Thermodynamic properties of phosphonium-based ionic liquid mixtures at different temperatures

by

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Preface

I, Kabane Bakusele, declare that:

(i) The research work reported in this thesis, besides where indicated, is my original work.

(ii) This work has not been submitted for any examination or degree at any other university.

(iii) This work does not contain other person's data, graphs or information, unless specifically stated.

Signed: 

Bakusele Kabane Date: 16/08/2018

Signed 

Prof. G. G. Redhi (Supervisor) Date: 16/08/2018

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Abstract

Ionic Liquids (ILs) are relatively newly formed types of solvents. As part of ongoing research, research groups and industries are focusing on solvents classified as ionic liquids, which have a low melting point, and they have been given great attention focusing on their thermophysical properties and applications. In order to utilize or industrially exploit these types of solvents, the understanding of intermolecular interactions and properties of pure liquids and their mixtures is important. Thermophysical properties of ionic liquid mixtures, especially density, viscosity and speed of sound are measured as a function of temperature. Accurate analysis on thermophysical properties of ionic liquids is more of paramount interest as they indicate the transformation of ionic liquids from small laboratory level to large-scale industrial implementation.

In this study, new data for the binary mixtures containing {trihexyltetradecylphosphonium chloride ($[P^{+}_{14,\,6,\,6,\,6}]$ $[Cl^{-}]$) IL and propanoic acid (PA)} and {1-ethyl-3-methylimidazolium tetrafluoroborate ([Emim][BF_4]) + benzaldehyde or ethyl acetoacetate} were investigated under atmospheric pressure (p equivalent to 0.1 MPa) and at temperatures (293.15 to 313.15) K. Densities (ρ), viscosities (η) as well as speeds of sound (u) were measured over the whole range of mole fraction (x_i = 0 to 1). The computed excess properties which includes excess molar volumes ($V_{\mathrm{m}}^{\mathrm{E}}$), apparent molar volume (V_ϕ), intermolecular free length (L_f), isentropic compressibility(k_s), deviations in viscosity ($\Delta\eta$), apparent molar isentropic compressibility (K_ϕ) and deviation in isentropic compressibility (Δk_s) were computed from the experimentally determined data of densities, viscosities and speeds of sound. In addition, measurements of activity coefficients at infinite dilution for volatile organic compounds (alkenes, alcohols, alkanes, cycloalkanes, aromatic hydrocarbons, thiophene, ketones, acetonitrile, water and tetrahydrofuran) in the IL [trihexyltetradecylphosphonium-bis-(2, 4, 4-trimethylpentyl)-phosphinate and trihexyltetradecylphosphonium chloride] were conducted at different temperatures.

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A_i	=	polynomial coefficient.
M_1	=	molar mass of organic solvent ($g \cdot mol^{-1}$).
M_2	=	molar mass of ionic liquid ($g \cdot mol^{-1}$).
σ	=	standard deviation.
x_1	=	mole fraction of the 1st component.
x_2	=	mole fraction of the 2nd component.
T	=	temperature (K).
$V_{m,1}^{E}$	=	molar volume of the first component ($cm^3 \cdot mol^{-1}$).
V_m	=	molar volume ($cm^3 \cdot mol^{-1}$).
V_m^{E}	=	excess molar volume ($cm^3 \cdot mol^{-1}$).
$V_{m,1}^{*}$	=	molar volume of the pure IL ($cm^3 \cdot mol^{-1}$).
$V_{m,2}^{*}$	=	molar volume of the pure organic solvent ($cm^3 \cdot mol^{-1}$).
ρ	=	density ($g \cdot cm^{-3}$).
k	=	polynomial degree.
n	=	number of experimental points.
u	=	speed of sound ($m \cdot s^{-1}$).
k_s	=	isentropic compressibility (Pa^{-1}).
Δk_s	=	deviation in isentropic compressibility (Pa^{-1}).
L_f	=	intermolecular free length (m).
η	=	viscosity (mPa · s).
$\Delta\eta$	=	deviation in viscosity (mPa · s).
p	=	atmospheric pressure (MPa).
m	=	molality (mol/kg).
V_ϕ	=	apparent molar volume ($m^3 \cdot mol^{-1}$).
K_ϕ	=	apparent molar isentropic compressibility ($m^3 \cdot mol^{-1} \cdot Pa^{-1}$).
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 (cm^3 min)

P_o = outlet pressure (kPa).

P_1^* = saturated vapour pressure of the solute.

B_{11} = second virial coefficient of pure solute (cm^3 · mol^{-1}).

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

V_1^* = molar volume of the solute (cm^3 · mol^{-1}).

V_1^{∞} = partial molar volume of solute at infinite dilution in the solvent (cm^3 · mol^{-1}).

A = solute peak area detected by gas chromatography (mV · min).

a = slope (min^{-1}).

D = pure carrier gas flow rate (cm^3 · min^{-1}).

R_b = radius of bubbles (cm).

T_b = boiling point temperature (K).

Z = compressibility factor.

ω = acentric factor.

ϕ = volume fraction

Abbreviations

PA	=	propanoic acid.
EAA	=	ethyl acetoacetate.
ILs	=	ionic liquids.
VOS	=	volatile organic solvent.
GC	=	gas chromatography.
PFP	=	Prigogine-Flory-Patterson.
SLE	=	solid-liquid extraction.
THF	=	tetrahydrofuran
IDAC	=	infinite dilution activity coefficient

Cations

$[P_{14,\ 6,\ 6,\ 6}]^+$	=	trihexyltetradecylphophonium.
$[EMIM]^+$	=	1-ethyl-3-methylimidazolium.
$[C_{16}MIM]^+$	=	1-hexadecyl-3-methylimidazolium.
$[MOIM]^+$	=	1-methyl-3-octylimidazolium.
$[P_{14,\ 4,\ 4,\ 4}]^+$	=	tributyltetradecylphosphonium.
$[DoMIM]^+$	=	1-dodecyl-3-methylimidazolium.
$[(C_6OC)_2\ IM]^+$	=	1,3dihexyloxymethyl-imidazolium.
$[C_8\ iQuin]^+$	=	*N*-octylisoquinolinium.
$[DMIM]^+$	=	1-decyl-3-methylimidazolium.
$[BMPYR]^+$	=	1-butyl-1-methylpyrrolidynium.
$[C_6\ Qui]^+$	=	hexylquinolinium.
$[P_{4,\ 4,\ 4,\ 1}]^+$	=	methyltributylphosphonium.
$[P_{4,\ 4,\ 4,\ 2}]^+$	=	tributylethylphosphonium

Anion

$[(C_8H_{17})_2\ PO_2]^-$	=	Dimethylpentylphosphinate
$[Cl]^-$	=	chloride.
$[DBS]^-$	=	dodecylbenzenesulfonate.
$[NTf_2]^-$	=	bis-(trfluoromethylsulfonyl) imide.
$[TCB]^-$	=	tetracynaborate.
$[BF_4]^-$	=	tetrafluoroborate.
$[TOS]^-$	=	tosylate.
$[FAP]^-$	=	trifluorotris-(perfluoroethyl) phosphate
$[(Et)_2\ PO_4]^-$	=	diethylphosphate

List of publications

1) **Bakusele Kabane**, Rajasekhar Chokkareddy, Natesh Kumar Bhajanthri and Gan G Redhi. 2018. Essence of the intermolecular interaction in binary mixtures of phosphonium based ionic liquid and propanoic acid. *Indian Journal of Chemistry A*, 57, 753-760.
2) **B. Kabane**, R. Chokkareddy, G.G. Redhi* Molecular interaction studies of binary systems comprising 1-ethyl-3-methylimidazolium tetrafluoroborate with organic solvents at different temperature (Under Review)
3) **B. Kabane**, G.G. Redhi* Separation of (water/butan-1-ol) binary systems based on activity coefficients at infinite dilution with phosphonium ionic liquid (Prepared for Journal Review)

Chapter 1

Introduction

1.1 Introduction on thermodynamics

The field of chemistry is concerned with the study of reactions and processes in solution and that is where liquids are used as solvents. In order to form a homogenous mixture, one or more solutes are mixed or dissolved and this results in the formation of the solvent. The use of solvents generates a lot of attention in chemistry research and including of the crucial ones used in the society. Lately, solvents are being employed in an expansive range of applications which include the making of food processing, plastic industries, medicine processing, extraction and separations [Goldrick, 2013]. Some of the setbacks with the use of solvents relate to safety issues or environmental, which has a huge impact in rigid legislation in many countries. Due to many adverse properties of solvents, which may include volatility, there are high risks related to atmospheric pollution, storage and transportation. These issues have caught the imagination of the research groups and industries in order to enhance the living standard of people. Inadequacy of innovation in the solvent technology area may result in severe consequences. Some of the goals of chemistry instruction and education should clearly aim at empowering non-chemists as well as equipping chemists to better understand the toxic potential of chemical solvents to the environment and living organisms. It should also improve the quality of research problems and obtain more insight into making the environment safer.

Thermodynamic properties of solutions are not only important for evaluating the feasibility of reactions in solution, but also provide more desirable methods to carry out systematic theoretical aspects of solution structure. Some of the principal goals of physical chemistry is to understand the properties and behaviour of actual systems, and to apply the understanding in an appropriate manner. An average change in temperature and pressure results in small changes in the volume of a liquid. According to the fundamentals of physics and mathematics to get quantitative relations, physical chemistry contributes towards the structure and dynamic matter. The main concern is with the phase and chemical equilibrium or dynamic

process, which includes phase transition, reaction kinetics, charge transport, and energy exchange between systems and surroundings. The study of physical analysis is mostly based on a small number of fundamental quantities [Rodriguez et al., 2001].

1.2 Overview on Ionic Liquids

Nowadays, it is essential to expand the green technologies to minimise the solvent contamination in the environment due to strict environmental regulations and the strong legal framework that we are living in. Any kind of salt that melts without decomposing or vaporizing usually yields an IL, which recently is enjoying tremendous interest, and is also described as having numerous applications. The research on ionic liquids has developed exceptionally over the past years with many of researchers focusing on their applications and properties as solvents, for a wide choice of chemical reactions. Without proper understanding of the physical properties of these solvents, none of these reactions would be industrially utilized [Deive et al., 2013, Redhi et al., 2015, Blahut et al., 2013, Esperança et al., 2006, Wei et al., 2015, Besbes et al., 2009, Domańska et al., 2014, Matkowska et al., 2013, Hwang et al., 2011].

Ionic liquids are composed of diverse alkyl functionalized or substituents group with large organic cations, and organic or inorganic anions. The main reason in support of the ILs low melting temperatures is their large and asymmetric features of their ions [Martins et al., 2016, Kirchner et al., 2009]. Attributable to their ionic nature, nearly all of the ILs are known to present attractive and useful properties, which include insignificant vapour pressure [Holbrey et al., 2008], non-flammability [Smiglak et al., 2006], high thermally stability [Pucheault et al., 2009], high conductivity [Bonhote et al., 1996], as well as considerable potential to dissolve inorganic and organic materials. These are liquids with feasible applications in several fields which include, electrochemistry (batteries, solar panels, fuel cells), chemistry (synthesis, catalysis, polymerization), chemical engineering (extraction, separation, liquid membranes), and biotechnology (bio-catalysis, protein purification) as well in pharmaceuticals industries. As a result, clear understanding of their properties and behaviour with organic solvents is essential for proper development of these applications [Vercher et al., 2015, Kumar et al., 2010].

ILs are environmentally friendly but they can also be pollutants if procedures used in handling these liquids are incorrect, because inappropriate handling may result in high possible soil and water contamination as a consequence of unexpected spills or incompetent waste water management [Bubalo et al., 2014]. If the ionic liquid is contains small traces of water, this can extremely influence the phase equilibrium and their thermodynamic properties [Neves et al., 2010, Neves et al., 2011]. As a result, in previous years, a notably large number of studies has been focussing on examining thermodynamic and physical properties which include density and viscosity for the water saturated ionic liquids [Carvalho et al., 2009, Zhang et al., 2009, Gardas et al., 2008, Rocha et al., 2013]. This clearly confirms that ILs can have an extensive range of properties which can be determined or influenced by the choice of cation or anion [Neves et al., 2013, Rodríguez et al., 2006].

Organic solvents are widely used in the production industries for several effective applications, ionic liquids possess greater advantages over the organic solvents, which may include: non-volatile, thermally stable [de Castro et al., 2010], wide liquid electro-chemical window [Martins et al., 2016], large liquidus temperature range [Vaid et al., 2015], and the potential to dissolve a broad range of inorganic, organic and also polymeric compounds, so they are treated as green solvents and can be easily recycled [Warke et al., 2016, Bhattacharjee et al., 2015, Neves et al., 2011]. Imidazolium-based ionic liquids are one of the most addressed ionic liquids according to the literature search; the number of industrial application concerning phosphonium-base ionic liquids is facing a tremendous increase [Joglekar et al., 2007]. One of the obstacles in developing the ILs for the industrial implementation is the insufficient understanding of thermophysical properties [Wei et al., 2015], for both pure and mixed with organic solvents, in a broad range of temperatures and pressures for method development purposes.

1.3 Aims and objectives of the research

The principal aim of this research work were to determine activity coefficients at infinite dilution of organic solutes and to experimentally determine density, viscosity and speed of sound data as well the derived properties (excess molar volume, isentropic compressibility, deviation in isentropic compressibility, intermolecular free length, deviation in viscosity, apparent molar isentropic compressibility and apparent molar volume) for the binary

mixtures of the IL trihexyltetradecylphosphonium chloride and 1-ethyl-3-methylimidazolium tetrafluoroborate.

The objectives are to:

- Investigate types of molecular interactions occurring in the binary mixtures by calculating excess molar volumes and isentropic compressibility.
- Investigate the separation potential of organic solutes in the ionic liquid trihexyltetradecylphosphonium-bis-(2, 4, 4-trimethylpentyl)-phosphinate.
- Calculate the selectivity of the solvent for binary mixtures of close boiling point.

1.4 Background to Phosphonium, Imidazolium based ILs

The first phosphonium salt was prepared with the combination of [Cl^-] and [Br^-] ions [Neves et al., 2010]. Phosphonium based ILs has grown widely during the previous years with extensive commercial accessibility. Phosphonium-based ionic liquids are produced in bulk by the Cytec industries, and many of pharmaceutical intermediates are developed by utilizing phosphonium-based ionic liquids [Deive and Rodríguez 2013]. Phosphonium based ILs possess many advantages as they are thermally more stable, less toxic, and less costly, and exhibit a wide range of properties and uses [Yoshii et al., 2013]. Because of the absence of the acidic proton, under nucleophilic and basic conditions, phosphonium based ILs is more stable in their moieties [Millero et al., 1971]. Several applications have been tested for phosphonium based ionic liquids which include electrolytes in batteries, extraction solvents, corrosion protection and chemical synthesis solvents [Atefi et al., 2009].

According to the literature search, the ionic liquids that have received the least amount of attention based on their physical properties with organic solvent mixtures are the phosphonium based ILs, whilst they provide a broad range of appealing properties [de Castro et al., 2010], and also electrochemical properties [Fraser and MacFarlane 2009, Blahušiak and Schlosser 2014].

Kilaru 2007 and Martins 2016, have studied some of the physical properties of a pure [$P^+_{14, 6, 6, 6}$] [Cl^-], (Figure 4.1.1), which includes density and viscosity, and surface tension. Recently, binary mixture studies using methanol and dodecane with [$P^+_{14, 6, 6, 6}$] cation have been reported by [McAtee and Heitz 2016]. The nature of the added diluents will decide if it prefers to move towards the non-polar or polar domain of the ionic liquid. The additions of

solvent results in reduction of viscosity via interruption of the ionic liquid ion pair association [Tsunashima and Sugiya 2007]. Often, addition of water may result in the change of the solution structure which may also result in the formation of micellar structures. Deeper knowledge in connection between the physicochemical properties of mixtures containing phosphonium based ionic liquids and appropriate diluents in the formulation of solvents and their make-up is required to optimize the ionic liquid composition for the various processes. The study of thermophysical properties of these solvents can initiate more insight into the interactions and structure.

In the field of ionic liquids, the imidazolium based cations are the most studied class of ionic liquids and these types of liquids have been utilized in most areas which include electrochemistry, catalysis, synthesis, as well industrial applications [Wasserscheid et al., 2000, Wilkes et al., 2004, Koch et al., 1996, Every et al., 2000]. Imidazolium based ionic liquids can also be useful in the technique of eliminating carbon dioxide from the natural gas [Bates et al., 2002] as well in extractive desulfurization of liquid fuels, principally with consideration of those of sulphur compounds that are extremely complex to remove by the ordinary hydrodesulfurization (HDS) process [Rao et al., 2016]. 1-ethy-3-methylimidazolium tetrafluoroborate [Emim] [BF_4] found usage in the recycling of osmium oxide [Yanada and Takemoto 2002]. In the capillary electrophoretic technique, 1-ethy-3-methylimidazolium tetrafluoroborate is mostly utilized in grape seed extract; is also used for settling phenolic compounds. Normally, the level of toxicity of imidazolium depends on the lower order n-alkyl chain which have low to average degree of damage, and in particular [Emim] [BF_4] is likely to cause harm when swallowed [Latała et al., 2009].

1.5 Organic Solvents used for binary systems

Carboxylic acids as a group are important as they are effective in many industrial applications which include use of polyester resins, pharmaceutical products, cleaning agents, separation processes, manufacturing of pharmaceutical products, catalysts and other chemical industries. In the family of aromatic aldehydes, benzaldehyde is one of the most industrially functional members in the group. Large numbers of industries have been using benzaldehyde as a raw material in organic synthesis, which also includes perfumery chemicals [Satrio and Doraiswamy 2001]. A notably large amount of benzaldehyde is used in the production of other aldehydes, such as cinnamic, methylcinnamic and hexylcinnamic. In the synthesis of

many organic compounds, ethyl acetoacetate is mostly used as an intermediate. It is also utilised in the manufacturing of synthetic drugs and dyes.

1.6 Activity Coefficients

The determination of activity coefficients at infinite dilution (γ_{13}^{∞}), for organic solutes in ionic liquid solvents provides an indispensable way for the successful evaluation of ionic liquids for prospective uses in solvent-enhanced separation processes for organic liquid systems [Kolbe et al., 1979]. Utilization of steady-state gas-chromatographic techniques to compute activity coefficients data at infinite dilution; has been done by many researchers; as it is comparatively quick and consistently yields good quality data [Poole et al., 2004]. The activity coefficients at infinite dilution gives clear knowledge concerning the interactions among the investigated compounds. Information of these values permits one to compute the selectivity, $S_{12}^{\infty} = \frac{\gamma_{13}^{\infty}}{\gamma_{23}^{\infty}}$ and capacity, $K_2^{\infty} = \frac{1}{\gamma_{23}^{\infty}}$, at infinite dilution. Methodical research of γ_{13}^{∞} supplies enough details about the impact of ionic liquid structure on the types of interactions occurring with numerous solvents, and the resultant feasibility to separate various components in systems.

Ionic liquids are specifically appropriate for the determination of activity coefficients at infinite dilution by the use of gas chromatography technique, due to their insignificant vapour pressure, which make them ideal stationery phase material for gas-liquid chromatography. A literature review for activity coefficients at infinite dilution (γ_{13}^{∞}) for phosphonium-based ionic liquids has revealed relatively few articles.

1.7 Distinctive properties of ionic liquids

Initial research based on examining the physical properties of pure and mixed ionic liquids has concentrated the development and clear understanding on the relationship amongst the structure and nature of the anion/cation and the related physical properties. Because ionic liquids are still under intensive research, their purity is essential when conducting the thermophysical property measurements. Before conducting any thermophysical property measurements of ionic liquids, it is important to first determine the water content by reliable means, as the water can be one of the major contaminants and influence. The chemical and

physical properties of ILs are strongly influenced by the type of ionic liquid, i.e. cation or anion [Wasserscheid et al., 2000]. The study of physical properties is important in all aspects of applied research, as they provide advisable material information for positive utilization. In liquid mixtures, these properties are also essential as they describe the types of molecular interaction that occurs especially where hydrogen bonding occurs.

1.8 Environmental Aspects

Ionic liquids represent the current effort to lessen the extremely number of coupling side products as well as the catalyst and solvent usage in chemical process. Utilization of ionic liquids can contribute hugely in this area, especially with concerns relating to catalyst and solvent utilization. In difference to volatile organic solvent and extraction media, ionic liquids have no measurable vapour pressure [Wasserscheid et al., 2000]. For these reasons, there is no loss of solvent via evaporation. By using ionic liquids, safety and environmental difficulties from the light of the usage of volatile solvent can be resolved. With the effort to reduce catalyst consumption, two aspects come to light in the usage of ionic liquids:

- The better solubility features of ionic reaction media allow a biphasic reaction procedure in many instances [Wasserscheid et al., 2000]. Utilization of the miscibility gap between the ionic catalyst phase and the product allows, for the catalyst to be separated efficiently from the product, and re-used again.
- The nature of the ionic liquids allows a more effective product separation; by the use of distillation.

In both instances, the overall reactivity of the applied catalyst is increased and catalyst usage relative to generated product is reduced. For the environmental and safety explanations, the use of ionic liquids could gain the quality of being worthy of attention especially in the process with a super acid catalyst.

1.9 Factors that influence thermophysical property measurements

1.9.1 Structure

In order to conduct proper thermophysical property measurements of ionic liquids, we use pure ionic liquids are used. These types of liquids have special properties that allow the appropriate manner of handling in order to avoid potential danger in sample characterization. In previous years, study of thermophysical and thermodynamic properties have been the topic of interest and they are by no means exhausted. Although, the pressure to issue new results hide the problems in getting samples of high purity and inappropriate handling of these materials. The contamination of water and dissolution of environmental with samples should be taken to considerations. In the year 2005 [Widegren et al., 2005, Widegren and Magee 2007], and co-workers could expressed the consequence of the existence of water in electrical conductivity and viscosity of some type of ionic liquids, although the consequences were well known; qualitatively. After the removal of any small traces of water, it is advisable to eliminate any chances of further water contamination during sample handling, as well as throughout the measurements.

1.9.2 Instrumental factors

In many laboratories, measurements of thermophysical properties (thermodynamic and mainly transport properties) are measured, but not always with the same degree of accuracy and precision regarding the different procedures and technique used. In laboratories, the use of any instrumentation without properly recognition of the ionic liquids properties can result in a significantly poor contribution to the experimental databases. In terms of the work done, it is proposed the best instrumental technique should be used, their classifications as secondary and primary, or relative and absolute, their adaptability to ionic liquids and the real achievable correctness.

1.10 Importance in the study of thermodynamic properties of liquid mixtures

During the recent years, the study of thermodynamic and physical properties has been extensively notably, but they are no means completed. The complexity of the molecular interaction occurring between these mixtures/liquids, makes the task difficult in predicting

thermodynamic quantities. Investigation of intermolecular interactions of ionic liquids with organic solvents is important; as these data decide the transformation of ionic liquids from small laboratory scale to large scale industrial applications. Examination of thermodynamic properties, including excess molar volumes and γ_{13}^{∞} are essential for the processing of suitable predictive models for mixtures comprising ionic liquids.

One of the main ambitions in investigating these properties of binary systems is to add to a list of data of thermodynamic properties of binary systems of ionic liquids, as well to determine or examine the relationship among the structures of ionic liquids and the related densities of binary systems appropriate for the process design of proper ionic liquids suitable for specific chemical extraction processes [Azevedo et al., 2004].

1.11 Ionic liquids Industrial Applications

Ionic liquids have been successfully applied for the industrial application [Welton et al., 1999], which include the following:

1.11.1 Nuclear industry

Ionic liquids are broadly utilised for innovative applications in the nuclear industries, which include application of ionic liquids as an entrainer in solvent extraction systems; as well as another possible electrolyte medium for excessive temperature in pyro-chemical development [Giridhar et al., 2007].

1.11.2 Cellulose processing

Cellulose are naturally organic materials which are found in large quantities on earth, it is also very essential in the paper industries, body care products, packing materials and textile fibres. It possesses great advantages, as these are renewable materials. Approximately 200 million tons of the 40 billion tons are renewable per year to be used as raw material. Due to strong intermolecular interactions of hydrogen bonding that subsists in the cellulose, it is insoluble in water or organic solvents and this prevents its usage extensively. Ionic liquids are effective in breaking the intermolecular hydrogen bonds and they are used to dissolve the cellulose [Hermanutz et al., 2008].

1.11.3 Pharmaceutical industries

These are well known manufacturing industries of medicines and drugs which are very useful. These industries have been facing setbacks connected with the consumption of medicines and related high waste discharged to the environment. The usage of ionic liquids has been used to recover active pharmaceutical ingredients, and this reduces high amount of pharmaceutical waste. This action was done by the use of aqueous biphasic system base of ionic liquid in a single step, and use of the ionic liquid aqueous solution as the extract, which was effective in extracting the pharmaceutical ingredients using solid-liquid extraction process (IL-based SLE).

1.12 Research work covered

In this research work, two different types of ionic liquids were used, the phosphonium based and imidazolium based ionic liquids, and three solvents were used (propanoic acid, ethyl acetoacetate and benzaldehyde) to study the thermodynamic properties of ($[P^{+}_{14, 6, 6, 6}]$ $[Cl^{-}]$ + propanoic acid) and ([Emim] $[BF_4]$ + benzaldehyde or ethyl acetoacetate). Water and 26 solutes which include (alkanes, alkenes, alcohols, aromatic hydrocarbons, acetonitrile, THF, acetone and thiophene) were used in the ionic liquids {trihexyltetradecylphosphonium-bis-(2, 4, 4-trimethylpentyl)-phosphinate and trihexyltetradecylphosphonium chloride} and the resulting data used to predict the activity coefficients at infinite dilution.

Chapter 2

Literature Review

Many authors have displayed the importance of studying the thermodynamics of ionic liquids for chemical and connected industries. The analysis work by [Zhao et al., 2006, Plechkov and Seldon 2008], review a notable use and attraction of ionic liquids in industries. However, some of the obstacles in the growth of ionic liquids for industrial use are the scarcity of their thermophysical properties [Rao et al., 2016], for both mixed and pure liquids in a broad range of temperatures and pressures.

In the family of phosphonium based ionic liquids, there is limited experimental data showing their thermodynamic properties of pure and binary/ternary systems available. Some of the important reasons necessary study the thermophysical properties of composite materials is because of their difference from the ideality, due to the particular implementation or mixing for the considered properties, [Blandmer et al., 1974, Franks and Reid 1973, Millero et al., 1971, Hoiland et al., 1986].

Nieto de Castro et al., (2010) conducted research work on thermophysical properties of ILs. Based on the obtained results, it was observed that the measurements of thermophysical properties of ILs is far from being compared to those actually found in molecular liquids. It was also recommended that measuring thermophysical properties of ILs should be performed with good precision, because the errors in their measurements can have a tremendous negative impact on upcoming design of mass transfer and heat apparatus.

Neves et al., (2011) measured thermodynamic properties of water-saturated and pure tetradecylphosphonium-based ILs. The results showed that the existence of water has a negligible impact on the ionic liquid densities; yet a huge effect via their viscosities, and less hydrophobic ILs are more influenced because of their large water content. Furthermore, from the density of water-saturated ILs, a simple technique was suggested to evaluate the water saturation data in each IL at constant temperature.

As much as phosphonium-based ionic liquids are denser as compared to water, the densities obtained for phosphonium ionic liquids are alike or even smaller as compared to the values recorded for pure water [Kolbe et al., 1979]. In addition, the obtained density results are as anticipated, following the rule of thumb that the densities of ionic liquids are approximately inversely proportional to the molecular volume. Experimentally determined results of refractive index, dynamic viscosity, speed of sound as well as densities of some of the phosphonium based ionic liquids were presented by [Deive et al., 2013]. Dale-Gladstone, Lorentz-Lorenz, Eykman, Arago-Biot, Oster, Newton and altered Eykman equations were utilized to correlate the relation among the refractive indices and densities of the chosen ionic liquids.

The solubility of hydrocarbons in three phosphonium based IL tributyl(ethyl)phosphonium diethylphosphate ([$P_{4,\ 4,\ 4,\ 2,}$] [$(C_2)_2PO_4$]), (trihexyltetradecylphosphonium chloride [($P_{6,\ 6,\ 6,\ 14}$] [Cl]) and tributyl(methyl)phosphonium methylsulfate ([$P_{4,\ 4,\ 4,\ 1,}$] [$CH_3\ SO_4$]) were investigated at various temperatures between (288.15 to 308.15) K and at atmospheric pressure by [Ferguson and Scovazzo 2007]. Based on their results, it was observed that the solubility values for CHF_3 and C_2HF_2 were more in ([$P_{4,\ 4,\ 4,\ 2,}$] [$(Et)_2\ PO_4$]) whereas CHF_3 showed large solubility values in [($P_{6,\ 6,\ 6,\ 14}$] [Cl]). The entropy and enthalpy values were examined by using the solubility dependence on temperature and were within the thermophysical predictions from the theory of regular systems in which for more soluble gases, the solubility is inversely related to the temperature.

Solubilities of 1,1,1,3,3-pentafluoropropane (R25fa), difluoromethane (R32), 1,1,2,2,3,3, 3-heptafluoropropane (R227ea) and 1,1,1,3,3,3-hexafluoropropane (R236fa) in trihexyltetradecylphosphonium at temperatures from 292 K to 344 K at 0.01 to 1.07 MPa were reported by [Liu 2016]. High gas solubility of hydrocarbons was found to be higher at low temperatures as compared to higher temperatures. The solubility gave high values as compared to their corresponding alkanes. The interactions such as dipole-dipole interaction, hydrogen bonding and dispersive forces were observed to occur among the hydrocarbons and the ionic liquid.

Blahusiak et al., (2014) reported on the physico-chemical properties of phosphonium based ionic liquids and its liquid systems with water or dodecane. Based on the obtained data, it was observed that the density and viscosity on the composition of binary and ternary systems are strongly nonlinear.

Bhattacharjee et al., (2015) reported the study of physical properties of phosphonium-based ionic liquids at different temperatures. It was observed that the densities of the investigated ionic liquid are generally smaller as compared to the imidazolium-based ones. It was also observed that the examined ILs display low entropies and surface enthalpy in contrast with molecular organic compounds.

Wlazlo et al., (2015) conducted a study on physicochemical properties and γ_{13}^{∞} for water and selected volatile organic solutes in the ionic liquid 4-(3-hydroxypropyl)-4-methylmorpholinium bis(trifluoromethylsulfonyl)-amide. Based on the results, it was seen that [N-C_3OHmMOR] [NTf_2] has higher activity coefficients at infinite dilution compared to [N-C_3OHPY] [NTf_2] and [COC_2mMOR] [NTf_2] with alike structures. Investigated ILs revealed the lowest of selectivity value at infinite dilution for butanol/water separation.

Martins et al., (2016) reported viscosities, densities, and computed thermodynamic properties of water-saturated imidazolium-based ionic liquid. Based on the obtained results, it was observed that in the two series of water-saturated ILs, the densities decrease with an increase in temperature. In addition, the existences of water result in reduction of density in the ionic liquid mixtures.

Warke el at., (2016) conducted a study on examining thermodynamic properties of aqueous solutions of tetraalkylphosphonium-based ionic liquids at atmospheric pressure and various temperatures. Based on their results, it was observed that the density values of aqueous solutions of [$P_{i\ (444)1}$] [Tos] and [$P_{4,4,4,1}$] [CH_3SO_4] are directly proportional to the mole fractions concentration while those of [$P_{4,4,4,1}$] [Cl] are inversely proportional to the mole fractions concentration, at all the chosen temperatures. These remarks imply an increase in ion-ion interactions with increase in mole fractions concentration.

Thermophysical properties such as viscosity, density and computed parameters in trihexyltetradecylphosphonium chloride IL with methanol binary systems were studied by [Mctee et al., 2016]. Based on the observed data, the calculated parameters of binary mixtures of ([$P^{+}_{14,\ 6,\ 6,\ 6}$] [Cl^{-}] + MeOH) show a negative deviation from ideal mixing behaviour at all temperatures and ionic liquid mole fractions.

Battez et al., (2016) conducted a study on phosphonium cation-based ionic liquids as pure lubricants, in terms of physcochemical and tribological performance. Based on the results, it was found that the structure and size symmetry of the two ions have a strong impact on conductivity, viscosity, thermal stability as well as corrosion. At 240 ^{o}C, all ionic liquids displayed thermal stability as expected, with higher values under inert atmosphere.

1-ethyl-3-methylimidazolium tetrafluoroborate found usage for the removal of carbon dioxide from natural gas. Yet, its relatively high viscosity set some boundaries on its usage as a pure liquid in large-scale at industries. This suggests the thermodynamic and thermophysical property studies of the ILs could be influenced advantageously in a careful manner, by the addition of organic solvent to the ionic liquids.

Vercher et al., (2015), worked on characterisation of thermodynamic properties of tetrafluoroborate-based ILs containing methanol at different temperatures. In both of the studied ionic liquids, speed of sound and density increase with the mole fraction, but decreases with an increase in temperature. The calculated excess molar properties were negative at all investigated temperatures and mole fractions implying strong interactions occurred in the studied binary mixtures. The results of fitting for both of the ionic liquid mixtures display good agreement with the experimental data. Deviation on viscosities were negative at all examined mole fraction compositions with an increase in temperature.

