

**Interaction studies of imidazolium based ionic liquids
with organic acids and acetophenone: Thermodynamic,
spectroscopic, and theoretical approaches**

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Declaration

I hereby declare that the thesis entitled “Interaction studies of imidazolium based ionic liquids with organic acids and acetophenone: thermodynamic, spectroscopic and theoretical approaches” submitted to the Department of Chemistry, North-West University, Mafikeng Campus for the fulfilment of the degree of Doctor of Philosophy in Chemistry is a faithful record of original research work carried out by me under the guidance and supervision of Prof Indra Bahadur. No part of this work has been submitted by any other researcher or student. Sources of my information have been properly acknowledged in the reference pages.

Signature.....

Date.....

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Prof Indra Bahadur

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Abstract

Ionic liquids (ILs) are salts that are primarily composed of cations and anions. They exist as liquids below 100°C or at room temperature, which is why they are sometimes referred to as room-temperature ionic liquids (RTILs). These salts are receiving a great deal of attention in a wide range of fields of chemistry and chemical engineering, this is due to their fascinating physicochemical properties like low volatility, vapour pressure, high thermal, chemical stability, good electrical conductivity and low flammability. Amongst these, the most appealing property is their ability to be customized to fulfil individual needs for various applications. This is done by making changes to the N-alkyl substituents or the hydrogen atoms attached to the imidazolium ring of the cation as well as the anion constituent, thus varying their structure. To use ILs as solvents, it is necessary to know how they behave in the presence of other chemicals, like conventional solvents such as alcohols or carboxylic acids as well as water, which are widely employed in extraction and separation processes. The nature of ILs therefore has a significant impact on the efficiency of chemical processes (e.g. synthesis, extraction, and separation). It is worth mentioning that, adding a small quantity of one or more conventional solvents, changes the physicochemical properties of ILs dramatically. Mixtures of ILs provide knowledge of different types of interactions which are absent in their pure state.

With the view of gaining a comprehensive and detailed understanding of the behaviour of ILs, in this work, binary mixtures of ILs 1-ethyl-3-methylimidazolium tetrafluoroborate [EMIM][BF₄] or 1-butyl-3-methylimidazolium tetrafluoroborate [BMIM][BF₄] or 1-ethyl-3-methylimidazolium methyl sulphate [EMIM][MeSO₄] or 1-butyl-3-methylimidazolium hexafluorophosphate [BMIM][PF₆] with acetic acid or propionic acid have been prepared. The different interactions in these binary mixtures were investigated by measuring their thermophysical properties at $T = (293.15-333.15)$ K and at pressure $p = 0.1$ MPa. Thermophysical properties including density (ρ), sound velocity (u), refractive index (n_D) and surface tension (γ) of these binary mixtures were investigated. Using the measured thermophysical properties, thermodynamic properties such as excess molar volumes (V_m^E), excess isentropic compressibilities (k_s^E), excess sound velocity (u^E), intermolecular free length (L_f), deviation in refractive index (Δn_D) and deviation in surface tension ($\Delta \gamma$) were determined and the Redlich–Kister polynomial equation was fitted to these thermodynamic properties data, where the ‘at least square’ method was utilized in determining the fitting parameters and standard errors. This was done to check the precision of the measured data and standard

deviations. The FTIR studies of pure components and binary mixtures at an equimolar composition were also conducted to clarify results obtained from thermodynamic properties and to further analyse the intermolecular interactions occurring in the mixtures.

From understanding these binary mixtures, the density (ρ_{123}), sound velocity (u_{123}), excess molar volume (V_{m123}^E) and deviation in isentropic compressibility (Δk_{s123}) for ternary mixtures of ILs [EMIM][BF₄] or [BMIM][BF₄] or [BMIM][PF₆] with acetophenone and acetic acid or propionic acid were obtained at temperatures ranging from (293.15 to 333.15) K and pressure of $p = 0.1$ MPa. The V_{m123}^E and Δk_{s123} properties of the ternary mixtures were modelled using the sum of the predictive term (no estimated parameter) and correlative term (with estimated parameters). The standardized deviations (σ) of the V_{m123}^E and Δk_{s123} properties of the ternary mixtures were determined to estimate the optimal number of parameters in the correlation. In order to accomplish the modelling of the V_{m123}^E and Δk_{s123} properties of the ternary mixtures, interactions of binary mixtures of acetophenone with acetic and propionic acid were also investigated through the measurement of thermophysical properties; ρ , u , n_D and γ at temperature ranges of (293.15-333.15) K and pressure, $p = 0.1$ MPa. Thermodynamic properties; V_m^E , k_s^E , Δk_s , u^E , L_f , Δn_D and $\Delta \gamma$ were determined and correlated using Redlich–Kister polynomial equation and the correlating parameters were obtained. The binary parameters obtained from correlating the binary data with the Redlich–Kister polynomial equation were further used in modelling the V_{m123}^E and Δk_{s123} properties of the ternary mixtures. The systems reported in the thesis produced four published article, except one manuscript for the ternary mixtures of IL [EMIM][BF₄] with acetophenone and acetic acid or propionic acid which is accepted for publication with minor revision.

Keywords: *Ionic liquids; binary mixture, ternary mixture; thermophysical properties, thermodynamic properties; Modelling; Redlich-Kister polynomial equation*

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+ acetophenone (x_3)} at (a) 293.15 K, (b) 303.15 K, (c) 313.15 K, (d) 323.15 K and (e) 333.15 K.

Figure 5.5E: Variations of deviation in isentropic compressibility (Δk_{s123}) with IL mole fraction (x_1) for the ternary mixtures of {[BMIM][BF₄] (x_1) + propionic acid (x_2) + acetophenone (x_3)} at (a) 293.15 K, (b) 303.15 K, (c) 313.15 K, (d) 323.15 K and (e) 333.15 K.

Figure 5.6E: Variations of deviation in isentropic compressibility (Δk_{s123}) with IL mole fraction (x_1) for the ternary mixtures of {[BMIM][PF₆] (x_1) + acetic acid (x_2) + acetophenone (x_3)} at (a) 293.15 K, (b) 303.15 K, (c) 313.15 K, (d) 323.15 K and (e) 333.15 K.

List of Symbols

x	-	Mole fraction
M	-	Molar mass
m	-	Mass
n	-	Mole
ρ	-	Density of the mixture
V_m	-	Molar volume
V_m^{id}	-	Molar volume of the ideal
V_m^{E}	-	Excess molar volume
u	-	Sound velocity of the mixture
u^{id}	-	Sound velocity of the ideal mixture
k_s	-	Isentropic compressibility of mixture
k_s^{id}	-	Isentropic compressibility of the ideal mixture
k_s^{E}	-	Excess isentropic compressibility
u^{E}	-	Excess sound velocity
ϕ	-	Volume fraction
α_p	-	Isobaric expansivity
c_p	-	Isobaric heat capacity
Δk_s	-	Deviation in isentropic compressibility
L_f	-	Intermolecular free length
k_j	-	Temperature dependent Jacobson's constant
n_D	-	Refractive index
n^{id}	-	Ideal refractive index of the mixture
Δn_D	-	Deviation in refractive index

γ	-	Surface tension
$\Delta\gamma$	-	Deviation in surface tension
v	-	Volume
T	-	Temperature
f	-	Frequency
c_o	-	Speed of light in a vacuum material
c	-	Speed of light in the material
ε	-	Relative permittivity
μ	-	Relative permeability
D_i	-	molar sound velocity
w_1	-	weight fraction of the components 1
w_2	-	weight fraction of the components 2
$f(n_D)$	-	function of the refractive index
k	-	Order of polynomial expansion in the Redlich–Kister equation
A_i	-	Coefficients in the Redlich–Kister equation
n	-	Experimental points in the Redlich–Kister equation
p	-	Number of parameters in the Redlich–Kister equation
σ	-	Standard deviation
Q	-	Quotient of the period of oscillation of the U-tube divided by
F	-	Force
R	-	Radius of the ring
r	-	Radius of the wire
$\%D$	-	percentage deviation
$AADu\%$	-	absolute average deviation for sound velocity
$AADn_D\%$	-	absolute average deviation for refractive index

List of Abbreviations

A-IL	-	Acidic ionic liquid
B-IL	-	Basic IL
C-IL	-	Chiral ionic liquid
DMAC	-	Dimethylacetamide
DMF	-	Dimethylformamide
DMSO	-	Dimethyl sulfoxide
FTIR	-	Fourier-transform infrared
HE-ILs	-	High energetic IL
[HF]	-	Hydrofluoric acid
[HBF ₄]	-	Tetrafluoroboronic acid
[HPF ₆]	-	Hexafluorophosphonic acid
HPLC	-	High-performance liquid chromatography
ICP-MS	-	Inductively coupled plasma-mass spectrometry
IL	-	Ionic liquid
Ms	-	Mass spectrometry
NMR	-	Nuclear magnetic resonance spectrometry
NMA	-	N-Methylaniline
NVP	-	N-Vinyl-2- pyrrolidinone
Poly-IL	-	Polymeric IL
RTIL	-	Room-temperature ionic liquid
S-IL	-	Supported ionic liquid
TS-IL	-	Task specific ionic liquid
THF	-	Tetrahydrofuran
VOC	-	Volatile organic solvent

[EMIM][OAc]	-	1-Ethyl-3-methylimidazolium acetate
[EMIM][MeSO ₄]	-	1-Ethyl-3-methylimidazolium methyl sulphate
[EMIM][BF ₄]	-	1-Ethyl-3-methylimidazolium tetrafluoroborate
[BMIM][Cl]	-	1-Butyl-3-methylimidazolium chloride
[BMIM][PF ₆]	-	1-Butyl-3-methylimidazolium hexafluorophosphate
[BMIM][NO ₃]	-	1-Butyl-3-methylimidazolium nitrate
[BMIM][ClO ₄]	-	1-Butyl-3-methylimidazolium perchlorate
[BMIM][BF ₄]	-	1-Butyl-3-methylimidazolium tetrafluoroborate
[BMIM][CF ₃ CO ₂]	-	1-Butyl-3-methylimidazolium trifluoroacetate
[OMIM][PF ₆]	-	1-Octyl-3-methylimidazolium hexafluorophosphate
[OMIM][SCN]	-	1-Octyl-3-methylimidazolium thiocyanate

List of Publications

- I. **K. Masilo**, I. Bahadur, “Intermolecular interactions between 1-ethyl-3-methylimidazolium-based ionic liquids with carboxylic acid at different temperatures via thermodynamic and spectroscopic studies” **Journal of Chemical & Engineering Data, 66 (2021) 1211-1230.**
- II. **K. Masilo**, S. Kumar Singh, I Bahadur, “Interactions between 1-butyl-3-methylimidazolium cation with various anions and carboxylic acids: Physicochemical and spectroscopic aspects”, **Colloids and Surfaces A: Physicochemical and Engineering Aspects, 617 (2021) 126376.**
- III. **K. Masilo**, I. Bahadur, “Investigation on the molecular interaction of binary mixtures of acetophenone with carboxylic acids at various temperature: thermodynamic and spectroscopic aspects” **Journal of Chemical Thermodynamics, 166 (2022) 106667.**
- IV. **K. Masilo**, I. Bahadur, M. L. L. Paredes, “Measurement and modelling of thermodynamic properties for ternary mixtures containing 1-butyl-3-methylimidazolium-based ionic liquids with acetophenone and acetic or propionic acid” **Journal of Chemical & Engineering Data, 66(12) (2021) 4368-4383.**
- V. **K. Masilo**, I. Bahadur, M. L. L. Paredes, “Volumetric and acoustic properties of ternary mixtures of 1-ethyl-3-methylimidazolium tetrafluoroborate with acetophenone and acetic or propionic acid: Experimental measurements, correlation and prediction Models” **Journal of Chemical & Engineering Data, (accepted for minor revision).**

List of Conference Presentations

- I. **K. Masilo**, I. Bahadur, Temperature dependence of thermophysical properties of imidazolium based ionic liquids with organic solvents: density, sound velocity, refractive index and surface tension in the **4th International Conference on Ionic Liquids in Separation and Purification Technology**, 08-11 September 2019, Sitges, Barcelona, Spain.

- II. **K. Masilo**, Thermodynamic properties of 1-butyl- 3-methylimidazolium-based ionic liquids mixtures with acetic acid and their structural studies by FTIR in the **6th SA-UNESCO Engineering, Science and Technology Conference**, 23 - 27 September 2019, North- West University, Mafikeng, South Africa.

INTRODUCTION

1.1. General Description of Ionic Liquids

Ionic liquids (ILs) are salts comprising solely of cations and anions and exist as liquid below 100°C, or at room temperature, hence they are also called room-temperature ionic liquids (RTILs) [1-3]. Throughout this thesis, the terms IL and RTIL will be used interchangeably. ILs are distinguished from other salts, in that, other salts become molten at extremely high temperatures while ILs melt at or below 100°C. For example, sodium chloride only becomes molten at temperatures $>800^{\circ}\text{C}$ because of its closely packed structure and strong ionic interactions [2,4,5]. Molten salts are composed of symmetric cations and anions, making a close packed ion structure with a well-defined lattice and therefore needs large energy to break the lattice (Figure 1.1) [1,5,6]. The lower melting point of an IL is mainly ascribed to the bulky and larger asymmetrical organic cation in combination with a weakly-coordinating anion [1,5,6]. The asymmetry nature of the cation lowers the lattice energy, thus lowering the melting point. In certain circumstance, anions are quite large and play part in lowering the melting point [7].

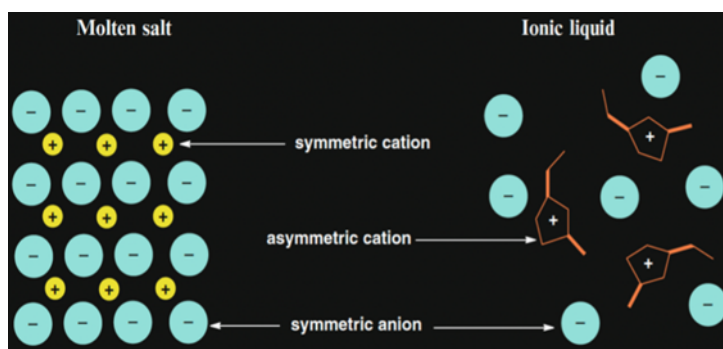


Figure 1.1: Comparison between molten salts and ILs structure [6].

ILs are generally regarded as environmentally friendly solvents due to their distinctive chemical and physical properties [8-12]. The status of ILs as environmentally friendly solvent is based primarily on their negligible vapour pressure [13], non-volatility, and recyclability [14]. Besides having low melting point, ILs have a higher thermal stability ($> 250^{\circ}\text{C}$) and are not flammable due to their negligible vapour pressure at ambient temperature, thus increasing their safety and possibility to be used in high temperatures [2]. ILs have properties such as high

ionic conductivities, higher thermal conductivities, large electrochemical window, wide liquid range, high polarity, non-corrosive, miscible with organic solvents and water, potential to dissolve and solvate various organic, inorganic, and organometallic constituents [15-23]. More importantly, ILs are referred to as designer solvents due to the ability to tailor their properties by varying the length and branching of the alkyl chain and the counter-anions of the IL, such that the designed IL possess a definite set of properties [15]. Being designer solvents, ILs can be modified to be specific for a certain application, thus earning the name task specific ILs. The specifically designed properties include both chemical properties such as acidity, basicity, electrophilicity and nucleophilicity and physical properties which include density, viscosity, surface tension, optical activity, electrical and thermal conductivity and many more [24].

ILs are regarded as highly valuable materials for various potential uses as greener and more suitable alternative to volatile organic solvents (VOCs), additives and reagents [1]. Volatility of organic solvents in industrial applications give rises to serious concern in the industry, mainly the toxicity of the organic solvents to the environment and human health, as well as the flammable nature of these solvents, which make them a potential explosion hazard [25]. The replacement of VOCs with ILs solves the environmental and safety issues that emerges from using VOCs.

1.2. History of Ionic Liquids

The early history ILs began with a discovery of a liquid known as red oil, which is a by-product of the AlCl_3 catalysed Friedel-Crafts reaction [26]. Friedel and Crafts (1887) [26] described that the red oil was prepared by adding small amounts of anhydrous aluminium chloride to amyl chloride, which resulted in a liquid divided into two layers. The red oil was later acknowledged as a carbocation containing a tetrachloroaluminate anion ($[\text{AlCl}_4]^-$). In 1888, Gabriel and Weiner [27] reported ethanol ammonium nitrate (m.p. 52 - 55°C), which was possibly the first organic salt with melting point of less than 100°C. Walden [28] developed and reported the first RTIL, ethylammonium nitrate, in 1914. He stated that ethylammonium nitrate is made by reacting ethylamine with strong nitric acid and its melting point is 12.1 °C. A similar RTIL reported by Walden (1914) was earlier synthesized by Rây [29] in 1911, unfortunately, it did not receive much attention due to unknown reasons.

In between the 1970s and 1980s [30], a new class of ILs were developed based on alkyl-imidazolium and pyridinium cations with halide or tetrahalogenoaluminate anions. The first

generation of ILs was discovered in 1982 [31] and were based on the dialkylimidazolium cation and tetrachloroaluminate anion. Throughout the 1980s, chloroaluminate ILs were investigated by different research groups [32,33] as solvents for transition metal complexes, predominantly through electrochemical and spectroscopic studies. The chloroaluminate ILs were however, found to be unstable in air and water, not inert towards various organic compounds and were to be synthesized and used under inert gas atmosphere, therefore, delaying their advancement in many industrial applications [34].

In the early 1992 [35], the second generation of ILs which are non-haloaluminate were reported. The second generation of ILs comprised of dialkylimidazolium cations and weakly coordinating anions such as hexafluorophosphate ($[\text{PF}_6]$) and tetrafluoroborate ($[\text{BF}_4]$). These ILs were originally thought to be stable in air and water but it was subsequently shown that they undergo hydrolysis under certain conditions, resulting in the formation of corrosive and/or toxic hydrolysis products. Unlike the aluminate ILs, they could be synthesized and safely kept outside an inert atmosphere. The third generation of ILs are termed task specific ILs (TS-ILs) and were established by Davis [12] and his acquaintance in 2004. TS-ILs are centred around more stable anions such as, alkyl sulphates, or alkyl phosphates or sugars or amino or organic acids and are said to be more hydrophilic than the second generation.

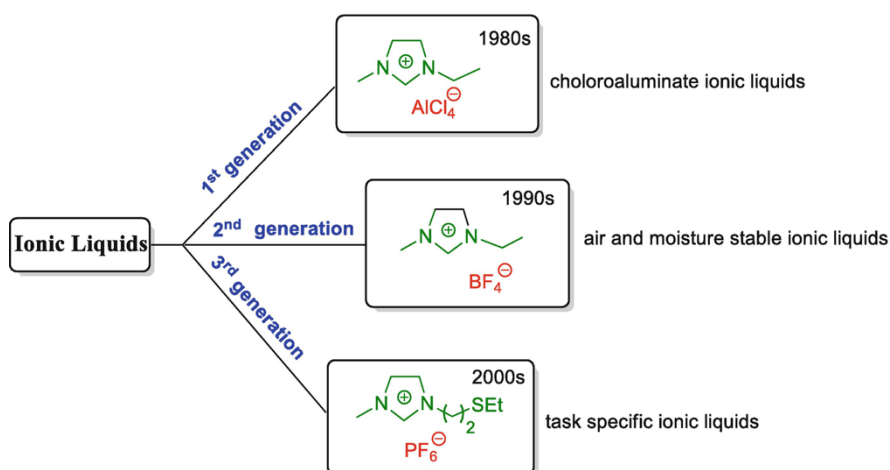


Figure 1.2: Generations of ILs through time [36].

1.3. Physical Properties of Ionic Liquids

ILs have been considered as valuable solvents due to their unique properties, which make them suitable for applications in which the traditional molecular solvents are either unsuitable or insufficiently effective. Their properties can be modified by mixing and/or matching different

cation and anion to meet the requirements of a particular process. Below is a list of physical properties of ILs and their relationships with their structure:

- **Melting point-** for a material to be regarded as an IL, its melting point should lie between 0 -100°C. The anion and cation constituents strongly affect the melting point of an IL. The longer the alkyl side chain length of the cation (mostly from 8 - 10 carbon atoms) and the bigger the size of an anion, the lower is the melting point. Factors that affect the melting point of ILs are the charge distribution and symmetry of ions, Van der Waals interactions and hydrogen bonding ability of ILs [37].
- **Viscosity-** ILs more viscous compared to the traditional molecular solvents [37]. The viscosities of ILs are greatly influenced by cation. ILs with branched or longer alkyl groups have higher viscosities [38]. The presence of hydrogen bonds and the Van der Waals force also controls the viscosities of ILs. The strength of Van der Waals forces in ILs is reduced by the presence of small anions, which also increase the energy required for molecular motion, thus decreasing in viscosity [39]. Symmetric or nearly spherical anions, resulting in more viscous ILs. This is due to the weakening of the hydrogen bonding between cations and anions [40].
- **Density-** generally, the density values for ILs range from 1.10 to 1.69 g·cm⁻³ and are much denser than most traditional molecular solvents and water. The density of IL depends on the, alkyl chain length and bulkiness of the cation as well as the size of the anion, which are associated with the free volume and molecular frame volume of the ILs [37]. The density of IL is lower for larger cations and anions. For fluorine-containing ILs, the densities values are higher.
- **Polarity-** by definition, polarity is the combined strength of specific and non-specific solute-solvent interactions [41] other than interactions resulting in chemical transformations of the solute [42]. The solute-solvent intermolecular interactions include hydrogen-bonding, Columbic interactions, various dipole interactions and electron pair donor–acceptor interactions [41]. Due to their salt nature, IL are highly polar.
- **Hydrophobic/hydrophilic behaviour-** the hydrophilic or hydrophobic behaviour of an IL is a significant feature for its solvation. The hydrophilic or hydrophobic behaviour of an IL is highly dependent on the alkyl chain length of the cation, nature of the anion, and

temperature. For hydrophilic ILs, water molecules become stabilized in the bulk by favourable intermolecular interactions like hydrogen bonding and dipole-dipole interactions. While for hydrophobic IL, the water molecules become less stable in the bulk, thus forming a miscibility gap or separation phase. ILs with the same cations but different anions may show different water miscibility behaviour, for instance, 1-butyl-3-methylimidazolium tetrafluoroborate is miscible in water, whereas 1-butyl-3-methylimidazolium hexafluorophosphate is water immiscible [43]. Hydrophobic ILs generally possess long alkyl chains, while IL with no alkyl chain branching or very short alkyl chain branching are hydrophilic. The longer the alkyl chain branching of ILs, the stronger the polarity they have [44].

- **Thermal stability-** the thermal stability of ILs is mostly depended on the anion group while the cation group displays a minor effect on the thermal stability of ILs. Organic anion based ILs are mostly found to be more thermally stable than ILs containing inorganic anions [45]. A relationship between the thermal stability of ILs with anion-coordinating nature, nucleophilicity and hydrophilicity has been established [46]. For example, the thermal decomposition decreases with increase in the hydrophilicity of anions. Other factors that have an impact on the thermal stability of ILs [47,48] include experimental conditions such as sample mass, atmosphere type, atmosphere heating rate, flowing rate and instrument type and contaminants like halides and water. Studies [12, 45] have showed that the IL thermal stability increases as follows and as based on the anion nature: chloride<bromide<iodide<tetrafluoroborate<triflate<bis(trifluoromethanesulfonic)imide<hexafluorophosphate. ILs containing halides have lower thermal stability due to their nucleophilic character. The order of thermal stability based on cation natures is as follows: phosphonium>imidazolium>tetraalkyl ammonium>pyrrolidinium [49].

- **Ionic conductivity-** ILs have a fairly good ionic conductivity compared to organic solvents. Interactions such as the Coulomb forces between ionic charges and the Van der Waals forces largely influence the ionic conductivities of ILs. The nature of these interactions is influenced by the structure and size of the ions, their polarizability and potential to form hydrogen bond. The large ion constituents of ILs decrease the ion mobility, which results in lower ionic conductivities. It is worth noting that ILs with higher viscosity demonstrate a lower conductivity [50]. Furthermore, an increase in temperature leads to an increase in conductivity and decrease in viscosity. An extension in the alkyl length of the imidazolium ring substituent results in a decrease in the ionic conductivity.

- **Electrochemical window-** ILs generally have a wide electrothermal stability window, which makes them favourable to be applied in electrochemistry processes. The electrothermal stability window of an IL range is equal or slightly wider to those seen in organic electrolytes, and significantly larger than that of aqueous electrolytes like water. The electrochemical stability of the imidazolium based ILs is as follows, based on the anion structure: hexafluorophosphate>tetrafluoroborate>triflate >bistriflimide [51].
- **Hydrolytic stability-** Hydrolytic stability is an important property of ILs anions in terms of their technical application and environmental stability, this is because hydrolytic processes of ILs can result in decomposition, lower technical performance, and decreased operational safety due to the formation of corrosive and/or toxic hydrolysis products [52]. Numerous ILs anions, such as $[\text{AlCl}_4]$, $[\text{PF}_6]$, and $[\text{BF}_4]$, have been observed to react with water, forming HCl or HF, as the case may [53]. Hydrolysis of fluorine-based anions are said to occur under certain conditions, such as pH and temperature. Studies [54-58] on imidazolium based ILs revealed that the $[\text{PF}_6]$ anion is chemically and thermally stable at moderate temperatures and in aqueous media, but its hydrolysis becomes noticeable at high temperatures (343 and 373 K) or under acidic conditions ($\text{pH} = 3$), producing hydrophilic $[\text{PO}_4^{3-}]$ and a significant amount of hydrofluoric acid ($[\text{HF}]$), which can dissolve glassware and cause corrosion to steel autoclaves and reactors. In contrast, $[\text{BF}_4]$ hydrolysis occurs in aqueous solutions and in acidic conditions even at ambient temperature. Additionally, it was shown that the hydrolysis potential of an imidazolium-based ILs containing $[\text{PF}_6]$, and $[\text{BF}_4]$ anion is substantially influenced by the type of cation linked to [55, 59, 60]. The extent of hydrolysis increased with the size of the imidazolium cation's side alkyl chain, owing to the decreased cation-anion interaction, which facilitated the interaction of water and the anion; $[\text{PF}_6]$ or $[\text{BF}_4]$, hence increasing their hydrolysis [55, 59, 60]. The $[\text{HF}]$ formed as hydrolysis products are corrosive and toxic, causing serious health problems; therefore, caution should be exercised when handling possible HF-containing compounds.

1.4. Chemical Composition and Structures of Ionic Liquids

As already mentioned above, ILs are acceptably defined as low-melting point salts consisting of a bulky organic cation with low symmetry/asymmetry and an organic or inorganic anion, which remain in a molten form at or near room temperature. There are various types of cations and anions, which allow for the synthesise of different ILs. The ability to vary the cations and

anions constituents of ILs gives an opening to alter the chemical and physical properties of the ILs. The choice of anion largely influences the properties of an IL, even when the cations are the same, thus a significant difference between ILs with varying anions is observed. For instance, the viscosity density, conductivity, hydrophobicity, solvation [61] and miscibility or immiscibility [61,62] of IL with a wide range of solvents may change by changing the anion.

Contrary to traditional molecular liquids, the Coulomb interactions are dominating between cations and anions of an IL, whereas for traditional molecular liquids, either the dipolar or multipolar electrostatic interactions are dominating. The coulomb interactions plays a key role in ILs. The solvation characteristics of ILs vary from strong Coulombic, specific, hydrogen bonding, ion-dipole interactions, dipole-dipole interaction, donor-acceptor complexes, charge-transfer forces, $n-\pi$ and $\pi-\pi$ interactions to weak and nonspecific interactions as well as Van der Waals forces [63-65]. The above solvation characteristics are commonly investigated using spectroscopic and chromatographic methods. Figures 1.3 and 1.4 below display a non-exhaustive list of selected common IL cations and anions used in the manufacture of ILs.

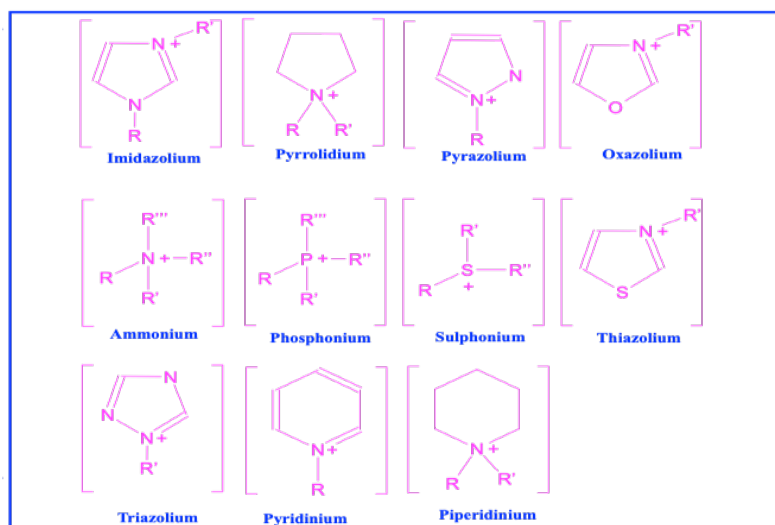


Figure 1.3: Cations used in IL synthesis.

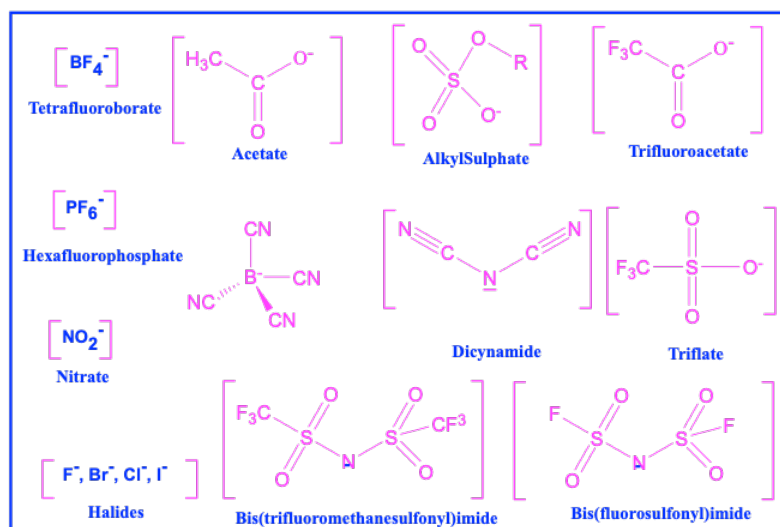


Figure 1.4: Anions used in IL synthesis.

1.5. Ionic Liquids Classification

The classification of ILs are based on their unique chemical structure (cation and anion constituents), biological properties, physicochemical properties such as hydrophilic and/or hydrophobic nature, acidity, basicity, solubility in organic solvents, ionic conductivity and the method of synthesis. Structural classification of ILs is discussed in detail below:

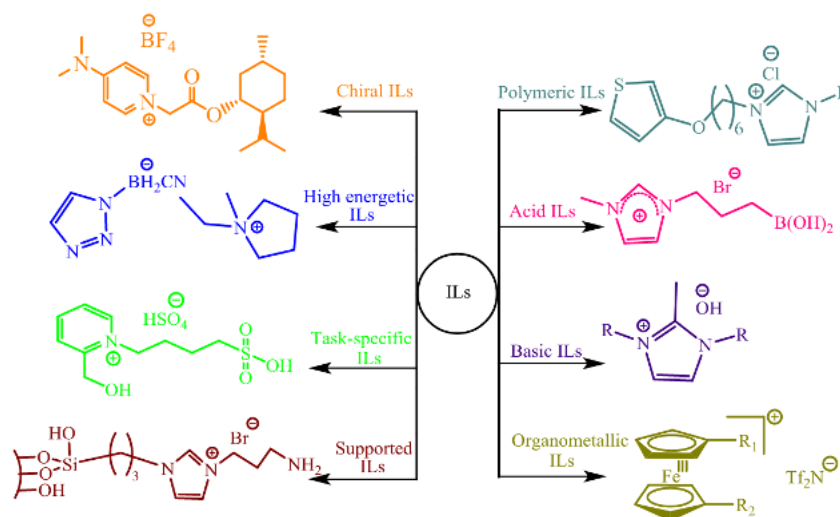


Figure 1.5: Classification of ILs [57].

1.5.1. Task specific Ionic Liquids

The term task specific ILs (TS-ILs) refers to ILs that have been functionalized to perform a specified task. A functional group is covalently incorporated to the anion or cation or both, which allows the design of the IL to meet the requirements of a specific purpose. The TS-ILs are usually aimed to accomplish a specific task. The incorporation of a functional group as a

part of the cation and/anion into an IL will, without a doubt, adjust the solvent properties of an IL. Properties such as dipolarity, basicity, acidity, polarizability, hydrogen bonding, and many more, are aspects that make an IL a good or bad solvent for a specific solute. The general classification of TS-ILs includes the chiral ILs, metal-containing ILs, acidic ILs, basic ILs, guanidinium ILs and ILs containing an -OH group [66-67].

1.5.2. Chiral Ionic Liquids

The characteristics of chiral ILs (C-ILs) are based on the chiral centre either at the cation (chiral cation) or anion (chiral anion) or both the chiral cation and chiral anion parts within the IL. The chiral anions, include amino acids (rich in several functional groups such as the, amino, amide thiol, thioether, hydroxyl and carboxyl), lactic acid, camphor sulfonates and borates [68]. Most of the currently available C-ILs are based on the chiral anion as the centre of the chirality with imidazolium, ammonium, and phosphonium cations. As a result of the high molecular diversity of the chiral cations and chiral anions, a wide range of optically active structures may be designed, extending the C-ILs applications.

1.5.3. High Energetic Ionic Liquids

High energetic ILs (HE-ILs) are ILs that can release a lot of energy due to combustion. The HE-ILs are more advantageous over common high-energy materials in that they have high density, low melting point, low viscosity, high thermal stability, less volatile, less toxic and are easy store and transport. The composition of HE-ILs consists of a series of cations including imidazolium, ammonium, triazolium, tetrazolium, triazanium, hydrazinium, iminium, other substituted N-heteroaromatic rings and anions such as dicyanamides, nitrocyanamides, dinitramides, nitrocyanomethanides, nitrates, metallic nitro complexes, methane-sulfonates, perchlorates, cyanoborates, borohydride, perchlorates, azolates or azides [69].

1.5.4. Supported Ionic Liquids

The notion of supported ILs (S-ILs) is based on the immobilization of ILs using various solid polymeric [70,71] and inorganic supports [72,73] including polystyrene resin [74], activated carbon, silica gel and aluminium oxide [75] so as to enhance their suitability for use in industrial processes. The ILs can be immobilized or supported on solid supports by physical and chemical techniques. The methods of preparation of S-ILs involve physical immobilization, whereby the ILs are immobilized or supported on solid supports through physical methods such as sol-gel method [76,77], simple impregnation [78], encapsulation [79]

and so on; and chemical immobilization, whereby the IL moieties are supported on solid supports through covalent bonds. The applications of S-ILs are significantly influenced by the type of the supporting method and solid support. The advantages of ILs together with the advantages of the solid support, improve the efficiency of S-ILs in separation and catalytic processes [80].

1.5.5. Polymeric Ionic Liquids

Polymeric ILs (poly-ILs) can be described as a form of polyelectrolytes in which repetitive monomer units carry the ILs molecules. In other words, the cationic and anionic constituents of ILs are bonded to polymer backbones [81-84]. The poly-ILs combine the distinctive properties of ILs with macromolecular features of the polymer. These compounds have improved stability, flexibility, durability, processability and improved control over their meso- to nano-structure [66,85]. The poly-ILs are used in the manufacture of polymer electrolytes, electrolytes for batteries, solar cells, lithium batteries and electrochemical supercapacitors, poly-ILs based antimicrobial materials, carbon dioxide responsive gels and adsorbents, corrosion inhibitors and photoresistors, stabilizers and dispersants, and many more materials [86-99].

1.5.6. Acid Ionic Liquids

Acidic ILs (A-ILs) are a type of low melting ILs with good acidic characteristics. The A-ILs are divided into the Lewis acid and Brønsted acid ILs. The Lewis acid ILs are defined as ILs with an electron accepting ability, whereby the electron accepting ability may be positioned on the cation or anion. On the other hand, Brønsted acidic ILs are described as ILs which have the ability to donate a hydrogen ion or proton. The most common positions, where acidic protons can be found are oxygen or nitrogen atoms, and in acidic functional groups such as CO₂H and SO₃H connected to the cation [100]. The good performance of A-ILs allows them to be widely utilised with most solvents and as catalysts in the organic reactions [101,102].

1.5.7. Basic Ionic Liquids

Basic ILs (B-ILs) are a class of ILs with high activity and selectivity and have been used as a potential replacement for traditional bases e.g. tetrabutylammonium acetate, sodium hydroxide, potassium hydroxide, sodium bicarbonate and potassium carbonate, since they demonstrated to be non-corrosive, non-volatile, stable, flexible and soluble with numerous organic solvents [103,104]. Similarly, to the A-ILs, the B-ILs are divided into the Lewis basic

and Brønsted basic ILs. The basic character of the B-ILs are linked with the anion or the cation of the IL. Using strong anionic bases such as the hydroxyl group may result in the instability of the IL due to attack of the cation by the anion [105]. High basicity anions may also result in IL with lower thermal stability compared to low basicity anions [106]. For basic cations comprising weaker bases like amine groups, the basicity may be weakened as a result of the cation positive charge reducing the availability of the amine to use an electron pair as a base [107,108]. Nonetheless, since cations tend to be more bulky and not as mobile as the anion, ILs consisting of the basic cations are usually more stable than ILs comprising basic anions [109]. B-ILs have been used in organic transformation reactions like the Markovnikov addition [110], Michael addition [111], Mannich reaction [112,113] Knoevenagel condensation [114-116] etc.

1.5.8. Organometallic Ionic liquids

Organometallic ILs are synthesized by utilizing inorganic cations of zinc or silver complexes with organic ligands like amides, amine-containing compounds and olefins [66]. Most of the organometallic ILs are prepared based on the organic cations such pyridinium and imidazolium and metallic anions [117] including $[\text{AlCl}_4]^-$, $[\text{Al}_3\text{Cl}_{10}]^-$, $[\text{Al}_2\text{Cl}_7]^-$, $[\text{AuCl}_4]^-$, $[\text{InCl}_4]^-$, $[\text{PdCl}_4]^{2-}$, $[\text{CoCl}_4]^{2-}$ and $[\text{CuX}_3]^-$ [118]. These IL possess unique properties such as low melting temperature, low viscosity, high conductivity and water insensitive.

1.6. Synthesis of Ionic liquids

For the synthesis of ILs, two primary approaches are employed: (1) the metathesis reaction of a halide salt or anion, and (2) the acid-base neutralization process (also known as neutralization reaction) (Figure 1.7) [119,120]. The first step is the quaternisation reaction of amines (NR_3) such as alkylation to obtain the corresponding ILs. Then the anion exchange reactions or metathesis exchange of anions takes place to obtain the desired anions. The anions exchange reaction is conducted by treatment of halides with Lewis acids to form Lewis acidic ILs. The metal salt (MA), brønsted acid (HA) or ion exchange resin are also used for metathesis reactions. Metathetic exchange of anions yields halide by-products (MX), which are not easy to remove by filtration, particularly in hydrophilic ILs, which makes it difficult to produce high-purity ILs [120]. The advanced way of synthesizing ILs of higher purity is the use of microwave-assisted or microwave radiation and ultrasound-assisted methods [121-124] to reduce by-product formation and improve the reaction rates and the extent of reaction. The

microwave-assisted and ultrasound-assisted methods have advantages, which will be discussed herein in detail.

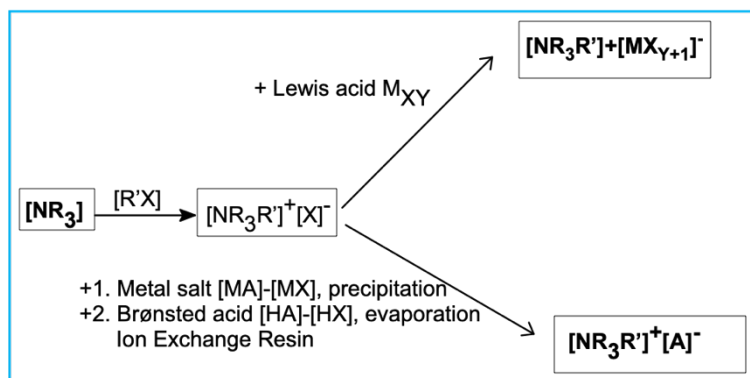


Figure 1.6: General routes for preparations of ILs.

1.6.1. Synthesis of Ionic Liquids Using the Microwave-assisted Method

The microwave-assisted method has displayed several advantages such as lower reaction time, selectivity and is environmentally friendly over other conventional synthesis methods. In the preparation of ILs by the microwave method, a safe source of heating in a solvent-free environment is used, which ensures high atomic efficiency by increasing the product selectivity with high yields in short reaction time. Varma and Namboodiri (2001) [125] were the first to report that microwave heating could be used to synthesize ILs. They prepared 1-butyl-3-methylimidazolium halides from 1-methylimidazole without any solvent and a 70% yields in less than 2 min was obtained with reduced organic waste. Soon afterwards, Deetlefs and Seddon (2003) [126] synthesized imidazolium, pyrazolium, pyridinium based IL using the microwave-assisted technique. The microwave-assisted technique can further be used to prepare the chiral ILs and Lewis acidic IL [127-129]. The benefits of combining microwave-assisted method with ILs are that [130]: (1) IL have negligible vapour pressure and if utilised as solvents, they will not be imposed to pressure constraints, irrespective of the temperature used, (2) ILs are effective microwave absorbers, and (3) high temperatures and fast reactions are readily acquired.

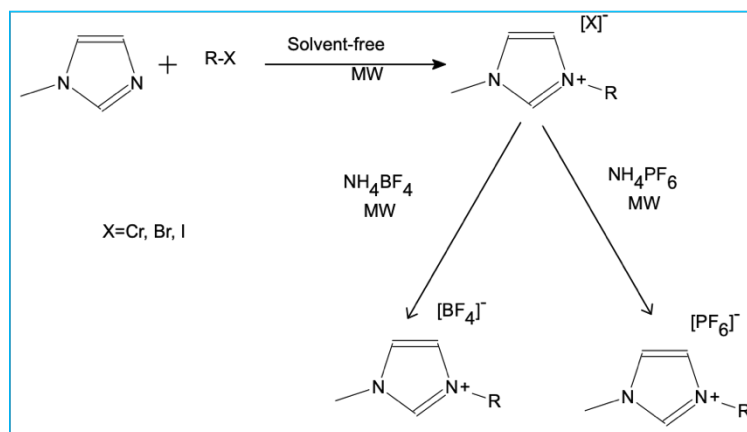


Figure 1.7: Microwave-assisted synthesis of ILs.

1.6.2. Synthesis of Ionic Liquids Using the Ultrasound-assisted Method

The application of ultrasound-assisted technology in the pharmaceutical and chemical sectors for the manufacture of medicinal compounds, biofuels, catalysts, and heterocyclic intermediates has caught the interest of many researchers and practitioners [131-133]. The goal of ultrasound-assisted technology is to meet the requirements of green chemistry as emerging prospective to the manufacture, design, and utilization of chemical products to reduce chemical hazards through the selection of safe and more effective means for the synthesis of compounds [134,135]. The major advantages of the ultrasound-assisted method is that it improves the rate of chemical reactions and transfer of materials, effectively reducing the reaction time, and enhanced yields and high purity of compounds is obtained [136-138]. At the same time, the selectivity is increased, and the method uses small amounts of solvents and producing less waste. The ultrasound-assisted method could, therefore, be considered as environmentally friendly [139]. The ultrasound-assisted method involves preparing ILs in a solvent free condition. In 2002, Varma's and Leveques groups [140] prepared 1-alkyl-3-methylimidazolium based ILs with anions such as chloride, bromide, iodide, tetrafluoroborate, hexafluorophosphate and trifluoromethanesulfonate, using the ultrasound-assisted method. It took 2 hours for Varma and Namboodiri (2002) [141] to prepare ILs based on the bromide and iodide anions and obtained a yield of 90%. In 2004, Leveque [142] further used the ultrasound-assisted method to prepare 1-butylmethylimidazolium chloride and the reaction took only 1 hour to complete. An N-methyl-2-pyrrolidinium hydrogen sulphate-based IL was produced in the absence of a solvent and a promising yield was obtained [143].

1.7.1. Chemistry/Chemical Engineering

Different ILs have been used as reaction media, reagents, solvents, catalyst, or combinations of these in many chemical processes [147,148]. In separation processes, ILs cover a broad range, such as extractive separation [149] and membrane separations [150]. In extractive separation processes such as liquid–liquid extraction, solid–phase extraction, solid–liquid extraction and induced–precipitation techniques, ILs are used as separating or extraction agents [151]. For supported liquid membrane separation, ILs are used as a liquid phase [152,153]. Using ILs in extractive separation processes results in higher extraction yields and improved purification compared to when conventional solvents are used. The selection of suitable separating/extraction agents is key for amplifying the process. ILs have further been used in chemical reactions such as acid-base, acid catalysed, electron transfer, transition metal catalysed and addition, substitutions, elimination reactions [154-158].

1.7.2. Physical Chemistry

Initially, ILs did not form any separate concepts in the physical chemistry areas. The unique physicochemical properties have led to more research projects regarding thermophysical and thermodynamic properties of ILs mixtures in the last few years. The increasing use of ILs in extraction or separation processes as well as chemical processes need reliable and systematic data of thermophysical and thermodynamic properties for example, activity coefficients, vapor–liquid equilibrium and liquid-liquid equilibrium data, enthalpy of mixing and gas solubility data, viscosity, densities and electric conductivity [159-165].

The activity coefficients are very helpful for characterization of the behaviour of liquid mixtures, estimation of mutual solubilities and predicting the existence of an azeotrope [159]. They also describe how solute–solvent interactions contribute to nonideal behaviour and are the activity coefficients data are mostly used by chemical engineers for modelling separation processes (e.g., extraction and distillation) [159,160]. The data on vapour-liquid equilibrium are required for distillation design and optimization [161,162]. Knowledge of the liquid-liquid equilibrium in binary and multicomponent systems is of essential importance in the design of efficient separation processes [163,164]. On the other hand, solid-liquid equilibrium data shows how components that need to be separated by solid-liquid extraction dissolve in mixtures [165]. Mixture enthalpy data are important for the determination of heat loads [160].

1.7.3. Electro-chemistry

In electrochemistry, ILs are commonly used as electrolytes due to their fantastic properties such as good ionic conductivity, high thermal stability, high viscosity, large electrochemical windows and large liquids range [166,167]. For electrochemical devices, the most important properties are their ionic conductivity and their electrochemical stability [168,169], together with other properties of interest, for instance, their non-flammability and negligible vapour pressure. Aqueous electrolytes like inorganic salt or water exhibit high ionic conductivities, however, the window for electrochemical stability is limited, therefore, not acceptable to be used at a large temperature range. Non-aqueous electrolytes also show a limited electrochemical windows mainly resulting from the decomposition of the solvent used. Using IL as electrolytes may combat the above limitations for electrochemical stability. The non-flammability property of IL makes them safer to be used as electrolytes in electrochemical or energy devices.

1.7.4. Pharmaceuticals

Other than their distinct physical and chemical properties, the high biological activity of ILs has attracted a lot of attention from ecologists, biochemists, and medical scientists. The biological activities of ILs include cytotoxic and antimicrobial properties (i.e. antimicrobial activity, antioxidant and anti-tumoral) [170-172]. ILs have been used in the pharmaceutical industry to address some of the drawbacks associated with solid-state pharmaceuticals drugs such as low solubility of formulations or delivery, stability, bioavailability, polymorphism and permeation [173]. However, some ILs are known to be toxic, which is the main issue for any chemical to be utilized in medicine, biomedicine, or biology related fields. To address the toxicity, biocompatible ILs containing more bio-compatible cations and anions have been developed [174,175]. Attaching the ether groups into the ester side chain of the IL cation was recently shown to remarkably reduce the toxicity [176]. Biocompatible ILs have significantly enhanced the pharmacodynamic and pharmacokinetic properties, together with the biological activities of the pharmaceuticals drugs. In the last two decades, the use of ILs has greatly increased in the pharmaceutical industry and medicinal chemistry, whereby they have been used as reagents, solvents, and anti-solvents in the synthesis of active pharmaceutical ingredients, as emulsifiers, solvents, co-solvents in drug formulations and in the development of improved drug-delivery systems [177].

1.7.5. Analytical Chemistry

The application of ILs in analytical chemistry, particularly in separating analytes, is merited because of some of the unique properties ILs possess. ILs are predominantly employed in the following areas directly related to analytical chemistry: (i) extraction such as solid phase microextraction, liquid phase microextraction and many more), (ii) gas chromatography [171], (iii) liquid chromatography [125,176,177], (iv) mass spectrometry, (v) spectroscopy, (vi) capillary electrophoresis [178,179], (vii) sensors [180,181] and (viii) electrochemistry [182-184]. It is worth noting that ILs are merely a starting materials and do not remain as liquids in other analytical chemistry applications. For instance, ILs are bonded to silica solid support to prepare solid phase microextraction fibres and liquid chromatography stationary phases [185,186].

1.8. Application of Ionic Liquids Based Binary and Ternary Mixtures

In order to expand the applicability of ILs in numerous fields, ILs-based mixed solvents appear to be a potential technique. The availability and diversity of media can be greatly expanded by combining neat ILs with other solvents in binary or ternary mixtures. The combining of an IL with a molecular solvent creates a medium with desired, intriguing, and versatile physicochemical properties. In a similar way, adding an IL to a molecular solvent can change its properties in a positive way.

ILs based on imidazolium cation are the most common and versatile ILs. Due to their miscibility with polar solvents and stability under both oxidative and reductive conditions, the imidazolium-based ILs were chosen for this work [187]. Imidazolium based IL are commonly used as environmentally friendly catalysts [188], electrolyte materials [189-193], nanomaterials, and pharmaceuticals materials [194]. The use of imidazolium-based IL as catalysts to enhance reaction time, yield, and chemo selectivity in a variety of chemical processes has been documented in a number of articles [195-198]. In addition, ILs are extremely beneficial in biotech applications, such as bio-catalysis [197,198], biomass dissolution, and separation and extraction technologies [201-206]. As a result of their high viscosity and basicity, ILs could not be used in some applications. This can be circumvented by diluting ILs with suitable co-solvents, which is also a good alternative way of expanding the uses of ILs and lowering their costs. For instance, a mixture of [EMIM][MeSO₄] and methanol was reported by Young *et al.* (2010) [207] to extract bio-oil from *Dunaliella spp.*

biomass. According to the results of the study, lipids were extracted in a satisfactory amount from the mixture.

In the current study, acetic acid, propionic acid, and acetophenone were used as co-solvents. The selection of these solvents was based on their miscibility with imidazolium based ILs, their versatility as solvents in chemical and technological processes, their low cost, and their ability to be obtained at high purity. Polar solvents were widely used in the extraction of medicinal plants in a manner similar to that of imidazolium based ILs [208]. Carboxylic acids have been utilised as catalysts, solvents in separation processes, and in the production of biodegradable plastic, cleaning agents, pharmaceuticals, fungicides, insecticides, and flavouring agents [209-215]. Wasserscheid *et al.* (2002) [216] reported the use of mixtures of imidazolium based IL and H₂SO₄ as a catalyst for the Friedel-Craft alkylation of benzene with 1-decene. In this reaction, adding a small amount of IL increased the amount of product made by 90% compared to using sulfuric acid alone. In addition, Zhang's group investigated the isobutane alkylation reaction using a binary mixture of strong acids with fluoride-containing ILs (e.g., [BMIM][PF₆] and [BMIM][BF₄]) as a catalyst [217-219]. Other researchers [220-226] have looked at the properties of carboxylic acid and acetophenone solutions in different solvents.

It would therefore be interesting to investigate and comprehend the behaviour of binary and ternary mixtures of imidazolium based ILs with acetic acid, propionic acid, and/or acetophenone, as these components have been used in a similar processes. Mixtures of ILs and co-solvents could have the potential to increase the efficiency of a process. This study will also add to the data bank of thermodynamic properties of mixtures of ILs. This will help establish principles for the molecular design of chemical separation processes and improve the use of ILs in certain areas of research or industry.

1.9. Purification and Recovery of Ionic Liquids

In the literature, various ways of manufacturing ILs on a laboratory and industrial scales have been documented. The resulting ILs are sometimes found to be contaminated with various impurities. The list of commonly encountered impurities includes water, halide ions, organics from unreacted starting materials or residual reaction solvents, metals and by-products formed during the reaction. Impurities in ILs are clearly detrimental to their physiochemical properties and consequently to some applications. The purification of ILs is important for economic and

environmental reasons, therefore, it is necessary to implement methods to measure and remove these contaminants.

Since ILs have low volatility, water can be removed by immersing the ILs under vacuum for hours, but this process does not apply to highly viscous ILs containing ions with hydrogen bonding groups. Alternatively, water can be removed by vacuum azeotropic distillation with toluene or by dissolving the IL in a low boiling solvent and placing over a dry molecular sieve [6,44,66]. Chemical drying agents such as magnesium chloride, magnesium sulphate and potassium metal may be used as mechanism to remove water [6]. Halide ions for water immiscible ILs can be removed by a repeated wash with water. Halide ions can further be removed by precipitation of insoluble halide salts, by ion-exchange chromatography or electrochemical oxidation, then followed by vacuum removal of the halogen gas [227]. Similarly, unreacted starting materials can also be removed under vacuum. Alternatively, in cases where the unreacted starting materials are less volatile, they can be removed by extracting them with an immiscible solvent of a low boiling point like diethyl ether or dichloromethane then this is followed by removal under vacuum [6,44]. Pre-purification of the starting materials is believed to be a good way to reduce the impurity content of the resulting products. Table 1.1 provides a comprehensive discussion on the various purification methods of ILs, their characteristic features, advantages and disadvantages [228].

Table 1.1: Purification methods, characteristic features, advantages, and disadvantages of ILs [228].

Purification/ recovery method	Characteristic feature	Advantage	Disadvantage
Distillation	Distillation of volatile compounds: ILs remained as a residue	Easy to perform	High energy requirement
Crystallization	Solution, melt and pressure induced crystallization: IL recovered as a crystal	High purity	High energy requirement
Membrane separation	Pervaporation and Pressure-driven membrane techniques and electrodialysis: water or volatile compound separation, ILs separation or elimination, cation or anion cross through an ion-exchange membrane	Selective separation, low energy requirement	Membrane fouling

Extraction	Extraction using water, organic solvents, supercritical carbon dioxide: recovery of hydrophilic, hydrophobic or both hydrophilic and hydrophobic ILs	Easy to perform economical	Special apparatus requirement, cross contamination
Force field	Centrifugation or gravity and magnetic separation: separated as emulsion, immiscible liquids, or magnetic field	Easy to perform, low energy requirement	Limited application, low separation rate
Biphasic separation	Based on chemicals addition in water or vice versa and temperature based biphasic separation: separation of biphasic by addition of salt, covered dioxide or polysaccharides	Economical, fast, scaleup	High concentration of salts or organic requirement
Combine method			
Membranes operation and distillation	Pressure-driven membrane techniques and distillation: separation or elimination of IL and removal of water or organic compounds	High purity	Economical process, membrane fouling
Centrifugation and distillation	Centrifugation and distillation: emulsion or immiscible ILs and separation as a residue	High purity	High energy requirement

1.10. Characterization of Impurities in Ionic Liquids

ILs play a critical role in the manufacturing of pharmaceutical products, healthcare-related solutions, catalysts, and other chemical products. The industries, laboratories, researchers, scientists, chemists, or inventors, who use ILs believe and trust that the manufactures of ILs have been properly identified and graded the chemicals and confirmed that the chemicals meet all regulatory and compliance standards for their intended use. However, before using the technical grade ILs, their impurities must be assessed and analysed. Table 1.2 shows the characterization of impurities in ILs [229-236].

Table 1.2: Characterization of impurities in ILs [229-236].

Impurity	Technique
Structure of the IL	Nuclear magnetic resonance spectrometry (NMR), Mass spectrometry (Ms), X-ray crystallography and elemental analysis
Quantification of cations and anions	Reversed phase or ion exchange, High-performance liquid chromatography (HPLC) coupled with a suitable detector like UV.
Imidazolium cations	Capillary electrophoresis
Presence of halide ions	Techniques based on varying degrees of uncertainties: ^{19}F , ^{35}Cl NMR (>1%) Ion selective electrodes (>0.01) Volhard procedure (>0.001%) Ion chromatography (>0.001%) Inductively coupled plasma-mass spectrometry (ICP-MS) (>0.000001)
Water content	Proton nuclear magnetic resonance (^1H) NMR or infrared spectroscopy (IR), however for low levels (<1,000 ppm) a Karl–Fischer titration is preferred.
Metal content	Atomic absorption spectroscopy (available for most metals) Ion selective electrodes (available for Na^+ , K^+ , Ag^+ , Ca^{2+} , Mg^{2+} , Cd^{2+} , Cu^{2+} and Pb^{2+}).
Volatility	Gas chromatography or Head-gas chromatography

1.11. Ionic Liquid as a Solvent

Mixing of the ILs with other solvents is one of alternative approach to minimize the use of ILs, which are currently considered expensive not only due to the price of raw materials, but also the complexity in their manufacturing processes. In 2015, Helmut Kaiser Consultancy predicted a phenomenal increase in demand for ILs in the next fifteen years, which may surely result in a decrease in their cost. Another factor is that ILs are highly viscous compared to typical organic solvents. The high viscosities of ILs have an influence on the conductivity of ILs, therefore mixing ILs with other solvents significantly reduces their viscosities.

Furthermore, improvement of the physicochemical properties of ILs is achieved by mixing them with other solvents. The physicochemical properties of ILs can easily be controlled by

mixing them with other solvents, thus saving time to prepare new ILs possessing the same or desired properties. The addition of suitable co-solvents to ILs may enhance the solute solubility properties associated with some ILs. Usually, ILs that are used to dissolve biopolymers are highly viscous and require high temperatures to reduce the viscosity. Rather than applying high temperatures, co-solvents may be used, for instance, Shamsuri *et al.* (2012) [237] used IL-co-solvent mixture containing 1-butyl-3-methylimidazolium chloride and dimethyl sulfoxide to dissolve a biopolymer such as cellulose, zein protein or rice starch. The approach of adding solvents to ILs has shown to have increased the efficiency and applications of ILs.

1.12. Importance of Thermophysical and Thermodynamic Properties

Due to the large number of new applications provided by ILs in recent years, ILs have become the main subject of research both on a laboratory and industrial scale. Among the huge number of research areas for ILs, one of the most important areas is the measurement of their thermophysical properties. Accurate and precise knowledge of thermophysical properties is valued as it is necessary to determine whether the use of ILs can possibly be expanded from the laboratory level to large scale industrial applications. Thermophysical studies of ILs are being established in parallel to industry advances, contributing to the design, development, and output of the processes. These properties can be modified through the selection of the cationic or anionic part of the IL or by the addition of a suitable co-solvents to an IL, thus forming an IL mixture.

Measurements of thermophysical properties of ILs are utilized to calculate the thermodynamic properties, which are crucial in designing future processes and equipment involving these ILs. Thermophysical and thermodynamic properties of ILs and their mixtures with other molecular solvents are developed to provide information about the molecular level structure of the IL mixture, as well as the structural properties and intermolecular interactions, such as solute–solvent, solute–solute and solute–cosolvent, taking place between the ions of ILs and solvent molecules, specifically where hydrogen bonding occurs [238-240].

Thermophysical properties of ILs mixtures are used in various industries which includes the, pharmaceutical, polymer and chemical industries [241]. ILs mixtures improve the thermodynamic and transport properties of working fluids as well as the efficiency of the electrochemical equipments such as batteries, photoelectrical cells, and others [242]. The

density and viscosity of mixtures containing ILs are necessary in various chemical engineering calculations involving chemical separations, fluid flow, mass, and heat transfer [243-245]. From all these reasons, it is important to further conduct research on the thermodynamic and thermophysical properties of ILs and ILs mixtures.

1.13. Scope of the Present Work

In the present work, the thermophysical properties such as the density (ρ), sound velocity (u), refractive index (n_D) and surface tension (γ) for ILs binary mixtures of {[EMIM][BF₄] (x_1) + acetic acid (x_2)} (*mix*₁), {[EMIM][MeSO₄] (x_1) + acetic acid (x_2)} (*mix*₂), {[EMIM][BF₄] (x_1) + propionic acid (x_2)} (*mix*₃), {[EMIM][MeSO₄] (x_1) + propionic acid (x_2)} (*mix*₄), {[BMIM][BF₄] (x_1) + acetic acid (x_2)} (*mix*₅), {[BMIM][PF₆] (x_1) + acetic acid (x_2)} (*mix*₆), {[BMIM][BF₄] (x_1) + propionic acid (x_2)} (*mix*₇) and {[BMIM][PF₆] (x_1) + acetic acid (x_2)} (*mix*₈) at varying compositions and temperatures ranging from (293.15 to 333.15) K under pressure of 0.1 MPa were studied. From the experimental results, the thermodynamic properties such as excess molar volumes (V_m^E), excess isentropic compressibilities (k_s^E), excess sound velocity (u^E), intermolecular free length (L_f), deviation in refractive index (Δn_D) and deviation in surface tension ($\Delta \gamma$), were calculated. Redlich-Kister polynomial type equation were fitted into the calculated thermodynamic properties in order to verify the calculated thermodynamic properties using the experimental values as well as values obtained from Redlich Kister equation. Furthermore, the standard deviations were calculated using the thermodynamic properties which calculated from experimental data and thermodynamic properties obtained from Redlich Kister equation to check accuracies of calculated thermodynamic data using experimental data.

