid-liquid equilibria

This technique measures the phase amounts, phase compositions, temperature, and pressure. However, the experimental requirement of high accuracy is not a simple task to obtain. In addition, one should ensure that when taking samples for analysis does not disturb the equilibrium, and that pressure and temperature are accurately measured at the equilibrium position and ensure that the equilibrium really exists.

4.5. Experimental techniques

4.5.1. Titration methods

In the titration method, the binodal curve can only defines the heterogeneous region and this does not make it useful since it yields an incomplete information on phase equilibria. This technique determines the composition of the conjugate phase when other parameters of the substances are known (Novak et al., 1987). The unlimited mixtures of immiscibility are preferred for determining the binodal curve and the tie-lines, these should be controlled at a constant temperature and allow to reach phase equilibrium and followed by analysis of each phase system by gas liquid chromatography. This is referred as a classical method for determining binodal curve and tie-lines. In a ternary diagram, tie-lines are given by joining all the experimental points related to the system, and binodal curve is given by joining all the points in the ternary diagram. The titration curve was introduced for the situation where one of the substances is non-volatile (Redhi, 2003).

4.5.2. The direct technique

This method involves a system whose compositions lie in the two-phase region. The two-phase system is shaken vigorously for a long period of time at a constant temperature, after reaching phase equilibrium, the samples are analysed. In this method, the conditions are complicated as compared to binary mixtures as the content of at least two components must be determined in each phase. The combination of chemical and physical techniques is used in determining the tie-lines. The technique based on gas chromatography can be utilised successfully (Moriyoshi et al., 1989).

4.5.3. Gas liquid chromatography

For this technique, unlimited immiscible mixtures are prepared and controlled at constant temperature, and the pressure is always monitored until the systems reaches equilibrium. The mixture concentrations are determined by gas liquid chromatography. The full details of the procedure are described below.

4.6. Procedure and experimental apparatus

4.6.1. Material

The list of volatile organic solvents used for the formation of binary mixtures to be separated [azeotropic mixture (hexane + ethyl acetate) and desulfurization (thiophene + octane or hexadecane)] are listed in the table below.

Table 4.4

Suppliers and purities of the material used in this work

Compound	Supplier	Mass fraction purity	Analysis method	CAS Number
Ethyl acetate	Merck	0.998	GC	141-78-6
Hexane	Sigma-Aldrich	0.995	GC	110-54-3
1-propanol	Sigma-Aldrich	0.995	GC	71-23-8
2-pentanone	Sigma-Aldrich	0.995	GC	107-87-9
Thiophene	Sigma-Aldrich	0.995	GC	110-02-1
Octane	Merck	0.998	GC	111-65-9
Hexadecane	Sigma-Aldrich	0.995	GC	544-76-3

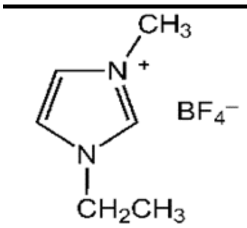
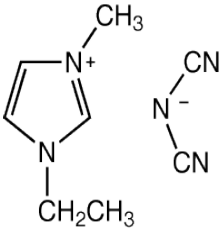
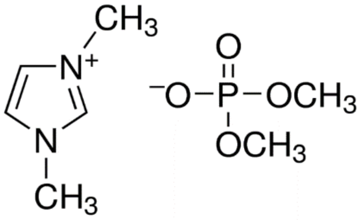
Purification method: molecular sieves

The ionic liquids used for LLE measurements are listed below including their structures.

Table 4.5

Properties of ionic liquids under investigation

Structure	Name, abbreviation, supplier, CAS	M (g/mol)	Mass fraction purity

	1-ethyl-3-methylimidazolium tetrafluoroborate, [EMIM][BF_4], Sigma-Aldrich, CAS:370865-89-7	197.21	0.985 (HPLC)
	1-ethyl-3-methylimidazolium dicynamide, [EMIM][DCA], Sigma-Aldrich, CAS:654058-04-5	222.18	0.98 (HPLC)
	1,3-dimethylimidazolium dimethylphosphate, [MMIM] [DMP], Sigma-Aldrich, CAS:654058-04-5	222.18	0.98 (HPLC)

Purification technique: Low pressure for 8 hr, T = 343.15 K, Analysis: Karl-Fischer technique. Water content for the purchased ionic liquids was less than $360 \cdot 10^{-6}$ %.

4.6.2. Method

The purification method for the ionic liquids has been briefly stated in section 4.2.6.1 and the g.l.c technique in 4.2.5. However, for this analysis, a flame ionization detector (FID) was used.

A 10 cm^3 jacketed glass cell was used to prepare the mixture composition to obtain the experimental liquid-liquid equilibria tie-lines. The mixture compositions were within the region of immiscibility. The mixtures were stirred using a coated magnetic stirrer bar. A possible evaporation of the mixtures or unwanted species were prevented by sealing the vessels. The jacketed vessels were connected to a thermostatic water bath maintained at a constant temperature, T = 298.15 K.

The thermodynamic equilibrium was ensured by stirring the mixtures for a period of 8 hr. After 13 hrs, the mixtures were analysed. A sample of approximately (0.1 – 0.4) cm^3 were taken from both phases of the system. A disposable plastic syringe coupled with a stainless-steel needle were used to withdraw the samples to be analysed. The withdrawn samples at each phase were placed in an ampoule containing 1 cm^3 of an internal standard. This was done to eliminate the phase splitting.

An internal standard was prepared by dissolution of pentanone in propanol in a mass ratio of 0.055. Gas liquid chromatography (g.l.c) coupled with flame ionization detector and a capillary column was used to analyse the mixtures. The g.l.c. instrument could only detect the volatile solutes; ionic liquid could not be detected due to its low vapor pressure.

The mole fraction of ionic liquids was determined by subtracting the composition of the two detected substances from the unity. This was accomplished by focussing at only two detected peaks (ethyl acetate and hexane, octane or hexadecane and thiophene). Total chrom workstation was used to process the results. To ensure the repeatability of the results, three sample injections of each sample were injected, and an average peak area was used to compute the mole fractions. Table 4.6.2 shows the operational conditions of the g.l.c. In determining the mole fraction composition, the estimated uncertainty is ± 0.005 mole fraction.

4.6.4. Flame ionization detector

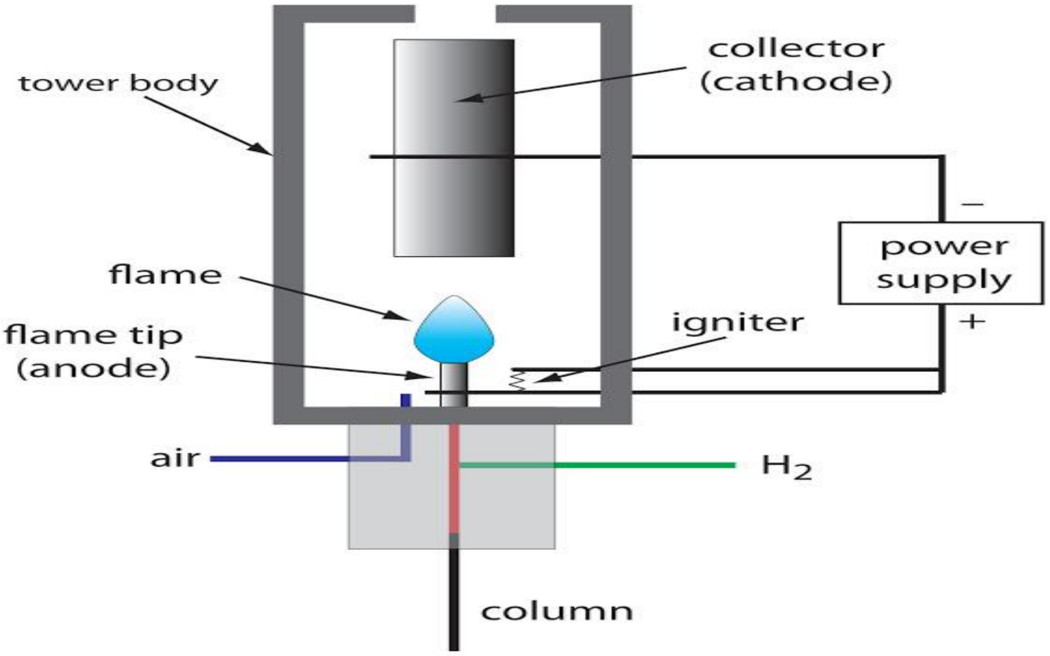


Figure 4.5: Schematic of a flame ionization detector (FID).

4.6.3. Gas chromatography operating conditions

The operating conditions for the instrument are as follows:

Table 4.6

Gas liquid chromatography operational conditions for the composition analysis of the equilibrium phases

Element	Characteristics	Description
Column	Type	ZB-WAXplus (polyethylene glycol), length 30 m, inner diameter 0.25 mm, film thickness 0.25 µm, temperature 20 °C to 250/260 °C
	Flow	1 mL.min^{-1}
	Carrier gas	Nitrogen
Oven	Temperature	323.15 K
Injector	Injection volume	0.0005 cm^3
	Split ratio	75:1
	Temperature	473.15 K

Detector	Type	Flame ionization detector (FID)
	Temperature	523.15 K

These were the operating parameters for the GC-FID, this also include the column used for the analysis of the hydrocarbons.

The advantages and disadvantages of the chromatographic technique are given below.

Table 4.7

Disadvantages and advantages of chromatographic technique

Disadvantages	Advantages
Technique is appropriate for low volatile solvents. The infinite dilution activity coefficients (IDAC) of the solvent in the solute cannot be determined.	Sample purity is not a major problem. The technique response is fast as the solutes can be injected once. Reactive systems can also be examined

The activity coefficients at infinite dilution of organic solutes in the entrainers can be easily determined by the technique of a gas liquid chromatography.

Chapter 5

Experimental Results

This chapter consists of results for two thermodynamic components (activity coefficients and liquid-liquid equilibria) data for possible solution to industrial separation problems.

5.1. Experimental Activity coefficients data

This factor is used in thermodynamics to account the deviations from the ideal behaviour in a binary mixture of chemical substances. Activity coefficients at infinite dilution of binary mixture are often reported at infinite of each component because activity coefficients models simply at infinite dilution, such empirical values can be used to estimate interaction energies. In separation processes, to avoid the loss of solvents, ionic liquids are very suitable due to low volatility and could be re-used. The types of interactions among the solutes and ionic liquids can be analysed from the values of γ_{13}^{∞}, the activity coefficients at infinite dilution data provides functional information in extraction and separation technology. The highest interaction among the solutes and investigated ionic liquid can be noticed by the lowest value of γ_{13}^{∞}. An excellent extracting solvent is determined from the selectivity and capacity values.

The following ionic liquids were used:

- 1,3-dimethylimidazolium dimethyphosphate [MMIM] [DMP]
- Trioctylmethylammonium chloride [N_{8881}] [Cl]
- Trihexyltetradecylphosphonium dicyanamide [$P_{666\,14}$] [DCA]
- 2,3-dihydroxypropyl-*N*-methyl-2-oxopyrrolidinium chloride [$(OH)_2$ C_3MPYR] [Cl]
- 2,3-epoxypropyl methyl-2-oxopyrrolidinium chloride [EPMpyr] [Cl]
- Deep eutectic solvent (DES) (1-butyl-3-methylimidazolium chloride + glycerol)

Table 5.1

Average activity coefficients at infinite dilution for the solutes in the ionic liquid ([$P_{6,\,6,\,6,\,14}$] [DCA]) at four different temperatures: for the standard state of solutes hypothetical liquid at zero pressure. [a]

Solute	Average γ_{13}^{∞} values			
	T = 313.15 K	T = 323.15 K	T = 333.15 K	T = 343.15 K
2,2-dimethylbutane	1.114	1.196	1.276	1.351
Pentane	1.001	1.065	1.121	1.185
Hexane	1.164	1.236	1.320	1.390
Heptane	1.357	1.434	1.518	1.613
n-Nonane	1.802	1.926	2.088	2.242
n-Decane	2.189	2.339	2.535	2.743
1-Pentene	0.7962	0.8583	0.9223	0.9940
1-Hexene	0.9152	0.9799	1.057	1.113
1-Heptene	1.0938	1.130	1.173	1.224
1-Nonene	1.412	1.532	1.668	1.820
1-Decene	1.585	1.770	1.978	2.190
Cyclohexene	0.6479	0.7097	0.7606	0.8135
Cyclohexane	0.7335	0.7806	0.8329	0.9013
Cyclooctane	0.8904	0.9284	0.9784	1.052
1-Pentyne	0.4132	0.4659	0.5475	0.6198
1-Hexyne	0.4420	0.5131	0.5937	0.6694
1-Heptyne	0.4857	0.5709	0.6448	0.7217
Benzene	0.3195	0.3638	0.4033	0.4405
Toluene	0.4194	0.4582	0.4899	0.5239
Ethylbenzene	0.5677	0.6067	0.6530	0.7004
m-Xylene	0.6338	0.6546	0.6897	0.7166
p-Xylene	0.6029	0.6404	0.6805	0.7067
o-Xylene	0.5252	0.5662	0.6134	0.6512
Methanol	0.3060	0.3239	0.3448	0.3617
Ethanol	0.3396	0.3598	0.3836	0.4019
Propan-1-ol	0.3962	0.4106	0.4244	0.4433
Butan-1-ol	0.4213	0.4454	0.4539	0.4708
THF	0.3514	0.3655	0.3840	0.4043
Acetonitrile	0.5743	0.6009	0.6242	0.6519
Thiophene	0.3722	0.3838	0.4121	0.4297
Acetone	0.3501	0.3634	0.3835	0.4053
2-butanone	0.4224	0.4481	0.4788	0.5139
Water	1.9549	1.823	1.7256	1.603

[a] Standard uncertainties: u are u(γ_{13}^{∞}) = 5 %, u(T) = 0.02 K and u(P) = 2 kPa.

Table 5.2

Limiting partial molar enthalpies $\Delta H_1^{\mathrm{E},\infty}$, Gibbs energies $\Delta G_1^{\mathrm{E},\infty}$ and entropies $T_{\mathrm{ref}}\,\Delta S_1^{\mathrm{E},\infty}$ for solutes in the investigated ionic liquid ([$P_{6,6,6,14}$] [DCA]) at the reference temperature T_{ref} = 323.15 K.

Solute	$\Delta H_1^{\mathrm{E},\infty}$ (kJ · mol^{-1})	$\Delta G_1^{\mathrm{E},\infty}$ (kJ · mol^{-1})	$T_{\mathrm{ref}}\,\Delta S_1^{\mathrm{E},\infty}$(kJ · mol^{-1})
2,2-dimethylbutane	-5.89	0.482	-6.37
Pentane	-4.94	0.169	-5.11
Hexane	-5.31	0.569	-5.88
Heptane	-5.12	0.968	-6.09
n-Nonane	-6.66	1.76	-8.43
n-Decane	-6.92	2.28	-9.20
1-Pentene	-6.58	-0.410	-6.17
1-Hexene	-5.90	-0.057	-5.84
1-Heptene	-3.36	0.328	-3.69
1-Nonene	-7.65	1.15	-8.79
1-Decene	-9.66	1.53	-11.2
Cyclohexene	-6.75	-0.93	-5.82
Cyclohexane	-6.10	-0.667	-5.43
Cyclooctane	-4.76	-0.201	-4.56
1-Pentyne	-12.3	-2.06	-10.3
1-Hexyne	-12.4	-1.79	-10.6
1-Heptyne	-11.7	-1.51	-10.2
Benzene	-9.55	-2.72	-6.83
Toluene	-6.51	-2.09	-4.41
Ethylbenzene	-6.29	-1.35	-4.94
m-Xylene	-3.78	-1.14	-2.64
p-Xylene	-4.80	-1.20	-3.60
o-Xylene	-6.51	-1.53	-4.98
Methanol	-4.98	-3.03	-1.95
Ethanol	-5.06	-2.75	-2.31
Propan-1-ol	-3.31	-2.39	-0.91
Butan-1-ol	-3.10	-2.17	-0.93
THF	-4.18	-2.71	-1.47
Acetonitrile	-3.72	-1.37	-2.35
Thiophene	-4.47	-2.58	-1.89
Acetone	-4.42	-2.72	-1.70
2-butanone	-5.79	-2.16	-3.63
Water	5.70	1.60	4.10

[a] Standard uncertainties: u are u(γ_{13}^{∞}) = 5 %, u(T) = 0.02 K and u(P) = 2 kPa.

Table 5.3

Selectivities (S_{ij}^{∞}) and capacities (K_j^{∞}) at infinite dilution for [$P_{6,\ 6,\ 6,\ 14}$] [DCA] for various separation problems at 328.15 K

Ionic Liquid	S_{ij}^{∞}			K_j^{∞}		
	Water/butan-1-ol	Heptane/benzene	Heptane/thiophene	Butan-1-ol	benzene	thiophene
[$P_{666\ 14}$][DCA]	3.95	3.87	3.72	2.23	2.62	2.527
[EMIM][DCA]^a	-	66.2	109	-	0.399	0.649
[$P_{666\ 14}$][TCM]^b	4.53	4.44	4.97	2.36	2.18	2.44
[BMIM][DCA]^c	0.292	44.7	71.5	0.907	0.519	0.823
[AMIM][DCA]^d	0.194	64.1	106	0.569	0.325	0.537
[P_{1444}][TOS]^e	1.74	12.6	19.7	3.14	0.780	1.22
[B^4MPY][DCA]^f	0.336	50.6	80.5	1.13	0.722	1.15

(^{a}Mutelet et al., 2010, ^{b}Marciniak and Wlazlo, 2018, ^{c}Domańska et al., 2016, ^{d}Wlazło et al., 2016, ^{e}Domańska and Paduszynski, 2010, ^{f}Królikowski and Królikowska, 2014)

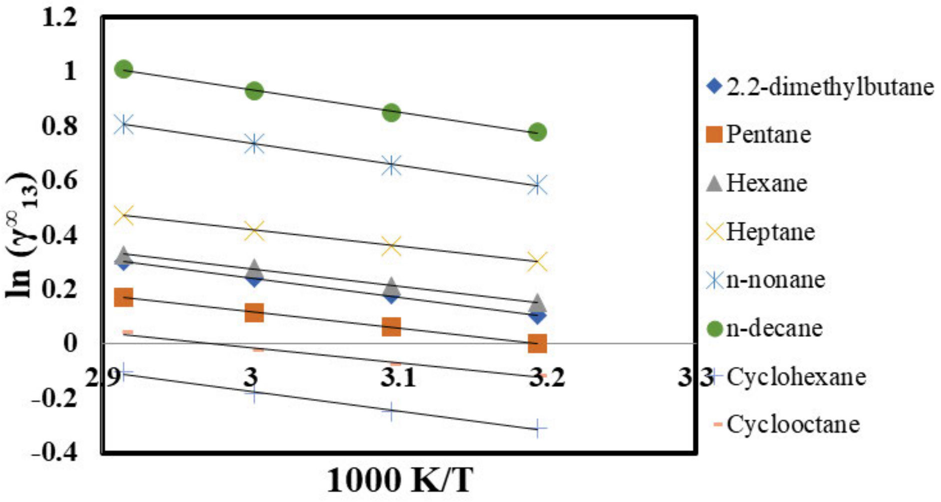


Figure 5.1: Plot of ln γ_{13}^{∞} against 1/T for the alkanes in ionic liquid [$P_{6,\ 6,\ 6,\ 14}$] [DCA] at T = (313.15 – 343.15) K.

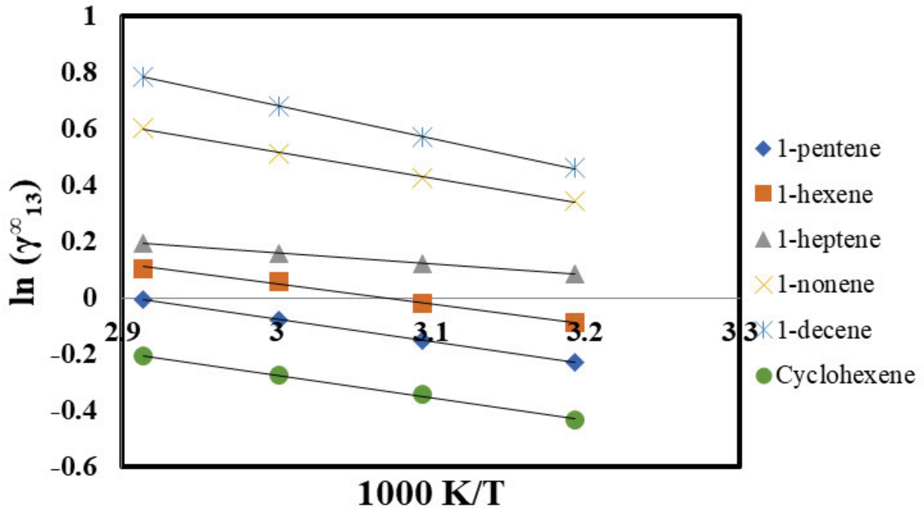


Figure 5.2: Plot of ln γ_{13}^{∞} against 1/T for the alkenes in ionic liquid [$P_{6,\,6,\,6,\,14}$] [DCA] at T = (313.15 – 343.15) K.

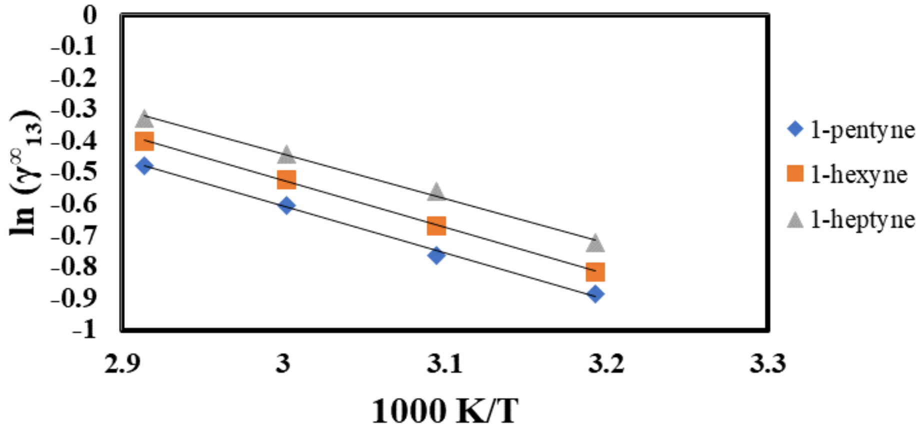


Figure 5.3: Plot of ln γ_{13}^{∞} versus 1/T for alkynes in ionic liquid [$P_{6,\,6,\,6,\,14}$] [DCA] at T = (313.15 – 343.15) K.

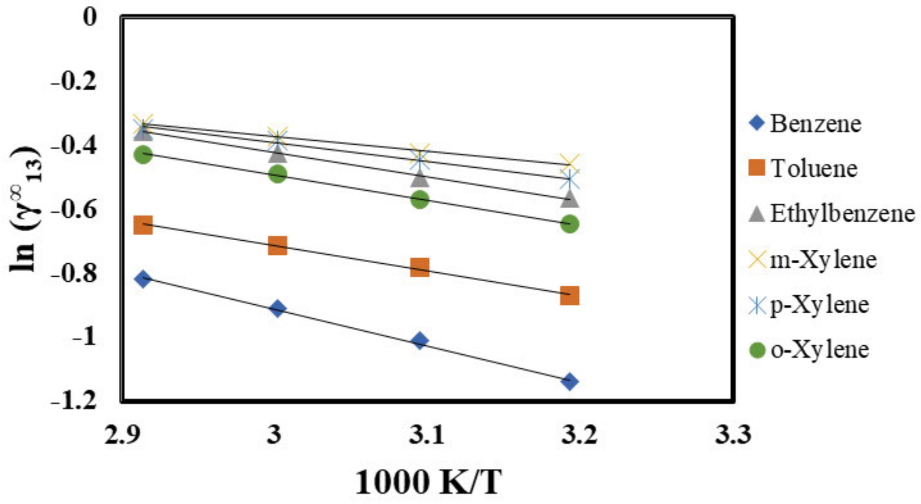


Figure 5.4: Plot of ln γ_{13}^{∞} versus 1/T for aromatic hydrocarbons in [$P_{6,\,6,\,6,\,14}$] [DCA] at T = (313.15 – 343.15) K.

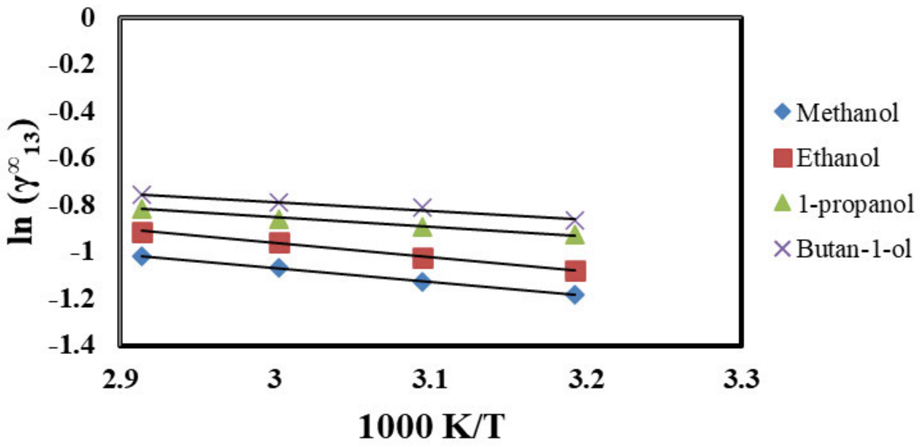


Figure 5.5: Plot of ln γ_{13}^{∞} versus 1/T for alcohols in ionic liquid [$P_{6,\,6,\,6,\,14}$] [DCA] at T = (313.15 – 343.15) K.

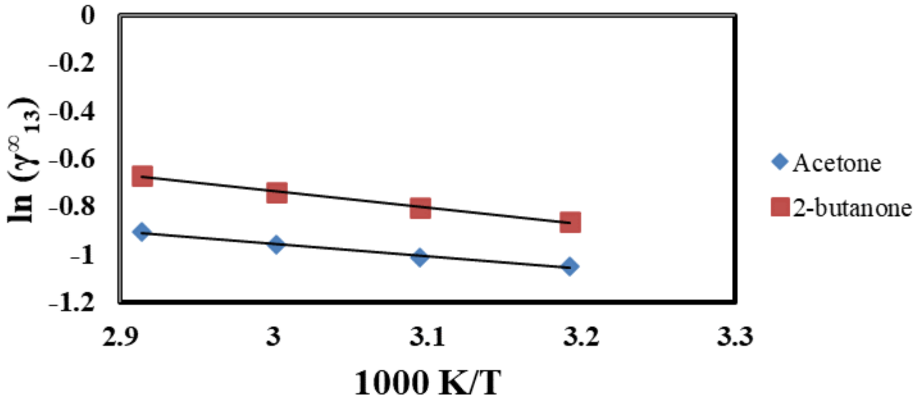


Figure 5.6: Plot of ln γ_{13}^{∞} versus 1/T for ketones in ionic liquid [$P_{6,6,6,14}$] [DCA] at T = (313.15 – 343.15) K.