Historically, 1-butyl-3-methylimidazolium tetrafluoroborate is the most significant and well-studied IL. Thermophysical functions such heat capacity, density as well as enthalpy change have been conducted at various temperatures [Kabo et al., 2004, Fredlake and Harris 2005, Chandrasekhar et al., 2003]. However, experimental data concerning the volumetric properties of ionic liquids remains scarce in the literature.

Gao et al., (2009) conducted a study on densities and excess parameters of binary systems of ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate containing benzaldehyde at temperature (298.15 to 313.15) K. According to the results of the study, the densities increases with the increase in mole fraction and decreases with increase in temperatures; the calculated excess molar volumes were negative across the entire mole fraction range; and this signifies more efficient packaging within the ionic liquid and organic solvent.

For the Prigogine-Flory-Patterson (PFP) theory, [Patterson and Delmas 1970, Prigogine et al., 1957, Flory et al., 1965], have frequently used this theory to access the excess thermodynamic functions. Calculated excess properties and the measured results of binary systems made by molecular interaction, which have different shape and size have been interpreted by this theory. In spite of the fact that in the formation of interactions of strongly electrostatic nature and hydrogen bonds are specifically not included in the theory, an absolutely empirical implementation of the Flory formalism can also give an interesting correlation among the excess volumes of more compound systems.

The implementation of Prigogine-Flory-Patterson theory to the excess molar volumes of systems containing 1-butyl-3-methylimidazolium ionic liquids and *N*-methyl-2-pyrrolidinone was conducted by [Qi et al., 2009]. From the obtained results of excess molar volumes of all the investigated ionic liquids, the Prigogine-Flory-Patterson theory has displayed a good achievement in estimating these liquids, although it showed a small deviation in 1-butyl-3-methylimidazolium hexafluorophosphate mixed with *N*-methyl-2-pyrrolidinone. In comparison to the results containing 1-butyl-3-methylimidazolium tetrafluoroborate, large molecular interaction values in the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate were observed.

Binary systems of 1-hexyl-3-methylimidazolium tetrafluoroborate with *N*-methyldiethanolamine were investigated by [Akbar et al., 2013]. In their work, measurements of thermophysical properties which includes density, refractive index, and dynamic viscosity were conducted across the temperature range, T = (303.15 to 323.15) K. In the results obtained, 1-hexyl-3-methylimidazolium tetrafluoroborate has high density and viscosity values when compared to *N*-methyldiethanolamine. In binary mixtures, density is directly proportional to the mole fraction and decreases with increase in temperatures. The roughly calculated excess molar volume displayed positive values across the entire mole fraction range and temperatures; this might be attributed towards several factors. These factors might be categorized into three types:

- Physical
- Chemical
- Structural

Physical cause which are not clearly defined as forces of interactions result in positive excess molar volumes. Calculated excess molar volumes which showed positive values might be the result of weak dipole–dipole interactions or dispersion forces in particular among different molecules because of the rupture of hydrogen bonds. Positive values explain that the structural breaking impacts of the constituents are more profound in these binary systems [Sovilj and Barjaktarovic 2000, Vural et al., 2011]. All measured properties were correlated as a function of temperatures and concentration.

Aniline, because of its high reactivity of the amine group that exist in the chemical structure, is widely utilized in many of the chemical industries. It is essential and non-associative in the manufacturing of methylene diphenyleneisocynate. Rao et al., (2017) conducted a study on characterising properties of 1-ethyl-3-methylimidazolium tetrafluoroborate with aniline from temperature ranging (293.15 to 323.15) K at p = 0.1 MPa. The types interactions that occurred in the binary systems between aniline and 1-ethyl-3-methylimidazolium tetrafluoroborate were determined by analysing excess parameters. The values for the excess parameters were negative across the entire mole fraction range, excess molar volumes which were negative indicate the more effective packing, negative values of isentropic compressibility are due to strong attractive interactions because of the solvation of ions in the systems and negative values for intermolecular free length point out the structural alteration in the liquid systems.

Martins et al., (2016) measured viscosities, densities and calculated excess parameters of water-saturated imidazolium-based ionic liquids. The action of symmetry of the cation and alkyl side chain length was accessed in this study for the water-saturated IL. For the studied ionic liquids (water-saturated and pure), the viscosity and density are inversely proportional to the temperature. The densities decrease with an increase in alkyl side chain length, whereas viscosity was observed to increase according to size of the aliphatic tails-trend, either for water-saturated or pure ionic liquids. In addition, the water-saturated symmetric series for the ionic liquids show low viscosities and densities as compared to their pure IL counterparts [Martins et al., 2016].

Experimental data of viscosities and densities for the binary mixtures of 1-ethyl-3-methylimidazolium tetrafluoroborate with water were presented by [Zhang et al., 2004]. According to the experimental results of densities and viscosities, both are inversely

proportional to the temperatures. The results displayed that the water content does influence the excess thermodynamic and physical properties.

Partial molar isentropic compressibilities and partial molar volumes of 1-butyl-3-methylimidazolium tetrafluoroborate containing N-methylaniline binary systems under atmospheric pressure and various temperatures (293.15 to 323.15) K were reported by [Rao et al., 2016]. The Redlich-Kister polynomial equation was utilized to fit the excess molar volumes in order to predict the standard deviations and polynomial coefficients among the experimental data as well as the calculated values. FT-IR spectrum was used to analyse the molecular interactions of the binary systems and were recorded at room temperature. The calculated derived properties were negative across the entire mole fraction range, and investigated temperatures indicated strong attractive interactions.

Thermophysical and thermodynamic properties are essential in all aspects of applied studies for prospective new solvents as these are the key in screening. Singh et al., (2015) investigated the impact of alkyl group on physical properties of propanoic acid or acetic acid in 1-butyl-3-methylimidazolium thiocyanate IL at different temperatures under atmospheric pressure. In their work, new data of physico-chemical properties which include sound velocity and densities were obtained. Redlich-Kister polynomial equation was utilized to test the derived properties by fitting the polynomial through the data. The calculated (derived) properties were negative across the whole mole fraction range at all examined temperatures.

Evaluation of solvents for the possible implementation in solvent-enhanced extraction technology of organic liquid systems can be predicted via the determination of the activity coefficients at infinite dilution of organic solutes. Many researchers and research groups have been using the steady-state gas liquid chromatography to investigate activity coefficients at infinite dilution values and have provided consistently good results in this respect. Based on good properties possessed by the ionic liquids which include low vapour pressure, this technique is suitable for examining γ_{13}^{∞} for the ionic liquid and also making an ideal stationary phase with ILs.

For the organic solutes, γ_{13}^{∞} measurements in the phosphonium based ionic liquid [trihexyltetradecylphosphonium-bis-(2, 4, 4-trimethylpentyl)-phosphinate] using gas-liquid chromatography at T = (303.15 to 318.15) were conducted by [Letcher et al., 2008]. According to the results of the computed γ_{13}^{∞}, it was seen that the investigated ionic liquid displayed minimum selectivity at infinite dilution of any ionic liquid before 2008. The low

selectivity values might indicate that the investigated ionic liquid is apparently of little use in solvent extraction processes in separating aromatic compounds from aliphatic compounds.

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

Activity coefficients at infinite dilution were also conducted by [Letcher et al., 2005] for the organic solutes (non-polar and polar) in the ionic liquid [trihexyltetradecyl phosphonium tris(pentafluoroethyl) trifluorophosphate] at various temperatures (308.15, 318.15 and 328.15) K. This was the earliest reported research work to be conducted and described for the phosphonium-based ionic liquids. Their results clearly showed the importance of the trial and error approach, and the subsequent utilization of ionic liquids for required usage.

Domańska et al., (2010) used a gas-liquid chromatography (g.l.c) to conduct measurements of γ_{13}^{∞} of 33 various organic solutes such as cycloalkanes, alkynes, alkanes, benzene, alkylbenzene, alkenes, water, tetrahydrofuran, methyl tert-butyl ether, alcohols and thiophene in tri-iso-butylmethylphosphonium tosylate ionic liquid which were reported at T = (298.15 to 368.15) K. Based on their results, it was observed that the examined ionic liquid displayed higher capacity and selectivity at infinite dilution, than the normally utilized solvents such as sulfolane or NMP for the separation of aliphatic hydrocarbons from aromatic hydrocarbons.

Examination of γ_{13}^{∞} of organic solutes in the ionic liquid (tributylmethylphosphonium methylsulphate) conducted by the use of g.l.c were also reported by [Letcher et al., 2007]. This was the first reported experimental activity coefficient data to be reported and described for this IL via the method of steady-state gas-liquid chromatography. The activity coefficient values obtained in this work for all chosen solutes in the latter, were unusual in being less than unity, of alcohols at lower temperatures, implying a strong affinity of the solutes for IL stationary phase.

Gas liquid chromatography was also used by [Domańska et al., 2009] to investigate the activity coefficients at infinite dilution for various solutes (water, alkenes, alkanes, cycloalkanes, alkynes, aromatic hydrocarbons, tert-butyl methyl ether, alcohols, thiophene, and THF) in the ionic liquid 1-butyl-1-methylpyrrolidinium trifluoromethanesulfonate at temperatures between (298.15 to 368.15) K. Based on their findings, it was observed that the

ionic liquid used displayed higher capacity and selectivity values at infinite dilution, than any other ionic liquid achieved in previous years for separating aliphatic from aromatics.

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

Table 2.1

Ionic liquids in contrast with volatile organic solvents (VOS)

Property	VOS	Ionic liquid
Density	(0.6 – 1.7) $g \cdot cm^{-1}$	(0.8 – 3.3) $g \cdot cm^{-1}$
Vapour Pressure	Obeys the Clausius-Clapeyron equation	Low vapour pressure under normal conditions
Viscosity	(0.2 – 100) 10^{-3} N s/m^2 cP	(22 – 40 000) 10^{-3} N s/m^2 cP
Cost	Relatively cheap	2 to 100 times more compared to organic solvents
Polarity	Traditional polarity concepts	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

In contrast with the past, about 10^{18} ionic liquids have been estimated [Endres and EL Abedin 2006] and could be developed by merging various ions which are displayed in Figure 2.1 below.

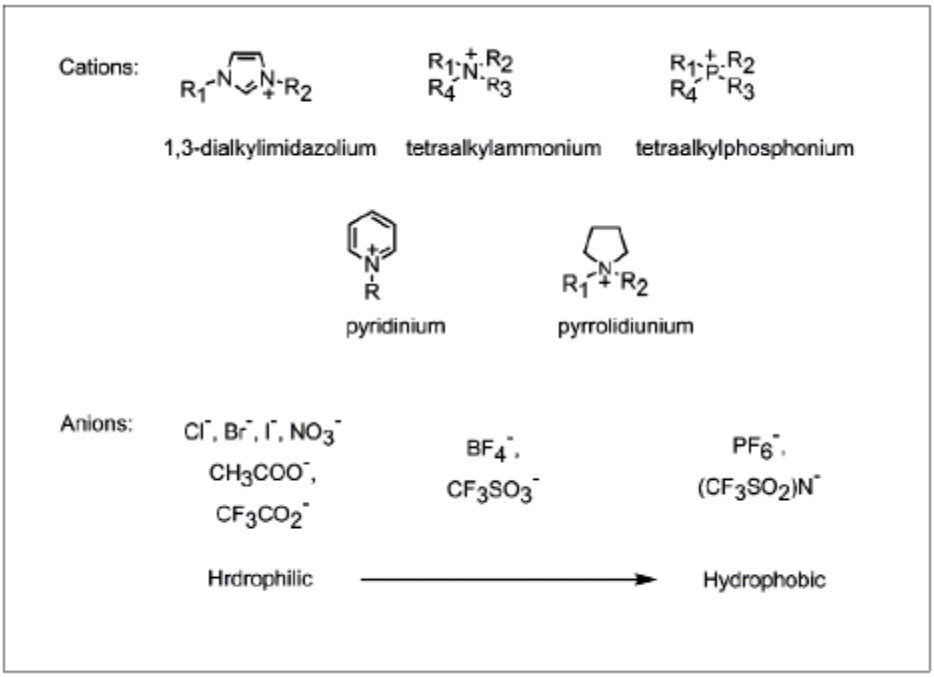

Figure 2.1 Structures of commonly used ions in synthesizing ionic liquids

Table 2.2

Excess molar volumes of ionic liquids and organic solvents from the literature including those obtained in this research work.

Author	Liquid mixtures	V_m^E ($cm^3 \cdot mol^{-1}$)
Gao et al., (2009)	([bmim][BF_4]+ benzaldehyde	
	T = 298.15 K	-1.1278
	T = 303.15 K	-1.1678
	T = 308.15 K	-1.2176
	T = 313.15 K	-1.2992
Vercher et al., (2015)	([emim] [BF_4] + methanol)	
	T = 278.15 K	-0.80
	T = 288.15 K	-0.85
	T = 298.15 K	-0.90
	T = 308.15 K	-0.97
	T = 318.15 K	-1.04
Singh et al., (2015)	($[BMIM]^+[SCN]^-$+ Propanoic acid)	
	T = 293.15 K	-1.551
	T= 298.15 K	-1.584
	T = 303.15 K	-1.650
	T = 308.15 K	-1.717
	T = 313.15 K	-1.786

Warke et al., (2016)	([P $_{4,4,4,1}$][CH_3SO_4] + H_2O)	
	T = 298.15 K	-0.0215
	T = 303.15 K	-0.0191
	T = 308.15 K	-0.0165
	T = 313.15 K	-0.0141
McAtee and Heitz (2016)	([$P^+_{14,6,6,6}$][Cl^-] + methanol)	
	T = 290.15 K	-0.646
	T = 293.15 K	-0.702
	T = 295.15 K	-0.735
	T= 298.15 K	-0.799
	T = 303.15 K	-0.870
	T = 308.15 K	-0.991
	T = 313.15 K	-1.050
Srinivasa et al., (2017)	([emim][BF_4] + aniline)	
	T = 293.15 K	-2.02
	T = 303.15 K	-2.08
	T = 313.15 K	-2.19
	T = 323.15 K	-2.27
In this research work	[$P^+_{14,6,6,6}$][Cl^-] + Propanoic	

acid	
T = 293.15 K	-0.6701
T= 298.15 K	-0.7621
T = 303.15 K	-0.7983
T = 308.15 K	-0.8524
T = 313.15 K	-0.9726
([emim][BF_4]+ benzaldehyde	
T = 293.15 K	-1.4648
T= 298.15 K	-1.4945
T = 303.15 K	-1.5244
T = 308.15 K	-1.5567
T = 313.15 K	-1.5901
([emim][BF_4]+ ethyl acetoacetate)	
T = 293.15 K	-1.5955
T= 298.15 K	-1.6509
T = 303.15 K	-1.7081
T = 308.15 K	-1.7678
T = 313.15 K	-1.8289

2.1 Advanced projects

Apart from the number of established industrial processes, some of the optimistic projects which are still in pilot plant stage include:

- Olefin trimerisation and metathesis conducted by Sasol (South Africa); [Tumba et al., 2010]
- BASF conducted solvent recovery by azeotrope-breaking for water-tetrahydrofuran and water-ethanol at minimum cost;
- Cellulose dissolution by BASF;
- Aluminium plating by BASF;
- Phosgene renewal by the use of ionic liquid in 1.4-diclorobutane production, attained by BASF.

2.2 Obstacles towards the use of Ionic Liquids

In the year 2002, the chemical vision 2020 technology partnership [Ford et al., 2004], a task force was appointed by the American industry-led organisation to consider the setbacks for the extensive utilization of ionic liquids and ways to master them. After two years, six obstacles were recognised by the vision 2020 ILs task force [Ford et al., 2004] towards the extensive utilization of these promising solvents in chemical industry as well as extraction processes:

- Insufficient performance data under industrial conditions;
- Insufficient safety and environmental data for many ionic liquids used;
- Insufficient economic benefit analysis
- Lack of basic knowledge of composition structure against performance;
- Scale-up and cost of manufacturing of ionic liquids;
- Institutional issues such as communication and intellectual property among researchers.

Based on the literature review, it can be concluded that the researchers have not put much focus on the thermophysical properties of phosphonium based ILs and therefore more work needs to be done on their physical properties.

Chapter 3

Theoretical Considerations

3.1 Thermophysical properties

The investigation of thermophysical properties of liquid mixtures is essential and important in all fields of applied chemistry as these are the key for screening in order to begin utilization of a proper material for definite application or modifying their distinctive physicochemical properties which will then increase and provide the materials function in certain features of research and industrial application [Bahadur et al., 2014]. These properties are also functional in examining the types of molecular interactions occurring between the liquid mixtures.

3.1.1 Sound Velocity

The speed of sound can be determined by using the distance and time of the sound waves propagated between the receiver and transmitter. Speed of sound can be calculated from equation 3.1.1. The sample of interest is placed into the sound velocity determining cell which is enclosed by an ultrasonic transmitter on one side and the other side is a receiver. The sound waves are sent by a transmitter for a known period of time via the sample.

$$u = \frac{l \times \left(\frac{1}{1 \times 10^{-5} \times \Delta T}\right)}{\left(\frac{P_S}{512}\right) - A \times f_3} \qquad (3.1.1)$$

From equation 3.1.1 sound waves of the original path length is represented by *l*, ΔT denotes the deviation in temperature to 278.15 K, P_s represents the oscillation interval of the sound waves received, A denotes constant speed of sound apparatus, and f_3 represents the correction term for temperature. The density and speed of sound are more temperature dependent; i.e. peltier elements are used to ensure that the measuring cells are thermostated correctly.

3.1.2 Excess Molar Volume

The simple definition of excess molar volume is the real liquid mixture volume with a decrease or increase in volume due to intermolecular interactions among components of the binary systems measured [Warke et al., 2016].

$$V_m^{\mathrm{E}} = V_{mixture} - \sum x_i V_i \quad (3.1.2)$$

Where x_i represents the mole fraction of the components, whilst $V_{mixture}$ and V_i represent molar volume of mixtures and pure components, respectively.

$$V_m^{\mathrm{E}} = V_{mixture} - (x_1 V_1^o + x_2 V_2^o) \quad (3.1.3)$$

The equation above represents the change in volume upon mixing of two compounds, subscript 2 and 1 are assigned to a number of processes:

(a) The breakdown of 2-2 as well as 1-1 molecular interactions which gives a positive impact on the volume.
(b) 1-2 molecular interactions gives a significant decrease in volume of the system.
(c) "packing impact" due to the give in size and shape of component species which may results in a negative or positive impact on specific species associated.
(d) result the formation of new chemical species [Redhi et al., 2003].

In thermodynamics, the change in volume upon mixing of binary systems, excess molar volume at constant temperature and pressure is an important parameter. This parameter implies the deviation from ideality of liquid systems, in a particular process, the existence of non-ideality in the binary systems can stipulate the applicability of liquid systems and volume, which is the function of temperature (T), number of moles (n) and pressure (p).

$$V = V(\mathrm{T}, \mathrm{P}, \mathrm{n}_1, \mathrm{n}_2, \mathrm{n}_3, \ldots\ldots \mathrm{n}_\mathrm{f}) \quad (3.1.4)$$

At constant temperature and pressure

$$V = V(\mathrm{n}_1, \mathrm{n}_2, \mathrm{n}_3, \ldots \mathrm{n}_\mathrm{f}) \quad (3.1.5)$$

The ideal volume of liquid mixtures (V_m) atmospheric pressure may be:

$$V_{m,ideal} = \sum x_i V_{m,i}^o \quad (3.1.6)$$

Where $V_{m,i}^o$ denotes molar volume of the pure components *i*.

After the two liquids are mixed, the volume of the system is not normal; the total volume of pure components is then given by:

$$V_{m,mix} = \left(V_{m,mix}\right) \neq x_i V_{m,1} + x_2 V_{m,2} + \ldots . x_i V_{m,i} = \sum x_i V_{m,i}^{o} \quad (3.1.7)$$

The excess molar volume is given by:

$$V_m^{\mathrm{E}} = V_{m,mix} - V_{m,pure} = V_{m,real} - V_{m,ideal} = \sum x_i \left(V_{m,i} - V_{m,i}^{o}\right) \quad (3.1.8)$$

V_m^{E} is the excess molar volume at constant pressure and temperature [Patil et al., 2011]

$V_{m,i}$ denotes the partial molar volume of the ith component and $V_{m,i}^{o}$ represent molar volume of the pure components, *i*.

3.2 Experimental technique for determining excess molar volume

The excess molar volume of component 1 mole fraction (x_1) and component 2 mole fraction (x_2) at constant concentration is given by:

$$V_m^{\mathrm{E}} = V_{m,mix} - \left(x_1 V_1 + x_2 V_2\right) \quad (3.1.9)$$

This parameter can be measured either directly or indirectly. The indirect technique is conducted by determining the density of pure components and density of the binary systems followed by computing the excess molar volume. Direct technique is conducted by measuring the volume change upon mixing, dilatometric technique is a typical example. The measurements are conducted with the use of densimeter followed by computing excess molar volume with the use of equation 3.1.7 and 3.1.8 [Mclure et al., 1967, Duncan et al., 1966, McLean and Yoshimine 1967].

3.2.1 Dilatometer technique

This technique is functional in measuring excess molar volumes; it measures the level of liquid in the dilatometer capillary before and after mixing with the use of a cathetometer. One of the advantages of this method is that it uses or requires less accurate weighing compared to the density method. This method is characterized into two methods which includes batch dilatometry and continuous dilution dilatometry. The setback of this method is the change in pressure of these components before and after mixing which can result in instrumental error.

3.2.2 Batch technique

This technique permits measurements of one data point per loading of the instrument. Here, known mass of pure liquids are filled into the dilatometer which are then separated by mercury. Before and after mixing the liquids, the heights of the mercury in the graduated column is determined, the difference in the mercury height implies the volume change. Proper mixing is achieved by applying a rotating dilatometer, excess molar volume is determined by measuring the change in mercury height. As much as it is not easy to fill the dilatometer, a narrow needle is used to fill the dilatometer. One of the setbacks involved with this technique is the accuracy, due to the fact that the dilatometer is weighed while containing the mercury. This results in an error in mass measurements which also affects the excess molar volume results [Redhi 2003].

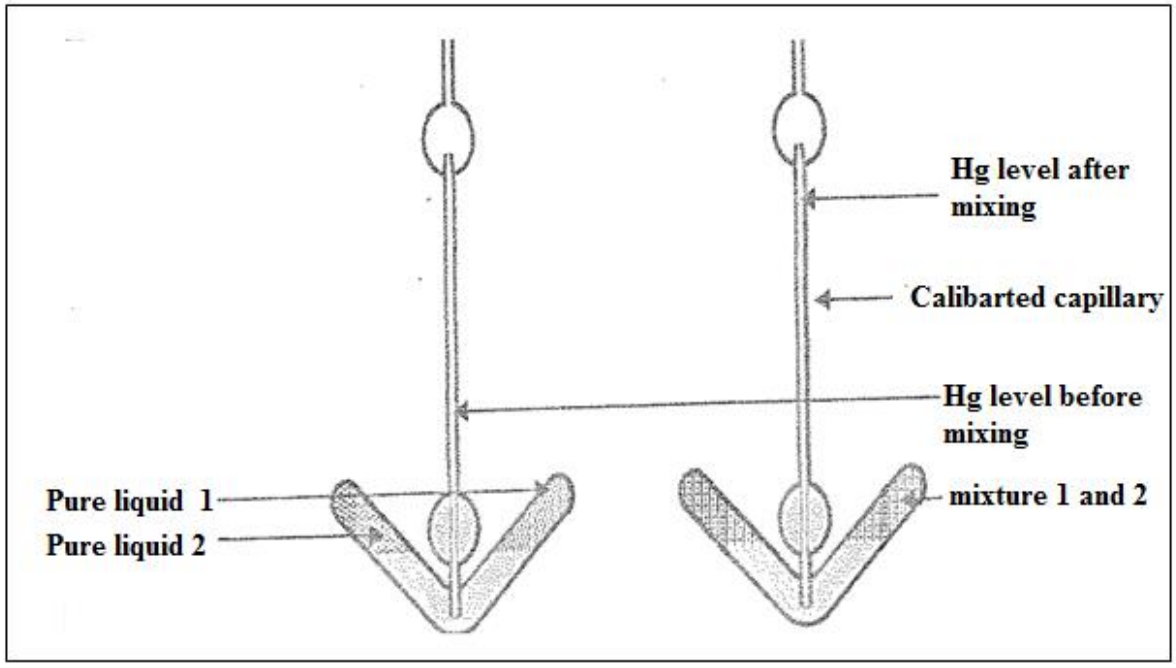

Figure 3.1 Diagram denoting a batch dilatometer [Nevines et al., 1997, Redhi et al., 2003].

3.2.3 Continuous dilution technique

This technique permits the measurements of a number of data points per loading of the instrument (see Figure 3.2). The liquid is filled into the reservoir which contains the other liquid. At this, the two liquids are separated by mercury and the height of the mercury is also measured before and after. The two liquids are then mixed in a closed system. The volume change upon mixing is specified by the change of the components, and the excess molar volume of the components is determined. Upon mixing the liquids, the change in pressure is observed, but this is one of the unconsidered instrumental errors when this technique is employed as compared to batch dilution technique.

From the diagram given in Figure 3.2 (e) is the burette where the volume is measured by filling with one of the pure liquids well as bulb (d) with the second liquid. Upon rotation of the dilatometer, the change in position of some part of mercury in the burette through the capillary (c) is observed. This process commences mixing of the liquids by allowing pure liquids in the burette into the bulb via the higher capillary (b). In the calibrated capillary (a) containing the mercury, the change in the level after mixing is considered as the volume change.

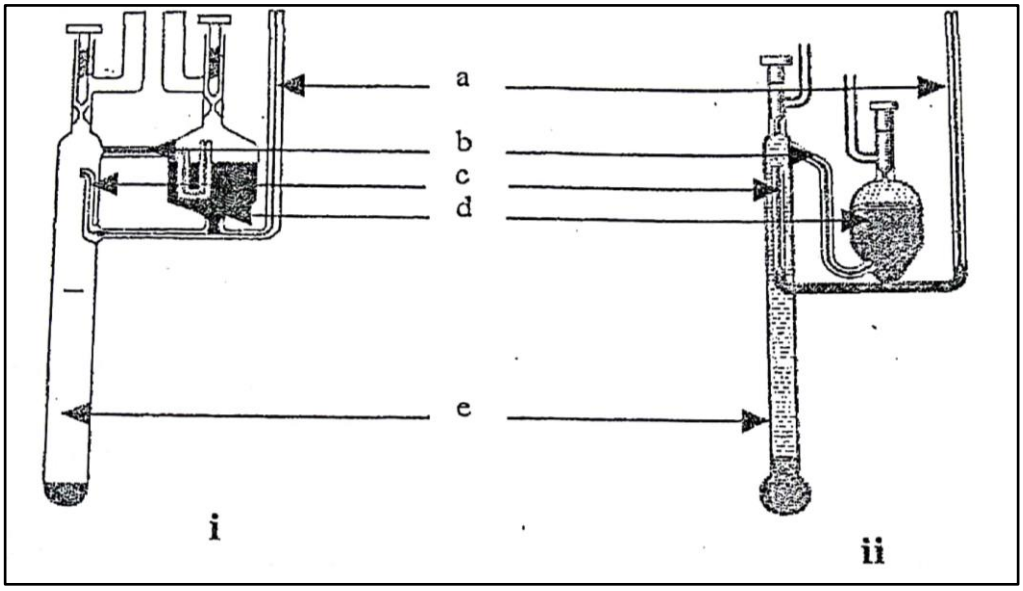

Figure 3.2 Diagram representing continuous dilution dilatometer [Bottomley and Scott 1974, Kumaran and McGlashan 1977].

3.2.4 Indirect technique

The developed dilatometer is accompanied by a greater accuracy than was possible from density measurement methods, the latter technique became less popular for the determination of excess molar volume [Redhi et al., 2003]. In this technique, an accurate automated vibrating densitometer is utilized to determine the densities which makes it more convenient and simple. The excess molar volume for the binary systems is computed from the experimentally determined densities.

3.3 Gas liquid chromatography

For examining activity coefficients at infinite dilution for volatile solutes in non-volatile solvents, gas liquid chromatography is one of the traditional techniques employed. This technique is mostly used to study high boiling solvents, for example ionic liquids. As the solute moves in and out of the column, it is always presumed that:

- The gas phase is an ideal mixture made up of carrier and solute;
- The stationary phase is a real liquid mixture with the solvent and solute.

3.3.1 Theory

The equation 4.2.1 below which was proposed by [Everett et al. 1965, Cruickshank 1969] was used to compute γ_{13}^{∞} of solute in the used ionic liquid.

$$\ln \gamma_{13}^{\infty} = \ln \left(\frac{N_3 RT}{V_N P_1^*}\right) - \frac{P_1^* (B_{11} - V_1^*)}{RT} + \frac{P_0 J_2^3 (2B_{12} - V_1^{\infty})}{RT} \qquad (3.2.1)$$

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

Equation 3.2.2 was used to determine the net retention volume of solute (V_N).

$$V_N = J_2^3(t_R - t_G)q_{ov,} \quad (3.2.2)$$

In the above equation, t_R refers to the retention time of a specified solute, q_{ov} is 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 (taken to be air). The equation (3.2.3) below was use to correct the carrier gas flow for the impact of water vapour.

$$q_{ov} = q_o\left(\frac{T}{T_f}\right)\left[1 - \left(\frac{P_w^*}{P_o}\right)\right] \quad (3.2.3)$$

Where $q_o$denotes the flow rate conducted 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 conducted by using a thermometer. The expression J_2^3 which appears in equation 3.2.1 and 3.2.2 is used to correct the impact of pressure drop through the column and is displayed in equation (3.2.4):

$$J_2^3 = \frac{2}{3}(P_i/P_o)^3 - 1 / (P_i/P_o)^2 - 1 \quad (3.2.4)$$

Where P_i in the above equation represents column inlet pressure.

McGlashan and Potter 1951, proposed an equation to determine the values of B_{11} and B_{12}.

$$\frac{B}{V_c} = 0.430 - 0.866\left(\frac{T_c}{T}\right) - 0.694\left(\frac{T_c}{T}\right)^2 - 0.0375\,(n-1)\left(\frac{T_c}{T}\right)^{4.5} \quad (3.2.5)$$

n is the number of carbon atoms. Utilizing the integrated rules of [Hudson and McCoubrey 1960], V_{12}^c and T_{12}^c could be computed from critical properties of pure elements.

Chapter 4

Experimental Work

4.1 Thermophysical property measurements

4.1.1. Materials

The investigated ionic liquids (trihexyltetradecylphosphonium chloride and 1-ethy-3-methylimidazolium tetrafluoroborate) shown in Figure 4.1.1 and 4.1.2 respectively, were provided by Sigma Aldrich (South Africa). Organic solvents used, propanoic acid was also provided by Sigma Aldrich (South Africa), ethyl acetoacetate was supplied by Acros Organics New Jersey (USA) and benzaldehyde by Merk industry (South Africa). The supplied solvents were degassed by the use of ultra sound, and the method used for the purification of the ionic liquids involved the use of vacuum drying. The water content of the chemicals used was determined by the Karl-Fischer auto titrator before commencement of the experimental work. The initial purity and the type of analysis for materials are given in Table 4.1.1. The measured properties (densities and speeds of sound) for pure liquids were compared with the experimental literature data and are shown in Table 4.1.2. The densities and speeds of sound for the pure ionic liquids and organic solvents are in good correspondence with literature values.