The Fourier-transform infrared (FTIR) spectroscopic studies of pure components and binary mixtures at an equimolar composition were also conducted to clarify results from thermodynamic properties. The selection of ILs were made in an order that, they contained same cations but different anions, while others contained same anions and different cations. As a result, the structural effect of the cation and anion constituents of the ILs on the thermophysical and thermodynamic properties were investigated as well the variations of the thermodynamic properties with composition and temperature were reported. The temperature ranging from 293.15-333.15K were chosen in order to analyse how properties of the studied mixtures varies with temperature and how temperature influence these properties.

Furthermore, the density (ρ_{123}), sound velocity (u_{123}), excess molar volume (V_{m123}^E) and deviation in isentropic compressibility (Δk_{s123}) for ternary mixtures of {[BMIM][BF₄] (x_1) + acetic acid (x_2) + acetophenone (x_3)} (*mix*₁), {[BMIM][BF₄] (x_1) + propionic acid (x_2) + acetophenone (x_3)} (*mix*₂), {[BMIM][PF₆] (x_1) + acetic acid (x_2) + acetophenone (x_3)} (*mix*₃), {[EMIM][BF₄] (x_1) + acetic acid (x_2) + acetophenone (x_3)} (*mix*₄), {[EMIM][BF₄] (x_1) + propionic acid (x_2) + acetophenone (x_3)} (*mix*₅), at different compositions and temperatures ranging from (293.15 to 333.15) K as well as under pressure of 0.1 MPa were explored. The V_{m123}^E and Δk_{s123} properties of the ternary mixtures were modelled using the sum of predictive term (no estimated parameter) and correlative term (with estimated parameters). The standardized deviations (σ) of the V_{m123}^E and Δk_{s123} properties of the ternary mixtures were determined to estimate the optimal number of parameters in the correlation. It was further necessary to evaluate the intermolecular interaction of binary mixtures {acetophenone (x_1) + acetic acid (x_2)} (*mix*₉) and {acetophenone (x_1) + propionic acid (x_2)} (*mix*₁₀), which was accomplished through the measurement of the thermophysical properties: ρ , u , n_D , n_D and γ at temperature ranges of (293.15-333.15) K and pressure, $p = 0.1$ MPa. The Redlich–Kister polynomial equation was fitted to the calculated thermodynamic properties V_m^E , k_s^E , Δk_s , u^E , L_f , Δn_D and $\Delta \gamma$ and the fitting parameters were obtained. The binary parameters obtained from correlating the data of the binary mixtures were further used in modelling the V_{m123}^E and Δk_{s123} properties of the ternary mixtures. The utmost intention of this work was to understand the various inter or intra-molecular interactions between a selected IL and its co-solvents as well as to understand the structure-property relationship of ILs in the presence of a co-solvent.

1.14. Research Aim and Objectives

The aim of the research was to investigate the inter-molecular interactions of imidazolium based ILs with organic acids and the effect of the third component acetophenone on the interactions of the binary mixtures at various temperatures using experimental and theoretical studies.

These are the objectives as is required herein:

- To measure the thermophysical properties such as density, sound velocity, refractive index and surface tension of imidazolium based ILs, organic compounds, as well as their binary/ternary mixtures at various temperatures and concentrations;

- To calculate the thermodynamic properties of pure ILs, organic compounds and their binary/ternary mixtures at same experimental conditions;
- To investigate the intermolecular interactions occurring between the ILs with organic acids;
- To investigate the effect of the third components, acetophenone on the intermolecular interactions of binary mixtures;
- To investigate the influence of cation and anion constituents on intermolecular interactions;
- To evaluate the effect of the organic acid chain length on the intermolecular interactions;
- To elucidate the effect of temperature on the thermophysical properties of the binary/ternary mixtures and their derived thermodynamic properties;
- To correlate the thermodynamic properties of the binary data using Redlich-Kister;
- To model the thermodynamic properties of the ternary data using predictive and correlation models;
- To provide experimental spectroscopic data, Fourier transform infrared (FT-IR) for pure ILs, organic solvents and their binary/ternary mixtures.

1.15. Outline of Chapters in the Thesis

The outline of this thesis is as follows:

Chapter 1 presents a comprehensive overview on ILs, thermophysical properties and thermodynamics properties of IL mixtures as well as aims and objectives.

Chapter 2 provides the theoretical background on the thermophysical and thermodynamic properties under study.

Chapter 3 gives a literature review based on the previously reported thermophysical and thermodynamic properties of ILs used in present study with various organic solvents.

Chapter 4 devoted to the experimental design and procedures.

Chapter 5 presents the experimental results obtained. The results are presented in tables, graphs or figures and are discussed.

Chapter 6 gives a summary and concluding statements.

THEORETICAL FRAMEWORK

This chapter provides a theoretical background of the thermophysical, and thermodynamic properties investigated in the present study. Ideally, thermophysical and thermodynamic properties are useful for:

- interpretation, correlation and prediction through molecular thermodynamic consideration,
- predicting the properties of mixtures of like nature,
- the design of industrial equipment with better precision, and
- testing current theories of solutions because of their sensitivity to the difference in magnitude of intermolecular forces and geometry of the component molecules.

2.1. Density

Density (ρ) is the most commonly measured attribute of ILs, as many applications require it and, once again, the feasibility of employing ILs in any application is often dependent on its density [246]. The ρ of ILs is mostly related to the engineering and mechanical components of a process and is used to evaluate parameters such as rates of liquid-liquid extraction, heat and mass transfer [247]. The ρ data are used to determine the excess molar volume (V_m^E), which is one of the key thermodynamic properties of IL mixtures utilized in investigating the ion-ion, ion-solvent and solvent-solvent interactions. The ρ of a chemical compound is defined as the mass per unit volume:

$$\rho = \frac{m}{v} \quad (2.1)$$

where, m and v represent the mass and volume respectively.

The ρ of a chemical compound can further be expressed as a temperature dependant:

$$\rho = kT + m' \quad (2.2)$$

where, k and m' are constants and T is temperature.

2.2. Excess Molar Volume

The excess molar volume (V_m^E) is defined as the volume changes between the molar volume of the mixture and the ideal molar volume of a mixture under the same pressure, temperature, and concentration conditions [248,249]. Volume changes is one of the significant ways to determine the degree of the non-ideal behaviour existing in a mixture. The V_m^E of a mixture can be determined either directly or indirectly. The direct determination of V_m^E involves measuring the volume changes occurring after the liquids are mixed. The techniques used for direct determination of V_m^E include the dilatometric methods such as batch dilatometer and continuous dilution dilatometer. The indirect determination of V_m^E involves measuring the ρ of pure liquids and their mixtures and then calculate V_m^E . The techniques used for indirect determination of V_m^E include pycnometry, magnetic float densitometer and mechanical oscillating (vibrating tube) densitometer. In the present study, the indirect determination of V_m^E were employed, in which the V_m^E for binary $V_{m,12}^E$ and ternary $V_{m,123}^E$ mixtures were determined from ρ measurements using the following expressions:

$$V_m^E = V_m - V_m^{id} \quad (2.3)$$

where, V_m and V_m^{id} represent the molar volume of the mixture and molar volume of the ideal mixture respectively. The V_m and V_m^{id} are calculated as follows:

$$V_m = \frac{\sum_i x_i M_i}{\rho_i} \quad (2.4)$$

$$V_m^{id} = \sum \frac{x_i M_i}{\rho_i^*} \quad (2.5)$$

where, M_i is the molar mass of component i , ρ and ρ_i^* represents the densities of a mixture with a mole fraction (x) of i and of pure component i , respectively.

The sign and magnitude of volume changes in a mixture are important in determining the molecular rearrangement caused by intermolecular interaction occurring amongst molecules in a mixtures and depends on the relative strength of volume expansion and contraction factors [250]. The factors that lead to volume contraction are the predominance of chemical effects or of strong specific interactions, which include the establishment of hydrogen bonds, ion-dipole interaction, dipole-dipole interaction, donor-acceptor complexes, charge-transfer forces, $n-\pi$ and $\pi-\pi$ interactions amongst dissimilar components in the mixture [251-253]. A part from

these interactions, another factor leading to volume contraction is the dominance of structural effects in which a favourable geometrical fitting among the component molecules exist. On the other hand, the disruption of stronger and specific interactions between dissimilar mixing components, leads to volume expansion. Furthermore, volume expansion is caused by the predominance of the physical effects or non-specific or weak interaction such as dispersion forces (London force) [252,253]. The steric hindrance caused by the structure of the mixing component molecules as well as unfavourable geometrical fitting between the mixed components contribute to volume expansion of a mixture [252]. An ideal behaviour exists in a mixture if no changes in volume occur. The volume changes in binary and ternary mixtures of the current study were evaluated using Equation 2.3.

2.3. Sound Velocity

The speed where an ultrasonic wave propagates in a liquid at low frequencies (f) is referred to as sound velocity (u) [254]. The u of a liquid is usually preconceived to be a mechanical quantity and not a thermodynamic quantity, however, the treatment of u as a thermodynamic quantity is feasible on condition that the sound frequency is relatively low [255]. In this regard, beside the density and viscosity of liquids, the accuracy of the u measurements is dependent on the frequencies of the ultrasound waves that propagate through a liquid. Therefore, it is important to be cautious when determining if the recorded u measurements is a thermodynamic quantity to be utilized for determining necessary derived properties. The u that was determined with the equipment of the current study was the thermodynamic speed.

Provided that the ρ of a liquid is known, the measurement of u is the only straightforward approach to compute the isentropic compressibility (k_s) of a mixture. A wide range of thermophysical and thermodynamic properties of the liquid mixtures which includes the isobaric thermal expansion coefficient, thermal pressure coefficient, isothermal compressibility, isobaric and isochoric heat capacity, Joule–Thomson coefficient, and the reduced bulk modulus can be derived from u measurement [254,256]. It is feasible to use u measurements of the ILs mixtures to investigate the nature of molecular interactions, structure packing effects, or to determine the vital thermodynamic parameters of IL mixtures that are useful in chemical and industrial processes.

2.4. Isentropic Compressibility

The term isentropic describes the behaviour of sound waves flowing through a fluid in which the temperature and pressure vary within each microscopic volume, but the entropy of the total system stays unchanged. This requirement remains true if the u is measured utilizing a low frequency generator (eg., the DSA 5000 M transducer produces around 3 MHz frequency) [257], but for frequencies higher than 100 MHz, velocity dispersion and absorption of sound waves prevails [257,259].

The Newton Laplace equation provides the basis for the experimental evaluation of isentropic compressibilities (k_s) of liquid mixtures. The Newton Laplace equation is employed to determine k_s of liquid mixtures, it links the measured u of a fluid at low frequency (e.g., 3MHz) with its ρ .

The Newton Laplace equation is given below:

$$k_s = \frac{1}{\rho u^2} \quad (2.6)$$

2.5. Excess Isentropic Compressibility

The excess isentropic compressibilities (k_s^E) of mixtures are calculated in a manner suggested by Douheret *et al.* (2005) [260]:

$$k_s^E = k_s - k_s^{id} \quad (2.7)$$

where, k_s is the isentropic compressibility defined in Equation 2.6 and k_s^{id} is the isentropic compressibility of the ideal mixture given by:

$$k_s^{id} = \phi_1 k_{s,1} + \phi_2 k_{s,2} + T \left[\frac{\phi_1 V_{m,1} (\alpha_{p,1})^2}{c_{p,1}} + \frac{\phi_2 V_{m,2} (\alpha_{p,2})^2}{c_{p,2}} - \frac{(V_m^{id} (\alpha_p^{id})^2)}{(c_p^{id})} \right] \quad (2.8)$$

where, ϕ , k_s , V_m , α_p and c_p symbolizes the volume fraction, isentropic compressibility, molar volume, isobaric expansivity and isobaric heat capacity respectively. The superscript 'id' is the ideal mixture and the subscripts 1 and 2 is the pure component 1 and 2 respectively. The values of ϕ , V_m^{id} , C_p^{id} , α_p and α_p^{id} were calculated using the equations:

$$\phi_i = \frac{x_i V_{m,i}}{\sum_{i=1} x_i V_{m,i}} \quad (2.9)$$

$$V_m^{id} = \sum_{i=1} x_i V_{m,i} \quad (2.10)$$

$$C_p^{id} = \sum_{i=1} x_i C_{p,i} \quad (2.11)$$

$$\alpha_p = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_p \quad (2.12)$$

$$\alpha_p^{id} = \sum_i^n \phi_i \alpha_{p,i} \quad (2.13)$$

2.6. Deviation in Isentropic Compressibility

The deviation in isentropic compressibility (Δk_s) for binary and ternary mixtures, is the change in the compressibility of an actual solution from an ideal one and it is calculated by Equation 2.14:

$$\Delta k_s = k_s - \sum_i^n x_i k_{s,i} \quad (2.14)$$

where, x_i and $k_{s,i}$ represent the mole fraction and isentropic compressibility of component i , respectively.

The definition of deviation in isentropic compressibility (Δk_s) on a volume fraction basis is derived according to the following equation:

$$\Delta k_s = k_s - \sum_i^n \phi_i k_{s,i} \quad (2.15)$$

where, ϕ_i and $k_{s,i}$ represent the volume fraction and isentropic compressibility of component i , respectively.

2.7. Excess Sound Velocity

The excess sound velocity (u^E) of a mixture is appropriately estimated using the following expression [260,261]:

$$u^E = u - u^{id} \quad (2.16)$$

where, u is the sound velocity of a mixture and u^{id} is sound velocity of an ideal mixture.

Calculation of u^{id} requires accurate estimations of ideal volumetric properties such as molar volumes (V_m^{id}) or ideal densities (ρ^{id}) with ideal isentropic compressibility (k_s^{id}) or ideal molar isentropic compressibility ($k_{s,m}^{id}$). The ideal densities (ρ^{id}) and molar volumes (V_m^{id}), are readily calculated using volume or mole fraction of pure component. Based on the volume or mole fraction of a pure component, the V_m^{id} and ρ^{id} values can be easily determined.

For the current study the u^{id} were calculated using the link between the ρ^{id} and k_s^{id} as follows:

$$u^{id} = (\rho^{id} k_s^{id})^{-\frac{1}{2}} \quad (2.17)$$

The k_s^{id} is calculated using Equation 2.8, in which, ϕ , V_m^{id} , C_P^{id} , α_P and α_P^{id} are defined in Equations 2.9 - 2.13.

The ρ^{id} is defined either on volume fraction or mole fraction as follows:

$$\rho^{id} = \sum_i^n x_i \rho_i \quad (2.18)$$

$$\rho^{id} = \sum_i^n \phi_i \rho_i \quad (2.19)$$

where, x_i , ϕ_i and ρ_i represent the mole fraction, volume fraction and density of component i , respectively.

2.8. Intermolecular Free Length

The intermolecular free length (L_f) have been used to determine the distance between the surfaces of two adjacent dissimilar molecules [262], and to further determine the intermolecular forces existing between the molecules in a mixture. Intermolecular forces such forces of

attraction or repulsion play a key role in deciding the value of (L_f). The attraction or repulsion are defined as forces which facilitate interaction that act amongst the mixing molecules and other types of neighbouring particle [262,267].

With attractive forces, the centre of attraction of the molecules plays a vital role and it is dependent on the distance between the molecules. The distance between the surfaces of molecules determines the repulsive forces in a mixture [262,263]. Due to the fact that the centres of attraction and structural centres of the solute and solvent molecules are not aligned with geometrical centres, obtaining the L_f between them is difficult. The distances between the molecules surfaces have a well-defined explanation and are simple to calculate.

The free length theory (FTL) [264-266] of Jacobson have been used to calculate the L_f . The L_f is given by a link between the Jacobson's empirical relation and isentropic compressibility as follows:

$$L_f = k_j (k_s)^{\frac{1}{2}} \quad (2.20)$$

where, k_j signifies the temperature dependent Jacobson's constant given by $k_j = (93.875 + 0.375 T) \times 10^{-8}$.

2.9. Refractive Index

Refractive index (n_D) is a dimensionless optical property of pure liquid and their mixtures [267]. It can be measured using small volume of sample in extensive temperature and pressure and with high precisions [268-270]. The n_D is useful in verifying a material, assessing the purity of substances, determining forces between molecules or their behaviour in solution [271], to calculate the molecular electronic polarizability [272], to estimate the boiling point with Meissner's method [272] and it is related closely with other thermophysical or electrical properties such as dielectric permittivity [273,274], density [275,276] and surface tension [277,278]. The values of n_D can further be used to estimate the values of other properties which are difficult to measure directly.

The n_D is referred to as the ratio of the speed of wave of light or sound wave in one medium to another [279]. Mainly, it has been utilized in the context of the speed of the wave of light

with a vacuum as a reference medium. In addition to air at standard pressure and temperature, other media have been used.

The n_D is defined as the ratio of the speed of light in vacuo to the speed of light in the material [279] expressed in the following equation:

$$n_D = \frac{c_o}{c} \quad (2.21)$$

where, c_o and c represents the speed of light in a vacuum and the speed of light in the material respectively.

From the Maxwell equations of electromagnetism, the n_D of a substance is related to the substance's relative permittivity (ϵ) and relative permeability (μ) at optical frequencies [280-282] through the following equation:

$$n_D = \sqrt{\epsilon\mu} \quad (2.22)$$

where, ϵ and μ denotes the material of both the permeability and permittivity, respectively. For non-magnetic mixtures, the μ is very close to 1, [214-216] and therefore,

$$\epsilon = n^2 \quad (2.23)$$

The Snell's law defines n_D as the ratio of the sine of the angle of incidence (material 1) θ_1 with the angle of refraction (material 2) θ_2 [283]:

$$n_D = \frac{\sin \theta_1}{\sin \theta_2} \quad (2.24)$$

2.10. Deviation in Refractive Index

The deviation in refractive index (Δn_D) is given by the changes between the refractive index of the liquid mixtures (n_D) and an ideal refractive index (n^{id}) of the mixture [270]:

$$\Delta n_D = n_D - n^{id} \quad (2.25)$$

The ideal refractive index (n^{id}) of the mixture is defined by Equation 2.26:

$$n^{id} = [\phi_1 n_{D1} + \phi_2 n_{D2}] \quad (2.26)$$

There are several approaches of describing the n^{id} of a liquid mixture based on volume fraction. The equation below was suggested by Iglesias-Otero *et al.* (2008) [217]:

$$n^{id} = \left[\frac{(n_{D,1})^2 (n_{D,2})^2 + 2\phi_1 (n_{D,1})^2 + 2\phi_2 (n_{D,2})^2}{2 + \phi_1 (n_{D,1})^2 + 2\phi_2 (n_{D,2})^2} \right] \quad (2.27)$$

Equation 2.27 can be simplified to Equation 2.26 provided that the disparity in n_D between component 1 and 2 is small [283].

The following equation for n^{id} was suggested by Reis *et al.* (2010) [283]:

$$n^{id} = [\phi_1 (n_{D,1})^2 + \phi_2 (n_{D,2})^2]^{\frac{1}{2}} \quad (2.28)$$

The ideal refractive index (n^{id}) in a mixture is defined in mole-fraction basis as follows [204]:

$$\Delta n_D = n_D - \sum_i^n x_i n_{D,i} \quad (2.29)$$

where, x_i and $n_{D,i}$ represent the mole fraction and refractive index of component i , respectively.

2.11. Surface Tension

The tension in the surface is the energy per unit surface area that needs to be applied parallel to the surface such that it balances the net inward pull [284]. The surface tension (γ) gives useful information on the cohesive forces between liquid component molecules present at the surface, intrinsic energies and their structural nature [285]. The ion-ion interaction existing between an IL molecule, make the IL have a stronger cohesive energy [286]. The γ of a liquid mixture yields useful knowledge about the specific intermolecular interactions that take place at the surface and in the bulk region of the liquid.

In chemical engineering the γ is considered a key property to obtain vital information about the transfer of mass and energy in processes such as distillation, liquid-liquid extraction condensation and gas absorption [287-290]. Furthermore, surface thermodynamic property

such as the surface entropy and the surface enthalpy can be estimated using the measured γ [290,291]. The u is directly linked to the γ with the theoretical Auerbach's relation [292]:

$$u = \left(\frac{\sigma}{6.33 \times 10^{-10} \rho} \right)^{\frac{2}{3}} \quad (2.30)$$

The γ measurements of liquids and liquid mixtures can be experimentally determined or through models. The commonly used methods for measurement of γ are classified as follows [293]: (a) drop shape methods such as the pendant drop and capillary rise; (b) methods based on menisci at the stability limit such as the drop weight/volume and maximum bubble pressure; (c) detachment methods such as the Wilhelmy plate and Du Noüy ring; (d) methods based on dynamic light scattering and the (e) spinning drop method. In the present study, the Du Noüy ring detachment method was employed. The Du Noüy ring method is most accurate when dealing with liquids with surface tension more than 20 mN/m⁻¹ and it is simple to operate, clean and repeats the tests.

2.12. Deviation in Surface Tension

The deviation in surface tension ($\Delta\gamma$) provides a better understanding regarding the mixture's ideal behaviour and the various distributions of unlike components in the bulk solution and at the surface. The ($\Delta\gamma$) were calculated from the surface tension (γ) values, according to the following equation:

$$\Delta\gamma = \gamma - \sum_i^n x_i \gamma_i \quad (2.31)$$

where, x_i and γ_i represent the mole fraction and surface tension of component i , respectively.

2.13. Correlation and Prediction Theories for Measured Thermophysical Properties

The experimental data for sound velocity of the binary mixtures were modelled using the Nomoto's relation [294], which is given by Equation 2.32:

$$u = \left(\frac{x_1 D_1 + x_2 D_2}{\frac{x_1}{\rho_1} + \frac{x_2}{\rho_2}} \right)^3 \quad (3.32)$$

where D_i stand the molar sound velocity and can be obtained by Equation 2.33:

$$D_i = \frac{1}{\rho_i} u_i^{1/3} \quad (2.33)$$

where, ρ_i is the experimental molar density of the pure components and u_i is the experimental sound velocity of the pure component.

The experimental refractive index of the mixtures, were predicted from the densities of the mixture together with the refractive indexes and densities of the pure components by a using a mixing rule [295] as in Equation 2.34:

$$\left(\frac{1}{\rho}\right) f(n_D) = \left(\frac{w_1}{\rho_1}\right) f(n_{D1}) + \left(\frac{w_2}{\rho_2}\right) f(n_{D2}) \quad 2.34$$

where w_1 and w_2 are the weight fraction of the components 1 and 2, respectively, and $f(n_D)$ is a function of the refractive index. The following mixing rules were used; Lorentz-Lorenz (LL), Gladstone-Dale (GD), Laplace (LP), and Eykman (EK). These mixing rules are given by Equation 2.35 – 2.38:

$$LL: f(n_D) = \frac{n_D^2 - 1}{n_D^2 + 2} \quad 2.35$$

$$GD: f(n_D) = n_D - 1 \quad 2.36$$

$$LP: f(n_D) = n_D^2 - 1 \quad 2.37$$

$$EK: f(n_D) = \frac{n_D^2 - 1}{n_D + 0.4} \quad 2.38$$

2.14. Correlation and Prediction Theories for Thermodynamic Properties

2.14.1. Binary Mixtures

The thermodynamic properties such V_m^E , k_s^E , u^E , Δn_D and $\Delta \gamma$ of the binary mixtures were correlated using the the Redlich-Kister polynomial equation [296] to check the accuracy of the

values of the experimental results. The Redlich-Kister polynomial equation was embedded on the Mathcad computer programme to conduct the correlation.

Redlich-Kister polynomial equation is given as:

$$X = x_1 x_2 \sum_{i=1}^p A_i (1 - 2x_i)^{i-1} \quad (2.39)$$

where x_1 and x_2 denotes the mole fraction of components 1 and 2. In other cases, volume fraction (ϕ_i) is used instead of mole fraction (x_i). X represents V_m^E or k_s^E or u^E or Δn_D or $\Delta\gamma$ coefficients (A_i) are the adjustable fitting parameters, which are acquired by the least square analysis. The optimum number of coefficients (A_i) were determined from an examination of the variation of the standard deviation (σ).

The corresponding standard deviations (σ) were determined as:

$$\sigma(X) = \left[\frac{\sum (X_{\text{exp}} - X_{\text{cal}})^2}{(n - p)} \right]^{\frac{1}{2}} \quad (2.40)$$

where, n and p denotes the number of experimental data points and the number of coefficients (A_i), which are considered to be $(i+1)$ in this work.

2.14.2. Ternary Mixtures

The thermodynamic properties of ternary mixtures were modelled using various predictive and correlative expressions proposed by Redlich-Kister (1948) [296], Cibulka (1948) [297], Tao-Smith (1953) [298], Kohler (1960) [299], Colinet (1967) [300], Scatchard *et al.* (1952) [301], Toop (1965) [302], Muggianu *et al.* (1975) [303], Hillert (1980) [304] and Rastogi *et al.* (1977) [305].

The models proposed by these authors are empirical and based on the Redlich-Kister model. They are alternatives for turning a binary polynomial model in composition into a ternary model. The Redlich-Kister expansion, used for binary mixtures, is based on the observation of calculated excess properties with the Lewis-Randall approach. For these properties, excess

values are always zero for the pure components. Hence, a model $Y = x_1 * x_2 * \{\text{polynomial in composition}\}$ guarantees the necessary mathematical requirements. Moreover, a constant in this polynomial is good enough for modelling accurately experimental data of simple systems (not so non-ideal), and a two parameters polynomial is good enough for several applications.

The question is how to turn this binary model into a ternary model. It is not so straightforward. Some of the models are presented as empirical extensions, purely mathematical approaches. Some present some basis that is, somehow, supported by empirical evidence that is not necessarily present in our data.

This modelling is the compendium of the most used ternary models based on the Redlich-Kister approach, and the choice of the model that better suits the correlation is purely based on statistical performance. Currently there is not enough information to try to understand why one model is better than the other. They are there for interpolation.

In this work, thermodynamic properties of the ternary mixtures were modelled with the sum of a predictive term (no estimated parameter) and a correlative term (with estimated parameters). The procedure to finding the best predictive and correlative model for each property is provided in the Chapter 5 together with the predictive and correlative expressions by these authors.

LITERATURE REVIEW

Since the history of ILs in 1914, which began with the invention of aluminium chloride-based salts for use in aluminium electroplating, a large number of research groups have concentrated their efforts on investigating ILs, resulting in the development of their novel uses. A survey of literature has revealed that significant data have been accumulated on the thermodynamic and thermophysical studies of ILs and their binary mixtures. Many of these studies involved the measurement of properties including ρ , u and n_D as well as determination of their excess/derived properties. The literature review herein focuses on the current studied imidazolium based ILs and their mixtures with various co-solvents.

3.1. A Review on the Thermophysical Properties of Ionic Liquid Binary Mixtures

3.1.1. [EMIM][BF₄] Mixtures

The thermophysical and thermodynamic properties of [EMIM][BF₄] and its binary mixtures with water [306], acetone, acetonitrile, dimethyl sulfoxide (DMSO) [307,308], dimethylacetamide (DMAC), dimethylformamide (DMF) [309,310], 2,2,2 trifluoroethanol [311], cyclopentanone, cyclohexanone [312], methyl ethyl ketone, 2-pyrrolidone, 1-methyl-2-pyrrolidone, N-methyl-2-pyrrolidone [313,314], aniline, 2-methyl aniline, N-methylaniline (NMA) [315-318], 2-methoxyethanol, 2-ethoxyethanol [319,320], methanol [321], 1,4-dioxane and ethylene glycol [322] have been reported by various researchers at different temperatures. Figure 3.1. represents the variation of V_m^E and k_s^E as a function of IL [EMIM][BF₄] mole fraction.

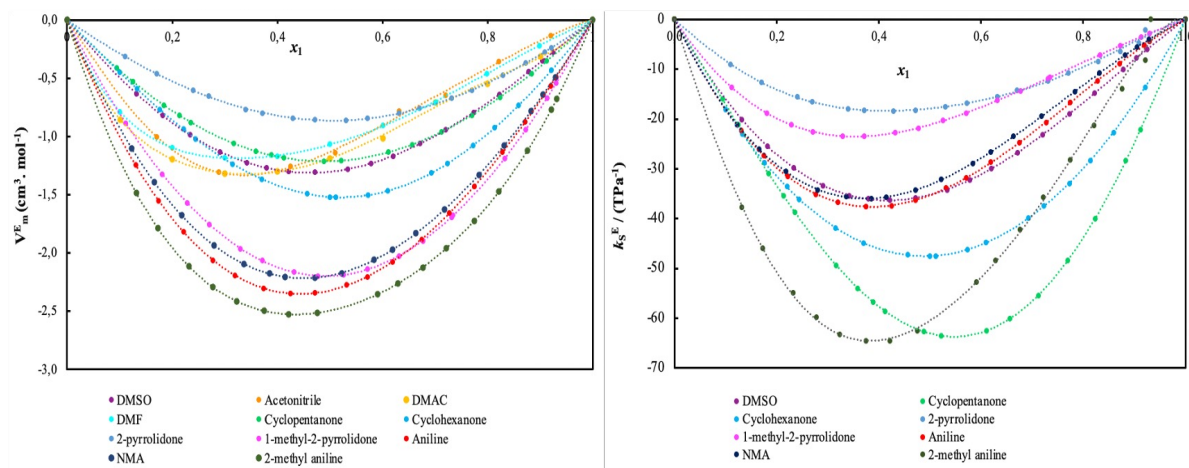


Figure 3.1: Variations of excess molar volume (V_m^E) and excess isentropic compressibility (k_s^E) with IL mole fraction (x_1) for the binary mixtures of [EMIM][BF₄] with DMSO [307] or acetonitrile [308] or DMAC or DMF [309] or cyclopentanone or cyclohexanone [312] or 2-pyrrolidone, 1-methyl-2-pyrrolidone [314] or aniline or 2-methyl aniline or NMA [317] at 303.15 K.

At $T = 303.15$ K, the values of V_m^E for all of binary mixtures as shown in Figure 3.1 are negative for the entire composition range. The presence of a strong forces between [EMIM][BF₄] and the co-solvent were suggested by the negative V_m^E values. For all mixtures, the minimum in the V_m^E values were found at an equimolar composition or at a lower IL mole fraction. This is commonly seen in the binary mixtures with a large difference in molar volumes of component molecules in the mixtures. The free molar volume of the mixtures decreases, due to the co-solvent fitting into the free volume of IL ions, which increase the interaction, hence the negative V_m^E values. The packing efficiency diminishes at a high IL mole fraction due to fewer dipoles in the mixtures. More negative values of V_m^E were seen for mixtures containing aniline, NMA, 2- methylaniline. This may be owing to the occurrence of an additional $\pi - \pi$ interaction between the π electrons of benzene and the imidazolium cation. Similarly, negative k_s^E values were obtained for all mixtures at 303.15K, with their minimums reached at a low IL mole fraction or equimolar composition. The negative values of k_s^E indicated that the solutions are less compressible than the ideal solution, possibly due to a stronger interaction between the components when the mixture is formed.

3.1.2. [EMIM][MeSO₄] Mixtures

The thermophysical and thermodynamic properties of mixtures of [EMIM][MeSO₄] mostly reported in literature are with alcohols [323-327] and water [328-330]. Bhanuprakash *et al.* (2016) [331] reported density, viscosity, and sound velocity for the binary mixtures of [EMIM][MeSO₄] with acetic and propionic acid at temperatures of 298.15, 303.15, 308.15 and 313.15 K. The values for density and sound velocity for the current studied binary mixtures, together with literature data reported by Bhanuprakash *et al.* (2016), are further discussed in Chapter 5. The variations of V_m^E and k_s^E as a function of IL [EMIM][MeSO₄] mole fraction are presented in Figure 3.2.

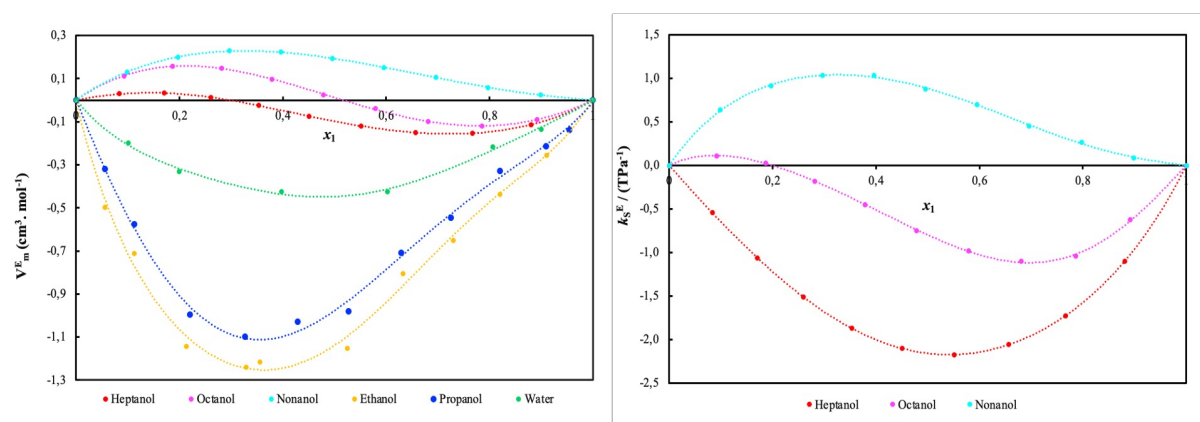


Figure 3.2: Variations of excess molar volume (V_m^E) and excess isentropic compressibility (k_s^E) with IL mole fraction (x_1) for the binary mixtures of [EMIM][MeSO₄] with heptanol or octanol or nonanol [323] or ethanol or propanol [327] or water [328] at 303.15 K.

The graph presented in Figure 3.2 demonstrates entirely negative values of V_m^E for mixtures of [EMIM][MeSO₄] with or ethanol or propanol or water, while for mixtures nonanol the V_m^E are entirely positive. The negative V_m^E behaviour may be attributed to the hydrogen bonding between the most acidic hydrogen of an imidazolium-IL cation and hydroxyl group of 1-alkanol or water and also due to the hydrogen bonding between methyl sulphate anion in IL and hydrogen atom of the alcohols and water molecule. The strong hydrogen bonding interactions reduced with increase in the alkyl chain length of 1-alcohols, this may be due to increase in non-polar nature, hence the observed positive V_m^E values. More negative values of V_m^E were seen for mixtures containing ethanol, propanol and water this may have been due to the small ethanol, propanol or water molecule fitting well into the free volumes between the relatively large ions of the IL, leading to a more efficient packing in the mixture. The values of

k_s^E presented in Figure 3.2 are entirely negative for mixtures of [EMIM][MeSO₄] with heptanol and entirely positive for mixtures of [EMIM][MeSO₄] with nonanol. The values of k_s^E mixtures of [EMIM][MeSO₄] with octanol shifted from positive to negative. The negative k_s^E values suggested the presence of strong specific interaction such as strong ion-dipole and hydrogen bonding interactions between the IL and alcohols, while positive values suggest the presence of a weak interaction. Similarly, with increase in alkyl chain length of the alcohol increase, the strength of the interaction is weakened.

3.1.3. [BMIM][BF₄] Mixtures

Various research groups have reported the thermodynamic properties of binary mixture of [EMIM][MeSO₄] mixtures with 2,2,2 trifluoroethanol [311], methanol [321], NMA, N-ethylaniline (NEA) [332,333], formamide [334], N-methylacetamide, [335], methyl acrylate [336], water, 2-propanol [337-339], 2-pyrrolidone, N-vinyl-2-pyrrolidinone (NVP), N-methyl-2-pyrrolidinone, N-octyl-2-pyrrolidone [340-344], cyclopentanone, cyclohexanone [345], 1,2-propanediol [346], aniline [347,348], benzene, acetonitrile, 1-propanol [349], hexane, heptane, cyclohexane [350], Benzaldehyde, ethyl acetoacetate [351], 1,2-propanediol and 1,3-propanediol [352] at different temperatures and composition. The variations of V_m^E and k_s^E as a function of IL [BMIM][BF₄] mole fraction are presented in Figure 3.3.

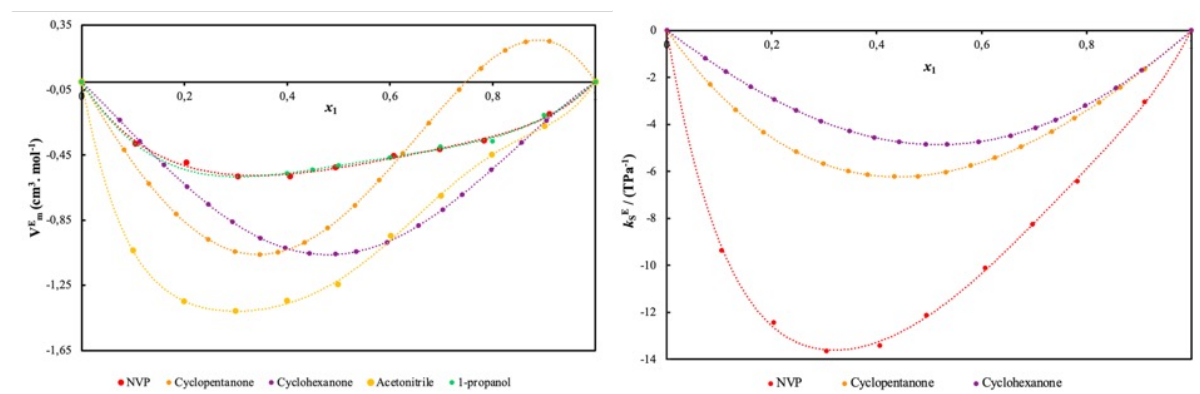


Figure 3.3: Variations of excess molar volume (V_m^E) with IL mole fraction (x_1) for the binary mixtures of [BMIM][BF₄] with NVP [341] or cyclopentanone or cyclohexanone [345] or acetonitrile, 1-propanol [349] at 303.15 K.

The graph presented in Figure 3.3 shows that entirely negative values of V_m^E for all the mixtures except for mixtures of [BMIM][BF₄] with cyclopentanone, whose values shifted from negative to positive. Minimums in the V_m^E values were found at lower IL mole fraction for all the

mixtures The π triple bonds in acetonitrile may be responsible for the more negative values of V_m^E for acetonitrile mixtures, which are absent in other mixtures. The values of k_s^E are entirely negative for all the mixtures [BMIM][BF₄] presented in Figure 3.3. More negative values of k_s^E are seen for mixtures containing NVP compared to cyclopentanone and cyclohexanone, this may be due the existence of an additional π interaction between the ethylene group of the NVP and the imidazolium cation.

3.1.4. [BMIM][PF₆] Mixtures

The thermophysical and thermodynamic properties of [BMIM][PF₆] and its binary mixtures with NMA [353], N-methylpyrrolidone [354], acetonitrile methanol, tetrahydrofuran (THF), formamide, N,N-dimethylformamide, DMSO [355-557], propylamine [358], ethyl methacrylate [359], benzyl alcohol, benzaldehyde [360], 2-methoxyethanol, 2-ethoxyethanol, 2-propoxyethanol [361,362], 2,2,2-trifluoroethanol [363], 2-Pyrrolidone and NVP [364-366] at various temperatures, and composition have been reported. The variation of V_m^E as a function of ILs [BMIM][PF₆] mole fraction is presented in Figure 3.4.

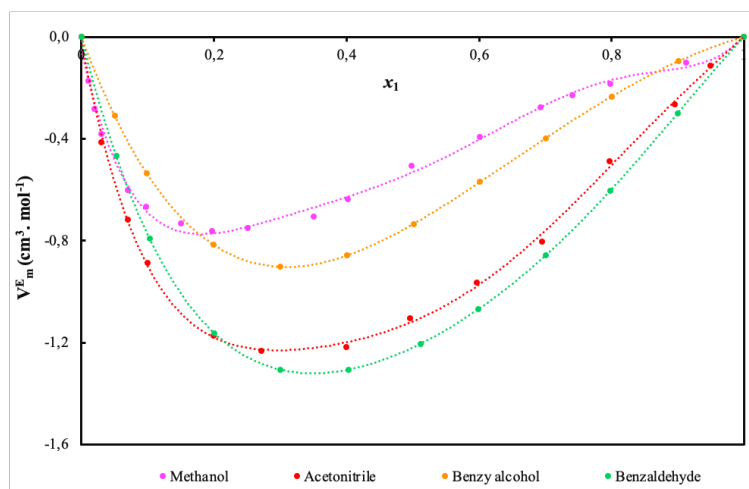


Figure 3.4: Variations of excess molar volume (V_m^E) and excess isentropic compressibility (k_s^E) with IL mole fraction (x_1) for the binary mixtures of [BMIM][PF₆] with methanol or acetonitrile [356] or benzyl alcohol or benzaldehyde [360] at 303.15 K.

It is evident from Figure 3.4 that the values of V_m^E for the mixtures of IL [BMIM][PF₆] are all negative. A minimum in V_m^E is reached at a low IL mole fraction for all binary mixtures. The negative V_m^E indicated that a more efficient packing and/or attractive interaction existent when the [BMIM][PF₆] and co-solvent were mixed. The co-solvent molecules can be accommodated

by the free volume of the [BMIM][PF₆] when the solution is created due to the significant difference in the molar volumes of the mixing components. When comparing mixtures methanol and benzyl alcohol, it appears that more negative V_m^E were obtained for mixtures of benzyl alcohol, this may be due to the additional $\pi - \pi$ interaction between the π electrons of benzene and the imidazolium cation. Moreover, the V_m^E values for benzaldehyde mixtures are more negative than those for the benzyl alcohol mixtures, which indicated that there are stronger interactions and packing effects in the benzaldehyde mixtures. According to the authors the molar volume for benzyl alcohol is greater than the molar volumes of benzyl alcohol, which means more benzaldehyde molecules can fit into the interstices upon mixing, resulting in an increase in interaction. The $C\equiv N\cdots H$ interaction between nitrogen of CH₃CN and most acidic hydrogen of an imidazolium-IL cation, interactions between the hydrogen of CH₃CN with [PF₆] anion and interactions between the imidazolium cation with π bonding of $C\equiv N$ of CH₃CN may be responsible for the more negative values of V_m^E for acetonitrile mixtures.

Table 3.1: A review summary on the thermophysical and thermodynamic properties of binary mixtures of [EMIM][BF₄], [EMIM][MeSO₄], [BMIM][BF₄] and [BMIM][PF₆] with solvents.

Binary mixture		Excess/derived propeties			
ILs	Solvent	V_m^E	$\Delta k_s/k_s^E$	u^E	Δn_D
[EMIM][BF ₄]	Water, acetonitrile DMSO, DMAC, DMF, Trifluoroethanol [304,308, 309,311]	Negative			
[EMIM][BF ₄]	Acetone, DMSO [309]	Negative	Negative		
[EMIM][BF ₄]	DMF, DMAC [310]	Negative and positive	Negative		
[EMIM][BF ₄]	Cyclopentanone or Cyclohexanone [312]	Negative	Negative		
[EMIM][BF ₄]	Methyl ethyl ketone, N-methyl-2-pyrrolidone [313]	Negative			
[EMIM][BF ₄],	2-pyrrolidone, 1-methyl-2-pyrrolidone [314]	Negative	Negative		

[EMIM][BF ₄],	Aniline, NMA, 2-methyl aniline, [315-317]	Negative	Negative		
[EMIM][BF ₄]	2- methoxyethanol, 2-ethoxyethanol [319,320]	Negative	Negative	Positive	Positive
[BMIM][BF ₄], [EMIM][BF ₄]	Methanol [321]	Negative	Negative		Positive
[BMIM][BF ₄], [EMIM][BF ₄]	1,4-dioxane, ethylene glycol [322]	Negative and positive			Negative and positive
[EMIM][MeSO ₄]	1-Alkanols (C ₇ -C ₉) [323]	Negative and positive	Negative and positive		
[EMIM][MeSO ₄]	1-Alkanols (C ₁ -C ₅), 2-propanol, ethanoic, propionic acid [324-327,331]	Negative	Negative		
[EMIM][MeSO ₄]	Water [328]	Negative			
[BMIM][BF ₄]	Aniline, NMA, N-ethylaniline [332,333,347,348]	Negative	Negative		Negative
[BMIM][BF ₄]	Formamide, N-methylacetamide, methyl acrylate [334-336],	Negative	Negative	Positive	Positive
[BMIM][BF ₄]	Water [337]	Positive	Positive		
[BMIM][BF ₄]	2-Pyrrolidone, N-methyl-2-pyrrolidinone, N-methyl-2-pyrrolidinone [340, 342,344]	Negative and positive	Negative		
BMIM][BF ₄]	NVP [341]	Negative	Negative		
[BMIM][BF ₄]	N-octyl-2-pyrrolidone [343]	Positive	Negative and positive		
[BMIM][BF ₄]	Cyclopentanone, cyclohexanone [345]	Negative and positive	Negative		
[BMIM][BF ₄]	1,2-Propanediol [346]	Positive	Negative and positive		

[BMIM][BF ₄]	Acetonitrile, benzene, 1-propanol [349]	Negative			
[BMIM][BF ₄]	Benzaldehyde, ethyl acetoacetate, NMA [351,353]	Negative	Negative		
[BMIM][BF ₄]	1,2-Propanediol, 1,3-propanediol [352]	Negative and positive	Positive	Negative	
[BMIM][PF ₆]	N-Methyl-2-pyrrolidone, 2-methoxyethanol, 2-ethoxyethanol, 2-propoxyethanol [354,361,362]	Negative	Negative	Positive	Positive
[BMIM][PF ₆]	methanol or acetonitrile [355]	Negative	Negative		
[BMIM][PF ₆]	DMF, formamide, DMSO, THF, methanol or acetonitrile [356]	Negative and positive	Negative		
[BMIM][PF ₆]	THF or propylamine [357,358]	Negative	Negative		Positive
[BMIM][PF ₆]	Ethyl methacrylate, benzyl alcohol, benzaldehyde [359,360]	Negative			
[BMIM][PF ₆]	2,2,2-trifluoroethanol [363]	Positive and negative			
[BMIM][PF ₆]	NVP [364]	Negative	Negative	Positive	Positive
[BMIM][PF ₆]	2-Pyrrolidone [365]	Negative and positive	Negative and positive	Negative and positive	Positive
[BMIM][PF ₆]	2-Pyrrolidone [366]	Negative and positive	Negative and positive	Negative and positive	Negative
[EMIM][BF ₄] [BMIM][BF ₄] [BMIM][PF ₆]	Acetophenone [367]	Negative and positive	Negative and positive		Negative and positive

3.2. A Review on the Thermophysical Properties of Ionic Liquid Ternary Mixtures

The ρ , u , V_m^E and k_s^E for ternary mixtures containing [BMIM][BF₄] or [EMIM][BF₄] with cyclopentanone and cyclohexanone were reported by Malik *et al.* (2021) [368] at 293.15 – 308.15K. The results obtained indicated that a strong interaction exists between the O atom of

cyclohexanone and the H atom attached to the imidazolium ring. The excess properties were analysed in terms of the Graph theory.

The intermolecular interaction of ternary mixtures containing [BMIM][BF₄] or [EMIM][BF₄] with cyclopentanone and cyclohexanone were investigated by Gupta *et al.* (2021) [369] through the measurement of the ρ and u data. From these measured data, the V_m^E and k_s^E were calculated. The graph theory was employed to obtain these excess properties.

Sharma *et al.* (2015) [370] determined the ρ , u , V_m^E and k_s^E for ternary mixtures comprising [EMIM][BF₄] + 1-methyl pyrrolidin-2-one or pyrrolidin-2-one or + cyclohexanone or cyclopentanone at temperatures ranging from 293.15 to 308.15 K. The Redlich-Kister equation was fitted to the V_m^E and k_s^E data to determine the ternary adjustable parameters along with their standard deviations. The V_m^E and k_s^E results were tested in terms of the Graph and Prigogine-Flory-Patterson (PFP) theories. The results calculated by the Graph theory were found to be comparable to the experimental values obtained in this study.

Sharma *et al.* (2014) [371] evaluated the ρ and u of the [EMIM][BF₄] + 2-methylaniline + pyridine or the α -, β -, or γ -picoline ternary mixtures measured over the whole range of compositions at 293.15 K, 298.15 K and 303.15 K. The Redlich-Kister equations was fitted to the V_m^E and k_s^E data. The thermodynamic properties of the ternary mixtures were analysed in terms of the Graph and Prigogine-Flory-Patterson (PFP) theories. The Graph and PFP theories correctly predicted the signs of the V_m^E and k_s^E data.

Sharma *et al.* (2013) [372] investigated the ρ and u for ternary mixtures containing [EMIM][BF₄] + 1-methyl pyrrolidin-2-one or pyrrolidin-2-one + water, measured over the entire mole fraction range at 293.15, 298.15, 303.15, and 308.15 K. The V_m^E and k_s^E were computed from the measured data and were correlated using the Redlich-Kister equation. Negative values were obtained for the V_m^E and k_s^E over the complete mole fraction range.

Sharma *et al.* (2013) [373] determined the V_m^E and k_s^E for ternary mixtures containing [EMIM][BF₄] + 2-methylaniline + aniline or N-methylaniline ternary mixtures at 293.15, 298.15, 303.15, 308.15 K under atmospheric pressure. The V_m^E and k_s^E were analysed utilizing the Graph theory and were described successfully.

The ρ , u , V_m^E and k_s^E data for ternary mixtures containing [EMIM][BF₄] + 1-methyl pyrrolidin-2-one or pyrrolidin-2-one + pyridine at T = 293.15 - 308.15 K under atmospheric pressure were reported by Sharma *et al.* (2013) [374]. The V_m^E and k_s^E were calculated using the Graph theory.

3.3. A Review on the Spectroscopic Studies of Ionic Liquid Binary Mixtures

The changes in the thermophysical and thermodynamic properties of IL mixtures as a function of composition and temperature allows for a quantitative evaluation of mixture behaviour. In mixtures of ILs and co-solvents, there are a variety of interactions that occur. As a result, thermodynamic analysis alone will not reveal the exact nature of solute–solvent interactions. In this regard, different types of spectroscopy, such as ¹H NMR, ¹³C NMR, and FTIR, are usually employed to perform spectroscopic studies to gain a better understanding of the interactions occurring between different moieties of binary mixtures and to verify assertions made by excess thermodynamic properties. Below is a summary of a few spectroscopic studies of the current studied ILs with various co-solvents conducted by other researchers.

Sharma *et al.* (2012) [314] presented FTIR measurements for equimolar mixtures of [EMIM][BF₄] and 2-pyrrolidinone or 1-methyl-2-pyrrolidone. It has been reported that the addition of [EMIM][BF₄] to 2-pyrrolidinone or 1-methyl-2-pyrrolidone affects the C₂-H vibration of the [EMIM] cation, B-F stretching of the [BF₄] anion, C=O vibration of 2-pyrrolidinone and 1-methyl-2-pyrrolidone, N–H stretching of 2-pyrrolidinone, and the C-N stretching of 1-methyl-2-pyrrolidone. The obtained result demonstrated a shift from lower to higher frequencies for the C₂-H vibration of the [EMIM] cation, the B-F stretching of the [BF₄] anion, and the N–H stretching of 2-pyrrolidinone. The C=O vibration of 2-pyrrolidinone and 1-methyl-2-pyrrolidone, as well as the C-N stretching of 1-methyl-2-pyrrolidone, exhibited a shift from higher to lower frequencies. The thermodynamic data of binary mixtures were supported by FTIR data.

Sharma and Solanki (2013) [317] reported the FTIR measurements of equimolar composition of [EMIM][BF₄] with aniline, N-methylaniline, or 2-methylaniline. The addition of [EMIM][BF₄] to anilines or vice versa was reported to influence the C₂-H vibration of the [EMIM] cation, the B-F stretching of the [BF₄] anion, and the N–H stretching of aniline, N-methylaniline, or 2-methylaniline. The obtained result demonstrated a shift from lower to

higher frequencies for the C₂-H vibration of the [EMIM] cation, B-F stretching of the [BF₄] anion, and N-H stretching of the aniline, N-methylaniline, or 2-methylaniline molecule. The authors suggested that the shift in the C₂-H vibration shows that the interactions between the hydrogen atom of the imidazolium ring of the [EMIM] cation and the fluorine atom of the [BF₄] anion are getting weaker.

The ¹H NMR, ¹³C NMR, and FTIR experiments were conducted by Chaudhary *et al.* (2014) [337] to offer physical information regarding the structure and molecular interactions of aqueous mixtures of [BMIM][BF₄]. According to the ¹H NMR data, the addition of [BMIM][BF₄] to water produced upfield shifts, which corresponded to the disruption of ion-pair interactions between the cation and anion of [BMIM][BF₄]. Also with addition of [BMIM][BF₄] to water, the broad OH band of water became more sharper. These results suggested that the network of hydrogen bonds between water molecules in aqueous mixtures had broken down. The data from ¹H NMR, ¹³C NMR, and FTIR, as well as the thermodynamic properties that were investigated, were all in close agreement.

By using spectroscopic technique like FTIR, Pal *et al.* (2016) [346] investigated the intermolecular interactions existing between the binary mixtures of [BMIM][BF₄] or [BMIM]MeSO₄ with 1,2-propanediol. The frequency of the OH broad stretching band in binary mixtures was investigated as a function of the IL mole fraction. With the addition of [BMIM]MeSO₄, a significant shift in the OH broad stretching band of 1,2-propanediol was identified, however this shifting was less when [BMIM][BF₄] was added. The establishment of hydrogen bonds between the hydroxyl group of 1,2-propanediol and component ions of [BMIM][BF₄] or [BMIM][MeSO₄], as well as the breakdown of inter and intramolecular hydrogen bonding in 1,2-propanediol, may have caused the frequency shifts. When compared to alkyl chain protons of imidazolium cation, the oxygen electron and hydroxyl protons of the 1,2-propanediol interacted strongly with aromatic ring protons of the cation, while the [MeSO₄] anion interacts strongly with the OH of 1,2-propanediol compared to the [BF₄] anion.

Prathipati *et al.* (2021) [354] presented the FTIR readings of [BMIM][PF₆] and N-methylpyrrolidone binary liquid mixtures. Due to the lower electron density on the C=N bond of the imidazolium cation of [BMIM][PF₆], the authors state that the hydrogen in C₂-H is more acidic than C₄-H and C₅-H. Understanding the characteristics of [BMIM][PF₆] hinges on the acidity of the resulting hydrogen atoms. In comparison to the C₄-H and C₅-H stretching

frequencies, a more prominent shift was observed for C₂-H stretching frequency, which indicated that the more acidic C₂-H plays the most critical role in the formation of H-bonds with the carbonyl oxygen of N-methylpyrrolidone. At the same time, a significant change was noticed in the N-methylpyrrolidone C=O stretching frequencies. This demonstrated the formation of intermolecular hydrogen bonds between the H atoms of the aromatic imidazolium ring and the carbonyl oxygen of NMP. The authors discovered an excellent correlation between thermodynamic measures and FTIR spectroscopy.

Krishna *et al.* (2016) [361] reported the FTIR measurements of binary liquid mixtures of [BMIM][PF₆] and 2-propoxyethanol at mole fractions ($x_1 = 0.3, 0.4, 0.5$, and 0.8). From the FTIR spectra, it was determined that a broad band of the terminal OH group of 2-propoxyethanol occurred at 3405.6 cm^{-1} . However, on addition of the IL (from $x_1 = 0$ to 0.4), a slight shift from lower frequencies to higher frequencies was observed, indicating that the addition of the IL caused the intermolecular hydrogen bonding in the mixture to break and the ion–dipole interactions to form. At ($x_1 \geq 0.5$) the intermolecular hydrogen bonds were reported to be weaken. The authors concluded that the strength of hydrogen bonding interactions between the ions of [BMIM][PF₆] and 2-propoxyethanol molecules decreases as the [BMIM][PF₆] mole fraction in the mixture increases. In addition, two bands formed between 3100 and 3200 cm^{-1} as a result of C–H stretching vibrations in the imidazolium ring at 3125.0 cm^{-1} and 3170.5 cm^{-1} in pure [BMIM][PF₆]. Upon addition of 2-propoxyethanol, these two peaks shifted toward lower frequencies, with the shift becoming more prominent as the mole fraction of 2-propoxyethanol increased ($x_2 = 0.6$ to 0.9). According to the authors, this shift may be due to ion–dipole interactions and hydrogen bonding between the nitrogen atoms of imidazolium cation of [BMIM][PF₆] and the dipolar OH group of 2-propoxyethanol.

Using FTIR spectroscopy, Jain and Kumar (2017) [375] revealed the intermolecular interactions in the binary mixture of [EMIM][EtSO₄] with water or methanol. The C₂-H absorption peak shifted from 3108 to 3111 cm^{-1} when water was added to the [EMIM] [EtSO₄]. As the water molecule was introduced to [EMIM][EtSO₄], it appeared that a strong hydrogen bond (OH—OSO₃H) was formed with water. This significantly decreased the H-bonding between cation and anion in [EMIM] [EtSO₄]. The C₂-H absorption peak of [EMIM] [EtSO₄] shifted also due to the water molecule's interaction with an anion. The C₂-H absorption peak, on the other hand, did not change when methanol was added to [EMIM] [EtSO₄]. Through the

use of ^1H NMR spectroscopy, Pal *et al.* (2011) [376] were able to explore the interactions that take place on a molecular scale between [BMIM][PF₆] and alkoxyalkanols. Based on the chemical shifts of the ^1H NMR, the researchers came to the conclusion that the hydroxyl groups of alkoxyalkanols and their deviations show hydrogen bonding interactions of varying strengths between ILs and alkoxyalkanol in their binary mixtures. This conclusion was based on the analysis of the chemical shifts of the ^1H NMR. When the results of thermodynamic and spectroscopic studies were compared, it was found that the hydroxyl group interactions that take place in the mixtures that were being investigated on a microscopic level are not represented in the mixing behaviour on a macroscopic level.

A survey of literature shows that no data has been reported for thermophysical and thermodynamic properties as well as the FTIR spectra analysis of the IL binary and ternary mixtures of the current study.

3.4. Ionic Liquids Interactions

The ILs physicochemical properties are generally understood to be structure dependent. The anion or cation variations affect their physicochemical properties and their effectiveness as a solvent. Due to single and multiple ion combinations, there are almost an infinite number of ILs that can be made. This forms a large pool of ILs with a wide range of properties and use that could theoretically be tuned for a specific need. It is therefore very important to have a clear understanding of the properties of ILs such that best ion combination can be selected for a process. Not only do these include the physicochemical properties of the pure ILs, but they also include how they act and interact with other compounds. ILs, as solvents, can form a variety of appealing interactions with solutes. These range from weak, nonspecific, and isotropic forces like van der Waals [377], solvophobic [378], and dispersion forces [379] to strong interactions like Coulombic forces and anisotropic forces like, dipole-dipole, magnetic dipole, hydrogen bonds [380], halogen bonds [381], and electron pair donor/acceptor interactions. The local arrangements in bulk and at the interface are determined by the diversity and strength of intermolecular forces in ILs.

3.4.1. Interactions Between Ionic Liquids and Co-Solvents

The structure-property relationship of ILs in the presence of a co-solvent and the type of interactions and strength of interaction that exist between ions of the IL and solutes can be

understood by performing measurement of their physicochemical measurements such as density (ρ), viscosity (η) and conductivity(κ).

Li *et al.* (2007) [382] reported the ρ , η and κ properties of [BMIM][PF₆], [BMIM][BF₄], and 1-butyl-3-methylimidazolium trifluoroacetate ([BMIM][CF₃CO₂]), as well as the effect of temperature and solvents including, water, dichloromethane, ethyl acetate, pyridine, acetone on these properties. The solvents used were all found to be completely miscible in the IL, while chloroform was only slightly miscible in [BMIM][PF₆]. Through experiments of the ρ , η and κ , it was discovered that the ρ of the ILs decreased linearly with increasing temperature and decreased with anions molecular mass: [PF₆] > [CF₃CO₂] > [BF₄]. The ILs, η and κ appeared to be responsive to temperature changes. The κ increased while the η dramatically decreased as the temperature was increased, demonstrating a close relation between these two properties. The η and κ of the mixtures were found to be more affected by the solvents with high dielectric constants such as pyridine, acetone, and acetonitrile. High dielectric constant solvents were effective at weakening the electrostatic attraction between the ions in ILs, which in turn reduced the η . Based on comparisons between the κ of the mixture and of pure ILs, it was discovered that solvents enhance the ionic association of the ILs, while water promotes a considerable dissociation. The high dielectric constant of water and its ability to form strong hydrogen bonds with the anions of the ILs caused the bonds of the ILs to be effectively broken, thus change the molecular structure of ILs.

In (2021), Losetty *et al.* [383], investigated anion structural effects on the solute-solvent interactions of ILs; 1-octyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide [OMIM][NTf₂], 1-octyl-3-methylimidazolium hexafluorophosphate [OMIM][PF₆] and 1-octyl-3-methylimidazolium thiocyanate [OMIM][SCN] with DMF by measurement of density, sound velocity viscosity properties. The results showed that the anion structural effects (shape and size) of the ILs with DMF solvent have a significant impact on the measured ρ , u and η properties. With an increase in the molality of the solute and a decrease in temperature, the ρ , u and η data of all mixtures changed. There was only a slight difference in ρ of the measured mixtures, the structural effects of anion were assumed to be responsible for the difference. According to the authors, anions may have a very minor role in the formation of strong intra- or intermolecular interactions because of the larger size of the cation and the fact that their alkyl side chains interfere with ionic approaches. The overall findings showed that DMF

interact strongly with [OMIM][NTf₂] compared to the other IL, as a result of strong ion-dipole interactions. It was found by the authors that the geometry of the cation and anion, namely steric hindrance and electro negativity of the atoms involved in the anion structure of IL, were the reason for the stronger ion-dipole interaction exhibited by mixtures of [OMIM][NTf₂] with DMF.