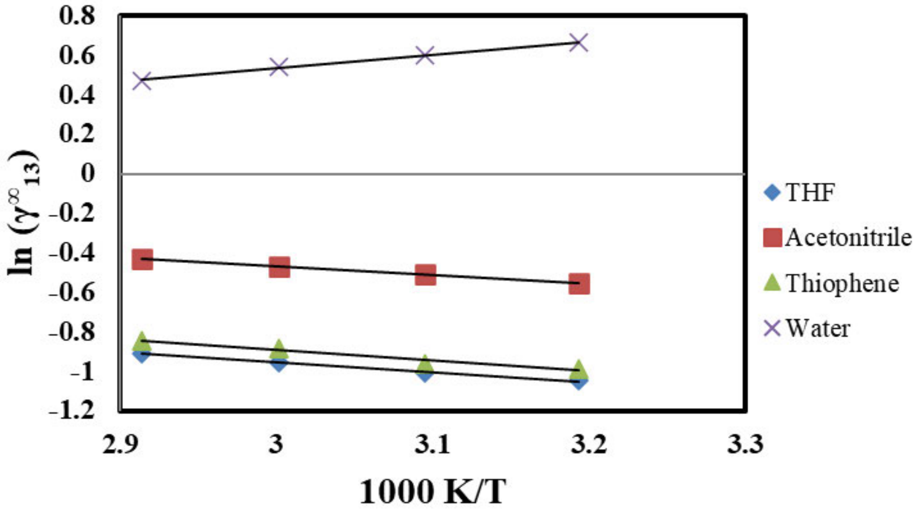


Figure 5.7: Plot of ln γ_{13}^{∞} versus 1/T for THF, acetonitrile, thiophene and water in ionic liquid [$P_{6,6,6,14}$] [DCA] at T = (313.15 – 343.15) K.

Table 5.4

Average activity coefficients at infinite dilution for the solutes in the ionic liquid [$N_{8\,8\,8\,1}$] [Cl] at four different temperatures: for the standard state of solutes hypothetical liquid at zero pressure. [a]

Solute	Average γ_{13}^{∞} values			
	T = 313.15 K	T = 323.15 K	T = 333.15 K	T = 343.15 K
2,2-dimethylbutane	1.455	1.544	1.609	1.713
Pentane	1.288	1.365	1.485	1.579
Hexane	1.504	1.580	1.686	1.826
Heptane	1.699	1.839	1.963	2.084
n-Nonane	2.126	2.348	2.557	2.755
n-Decane	2.389	2.627	2.884	3.156
1-Pentene	1.083	1.151	1.236	1.347
1-Hexene	1.257	1.311	1.404	1.505
1-Heptene	1.448	1.535	1.637	1.733
1-Nonene	1.819	1.934	2.094	2.285
1-Decene	2.019	2.163	2.346	2.517
Cyclohexene	0.9316	0.9966	1.072	1.167
Cyclohexane	1.006	1.096	1.213	1.313
Cyclooctane	1.140	1.233	1.332	1.426
1-Pentyne	0.3667	0.4266	0.4963	0.5795
1-Hexyne	0.3975	0.4524	0.5344	0.6190
1-Heptyne	0.4277	0.4929	0.5694	0.6646
Benzene	0.4396	0.4767	0.5262	0.5845
Toluene	0.5674	0.6086	0.6577	0.7103
Ethylbenzene	0.6678	0.7378	0.8109	0.8788
m-Xylene	0.7445	0.8195	0.8824	0.9627
p-Xylene	0.7279	0.7844	0.8526	0.9326
o-Xylene	0.6548	0.7152	0.7764	0.8537
Methanol	0.3015	0.3276	0.3524	0.3785
Ethanol	0.4234	0.4382	0.4616	0.4814
Propan-1-ol	0.5336	0.5583	0.5979	0.6372
Butan-1-ol	0.6877	0.7140	0.7530	0.7906
THF	0.5874	0.6329	0.6753	0.7133
Acetonitrile	1.245	1.0815	0.9842	0.8975
Thiophene	0.3106	0.3326	0.3734	0.4208
Acetone	0.7912	0.7647	0.7463	0.7313
2-butanone	0.8539	0.8106	0.7825	0.7609
Water	0.2690	0.3038	0.3347	0.3714

[a] Standard uncertainties u are u (γ_{13}^{∞}) = 5 %, u(T) = 0.02 K and u(P) = 2 kPa.

Table 5.5

Limiting partial molar enthalpies $\Delta H_1^{\mathrm{E},\infty}$, Gibbs energies $\Delta G_1^{\mathrm{E},\infty}$ and entropies $T_{\mathrm{ref}}\,\Delta S_1^{\mathrm{E},\infty}$ for solutes in the ionic liquid [$N_{8\,8\,8\,1}$] [Cl] at the reference temperature T_{ref} = 323.15 K.

Solute	$\Delta H_1^{\mathrm{E},\infty}$ (kJ · mol^{-1})	$\Delta G_1^{\mathrm{E},\infty}$ (kJ · mol^{-1})	$T_{\mathrm{ref}}\,\Delta S_1^{\mathrm{E},\infty}$(kJ · mol^{-1})
2,2-dimethylbutane	-4.73	1.16	-5.88
Pentane	-6.27	0.825	-7.09
Hexane	-5.57	1.23	-6.80
Heptane	-6.15	1.62	-7.77
n-Nonane	-7.72	2.28	-10.0
n-Decane	-8.34	2.58	-10.9
1-Pentene	-6.29	0.369	-6.66
1-Hexene	-5.48	0.734	-6.21
1-Heptene	-5.44	1.15	-6.59
1-Nonene	-6.84	1.77	-8.61
1-Decene	-6.65	2.07	-8.72
Cyclohexene	-6.37	-0.011	-6.36
Cyclohexane	-8.07	0.228	-8.29
Cyclooctane	-6.49	0.560	-7.05
1-Pentyne	-13.6	-2.29	-11.3
1-Hexyne	-13.4	-2.13	-11.3
1-Heptyne	-13.1	-1.91	-11.2
Benzene	-8.54	-1.99	-6.55
Toluene	-6.72	-1.34	-5.38
Ethylbenzene	-8.20	-0.818	-7.38
m-Xylene	-7.42	-0.537	-6.88
p-Xylene	-7.57	-0.652	-6.92
o-Xylene	-7.85	-0.900	-6.95
Methanol	-6.76	-3.00	-3.76
Ethanol	-3.92	-2.216	-1.70
Propan-1-ol	-5.39	-1.57	-3.82
Butan-1-ol	-4.21	-0.907	-3.30
THF	-5.79	-1.232	-4.56
Acetonitrile	9.66	0.210	9.45
Thiophene	-9.14	-2.97	-6.17
Acetone	2.34	-0.723	3.06
2-butanone	3.42	-0.566	3.98
Water	-9.56	-3.21	-6.35

[a] Standard uncertainties: u are u(γ_{13}^{∞}) = 5 %, u(T) = 0.02 K and u(P) = 2 kPa.

Table 5.6

Selectivities (S_{ij}^{∞}) and capacities (K_j^{∞}) at infinite dilution for [$N_{8\ 8\ 8\ 1}$] [Cl] for various separation problems at T = 323.15 K.

Separation mixtures	S_{ij}^{∞}	K_j^{∞}
Heptane/benzene	4.27	2.81
Heptane/thiophene	5.51	3.02
Hexane/toluene	2.60	1.62
Hexane/hexene	1.20	0.77
Cyclohexane/cyclohexene	1.09	1.00

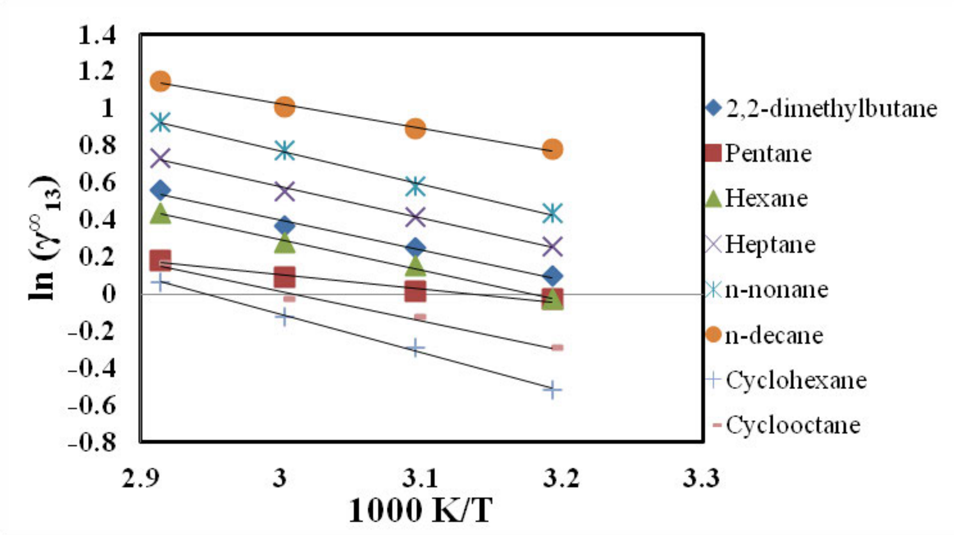


Figure 5.8: Plot of ln γ_{13}^{∞} against 1/T for the alkanes in the ionic liquid [$N_{8\,8\,8\,1}$] [Cl] at T = (313.15 – 343.15) K.

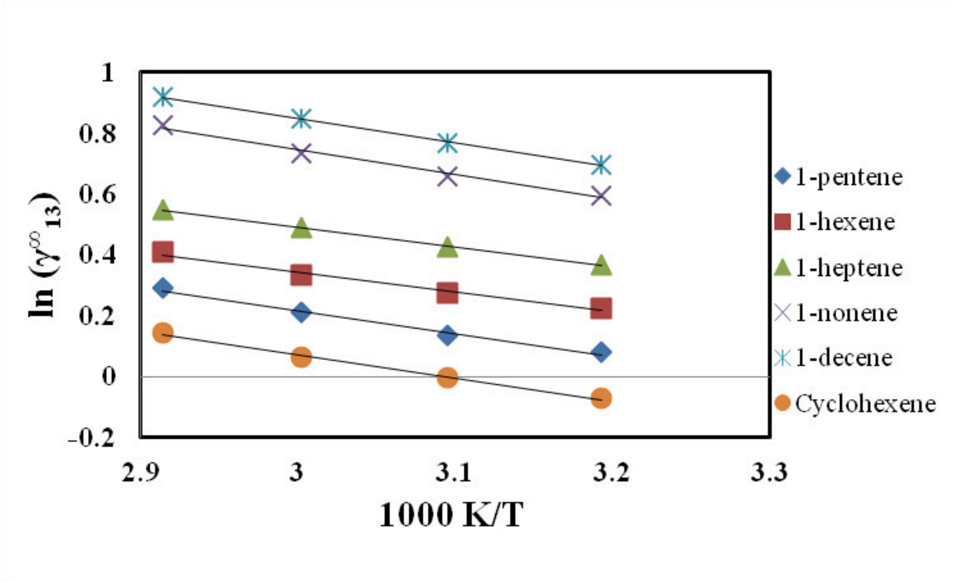


Figure 5.9: Plot of ln γ_{13}^{∞} versus 1/T for alkenes in the ionic liquid [$N_{8\,8\,8\,1}$] [Cl] at T = (313.15 – 343.15) K.

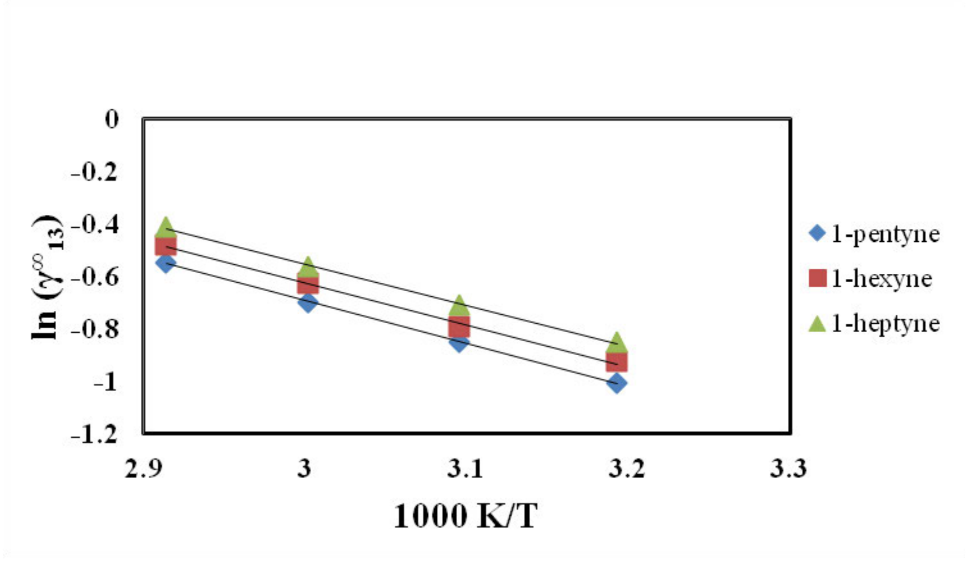


Figure 5.10: Plot of ln γ_{13}^{∞} versus 1/T for alkynes in the ionic liquid [$N_{8\,8\,8\,1}$] [Cl] at T = (313.15 – 343.15) K.

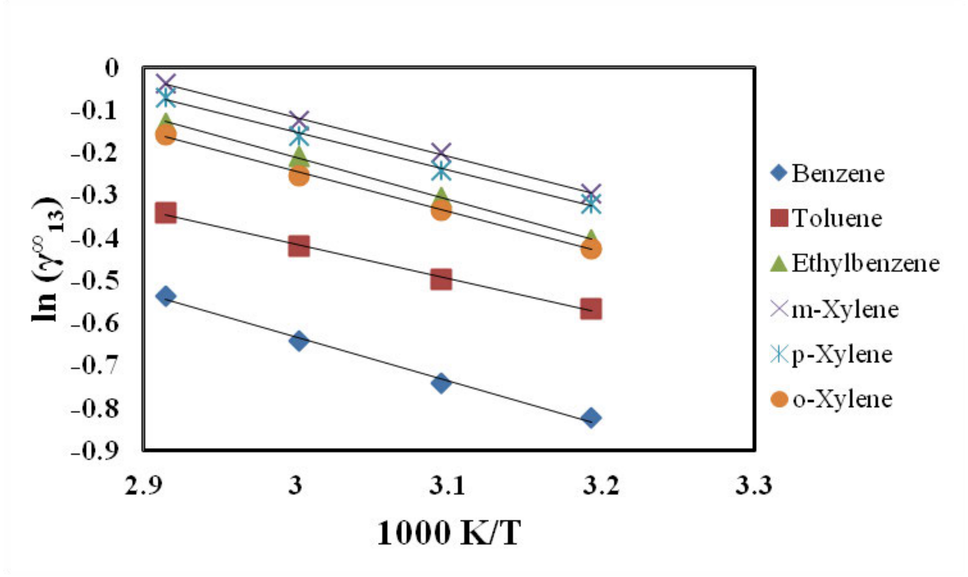


Figure 5.11: Plot of ln γ_{13}^{∞} versus 1/T for aromatic hydrocarbons in the ionic liquid [$N_{8\,8\,8\,1}$] [Cl] at T = (313.15 – 343.15) K.

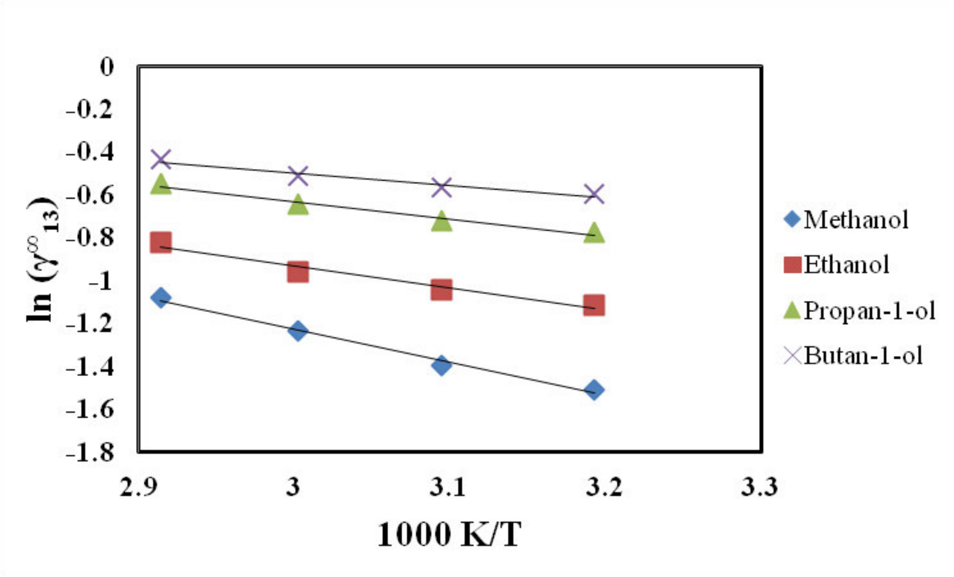


Figure 5.12: Plot of ln γ_{13}^{∞} versus 1/T for alcohols in the ionic liquid [$N_{8\,8\,8\,1}$] [Cl] at T = (313.15 – 343.15) K.

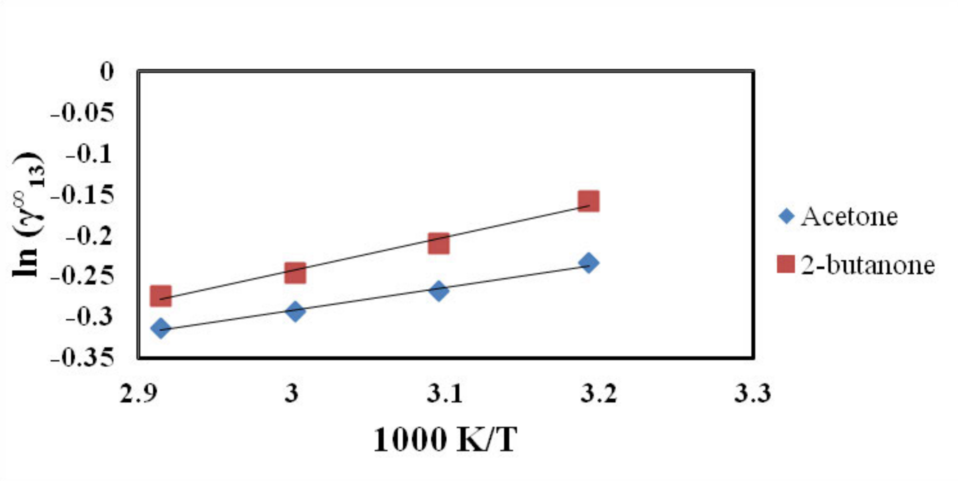


Figure 5.13: Plot of ln γ_{13}^{∞} versus 1/T for ketones in the ionic liquid [$N_{8\,8\,8\,1}$] [Cl] at T = (313.15 – 343.15) K.

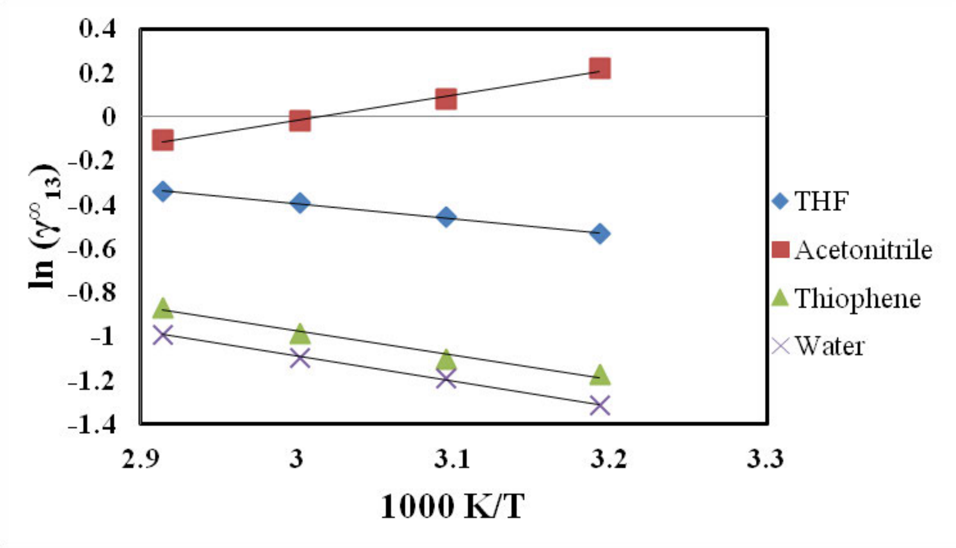


Figure 5.14: Plot of ln γ_{13}^{∞} versus 1/T for THF, acetonitrile, thiophene and water in the ionic liquid [$N_{8\,8\,8\,1}$] [Cl] at T = (313.15 – 343.15) K.

Table 5.7

Average activity coefficients at infinite dilution for the solutes in the ionic liquid [(OH)$_2$ C$_3$MPyr] [Cl] at four different temperatures: for the standard state of solutes hypothetical liquid at zero pressure. [a]

Solute	Average γ_{13}^{∞} values			
	T = 313.15 K	T = 323.15 K	T = 333.15 K	T = 343.15 K
2,2-dimethylbutane	15.31	13.80	12.14	10.74
Pentane	11.55	10.83	9.440	8.167
Hexane	18.09	17.12	14.69	12.98
Heptane	26.39	23.64	22.09	19.65
n-Nonane	47.80	43.90	41.17	38.94
n-Decane	66.64	61.93	56.80	54.57
1-Pentene	7.912	7.465	7.508	7.472
1-Hexene	10.12	9.823	9.859	9.709
1-Heptene	14.20	14.08	13.35	12.74
1-Nonene	24.58	23.39	22.31	22.19
1-Decene	29.93	28.89	27.56	27.12
Cyclohexene	4.227	4.154	4.110	3.986
Cyclohexane	4.501	4.311	4.170	3.987
Cyclooctane	7.123	6.494	6.019	5.638
1-Pentyne	2.566	2.700	2.870	3.101
1-Hexyne	3.452	3.620	3.772	3.979
1-Heptyne	4.035	4.217	4.444	4.806
Benzene	1.510	1.615	1.737	1.853
Toluene	1.893	2.004	2.111	2.279
Ethylbenzene	2.875	3.008	3.192	3.363
m-Xylene	3.321	3.552	3.761	3.942
p-Xylene	3.160	3.357	3.550	3.733
o-Xylene	2.535	2.673	2.851	3.003
Methanol	0.1773	0.2369	0.3197	0.4434
Ethanol	0.2094	0.2814	0.3819	0.5181
Propan-1-ol	0.3356	0.4295	0.5347	0.6720
Butan-1-ol	0.4566	0.5393	0.6496	0.7923
THF	1.053	1.220	1.4374	1.659
Acetonitrile	2.630	2.845	3.038	3.207
Thiophene	0.8114	0.9485	1.097	1.256
Acetone	0.6769	0.8843	1.115	1.430
2-butanone	1.129	1.352	1.636	2.016
Water	0.9320	0.8392	0.7629	0.6989

[a] Standard uncertainties: u are u(γ_{13}^{∞}) = 5 %, u(T) = 0.02 K and u(P) = 2 kPa.

Table 5.8

Limiting partial molar enthalpies $\Delta H_1^{E,\infty}$, Gibbs energies $\Delta G_1^{E,\infty}$ and entropies $T_{ref}\,\Delta S_1^{E,\infty}$ for solutes in the investigated ionic liquid [(OH)$_2$ C$_3$MPyr] [Cl] at the reference temperature T_{ref} = 323.15 K.

Solute	$\Delta H_1^{E,\infty}$ (kJ · mol^{-1})	$\Delta G_1^{E,\infty}$ (kJ · mol^{-1})	$T_{ref}\,\Delta S_1^{E,\infty}$(kJ · mol^{-1})
2,2-dimethylbutane	10.2	7.05	3.18
Pentane	10.5	6.40	4.07
Hexane	10.6	7.63	3.00
Heptane	8.51	8.50	0.0126
n-Nonane	6.08	10.2	-4.08
n-Decane	6.15	11.1	-4.94
1-Pentene	1.50	5.40	-3.90
1-Hexene	1.08	6.14	-5.06
1-Heptene	3.38	7.11	-3.73
1-Nonene	3.17	8.47	-5.30
1-Decene	3.08	9.04	-5.96
Cyclohexene	1.58	3.83	-2.25
Cyclohexane	3.54	3.93	-0.396
Cyclooctane	6.96	5.03	1.94
1-Pentyne	-5.61	2.67	-8.28
1-Hexyne	-4.18	3.46	-7.63
1-Heptyne	-5.15	3.87	-9.01
Benzene	-6.14	1.29	-7.43
Toluene	-5.43	1.87	-7.30
Ethylbenzene	-4.73	2.96	-7.69
m-Xylene	-5.11	3.41	-8.52
p-Xylene	-4.97	3.25	-8.22
o-Xylene	-5.12	2.64	-7.76
Methanol	-27.3	-3.88	-23.4
Ethanol	-27.1	-3.41	-23.7
Propan-1-ol	-19.0	-2.28	-16.7
Butan-1-ol	-16.4	-1.66	-14.7
THF	-13.7	0.539	-14.2
Acetonitrile	-5.91	2.81	-8.72
Thiophene	-13.0	-0.147	-12.9
Acetone	-22.2	-0.330	-21.8
2-butanone	-17.2	0.813	-18.0
Water	8.61	-0.475	9.08

[a] Standard uncertainties: u are u(γ_{13}^{∞}) = 5 %, u(T) = 0.02 K and u(P) = 2 kPa.

Table 5.9

Selectivities (S_{ij}^{∞}) and capacities (K_{j}^{∞}) at infinite dilution for $[(OH)_2\ C_3MPyr]\ [Cl]$ for various separation problems at 328.15 K.