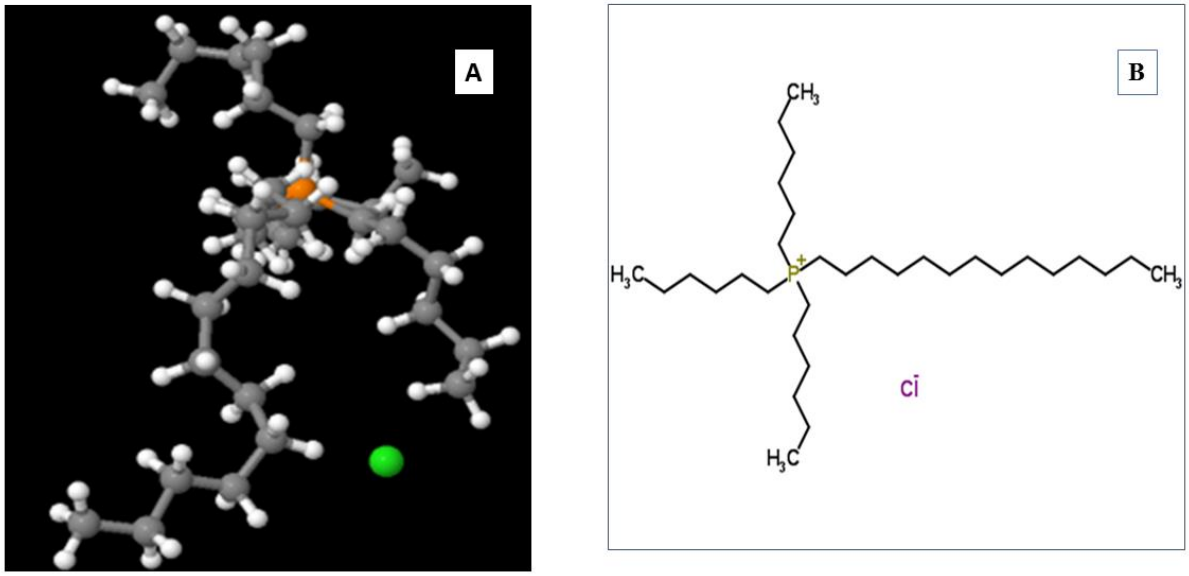

Figure 4.1.1 A) 3-Dimensional geometry of [$P^{+}_{14, 6, 6, 6}$] [Cl^{-}], B) 2-Dimensional geometry of [$P^{+}_{14, 6, 6, 6}$] [Cl^{-}]

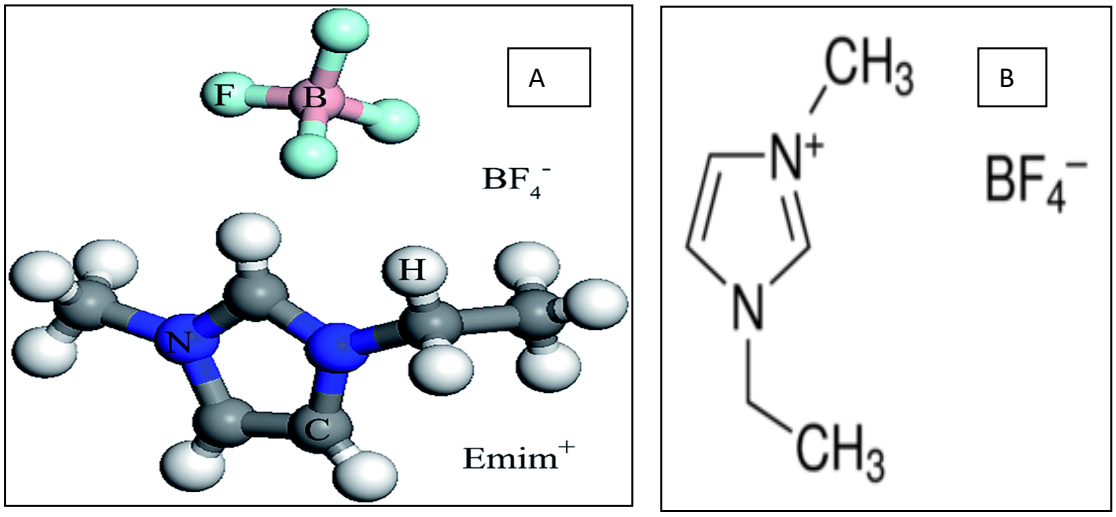

Figure 4.1.2 A) 3-Dimensional geometry of [$Emim^{+}$] [BF_4^{-}], B) 2-Dimensional geometry of [$Emim^{+}$] [BF_4^{-}]

Table 4.1.1

The Table below shows the list of materials, supplier, purification method, purity and analysis method.

Chemical Name	Supplier	Method used for purification	Initial Purity (%)	Analysis method	CAS number
$[P_{4,4,4,14}]$ $[Cl^-]$	Sigma Aldrich	Vacuum drying and kept under molecular sieves 4 Å	≥ 95	--	258864-54-9
[Emim][BF_4^-]	Sigma Aldrich	Vacuum drying and kept under molecular sieves 4 Å	≥ 98	HPLC	143314-16-7
Propanoic Acid	Sigma Aldrich	Degassed by the use of ultrasound (content of water were checked before the analysis by the use of Karl-Fischer titrator)	≥ 995	GC	79-09-4
Ethyl Acetoacetate	Acros Organics	Degassed by the use of ultrasound (content of water were checked before the analysis by the use of Karl-Fischer titrator)	≥ 99	GC	141-97-9
Benzaldehyde	Merck	Degassed by the use of ultrasound (content of water were checked before the analysis by the use of Karl-Fischer titrator)	≥99	GC	100-52-7

Table 4.1.2

Speed of sound and density differentiation among literature and experimental values of **[**$P^{+}_{14, 6, 6, 6}$] [Cl^{-}] and propanoic acid

Component	T/K	ρ/g·cm^{-3}			u/(m·s^{-1})		
		Expt.	Lit.	Ref.	Expt.	Lit.	Ref.
Propanoic acid	293.15	0.9934	0.9938	a	1165.32	1165.6	a
			0.9939	b		1165.0	b
	298.15	0.9881	0.9984	a	1146.65	1127.7	a
			0.9985	b		1147.0	b
	303.15	0.9826	0.9831	a	1127.77	1127.0	a
			0.9831	b		1128.0	b
	308.15	0.9772	0.9776	a	1110.98	1108	a
			0.9777	b		1108	b
	313.15	0.9718	0.9723	a	1090.41	1109.0	a
			0.9722	b		1109.2	b
$[P^{+}_{14,6,6,6}][Cl^{-}]$	293.15	0.8950	0.8928	c	-	-	-

		0.8951	d			
298.15	0.8913	0.8899	c	-	-	-
		0.8919	d			
303.15	0.8890	0.8870	c	-	-	-
		0.8891	d			
308.15	0.8856	0.8840	c	-	-	-
		0.8860	d			
313.15	0.8832	0.8817	c	-	-	-
		0.8829	d			

(Singh et al., 2015) [a]

(Bhanuprakash et al.,2016) [b]

(Wei et al.,2015) [c]

(McAtee and Heitz 2016) [d]

Table 4.1.3

Density and speeds of sound comparison between experimental and literature values of [Emim][BF_4], benzaldehyde and ethyl acetoacetate.

Component	T/K	ρ/(g·cm^{-3})			u/(m· s^{-1})		
		Expt.	Lit.	Ref.	Expt.	Lit.	Ref.
Benzaldehyde	293.15	1.0450	1.0455	a	1477.15	1476.7	a
	298.15	1.0405	1.0442	b	1458.96	1458.2	a
	303.15	1.0360	1.040	b	1440.58	1439.7	a
	308.15	1.0315	1.0361	b	1422.26	1421.2	a
	313.15	1.0270	1.0321	b	1404.04	1402.9	a
[Emim] [BF_4]	293.15	1.2844	1.283	d	1640.25	1631.05	d
	298.15	1.2806	1.2887	c	1628.62	1629	c
	303.15	1.2768	1.2761	d	1616.88	1609.49	d
	308.15	1.2730	1.2824	c	1605.19	1606	c
	313.15	1.2692	1.2685	d	1593.58	1586.19	d
Ethyl Acetoacetate	293.15	1.0283	1.029	e	1350.86	1351.9	e
	298.15	1.0231	1.023	f	1332.06	1332.9	f
	303.15	1.0179	1.015	g	1313.06	1313.5	e
	308.15	1.0127	1.013	f	1294.13	1294.6	e
	313.15	1.0074	1.008	g	1275.32	1276.1	e

(Malek et al., 2012) [a]

(Gao et al., 2009) [b]

(Vercher et al., 2015) [c]

(Rao et al.,2017) [d]

(Amalundi et al., 2013) [e]

(Bermudez-Salguero et al., 2011) [f]

(Gao et al., 2008) [g]

4.2. Methodologies

4.2.1 Preparation of the binary mixtures

The binary systems were prepared by syringing exact amounts of pure compounds of [Emim] [BF_4] and ethyl acetoacetate or benzaldehyde and [$P^+_{14, 6, 6, 6}$] [Cl^-] + propanoic acid into air tight stoppered glass vials. The mass of each component was determined by using an OHAUS analytical mass balance with an accuracy of ± 0.0001 g. Since ionic liquids are viscous, to ensure that absolute homogeneity of both components is achieved, the binary mixtures were shaken thoroughly. Every safeguard was taken to minimise any type of contamination.

4.2.2 Instrument used for thermophysical property measurements

Figure 4.2.1 Anton Paar DSA 5000 M densitometer (taken from densitometer manual).

Figure 4.2.2 DSA 5000 M coupled with RXA 156 and X sampler 452 (taken from densitometer manual).

Measurements of sound velocity and density for the binary mixtures and pure liquids were conducted by the use of a digital vibrating tube density meter and sound velocity analyser (Anton Paar DSA 5000 M) with accuracy of ± 5 × 10^{-6} g · cm^3 in density, ± 0.5 m · s^{-1} in sound velocity, and ± 0.01 K in temperature. Before any experimental analysis was done, ethanol was used to clean the cell, and this was followed by drying with acetone utilizing the fully automatic X sampler 452 module. Cleaning routine was carried out by the X sampler 452 after each measurement. The DSA 5000 M instrument is made of a built-in thermostat controller with the ability to maintain the temperature exactly to ±0.01 K whilst measuring density.

For density measurements, the principle employed by the instrument is a well-known oscillating U-tube, DSA 5000 M which is able to measure simultaneously density over a wide range of 0-3 × 10^3 kg · m^{-3}, and speed of sound between 1000 to 2000 m · s^{-1}, at temperatures ranging between 273. 15 to 343.15 K, with a pressure difference of 0-0.3 MPa, and at a low frequency of about 3 MHz. The approximate density and sound velocity uncertainty measurements were below ± 2 × 10^{-5} g · cm^{-3} for the density and ±0.8 m · s^{-1} for sound velocity, and the temperature was maintained at ±0.02 K. For the derived properties (k_s, Δk_s and V_m^E), the estimated uncertainty was approximately ± 2 × 10^{-8} Pa^{-1}, ± 0.7 × 10^{-8} Pa^{-1} and ±0.004 cm^3 · mol^{-1}, respectively.

4.2.3 Instrumental Accuracy

The technology used in Anton Paar (DSA 5000 M) densitometer make it well more developed and advanced digital instrument. This includes:

- The instrument can be adjusted, especially with standards of high density and high viscosity, and this increases the precision when working with samples of high density and viscosity.
- The instrument is equipped with a thermobalance which acts as an additional reference oscillator that supplies long-term stability and also permits precise measurements.
- Across the full range of viscosity, the errors related to viscosity are corrected automatically by simply determining the damping impact of the viscous compounds then followed by numerical correction for density data.

4.2.4 Detection of Error

- A warning message is shown on the instrument screen anytime there's a filling error. In addition, gas bubbles in the density measuring cell are detected automatically by the instrument by determination of its oscillating pattern.
- When using the speed of sound and density meter, the important source of measuring errors are gas bubbles on the measuring cell. New features of the instrument include a U-view using a real-time camera with zoom functions initiated by Anton Paar institute in order to minimize the occurrence of gas bubbles, the U-tube can be visually examined for gas bubbles in the density measuring cell.

Table 4.2.1

DSA 5000 M instrument specifications

Property	Range
Measurement range for density	0 to 3 $g \cdot cm^{-3}$
Measurement range for speed of sound	1000 to 2000 $m \cdot s^{-1}$
Range of pressure	0 to 3 MPa
Repeatability density	0.000001 $g \cdot cm^{-3}$
Measurement range of temperature	298.15 to 343.15 K
Repeatability speed of sound	0.1 $m \cdot s^{-1}$
Measurement time per sample	1 to 4 min
Repeatability temperature	298.15 K
Sample volume	approximately 3 ml
Automatic bubble detection	Yes
Reference oscillator	Yes
Visual check of the density measuring cell	Camera
Ambient air pressure sensor	yes

4.2.5 Experimental validation method

The experimental method was evaluated by calculating the excess molar volume for the binary test systems of diethyl carbonate + ethanol at a temperature of 298.15 K and comparing with the data from literature [Rogrigueze et al., 2001]. The test system data display that the dissimilarities among the literature and experimental excess molar volume is within the experimental error. Figure 4.2.3 shows the contrast among the experimental and literature values for the excess molar volumes.

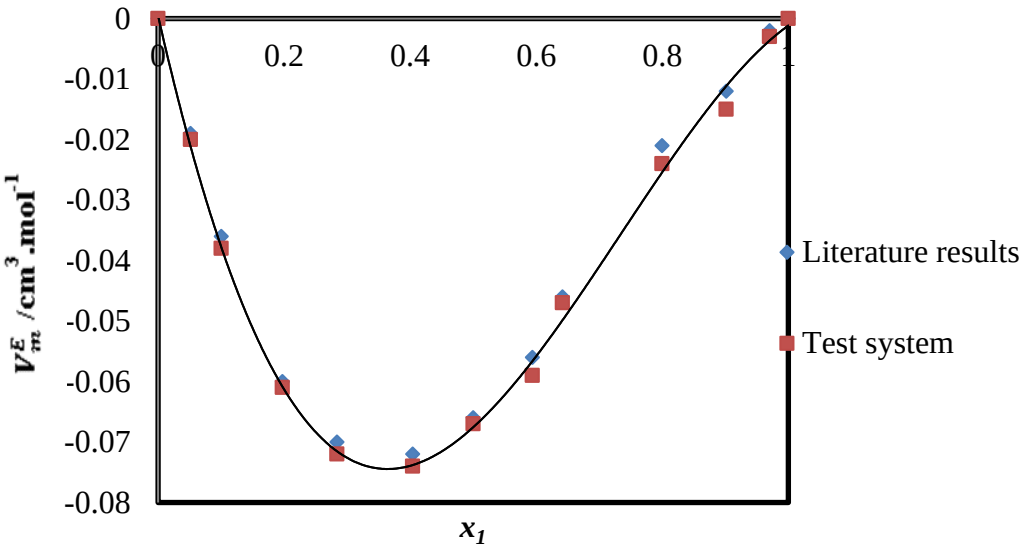

Figure 4.2.3 excess molar volume graph for the comparison of literature results and results for the test system of [ethanol (1) + diethyl carbonate (2)] at T = 298.15 K.

4.3 Activity coefficient measurements

For a proper preference of applicable solvents for aromatic / aliphatic hydrocarbon separation by extractive distillation and liquid-liquid extraction, the understanding of activity coefficients at infinite dilution is essential and important [Meindersma et al., 2010]. The obtained data are important for identifying ionic liquids in solvent which increased separation potential and produced information about types of interactions needed to achieve correlative and predictive excess Gibbs free energy models.

4.3.1 Chemicals

The chemical solutes utilized to conduct the activity coefficients at infinite dilution were provided by Sigma Aldrich (South Africa) and utilized without any further purification, due to the fact that gas liquid chromatography method can easily remove any unwanted species in the column. A vacuum evaporator was used to eliminate any traces of volatile compounds and water contained in the ionic liquid. Karl-Fischer auto titrator was used to examine the water content in the purified ionic liquid, and was found to contain mass percent of 0.0003%. The experimental densities were then conducted to further assess the purity of the ionic liquid in comparison to the literature data. Chromosorb (WHP 80/100) mesh which was provided by Supelco was utilized as a solid support material. Purification technique for this substance was the one applied for the ionic liquid. Helium which is an inert gas with purity of more than 0.99999, was used as a g.l.c carrier gas and was provided by Afrox.

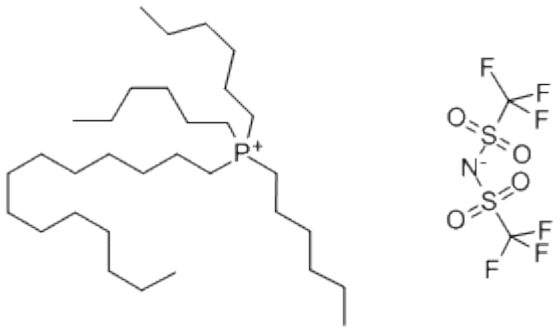

Figure 4.3.1 Structure of trihexyltetradecylphosphonium-bis-(2,4,4-trimethylpentyl)-phosphinate used to study activity coefficients measurements.

The list of chemicals, purity, and suppliers are listed in Table 4.3.1.

Table 4.3.1

Solutes used in this research work, together with suppliers and purity

Solute	Supplier	Mass fraction purity	CAS number
2,2-dimethylbutane	Sigma-Aldirich	>0.99	75-83-2
2,2,4-trimethylpentane	Fluka	>0.995	540-84-1
Methylcyclohexane	Sigma-Aldirich	>0.99	108-87-2
Cyclooctane	Sigma-Aldirich	>0.98	294-64-8
n-Nonane	Merk	>0.99	111-84-2
n-Decane	Merk	>0.99	124-18-5
Hep-1-ene	Sigma-Aldirich	>0.98	592-76-7
Non-1-ene	Sigma-Aldirich	>0.98	124-11-8
Dec-1-ene	Sigma-Aldirich	>0.97	872-05-9
Cyclohexene	Sigma-Aldirich	>0.997	110-83-8
Benzene	Riedel-deHaen	>0.997	71-43-2
Toluene	Sigma-Aldirich	>0.995	108-88-3
Ethylbenzene	Riedel-deHaen	>0.997	100-41-4
m-xylene	Fluka	>0.99	108-38-3
o-xylene	Fluka	>0.99	95-47-6
p-xylene	Fluka	>0.99	106-42-3
Methanol	Sigma-Aldirich	>0.999	67-56-1
Ethanol	Sigma-Aldrich	>0.999	64-17-5
Propan-1-nol	Fluka	>0.995	71-23-8
Butan-1-nol	Riedel-deHaen	>0.995	71-36-3
Acetone	Merk	>0.99	67-64-1
Butanone	Merk	>0.995	78-93-3
THF	Sigma-Aldirich	>0.995	109-99-9
Acetonitrile	Fluka	>0.997	75-05-5
Thiophene	Sigma-Aldirich	>0.99	110-021
Water	Sigma-Aldirich	>0.999	7732-18-5

4.3.2 Procedure

DSA 5000 M densitometer was utilized to conduct the density measurements of the investigated ionic liquid, and the results including the literature results are shown in Table 4.3.2 below.

Table 4.3.2

Differentiation of experimental and literature values for density of trihexyltetradecylphosphonium-bis-(2,4,4-trimethylpentyl)-phosphinate at four different temperatures.

T/K	ρ/g · cm^{-3}	
	Exp.	Lit. [a]
298.15	0.9067	0.9073
303.15	0.9036	0.9039
308.15	0.9001	0.9005
313.15	0.8974	0.8972

(Neves et al., 2011) [a]

4.3.3 Gas chromatography experimental

A gas chromatography (Shimadzu 2014) which is coupled with a thermal conductivity detector was used to conduct the experiments. Total chrom workstation software was used to process and collect the data. A soap bubble flow meter which was located at the outlet of the detector was used to examine the carrier gas flow rate. A stainless steel column of 1 m in length and an internal diameter of 4 mm were used. The use of hot soapy water, hot water and acetone were for the cleaning of the column and followed by rinsing with distilled water. For the development of stationary phase, a definite portion of chromosorb was dispersed in the ionic liquid with dichloromethane followed by the use of the rotary evaporator to evaporate the solvent. The column was packed under vacuum pressure and this is the critical step when undertaking measurements with g.l.c.

The mass of each solid support and stationary phase were weighed in a precision of about 0.0001 g. The loading of column by solvent varied between 28-36 mass percent of ionic liquid, high enough to avoid any unwanted absorption onto the column loading. For each investigated temperature, two different columns with different mass percent loading were used to repeat the measurements. Before commencement of the experiments, carrier gas was passed through each column at a flow rate of 30 cm^3s^{-1}, and high temperature of 360 K in order to condition the columns for an interval of about 8h. A pressure transducer application in the g.l.c was utilized to measure the pressure drop with uncertainty of about 0.1 hPa. A digital barometer was used to measure an atmospheric pressure which has an uncertainty of about 0.1 hPa. Range of (0.2 - 0.3) μL of the sample solute was injected manually and these volumes were regarded small enough to make sure the state of infinite dilution of the solute on the column. The experimental work was carried out at various temperatures, T = (313.15 to 343.15) K. The column temperature was kept constant at about 0.02 K. The reproducibility was checked by repeating the experiments 2-3 times at all given temperatures. The approximate overall error in activity coefficients at infinite dilution were not more than 3%, the feasible errors in examining the solute vapour pressure, retention time, and column loading were taken to consideration. The system of (hexane and hexadecane) was used to validate the g.l.c method at 298.15 K, and the results obtained were within 1% of the literature results reported by [Tiegs et al., 1986].

4.3.4 Instrumentation

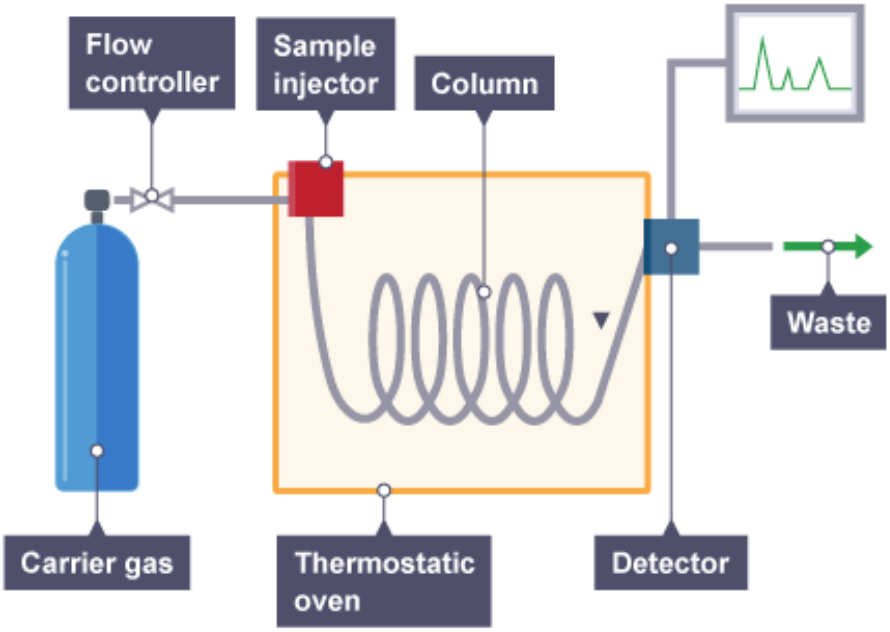

Figure 4.3.2 A typical schematic diagram of gas liquid chromatograph used (taken from g.l.c manual).

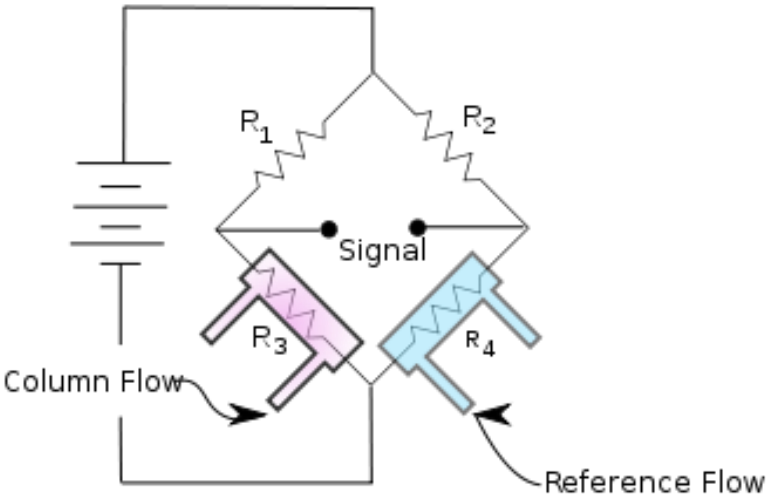

Figure 4.3.3 A Schematic diagram of thermal conductivity detector (TCD) which is also known as a "Katharometer" (taken from TCD instruction manual).

This is a chemical specific detector and a bulk property detector mostly used in gas chromatography. Because most of the used compounds have less thermal conductivity 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 good purpose. As much as the detector is not sensitive in comparison to other detectors, it is non-specific and non-destructive.

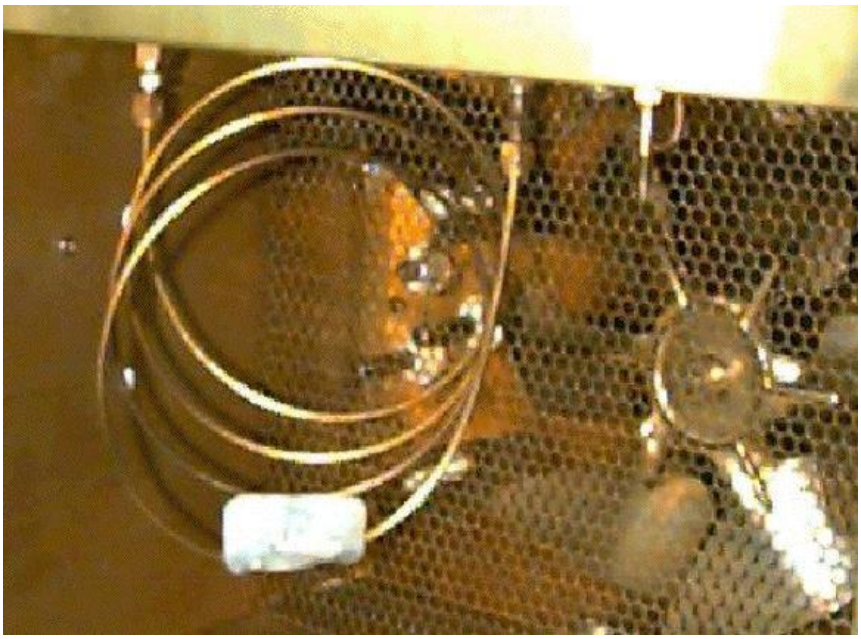

Figure 4.3.4 A diagram showing a packed column inserted into a gas liquid chromatography oven.

The column was fully packed of 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 thermal conductivity detector.

Table 4.3.3

Disadvantages and advantages of chromatographic technique

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

Chapter 5

Results

5.1 Measured thermodynamic properties

The densities and sound velocity of the measured binary systems: of (trihexyltetradecylphosphonium chloride + propanoic acid), and binary mixtures of (1-ethyl-3-methylimidazolium tetrafluoroborate + ethyl acetoacetate or benzaldehyde) are shown in Tables 5.1.1 and 5.1.3 below. The derived properties which include (excess molar volume, isentropic compressibility and deviation in isentropic compressibility) were computed from the experimentally determined densities and speeds of sound. For the binary mixtures of (trihexyltetradecylphosphonium chloride + propanoic acid), apparent molar volume was calculated from the densities and molalities, intermolecular free length was calculated by using Jacobson's empirical relation, and apparent molar isentropic compressibilities were computed from densities, molalities as well as isentropic compressibilities. For the systems containing (1-ethyl-3-methylimidazolium tetrafluoroborate + ethyl acetoacetate or benzaldehyde), viscosity was measured and deviations in viscosity were determined on a mole fraction basis. The thermodynamic properties were conducted at T = (293.15, 298.15, 303.15, 308.15 and 313.15) K, and at 0.1 MPa across the whole mole fraction range (0 to 1).

The derived excess parameters of the binary systems of (trihexyltetradecylphosphonium chloride + propanoic acid) and binary systems of (1-ethyl-3-methylimidazolium tetrafluoroborate + ethyl acetoacetate or benzaldehyde) were fitted by a technique of non linear least squares to a Redlich-Kister equation (5.1).

$$X = x_1 x_2 \sum_{i=1}^{k} A_i \, (1 - 2x_1)^{i-1} \qquad (5.1)$$

In equation 5.1 above, *x* represents the excess molar volume or deviation in isentropic compressibility. The least squares method was used to determine the values of the fitting parameters A_i.

The results of the measured and derived properties of the binary mixtures are shown in the tables below as well as their plots.

Table 5.1.1

Densities (ρ), excess molar volume (V_m^E), sound velocity (u), of [$P^+_{14, 6, 6, 6}$] [Cl^-] + propanoic acid binary systems at p = 0.1 MPa.

x_1	ρ/g · cm^{-3}	V_m^E/cm^3 ·mol^{-1}	u/m · s^{-1}
		293.15 K	
0	0.9934	0	1165.32
0.0105	0.9876	-0.0612	1188.89
0.0203	0.9810	-0.1071	1208.89
0.0305	0.9756	-0.1415	1227.81
0.0699	0.9591	-0.2230	1288.49
0.1088	0.9476	-0.2838	1330
0.2131	0.9298	-0.5559	1392.17
0.3301	0.9187	-0.6701	1425.44
0.4361	0.9116	-0.6075	1450.53
0.5301	0.9069	-0.4833	1467.69
0.6333	0.9031	-0.3557	1483.53
0.7601	0.9001	-0.1895	1490.27
1	0.8950	0	1515.13
		298.15 K	
0	0.9881	0	1146.65
0.0105	0.9816	-0.0735	1170.64
0.0203	0.9761	-0.1298	1190.94
0.0305	0.9709	-0.1798	1210.12
0.0699	0.9549	-0.2909	1271.56
0.1088	0.9436	-0.3577	1313.53
0.2131	0.9259	-0.6345	1376.32
0.3301	0.9150	-0.7621	1409.38
0.4361	0.9079	-0.6928	1433.97
0.5301	0.9032	-0.5497	1450.92
0.6333	0.8994	-0.4206	1470.57

0.7601	0.8964	0.2520	1475.73
1	0.8913	0	1495.30

303.15 K

0	0.9826	0	1127.77
0.0105	0.9765	-0.077	1152.22
0.0203	0.9712	-0.1360	1172.83
0.0305	0.9662	-0.1772	1192.26
0.0699	0.9507	-0.2984	1254.44
0.1088	0.9398	-0.3716	1296.89
0.2131	0.9229	-0.6828	1360.31
0.3301	0.9122	-0.7983	1393.35
0.4361	0.9053	-0.7300	1417.58
0.5301	0.9007	-0.5970	1433.83
0.6333	0.8970	-0.4576	1447.93
0.7601	0.8940	-0.2819	1450.48
1	0.8890	0	1476.21

308.15 K

0	0.9772	0	1108.98
0.0105	0.9714	-0.0888	1133.91
0.0203	0.9663	-0.1566	1154.81
0.0305	0.9615	-0.2112	1174.48
0.0699	0.9466	-0.3555	1237.41
0.1088	0.9359	-0.4369	1280.33
0.2131	0.9191	-0.7215	1344.41
0.3301	0.9086	-0.8524	1377.45
0.4361	0.9018	-0.7914	1401.38
0.5301	0.8973	-0.6589	1417.16
0.6333	0.8936	-0.5259	1430.76
0.7601	0.8907	-0.3378	1439.79

1	0.8856	0	1457.47
		313.15 K	
0	0.9718	0	1090.41
0.0105	0.9663	-0.0939	1115.83
0.0203	0.9615	-0.1649	1136.94
0.0305	0.9569	-0.2217	1156.83
0.0699	0.9424	-0.3693	1220.45
0.1088	0.9326	-0.5184	1263.87
0.2131	0.9160	-0.7752	1328.62
0.3301	0.9060	-0.9726	1361.73
0.4361	0.8991	-0.8411	1385.39
0.5301	0.8947	-0.7262	1400.83
0.6333	0.8911	-0.5622	1414.06
0.7601	0.8882	-0.3702	1422.67
1	0.8832	0	1439.33

Table 5.1.2

Molality (m), apparent molar volume (V_ϕ), intermolecular free length (L_f), isentropic compressibility (k_s), apparent molar isentropic compressibility (K_ϕ), and deviation in isentropic compressibility (Δk_s) for ($[P^+_{14, 6, 6, 6}]$ $[Cl^-]$ + propanoic acid) binary systems at p = 0.1 MPa.

x_1	m (mol/kg)	$10^8 \cdot k_s/Pa^{-1}$	$10^8 \cdot \Delta k_s/Pa^{-1}$	$V_\phi(m^3 \cdot mol^{-1})$	$L_f/(10^{-7}m)$	$10^{15} \cdot K_\phi/m^3 \cdot mol^{-1} \cdot Pa^{-1}$
		293.15 K				
0		74.13	0	0	1.755	0
0.0105	0.1438	71.70	-2.16	573.91	1.726	23.62
0.0203	0.2802	69.75	-3.89	574.71	1.702	24.37
0.0305	0.4217	67.99	-5.40	575.75	1.680	24.51
0.0699	1.0143	62.80	-9.55	577.00	1.615	25.00
0.1088	1.6377	59.66	-11.83	577.72	1.574	25.58
0.2131	3.4230	55.49	-14.02	578.63	1.518	26.63
0.3301	5.6535	53.57	-14.75	579.73	1.492	27.93
0.4361	9.0791	52.14	-13.39	579.75	1.472	28.13
0.5301	13.5314	51.49	-11.22	579.77	1.466	28.03
0.6333	20.7076	50.31	-9.76	579.89	1.458	28.02
0.7601	31.8278	50.18	-7.73	580.23	1.441	28.62
1		48.67	0	0	1.422	0
		298.15 K				
0		76.98	0	0	1.804	0
0.0105	0.1438	74.34	-2.36	575.47	1.773	24.22
0.0203	0.2802	72.23	-4.23	576.16	1.747	24.47
0.0305	0.4217	70.33	-5.87	577.19	1.724	24.65
0.0699	1.0143	64.77	-10.34	578.49	1.655	25.29
0.1088	1.6377	61.42	-12.78	579.45	1.611	25.98
0.2131	3.4230	57.01	-15.09	580.67	1.552	27.20
0.3301	5.6535	55.02	-15.81	581.84	1.525	28.39
0.4361	9.0791	53.56	-14.33	581.85	1.504	28.83

0.5301	13.5314	52.59	-12.45	581.99	1.491	28.86
0.6333	20.7076	51.41	-10.75	582.19	1.474	28.75
0.7601	31.8278	51.29	-7.86	582.56	1.471	29.06
1		50.18	0	0	1.456	0
		303.15 K				
0		80.01	0	0	1.856	0
0.0105	0.1438	77.14	-2.57	576.62	1.822	24.63
0.0203	0.2802	74.85	-4.61	577.37	1.795	24.69
0.0305	0.4217	72.81	-6.37	578.44	1.771	24.75
0.0699	1.0143	66.84	-11.19	579.89	1.696	25.55
0.1088	1.6377	63.26	-13.81	580.85	1.650	26.34
0.2131	3.4230	58.56	-16.26	581.92	1.588	27.35
0.3301	5.6535	56.47	-16.97	583.20	1.559	29.00
0.4361	9.0791	54.97	-15.36	583.23	1.538	29.63
0.5301	13.5314	54	-13.31	583.41	1.525	29.55
0.6333	20.7076	53.18	-1108	583.64	1.514	29.72
0.7601	31.8278	53.16	-7.91	584.02	1.513	29.97
1		51.62	0	0	1.491	0
		308.15 K				
0		83.21	0	0	1.910	0
0.0105	0.1438	80.07	-2.82	577.76	1.874	24.84
0.0203	0.2802	77.59	-5.03	578.57	1.844	24.96
0.0305	0.4217	75.39	-6.95	579.68	1.818	25.04
0.0699	1.0143	68.99	-12.12	581.29	1.739	25.76
0.1088	1.6377	65.18	-14.19	582.47	1.691	26.70
0.2131	3.4230	60.19	-17.52	583.94	1.625	27.82
0.3301	5.6535	58.01	-18.19	585.23	1.595	29.69
0.4361	9.0791	56.47	-16.45	585.29	1.574	30.39
0.5301	13.5314	55.49	-14.24	585.50	1.559	30.39
0.6333	20.7076	54.66	-11.84	585.74	1.548	30.61

0.7601	31.8278	54.16	-8.95	586.16	1.541	30.81
1		53.16	0	0	1.527	0
		313.15 K				
0		86.54	0	0	1.966	0
0.0105	0.1438	83.12	-3.09	578.87	1.926	24.96
0.0203	0.2802	80.46	-5.46	579.77	1.895	25.17
0.0305	0.4217	78.09	-7.52	580.93	1.867	25.36
0.0699	1.0143	71.24	-13.07	582.69	1.783	25.99
0.1088	1.6377	67.13	-16.10	583.31	1.731	26.96
0.2131	3.4230	61.85	-18.83	585.26	1.662	28.07
0.3301	5.6535	59.52	-19.52	586.42	1.630	30.29
0.4361	9.0791	57.95	-17.61	586.75	1.609	31.11
0.5301	13.5314	56.96	-15.22	586.96	1.592	31.18
0.6333	20.7076	56.16	-12.60	587.23	1.583	31.47
0.7601	31.8278	55.63	-9.53	587.71	1.576	31.70
1		54.65	0	0	1.562	0

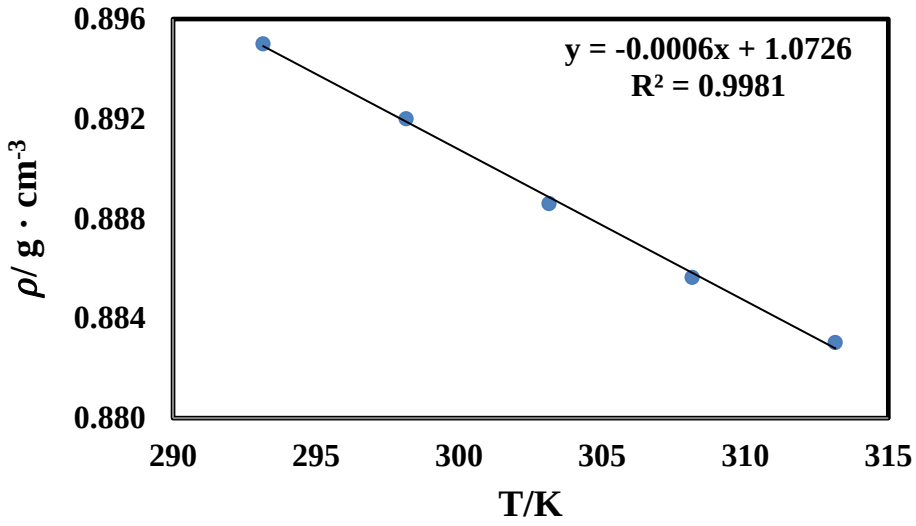

Figure 5.1.1: Density (ρ) of IL [$P^{+}_{14,\ 6,\ 6,\ 6}$] [Cl^{-}] against temperature range (293.15 to 313.15)K.