The publication by Papovic *et al.* (2016) [384] reported the effect of the alkyl chain length on physicochemical properties of mixtures of 1-n-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ILs (where n = ethyl, hexyl, octyl) and butyrolactone. The ρ , η and apparent molar volumes (V_ϕ) of the mixtures were determined and analysed. It was evident from the examination of the data that ρ increased with IL mole fraction and decreased with temperature. The findings of the V_ϕ showed that when butyrolactone is added to ILs with longer alkyl chains ($n \geq 4$) the volume of the solution changes less than in binary mixtures with shorter alkyl chains of IL ($n \leq 3$). The author suggested that it might be caused by hydrophilic domains in mixture with longer alkyl chains, which allows for more exposure of the polar regions of the IL and, thus, better interaction with butyrolactone. Butyrolactone was also seen to promote ion solvation, break ion-ion interactions, and reduces the η of the mixtures. The [OMIM][NTf₂] + butyrolactone binary mixture showed slightly higher viscosity values.

The 1-butyl-3-methylimidazolium cation was studied with several fluorinated anions, including [NTf₂], [OTf], [PF₆], [CF₃CO₂], and [BF₄] by Tokuda, *et al.* (2004) [385]. Through self-diffusion and conductivity experiments, it was found that the high rate of ions contributing to the ionic conductivity within the diffusion component is related to the poor interaction of the anion with the cation. The distribution of the anionic charge in phosphate, borate, and imide, respectively, is influenced by the electronegative fluorine atoms and perfluorosulfonyl groups in the anion. Thus, only the anion character determines which diffusive species in the IL contribute to ionic conduction. The obtained results made it clear that the size, geometry, and shape of the anion affect how strongly the cation and anion interact electrostatically.

A study on the influence of alkyl chain length was published in 2005 by Hayamizu *et al.* [386] It involved varying the alkyl chain length of 1-alkyl-3-methylimidazolium bis(trifluoromethane sulfonyl) imide [C_nMIM][NTf₂] (n = 1, 2, 4, 6, 8). The combined effect of the electrostatic contact between the ionic species and the inductive interactions between the

ions were investigated to determine the influence of alkyl chain length of the ILs. The [C₂MIM][NTF₂] showed to have the best electrical conductivity, the lowest viscosity, and the maximum diffusivity. The acquired results demonstrated that the alkyl chain length caused changes in the interaction forces.

3.4.2. Ion Exchange in Ionic Liquid Mixtures

In-theory, ion exchange can occur between an IL and any other ionic compound, such as salts or acid. Even though the idea of ion pairs in an IL is controversial [376], it stands to reason that in any mixture of two cations and two anions, one ion would associate preferentially with another. Ion exchange in ILs mixtures is a phenomenon that has been mostly ignored up, with the exception of the fact that it can be used in ILs synthesis to introduce a specific anion of choice [388; 389]. The key factor of ion exchange is the formation of a mixture that maximises the interaction between each ion and its neighbouring species. Understanding of the interactions between an ion and a solvent, is therefore crucial for predicting ion exchange. Naert et al. (2018) [390] postulated that interaction energy can be utilised as a quantitative variable to predict IL ion exchange by determining the potential of an anion and cation to form a pair and the strength of the formed pair. The interaction energy is governed by the strength of electrostatic attraction, which is dictated by the anion size and potential for charge delocalization. The anion charge density is determined by the charge delocalisation. In acetate, nitrate, and perchlorate, for instance, the negative charge is distributed among two, three, and four oxygen atoms, resulting in a decrease in charge density. The size and charge delocalization of cations also assess the strength of interactions. The cations of ILs are relatively bulky with alkyl chains surrounding the positive charge, this hinders the anion ability to approach the cation and shields the charge. This shielding prevents the anion from approaching the positive charge too closely, resulting in a significant reduction in the anion electrostatic interaction. Increasing the length of the alkyl chain, increases the bulkiness of the cation.

When an IL is in contact with a salt, ion exchange is anticipated provided the salt cation and the IL anion may form a pair with a greater interaction energy than the salt cation and anion pair. In order to maintain charge neutrality, the cation of the IL must pair with the anion of the salt. This only hold, for instance, when the anion of the IL is one with a high charge density, such as halides, HSO₄, NO₃, or carboxylates. The majority of IL studies to date, comprises low charge density anions such as NTf₂, BF₄, PF₆ and N(CN)₂ [390; 391]. These anions exhibit a weak electrostatic contact with the cation; hence, it is unlikely that a cation can acquire

interaction energy by exchanging its anion for the IL anion. Naert *et al.* (2018) [390] highlighted that the IL ion exchange is dependent on the charge density of the anion. Experiments involving mixtures of solid salt and IL; 1-butyl-3-methylimidazolium chloride ([BMIM][Cl]), 1-butyl-3-methylimidazolium nitrate ([BMIM][NO₃]) and 1-butyl-3-methylimidazolium perchlorate ([BMIM][ClO₄]) clearly demonstrated this. To [BMIM][Cl], [BMIM][NO₃] and [BMIM][Cl], the solid sodium salts of chloride, acetate, nitrate, iodide, and perchlorate were added. A significant anion exchange occurred when the sodium salts were added to [BMIM][Cl]. In [BMIM][NO₃], a substantial exchange was seen with sodium salts of iodide and perchlorate, but exchange for sodium salts of iodide acetate and chloride was low or negligible. For [BMIM][ClO₄], no substantial exchange was seen, nevertheless, added anions interact more strongly with sodium. The trend for anion exchange decreases in the order chloride > acetate > nitrate > iodide > perchlorate. The more to the right in this order, the lower the charge density. Since chloride has the highest charge density and exhibits the most electrostatic attraction, it will gravitate toward the sodium cation, which has the highest charge density. Perchlorate is a low charge density cation, and acetate and nitrate are intermediate charge density anions.

EXPERIMENTAL METHODS

4.1. Materials

All chemicals used in the present study are listed in Figure 4.1. A detailed description of the chemicals is summed up in Table 4.1. The purities of the pure chemicals were confirmed by GC analysis and due to their high mass fraction purity, no additional purification of the chemicals was required.

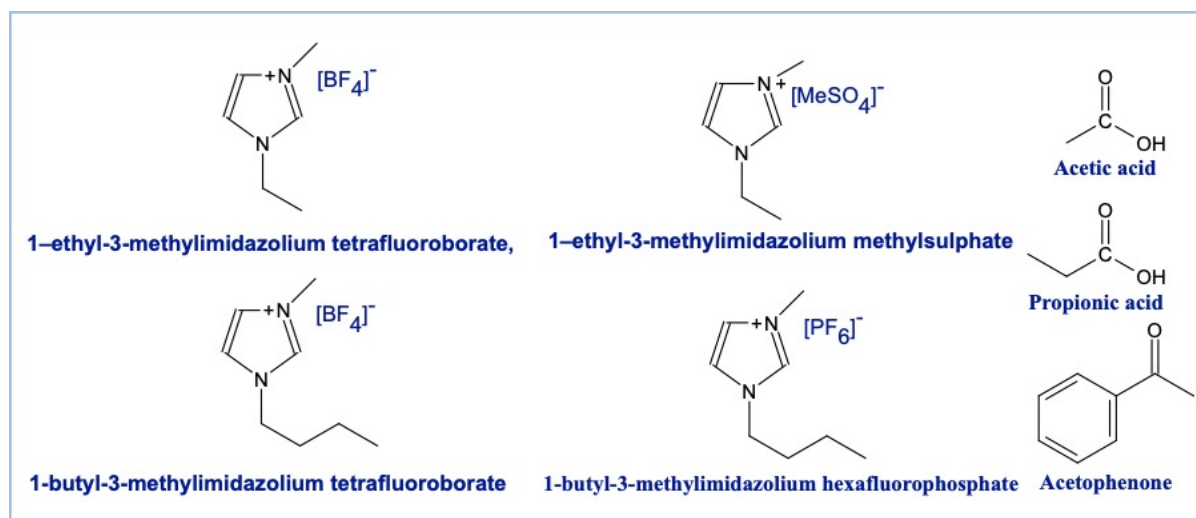


Figure 4.1: Chemical structure of the ILs and solvents used in the present work.

Table 4.1: Chemicals, molar mass, CAS number, supplier, and mass fraction purity.

Pure chemical	Molar mass (g.mol ⁻¹)	CAS Number	Supplier	Mass fraction purity (stated by the supplier)	Mass fraction purity GC analysis (final)
[EMIM][BF ₄]	197.97	143314-16-3	Ionic Liquids Technologies Inc.	>98%	>97%
[EMIM][MeSO ₄]	222.26	516474-01-4	Ionic Liquids Technologies Inc.	>98%	>98%
[BMIM][BF ₄]	226.02	174501-65-6	Ionic Liquids Technologies Inc.	>99%	>98%
[BMIM][PF ₆]	284.18	174501-64-5	Ionic Liquids Technologies Inc.	>99%	>99%

Acetic acid	60.05	64-19-7	Sigma-Aldrich (Pty) Ltd.	$\geq 99\%$	$\geq 99\%$
Propionic acid	74.08	79-09-4	Sigma-Aldrich (Pty) Ltd.	$\geq 99.5\%$	$\geq 99.5\%$
Acetophenone	120.15	98-86-2	Sigma-Aldrich (Pty) Ltd.	$>99\%$	$>98\%$

4.2. Water Content Determination

An accurate and precise moisture determination is usually important in issues where water is involved. Water has been identified as a contaminant factor or impurity, which limits the accuracy of other measurements. The physiochemical properties of ILs like conductivity, density and rheological behaviour [392] have shown to be affected by the presence of water. Residual water in ILs may be present due to the hygroscopic nature of many ILs [44]. Therefore, it is essential to determine their water content and ensure that such water content is low or undetectable. High volume of water in ILs may influence the overall results obtained. The removal of water content present in ILs can be accomplished by placing the ILs under high vacuum for a minimum of 3 hours and heating at 343.15K. Another technique that can be used is the azeotropic distillation to remove any trace of water that remained [44]. In this study, the Karl Fisher coulometer was employed to evaluate the concentration of water in the pure chemicals prior to preparation of mixtures. A water content of about $\leq 0.06\%$ was obtained.

4.3. Liquid Mixtures that were Studied

The mixtures studied contained ILs with an imidazolium cation and different anion constituents. There are two portions to an imidazolium cation: a polar (imidazole ring) and nonpolar (alkyl chain) domains. The alkyl chains (nonpolar) tend to aggregate when they exceed some critical length, just as other amphiphilic systems do [393,394]. Imidazolium based ILs are comparatively more versatile amongst other ILs. Modifications to imidazolium cations involves changes to the N-alkyl substituents and the hydrogen atoms attached to the imidazolium ring can be substituted with another atom or compound to produce desired properties.

Polar co-solvents used in the current study included acetic acid, propionic acid and acetophenone. Carboxylic acids are hydrocarbon derivatives containing a carboxyl ($-\text{COOH}$)

functional group. In the carboxylic acids functional group, carbon creates a double bond to one oxygen atom, generating a carbonyl (C=O) moiety, and a single bond to another oxygen, forming a hydroxyl group (-OH). Another bond is formed with another carbon atom in case of formic acid. Since carboxylic acids contain the (C=O) and (OH) moieties they have similar physicochemical properties with aldehydes, ketones and alcohols. In other words, their physicochemical behaviour is described by the carboxyl (COOH) moiety. The dipoles of carboxylic acids allow them to participate in energetically beneficial hydrogen bonding (H-bonding) interactions with other molecules such as water, acting as both a donor and acceptor of H-bonds.

Acetophenone, also known as 1-phenylethanone or acetylbenzene, is the simplest ketone derivative of benzene, which belongs to the class of organic compounds known as alkyl-phenyl ketones. It is a relatively weak basic (almost neutral) compound (based on its pKa). Acetophenone has been used as a solvent for manufacture of pharmaceuticals [394;395], agrochemicals [396], resins, plastics [397-399] .

As a result of the attractive properties of selected ILs, acetophenone, and carboxylic acids in a variety of industries, it has thus become necessary to investigate the intermolecular interactions of acetophenone with carboxylic acid through the measurement of thermophysical properties.

Table 4.2: Liquid mixtures that were studied.

IL	Solvent	Temperature
1. [EMIM][BF ₄] (x_1)	acetic acid (x_2)	(293.15, 303.15, 313.15, 323.15, 333.15) K
2. [EMIM][MeSO ₄] (x_1)	acetic acid (x_2)	(293.15, 303.15, 313.15, 323.15, 333.15) K
3. [BMIM][BF ₄] (x_1)	acetic acid (x_2)	(293.15, 303.15, 313.15, 323.15, 333.15) K
4. [BMIM][PF ₆] (x_1)	acetic acid (x_2)	(293.15, 303.15, 313.15, 323.15, 333.15) K
5. [EMIM][BF ₄] (x_1)	propionic acid (x_2)	(293.15, 303.15, 313.15, 323.15, 333.15) K

6. [EMIM][MeSO ₄] (x_1)	propionic acid (x_2)	(293.15, 303.15, 313.15, 323.15, 333.15) K
7. [BMIM][BF ₄] (x_1)	propionic acid (x_2)	(293.15, 303.15, 313.15, 323.15, 333.15) K
8. [BMIM][PF ₆] (x_1)	propionic acid (x_2)	(293.15, 303.15, 313.15, 323.15, 333.15) K
9. acetophenone (x_1)	acetic acid (x_2)	(293.15, 303.15, 313.15, 323.15, 333.15) K
10. acetophenone (x_1)	propionic acid (x_2)	(293.15, 303.15, 313.15, 323.15, 333.15) K
11. [BMIM][BF ₄] (x_1)	acetic acid (x_2) + acetophenone (x_3)	(293.15, 303.15, 313.15, 323.15, 333.15) K
12. [BMIM][BF ₄] (x_1)	propionic acid (x_2) + acetophenone(x_3)	(293.15, 303.15, 313.15, 323.15, 333.15) K
13. [BMIM][PF ₆] (x_1)	acetic acid (x_2) + acetophenone (x_3)	(293.15, 303.15, 313.15, 323.15, 333.15) K
14. [EMIM][BF ₄] (x_1)	acetic acid (x_2) + acetophenone (x_3)	(293.15, 303.15, 313.15, 323.15, 333.15) K
15. [EMIM][BF ₄] (x_1)	propionic acid (x_2) + acetophenone (x_3)	(293.15, 303.15, 313.15, 323.15, 333.15) K

4.4. Preparation of Mixtures

The preparation of the binary and ternary mixtures was accomplished by weighing out appropriate amounts of pure compounds into air-tight 10 cm³ glass vials with the aid of a disposable syringe. A precision of ± 0.0004 g was achieved while measuring the appropriate masses of pure compounds using an analytical electronic balance (CNW FA-2104). Care was taken to first add the least volatile chemical into the vial, this was to ensure that the most volatile chemical does not evaporate while transferring other chemicals, and that the completed mixture left a small space, just enough to aid mixing in the vial. This order minimized the possibility of loss of chemicals mass. To prevent evaporation and adsorption of moisture from the surrounding environment, the mixtures were stored in vials with screw caps that were tightly closed until further use. Before injecting the mixtures into the measuring devices, they were shaken to ensure that total dissolution of the mixture is achieved. The binary and ternary

compositions were calculated using an excel spreadsheet to give an accurate mole fraction (x_i) range of the samples. The mole fraction (x_i) of components in the mixture is defined as the amount of moles of a compound (n_i) divided by the total amount of moles (n_{total}) of all compounds in a mixture.

$$x_i = \frac{n_i}{n_{total}} \quad (4.1)$$

4.5. Thermophysical Measurements and Instrumentation

4.5.1. Density and Sound Velocity Measurements

An Anton Paar DSA-5000 M density and sound velocity analyser was used to record density (ρ) and sound velocity (u) measurements for pure ILs, organic acids, acetophenone, and their mixtures. The instrument contains a density cell and a sound velocity cell, which are equipped with a temperature regulator (built-in Pt-100 platinum thermometers alongside with the Peltier elements) that maintains the samples within a specified temperature. The two integrated Pt 100 platinum thermometers provide accurate temperature control of ± 0.02 K. The measurements were repeated three times for ρ and u . This was done to ensure the consistency of results.

The density cell or vibration tube, which consists of an oscillating U-shaped borosilicate glass tube that is being excited to vibrate at a natural or characteristic frequency (f), was used to measure the ρ . The f , changes are dependent on the ρ of the sample, and the ρ of the sample is assessed by precisely determining the f .

The density (ρ) is determined from the quotient of the period of oscillations of the U-shaped borosilicate glass tube and the reference oscillator as follows:

$$\rho = KA \times Q^2 \times f_1 - KB \times f_2 \quad (4.2)$$

where, KA and KB are apparatus constants, Q is the quotient of the period of oscillation of the U-tube divided by the period of oscillation of the reference oscillator, f_1 and f_2 represent the correction terms for temperature, viscosity and nonlinearity.

The sound velocity (u) measurements were performed by placing the sample mixture in a sound velocity cell with two piezoelectric ultrasound transducers. The first transducer releases sound waves at a frequency of roughly 3 MHz through the sample-filled chamber, while the second

transducer receives those waves. The first transducer sends sound waves through the sample with a defined period. The sound velocity (u) can be computed by calculating the period of received sound waves and taking into account the distance between the transmitter and receiver.

$$v = \frac{\text{original length} \times (1 + 1.6 \times 10^{-5} \times \Delta \text{temp})}{\frac{p_s}{\text{divisor}} - \text{TAU} \times f_3} \quad (4.3)$$

where, original length is the original path length of the sound waves (factory default = 5000 μm), Δtemp denotes the temperature deviation from 273.15K, p_s is the oscillation period of the sound waves received, divisor is 512, TAU represents the apparatus constant for sound velocity and f_3 denotes the correction term for temperature.

The DSA-5000 M, density and sound velocity analyser instrument is coupled with an Xsampler 452 (an automatic sample filling unit), which automatically fills the sample mixture from the vials into the instrument. The vials are lined up on the Xsampler 452's magazine, which allows measurement of sample mixtures directly after one another thus reducing time. Prior to each measurement, the measuring cells are automatically cleaned with two liquids; firstly, water then ethanol and then thereafter dried by measuring dry air to dissolve any residues in the measuring cell. The results are automatically saved and displayed on the TFT LCD display on the instrument. The instrument supports the direct print out and export of result data files with an aid of USB flash drive.

A certified standard liquid was used in the calibration of the instrument, and the results were compared with a standard liquid calibration certificate that contained a reference value for the standard liquid. The ρ and u measurements of water were taken after a series of measurements of the sample mixtures were taken in order to validate the accuracy of the ρ and u measurements.

Table 4.3: A complete specifications list of the DSA 5000 M instrument.

Density measuring range	0 to 3 g/cm ³
Sound velocity measuring range	1000 to 2000 m/s ⁻¹
Temperature measuring range	273.15 to 343.15 K (32 to 158 °F)
Pressure measuring range	0 to 3 bars (0 to 44 psi)

Repeatability density	0.000001 g/cm ³
Repeatability sound velocity	0.1 m/s
Repeatability temperatures	273.151 (0.002 °F)
Measuring time per sample	1- 4 minutes
Sample volume	Approx. 3 ml
Ambient air pressure sensor	Yes
Reference oscillator	Yes
Automatic bubble detection	Yes
Visual check of the density measuring cell	Camera

4.5.2. Refractive Index Measurements

The Abbemat digital automated refractometer (Anton Paar RXA 156) with an accuracy of $T = \pm 0.03$ K was used to measure the refractive index (n_D) of pure ILs, organic acids, acetophenone, and their mixtures. The measurements were repeated three times for each sample mixture in order to guarantee that the results were consistent. Before each measurement, the instrument was thoroughly cleaned with deionized water and acetone. The instrument is equipped with an external computer embedded with a software program and the results obtained displayed onto the computer LCD monitor. Experimental measurements were replicated three times for each of data set to ascertain the accuracy.

Table 4.4: A complete specifications list of the of Abbemat digital automatic refractometer (RXA 156) instrument.

Refractive index measuring range	1.32 – 1.56 n_D
Temperature measuring range	273.15 to 343.15 K (32 to 158 °F)
Refractive index resolution	± 0.000001 n_D
Temperature resolution	273.16K (32.018 °F)
Refractive index accuracy	± 0.00004 n_D
Temperature accuracy	273.18K (32.054 °F)
Temperature stability	273.17K (32.036 °F)
Measuring time per sample	5 seconds (after temp. equilibration)
Temperature control speed	20 seconds
Minimum sample volume	approx. 0.2 ml

4.5.3. Surface Tension Measurements

The surface tension (γ) of pure ILs, organic acids, acetophenone and their mixtures were measured by an Attension Sigma 702 tensiometer from Biolin scientific Inc. The Sigma 702 tensiometer allows precise temperature control via its integrated water-jacket vessel holder which is directly mounted on the motorized sample stage. Prior to each measurement, the ring was cleaned with a flaming torch. Each γ value is an average of five measurements. Due to equipment limitations related to temperature control, the measurements were made only at 298.15 K .

The Du-Noüy ring method was used for the γ measurements, taking into account the Huh and Mason correction factors [400]. The Du-Noüy ring method is ideal for measuring highly viscous liquids because it is extremely resistant to the build-up of contaminants in the surface layer [401]. This method utilizes the interaction of a platinum ring with the surface of the liquid. Through the movement of the stage on which the liquid container is mounted, the ring is submerged below the interface. Once immersed, the stage is gradually lowered, and the ring gradually raised to the meniscus of the liquid until the meniscus splits away from the ring [402]. Before the liquid meniscus ruptures, the volume of the meniscus and the force required to pull up the meniscus have reached their maximum values and have begun to decline before the actual tearing of the meniscus occurs. The calculation of the surface tension by the Du Noüy ring method is based on the measurement of the maximum force necessary to detach the ring from the surface of the liquid.

By measuring the maximum force (F) to pull out the ring from the liquid surface, the surface tension can be calculated using the equation given below [400]:

$$\gamma = \frac{F}{4\pi R} f\left(\frac{R}{r}, \frac{R^3}{V}\right) \quad (4.4)$$

where, f is the Harkins correction factor [403] that is a function of the volume (V) of the liquid raised above the flat level of the liquid surface by the ring when the maximum force (F) is reached, of the radius of the ring (R) and of the radius of the ring's wire (r). Huh and Mason [400] are the most recent functional forms for f , based on a rigorous theory and were used in the present study.

Table 4.5: A complete specification list of the Sigma 702 tensiometer.

Surface tension measurement	Yes
Interfacial Tension	Yes
Critical micelle concentration measurement	Manual
Surface free energy measurement	No
Density measurement	Yes
Surface & interfacial tension measuring range	1 – 1000 mN.m ⁻¹
Displayed resolution	0.01
Density range	0 – 2.2 g/cm ³
Density resolution	0.0001
Weighing resolution	5 g
Maximum load	0.01 mg
Force resolution	0.1 µN
Calibration & locking	Manual

4.6. Determination of Thermodynamic Properties

The thermodynamic properties such as excess molar volume (V_m^E), isentropic compressibility (k_s), excess isentropic compressibilities (k_s^E), deviation in isentropic compressibility (Δk_s), excess sound velocity (u^E), intermolecular free length (L_f), deviation in refractive index (Δn_D) and deviation in surface tension ($\Delta\gamma$) for the binary mixtures were determined from the experimental densities (ρ), sound velocities (u), refractive indexes (n_D) and surface tension (γ) values, using thermodynamic equations provided in Chapter 2. For ternary mixtures, the excess molar volumes (V_m^E) and deviation in isentropic compressibility (Δk_s) were examined.

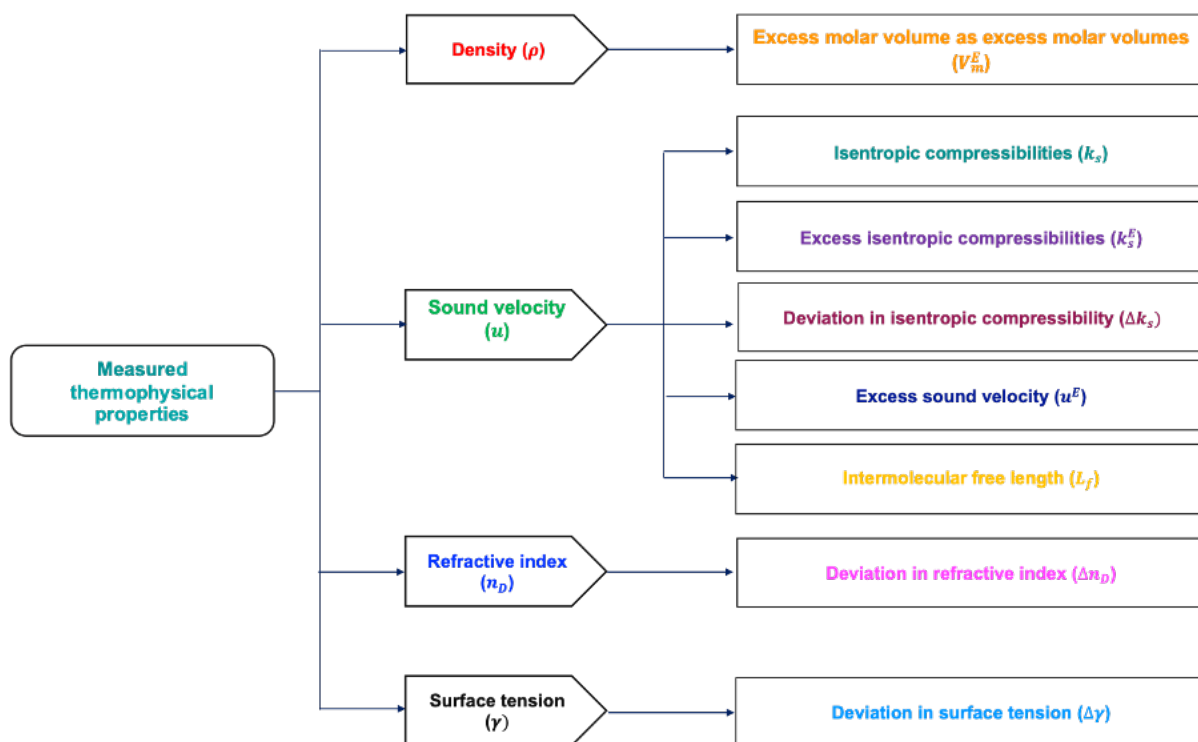


Figure 4.2: Classification of thermophysical and thermodynamic properties.

4.7. FTIR Measurements

FTIR measurements of the pure ILs, organic acids and their mixtures at an equimolar composition ($x_1 = 0.5$) were performed at room temperature using the FTIR spectrometer (Alpha II FT-IR, Bruker South Africa (Pty) Ltd) at room temperature. The measurements were made at a 4.0 cm^{-1} resolution with wavelength ranging between 400 cm^{-1} and 4000 cm^{-1} .

RESULTS AND DISCUSSION

5.1 Comparison of the Experimental Data of the Pure Ionic Liquids with Literature Data

To verify the purity of the pure ILs [EMIM][BF₄], [EMIM][MeSO₄], [BMIM][BF₄] and [BMIM][PF₆] and the reliability of the equipment used in the present study, the density (ρ), sound velocity (u), refractive index (n_D) and surface tension (γ) of pure ILs measured at T = 293.15 - 333.15K are compared with the data reported by the other authors. The results of the comparative study are shown in Tables 5.1A - 5.2A of Appendix A. The percentage deviations of the experimental data from the literature data were calculated using Equation 5.1.

$$\% \text{ Deviation } (\%D) = \left(\frac{Y_{exp} - Y_{lit}}{Y_{exp}} \right) \times 100 \quad (5.1)$$

where Y represents density (ρ) or sound velocity (u) or refractive index (n_D) or surface tension (γ). The subscripts “exp” and “lit” denotes the experimental values of this work and the literature values, respectively.

The experimental ρ values for [EMIM][BF₄] were compared with the ρ values published by Montalban *et al.* (2015) [404], Soriano *et al.* (2010) [405] and Zarei *et al.* (2017) [406]. Maximum deviations obtained were 0.00%, 0.39% and 0.32%, respectively. The experimental u values were compared with the u values reported by Zarei *et al.* (2017) [406], Sharma *et al.* (2013) [407], Rao *et al.* (2017) [408], with the maximum deviations found to be 0.13%, 0.67% and 0.61%, respectively. The experimental n_D values were compared with n_D values published by Montalban *et al.* (2015) [404], Neves *et al.* (2013) [409] and Seki *et al.* (2013) [410]. Maximum deviations obtained were 0.14%, 0.14% and 0.07%, respectively. The γ values for [EMIM][BF₄] supplied by Xu *et al.* (2012) [411] and Shojaeian *et al.* (2019) [412] showed maximum deviation of 2.83% and 0.95%, respectively. Since the deviations of experimental ρ , u and n_D are small, being in the range of 0.08% - 0.67%, it can be concluded that the experimental measurements are in good agreement with the data reported by these authors. It is worth noticing that the higher deviations were found with the γ data presented by seki *et al.*

(2012) [410], a possible explanation for this difference is that the equipment used in taking the measurements.

For [EMIM][MeSO₄] scarce literature is available, particularly for u and n_D at the current studied temperatures. The ρ values published by Wang *et al.* (2011) [413], Costa *et al.* (2011) [414] and Bhanuprakash *et al.* (2016) [331] showed a maximum difference of about 2.40%, 0.54% and 0.54%, respectively. Bhanuprakash *et al.* (2016) [331] determined the u for [EMIM][MeSO₄] at $T = 303.15 - 313.15\text{K}$, and maximum deviations of about 0.17% were obtained. The maximum deviation found for γ data is about 1.37% with respect to Wang *et al.* (2011) [413]. The deviations of ρ , u , n_D and γ are small and suggest that the literature values are in good agreement with the experimental results obtained in this work.

Concerning the deviations between experimental and literature values for [BMIM][BF₄], the maximum deviations found for ρ values were about 0.17%, 0.08% and 0.00% with respect to Montalban *et al.* (2015) [404], Taib *et al.* (2012) [415] and Yin *et al.* (2016) [416]. The experimental u values were compared with the u values reported by Rao *et al.* (2016) [417], Pal *et al.* (2012) [418] and Chaudhary *et al.* (2020) [419] with the maximum deviations found to be 0.13%. Taib *et al.* (2012) [415], Montalban *et al.* (2015) [404] and Chaudhary *et al.* (2020) [419] evaluated the values of n_D and the maximum deviation obtained were 0.28%, 0.28% and 0.07%, respectively. The γ values for [BMIM][BF₄] supplied by Li *et al.* (2019) [420], Pandit *et al.* (2016) [421] and Wang *et al.* (2011) [422] showed maximum deviations of 3.78%, 3.96% and 3.43%, respectively. Similarly, higher deviations were obtained for γ data probably due to the different equipment used in measuring the γ .

Montalban *et al.* (2015) [404], Pereiro *et al.* (2007) [423] and Currás *et al.* (2017) [424] measured ρ values for pure [BMIM][PF₆]. The maximum deviations of about 0.07% were obtained by these authors. The u values published by Pereiro *et al.* (2007) [423] and AlTuwaim *et al.* (2014) [425] showed a maximum difference of about 0.28% and 0.14%, respectively. The experimental n_D values for [BMIM][PF₆] were compared with the u values published by Montalban *et al.* (2015) [404], Pereiro *et al.* (2007) [423] and AlTuwaim *et al.* (2014) [425]. The maximum deviations obtained were 0.07%, 0.07% and 0.29%, respectively. The maximum deviations found for γ values were about 0.18% and 2.35%, 2.80% with respect to

Li *et al.* (2019) [420], Pereiro *et al.* (2007) [423] and AlTuwaim *et al.* (2014) [425]. The experimental measurements show a good agreement with the data reported by these authors.

The ρ and u data indicated lower variations in the overall comparison analysis, which may be reasoned to the fact that most authors employed different types of models of the vibrating densimeter and sound velocity analyser from Anton Paar. Other sources of observed deviations can be due to the differences in water content, the presence of contaminants due to the starting material in the synthesis, a different source of supply, a different measuring device, and a different level of measurement accuracy.

5.2 Theoretical Modelling of the Measured Thermophysical Properties

The experimental data for sound velocity (u) and refractive index (n_D) of the binary mixtures of ILs + acetic acid or propionic acid and acetophenone + acetic acid or propionic acid were modelled using predictive approaches: Nomoto's relation and four mixing rules for the refractive index (Nomoto's relation and refractive index mixing rules equations are presented in Chapter 2).

The absolute average deviation for sound velocity ($AADu\%$) of the mixtures and refractive index of the mixtures ($AADn_D\%$) were obtained using Equation 5.2-5.3 respectively:

$$AADu\% = \frac{100}{n} \sum_{i=1}^n \frac{|u_i^{exp} - u_i^{theo}|}{u_i^{exp}} \quad 5.2$$

$$AADn_D\% = \frac{100}{n} \sum_{i=1}^n \frac{|n_{D,i}^{exp} - n_{D,i}^{theo}|}{n_{D,i}^{exp}} \quad 5.3$$

where n is the number of experimental points, *exp* and *theo* are experimental and theoretical value, respectively.

The absolute average deviations in sound velocity ($AADu\%$) and refractive index ($AADn_D\%$) of the mixtures are summarized in Table 5.3A. According to Table 5.3A, the overall deviation for u was 1.573% and all the mixing rules were capable of correctly predicting the n_D , however, the Laplace mixing rule was the best option (with overall deviation = 0.156%). Good results in u and n_D prediction have already been obtained using the same models in [426-428].

Figures 5.1 - 5.10 illustrate the behavior of u for all the mixtures at the different temperatures. According to these figures, Nomoto's relation underpredicted the u for all the mixtures studied. The lowest deviation for u was obtained for acetophenone + acetic acid (0.544%, see Figure 5.9), and the highest deviation was obtained for [EMIM][BF₄] + propionic acid (2.605%, see Figure 5.2).

Since the Laplace (LP) mixing rule predicted the n_D with the least deviation, this rule was used to show the variation of the n_D with the mole fraction of the ILs (see Figures 5.11 – 5.20). According to see Figures 5.11 – 5.20), LP mixing rule overpredicted and underpredicted the measured properties in some mixtures. The lowest deviation was obtained for [BMIM][BF₄] + propionic acid (0.048%, see Figure 5.16) and the highest deviation was obtained for [BMIM][BF₆] + propionic acid (0.513%, see Figure 5.18). It is worth to mention that the refractive index mixing rules require density data for the pure component and binary mixtures. Good results are expected in the prediction of the refractive index, provided good results in the density of the pure components and binary mixtures are obtained.

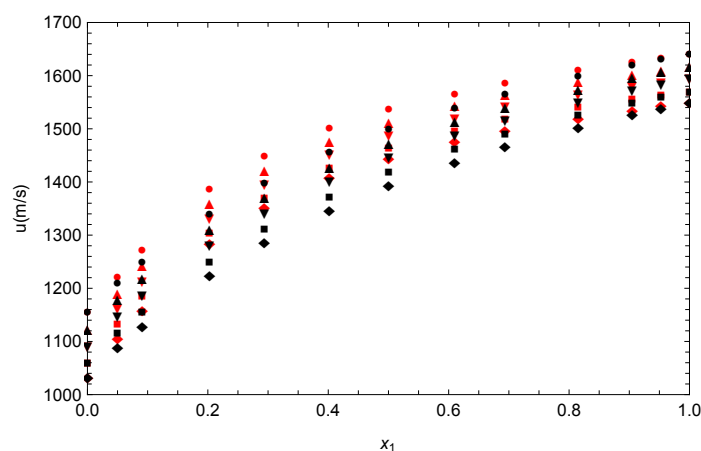


Figure 5.1: Comparison between experimental and calculated sound velocity using Nomoto's relation for the binary mixture of [EMIM][BF₄] (x_1) + acetic acid (x_2) at different temperatures. Symbols: (circle) 293.15 K, (triangle) 303.15 K, (down triangle) 313.15 K, (square) 323.15 K, (diamond) 333.15 K. Colours: (red) experimental data, (black) Nomoto's relation.

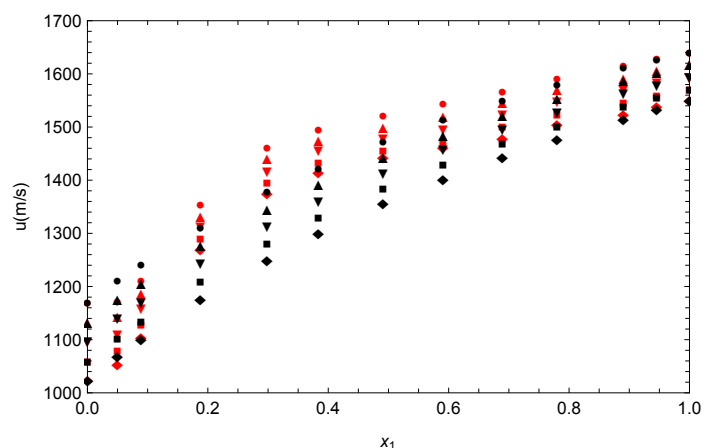


Figure 5.2: Comparison between experimental and calculated speeds of sound using Nomoto's relation for the binary mixture of [EMIM][BF₄] (x_1) + propionic acid (x_2) at different temperatures. Symbols: (circle) 293.15 K, (triangle) 303.15 K, (down triangle) 313.15 K, (square) 323.15 K, (diamond) 333.15 K. Colours: (red) experimental data, (black) Nomoto's relation.

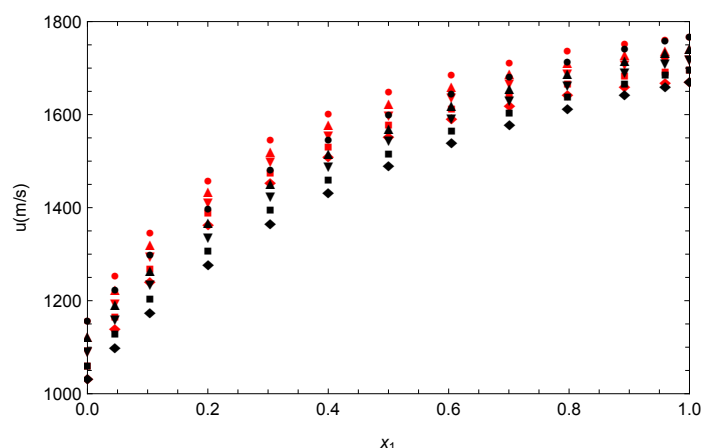


Figure 5.3: Comparison between experimental and calculated speeds of sound using Nomoto's relation for the binary mixture of [EMIM][MeSO₄] (x_1) + acetic acid (x_2) at different temperatures. Symbols: (circle) 293.15 K, (triangle) 303.15 K, (down triangle) 313.15 K, (square) 323.15 K, (diamond) 333.15 K. Colours: (red) experimental data, (black) Nomoto's relation.

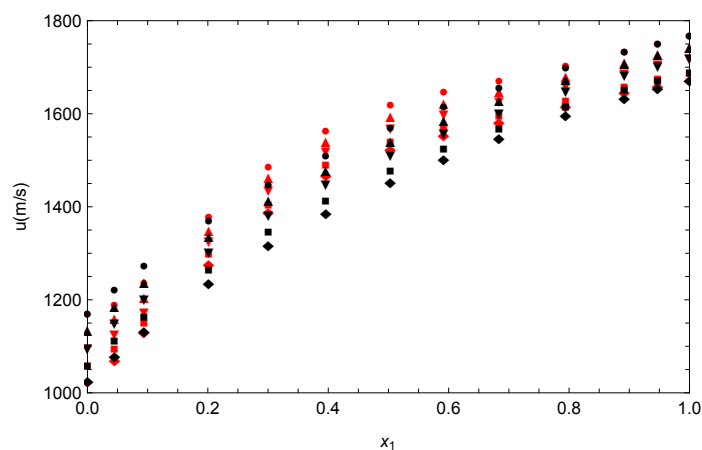


Figure 5.4: Comparison between experimental and calculated speeds of sound using Nomoto's relation for the binary mixture of [EMIM][MeSO₄] (x_1) + propionic acid (x_2) at different temperatures. Symbols: (circle) 293.15 K, (triangle) 303.15 K, (down triangle) 313.15 K, (square) 323.15 K, (diamond) 333.15 K. Colours: (red) experimental data, (black) Nomoto's relation.

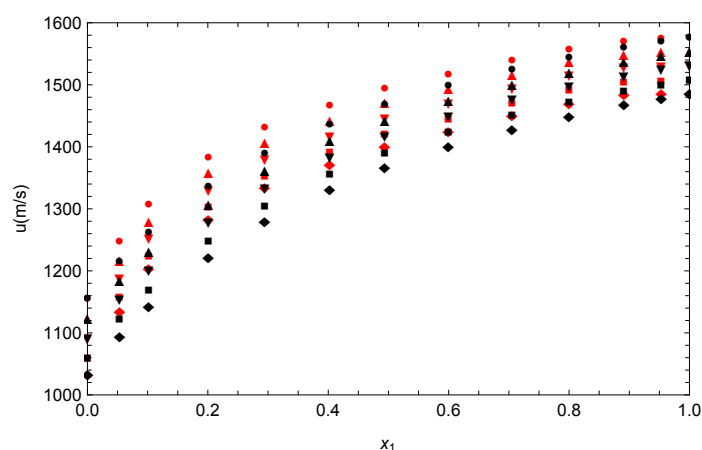


Figure 5.5: Comparison between experimental and calculated speeds of sound using Nomoto's relation for the binary mixture of [BMIM][BF₄] (x_1) + acetic acid (x_2) at different temperatures. Symbols: (circle) 293.15 K, (triangle) 303.15 K, (down triangle) 313.15 K, (square) 323.15 K, (diamond) 333.15 K. Colours: (red) experimental data, (black) Nomoto's relation.

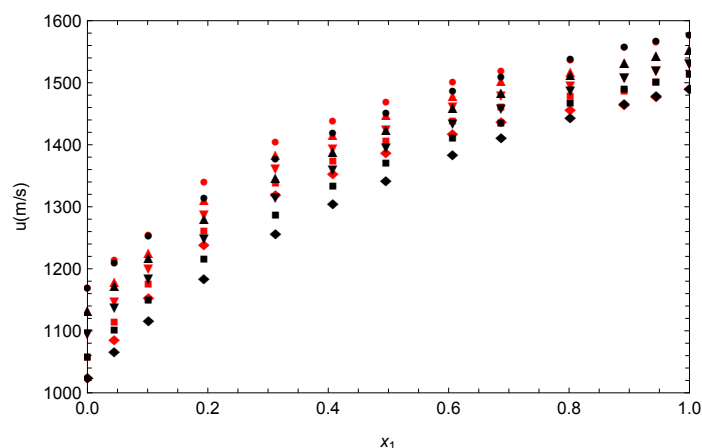


Figure 5.6: Comparison between experimental and calculated speeds of sound using Nomoto's relation for the binary mixture of [BMIM][BF₄] (x_1) + propionic acid (x_2) at different temperatures. Symbols: (circle) 293.15 K, (triangle) 303.15 K, (down triangle) 313.15 K, (square) 323.15 K, (diamond) 333.15 K. Colours: (red) experimental data, (black) Nomoto's relation.

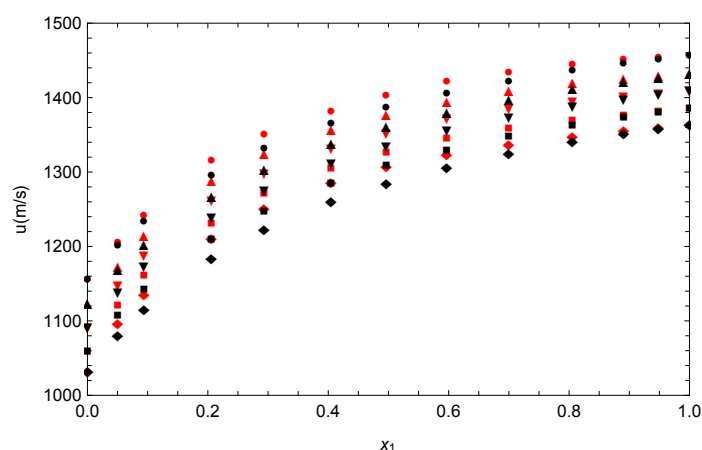


Figure 5.7: Comparison between experimental and calculated speeds of sound using Nomoto's relation for the binary mixture of [BMIM][PF₆] (x_1) + acetic acid (x_2) at different temperatures. Symbols: (circle) 293.15 K, (triangle) 303.15 K, (down triangle) 313.15 K, (square) 323.15 K, (diamond) 333.15 K. Colours: (red) experimental data, (black) Nomoto's relation.

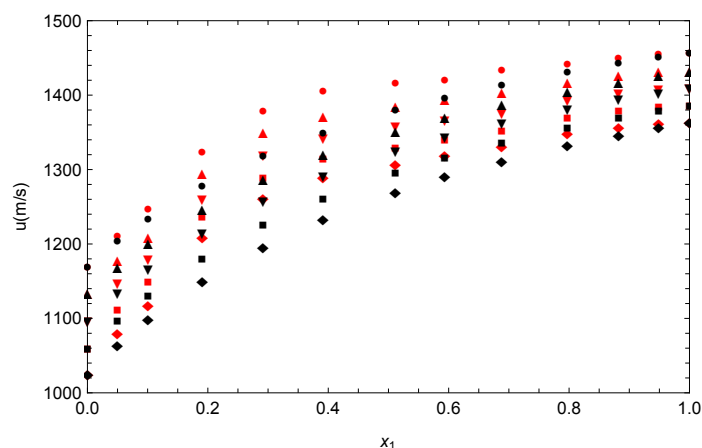


Figure 5.8: Comparison between experimental and calculated speeds of sound using Nomoto's relation for the binary mixture of [BMIM][PF₆] (x_1) + propionic acid (x_2) at different temperatures. Symbols: (circle) 293.15 K, (triangle) 303.15 K, (down triangle) 313.15 K, (square) 323.15 K, (diamond) 333.15 K. Colours: (red) experimental data, (black) Nomoto's relation.

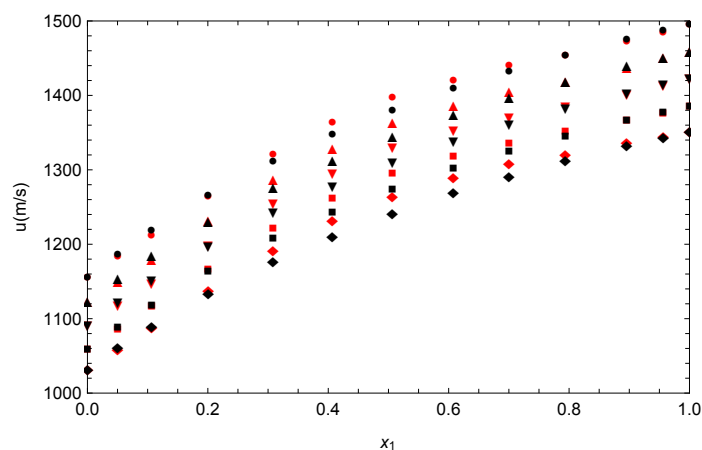


Figure 5.9: Comparison between experimental and calculated speeds of sound using Nomoto's relation for the binary acetophenone mixture of (x_1) + acetic acid (x_2) at different temperatures. Symbols: (circle) 293.15 K, (triangle) 303.15 K, (down triangle) 313.15 K, (square) 323.15 K, (diamond) 333.15 K. Colours: (red) experimental data, (black) Nomoto's relation.

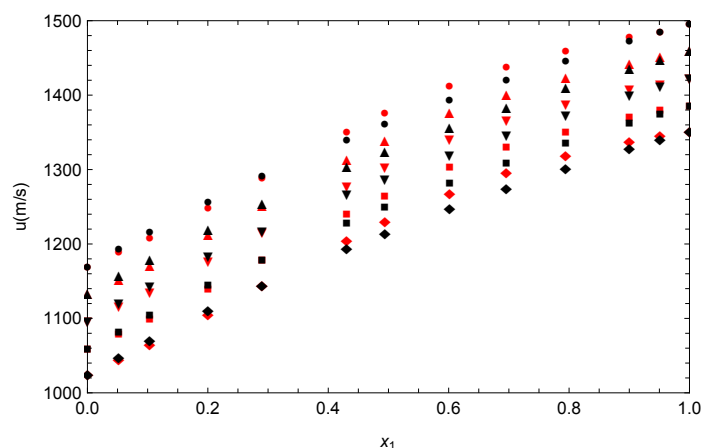


Figure 5.10: Comparison between experimental and calculated speeds of sound using Nomoto's relation for the binary acetophenone mixture of (x_1) + propionic acid (x_2) at different temperatures. Symbols: (circle) 293.15 K, (triangle) 303.15 K, (down triangle) 313.15 K, (square) 323.15 K, (diamond) 333.15 K. Colours: (red) experimental data, (black) Nomoto's relation.

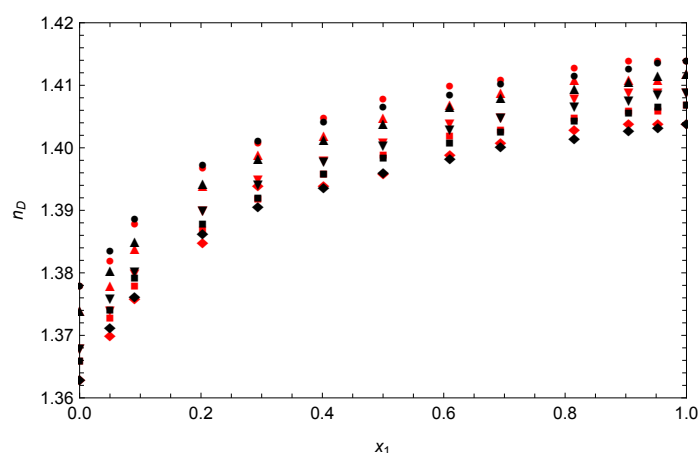


Figure 5.11: Comparison between experimental and calculated refractive index using Laplace mixing rule for the binary mixture of [EMIM][BF₄] (x_1) + acetic acid (x_2) at different temperatures. Symbols: (circle) 293.15 K, (triangle) 303.15 K, (down triangle) 313.15 K, (square) 323.15 K, (diamond) 333.15 K. Colours: (red) experimental data, (black) Laplace mixing rule.

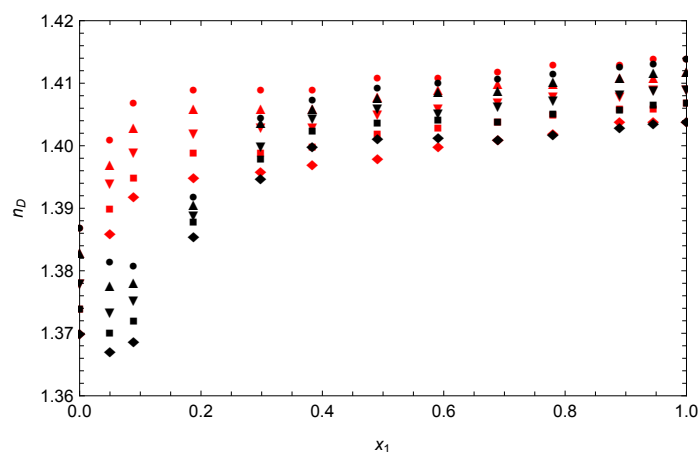


Figure 5.12: Comparison between experimental and calculated refractive index using Laplace mixing rule for the binary mixture of [EMMN][BF₄] (x_1) + propionic acid (x_2) at different temperatures. Symbols: (circle) 293.15 K, (triangle) 303.15 K, (down triangle) 313.15 K, (square) 323.15 K, (diamond) 333.15 K. Colours: (red) experimental data, (black) Laplace mixing rule.

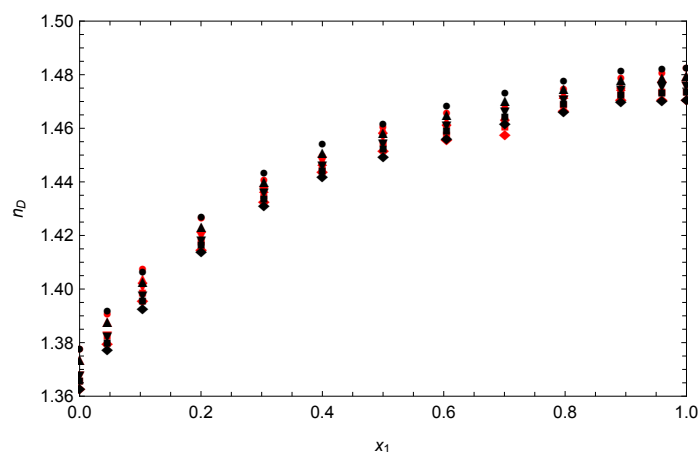


Figure 5.13: Comparison between experimental and calculated refractive index using Laplace mixing rule for the binary mixture of [EMIM][MeSO₄] (x_1) + acetic acid (x_2) at different temperatures. Symbols: (circle) 293.15 K, (triangle) 303.15 K, (down triangle) 313.15 K, (square) 323.15 K, (diamond) 333.15 K. Colours: (red) experimental data, (black) Laplace mixing rule.

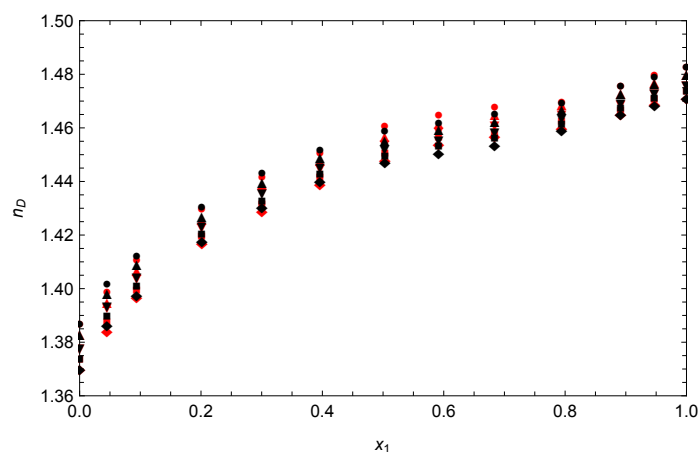


Figure 5.14: Comparison between experimental and calculated refractive index using Laplace mixing rule for the binary mixture of [EMIM][MeSO₄] (x_1) + propionic acid (x_2) at different temperatures. Symbols: (circle) 293.15 K, (triangle) 303.15 K, (down triangle) 313.15 K, (square) 323.15 K, (diamond) 333.15 K. Colours: (red) experimental data, (black) Laplace mixing rule.

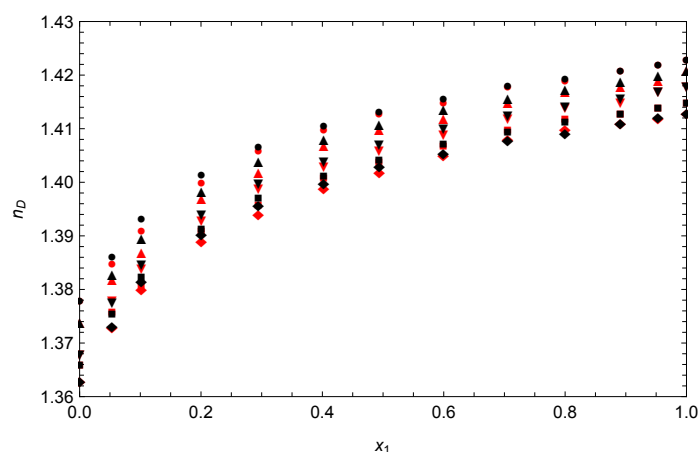


Figure 5.15: Comparison between experimental and calculated refractive index using Laplace mixing rule for the binary mixture of [BMIM][BF₄] (x_1) + acetic acid (x_2) at different temperatures. Symbols: (circle) 293.15 K, (triangle) 303.15 K, (down triangle) 313.15 K, (square) 323.15 K, (diamond) 333.15 K. Colours: (red) experimental data, (black) Laplace mixing rule.

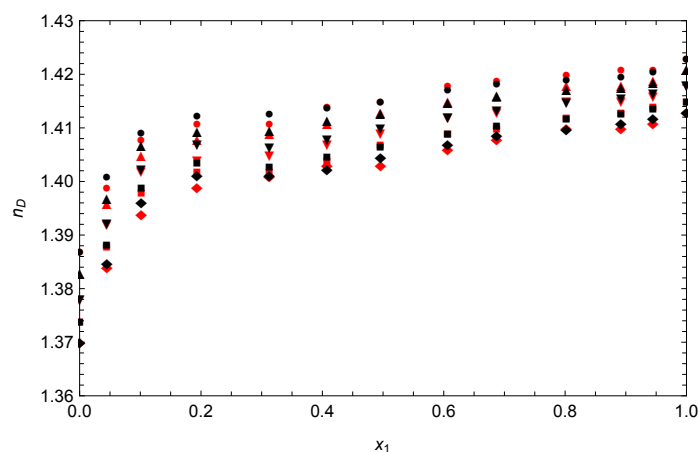


Figure 5.16: Comparison between experimental and calculated refractive index using Laplace mixing rule for the binary mixture of [BMIM][BF₄] (x_1) + propionic acid (x_2) at different temperatures. Symbols: (circle) 293.15 K, (triangle) 303.15 K, (down triangle) 313.15 K, (square) 323.15 K, (diamond) 333.15 K. Colours: (red) experimental data, (black) Laplace mixing rule.

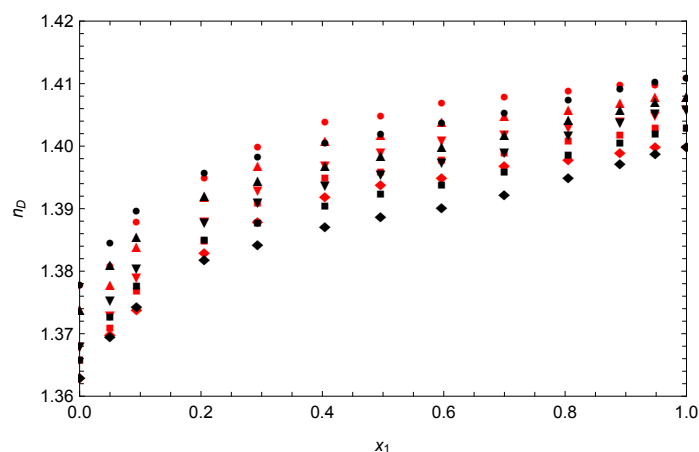


Figure 5.17: Comparison between experimental and calculated refractive index using Laplace mixing rule for the binary mixture of [BMIM][PF₆] (x_1) + acetic acid (x_2) at different temperatures. Symbols: (circle) 293.15 K, (triangle) 303.15 K, (down triangle) 313.15 K, (square) 323.15 K, (diamond) 333.15 K. Colours: (red) experimental data, (black) Laplace mixing rule.

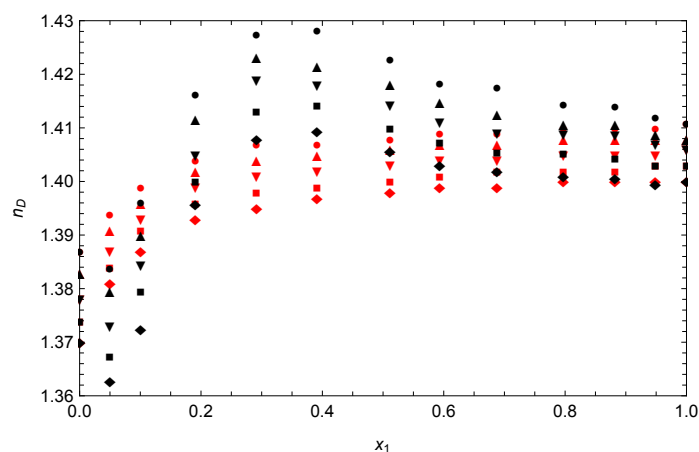


Figure 5.18: Comparison between experimental and calculated refractive index using Laplace mixing rule for the binary mixture of [BMIM][PF₆] (x_1) + propionic acid (x_2) at different temperatures. Symbols: (circle) 293.15 K, (triangle) 303.15 K, (down triangle) 313.15 K, (square) 323.15 K, (diamond) 333.15 K. Colours: (red) experimental data, (black) Laplace mixing rule.

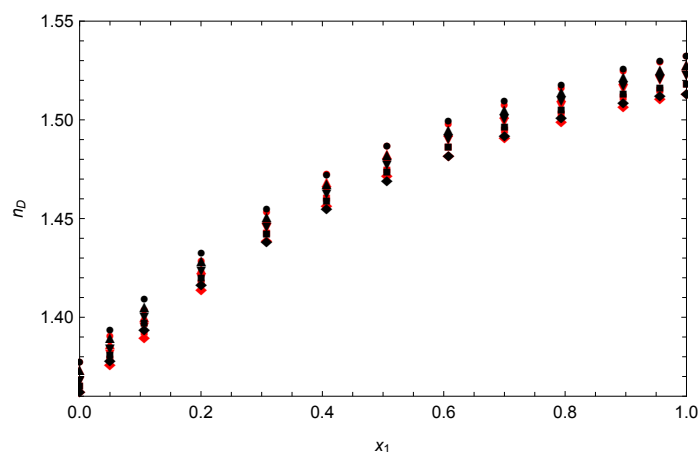


Figure 5.19: Comparison between experimental and calculated refractive index using Laplace mixing rule for the binary mixture of acetophenone (x_1) + acetic acid (x_2) at different temperatures. Symbols: (circle) 293.15 K, (triangle) 303.15 K, (down triangle) 313.15 K, (square) 323.15 K, (diamond) 333.15 K. Colours: (red) experimental data, (black) Laplace mixing rule.