Ionic Liquid	S_{ij}^{∞}			K_{j}^{∞}		
	heptane/ benzene	heptane/ thiophene	heptane/1-heptyne	benzene	thiophene	1-heptyne
$[(OH)_2\ C_3MPyr]\ [Cl^-]$	14.7	24.9	5.61	0.621	1.05	0.233
[BMPYR][SCN][a]	28.4	48.8	6.26	0.524	0.905	0.127
[BMPYR][TCM][b]	30.6	43.6	7.66	0.965	1.37	0.246
$[BMPYR][\ CF_3SO_3]$[c]	36.6	50.2	9.91	0.688	0.938	0.188
[BMPYR][DCA][d]	53.3	88.3	12.0	0.713	1.18	0.173
$[BMPYR][B(CN)_4]$[e]	26.3	32.4	6.14	1.23	1.51	0.295
$[B^4MPY][DCA]$[f]	50.6	80.5	11.0	0.723	1.15	0.163

Interpolated values (This work)

([a]Domańska and Królikowska, 2010, [b]Domańska and Lukoshko, 2013, [c]Domańska et al., 2009, [d]Durski et al., 2018, [e]Domańska et al., 2011, [f]Królikowski and Królikowska, 2014)

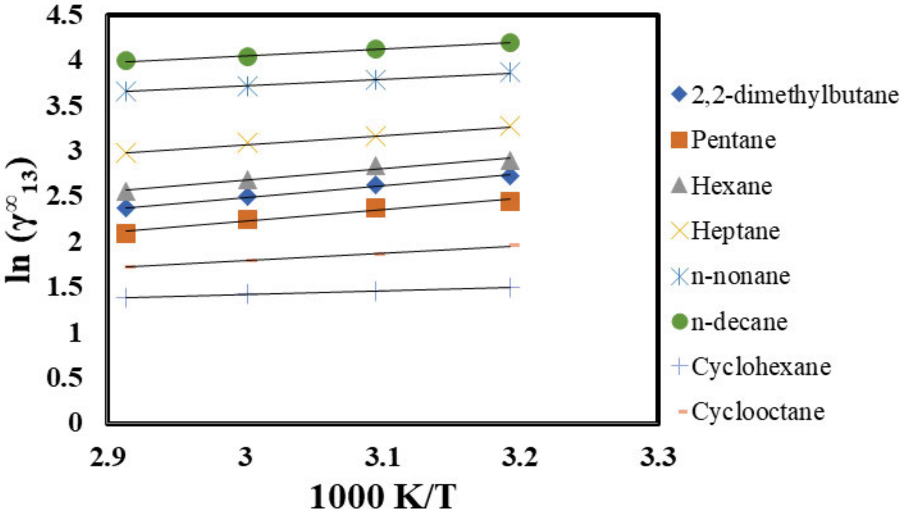


Figure 5.15: Plot of ln γ_{13}^{∞} against 1/T for the alkanes in the ionic liquid [(OH)$_2$ C$_3$MPyr] [Cl] at T = (313.15 – 343.15) K.

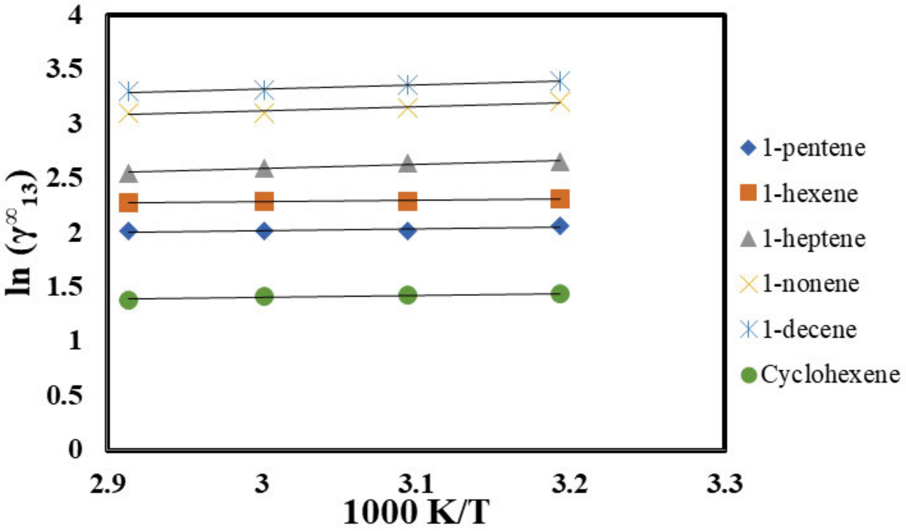


Figure 5.16: Plot of ln γ_{13}^{∞} against 1/T for the alkenes in the ionic liquid [(OH)$_2$ C$_3$MPyr] [Cl] at T = (313.15 – 343.15) K.

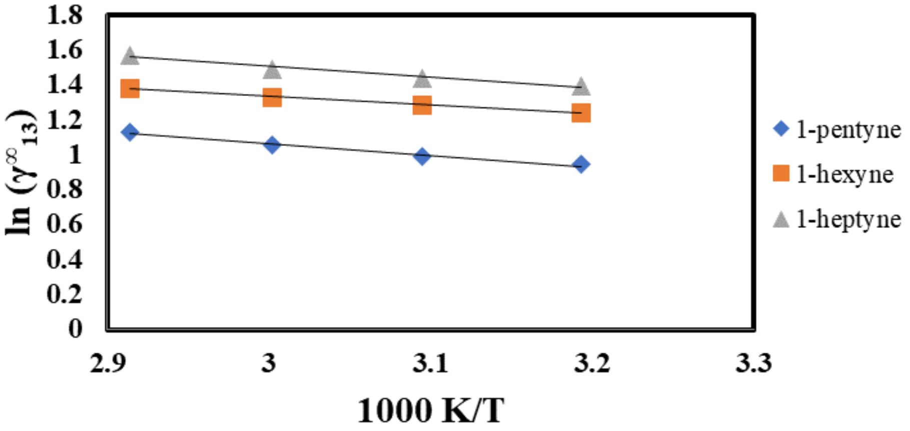


Figure 5.17: Plot of ln γ_{13}^{∞} versus 1/T for alkynes in the ionic liquid [$(OH)_2$ C_3MPyr] [Cl] at T = (313.15 – 343.15) K.

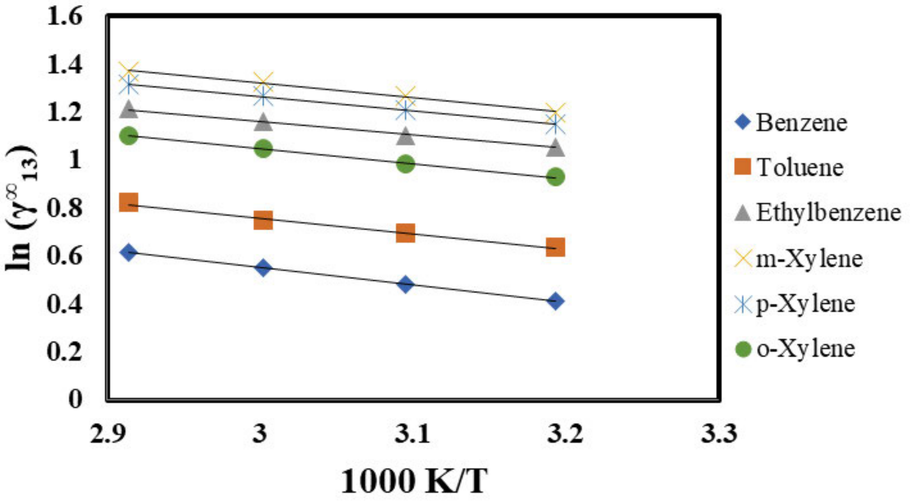


Figure 5.18: Plot of ln γ_{13}^{∞} versus 1/T for aromatic hydrocarbons in the ionic liquid [$(OH)_2$ C_3MPyr] [Cl] at T = (313.15 – 343.15) K.

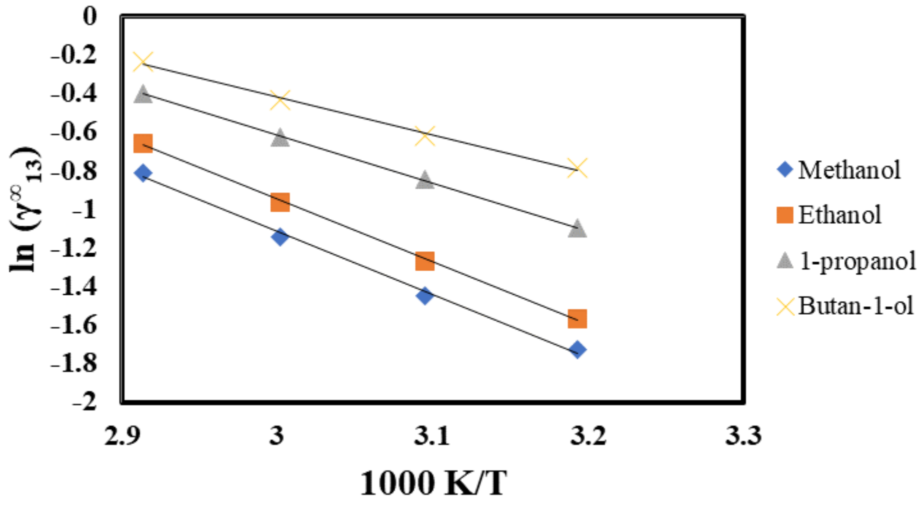


Figure 5.19: Plot of ln γ_{13}^{∞} versus 1/T for alcohols in the ionic liquid [(OH)$_2$ C$_3$MPyr] [Cl] at T = (313.15 – 343.15) K.

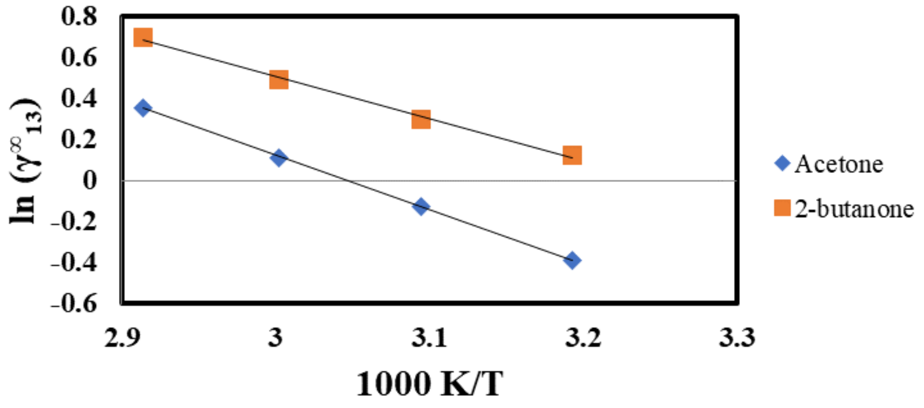


Figure 5.20: Plot of ln γ_{13}^{∞} versus 1/T for ketones in the ionic liquid [(OH)$_2$ C$_3$MPyr] [Cl] at T = (313.15 – 343.15) K.

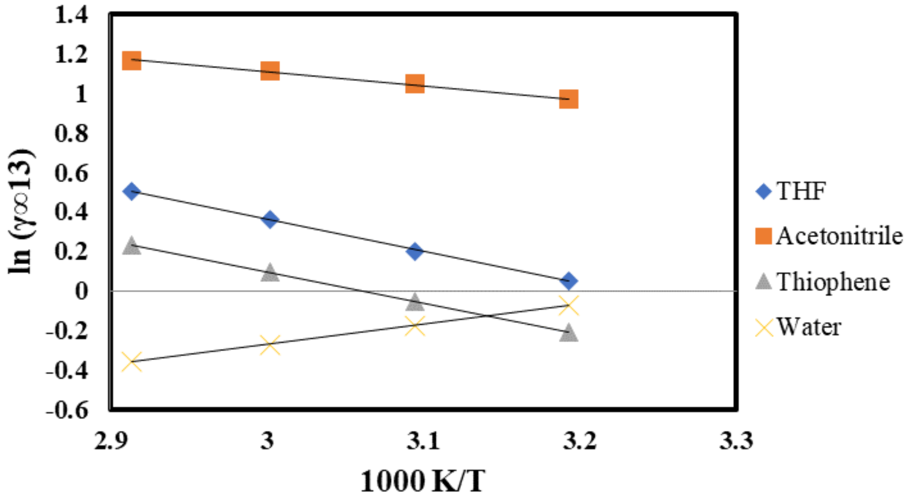


Figure 5.21: Plot of ln γ_{13}^{∞} versus 1/T for THF, acetonitrile, thiophene and water in the ionic liquid $[(OH)_2C_3MPyr]$ [Cl] at T = (313.15 – 343.15) K.

Table 5.10

Average activity coefficients at infinite dilution for the solutes in the ionic liquid [MMIM] [DMP] at four different temperatures: for the standard state of solutes hypothetical liquid at zero pressure. [a]

Solute	Average γ_{13}^{∞} values			
	T = 313.15 K	T = 323.15 K	T = 333.15 K	T = 343.15 K
2,2-dimethylbutane	141.6	114.2	104.2	92.62
Pentane	90.70	73.15	66.42	60.70
Hexane	239.7	194.1	170.4	151.3
Heptane	574.2	470.6	396.7	362.2
n-Nonane	2504	2050	1810	1625
n-Decane	4711	3697	3280	3115
1-Pentene	59.34	53.69	45.66	43.42
1-Hexene	150.4	133.9	112.2	107.3
1-Heptene	372.4	311.6	252.6	238.0
1-Nonene	1305	1183	1054	1016
1-Decene	2058	1935	1825	1636
Cyclohexene	112.8	97.96	86.02	82.22
Cyclohexane	197.8	161.6	134.7	120.5
Cyclooctane	652.1	593.8	535.2	466.1
1-Pentyne	15.94	15.55	15.10	15.56
1-Hexyne	30.75	29.75	28.92	28.66
1-Heptyne	48.55	48.17	47.22	47.43
Benzene	12.01	12.44	13.56	15.10
Toluene	23.22	25.82	27.45	31.40
Ethylbenzene	41.10	48.58	52.06	60.83
m-Xylene	45.56	52.70	56.25	64.54
p-Xylene	43.61	49.70	55.97	60.47
o-Xylene	35.92	39.73	45.87	54.47
THF	12.83	12.89	13.12	13.52
Acetonitrile	4.654	4.635	4.429	4.417
Thiophene	4.723	4.918	5.425	6.303
Acetone	6.437	6.605	6.583	7.409
2-butanone	11.34	11.39	11.51	12.92
	T = 343.15 K	T = 353.15 K	T = 363.15 K	T = 373.15 K
Methanol	0.1851	0.1914	0.2007	0.2088
Ethanol	--	0.2598	0.2739	0.2883
Propan-1-ol		0.2895	0.3083	0.3275
Butan-1-ol	--	--	0.5089	0.5332
Water		0.4402	0.4622	0.4918

[a] Standard uncertainties: u are u(γ_{13}^{∞}) = 5 %, u(T) = 0.02 K and u(P) = 2 kPa.

Table 5.11

Limiting partial molar enthalpies $\Delta H_1^{\mathrm{E},\infty}$, Gibbs energies $\Delta G_1^{\mathrm{E},\infty}$ and entropies $T_{\mathrm{ref}}\,\Delta S_1^{\mathrm{E},\infty}$ for solutes in the investigated ionic liquid [MMIM] [DMP] at the reference temperature T_{ref} = 323.15 K.

Solute	$\Delta H_1^{\mathrm{E},\infty}$ (kJ · mol^{-1})	$\Delta G_1^{\mathrm{E},\infty}$ (kJ · mol^{-1})	$T_{\mathrm{ref}}\,\Delta S_1^{\mathrm{E},\infty}$(kJ · mol^{-1})
2,2-dimethylbutane	12.2	12.7	-12.7
Pentane	11.7	11.5	0.165
Hexane	13.6	14.2	-0.612
Heptane	13.9	16.5	-2.60
n-Nonane	12.7	20.5	-7.75
n-Decane	12.23	22.1	-9.82
1-Pentene	9.86	10.7	-0.859
1-Hexene	10.7	13.2	-2.49
1-Heptene	13.9	15.4	-1.50
1-Nonene	7.76	19.0	-11.3
1-Decene	6.66	20.3	-13.7
Cyclohexene	13.8	12.3	1.49
Cyclohexane	14.9	13.7	1.31
Cyclooctane	9.90	17.2	-7.26
1-Pentyne	0.519	7.37	-6.86
1-Hexyne	1.81	9.12	-7.31
1-Heptyne	0.819	10.4	-9.60
Benzene	-6.89	6.77	-13.7
Toluene	-8.63	8.74	-17.4
Ethylbenzene	-11.1	10.4	-21.6
m-Xylene	-9.93	10.7	-20.6
p-Xylene	-9.85	10.5	-20.3
o-Xylene	-12.4	9.89	-22.3
Methanol	-4.13	-4.44	0.329
Ethanol	-5.92	-3.93	-2.00
Propan-1-ol	-6.89	-3.56	-3.33
Butan-1-ol	-5.73	-2.05	-3.69
THF	-1.56	6.87	-8.42
Acetonitrile	1.84	4.13	-2.27
Thiophene	-8.57	4.28	-12.8
Acetone	-3.72	5.07	-8.79
2-butanone	-3.53	6.55	-10.1
Water	-6.05	-2.33	-3.72

[a] Standard uncertainties: u are u(γ_{13}^{∞}) = 5 %, u(T) = 0.02 K and u(P) = 2 kPa.

Table 5.12

Selectivities (S_{ij}^{∞}) and capacities (K_j^{∞}) at infinite dilution for [MMIM] [DMP] for different separation problems at T = 328.15 K.

Ionic Liquid	S_{ij}^{∞}			K_j^{∞}		
	heptane/ benzene	heptane/ thiophene	heptane/1-heptyne	benzene	thiophene	1-heptyne
[MMIM] [DMP]	37.8	95.7	9.70	0.083	0.200	0.0257
[EMIM] [DCA][a]	66.2	109	11.8	0.395	0.644	0.0783
[BMIM] [DCA][b]	44.7	71.5	10.1	0.519	0.828	0.1240
[AMIM] [DCA][c]	64.1	106	11.1	0.322	0.534	0.0573
[BzMIM] [DCA][d]	59.0	100	11.2	0.410	0.699	0.0858
[BMPYR][B(CN)$_4$][e]	26.3	32.4	6.14	1.23	1.51	0.2926
[B^{4}MPY][DCA][f]	50.6	80.5	11.0	0.727	1.15	0.1682

([a]Mutelet et al., 2010, [b]Domańska et al., 2016, [c]Wlazło et al., 2016, [d]Design Institute for Physical Properties, [e]Domańska et al., 2011, [f]Krolikowski and Krolikowska 2014)

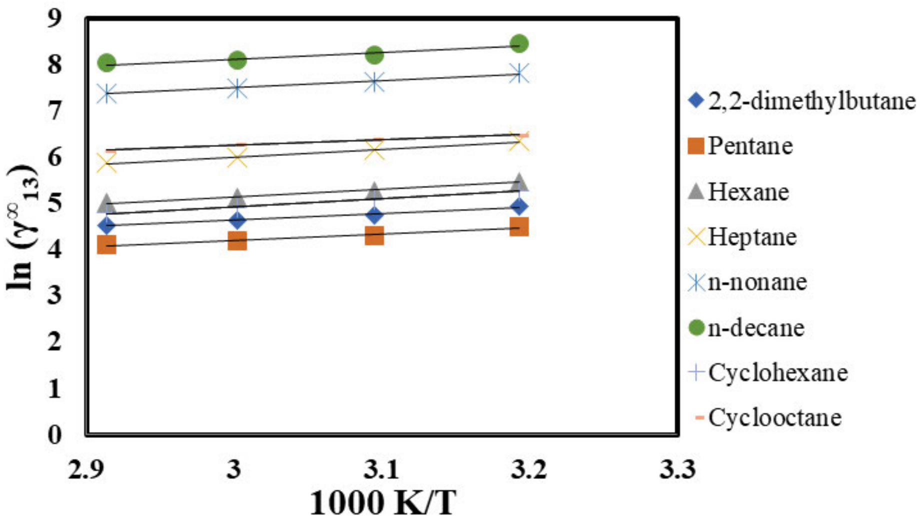


Figure 5.22: Plot of ln γ_{13}^{∞} versus 1/T for alkanes in the ionic liquid [MMIM] [DMP] at T = (313.15 – 343.15) K.

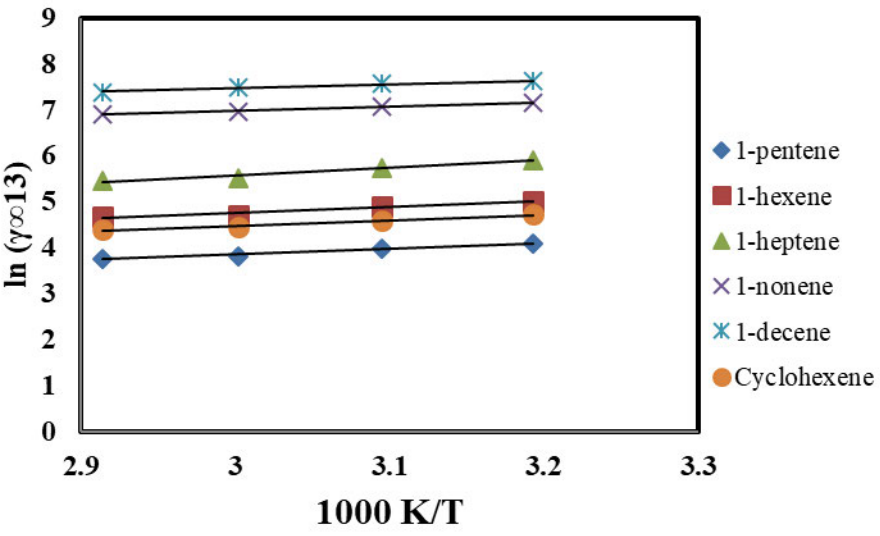


Figure 5.23: Plot of ln γ_{13}^{∞} versus 1/T for alkenes in the ionic liquid [MMIM] [DMP] at T = (313.15 – 343.15) K.

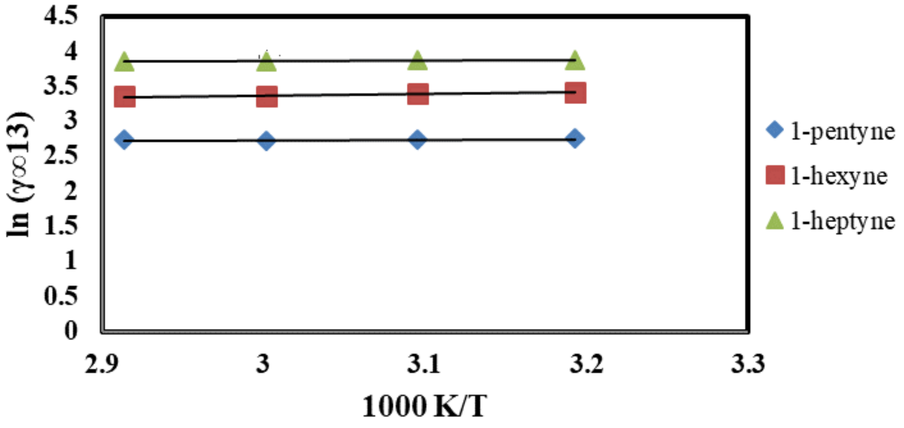


Figure 5.24: Plot of ln γ_{13}^{∞} versus 1/T for alkynes in the ionic liquid [MMIM] [DMP] at T = (313.15 – 343.15) K.

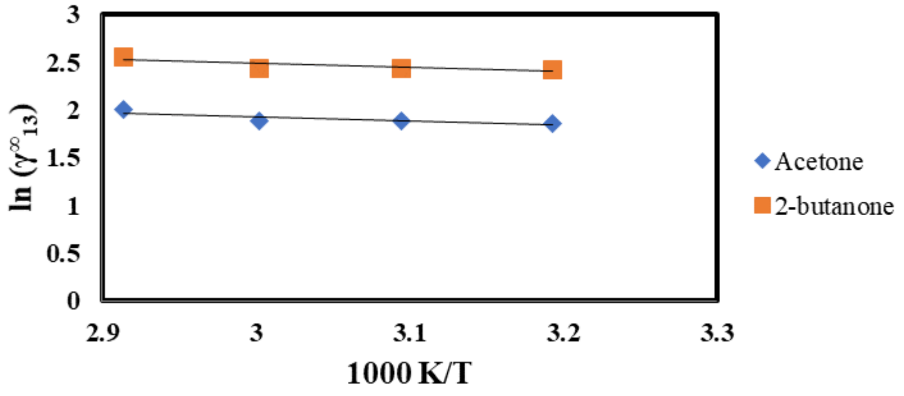


Figure 5.25: Plot of ln γ_{13}^{∞} versus 1/T for ketones in the ionic liquid [MMIM] [DMP] at T = (313.15 – 343.15) K.

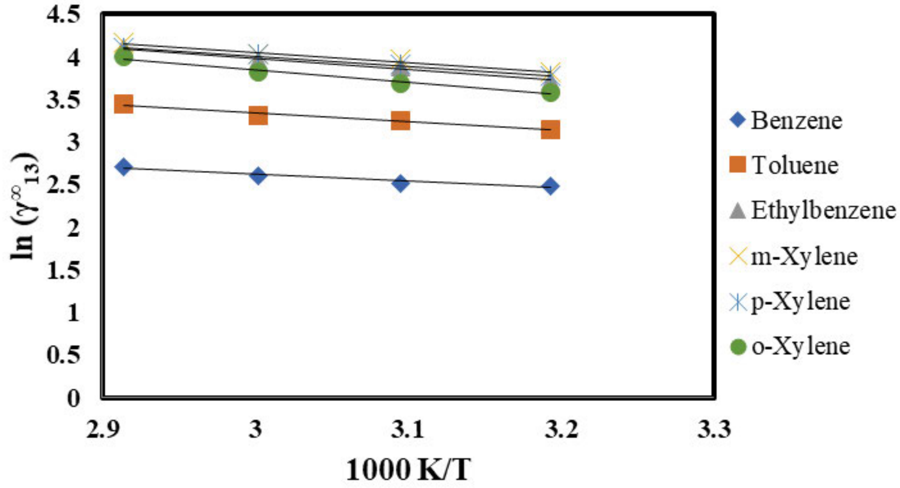


Figure 5.26: Plot of ln γ_{13}^{∞} versus 1/T for aromatic hydrocarbons in the ionic liquid [MMIM] [DMP] at T = (313.15 – 343.15) K.