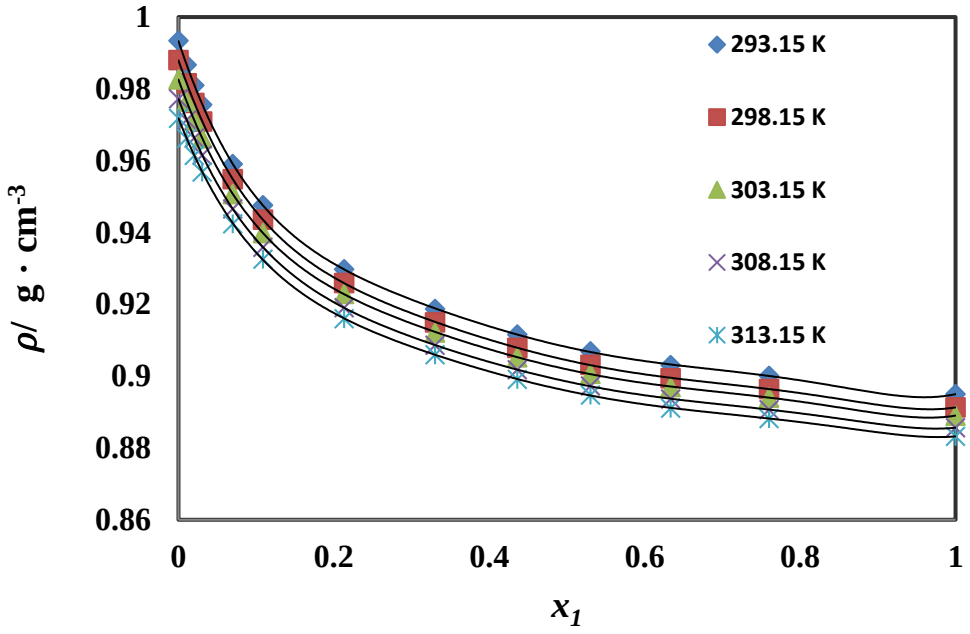

Figure 5.1.2: Density of the binary mixtures of {[$P^{+}_{14,\ 6,\ 6,\ 6}$] [Cl^{-}] (x_1) + propanoic acid (x_2)} at T = (293.15, 298.15, 303.15, 308.15 and 313.15) K.

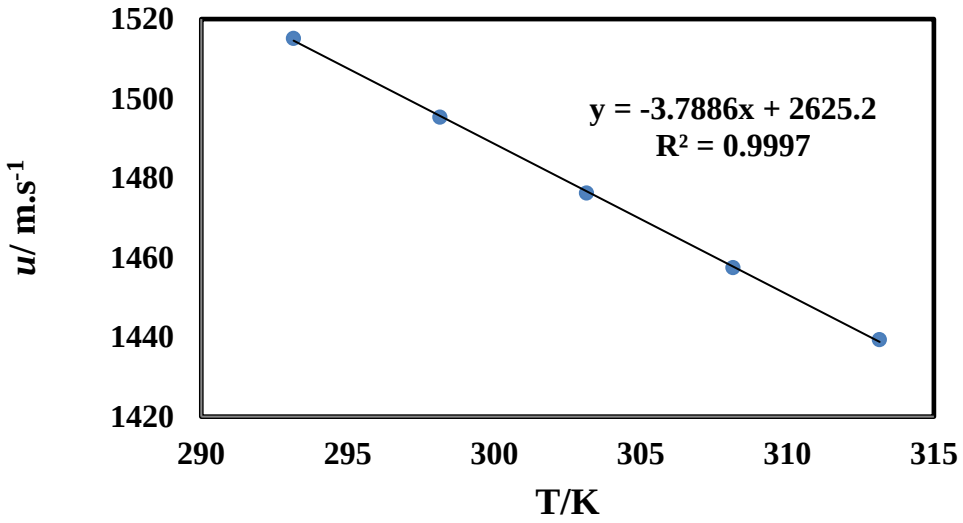

Figure 5.1.3: Speed of sound (u) of IL ([$P^{+}_{14,6,6,6}$] [Cl^{-}]) against temperature range (293.15 to 313.15) K

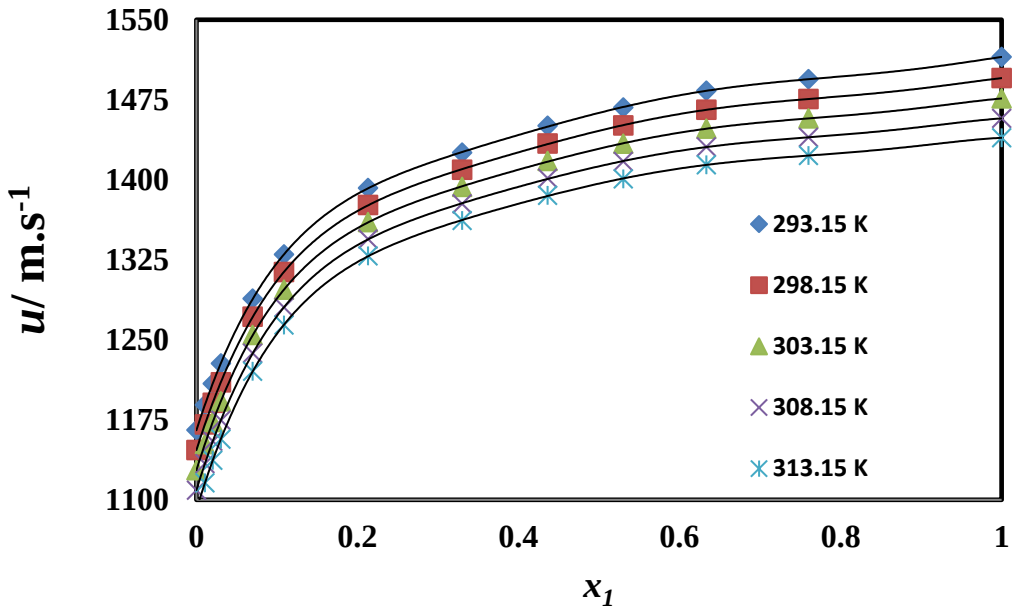

Figure 5.1.4: Speed of sound (u) graph for the binary mixtures of {[$P^{+}_{14,6,6,6}$] [Cl^{-}] (x_1) + propanoic acid (x_2)} at T = (293.15, 298.15, 303.15, 308.15 and 313.15) K.

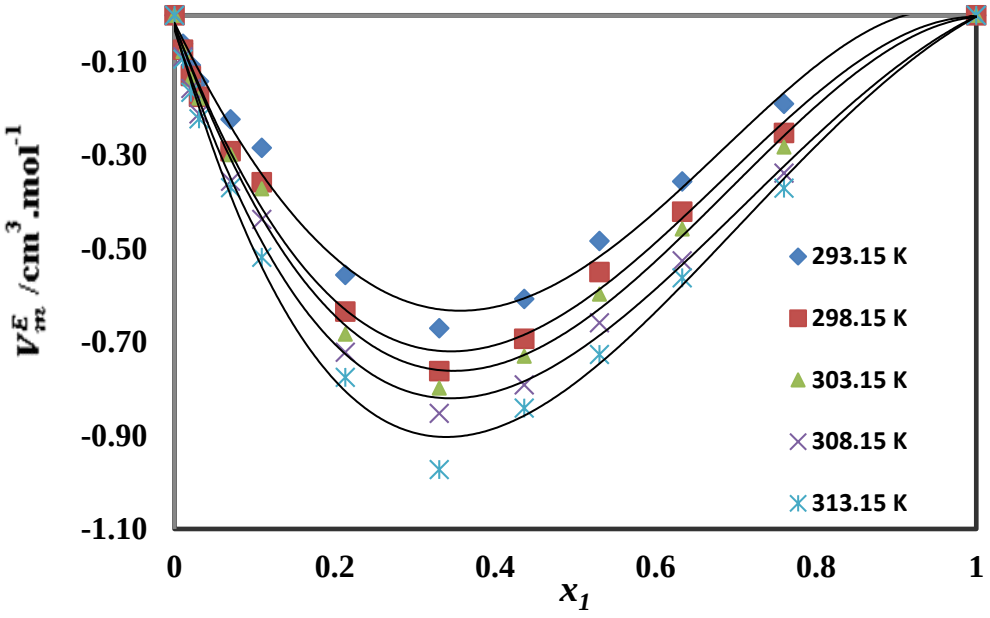

Figure 5.1.5: Excess molar volume (V_m^E) of the miscible prepared mixtures for {[$P^+_{14, 6, 6, 6}$] [Cl^-] (x_1) + propanoic acid (x_2)} as a function of mole fraction of ionic liquid at T = (293.15, 298.15, 303.15, 308.15 and 313.15) K. The plot was fitted by using the Redlich-Kister equation.

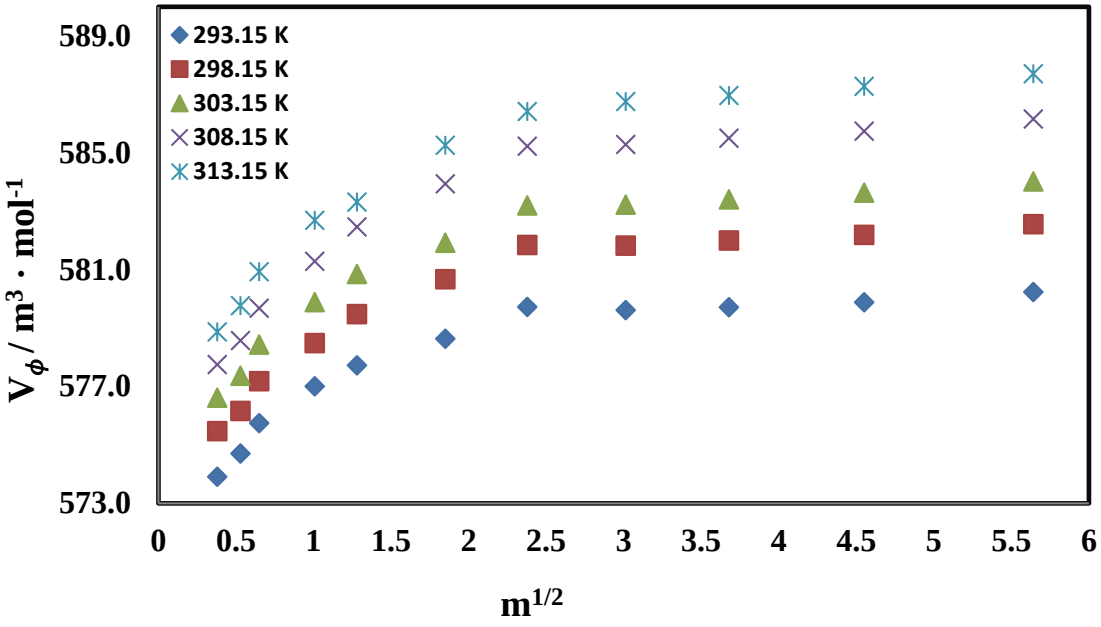

Figure 5.1.6: Apparent molar volume(V_ϕ), of binary mixtures {[$P^+_{14, 6, 6, 6}$] [Cl^-] (x_1) + propanoic acid(x_2)} at T = (293.15, 298.15, 303.15, 308.15 and 313.15) K. [m = molality of mixture]

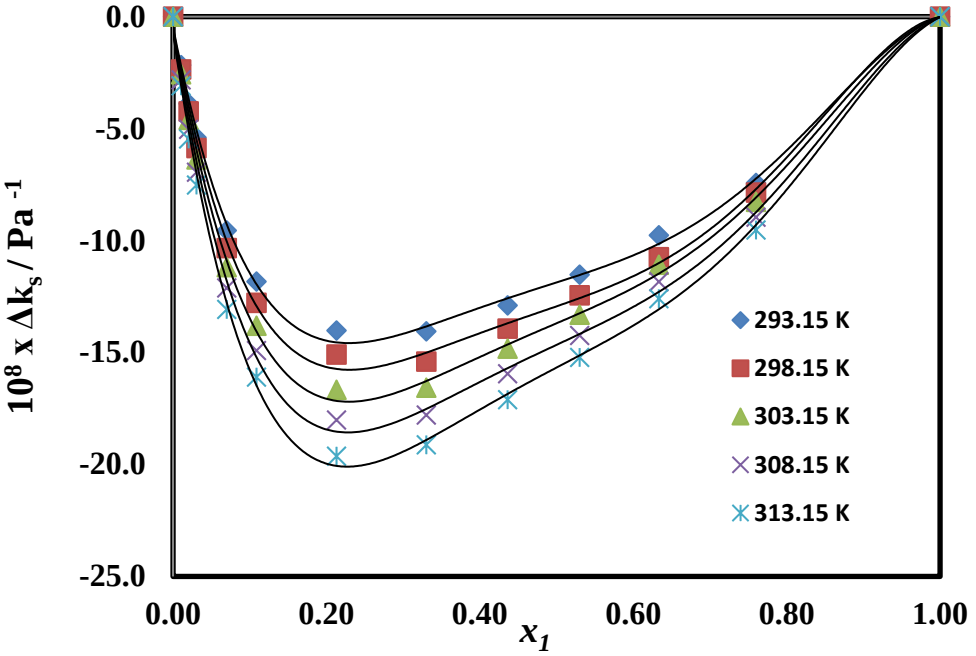

Figure 5.1.7: Deviation in isentropic compressibility (Δk_s) of the binary mixtures of {[$P^+_{14,\ 6,\ 6,\ 6}$] [Cl^-] (x_1) + propanoic acid(x_2)} expressed in mole fraction of [$P^+_{14,\ 6,\ 6,\ 6}$] [Cl^-] at (293.15, 298.15, 303.15, 308.15 and 313.15) K.

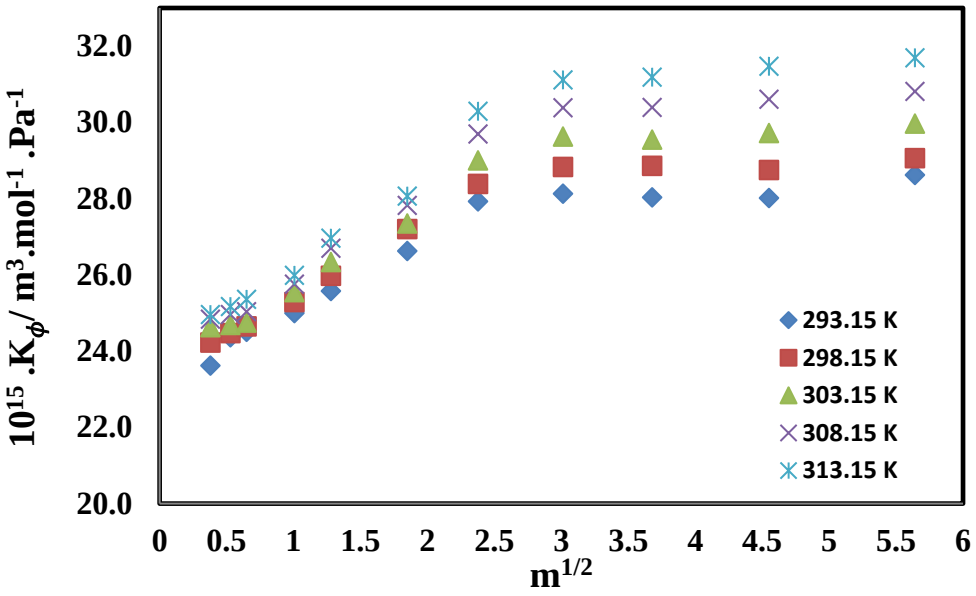

Figure 5.1.8: Apparent molar isentropic compressibility (K_ϕ) of binary mixtures {[$P^+_{14,\ 6,\ 6,\ 6}$] [Cl^-] (x_1) + propanoic acid (x_2)} plotted against $(m)^{1/2}$ at T = (293.15, 298.15, 303.15, 308.15 and 313.15) K.

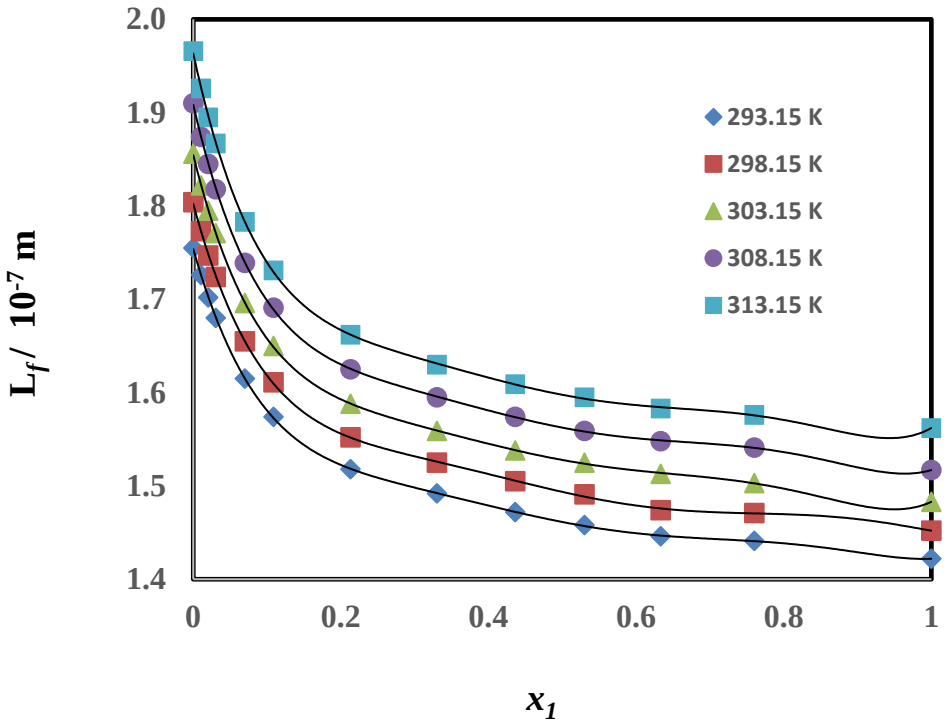

Figure 5.1.9: Intermolecular free length (L_f), of the binary mixtures of {[$P^+_{14, 6, 6, 6}$] [Cl^-] (x_1)+ propanoic acid (x_2) given as a function of mole fraction of IL at T = (293.15, 298.15, 303.15, 308.15 and 313.15) K.

Table 5.1.3

Densities (ρ), excess molar volume (V_m^E), sound velocity (u), intermolecular free length (L_f), deviation in isentropic compressibility (Δk_s), and isentropic compressibility (k_s) of {[Emim] [BF_4] (x_1) + benzaldehyde (x_2)} binary systems at T = (293.15, 298.15, 303.15, 308.15 and 313.15) K and at p = 0.1 MPa.

x_1	ρ/g·cm^{-3}	V_m^E/cm^3· mol^{-1}	u/m · s^{-1}	L_f /(10^{-7} m)	10^8 · Δk_s /Pa^{-1}	10^8 · k_s /Pa^{-1}
		293.15 K				
0	1.0450	0	1477.15	1.35	0	43.9
0.0182	1.0540	-0.2323	1485.48	1.34	-0.59	43.0
0.0416	1.0644	-0.4516	1493.58	1.32	-1.12	42.1
0.0803	1.0805	-0.7295	1505.00	1.30	-1.79	40.9
0.1062	1.0907	-0.8893	1511.97	1.29	-2.16	40.1
0.2053	1.1250	-1.2567	1535.34	1.25	-3.09	37.7
0.3051	1.1548	-1.4321	1555.75	1.22	-3.53	35.8
0.4059	1.1810	-1.4648	1573.63	1.19	-3.61	34.2
0.5056	1.2037	-1.3885	1589.24	1.17	-3.42	32.9
0.6051	1.2237	-1.2250	1602.63	1.15	-3.01	31.8
0.7056	1.2417	-0.9925	1614.55	1.13	-2.44	30.9
0.8054	1.2577	-0.7025	1624.73	1.12	-1.72	30.1
0.9060	1.2722	-0.3638	1633.45	1.11	-0.88	29.5
1	1.2844	0	1640.25	1.09	0	28.9
		298.15 K				
0	1.0405	0	1458.96	1.38	0	45.2
0.0182	1.0495	-0.2377	1467.57	1.37	-0.62	44.2
0.0416	1.0600	-0.4622	1475.96	1.35	-1.19	43.3
0.0803	1.0761	-0.7456	1487.80	1.33	-1.91	42.0
0.1062	1.0863	-0.9082	1495.03	1.32	-2.30	41.2
0.2053	1.1208	-1.2825	1519.37	1.28	-3.28	38.6
0.3051	1.1507	-1.4610	1540.67	1.24	-3.75	36.6
0.4059	1.1769	-1.4945	1559.36	1.22	-3.83	34.9
0.5056	1.1997	-1.4164	1575.65	1.19	-3.63	33.6
0.6051	1.2197	-1.2497	1589.61	1.17	-3.20	32.4
0.7056	1.2378	-1.0123	1601.93	1.15	-2.58	31.5
0.8054	1.2538	-0.7164	1612.51	1.14	-1.82	30.7
0.9060	1.2684	-0.3707	1621.23	1.13	-0.92	30.0
1	1.2806	0	1628.62	1.12	0	29.4
		303.15 K				
0	1.0360	0	1440.58	1.42	0	46.5
0.0182	1.0451	-0.2439	1449.46	1.4	-0.66	45.5
0.0416	1.0556	-0.4731	1458.12	1.39	-1.27	44.6

0.0803	1.0718	-0.7622	1470.37	1.36	-2.03	43.2
0.1062	1.0820	-0.9279	1477.86	1.34	-2.44	42.3
0.2053	1.1166	-1.3093	1503.18	1.31	-3.48	39.6
0.3051	1.1466	-1.4911	1525.42	1.27	-3.98	37.5
0.4059	1.1729	-1.5244	1544.92	1.24	-4.07	35.7
0.5056	1.1957	-1.4442	1561.89	1.21	-3.86	34.3
0.6051	1.2158	-1.2746	1576.43	1.19	-3.39	33.1
0.7056	1.2339	-1.0328	1589.25	1.18	-2.74	32.1
0.8054	1.2500	-0.7307	1600.19	1.16	-1.94	31.2
0.9060	1.2645	-0.3782	1609.26	1.15	-0.98	30.5
1	1.2768	0	1616.88	1.14	0	30.0
		308.15 K				
0	1.0315	0	1422.26	1.45	0	47.9
0.0182	1.0406	-0.2502	1431.40	1.43	-0.71	46.9
0.0416	1.0512	-0.4848	1440.33	1.42	-1.35	45.9
0.0803	1.0675	-0.7801	1453.01	1.39	-2.25	44.4
0.1062	1.0777	-0.9491	1460.75	1.38	-2.59	43.5
0.2053	1.1124	-1.3376	1487.07	1.34	-3.69	40.7
0.3051	1.1425	-1.5230	1510.22	1.29	-4.23	38.4
0.4059	1.1689	-1.5567	1530.56	1.27	-4.33	36.5
0.5056	1.1917	-1.4741	1548.23	1.24	-4.10	35.0
0.6051	1.2119	-1.3008	1563.33	1.22	-3.61	33.8
0.7056	1.2300	-1.0542	1576.60	1.2	-2.91	32.7
0.8054	1.2461	-0.7461	1587.81	1.19	-2.05	31.8
0.9060	1.2607	-0.3863	1597.39	1.18	-1.04	31.1
1	1.2730	0	1605.19	1.16	0	30.5
		313.15 K				
0	1.0270	0	1404.04	1.49	0	49.4
0.0182	1.0361	-0.2567	1413.44	1.47	-0.75	48.3
0.0416	1.0468	-0.4968	1422.65	1.45	-1.43	47.2
0.0803	1.0631	-0.7984	1435.72	1.43	-2.28	45.6
0.1062	1.0734	-0.9705	1443.73	1.41	-2.75	44.7
0.2053	1.1082	-1.3670	1471.04	1.36	-3.92	41.7
0.3051	1.1384	-1.5560	1495.13	1.32	-4.49	39.3
0.4059	1.1648	-1.5901	1516.30	1.29	-4.60	37.3
0.5056	1.1878	-1.5056	1534.67	1.26	-4.36	35.7
0.6051	1.2080	-1.3273	1550.34	1.24	-3.84	34.4
0.7056	1.2262	-1.0749	1563.88	1.22	-3.09	33.3
0.8054	1.2423	-0.7613	1575.60	1.2	-2.17	32.4
0.9060	1.2569	-0.3939	1585.61	1.19	-1.11	31.6
1	1.2692	0	1593.58	1.18	0	31.0

Table 5.1.4

Densities (ρ), excess molar volume (V_m^E), sound velocity (u), intermolecular free length (L_f), deviation in isentropic compressibility (Δk_s), and isentropic compressibility (k_s), of {[Emim] [BF_4] (x_1) + ethyl acetoacetate (x_2)} binary systems at T = (293.15, 298.15, 303.15, 308.15 and 313.15) K and at p = 0.1 MPa.

x_1	ρ/g·cm^{-3}	V_m^E/cm^3· mol^{-1}	u/m · s^{-1}	L_f /(10^{-7} m)	10^8· Δk_s /Pa^{-1}	10^8 · k_s /Pa^{-1}
		293.15 K				
0	1.0283	0	1350.86	1.49	0	53.3
0.0167	1.0353	-0.2245	1360.12	1.47	-0.67	52.2
0.0455	1.0464	-0.5028	1373.10	1.45	-1.50	50.7
0.0885	1.0618	-0.7814	1390.18	1.42	-2.40	48.7
0.1056	1.0680	-0.9108	1396.77	1.41	-2.73	48.0
0.2055	1.1007	-1.3241	1432.93	1.36	-4.04	44.2
0.3057	1.1306	-1.5349	1467.28	1.31	-4.76	41.1
0.4053	1.1579	-1.5955	1499.45	1.26	-5.01	38.4
0.5053	1.1832	-1.5319	1529.68	1.22	-4.87	36.1
0.6054	1.2066	-1.3649	1557.25	1.19	-4.37	34.2
0.7055	1.2284	-1.1112	1581.89	1.16	-3.58	32.5
0.8058	1.2487	-0.7843	1604.09	1.14	-2.54	31.1
0.9053	1.2677	-0.4137	1623.63	1.11	-1.32	29.9
1	1.2844	0	1640.25	1.10	0	28.9
		298.15 K				
0	1.0231	0	1332.06	1.53	0	55.1
0.0167	1.0302	-0.2328	1341.59	1.51	-0.72	53.9
0.0455	1.0414	-0.5210	1354.84	1.49	-1.61	52.3
0.0885	1.0569	-0.8097	1372.28	1.46	-2.57	50.2
0.1056	1.0631	-0.9429	1379.03	1.45	-2.92	49.5
0.2055	1.0960	-1.3697	1416.06	1.39	-4.31	45.5
0.3057	1.1260	-1.5876	1451.28	1.34	-5.08	42.2
0.4053	1.1535	-1.6509	1484.30	1.29	-5.34	39.3
0.5053	1.1790	-1.5859	1515.32	1.25	-5.19	36.9
0.6054	1.2025	-1.4128	1543.62	1.21	-4.66	34.9
0.7055	1.2244	-1.1507	1568.90	1.18	-3.81	33.2
0.8058	1.2448	-0.8123	1591.65	1.16	-2.71	31.7
0.9053	1.2638	-0.4279	1611.42	1.13	-1.39	30.5
1	1.2806	0	1628.62	1.12	0	29.4

303.15 K

0	1.0179	0	1313.06	1.57	0	57.0
0.0167	1.0250	-0.2419	1322.80	1.55	-0.78	55.8
0.0455	1.0364	-0.5403	1336.34	1.53	-1.72	54.0
0.0885	1.0519	-0.8398	1354.17	1.49	-2.75	51.8
0.1056	1.0582	-0.9764	1361.07	1.48	-3.12	51.0
0.2055	1.0913	-1.4180	1398.97	1.42	-4.61	46.8
0.3057	1.1215	-1.6431	1435.05	1.37	-5.42	43.3
0.4053	1.1492	-1.7081	1468.93	1.32	-5.70	40.3
0.5053	1.1748	-1.6399	1500.77	1.28	-5.53	37.8
0.6054	1.1984	-1.4605	1529.82	1.24	-4.97	35.7
0.7055	1.2204	-1.1901	1555.78	1.21	-4.06	33.9
0.8058	1.2408	-0.8409	1579.06	1.18	-2.89	32.3
0.9053	1.2599	-0.4429	1599.41	1.16	-1.49	31.0
1	1.2768	0	1616.88	1.14	0	30.0