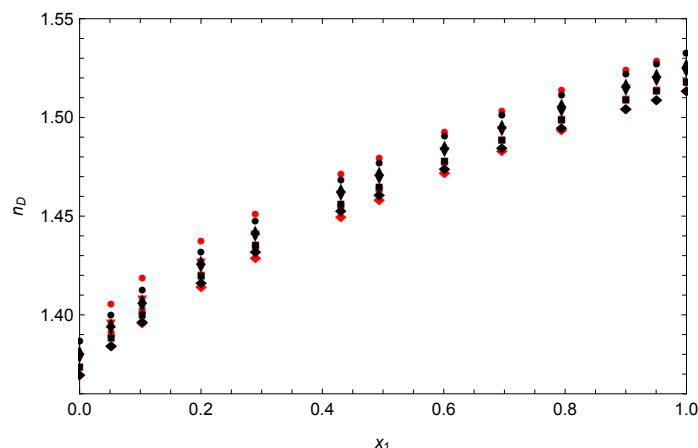


Figure 5.20: Comparison between experimental and calculated refractive index using Laplace mixing rule for the binary mixture of acetophenone (x_1) + propionic acid (x_2) at different temperatures. Symbols: (circle) 293.15 K, (triangle) 303.15 K, (down triangle) 313.15 K, (square) 323.15 K, (diamond) 333.15 K. Colours: (red) experimental data, (black) Laplace mixing rule.

5.3 Summary of Publications

5.3.1. Mixtures of [EMIM][MeSO₄] or [EMIM][BF₄] with Acetic or Propionic Acid

This research publication presented the experimental values of ρ , u , n_D and γ over the whole range of composition of {[EMIM][BF₄] (x_1) + acetic acid (x_2)} (mix_1), {[EMIM][MeSO₄] (x_1) + acetic acid (x_2)} (mix_2), {[EMIM][BF₄] (x_1) + propionic acid (x_2)} (mix_3) and {[EMIM][MeSO₄] (x_1) + propionic acid (x_2)} (mix_4) at temperatures between 293.15 and 333.15 K under atmospheric pressure. The V_m^E , k_s , k_s^E , u^E , L_f , Δn_D and $\Delta\gamma$ were determined from the experimental values (using the theoretical equations provided in Chapter 2) and were then correlated with the Redlich-Kister type equation. The FTIR analysis of the pure ILs, acetic and propionic acid as well their binary mixtures at an equimolar composition were carried out. The results obtained are tabulated in Tables 5.1B - 5.13B and graphically illustrated in Figures 5.1B - 5.11B of Appendix B. The full discussions of the results were published in [429].

The thermophysical properties, ρ , u and n_D of the ILs and their corresponding binary mixtures increased with increase in ILs mole fraction and temperature. An increase in ρ values with ILs mole fraction was expected since ILs are denser and more viscous than carboxylic acids. The addition of carboxylic acids into ILs decreased their viscosity, leading to an increase in their

ion pair mobility. The values of γ appeared to have increased with an increase in IL mole fraction (Figure 5.4B). According to Ghatee *et al.* (2008) [430], if an IL has a shorter alkyl side chain length of the cation, the γ is predominantly dependent on the nature of anion, which is responsible for higher γ values. In other words, the anion constituent of the IL significantly affects the imidazolium IL- solvent interactions. It was also evident from Figures 5.1A - 5.3A that temperature has a significant influence on the interaction amongst the mixing components, hence the decrease in ρ , u and n_D values with increasing temperature.

The values for ρ and u for the binary mixtures {[EMIM][MeSO₄] (x_1) + acetic acid (x_2)} (mix_2) and {[EMIM][MeSO₄] (x_1) + propionic acid (x_2)} (mix_2), together with literature ρ and u data reported by Bhanuprakash *et al.* (2016) [331], are given in Figure 5.21 for comparison purposes. From Figure 5.21, it can be observed that the ρ and u values shows notable deviations, especially for u . The deviations in ρ is within the experimental error. On the other hand, the deviation in u values may be related to experimental techniques and/instruments used as well as preparation of the samples etc. In the present study the instruments used is known to have high precision and accuracy as compared to the instruments used in the literature. In general, notable deviation were always observed for u values while comparing the data measured in these two instruments in literature.

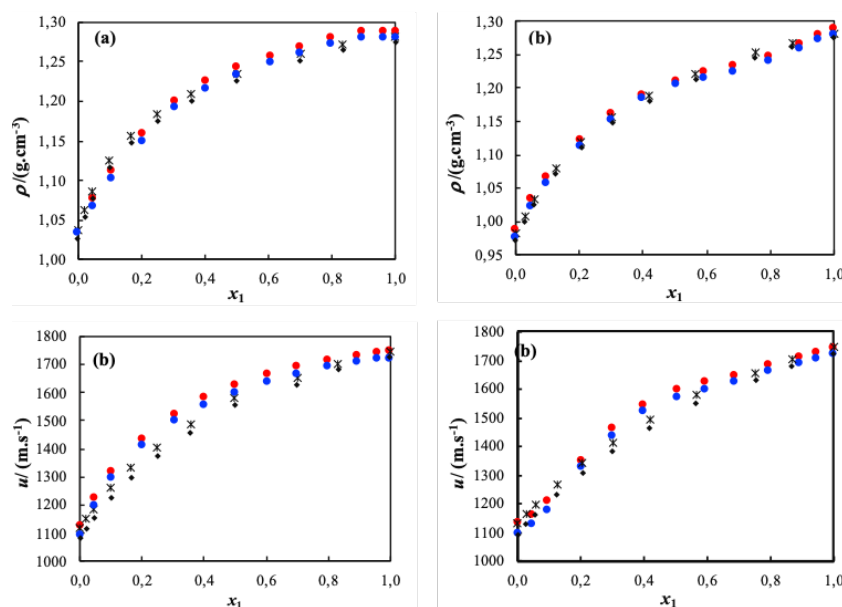


Figure 5.21: Comparison of density (ρ) and sound velocity (u) for the binary mixtures of [EMIM][MeSO₄] with (a) acetic acid or (b) propionic acid at (●) 303.15 K and (●) 313.15 K together with literature [331] at (*) 303.15 K and (♦) 313.15 K.

The graphs for thermodynamic properties; V_m^E , k_s , k_s^E , u^E , L_f , Δn_D and $\Delta\gamma$ as a function of IL mole fraction for the binary mixture {[EMIM][BF₄] (x_1) + acetic acid (x_2)} (*mix*₁), {[EMIM][MeSO₄] (x_1) + acetic acid (x_2)} (*mix*₂), {[EMIM][BF₄] (x_1) + propionic acid (x_2)} (*mix*₃) and {[EMIM][MeSO₄] (x_1) + propionic acid (x_2)} (*mix*₄) are presented in Figures 5.5B-5.10B. Figure 5.5B shows that the values of V_m^E were completely negative throughout the entire IL mole fraction for the [EMIM]⁺ based IL with acetic acid mixture and changed sign from negative to positive and vice versa for the [EMIM]⁺ based IL with propionic acid. The sign and magnitude of the values of the excess or derived properties plays a vital part in evaluating the molecular rearrangement caused by molecular interaction taking place between the component molecules in the mixtures and relies on the strength of volume expansion and contraction factors. The negative V_m^E values were attributed to the hydrogen bonding between the mixing components and ion-dipole interactions, which resulted from the ILs ions and dipoles of the carboxylic acids. The small carboxylic acid molecule were capable of fitting into the free volume of IL ions, resulting in a decrease in the free volume of IL, hence the negative V_m^E values. Thus the negative values of V_m^E favours structure making effects. The positive V_m^E values suggested the existence of weak interaction such as dispersion forces between the mixing components. In all cases, the values of V_m^E were seen to have decreased with temperatures increase. The inversion of sign in the V_m^E values observed for binary mixtures of [EMIM]⁺ based IL with propionic acid, shifting from positive values at negative values and vice versa which indicated that the structure breaking and structure making factors are competing with each other at different levels. For {[EMIM][BF₄] (x_1) + propionic acid (x_2)} (*mix*₃), positive values were found at a lower IL mole fraction ($x_1=0.2-0.3$) and negative were found at a higher IL mole fraction ($x_1=0.1-0.2$). The addition of the IL lead to the propionic acid lead to the distraction of the self-associated propionic acid molecule resulting in positive V_m^E values. A further addition of the IL lead to the establishment of cross hydrogen-bonding between the carboxylic acid and IL, resulting into negative V_m^E values at higher IL mole fraction.

The minimums in the V_m^E values were found to be -1.599 cm³.mol⁻¹, -1.881 cm³.mol⁻¹, -2.786 cm³.mol⁻¹ and -3.397 cm³.mol⁻¹, which occurred at IL mole fractions of $x_1 \approx 0.3$, $x_1 \approx 0.4$, $x_1 \approx 0.4$ and $x_1 \approx 0.3$, from *mix*₁ to *mix*₄ respectively. The magnitude of the minimums in the V_m^E values decreased in the following order: *mix*₄<*mix*₃<*mix*₂<*mix*₁. This order suggested that the values of V_m^E decreased with increase in the size of the anion. Furthermore, the order

suggested that the minimums in the V_m^E values increased as the alkyl chain length of the acid decreased. As the alkyl chain length of carboxylic acid increased, the intermolecular interaction between mixing components increased, this is because of the more positive inductive effect of the larger ethyl (C_2H_5) group in propionic acid than methyl (CH_3) group in acetic acid [431,432].

The results presented in Figure 5.6B show that the k_s^E values were negative for the binary mixtures, except for the $\{[EMIM][BF_4](x_1) + \text{propionic acid}(x_2)\}$ (*mix*₃) binary mixture, which shifted from positive to negative. The negative values of k_s^E implied that solvent molecules around solute are less compressible than the solvent molecules in the bulk solutions. This is due to a closer approach of unlike molecules and a stronger interaction between components of mixtures that leads to a decrease in compressibility as seen in Table 5.8 – 5.11B. The positive values of k_s^E were attributed to a weak interaction between mixing components, thus making the mixtures to be more compressible than the corresponding ideal mixture. The values of k_s^E were seen to have decreased with temperatures increase. As seen from results in Figure 5.6B the values of k_s^E for the $\{[EMIM][BF_4](x_1) + \text{propionic acid}(x_2)\}$ (*mix*₃) are both positive and negative. The positive values were found at higher propionic acid mole fraction. The addition of $\{[EMIM][BF_4](x_1)\}$. The addition of the IL lead to the propionic acid resulted in a the rupture of intermolecular hydrogen bond in the propionic acid molecule. It was followed by the association through cross hydrogen bonding between the most acidic hydrogen which was at the C₂ position of an imidazolium cation and negative pole oxygen of carbonyl group of the carboxylic acid. The values of k_s^E became more negative with increase in temperature. Minimums in the k_s^E values were found to be -153 TPa¹, -182 TPa⁻¹, -217 TPa⁻¹ and -189 TPa⁻¹, which occurred at IL mole fractions of $x_1 \approx 0.2$ for the $[EMIM]^+$ based IL with acetic acid mixtures and $x_1 \approx 0.3$ for the $[EMIM]^+$ based IL with propionic acid mixtures respectively. Similarly, the minimums in the k_s^E values were more negative for mixtures containing propionic acid.

Figure 5.7B shows that the values of u^E were completely negative for mixtures of the $[EMIM]^+$ based IL with acetic acid and changed sign from negative to positive for the $[EMIM]^+$ based IL with propionic acid mixtures. Maximums in the positive u^E values were found to be 127 m.s⁻¹, 180 m.s⁻¹, 196 m.s⁻¹ and 193 m.s⁻¹, which occurred at IL mole fractions of $x_1 \approx 0.3$, $x_1 \approx 0.3$, $x_1 \approx 0.3$ and $x_1 \approx 0.4$, x_1 from *mix*₁ to *mix*₄ respectively. The positive u^E values indicated

the existence of strong intermolecular forces. Strong molecular interactions between component molecules in the mixture lead to an increase in compactness and closer packing of the molecules, which raised the u^E value and resulted in positive u^E values. To the contrary, if bond dissociation dominates, it causes the volume of the binary mixtures to expand, which yielded negative u^E values. The negative values for {[EMIM][BF₄](x_1) + propionic acid (x_2)} (*mix*₃) and {[EMIM][MeSO₄](x_1) + propionic acid (x_2)} (*mix*₄) binary mixtures were at high propionic acid mole fraction. This suggested that the dissociation of propionic acid molecule dominated. The u^E values for the [EMIM]⁺ based IL with propionic acid mixtures appeared to be slightly higher compared to the [EMIM]⁺ based IL with acetic acid. The effect of interaction increased, as the alkyl chain length of carboxylic acid increases, this is due to the positive inductive effect of the alkyl chain. Therefore the more positive maximum values of the [EMIM]⁺ based IL with propionic acid mixtures are due to the more positive inductive effect of larger ethyl (C₂H₅) group in propionic acid than methyl (CH₃) group in acetic acid. The values of u^E increased with temperatures increasing.

The results presented in Figure 5.8B show that the values of L_f for the binary mixtures decreased with an increase in IL mole fraction and increased temperature. An increase in the IL concentration lead to an increase in the number of ILs molecules in a mixtures, which resulted in an increase in attractive forces between molecules and consequently decreasing L_f . Moreover, it has been proposed by Kincaid and Eyring (1938) [433] that the variation of u in a mixture is dependent upon the increase or decrease of L_f after the components molecules have mixed. The L_f and u are related inversely as is seen in Figures 5.2A and 5.8A and it is proven that molecules with spherical or symmetrical shape have short L_f resulting in higher u values.

It is evident from Figure 5.9B that the values of Δn_D were positive and increased with temperature throughout the entire composition range. The values of Δn_D sharply increased until reaching a maximum at of $x_1 \approx 0.3$, $x_1 \approx 0.3$, $x_1 \approx 0.1$ and $x_1 \approx 0.4$ from *mix*₁ to *mix*₄ respectively. A further addition of IL in to the carboxylic acid appeared have a decreased the packing efficiency between IL and carboxylic acids, which contributed to a decrease in the positive values of Δn_D . The positive Δn_D results suggested the formation of chemical interactions, which may include association brought on by ion-dipole contact and H-bonding between dissimilar molecules in the mixtures [434, 435]. The maximums in the Δn_D values

were more positive for mixtures with a larger anion and also for mixtures containing propionic acid. Furthermore, a strong negative correlation between the Δn_D and V_m^E values was observed, whereby the sign of the Δn_D values were opposite to the sign of the V_m^E values for mixtures of the [EMIM]⁺ based IL with acetic acid as depicted in Figures 5.5B and 5.9B. This observation is in agreement with the view proposed by Brocos *et al.* (2003) [436] in that the values of Δn_D can be directly interpretable as a sign-reverse of the deviation of a reduced free volume from ideality and consequently of changes in intermolecular interactions. It should be noted that the Δn_D and V_m^E values for the [EMIM]⁺ based IL with propionic acid mixtures, failed to comply with the proposed rule, which has been in some literatures [436-438]. Also, with an increase in temperature, V_m^E tends to become more negative, and accordingly Δn_D becomes more positive.

The results displayed in Figure 5.10B show that the $\Delta\gamma$ values were entirely negative for the {[EMIM][BF₄] (x_1) + propionic acid (x_2)} (*mix*₃), {[EMIM][MeSO₄] (x_1) + propionic acid (x_2)} (*mix*₃), and shifted from positive to negative for mixtures of the {[EMIM][BF₄] (x_1) + acetic acid (x_2)} (*mix*₁) and {[EMIM][MeSO₄] (x_1) + acetic acid (x_2)} (*mix*₂). Changes in γ are due to the different distributions of unlike components in the bulk solution and at the surface [439,440]. The negative values of $\Delta\gamma$ indicated that the surface concentration of the component with lower γ is higher than its bulk concentration. Minimums in the $\Delta\gamma$ values were found to be -2.34 mN.m⁻¹, -1.76 mN.m⁻¹, -7.16 mN.m⁻¹ and -4.44 mN.m⁻¹, which occurred at IL mole fractions of $x_1 \approx 0.2$, $x_1 \approx 0.2$, $x_1 \approx 0.6$ and $x_1 \approx 0.9$ from *mix*₁ to *mix*₄ respectively. Minimums in $\Delta\gamma$ values were more negative for mixtures containing the IL [EMIM][BF₄], and for mixtures containing propionic acid. The more negative values for the [EMIM][BF₄] containing binary mixtures indicated that the strength of the intermolecular interaction is in the order; [EMIM][BF₄] > [EMIM][MeSO₄], which could have been caused by the less steric hindrance of the [BF₄]⁻ anion compared to the [MeSO₄]⁻ anion. Stronger interactions were thus established between an IL with a small anion and the acids.

The FTIR spectrums for pure [EMIM][BF₄], [EMIM][MeSO₄], acetic acid, propionic acid and their corresponding binary mixtures (Figure 5.11B) were recorded to further investigate their solute and solvent interactions in the binary mixture. The FTIR spectrums for the binary mixtures were examined at an IL mole fraction of 0.5. The FTIR spectrums displayed that the addition of ILs to carboxylic acids does affect the C=O vibrations of the carboxylic acids. The

evaluation of FTIR spectra gave better clarification about the ion + dipole interaction between IL and acids.

5.3.2. Mixtures of [BMIM][BF₄] or [BMIM][PF₆] with Acetic or Propionic Acid

In this research publication [441], the study was extended to investigate the above-mentioned thermophysical and thermodynamic properties for the binary mixtures of {[BMIM][BF₄] (x_1) + acetic acid (x_2)} (*mix*₅), {[BMIM][PF₆] (x_1) + acetic acid (x_2)} (*mix*₆), {[BMIM][BF₄] (x_1) + propionic acid (x_2)} (*mix*₇) and {[BMIM][PF₆] (x_1) + propionic acid (x_2)} (*mix*₈) at the same experimental conditions and the results obtained are tabulated in Tables 5.1C-5.12C and graphically illustrated in Figures 5.1B - 5.11C (see Appendix C for results). Complete discussion regarding thermophysical properties for studied systems were found elsewhere [441].

The results presented in Figure 5.5C show that the V_m^E values changed from negative for all binary mixtures except for {[BMIM][PF₆] (x_1) + propionic acid (x_2)} (*mix*₈) binary mixtures, which changed from positive to negative. The negative values of V_m^E confirmed the presence of ion-dipole interactions and stronger structure packing effects between the component molecules in the mixtures. The V_m^E values changed sign from negative to positive for *mix*₅, *mix*₆ and *mix*₇, where negative V_m^E values were found at a higher carboxylic acid mole fraction and the positive V_m^E values were located at a higher IL mole fraction.

An increase in the IL in the mixtures reduced the structure packing efficiency, due to the increase in the free volume between the IL ions, and fewer dipoles of carboxylic acids to fit into those free volumes to increase the interactions [355]. As a result, the magnitude of the negative V_m^E values decreased and consequently shifted to positive V_m^E values. Also with further addition of IL in to the carboxylic acid, interactions between the molecules of IL and carboxylic acids are broken in the mixing process, the breaking leads to positive V_m^E values. The V_m^E values shifted from positive to negative for the mixtures of {[BMIM][PF₆] (x_1) + propionic acid (x_2)} (*mix*₈), the addition of the IL to the carboxylic acid caused the self-associated carboxylic acid molecule to be distracted, resulting in positive V_m^E values. Adding more ILs caused hydrogen bonds to form between the carboxylic acid and the ILs, [355,442,443], which lead to negative V_m^E values.

In all the binary mixtures, negative values of k_s^E were obtained as seen in Figure 5.6C, which signified that the mixtures are less compressible than their corresponding ideal mixtures. The free volume in the mixtures was reduced because of a stronger interaction between the mixing molecules, which contributed to the negative k_s^E . Dissimilar molecules approached each other closely in these binary mixtures, forming a stronger interaction. Another point that could have caused the sign of k_s^E to be negative is the loss of mutual dipolar association and the difference in size and shape of the molecules that make up the mixtures. This could cause the free length between the molecules to decrease, making the k_s^E negative. Minimums in the k_s^E values were found to be -141 TPa^{-1} , -94.08 TPa^{-1} , -167.85 TPa^{-1} and -172.46 TPa^{-1} , which occurred at IL mole fractions of $x_1 \approx 0.1$, $x_1 \approx 0.2$, $x_1 \approx 0.2$ and $x_1 \approx 0.3$ from *mix*₅ to *mix*₈ respectively. The minimums in the k_s^E values decreased as the alkyl chain length of the carboxylic acid increased.

The results in Figures 5.7C - 5.8C show that the u^E and Δn_D values were entirely positive for all binary mixtures and increased with increasing IL mole fraction and temperature. Maximums in the positive u^E values were found to be $101.45 \text{ m.s}^{-1} \cdot \text{s}^{-1}$, 38 m.s^{-1} , 114 m.s^{-1} and 89 m.s^{-1} , which occurred at IL mole fractions of $x_1 \approx 0.2$, $x_1 \approx 0.2$, $x_1 \approx 0.3$ and $x_1 \approx 0.3$, from *mix*₅ to *mix*₈ respectively. The maximums in the positive deviations of Δn_D were found to be, 0.017, 0.015, 0.021 and 0.017, which occurred at IL mole fractions of $x_1 \approx 0.3$, $x_1 \approx 0.3$, $x_1 \approx 0.2$ and $x_1 \approx 0.2$, from *mix*₅ to *mix*₈ respectively. The observed positive values the u^E and Δn_D for these binary mixtures suggested the presence of significant interactions involving formation of ion-dipole interactions between the component molecules of the mixture. The magnitude of the positive deviation of u^E and Δn_D increased as the alkyl chain length of the carboxylic acid increased and decreased with increase in the anion constituent of the IL.

With increasing temperature and decreasing IL mole fraction, the L_f increased as seen in Figure 5.9C. The attractive or repulsive forces between molecules in a mixture were explained by intermolecular free length. Although the magnitudes of the forces are identical, the directions of the forces are different. Under external conditions, the forces have the same numerical sign but are in opposing directions.

The results displayed in Figure 5.10C show that the $\Delta\gamma$ values were entirely negative for ILs mixtures with propionic acid and shifted from positive to negative for the IL binary mixture with propionic acid. Knowledge of the surface tension (γ), is essential to comprehend how

microscopic effects influence the macroscopic bulk and surface properties of IL mixtures [355]. The obtained negative $\Delta\gamma$ values suggested that the concentration of the carboxylic acids in the surface region were higher than its concentration in the bulk region. The positive $\Delta\gamma$ values implied that the components were distributed unevenly between the surface and bulk regions of the system. Minimum in the $\Delta\gamma$ values were found to be -0.263 mN.m^{-1} , -0.111 mN.m^{-1} , -1.545 mN.m^{-1} and -1.228 mN.m^{-1} , which occurred at IL mole fractions of $x_1 \approx 0.1$, $x_1 \approx 0.05$, $x_1 \approx 0.7$ and $x_1 \approx 0.8$, from *mix*₅ to *mix*₈ respectively. The magnitude of the negative deviation of $\Delta\gamma$ increased as the alkyl chain length of the carboxylic acid increased and also increased with a decrease in the size of the anion constituent of the IL. Similarly, stronger interactions were established between an IL with a small anion and the acids.

The evaluation of FTIR spectrums in Figure 5.11C confirmed that the addition of [BMIM][BF₄] or [BMIM][PF₆] to acetic or propionic acid influenced the C=O vibrations of the carboxylic acids, indicating the existing ion–dipole interactions between the binary mixtures. The Redlich-Kister polynomial equation was employed to correlate the V_m^E , k_s , k_s^E , u^E , Δn_D and $\Delta\gamma$ and a good and satisfactory correlation was obtained for the binary mixtures and at all investigated temperatures.

5.3.3. Mixtures of Acetophenone with Acetic or Propionic Acid

At temperatures ranging from (293.15 to 333.15) K and pressure of 0.1 MPa, the thermophysical properties of binary mixtures of {acetophenone (x_1) + acetic acid (x_2)} (*mix*₉) and {acetophenone (x_1) + propionic acid (x_2)} (*mix*₁₀). The thermophysical properties measured included of ρ , u , n_D and γ . From the experimentally determined thermophysical properties as a function of acetophenone mole fraction, we calculated the thermodynamic properties of the binary mixtures. The results obtained are summarized in Tables 5.1D-5.8D and graphically displayed in Figures 5.1D - 5.10D (see Appendix D for results). Correlation of the calculated thermodynamic properties was done using the Redlich-Kister polynomial equation, which satisfactory correlated the experimental data for all binary mixtures at the investigated temperatures. The FTIR spectra of pure acetophenone and carboxylic acids as well as their binary mixtures were measured at an equimolar composition (Figure 5.11D). The effects of acetophenone mole fraction, composition and temperature on the thermodynamic properties were discussed. Complete discussion regarding thermophysical properties for studied systems were found elsewhere [444].

The values for ρ and γ for the binary mixtures of acetophenone with acetic acid or propionic acid at temperature of 303.15 and 313.15 K, together with literature data reported by Ahluwalia *et al.* (2016) [445], are given in Figure 5.22 – 5.23 for the comparison purpose. The ρ measurement for the binary mixtures of acetophenone with acetic acid or propionic acid at temperatures at the exact studied temperature is not available, the closest available set of data for the binary mixtures of acetophenone with acetic acid or propionic acid were found at $T=308.15$ and 318.15 K. The values of ρ reported in the literature and our experimental data decreased with increase in acetophenone mole fraction for binary mixtures of acetophenone with acetic acid and further decreased with temperature, while for binary mixtures of acetophenone with propionic acid, the values of ρ reported in the literature and our experimental data increased in acetophenone mole fraction and decreased with temperature. Similar trends were observed between the current work and literature. From Figure. 5.23, it can be observed that γ values shows a notable deviation, which may be related to experimental techniques and/instruments used. In the present method a Du Noüy ring method (Sigma 702, tensiometer) was used in taking the measurement. The Sigma 702 tensiometer allows precise temperature control via its integrated water-jacket vessel holder. In literature, a capillary rise method was used in the taking the measurement and an external temperature regular (Ultra-Cryostat Circulating Bath) was used in regulating the temperature. The use of external temperature regulators increases the probability of human error to occur. Moreover, the γ measurement may be strongly influenced by inter-facially active solutes or impurities that are accidentally introduced into the fluid-fluid system or present on solid surfaces that act as part of the measurement system. Some inter-facially active contaminants can be introduced from the skin or breath of the person taking the measurements.

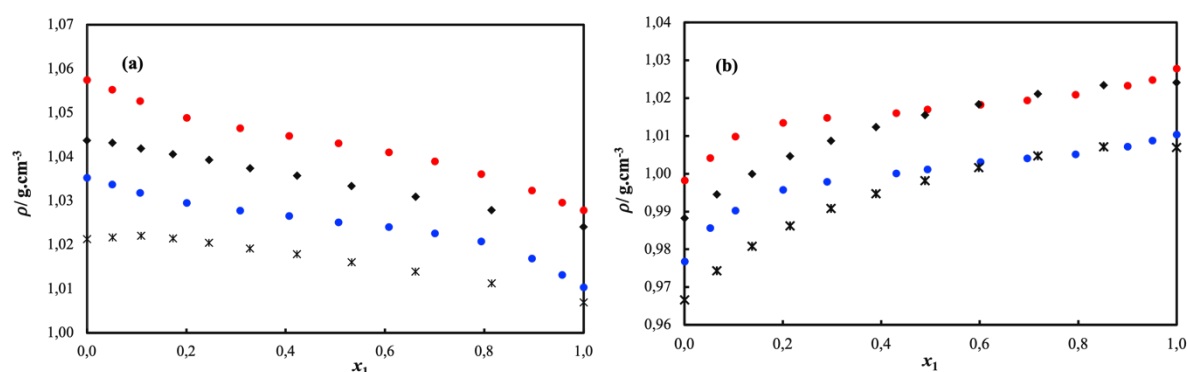


Figure 5.22: Comparison between experimental density (ρ) for the binary mixtures of acetophenone with (a) acetic acid or (b) propionic acid at 293.15 K (●) and 313.15 K (●) and literature density (ρ) [445] at 298.15 K (◆) and 318.15 K (*).

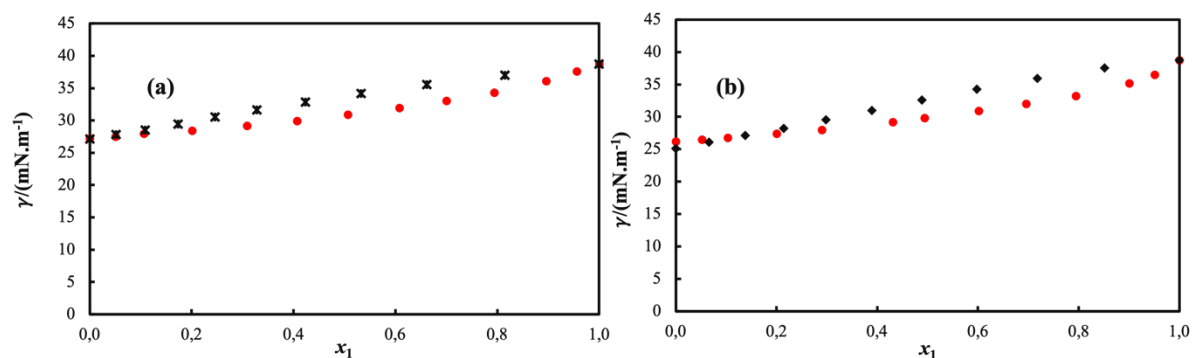


Figure 5.23: Comparison between experimental surface tension (γ) for the binary mixtures of acetophenone with (a) acetic acid or (b) propionic acid at 298.15 K (●) and literature surface tension (γ) [445] at 298.15 K (◆).

The graphs for thermodynamic properties; V_m^E , k_s , k_s^E , u^E , L_f , Δn_D and $\Delta\gamma$ as a function of acetophenone the binary mixture {acetophenone (x_1) + acetic acid (x_2)} (*mix*₉) and {acetophenone (x_1) + propionic acid (x_2)} (*mix*₁₀) are presented in Figures 5.4D-5.10D. The results in Figure 5.55D reveal that the V_m^E values were completely negative for the {acetophenone (x_1) + acetic acid (x_2)} (*mix*₉) binary mixture, and shifted from negative to positive for the {acetophenone (x_1) + propionic acid (x_2)} (*mix*₁₀) binary mixture. A hydrogen bond was formed between the oxygen atom of the C=O group in the acetophenone and the hydrogen atom of the O–H group in carboxylic acids, which resulted in negative V_m^E values [251]. The structural differences between acetophenone and carboxylic acids explained the observed negative values of V_m^E [446, 447]. Due to the fact that acetophenone and carboxylic acids are both polar solvents, a dipole-dipole interaction existed between the components, which contributed to the reduction in free volume, hence negative values [448]. No significant interactions between unlike components were indicated by the positive V_m^E values for {acetophenone (x_1) + propionic acid (x_2)}. Furthermore, Figure 5.5D also demonstrates that the positive V_m^E values were more prevalent at a higher acetophenone mole fraction. When acetophenone were added to propionic acid, it caused the dissociation of hydrogen bonds in the self-associated propionic acid molecule and also disrupted the dipole–dipole interactions between the propionic acid monomers [250,449].

The results displayed in Figure 5.6D show that the values of k_s^E were negative acetophenone binary mixtures. Negative k_s^E values implied that the molecules were close together, which was caused by strong molecular interactions. On the other hand, positive k_s^E values implied a weak

interaction dissimilar component molecules. The sign of k_s^E is a key factor in determining the compactness of a mixture. This is because molecules interact in mixtures through hydrogen bonds, charge transfer, dipole-dipole interactions and dipole-induced dipole interactions, interstitial accommodation, and orientational ordering, which leads to a more compact structure making negative k_s^E values. So, the negative values of k_s^E for both the acetophenone binary mixtures suggested that dipole-dipole interactions are prevailing through H-bonding in the liquid mixtures.

Figure 5.7D present that for both binary mixtures positive u^E values were observed. The u^E indicated an increase in the strength of interaction between component molecules of binary liquid mixtures. Stronger interactions in a mixture, lead to the formation of molecular aggregates and more compact structures. Whereas if the structure-breaking factor in the mixture predominates, resulting in expansion, resulting into negative u^E values.

The variations of Δn_D as a function of the acetophenone volume fraction are shown Figure 5.9D. The results presented in Figure 5.9D show that the Δn_D values changed from negative to positive for the {acetophenone (x_1) + acetic acid (x_2)} (*mix*₉) binary mixture, and entirely positive for the {acetophenone (x_1) + propionic acid (x_2)} (*mix*₁₀) binary mixture. Positive Δn_D values were due to the presence of significant interactions in the mixtures, which included the formation of dipole-dipole interactions and hydrogen bonding between unlike components in the mixture [434,435].

Figure 5.10D show that the $\Delta\gamma$ values were entirely negative for both binary mixtures. Minimums in the $\Delta\gamma$ value were reached at IL mole fractions of $x_1 \approx 0.6$ and $x_1 \approx 0.8$, where $\Delta\gamma$ was found to be -2.286 mN.m^{-1} and -2.944 mN.m^{-1} for the {acetophenone (x_1) + acetic acid (x_2)} (*mix*₉) and {acetophenone (x_1) + propionic acid (x_2)} (*mix*₁₀) binary mixtures respectively. The negative $\Delta\gamma$ values indicated that the concentration of the carboxylic acids in the surface region, which was the component with lower surface tension, was higher than its concentration in the bulk region. The FTIR spectra of both binary mixtures at an equimolar composition Figure 5.11D indicated a change in the C=O stretching vibrations of acetophenone from 1572 cm^{-1} to 1599 cm^{-1} . This indicated the formation of a hydrogen bond ($\text{O-H}\cdots\text{O=C}$) between the mixture components.

5.3.4. Mixtures of [EMIM][BF₄] or [BMIM][BF₄] or [BMIM][PF₆] with Acetophenone

The binary mixtures of current studied ILs with acetophenone were previously studied as a masters research project and published in [367]. The interactions between the binary mixtures of ILs with acetophenone were also investigated through the measurement of thermophysical properties; ρ , u , n_D and viscosity (η) at temperature ranges of (293.15-333.15) K and pressure, $p = 0.1$ MPa. The thermodynamic properties such as V_m^E , Δk_s , Δn_D and deviation in viscosity ($\Delta\eta$) were determined from the measured thermophysical properties and further correlated with the Redlich–Kister polynomial equation. The binary parameters obtained from correlating the binary data with the Redlich–Kister polynomial equation were further used in modelling the V_{m123}^E and Δk_{s123} properties of the ternary mixtures of the current study. Similar to the binary mixtures of IL with the carboxylic acids, the ρ and u values of binary mixtures of ILs with acetophenone increased with increase in IL mole fraction and decreased temperature. In the contrary, the values of n_D decreased with increase in the IL mole fraction.

The results obtained for the V_m^E for binary mixture were positive for binary mixtures containing ILs [BMIM][BF₄] or [BMIM][PF₆], while both positive and negative values were obtained for binary mixture containing [EMIM][BF₄]. The negative values of V_m^E were found at a lower IL mole fraction and became positive at a high IL mole fraction. This was due to the weakening of the ion-dipole interaction and the dominance of IL-IL interaction at high IL mole fraction. Moreover, the negative values of V_m^E reveal that a more efficient packing occurred at a low IL mole fraction due to the difference in size between the components in the mixture. On the other hand the positive values of V_m^E suggested that the interactions between unlike are weaker compared to like molecules. The results obtained for the Δk_s , displayed shift from negative to and positive values, with positive values found at a high IL mole fraction. The negative Δk_s values were attributed to the strong attractive interactions of the ions in the mixtures. The positive Δk_s might be due to a decrease in attraction of acetophenone and that between IL to acetophenone decreases. The results obtained for the Δn_D for binary mixture were both positive and negative. The positive values of Δn_D indicated the stronger interactions of ions of ILs with acetophenone and negative values attributed to weaker interaction ions of ILs with acetophenone. The positive or negative V_m^E values corresponded with the negative or positive Δn_D values of the corresponding binary mixture whereby the minimum or maximum of both properties existed at almost the same mole fraction of IL. This observation was in agreement with the view proposed by Brocos *et al.* (2003) [436].

5.3.5. Mixtures of [BMIM]⁺ Based Ionic Liquids with Acetophenone and Acetic or Propionic Acid

This section presents the experimental results of ρ_{123} , u_{123} , V_{m123}^E and Δk_{s123} for the ternary mixtures of {[BMIM][BF₄](x_1) + acetic acid (x_2) + acetophenone (x_3)}(*mix*₁), {[BMIM][BF₄]⁻(x_1) + propionic acid (x_2) + acetophenone (x_3)}(*mix*₂), and {[BMIM][PF₆](x_1) + acetic acid (x_2) + acetophenone (x_3)}(*mix*₃) at 293.15 - 333.15 K and pressure 0.1 MPa. The obtained results are listed in Tables 5.1E - 5.3E of Appendix E. The computed values of V_{m123}^E and Δk_{s123} were found to be both positive and negative. This proposed that the ternary mixtures are not ideal mixtures in terms of binary components. Complete discussion regarding thermophysical and thermodynamic properties for studied systems were found elsewhere [450].

The V_{m123}^E and Δk_{s123} properties of the ternary mixtures were modelled using the sum of a predictive term (no estimated parameter) and a correlative term (estimated parameters) as shown in Equation 5.4. The entire model was a correlative model, which became a predictive model only when all parameters of the correlative term were set to zero.

$$Y_{123} = Y_{123}^{predictive} + Y_{123}^{correlative} \quad (5.4)$$

The predictive term ($Y_{123}^{predictive}$) was derived from the binary mixtures using Equation 5.5 below.

$$Y_{ij}(x_i, x_j) = x_i x_j \sum_{k=1}^{N^{parbin}} A_k^{i,j} (x_j - x_i)^{k-1} \quad (5.5)$$

whereby, N^{parbin} denotes the number of parameters utilized to model the binary property and $A_k^{i,j}$ represents the binary property's k-th parameter (i,j). All of the binary parameters were calculated by correlating the respective binary data (Tables 5.33 - 5.35D) of Appendix D. Tables 5.1 -5.2 shows the predictive and correlative terms that were tested [305,451].

Table 5.1: Predictive terms that were tested in this work.

Model	$\mathbf{Y}_{123}^{predictive}$
1. Redlich-Kister [451]	$Y_{12}(x_1, x_2) + Y_{13}(x_1, x_3) + Y_{23}(x_2, x_3)$
2. Tao-Smith [451]	$\frac{x_2}{1-x_1} Y_{12}(x_1, 1-x_1) + \frac{x_3}{1-x_1} Y_{13}(x_1, 1-x_1) + (1-x_1) Y_{23}(x'_2, x'_3)$
3. Kohler [451]	$(x_1 + x_2)^2 Y_{12}(x'_1, x'_2) + (x_1 + x_3)^2 Y_{13}(x'_1, x'_3) + (x_2 + x_3)^2 Y_{23}(x'_2, x'_3)$
4. Colinet [451]	$\frac{1}{2} \left[\frac{x_2}{1-x_1} Y_{12}(x_1, 1-x_1) + \frac{x_1}{1-x_2} Y_{12}(1-x_2, x_2) + \frac{x_3}{1-x_1} Y_{13}(x_1, 1-x_1) \right.$ $+ \frac{x_1}{1-x_3} Y_{13}(1-x_3, x_3) + \frac{x_3}{1-x_2} Y_{23}(x_2, 1-x_2)$ $\left. + \frac{x_2}{1-x_3} Y_{23}(1-x_3, x_3) \right]$
5. Scatchard <i>et al.</i> [451]	$\frac{x_2}{1-x_1} Y_{12}(x_1, 1-x_1) + \frac{x_3}{1-x_1} Y_{13}(x_1, 1-x_1) + Y_{23}(x_2, x_3)$
6. Toop [451]	$\frac{x_2}{1-x_1} Y_{12}(x_1, 1-x_1) + \frac{x_3}{1-x_1} Y_{13}(x_1, 1-x_1) + (1-x_1)^2 Y_{23}(x'_2, x'_3)$
7. Muggianu <i>et al.</i> [451]	$\frac{x_1 x_2}{\chi_1^{12} \chi_2^{12}} Y_{12}(\chi_1^{12}, \chi_2^{12}) + \frac{x_1 x_3}{\chi_1^{13} \chi_3^{13}} Y_{13}(\chi_1^{13}, \chi_3^{13}) + \frac{x_2 x_3}{\chi_2^{23} \chi_3^{23}} Y_{23}(\chi_2^{23}, \chi_3^{23})$ $\chi_i^{ij} = \frac{1 + x_i - x_j}{2}$
8. Hiller [451]	$\frac{x_2}{1-x_1} Y_{12}(x_1, 1-x_1) + \frac{x_3}{1-x_1} Y_{13}(x_1, 1-x_1) + \frac{x_2 x_3}{\chi_2^{23} \chi_3^{23}} Y_{23}(\chi_2^{23}, \chi_3^{23})$ $\chi_i^{ij} = \frac{1 + x_i - x_j}{2}$
9, “average” [305]	$\frac{(x_1 + x_2)Y'_{12} + (x_2 + x_3)Y'_{23} + (x_1 + x_3)Y'_{13}}{2}$

Table 5.2: Correlative terms that were tested in this work.

Model	$\mathbf{Y}_{123}^{correlative}$	Ref.
1. Cibulka	$x_1 x_2 x_3 [A_0 + A_1 x_1 + A_2 x_2]$	[297]

2. 1p-Cibulka	$x_1x_2x_3A_0$	[297], tw
3. Rastogi <i>et al.</i>	$x_1x_2x_3[A_0 + A_1x_1(x_2 - x_3) + A_2x_1^2(x_2 - x_3)^2]$	[305]
4. 5p-model	$x_1x_2x_3[A_0 + A_1(x_2 - x_1) + A_2(x_3 - x_2) + A_3(x_2 - x_1)^2 + A_4(x_3 - x_2)^2]$	[452], tw
5. 7p-model	$x_1x_2x_3[A_0 + A_1(x_2 - x_1) + A_2(x_3 - x_2) + A_3(x_2 - x_1)^2 + A_4(x_3 - x_2)^2 + A_5(x_2 - x_1)^3 + A_6(x_3 - x_2)^3]$	tw
6. 9p-model	$x_1x_2x_3[A_0 + A_1(x_2 - x_1) + A_2(x_3 - x_2) + A_3(x_2 - x_1)^2 + A_4(x_3 - x_2)^2 + A_5(x_2 - x_1)^3 + A_6(x_3 - x_2)^3 + A_7(x_2 - x_1)^4 + A_8(x_3 - x_2)^4]$	tw
7. 11p-model	$x_1x_2x_3[A_0 + A_1(x_2 - x_1) + A_2(x_3 - x_2) + A_3(x_2 - x_1)^2 + A_4(x_3 - x_2)^2 + A_5(x_2 - x_1)^3 + A_6(x_3 - x_2)^3 + A_7(x_2 - x_1)^4 + A_8(x_3 - x_2)^4 + A_9(x_2 - x_1)^5 + A_{10}(x_3 - x_2)^5]$	tw

tw stands for this work

The standardized deviation of the parameter was given by Equation 5.6 below:

$$\sigma = \sqrt{\sum_{i=1}^{Nexp} \frac{(Y_{calc_i} - Y_{exp_i})^2}{Nexp - Npar}} \quad (5.6)$$

where, Y denotes the modelled property, $Nexp$ represents the number of experimental data, and $Npar$ is the number of estimated parameters. Since this metric applied the number of degrees of freedom in the parameter estimation, a model with more parameters than the other may present a higher σ .

All the predictive models were tested along with correlative models, with each predictive term combining with each correlative term to produce 63 correlative models. The metric below was used to select the best model among the 63 possibilities (9 predictive terms with each of the 7

correlative terms), and also to exclude of the modelling highly nonideal data. The procedure was as follows:

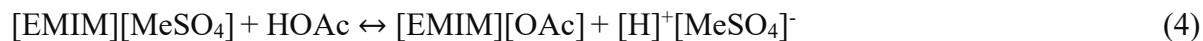
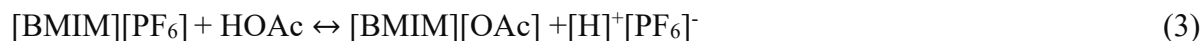
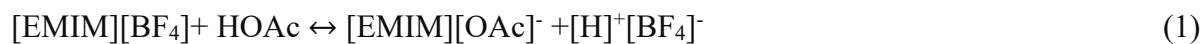
- the parameters for all the 63 models were determined and the model with the lowest σ was selected to test the datum for which this best model had the highest absolute deviation;
- this data was temporarily excluded and a new parameter estimation was performed using the previously selected model;
- if the model deviation for the tested datum was inside the 95% confidence level of the deviations for the rest of the data, the datum was kept in the modelling and this evaluation procedure was stopped;
- however, if the model deviation for the tested datum was outside the 95% confidence level of the deviations for the rest of the data, the datum was removed from the modelling and this evaluation was repeated up to a maximum of 3 data removed.
- The procedure cited allowed finding the best model for each property at each temperature for each mixture.

Tables 5.7E - 5.9E of Appendix E summarize the modelling results of V_{m123}^E and Δk_{s123} with contour plots from the best models displayed in Figures 5.1E - 5.6E of Appendix E. The best predictive term for the ternary mixture of {[BMIM][BF₄](x_1) + acetic acid (x_2) + acetophenone (x_3)} (mix_1) was the 1 (Redlich-Kister), while for {[BMIM][BF₄](x_1) + propionic acid (x_2) + acetophenone (x_3)} (mix_2) and {[BMIM][BF₄](x_1) + acetic acid (x_2) + acetophenone (x_3)} (mix_3) was the 9 (“average”). For the correlative term, the best models were 2 (1p-Cibulka) (mix_1 , Δk_{s123}), 4 (5p-model) (mix_1 and mix_2 , V_{m123}^E), 5 (7p-model) and 6 (9p-model) (mix_3 , Δk_{s123}) depending on the temperature; and 7 (11p-model) (mix_2 , Δk_{s123} , mix_3 , V_{m123}^E , and mix_3 , Δk_{s123} at 333.15 K), hence all the parameters might be presented as model 7. These results show that the mix_1 properties were easier to correlate with fewer parameters than properties of mix_2 and mix_3 .

The average standardized deviation (σ) for the V_{m123}^E of mix_3 was about twice the values for mixtures mix_1 and mix_2 , even using more parameters. The σ for Δk_{s123} were in the same range for the three mixtures, even though only one parameter was used in each temperature for mix_1 and up to eleven in mix_2 and mix_3 . These results indicated that the non-ideality qualitatively was in the order: $mix_3 > mix_2 > mix_1$.

5.4 Anion Exchange in Ionic Liquids-Carboxylic Acid Binary Mixtures

In this section, the possibility of anion exchange in mixtures of IL and carboxylic acid is discussed. In-theory, ion exchange can occur between an IL and any other ionic compound, such as salts or acid. Even though the idea of ion pairs in an IL is controversial [376], it stands to reason that in any mixture of two cations and two anions, one ion would associate preferentially with another. To evaluate the possibility of anion exchange in the current studied binary mixtures, the equimolar composition of the binary mixtures will be taken into consideration. The acetic acid (CH_3COOH) dissociate into H^+ and CH_3COO^- and anion exchange reactions for the binary mixture of $\{[\text{EMIM}][\text{BF}_4] (x_1) + \text{acetic acid} (x_2)\}$ (mix_1), $[\text{EMIM}][\text{MeSO}_4] (x_1) + \text{acetic acid} (x_2)\}$ (mix_2), $\{[\text{BMIM}][\text{BF}_4] (x_1) + \text{acetic acid} (x_2)\}$ (mix_5) and $\{[\text{BMIM}][\text{PF}_6] (x_1) + \text{acetic acid} (x_2)\}$ (mix_6) at an equimolar composition may be represented as:



From the reactions above, there is a possibility of two different ILs forming at an equimolar composition, which are 1-ethyl-3-methylimidazolium acetate ($[\text{EMIM}][\text{OAc}]$) and 1-butyl-3-methylimidazolium acetate ($[\text{BMIM}][\text{OAc}]$). In order to establish that anion exchange occurred, the ρ data of binary mixtures of $\{[\text{EMIM}][\text{BF}_4] (x_1) + \text{acetic acid} (x_2)\}$ (mix_1), $[\text{EMIM}][\text{MeSO}_4] (x_1) + \text{acetic acid} (x_2)\}$ (mix_2), $\{[\text{BMIM}][\text{BF}_4] (x_1) + \text{acetic acid} (x_2)\}$ (mix_5) and $\{[\text{BMIM}][\text{PF}_6] (x_1) + \text{acetic acid} (x_2)\}$ (mix_6) at an equimolar composition is compared with existing ρ data of pure $[\text{EMIM}][\text{OAc}]$ and $[\text{BMIM}][\text{OAc}]$ from the literature.

Tables 5.3-5.6B and Table 5.3C-5.6C of Appendix A and B shows that the values the ρ data for the binary mixtures of $\{[\text{EMIM}][\text{BF}_4] (x_1) + \text{acetic acid} (x_2)\}$ (mix_1), $[\text{EMIM}][\text{MeSO}_4] (x_1) + \text{acetic acid} (x_2)\}$ (mix_2), $\{[\text{BMIM}][\text{BF}_4] (x_1) + \text{acetic acid} (x_2)\}$ (mix_5) and $\{[\text{BMIM}][\text{PF}_6] (x_1) + \text{acetic acid} (x_2)\}$ (mix_6) at an equimolar composition and at temperature 293.15K are

1.230 g.cm⁻³, 1.251 g.cm⁻³, 1.173 g.cm⁻³, 1.251 g.cm⁻³ and 1.296 g.cm⁻³ respectively. On the other hand, the literature ρ data of pure [EMIM][OAc] were found to be ± 1.1030 g.cm⁻³ [453; 454], while for [BMIM][OAc] the ρ values were found to be ± 1.1056 g.cm⁻³ [455; 456]. It is clearly evident that the experimental ρ values of the current studied binary mixtures at an equimolar composition are different from the ρ data of the pure [EMIM][OAc] and [BMIM][OAc] obtained from the literature. This finding suggested that anion exchange between the IL and the acid may have not occur rather the components in the mixtures interacted with each other through other forces which include the ion-dipole interaction as well as hydrogen bonding.

Naert *et al.* (2018) [390] proposed a theory that the IL anion exchange is dependent on the charge density of the anion and that anion exchange is anticipated with higher charge density anion. They also stated that fluorinated low charge density anions is unsuceptible to anion exchange. These anions exhibit a weak electrostatic interaction with the cation. The typical higher charge density anion such as HSO₄, NO₃ and carboxylates, are inherently more susceptible to anion exchange. According to the theory proposed by Naert *et al.* (2018), it can be assumed that there is no substantial exchange take place in IL [EMIM][BF₄], [BMIM][BF₄] and [BMIM][BF₆] and acetic acid mixtures and there is a possible of ion-exchange for binary mixture of [EMIM][MeSO₄] with the acetic acid. The [MeSO₄] is a high-density anion.

Even through, ion exchange can theoretically take place in a mixture of two cations and two anions, in the current study the possible anion exchange results were inconclusive. The thermodynamic analysis alone cannot predict anion exchange in the mixtures. Different types of techniques needs to be employed to determine the structure formed at an equimolar composition and thus confirm the anion exchange.

5.5 Influence of the Anion and Alkyl Side Chain Length on Thermophysical Properties

The chosen ILs allows us to investigate the effect of the nature of the anion, its sphericity, and size and the effect of the alkyl side chain length attached to the nitrogen of the imidazolium cation. In this section the effect of the anion on the thermophysical properties were investigated between [EMIM][BF₄] and [EMIM][MeSO₄]; as well as [BMIM][BF₄] and [BMIM][PF₆]. The

influence of the alkyl side chain length attached to the nitrogen of the imidazolium cation were discussed between [BMIM][BF₄] and [EMIM][BF₄].

The binary mixtures containing [EMIM][MeSO₄] and [BMIM][PF₆] appeared to have higher values of ρ than the binary mixtures containing [EMIM][BF₄] and [BMIM][BF₄]. This indicated that, for ILs with a common cation but different anions, the ρ values increased with the size of the anion; this observation was consistent with existing reports [450, 457-459]. The values of u and Δn_D for the binary mixtures containing [EMIM][MeSO₄] were higher than the [EMIM][BF₄] containing binary mixtures. The u and Δn_D values increased with increase in the size of the anion ([MeSO₄]⁻ > [BF₄]⁻). In contrast to the latter, the values of u and Δn_D for the [BMIM][PF₆] containing binary mixture were lower than the [BMIM][BF₄] containing binary mixtures. These values decreased with increase in size of the anion ([PF₆]⁻ < [BF₄]⁻). The decrease in u and Δn_D values with increase in size of an anion was linked to a decrease in the ion-ion interaction, which was due to an increase in the distance between the cation and anion in solution. It was simple for a smaller anion to hold a position closer relative to the large cation. The [PF₆]⁻ anion is greater in size compared to the [BF₄]⁻ ion. Only a slight difference in size between the [MeSO₄]⁻ and [BF₄]⁻ ions is observed. The γ for binary mixtures containing [EMIM][MeSO₄] and [BMIM][PF₆] appeared to have higher values of γ as compared to the [EMIM][BF₄] and [BMIM][BF₄] containing binary mixtures. The γ of IL binary mixture containing the same cation increased with increasing molecular size of the anion.

Moving to the influence of alkyl side chain length attached to the nitrogen of the imidazolium cation on the thermophysical properties of IL binary mixtures, it was found that for the studied ILs binary mixtures, the values of ρ decreased when the side alkyl chain length of the cation increased. The decrease in mixtures ρ were reasoned in terms of the packing efficiency of the molecules. With an elongation in the alkyl side chain length of the cation, the density charge on the cation decreased and the molar volume increased, leading to a less packing efficiency, thus a decrease in ρ values [460,461].

Similar to the ρ data, the values of u for the investigated IL binary mixtures increased as alkyl chain length of the cation decreased. This order indicated that ILs with a lower alkyl side chain length interacted more strongly with the carboxylic acids than ILs with a longer alkyl side chain length. The values of Δn_D of the studied ILs binary mixtures, increased with increase in the

side alkyl chain length of the cation. There was an inverse relationship established between the variation of Δn_D and the variation in ρ , whereby the two were nearly mirror images of one another. Given that the n_D of a molecule is used as a measure of its electronic polarizability and gives important information, from a qualitative point of view, when investigating the forces existing between molecules or their behaviour in solution [462], our findings were consistent with the assertion that the length of an alkyl chain is proportional to the Δn_D [463]. The values of γ for the studied ILs binary mixtures appeared to have decreased as the alkyl chain length of the cation increased. For the imidazolium-based ILs, this phenomenon was reported by various groups [464-466].

5.6 Influence of Temperature on the Thermodynamic Properties

In this section, the variations of the thermodynamic properties V_m^E , k_s , k_s^E , u^E , L_f and Δn_D with temperature were discussed. As already mentioned, the thermodynamic properties for the binary mixtures [EMIM][BF₄] or [BMIM][BF₄] or [BMIM][PF₆] or [EMIM][MeSO₄] with acetic acid or propionic acid were investigated at temperatures between 293.15 and 333.15 K with 10 K intervals. The type of interactions taking place between the binary mixtures have already been established in this discussion.

The values of V_m^E and k_s^E decreased with increase in temperature for all of the IL binary mixtures examined, except for V_m^E values for binary mixtures of [BMIM][PF₆] with acetic or propionic acid binary mixtures. The decrease was due to weakening of interaction between like molecules (IL+IL) or (carboxylic acid + carboxylic acid), and the strengthening of ion-dipole interactions between unlike components [467-469]. In other words, ion-dipole interactions between unlike components in mixtures dominated at high temperatures. Also with increase in temperature, there was a better packing efficiency between the mixing components, which were caused by the expansion in free volume between the IL ions [470]. The increase in V_m^E values with temperature were related to a decrease in the magnitude of hydrogen bonding between dissimilar component molecules in the mixtures. Literature [471-473] has reported a similar effect of temperature on in V_m^E values.

The values of u^E and Δn_D became more positive with increase in temperature for all of the IL binary mixtures examined. The larger the positive values of u^E and Δn_D in binary mixtures, the stronger was the intermolecular interaction taking place in the mixtures. Furthermore, for all

ILs binary mixtures examined, the values of L_f were found to be directly proportional to temperature. High temperatures disrupted the intermolecular interaction of the mixing components in such a way that the structure and bonds established after the molecules had mixed, became disordered or break, causing the molecules to move apart, thus increasing the values of L_f [3, 474,475]. The compressibility increased as the temperature increased, and the u decreased, resulting in an increase in the values of L_f [476].

5.7 Mixtures of [EMIM] Based Ionic Liquid with Acetophenone and Acetic or Propionic Acid

The thermophysical and thermodynamic properties including ρ_{123} , u_{123} , V_{m123}^E and Δk_{s123} of pure IL, carboxylic acids and acetophenone as well as their ternary mixtures were examined throughout the mole fraction of {[EMIM][BF₄](x_1) + acetic acid (x_2) + acetophenone (x_3)} (*mix*₄) and {[EMIM][BF₄](x_1) + propionic acid (x_2) + acetophenone (x_3)} (*mix*₅) at (293.15 to 333.15) K and pressure 0.1 MPa. The results obtained are presented in Tables 5.3 – 5.4.