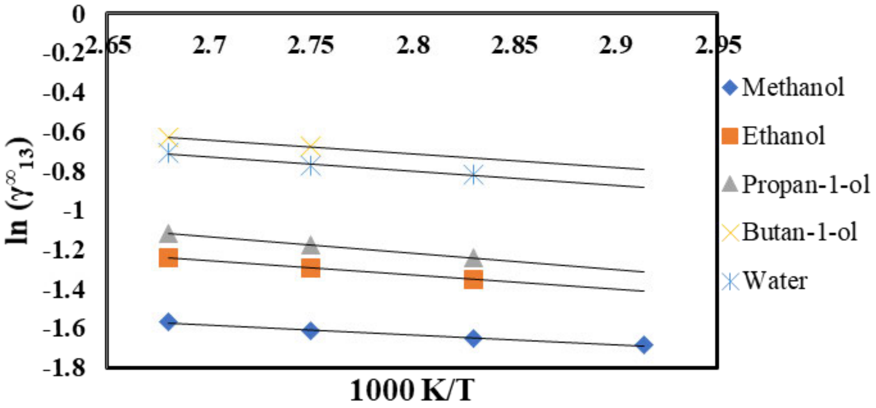


Figure 5.27: Plot of ln γ_{13}^{∞} versus 1/T for water and alcohols in the ionic liquid [MMIM] [DMP] at T = (313.15 – 343.15) K.

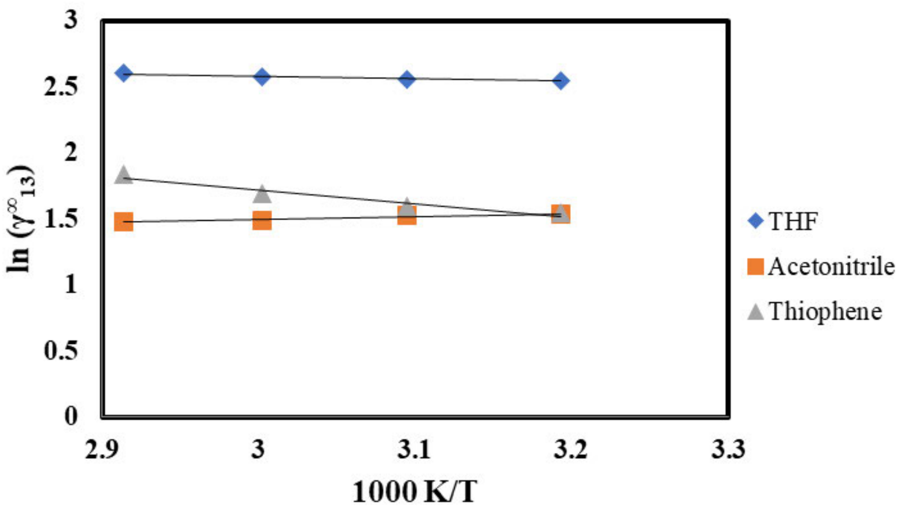


Figure 5.28: Plot of ln γ_{13}^{∞} versus 1/T for THF, acetonitrile and thiophene in the ionic liquid [MMIM] [DMP] at T = (313.15 – 343.15) K.

Table 5.13

Density and speed of sound for DES (1-butyl-3-methylimidazolium chloride + glycerol) at 2:1 mole ratio, measured at T = (313.15 – 343.15) K at atmospheric pressure.

	DES				
	T = 293.15 K	T = 298.15 K	T = 303.15 K	T = 308.15 K	T = 313.15 K
ρ/g · cm^{-3}	1.1709	1.1678	1.1647	1.1616	1.1585
u/m · s^{-1}	1851.3	1838.8	1826.5	1814.4	1802.4

The standard uncertainties u are u(T) = ±0.02 K, u(p) = ±0.04 MPa, u(ρ) = ±2.10^{-5}g.cm^{-3} and u(u) = ±0.8 m. s^{-1}.

Table 5.14

Average activity coefficients at infinite dilution for the solutes in the DES at four different temperatures: for the standard state of solutes hypothetical liquid at zero pressure. [a]

Solutes	Average γ_{13}^{∞} values			
	T = 313.15 K	T = 323.15 K	T = 333.15 K	T = 343.15 K
2,2-dimethylbutane	99.50	81.89	68.97	56.00
Pentane	64.19	53.11	43.82	37.21
Hexane	175.9	137.9	112.3	95.03
Heptane	431.0	341.3	271.1	222.5
n-Nonane	1444	1315	1078	946.5
n-Decane	2059	1935	1737	1558
1-Pentene	48.04	39.69	31.59	28.60
1-Hexene	124.6	103.7	83.72	66.77
1-Heptene	296.2	238.6	197.9	167.3
1-Nonene	1103	985.9	826.1	697.7
1-Decene	1486	1432	1273	1146
Cyclohexene	107.2	94.32	78.56	59.40
Cyclohexane	165.1	135.6	111.8	93.66
Cyclooctane	559.5	495.4	426.4	359.1
1-Pentyne	29.12	26.40	24.13	21.68
1-Hexyne	63.65	58.12	51.49	44.94
1-Heptyne	110.3	105.4	96.01	88.17
Benzene	20.06	20.19	19.13	18.28
Toluene	43.75	42.97	40.05	38.46
Ethylbenzene	88.18	85.69	79.05	75.03
m-Xylene	94.34	89.13	84.56	79.29
p-Xylene	93.27	88.64	84.37	78.85
o-Xylene	78.11	73.81	71.17	66.98
Methanol	1.184	1.127	1.073	1.008
Ethanol	1.589	1.464	1.379	1.339
Propan-1-ol	1.956	1.750	1.630	1.543
Butan-1-ol	2.803	2.519	2.224	2.039
THF	6.676	6.685	6.933	7.048
Acetonitrile	7.293	6.829	6.576	6.053
Thiophene	11.43	11.43	11.77	11.08
Acetone	4.940	4.842	4.705	4.628
2-butanone	9.353	9.138	8.958	8.653
Water	1.719	1.597	1.423	1.365

[a] Standard uncertainties: u are u(γ_{13}^{∞}) = 5 %, u(T) = 0.02 K and u(P) = 2 kPa.

Table 5.15

Limiting partial molar enthalpies $\Delta H_1^{\mathrm{E},\infty}$, Gibbs energies $\Delta G_1^{\mathrm{E},\infty}$ and entropies $T_{\mathrm{ref}}\,\Delta S_1^{\mathrm{E},\infty}$ for solutes in the investigated DES at the reference temperature T_{ref} = 323.15 K.

Solutes	$\Delta H_1^{\mathrm{E},\infty}$ (kJ · mol^{-1})	$\Delta G_1^{\mathrm{E},\infty}$ (kJ · mol^{-1})	$T_{\mathrm{ref}}\,\Delta S_1^{\mathrm{E},\infty}$(kJ · mol^{-1})
2,2-dimethylbutane	16.9	11.8	5.08
Pentane	16.3	10.7	5.65
Hexane	16.6	13.2	3.33
Heptane	19.8	15.7	4.13
n-Nonane	13.1	19.3	-6.20
n-Decane	8.41	20.3	-11.9
1-Pentene	15.9	9.89	6.06
1-Hexene	18.6	12.5	6.13
1-Heptene	17.0	14.7	2.30
1-Nonene	13.8	18.5	-4.68
1-Decene	7.97	19.5	-11.6
Cyclohexene	17.4	12.2	5.18
Cyclohexane	16.9	13.2	3.74
Cyclooctane	13.2	16.7	-3.47
1-Pentyne	8.67	8.79	-0.129
1-Hexyne	10.4	10.9	-0.537
1-Heptyne	6.82	12.5	-5.69
Benzene	2.93	8.07	-5.15
Toluene	4.07	10.2	-6.03
Ethylbenzene	5.21	11.9	-6.75
m-Xylene	5.12	12.1	-6.94
p-Xylene	4.93	12.1	-7.12
o-Xylene	4.44	11.6	-7.11
Methanol	4.83	0.30	4.53
Ethanol	5.27	1.02	4.24
Propan-1-ol	6.99	1.51	5.48
Butan-1-ol	9.72	2.47	7.25
THF	-1.79	5.10	-6.89
Acetonitrile	5.31	5.16	0.159
Thiophene	0.53	6.54	-6.02
Acetone	1.56	4.24	-2.68
2-butanone	2.22	5.94	-3.72
Water	7.15	1.25	5.90

[a] Standard uncertainties: u are u(γ_{13}^{∞}) = 5 %, u(T) = 0.02 K and u(P) = 2 kPa.

Table 5.16

Selectivities (S_{ij}^{∞}) and capacities (k_j^{∞}) at infinite dilution for investigated DES for various separation problems at 313.15 K.

Solvent	S_{ij}^{∞}				k_j^{∞}	
	hexane/ benzene	cyclohexane/ benzene	Acetone /ethanol	cyclohexane/ ethanol	benzene	ethanol
[BMIM][Cl]+ [Gly] 2:1	8.77	8.23	3.12	104	0.0493	0.638
[ChCl]+[Gly]1:1[a]	22.0	8.71	2.46	98.1	0.0405	0.486
[ChCl]+[Gly] 1:2[a]	30.8	12.2	3.05	121	0.0656	0.593
[$4C_1$NCl]+[Gly] 1:2[b]	4.05	3.71	1.63	63.7	0.0187	0.311
Sulfolane[c]	18.3	9.98	0.677	10.8	0.424	0.323
NMP[d]	16.1	9.07	–	–	0.515	–
[BMIM][SCN][e]	82.4	23.2	–	71.1	0.463	1.43
[BMIM][SbF_6][f]	11.3	12.5	0.179	6.63	0.813	0.429

([a]Verevkin et al., 2015, [b]Nkosi et al., 2018, [c]Mollmann and Gmehling, 1997, [d]Krummen and Gmehling, 2004, [e]Domanska and Marciniak, 2008, [f]Olivier et al., 2011)

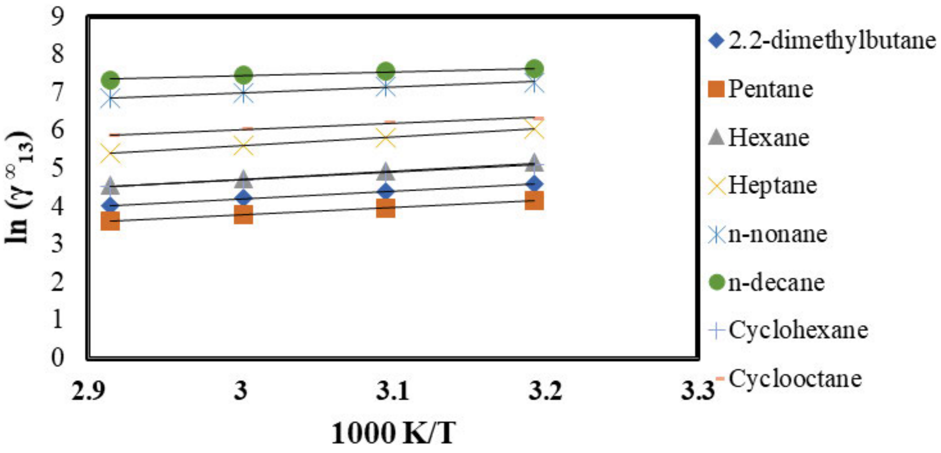


Figure 5.29: Plot of ln γ_{13}^{∞} versus 1/T for the alkanes in the DES at T = (313.15 – 343.15) K.

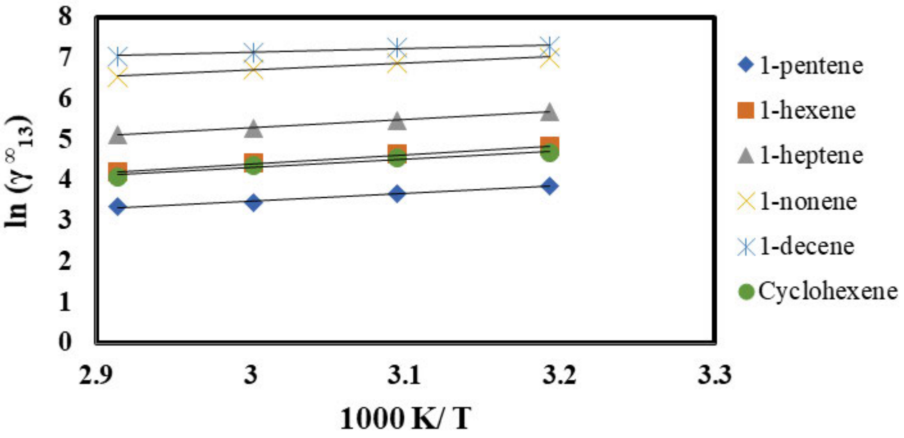


Figure 5.30: Plot of ln γ_{13}^{∞} versus 1/T for alkenes in the DES at T = (313.15 – 343.15) K.

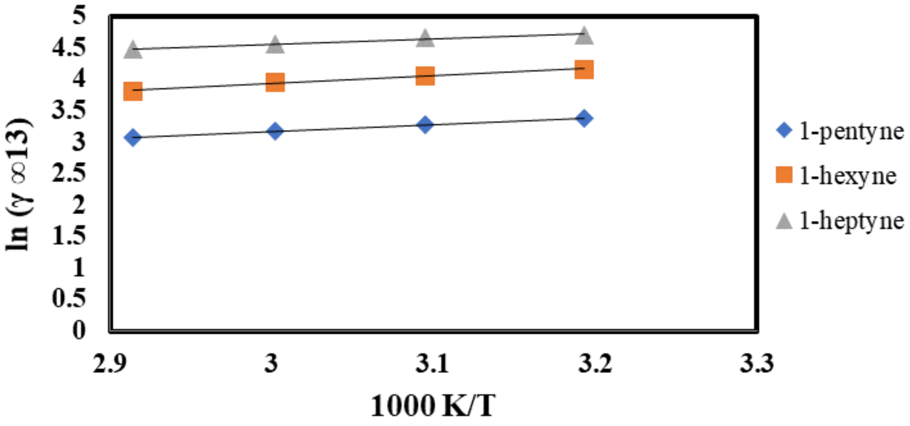


Figure 5.33: Plot of ln γ_{13}^{∞} versus 1/T for alkyne in the DES at T = (313.15 – 343.15) K.

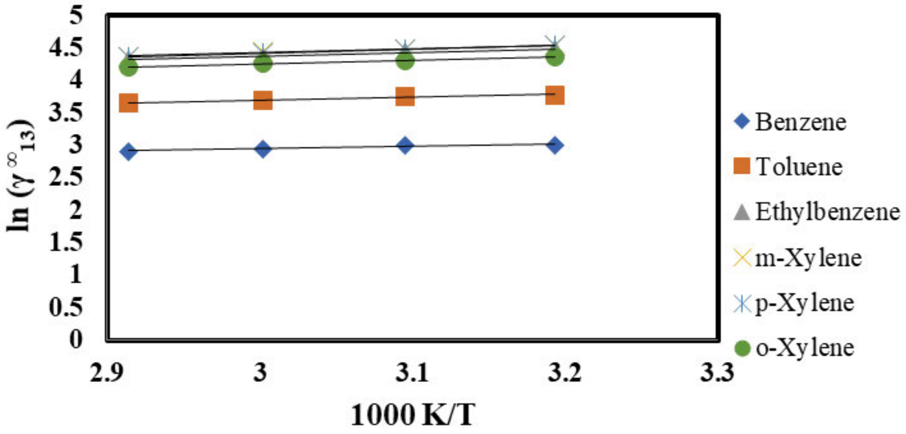


Figure 5.32: Plot of ln γ_{13}^{∞} versus 1/T for aromatic hydrocarbons in the DES at T = (313.15 – 343.15) K.

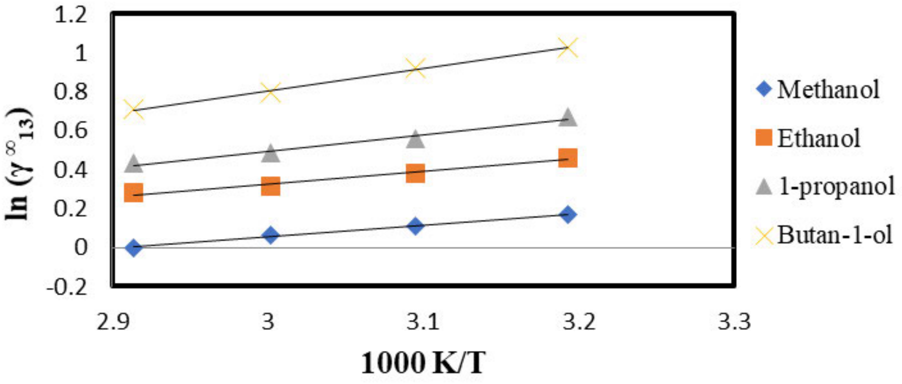


Figure 5.33: Plot of ln γ_{13}^{∞} versus 1/T for alcohols in the DES at T = (313.15 – 343.15) K.

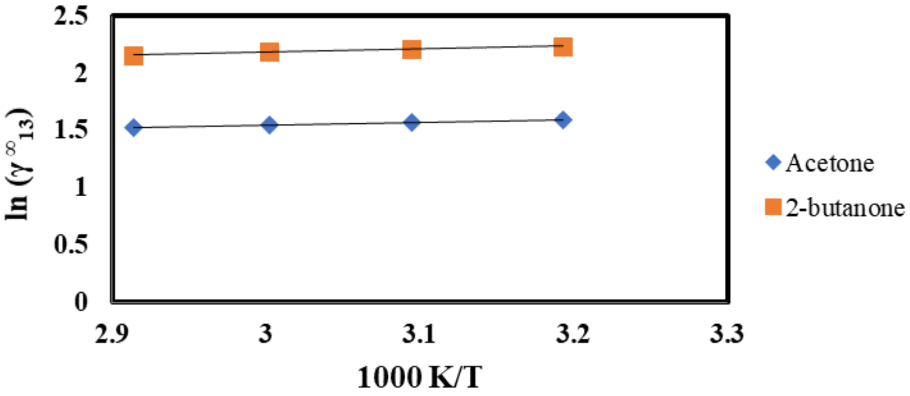


Figure 5.34: Plot of ln γ_{13}^{∞} versus 1/T for ketones in the DES at T = (313.15 – 343.15) K.

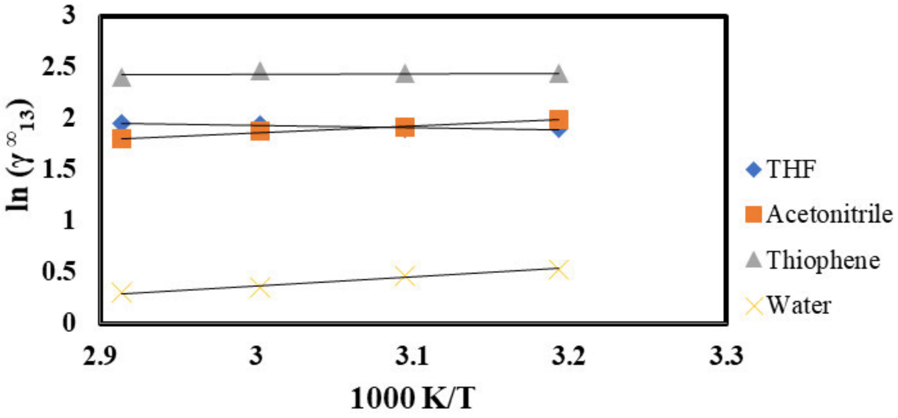


Figure 5.35: Plot of ln γ_{13}^{∞} against 1/T for THF, acetonitrile, thiophene water in the DES at T = (313.15 – 343.15) K.

Table 5.17

Average activity coefficients at infinite dilution for the solutes in the ionic liquid [EPMpyr] [Cl] at four different temperatures: for the standard state of solutes hypothetical liquid at zero pressure. [a]

Solutes	Average γ_{13}^{∞} values			
	T = 343.15 K	T = 323.15 K	T = 333.15 K	T = 343.15 K
2.2-dimethylbutane	67.80	92.20	114.1	145.5
Pentane	39.04	49.54	70.34	98.68
Hexane	120.2	148.9	193.5	243.7
Heptane	182.5	264.1	357.7	415.6
n-Nonane	461.3	614.7	811.7	1088
n-Decane	1174	1415	1816	2423
1-Pentene	29.58	40.10	56.31	67.10
1-Hexene	91.12	111.4	130.8	148.3
1-Heptene	220.8	291.6	332.6	373.7
1-Nonene	646.6	839.6	1028	1159
1-Decene	863.9	1134	1338	1539
Cyclohexene	19.01	26.06	37.20	47.42
Cyclohexane	19.81	27.35	37.48	50.57
Cyclooctane	26.57	34.15	46.28	65.10
1-Pentyne	3.052	5.396	9.682	16.41
1-Hexyne	5.824	9.463	15.16	24.72
1-Heptyne	11.24	18.62	30.62	49.06
Benzene	29.62	44.28	75.54	117.6
Toluene	47.54	75.54	120.2	194.4
Ethylbenzene	155.8	221.5	338.1	415.3
m-Xylene	274.2	434.6	587.7	703.8
p-Xylene	220.1	302.6	466.5	572.8
o-Xylene	114.2	167.6	238.2	345.6
Methanol	30.36	40.86	56.16	69.99
Ethanol	55.32	77.98	98.85	116.4
Propanol	80.92	103.2	138.0	171.6
Butanol	123.6	160.6	205.5	250.3
THF	118.4	89.84	64.94	47.34
Acetonitrile	111.9	139.2	191.0	229.8
Thiophene	87.61	121.9	153.9	186.7
Acetone	88.86	72.12	58.01	51.95
MEKP	82.52	116.6	159.5	203.0
Water	23.83	35.27	51.59	79.04

[a] Standard uncertainties: u are u(γ_{13}^{∞}) = 5 %, u(T) = 0.02 K and u(P) = 2 kPa.

Table 5.18

Limiting partial molar enthalpies $\Delta H_1^{E,\infty}$, Gibbs energies $\Delta G_1^{E,\infty}$ and entropies $T_{ref}\,\Delta S_1^{E,\infty}$ for solutes in the investigated ionic liquid [EPMpyr] [Cl] at the reference temperature T_{ref} = 323.15 K.

Solutes	$\Delta H_1^{E,\infty}$ (kJ · mol^{-1})	$\Delta G_1^{E,\infty}$ (kJ · mol^{-1})	$T_{ref}\,\Delta S_1^{E,\infty}$(kJ · mol^{-1})
2.2-dimethylbutane	-22.4	12.2	-34.6
Pentane	-27.9	10.5	-38.4
Hexane	-21.3	13.4	-34.7
Heptane	-24.9	15.0	-39.9
n-Nonane	-25.5	17.3	-42.8
n-Decane	-21.6	19.5	-41.1
1-Pentene	-25.0	9.91	-35.0
1-Hexene	-14.5	12.7	-27.2
1-Heptene	-15.4	15.2	-30.6
1-Nonene	-17.5	18.1	-35.6
1-Decene	-17.0	18.9	-35.9
Cyclohexene	-27.7	8.82	-36.5
Cyclohexane	-27.9	8.93	-36.8
Cyclooctane	-18.4	9.51	-27.9
1-Pentyne	-50.3	4.57	-54.9
1-Hexyne	-43.0	6.02	-49.0
1-Heptyne	-44.0	7.93	-51.8
Benzene	-41.7	10.2	-51.9
Toluene	-41.9	11.6	-53.5
Ethylbenzene	-30.1	14.5	-44.6
m-Xylene	-28.1	16.3	-44.4
p-Xylene	-29.6	15.3	-44.9
o-Xylene	-32.8	13.8	-46.6
Methanol	-25.3	10.0	-35.2
Ethanol	-22.1	11.7	-33.9
Propanol	-22.8	12.5	-35.2
Butanol	-21.1	13.6	-34.8
THF	27.4	12.1	15.4
Acetonitrile	-22.1	13.3	-35.4
Thiophene	-22.4	12.9	-35.3
Acetone	16.4	11.5	4.92
MEKP	-20.3	12.8	-33.1
Water	-35.5	9.65	-45.1

[a] Standard uncertainties u are u(γ_{13}^{∞}) = 5 %, u(T) = 0.02 K and u(P) = 2 kPa.

Table 5.19

Selectivities (S_{ij}^{∞}) and capacities (K_j^{∞}) at infinite dilution for [EPPYR] [Cl] for various separation problems at T = 328.15 K.

Ionic Liquid	S_{ij}^{∞}			K_j^{∞}		
	Water/butan-1-ol	Heptane/benzene	Heptane/thiophene	Butan-1-ol	benzene	thiophene
[EPPYR][Cl]	0.220	5.96	2.17	0.006	0.02	0.01
[$P_{666\ 14}$][DCA][a]	3.95	3.87	3.72	2.23	2.62	2.52
[EMIM][DCA][b]	-	66.2	109.0	-	0.39	0.64
[$P_{666\ 14}$][TCM][c]	4.53	4.44	4.97	2.36	2.18	2.44
[BMIM][DCA][d]	0.29	44.7	71.5	0.90	0.51	0.82
[AMIM][DCA][e]	0.19	64.1	106.9	0.56	0.32	0.53
[P_{1444}][TOS][f]	1.74	12.6	19.7	3.14	0.78	1.22
[B^4MPY][DCA][g]	0.33	50.6	80.5	1.13	0.72	1.15

([a]Kabane and Redhi, 2019, [b]Mutelet et al., 2010, [c]Marciniak and Wlazlo, 2018, [d]Domańska et al., 2016, [e]Wlazło et al., 2016, [f]Domańska and Paduszynski, 2010, [g]Królikowski and Królikowska, 2014)

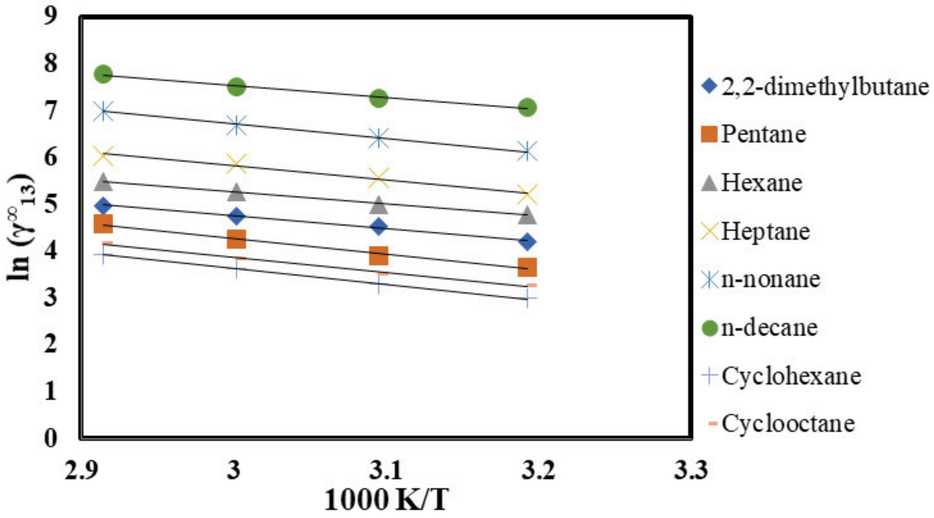


Figure 5.36: Plot of ln γ_{13}^{∞} against 1/T for alkanes in the ionic liquid [EPMpyr] [Cl] at T = (313.15 – 343.15) K.