308.15 K

0	1.0127	0	1294.13	1.61	0	59.0
0.0167	1.0199	-0.2512	1304.09	1.59	-0.83	57.7
0.0455	1.0313	-0.5606	1317.94	1.56	-1.84	55.8
0.0885	1.0470	-0.8708	1336.15	1.53	-2.94	53.5
0.1056	1.0533	-1.0120	1343.20	1.52	-3.34	52.6
0.2055	1.0866	-1.4684	1381.95	1.45	-4.92	48.2
0.3057	1.1171	-1.7008	1418.92	1.40	-5.79	44.5
0.4053	1.1448	-1.7678	1453.67	1.35	-6.09	41.3
0.5053	1.1706	-1.6971	1486.34	1.30	-5.90	38.7
0.6054	1.1943	-1.5112	1516.13	1.26	-5.30	36.4
0.7055	1.2164	-1.2317	1542.74	1.23	-4.33	34.5
0.8058	1.2369	-0.8707	1566.47	1.20	-3.07	32.9
0.9053	1.2561	-0.4587	1587.45	1.18	-1.59	31.6
1	1.2730	0	1605.19	1.16	0	30.5

313.15 K

0	1.0074	0	1275.32	1.65	0	61.0
0.0167	1.0147	-0.2611	1285.49	1.63	-0.89	59.6
0.0455	1.0263	-0.5816	1299.61	1.60	-1.97	57.7
0.0885	1.0421	-0.9035	1318.23	1.57	-3.15	55.2
0.1056	1.0484	-1.0485	1325.44	1.56	-3.57	54.3
0.2055	1.0819	-1.5202	1365.05	1.49	-5.26	49.6
0.3057	1.1126	-1.7607	1402.90	1.43	-6.19	45.7
0.4053	1.1405	-1.8298	1438.51	1.38	-6.50	42.4
0.5053	1.1664	-1.7565	1472.01	1.33	-6.30	39.6
0.6054	1.1903	-1.5640	1502.56	1.29	-5.65	37.2
0.7055	1.2124	-1.2740	1529.83	1.25	-4.62	35.2
0.8058	1.2330	-0.9007	1554.10	1.22	-3.27	33.6

0.9053	1.2522	-0.4745	1575.55	1.20	-1.70	32.2
1	1.2692	0	1593.58	1.18	0	31.0

Table 5.1.5

Apparent molar isentropic compressibility K_ϕ ($m^3 \cdot mol^{-1}Pa^{-1}$) for the binary mixtures of ([Emim] [BF_4] + ethyl acetoacetate or benzaldehyde) at T = (293.15 to 313.15) K as a function of molality m (mol/kg).

m	K_ϕ				
	T = 293.15 K	T = 298.15 K	T = 303.15 K	T = 308.15 K	T = 313.15 K
	[Emim] [BF_4] + Benzaldehyde				
0.1746	1.15	0.75	0.92	1.10	0.72
0.4088	1.82	1.75	1.92	1.86	1.56
0.8231	2.45	2.37	2.42	2.35	2.16
1.1201	2.59	2.58	2.57	2.57	2.48
2.4348	3.14	3.12	3.15	3.20	3.15
4.1370	3.48	3.48	3.53	3.55	3.56
6.4389	3.71	3.72	3.78	3.82	3.84
9.6378	3.89	3.94	3.99	4.04	4.08
14.4395	4.04	4.09	4.17	4.24	4.28
22.5817	4.17	4.24	4.31	4.38	4.45
39.0043	4.27	4.36	4.43	4.52	4.60
90.8327	4.38	4.46	4.55	4.64	4.72
	[Emim] [BF_4] + Ethyl acetoacetate				
0.1306	-0.84	-1.40	-1.18	-1.71	-2.27
0.3661	0.35	0.01	-0.32	-0.64	-0.68
0.7459	1.08	0.88	0.69	0.51	0.33
0.9069	1.30	1.17	0.94	0.71	0.59
1.9873	2.07	2.01	1.89	1.78	1.68
3.3837	2.62	2.58	2.50	2.44	2.38
5.2367	3.00	2.97	2.95	2.90	2.89
7.8502	3.32	3.32	3.34	3.33	3.33
11.7897	3.62	3.64	3.67	3.68	3.70
18.4088	3.86	3.92	3.97	3.99	4.04
31.8798	4.09	4.15	4.21	4.27	4.35
73.4829	4.29	4.37	4.44	4.53	4.62

Table 5.1.6

Apparent molar volume V_ϕ ($m^3 \cdot mol^{-1}$) for the binary mixtures of ([Emim] [BF_4] + ethyl acetoacetate or benzaldehyde) at T = (293.15 to 313.15) K as a function of molality, m (mol/kg)

m	V_ϕ				
	T = 293.15 K	T = 298.15 K	T = 303.15 K	T = 308.15 K	T = 313.15 K
			[Emim] [BF_2] + Benzaldehyde		
0.1747	141.38	141.54	141.66	141.78	141.88
0.4088	143.27	143.47	143.67	143.85	144.03
0.8232	145.05	145.31	145.57	145.81	146.04
1.1202	145.76	146.04	146.32	146.58	146.84
2.4349	148.01	148.34	148.68	149.00	149.32
4.1370	149.43	149.80	150.16	150.52	150.88
6.4389	150.52	150.91	151.30	151.68	152.06
9.6378	151.38	151.79	152.20	152.60	153.00
14.4395	152.10	152.52	152.94	153.36	153.78
22.5818	152.72	153.15	153.59	154.02	154.45
39.0044	153.26	153.70	154.14	154.59	155.03
90.8327	153.73	154.18	154.63	155.09	155.54
			[Emim] [BF_4] + Ethyl acetoacetate		
0.1307	140.71	140.67	140.59	140.49	140.37
0.3662	143.08	143.14	143.18	143.19	143.19
0.7460	145.30	145.44	145.56	145.68	145.77
0.9070	145.50	145.66	145.80	145.93	146.05
1.9874	147.68	147.92	148.15	148.37	148.58
3.3838	149.11	149.40	149.68	149.95	150.22
5.2368	150.19	150.52	150.84	151.15	151.46
7.8502	151.10	151.45	151.81	152.16	152.50
11.7897	151.87	152.26	152.64	153.02	153.39
18.4088	152.55	152.96	153.36	153.77	154.17
31.8798	153.16	153.58	154.01	154.43	154.86
73.4829	153.67	154.12	154.56	155.01	155.45

Table 5.1.7

Viscosity η (mPa · s) for the binary mixtures of {[Emim] [BF_4] (x_1)+ ethyl acetoacetate (x_2) or benzaldehyde (x_2)} at T = (293.15 to 313.15) K and p = 0.1 MPa, as a function of mole fraction.

x_1	η				
	T = 293.15 K	T = 298.15 K	T = 303.15 K	T = 308.15 K	T = 313.15 K
[Emim] [BF_4] + Ethyl acetoacetate					
0	1.82	1.65	1.51	1.39	1.29
0.0167	1.99	1.81	1.65	1.51	1.39
0.0455	2.29	2.07	1.88	1.72	1.58
0.0885	2.77	2.49	2.25	2.05	1.88
0.1056	2.99	2.68	2.42	2.20	2.01
0.2055	4.43	3.93	3.52	3.18	2.88
0.3057	6.33	5.56	4.93	4.41	3.97
0.4053	8.78	7.66	6.73	5.97	5.33
0.5053	11.85	10.30	8.99	7.91	7.01
0.6054	15.75	13.63	11.80	10.31	9.08
0.7055	20.86	17.82	15.29	13.27	11.61
0.8058	26.98	23.01	19.53	16.86	14.64
0.9053	34.83	29.69	25.55	21.34	18.38
1	49.32	41.01	34.71	28.80	22.63
[Emim] [BF_4] + Benzaldehyde					
0	1.57	1.45	1.34	1.25	1.16
0.0182	1.77	1.62	1.49	1.38	1.29
0.0416	2.01	1.84	1.68	1.56	1.45
0.0803	2.47	2.24	2.05	1.88	1.73
0.1062	2.82	2.55	2.32	2.13	1.96
0.2053	4.49	3.99	3.58	3.24	2.95
0.3051	6.84	6.01	5.31	4.75	4.27
0.4059	10.01	8.70	7.61	6.72	5.98
0.5056	14.02	12.07	10.45	9.12	8.03
0.6051	19.00	16.17	13.84	11.98	10.47
0.7056	24.94	20.7	17.83	15.32	13.28
0.8054	30.99	25.68	22.18	18.92	16.33
0.906	37.98	31.68	27.75	23.46	19.60
1	49.32	41.01	34.71	28.80	22.63

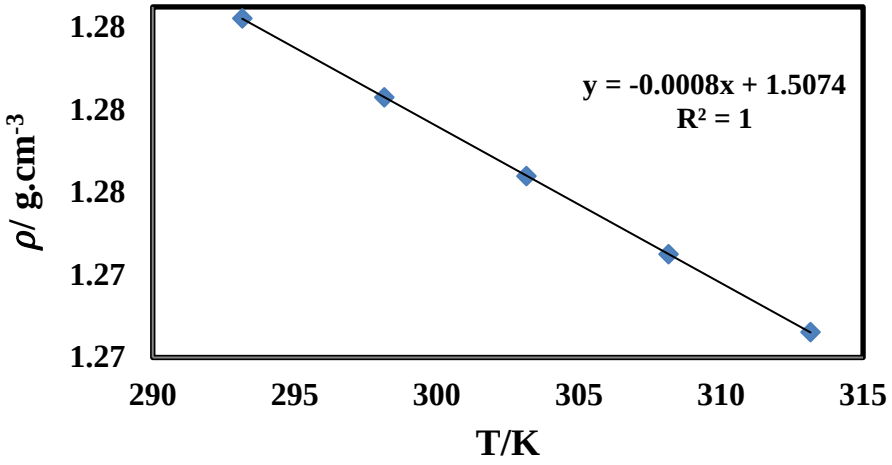

Figure 5.1.10: Density (ρ) plot of the pure ionic liquid [Emim] [BF_4] at T = (293.15, 298.15, 303.15, 308.15 and 313.15) K.

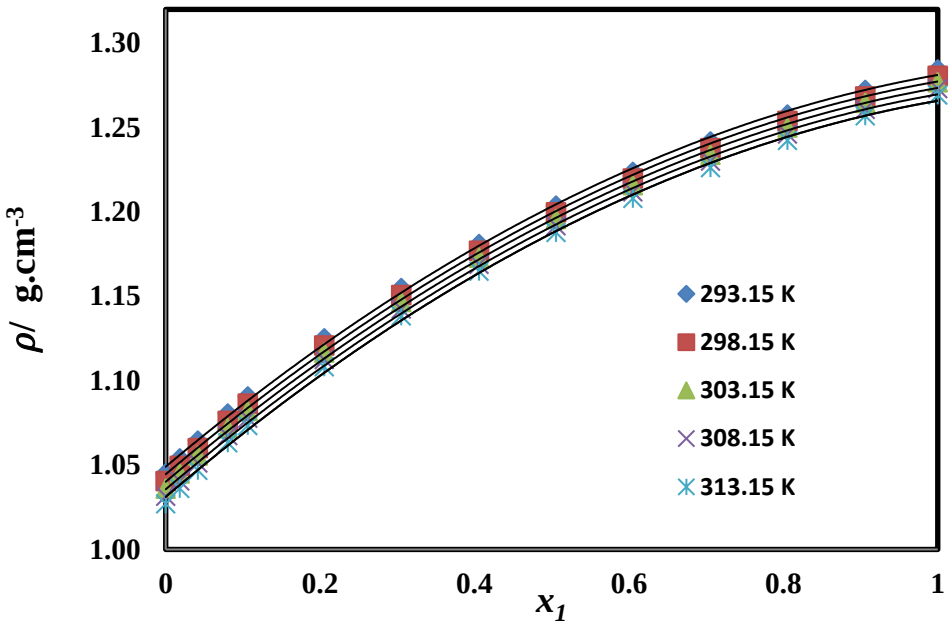

Figure 5.1.11: Density of the binary mixtures of {[Emim] [BF_4] (x_1) + benzaldehyde (x_2)} at T = (293.15, 298.15, 303.15, 308.15 and 313.15) K.

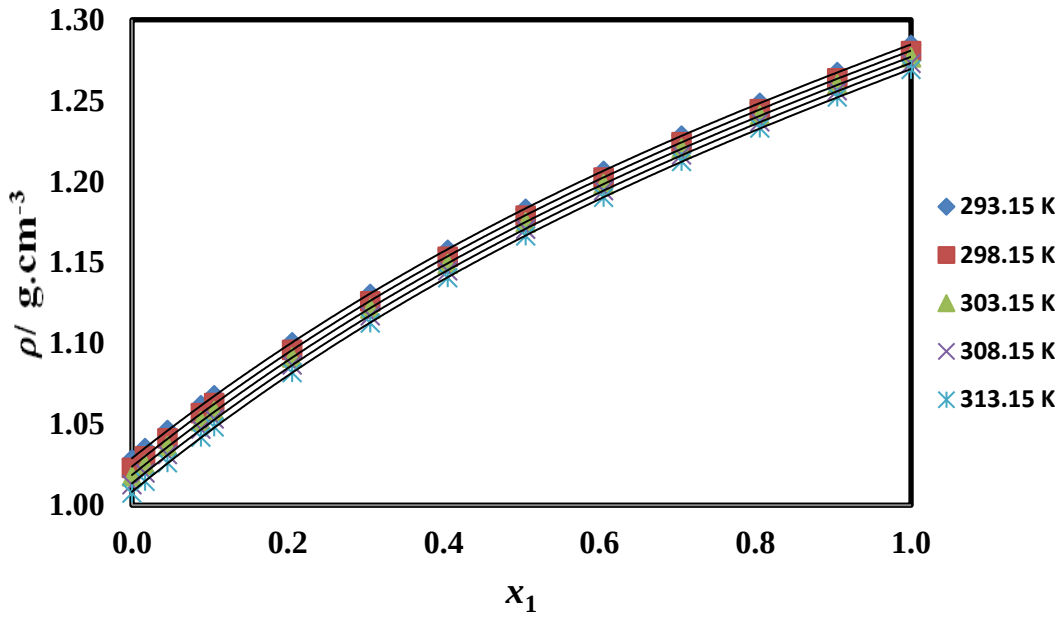

Figure 5.1.12: Density of the binary mixtures of {[Emim] [BF_4] (x_1) + ethyl acetoacetate (x_2)} at T = (293.15, 298.15, 303.15, 308.15 and 313.15) K.

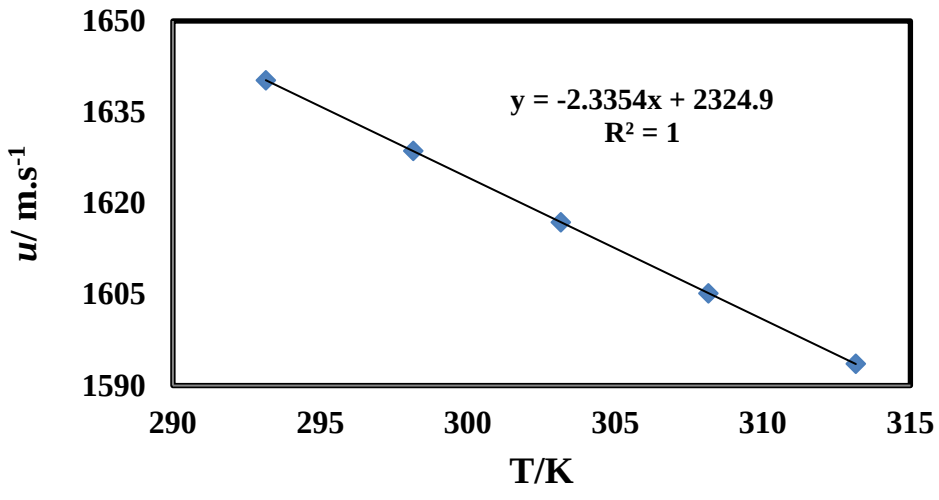

Figure 5.1.13: Speed of sound (u) of IL against temperature ranges (293.15, 298.15, 303.15, 308.15 and 313.15) K.

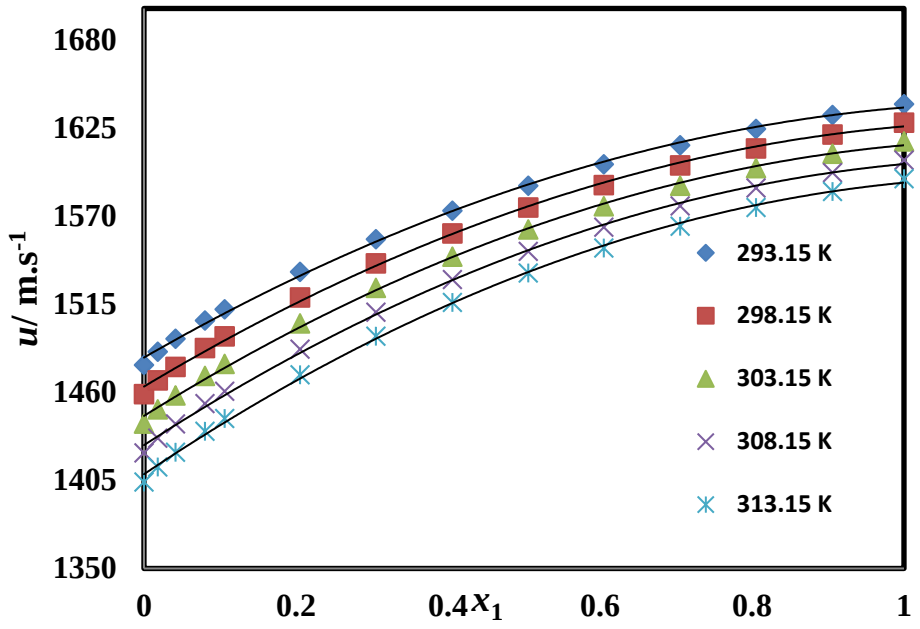

Figure 5.1.14: Speed of sound (u) graph for the binary mixtures of {[Emim] [BF_4] (x_1) + benzaldehyde (x_2)} at T = (293.15, 298.15, 303.15, 308.15 and 313.15) K.

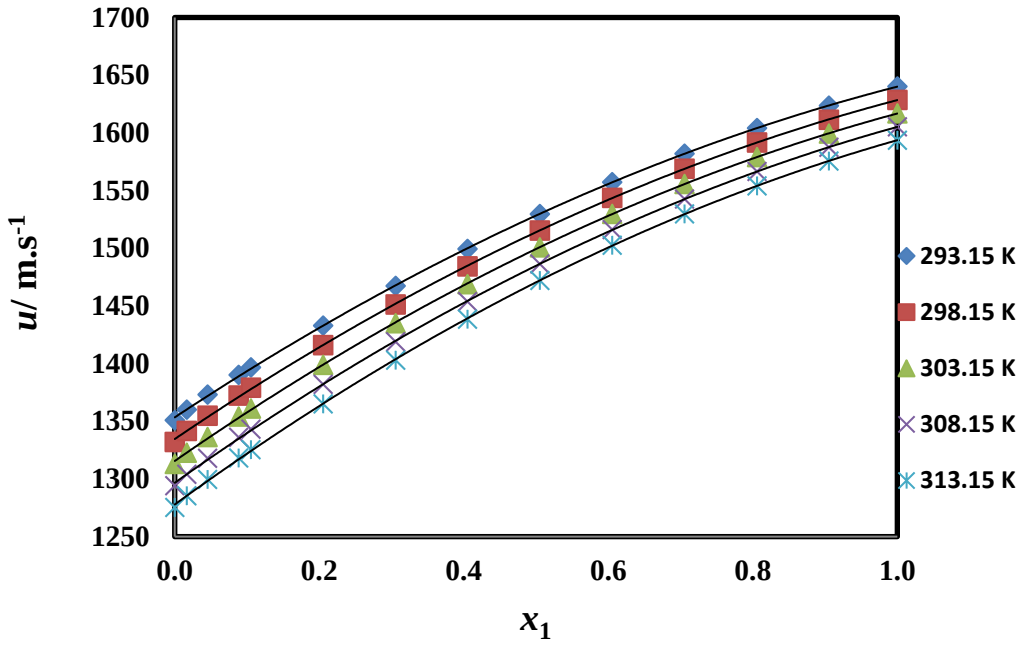

Figure 5.1.15: Speed of sound (u) graph for the binary mixtures of {[Emim] [BF_4] (x_1) + ethyl acetoacetate (x_2)} at T = (293.15, 298.15, 303.15, 308.15 and 313.15) K.

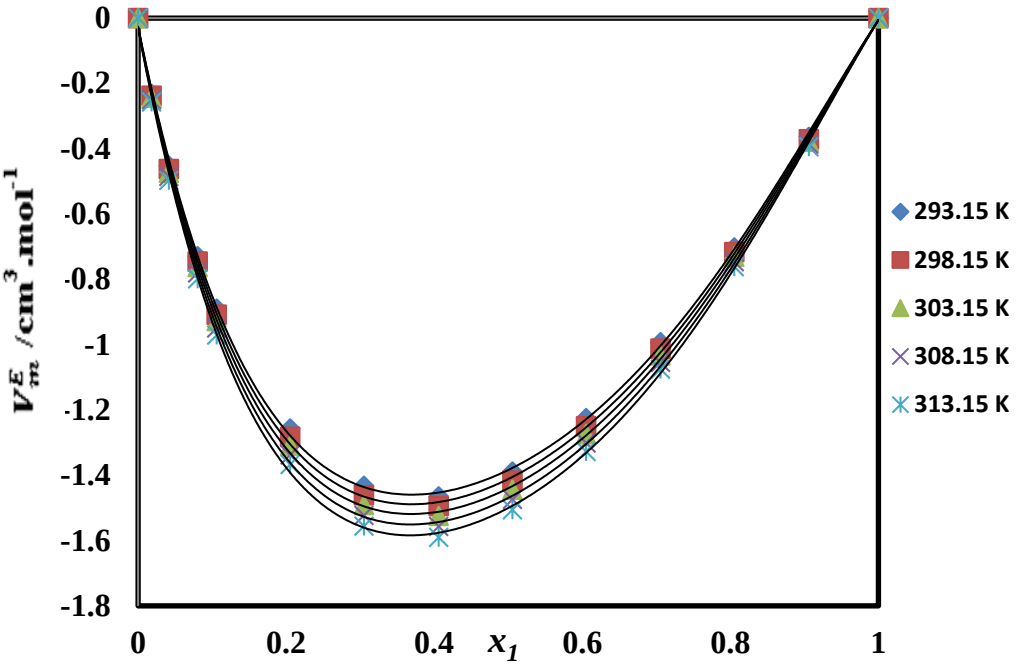

Figure 5.1.16: Excess molar volume (V_m^E) of the miscible prepared mixtures of {[Emim][BF_4] (x_1) + benzaldehyde (x_2)} as a function of mole fraction of ionic liquid at T = (293.15, 298.15, 303.15, 308.15 and 313.15) K. The plot was fitted by using the Redlich-Kister equation.

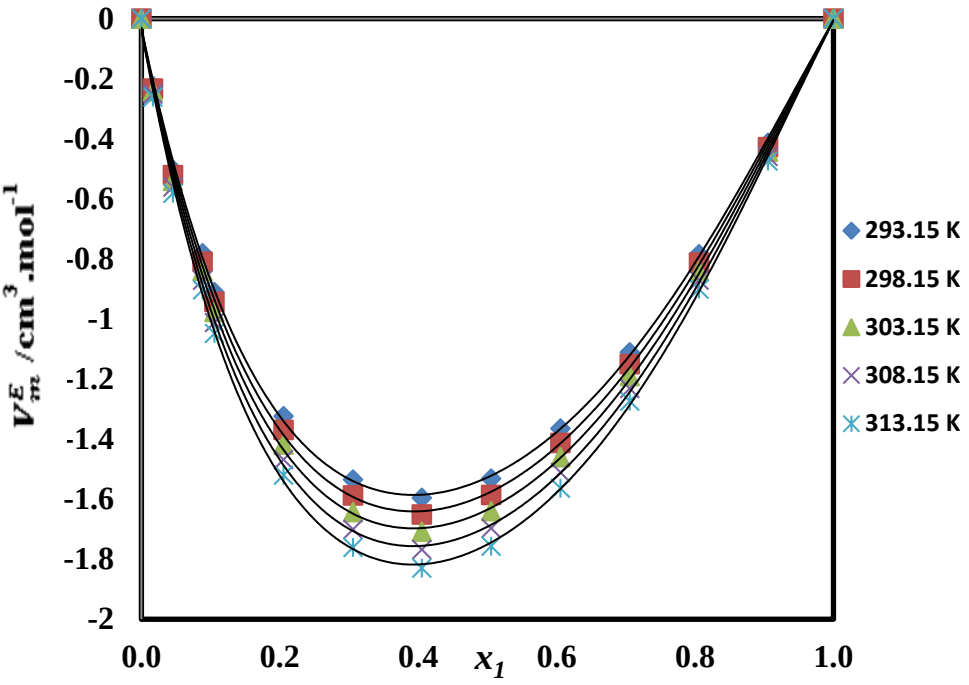

Figure 5.1.17: Excess molar volume (V_m^E) of the miscible prepared mixtures of {[Emim] [BF_4] (x_1) + ethyl acetoacetate (x_2)} as a function of mole fraction of ionic liquid, at T = (293.15, 298.15, 303.15, 308.15 and 313.15) K. The plot was fitted by using the Redlich-Kister equation.

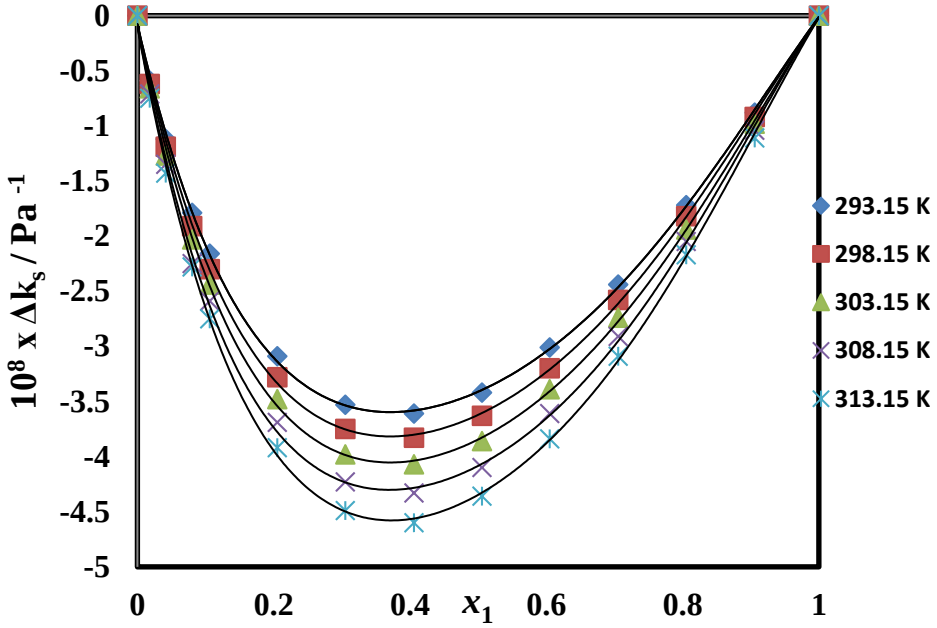

Figure 5.1.18: Deviation in isentropic compressibility (Δk_s) of the binary mixtures of {[Emim] [BF_4] (x_1) + benzaldehyde (x_2)} expressed in mole fraction of [Emim] [BF_4] at T= (293.15, 298.15, 303.15, 308.15 and 313.15) K. The plot was fitted by using the Redlich-Kister equation.

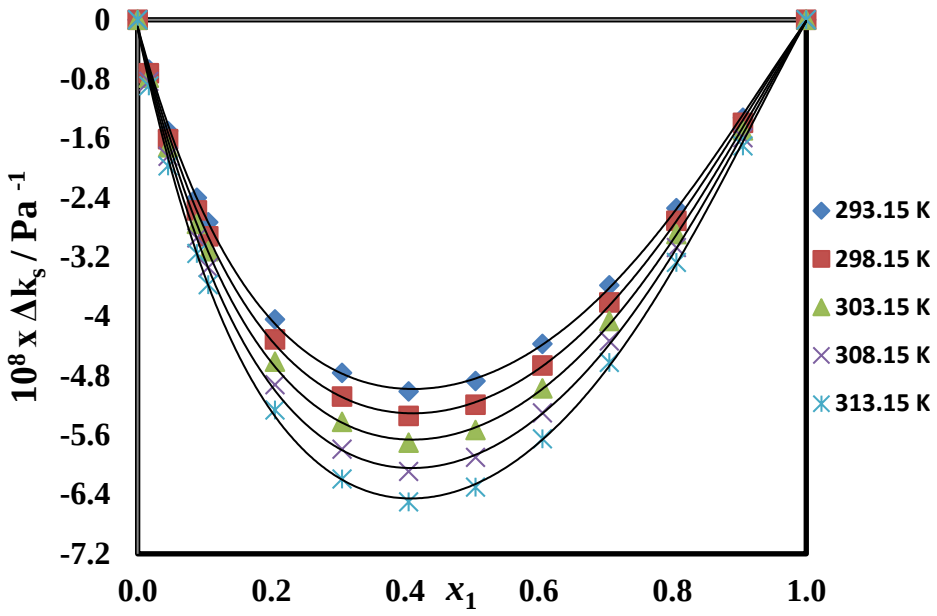

Figure 5.1.19: Deviation in isentropic compressibility (Δk_s) of the binary mixtures of {[Emim] [BF_4] (x_1) + ethyl acetoacetate (x_2)} expressed in mole fraction of [Emim] [BF_4] at T = (293.15, 298.15, 303.15, 308.15 and 313.15) K. The plot was fitted by using the Redlich-Kister equation.

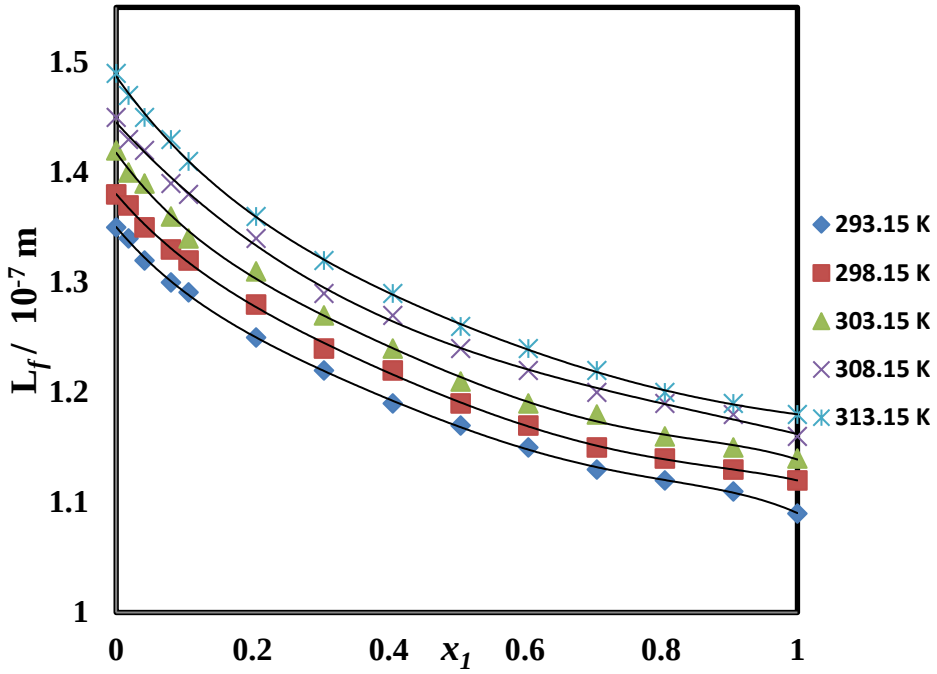

Figure 5.1.20: Intermolecular free length (L_f) of the binary mixtures of {[Emim] [BF_4] (x_1) + benzaldehyde (x_2)} as a function of mole fraction of IL at T = (293.15, 298.15, 303.15, 308.15 and 313.15) K.