Table 5.3: Mole fraction (x_1 , x_2 , x_3), density (ρ_{123}), sound velocity (u_{123}), excess molar volume (V_{m123}^E) and deviation in isentropic compressibility (Δk_{s123}) for the ternary mixture of {[EMIM][BF₄](x_1) + acetic acid (x_2) + acetophenone (x_3)} (*mix*₄) at T = 293.15 – 333.15 K and at pressure, p = 0.1 Mpa.

x_1	x_2	x_3	ρ / g.cm ⁻³	u / m.s ⁻¹	V_{m123}^E / cm ⁻³ .mol ⁻¹	Δk_{s123} / Tpa ⁻¹
293.15 K						
0.2688	0.5254	0.2058	1.1552	1500	-0.599	267206
0.3724	0.3465	0.2812	1.1691	1527	-0.269	159385
0.4331	0.2400	0.3269	1.1841	1559	-0.935	126187
0.1291	0.8333	0.0376	1.1265	1338	-0.524	177717
0.3097	0.5997	0.0906	1.1794	1476	-0.701	239274
0.4363	0.4327	0.1310	1.1879	1536	-	234980
0.5060	0.3507	0.1433	1.2120	1563	-0.532	196258
0.5856	0.2451	0.1693	1.1946	1578	-	175145
0.6819	0.1224	0.1956	1.2301	1606	-0.250	82245
0.4120	0.5490	0.0390	1.2045	1507	-0.352	238505
0.5680	0.3683	0.0637	1.2299	-	-0.402	-
0.6780	0.2570	0.0651	-	-	-	-
0.7909	0.1349	0.0741	1.2556	-	-0.162	-
0.8563	0.0599	0.0837	1.2608	1625	-0.073	37185
0.0372	0.6556	0.3072	-	-	-	-

0.0493	0.5433	0.4074	1.0651	1361	-	58786
0.0616	0.4317	0.5067	1.0678	-	-0.541	-
0.0737	0.3223	0.6039	1.0687	-	-0.606	-
0.0841	0.2230	0.6928	1.0691	1484	-	89391
0.0967	0.1069	0.7964	1.0697	1505	-0.736	43062
0.1083	0.7056	0.1861	1.1041	1373	-0.491	178315
0.1935	0.4767	0.3297	1.1261	1466	-0.857	178474
0.2283	0.3815	0.3902	1.1032	1468	-	138254
0.2947	0.2073	0.4980	1.1419	1535	-1.074	95357
303.15 K						
0.2688	0.5254	0.2058	1.1466	-	-0.651	-
0.3724	0.3465	0.2812	1.1605	1498	-0.284	161 931
0.4331	0.2400	0.3269	1.1759	1532	-0.986	132 401
0.1291	0.8333	0.0376	1.1170	1307	-0.558	179 344
0.3097	0.5997	0.0906	1.1707	1448	-0.742	242 676
0.4363	0.4327	0.1310	1.1795	1509	-	236 832
0.5060	0.3507	0.1433	1.2038	1537	-0.571	200 154
0.5856	0.2451	0.1693	1.1859	1552	-	179 543
0.6819	0.1224	0.1956	1.2223	1581	-0.280	86 320
0.4120	0.5490	0.0390	1.1960	1480	-0.383	241 952
0.5680	0.3683	0.0637	1.2218	-	-0.433	-
0.6780	0.2570	0.0651	-	-	-	-
0.7909	0.1349	0.0741	1.2496	-	-0.376	-
0.8563	0.0599	0.0837	1.2530	1601	-0.080	38491
0.0372	0.6556	0.3072	1.0540	-	-0.242	-
0.0493	0.5433	0.4074	1.0555	-	-0.321	-
0.0616	0.4317	0.5067	1.0588	1404	-0.562	155 149
0.0737	0.3223	0.6039	1.0598	1428	-0.633	119 637
0.0841	0.2230	0.6928	1.0604	1449	-0.698	89 772
0.0967	0.1069	0.7964	1.0612	1471	-0.774	44 669
0.1083	0.7056	0.1861	1.0947	1341	-0.517	179156
0.1935	0.4767	0.3297	1.1173	1435	-	179 867
0.2283	0.3815	0.3902	1.0944	1436	-	139844
0.2947	0.2073	0.4980	1.1336	1504	-1.128	99 172
313.15 K						
0.2688	0.5254	0.2058	1.1381	-	-0.731	-
0.3724	0.3465	0.2812	1.1519	1470	-0.308	165247
0.4331	0.2400	0.3269	1.1679	1504	-1.052	135955
0.1291	0.8333	0.0376	1.1074	1278	-0.628	181323
0.3097	0.5997	0.0906	1.1620	1421	-0.813	243465
0.4363	0.4327	0.1310	1.1712	1482	-	239380
0.5060	0.3507	0.1433	1.1957	1511	-0.628	202554
0.5856	0.2451	0.1693	1.1767	1527	-	184335
0.6819	0.1224	0.1956	1.2145	1556	-0.318	90023
0.4120	0.5490	0.0390	1.1875	1454	-0.441	243186
0.5680	0.3683	0.0637	1.2137	-	-0.481	-
0.6780	0.2570	0.0651	-	-	-	-
0.7909	0.1349	0.0741	1.2426	-	-0.485	-
0.8563	0.0599	0.0837	1.2453	1577	-0.088	40259
0.0372	0.6556	0.3072	1.0444	-	-0.279	-
0.0493	0.5433	0.4074	1.0459	-	-0.330	-
0.0616	0.4317	0.5067	1.0497	1373	-0.602	159072
0.0737	0.3223	0.6039	1.0510	1395	-0.676	121979
0.0841	0.2230	0.6928	1.0517	1416	-0.742	90249

0.0967	0.1069	0.7964	1.0527	1436	-0.819	45545
0.1083	0.7056	0.1861	1.0853	1435	-0.574	183046
0.1935	0.4767	0.3297	1.1085	1405	-	181601
0.2283	0.3815	0.3902	1.0856	1406	-	141872
0.2947	0.2073	0.4980	1.1253	1474	-1.195	101765
323.15 K						
0.2688	0.5254	0.2058	1.1297	-	-0.787	-
0.3724	0.3465	0.2812	1.1433	1442	-0.309	166047
0.4331	0.2400	0.3269	1.1598	1477	-1.108	138400
0.1291	0.8333	0.0376	1.0980	1252	-0.655	185447
0.3097	0.5997	0.0906	1.1534	1394	-0.855	243515
0.4363	0.4327	0.1310	1.1630	1457	-	241191
0.5060	0.3507	0.1433	1.1876	1486	-0.669	204271
0.5856	0.2451	0.1693	1.1674	1502	-	188767
0.6819	0.1224	0.1956	1.2068	1531	-0.351	93213
0.4120	0.5490	0.0390	1.1791	1429	-0.473	243764
0.5680	0.3683	0.0637	1.2056	-	-0.508	-
0.6780	0.2570	0.0651	-	-	-	-
0.7909	0.1349	0.0741	1.2356	-	-0.584	-
0.8563	0.0599	0.0837	1.2377	1553	-0.101	42090
0.0372	0.6556	0.3072	1.0348	-	-0.280	-
0.0493	0.5433	0.4074	1.0331	-	-0.038	-
0.0616	0.4317	0.5067	1.0406	1343	-0.619	164478
0.0737	0.3223	0.6039	1.0421	1364	-0.702	124614
0.0841	0.2230	0.6928	1.0430	1382	-0.775	90645
0.0967	0.1069	0.7964	1.0441	1402	-0.860	46059
0.1083	0.7056	0.1861	1.0759	1285	-0.593	188852
0.1935	0.4767	0.3297	1.0998	1376	-1.007	183194
0.2283	0.3815	0.3902	1.0768	1377	-	143873
0.2947	0.2073	0.4980	1.1171	1444	-1.254	104149
333.15 K						
0.2688	0.5254	0.2058	1.1213	1390	-1.092	270825
0.3724	0.3465	0.2812	1.1347	1416	-0.474	168735
0.4331	0.2400	0.3269	1.1519	1451	-1.284	139595
0.1291	0.8333	0.0376	1.0885	1230	-1.074	189368
0.3097	0.5997	0.0906	1.1449	1372	-1.182	246624
0.4363	0.4327	0.1310	1.1548	1435	-	245323
0.5060	0.3507	0.1433	1.1797	1463	-0.878	206956
0.5856	0.2451	0.1693	1.1590	1478	-	188975
0.6819	0.1224	0.1956	1.1991	1507	-0.447	94631
0.4120	0.5490	0.0390	-	-	-	-
0.5680	0.3683	0.0637	-	-	-	-
0.6780	0.2570	0.0651	-	-	-	-
0.7909	0.1349	0.0741	1.2287	-	-0.752	-
0.8563	0.0599	0.0837	1.2301	1530	-0.135	43176
0.0372	0.6556	0.3072	1.0253	-	-0.589	-
0.0493	0.5433	0.4074	1.0266	1234	-	62917
0.0616	0.4317	0.5067	1.0315	-	-0.842	-
0.0737	0.3223	0.6039	1.0333	-	-0.886	-
0.0841	0.2230	0.6928	1.0344	1351	-0.921	90987
0.0967	0.1069	0.7964	1.0356	1369	-0.961	44476
0.1083	0.7056	0.1861	1.0666	1264	-0.946	200160
0.1935	0.4767	0.3297	1.0912	1350	-1.280	186394
0.2283	0.3815	0.3902	1.0679	1351	-	148442

0.2947	0.2073	0.4980	1.1089	1415	-1.420	103429
Standard uncertainties u are; $u(T) = 0.02$ K, $u(p) = 0.04$ MPa and the combined expanded uncertainty Uc in mole fraction, density and sound velocity were $Uc(x) = 0.0005$, $Uc(\rho) = 0.006$ g.cm ⁻³ and $Uc(u) = 2$ m.s ⁻¹ , respectively, (0.95 level of confidence).						

Table 5.4: Mole fraction (x_1 , x_2 , x_3), density (ρ_{123}), sound velocity (u_{123}), excess molar volume (V_{m123}^E) and deviation in isentropic compressibility (Δk_{s123}) for the ternary mixture of {[EMIM][BF₄] (x_1) + propionic acid (x_2) + acetophenone (x_3)} (mix_5) at T = 293.15 – 333.15 K and at pressure, p = 0.1 Mpa.

x_1	x_2	x_3	ρ / g.cm ⁻³	u / m.s ⁻¹	V_{m123}^E / cm ³ .mol ⁻¹	Δk_{s123} / Tpa ⁻¹
293.15 K						
0.2990	0.4743	0.2266	1.1390	1463	-1.112	104590
0.4019	0.2944	0.3037	1.1598	1521	-0.512	83831
0.4526	0.2054	0.3420	1.1727	1550	-0.664	71483
0.1544	0.8013	0.0444	1.0337	1492	3.672	632406
0.3490	0.5490	0.1020	1.1608	1460	-1.421	127673
0.4789	0.3764	0.1447	1.1886	1526	-0.916	120147
0.5425	0.3044	0.1531	1.2031	1552	-	110544
0.6131	0.2090	0.1779	1.2107	1574	-0.238	82283
0.7004	0.1012	0.1984	1.2307	1604	-0.688	46092
0.4614	0.4952	0.0434	1.1889	1495	-0.969	135332
0.6254	0.3154	0.0593	1.2276	1542	-	61202
0.7130	0.2195	0.0675	1.2362	1587	-0.340	89882
0.8131	0.1110	0.0759	-	-	-	-
0.8711	0.0440	0.0850	1.3109	1624	-5.831	-64437
0.0507	0.5344	0.4149	1.0441	1384	-0.710	89464
0.0554	0.4904	0.4542	-	-	-	-
0.0672	0.3810	0.5517	1.0540	-	-0.845	-
0.0782	0.2786	0.6432	1.0577	1462	-0.709	71321
0.0880	0.1881	0.7239	1.0635	-	-0.890	-
0.0989	0.0889	0.8122	1.0419	1484	1.974	15008
0.1252	0.6615	0.2132	1.0500	1416	1.340	273479
0.2122	0.4258	0.3619	1.1099	1457	-1.205	93433
0.2477	0.3314	0.4210	1.1198	1489	-	88428
0.3054	0.1743	0.5203	1.1356	1536	-1.232	62688
303.15 K						
0.2990	0.4743	0.2266	1.1305	1434	-1.195	112812
0.4019	0.2944	0.3037	1.1516	1492	-0.576	89762
0.4526	0.2054	0.3420	1.1646	1522	-0.719	77148
0.1544	0.8013	0.0444	1.0277	1471	3.384	653299
0.3490	0.5490	0.1020	1.1544	1433	-1.698	134488
0.4789	0.3764	0.1447	1.1804	1499	-0.988	127636
0.5425	0.3044	0.1531	1.1950	1526	-0.982	117231
0.6131	0.2090	0.1779	1.2027	1547	-	86923
0.7004	0.1012	0.1984	1.2230	1578	-0.733	50702

0.4614	0.4952	0.0434	1.1808	1465	-1.065	136023
0.6254	0.3154	0.0593	1.2098	1517	-	82937
0.7130	0.2195	0.0675	1.2280	1562	-0.343	94975
0.8131	0.1110	0.0759	-	-	-	-
0.8711	0.0440	0.0850	1.3038	1600	-5.980	-60259
0.0507	0.5344	0.4149	1.0350	1349	-0.755	90305
0.0554	0.4904	0.4542	1.0383	1365	-0.817	92327
0.0672	0.3810	0.5517	1.0451	1399	-0.893	85056
0.0782	0.2786	0.6432	1.0489	1427	-0.754	72802
0.0880	0.1881	0.7239	1.0549	1450	-	54437
0.0989	0.0889	0.8122	1.0342	1449	1.883	11606
0.1252	0.6615	0.2132	1.0443	1386	0.995	276012
0.2122	0.4258	0.3619	1.1013	1426	-1.281	99355
0.2477	0.3314	0.4210	1.1113	1459	-	94544
0.3054	0.1743	0.5203	1.1274	1505	-1.301	67743
313.15 K						
0.2990	0.4743	0.2266	1.1221	1405	-1.292	121321
0.4019	0.2944	0.3037	1.1434	1464	-0.647	95973
0.4526	0.2054	0.3420	1.1566	1494	-0.784	83004
0.1544	0.8013	0.0444	1.0214	1457	3.104	693070
0.3490	0.5490	0.1020	1.1464	1407	-1.843	146799
0.4789	0.3764	0.1447	1.1723	1473	-1.071	135227
0.5425	0.3044	0.1531	1.1870	1500	-1.058	123910
0.6131	0.2090	0.1779	1.1948	-	-0.336	-
0.7004	0.1012	0.1984	1.2152	1553	-0.782	55511
0.4614	0.4952	0.0434	1.1718	1438	-	140372
0.6254	0.3154	0.0593	1.1910	1490	-	100184
0.7130	0.2195	0.0675	1.2198	1538	-0.350	100812
0.8131	0.1110	0.0759	-	-	-	-
0.8711	0.0440	0.0850	1.2957	1576	-6.015	-55289
0.0507	0.5344	0.4149	1.0258	1314	-0.812	90701
0.0554	0.4904	0.4542	1.0292	1330	-0.875	92910
0.0672	0.3810	0.5517	1.0363	-	-0.951	-
0.0782	0.2786	0.6432	1.0402	1392	-0.807	73959
0.0880	0.1881	0.7239	1.0463	-	-0.993	-
0.0989	0.0889	0.8122	1.0265	1413	1.7881	8238
0.1252	0.6615	0.2132	1.0365	1357	0.828	282272
0.2122	0.4258	0.3619	1.0928	1395	-1.369	105457
0.2477	0.3314	0.4210	1.1029	1428	-	99661
0.3054	0.1743	0.5203	1.1192	1475	-1.379	72881
323.15 K						
0.2990	0.4743	0.2266	1.1138	1378	-1.393	129601
0.4019	0.2944	0.3037	1.1353	1436	-0.718	102535
0.4526	0.2054	0.3420	1.1485	1467	-0.849	88680
0.1544	0.8013	0.0444	1.0130	1435	3.011	711939
0.3490	0.5490	0.1020	1.1380	1379	-1.948	152101
0.4789	0.3764	0.1447	1.1643	1447	-1.141	142729
0.5425	0.3044	0.1531	1.1791	1474	-1.137	130226
0.6131	0.2090	0.1779	1.1689	1496	-0.385	97592
0.7004	0.1012	0.1984	1.2075	1528	-0.834	60097
0.4614	0.4952	0.0434	1.1607	-	-1.103	-
0.6254	0.3154	0.0593	1.1761	1464	-	114508
0.7130	0.2195	0.0675	1.2118	1514	-0.367	106200
0.8131	0.1110	0.0759	-	-	-	-

0.8711	0.0440	0.0850	1.2876	1553	-6.047	-50530
0.0507	0.5344	0.4149	1.0167	1279	-0.868	90809
0.0554	0.4904	0.4542	1.0202	1296	-0.933	93182
0.0672	0.3810	0.5517	1.0274	1330	-1.011	86968
0.0782	0.2786	0.6432	1.0315	1358	-0.861	74989
0.0880	0.1881	0.7239	1.0377	1382	-1.050	58004
0.0989	0.0889	0.8122	1.0158	1378	1.692	4799
0.1252	0.6615	0.2132	1.0274	1326	0.790	285907
0.2122	0.4258	0.3619	1.0843	1365	-1.460	111292
0.2477	0.3314	0.4210	1.0946	1398	-1.389	104838
0.3054	0.1743	0.5203	1.1111	1445	-1.460	77427
333.15 K						
0.2990	0.4743	0.2266	1.1055	1351	-1.504	136944
0.4019	0.2944	0.3037	1.1272	1409	-0.796	108183
0.4526	0.2054	0.3420	1.1405	1440	-0.920	93810
0.1544	0.8013	0.0444	1.0061	1425	2.776	758883
0.3490	0.5490	0.1020	1.1291	1358	-	172919
0.4789	0.3764	0.1447	1.1564	1422	-1.253	148930
0.5425	0.3044	0.1531	1.1713	1449	-1.224	135846
0.6131	0.2090	0.1779	1.1791	1471	-0.439	102254
0.7004	0.1012	0.1984	1.1999	1504	-0.892	64128
0.4614	0.4952	0.0434	1.1534	1389	-1.053	162564
0.6254	0.3154	0.0593	1.1603	1439	-	129188
0.7130	0.2195	0.0675	1.2039	-	-0.392	-
0.8131	0.1110	0.0759	-	-	-	-
0.8711	0.0440	0.0850	1.2796	1530	-	-46036
0.0507	0.5344	0.4149	1.0076	1249	-0.933	100051
0.0554	0.4904	0.4542	1.0111	1262	-1.000	93672
0.0672	0.3810	0.5517	1.0186	-	-1.079	-
0.0782	0.2786	0.6432	1.0228	1325	-0.925	75007
0.0880	0.1881	0.7239	1.0291	1349	-1.117	58696
0.0989	0.0889	0.8122	1.0110	1343	1.585	594
0.1252	0.6615	0.2132	1.0191	1296	0.856	286795
0.2122	0.4258	0.3619	1.0758	1336	-1.562	116111
0.2477	0.3314	0.4210	1.0863	1369	-1.486	109214
0.3054	0.1743	0.5203	1.1030	1416	-1.552	81306

Standard uncertainties u are; $u(T) = 0.02$ K, $u(p) = 0.04$ MPa and the combined expanded uncertainty Uc in mole fraction, density and sound velocity were $Uc(x) = 0.0005$, $Uc(\rho) = 0.006$ g.cm⁻³ and $Uc(u) = 2$ m.s⁻¹, respectively, (0.95 level of confidence).

5.4.1. Excess Molar Volume and Deviation in Isentropic Compressibility

As seen from Tables 5.3 – 5.4, the results obtained revealed that the values of V_{m123}^E were entirely negative for the ternary mixture {[EMIM][BF₄](x_1) + acetic acid (x_2) + acetophenone (x_3)} (mix_4), with the most negative value about -1.4 cm³.mol⁻¹, while for the {[EMIM][BF₄](x_1) + propionic acid (x_2) + acetophenone (x_3)} (mix_5) ternary mixture, the V_{m123}^E values were found to be both positive and negative, from (-6.0 to 3.7) cm³.mol⁻¹. On the other hand, the Δk_{s123} values were found to be entirely positive for the ternary mixture of {[EMIM][BF₄](x_1) + acetic acid (x_2) + acetophenone (x_3)} (mix_4), up to about 2.7×10^5 TPa⁻¹, and for

$\{[\text{EMIM}][\text{BF}_4](x_1) + \text{propionic acid}(x_2) + \text{acetophenone}(x_3)\}$ (*mix*₅) ternary mixture, positive and negative values from $(-0.6 \text{ to } 7.1) \times 10^5 \text{ TPa}^{-1}$ were obtained. From these results one can infer that the mixture with acetic acid is closer to an ideal solution than the mixture with propionic acid.

It is evident also from Tables 5.2 – 5.3, that the values of V_{m123}^E for the $\{[\text{EMIM}][\text{BF}_4](x_1) + \text{propionic acid}(x_2) + \text{acetophenone}(x_3)\}$ (*mix*₅) were more negative when compared to the V_{m123}^E of the $\{[\text{EMIM}][\text{BF}_4](x_1) + \text{acetic acid}(x_2) + \text{acetophenone}(x_3)\}$ (*mix*₄) ternary mixture. Similarly, less positive values of Δk_{s123} were observed for the $\{[\text{EMIM}][\text{BF}_4](x_1) + \text{propionic acid}(x_2) + \text{acetophenone}(x_3)\}$ (*mix*₅) ternary mixtures. The effect of interaction increased with increase in the alkyl chain length of carboxylic acid, this was due to the higher electron – donor capacity of propionic acid than acetic acid [478].

Furthermore, the magnitude of the negative V_{m123}^E values for both ternary mixtures decreased with increase in temperature, becoming more negative. With increase in temperature, the thermal motion of component molecules was increased, allowing a more effective occupation of the free volumes between the IL ions, leading to an increase in the negative V_{m123}^E values. The changes in the values of Δk_{s123} with temperature were explained based on the thermal stress that took place when the components were mixed [355,479].

5.4.2. Modelling of the Excess Molar Volume and Deviation in Isentropic Compressibility

The V_{m123}^E and Δk_{s123} properties of ternary mixtures were well modelled using the sum of a predictive term (no estimated parameter) and a correlative term (estimated parameters), provided in Equation 5.1. The empirical predictive and correlative terms, which were used are provided in Tables 5.1 – 5.2. The V_{m123}^E and Δk_{s123} parameters obtained for the ternary mixtures of $\{[\text{EMIM}][\text{BF}_4](x_1) + \text{acetic acid}(x_2) + \text{acetophenone}(x_3)\}$ (*mix*₄) and $\{[\text{EMIM}][\text{BF}_4](x_1) + \text{propionic}(x_2) + \text{acetophenone}(x_3)\}$ (*mix*₅) are presented in Tables 5.5 - 5.6, with their corresponding standardized deviations (σ) determined using Equation 5.3. The plots from the best models are displayed in Figures 5.24 - 5.27.

Table 5.5: Parameters for the ternary mixture of {[EMIM][BF₄] (x_1) + acetic acid (x_2) + acetophenone (x_3)} (mix_4). For V_{m123}^E , the model is 5 (Scatchard) + 7 (11p-model). For Δk_{s123} , the model is 1 (Redlich-Kister) + 7 (11p-model).

$Y_{123} = V_{m123}^E$, parameters in $cm^3 \cdot mol^{-1}$												
T / K	A_0	A_1	A_2	A_3	A_4	A_5	A_6	A_7	A_8	A_9	A_{10}	σ
293.15	-13.1	167	69.6	-338	-151	-769	-443	757	-93	1971	1094	0.08
303.15	-20.1	182	56.6	-189	-169	-631	-84	346	-41	1701	504	0.13
313.15	-20.6	188	59.3	-197	-184	-606	-74	373	-31	1669	503	0.14
323.15	-24.0	166	78.9	-215	-172	-402	-210	339	-31	1526	716	0.32
333.15	-21.3	214	92.8	-421	-152	-964	-460	822	-134	2430	1287	0.20
$Y_{123} = \Delta k_{s123}$, parameters in $10^5 \cdot TPa^{-1}$												
T / K	A_0	A_1	A_2	A_3	A_4	A_5	A_6	A_7	A_8	A_9	A_{10}	σ
293.15	-10.7	7.83	-63.0	-50.9	159	-308	276	145	-208	885	-362	0.32
303.15	-11.3	-25.8	-52.4	120	95.4	238	355	-186	-79.6	-179	-521	0.12
313.15	-9.57	-31.9	-49.5	128	83.9	268	350	-214	-50.1	-301	-524	0.11
323.15	-8.11	-36.4	-47.2	135	82.2	293	342	-236	-36.7	-393	-514	0.11
333.15	-7.47	-20.1	-23.2	-6.11	99.5	0	0	0	0	0	0	0.28

For Δk_{s123} with parameters A_7 to A_{10} equal to 0, the model is equivalent to 9 (“average”) + 5 (7p-model); and with parameters A_5 and A_{10} equal to 0, the model is equivalent to 1 (“Redlich-Kister”) + 4 (5p-model).

Table 5.6: Parameters for the model 3 (Kohler) + 7 (11p-model) for the ternary mixture of {[EMIM][BF₄] (x_1) + propionic acid (x_2) + acetophenone (x_3)} (mix_5).

$Y_{123} = V_{m123}^E$, parameters in $cm^3 \cdot mol^{-1}$												
T / K	A_0	A_1	A_2	A_3	A_4	A_5	A_6	A_7	A_8	A_9	A_{10}	σ
293.15	26.6	391	224	-1790	-303	-5757	-2395	5443	394	17750	5386	0.26
303.15	1.53	347	101	-1133	-248	-5068	-1226	3320	701	15825	3358	0.25
313.15	11.0	386	171	-1184	-254	-4997	-2218	3113	874	15247	4722	0.39
323.15	-29.2	320	129	-297	88.9	-3816	-2441	-112	842	11194	4748	0.62
333.15	-36.3	153	179	488	-10.8	-765	-3195	-4412	2196	4072	4603	0.44
$Y_{123} = \Delta k_{s123}$, parameters in $10^5 \cdot TPa^{-1}$												
T / K	A_0	A_1	A_2	A_3	A_4	A_5	A_6	A_7	A_8	A_9	A_{10}	σ
293.15	-5.68	-19.8	-51.9	-468	-173	-473	871	2171	858	3350	-2317	0.22
303.15	-4.35	-34.1	-42.3	-345	-211	-250	723	1767	942	2580	-2151	0.21
313.15	-3.04	-40.0	-65.6	-360	-170	-337	1026	1885	773	2787	-2473	0.19
323.15	-4.85	-39.3	-64.5	56.9	-363.7	47.6	1227	-430	1570	-96.4	-3544	0.35
333.15	-6.73	-35.1	-36.9	85.5	-256.9	-57.8	840	-654	1238	-41.6	-2696	0.29

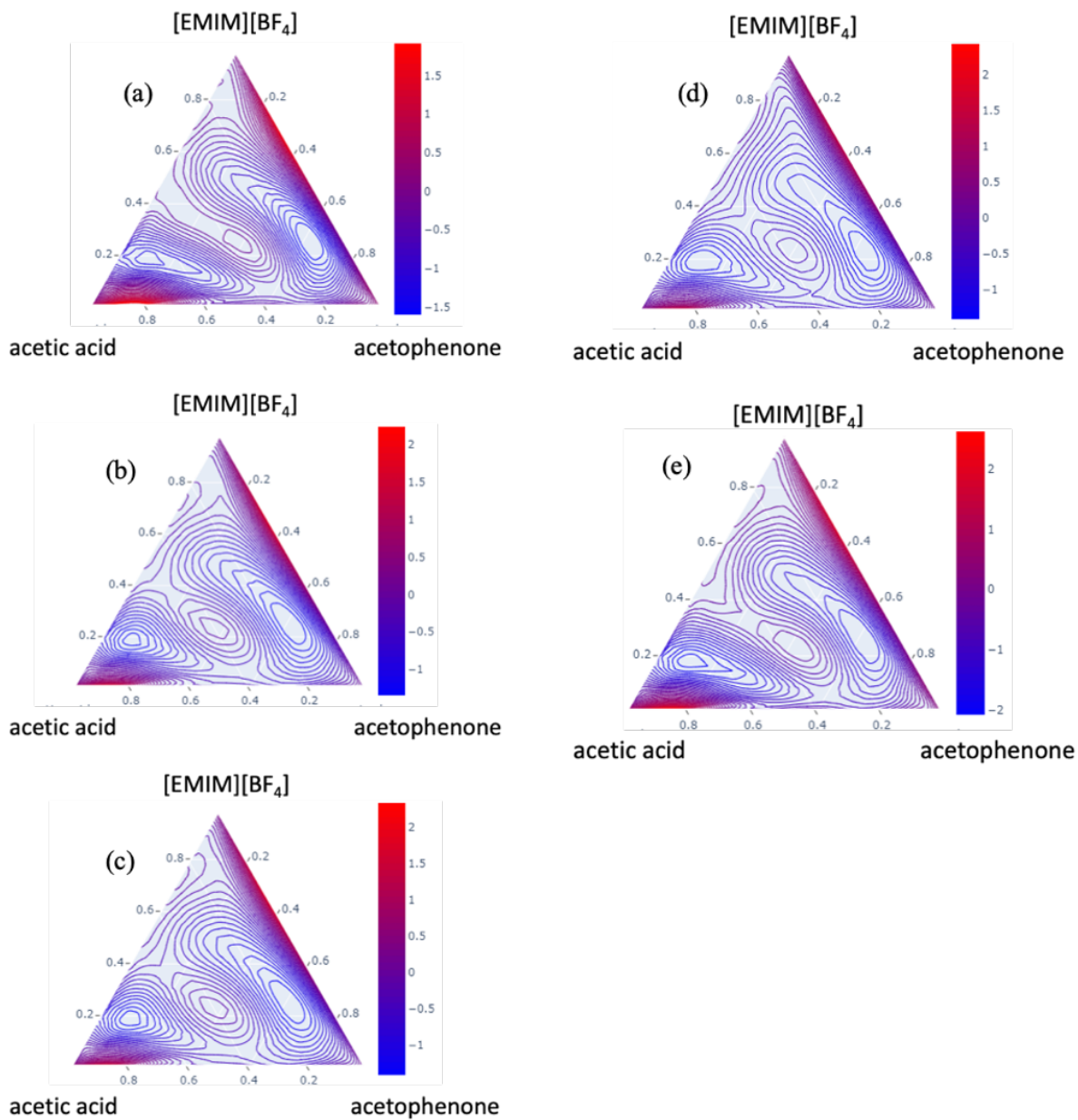


Figure 5.24: Variations of excess molar volume (V_{m123}^E) with IL mole fraction (x_1) for the ternary mixtures of {[EMIM][BF₄] (x_1) + acetic acid (x_2) + acetophenone (x_3)} at (a) 293.15 K, (b) 303.15 K, (c) 313.15 K, (d) 323.15 K and (e) 333.15 K.

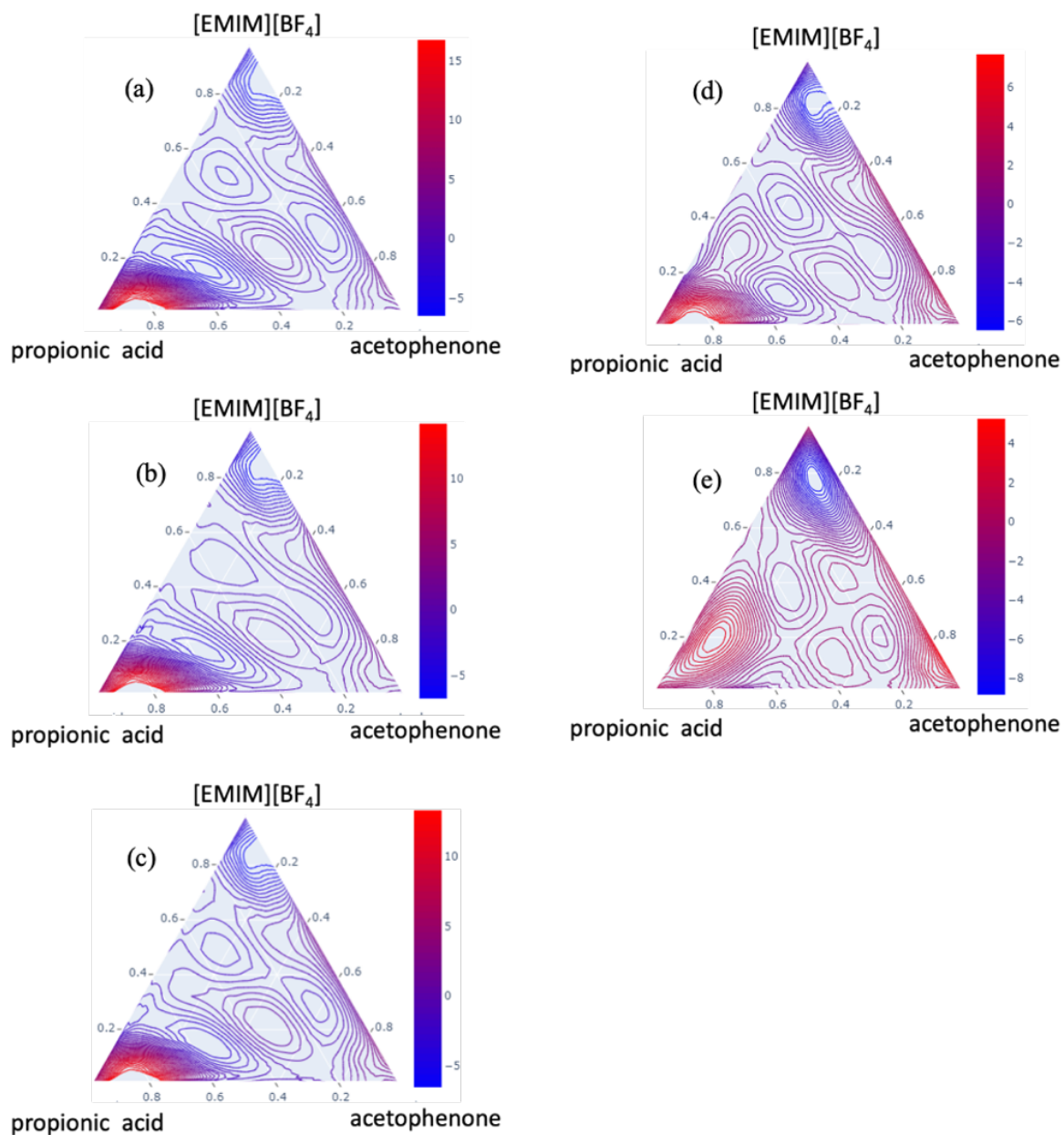


Figure 5.25: Variations of excess molar volume (V_{m123}^E) with IL mole fraction (x_1) for the ternary mixtures of $\{[EMIM][BF_4] (x_1) + \text{propionic acid} (x_2) + \text{acetophenone} (x_3)\}$ at (a) 293.15 K, (b) 303.15 K, (c) 313.15 K, (d) 323.15 K and (e) 333.15 K.

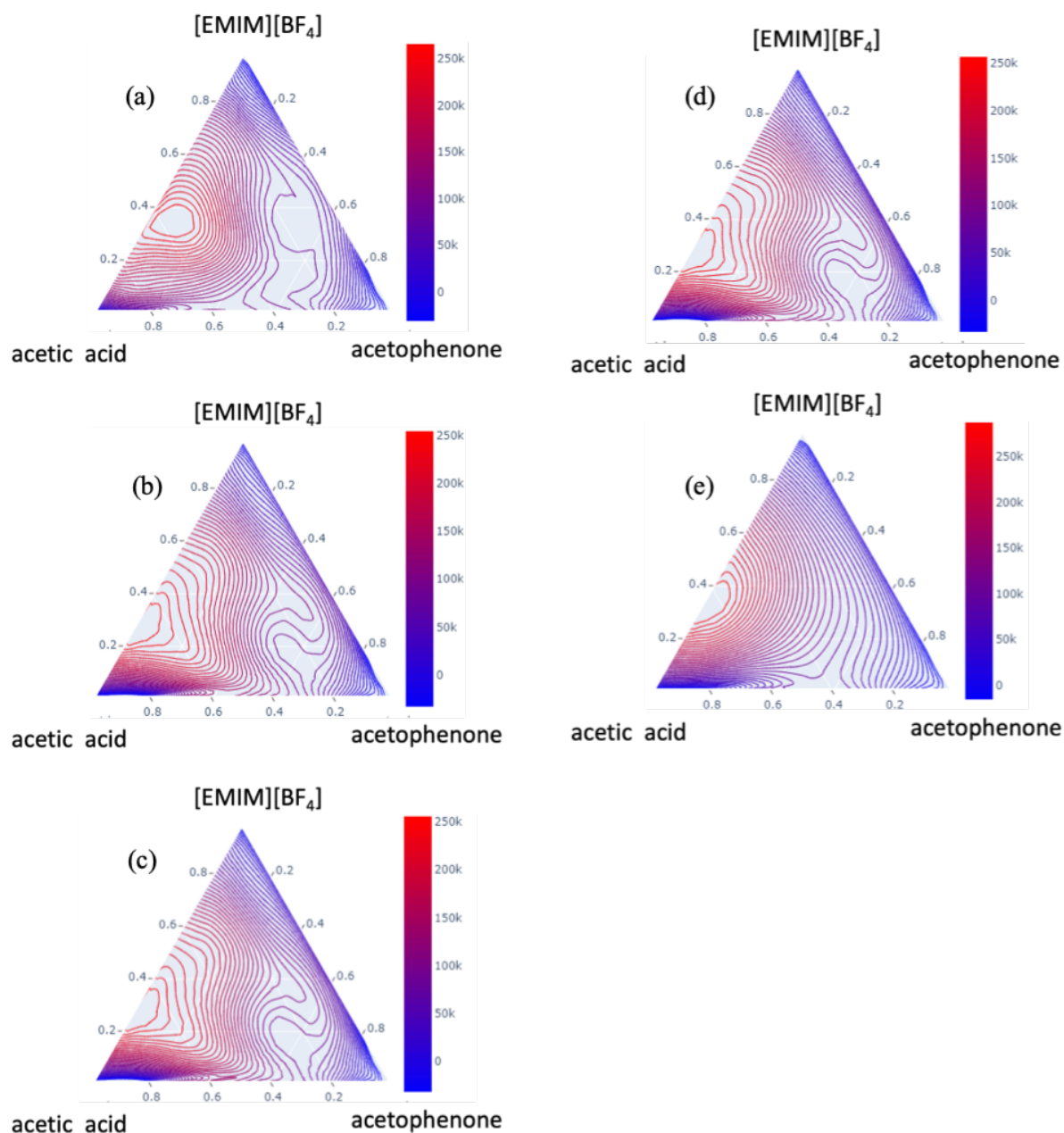


Figure 5.26: Variations of deviation in isentropic compressibility (Δk_{s123}) with IL mole fraction (x_1) for the ternary mixtures of $\{[EMIM][BF_4] (x_1) + \text{acetic acid} (x_2) + \text{acetophenone} (x_3)\}$ at 293.15 K, (b) 303.15 K, (c) 313.15 K, (d) 323.15 K and (e) 333.15 K.

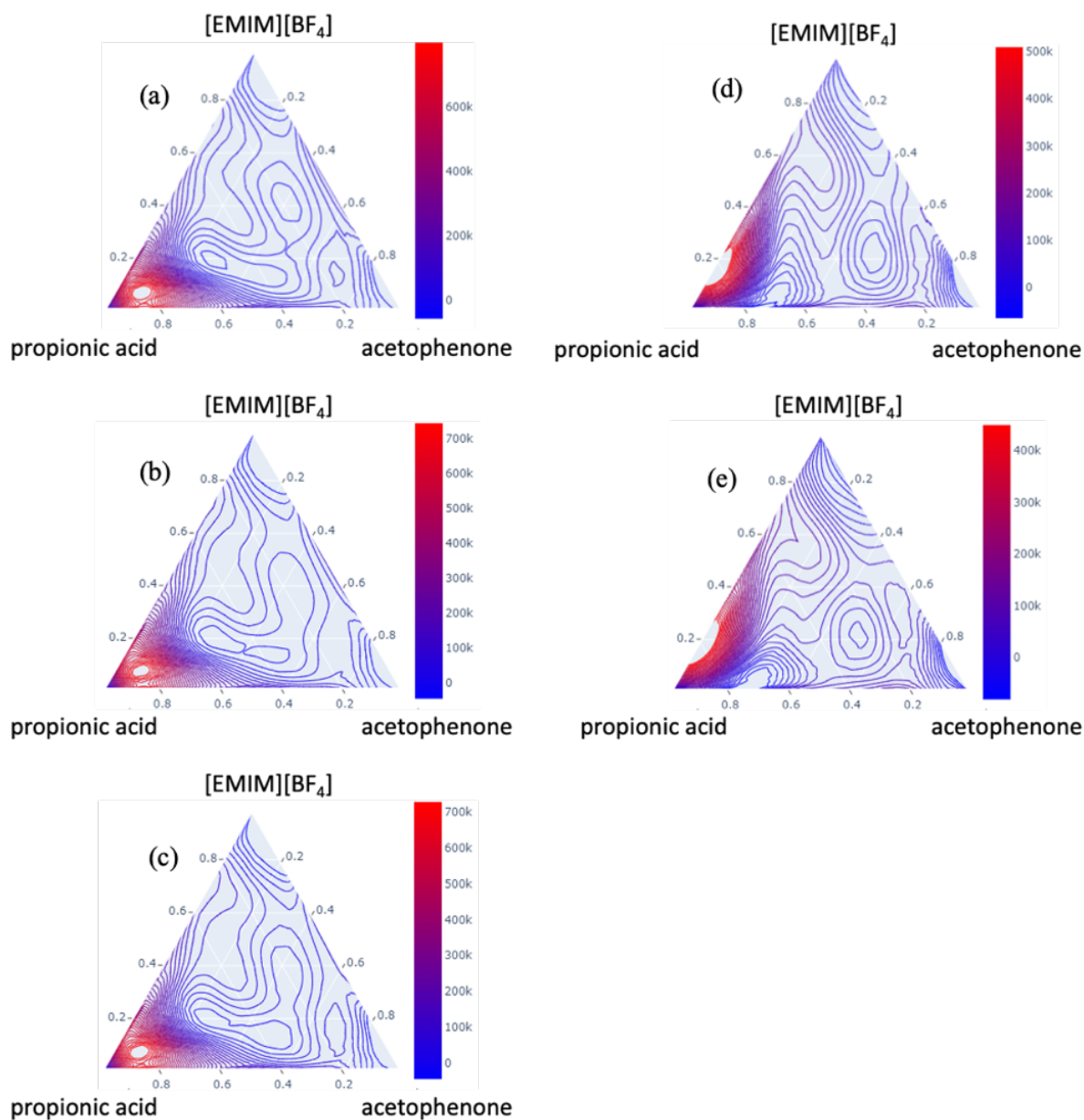


Figure 5.27: Variations of deviation in isentropic compressibility (Δk_{s123}) with IL mole fraction (x_1) for the ternary mixtures of $\{[\text{EMIM}][\text{BF}_4] (x_1) + \text{propionic acid} (x_2) + \text{acetophenone} (x_3)\}$ at 293.15 K, (b) 303.15 K, (c) 313.15 K, (d) 323.15 K and (e) 333.15 K.

The best models for the predictive term for the ternary mixture of {[EMIM][BF₄](x_1) + acetic acid (x_2) + acetophenone (x_3)} (mix_4) was the 5 (Scatchard) for V_{m123}^E and for Δk_{s123} , it was found to be 1 (Redlich-Kister) and 9 (“average”), while for the {[EMIM][BF₄](x_1) + propionic acid (x_2) + acetophenone (x_3)} (mix_5), the best predictive term was 3 (Kohler) for both V_{m123}^E and for Δk_{s123} . The best correlative terms were found to be 4(5p-model) and 5(7p-model) for Δk_{s123} of mix_4 based on the temperature and 7 (11p-model) for V_{m123}^E and Δk_{s123} of mix_4 as well as V_{m123}^E and Δk_{s123} of mix_5 . As would be expected, the best modelling for mix_1 was obtained with a simpler model than for mix_2 , and so the most non-ideal mixture needed a more complex model.

The average standardized deviation (σ) for V_{m123}^E of mix_5 was about triple the values for mix_4 at temperatures 293.15 and 313.15K, and double the values at 303.15, 323.15 and 333.15 K. The σ for Δk_{s123} of mix_5 were in the same range for both ternary mixtures at 293.15 and 333.15K, for temperatures of 303.15 and 313 K the σ for (Δk_{s123}) of mix_5 was double the values of Δk_{s123} of mix_4 and triple at 323.15 K. These results corroborates that non-ideality follows the order: $mix_5 > mix_4$

CONCLUSION

The first part of this thesis dealt with the studies on thermophysical properties such as ρ , u and n_D of imidazolium based ILs [EMIM][BF₄], [EMIM][MeSO₄], [BMIM][BF₄], [BMIM][PF₆], with acetic or propionic acid at temperatures of 293.15, 303.15, 313.15, 323.15 and 333.15 K and $p = 0.1$ MPa. The γ of the mixtures were also evaluated at 298.15 K. To further understand the nature of intermolecular interactions existing between mixing components, the thermodynamic properties of the mixtures such as V_m^E , k_s^E , u^E , L_f , Δn_D and $\Delta\gamma$ were determined from the experimental results at the same experimental conditions. The thermodynamic properties were correlated by the Redlich–Kister polynomial equation and the FTIR studies were carried out for the pure and the mixing components at equimolar compositions ($x_1 = 0.5$).

The results obtained revealed that the values of ρ , u , n_D and γ decreased with addition of acetic or propionic acid to the pure ILs with IL mole fraction. The decrease in ρ , u , n_D and γ values with addition of acetic or propionic acid in pure ILs resulted from the disruption of three-dimensional hydrogen bonded network formed by the cations and anions in pure ILs. Acetic or propionic acid formed hydrogen bonds with cations and as a consequence cation-anion interaction in ILs becomes weaker. The increase in values of ρ , u , n_D and γ with IL mole fraction were due to the dominance of hydrogen bonding between the acetic or propionic acid and either the cation or anion of the IL.

To study the influence of the anion of the IL on the ρ , u , n_D and γ of the binary mixtures, the results obtained for ILs [EMIM][BF₄] and [EMIM][MeSO₄] as well as [BMIM]BF₄] and [BMIM][PF₆] containing binary mixtures were analysed. It was found that the values of ρ , u , n_D and γ appeared to have increased with an increase in the size of the anion; [EMIM][BF₄] < [EMIM][MeSO₄]; [BMIM]BF₄] < [BMIM][PF₆]. ILs containing anions, having higher molar masses exhibited higher densities. Unexpectedly, the values of u and n_D for binary mixtures containing ILs [BMIM][BF₄] and [BMIM][PF₆] decreased with increase in size of the anion constituent of the ILs; [BMIM][BF₄] > [BMIM][PF₆]. This was due to the fact that the

smaller anion $[\text{BF}_4]$ held a position relatively close to the large cation, leading to an increase in the ion-ion interaction.

The effect of the alkyl side chain length attached to the nitrogen atom of the imidazolium cation of the IL on these properties was also studied. It was found that the values of ρ , u , and γ appeared to have decreased with increase in the alkyl side chain length attached to the nitrogen atom of the imidazolium cation; $[\text{BMIM}][\text{BF}_4] < [\text{EMIM}][\text{BF}_4]$. The decrease in the values of ρ , u , and γ were reasoned in terms of the packing efficiency of the molecules, which decreased with an increase in the length of the alkyl side chain due to an increase in the molar volume of the cation. Contrary to the latter, the values of n_D increased with increase in the length of the alkyl side chain attached to the nitrogen atom of the imidazolium cation. An inverse relationship between the variation of n_D and ρ with length of the alkyl side chain was established.

The results obtained for V_m^E shifted from negative to positive for the binary mixtures of $\{[\text{EMIM}][\text{MeSO}_4](x_1) + \text{propionic acid}(x_2)\}$ (mix_4), $\{[\text{BMIM}][\text{BF}_4](x_1) + \text{acetic acid}(x_2)\}$ (mix_5), $\{[\text{BMIM}][\text{BF}_4](x_1) + \text{propionic acid}(x_2)\}$ (mix_6), $\{[\text{BMIM}][\text{PF}_6](x_1) + \text{acetic acid}(x_2)\}$ (mix_7), and from positive to negative for the binary mixtures of $\{[\text{EMIM}][\text{BF}_4](x_1) + \text{propionic acid}(x_2)\}$ (mix_3) and $\{[\text{BMIM}][\text{PF}_6](x_1) + \text{propionic acid}(x_2)\}$ (mix_8). Entirely negative V_m^E values were obtained for the $\{[\text{EMIM}][\text{BF}_4](x_1) + \text{acetic acid}(x_2)\}$ (mix_1) and $\{[\text{EMIM}][\text{MeSO}_4](x_1) + \text{acetic acid}(x_2)\}$ (mix_2). Minimums in the V_m^E values were found to be $-1.599 \text{ cm}^3 \cdot \text{mol}^{-1}$, $-1.881 \text{ cm}^3 \cdot \text{mol}^{-1}$, $-2.786 \text{ cm}^3 \cdot \text{mol}^{-1}$, $-3.397 \text{ cm}^3 \cdot \text{mol}^{-1}$, $-1.237 \text{ cm}^3 \cdot \text{mol}^{-1}$, $-0.320 \text{ cm}^3 \cdot \text{mol}^{-1}$, $-4.321 \text{ cm}^3 \cdot \text{mol}^{-1}$ and $-7.439 \text{ cm}^3 \cdot \text{mol}^{-1}$, which occurred at IL mole fractions of $x_1 \approx 0.3$, $x_1 \approx 0.4$, $x_1 \approx 0.4$, $x_1 \approx 0.3$, $x_1 \approx 0.2$, $x_1 \approx 0.1$, $x_1 \approx 0.1$ and $x_1 \approx 0.4$ from mix_1 to mix_8 respectively. The magnitude of the minimums in the V_m^E values decreased as follows: $\text{mix}_8 < \text{mix}_7 < \text{mix}_4 < \text{mix}_3 < \text{mix}_2 < \text{mix}_1 < \text{mix}_5 < \text{mix}_6$. In all cases the minimums in the V_m^E were skewed towards the lower IL mole fraction, which were seen in the binary mixtures with a large difference in molar volumes of mixing component molecules. The sign and magnitude of the values of the excess or derived properties play a key role in evaluating the molecular rearrangement caused by molecular interaction taking place between the component molecules in the mixtures and relies on the structure making and breaking effects. The negative V_m^E values were attributed to the hydrogen bonding between the mixing components and ion-dipole interactions, which resulted from the ILs ions and dipoles of the carboxylic acids. The negative

V_m^E values were also caused by the fitting effect of the carboxylic acid molecule into the free volume of IL ions, which result in a decrease in the free volume of IL. The negative values of V_m^E favours structure making effects.

Negative k_s^E values were obtained for all binary mixtures except for {[EMIM][BF₄]} (x_1) + propionic acid (x_2) (*mix*₃) mixtures which shifted from positive to negative and decreased with temperature. Minimums in the k_s^E values were found to be -153 TPa⁻¹, -182 TPa⁻¹, -217 TPa⁻¹, -189 TPa⁻¹, -141 TPa⁻¹, -94.08 TPa⁻¹, -167.85 TPa⁻¹ and -172.46 TPa⁻¹, which occurred at IL mole fractions of $x_1 \approx 0.2$, $x_1 \approx 0.2$, $x_1 \approx 0.3$, $x_1 \approx 0.2$, $x_1 \approx 0.1$, $x_1 \approx 0.2$, $x_1 \approx 0.2$ and $x_1 \approx 0.3$ from *mix*₁ to *mix*₈ respectively. The magnitude of the minimums in the k_s^E values decreased as follows: *mix*₃ < *mix*₄ < *mix*₂ < *mix*₈ < *mix*₇ < *mix*₁ < *mix*₅ < *mix*₆. Similarly the minimums in the k_s^E were skewed towards the lower IL mole fractions. The negative values of k_s^E suggested that the molecules of solvent around the solute were less compressed than the molecules of solvent in the bulk solution. This is because dissimilar molecules are approached closer together, and thus interactions between the components in the mixture became stronger. Positive values of k_s^E were thought to be caused by weak interactions between the mixing components, which made the mixtures to be more compressible than the corresponding ideal mixture.

The results obtained for u^E were positive for all binary mixtures except for {[EMIM][BF₄]} (x_1) + propionic acid (x_2) (*mix*₃) and {[EMIM][MeSO₄]} (x_1) + propionic acid (x_2) (*mix*₄), which shifted from positive to negative and decreased with temperature. Maximums in the positive u^E values were found to be 127 m.s⁻¹, 180 m.s⁻¹, 196 m.s⁻¹, 193 m.s⁻¹, 101.45 m.s⁻¹, 38 m.s⁻¹, 114 m.s⁻¹ and 89 m.s⁻¹, which occurred at IL mole fractions of $x_1 \approx 0.3$, $x_1 \approx 0.3$, $x_1 \approx 0.3$, $x_1 \approx 0.4$, $x_1 \approx 0.2$, $x_1 \approx 0.2$, $x_1 \approx 0.3$ and $x_1 \approx 0.3$, from *mix*₁ to *mix*₈ respectively. Positive u^E values suggested the existence of strong intermolecular forces. Strong molecular interactions between component molecules in the mixture lead to an increase in compactness and closer packing of the molecules. This increased the u^E value and resulted in positive u^E values. On the other hand, when the bond dissociation dominated, it caused the volume of the binary mixtures to expand, which yielded negative u^E values.

The results obtained for L_f for all investigated the binary mixtures decreased with an increasing IL mole fraction and increased with temperature. The attractive or repulsive forces between

molecules in a mixture were explained by intermolecular free length. An increase in the IL content in the mixture lead to an increase in the number of ILs molecules in a mixtures, which resulted in an increase in attractive forces between molecules and consequently decreasing L_f . With increase in temperature, the bonds formed became disrupted, causing the molecules to move apart, thus increasing the L_f between the surfaces of the mixing components.

The values of Δn_D were found to be positive and increased with increase in temperature. Maximums in the positive deviations were found to be 0.016, 0.038, 0.019, 0.030, 0.017, 0.015, 0.021 and 0.017, which occurred at IL mole fractions of $x_1 \approx 0.3$, $x_1 \approx 0.3$, $x_1 \approx 0.1$, $x_1 \approx 0.4$, $x_1 \approx 0.3$, $x_1 \approx 0.3$, $x_1 \approx 0.2$ and $x_1 \approx 0.2$ from *mix*₁ to *mix*₈ respectively. The magnitude of the maximums in the positive deviations increased as follows: *mix*₂>*mix*₄>*mix*₇>*mix*₃>*mix*₅>*mix*₉> *mix*₁>*mix*₆. The positive Δn_D results suggested the formation of chemical interactions, which may include association brought on by ion-dipole contact and H-bonding between dissimilar molecules in the mixtures. The maximums in the Δn_D values were more positive for mixtures with a larger anion and also for mixtures containing propionic acid

The results obtained for $\Delta\gamma$ were entirely negative for all IL binary mixtures with propionic acid and shifted from positive to negative for IL binary mixtures with acetic acid. The negative $\Delta\gamma$ values indicated that the concentration of the acids in the surface region was higher than its concentration in the bulk region and the positive $\Delta\gamma$ values suggested that the components in the mixtures were unevenly distributed between the surface and the bulk regions of the system. Minimums in the $\Delta\gamma$ values were found to be -2.34 mN.m⁻¹, -1.76 mN.m⁻¹, -7.16 mN.m⁻¹, -4.44 mN.m⁻¹, -0.263 mN.m⁻¹, -0.111 mN.m⁻¹, -1.545 mN.m⁻¹ and -1.228 mN.m⁻¹, which occurred at IL mole fractions of $x_1 \approx 0.2$, $x_1 \approx 0.2$, $x_1 \approx 0.6$, $x_1 \approx 0.9$, $x_1 \approx 0.1$, $x_1 \approx 0.05$, $x_1 \approx 0.7$ and $x_1 \approx 0.8$ from *mix*₁ to *mix*₈ respectively. The magnitude of the minimums in the negative deviations increased as follows: *mix*₃>*mix*₄>*mix*₁>*mix*₂>*mix*₇>*mix*₈>*mix*₅>*mix*₆.

The FTIR studies suggested that the addition of ILs [EMIM][BF₄], [EMIM][MeSO₄], [BMIM][BF₄], [BMIM][PF₆] to acetic or propionic acid influenced the C=O vibrations of the acetic and propionic acid, confirming the existence of ion–dipole interactions between the binary mixtures. Furthermore, the Redlich–Kister model correlated the experimental data satisfactorily for the mixtures at all investigated temperatures.

The second part of this thesis dealt with the studies of the thermophysical and thermodynamic properties such as ρ , u , V_{m123}^E and Δk_{s123} of ternary mixtures $\{[\text{BMIM}][\text{BF}_4](x_1) + \text{acetic acid}(x_2) + \text{acetophenone}(x_3)\}$ (mix_1), $\{[\text{BMIM}][\text{BF}_4](x_1) + \text{propionic acid}(x_2) + \text{acetophenone}(x_3)\}$ (mix_2), $\{[\text{BMIM}][\text{PF}_6](x_1) + \text{acetic acid}(x_2) + \text{acetophenone}(x_3)\}$ (mix_3), $\{[\text{EMIM}][\text{BF}_4](x_1) + \text{acetic acid}(x_2) + \text{acetophenone}(x_3)\}$ (mix_4) and $\{[\text{EMIM}][\text{BF}_4](x_1) + \text{propionic acid}(x_2) + \text{acetophenone}(x_3)\}$ (mix_5), at temperatures of 293.15, 303.15, 313.15, 323.15 and 333.15 K and pressure of 0.1 MPa. The V_{m123}^E and Δk_{s123} properties of the were modelled using the sum of various predictive and correlative models. The calculated values of V_{m123}^E and Δk_{s123} were found to be both positive and negative. This suggested that the ternary mixtures were not ideal mixtures in terms of their binary components. The negative values of V_{m123}^E and Δk_{s123} indicated formation of strong hydrogen bonding between acetic acid or propionic acid and ILs and between the acetic acid or propionic acid and acetophenone. The positive values of (Δk_{s123}) indicated that there was no presence of any specific interaction between the mixing molecules because of the breakage of the hydrogen bond in pure acetic or propionic acid and loss of their dipolar association, which occurred when acetic or propionic acid mixed with the binary mixtures of $[\text{BMIM}][\text{BF}_4]$ or $[\text{BMIM}][\text{PF}_6]$ or $[\text{EMIM}][\text{BF}_4]$ with acetophenone. The strength in the intermolecular interactions of the ternary mixtures followed the trend: $\text{mix}_5 > \text{mix}_4 > \text{mix}_3 > \text{mix}_2 > \text{mix}_1$.

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APPENDICES

Appendix A: This section presents the results of the comparative study between the experimental values of pure ILs with corresponding literature values.

Table 5.1A: Comparison between experimental and literature data for ρ , u , n_D and γ of pure [EMIM][BF₄] and [EMIM][MeSO₄] at T = 293.15 - 333.15 K and at pressure, $p = 0.1$ MPa.

IL	T/K	$\rho/(\text{g}\cdot\text{cm}^{-3})$			$u/\text{m}\cdot\text{s}^{-1}$			n_D			$\gamma^{298.15\text{K}}/(\text{mN}\cdot\text{m}^{-1})$		
		Expt.	Lit.	%D	Expt.	Lit.	%D	Expt.	Lit.	%D	Expt.	Lit.	%D
[EMIM][BF ₄]	293.15	1.283	1.283 ^a	0.08%	1642	1640 ^c	0.12%	1.414	1.415 ^a	0.07%	51.56	50.10 ^h	2.83%
			1.288 ^b	0.39%		1631 ^d	0.67%		1.416 ^f	0.14%		52.05 ⁱ	0.95%
			1.286 ^c	0.23%		1632 ^e	0.61%		1.413 ^g	0.07%			
	303.15	1.275	1.276 ^a	0.08%	1618	1616 ^c	0.12%	1.412	1.410 ^a	0.14%			
			1.279 ^b	0.31%		1608 ^d	0.62%		1.413 ^f	0.07%			
			1.278 ^c	0.24%		1609 ^e	0.56%		1.411 ^g	0.07%			
	313.15	1.267	1.268 ^a	0.08%	1595	1593 ^c	0.13%	1.409	1.407 ^a	0.14%			
			1.271 ^b	0.32%		1586 ^e	0.56%		1.410 ^f	0.07%			
			1.271 ^c	0.32%					1.408 ^g	0.07%			
	323.15	1.260	1.261 ^a	0.08%	1572	1571 ^c	0.06%	1.407	1.406 ^a	0.07%			
			1.264 ^b	0.32%		1563 ^e	0.57%		1.408 ^f	0.07%			
			1.263 ^c	0.24%					1.406 ^g	0.07%			
	333.15	1.253	1.253 ^a	0.00%	1550	1548 ^c	0.13%	1.404	1.404 ^a	0.00%			
			1.257 ^b	0.32%					1.403 ^g	0.07%			
			1.256 ^c	0.24%									

[EMIM][MeSO ₄]	293.15	1.297	1.267 ^j 1.290 ^k	2.31% 0.54%	1769	-		1.483	-	53.35	52.62 ^j	1.37%
	303.15	1.290	1.259 ^j 1.288 ^k 1.283 ^l	2.40% 0.16% 0.54%	1744	1745 ^l	0.06%	1.480	-			
	313.15	1.282	1.276 ^k 1.276 ^l	0.47% 0.47%	1720	1723 ^l	0.17%	1.476	-			
	323.15	1.274	1.247 ^j 1.269 ^k	2.12% 0.39%	1697	-		1.474	-			
	333.15	1.267	1.240 ^j 1.262 ^k	2.13% 0.39%	1673	-		1.471	-			

^a [Montalban *et al.* 2015], ^b [Soriano *et al.* 2010], ^c [Zarei *et al.* 2017], ^d [Sharma *et al.* 2013], ^e [Rao *et al.* 2017], ^f [Neves *et al.* 2013], ^g [Seki *et al.* 2012], ^h [Xu *et al.* 2012], ⁱ [Shojaeian *et al.* 2019], ^j [Wang *et al.* 2011], ^k [Costa *et al.* 2011], ^l [Bhanuprakash *et al.* 2016]

Table 5.2A: Comparison between experimental and literature data for ρ , u , n_D and γ of pure [BMIM][BF₄] and [BMIM][PF₆] at T = 293.15 - 333.15 K and at pressure, $p = 0.1$ MPa.

IL	T/K	ρ / g.cm ⁻³			u / m.s ⁻¹			n_D			$\gamma^{298.15\text{K}}/(\text{mN.m}^{-1})$		
		Expt.	Lit.	%D	Expt.	Lit.	%D	Expt.	Lit.	%D	Expt.	Lit.	%D
[BMIM][BF ₄]	293.15	1.205	1.204 ^a	0.08%	1579	1577 ^d	0.13%	1.423	1.426 ^a	0.21%	42.90	44.52 ^g	3.78%
			1.205 ^b	0.00%		1577 ^e	0.13%		1.422 ^c	0.07%		44.60 ^h	3.96%
			1.203 ^c	0.17%		1577 ^f	0.13%		1.423 ^f	0.00%		44.37 ⁱ	3.43%
	303.15	1.198	1.197 ^a	0.08%	1555	1553 ^d	0.13%	1.421	1.424 ^a	0.21%			
			1.198 ^b	0.00%		1554 ^e	0.06%		1.420 ^c	0.07%			
			1.197 ^c	0.08%		1556 ^f	0.06%		1.420 ^f	0.07%			
	313.15	1.191	1.190 ^a	0.08%	1532	1530 ^d	0.13%	1.418	1.421 ^a	0.21%			
			1.191 ^b	0.00%		1531 ^e	0.07%		1.418 ^c	0.00%			
			1.191 ^c	0.00%		1531 ^f	0.07%		1.419 ^f	0.07%			
	323.15	1.184	1.183 ^a	0.08%	1509	1507 ^d	0.13%	1.415	1.419 ^a	0.07%			
			1.184 ^b	0.00%					1.416 ^c	0.28%			
			1.183 ^c	0.08%									
	333.15	1.177	1.176 ^a	0.08%	1487	-		1.413	1.417 ^a	0.28%			
			1.177 ^b	0.00%					1.415 ^c	0.14%			
			1.176 ^c	0.08%									
[BMIM][PF ₆]	293.15	1.371	1.371 ^c	0.00%	1458	1455 ^j	0.21%	1.411	1.410 ^c	0.07%	44.24	44.32 ^g	2.35%
			1.372 ^j	0.07%					1.411 ^j	0.00%		43.20 ^j	2.80%
			1.372 ^k	0.07%								43.00 ^l	0.18%
	303.15	1.363	1.362 ^c	0.07%	1433	1431 ^j	0.14%	1.408	1.408 ^c	0.00%			
			1.363 ^j	0.00%		1432 ^l	0.07%		1.408 ^j	0.00%			
			1.363 ^k	0.00%					1.409 ^l	0.07%			
	313.15	1.354	1.354 ^c	0.00%	1410	1406 ^j	0.28%	1.406	1.406 ^c	0.00%			

		1.355 ^j	0.07%		1408 ^l	0.14%		1.405 ^j	0.07%
		1.355 ^k	0.07%					1.407 ^l	0.07%
323.15	1.346	1.346 ^c	0.00%	1387	1384 ^j	0.22%	1.403	1.403 ^c	0.00%
		1.346 ^j	0.00%		1386 ^l	0.07%		1.403 ^j	0.00%
		1.347 ^k	0.07%					1.406 ^l	0.21%
333.15	1.338	1.337 ^c	0.07%	1364	1361 ^j	0.22%	1.400	1.401 ^c	0.07%
		1.338 ^j	0.00%		1364 ^l	0.00%		1.400 ^j	0.00%
		1.338 ^k	0.00%					1.404 ^l	0.29%

^a [Taib *et al.* 2012], ^b [Yin *et al.* 2016], ^c [Montalban *et al.* 2015], ^d [Rao *et al.* 2016], ^e [Pal *et al.* 2012], ^f [Chaudhary *et al.* 2020], ^g [Li *et al.* 2019], ^h [Pandit, *et al.* 2016], ⁱ [Wang *et al.* 2011], ^j [Pereiro *et al.* 2007], ^k [Currás *et al.* 2017], ^l [AlTuwaim *et al.* 2014]

Table 5.3A: Statistical deviation for the sound velocity and refractive index of the binary mixtures at. T = 293.15 - 333.15 K.