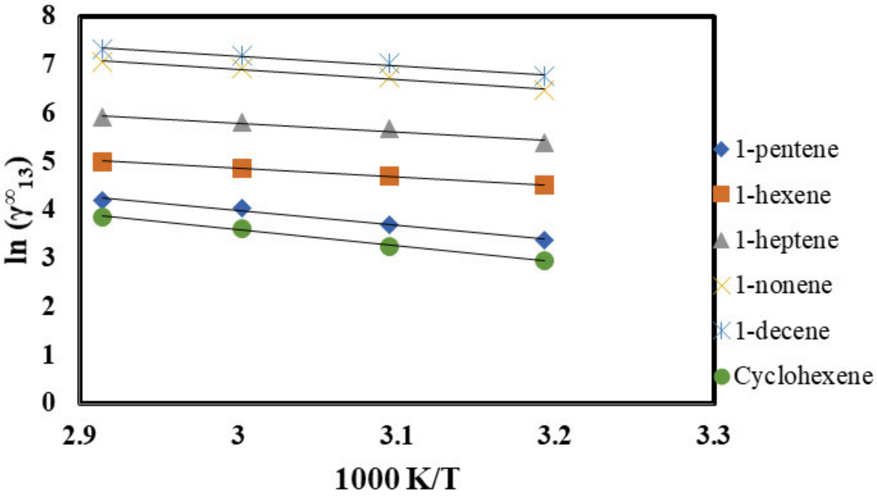


Figure 5.37: Plot of ln γ_{13}^{∞} against 1/T for alkenes in the ionic liquid [EPMpyr] [Cl] at T = (313.15 – 343.15) K.

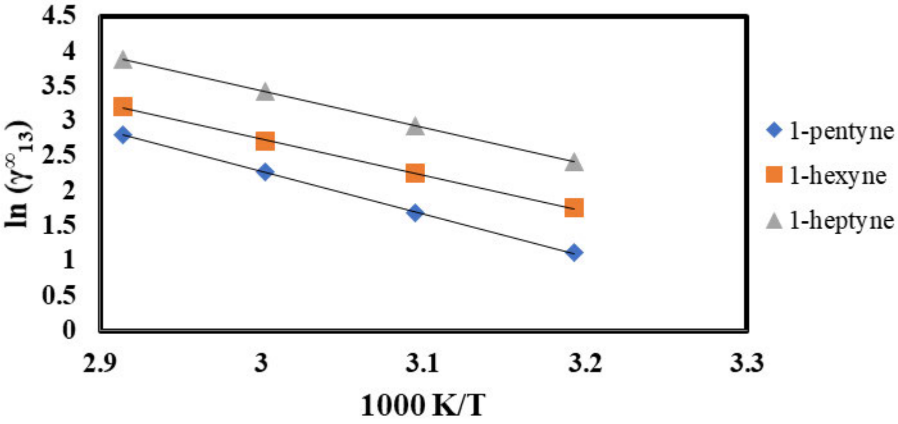


Figure 5.38: Plot of ln γ_{13}^{∞} against 1/T for alkynes in the ionic liquid [EPMpyr] [Cl] at T = (313.15 – 343.15) K.

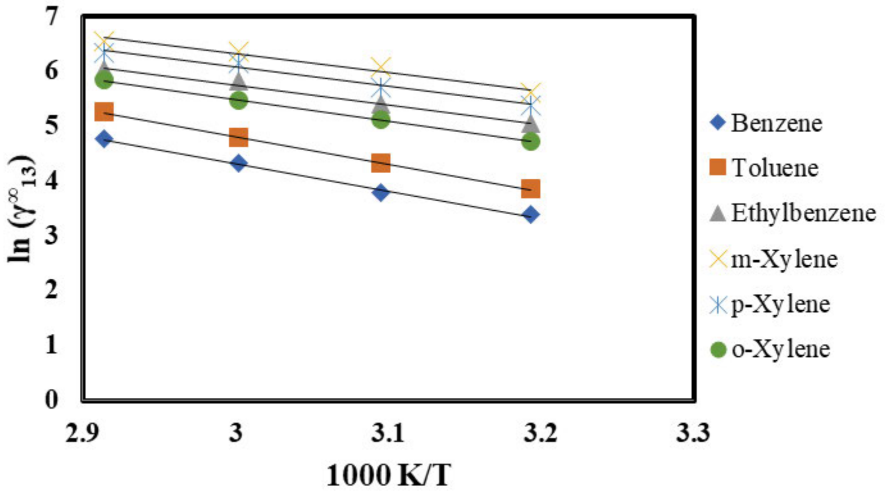


Figure 5.39: Plot of ln γ_{13}^{∞} against 1/T for aromatic hydrocarbons in the ionic liquid [EPMpyr] [Cl] at T = (313.15 – 343.15) K.

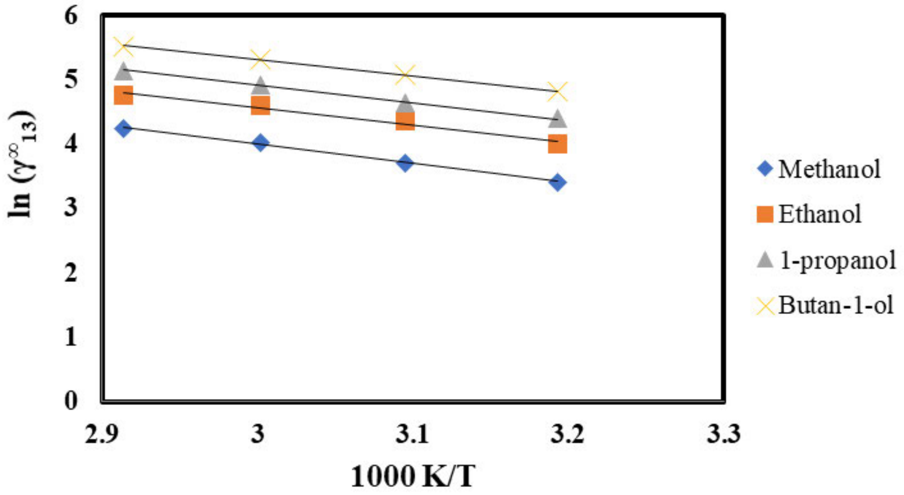


Figure 5.40: Plot of ln γ_{13}^{∞} against 1/T for alcohols in the ionic liquid [EPMpyr] [Cl] at T = (313.15 – 343.15) K.

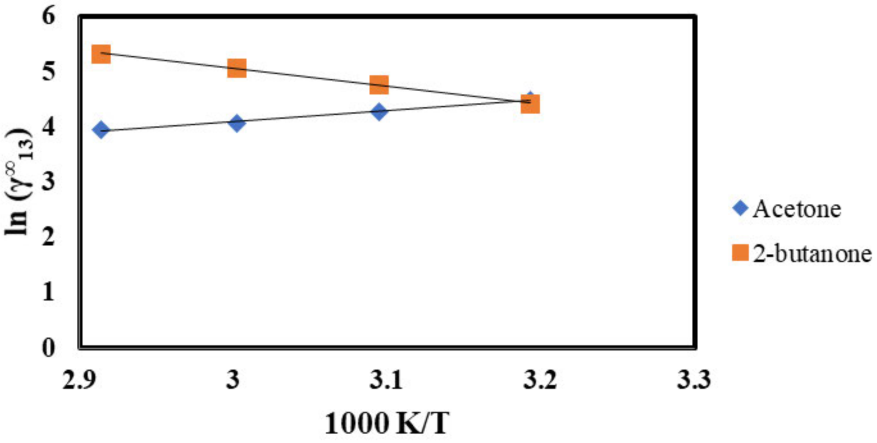


Figure 5.41: Plot of ln γ_{13}^{∞} against 1/T for ketones in the ionic liquid [EPMpyr] [Cl] at T = (313.15 – 343.15) K.

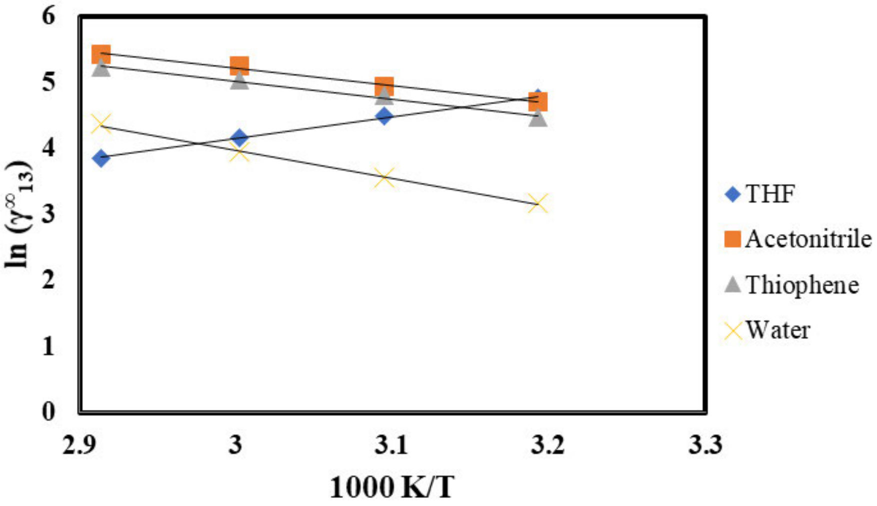


Figure 5.42: Plot of ln γ_{13}^{∞} against 1/T for THF, acetonitrile, thiophene and water in the ionic liquid [EPMpyr] [Cl] at T = (313.15 – 343.15) K.

5.2. Liquid-liquid equilibrium data

Liquid-liquid extraction is based on the distribution of an analyte between two essentially immiscible solvents. The distribution ratio of an analyte is defined as the ratio of its total concentration in the organic phase to that in the aqueous phase at equilibrium. LLE is used for clean-up of the sample. This technique extract compounds based on their relative solubilities in two different immiscible liquids. The main setback of this technique is that it is time consuming, can require large quantities of extracting solvent, toxic solvents that pose a potential threat to human health and environment.

The following ionic liquids were used:

- 1-ethyl-3-methylimidazolium tetrafluoroborate [EMIM] [BF_4]
- 1-ethyl-3-methylimidazolium dicyanamide [EMIM] [DCA]
- 1,3-dimethylimidazolium dimethylphosphate [MMIM] [DMP]

Table 5.20

Composition of experimental tie-lines in mole fractions, selectivity (*S*) and distribution ratio (*β*) for the ternary systems{[EMIM] [DCA] or [EMIM] [BF$_4$] (1) + hexane (2) + ethyl acetate (3)} at T = 298.15 K and atmospheric pressure.

Hydrocarbon-rich phase		IL-rich phase		*S*	*β*
x_1^{HC}	x_2^{HC}	x_1^{IL}	x_2^{IL}		
[EMIM][DCA]					
0.000	0.000	0.008	0.000	---	---
0.000	0.170	0.027	0.018	10.9	1.15
0.000	0.295	0.031	0.023	17.2	1.34
0.000	0.406	0.040	0.032	19.8	1.56
0.000	0.531	0.067	0.039	25.9	1.90
0.000	0.629	0.106	0.043	33.6	2.29
0.000	0.717	0.147	0.035	59.2	2.89
0.000	0.736	0.225	0.051	39.6	2.75
0.000	0.801	0.315	0.033	79.5	3.28
0.000	0.860	0.465	0.034	90.5	3.58
0.000	0.937	0.690	0.035	116	4.37
0.000	0.948	0.700	0.033	147	5.13
0.000	0.963	0.735	0.031	200	6.46
0.000	1.000	0.958	0.042	---	---
[EMIM][BF$_4$]					
0.000	0.000	0.004	0.000	---	---
0.000	0.160	0.059	0.009	19.7	1.11
0.000	0.294	0.095	0.012	31.1	1.26
0.000	0.422	0.145	0.015	40.9	1.46
0.000	0.521	0.208	0.017	49.6	1.62
0.000	0.615	0.249	0.018	65.0	1.90
0.000	0.711	0.270	0.019	92.1	2.46
0.000	0.756	0.290	0.020	107.0	2.83
0.000	0.808	0.350	0.025	106.2	3.29
0.000	0.874	0.551	0.029	100.5	3.33
0.000	0.933	0.639	0.025	187.2	5.01
0.000	0.940	0.674	0.030	154.6	4.93
0.000	0.948	0.706	0.030	159.8	5.06
0.000	1.000	0.993	0.007	---	---

Standard uncertainties are u(*x*) = 0.005; u(*S*) = 0.005; u(β) = 0.005; u(*T*) = 0.1 K; u(p) = 1 kPa.

Table 5.21

Summary of results (*S* and β) from previously published related literature using ionic liquids for liquid-liquid equilibrium data with azeotropic mixture (hexane + ethyl acetate).

IL	LLE system	*T*/K	S_{av}	β_{av}
[EMIM][DCA]	IL+hexane +ethyl acetate	298.15	70.01	3.06
[EMIM][BF_4]	IL+hexane+ethyl acetate	298.15	92.81	2.86
[HMIM][PF_6][a]	IL+hexane+ethyl acetate	298.15	28.02	1.51
[OMIM][PF_6][a]	IL+hexane+ethyl acetate	298.15	14.87	2.21
[DES][b]	DES+hexane+ethyl acetate	298.15	52.23	0.110
[HMIM][BF_4][c]	IL+hexane+ethylacetate	298.15	9.300	0.818
[OMIM][BF_4][c]	IL+hexane+ethylacetate	298.15	6.770	1.147
[HMIM][BF_4][c]	IL+hexane+ethylacetate	308.15	10.70	0.629

([a]Pereiro and Rogriguez, 2008, [b]Gonzalez et al., 2013, [c]Wen et al., 2018)

Table 5.22

Binary interaction parameters set, non-randomness parameter α_{ij} and root mean square deviation (σ_x) for NRTL equation for ternary mixtures {[EMIM] [DCA] or [EMIM] [BF_4] (1) + hexane (2) + ethyl acetate (3)} at T = 298.15 K and atmospheric pressure.

IL	ij	g_{ij}/ J·mol^{-1}	g_{ji}/ J·mol^{-1}	α_{ij}	σ_x
		hexane			
[EMIM] [DCA]	12	−186.245	57603.2	0.300	0.009
	13	31022.3	24271.1		
	23	7169.14	764.345		
[EMIM] [BF_4]	12	27626.6	47511.1	0.300	0.011
	13	26260.6	9685.37		
	23	35460.7	286677		

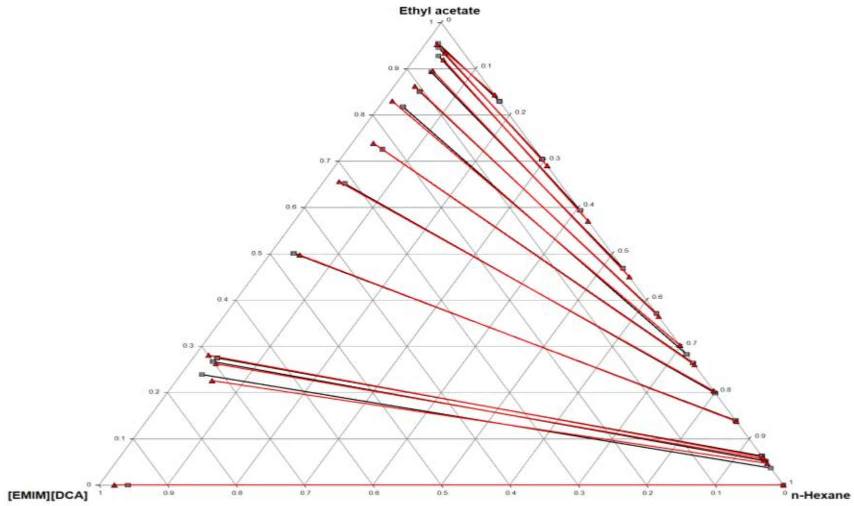


Figure 5.43: Plot of the experimental (■, solid lines) versus calculated with NRTL equation (▲ , red lines) for the composition tie lines of the ternary mixtures {[EMIM] [DCA] (1) + hexane (2) + ethyl acetate (3)} in mole fraction at T = 298.15 K, p = 101 kPa.

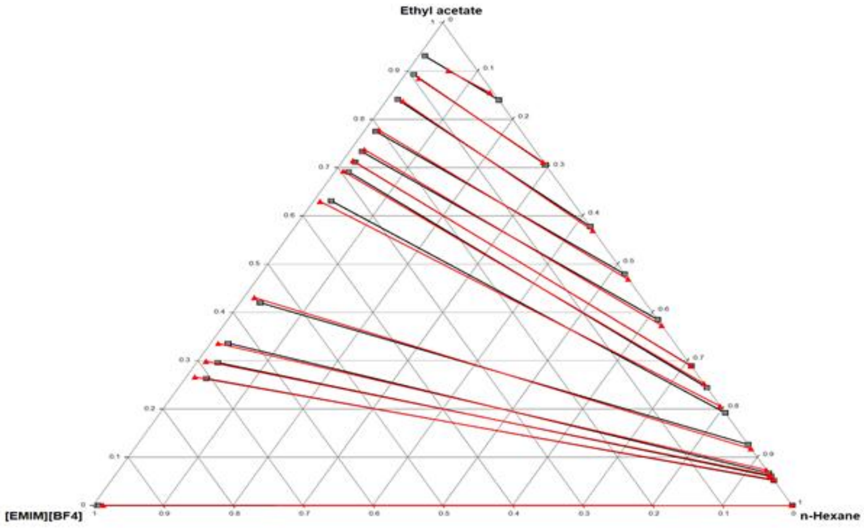


Figure 5.44: Plot of the experimental (■, solid lines) versus calculated with NRTL equation (▲ , red lines) for the composition tie lines of the ternary mixtures {[EMIM] [BF_4] (1) + hexane (2) + ethyl acetate (3)} in mole fraction at T = 298.15 K, p = 101 kPa.

Table 5.23

Composition of experimental tie-lines in mole fractions, selectivity (*S*) and distribution ratio (*β*) for the ternary systems{[EMIM] [BF_4] or [MMIM] [DMP] (1) + thiophene (2) + octane (3)} at T = 308.15 K and p = 101 kPa.

Hydrocarbon-rich phase		IL-rich phase		*S*	*β*
x_1^{HC}	x_2^{HC}	x_1^{IL}	x_2^{IL}		
[EMIM][BF_4]					
0.000	0.000	0.998	0.000	--	--
0.000	0.134	0.899	0.084	31.7	0.63
0.000	0.273	0.851	0.136	27.4	0.50
0.000	0.328	0.793	0.198	49.3	0.60
0.000	0.401	0.784	0.207	35.7	0.52
0.000	0.467	0.769	0.223	34.6	0.48
0.000	0.556	0.724	0.270	37.3	0.49
0.000	0.674	0.690	0.305	30.1	0.45
0.000	0.709	0.676	0.319	29.0	0.45
0.000	0.739	0.655	0.341	28.9	0.46
0.000	0.800	0.641	0.355	23.4	0.44
0.000	0.881	0.633	0.364	14.4	0.41
0.000	0.920	0.586	0.411	11.9	0.45
0.000	1.000	0.391	0.609	--	--
[MMIM][DMP]					
0.000	0.000	0.997	0.000	--	--
0.000	0.138	0.841	0.138	42.9	1.00
0.000	0.256	0.804	0.179	29.6	0.70
0.000	0.342	0.724	0.260	30.4	0.76
0.000	0.498	0.659	0.326	21.3	0.65
0.000	0.557	0.624	0.361	19.6	0.65
0.000	0.695	0.590	0.397	13.6	0.57
0.000	0.742	0.540	0.449	13.8	0.61
0.000	0.834	0.512	0.478	9.7	0.57
0.000	0.870	0.483	0.510	10.3	0.59
0.000	0.885	0.438	0.556	13.3	0.63
0.000	0.909	0.422	0.574	14.9	0.63
0.000	0.927	0.386	0.611	15.3	0.66
0.000	1.000	0.182	0.818	--	--

Standard uncertainties are u(x) = 0.005; u(S) = 0.005; u(β) = 0.005; u(T) = 0.1 K; u(p) = 1 kPa.

Table 5.24

Composition of experimental tie-lines in mole fractions, selectivity (*S*) and distribution ratio (*β*) for the ternary systems{[EMIM] [BF_4] or [MMIM] [DMP] (1) + thiophene (2) + hexadecane (3)} at T = 308.15 K and p = 101 kPa.

Hydrocarbon- rich phase		IL-rich phase		*S*	*β*
x_1^{HC}	x_2^{HC}	x_1^{IL}	x_2^{IL}		
[EMIM] [BF_4]					
0.000	0.000	0.997	0.000	---	---
0.000	0.066	0.941	0.048	65.6	0.73
0.000	0.151	0.922	0.068	38.2	0.45
0.000	0.213	0.851	0.141	64.2	0.66
0.000	0.257	0.791	0.201	77.5	0.78
0.000	0.397	0.735	0.260	84.1	0.65
0.000	0.428	0.715	0.281	99.4	0.66
0.000	0.527	0.687	0.310	82.9	0.59
0.000	0.608	0.651	0.346	74.3	0.57
0.000	0.738	0.577	0.421	66.4	0.57
0.000	0.802	0.505	0.493	66.2	0.62
0.000	0.888	0.482	0.516	43.7	0.58
0.000	0.946	0.461	0.538	26.4	0.57
0.000	1.000	0.391	0.609	---	---
[MMIM] [DMP]					
0.000	0.000	0.999	0.000	---	---
0.000	0.210	0.645	0.329	47.9	1.57
0.000	0.321	0.599	0.381	39.8	1.19
0.000	0.515	0.535	0.446	21.9	0.87
0.000	0.570	0.483	0.500	23.2	0.88
0.000	0.664	0.368	0.618	22.2	0.93
0.000	0.744	0.309	0.682	24.6	0.92
0.000	0.811	0.260	0.732	22.1	0.90
0.000	0.846	0.213	0.781	24.0	0.92
0.000	0.874	0.176	0.820	28.1	0.94
0.000	0.897	0.162	0.835	32.5	0.93
0.000	0.930	0.157	0.841	27.4	0.90
0.000	0.963	0.136	0.862	18.0	0.89
0.000	1.000	0.391	0.609	---	---

Standard uncertainties are u(*x*) = 0.005; u(*S*) = 0.005; u(β) = 0.005; u(T) = 0.1 K; u(p) = 1 kP

Table 5.25

Summary of results (S and β) from previously published related literature using ionic liquids for liquid-liquid equilibrium data with sulphur compounds.

IL	LLE system	T/K	S_{av}	β_{av}
[EMIM][BF_4]	IL + thiophene + octane	308.15	29.5	0.49
[MMIM][DMP]	IL + thiophene + octane	308.15	19.6	0.69
[EMIM][BF_4]	IL + thiophene + hexadecane	308.15	59.4	1.81
[MMIM][DMP]	IL + thiophene + hexadecane	308.15	27.6	0.99
[EMIM][$EtSO_4$][a]	IL + thiophene + hexadecane	298.15	50.5	0.82
[EMIM][$MeSO_3$][a]	IL + thiophene + hexadecane	298.15	56.3	1.09
[C_8MIM][BF_4][b]	IL + thiophene + hexadecane	298.15	6.84	0.69
[HMIM][SCN][c]	IL + thiophene + octane	298.15	80.2	1.82
[BMIM][OTf][d]	IL + thiophene + octane	308.15	43.9	1.25
[BMIM][OTf][d]	IL + thiophene + hexadecane	308.15	209	0.93
[EMIM][NTf_2][e]	IL + thiophene + heptane	298.15	74.6	1.96

([a]Ramalingam and Balaji, 2015, [b]Alonso et al., 2008, [c]Mafi et al., 2016, [d]Ge et al., 2015, [e]Rodriguez-Cabo et al., 2013)

Table 5.26

Binary interaction parameters set, non-randomness parameter α_{ij} and root mean square deviation (σ_x) for NRTL equation for ternary mixtures {[EMIM] [BF_4] or [MMIM] [DMP] (1) + thiophene (2) + octane or hexadecane (3)} at T = 308.15 K and p = 101 kPa.

IL	ij	g_{ij}/ J·mol^{-1}	g_{ji}/ J·mol^{-1}	α_{ij}	σ_x
		Octane			
[EMIM][BF_4]	12	38983.88	15319.48	0.3	0.006
	13	16661.44	78787.03		
	23	78641.17	3056.68		
[MMIM][DMP]	12	31037.22	11058.75	0.3	0.010
	13	30647.97	24493.47		
	23	31369.50	5208.94		
		Hexadecane			
[EMIM][BF_4]	12	-1345.70	11161.21	0.3	0.004
	13	15470.36	14843.81		
	23	6525.95	-3431.23		
[MMIM][DMP]	12	1968.38	8597.35	0.3	0.011
	13	9479.98	20150.21		
	23	11549.66	18414.77		

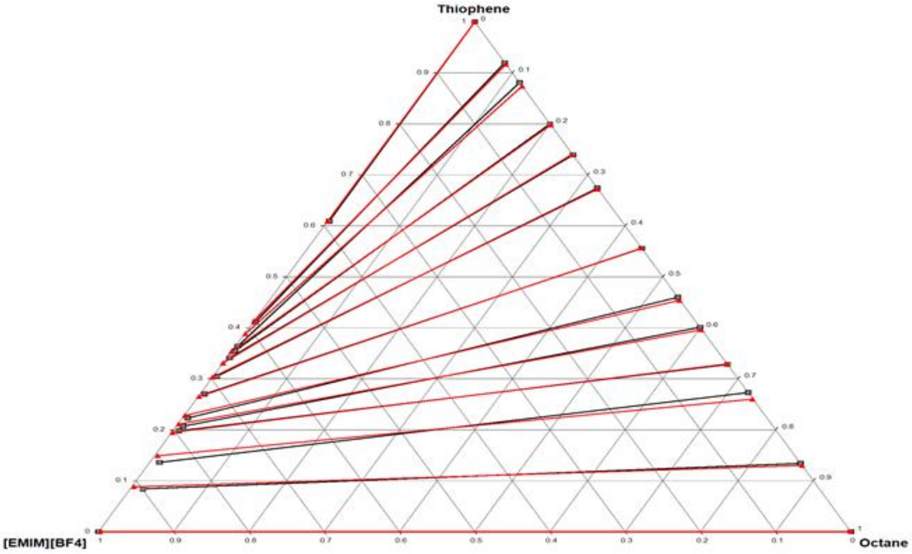


Figure 5.45: Plot of the experimental (■, solid lines) versus calculated with NRTL equation (▲ , red lines) for the composition tie lines of the ternary mixtures {[EMIM] [BF_4] (1) + thiophene (2) + octane (3)} in mole fraction at T = 308.15 K, p = 101 kPa.