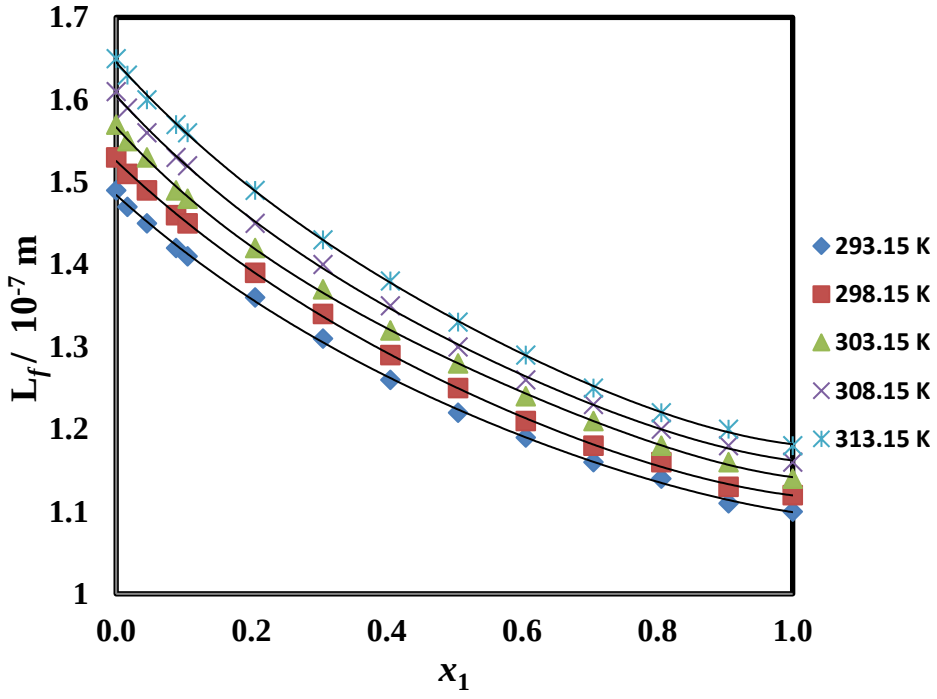

Figure 5.1.21: Intermolecular free length (L_f) of the binary mixtures of {[Emim] [BF_4] (x_1) + ethyl acetoacetate (x_2)} given as a function of mole fraction of IL (x_2) at T = (293.15, 298.15, 303.15, 308.15 and 313.15) K.

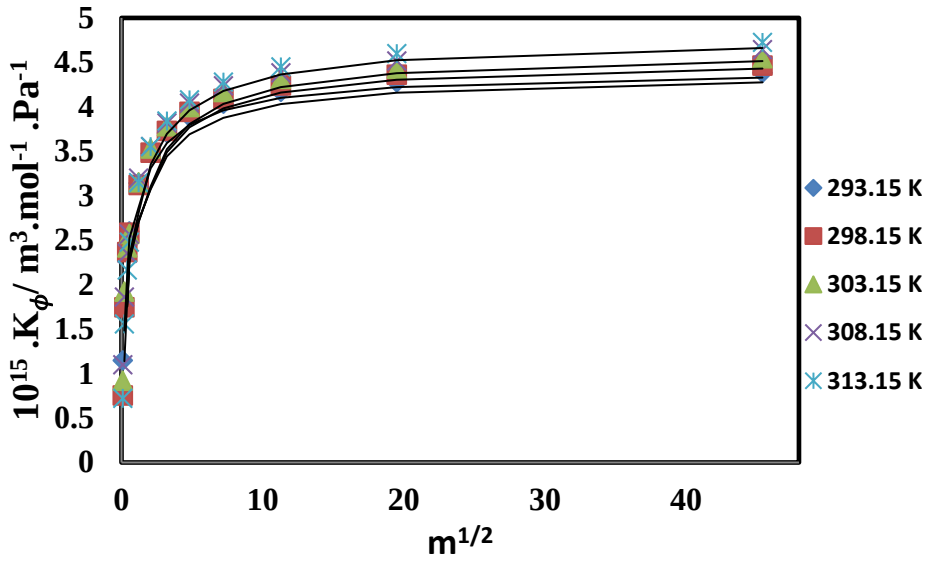

Figure 5.1.22: Apparent molar isentropic compressibility (K_ϕ) of binary mixtures ([Emim] [BF_4] + benzaldehyde) plotted against $(m)^{1/2}$ at T = (293.15, 298.15, 303.15, 308.15 and 313.15) K. [m = molality of mixture]

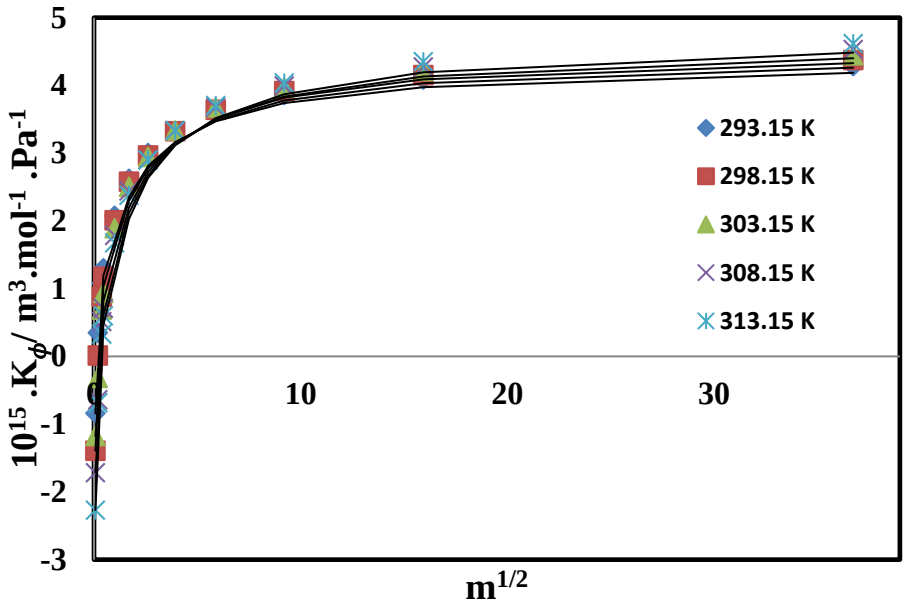

Figure 5.1.23: Apparent molar isentropic compressibility(K_ϕ) of binary mixtures ([Emim] [BF_4] + ethyl acetoacetate) plotted against $(m)^{1/2}$ at T = (293.15, 298.15, 303.15, 308.15 and 313.15) K. [m = molality of mixture]

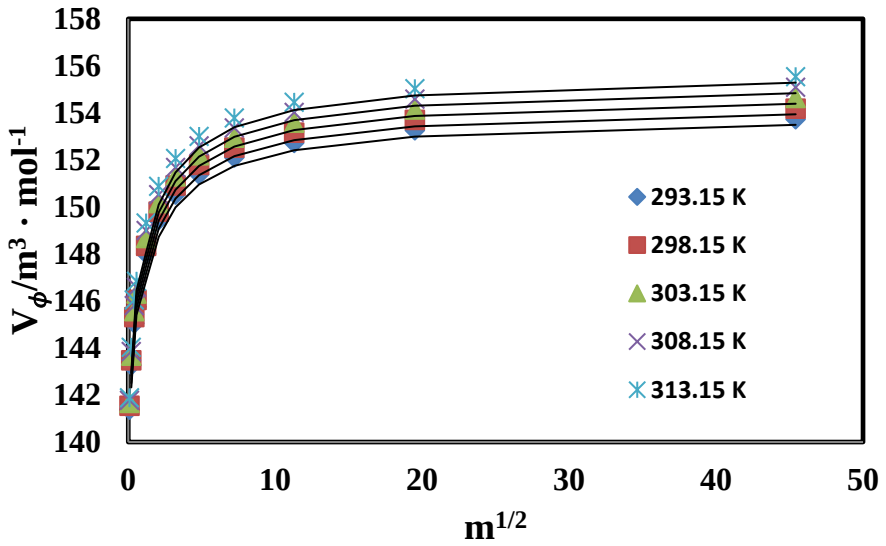

Figure 5.1.24: Apparent molar volume(V_ϕ) of binary mixtures ([Emim] [BF_4] + benzaldehyde) plotted against $(m)^{1/2}$ at T = (293.15, 298.15, 303.15, 308.15 and 313.15) K. [m = molality of mixture]

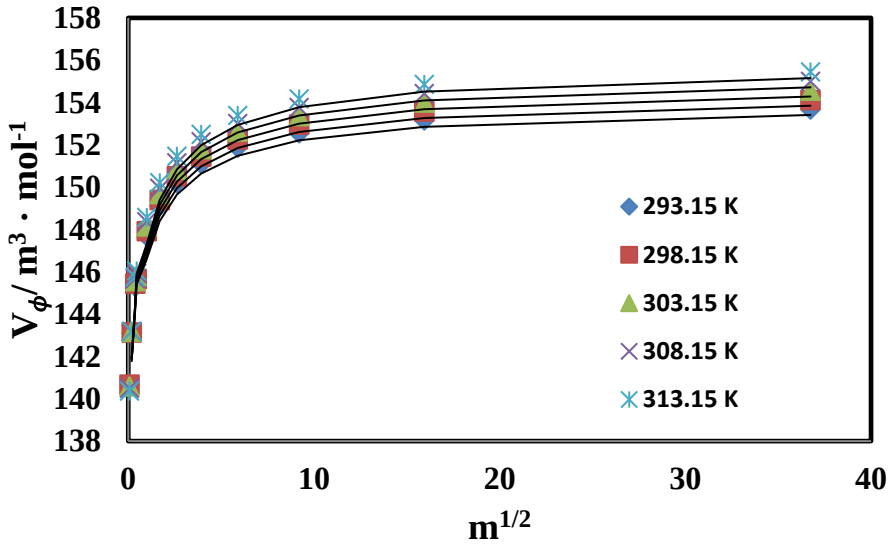

Figure 5.1.25: Apparent molar volume(V_ϕ) of binary mixtures ([Emim] [BF_4] + ethyl acetoacetate) plotted against $(m)^{1/2}$ at T = (293.15, 298.15, 303.15, 308.15 and 313.15) K. [m = molality of mixture]

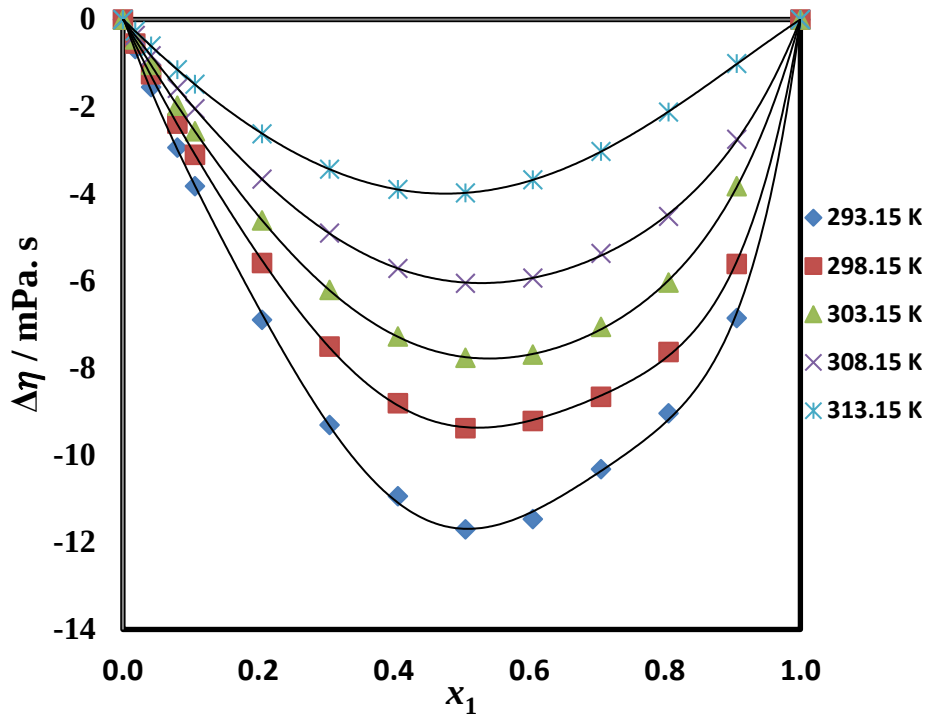

Figure 5.1.26: Deviations in viscosity ($\Delta\eta$) for the binary mixtures of {[Emim] [BF_4] (x_1) + benzaldehyde (x_2)} given as a function of mole fraction of IL (x_1) at T = (293.15, 298.15, 303.15, 308.15 and 313.15) K.

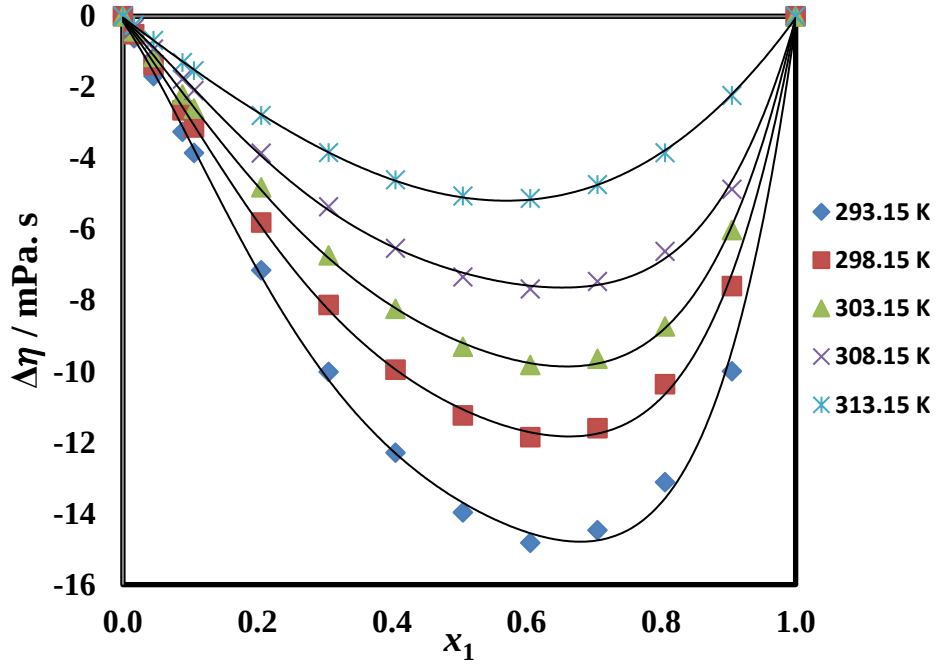

Figure 5.1.27: Deviations in viscosity ($\Delta\eta$) for the binary mixtures of {[Emim] [BF_4] (x_1) + ethyl acetoacetate (x_2)} given as a function of mole fraction of IL (x_1) at T = (293.15, 298.15, 303.15, 308.15 and 313.15) K.

Standard deviation and coefficients are given in Table 5.1.8 and 5.1.9 for both of the studied systems. The Redlich-Kister equation was fitted for the following properties (V_m^E, Δk_s and L_f). The standard deviation (σ) was calculated from the given equation (5.2) below, for the correlation.

$$\sigma(X) = \sum_{i=1}^{n} \left[\frac{X_{expt} - X_{calc}}{(N-K)}\right]^{1/2} \quad (5.2)$$

Where N is the number of experimental points and K represents the coefficient used in the Redlich-Kister equation.

Table 5.1.8

Standard deviations σ, and coefficients A_i, achieved for the binary solution ($[P^+_{14,6,6,6}]$ $[Cl^-]$ + propanoic acid) at pressure p = 0.1 MPa and different temperatures, for Redlich-Kister equation (5.1).

	T/K	A_0	A_1	A_2	A_3	σ
$V^E_m/cm^3.mol$	293.15	-2.151	-2.498	0.039	1.368	0.022
	298.15	-2.445	-2.589	-0.412	1.075	0.024
	303.15	-2.612	-2.656	-0.487	1.21	0.024
	308.15	-2.861	-2.377	-0.637	0.175	0.025
	313.15	-3.108	-2.809	-0.931	0.72	0.026
$10^8.\ \Delta k_s/Pa^{-1}$	293.15	-48.683	-24.714	-41.522	-63.732	0.381
	298.15	-52.237	-24.867	-47.087	-71.276	0.412
	303.15	-55.92	-29.116	-45.771	-81.363	0.46
	308.15	-59.355	-30.564	-55.792	-83.602	0.535
	313.15	-63.528	-32.567	-60.440	-91.993	0.587
L_f / (10^{-7} m)	293.15	3.153	-2.187	15.381	11.639	0.310
	298.15	3.368	-2.382	15.693	12.489	0.326
	303.15	3.590	-2.541	16.264	12.208	0.381
	308.15	3.619	-2.840	16.539	12.893	0.401
	313.15	3.831	-3.085	16.721	13.047	0.417

Table 5.1.9

Standard deviations σ, and coefficients A_i, achieved for the binary solution ([Emim] [BF_4] + Benzaldehyde or ethyl acetoacetate) at pressure p = 0.1 MPa and different temperatures for Redlich-Kister equation (5.1).

	T/K	A_0	A_1	A_2	A_3	σ
[Emim] [BF_4] + Benzaldehyde						
	293.15	-5.524	-2.134	-1.985	-1.943	0.019
	298.15	-5.635	-2.174	-2.032	-2.007	0.020
V^E_m/cm^3.mol	303.15	-5.747	-2.217	-2.090	-2.069	0.020
	308.15	-5.866	-2.265	-2.153	-2.13	0.021
	313.15	-5.988	-2.322	-2.208	-2.187	0.022
10^8. Δk_s/Pa^{-1}	293.15	-13.614	-5.287	-4.686	-4.775	0.052
	298.15	-14.454	-5.604	-4.909	-5.277	0.054
	303.15	-15.345	-5.952	-5.256	-5.556	0.060
	308.15	-16.297	-6.182	-5.724	-6.570	0.073
	313.15	-17.346	-6.720	-5.752	-6.273	0.075
L_f / (10^{-7} m)	293.15	3.952	-2.058	13.895	10.191	0.666
	298.15	4.025	-2.083	14.197	10.44	0.682
	303.15	4.1	-2.141	14.574	10.735	0.699
	308.15	4.189	-2.205	14.876	11.001	0.713
	313.15	4.259	-2.274	15.119	11.48	0.730
[Emim][BF_4] + Ethyl acetoacetate						
	293.15	-6.099	-2.055	-1.671	-1.762	0.022
	298.15	-6.312	-2.11	-1.731	-1.854	0.023
V^E_m/cm^3.mol	303.15	-6.527	-2.188	-1.813	-1.923	0.024
	308.15	-6.754	-2.263	-1.894	-2.007	0.025
	313.15	-6.989	-2.343	-1.97	-2.101	0.027

	293.15	-19.369	-5.48	-4.272	-5.591	0.064
	298.15	-20.648	-5.81	-4.559	-6.253	0.069
10^8. Δk_s/Pa^{-1}	303.15	-22.012	-6.256	-4.954	-6.621	0.075
	308.15	-23.491	-6.745	-5.325	-7.075	0.081
	313.15	-25.069	-7.277	-5.764	-7.528	0.088
	293.15	4.154	-1.871	14.495	11.1	0.716
	298.15	4.239	-1.899	14.836	11.477	0.734
L_f / (10^{-7} m)	303.15	4.341	-1.959	15.152	11.769	0.753
	308.15	4.415	-1.966	15.513	12.073	0.770
	313.15	4.512	-2.003	15.85	12.493	0.788

The standard uncertainties u are u (T) = ±0.02 K, u (p) = ±0.04 MPa and the joined expanded uncertainty U_c in mole fractions, density and sound velocity measurements were not above U_c(x) = ±0.0004, U_c (ρ) = ±2.10^{-5}g.cm^{-3} and U_c (u) = ±0.8 m. s^{-1}.

5.2 Results for Activity coefficients at infinite dilution

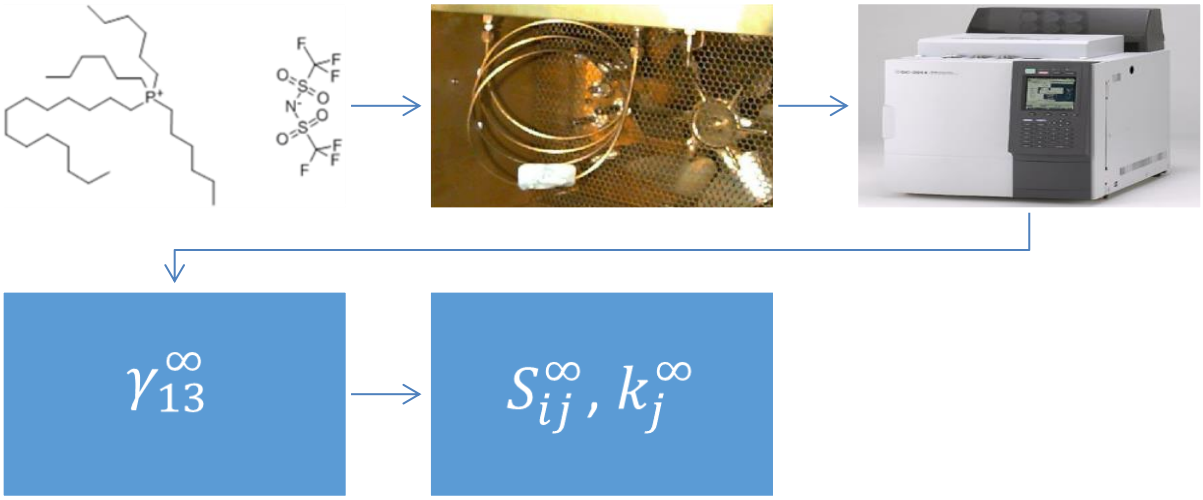

Figure 5.2.1: Schematic diagram showing the process for determining activity coefficients at infinite dilution for [3 C_6 C_{14} P] [$(C_8H_{17})_2$ PO_2].

Table 5.2.1

Activity coefficients at infinite dilution for the solutes in the ionic liquid [3 C_6 C_{14} P] [$(C_8H_{17})_2$ PO_2] at four different temperatures

Solute	γ_{13}^{∞} values			
	T = 313.15 K	T = 323.15 K	T = 333.15 K	T = 343.15 K
2.2-dimethylbutane	0.78	0.82	0.90	0.97
2.2.4-trimethylpentane	0.92	0.96	1.04	1.14
Methylcyclohexane	0.64	0.68	0.73	0.78
Cyclooctane	0.70	0.71	0.77	0.79
n-Nonane	1.04	1.11	1.23	1.25
n-Decane	1.22	1.28	1.33	1.39
1-Heptene	0.77	0.81	0.88	0.95
1-Nonene	0.91	0.95	1.08	1.14
1-Decene	0.98	1.04	1.15	1.18
Cyclohexene	0.57	0.59	0.64	0.68
Benzene	0.42	0.45	0.49	0.52
Toluene	0.50	0.51	0.56	0.59
Ethylbenzene	0.57	0.60	0.65	0.68
m-Xylene	0.63	0.65	0.67	0.70
p-Xylene	0.60	0.63	0.65	0.69
o-Xylene	0.60	0.62	0.64	0.67
Methanol	0.03	0.04	0.05	0.06
Ethanol	-	0.04	0.06	0.07
Propan-1-ol	-	0.07	0.08	0.09
Butan-1-ol	-	-	0.11	0.12
Acetone	0.70	0.72	0.78	0.83
2-Butanone	0.65	0.67	0.72	0.77
THF	0.43	0.45	0.49	0.52
Acetonitrile	1.34	1.40	1.41	1.46
Thiophene	0.35	0.40	0.41	0.44
Water	0.26	0.27	0.30	0.31

Standard uncertainties u are u (γ_{13}^{∞}) < 3 %, u(T) = 0.02 K.

Table 5.2.2

Linear regression and excess molar enthalpies computed from the activity coefficients at infinite dilution of the ionic liquid [3 C_6 C_{14} P] [$(C_8H_{17})_2$ PO_2].

Solute	Linear regression		$\Delta H_1^{E\infty}$ / (kJ · mol^{-1})
	Gradient	R^2	
2.2-dimethylbutane	-0.823	0.981	-6.84
2.2.4-trimethylpentane	-0.779	0.979	-6.48
methylcyclohexane	-0.714	0.997	-5.94
cyclooctane	-0.489	0.954	-4.07
n-nonane	-0.699	0.949	-5.82
n-decane	-0.463	0.999	-3.85
1-heptene	-0.761	0.983	-6.33
1-nonene	-0.848	0.948	-7.05
1-decene	-0.697	0.961	-5.79
cyclohexene	-0.655	0.979	-5.45
benzene	-0.762	0.995	-6.34
toluene	-0.620	0.938	-5.16
ethylbenzene	-0.635	0.978	-5.28
m-xylene	-0.361	0.988	-3.01
p-xylene	-0.459	0.997	-3.82
o-xylene	-0.443	0.991	-3.68
methanol	-2.167	0.993	-18.0
ethanol	-2.561	0.987	-21.3
propan-1-ol	-0.97	0.989	-8.06
butan-1-ol	-0.697	1.000	-5.79
acetone	-0.648	0.987	-5.39
2-butanone	-0.656	0.98	-5.46
THF	-0.722	0.993	-6.01
acetonitrile	-0.263	0.993	-2.19
thiophene	-0.716	0.984	-5.96
water	-0.703	0.991	-5.84

Standard uncertainties u are u (γ_{13}^{∞}) < 3 %, u (T) = 0.02 K.

Table 5.2.3

Comparison of selectivities (S_{ij}^{∞}) and capacities $\left(K_j^{\infty}\right)$ for (water/butan-1-ol) separation problems for selected ionic liquids 333.15 K.

Ionic liquid	S_{ij}^{∞} water/butan-1-ol	K_j^{∞} butan-1-ol	Ref.
[3 C_6 C_{14} P] [$(C_8H_{17})_2$ PO_2]	2.70	8.90	This work
[$P_{14,4,4,4}$] [DBS]	3.77	5.29	a
[DoMIM] [NTf_2]	2.76	0.64	b
[$(C_6OC)_2$ IM] [NTf_2]	2.67	0.91	c
[$N_{8,2,2,2}$] [NTf_2]	2.46	0.52	d
[C_8 iQuin] [NTf_2]	2.22	0.63	e
[DMIM] [TCB]	2.04	0.96	f
[BMPYR] [FAP]	2.03	0.26	g
[C_6 Qui] [NTf_2]	1.99	0.58	h
[$P_{4,4,4,1}$] [TOS]	1.74	3.14	i
[EMIM] [FAP]	1.49	0.25	j

(Wlalzo et al., 2017)[a]

(Domanska and Wlalzo 2016)[b]

(Domanska and Marciniak 2009)[c]

(Wlalzo and Domanska 2016)[d]

(Domanska et al., 2011)[e]

(Domanska and Marciniak 2010)[f]

(Domanska et al., 2012)[g]

(Ayad et al., 2016)[h]

(Domanska and Paduszynski 2010)[i]

(Wlazlo et al., 2015)[j]

Table 5.2.4

Comparison of selectivities (S_{ij}^{∞}) and capacities (K_j^{∞}) for (methanol/benzene) separation problems for selected ionic liquids at 333.15 K.

Ionic Liquid	S_{ij}^{∞} methanol/benzene	K_j^{∞} benzene	Ref.
[3 C_6 C_{14} P] [$(C_8H_{17})_2$ PO_2]	0.07	2.36	This work
[3C_6C_{14}P] [BF_4]	1.31	0.90	a
[3C_6C_{14}P] [TF_2N]	2.77	1.10	a
[3C_6C_{14}P] [PF_6]	3.12	1.47	b
[3C_6C_{14}P] [(C_2F_5) PF_3]	5.83	5.00	c
[C_{16}MIM] [BF_4]	1.52	1.27	d
[MOIM] [PF_6]	1.88	1.04	b
Sulfolane	0.91	0.43	e

(Tumba et al., 2010)[a]

(Heintz et al., 2006)[b]

(Letcher et al., 2008)[c]

(Mutelet and Jaubert 2007)[d]

(Mollmann and Gmehling 1997)[e]

Table 5.2.5

Comparison of selectivities (S_{ij}^{∞}) and capacities (K_j^{∞}) for (ethanol/2-butanone) separation problems for selected ionic liquids at 333.15 K.

Ionic Liquid	S_{ij}^{∞} ethanol/2-butanone	K_j^{∞} 2-butanone	Ref.
[3 C_6 C_{14} P] [$(C_8H_{17})_2$ PO_2]	0.06	1.48	This work
[3C_6C_{14}P] [BF_4]	1.31	0.90	a
[3C_6C_{14}P] [TF_2N]	2.77	1.10	a
[3C_6C_{14}P] [PF_6]	3.12	1.47	b
[3C_6C_{14}P] [(C_2F_5) PF_3]	5.83	5.00	c
[C_{16}MIM] [BF_4]	1.52	1.27	d
[MOIM] [PF_6]	1.88	1.04	b
Sulfolane	0.91	0.43	e

(Tumba et al., 2010)[a]

(Heintz et al., 2006)[b]

(Letcher et al., 2008)[c]

(Mutelet and Jaubert 2007)[d]

(Mollmann and Gmehling 1997)[e]

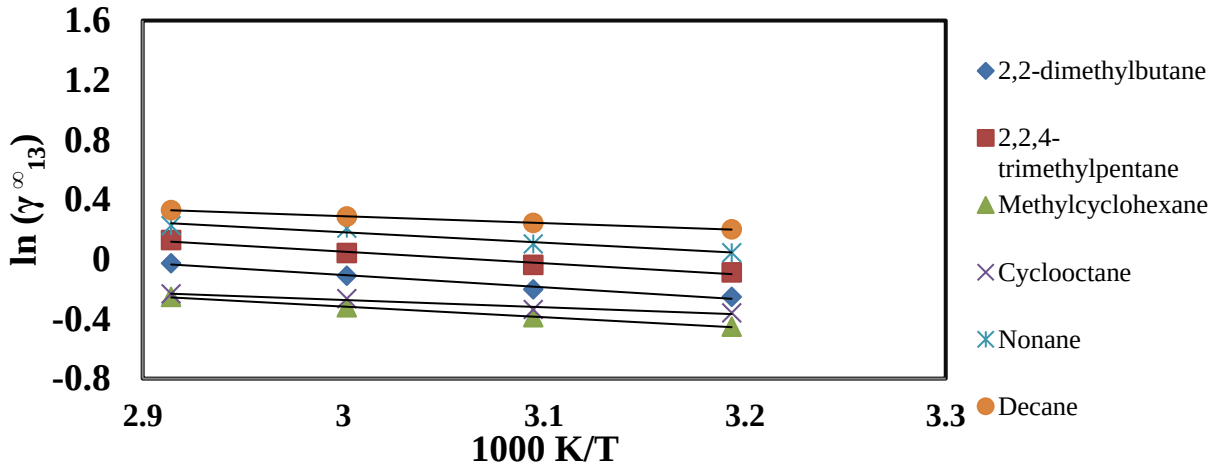

Figure 5.2.2: Plots of ln γ_{13}^{∞} versus 1/T for the alkanes in [3 C_6 C_{14} P] [$(C_8H_{17})_2$ PO_2].

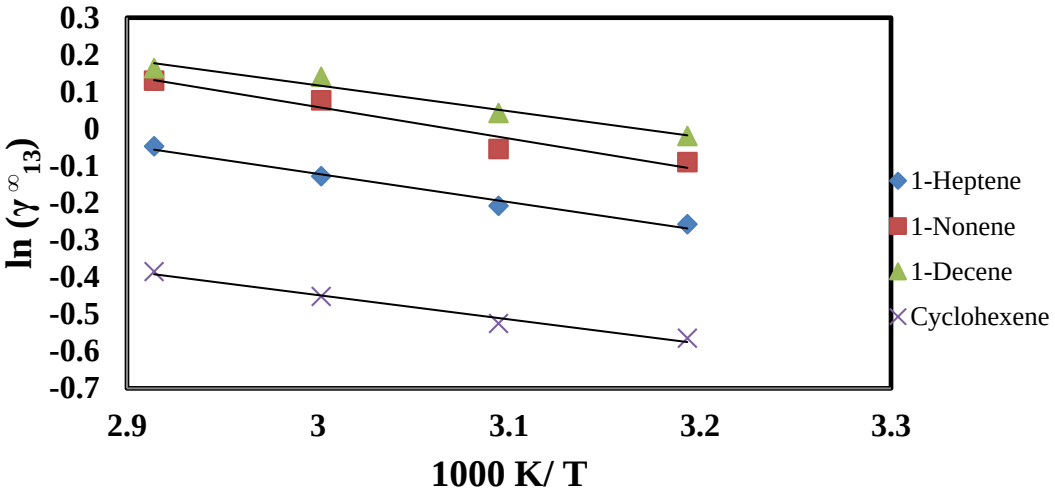

Figure 5.2.3: Plots of ln γ_{13}^{∞} versus 1/T for alkenes in [3 C_6 C_{14} P] [$(C_8H_{17})_2$ PO_2].

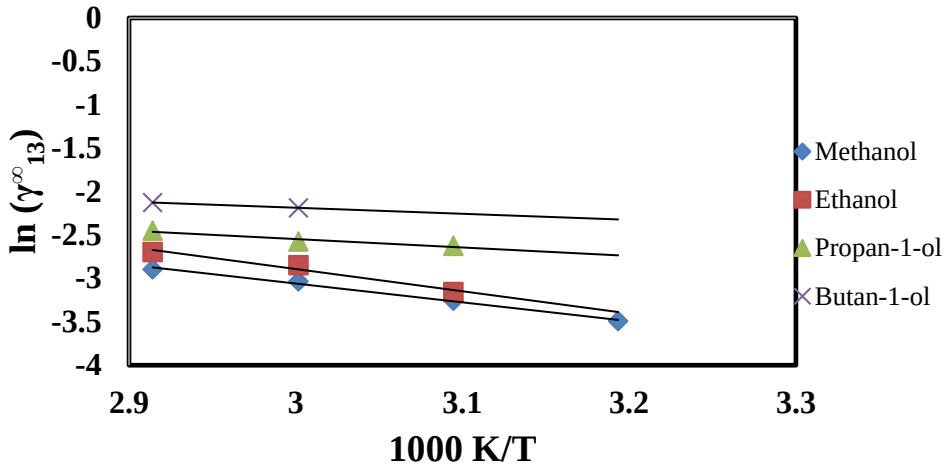

Figure 5.2.4: Plots of ln γ_{13}^{∞} versus 1/T for alcohols in [3 C_6 C_{14} P] [$(C_8H_{17})_2$ PO_2].