Mixture	T [K]	AADu%	AADn _D %			
			LL	GD	LP	EK
[EMIM][BF ₄] + acetic acid	293.15	1.461	0.063	0.060	0.056	0.061
	303.15	1.620	0.057	0.051	0.053	0.052
	313.15	1.751	0.054	0.045	0.043	0.048
	323.15	1.947	0.060	0.049	0.039	0.054
	333.15	2.183	0.076	0.069	0.064	0.072
	Average	1.792	0.062	0.055	0.051	0.057
[EMIM][MeSO ₄] + acetic acid	293.15	2.081	0.157	0.146	0.137	0.152
	303.15	2.322	0.132	0.119	0.110	0.124
	313.15	2.574	0.114	0.102	0.091	0.105
	323.15	2.808	0.118	0.106	0.098	0.109
	333.15	3.040	0.098	0.095	0.095	0.093
	Average	2.565	0.124	0.114	0.106	0.117
[EMIM][BF ₄] + propionic acid	293.15	2.089	0.415	0.411	0.407	0.412
	303.15	2.324	0.399	0.375	0.353	0.386
	313.15	2.583	0.395	0.374	0.359	0.382
	323.15	2.833	0.407	0.368	0.338	0.386
	333.15	3.194	0.405	0.369	0.341	0.385
	Average	2.605	0.332	0.379	0.360	0.390
[EMIM][MeSO ₄] + propionic acid	293.15	1.401	0.150	0.119	0.089	0.133
	303.15	1.576	0.148	0.118	0.090	0.131
	313.15	1.811	0.115	0.086	0.062	0.099
	323.15	1.913	0.132	0.108	0.084	0.119
	333.15	2.085	0.133	0.106	0.081	0.118
	Average	1.757	0.136	0.107	0.081	0.120
[BMIM][BF ₄] + acetic acid	293.15	1.532	0.058	0.053	0.048	0.056
	303.15	1.703	0.080	0.077	0.074	0.080
	313.15	1.844	0.047	0.045	0.043	0.047

[BMIM][PF ₆] + acetic acid	323.15	1.979	0.043	0.038	0.032	0.040
	333.15	2.259	0.072	0.060	0.046	0.066
	Average	1.863	0.060	0.055	0.049	0.058
	293.15	0.720	0.150	0.137	0.124	0.143
	303.15	0.788	0.172	0.157	0.141	0.164
	313.15	0.857	0.141	0.128	0.113	0.134
	323.15	0.930	0.174	0.158	0.140	0.165
	333.15	1.129	0.205	0.188	0.169	0.195
	Average	0.885	0.168	0.154	0.137	0.160
	293.15	0.656	0.143	0.101	0.058	0.120
[BMIM][BF ₄] + propionic acid	303.15	0.973	0.130	0.085	0.041	0.106
	313.15	1.318	0.137	0.094	0.047	0.114
	323.15	1.616	0.126	0.080	0.033	0.101
	333.15	2.022	0.153	0.106	0.061	0.128
	Average	1.317	0.138	0.093	0.048	0.114
	293.15	1.581	0.842	0.727	0.606	0.777
[BMIM][PF ₆] + propionic acid	303.15	1.610	0.741	0.634	0.521	0.681
	313.15	1.662	0.733	0.632	0.525	0.677
	323.15	1.829	0.681	0.587	0.486	0.629
	333.15	2.053	0.611	0.524	0.428	0.564
	Average	1.747	0.722	0.621	0.513	0.666
	293.15	0.428	0.097	0.095	0.115	0.093
Acetophenone + acetic acid	303.15	0.462	0.111	0.106	0.116	0.106
	313.15	0.521	0.113	0.106	0.105	0.108
	323.15	0.581	0.120	0.103	0.099	0.106
	333.15	0.726	0.132	0.116	0.108	0.119
	Average	0.544	0.115	0.105	0.109	0.106
	293.15	0.575	0.321	0.254	0.193	0.272
Acetophenone + propionic acid	303.15	0.626	0.257	0.194	0.137	0.211
	313.15	0.668	0.175	0.120	0.070	0.134
	323.15	0.683	0.104	0.054	0.046	0.066

	333.15	0.717	0.026	0.049	0.082	0.042
	Average	0.654	0.177	0.134	0.106	0.145
	Overall deviation	1.573	0.203	0.182	0.156	0.193

Appendix B: This section presents the results obtained for binary mixtures of IL; [EMIM][BF₄] or [EMIM][MeSO₄] with acetic or propionic acid.

Table 5.1B – 5.2B below presents the isobaric heat capacities (C_p) and isobaric expansivity coefficients (α_p) required to calculate excess isentropic compressibility (k_s^E). The C_p values of the pure [EMIM][BF₄], [EMIM][MeSO₄], acetic acid and propionic acid were taken from the literature, and the for acetic acid and propionic acid at $T = 323.15$ and 333.15 K were not available in the literature and were therefore extrapolated using the correlative equations. The α_p values for the pure [EMIM][BF₄], [EMIM][MeSO₄], acetic acid and propionic acid were calculated from the experimental density data using Equations 2.12 in Section 2.5 of Chapter 2

Table 5.1B: Isobaric heat capacities, c_p of pure [EMIM][BF₄], [EMIM][MeSO₄], acetic acid and propionic acid at $T = 293.15 - 333.15$ K.

T/K	$c_p/\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$			
	[EMIM][BF ₄]	[EMIM][MeSO ₄]	Acetic acid	Propionic acid
293.15	306.5 ^a	320.0 ^b	94.7 ^c	112.3 ^c
303.15	309.8 ^a	332.0 ^b	101.0 ^c	118.3 ^c
313.15	313.2 ^a	337.0 ^b	107.7 ^c	122.3 ^c
323.15	316.8 ^a	343.0 ^b	114.1	127.7
333.15	320.6 ^a	347.0 ^b	120.5	132.7

^a [Waliszewski *et al.* 2005], ^b [Ficke *et al.* 2010], ^c [Parveen *et al.* 2012]

Table 5.2B: Isobaric expansivity coefficients, α_p of pure [EMIM][BF₄], [EMIM][MeSO₄], acetic acid and propionic acid at $T = 293.15 - 333.15$ K.

T/K	α_p/kK^{-1}			
	[EMIM][BF ₄]	[EMIM][MeSO ₄]	Acetic acid	Propionic acid
293.15	0.000624	0.000617	0.001135	0.001102
303.15	0.000627	0.000620	0.001146	0.001114
313.15	0.000631	0.000624	0.001159	0.001126
323.15	0.000635	0.000628	0.001171	0.001139
333.15	0.000639	0.000631	0.001192	0.001151

Table 5.3B: Mole fraction of [EMIM][BF₄] (x_1), density (ρ), sound velocity (u) and refractive index (n_D) for the binary mixtures of {[EMIM][BF₄] (x_1) + acetic acid (x_2)} (mix_1) at T = 293.15 - 333.15 K and at pressure, $p = 0.1$ MPa.

x_1	$\rho/\text{g}\cdot\text{cm}^{-3}$	$u/\text{m}\cdot\text{s}^{-1}$	n_D	x_1	$\rho/\text{g}\cdot\text{cm}^{-3}$	$u/\text{m}\cdot\text{s}^{-1}$	n_D
293.15K							
0.0000	1.057	1158	1.378	0.6100	1.229	1520	1.404
0.0499	1.089	1223	1.382	0.6937	1.240	1542	1.405
0.0908	1.115	1273	1.388	0.8150	1.252	1565	1.408
0.2027	1.165	1389	1.397	0.9047	1.259	1581	1.409
0.2939	1.191	1450	1.401	0.9528	1.264	1588	1.409
0.4019	1.213	1503	1.405	1.0000	1.267	1595	1.409
0.5002	1.230	1539	1.408	323.15K			
0.6100	1.245	1568	1.410	0.0000	1.025	1061	1.366
0.6937	1.256	1588	1.411	0.0499	1.064	1135	1.373
0.8150	1.267	1612	1.413	0.0908	1.090	1187	1.378
0.9047	1.275	1627	1.414	0.2027	1.138	1306	1.387
0.9528	1.280	1635	1.414	0.2939	1.164	1372	1.392
1.0000	1.283	1642	1.414	0.4019	1.188	1429	1.396
303.15K				0.5002	1.205	1465	1.399
0.0000	1.047	1124	1.374	0.6100	1.221	1498	1.402
0.0499	1.081	1192	1.378	0.6937	1.232	1520	1.403
0.0908	1.105	1243	1.384	0.8150	1.244	1543	1.405
0.2027	1.156	1360	1.394	0.9047	1.252	1558	1.406
0.2939	1.182	1423	1.399	0.9528	1.257	1566	1.407
0.4019	1.204	1477	1.402	1.0000	1.260	1572	1.407
0.5002	1.221	1513	1.405	333.15K			
0.6100	1.238	1544	1.407	0.0000	1.006	1033	1.363
0.6937	1.248	1565	1.409	0.0499	1.047	1107	1.370
0.8150	1.259	1589	1.411	0.0908	1.073	1160	1.376
0.9047	1.267	1604	1.411	0.2027	1.128	1285	1.385
0.9528	1.272	1611	1.411	0.2939	1.156	1353	1.390
1.0000	1.275	1618	1.412	0.4019	1.179	1409	1.394
313.15K				0.5002	1.197	1445	1.396
0.0000	1.035	1092	1.368	0.6100	1.213	1477	1.399
0.0499	1.073	1163	1.374	0.6937	1.225	1498	1.401
0.0908	1.095	1213	1.380	0.8150	1.236	1521	1.403
0.2027	1.147	1333	1.390	0.9047	1.245	1536	1.404
0.2939	1.173	1397	1.395	0.9528	1.249	1544	1.404
0.4019	1.196	1452	1.398	1.0000	1.253	1550	1.404
0.5002	1.213	1488	1.401				

Standard uncertainties u are; $u(T) = 0.02$ K, $u(p) = 0.04$ MPa and the combined expanded uncertainty U_c in mole fraction, density, sound velocity and refractive index were $U_c(x) = 0.0006$, $U_c(\rho) = 0.006$ g·cm⁻³, $U_c(u) = 1$ m·s⁻¹ and $U_c(n) = 0.004$, respectively, (0.95 level of confidence).

Table 5.4B: Mole fraction of [EMIM][MeSO₄] (x_1), density (ρ), sound velocity (u) and refractive index (n_D) for the binary mixtures of {[EMIM][MeSO₄] (x_1) + acetic acid (x_2)} (mix_2) at T = 293.15 - 333.15 K and at pressure, $p = 0.1$ MPa.

x_1	$\rho/\text{g.cm}^{-3}$	$u/\text{m.s}^{-1}$	n_D	x_1	$\rho/\text{g.cm}^{-3}$	$u/\text{m.s}^{-1}$	n_D
293.15 K							
0.0000	1.057	1158	1.378	0.6047	1.250	1638	1.460
0.0456	1.089	1256	1.391	0.7010	1.262	1667	1.462
0.1037	1.122	1347	1.408	0.7974	1.273	1690	1.471
0.2005	1.170	1460	1.427	0.8922	1.281	1708	1.474
0.3039	1.210	1547	1.441	0.9596	1.282	1717	1.476
0.3999	1.235	1604	1.450	1.0000	1.282	1720	1.476
0.5002	1.251	1651	1.461				
0.6047	1.266	1687	1.466	323.15 K			
0.7010	1.277	1714	1.468	0.0000	1.025	1061	1.366
0.7974	1.288	1738	1.475	0.0456	1.057	1168	1.383
0.8922	1.296	1755	1.479	0.1037	1.095	1270	1.399
0.9596	1.297	1763	1.481	0.2005	1.143	1391	1.418
1.0000	1.297	1769	1.483	0.3039	1.185	1477	1.435
				0.3999	1.209	1533	1.446
303.15 K				0.5002	1.227	1579	1.455
0.0000	1.047	1124	1.374	0.6047	1.243	1614	1.458
0.0456	1.078	1225	1.388	0.7010	1.255	1644	1.461
0.1037	1.113	1321	1.404	0.7974	1.266	1668	1.469
0.2005	1.161	1435	1.423	0.8922	1.273	1685	1.473
0.3039	1.202	1522	1.438	0.9596	1.274	1693	1.474
0.3999	1.227	1580	1.448	1.0000	1.274	1697	1.474
0.5002	1.243	1624	1.460				
0.6047	1.258	1662	1.463	333.15 K			
0.7010	1.270	1690	1.465	0.0000	1.006	1033	1.363
0.7974	1.281	1714	1.473	0.0456	1.041	1141	1.380
0.8922	1.288	1731	1.476	0.1037	1.078	1243	1.396
0.9596	1.289	1739	1.479	0.2005	1.131	1365	1.415
1.0000	1.290	1744	1.480	0.3039	1.174	1455	1.433
313.15 K				0.3999	1.201	1510	1.444
0.0000	1.035	1092	1.368	0.5002	1.218	1555	1.452
0.0456	1.067	1195	1.383	0.6047	1.234	1593	1.456
0.1037	1.103	1296	1.401	0.7010	1.247	1620	1.458
0.2005	1.151	1412	1.420	0.7974	1.258	1645	1.467
0.3039	1.194	1500	1.437	0.8922	1.267	1662	1.471
0.3999	1.217	1556	1.448	0.9596	1.267	1671	1.471
0.5002	1.235	1600	1.457	1.0000	1.267	1673	1.471

Standard uncertainties u are; $u(T) = 0.02$ K, $u(p) = 0.04$ MPa and the combined expanded uncertainty Uc in mole fraction, density, sound velocity and refractive index were $Uc(x) = 0.0006$, $Uc(\rho) = 0.006$ g.cm⁻³, $Uc(u) = 1$ m.s⁻¹ and $Uc(n) = 0.004$, respectively, (0.95 level of confidence).

Table 5.5B: Mole fraction of [EMIM][BF₄] (x_1), density (ρ), sound velocity (u) and refractive index (n_D) for the binary mixtures of {[EMIM][BF₄] (x_1) + propionic acid (x_2)} (mix_3) at T = 293.15 – 333.15 K and at pressure, $p = 0.1$ MPa.

x_1	$\rho/\text{g.cm}^{-3}$	$u/\text{m.s}^{-1}$	n_D	x_1	$\rho/\text{g.cm}^{-3}$	$u/\text{m.s}^{-1}$	n_D
293.15 K							
0.0000	0.998	1171	1.387	0.5907	1.208	1496	1.406
0.0497	1.001	1173	1.401	0.6891	1.225	1524	1.407
0.0888	1.013	1213	1.407	0.7800	1.239	1549	1.408
0.1876	1.078	1356	1.409	0.8899	1.254	1571	1.408
0.2982	1.148	1463	1.409	0.9453	1.262	1584	1.409
0.3836	1.176	1496	1.409	1.0000	1.267	1595	1.409
0.4908	1.203	1522	1.411	323.15 K			
0.5907	1.222	1545	1.411	0.0000	0.966	1060	1.374
0.6891	1.238	1568	1.412	0.0497	0.973	1080	1.390
0.7800	1.252	1593	1.413	0.0888	0.992	1130	1.395
0.8899	1.268	1617	1.413	0.1876	1.071	1291	1.399
0.9453	1.275	1629	1.414	0.2982	1.131	1396	1.399
1.0000	1.283	1642	1.414	0.3836	1.164	1435	1.400
303.15 K				0.4908	1.188	1457	1.402
0.0000	0.988	1134	1.383	0.5907	1.205	1474	1.403
0.0497	0.991	1145	1.397	0.6891	1.217	1501	1.404
0.0888	1.006	1187	1.403	0.7800	1.232	1525	1.405
0.1876	1.075	1332	1.406	0.8899	1.246	1547	1.406
0.2982	1.146	1442	1.406	0.9453	1.254	1561	1.406
0.3836	1.172	1476	1.406	1.0000	1.260	1572	1.407
0.4908	1.198	1500	1.408	333.15 K			
0.5907	1.217	1521	1.409	0.0000	0.955	1025	1.370
0.6891	1.231	1548	1.410	0.0497	0.965	1054	1.386
0.7800	1.247	1572	1.410	0.0888	0.983	1105	1.392
0.8899	1.261	1593	1.411	0.1876	1.065	1270	1.395
0.9453	1.269	1607	1.411	0.2982	1.123	1376	1.396
1.0000	1.275	1618	1.412	0.3836	1.158	1415	1.397
313.15 K				0.4908	1.182	1443	1.398
0.0000	0.977	1097	1.378	0.5907	1.198	1463	1.400
0.0497	0.982	1111	1.394	0.6891	1.210	1480	1.401
0.0888	1.001	1160	1.399	0.7800	1.225	1506	1.402
0.1876	1.073	1313	1.402	0.8899	1.239	1525	1.404
0.2982	1.137	1418	1.403	0.9453	1.247	1539	1.404
0.3836	1.170	1456	1.403	1.0000	1.253	1550	1.404
0.4908	1.195	1480	1.405				

Standard uncertainties u are; $u(T) = 0.02$ K, $u(p) = 0.04$ MPa and the combined expanded uncertainty Uc in mole fraction, density, sound velocity and refractive index were $Uc(x) = 0.0006$, $Uc(\rho) = 0.006 \text{ g.cm}^{-3}$, $Uc(u) = 1 \text{ m.s}^{-1}$ and $Uc(n) = 0.004$, respectively, (0.95 level of confidence).

Table 5.6B: Mole fraction of [EMIM][MeSO₄] (x_1), density (ρ), sound velocity (u) and refractive index (n_D) for the binary mixtures of {[EMIM][MeSO₄] (x_1) + propionic acid (x_2)} (mix_4) at T = 293.15 - 333.15 K and at pressure, $p = 0.1$ MPa.

x_1	$\rho/\text{g.cm}^{-3}$	$u/\text{m.s}^{-1}$	n_D	x_1	$\rho/\text{g.cm}^{-3}$	$u/\text{m.s}^{-1}$	n_D
293.15 K							
0.0000	0.998	1171	1.387	0.5917	1.216	1600	1.459
0.0449	1.044	1191	1.399	0.6837	1.226	1627	1.461
0.0939	1.076	1238	1.411	0.7941	1.242	1660	1.465
0.2013	1.132	1380	1.430	0.8916	1.260	1688	1.469
0.3004	1.171	1487	1.442	0.9472	1.273	1706	1.473
0.3959	1.199	1565	1.451	1.0000	1.282	1720	1.476
0.5029	1.221	1621	1.461	323.15 K			
0.5917	1.231	1648	1.465	0.0000	0.966	1060	1.374
0.6837	1.241	1672	1.468	0.0449	1.014	1096	1.388
0.7941	1.254	1704	1.470	0.0939	1.048	1153	1.400
0.8916	1.275	1735	1.476	0.2013	1.107	1300	1.420
0.9472	1.285	1751	1.480	0.3004	1.146	1407	1.432
1.0000	1.297	1769	1483	0.3959	1.177	1491	1.442
303.15 K				0.5029	1.198	1542	1.451
0.0000	0.988	1134	1.383	0.5917	1.209	1571	1.457
0.0449	1.034	1161	1.395	0.6837	1.219	1598	1.459
0.0939	1.067	1206	1.407	0.7941	1.235	1630	1.463
0.2013	1.123	1351	1.426	0.8916	1.254	1660	1.467
0.3004	1.162	1463	1.439	0.9472	1.266	1677	1.471
0.3959	1.192	1541	1.448	1.0000	1.274	1690	1.474
0.5029	1.212	1596	1.457	333.15 K			
0.5917	1.225	1624	1.462	0.000	0.955	1025	1.370
0.6837	1.234	1648	1.465	0.0449	1.004	1071	1.384
0.7941	1.249	1682	1.469	0.0939	1.038	1131	1.397
0.8916	1.268	1711	1.473	0.2013	1.100	1277	1.417
0.9472	1.280	1729	1.477	0.3004	1.139	1389	1.429
1.0000	1.290	1744	1.480	0.3959	1.169	1469	1.439
313.15 K				0.5029	1.192	1524	1.448
0.0000	0.977	1097	1.378	0.5917	1.202	1554	1.454
0.0449	1.024	1126	1.393	0.6837	1.212	1583	1.457
0.0939	1.057	1174	1.404	0.7941	1.230	1616	1.460
0.2013	1.115	1326	1.423	0.8916	1.249	1646	1.465
0.3004	1.154	1436	1.436	0.9472	1.259	1660	1.469
0.3959	1.185	1519	1.445	1.0000	1.267	1673	1.471
0.5029	1.206	1570	1.454				

Standard uncertainties u are; $u(T) = 0.02$ K, $u(p) = 0.04$ MPa and the combined expanded uncertainty Uc in mole fraction, density, sound velocity and refractive index were $Uc(x) = 0.0006$, $Uc(\rho) = 0.006 \text{ g.cm}^{-3}$, $Uc(u) = 1 \text{ m.s}^{-1}$ and $Uc(n) = 0.004$, respectively, (0.95 level of confidence).

Table 5.7B: Mole fraction (x_1) and surface tension (γ) for the binary mixture of {[EMIM][BF₄] + acetic acid or propionic acid} or {[EMIM][MeSO₄] + acetic acid or propionic acid} at T = 298.15 K and at pressure, $p = 0.1$ MPa.

x_1	$\gamma / \text{mN.m}^{-1}$	x_1	$\gamma / \text{mN.m}^{-1}$
{[EMIM][BF₄] (x_1) + acetic acid (x_2)}		{[EMIM][MeSO₄] (x_1) + acetic acid (x_2)}	
0.0000	27.21	0.0000	27.21
0.0499	27.43	0.0456	27.52
0.0908	27.94	0.1037	28.66
0.2027	29.81	0.2005	30.69
0.2939	32.06	0.3039	33.91
0.4019	35.08	0.3999	38.17
0.5002	38.14	0.5002	42.27
0.6157	41.89	0.6047	45.40
0.6937	45.42	0.7010	48.15
0.8269	49.42	0.7974	50.95
0.9313	51.08	0.8922	52.77
0.9528	51.30	0.9596	52.99
1.0000	51.56	1.0000	53.35
{[EMIM][BF₄] (x_1) + propionic acid (x_2)}		{[EMIM][MeSO₄] (x_1) + propionic acid(x_2)}	
0.0000	26.20	0.0000	26.20
0.0497	26.30	0.0449	26.36
0.0888	26.49	0.0939	26.88
0.1876	27.57	0.2013	28.29
0.2982	28.30	0.3004	30.85
0.3836	29.69	0.3959	33.58
0.4908	31.75	0.5029	36.18
0.5907	34.02	0.5917	38.25
0.6891	37.04	0.6837	40.52
0.7800	40.05	0.7941	43.32
0.8899	44.07	0.8916	46.85
0.9453	47.33	0.9472	50.05
1.0000	51.56	1.0000	53.35

Standard uncertainties u are; $u(T) = 0.02$ K, $u(p) = 0.04$ MPa and the combined expanded uncertainty Uc in mole fraction and surface tension were $Uc(x) = 0.0006$ and $Uc(\gamma) = 0.5 \text{ mN.m}^{-1}$, respectively, (0.95 level of confidence).

Table 5.8B: Mole fraction of [EMIM][BF₄] (x_1), excess molar volume (V_m^E), isentropic compressibility (k_s), excess isentropic compressibility (k_s^E), excess sound velocity (u^E), intermolecular free-length (L_f) and deviation in refractive index (Δn_D) for the binary mixtures of {[EMIM][BF₄] (x_1) + acetic acid (x_2)} (mix_1) at T = 293.15 - 333.15 K and at pressure, p = 0.1 MPa.

x_1	$V_m^E/\text{cm}^3\text{mol}^{-1}$	$10^9 k_s/\text{TPa}^{-1}$	k_s^E/TPa^{-1}	$u^E/\text{m.s}^{-1}$	$L_f/10^9\text{m}$	Δn_D
293.15 K						
0.0000	0.000	705	0	0	1.711	0.000
0.0499	-0.214	613	-40	26	1.596	0.002
0.0908	-0.572	554	-63	46	1.516	0.007
0.2027	-1.017	445	-90	87	1.360	0.012
0.2939	-0.977	399	-85	95	1.288	0.013
0.4019	-0.796	365	-71	90	1.231	0.012
0.5002	-0.668	343	-58	79	1.194	0.012
0.6100	-0.494	327	-42	60	1.165	0.010
0.6937	-0.471	316	-32	48	1.145	0.008
0.8150	-0.198	304	-18	28	1.123	0.006
0.9047	-0.060	296	-8	14	1.109	0.003
0.9528	-0.120	292	-4	7	1.102	0.002
1.0000	0.000	289	0	0	1.096	0.000
303.15 K						
0.0000	0.000	756	0	0	1.805	0.000
0.0499	-0.325	651	-48	30	1.675	0.002
0.0908	-0.603	586	-73	50	1.589	0.007
0.2027	-1.080	468	-102	93	1.420	0.012
0.2939	-1.023	418	-96	101	1.342	0.014
0.4019	-0.811	381	-81	98	1.280	0.013
0.5002	-0.701	358	-65	86	1.241	0.012
0.6100	-0.585	339	-48	67	1.209	0.010
0.6937	-0.497	327	-36	54	1.188	0.009
0.8150	-0.228	315	-20	32	1.164	0.006
0.9047	-0.079	307	-10	16	1.150	0.003
0.9528	-0.126	303	-5	8	1.142	0.002
1.0000	0.000	299	0	0	1.136	0.000
313.15 K						
0.0000	0.000	810	0	0	1.902	0.000
0.0499	-0.508	689	-59	33	1.754	0.004
0.0908	-0.673	620	-84	54	1.664	0.008
0.2027	-1.166	491	-116	99	1.481	0.013
0.2939	-1.102	437	-109	108	1.397	0.014
0.4019	-0.893	396	-92	105	1.331	0.013
0.5002	-0.765	372	-73	92	1.289	0.013

0.6100	-0.625	352	-54	74	1.254	0.011
0.6937	-0.542	339	-41	60	1.231	0.009
0.8150	-0.269	326	-23	35	1.207	0.003
0.9047	-0.084	318	-11	18	1.191	0.004
0.9528	-0.127	313	-6	9	1.183	0.002
1.0000	0.000	310	0	0	1.177	0.000
323.15 K						
0.0000	0.000	866	0	0	2.001	0.000
0.0499	-0.594	730	-69	36	1.838	0.005
0.0908	-0.939	652	-99	58	1.736	0.008
0.2027	-1.205	515	-130	104	1.544	0.014
0.2939	-1.154	456	-122	115	1.453	0.015
0.4019	-0.957	412	-103	113	1.381	0.014
0.5002	-0.816	387	-82	99	1.337	0.013
0.6100	-0.654	365	-61	81	1.299	0.011
0.6937	-0.576	351	-47	65	1.275	0.009
0.8150	-0.299	338	-26	39	1.249	0.006
0.9047	-0.109	329	-13	20	1.234	0.004
0.9528	-0.138	325	-6	10	1.225	0.002
1.0000	0.000	321	0	0	1.218	0.000
333.15 K						
0.0000	0.000	931	0	0	2.112	0.000
0.0499	-0.639	779	-79	38	1.932	0.005
0.0908	-0.950	692	-114	62	1.821	0.009
0.2027	-1.586	537	-153	114	1.603	0.014
0.2939	-1.599	473	-145	127	1.504	0.015
0.4019	-1.282	427	-120	124	1.430	0.014
0.5002	-1.090	400	-96	109	1.384	0.013
0.6100	-0.771	378	-70	89	1.346	0.011
0.6937	-0.759	364	-54	73	1.320	0.009
0.8150	-0.347	349	-30	44	1.294	0.006
0.9047	-0.172	341	-15	22	1.277	0.004
0.9528	-0.165	336	-7	12	1.268	0.002
1.0000	0.000	332	0	0	1.261	0.000

Standard uncertainties u are; $u(T) = 0.02$ K, $u(p) = 0.04$ MPa and the combined expanded uncertainty Uc in mole fraction, density, sound velocity and refractive index were $Uc(x) = 0.0006$, $Uc(\rho) = 0.006$ g.cm⁻³, $Uc(u) = 1$ m.s⁻¹ and $Uc(n) = 0.004$, respectively, (0.95 level of confidence).

Table 5.9B: Mole fraction of [EMIM][MeSO₄] (x_1), excess molar volume (V_m^E), isentropic compressibility (k_s), excess isentropic compressibility (k_s^E), excess sound velocity (u^E), intermolecular free-length (L_f) and deviation in refractive index (Δn_D) for the binary mixtures of {[EMIM][MeSO₄] (x_1) + acetic acid (x_2)} (mix_2) at T = 293.15 - 333.15 K and at pressure, $p = 0.1$ MPa.

x_1	$V_m^E / \text{cm}^3 \cdot \text{mol}^{-1}$	$10^9 k_s / \text{TPa}^{-1}$	k_s^E / TPa^{-1}	$u^E / \text{m} \cdot \text{s}^{-1}$	$L_f / 10^9 \text{m}$	Δn_D
293.15 K						
0.0000	0.000	705	0	0	1.711	0.000
0.0456	-0.068	582	-65	53	1.555	0.008
0.1037	-0.137	491	-95	92	1.428	0.020
0.2005	-0.619	401	-107	125	1.290	0.028
0.3039	-1.237	345	-99	136	1.197	0.031
0.3999	-1.453	315	-84	129	1.143	0.031
0.5002	-1.245	293	-67	116	1.103	0.031
0.6047	-1.103	277	-51	95	1.074	0.025
0.7010	-0.998	267	-37	74	1.052	0.017
0.7974	-1.081	257	-25	53	1.033	0.013
0.8922	-0.955	250	-14	30	1.020	0.008
0.9596	-0.346	248	-5	10	1.015	0.003
1.0000	0.000	246	0	0	1.012	0.000
303.15 K						
0.0000	0.000	756	0	0	1.805	0.000
0.0456	-0.072	617	-76	58	1.631	0.009
0.1037	-0.215	515	-112	101	1.490	0.020
0.2005	-0.654	418	-122	136	1.343	0.028
0.3039	-1.310	359	-113	147	1.244	0.032
0.3999	-1.509	326	-95	141	1.186	0.031
0.5002	-1.315	305	-75	123	1.146	0.033
0.6047	-1.164	288	-57	103	1.114	0.025
0.7010	-1.142	276	-42	81	1.090	0.017
0.7974	-1.144	266	-28	57	1.070	0.014
0.8922	-1.019	259	-15	33	1.056	0.008
0.9596	-0.386	256	-5	12	1.051	0.003
1.0000	0.000	255	0	0	1.048	0.000
313.15 K						
0.0000	0.000	810	0	0	1.902	0.000
0.0456	-0.081	656	-86	60	1.711	0.010
0.1037	-0.301	540	-130	109	1.553	0.021
0.2005	-0.698	436	-140	147	1.395	0.031
0.3039	-1.454	372	-129	159	1.289	0.036
0.3999	-1.521	339	-107	151	1.231	0.036
0.5002	-1.353	316	-84	132	1.188	0.035
0.6047	-1.254	298	-63	110	1.154	0.027

0.7010	-1.228	285	-47	87	1.128	0.019
0.7974	-1.210	275	-31	63	1.108	0.017
0.8922	-1.033	268	-17	36	1.093	0.010
0.9596	-0.421	265	-6	14	1.087	0.004
1.0000	0.000	264	0	0	1.085	0.000

323.15 K

0.0000	0.000	866	0	0	2.001	0.000
0.0456	-0.081	693	-99	64	1.791	0.012
0.1037	-0.367	566	-148	116	1.618	0.022
0.2005	-0.801	453	-160	158	1.447	0.031
0.3039	-1.535	387	-144	169	1.337	0.036
0.3999	-1.599	352	-120	160	1.275	0.038
0.5002	-1.419	327	-95	143	1.230	0.035
0.6047	-1.361	309	-71	117	1.195	0.027
0.7010	-1.297	295	-52	94	1.168	0.019
0.7974	-1.324	284	-35	68	1.146	0.017
0.8922	-1.095	277	-19	39	1.131	0.011
0.9596	-0.459	274	-7	15	1.125	0.004
1.0000	0.000	273	0	0	1.123	0.000

333.15 K

0.0000	0.000	931	0	0	2.112	0.000
0.0456	-0.145	738	-113	67	1.880	0.013
0.1037	-0.377	600	-167	120	1.695	0.022
0.2005	-1.026	474	-181	165	1.507	0.031
0.3039	-1.701	402	-164	180	1.388	0.038
0.3999	-1.881	365	-136	170	1.323	0.038
0.5002	-1.598	340	-107	151	1.275	0.036
0.6047	-1.450	319	-81	128	1.237	0.028
0.7010	-1.446	305	-59	101	1.209	0.020
0.7974	-1.397	294	-40	74	1.186	0.017
0.8922	-1.243	286	-22	42	1.169	0.011
0.9596	-0.492	283	-8	17	1.163	0.005
1.0000	0.000	282	0	0	1.162	0.000

Standard uncertainties u are; $u(T) = 0.02$ K, $u(p) = 0.04$ MPa and the combined expanded uncertainty Uc in mole fraction, density, sound velocity and refractive index were $Uc(x) = 0.0006$, $Uc(\rho) = 0.006$ g.cm⁻³, $Uc(u) = 1$ m.s⁻¹ and $Uc(n) = 0.004$, respectively, (0.95 level of confidence).

Table 5.10B: Mole fraction of [EMIM][BF₄] (x_1), excess molar volume (V_m^E), isentropic compressibility (k_s), excess isentropic compressibility (k_s^E), excess sound velocity (u^E), intermolecular free-length (L_f) and deviation in refractive index (Δn_D) for the binary mixtures of {[EMIM][BF₄] (x_1) + propionic acid (x_2)} (mix_3) at T = 293.15 - 333.15 K and at pressure, $p = 0.1$ MPa.

x_1	$V_m^E / \text{cm}^3 \cdot \text{mol}^{-1}$	$10^9 k_s / \text{TPa}^{-1}$	k_s^E / TPa^{-1}	$u^E / \text{m} \cdot \text{s}^{-1}$	$L_f / 10^9 \text{m}$	Δn_D
293.15 K						
0.0000	0.000	731	0	0	1.742	0.000
0.0497	1.990	726	39	-25	1.737	0.013
0.0888	2.631	671	14	-7	1.669	0.017
0.1876	1.057	505	-83	83	1.448	0.017
0.2982	-1.413	407	-117	136	1.300	0.014
0.3836	-1.582	380	-102	127	1.256	0.012
0.4908	-1.396	359	-77	102	1.221	0.011
0.5907	-1.075	343	-57	80	1.193	0.008
0.6891	-0.608	328	-40	60	1.168	0.007
0.7800	-0.417	315	-27	45	1.143	0.005
0.8899	-0.191	302	-13	22	1.119	0.002
0.9453	-0.036	295	-6	11	1.108	0.001
1.0000	0.000	289	0	0	1.096	0.000
303.15 K						
0.0000	0.000	788	0	0	1.843	0.000
0.0497	1.963	769	29	-16	1.821	0.013
0.0888	2.404	706	-0.2	4	1.744	0.018
0.1876	0.441	524	-106	98	1.502	0.018
0.2982	-2.066	419	-140	152	1.344	0.015
0.3836	-2.057	392	-121	143	1.299	0.012
0.4908	-1.766	371	-92	116	1.264	0.011
0.5907	-1.375	356	-66	90	1.238	0.009
0.6891	-0.763	339	-48	72	1.208	0.007
0.7800	-0.673	325	-33	54	1.182	0.005
0.8899	-0.207	313	-14	25	1.160	0.002
0.9453	-0.158	305	-7	13	1.147	0.001
1.0000	0.000	299	0	0	1.136	0.000
313.15 K						
0.0000	0.000	851	0	0	1.950	0.000
0.0497	1.918	826	27	-13	1.920	0.014
0.0888	2.036	743	-18	15	1.821	0.018
0.1876	-0.254	541	-136	116	1.554	0.018
0.2982	-2.150	437	-161	165	1.397	0.015
0.3836	-2.738	403	-144	160	1.342	0.013
0.4908	-2.440	382	-109	131	1.306	0.011

0.5907	-1.429	370	-77	99	1.285	0.009
0.6891	-1.016	351	-56	80	1.253	0.007
0.7800	-0.717	337	-39	61	1.226	0.005
0.8899	-0.346	323	-18	30	1.201	0.003
0.9453	-0.286	316	-9	15	1.188	0.002
1.0000	0.000	310	0	0	1.177	0.000

323.15 K

0.0000	0.000	920	0	0	2.063	0.000
0.0497	1.790	880	18	-7	2.018	0.014
0.0888	1.946	789	-31	22	1.910	0.018
0.1876	-0.904	560	-168	131	1.610	0.019
0.2982	-2.510	454	-188	179	1.449	0.015
0.3836	-3.073	417	-167	176	1.389	0.013
0.4908	-2.651	396	-126	144	1.354	0.012
0.5907	-1.943	382	-91	111	1.329	0.010
0.6891	-1.104	365	-64	89	1.299	0.007
0.7800	-0.875	349	-45	67	1.270	0.006
0.8899	-0.370	335	-20	33	1.245	0.003
0.9453	-0.299	327	-10	17	1.230	0.002
1.0000	0.000	321	0	0	1.218	0.000

333.15 K

0.0000	0.000	996	0	0	2.183	0.000
0.0497	1.649	933	1	2	2.114	0.014
0.0888	1.892	833	-53	33	1.997	0.019
0.1876	-1.249	582	-201	147	1.669	0.019
0.2982	-2.721	470	-217	196	1.501	0.016
0.3836	-3.397	431	-194	192	1.437	0.014
0.4908	-2.968	406	-150	165	1.395	0.012
0.5907	-2.222	390	-111	134	1.366	0.010
0.6891	-1.283	377	-75	100	1.344	0.008
0.7800	-0.925	360	-53	77	1.313	0.006
0.8899	-0.395	347	-23	37	1.289	0.004
0.9453	-0.319	339	-12	20	1.273	0.002
1.0000	0.000	332	0	0	1.261	0.000

Standard uncertainties u are; $u(T) = 0.02$ K, $u(p) = 0.04$ MPa and the combined expanded uncertainty Uc in mole fraction, density, sound velocity and refractive index were $Uc(x) = 0.0006$, $Uc(\rho) = 0.006$ g.cm⁻³, $Uc(u) = 1$ m.s⁻¹ and $Uc(n) = 0.004$, respectively, (0.95 level of confidence).

Table 5.11B: Mole fraction of [EMIM][MeSO₄] (x_1), excess molar volume (V_m^E), isentropic compressibility (k_s), excess isentropic compressibility (k_s^E), excess sound velocity (u^E), intermolecular free-length (L_f) and deviation in refractive index (Δn_D) for the binary mixtures of {[EMIM][MeSO₄] (x_1) + propionic acid (x_2)} (mix_4) at T = 293.15 - 333.15 K and at pressure, $p = 0.1$ MPa.

x_1	$V_m^E / \text{cm}^3 \cdot \text{mol}^{-1}$	$10^9 k_s / \text{TPa}^{-1}$	k_s^E / TPa^{-1}	$u^E / \text{m} \cdot \text{s}^{-1}$	$L_f / 10^9 \text{m}$	Δn_D
293.15 K						
0.0000	0.000	731	0	0	1.742	0.000
0.0449	-1.272	675	-8	-12	1.675	0.007
0.0939	-1.554	607	-31	1	1.587	0.015
0.2013	-1.944	464	-89	73	1.388	0.024
0.3004	-2.070	386	-104	117	1.267	0.026
0.3959	-1.965	340	-99	137	1.189	0.026
0.5029	-1.320	312	-80	130	1.138	0.025
0.5917	-0.247	299	-59	106	1.115	0.022
0.6837	0.783	288	-39	78	1.094	0.015
0.7941	1.613	275	-21	48	1.068	0.007
0.8916	0.937	261	-10	25	1.041	0.003
0.9472	0.666	254	-4	12	1.026	0.002
1.0000	0.000	246	0	0	1.012	0.000
303.15 K						
0.0000	0.000	788	0	0	1.843	0.000
0.0449	-1.330	717	-19	-4	1.758	0.008
0.0939	-1.649	645	-41	8	1.667	0.015
0.2013	-2.111	488	-105	82	1.450	0.024
0.3004	-2.222	402	-121	131	1.316	0.027
0.3959	-2.148	354	-114	151	1.234	0.027
0.5029	-1.361	324	-91	142	1.182	0.025
0.5917	-0.512	310	-68	118	1.155	0.022
0.6837	0.584	298	-46	88	1.134	0.015
0.7941	1.263	283	-26	58	1.104	0.009
0.8916	0.867	269	-12	31	1.077	0.003
0.9472	0.316	261	-6	16	1.061	0.003
1.0000	0.000	255	0	0	1.048	0.000
313.15 K						
0.0000	0.000	851	0	0	1.950	0.000
0.0449	-1.406	770	-24	-2	1.854	0.010
0.0939	-1.764	686	-53	14	1.750	0.016
0.2013	-2.264	510	-126	96	1.509	0.025
0.3004	-2.397	420	-140	143	1.369	0.028
0.3959	-2.435	366	-133	168	1.278	0.028
0.5029	-1.682	336	-105	153	1.226	0.027
0.5917	-0.563	321	-79	130	1.197	0.023

0.6837	0.492	308	-54	101	1.173	0.016
0.7941	1.060	292	-31	67	1.142	0.010
0.8916	0.789	278	-15	35	1.115	0.004
0.9472	0.226	270	-8	19	1.098	0.003
1.0000	0.000	264	0	0	1.085	0.000

323.15 K

0.0000	0.000	920	0	0	2.063	0.000
0.0449	-1.477	820	-8	6	1.947	0.010
0.0939	-1.874	718	-79	30	1.823	0.016
0.2013	-2.440	535	-150	108	1.573	0.025
0.3004	-2.591	440	-161	154	1.427	0.028
0.3959	-2.627	382	-152	179	1.329	0.028
0.5029	-1.797	351	-119	165	1.274	0.027
0.5917	-0.661	335	-90	140	1.245	0.023
0.6837	0.415	321	-63	111	1.219	0.016
0.7941	0.929	305	-36	74	1.187	0.009
0.8916	0.587	289	-18	41	1.157	0.004
0.9472	0.151	281	-9	22	1.140	0.003
1.0000	0.000	275	0	0	1.127	0.000

333.15 K

0.0000	0.000	996	0	0	2.183	0.000
0.0449	-1.549	868	-59	16	2.038	0.010
0.0939	-1.986	753	-107	44	1.899	0.010
0.2013	-2.760	557	-179	123	1.633	0.025
0.3004	-2.786	455	-189	172	1.476	0.028
0.3959	-2.755	397	-173	193	1.378	0.028
0.5029	-2.034	362	-137	181	1.316	0.027
0.5917	-0.862	345	-104	156	1.284	0.023
0.6837	0.267	329	-74	126	1.255	0.016
0.7941	0.646	311	-44	86	1.221	0.009
0.8916	0.291	296	-23	50	1.189	0.004
0.9472	0.126	288	-11	25	1.175	0.003
1.0000	0.000	282	0	0	1.162	0.000

Standard uncertainties u are; $u(T) = 0.02$ K, $u(p) = 0.04$ MPa and the combined expanded uncertainty Uc in mole fraction, density, sound velocity and refractive index were $Uc(x) = 0.0006$, $Uc(\rho) = 0.006$ g.cm⁻³, $Uc(u) = 1$ m.s⁻¹ and $Uc(n) = 0.004$, respectively, (0.95 level of confidence).

Table 5.12B: Mole fraction (x_1) and deviation in surface tension ($\Delta\gamma$) for the binary mixture of {[EMIM][BF₄] + acetic acid or propionic acid} or {[EMIM][MeSO₄] + acetic acid or propionic acid} at T = 298.15 K and at pressure, $p = 0.1$ MPa.

x_1	$\Delta\gamma/\text{mN.m}^{-1}$	x_1	$\Delta\gamma/\text{mN.m}^{-1}$
{[EMIM][BF₄](x_1) + acetic acid (x_2)}		{[EMIM][MeSO₄](x_1) + acetic acid (x_2)}	
0.0000	0.00	0.0000	0.00
0.0499	-1.00	0.0456	-0.88
0.0908	-1.48	0.1037	-1.26
0.2027	-2.34	0.2005	-1.76
0.2939	-2.31	0.3039	-1.24
0.4019	-1.92	0.3999	0.51
0.5002	-1.25	0.5002	1.99
0.6157	-0.17	0.6047	2.38
0.6937	1.32	0.7010	2.62
0.8269	2.36	0.7974	2.90
0.9313	1.84	0.8922	2.24
0.9528	0.89	0.9596	0.70
1.0000	0.00	1.0000	0.00
{[EMIM][BF₄](x_1) + propionic acid (x_2)}		{[EMIM][MeSO₄](x_1) + propionic acid(x_2)}	
0.0000	0.00	0.0000	0.00
0.0497	-1.16	0.0449	-1.06
0.0888	-1.96	0.0939	-1.87
0.1876	-3.39	0.2013	-3.38
0.2982	-5.46	0.3004	-3.51
0.3836	-6.24	0.3959	-3.37
0.4908	-6.90	0.5029	-3.67
0.5907	-7.16	0.5917	-4.02
0.6891	-6.64	0.6837	-4.24
0.7800	-5.93	0.7941	-4.44
0.8899	-4.70	0.8916	-3.56
0.9453	-2.84	0.9472	-1.87
1.0000	0.00	1.0000	0.00

Standard uncertainties u are; $u(T) = 0.02$ K, $u(p) = 0.04$ MPa and the combined expanded uncertainty Uc in mole fraction and surface tension were $Uc(x) = 0.0006$ and $Uc(\gamma) = 0.5 \text{ mN.m}^{-1}$, respectively.

Table 5.13B: Redlich-Kister coefficients (A_i) and standard deviation (σ) obtained for the binary mixtures of {[EMIM][BF₄] (x_1) + acetic acid (x_2)} (mix_1), {[EMIM][MeSO₄] (x_1) + acetic acid (x_2)} (mix_2), {[EMIM][BF₄] (x_1) + propionic acid (x_2)} (mix_3) and {[EMIM][MeSO₄] (x_1) + propionic acid (x_2)} (mix_4) at T = 293.15 - 333.15 K and at pressure, $p = 0.1$ MPa.

	T/K	A_0	A_1	A_2	A_3	A_4	σ
{[EMIM][BF₄] (x_1) + acetic acid (x_2)}							
$V_m^E/\text{cm}^3\cdot\text{mol}^{-1}$	293.15	-2.526	-3.487	-6.003	0.164	6.134	0.070
	303.15	-2.775	-3.244	-5.550	-0.887	4.779	0.060
	313.15	-3.055	-3.201	-5.060	-2.185	2.727	0.056
	323.15	-3.280	-2.910	-4.001	-4.290	-1.142	0.036
	333.15	-4.259	-5.263	-7.051	-1.156	4.016	0.065
k_s^E/TPa^{-1}	293.15	-227	-300	-314	-157	19	1
	303.15	-259	-328	-331	-222	-48	1
	313.15	-294	-360	-354	-297	-123	1
	323.15	-331	-392	-373	-388	-222	1
	333.15	-385	-477	-478	-408	-177	1
$u^E/\text{m}\cdot\text{s}^{-1}$	293.15	311	309	215	-93	-204	1
	303.15	354	315	201	-16	-103	1
	313.15	368	314	216	-47	-166	1
	323.15	397	317	216	-27	-150	1
	333.15	437	352	249	-61	-204	1
Δn_D	293.15	0.045	0.030	0.048	-0.012	-0.047	0.001
	303.15	0.048	0.039	0.051	-0.018	-0.053	0.001
	313.15	0.050	0.033	0.038	0.002	-0.017	0.001
	323.15	0.051	0.031	0.033	0.013	0.007	0.001
	333.15	0.053	0.037	0.037	0.010	0.004	0.001
$\Delta\gamma$	298.15	-5.25	-19.76	18.97	-9.09	-11.45	0.19
{[EMIM][MeSO₄] (x_1) + acetic acid (x_2)}							
$V_m^E/\text{cm}^3\cdot\text{mol}^{-1}$	293.15	-5.177	-2.877	-0.758	12.390	0.202	0.090
	303.15	-5.452	-2.577	-1.396	12.053	0.414	0.087
	313.15	-5.648	-2.482	-2.821	11.593	1.960	0.091
	323.15	-5.929	-2.487	-4.063	11.741	2.961	0.084
	333.15	-6.664	-3.598	-4.450	13.959	3.011	0.084
k_s^E/TPa^{-1}	293.15	-273	-289	-218	-452	-471	3
	303.15	-307	-326	-260	-548	-566	3
	313.15	-343	-373	-327	-642	-631	3
	323.15	-384	-417	-374	-751	-732	3
	333.15	-435	-476	-422	-847	-838	4
	293.15	463	329	190	180	172	2
	303.15	498	357	238	188	166	2

$u^E/\text{m.s}^{-1}$	313.15	532	390	303	184	128	1
	323.15	569	411	324	196	134	1
	333.15	608	425	335	181	132	1
Δn_D	293.15	0.118	0.079	-0.005	-0.001	0.064	0.001
	303.15	0.123	0.077	-0.025	0.002	0.093	0.001
	313.15	0.135	0.096	-0.014	-0.038	0.094	0.001
	323.15	0.138	0.096	-0.036	-0.034	0.148	0.001
	333.15	0.139	0.010	-0.028	-0.040	0.145	0.001
$\Delta\gamma$	298.15	6.87	-22.61	-19.19	-1.60	21.18	0.26
{[EMIM][BF₄] (x_1) + propionic acid (x_2)}							
$V_m^E/\text{cm}^3\cdot\text{mol}^{-1}$	293.15	-5.771	-10.553	3.855	44.793	39.201	0.158
	303.15	-7.106	-13.575	-2.011	47.596	46.778	0.170
	313.15	-8.925	-16.012	1.354	49.141	39.481	0.117
	323.15	-10.078	-17.156	-2.416	48.119	44.479	0.213
	333.15	-11.321	-17.844	-1.081	47.555	42.996	0.268
k_s^E/TPa^{-1}	293.15	-288	-679	-905	1224	2046	8
	303.15	-342	-770	-1037	1214	2132	8
	313.15	-401	-887	-1199	1244	2271	11
	323.15	-467	-1006	-1374	1262	2437	12
	333.15	-557	-1101	-1429	1165	2364	13
$u^E/\text{m.s}^{-1}$	293.15	398	642	669	-1184	-1711	4
	303.15	452	671	717	-1137	-1697	4
	313.15	504	724	764	-1152	-1698	4
	323.15	558	765	793	-1147	-1708	4
	333.15	639	761	694	-1044	-1524	5
Δn_D	293.15	0.041	0.020	0.016	0.139	0.140	0.001
	303.15	0.043	0.023	0.025	0.138	0.133	0.001
	313.15	0.044	0.023	0.021	0.138	0.146	0.001
	323.15	0.046	0.024	0.022	0.138	0.152	0.001
	333.15	0.048	0.027	0.017	0.133	0.164	0.001
$\Delta\gamma$	298.15	-28.18	4.99	3.54	16.64	-24.00	0.13
{[EMIM][MeSO₄] (x_1) + propionic acid (x_2)}							
$V_m^E/\text{cm}^3\cdot\text{mol}^{-1}$	293.15	-5.318	-17.823	22.728	-1.679	-31.764	0.118
	303.15	-5.900	-17.484	20.502	-0.727	-31.748	0.083
	313.15	-6.813	-18.425	21.778	0.982	-34.669	0.103
	323.15	-7.316	-19.362	20.710	2.896	-35.529	0.107
	333.15	-7.934	-19.431	17.091	3.461	-33.182	0.130
k_s^E/TPa^{-1}	293.15	-316	-491	-232	472	539	3
	303.15	-366	-547	-255	455	486	2
	313.15	-420	-627	-358	467	574	3
	323.15	-480	-685	-381	328	383	2
	333.15	-552	-746	-446	144	207	1
$u^E/\text{m.s}^{-1}$	293.15	514	400	-252	-810	-473	2

Δn_D	303.15	567	413	-262	-809	-393	2
	313.15	619	432	-179	-815	-491	2
	323.15	664	432	-198	-722	-311	2
	333.15	736	419	-298	-621	-343	2
$\Delta \gamma$	293.15	0.101	0.070	-0.045	0.021	0.074	0.070
	303.15	0.101	0.068	-0.027	0.028	0.058	0.001
	313.15	0.107	0.067	-0.032	0.036	0.077	0.001
	323.15	0.108	0.066	-0.025	0.041	0.072	0.001
	333.15	0.111	0.065	-0.016	0.049	0.063	0.001
	298.15	-14.31	4.34	-31.00	5.73	11.26	0.13

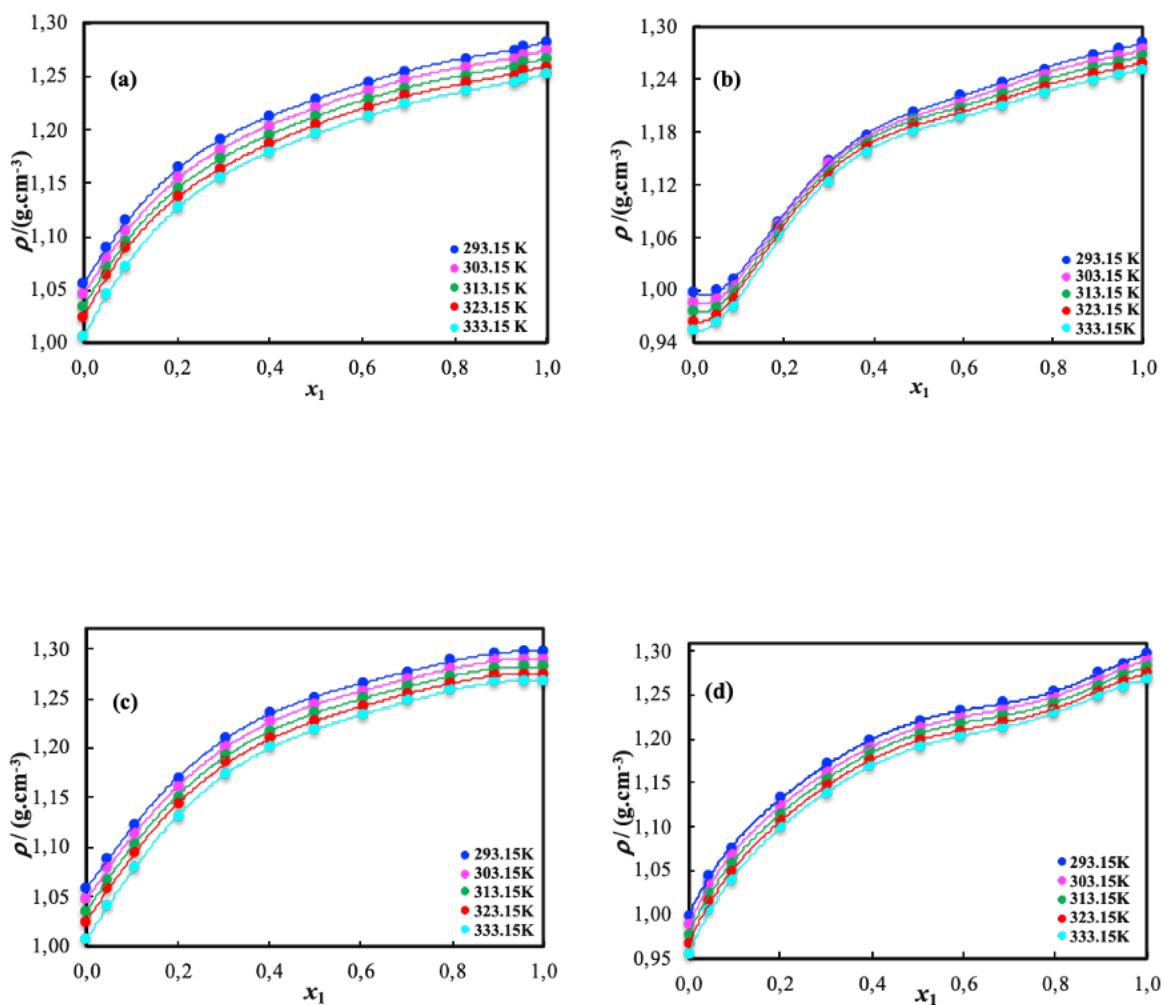


Figure 5.1B: Variations of density (ρ) with IL mole fraction (x_1) for the binary mixtures of [EMIM][BF₄] with (a) acetic acid or (b) propionic acid and [EMIM][MeSO₄] with (c) acetic acid or (d) propionic acid at $T = 293.15 - 333.15$ K. The dotted lines show the smoothness of these data.

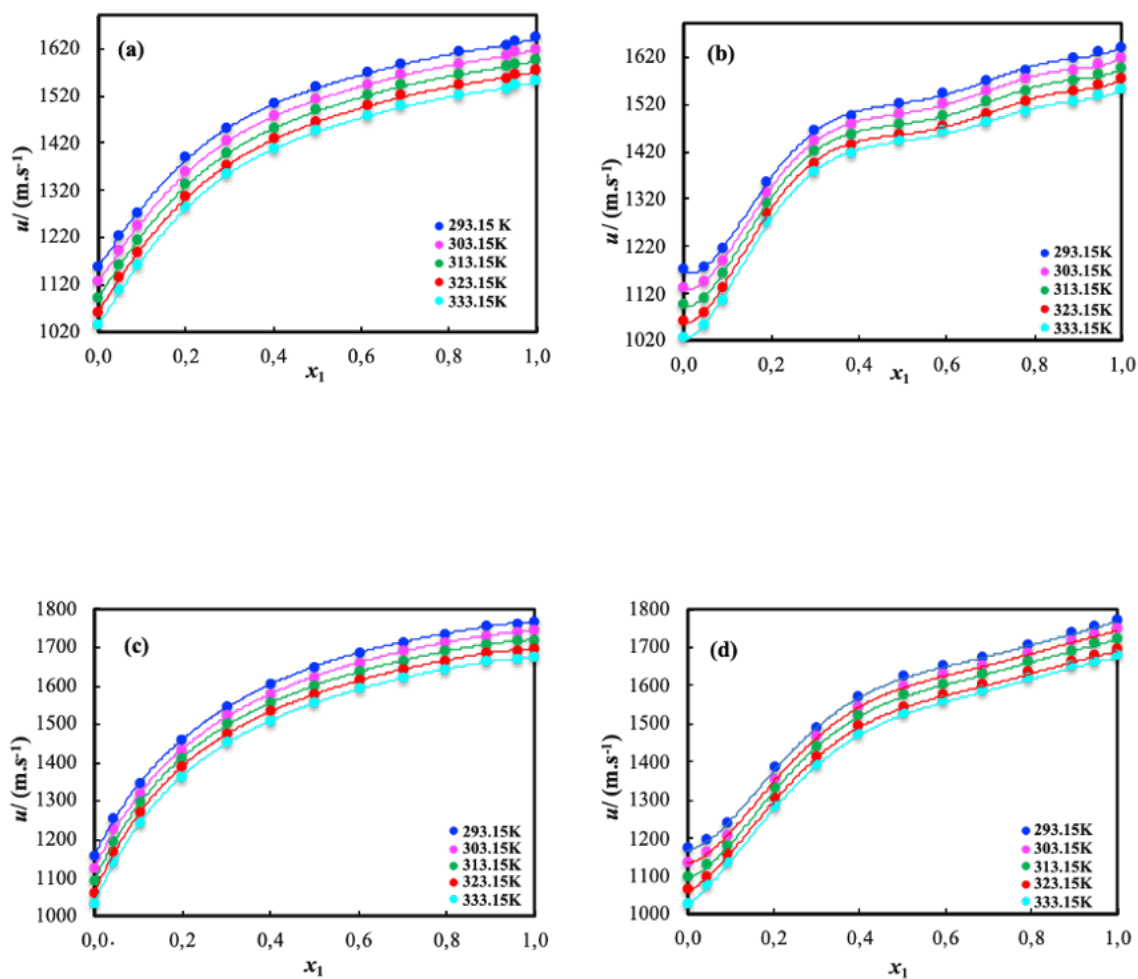


Figure 5.2B: Variations of sound velocity (u) with IL mole fraction (x_1) for the binary mixtures of [EMIM][BF₄] with (a) acetic acid or (b) propionic acid and [EMIM][MeSO₄] with (c) acetic acid or (d) propionic acid at $T = 293.15 - 333.15$ K. The dotted lines show the smoothness of these data.