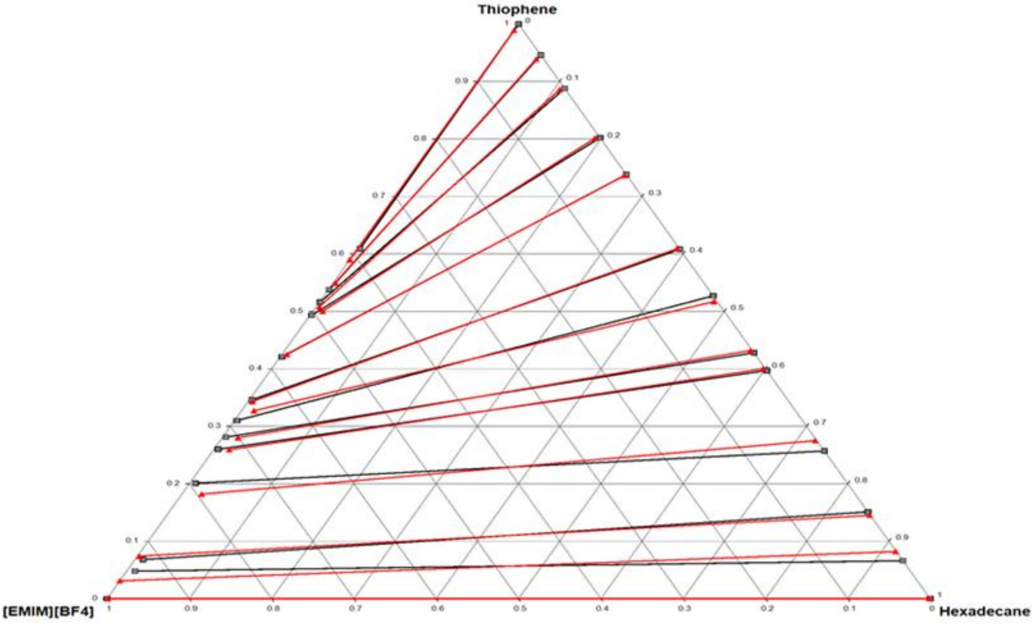


Figure 5.46: Plot of the experimental (■, solid lines) versus calculated with NRTL equation (▲, red lines) for the composition tie lines of the ternary mixtures {[EMIM] [BF_4] (1) + thiophene (2) + hexadecane (3)} in mole fraction at T = 308.15 K, p = 101 kPa.

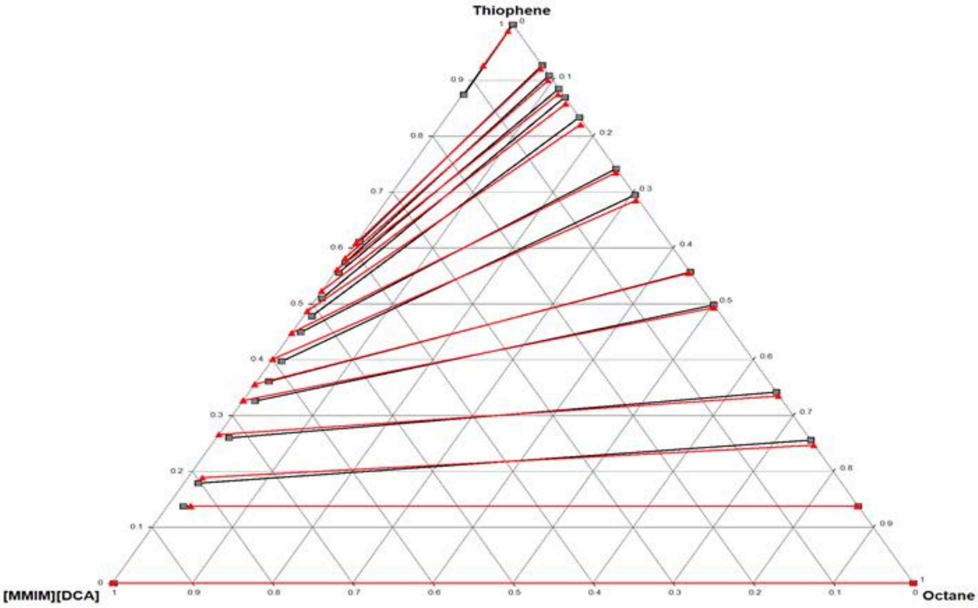


Figure 5.47: Plot of the experimental (■, solid lines) versus calculated with NRTL equation (▲, red lines) for the composition tie lines of the ternary mixtures {[MMIM] [DMP] (1) + thiophene (2) + octane (3)} in mole fraction at T = 308.15 K, p = 101 kPa.

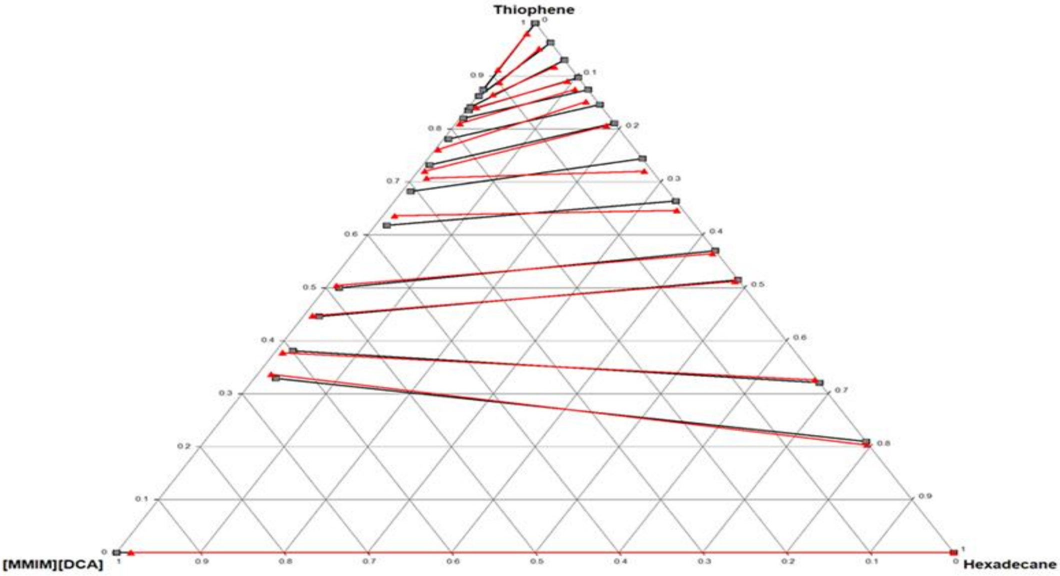


Figure 5.48: Plot of the experimental (■solid lines) versus calculated with NRTL equation (▲red lines) for the composition tie lines of the ternary mixtures {[MMIM] [DMP] (1) + thiophene (2) + hexadecane (3)} in mole fraction at T = 308.15 K, p = 101 kPa.

Chapter 6

Discussion

This chapter explains the intermolecular interactions of selected ionic liquids with solutes under investigation, and reveals the feasibility of these ionic liquids as possible entrainers for industrial separation problems. The different industrially selected separation problems are chosen based on the effectiveness of the ionic liquids for the separation processes.

6.1. Infinite dilution activity coefficients

This section comprises the evaluation of ionic liquids and explain the possible use of these ionic liquids for industrial applications. The possible intermolecular interaction between the solutes and ionic liquids are discussed.

Group 1: Application of trihexyltetradecylphosphonium dicyanamide ionic liquid for various types of separations problems: Activity coefficients at infinite dilution measurements utilizing GLC method:

The investigated phosphonium based IL generally reveals low γ_{13}^{∞} values for all solutes under investigation. For all chosen solutes, alkanes showed relatively high values viz., decane (γ_{13}^{∞} = 2.744) at 343.15 K. The lower γ_{13}^{∞} values are evident of increase in measured retention times between the solute and long alkyl chain of the investigated IL. In the ionic liquid with similar alkyl chains in phosphonium cation containing bis-(2, 4, 4-trimethylpentyl)-phosphinate and tris-(pentafluoroethyl) trifluorophosphate anion, low values of activity coefficients at infinite dilution were obtained viz., n-octane (γ_{13}^{∞} = 0.86) at 318.15 K and octane (γ_{13}^{∞} = 0.77) at 323.15 K, respectively (Letcher and Reddy, 2005, Letcher et al., 2008). This imply that weaker interactions occur in phosphonium cation with dicynamide anion, as compared to bis-(2, 4, 4-trimethylpentyl)-phosphinate and tris-(pentafluoroethyl) trifluorophosphate anion.

The average γ_{13}^{∞} data obtained in this work with the column loading of 0.3003 mass fraction of the IL at the series of four temperatures (313.15 to 343.15) K are presented in table 5.1. The plot of natural logarithm of $\ln \gamma_{13}^{\infty}$ as a function of inverse absolute temperature for all examined compounds, is shown in figure (5.1 – 5.7). In each class of investigated solutes, the γ_{13}^{∞} is directly proportional to the solute alkyl chain. The strength of higher interactions between the IL and solutes is as a consequence of branched structures, multiple bonds, aromatic rings or cyclic structures. The sequence of magnitude for γ_{13}^{∞} data is as follows: alcohols < ketones < aromatic hydrocarbons < alkynes < cycloalkenes < cycloalkanes < alkenes < alkanes. In the case of alkynes and alkenes, alkynes show stronger interactions via the triple bond as compared to the double bonds in alkenes. The interactions between the IL and π-delocalized electrons were revealed by the aromatic compounds and the γ_{13}^{∞} values are not far as compared to those of the polar compounds. Activity coefficient values ($\gamma_{13}^{\infty} < 1$) were obtained for these solutes except for water. The lower γ_{13}^{∞} values for the branched and cyclic solutes are due to the close packing impact, which then results in better interactions with the ionic liquid. Methanol gave lower γ_{13}^{∞} values as compared to the other compounds (γ_{13}^{∞} = 0.36) at 343.15 K, this effect could possibly be the consequence of interactions through dispersive interactions as well as hydrogen bonding formation by the short alkyl chain.

The results obtained in this work with a packed column loading (0.3003 mass fraction of the IL) are 1.5 times lower (except for alcohols), as compared to activity coefficient values with the same ionic liquid, using a capillary column (Ronco et al., 2019). This effect might be due to the use of the different types of columns. Packed columns are suitable for liquid-liquid extraction and contain a fully packed stationary phase made up of fine particles. In contrast, in the capillary column, the stationary phase is coated only on the inner surface. Packed column requires a larger amount of the sample so that solutes can be exposed to a large surface (in this regard, IL) as compared to capillary column where solutes are exposed to significantly reduced solvent which can lessen the interactions, resulting in relatively large activity coefficient values obtained. In capillary columns, some liquids of low viscosities would not form a uniform film on the silica walls which can then affect the precision in activity coefficient measurements (Gonzalez, 2004, Sizman, 1972).

The flow rate typically required with high precision and exact amount of volume (in this case, IL) is not easily determined when using capillary column and this may also affect the activity coefficient values. These are apparent drawbacks when using capillary column for the determination of activity coefficients, and may cause errors. Both the results (using packed and capillary columns) suggest a significant influence of the polarity of the ionic liquid on the activity coefficients obtained.

The following excess thermodynamic functions at infinite dilution ($\Delta H_1^{\mathrm{E}\infty}$, $\Delta S_1^{\mathrm{E},\infty}$and $\Delta G_1^{\mathrm{E},\infty}$) are related to activity coefficients at infinite dilution.

The $T_{\mathrm{ref}}\Delta S_1^{\mathrm{E},\infty}$ values at reference temperature 323.15 K are negative for almost all the studied solutes except for water. These negative values show that the solute molecules organize themselves in the ionic liquid structure. The positive value for water implies breaking of hydrogen bonds throughout their dissolution process in the ionic liquid under investigation. Negative values for computed $\Delta H_1^{\mathrm{E},\infty}$ were observed for almost all the chosen solutes except for water. The negative values of $\Delta H_1^{\mathrm{E},\infty}$ obtained imply that the interactions are related to solute-solvent pairs. This type of behaviour is due to interactions among the polar anions of the ionic liquid and double bonds in alkenes, triple bonds in alkynes as well as polarisable π-electrons in thiophene and aromatic compounds. The positive value for water ($\Delta H_1^{\mathrm{E},\infty}$ = 5.70 kJ mol $^{-1}$) can be explained as strong energetic interactions among the molecules of the IL and the particles of water. This implies that exothermic dissolution is due to the formation of hydrogen bonds between the IL and water. The calculated $\Delta G_1^{\mathrm{E},\infty}$ values are negative apart from alkanes, water and alkenes (≤ 6 carbons for alkenes are negative). These solutes possessed low values of γ_{13}^{∞} which are less than one, and this can be elucidated as negative deviation from Raoult's law. From figure (5.1 – 5.7), it can be noticeable that the $\ln \gamma_{13}^{\infty}$ values vary prominently with temperature for the alkanes, aromatic hydrocarbons, xylenes and ketones.

Separation potential of trihexyltetradecylphosphonium dicyanamide ionic liquid:

The selectivity and capacity data for the chosen extraction difficulties at 323.15 K (water/butan-1-ol, heptane/thiophene and heptane/benzene) are reported in table 5.3. In this work, selectivity for chosen separation problems ranges between (S_{ij}^{∞} = 3.75 to 4.08) and the capacity (K_j^{∞} = 2.24 to 3.75). In the ionic liquid [EMMor] (Domańska et al., 2018), [AMIM] (Wlazło et al., 2016), [BzMIM] (Design Institute for Physical Properties, 2005, 2008, 2009, 2010) and [N-C_3CNMIM] (Revelli, 2010) containing [DCA] anion, corresponding high selectivity values were obtained viz; (S_{ij}^{∞} = 273.3, 106.95, 100.0 and 138.0) respectively, and in the separation problem comprising (heptane/thiophene), the low capacity values (K_j^{∞} < 1) obtained indicate that large amounts of separating solvents would be required. The investigated ionic liquid revealed high capacity value (K_j^{∞} = 2.61) as compared to the above-mentioned ionic liquids implying smaller amounts of solvent would be required in the separation of (heptane/thiophene). Based on the literature regarding the separation involving (water/butan-1-ol), the capacity for most of the measured ionic liquids are less than one, except for tributyltetradecylphosphonium dodecylbenzenesulfonate (K_j^{∞} = 5.29) (Wlazlo et al., 2018), and tributylmethylphosphonium tosylate (K_j^{∞} = 3.14) (Domańska and Paduszynski, 2010). Again, high selectivity and relatively high capacity was observed for the investigated ionic liquid. In this regard, it is worth pointing out that large phosphonium cations give large selectivities.

Group 2: Methyltrioctylammonium chloride as a separation solvent for binary mixtures: Evaluation based on experimental activity coefficients:

The possibility of adsorption of solutes on to the solid support always raises some doubts about the measurements of γ_{13}^{∞} utilizing gas liquid chromatography. However, the peaks obtained by the gas liquid chromatography were symmetrical and γ_{13}^{∞} were free of helium gas flow, showing that no notable adsorption took place. This indicates adequate solvent on the column loading. The existing interactions at vapour phase between solvent and solutes at infinite dilution can be described by the values of γ_{13}^{∞}. In this present work, the ammonium ionic liquid [$N_{8\,8\,8\,1}$] [Cl], display low γ_{13}^{∞} data for all the solutes being examined. However, the relatively high γ_{13}^{∞} values were only revealed by alkanes, as decane (γ_{13}^{∞} = 3.15) at 343.15 K. The low γ_{13}^{∞} data presented by the investigated ionic liquid are due to an obvious increase in measured retention time between the solutes and ionic liquid under investigation. In recently published IL (*N*-benzyl-*N*-dimethyl-*N*-tetradecylammonium cinnamate), lowest data of γ_{13}^{∞} were presented by this ionic liquid, with far example of the alcohols and aromatic hydrocarbons: butan-1-ol (γ_{13}^{∞} = 0.173) and benzene (γ_{13}^{∞} = 1.55) at 338.15 K (Domanska et al., 2018). The other solutes including ketones, alkanes and alkenes revealed γ_{13}^{∞} values with magnitude of a small degree larger than one.

A column packing of 0.3001 by mass fraction of the ionic liquid was used to obtain the average γ_{13}^{∞} data at four different temperatures for the experimental work, and the results are shown in table 5.4. The γ_{13}^{∞} increase with an increase in solute alkyl chain in each class of the investigated solutes. From the γ_{13}^{∞} data, it is evident that the cyclic structures of alkanes show increased interactions as compared to linear alkanes with same number of carbon atoms. The observed effect is due to the stronger attractive interactions between the cyclic structures and the ammonium chains. The presence of the double bond in alkenes with equivalent number of carbon atoms as alkanes, caused an increased interaction with the polar ammonium IL as compared to alkanes. Alkenes, alkanes, cycloalkenes and cycloalkanes have high γ_{13}^{∞} in contrast to aromatic hydrocarbons except for alkynes, and this results from the strong attractive interactions between the investigated polar ammonium ionic liquid and the six π-delocalized electrons contained in the structure of benzene. The benzene molecule has delocalized π-electrons which can strongly interact with the investigated IL via (n-π) which is stronger when compared to van der Waal's interactions. In the group of alcohols, low values of γ_{13}^{∞} were observed implying an increased interaction with the IL under investigation. The strong interactions of alcohols with the ionic liquid result from the increased hydrogen bonding.

The following physicochemical properties at infinite dilution ($\Delta H_1^{\mathrm{E}\infty}$, $\Delta S_1^{\mathrm{E},\infty}$and $\Delta G_1^{\mathrm{E},\infty}$) are connected to γ_{13}^{∞}.

The calculated data is shown in table 5.5. The computed values for partial excess molar entropies at reference temperature 323.15 K are small, and some are positive and negative for various solutes. Ketones and acetonitrile are positive. The negative entropy values imply that a distinct solute molecule easily arranges itself in the investigated IL structure. The breaking of the hydrogen bond is specified by the positive entropy values (ketones and acetonitrile). This occurs through their dissolution process in the studied ammonium-based IL. The obtained negative values for $\Delta H_1^{\mathrm{E},\infty}$, except for ketones and acetonitrile, suggest that the types molecular interactions occurring between the solvent and solute result from the solute-solvent pairs. This result from the interactions between the double bonds in alkenes and lone pair of electrons on [Cl$^-$] anion of the ionic liquid, and the polarisable π-electrons in thiophene as well as aromatic hydrocarbons. The positive values for acetonitrile ($\Delta H_1^{E,\infty}$ = 10.3 kJ mol^{-1}), acetone ($\Delta H_1^{E,\infty}$ = 6.18 kJ mol^{-1}) and 2-butanone ($\Delta H_1^{E,\infty}$ = 7.17 kJ mol^{-1}) are due to strong energetic interactions occurring between the particles of the ionic liquid and the solutes. This suggests that the exothermic dissolution results from the hydrogen bonds between the IL and solute. Negative values for the calculated $\Delta G_1^{E,\infty}$ were observed apart from alkenes and alkanes. This is described as a negative deviation from ideality.

Separation potential of methyltrioctylammonium chloride:

The capacity and selectivity values for the chosen separation problems at 323.15 K (hexane/toluene, hexane/hexene, heptane/thiophene, cyclohexane/cyclohexene as well as heptane/benzene) are listed in table 5.6, and in contrast with the literature for the (heptane/thiophene) separation problems in figure1. For the investigated ammonium ionic liquid [$N_{8\,8\,8\,1}$] [Cl], the selectivity for the selected extraction problems ranges between (S_{ij}^{∞} = 1.09 to 5.51) and the capacity (K_j^{∞} = 0.76 to 3.02). In the IL *N*-benzyl-*N*-dimethyl-*N*-tetradecylammonium cinnamate for same separation difficulties, selectivity values range between (S_{ij}^{∞} = 1.23 to 3.90) and capacity (K_j^{∞} = 0.28 to 0.81) (Domanska et al., 2018). In [$N_{8\ 8\ 8\ 1}$] [NTf_2] published earlier (Gwalaet al., 2008), the selectivity for some of the petrochemical difficulties: (hexane/hexene, S_{ij}^{∞} = 1.30), (heptane/benzene, S_{ij}^{∞} = 4.00) at temperature, T = 323.15 K (Gwala et al., 2008). For hexane/hexene, the investigated ionic liquid presents larger capacity value (K_j^{∞} = 0.76) in contrast to the other ILs, 1-benzyl-3methylimidazolium dicynamide, (K_j^{∞} = 0.03), for [$N_{Bz\,1\,1\,14}$] [Cyn], (K_j^{∞} = 0.28) (Domanska et al., 2018) and for 1-benzyl-3-methylimidazolium bis{(triflouromethyl) sulfonyl} imide, (K_j^{∞} = 0.11) at temperature, T = 328.15 K. The presented ionic liquid offers possible industrial application in the separation of heptane/thiophene where it reveals selectivity of (S_{ij}^{∞} = 5.51) and large capacity (K_j^{∞} = 3.02), as compared to the ionic liquid that present selectivity of (S_{ij}^{∞} = 3.90) and capacity (K_j^{∞} = 0.81) (Domanska et al., 2018), and also the recent published ionic liquid (trihexyltetradecylphosphonium dicyanamide) with (S_{ij}^{∞} = 3.72) and capacity (K_j^{∞} = 2.52) (Kabane and Redhi, 2019). The published work for the ionic liquid [N-C_3OHmMOR] [NTf_2] showed high selectivity for the separation of heptane/thiophene (S_{ij}^{∞} = 118) but lower capacity (K_j^{∞} = 0.53) (Wlazlo, et al., 2015).

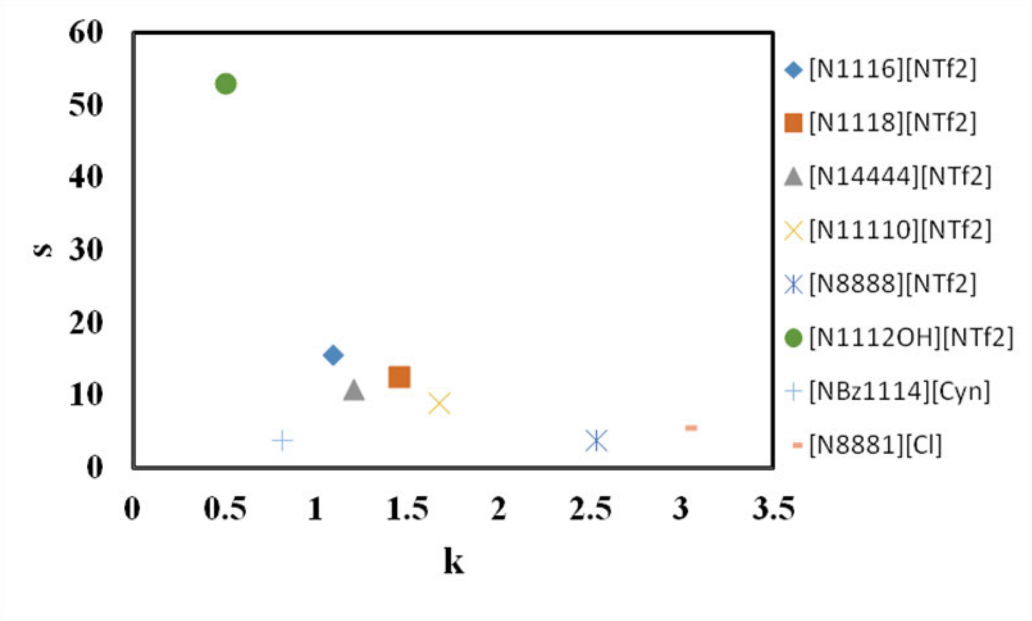


Figure 6.1: Selectivity (s) plotted against capacity (k) for the other ammonium based ionic liquids with [NTf_2]$^-$ and [Cyn]$^-$ anions in the separation of (heptane/thiophene) problem at temperature, T = 323.15 K.

Group 3: Assessment of 2,3-dihydroxypropyl-*N*-methyl-2-oxopyrrolidinium chloride ionic liquid for the separation of binary mixtures based on activity coefficients at infinite dilution:

The existing interactions at vapour phase between solvent and solutes at infinite dilution can be described by the values of activity coefficients at infinite dilution. The activity coefficients at infinite dilution data provide functional information in extraction and separation technology. The highest interaction among the solutes and investigated ionic liquid can be detected by the lowest value of γ_{13}^{∞}, and an increase in activity coefficients at infinite dilution result from a decrease in measured retention time as well as a decrease in strength of the interactions between the evaluated ionic liquid and solutes. For all chosen solutes, alkanes, alkenes and alkynes showed relatively high values viz., decane (γ_{13}^{∞} = 66.65), decene (γ_{13}^{∞} = 29.94) at 313.15 K and heptyne (γ_{13}^{∞} = 4.81) at 343.15 K. The evaluated ionic liquid showed increased interactions with solutes as compared to previously published pyrrolidinium based ionic liquid, for decane (γ_{13}^{∞} = 195) at 298.15 K, (Singh et al., 2016) and n-nonane (γ_{13}^{∞} = 172) at 313.15 K (Cruickshank et al., 1996). A similar occurrence with these pyrrolidinium based ionic liquids was observed as the activity coefficients at infinite dilution decreases with an increase in temperatures for alkanes and alkenes, whilst an opposite trend was observed for alkynes.

The average γ_{13}^{∞} data obtained in this work with the column loading of 0.3003 mass fraction of the IL at a series of four temperatures (313.15 to 343.15) K are presented in table 5.7. In each class of investigated solutes, the γ_{13}^{∞} is directly proportional to the solute alkyl chain. The strength of higher interactions between the IL and solute is related to branched structure, multiple bonds, aromatic rings or cyclic structures. The sequence for γ_{13}^{∞} data is as follows: alcohols < ketones < aromatic hydrocarbons < alkynes < cycloalkenes < cycloalkanes < alkenes < alkanes. In the case of alkynes and alkenes, alkynes show stronger interactions via the triple bond as compared to the double bonds in alkenes. The interactions between the IL and aromatic compounds are due to the π-delocalized electrons and the γ_{13}^{∞} values are within the polar compounds. Methanol gave lower γ_{13}^{∞} values as compared to the other compounds (γ_{13}^{∞} = 0.443) at 343.15 K, and this effect may possibly be the consequence of interactions through dispersive interactions as well as hydrogen bonding formation by the short alkyl chain.

The following excess thermodynamic functions at infinite dilution ($\Delta H_1^{\mathrm{E}\infty}$, $\Delta S_1^{\mathrm{E},\infty}$and $\Delta G_1^{\mathrm{E},\infty}$) are related to activity coefficients at infinite dilution.