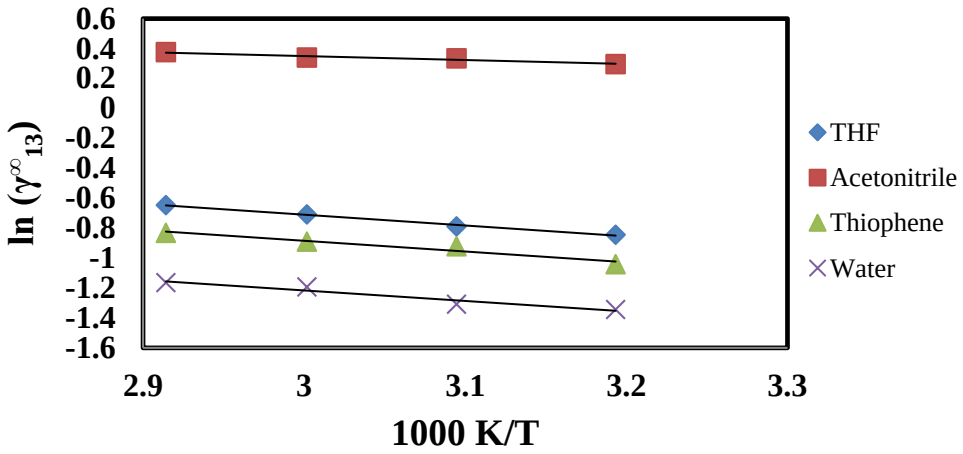

Figure 5.2.5: Plots of ln γ_{13}^{∞} versus 1/T for solute (THF, acetonitrile, thiophene and water) in [3 C_6 C_{14} P] [$(C_8H_{17})_2$ PO_2].

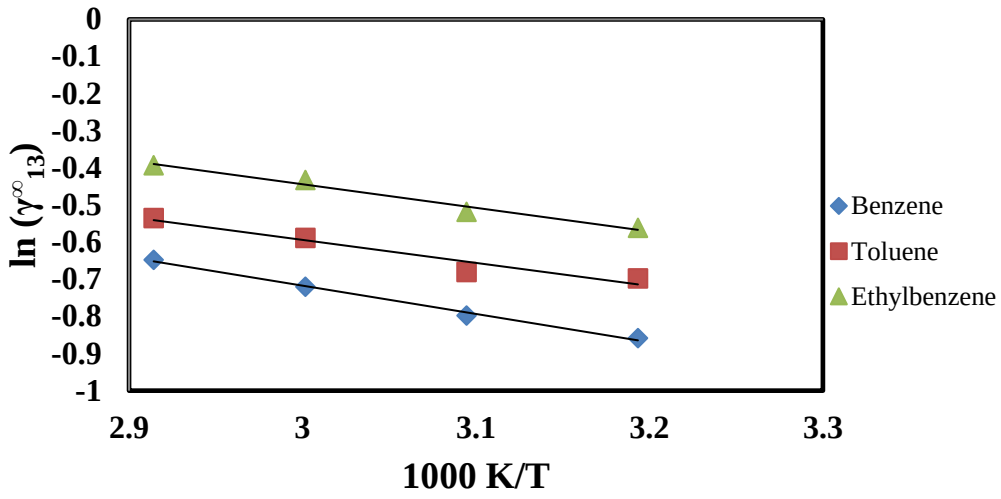

Figure 5.2.6: Plots of ln γ_{13}^{∞} versus 1/T for aromatic hydrocarbons in [3 C_6 C_{14} P] [$(C_8H_{17})_2$ PO_2].

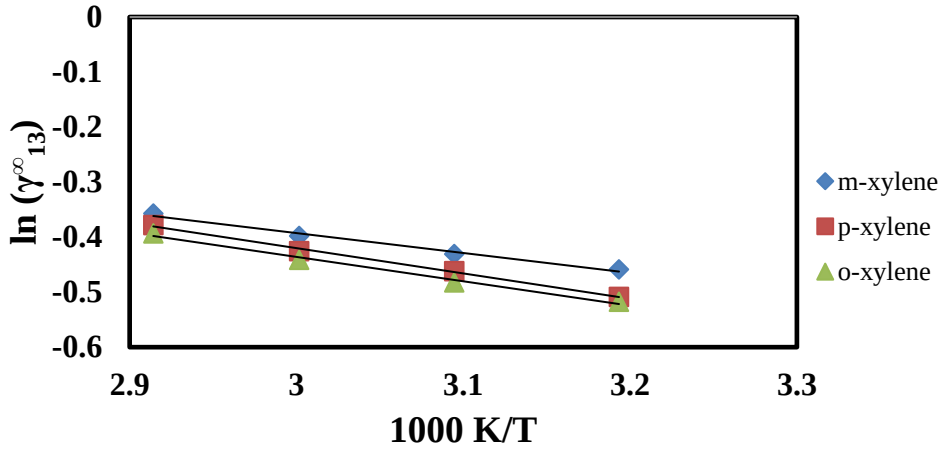

Figure 5.2.7: Plost of ln γ_{13}^{∞} versus 1/T for xylene in [3 C_6 C_{14} P] [$(C_8H_{17})_2$ PO_2].

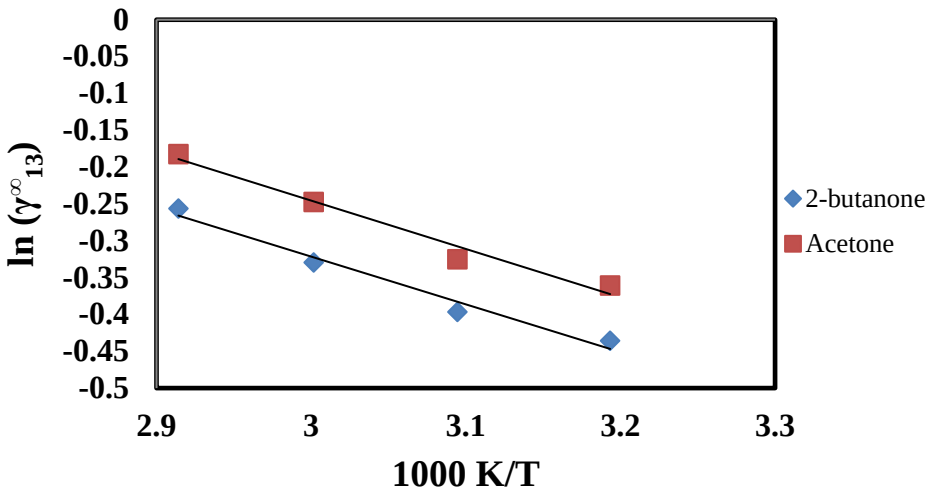

Figure 5.2.8: Plots of ln γ_{13}^{∞} versus 1/T for ketones in [3 C_6 C_{14} P] [$(C_8H_{17})_2$ PO_2].

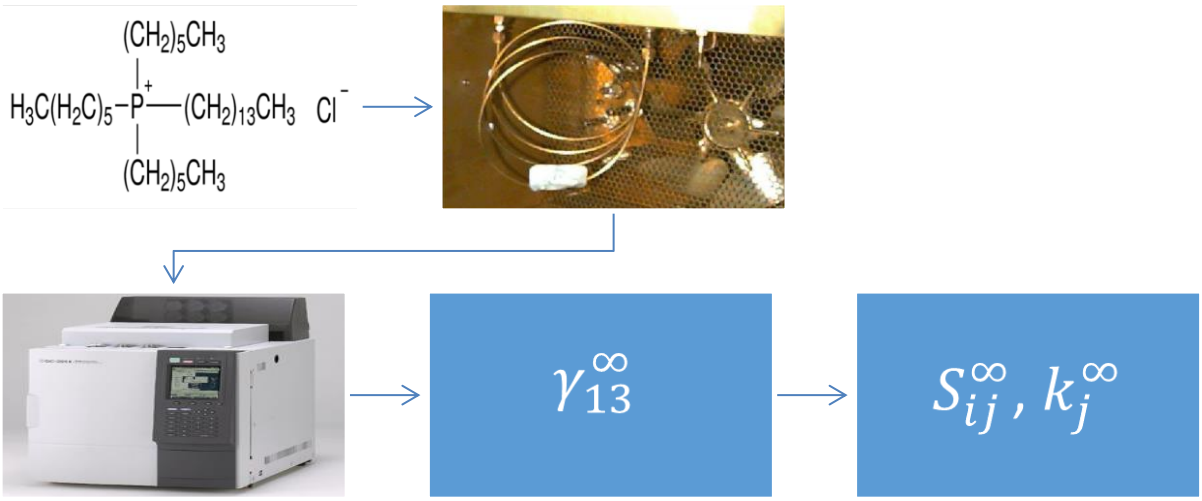

Figure 5.2.9: Schematic diagram showing the process for determining activity coefficients at infinite dilution for $[P^{+}_{14,\,6,\,6,\,6}]\,[Cl^{-}]$.

Table 5.2.6

Activity coefficients at infinite dilution for the solutes in the ionic liquid trihexyltetradecylphosphonium chloride at four different temperatures

Solute	γ_{13}^{∞} values			
	T = 313.15 K	T = 323.15 K	T = 333.15 K	T = 343.15 K
2.2-dimethylbutane	1.36	1.33	1.29	1.27
2.2.4-trimethylpentane	1.74	1.66	1.62	1.57
methylcyclohexane	1.18	1.11	1.06	1.04
cyclooctane	1.29	1.22	1.13	1.09
n-nonane	2.04	1.97	1.94	1.87
n-decane	2.41	2.32	2.22	2.11
1-heptene	1.32	1.29	1.27	1.25
1-nonene	1.73	1.62	1.56	1.53
1-decene	1.91	1.87	1.82	1.74
cyclohexene	0.92	0.90	0.88	0.87
benzene	0.53	0.51	0.50	0.49
toluene	0.60	0.61	0.62	0.63
ethylbenzene	0.85	0.80	0.76	0.73
m-xylene	0.87	0.82	0.78	0.75
p-xylene	0.85	0.79	0.75	0.72
o-xylene	0.77	0.74	0.71	0.69
methanol	0.18	0.16	0.14	0.11
ethanol	0.24	0.21	0.17	0.13
propan-1-ol	0.27	0.24	0.20	0.17
butan-1-ol	-	0.29	0.24	0.19
acetone	0.67	0.68	0.70	0.71
2-butanone	0.69	0.70	0.71	0.72
THF	0.62	0.60	0.59	0.58
acetonitrile	1.00	0.95	0.91	0.87
thiophene	0.34	0.37	0.38	0.40
water	0.29	0.27	0.24	0.23

Standard uncertainties u are u(γ_{13}^{∞}) < 3 %, u(T) = 0.02 K.

Table 5.2.7

Linear regression and excess molar enthalpies computed from the activity coefficients at infinite dilution for the ionic liquid trihexyltetradecylphosphonium chloride

Solute	Linear regression		$\Delta H_1^{E\infty}$ / (kJ · mol^{-1})
	Gradient	R^2	
2.2-dimethylbutane	0.231	0.978	1.92
2.2.4-trimethylpentane	0.361	0.989	3.00
methylcyclohexane	0.427	0.956	3.55
cyclooctane	0.630	0.985	5.24
n-nonane	0.308	0.969	2.56
n-decane	0.484	0.996	4.02
1-heptene	0.205	0.994	1.70
1-nonene	0.434	0.954	3.61
1-decene	0.322	0.973	2.68
cyclohexene	0.210	0.998	1.74
benzene	0.256	0.973	2.13
toluene	-0.067	0.975	-0.56
ethylbenzene	0.516	0.985	4.29
m-xylene	0.551	1.000	4.58
p-xylene	0.624	0.998	5.19
o-xylene	0.404	0.996	3.36
methanol	1.677	0.993	13.94
ethanol	2.249	0.981	18.70
propan-1-ol	1.692	0.979	14.07
butan-1-ol	2.474	0.997	20.57
acetone	-0.188	0.998	-1.56
2-butanone	-0.119	0.995	-0.99
THF	0.259	0.985	2.15
acetonitrile	0.480	0.993	3.99
thiophene	-0.547	0.989	-4.55
water	0.918	0.991	7.63

Table 5.2.8

Comparison of selectivities (S_{ij}^{∞}) and capacities (K_j^{∞}) for (water/butan-1-ol) separation problems for selected ionic liquids at 333.15 K.

Ionic liquid	S_{ij}^{∞} water/butan-1-ol	K_j^{∞} butan-1-ol	Ref.
$[P_{14,6,6,6}]$ [Cl]	0.90	3.39	This work
$[P_{14,4,4,4}]$ [DBS]	3.77	5.29	a
[DoMIM] $[NTf_2]$	2.76	0.64	b
$[(C_6OC)_2$ IM] $[NTf_2]$	2.67	0.91	c
$[N_{8,2,2,2}]$ $[NTf_2]$	2.46	0.52	d
$[C_8$ iQuin] $[NTf_2]$	2.22	0.63	e
[DMIM] [TCB]	2.04	0.96	f
[BMPYR] [FAP]	2.03	0.26	g
$[C_6$ Qui] $[NTf_2]$	1.99	0.58	h
$[P_{4,4,4,1}]$ [TOS]	1.74	3.14	i
[EMIM] [FAP]	1.49	0.25	j

(Wlalzo et al., 2017)[a]

(Domanska and Wlalzo 2016)[b]

(Domanska and Marciniak 2009)[c]

(Wlalzo and Domanska 2016)[d]

(Domanska et al., 2011)[e]

(Domanska and Marciniak 2010)[f]

(Domanska et al., 2012)[g]

(Ayad et al., 2016)[h]

(Domanska and Paduszynski 2010)[i]

(Wlazlo et al., 2015)[j]

Table 5.2.9

Comparison of selectivities (S_{ij}^{∞}) and capacities (K_j^{∞}) for (methanol/benzene) separation problems for selected ionic liquids at 333.15 K.

Ionic Liquid	S_{ij}^{∞} methanol/benzene	K_j^{∞} benzene	Ref.
$[P_{14,6,6,6}]$ [Cl]	0.34	1.88	This work
$[3C_6C_{14}P]$ $[BF_4]$	1.31	0.90	a
$[3C_6C_{14}P]$ $[TF_2N]$	2.77	1.10	a
$[3C_6C_{14}P]$ $[PF_6]$	3.12	1.47	b
$[3C_6C_{14}P]$ $[(C_2F_5)\ PF_3]$	5.83	5	c
$[C_{16}MIM]$ $[BF_4]$	1.52	1.27	d
[MOIM] $[PF_6]$	1.88	1.04	b
Sulfolane	0.91	0.43	e

(Tumba et al., 2010)[a]

(Heintz et al., 2006)[b]

(Letcher et al., 2008)[c]

(Mutelet and Jaubert 2007)[d]

(Mollmann and Gmehling 1997)[e]

Table 5.2.10

Comparison of selectivities (S_{ij}^{∞}) and capacities (K_j^{∞}) for (ethanol/2-butanone) separation problems for selected ionic liquids at 333.15 K.

Ionic Liquid	S_{ij}^{∞} ethanol/2-butanone	K_j^{∞} 2-butanone	Ref.
$[P_{14,6,6,6}]$ [Cl]	0.36	1.45	This work
$[3C_6C_{14}P]$ $[BF_4]$	1.31	0.90	a
$[3C_6C_{14}P]$ $[TF_2N]$	2.77	1.10	a
$[3C_6C_{14}P]$ $[PF_6]$	3.12	1.47	b
$[3C_6C_{14}P]$ $[(C_2F_5)\ PF_3]$	5.83	5	c
$[C_{16}MIM]$ $[BF_4]$	1.52	1.27	d
[MOIM] $[PF_6]$	1.88	1.04	b
Sulfolane	0.91	0.43	e

(Tumba et al., 2010)[a]

(Heintz et al., 2006)[b]

(Letcher et al., 2008)[c]

(Mutelet and Jaubert 2007)[d]

(Mollmann and Gmehling 1997)[e]

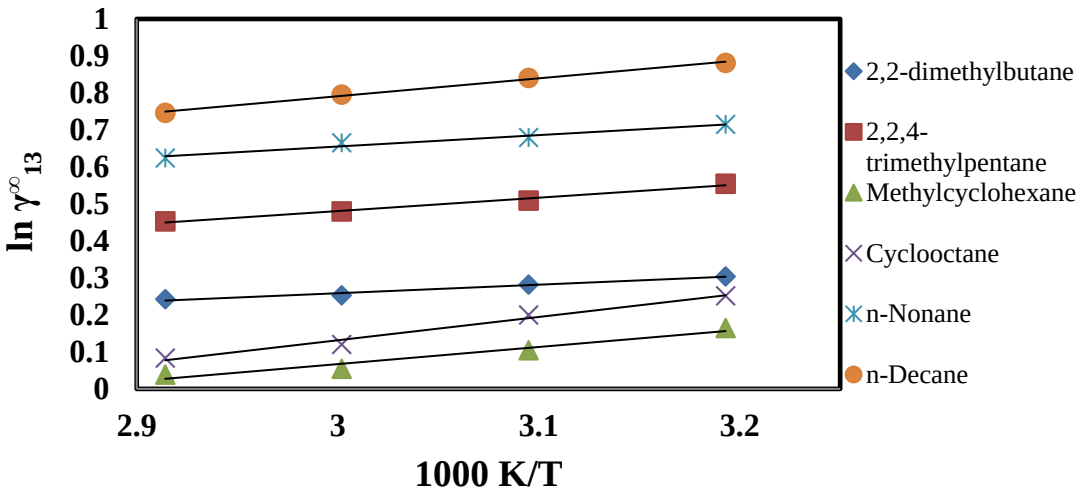

Figure 5.2.10: Plots of ln γ^{∞}_{13} versus 1/T for the alkanes in [$P^{+}_{14, 6, 6, 6}$] [Cl^{-}].

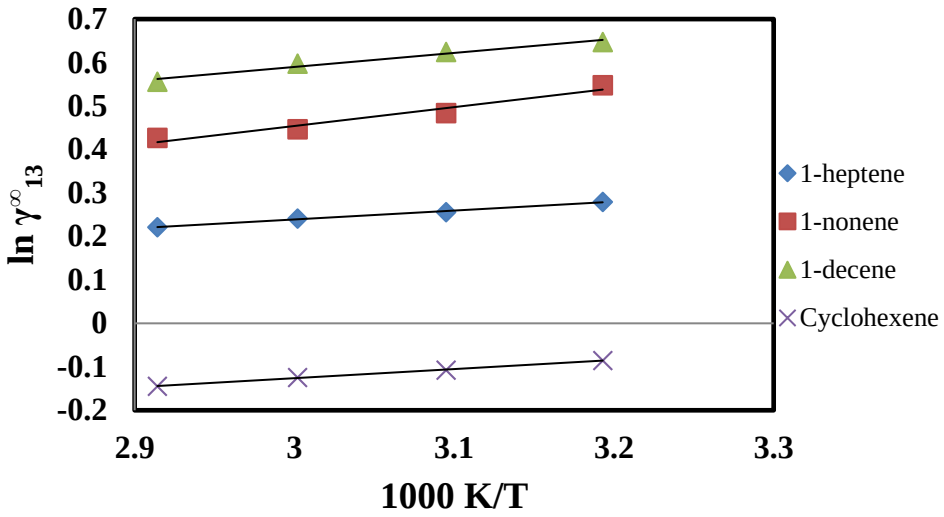

Figure 5.2.11: Plots of ln γ^{∞}_{13} versus 1/T for the alkenes in [$P^{+}_{14, 6, 6, 6}$] [Cl^{-}].

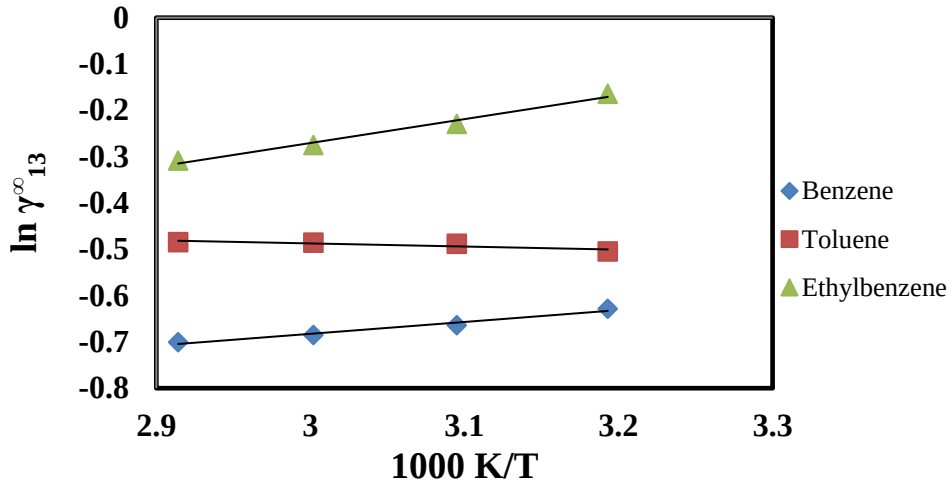

Figure 5.2.12: Plots of ln γ_{13}^{∞} versus 1/T for aromatic hydrocarbons in [$P^{+}_{14, 6, 6, 6}$] [Cl^{-}].

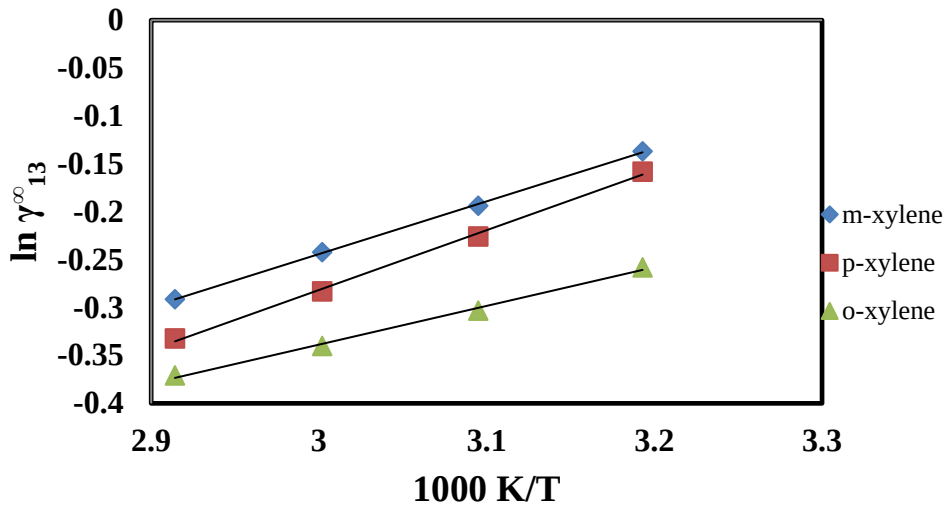

Figure 5.2.13: Plots of ln γ_{13}^{∞} versus 1/T for xylene in [$P^{+}_{14, 6, 6, 6}$] [Cl^{-}].

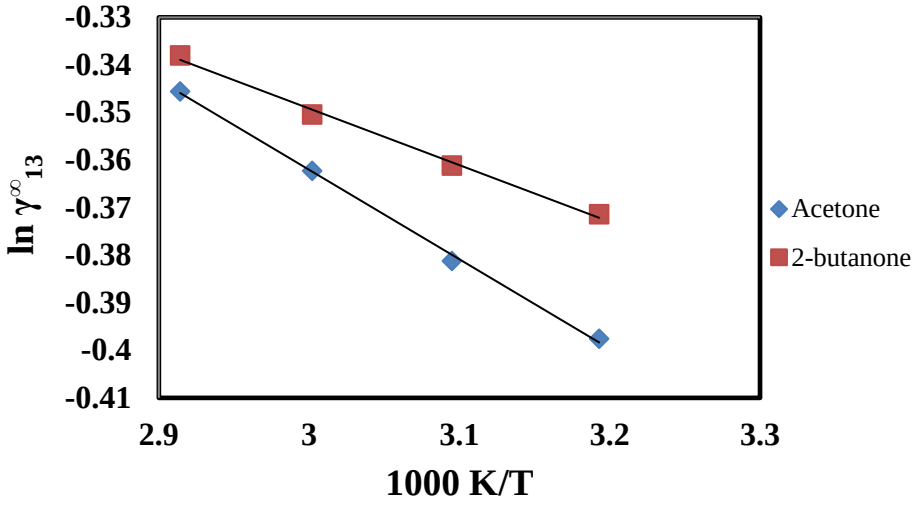

Figure 5.2.14: Plots of ln γ_{13}^{∞} versus 1/T for ketones in [$P^{+}_{14, 6, 6, 6}$] [Cl^{-}].

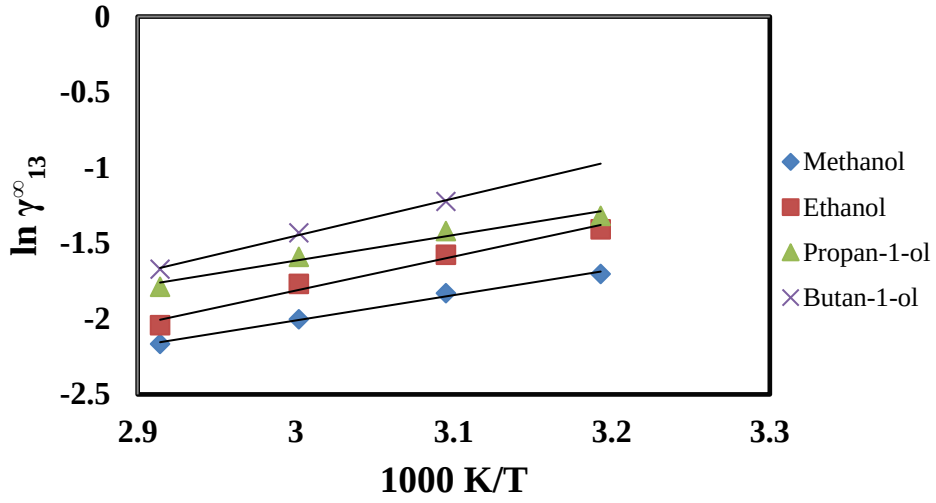

Figure 5.2.15: Plots of ln γ_{13}^{∞} versus 1/T for alcohols in [$P^{+}_{14, 6, 6, 6}$] [Cl^{-}].

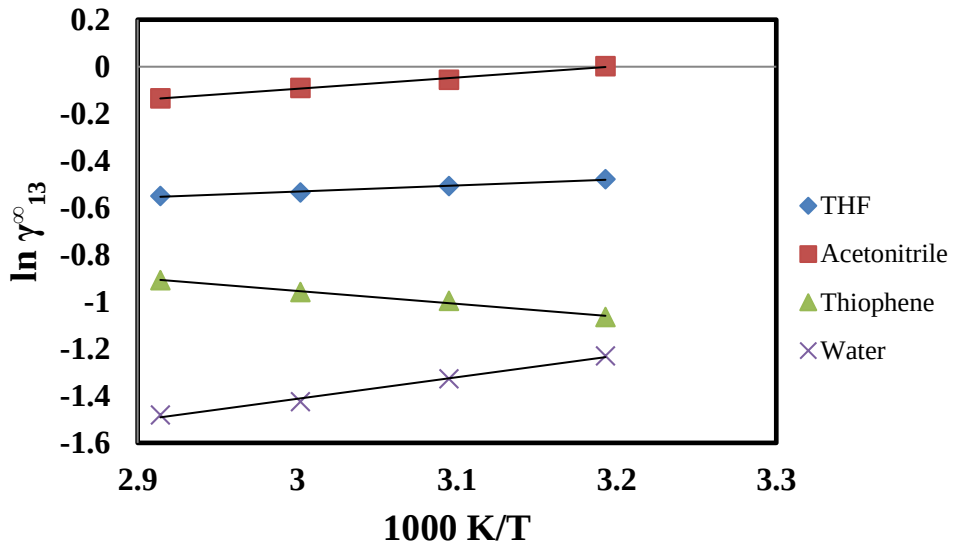

Figure 5.2.16: Plots of ln γ_{13}^{∞} versus 1/T for solute (THF, acetonitrile, thiophene and water) in $[P^{+}_{14,6,6,6}]$ $[Cl^{-}]$.

Chapter 6

Discussion

The chosen ionic liquids have a broad range of properties, including electrochemical properties, lower toxicity and thermally more stable. Several applications include their utility as electrolytes in batteries, as solvents for extraction, corrosion prevention and as solvents for chemical synthesis [Warke et al., 2016]. Carboxylic acids as a group are important since they are effective in many industrial applications, which include use in polyester resins, pharmaceutical products, catalysts and other chemical industries [Singh et al., 2015]. A notably large amount of benzaldehyde is used in the production of other aromatic aldehydes. In the synthesis of many organic compounds, ethyl acetoacetate is frequently used as an intermediate [Satrio and Doraiswamy 2001]. Mixtures of ionic liquids containing these organic solvents are reported to have potential industrial applications [Domanska et al., 2017].

The mixtures are composed of two components containing cations and anion, interacting with each other by self-association, often through hydrogen bond interaction, forming a eutectic mixture with a melting temperature far below that of its constituents [Zhang et al., 2012]. The mixture is referred as deep eutectic solvent.

6.1 Measured properties

6.1.1 Density

Among the studies occurring in the interesting field of ILs, density is the most studied parameter [Harris et al., 2005], although data regarding phosphonium based ILs remains scarce in the literature. Since ionic liquids are relatively more expensive as compared to the organic solvents, the use of pycnometric techniques in studying density is generally limited on ionic liquids due to the fact that pycometers requires a large sample of liquid and large-scale volume for calibration and measurement. Density measurements are mostly carried out at various temperatures in order to investigate the behaviour of the liquids by using for example the Rudolph Research Analytical DDM 2911 automatic densimeter or Anton Paar

DMA-5000 M digital vibrating tube densitometer. Density measurements are crucial in determining the characteristics of the materials, eg whether the material will sink or float on aqueous systems, it is also important because it also gives a clue about the speed sound. The denser the medium, the lower the speed of sound. From to the density measurements, some of the important ionic liquids derived parameters such as excess molar volume, isentropic compressibility, etc, can be computed.

In this research work, the Anton Paar DSA 5000 M densitometer which was controlled at different temperatures, T = (293.15 to 313.15) K was utilized to conduct the measurements of densities. Densities of the binary mixtures and pure compounds were measured at atmospheric pressure. Based on the represented results of density in Chapter 5 and Figures (5.1.1, 5.1.2, 5.1.10, 5.1.11 and 5.1.12) it can be seen that the densities are inversely proportional to the temperature at all intervals. Represented figures for the mixtures of ($[P^{+}_{14, 6, 6, 6}]$ $[Cl^{-}]$ and PA) clearly shows that the densities decrease as the concentration of the investigated IL increases. This observed change might rise from the weakening of $[P^{+}_{14, 6, 6, 6}]$ $[Cl^{-}]$ and PA interactions when both components were mixed [Sanmamed et al., 2007, Singh et al., 2015]. For the binary mixtures of ([Emim] $[BF_4]$ with benzaldehyde or ethyl acetoacetate), a different behaviour as compared to the mixtures of ($[P^{+}_{14, 6, 6, 6}]$ $[Cl^{-}]$ and PA) was observed. Here the density of the mixtures increases as the concentration of the ionic liquid increases for both of the studied systems. This effect is due to the dispersive interactions in the ionic liquid that occur with an increase in alkyl chain length. All the plotted figures of the binary mixtures show a simple linear correlation with the mole fraction.

6.1.2 Sound velocity

This is an important and essential parameter which gives a clear sign about the density as well as viscosity, eg (the lower the speed of sound, the denser the medium). As much as it is not that much easy to give a clear detailed report on types of interactions occurring between the liquid mixtures, this parameter is functional, because it also describes the interactions such as solvent-solvent, solvent-solute and solute-solute interactions existing between the liquid mixtures [Gowrisankar et al., 2013]. Speed of sound was measured simultaneously with the density at all investigated temperatures and mole fraction measurements, and the results are given in Chapter 5 in Table 5.1.1, 5.1.3 and 5.1.4 for the measured binary mixtures

studied in this research work. All the speed of sound Figures show the dependence of this parameter with temperature, and it can be seen that speed of sound is inversely proportional to the temperature. From Figures for the speed of sound, it can be observed that the speed of sound increases as the concentration of ([Emim] [BF_4] or [$P^+_{14, 6, 6, 6}$] [Cl^-]) increases, but decrease as the temperature increases.

6.1.3 Viscosity

By a simple definition, viscosity is the resistance to flow of liquid. Viscosity is one of the most commonly studied parameters which yield thermodynamic insight regarding insight to the activation energy for viscous flow. It is also a highly sensitive parameters relating to the presence of impurities. Safety precautions were taken to avoid the adsorption of moisture by drying the solvents over 4 Å molecular sieves during the experimental handling, which have a huge impact on the accuracy of results.