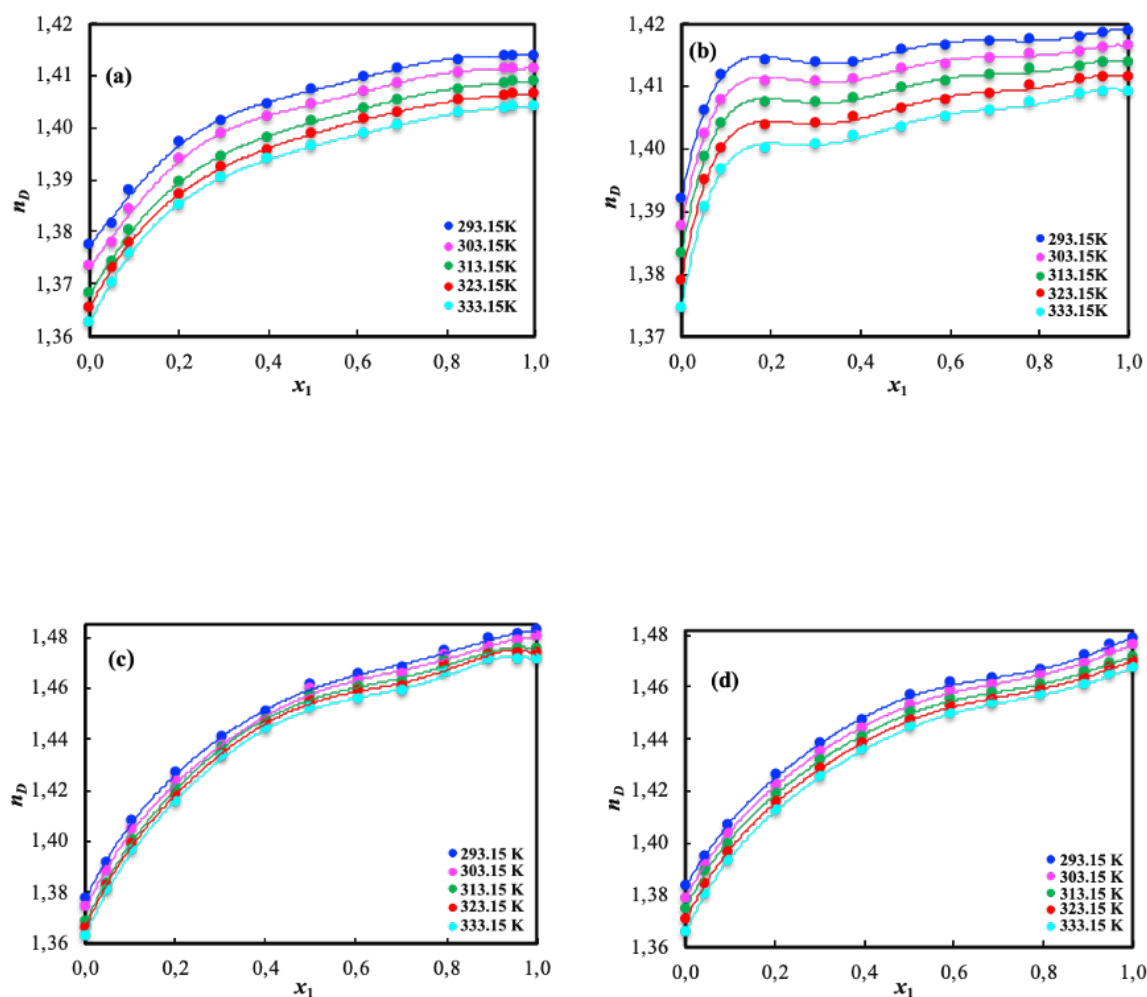


Figure 5.3B: Variations of refractive (n_D) with IL mole fraction (x_1) for the binary mixtures of [EMIM][BF₄] with (a) acetic acid or (b) propionic acid and [EMIM][MeSO₄] with (c) acetic acid or (d) propionic acid at $T = 293.15 - 333.15$ K. The dotted lines show the smoothness of these data.

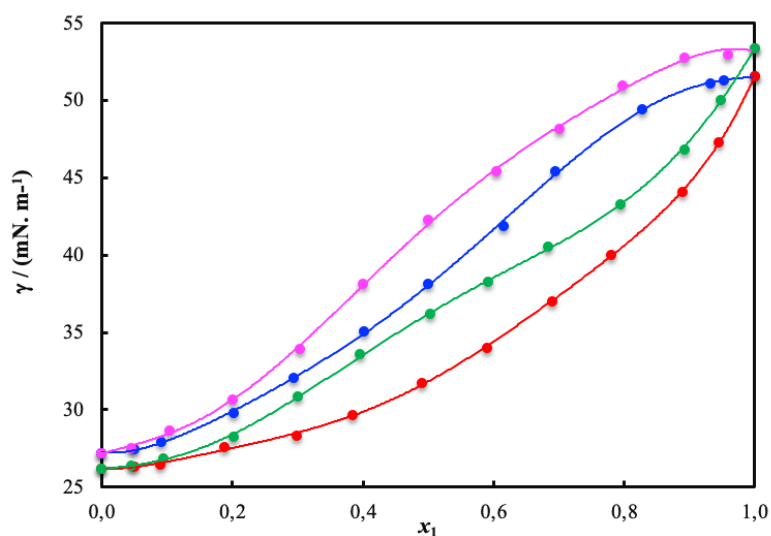


Figure 5.4B: Variations of surface tension (γ) with IL mole fraction (x_1) for the binary mixtures (•){[EMIM][BF₄](x_1) + acetic acid (x_2)}, (•){[EMIM][MeSO₄](x_1) + acetic acid (x_2)}, (•){[EMIM][BF₄](x_1) + propionic acid (x_2)} and (•){[EMIM][MeSO₄](x_1) + propionic acid (x_2)} at T = 298.15 K. The dotted lines show the smoothness of these data.

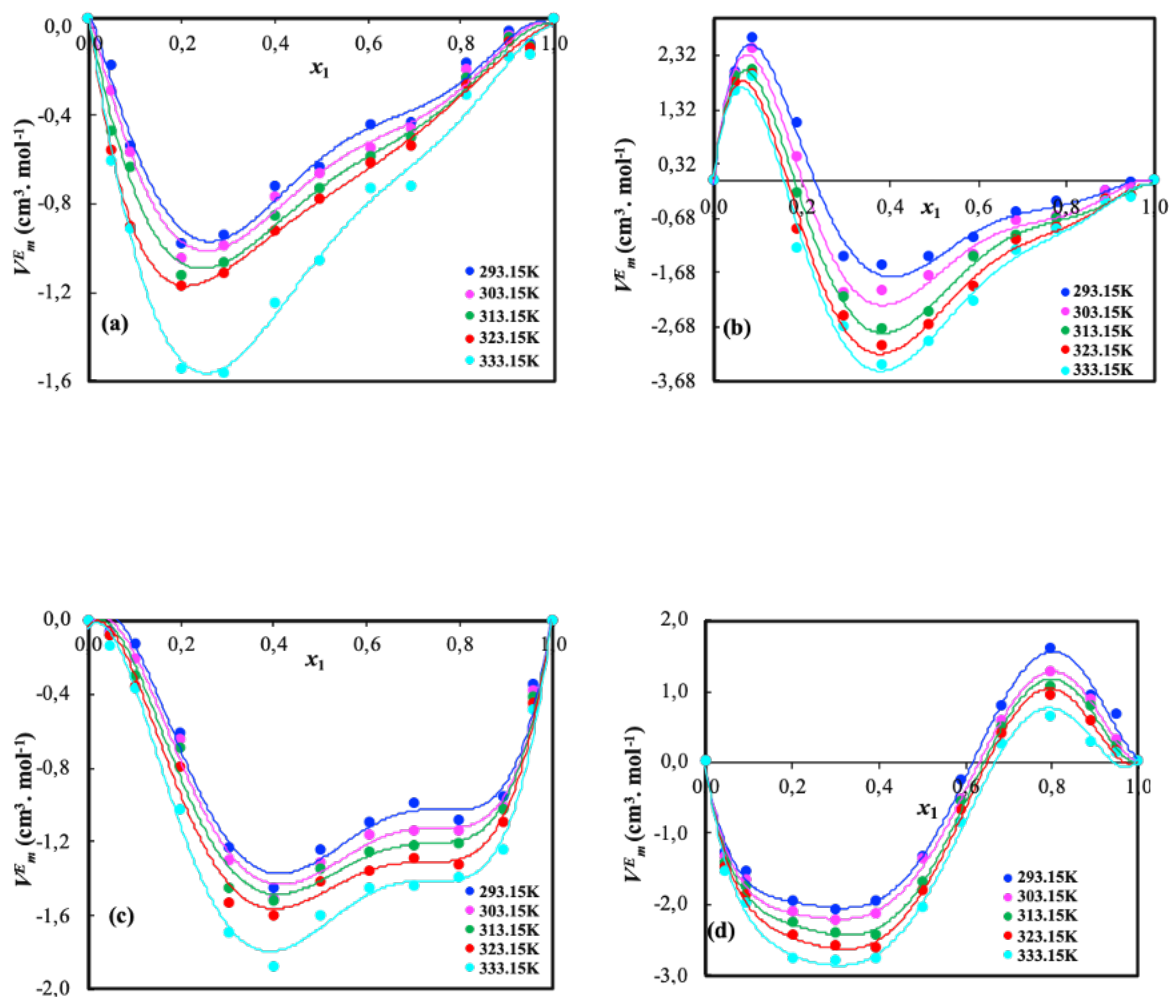


Figure 5.5B: Variations of excess molar volume (V_m^E) with IL mole fraction (x_1) for the binary mixtures of [EMIM][BF₄] with (a) acetic acid or (b) propionic acid and [EMIM][MeSO₄] with (c) acetic acid or (d) propionic acid at $T = 293.15 - 333.15$ K. The dotted lines were generated using the Redlich-Kister curve-fitting.

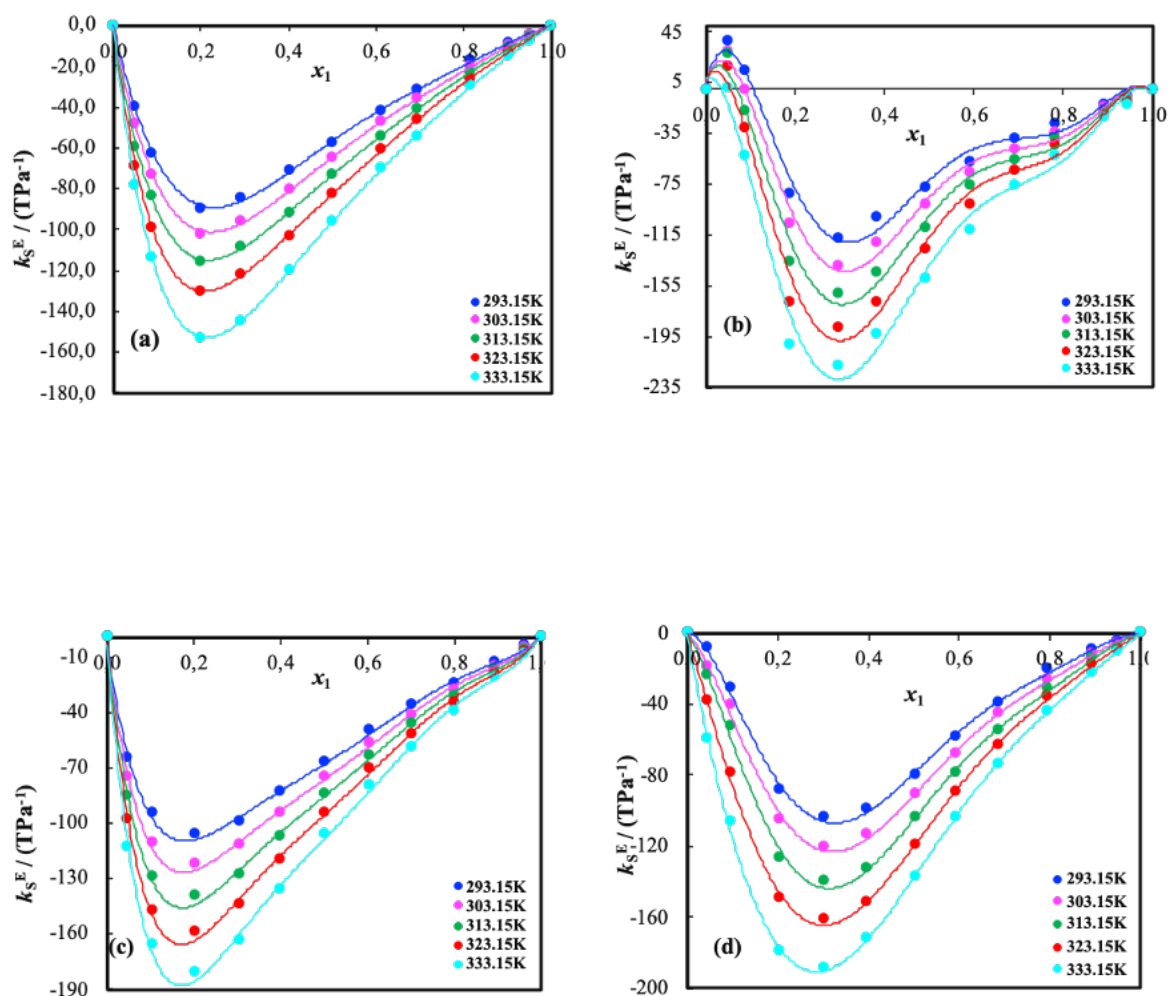


Figure 5.6B: Variations of excess isentropic compressibility (k_s^E) with IL mole fraction (x_1) for the binary mixtures of [EMIM][BF₄] with (a) acetic acid or (b) propionic acid and [EMIM][MeSO₄] with (c) acetic acid or (d) propionic acid at $T = 293.15 - 333.15$ K. The dotted lines were generated using the Redlich-Kister curve-fitting.

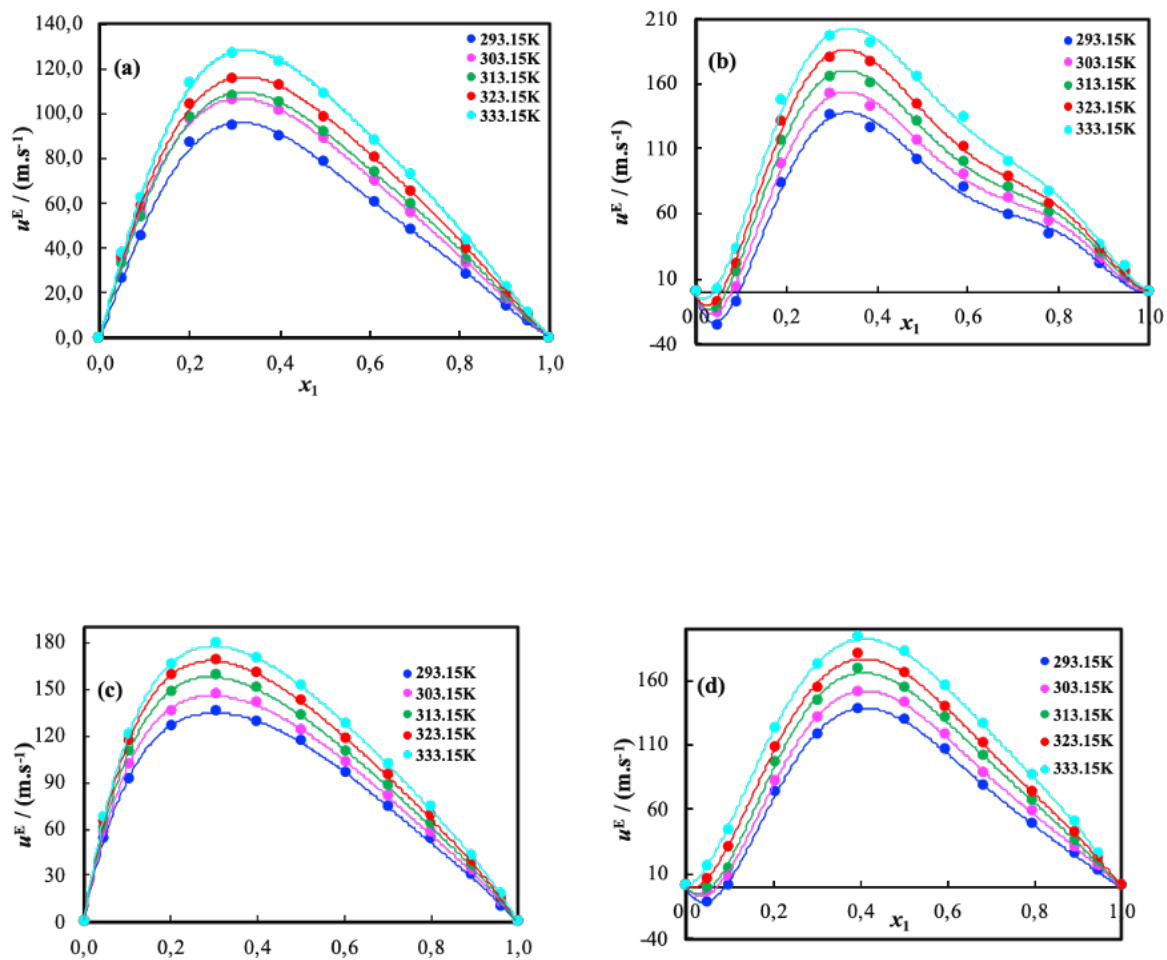


Figure 5.7B: Variations of excess sound velocity (u^E) with IL mole fraction (x_1) for the binary mixtures of [EMIM][BF₄] with (a) acetic acid or (b) propionic acid and [EMIM][MeSO₄] with (c) acetic acid or (d) propionic acid at $T = 293.15 - 333.15$ K. The dotted lines were generated using the Redlich-Kister curve-fitting.

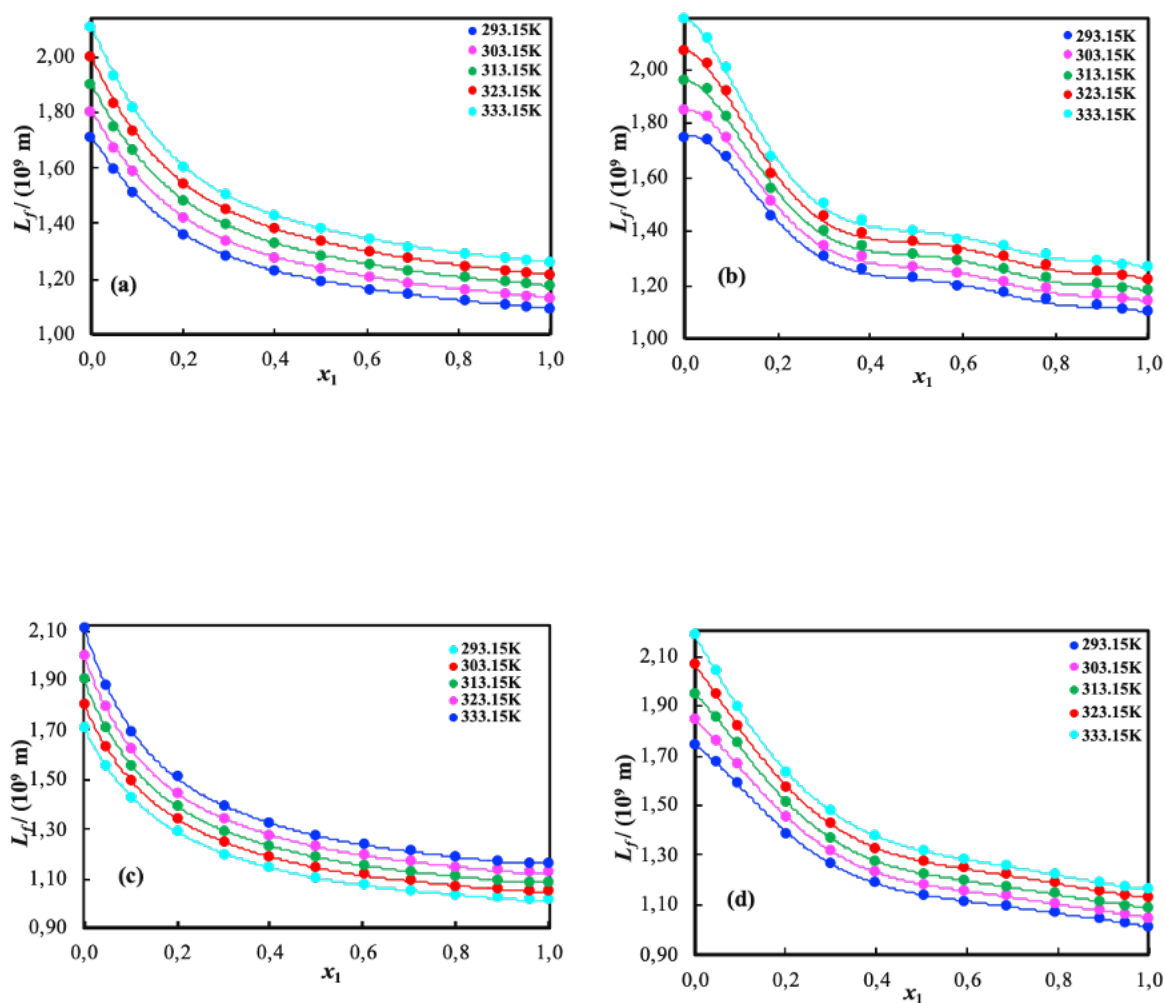


Figure 5.8B: Variations of intermolecular free-length (L_f) with IL mole fraction (x_1) for the binary mixtures of [EMIM][BF₄] with (a) acetic acid or (b) propionic acid and [EMIM][MeSO₄] with (c) acetic acid or (d) propionic at $T = 293.15 - 333.15$ K.

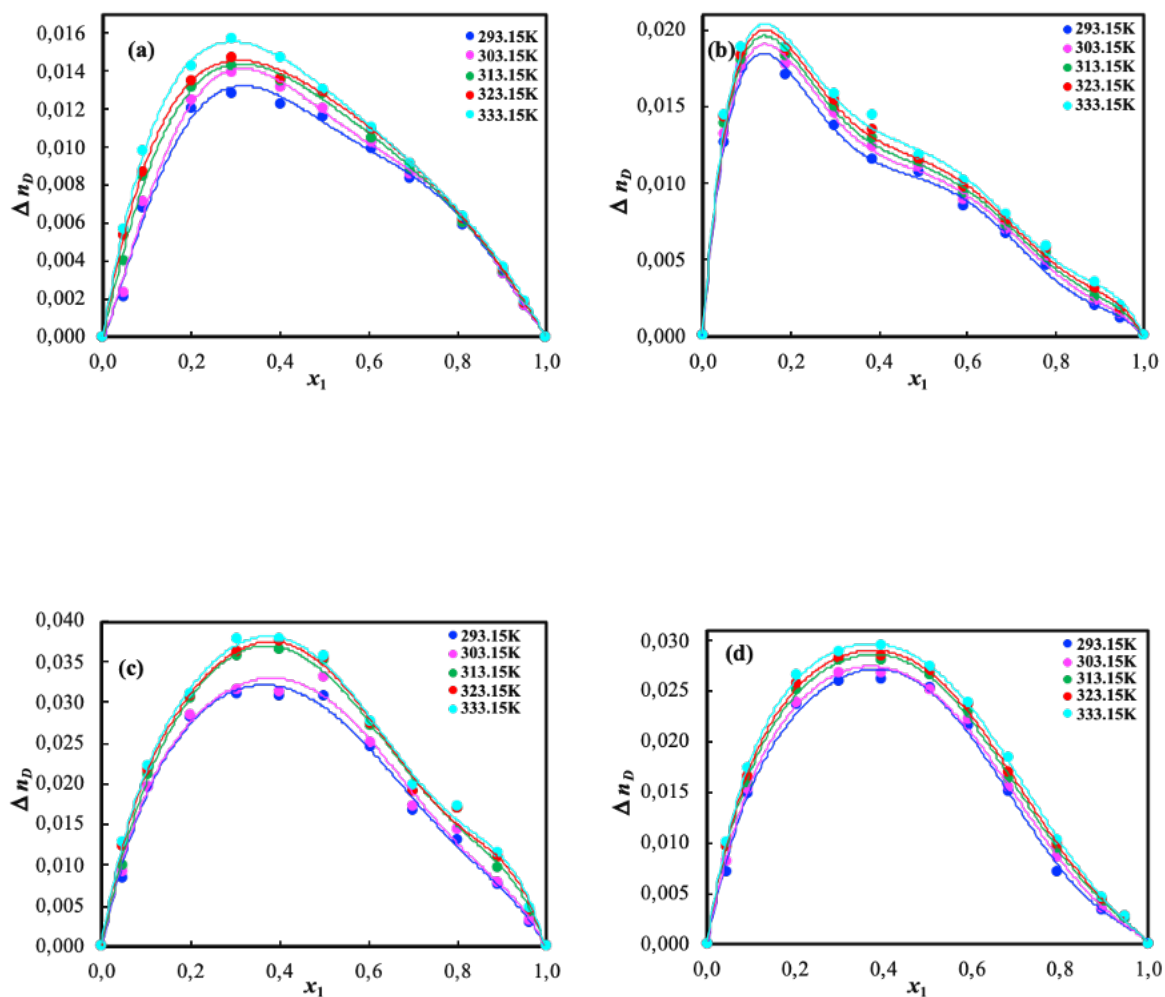


Figure 5.9B: Variations of deviation in refractive index (Δn_D) with IL mole fraction (x_1) for the binary mixtures of [EMIM][BF₄] with (a) acetic acid or (b) propionic acid and [EMIM][MeSO₄] with (c) acetic acid or (d) propionic at T = 293.15 - 333.15 K. The dotted lines were generated using the Redlich-Kister curve-fitting.

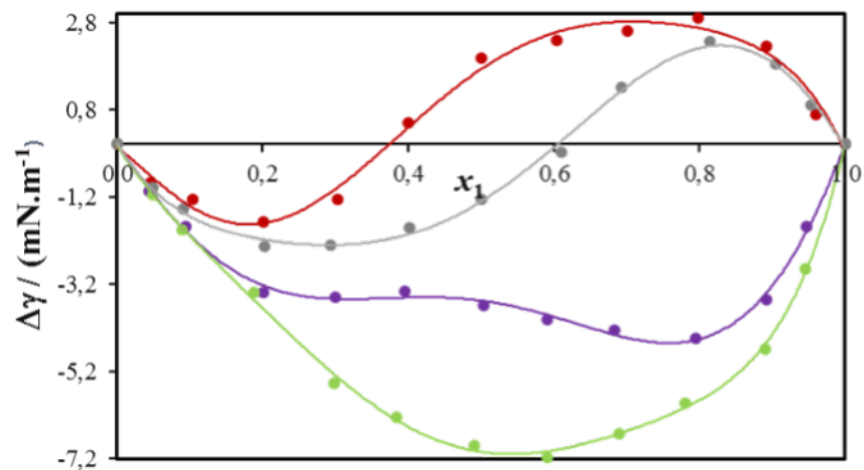


Figure 5.10B: Variations of deviation in surface tension ($\Delta\gamma$) with IL mole fraction (x_1) for binary mixtures (●){[EMIM][BF₄](x_1) + acetic acid (x_2)}, (●){[EMIM][MeSO₄](x_1) + acetic acid (x_2)}, (●){[EMIM][BF₄](x_1) + propionic acid (x_2)} and (●){[EMIM][MeSO₄](x_1) + propionic acid (x_2)} at T = 298.15 K. The dotted lines were generated using the Redlich-Kister curve-fitting.

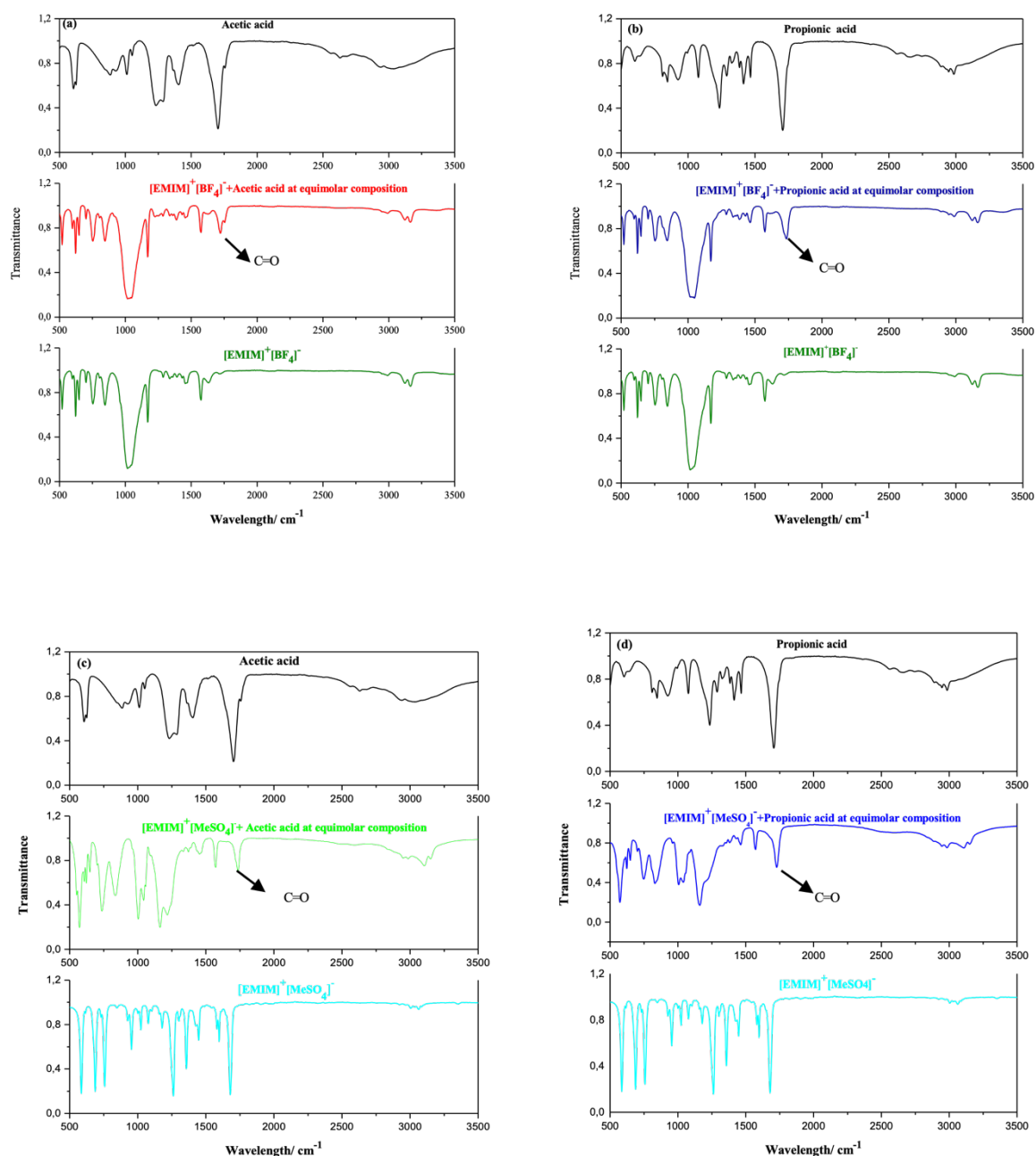


Figure 5.11B: FTIR spectrums of pure $[\text{EMIM}][\text{BF}_4]$, $[\text{EMIM}][\text{MeSO}_4]$, acetic acid, propionic acid and their binary mixtures at an equimolar composition

Appendix C: This section presents the results obtained for binary mixtures of IL; [BMIM][BF₄] or [BMIM][PF₆] with acetic or propionic acid.

Table 5.1C below presents the isobaric heat capacities (C_p) and isobaric expansivity coefficients (α_p) required to calculate excess isentropic compressibility (k_s^E). The C_p values of the pure [BMIM][BF₄] and [BMIM][PF₆] were taken from the literature. The α_p values for the pure [BMIM][BF₄] and [BMIM][PF₆] were calculated from the experimental density data using Equations 2.12 in Section 2.5 of Chapter 2.

Table 5.1C: Isobaric heat capacities (c_p) and isobaric expansion coefficients (α_p) of the pure [BMIM][BF₄] and [BMIM][PF₆] at T = 293.15 - 333.15 K.

T/K	$c_p/\text{J. mol}^{-1} \cdot \text{K}^{-1}$		α_p/kK^{-1}	
	[BMIM][BF ₄]	[BMIM][PF ₆]	[BMIM][BF ₄]	[BMIM][PF ₆]
293.15	362.5 ^a	405.0 ^b	0.000581	0.000583
303.15	367.2 ^a	410.3 ^b	0.000584	0.000587
313.15	371.9 ^a	416.0 ^b	0.000588	0.000591
323.15	376.6 ^a	421.9 ^b	0.000591	0.000594
333.15	381.4 ^a	430.2 ^c	0.000595	0.000598

^a[Waliszewski *et al.* 2005], ^b[Troncoso *et al.* 2006], ^c[Yu *et al.* 2009], ^d[Parveen *et al.* 2012]

Table 5.2C: Mole fraction of [BMIM][BF₄] (x_1), density (ρ), sound velocity (u) and refractive index (n_D) for the binary mixtures of {[BMIM][BF₄] (x_1) + acetic acid (x_2)} (mix_5) at T = 293.15 - 333.15 K and at pressure, $p = 0.1$ MPa.

x_1	$\rho/\text{g.cm}^{-3}$	$u/\text{m.s}^{-1}$	n_D	x_1	$\rho/\text{g.cm}^{-3}$	$u/\text{m.s}^{-1}$	n_D
293.15 K							
0.0000	1.057	1158	1.378	0.5993	1.166	1471	1.409
0.0532	1.084	1249	1.385	0.7052	1.174	1495	1.412
0.1015	1.107	1310	1.391	0.7997	1.179	1515	1.414
0.2007	1.134	1386	1.400	0.8909	1.184	1529	1.415
0.2945	1.151	1433	1.406	0.9529	1.188	1531	1.417
0.4021	1.164	1469	1.410	1.0000	1.191	1532	1.418
0.4935	1.173	1497	1.413	323.15 K			
0.5993	1.181	1519	1.415	0.0000	1.025	1061	1.366
0.7052	1.189	1541	1.418	0.0532	1.056	1160	1.376
0.7997	1.193	1559	1.419	0.1015	1.078	1225	1.382
0.8909	1.199	1573	1.421	0.2007	1.107	1305	1.391
0.9529	1.202	1577	1.422	0.2945	1.126	1355	1.396
1.0000	1.205	1579	1.423	0.4021	1.139	1393	1.401
303.15 K				0.4935	1.149	1423	1.404
0.0000	1.047	1124	1.374	0.5993	1.159	1447	1.407
0.0532	1.075	1217	1.382	0.7052	1.166	1473	1.410
0.1015	1.097	1280	1.387	0.7997	1.172	1493	1.412
0.2007	1.125	1359	1.397	0.8909	1.177	1506	1.413
0.2945	1.143	1407	1.402	0.9529	1.181	1508	1.414
0.4021	1.156	1443	1.407	1.0000	1.184	1509	1.415
0.4935	1.165	1472	1.410	333.15 K			
0.5993	1.174	1495	1.412	0.0000	1.006	1033	1.363
0.7052	1.181	1518	1.415	0.0532	1.040	1135	1.373
0.7997	1.186	1538	1.417	0.1015	1.068	1205	1.380
0.8909	1.191	1550	1.418	0.2007	1.098	1284	1.389
0.9529	1.195	1554	1.419	0.2945	1.117	1336	1.394
1.0000	1.198	1555	1.421	0.4021	1.131	1373	1.399
313.15 K				0.4935	1.142	1402	1.402
0.0000	1.035	1092	1.368	0.5993	1.151	1426	1.405
0.0532	1.065	1188	1.378	0.7052	1.159	1451	1.408
0.1015	1.088	1253	1.384	0.7997	1.164	1470	1.410
0.2007	1.116	1331	1.393	0.8909	1.170	1485	1.411
0.2945	1.134	1381	1.399	0.9529	1.174	1487	1.412
0.4021	1.147	1418	1.403	1.0000	1.177	1487	1.413
0.4935	1.157	1447	1.406				

Standard uncertainties u are; $u(T) = 0.02$ K, $u(p) = 0.04$ MPa and the combined expanded uncertainty Uc in mole fraction, density, sound velocity and refractive index were $Uc(x) = 0.0006$, $Uc(\rho) = 0.006$ g.cm⁻³, $Uc(u) = 1$ m.s⁻¹ and $Uc(n) = 0.004$, respectively, (0.95 level of confidence).

Table 5.3C: Mole fraction of [BMIM][PF₆] (x_1), density (ρ), sound velocity (u) and refractive index (n_D) for the binary mixtures of {[BMIM][PF₆] (x_1) + acetic acid (x_2)} (mix_6) at T = 293.15 - 333.15 K and at pressure, $p = 0.1$ MPa.

x_1	$\rho/\text{g.cm}^{-3}$	$u/\text{m.s}^{-1}$	n_D	x_1	$\rho/\text{g.cm}^{-3}$	$u/\text{m.s}^{-1}$	n_D
293.15 K							
0.0000	1.057	1158	1.378	0.5966	1.294	1372	1.401
0.0500	1.112	1208	1.381	0.6997	1.309	1386	1.402
0.0937	1.152	1244	1.388	0.8053	1.327	1396	1.403
0.2056	1.216	1318	1.395	0.8904	1.340	1402	1.404
0.2933	1.248	1352	1.400	0.9484	1.349	1406	1.405
0.4044	1.277	1384	1.404	1.0000	1.354	1410	1.406
0.4962	1.296	1405	1.405	323.15 K			
0.5966	1.314	1423	1.407	0.0000	1.025	1061	1.366
0.6997	1.330	1436	1.408	0.0500	1.079	1123	1.371
0.8053	1.346	1446	1.409	0.0937	1.118	1163	1.377
0.8904	1.358	1453	1.410	0.2056	1.184	1233	1.385
0.9484	1.366	1456	1.411	0.2933	1.216	1273	1.391
1.0000	1.371	1458	1.411	0.4044	1.246	1307	1.395
303.15 K				0.4962	1.266	1328	1.396
0.0000	1.047	1124	1.374	0.5966	1.283	1347	1.398
0.0500	1.103	1174	1.378	0.6997	1.300	1360	1.399
0.0937	1.141	1216	1.384	0.8053	1.318	1371	1.401
0.2056	1.206	1289	1.392	0.8904	1.331	1378	1.402
0.2933	1.237	1325	1.397	0.9484	1.340	1383	1.403
0.4044	1.267	1358	1.401	1.0000	1.346	1387	1.403
0.4962	1.286	1378	1.402	333.15 K			
0.5966	1.303	1395	1.404	0.0000	1.006	1033	1.363
0.6997	1.320	1410	1.405	0.0500	1.061	1097	1.370
0.8053	1.337	1421	1.406	0.0937	1.100	1136	1.374
0.8904	1.349	1427	1.407	0.2056	1.169	1211	1.382
0.9484	1.357	1431	1.408	0.2933	1.201	1251	1.388
1.0000	1.363	1433	1.408	0.4044	1.233	1287	1.392
313.15 K				0.4962	1.253	1308	1.394
0.0000	1.035	1092	1.368	0.5966	1.270	1324	1.395
0.0500	1.090	1148	1.373	0.6997	1.288	1337	1.397
0.0937	1.129	1188	1.379	0.8053	1.307	1349	1.398
0.2056	1.194	1262	1.388	0.8904	1.321	1356	1.399
0.2933	1.227	1299	1.393	0.9484	1.331	1361	1.400
0.4044	1.257	1332	1.397	1.0000	1.338	1364	1.400
0.4962	1.276	1352	1.399				

Standard uncertainties u are; $u(T) = 0.02$ K, $u(p) = 0.04$ MPa and the combined expanded uncertainty Uc in mole fraction, density, sound velocity and refractive index were $Uc(x) = 0.0006$, $Uc(\rho) = 0.006 \text{ g.cm}^{-3}$, $Uc(u) = 1 \text{ m.s}^{-1}$ and $Uc(n) = 0.004$, respectively, (0.95 level of confidence).

Table 5.4C: Mole fraction of [BMIM][BF₄] (x_1), density (ρ), sound velocity (u) and refractive index (n_D) for the binary mixtures of {[BMIM][BF₄] (x_1) + propionic acid (x_2)} (mix_7) at T = 293.15 - 333.15 K and at pressure, $p = 0.1$ MPa.

x_1	$\rho/\text{g.cm}^{-3}$	$u/\text{m.s}^{-1}$	n_D	x_1	$\rho/\text{g.cm}^{-3}$	$u/\text{m.s}^{-1}$	n_D
293.15 K							
0.0000	0.998	1171	1.387	0.6065	1.154	1462	1.413
0.0448	1.051	1215	1.399	0.6871	1.163	1481	1.413
0.1014	1.088	1256	1.408	0.8020	1.173	1496	1.415
0.1935	1.113	1342	1.411	0.8919	1.179	1509	1.415
0.3124	1.129	1406	1.411	0.9446	1.184	1521	1.416
0.4076	1.143	1440	1.414	1.0000	1.191	1532	1.418
0.4957	1.152	1470	1.415				
0.6065	1.168	1503	1.418	323.15 K			
0.6871	1.176	1520	1.419	0.0000	0.966	1060	1.374
0.8020	1.184	1538	1.420	0.0448	1.019	1116	1.388
0.8919	1.190	1559	1.421	0.1014	1.063	1177	1.398
0.9446	1.195	1568	1.421	0.1935	1.092	1262	1.402
1.0000	1.205	1579	1.423	0.3124	1.104	1340	1.402
				0.4076	1.119	1375	1.404
303.15 K				0.4957	1.132	1407	1.407
0.0000	0.988	1134	1.383	0.6065	1.147	1440	1.409
0.0448	1.040	1180	1.396	0.6871	1.156	1463	1.410
0.1014	1.082	1227	1.405	0.8020	1.166	1481	1.412
0.1935	1.105	1312	1.408	0.8919	1.173	1489	1.413
0.3124	1.120	1385	1.409	0.9446	1.178	1502	1.414
0.4076	1.135	1417	1.411	1.0000	1.184	1515	1.415
0.4957	1.146	1449	1.413				
0.6065	1.160	1480	1.415	333.15 K			
0.6871	1.169	1505	1.416	0.0000	0.955	1025	1.370
0.8020	1.178	1519	1.418	0.0448	1.009	1087	1.384
0.8919	1.183	1533	1.418	0.1014	1.055	1154	1.394
0.9446	1.188	1545	1.419	0.1935	1.085	1240	1.399
1.0000	1.198	1555	1.421	0.3124	1.099	1321	1.401
				0.4076	1.111	1354	1.403
313.15 K				0.4957	1.125	1388	1.403
0.0000	0.977	1097	1.378	0.6065	1.140	1419	1.406
0.0448	1.030	1148	1.392	0.6871	1.150	1439	1.408
0.1014	1.072	1202	1.402	0.8020	1.159	1458	1.410
0.1935	1.101	1289	1.404	0.8919	1.166	1465	1.410
0.3124	1.113	1362	1.405	0.9446	1.171	1479	1.411
0.4076	1.127	1395	1.407	1.0000	1.177	1492	1.413
0.4957	1.140	1425	1.409				

Standard uncertainties u_i are $u(T) = 0.02$ K, $u(p) = 0.04$ MPa and the combined expanded uncertainty Uc in mole fraction, density, sound velocity and refractive index were $Uc(x) = 0.0006$, $Uc(\rho) = 0.006$ g.cm⁻³, $Uc(u) = 1$ m.s⁻¹ and $Uc(n) = 0.004$, respectively, (0.95 level of confidence).

Table 5.5C: Mole fraction of [BMIM][PF₆] (x_1), density (ρ), sound velocity (u) and refractive index (n_D) for the binary mixtures of {[BMIM][PF₆] (x_1) + propionic acid (x_2)} (mix_8) at T = 293.15 - 333.15 K and at pressure, $p = 0.1$ MPa.

x_1	$\rho/\text{g.cm}^{-3}$	$u/\text{m.s}^{-1}$	n_D	x_1	$\rho/\text{g.cm}^{-3}$	$u/\text{m.s}^{-1}$	n_D
293.15 K							
0.0000	0.998	1171	1.387	0.5933	1.319	1366	1.404
0.0497	1.026	1212	1.394	0.6878	1.327	1376	1.404
0.1005	1.098	1248	1.399	0.7970	1.342	1394	1.405
0.1905	1.213	1325	1.404	0.8821	1.352	1403	1.405
0.2914	1.295	1380	1.407	0.9485	1.353	1408	1.405
0.3912	1.331	1407	1.407	1.0000	1.354	1410	1.406
0.5112	1.342	1417	1.408	323.15 K			
0.5933	1.343	1422	1.409	0.0000	0.966	1060	1.374
0.6878	1.357	1435	1.409	0.0497	0.982	1112	1.384
0.7970	1.361	1443	1.410	0.1005	1.051	1150	1.391
0.8821	1.370	1451	1.410	0.1905	1.165	1237	1.396
0.9485	1.370	1457	1.410	0.2914	1.251	1290	1.398
1.0000	1.371	1458	1.411	0.3912	1.287	1315	1.399
303.15 K				0.5112	1.301	1330	1.401
0.0000	0.988	1134	1.383	0.5933	1.308	1341	1.401
0.0497	1.015	1179	1.391	0.6878	1.317	1353	1.402
0.1005	1.080	1210	1.396	0.7970	1.332	1371	1.402
0.1905	1.200	1295	1.402	0.8821	1.339	1380	1.402
0.2914	1.283	1351	1.404	0.9485	1.341	1385	1.403
0.3912	1.310	1372	1.405	1.0000	1.346	1387	1.493
0.5112	1.328	1386	1.406	333.15 K			
0.5933	1.333	1395	1.407	0.0000	0.955	1025	1.370
0.6878	1.341	1404	1.407	0.0497	0.969	1080	1.381
0.7970	1.350	1418	1.408	0.1005	1.030	1118	1.387
0.8821	1.361	1427	1.408	0.1905	1.152	1210	1.393
0.9485	1.362	1432	1.408	0.2914	1.235	1262	1.395
1.0000	1.363	1433	1.408	0.3912	1.272	1290	1.397
313.15 K				0.5112	1.288	1308	1.398
0.0000	0.977	1097	1.378	0.5933	1.295	1319	1.399
0.0497	0.999	1147	1.387	0.6878	1.307	1332	1.399
0.1005	1.065	1180	1.393	0.7970	1.319	1349	1.400
0.1905	1.179	1261	1.399	0.8821	1.328	1357	1.400
0.2914	1.269	1320	1.401	0.9485	1.331	1363	1.400
0.3912	1.298	1343	1.402	1.0000	1.338	1364	1.400
0.5112	1.314	1359	1.403				

Standard uncertainties u are; $u(T) = 0.02$ K, $u(p) = 0.04$ MPa and the combined expanded uncertainty Uc in mole fraction, density, sound velocity and refractive index were $Uc(x) = 0.0006$, $Uc(\rho) = 0.006$ g.cm⁻³, $Uc(u) = 1$ m.s⁻¹ and $Uc(n) = 0.004$, respectively, (0.95 level of confidence).

Table 5.6C: Mole fraction (x_1) and surface tension (γ) for the binary mixture of {[BMIM][BF₄] + acetic acid or propionic acid} and {[BMIM][PF₆] + acetic acid or propionic acid} at T = 298.15 K and at pressure, $p = 0.1$ MPa.

x_1	$\gamma/\text{mN.m}^{-1}$	x_1	$\gamma/\text{mN.m}^{-1}$
{[BMIM][BF₄] (x_1) + acetic acid (x_2)}		{[BMIM][PF₆] (x_1) + acetic acid (x_2)}	
0.0000	27.2	0.0000	27.2
0.0532	27.8	0.0500	27.9
0.1015	28.5	0.0937	28.7
0.2007	30.2	0.2056	30.7
0.2945	31.8	0.2933	32.5
0.4021	34.1	0.4044	35.2
0.4935	35.7	0.4962	37.2
0.5993	37.5	0.5966	38.9
0.7052	39.1	0.6997	40.4
0.7997	40.4	0.8053	41.7
0.8909	41.5	0.8904	42.9
0.9529	42.5	0.9484	43.7
1.0000	42.9	1.0000	44.2
{[BMIM][BF₄] (x_1) + propionic acid (x_2)}		{[BMIM][PF₆] (x_1) + propionic acid(x_2)}	
0.0000	26.20	0.0000	26.20
0.0448	26.4	0.0497	26.8
0.1014	27.1	0.1005	27.5
0.1935	28.5	0.1905	29.0
0.3124	30.4	0.2914	30.8
0.4076	31.9	0.3912	32.5
0.4957	33.2	0.5112	34.5
0.6065	34.8	0.5933	35.9
0.6871	36.1	0.6878	37.5
0.8020	38.1	0.7970	39.4
0.8919	39.9	0.8821	41.0
0.9446	41.0	0.9485	42.4
1.0000	42.9	1.0000	42.9

Standard uncertainties u are; are $u(T) = 0.02$ K, $u(p) = 0.04$ MPa and the combined expanded uncertainty Uc in mole fraction and surface tension were $Uc(x) = 0.0006$ and $Uc(\gamma) = 0.5 \text{ mN.m}^{-1}$, respectively.

Table 5.7C: Mole fraction of [BMIM][BF₄] (x_1), excess molar volume (V_m^E), isentropic compressibility (k_s), excess isentropic compressibility (k_s^E), excess sound velocity (u^E), intermolecular free-length (L_f) and deviation in refractive index (Δn_D) for the binary mixtures of {[BMIM][BF₄] (x_1) + acetic acid (x_2) } (mix_5) at T = 293.15 - 333.15 K and at pressure, p = 0.1 MPa.

x_1	$V_m^E / \text{cm}^3 \cdot \text{mol}^{-1}$	$10^9 k_s / \text{TPa}^{-1}$	k_s^E / TPa^{-1}	$u^E / \text{m} \cdot \text{s}^{-1}$	$L_f / 10^9 \text{m}$	Δn_D
293.15 K						
0.0000	0.000	705	0.00	0.00	1.711	0.000
0.0532	-0.211	592	-55.04	43.79	1.568	0.005
0.1015	-0.572	526	-77.56	67.70	1.479	0.008
0.2007	-0.684	459	-77.41	76.72	1.381	0.013
0.2945	-0.654	423	-66.50	71.03	1.325	0.014
0.4021	-0.416	398	-50.26	56.01	1.286	0.014
0.4935	-0.292	380	-40.77	47.75	1.257	0.012
0.5993	-0.104	367	-28.82	34.08	1.234	0.010
0.7052	-0.016	354	-20.53	25.44	1.213	0.008
0.7997	0.193	345	-14.49	20.28	1.196	0.005
0.8909	0.216	337	-8.81	14.05	1.184	0.002
0.9529	0.140	334	-4.04	6.92	1.179	0.001
1.0000	0.000	333	0.00	0.00	1.176	0.000
303.15 K						
0.0000	0.000	756	0.00	0.00	1.805	0.000
0.0532	-0.250	628	-63.95	46.80	1.645	0.006
0.1015	-0.602	556	-88.83	72.04	1.548	0.009
0.2007	-0.724	482	-88.67	82.68	1.440	0.014
0.2945	-0.692	442	-76.31	77.56	1.380	0.015
0.4021	-0.445	415	-57.66	61.79	1.338	0.014
0.4935	-0.314	396	-46.77	53.06	1.306	0.013
0.5993	-0.178	381	-33.34	38.50	1.282	0.011
0.7052	-0.040	367	-24.11	29.84	1.258	0.008
0.7997	0.151	357	-17.66	24.89	1.239	0.005
0.8909	0.173	349	-10.60	16.62	1.227	0.003
0.9529	0.127	346	-4.78	7.98	1.222	0.001
1.0000	0.000	345	0.00	0.00	1.219	0.000
313.15 K						
0.0000	0.000	810	0.00	0.00	1.902	0.000
0.0532	-0.341	665	-74.51	49.86	1.724	0.007
0.1015	-0.669	586	-102.31	77.04	1.617	0.011
0.2007	-0.798	506	-100.39	87.30	1.503	0.015
0.2945	-0.761	462	-86.51	82.80	1.437	0.016
0.4021	-0.502	434	-65.55	66.84	1.391	0.015
0.4935	-0.364	413	-53.21	57.82	1.357	0.013

0.5993	-0.214	396	-38.06	42.56	1.330	0.011
0.7052	-0.051	381	-27.96	34.06	1.304	0.009
0.7997	0.146	370	-20.10	27.48	1.285	0.006
0.8909	0.121	361	-12.86	19.77	1.270	0.003
0.9529	0.095	359	-5.45	8.68	1.266	0.001
1.0000	0.000	358	0.00	0.00	1.264	0.000

323.15 K

0.0000	0.000	866	0.00	0.00	2.001	0.000
0.0532	-0.413	703	-85.97	52.97	1.804	0.007
0.1015	-0.687	618	-114.75	80.21	1.691	0.011
0.2007	-0.830	530	-112.80	91.98	1.566	0.015
0.2945	-0.793	484	-96.73	87.24	1.496	0.016
0.4021	-0.530	453	-73.43	71.15	1.447	0.015
0.4935	-0.386	430	-59.63	61.95	1.410	0.014
0.5993	-0.252	412	-42.84	46.15	1.381	0.012
0.7052	-0.059	395	-31.88	37.93	1.352	0.009
0.7997	0.080	383	-23.31	30.98	1.331	0.006
0.8909	0.118	374	-14.94	22.42	1.315	0.003
0.9529	0.063	373	-5.29	7.59	1.313	0.001
1.0000	0.000	371	0.00	0.00	1.309	0.000

333.15 K

0.0000	0.000	931	0.00	0.00	2.112	0.000
0.0532	-0.476	746	-101.23	57.19	1.890	0.007
0.1015	-1.126	644	-141.01	90.01	1.756	0.011
0.2007	-1.237	552	-134.83	101.45	1.626	0.015
0.2945	-1.157	502	-115.86	97.72	1.550	0.016
0.4021	-0.837	469	-88.07	80.53	1.499	0.015
0.4935	-0.639	446	-70.58	69.22	1.461	0.015
0.5993	-0.420	427	-51.22	52.96	1.430	0.011
0.7052	-0.208	410	-37.23	41.99	1.401	0.009
0.7997	0.063	398	-26.14	32.80	1.380	0.006
0.8909	0.108	388	-16.40	23.15	1.363	0.003
0.9529	0.039	385	-7.21	10.44	1.358	0.001
1.0000	0.000	384	0.00	0.00	1.356	0.000

Standard uncertainties u are; $u(T) = 0.02$ K, $u(p) = 0.04$ MPa and the combined expanded uncertainty Uc in mole fraction, density, sound velocity and refractive index were $Uc(x) = 0.0006$, $Uc(\rho) = 0.006$ g.cm⁻³, $Uc(u) = 1$ m.s⁻¹ and $Uc(n) = 0.004$, respectively, (0.95 level of confidence).

Table 5.8C: Mole fraction of [BMIM][PF₆] (x_1), excess molar volume (V_m^E), isentropic compressibility (k_s), excess isentropic compressibility (k_s^E), excess sound velocity (u^E), intermolecular free-length (L_f) and deviation in refractive index (Δn_D) for the binary mixtures of {[BMIM][PF₆] (x_1) + acetic acid (x_2)} (mix_6) at T = 293.15 - 333.15 K and at pressure, $p = 0.1$ MPa.

x_1	$V_m^E / \text{cm}^3 \cdot \text{mol}^{-1}$	$10^9 k_s / \text{TPa}^{-1}$	k_s^E / TPa^{-1}	$u^E / \text{m} \cdot \text{s}^{-1}$	$L_f / 10^9 \text{m}$	Δn_D
293.15 K						
0.0000	0.000	705	0.00	0.00	1.711	0.000
0.0500	-0.253	616	-30.44	7.42	1.600	0.002
0.0937	-0.520	561	-44.96	11.79	1.526	0.007
0.2056	-0.429	474	-55.27	19.63	1.403	0.011
0.2933	-0.107	438	-48.69	15.68	1.349	0.013
0.4044	0.378	409	-38.43	10.12	1.303	0.013
0.4962	0.689	391	-31.11	7.35	1.274	0.011
0.5966	0.880	376	-23.75	4.88	1.249	0.009
0.6997	0.950	364	-16.61	2.59	1.230	0.007
0.8053	0.705	355	-10.47	1.28	1.214	0.004
0.8904	0.427	349	-5.91	0.82	1.204	0.003
0.9484	0.083	345	-2.92	0.24	1.198	0.001
1.0000	0.000	343	0.00	0.00	1.194	0.000
303.15 K						
0.0000	0.000	756	0.00	0.00	1.805	0.000
0.0500	-0.316	658	-34.32	7.97	1.683	0.003
0.0937	-0.472	593	-53.86	17.46	1.599	0.007
0.2056	-0.412	499	-63.70	24.96	1.466	0.011
0.2933	-0.048	460	-56.09	21.40	1.408	0.013
0.4044	0.412	428	-44.37	15.34	1.358	0.013
0.4962	0.804	410	-34.47	9.98	1.329	0.011
0.5966	1.123	394	-25.50	6.32	1.303	0.010
0.6997	1.223	381	-18.18	4.71	1.281	0.007
0.8053	0.817	370	-11.61	2.68	1.263	0.005
0.8904	0.513	364	-6.12	0.87	1.252	0.003
0.9484	0.137	360	-3.04	0.34	1.245	0.002
1.0000	0.000	357	0.00	0.00	1.240	0.000
313.15 K						
0.0000	0.000	810	0.00	0.00	1.902	0.000
0.0500	-0.244	696	-44.44	14.48	1.762	0.003
0.0937	-0.439	627	-63.71	22.70	1.673	0.007
0.2056	-0.344	526	-71.94	29.18	1.533	0.012
0.2933	0.021	483	-63.59	26.10	1.469	0.014
0.4044	0.480	448	-50.28	19.67	1.415	0.014
0.4962	0.837	429	-39.16	13.70	1.383	0.012
0.5966	1.214	411	-29.74	10.90	1.355	0.010
0.6997	1.386	398	-20.50	7.33	1.332	0.007

0.8053	1.060	387	-12.01	3.02	1.315	0.005
0.8904	0.630	380	-6.37	1.06	1.302	0.003
0.9484	0.162	375	-3.20	0.41	1.294	0.002
1.0000	0.000	372	0.00	0.00	1.288	0.000
323.15 K						
0.0000	0.000	866	0.00	0.00	2.001	0.000
0.0500	-0.193	735	-54.27	19.53	1.844	0.004
0.0937	-0.398	662	-74.23	27.65	1.749	0.008
0.2056	-0.316	555	-79.50	31.61	1.602	0.012
0.2933	0.073	507	-71.25	30.12	1.532	0.014
0.4044	0.652	469	-56.13	23.82	1.474	0.014
0.4962	0.988	448	-44.36	18.23	1.439	0.012
0.5966	1.424	429	-32.85	13.68	1.409	0.010
0.6997	1.493	416	-21.39	7.10	1.387	0.008
0.8053	1.073	403	-13.18	3.82	1.366	0.005
0.8904	0.652	396	-6.75	1.15	1.353	0.003
0.9484	0.209	390	-3.37	0.55	1.343	0.002
1.0000	0.000	386	0.00	0.00	1.337	0.0000
333.15 K						
0.0000	0.000	931	0.00	0.00	2.112	0.000
0.0500	-0.171	783	-64.54	22.96	1.937	0.006
0.0937	-0.320	705	-84.36	30.41	1.837	0.008
0.2056	-0.298	583	-94.08	38.82	1.671	0.012
0.2933	0.234	532	-83.93	38.04	1.595	0.015
0.4044	0.801	490	-66.99	32.05	1.531	0.014
0.4962	1.182	466	-53.24	25.99	1.494	0.012
0.5966	1.747	449	-37.46	17.60	1.466	0.010
0.6997	1.811	434	-24.52	10.31	1.442	0.008
0.8053	1.337	420	-14.95	5.84	1.419	0.005
0.8904	0.922	412	-7.44	2.30	1.404	0.003
0.9484	0.233	406	-3.89	1.06	1.394	0.002
1.0000	0.000	402	0.00	0.00	1.387	0.000

Standard uncertainties u are; $u(T) = 0.02$ K, $u(p) = 0.04$ MPa and the combined expanded uncertainty Uc in mole fraction, density, sound velocity and refractive index were $Uc(x) = 0.0006$, $Uc(\rho) = 0.006$ g.cm⁻³, $Uc(u) = 1$ m.s⁻¹ and $Uc(n) = 0.004$, respectively, (0.95 level of confidence).