The obtained data is presented in table 5.8. The $T_{\mathrm{ref}}\Delta S_1^{\mathrm{E},\infty}$ values at reference temperature 323.15 K are negative for almost all the studied solutes, except for water and alkanes ($C \leq 8$). These negative values show that the solute molecules organize itself in the ionic liquid structure. The positive value for water implies breaking of hydrogen bonds throughout their dissolution process in the ionic liquid under investigation. Negative values for computed $\Delta H_1^{\mathrm{E},\infty}$ were observed for almost all the chosen solutes except for water, alkanes and alkenes. The negative values of $\Delta H_1^{\mathrm{E},\infty}$ obtained imply that the interactions are related to solute-solvent pairs. This type of behaviour is due to interactions among the polar anions of the ionic liquid and triple bonds in alkynes as well as polarisable π-electrons in thiophene and aromatic compounds. The positive value for water ($\Delta H_1^{\mathrm{E},\infty}$ = 8.61 kJ mol^{-1}), alkanes ($\Delta H_1^{\mathrm{E},\infty}$ = 3.54 to 10.63) kJ mol^{-1} and alkenes ($\Delta H_1^{\mathrm{E},\infty}$ = 1.08 to 3.38) kJ mol^{-1} can be explained as strong energetic interactions among the molecules of the IL and the particles of alkanes, alkenes or water. This implies that exothermic dissolution is due to the hydrogen bonds between the IL and water, alkanes or alkenes. The calculated $\Delta G_1^{\mathrm{E},\infty}$ values are positive except for alcohols, acetone thiophene and water. These solutes possessed low values of γ_{13}^{∞} which are less than one, and this can be elucidated as negative deviation from the Raoult's law. From figure 5.16 to 5.21, it can be ascertained that the $\ln \gamma_{13}^{\infty}$ values vary prominently with temperature for all the studied solutes.

Separation potential of 2,3-dihydroxypropyl-N-methyl-2-oxopyrrolidinium chloride:

The selectivity and capacity data for the chosen extraction problems are calculated at 328.15 K (interpolated values) and compared to the other ionic liquids in the literature: (heptane/1-heptyne, heptane/thiophene and heptane/benzene) are reported in table 5.9. The selectivity values for the chosen separation problems, ranges from (S_{ij}^{∞} = 5.61 to 24.94) and the capacity (K_j^{∞} = 0.23 to 1.05) at 328.15 K. The results obtained are also compared to the other ionic liquids, including pyrrolidinium based ionic liquids. In the IL [BMPYR] [SCN], the selectivity and capacity values for the same separation problems ranges between (S_{ij}^{∞} = 6.26 to 48.8) and the capacity (K_j^{∞} = 0.12 to 0.90) at 328.15 K (Domańska and Królikowska 2010). With previous ionic liquid [BMPYR] [CF_3SO_3] published earlier (Domańska et al., 2009), the selectivity for (heptane/thiophene, S_{ij}^{∞} = 50.2; heptane/benzene, S_{ij}^{∞} = 36.6; and heptane/heptyne, S_{ij}^{∞} = 9.91) with relative low capacity values (K_j^{∞} = 0.93; 0.68 and 0.18) respectively. Although the pyrrolidinium based ionic liquids published earlier (Domańska and Królikowska, 2010, Domańska et al., 2009), revealed high selectivity values as compared to the investigated ionic liquid in this work, the relatively large capacity values presented by [$(OH)_2$ C_3MPyr] [Cl] are useful. Morpholinium based ionic liquid [EMMor] [DCA] revealed better a separation, S_{ij}^{∞} = 13.9 at 328.15 K for the separation of heptane/heptyne as compared to pyrrolidinium based ionic liquids, but with lower capacity values (K_j^{∞} = 0.02) (Durski et al., 2018). This reducing effect most probably results from the additional n-π interaction coming from the electron pair on the oxygen atom with the triple bonds of 1-heptyne.

It is also important to outline the separation of hexane/hexene as description of paraffins and olefins with [$(OH)_2$ C_3MPyr] [Cl] ionic liquid. For hexane/hexene separation, S_{ij}^{∞} = 1.74, and capacity, K_j^{∞} = 0.10 at 323.15 K, and the ionic liquid [$(OH)_2$ C_3MPyr] [Cl] certainly presents a better separation mechanism. A better selectivity, S_{ij}^{∞} = 2.58 but lower capacity, K_j^{∞} = 0.046 (Domańska et al., 2009) was obtained with the ionic liquid [BMPYR] [CF_3SO_3] at 298.15 K.

Group 4: Evaluation of 1,3-dimethylimidazolium dimethylphosphate as a separation solvent for binary mixtures based on limiting activity coefficients data:

The activity coefficients data obtained with 0.303 by mass fraction of the ionic liquid in the column is presented in table 5.10. The peaks obtained by the g.l.c. were symmetrical and free of helium gas flow implying that no appreciable adsorption took place. This also implies sufficient ionic liquid on the column packing. The existing interactions at the vapour phase between solvent and solute can be elucidated by the values of γ_{13}^{∞}. The effect of temperature on the investigated solutes is also shown graphically (figures 5.22 – 5.28). The solubility of the ionic liquid can also be revealed by the γ_{13}^{∞} values. In this work, a decrease in solubility was revealed by almost all the examined solutes, except for water and alcohols and acetonitrile. A decrease in solubility results from lower interactions of solutes with the ionic liquid.

The imidazolium ionic liquid (1,3-dimethylimidazolium dimethylphosphate) results obtained show a decrease of intermolecular interactions with the solutes under investigation. The highest γ_{13}^{∞} values were revealed by non-polar solutes (alkanes) at 313.15 K, as decane (γ_{13}^{∞} = 4711.71). The lowest values observed was for water and alcohols at 343.15 K, as for methanol (γ_{13}^{∞} = 0.185). The highest solubility of (ionic liquid + water or alcohols) showed high intermolecular interaction. In addition, this impact resulted in different experimental temperatures for these solutes i.e. (343.15 – 373.15) K, with 10 K interval. The investigated ionic liquid showed enhanced solubility of these solutes and water. The γ_{13}^{∞} values were in the following order of solutes: water < alcohol < acetonitrile < thiophene < ketones < aromatic hydrocarbons < cyclic alkenes < cyclic alkanes < alkynes < alkenes < alkanes. The cyclic alkanes showed increased interactions as compared to their corresponding linear alkanes, and this results from an increased polarity possessed by cyclic alkanes. The presence of polarisable electrons contained in triple bonds of alkynes increased the molecular interactions with 1,3-dimethylimidazolium dimethylphosphate and resulted in lower γ_{13}^{∞} as compared to alkenes and alkanes. The smaller values for alcohols are the consequence of dipole-dipole interactions and hydrogen bonding between ionic liquid and solutes. For heterocyclics, the molecular interactions are due to delocalized π-electrons with positive sites of 1,3-dimethylimidazolium dimethylphosphate. Furthermore, the obtained activity coefficients at infinite dilution in this work using 0.303 by mass fraction of the ionic liquid are high as compared to the same ionic liquid with column loading of 35.98 % by mass percent, for example, benzene (γ_{13}^{∞} = 3.64) and toluene (γ_{13}^{∞} = 7.56) at T = 313.15 K (Ge et al., 2015). These γ_{13}^{∞} values are about four times smaller as compared to those obtained with 30.3 % of ionic liquid in this work, example for benzene (γ_{13}^{∞} = 15.69) and toluene (γ_{13}^{∞} = 30.36) at T = 313.15 K. This implies a reduced molecular interaction in smaller quantities of 1,3-dimethylimidazolium dimethylphosphate, and result in a better separation of volatile organic solutes.

The molecular interactions comprising solutes and ionic liquids can be further described by the following thermodynamic functions at infinite dilution ($\Delta H_1^{\mathrm{E}\infty}$, $\Delta S_1^{\mathrm{E},\infty}$and $\Delta G_1^{\mathrm{E},\infty}$), at T_{ref} = 323.15 K. The values for these physicochemical parameters are listed in table 5.11.

The limiting partial molar enthalpies are positive for non-polar solutes (alkanes, alkenes, alkynes) and acetonitrile. Alcohols, aromatic hydrocarbons, water, thiophene and ketones are characterized by negative values of $\Delta H_1^{\mathrm{E}\infty}$. The negative values are associated with strong arrangement of solutes on the ionic liquid structure. The breaking of hydrogen bonds in dissociation process was strongly influenced by the positive value of acetonitrile, ($\Delta H_1^{\mathrm{E}\infty}$ = 1.84 kJ mol^{-1}). Positive values of $\Delta G_1^{\mathrm{E},\infty}$ were observed for almost all the solutes except for water and alcohols. Negative values of $\Delta G_1^{\mathrm{E},\infty}$ were observed for alcohol and water (negative deviation from Raoult's law), eg, water ($\Delta G_1^{\mathrm{E},\infty}$ = -4.8 kJ mol^{-1}) at T = 363.15 K. The solutes with positive $\Delta G_1^{\mathrm{E},\infty}$ values showed relatively high γ_{13}^{∞} values of more than one (γ_{13}^{∞} > 1).

Separation potential of 1,3-dimethylimidazolium dimethylphosphate:

The following separation parameters form an important aspect for thermodynamic functions in separation technology. Capacity and selectivity at infinite dilution for (heptane/thiophene, heptane/benzene and heptane/heptyne) were computed.

Separation parameters (selectivity and capacity) for chosen extraction problems range between (S_{ij}^{∞} = 9.77 – 95.74) and low capacity values (K_{j}^{∞} = 0.02 – 0.2). The values for these separation parameters are listed in table 5.12 and in comparison, with the literature values. The investigated 1,3-dimethylimidazolium dimethylphosphate present low selectivity and capacity values for the separation of heptane/benzene (S_{ij}^{∞} = 37.84 and K_{j}^{∞} = 0.08) when compared to the other imidazolium ionic liquids, i.e. [EMIM] [DCA] (Mutelet et al., 2009), [BMIM] [DCA] (Domanska et al., 2016) and [BzMIM] [DCA] (Design institute of physical properties) with (S_{ij}^{∞} = 66.2; 44.7 and 59) and (K_{j}^{∞} = 0.3; 0.51 and 0.41), respectively. It is also important to highlight the high selectivity and capacity values obtained for the separation of azeotropic mixtures (THF/methanol) S_{ij}^{∞} = 73.94 and K_{j}^{∞} = 5.40 at T = 343.15 K. These results show a possible application of [MMIM] [DMP] in this separation. Table 5.12 also displays the separation of heptane/heptyne, the low selectivity and capacity values (S_{ij}^{∞} = 9.77 and K_{j}^{∞} = 0.02) compared to [DCA] anion (Domanska et al., 2016) are characterised by the additional n-n interaction from the electron pairs on the oxygen atom contained in [DMP] anion and triple bond of heptyne.

Group 5: Thermodynamic properties and activity coefficients at infinite dilution for different solutes in deep eutectic solvent: 1-butyl-3-methylimidazolium chloride + glycerol:

The experimental density and speed of sound for the prepared deep eutectic solvent were simultaneously measured with the use of the Anton Paar DSA 500 M at T = (298.15 –

313.15) K and at atmospheric pressure. The measured physical properties are listed in table 5.13.

The results of γ_{13}^{∞} for 33 solutes partitioning between carrier gas (He) and (1-butyl-3-methylimidazolium chloride + glycerol) as an extracting DES solvent were calculated from the retention data acquired by gas liquid chromatography, and the results are listed in table 5.14 at corresponding temperatures. The γ_{13}^{∞} values reveals that lower interactions occurred within the DES and investigated solutes. The investigated deep eutectic solvents better separate at low temperatures, for example, hexane (γ_{13}^{∞} = 175.92) at 313.15 K and (γ_{13}^{∞} = 95.03) at 343.15 K, except for tetrahydrofuran (γ_{13}^{∞} = 6.67) at 313.15 K and (γ_{13}^{∞} = 7.04) at 343.15 K. This also shows that an increase in temperature results in a reduced yield of an extraction. This effect can be associated to a decrease in viscosity and hence the mass transfer due to an increase in solubility at high temperatures. However, tetrahydrofuran showed an opposite trend from the rest of the investigated solutes. This impact might rise from the heterocyclic structure of the compound containing the oxygen. In addition, the polarity and a wide liquid range might also be the cause of the opposite trend.

The γ_{13}^{∞} data increase with an increase in the alkyl chain of solutes. The highest obtained γ_{13}^{∞} value is for decane (γ_{13}^{∞} = 2059.58) at 313.15 K. The strength of interactions between DES and solutes are facilitated by the aromatic ring, branched or cyclic structure or multiple bonding. In the case of alkynes, triple bond gave stronger interactions as compared to double bonds contained in alkenes. A better packing impact was observed for cyclic and branched structure as compared to linear alkanes due to a slight increase of polarity, and this consequently leads to a better solution with the DES. The investigated DES showed increased interaction as compared to the recently published ammonium based DES (tetramethylammonium chloride + glycerol) at a 1:2 molar ratios, eg, hexane (γ_{13}^{∞} = 314.98) at 343.15 K (Nkosi et al., 2018). The reduced extraction efficiency of the investigated DES can be associated with an increase of molar ratio (HBA to HBD). An increase of carbon atom chains which results from an increase in hydrogen bond donor which in turn reduces the effect of hydrogen bond interactions resulting from steric impact. The packing impact of solutes in DES can be affected by an increase of HBD, because the HBD wraps around the anion and gives higher active hydrogens which result in higher separation. Furthermore, an increase in the number of carbon chains result in higher immiscibility which results to reduced interactions between DES and solutes. The (tetramethylammonium chloride + glycerol) DES gives better separation at high temperatures as compared to the investigated DES that separates better at lower temperatures. The temperature dependence of activity coefficients at infinite dilution for the solutes is shown in figures (5.29 – 5.35).

Excess thermodynamic parameters ($\Delta H_1^{\mathrm{E}\infty}$, $\Delta S_1^{\mathrm{E},\infty}$ and $\Delta G_1^{\mathrm{E},\infty}$) calculated at infinite dilution can be used to discuss the types of interactions between the DES and solutes. The Van't Hoff relation was used to compute the values of entropies and enthalpies at infinite dilution.

Table 5.15 shows the calculated values for the excess thermodynamic properties at infinite dilution. Thermodynamic parameters listed in Table 5.15 reveals better information and understanding regarding interactions between investigated DES and solutes. Partial excess enthalpies are positive except for tetrahydrofuran. The negative value for THF ($\Delta H_1^{\mathrm{E},\infty} = -1.79\ \mathrm{kJ \cdot mol^{-1}}$) is associated with stronger energetic (solute-solvent) interactions in contrast to solute-solute interactions. In addition, this shows that the investigated DES exhibits strong hydrophilic properties with THF. The positive $\Delta H_1^{\mathrm{E},\infty}$ values indicate an exothermic dissolution through hydrogen bonds between DES and solutes characterised by positive values. For any process, the changes in entropy and enthalpy is related to the change in Gibbs free energy. When Gibbs free energy is below zero, there is a thermodynamic driving force for the process in the forward direction. The Gibbs free energies are characterised by positive values, and the highest values are observed for aliphatic hydrocarbons ($\Delta G_1^{\mathrm{E},\infty}$ = 20.3) for decane. These positive values suggest weak interactions with the investigated DES. The low values of polar compounds, for example methanol ($\Delta G_1^{\mathrm{E},\infty}$ = 0.302) confirm the formation of hydrogen bonds with the DES. The $\Delta S_1^{\mathrm{E},\infty}$ values are both positive and negative for the studied solutes. The negative values imply arrangements of solutes in the voids of DES, while positive values are associated with the breaking of hydrogen bonds.

Separation potential of deep eutectic solvent (1-butyl-3-methylimidazolium chloride + glycerol)*:*

The extraction capacity of the investigated DES can be determined by calculating extraction parameters (capacity and selectivity). These were determined at 313.15 K and compared to those found in literature. These separation parameters are important as they provide clear insight regarding specific extraction problems. Capacity and selectivity for extraction problems (hexane/benzene; cyclohexane/benzene; acetone/ethanol and cyclohexane/ethanol) were calculated.

High selectivity values were obtained for all the selected extraction problems, and relatively low capacity values ($\mathrm{k}_j^\infty < 1$) at T = 313.15 K. The number of equilibrium stages for a specific extraction can be determined from the selectivity values, while the volume of extraction solvent can be revealed by the capacity values. For the extraction problems selected in this work, the investigated DES shows that large quantities of 1-butyl-3-methylimidazolium chloride and glycerol would be required. The selectivity values for the investigated DES ranges between (S_{ij}^{∞} = 3.12 – 104.4) and capacity values (K_{j}^{∞} = 0.05 – 0.63). The investigated DES showed better selectivity values as compared to other investigated DES in the literature. For example, in tetramethylammonium chloride + glycerol at 1:2 molar ratio, selectivity values range between (S_{ij}^{∞} = 1.60 – 63.7) and capacity (K_{j}^{∞} = 0.02 – 0.31) (Nkosi et al., 2018), while in choline chloride + glycerol at 1:2 molar ratio, selectivity values are within (S_{ij}^{∞} = 3.05 – 121.6) and capacity (K_{j}^{∞} = 0.06 – 0.59) (Verevkin et al., 2015). For choline chloride + glycerol at 1:1 molar ratio, a significant change in selectivity values was observed (S_{ij}^{∞} = 2.46 – 98.12) and capacity between (K_{j}^{∞} = 0.04 – 0.48) (Verevkin et al., 2015). These were compared at T = 313.15 K. The examined DES also gives a better separation as compared to the currently used extraction solvents (sulfolane and NMP), for the same extraction problems, the selectivity values for sulfolane as a separation solvent range between (0.67 – 18.31) and capacity (K_{j}^{∞} = 0.32 – 0.42) (Mollmann and Gmehling, 1997), and NMP with selectivity (S_{ij}^{∞} = 9.07 – 16.08) and capacity for benzene (K_{j}^{∞} = 0.52) (Krummen and Gmehling, 2004) at T = 313.15 K. It is also worth to outline the influence of glycerol on [BMIM] [Cl] in DES as the investigated DES gave low selectivity values as compared to the ionic liquid with same cation but different anion [BMIM] [SCN] (S_{ij}^{∞} = 82.41) and capacity (K_{j}^{∞} = 0.46) for (hexane/benzene) at T = 313.15 K (Domanska and Marciniak, 2008). For the extraction of (cyclohexane/ethanol and acetone/ethanol), low selectivity and capacity values were observed (Domanska and Marciniak 2008). A similar occurrence was also observed for the ionic liquid [BMIM] [SbF_6] (Olivier et al., 2011).

Group 6: Rapid measurement of activity co-efficient at infinite dilution of organic solvent using novel ionic liquid 2′,3′-epoxypropyl-N-methyl-2-oxopyrrolidinium chloride by GLC.

Three different concentrations of N-(2′, 3′-epoxypropyl)-N-methyl-2-oxopyrrolidinium chloride ionic liquid, namely, 20, 30 and 40 % were prepared. At 40 % coating of ionic liquid on the chromosorb resulted in a surface which appeared to be a sticky semi solid. Thus, it was not suitable for preparing an IL - coated column. Therefore, 20 % and 30 % of ionic liquid were used to make two columns separately. These were used to investigate the activity coefficients for 33 organic solutes and water at four different temperatures. However, it was found that there were large deviations in data obtained from the two coated columns. In comparing the results for both 20 % and 30 %, it was found that the 30% coated column results were generally higher, than that for 20% coated column. These observations suggest that at 20 % of ionic liquid, the coverage of the chromosorb by the ionic liquid is not optimal. In the light of this, the data from 20% coated was omitted. The measured retention time was directly proportional to the magnitude of the interaction between solute and IL.

The highest value of limiting activity coefficients at infinite dilution (2423) was obtained at T = 343.15 K for alkanes, with n-decane as a solute. Lowest values of the activity coefficients were observed for ketones, namely, cyclopentanone and cyclohexanone as (γ_{13}^{∞} = 23.57 and 66.44), respectively. This implies that these solutes interact strongly with the investigated IL in comparison with other solutes. These strong intermolecular interactions were observed between polar solutes with polar anion of IL. For non-polar solutes, it was found that, the activity coefficient values for alkenes are (γ_{13}^{∞} = 24.13 to 1810.34) K, and for alkanes are (γ_{13}^{∞} = 24.96 to 254423) at T = (313.15 to 343.15) K, respectively. Furthermore, an opposite trend (γ_{13}^{∞} values decreases with an increase in temperatures) and this was observed for the following solutes, namely, acetone, dichloromethane and isopropyl methyl ketone. The interactions between the solute and anion of IL is attributed to the presence of the non-aromatic ring as well an epoxy group in this pyrrolidinium-based IL. H-bonds play an important role in the interactions of IL with alcohol. However, it was noted that acetonitrile also interacts via H-bond as well as through n-p orbital interactions with the epoxy functional group of the IL. Low activity coefficient values of alcohols are believed to be responsible for the formation of new H-bonds between alcohol and IL, and the existing self-associated H-bonds in alcohol molecules are broken. The double bonds of respective alkenes specifically interacted with polar anion of the IL, resulting in lower activity coefficient values. However, the same number of carbon atoms contained in alkanes were found to have higher values than the corresponding alkenes. It is noted that the n-n interactions occurred between the anion of the IL with the alkane or alkene. It is evident that the magnitude of activity coefficients play an important role in the separation of aliphatic from aromatics. The values of aromatic compounds namely benzene, m-xylene, p-xylene and o-xylene are (γ_{13}^{∞} = 202.92, 770.58, 599.01 and 562.05) at T = 343.15, respectively. A complex is formed between the double bond of an aromatic compounds and a lone pair of electrons on the Cl^- anion of the IL. In this complex, there is a potential for n-π interactions which will result in stronger binding between IL and aromatics than for other compounds, which do not have aromatic character. The multiple lone pair of electrons on the chloride anion is suggested as the reason for the H-bond basicity of [EPMpyr][Cl] IL.

During interaction of solute with IL, the effects of exothermic and endothermic properties were evident. Figures (5.36 – 5.41) shows the results for the plots of ln γ_{13}^{∞} as a function of the inverse absolute temperature using 30 % loading of the IL for all the solutes, which were selected for this study. The results show that the values for alkanes, alkenes and aromatics increase with increasing temperatures while the converse was observed for THF, acetone as well as isopropyl methyl ketone. The same type of dependence is shown by methanol whereas other chosen alcohols show weak dependence on temperature. Based on the chain length of the alkanes, ethers display both types of interactions. The behaviour of ketones is like those of aromatic hydrocarbons. In general, the effect of temperature is not significant for most of the solutes except for alkanes. In addition to the usefulness of what has been mentioned above, from the experimental values of γ_{13}^{∞} limiting partial molar enthalpies of organic solutes in IL at investigated temperatures were computed. The increasing order for organic solutes is: alkanes > cycloalkanes > alkenes > aromatic hydrocarbons. Stronger interactions were observed between solute and solvent pairs as well as between solute and solute for polar compounds (excluding water and higher alcohols), namely, aromatic hydrocarbons. This is attributed to negative values. These negative values may be ascribed to relatively strong solute-solvent interactions. The substituents of the epoxy group and chlorine anion exhibit strong hydrophobic properties which leads to these strong interactions of IL with various organic solutes. Gibb's free energies and entropies of organic solutes are shown in Table 5.18. It was also observed that the Gibb's free energies of higher alkanes and aromatic hydrocarbons have higher values; strong H-bonding between IL and solutes. Relatively low values of Gibb's free energy were observed for dichloromethane, cyclopentanone, cyclohexane, cyclohexene, tetrahydrofuran, acetone and ether. All organic solutes gave high entropy values, except for 1-hexene, cyclohexene and benzene. This is taken to imply that there are strong H-bonds between organic solutes and IL. Additionally, tetrahydrofuran and acetone gave negative entropy values. This suggests that there are strong interactions between these solutes and IL. The partial excess molar entropies of all solutes are positive except for THF and acetone; the negative entropy may suggest that the solute molecule arrange itself in the structure of IL.

Separation potential of 2′,3′-epoxypropyl-N-methyl-2-oxopyrrolidinium chloride ionic liquid:

Many separation problems were overcome using the selectivity data which is derived from activity coefficients at infinite dilution. For developing several extraction processes, the separation factor at infinite dilution needs to be known (Wlazlo et al., 2012). Therefore, the data from the interaction of IL with organic solutes is very useful for extraction of various materials using ILs as solvents. The selectivity and capacity values in contrast to those found in the literature are listed in Table 5.19. The ionic liquid [EPPYR] [Cl] revealed low selectivity and capacity values for the separation of (heptane/benzene; heptane/thiophene and water/butanol) compared to those found in the literature. The selectivity values for the chosen separation processes ranges between (S_{ij}^{∞} = 0.220 – 5.97) and capacity data between (K_j^{∞} = 0.006 – 0.20). Even though the calculated separation parameters show that the investigated ionic liquid cannot be used for the extraction of these mixtures, but the activity coefficients values indicate a hydrophobic character of the ionic liquid as water gave an activity coefficient value of 35.27 at T = 323.15 K. The capacity values obtained for these separation problems shows that large quantities of [EPPYR] [Cl] would be required for the extraction as the capacity values are less than one and this impact does not favour the separation process. This effect also indicates that this variation could be due to the differences of polarities of organic solutes.

6.2. Liquid-liquid equilibria

This section discusses the possible extraction of azeotropic mixture and desulfurization using liquid-liquid extraction.

Group 7: Separation of azeotropic mixture (ethyl acetate + hexane) using 1-ethyl-3-methylimidazolium tetrafluoroborate and 1-ethyl-3-methylimidazolium dicyanamide:

In binary systems comprising [IL (1) + ethyl acetate (3)], the solubility of ethyl acetate in [EMIM][DCA] and [EMIM][BF_4] is up to the mole fraction of ethyl acetate, x_3^{IL} = 0.949 and x_3^{IL} = 0.996, respectively. It was expected that the solubility of hexane should be very low in the investigated ionic liquids as x_2^{IL} = 0.007 in [EMIM][BF_4] and x_2^{IL} = 0.042 in [EMIM][DCA]. Figures 5.43 and 5.44 shows the ternary diagrams with the experimental tie-lines for the three component systems. The relative solubility of ethyl acetate in [EMIM]

[BF_4] or [EMIM] [DCA] is evident from the tie-lines. The gradient of the tie-lines obtained in this work show that ethyl acetate is more soluble in [EMIM] [BF_4] than the hexane mixture. A similar effect is noted for the ternary system {[EMIM] [DCA] (1) + hexane (2) + ethyl acetate (3)}. The size of difference in miscibility can also be observed in the figures, including the slopes of the tie-lines. The positive slope implies that the solute (ethyl acetate) is located in the solvent rich phase. Thermophysical properties such as viscosity and density are important to design a separation process using ionic liquids. The density and viscosity of [EMIM][BF_4] previously measured in the laboratory was found to be 1.2806 g $\cdot$ cm^{-3} and 41.01 mPa $\cdot$ s at T = 298.15 K (Kabane et al., 2018) and for [EMIM][DCA] was 1.1019 g $\cdot$ cm^{-3} and 14.90 mPa $\cdot$ s at T = 298.15 K (Quijada-Maldonado et al., 2012).