Based on the scale-up of ionic liquids, viscosity is the most defensible physical property when evaluating their applications. The internal resistance of various liquids to a shear stress can be described by viscosity, hence it is one of the major parameter to be studied in terms of liquid mixtures [McAtee and Heitz 2016]. As can be observed from the previous studies, viscosity of the ionic liquids is relatively low as compared to the organic solvents, and this results from their high molecular weight or complex structures.

This parameter was also measured by using Anton Paar (DSA 5000 M) densitometer which was operated over the temperature range T = (293.15 to 313.15) K and at atmospheric pressure (p = 0.1 MPa). Measured viscosity results of pure components and both of the binary systems of ([Emim] [BF_4] with benzaldehyde or ethyl acetoacetate) are given in Table 5.1.6. The viscosity of the ionic liquids is strongly influenced by hydrogen bonding and Van der Waals forces.

6.2 Derived properties

6.2.1 Excess Molar Volumes

The equation (6.2.1) below was used to determine excess molar volumes, which was computed from the experimentally determined densities of the binary systems and pure liquids at corresponding mole fractions and different temperatures (293.15 to 313.15) K respectively.

$$V_m^E = \sum_{i=1}^{2} x_i M_i (\rho^{-1} - \rho_i^{-1}) \quad (6.2.1)$$

From the equation (6.2.1) above, x_i indicates the mole fraction, ρ and ρ_i represent the densities of the pure liquids and binary systems of ([Emim] [BF_4] + benzaldehyde or ethyl acetoacetate) or ([$P^+_{14, 6, 6, 6}$] [Cl^-] and PA) respectively, M_1 and M_2 denotes the molar mass of the IL and molar mass of benzaldehyde, ethyl acetoacetate or propanoic acid. The calculated results are summarised in Tables 5.1.1, 5.1.3 to 5.1.4. Negative values were observed for the calculated excess molar volumes across the entire mole fraction range and at all examined temperatures for all of the studied systems. The negative values for the calculated $V_{\mathrm{m}}^{\mathrm{E}}$ increase as the temperatures increases and the shape of the profile changes as well. Such occurrence has been also noticed for other binary systems containing ionic liquids [Han *et al* 2009]. By closely looking at the values given in table 5.1.1 to 5.1.4 of the binary systems, they clearly show that [Emim] [BF_4] or [$P^+_{14, 6, 6, 6}$] [Cl^-] has a capacity to strongly interact with benzaldehyde, ethyl acetoacetate or propanoic acid molecules resulting in volume contraction, this effect possibly occurs from the dipolar interactions and hydrogen bonding [McAtee and Heitz 2016]. The observed negative values simply stipulate that a more systematic packing or attractive interactions occurred when the investigated ionic liquids and benzaldehyde, ethyl acetoacetate or propanoic acid molecules were assorted. The other factor that contributes towards negative values of $V_{\mathrm{m}}^{\mathrm{E}}$ might rise from the unlike molecular interactions, which leads to the action of hydrogen bonding and charge transfer. Over the whole temperature range described in this research work, the change in $V_{\mathrm{m},min}^{\mathrm{E}}$ for the binary mixtures of ([Emim] [BF_4] + benzaldehyde or ethyl acetoacetate) ranges from (-1.4648 to -1.5901) $cm^3 \cdot mol^{-1}$ and (-1.5955 to -1.8298) $cm^3 \cdot mol^{-1}$ and occurs at x_i = 0.4059 and 0.4053 for benzaldehyde and ethyl acetoacetate, respectively, which are not far off from the values reported by [Rao et al., 2016] for binary systems of ([Emim] [BF_4] + aniline). For the binary

mixtures of ([$P^{+}_{14,6,6,6}$] [Cl^{-}] and PA), the change in $V^{E}_{m,min}$ ranges from (-0.6701 to -0.9726) $cm^3 \cdot mol^{-1}$, and occurs at x_1 = 0.3301, which are also within close proximity to the values reported by [McAtee and Heitz 2016] for systems containing ([$P^{+}_{14,6,6,6}$] [Cl^{-}] + methanol).

6.2.2 Apparent Molar Volume

The apparent molar volume is the limiting volume that a substance occupies in one mole of the substance. It shows the change in corresponding solution property when that entire component is added to the solution per mole of component added. As previously discussed, the density measurements are one of the important parameters, density data was used to determine the data of apparent molar volume (V_ϕ) with the use of equation (6.2.2).

$$V_\phi = \frac{M}{\rho} + \frac{1000}{m}\left(\frac{\rho_1 - \rho}{\rho_1 \rho}\right) \quad (6.2.2)$$

In equation (6.2.2) above, molar mass of solute is represented by M, ρ and ρ_1 denotes densities of the solution and the solvent correspondingly; molality of the mixture represented by m. Table 5.1.2 and 5.1.6 shows the results for the computed values of V_ϕ for the binary mixtures of ([$P^{+}_{14,6,6,6}$] [Cl^{-}] and PA) as well as for ([Emim] [BF_4] + benzaldehyde or ethyl acetoacetate). The derived apparent molar volume properties are directly proportional to the temperatures which suggest the strong solute-solute interaction as well as the solute concentration in the binary mixtures with increase in temperature is observed. At small concentration of the ionic liquid, the ions are enclosed by the solvent molecules which indicate pronounced ion-solvent interaction and an enlargement in the ionic liquid molality, increases the ion-ion interaction resulting in high V_ϕ values.

6.2.3 Isentropic compressibility and deviation in isentropic compressibility

The word isentropic implies that as the sound waves passes into and out of a liquid, the temperature and pressure fluctuates inside each microscopic volume but the entropy of the entire system remain unchanged. By measuring speed of sound using a low frequency generator (DSA 5000 M transducer that yields about 3 MHz frequencies) this statement holds true, velocity dispersion and absorption of waves occurs at high frequency more than 100 MHz, this is due to coupling with molecular processes with liquids [Rajitha et al., 2017]. The k_s values were calculated with the use of the Newton Laplace equation (6.2.3), k_s.

$$k_s = \frac{1}{\rho u^2} \quad (6.2.3)$$

In the Newton Laplace equation (6.2.3), ρ represents the densities and *u* denotes the speed of sound for the prepared binary systems. Δk_s values were computed with the use of equation (6.2.4) below.

$$\Delta k_s = k_s - \sum_i^2 \phi_i k_s, i \quad (6.2.4)$$

In the above equation (6.2.4), k_s and ϕ_i, are isentropic compressibilities and volume fractions of the pure liquids respectively. The calculated values for k_s and k for the binary mixtures of ([Emim] [BF_4] + benzaldehyde or ethyl acetoacetate) and ([$P^+_{14, 6, 6, 6}$] [Cl^-] and PA) at all investigated temperatures are reported in Tables 5.1.2, 5.1.3 to 5.1.4. Based on the calculated results for k and Δk_s , it is clearly noticeable that the k_s values are inversely proportional to the mole fraction of the investigated ILs at all temperatures; this effect arises from the increase in thermal agitation making the soluble liquids more compressible [Singh et al., 2015, Gowrisankar et al., 2013]. Interactions that occurred in the binary systems contributed towards a decrease in free-space, and this effect lead to negative Δk_s values [Bahadur et al., 2014]. The Δk_s negative values show that these miscible solutions are less compressible as compared to the ideal mixtures. Due to the stronger interactions and closer approach of unlike molecules between benzaldehyde or ethyl acetoacetate and [Emim] [BF_4] or propanoic acid and [$P^+_{14, 6, 6, 6}$] [Cl^-] binary mixtures lead to a decrease in compressibility of the mixtures, and this observed effect is most likely. According to the volumetric studies, these observations are in good agreement. In addition, the Δk_s values across the mole fraction range of [Emim] [BF_4] and [$P^+_{14, 6, 6, 6}$] [Cl^-] are inversely proportional to the temperature. The $\Delta k_{s,\,\min}$ values obtained are (-3.61 to -4.60) x10^{-8} Pa^{-1} and (-5.01 to -6.50) x10^{-8} Pa^{-1} which occurs at x_i = 0.4059 and 0.4053, for ([Emim] [BF_4] + benzaldehyde or ethyl acetoacetate), respectively, and for the mixtures of ([$P^+_{14, 6, 6, 6}$] [Cl^-] and PA), the $\Delta k_{s,\,\min}$ values obtained are (-14.95 to -19.52) x10^{-8} Pa^{-1} and was observed at x_i = 0.3301, at all examined temperatures.

6.2.4. Apparent molar isentropic compressibility

Equation (6.2.5) below was utilized to determine the apparent molar isentropic compressibility (K_ϕ) values for the studied binary mixtures.

$$K_\phi = \left[\frac{1000(\rho_0\, k_s - k_0\, \rho)}{m\, \rho \rho_0}\right] + \left[\frac{M k_s}{\rho}\right] \quad (6.2.5)$$

Where ρ_0 *and* ρ indicates densities of the pure solvent and binary mixtures correspondingly; m and M denotes the molality of the solution and molar mass of solute, k_s and k_0 represents

the isentropic compressibilities of the solution and solvent, correspondingly. The dissimilarities among these quantities contemplate the degree of solute-solute and solute-solvent interactions. The data for $K_{\emptyset}$ are also displayed in Table 5.1.2 and 5.1.5. It is clearly observed that the K_{ϕ} values are directly proportional to the concentration of solute except for the molality of 13.53 mol/kg and 20.71 mol/kg at 298.15 K and 303.15 K in the binary mixtures of $[P^{+}_{14,\ 6,\ 6,\ 6}]$ $[Cl^{-}]$ + propanoic acid, as well as the temperature for the binary systems at all examined temperatures. A similar trend was observed for the systems of methanol and methyl acetate at low molality, which occurred at 298.15 K and 303.15 K [Bahadur and Deenadayalu 2011]. Negative values in the system containing ethyl acetoacetate at lower concentration of the ionic liquid were also observed. This effect reflects that ethyl acetoacetate molecules are less compressible than in the higher concentrations of the ionic liquid.

Hall et al., 1948 and [Mehta and Chauhan 1997] proposed the "analysis of disagreement at lower values" in terms of geometrical and structural compressibility. The geometrical compressibility results from simultaneous compression of the molecules whereas structural compressibility is due from the breakdown of intermolecular bonds resulting in a decrease in the average intermolecular length. A slight change in the apparent molar isentropic compressibility of solute at all investigated temperatures against $(m)^{1/2}$ have been shown in Figure 5.1.8, 5.1.22 and 5.1.23.

6.2.5 Intermolecular free length

Intermolecular forces (IMFs) are the forces which mediate interactions between molecules, including forces of attraction or repulsion which act between molecules and other types of neighbouring particles, e.g., atoms or ions. Intermolecular free length (L_f), equation (6.2.6) is determined from the Jacobson empirical relation and this helps to interpret the nature of intermolecular interaction [Jacobson et al 1952].

$$L_f = k_j\,(k_s)^{1/2} \tag{6.2.6}$$

In the equation above, k_j is the Jacobson's temperature dependent constant (93.875 + 0.375 T) $\cdot$ 10^{-8}, and k_s denotes the isentropic compressibility. The intermolecular free length values for the calculated binary mixtures at various temperatures are given in Tables 5.1.2 to 5.1.4.

The values of L_f for benzaldehyde, ethyl acetoacetate or propanoic acid are higher in comparison to that of pure [Emim] [BF_4] or [$P^+_{14,\ 6,\ 6,\ 6}$] [Cl^-], respectively, but they are noticed to be inversely proportional to the concentration of [Emim] [BF_4] or [$P^+_{14,\ 6,\ 6,\ 6}$] [Cl^-] in the mixtures. These conditions clearly specify the occurrence of the molecular interactions amongst the components of the mixtures. Furthermore, the intermolecular free length is directly proportional to the temperature. The length among the surfaces of the two molecules which result to a decrease in the sound velocity is caused by the progressive increase in the intermolecular free length. By closely inspecting Figures 5.1.9 and 5.1.20 to 5.1.21 as well as Tables 5.1.2 to 5.1.4, it can be seen that the L_f and sound velocity are connected in an inverse manner. Intermolecular free lengths were used to investigate the properties that exist in the binary mixtures that comprised of attractive and repulsive forces, and a simple linear correlation with the mole fraction of the ionic liquid was observed.

6.2.6 Deviations in viscosity

Like any other deviation of physical properties of liquid mixtures, the dissimilarity between the viscosity of mixtures and the viscosity of the ideal-mixture at the equivalent thermodynamic state (η^{id}) is explained as the deviation in viscosity ($\Delta\eta$). Equation (6.2.7) below was used to determine the deviations in viscosity of liquid mixtures.

$$\Delta\eta = \eta - \eta^{id} \tag{6.2.7}$$

As much as there are many methods to determine η^{id}, the most commonly used procedure by the research groups is that determined on a mole fraction basis, equation (6.2.8).

$$\eta^{id} = x_1\ \eta_1{}^0 + x_2\ \eta_2{}^0 \tag{6.2.8}$$

In the equation above, $\eta_i{}^0$ represents viscosity of pure liquid *i* at the mixture temperature and pressure, x_1 and x_2 represents mole fraction of ionic liquid and ethyl acetoacetate or benzaldehyde, respectively. The deviation in viscosities values against mole fraction are plotted in Figure 5.1.26 and 5.1.27 for both of the studied binary systems of ([Emim] [BF_4] + benzaldehyde or ethyl acetoacetate) for all experimental temperatures. When benzaldehyde or ethyl acetoacetate is mixed with the investigated [Emim] [BF_4] ionic liquid, a dramatic decrease in viscosities of the mixtures mainly at high temperatures was observed. In the dilute solutions containing organic compounds in the IL, the decrease is specifically strong. Between [Emim] and tetrafluoroborate anions, the strong coulomb interactions are weakened

when mixed with benzaldehyde or ethyl acetoacetate, which results in a greater mobility of the ions leading to a reduced viscosities of the binary mixtures [Tian et al., 2008]. Negative values of deviation in viscosity are observed in all cases.

6.2.7 Correlation of the calculated properties

The values for the derived thermophysical properties (excess molar volumes, deviation in isentropic compressibility and intermolecular free length) for the binary mixtures of {[$P^{+}_{14, 6, 6, 6}$] [Cl^{-}] + propanoic acid} and {[Emim] [BF_4] with benzaldehyde or ethyl acetoacetate} are given in Tables 5.1.8 and 5.1.9. Redlich-Kister polynomial equation (6.2.9) given below was used to fit these properties by the technique of non linear least squares.

$$X = x_1 x_2 \sum_{i=1}^{k} A_i \, (1 - 2x_1)^{i-1} \qquad (6.2.9)$$

In the equation above, *x* represents the excess molar volume or deviation in isentropic compressibility. The values of the fitting parameters A_i were determined by the least square method. Standard deviation results are also given in Tables 5.1.8 and 5.1.9.

For the correlation, the equation (6.2.10) below was utilised to calculate the standard deviation (σ).

$$\sigma(X) = \sum_{i=1}^{n} \left[\frac{X_{expt} - X_{calc}}{(N-K)}\right]^{1/2} \qquad (6.2.10)$$

The number of experimental points is represented by N, whilst K represents the coefficients used in the Redlich-Kister equation. For all of the derived properties, the standard deviation showed low values at all studied temperatures. Based on these data, it can be seen that there is good correlation with the experimental results.

6.3 Activity coefficients at infinite dilution

6.3.1 Phosphonium based ionic liquid

The average γ_{13}^{∞} data obtained in this work with the column loading of 28 % (by mass) of the ILs at four various temperatures between the range of (313.15 to 343.15) K, are presented in

Tables 5.2.1 and 5.2.6. The natural logarithm of γ_{13}^{∞} are shown in Figures 5.2.2 to 5.2.8 and 5.2.10 to 5.2.16 as a function of inverse absolute temperature, for all examined solutes. In each class of investigated compounds, the γ_{13}^{∞} values are directly proportional to the solute alkyl chain for both of the studied ionic liquids. From the γ_{13}^{∞} data, it can be noticed that cycloalkanes have lower values in contrast to linear alkanes because of the stronger attractive interactions amongst the cyclic structure and the phosphonium chain. Low values of alkenes as compared to alkanes with similar number of carbon atoms were observed, this is due to the interaction generated by the double bonds in the alkenes with the polar ionic liquid. Alkanes, alkenes and cycloalkanes have high γ_{13}^{∞} as compared to the aromatic hydrocarbons and this might be due to the strong attractive interactions between the six π-delocalized electrons in the benzene structure and polar IL. The benzene molecule contains delocalized π electrons that can highly interact with the ionic liquid by (n-π), which is stronger as compared to van der Waal's interactions. For methanol, ethanol and 1-propanol low values below unity of γ_{13}^{∞} were observed in the ionic liquid trihexyltetradecylphosphonium-bis-(2,4,4-trimethylpentyl)-phosphinate specifying strongest interactions with the investigated ionic liquid due to increased hydrogen bonding.

In the ionic liquid trihexyltetradecylphosphonium-bis-(2,4,4-trimethylpentyl)-phosphinate, the γ_{13}^{∞} values are directly proportional to the temperature. The opposite trend was observed in the ionic liquid trihexyltetradecylphosphonium chloride except for thiophene, toluene and ketones. A similar behaviour was also observed for some phosphonium based ionic liquid (tri-*iso*-butylmethylphosphonium tosylate) [Domanska and Paduszynski 2010]. Small values of γ_{13}^{∞} simply imply strong interactions amongst the solute and solvent. Alcohols have the smallest values of γ_{13}^{∞} for both of the ionic liquid studied.

6.3.2 Partial molar excess enthalpies

The Gibbs-Helmholtz equation given below was used to compute partial molar excess enthalpies at infinite dilution for the organic solutes in the ionic liquids which was determined from the temperature dependency of the ln γ_{13}^{∞} against temperature plots.

$$\frac{\Delta(\ln \gamma_{13}^{\infty})}{\Delta(\frac{1}{T})} = \frac{\Delta H_1^{\mathrm{E},\infty}}{R} \tag{6.3.1}$$

The computed data for $\Delta H_1^{\mathrm{E}\infty}$ are listed in Tables 5.2.2 and 5.2.7. Negative values for computed $\Delta H_1^{\mathrm{E}\infty}$ were observed for all chosen solutes in the ionic liquid trihexyltetradecylphosphonium-bis-(2,4,4-trimethylpentyl)-phosphinate. For ethanol and methanol, lowest values were observed, (-21.3 and -18.02) kJ · mol^{-1}, respectively. The strong interactions with the ionic liquid cause a very long retention time for alcohols. The obtained negative values of $\Delta H_1^{\mathrm{E}\infty}$ imply the existence of interactions due to solute-solvent pairs. This type of behaviour is due to interaction among the polar anions of the ionic liquid and the double bond in alkenes, and also polarisable π-electrons in thiophene and aromatic compounds.

Positive partial molar excess enthalpies were observed in the investigated ionic liquid trihexyltetradecylphosphonium chloride except for thiophene, toluene and ketones. The positive data of $\Delta H_1^{\mathrm{E}\infty}$ suggest that activity coefficients are inversely proportional to the temperature. Furthermore, this also implies that at infinite dilution, partial molar excess enthalpies stipulate that the dissociation impact is greater than association impact in very dilute mixtures comprising the ionic liquid as well as solute investigated. Water and alcohols have high positive values of $\Delta H_1^{\mathrm{E}\infty}$ indicating the breaking of hydrogen bonds during the dissolution process in the ionic liquid trihexyltetradecylphosphonium chloride.

6.3.3 Effect of structure of organic solutes in the phosphonium based ionic liquid

The interaction of non polar organic solutes such as linear alkanes with the phosphonium-based ionic liquid is mostly through a small range of van der Waals forces which are weaker as compared to induced interactions through dipole-dipole existing in system comprising aromatic hydrocarbons, alkynes and alkanes. These types of compounds contain delocalized

electrons that increase polarisability. Limiting activity coefficients are inversely proportional to the polarisability. The γ_{13}^{∞} values for alcohols are smaller because of the nature of their polarity as well as the existence of oxygen atom which is electronegative, and is more likely to strongly interact with the positive charge contained in the ionic liquid cation. Ketones interact through solute-solvent interactions and this type of interaction can be due to the two pairs of oxygen atoms with cation of the investigated ionic liquids.

In the phosphonium-based ionic liquids there are no delocalised electrons and this implies that association with volatile organic compounds is more likely to be strong. As the alkyl chain of solute increases, this weakens the interaction of ionic liquid with solute under investigation, as the activity coefficients at infinite dilution increase with increasing the number of carbons of solute. In the existence of coulombic forces and hydrogen bonds that are mostly common in the ionic liquids, extended chained ionic liquids are closely packed and possibly too large to accommodate solutes. As far as the impact of ionic liquid anion is concerned, polarity, size and shape have to be taken into consideration in interpreting activity coefficients at infinite dilution in terms of the experimental data.

6.4 Limiting capacity and selectivity

The extraction mechanism of mixtures of hydrocarbons utilizing polar agents is elucidated by the theory of [Prausnitz and Anderson 1961]. It is also functional for the ionic liquids. For a proper functional entrainer, an IL has to interact separately with the mixed components. This transpires when one of the constituents is saturated while the other one is not. The non-saturated component is polarised by the ionic liquid. The former interact more positively with the solvent and is then transported along as the bottom product. The selectivity of a solvent is a measure of the ability of a solvent to separate a mixture into its individual components [Perry and Green 1997]. The selectivity values are determined based on the relative polarizability of two constituents to be isolated. Capacity is the numerical amount of solute withdrawn from the two systems by removing solvent. Normally, the selectivity decrease with temperature and frequently follows a different trend from the solvent capacity. When examining the selectivity and capacity trends, it is important to incorporate in addition to

polarizability, size and shape of the species including hydrogen bonding capacity with the ionic liquid.

6.4.1 Water/butan-1-ol separation problem

The importance in determining γ_{13}^{∞} is to determine the suitability of [$3C_6C_{14}P$] [$(C_8H_{17})_2$ PO_2] or [$P^+_{14,\,6,\,6,\,6}$] [Cl^-] for the use in solvent enhanced processes. Selectivity and capacities values at infinite dilution were determined with the use of equation (6.3.2 and 6.3.3) below, for separation problems at 333.15 K.

$$S_{ij}^{\infty} = \frac{\gamma_{13}^{\infty}}{\gamma_{13}^{\infty}} \qquad 6.3.2$$

$$\mathrm{K}_j^{\infty} = \frac{1}{\gamma_{13}^{\infty}} \qquad 6.3.3$$

Where *i* denotes water, and *j* refer to butan-1-ol and the values are listed in table 5.2.3 and 5.2.8. The selectivity for (water/butan-1-ol) S_{ij}^{∞} = 2.70 and 0.9 for [$3C_6C_{14}P$] [$(C_8H_{17})_2$ PO_2] and [$P^+_{14,\,6,\,6,\,6}$] [Cl^-] at T = 333.15 K, respectively. These values are not far from the value for [$P_{14,\,4,\,4,\,4}$] [DBS], S_{ij}^{∞} = 3.77 [Wlalzo et al., 2017]. The selectivities were compared to other phosphonium based ionic liquids and some of the measured ionic liquids with different cation and anion as determined by other workers. Similar selectivity values were observed for [$(C_6OC)_2$ IM] [NTf_2] S_{ij}^{∞} = 2.67 [Domanska and Marciniak 2009], [DoMIM] [NTf_2] S_{ij}^{∞} = 2.76 [Domanska and Wlalzo 2016] and [$N_{8,\,2,\,2,\,2}$] [NTf_2] S_{ij}^{∞} = 2.46 [Wlalzo and Domanska 2016].

Based on the literature regarding the separation problem for water/butan-1-ol, the capacity for most of the measured ionic liquids are less than one, with the exception of tributyltetradecylphosphonium dodecylbenzenesulfonate (K_j^{∞} = 5.29) [Wlalzo 2017] and tributylmethylphosphonium tosylate (K_j^{∞} = 3.14) [Domanska and Paduszynski 2010]. The ionic liquid [$3C_6C_{14}P$] [$(C_8H_{17})_2$ PO_2] revealed the highest capacity (K_j^{∞} = 8.9) and (K_j^{∞} 3.39) for [$P^+_{14,\,6,\,6,\,6}$] [Cl^-].

6.4.2 Methanol/benzene separation problem

The order of the selectivities for the examined ILs when compared to other selected data in the literature is as follows:

[$3C_6C_{14}P$] [$(C_2F5)3PF_3$] > [$3C_6C_{14}P$] [PF_6] > [$3C_8C_1N$] [Tf_2N] > [$3C_6C_{14}P$] [Tf2N] > [MOIM] [PF_6] > [MOIM] [Tf_2N] > [HMIM] [Tf_2N] > [HMIM] [PF_6] > [C_{16}MIM] [BF_4] > [BMIM] [SbF_6] > [$3C_6C_{14}P$] [BF_4] > [Et3S] [Tf_2N] > [EMIM] [Tf_2N] > [BMIM] [Tf_2N] > [$3C_1C_4N$] [Tf2N] > [Epy] [Tf_2N] > [BMPy] [BF_4] > [MOIM] [BF_4] > [BMIM] [BF_4] > [BMIM] [TfO] > [HMIM] [BF_4] > [EMIM] [TfO] > [DMPIM] [BF_4] > [EMIM] [BF_4] > [EMIM] [TFA]

The selectivities for (methanol/benzene) S_{ij}^{∞} = 0.07 and 0.34, for [$3C_6C_{14}P$] [$(C_8H_{17})_2$ PO_2] and [$P^+_{14,\ 6,\ 6,\ 6}$] [Cl^-] at T = 333.15 K, respectively. This implies that [$P^+_{14,\ 6,\ 6,\ 6}$] [Cl^-] can better separate methanol from benzene as compared to [$3C_6C_{14}P$] [$(C_8H_{17})_2$ PO_2].

Capacity indices are in the following order:

[$3C_6C_{14}P$] [$(C_2F_5)3PF_3$] > [$3C_6C_{14}P$] [Tf_2N] > [$3C_6C_{14}P$] [PF_6] > [$3C_8C_1N$] [Tf_2N] > [$3C_6C_{14}P$] [BF_4] > [MOIM] [Tf_2N] > [HMIM] [Tf_2N] > [MOIM] [PF_6] > [C_{16}MIM] [BF_4] > [HMIM] [PF_6] > [BMIM] [Tf_2N] > [Et3S] [Tf_2N] > [EDMIM] [Tf_2N] > [BMIM] [SbF_6] > [EMIM] [Tf_2N] > [$3C_1C_4N$] [Tf_2N] > [Epy] [Tf_2N] > [MOIM] [BF_4] > [BMPy] [BF_4] > [BMIM] [TfO] > [BMIM][BF_4] > [HMIM][BF_4] > [EMIM] [TfO] > [EMIM] [BF_4] > [EMIM] [TFA].

6.4.3 Ethanol/2-butanone separation problem

The order of the infinite dilution selectivities for the studied ionic liquids compared to the data in the literature is as follows:

Chlorobenzene > [BMIM] [SbF_6] > [$3C_6C_{14}P$] [Tf2N] > [EMIM] [Tf_2N] > [HMIM] [Tf_2N] > [$3C_8C_1N$] [Tf_2N] > [BMPyrr] [Tf_2N] > [$3C_6C_{14}P$] [PF_6] > [Epy] [Tf_2N] > [BMIM] [PF_6] > [BMPy] [BF_4] > [MOIM] [BF_4] > [C_{16}MIM] [BF_4] > [HMIM] [BF_4] > [$3C_6C_{14}P$] [BF_4] > [BMIM] [BF_4] > [EMIM] [BF_4].

Capacity indices are in the following order:

[$3C_6C_{14}P$] [Tf_2N] > [$3C_8C_1N$] [Tf_2N] > [EMIM] [Tf_2N] > [HMIM] [Tf_2N] > [BMPyrr] [Tf_2N] > [BMIM] > [SbF_6] > [Epy] [Tf_2N] > [$3C_6C_{14}P$] [PF_6] > Chlorobenzene > [BMIM] [PF_6] > [BMPy] [BF_4] > [$3C_6C_{14}P$] [BF4] > [MOIM] [BF_4] > [C_{16}MIM] [BF_4] > [HMIM] [BF_4] > [BMIM] [BF_4] > [EMIM] [BF_4].

The selectivities for (ethanol/2-butanone) S_{ij}^{∞} = 0.06 and 0.36, for [$3C_6C_{14}P$] [$(C_8H_{17})_2$ PO_2] and [$P^+_{14,\ 6,\ 6,\ 6}$] [Cl^-] at T = 333.15 K, respectively. This implies that [$P^+_{14,\ 6,\ 6,\ 6}$] [Cl^-] can better separate ethanol from 2-butanone as compared to [$3C_6C_{14}P$] [$(C_8H_{17})_2$ PO_2].

Chapter 7

Conclusions

The primary objectives of this research work were to examine the impact of temperature and structure on the ionic liquids as well as the separation potential on volatile organic solvents. Capacities and selectivities were determined from the computed values of activity coefficients at infinite dilution in order to examine the effectiveness of these promising liquids as separation agents.

Thermophysical property measurements at various temperatures were conducted with the aid of the Anton Paar digital vibrating tube density meter and sound velocity analyser with automatic micro-viscometer in two ionic liquids:

- Trihexyltetradecylphosphonium chloride [$P^{+}_{14, 6, 6, 6}$] [Cl^{-}]
- 1-ethyl-3-methylimidazolium tetrafluoroborate [Emim] [BF_4]

Gas chromatography was utilised to determine γ_{13}^{∞} of different solutes over a broad range of temperatures for the ionic liquids:

- Trihexyltetradecylphosphonium chloride [$P^{+}_{14, 6, 6, 6}$] [Cl^{-}]
- Trihexyltetradecylphosphonium-bis-(2,4,4-trimethylpentyl)-phosphinate [$P^{+}_{14, 6, 6, 6}$] [$(C_8H_{17})_2$ PO_2]

New data for thermophysical properties measurements, which includes density, viscosity and speed of sound, have been measured as a function of temperature for [$P^{+}_{14, 6, 6, 6}$] [Cl^{-}] + propanoic acid and [EMIM] [BF_4] + benzaldehyde or ethyl acetoacetate and their binary mixtures have been reported over the entire range of mole fractions (x_i = 0 to 1).

Excess parameters which include excess molar volumes, isentropic compressibilities, deviation in isentropic compressibilities, apparent molar volume, apparent molar isentropic compressibility, intermolecular free length and deviation in viscosity were calculated to investigate the types of interactions occurring in the binary systems. For the derived properties (excess molar volumes and deviation in isentropic compressibilities), negative

differences were observed for the investigated mixtures at all given temperatures, these results suggests strong interactions that occurs in the binary systems of {[Emim] [BF_4] with benzaldehyde or ethyl acetoacetate} and {[$P^+_{14,\ 6,\ 6,\ 6}$] [Cl^-] + propanoic acid} molecules. Larger ion dipole interactions were observed for the ionic liquid [Emim] [BF_4] containing ethyl acetoacetate as compared to the other binary systems.

Negative deviations on viscosity across the temperatures and whole range of compositions were observed, and they are increasing, i.e. becomes less negative with increasing temperatures.

Low values of γ_{13}^{∞} were observed for both of the ionic liquids, with the values increasing as the alkyl chain increased. These results revealed that [$P^+_{14,\ 6,\ 6,\ 6}$] [$(C_8H_{17})_2\ PO_2$] strongly interact with the solute as compared to [$P^+_{14,\ 6,\ 6,\ 6}$] [Cl^-] and this suggests that [$P^+_{14,\ 6,\ 6,\ 6}$] [Cl^-] is a better entrainer as compared to [$P^+_{14,\ 6,\ 6,\ 6}$] [$(C_8H_{17})_2\ PO_2$].

In relation to some of the separation difficulties and challenges undertaken among the important and interesting ones for the chemical industry by this study involving ILs covered in this study:

- **Water/butan-1-ol separation problem:** The surprising properties of the ionic liquid [$3C_6C_{14}P$] [$(C_8H_{17})_2\ PO_2$] obtained gave favourable capacity and selectivity values in the chosen separation process, and may be utilized for new technological projects. This revealed that there is a feasible application of trihexyltetradecylphosphonium-bis-(2,4,4-trimethylpentyl)-phosphinate in comparison to trihexyltetradecylphosphonium chloride and other ionic liquids in the literature in the water/butan-1-ol separation processes with impact to extractive distillation to replace some less efficient operational technique of separation.
- **Methanol/benzene system:** Both of the studied ionic liquids were found to be poor extractants for the extraction problem, but trihexyltetradecylphosphonium chloride was better able to separate benzene from methanol as compared to trihexyltetradecylphosphonium-bis-(2,4,4-trimethylpentyl)-phosphinate.

- **Ethanol/2-butanone system:** Comparing the studied ionic liquids, trihexyltetradecylphosphonium chloride was found to be a better potential extractant on the basis of both selectivity and capacity.

According to the capacity index values, it can be seen that the ionic liquid trihexyltetradecylphosphonium-bis-(2, 4, 4-trimethylpentyl)-phosphinate would be a rational separation solvent for the investigated mixtures.

The obtained results highlight the significant role played by the ions within the ionic liquid in examining the immensity of activity coefficient values, and its potential for providing insight into extractant behaviour.

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