Analysis of [EMIM][BF_4] and [EMIM][DCA] as an extracting solvent:

The values of selectivity (S) and distribution ratio (β) are also shown in Table 5.20.

The amount of solvent required for an extraction process can be inferred by the β values, whilst selectivity implies the selectivity of the separating solvent towards the solute to be separated. The selectivities obtained using two selected ionic liquids in this work is promising for future separation of ethyl acetate from hexane. Better selectivity and distribution ratios were observed with ionic liquid containing the [DCA] anion at low concentrations of ethyl acetate. For the other range, [EMIM][BF4] revealed higher selectivities. This effect is due to the higher viscosity and bulky anion which cause the steric effects compared to [EMIM][DCA]. Furthermore, the DCA anion interacted more strongly (additional $\pi - \pi$ interactions in addition to electrostatic interactions). Many studies revealed that ionic liquids containing [DCA] anion give high selectivity values (Durski et al., 2019, Domańska et al., 2019). However, this cannot be concluded as there is a need for liquid-liquid equilibrium studies involving ionic liquids. Both investigated ionic liquids showed high selectivities and distribution ratios when compared to ionic liquids found in the literature measured at the same temperature. The extraction process is also driven by the net transfer from one liquid into another liquid phase, generally from hydrocarbon (HC)-rich phase to IL-rich phase. This transfer is given by the chemical potential, i.e. once the transfer is complete, the overall system of the chemical components that makes up to solutes and the solvent are in a more stable configuration (lower free energy). The physical and chemical interactions of a solute is capable of changing its apparent partition coefficient. In this regard, ethyl acetate makes stronger interactions with the investigated ionic liquids as compared to hexane.

With respect to recently published work in the literature on ionic liquids for the separation of ethyl acetate from hexane, the following results were reported at T = 298.15 K: In [HMIM][PF_6] selectivity of (S = 186.19) and distribution ratio (β = 3.66); [OMIM][PF_6] (S = 83.29) and (β = 7.45) (Pereiro et al., 2008), in ionic liquid [HMIM][BF_4] selectivity (S = 20.51) and (β = 0.922) and in ionic liquid [OMIM][BF_4] (S = 10.75) and (β = 1.493) (Wen et al., 2018). Values for deep eutectic solvent comprising (choline chloride + lactic acid) at (2 : 1) molar ratio, selectivity (S = 133.69) and distribution ratio (β = 0.170) (Gonzalez et al., 2013). The presented selectivities and distribution ratios from the literature are the maximum values obtained from tie-lines of ternary systems. It is not surprising therefore that [EMIM][BF_4] gave high separation parameters as compared to [HMIM][BF_4] and [OMIM][BF_4], this effect is certainly due to the extended carbon alkyl chain from 2 (this work) to 6 or 8. In deep eutectic solvents, the effect is due to the ratio of HBA – HBD which affects the yield of an extract. There is also no doubt that the [DCA] anion has a huge impact. The investigated ionic liquids better separate at lower concentrations of ethyl acetate.

Summary of results (S_{av} and β_{av}) from previously published related literature using ionic liquids for liquid-liquid equilibrium data for the separation of azeotropic mixture (hexane + ethyl acetate) are shown in Table 5.21 and also presented in the Figures (6.2 and 6.3) as a mole fraction of ethyl acetate at IL-rich phase.

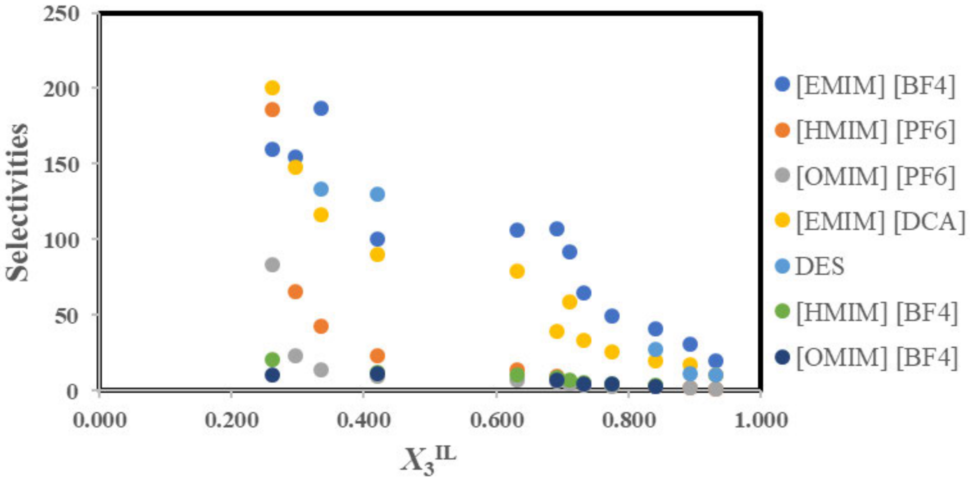


Figure 6.2: Comparison of selectivities (S) for the ternary mixture of {[EMIM][BF$_4$] or [EMIM][DCA] (1) + hexane (2) + ethyl acetate (3)} as a function of mole fraction of ethyl acetate at IL-rich phase with other ionic liquids from the literature for the separation of (hexane + ethyl acetate). (Pereiro and Rogriguez, 2008, Gonzalez et al., 2013, Wen et al., 2018)

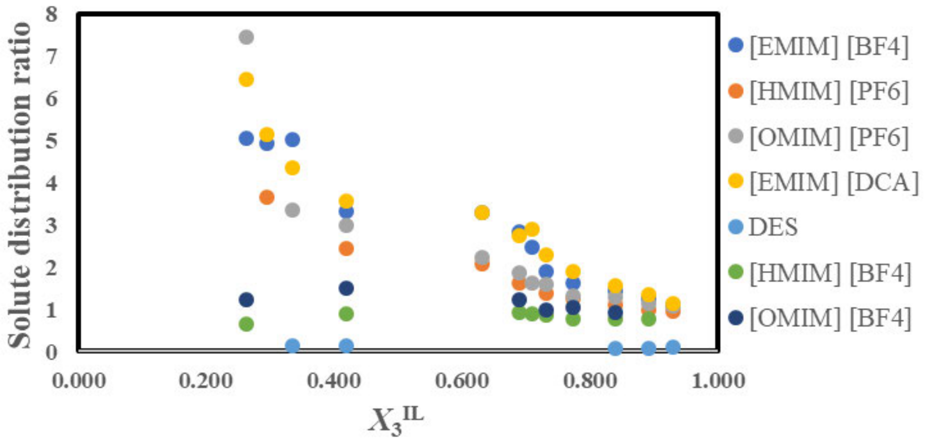


Figure 6.3: Comparison of solute distribution ratios (β) for the ternary mixture of {[EMIM][BF_4] or [EMIM][DCA] (1) + hexane (2) + ethyl acetate (3)} as a function of mole fraction of ethyl acetate at IL-rich phase with other ionic liquids from the literature for the separation of (hexane + ethyl acetate). (Pereiro and Rogriguez, 2008, Gonzalez et al., 2013, Wen et al., 2018)

Group 8: Desulfurization utilizing 1,3-dimethylimidazolium dimethylphosphate, and 1-ethyl-3-methylimidazolium tetrafluoroborate:

The phase equilibrium data for the four ternary systems studied: {[MMIM] [DMP] or [EMIM] [BF_4] (1) + thiophene (2) + hexadecane or octane (3)} measured at T = 308.15 K and at atmospheric pressure are listed in Table 5.22 and 5.23. Figures (5.45 – 5.48) shows the corresponding triangular diagrams with the experimental tie-lines. The investigated ionic liquids were not observed through the analysis of the upper phase (hydrocarbon-rich phase). Besides, a small amount of ionic liquid may be present in the hydrocarbon-rich phase. Furthermore, for this analysis, the amount of ionic liquid is too small. Nevertheless, this is an added advantage in using ionic liquids and for industrial applications, this effect also results in a less cost procedure of extraction and solvent recovery.

In binary systems involving [IL (1) + hexadecane (3)], the solubility of hexadecane in ionic liquid was observed from mole fraction x_3^{IL} = 0.0031 and x_3^{IL} = 0.0013 for [EMIM][BF_4] and [MMIM][DMP], respectively. The complete solubility up to the mole fraction of octane was observed from x_3^{IL} = 0.0016 and x_3^{IL} = 0.0023 for [EMIM][BF_4] and [MMIM][DMP], respectively. In the ionic liquid [HMIM][SCN], the solubility of octane in the ionic liquid was x_3^{IL} = 0.019 (Mafi et at., 2016). For the sake of comparison with the other ionic liquids [BMIM][OTf] and [OHOHIM][NTf_2], the solubility of octane in the IL was x_3^{IL} = 0.025 and x_3^{IL} = 0.008, respectively, as well as up to the mole fraction of hexadecane, x_3^{IL} = 0.004, and

x_3^{IL} = 0.019 for the [OHOHIM][NTf$_2$] and [BMIM][OTf], respectively (Durski et al., 2019). In ionic liquid [MMIM][DMP], the complete solubility of octane in the ionic liquid derived from the activity coefficients values was approximately x_3^{IL} = 0.0016 which is 1.4 times less as compared to the one measured in this work, and at T = 303.15 K (Kato and Gmehling, 2004) and at T = 343.15 K was approximately x_3^{IL} = 0.0032 (Ge et al., 2015) which is 1.3 times more compared to the solubility of octane measured in this work. The observed deviation is due to the different temperature measurements (303.15 and 343.15) K compared to 308.15 K in this study. This deviation can also be influenced by the different techniques applied for determining the solubility of the octane in the ionic liquid. The extract (thiophene) is expected to be soluble in ionic liquid, and the observed mole fraction x_2^{IL} = 0.609 and x_2^{IL} = 0.874 for [EMIM][BF$_4$] and [MMIM][DMP], respectively. In ionic liquids [BMIM][OTf] and [OHOHIM][NTf$_2$], the solubility of thiophene in the IL was x_2^{IL} = 0.472 and x_2^{IL} = 0.828, respectively (Durski et al., 2019). In addition, the solubility of thiophene in ionic liquid [HMIM][SCN] measured at T = 308.15 K was x_2^{IL} = 0.807 (Mafi et al., 2016). The relative high solubility of thiophene in [EMIM][BF$_4$] or [MMIM][DMP] is evident from the tie lines. The gradient of the tie lines obtained in this work shows that thiophene is more soluble in [EMIM][BF$_4$] than octane or hexadecane mixture. A similar impact is noted for the other ternary mixture {[MMIM][DMP] (1) + thiophene (2) + octane or hexadecane (3)}. Thermophysical properties such as viscosity and density are important to design a separation process using ionic liquids. The density and viscosity of [EMIM][BF$_4$] previously measured in the laboratory was found to 1.2806 g · cm^{-3} and 41.01 mPa · s at T = 298.15 K (Kabane et al., 2018) and for [MMIM][DMP] was 1.2613 g · cm^{-3} and 290.8 mPa · s at T = 298.15 K (Zhang et al., 2014).

Analysis of [EMIM][BF$_4$] and [MMIM][DMP] as an extracting solvent:

The amount of solvent required for a specific extraction is revealed by the distribution ratio, while the selectivity towards the solute in an extraction is determined by the selectivity values. The separation parameters displayed that the investigated ionic liquids are satisfactory for extractive-desulfurization. Table 5.24 and 5.25 also shows that the ionic liquids under investigation better separates at low concentration of thiophene. This impact has been observed in previously published work using ionic liquids (Durski et al., 2019, Królikowski and Lipinska, 2019). High selectivity values imply less interactions of the ionic liquid. This also shows complete immiscibility of aliphatic hydrocarbons in the ionic liquids under investigation. High distribution coefficients values imply lower operating cost and lower solvent to feed ratio. For both ionic liquids, the distribution is below unity ($1 < \beta$).

Table 5.2.6 shows a summary of results from previously published related literature using ionic liquids for liquid-liquid equilibrium data with sulphur compounds. For the investigated ionic liquids, better results were observed in the measured ternary system {[EMIM] [BF_4] (1) + thiophene (2) + hexadecane (3)} with (S_{av} = 59. 39) and higher average distribution ratio (β_{av} = 1.81) compared to those found in the literature. In ionic liquids [EMIM] [$EtSO_4$] and [EMIM] [$MeSO_4$], average selectivity and distribution ratio obtained are (S_{av} = 50.5 and 56.3) and (β_{av} = 0.82 and 1.09) at T = 298.15 K, respectively (Ramalingam and Balaji, 2015). These results show the influence of temperature and anion in the ionic liquids. For the ternary systems {[EMIM] [BF_4] (1) + thiophene (2) + octane (3)}, low average selectivity was observed, but high as compared to the phosphonium based ionic liquid with (S_{av} = 12.38) and (β_{av} = 1.27) at T = 308.15 K (Durski et al., 2020). Relatively high distribution ratio observed in phosphonium based ionic liquid is not surprising as they are characterized by high molecular weight which gives high capacity to hold solvents in extraction process. It is also worth mentioning the influence of long alkyl chain of ionic liquids and temperature on LLE. Average selectivity and distribution ratio showed by [EMIM] [BF_4] are almost 9 and 3 times higher as compared to [C_8MIM] [BF_4] measured at T = 298.15 K, respectively (Alonso et al., 2008). 1-ethyl-3-methylimidazolium tetrafluoroborate showed better results as compared to 1,3-dimethylimidazolium dimethylphosphate for both measured systems at T = 308.15 K and at p = 101 kPa. The results for selectivities and solute distribution ratio in comparison with literature data are also summarized in Figures (6.4 – 6.7).

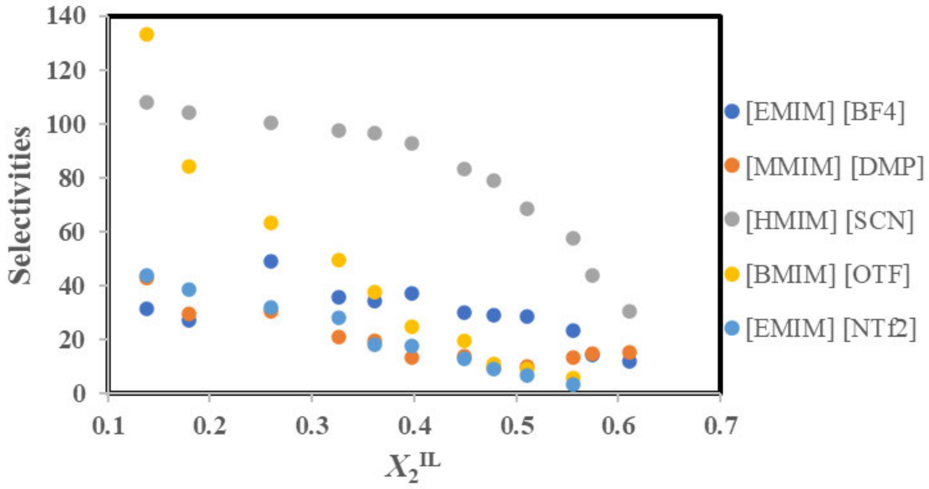


Figure 6.4: Comparison of selectivities (*S*) for ternary mixtures of {[EMIM][BF_4] or [MMIM][DMP] (1) + thiophene (2) + octane (3)} as a function of mole fraction of thiophene at IL-rich phase with other ionic liquids from the literature for desulfurization. (Mafi et al., 2016, Rodrguez-Cabo et al., 2013, Durski et al., 2020)

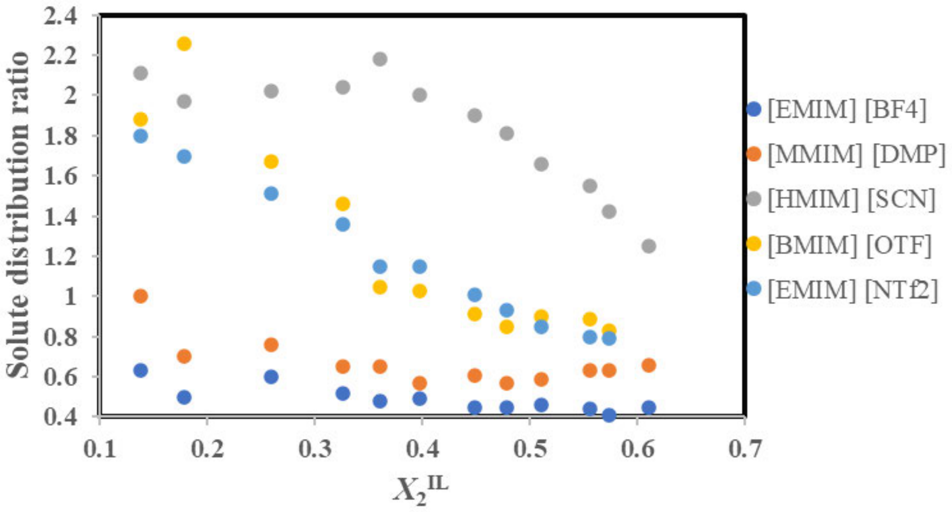


Figure 6.5: Comparison of solute distribution ratio (β) for ternary mixtures of {[EMIM][BF_4] or [MMIM][DMP] (1) + thiophene (2) + octane (3)} as a function of mole fraction of thiophene at IL-rich phase with other ionic liquids from the literature for desulfurization. (Mafi et al., 2016, Rodrguez-Cabo et al., 2013, Durski et al., 2020)

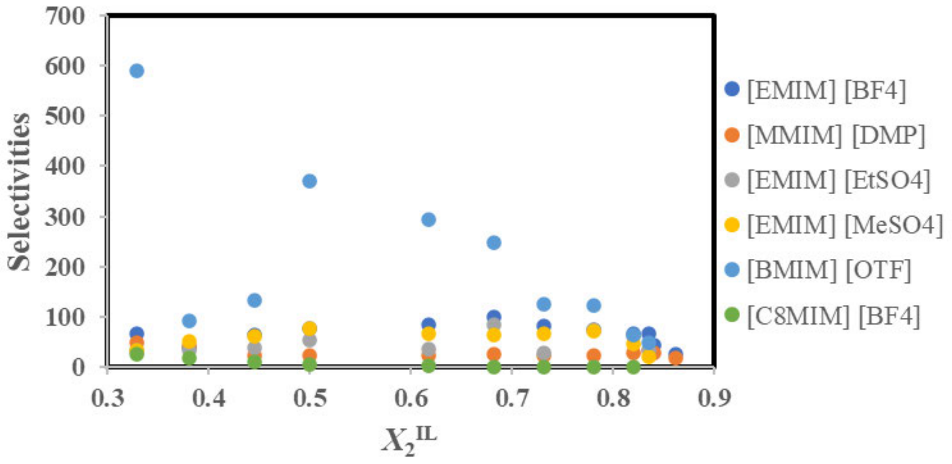


Figure 6.6: Comparison of selectivities (*S*) for ternary mixtures of {[EMIM][BF$_4$] or [MMIM][DMP] (1) + thiophene (2) + hexadecane (3)} as a function of mole fraction of thiophene at IL-rich phase with other ionic liquids from the literature for desulfurization. (Alonso et al., 2008, Ramalingam and Balaji, 2015, Durski et al., 2020)

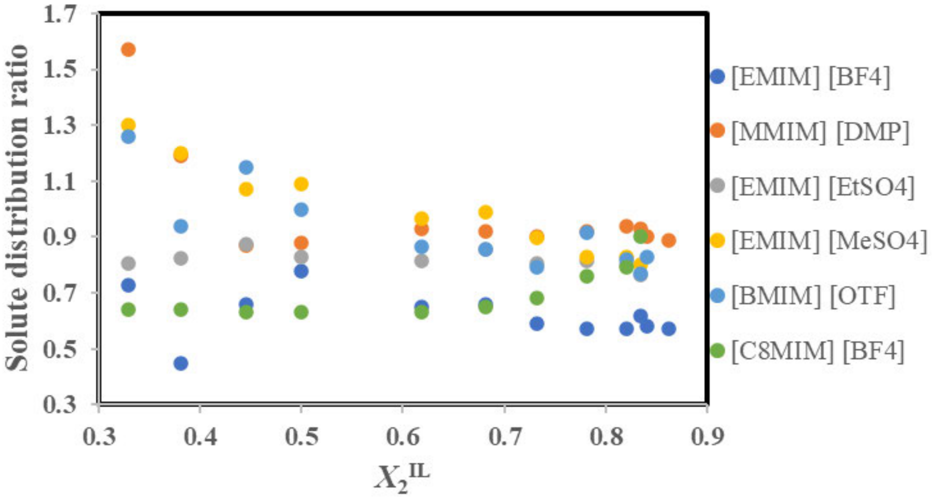


Figure 6.7: Comparison of solute distribution ratio (β) for ternary mixtures of {[EMIM][BF$_4$] or [MMIM][DMP] (1) + thiophene (2) + hexadecane (3)} as a function of mole fraction of thiophene at IL-rich phase with other ionic liquids from the literature for desulfurization. (Alonso et al., 2008, Ramalingam and Balaji, 2015, Durski et al., 2020)

Chapter 7

Conclusions

One of the main objectives of this research work were to conduct the experimental analysis to investigate the separation potential, intermolecular interactions and the effect of temperature and anion on ionic liquid mixtures with volatile organic solvents. The intermolecular interactions were further described by computing thermodynamic properties at infinite dilution (enthalpies, entropies, and Gibbs free energy). The pre-screening of selected ionic liquids for extraction was based on the activity coefficients at infinite dilution of organic solutes. In addition, separation of azeotropic mixture (hexane + ethyl acetate) and desulfurization (thiophene + octane or hexadecane) were also assessed using ionic liquids at temperature, T = 298.15 K and 308.15 K, respectively. The separation problems discussed in this work were based on the selectivities, capacities or distribution ratios.

Five ionic liquids and one deep eutectic solvent were determined in pre-screening for possible industrial application in extraction processes. These extracting solvents includes:

- 1,3-dimethylimidazolium dimethyphosphate [MMIM] [DMP]
- Trioctylmethylammonium chloride [N $_{8881}$] [Cl]
- Trihexyltetradecylphosphonium dicyanamide [P $_{666\,14}$] [DCA]
- 2,3-dihydroxypropyl-*N*-methyl-2-oxopyrrolidinium chloride [$(OH)_2$ C_3MPYR] [Cl]
- 2,3-epoxypropyl methyl-2-oxopyrrolidinium chloride [EPMpyr] [Cl]
- Deep eutectic solvent (DES) (1-butyl-3-methylimidazolium chloride + glycerol)

Furthermore, three different ionic liquids were investigated through liquid-liquid extraction of (hexane/ethyl acetate) and (thiophene/octane or hexadecane). These ionic liquids include:

- 1-ethyl-3-methylimidazolium tetrafluoroborate [EMIM] [BF_4]
- 1-ethyl-3-methylimidazolium dicyanamide [EMIM] [DCA]
- 1,3-dimethylimidazolium dimethylphosphate [MMIM] [DMP]

Some of the important industrial separation processes chosen were the following:

Heptane/benzene: selectivity and capacity values were calculated for heptane/benzene as a description of petrochemical extraction problems. The order of separating potential using the investigated extracting solvents based on selectivities were as follows: [MMIM] [DMP] > DES > [$(OH)_2$ C_3MPyr] [Cl] > [EPMpyr] [Cl] > [N $_{8881}$] [Cl] > [P $_{666\,14}$] [DCA].

The capacity trends for the investigated ionic liquids are as follows: [N $_{8881}$] [Cl] > [P $_{666\ 14}$] [DCA] > [(OH)$_2$ C$_3$MPyr] [Cl] > [MMIM] [DMP] > DES > [EPMpyr] [Cl].

Heptane/thiophene: For this industrial extraction problem, the investigated ionic liquids revealed promising results. The order of weak intermolecular energy was as follows: [MMIM] [DMP] > DES > [(OH)$_2$ C$_3$MPyr] [Cl] > [N $_{8881}$] [Cl] > [P $_{666\ 14}$] [DCA] > [EPMpyr] [Cl].

The capacity was as follows: [N $_{8881}$] [Cl] > [P $_{666\ 14}$] [DCA] > [(OH)$_2$ C$_3$MPyr] [Cl] > [MMIM] [DMP] > DES > [EPMpyr] [Cl].

The other interesting separation problems are discussed in Chapter 6. For the two separation problems (heptane/benzene) and (heptane/thiophene), the ionic liquid [MMIM] [DMP] is highly selective towards the petrochemical separation problems. Moreover, large quantities of separating agent would be required when using [EPMpyr] [Cl] ionic liquid as a separating solvent for (heptane/benzene or heptane/thiophene), and this effect can disadvantage this ionic liquid for these separations. The effect of anion is also observed as the Cl anion have the lone pairs of electrons which contributes towards the interactions. In DES, the selection for extraction processes can be affected by various factors, which include ratio of HBA – HBD and the extraction temperatures which can then affect the yield.

Ionic liquids (1-ethyl-3-methylimidazolium tetrafluoroborate and 1-ethyl-3-methylimidazolium dicyanamide) were investigated in the separation of azeotropic mixture (hexane + ethyl acetate) at T = 298.15 K. Better average selectivity value was observed in the ionic liquid containing [BF$_4$] anion with similar distribution ratios. This shows the hydrophobic character brought by the anion in the alky chain of the ionic liquid compared to [DCA] anion.

In desulfurization (thiophene/octane or hexadecane) as a description of model fuels, ionic liquids (1-ethyl-3-methylimidazolium tetrafluoroborate and 1,3-dimethylimidazolium dimethylphosphate) were investigated at temperature, T = 308.15 K and at atmospheric pressure. The optimum extraction efficiency was obtained for deep desulfurization of liquid fuels (for the low sulphur concentration in the feed). The average selectivity (S_{av} = 59.4) especially for [EMIM][BF_4] show some possible application for the separation of thiophene from hexadecane. The liquid-liquid equilibria data provided good correlation using the non-random two liquid equation.

In concluding, the data concerning liquid-liquid extraction is required to make an appropriate conclusion regarding the employment of ionic liquids for industrial separation problems. In addition, the data concerning DES is also required as it is easy and cheap to prepare compared to the ionic liquids, but the measurements and calculations comprising deep eutectic solvents binary mixtures need to be carefully determined to avoid incorrect data in the literature. From the experimental data presented in study, the selected and investigated ionic liquids could be used in refineries to improve the separation and efficiency.

Chapter 8

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