Table 5.9C: Mole fraction of [BMIM][BF₄] (x_1), excess molar volume (V_m^E), isentropic compressibility (k_s), excess isentropic compressibility (k_s^E), excess sound velocity (u^E), intermolecular free-length (L_f) and deviation in refractive index (Δn_D) for the binary mixtures of {[BMIM][BF₄] (x_1) + propionic acid (x_2) } (mix_7) at T = 293.15 - 333.15 K and at pressure, $p = 0.1$ MPa.

x_1	$V_m^E / \text{cm}^3 \cdot \text{mol}^{-1}$	$10^9 k_s / \text{TPa}^{-1}$	k_s^E / TPa^{-1}	$u^E / \text{m} \cdot \text{s}^{-1}$	$L_f / 10^9 \text{m}$	Δn_D
293.15 K						
0.0000	0.000	731	0.00	0.00	1.742	0.000
0.0448	-2.294	645	-44.08	14.67	1.636	0.011
0.1014	-3.451	583	-59.86	20.25	1.556	0.018
0.1935	-3.132	499	-81.97	54.59	1.439	0.017
0.3124	-1.939	448	-69.91	58.32	1.365	0.013
0.4076	-1.349	422	-56.37	50.66	1.324	0.012
0.4957	-0.840	401	-46.05	45.01	1.291	0.011
0.6065	-0.589	379	-34.94	36.89	1.255	0.009
0.6871	-0.343	368	-25.61	27.37	1.236	0.007
0.8020	0.462	357	-11.36	11.44	1.218	0.005
0.8919	0.871	346	-5.17	6.95	1.199	0.002
0.9446	0.896	340	-1.61	3.12	1.189	0.000
1.0000	0.000	333	0.00	0.00	1.176	0.000
303.15K						
0.0000	0.000	788	0.00	0.00	1.843	0.000
0.0448	-2.322	690	-51.11	17.16	1.724	0.012
0.1014	-3.831	614	-76.47	28.81	1.626	0.018
0.1935	-3.328	526	-95.15	60.59	1.506	0.017
0.3124	-2.024	465	-86.69	73.63	1.416	0.014
0.4076	-1.543	439	-68.49	61.56	1.375	0.012
0.4957	-0.952	416	-56.94	56.98	1.338	0.011
0.6065	-0.637	394	-42.40	45.85	1.302	0.009
0.6871	-0.459	378	-35.25	42.27	1.276	0.007
0.8020	0.165	368	-16.65	19.37	1.259	0.005
0.8919	0.744	360	-5.87	7.15	1.245	0.002
0.9446	0.821	353	-2.41	4.27	1.233	0.000
1.0000	0.000	345	0.00	0.00	1.219	0.000
313.15 K						
0.0000	0.000	851	0.00	0.00	1.950	0.000
0.0448	-2.376	737	-61.99	21.56	1.815	0.012
0.1014	-3.876	646	-96.27	40.37	1.699	0.019
0.1935	-3.865	547	-119.28	74.81	1.562	0.018
0.3124	-2.234	484	-104.52	86.47	1.470	0.014
0.4076	-1.620	456	-83.47	75.08	1.426	0.013
0.4957	-1.255	432	-68.52	66.85	1.389	0.011

0.6065	-0.943	405	-54.09	59.50	1.345	0.009
0.6871	-0.704	392	-41.67	48.51	1.323	0.008
0.8020	-0.143	381	-21.27	24.87	1.304	0.005
0.8919	0.314	373	-7.96	8.74	1.290	0.002
0.9446	0.287	365	-3.90	4.78	1.277	0.001
1.0000	0.000	358	0.00	0.00	1.264	0.000

323.15 K

0.0000	0.000	920	0.00	0.00	2.063	0.000
0.0448	-2.422	788	-74.26	25.75	1.910	0.012
0.1014	-4.041	679	-120.00	51.88	1.772	0.019
0.1935	-4.054	575	-139.20	83.42	1.630	0.019
0.3124	-2.294	505	-122.71	98.11	1.528	0.015
0.4076	-1.742	473	-99.13	87.17	1.478	0.013
0.4957	-1.366	446	-82.39	79.78	1.436	0.012
0.6065	-1.007	421	-61.59	65.64	1.395	0.010
0.6871	-0.740	405	-49.05	56.81	1.368	0.008
0.8020	-0.312	391	-26.96	32.55	1.345	0.005
0.8919	0.184	385	-9.25	9.87	1.334	0.002
0.9446	0.208	376	-4.62	5.49	1.319	0.001
1.0000	0.000	368	0.00	0.00	1.305	0.000

333.15 K

0.0000	0.000	996	0.00	0.00	2.183	0.000
0.0448	-2.493	839	-92.71	32.48	2.004	0.012
0.1014	-4.321	712	-149.46	64.30	1.846	0.020
0.1935	-4.330	599	-167.85	97.47	1.693	0.021
0.3124	-2.675	522	-148.76	114.34	1.581	0.018
0.4076	-1.764	491	-117.57	100.48	1.533	0.015
0.4957	-1.473	462	-98.80	93.54	1.487	0.012
0.6065	-1.216	436	-73.41	76.14	1.444	0.010
0.6871	-1.004	420	-56.92	63.04	1.418	0.008
0.8020	-0.346	406	-31.16	36.78	1.394	0.005
0.8919	0.059	399	-10.78	11.11	1.383	0.002
0.9446	0.134	391	-5.11	5.60	1.368	0.001
1.0000	0.000	382	0.00	0.00	1.352	0.000

Standard uncertainties u are; $u(T) = 0.02$ K, $u(p) = 0.04$ MPa and the combined expanded uncertainty Uc in mole fraction, density, sound velocity and refractive index were $Uc(x) = 0.0006$, $Uc(\rho) = 0.006$ g.cm⁻³, $Uc(u) = 1$ m.s⁻¹ and $Uc(n) = 0.004$, respectively, (0.95 level of confidence)

Table 5.10C: Mole fraction of [BMIM][PF₆] (x_1), excess molar volume (V_m^E), isentropic compressibility (k_s), excess isentropic compressibility (k_s^E), excess sound velocity (u^E), intermolecular free-length (L_f) and deviation in refractive index (Δn_D) for the binary mixtures of {[BMIM][PF₆] (x_1) + propionic acid (x_2)} (mix_8) at T = 293.15 - 333.15 K and at pressure, $p = 0.1$ MPa.

x_1	$V_m^E / \text{cm}^3 \cdot \text{mol}^{-1}$	$10^9 k_s / \text{TPa}^{-1}$	k_s^E / TPa^{-1}	$u^E / \text{m} \cdot \text{s}^{-1}$	$L_f / 10^9 \text{m}$	Δn_D
293.15K						
0.0000	0.000	731	0.00	0.00	1.742	0.000
0.0497	1.585	664	-17.38	10.34	1.661	0.006
0.1005	-0.871	585	-53.39	17.98	1.559	0.010
0.1905	-5.481	470	-107.21	51.61	1.397	0.013
0.2914	-8.482	405	-118.29	66.88	1.297	0.013
0.3912	-8.836	380	-102.26	60.16	1.256	0.012
0.5112	-6.968	371	-70.74	37.35	1.242	0.009
0.5933	-5.172	368	-51.22	23.81	1.237	0.008
0.6878	-4.590	358	-39.24	18.49	1.219	0.006
0.7970	-2.718	353	-22.24	8.69	1.211	0.004
0.8821	-2.251	346	-14.21	6.01	1.200	0.002
0.9485	-0.937	344	-6.82	4.42	1.195	0.001
1.0000	0.000	343	0.00	0.00	1.194	0.000
303.15K						
0.0000	0.000	788	0.00	0.00	1.843	0.000
0.0497	1.632	708	-25.07	15.34	1.747	0.006
0.1005	-0.290	632	-53.90	17.90	1.650	0.011
0.1905	-5.368	497	-120.44	58.13	1.464	0.014
0.2914	-8.439	427	-130.98	72.89	1.357	0.014
0.3912	-7.953	405	-106.54	60.04	1.321	0.012
0.5112	-6.645	392	-75.67	39.39	1.299	0.010
0.5933	-5.155	385	-56.94	28.34	1.289	0.009
0.6878	-3.824	378	-39.29	17.55	1.277	0.007
0.7970	-2.542	368	-24.96	12.24	1.260	0.005
0.8821	-2.183	361	-15.82	7.97	1.247	0.003
0.9485	-0.870	358	-7.22	4.76	1.242	0.001
1.0000	0.000	357	0.00	0.00	1.240	0.000
313.15K						
0.0000	0.000	851	0.00	0.00	1.950	0.000
0.0497	2.154	761	-29.50	19.97	1.843	0.007
0.1005	0.066	674	-63.55	24.26	1.735	0.012
0.1905	-4.544	534	-128.28	60.69	1.544	0.015
0.2914	-8.285	452	-143.80	77.46	1.421	0.015
0.3912	-7.897	427	-117.26	64.78	1.381	0.013
0.5112	-6.199	412	-82.76	44.73	1.356	0.011
0.5933	-4.663	406	-60.46	30.29	1.347	0.010
0.6878	-3.270	398	-41.11	18.88	1.333	0.007

0.7970	-2.624	383	-28.66	16.05	1.308	0.005
0.8821	-2.177	376	-17.78	10.11	1.295	0.003
0.9485	-0.909	373	-8.06	5.50	1.290	0.001
1.0000	0.000	372	0.00	0.00	1.288	0.000
323.15K						
0.0000	0.000	920	0.00	0.00	2.063	0.000
0.0497	2.711	823	-30.09	21.45	1.951	0.008
0.1005	0.370	719	-75.95	31.09	1.823	0.014
0.1905	-4.366	561	-149.37	72.52	1.611	0.016
0.2914	-7.683	480	-156.78	82.92	1.490	0.016
0.3912	-7.807	449	-129.78	70.58	1.442	0.014
0.5112	-5.903	435	-89.51	47.61	1.418	0.012
0.5933	-4.528	425	-67.53	35.68	1.403	0.010
0.6878	-3.179	415	-46.94	24.58	1.386	0.008
0.7970	-2.554	399	-32.54	20.12	1.359	0.005
0.8821	-1.538	392	-18.87	12.64	1.347	0.003
0.9485	-0.275	389	-7.87	6.58	1.341	0.001
1.0000	0.000	386	0.00	0.00	1.337	0.000
333.15K						
0.0000	0.000	996	0.00	0.00	2.183	0.000
0.0497	2.970	885	-36.12	24.23	2.059	0.009
0.1005	1.317	776	-80.16	34.34	1.928	0.014
0.1905	-4.215	592	-170.49	81.25	1.684	0.017
0.2914	-7.285	509	-172.46	88.61	1.560	0.017
0.3912	-7.439	473	-144.37	78.73	1.504	0.015
0.5112	-5.580	454	-101.27	56.77	1.475	0.012
0.5933	-4.063	444	-76.51	44.19	1.458	0.011
0.6878	-3.036	431	-54.77	32.58	1.437	0.008
0.7970	-1.898	417	-35.59	24.39	1.412	0.005
0.8821	-1.154	409	-20.66	15.22	1.399	0.003
0.9485	-0.068	405	-8.58	7.74	1.392	0.001
1.0000	0.000	402	0.00	0.00	1.387	0.000

Standard uncertainties u are; $u(T) = 0.02$ K, $u(p) = 0.04$ MPa and the combined expanded uncertainty Uc in mole fraction, density, sound velocity and refractive index were $Uc(x) = 0.0006$, $Uc(\rho) = 0.006$ g.cm⁻³, $Uc(u) = 1$ m.s⁻¹ and $Uc(n) = 0.004$, respectively, (0.95 level of confidence).

Table 5.11C: Mole fraction (x_1) and deviation in surface tension ($\Delta\gamma$) for the binary mixture of {[BMIM][BF₄] + acetic acid or propionic acid} or {[BMIM][PF₆] + acetic acid or propionic acid} at T = 298.15 K and at pressure, $p = 0.1$ MPa.

x_1	$\Delta\gamma/\text{mN.m}^{-1}$	x_1	$\Delta\gamma/\text{mN.m}^{-1}$
{[BMIM][BF₄] (x_1) + acetic acid (x_2)}		{[BMIM][PF₆] (x_1) + acetic acid (x_2)}	
0.0000	0.000	0.0000	0.000
0.0532	-0.205	0.0500	-0.111
0.1015	-0.263	0.0937	-0.095
0.2007	-0.149	0.2056	-0.002
0.2945	0.039	0.2933	0.336
0.4021	0.561	0.4044	1.112
0.4935	0.757	0.4962	1.549
0.5993	0.907	0.5966	1.590
0.7052	0.836	0.6997	1.304
0.7997	0.592	0.8053	0.816
0.8909	0.291	0.8904	0.486
0.9529	0.289	0.9484	0.359
1.0000	0.000	1.0000	0.000
{[BMIM][BF₄] (x_1) + propionic acid (x_2)}		{[BMIM][PF₆] (x_1) + propionic acid}	
0.0000	0.000	0.0000	0.000
0.0448	-0.548	0.0497	-0.337
0.1014	-0.774	0.1005	-0.524
0.1935	-0.962	0.1905	-0.626
0.3124	-1.018	0.2914	-0.637
0.4076	-1.116	0.3912	-0.717
0.4957	-1.248	0.5112	-0.881
0.6065	-1.498	0.5933	-0.983
0.6871	-1.545	0.6878	-1.108
0.8020	-1.503	0.7970	-1.228
0.8919	-1.224	0.8821	-1.094
0.9446	-1.005	0.9485	-0.871
1.0000	0.000	1.0000	0.000

Standard uncertainties u are; $u(T) = 0.02$ K, $u(p) = 0.04$ MPa and the combined expanded uncertainty U_c in mole fraction and surface tension were $U_c(x) = 0.0006$ and $U_c(\gamma) = 0.5 \text{ mN.m}^{-1}$, respectively.

Table 5.12C: Redlich-Kister Coefficients (A_i) and standard deviation (σ) obtained for the binary mixtures of {[BMIM][BF₄] (x_1) + acetic acid (x_2)} (*mix*₅), {[BMIM][PF₆] (x_1) + acetic acid (x_2)} (*mix*₆), {[BMIM][BF₄] (x_1) + propionic acid (x_2)} (*mix*₇) and {[BMIM][PF₆] (x_1) + propionic acid (x_2)} (*mix*₈) at T = 293.15 - 333.15 K and at pressure, $p = 0.1$ MPa.

	T/K	A_0	A_1	A_2	A_3	A_4	σ
{[BMIM][BF₄] (x_1) + acetic acid (x_2)}							
$\nu_m^E/\text{cm}^3\cdot\text{mol}^{-1}$	293.15	-1.046	-3.532	-3.321	-2.252	4.024	0.049
	303.15	-1.202	-3.408	-3.387	-2.535	1.275	0.045
	313.15	-1.416	-3.716	-2.733	-2.532	3.523	0.041
	323.15	-1.533	-3.624	-2.682	-2.848	0.452	0.027
	333.15	-2.479	-5.037	-4.356	-3.999	1.016	0.084
k_s^E/TPa^{-1}	293.15	-156.17	-187.19	-246.94	-425.24	-397.99	2.15
	303.15	-180.02	-212.18	-272.68	-495.19	-474.42	2.40
	313.15	-205.74	-233.67	-286.07	-588.26	-594.61	2.88
	323.15	-231.39	-255.58	-304.29	-680.93	-708.05	3.37
	333.15	-275.93	-305.37	-364.77	-838.66	-849.51	3.80
$u^E/\text{m}\cdot\text{s}^{-1}$	293.15	176.89	222.18	331.12	182.67	165.91	3.35
	303.15	197.90	238.36	343.04	187.99	178.03	3.35
	313.15	216.87	245.32	342.02	206.84	219.02	3.50
	323.15	233.15	252.08	347.45	219.09	242.98	3.51
	333.15	264.52	277.58	371.72	252.14	260.63	3.52
Δn_D	293.15	0.0488	0.0363	0.0330	0.0132	-0.0252	0.0002
	303.15	0.0511	0.0367	0.0278	0.0156	-0.0138	0.0002
	313.15	0.0530	0.0376	0.0347	0.0305	-0.0056	0.0001
	323.15	0.0544	0.0354	0.0360	0.0326	0.0020	0.0002
	333.15	0.0577	0.0347	0.0384	0.0420	0.0113	0.0003
$\Delta\gamma$	298.15	3.22	-4.08	-7.05	-0.22	4.30	0.059
{[BMIM][PF₆] (x_1) + acetic acid (x_2)}							
$\nu_m^E/\text{cm}^3\cdot\text{mol}^{-1}$	293.15	2.799	-6.231	-4.602	0.805	-1.583	0.048
	303.15	3.346	-7.730	-3.702	2.526	-3.348	0.041
	313.15	3.525	-8.539	-0.657	3.186	-6.205	0.045
	323.15	4.316	-8.877	-3.804	3.916	-2.254	0.052
	333.15	5.210	-10.358	-2.772	4.844	-2.975	0.091
k_s^E/TPa^{-1}	293.15	2.30	-155.28	-188.65	-206.28	-113.56	0.31
	303.15	-136.01	-186.43	-235.18	-238.11	-118.14	0.62
	313.15	-157.35	-195.98	-206.68	-340.35	-263.38	1.50
	323.15	-177.75	-212.67	-169.29	-426.89	-429.99	0.58
	333.15	-210.80	-264.93	-185.11	-468.82	-503.95	2.23
	293.15	27.05	76.00	126.06	19.31	-78.56	0.91
	303.15	38.48	100.45	174.43	21.44	-123.01	0.91

$u^E/\text{m.s}^{-1}$	313.15	57.11	96.53	133.00	95.40	-17.17	0.49
	323.15	74.39	106.10	58.86	130.36	130.21	0.66
	333.15	102.09	141.39	49.17	106.38	148.31	0.99
Δn_D	293.15	0.0438	0.0408	0.0213	-0.0245	-0.025	0.0006
	303.15	0.0458	0.0410	0.0198	-0.0197	-0.0190	0.0004
	313.15	0.0478	0.0413	0.0186	-0.0167	-0.0135	0.0003
	323.15	0.0495	0.0399	0.0110	-0.0048	0.0086	0.0004
	333.15	0.0506	0.0396	0.0022	0.0013	0.0322	0.0004
$\Delta\gamma$	298.15	6.17	-5.35	-15.20	1.59	13.46	0.04

{[BMIM][BF₄] (x_1) + propionic acid (x_2)}							
$\nu_m^E/\text{cm}^3\cdot\text{mol}^{-1}$	293.15	-3.598	-4.464	-10.371	-40.169	-8.474	0.084
	303.15	-3.925	-4.336	-13.334	-41.235	-8.371	0.144
	313.15	-4.756	-5.220	-16.047	-36.757	-11.081	0.086
	323.15	-5.058	-5.529	-17.229	-36.393	-12.189	0.123
	333.15	-5.550	-5.698	-21.437	-37.931	-8.676	0.108
k_s^E/TPa^{-1}	293.15	-184.04	-234.94	-244.57	-301.67	-112.64	3.19
	303.15	-226.93	-262.45	-315.66	-392.12	-103.13	2.36
	313.15	-275.22	-315.81	-408.41	-501.73	-135.31	2.05
	323.15	-325.86	-362.85	-446.33	-635.09	-264.58	1.35
	333.15	-389.76	-436.00	-505.98	-815.45	-422.41	2.09
$u^E/\text{m.s}^{-1}$	293.15	179.15	213.74	170.07	-97.76	-270.98	4.15
	303.15	226.06	205.45	244.09	-37.94	-395.99	3.67
	313.15	272.78	227.13	283.28	27.40	-408.57	3.17
	323.15	316.39	241.81	291.60	74.74	-376.75	2.12
	333.15	368.22	283.73	288.35	124.63	-323.44	2.35
Δn_D	293.15	0.0426	0.0162	0.0272	0.1494	0.1110	0.0006
	303.15	0.0436	0.0199	0.0305	0.1444	0.1053	0.0004
	313.15	0.0448	0.0209	0.0362	0.1474	0.1053	0.0005
	323.15	0.0467	0.0228	0.0408	0.1508	0.1009	0.0004
	333.15	0.0507	0.0401	0.0642	0.1301	0.0691	0.0006
$\Delta\gamma$	298.15	-5.21	3.28	-3.08	-0.33	-10.65	0.06

{[BMIM][PF₆] (x_1) + propionic acid (x_2)}							
$\nu_m^E/\text{cm}^3\cdot\text{mol}^{-1}$	293.15	-28.267	-40.543	-28.312	76.338	82.134	0.355
	303.15	-26.515	-41.319	-29.884	79.393	85.458	0.370
	313.15	-25.095	-44.299	-29.698	91.933	88.682	0.283
	323.15	-23.929	-41.514	-36.505	85.302	111.065	0.307
	333.15	-22.504	-42.573	-36.909	88.771	121.72	0.306
k_s^E/TPa^{-1}	293.15	-291.60	-574.47	-629.30	443.52	821.98	3.35
	303.15	-309.79	-626.85	-725.95	467.47	914.57	4.74
	313.15	-338.57	-686.37	-746.8	501.93	882.42	3.45
	323.15	-366.60	-744.88	-948.55	479.95	1117.42	4.69
	333.15	-412.01	-814.40	-1056.48	501.79	1262.09	6.91

$u^E/\text{ m.s}^{-1}$	293.15	162.70	373.62	248.84	-411.50	-410.89	2.59
	303.15	169.36	384.69	310.86	-405.38	-453.46	4.08
	313.15	186.59	391.87	274.57	-384.92	-334.64	3.89
	323.15	200.82	397.30	404.46	-341.28	-458.93	3.27
	333.15	235.66	391.76	406.44	-303.91	-458.79	3.93
Δn_D	293.15	0.0386	0.0386	0.0448	0.0308	-0.0027	0.0004
	303.15	0.0420	0.0364	0.0475	0.0367	-0.0000	0.0002
	313.15	0.0451	0.0385	0.0433	0.0409	0.0115	0.0001
	323.15	0.0466	0.0385	0.0476	0.0577	0.0254	0.0002
	333.15	0.0505	0.0407	0.0398	0.0599	0.0381	0.0002
$\Delta\gamma$	298.15	-3.48	2.26	-2.77	2.86	-9.38	0.05

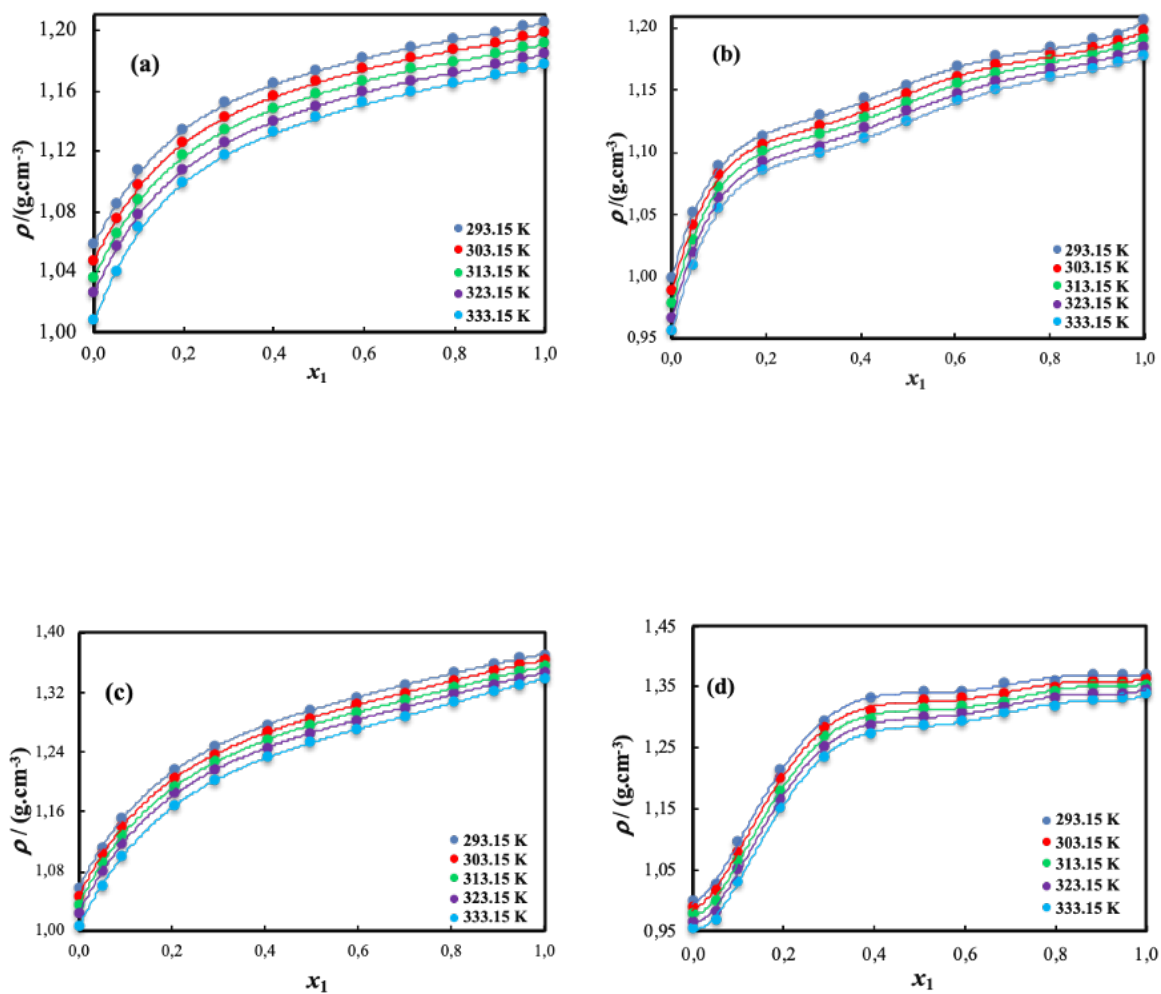


Figure 5.1C: Variations of density (ρ) with IL mole fraction (x_1) for the binary mixtures of [BMIM][BF₄] with (a) acetic acid or (b) propionic acid and [BMIM][PF₆] with (c) acetic acid or (d) propionic acid at $T = 293.15 - 333.15$ K. The dotted lines show the smoothness of these data.

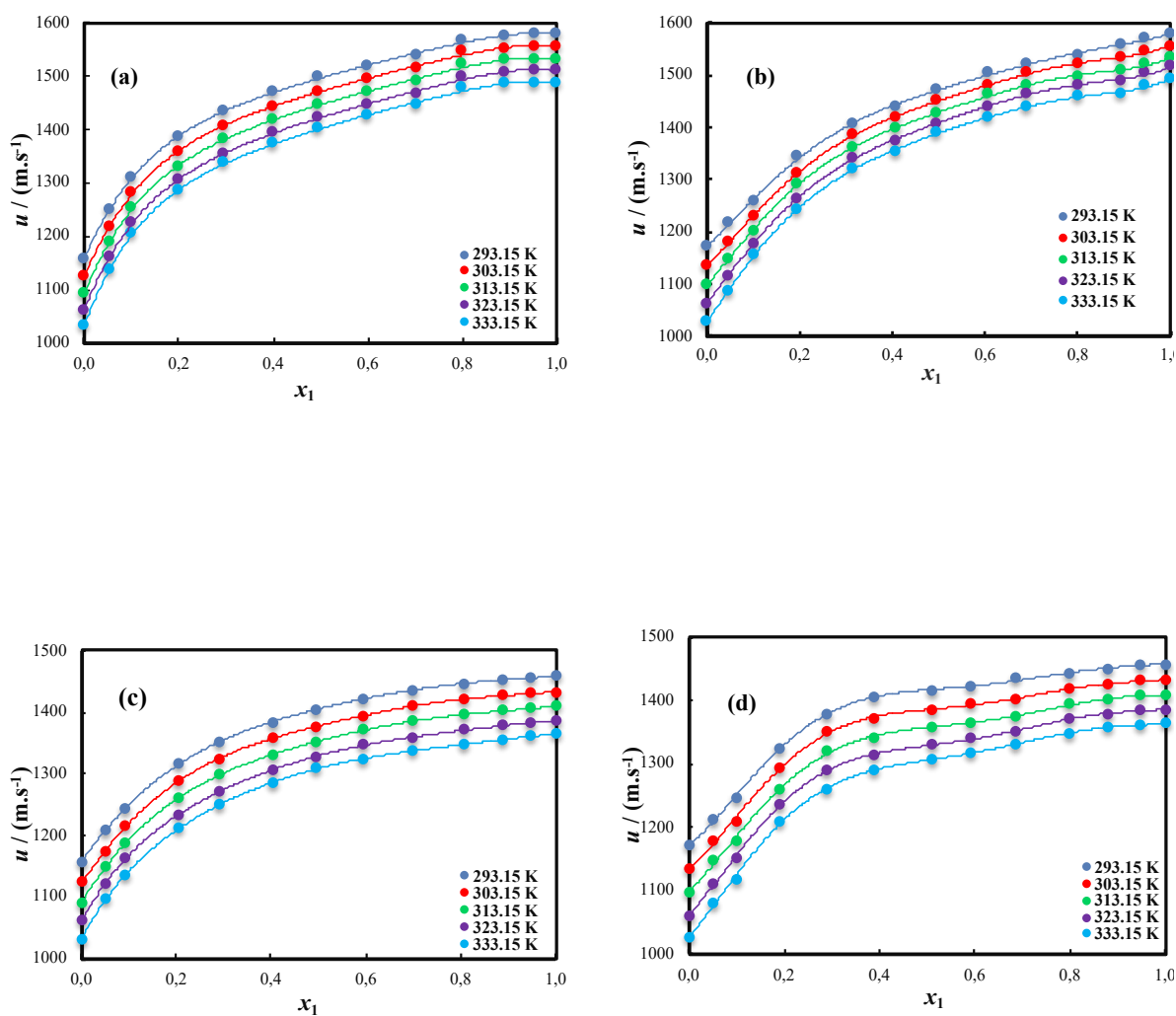


Figure 5.2C: Variations of sound velocity (u) with IL mole fraction (x_1) for the binary mixtures of [BMIM][BF₄] with (a) acetic acid or (b) propionic acid and [BMIM][PF₆] with (c) acetic acid or (d) propionic acid at $T = 293.15 - 333.15$ K. The dotted lines show the smoothness of these data.

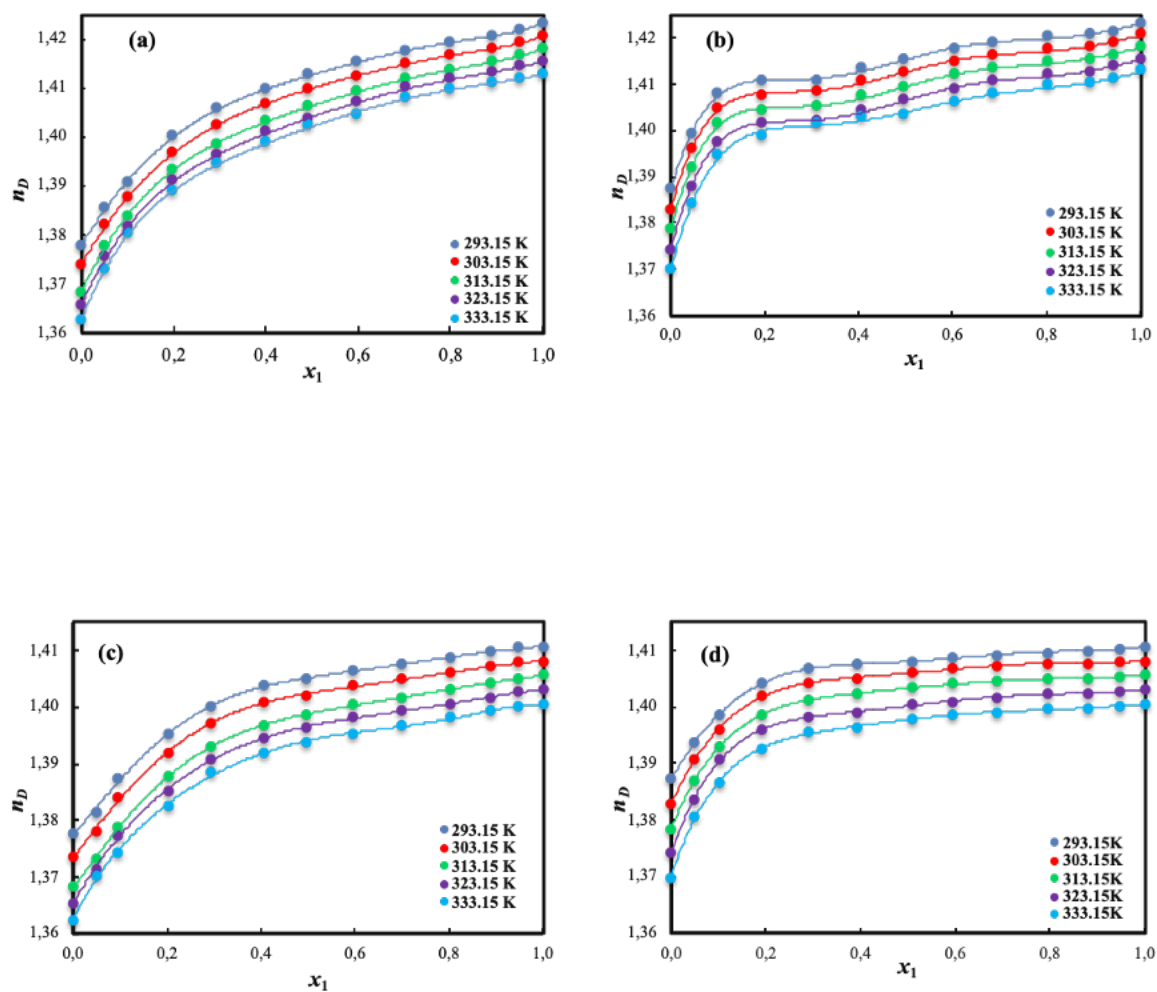


Figure 5.3C: Variations of refractive index (n_D) with IL mole fraction (x_1) for the binary mixtures of [BMIM][BF₄] with (a) acetic acid or (b) propionic acid and [BMIM][PF₆] with (c) acetic acid or (d) propionic acid at $T = 293.15 - 333.15$ K. The dotted lines show the smoothness of these data.

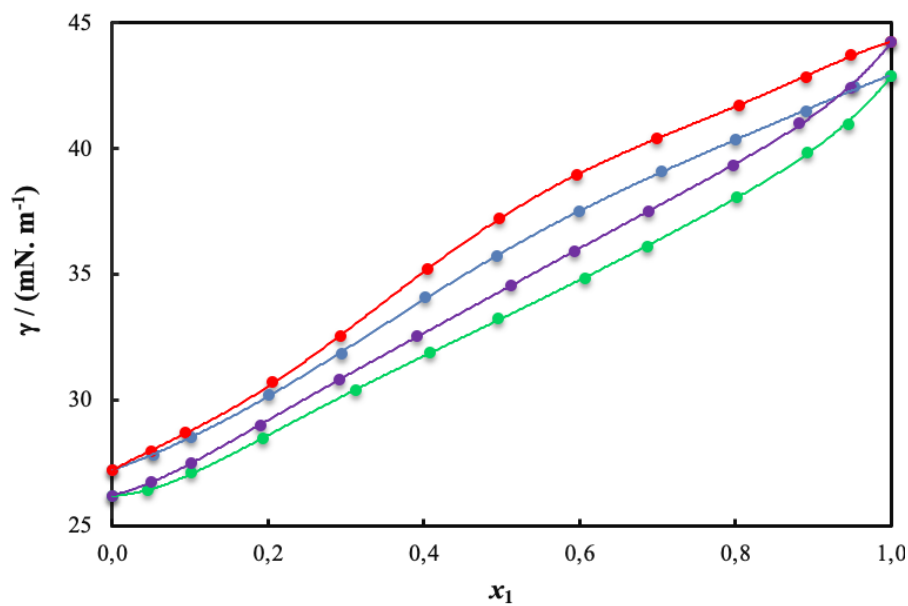


Figure 5.4C: Variations of surface tension (γ) with IL mole fraction (x_1) for the binary mixtures of (•){[BMIM][BF₄] (x_1) + acetic acid (x_2)}, (•){[BMIM][PF₆] (x_1) + acetic acid (x_2)}, (•){[BMIM][BF₄] (x_1) + propionic acid (x_2)} and (•){[BMIM][PF₆] (x_1) + propionic acid (x_2) at $T = 298.15$ K. The dotted lines show the smoothness of these data.

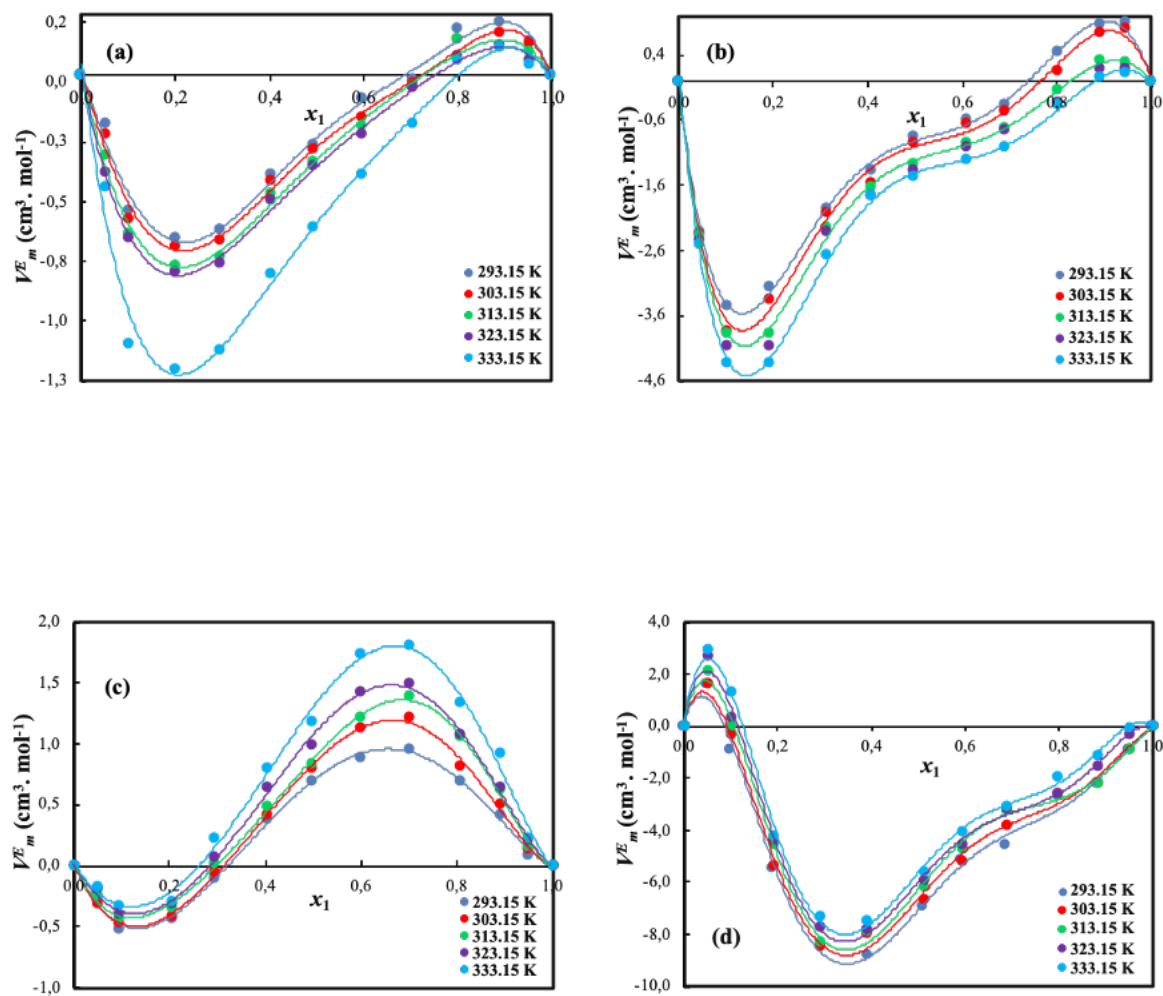


Figure 5.5C: Variations of excess molar volume (V_m^E) with IL mole fraction (x_1) for the binary mixtures of [BMIM][BF₄] with (a) acetic acid or (b) propionic acid and [BMIM][PF₆] with (c) acetic acid or (d) propionic acid at T = 293.15 - 333.15 K. The dotted lines were generated using the Redlich-Kister curve-fitting.

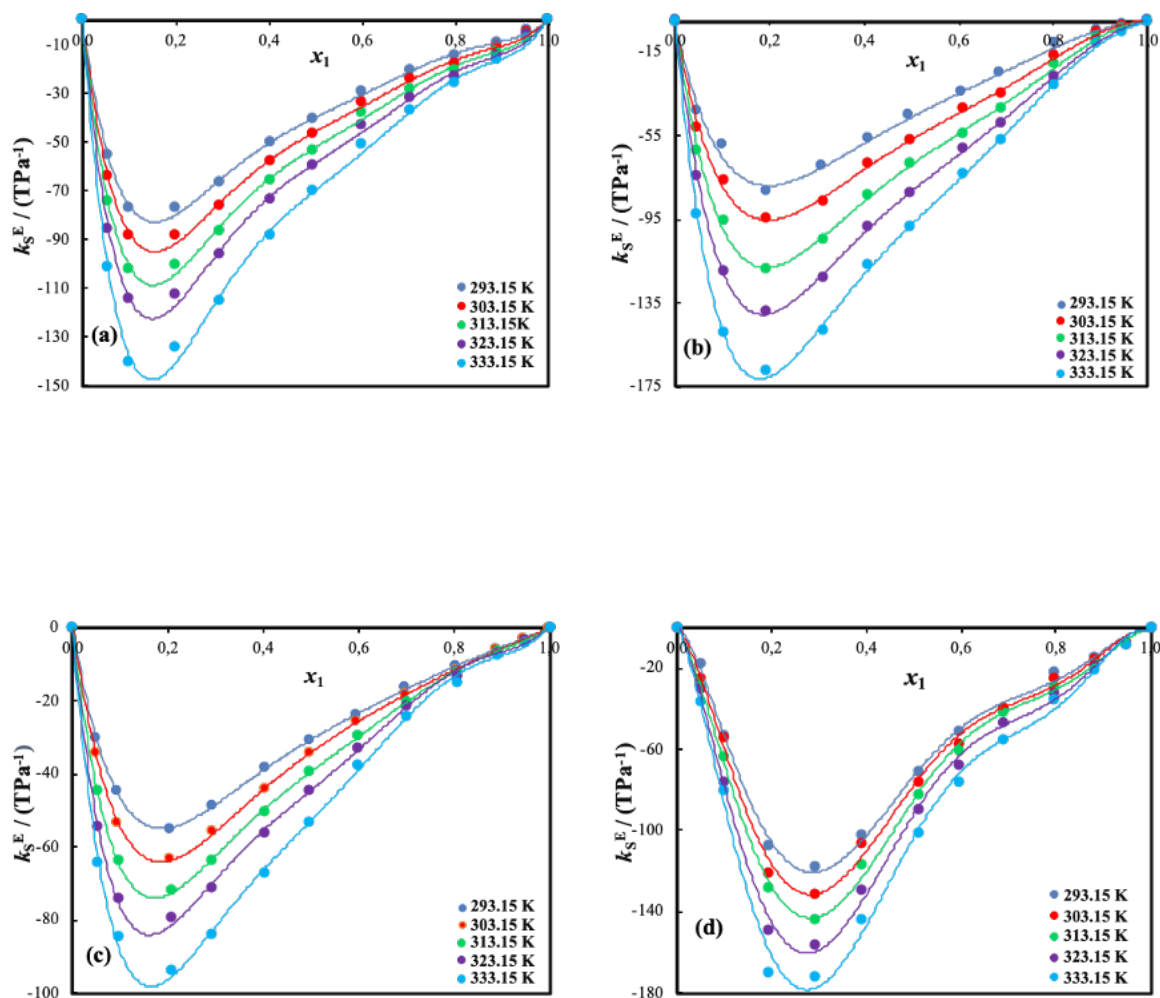


Figure 5.6C: Variations of excess isentropic compressibility (k_s^E) with IL mole fraction (x_1) for the binary mixtures of [BMIM][BF₄] with (a) acetic acid or (b) propionic acid and [BMIM][PF₆] with (c) acetic acid or (d) propionic acid at $T = 293.15 - 333.15$ K. The dotted lines were generated using the Redlich-Kister curve-fitting.

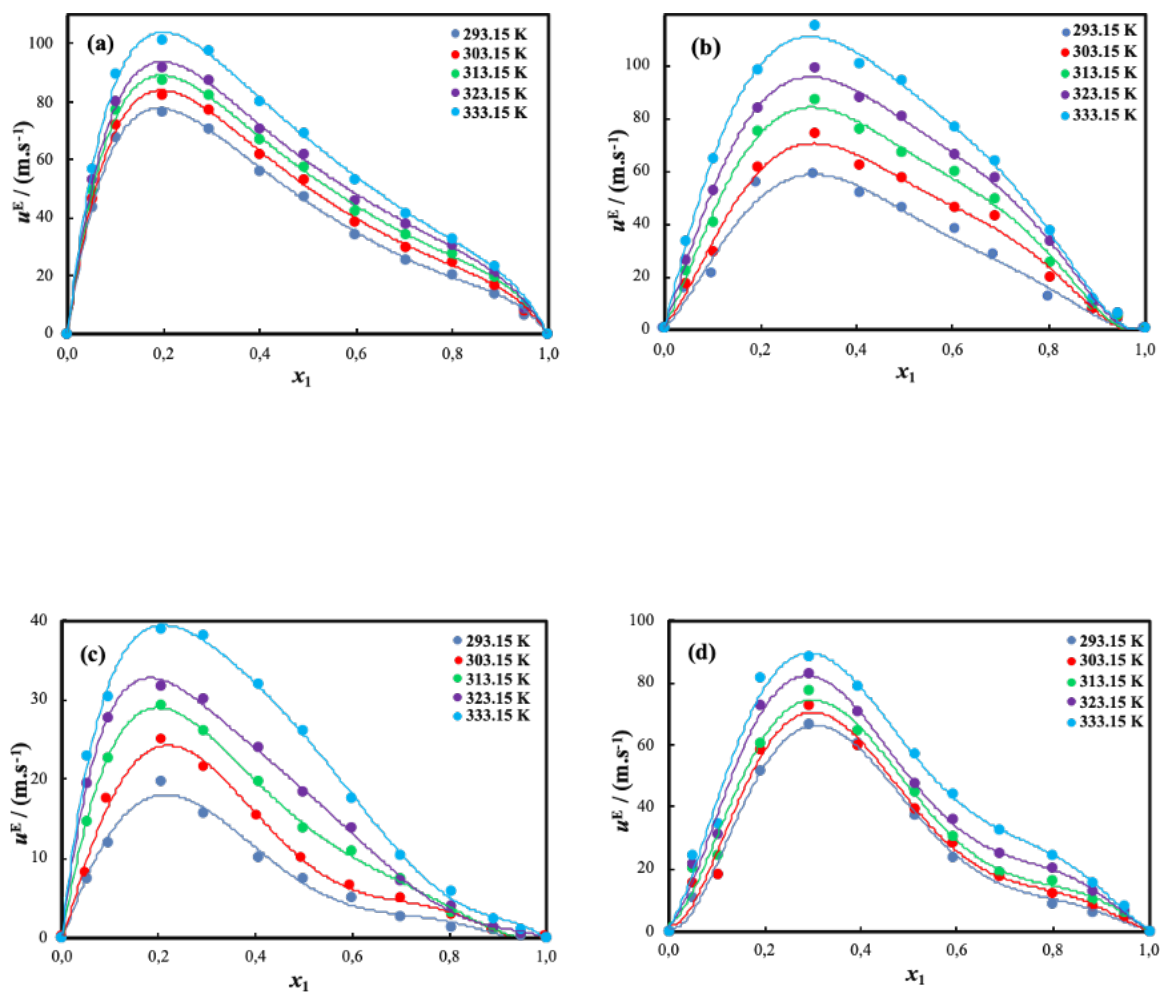


Figure 5.7C: Variations of excess sound velocity (u^E) with IL mole fraction (x_1) for the binary mixtures of [BMIM][BF₄] with (a) acetic acid or (b) propionic acid and [BMIM][PF₆] with (c) acetic acid or (d) propionic acid at $T = 293.15 - 333.15$ K. The dotted lines were generated using the Redlich-Kister curve-fitting.

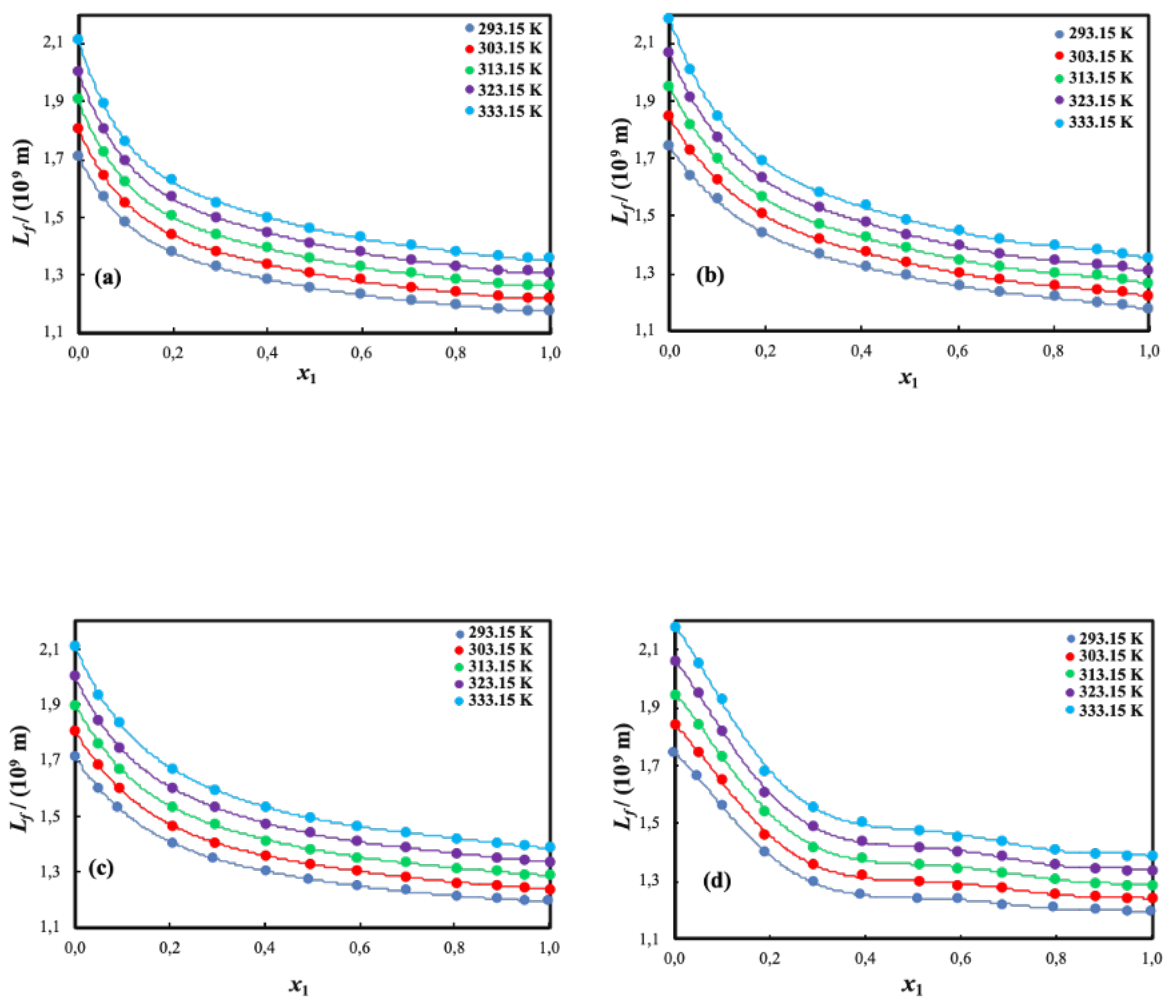


Figure 5.8C: Variations of intermolecular free-length (L_f) with IL mole fraction (x_1) for the binary mixtures of [BMIM][BF₄] with (a) acetic acid or (b) propionic acid and [BMIM][PF₆] with (c) acetic acid or (d) propionic acid at T = 293.15 - 333.15 K.

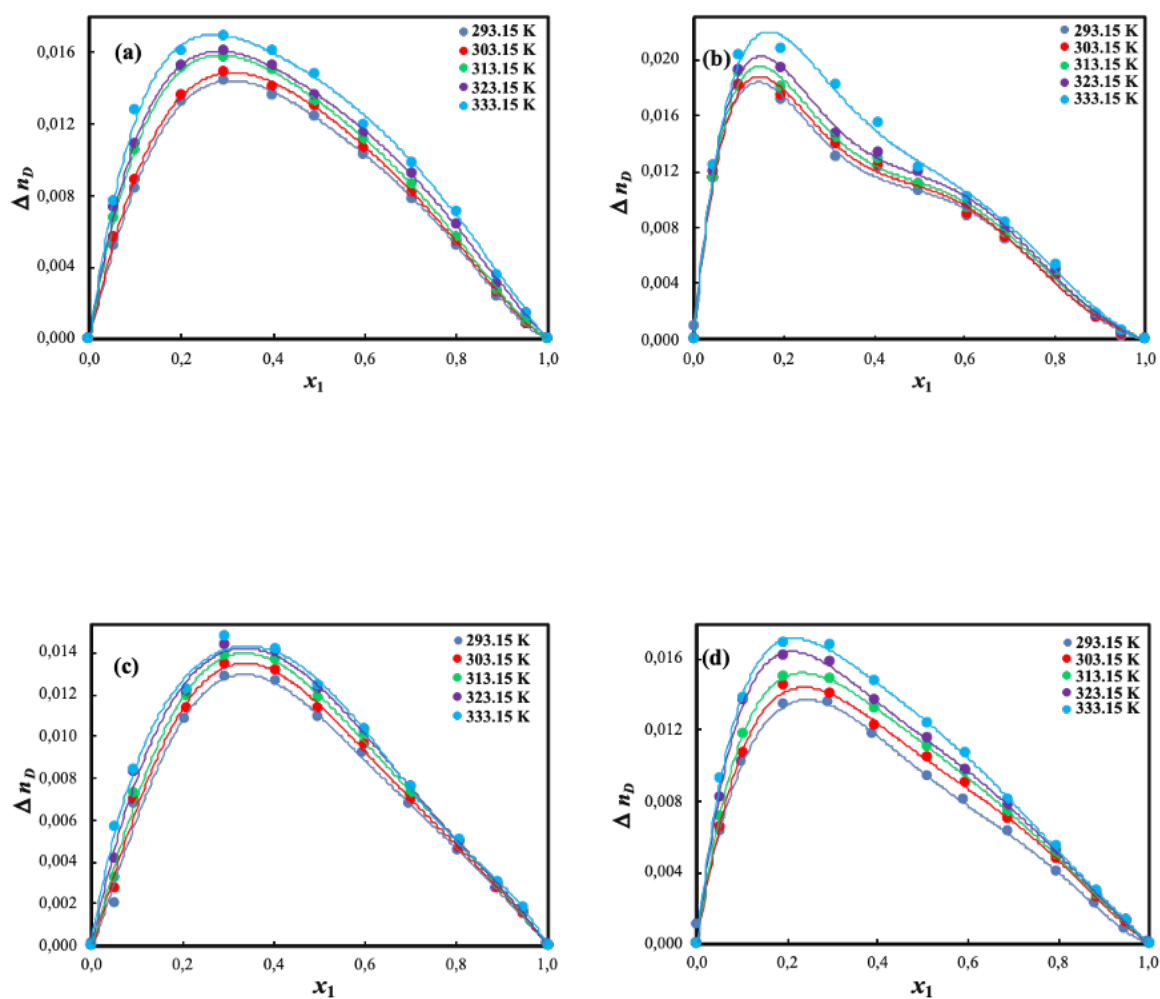


Figure 5.9C: Variations of deviation in refractive index (Δn_D) with IL mole fraction (x_1) for the binary mixtures of [BMIM][BF₄] with (a) acetic acid or (b) propionic acid and [BMIM][PF₆] with (c) acetic acid or (d) propionic acid at $T = 293.15 - 333.15$ K. The dotted lines were generated using the Redlich-Kister curve-fitting.

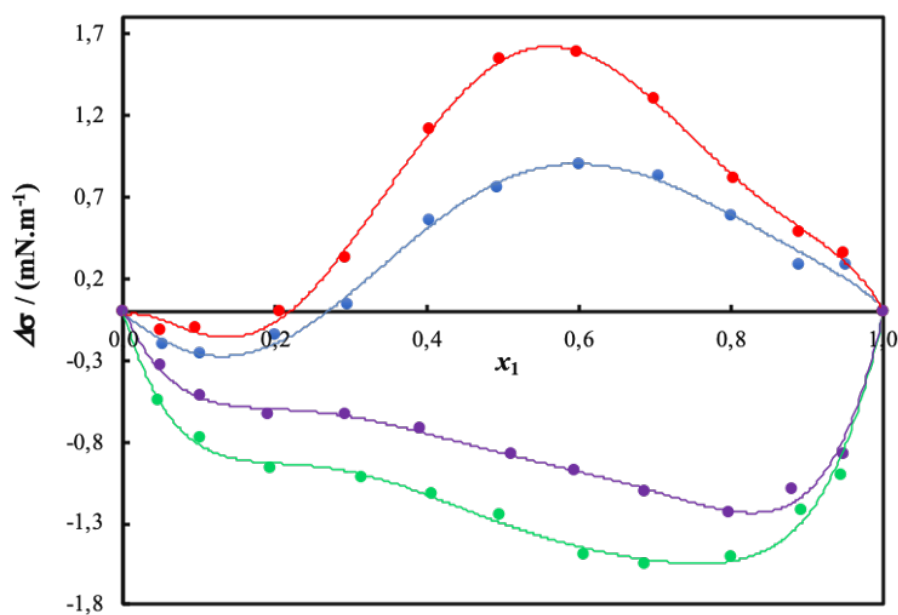


Figure 5.10C: Variations of deviation in surface tension ($\Delta\gamma$) with IL mole fraction (x_1) for the binary mixtures of (•){[BMIM][BF₄] (x_1) + acetic acid (x_2)}, (•){[BMIM][PF₆] (x_1) + acetic acid (x_2)}, (•){[BMIM][BF₄] (x_1) + propionic acid (x_2)} and (•){[BMIM][PF₆] (x_1) + propionic acid (x_2)} at T = 298.15 K. The dotted lines were generated using the Redlich-Kister curve-fitting.

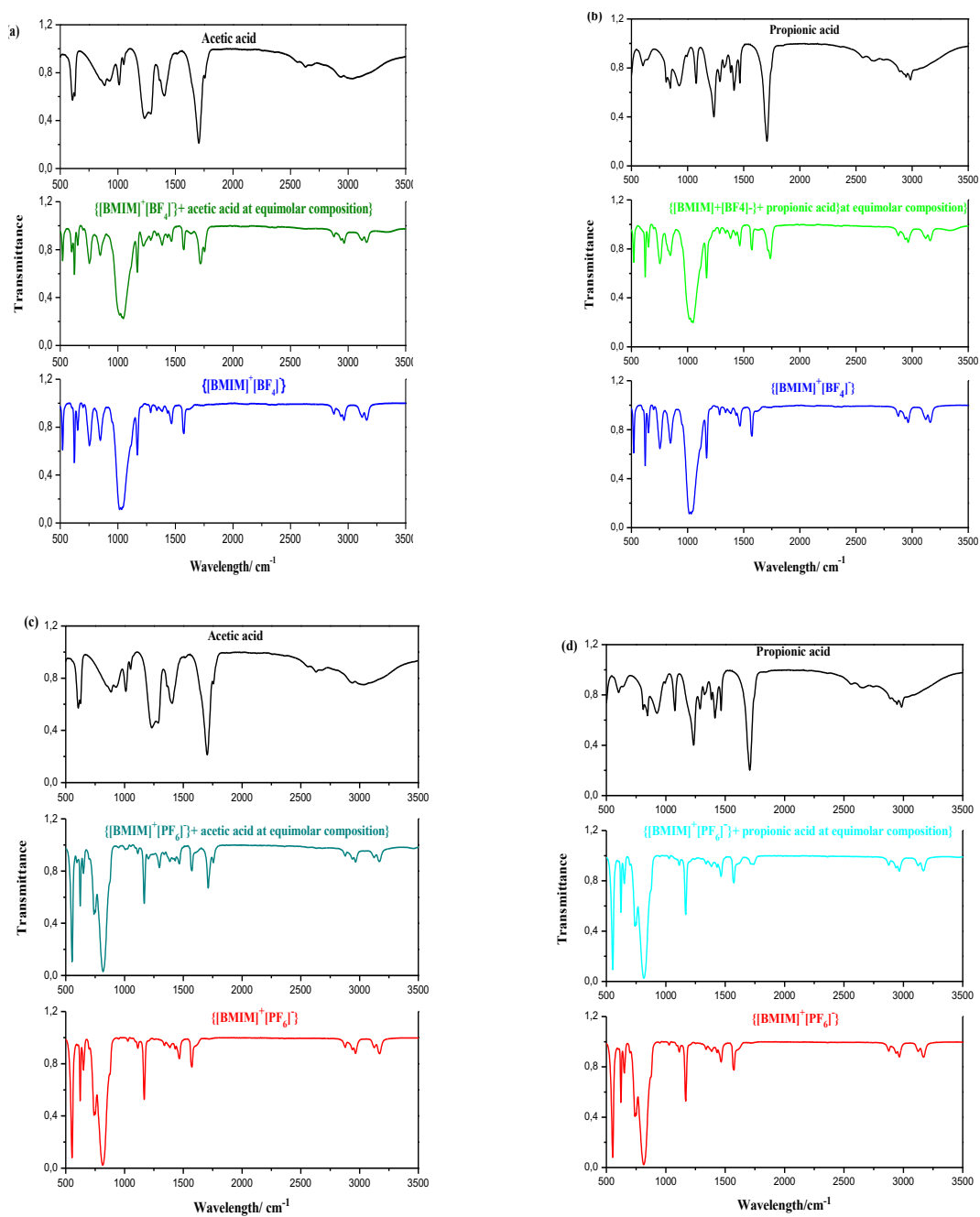


Figure 5.11C: FTIR spectrums of pure [BMIM][BF₄], [BMIM][PF₆] acetic acid, propionic acid and their binary mixtures at an equimolar composition.

Appendix D: This section presents the results obtained for binary mixtures of acetophenone and acetic or propionic acid.

Table 5.1D below presents the isobaric heat capacities (c_p) and isobaric expansivity coefficients (α_p) required to calculate excess isentropic compressibility (k_s^E). The c_p values of the pure acetophenone were taken for the literature, and the c_p at $T = 323.15 - 333.15\text{K}$ were not available in the literature and were therefore extrapolated using the correlative equations. The α_p values for the pure acetophenone were calculated at each temperature from the experimental density using Equation 2.12 in Section 2.5 of Chapter 2.

Table 5.1D: Isobaric heat capacities (c_p) and Isobaric thermal expansivity coefficients (α_p) of pure acetophenone at $T = 293.15 - 333.15\text{ K}$.

T/K	$c_p/\text{J. mol}^{-1} \cdot \text{K}^{-1}$	α_p/K^{-1}
293.15	205.9	0.000876
303.15	209.1 ^a	0.000883
313.15	212.4 ^a	0.000891
323.15	215.6	0.000898
333.15	218.9	0.000907

^a [Rihani *et al.* 2005], ^b [Parveen *et al.* 2012]

Table 5.2D: Mole fraction of acetophenone (x_1), density (ρ), sound velocity (u) and refractive index (n_D) for the binary mixtures of {acetophenone (x_1) + acetic acid (x_2)} (*mix9*) at T = 293.15 - 333.15 K and pressure, $p = 0.1$ MPa.

x_1	$\rho/\text{g.cm}^{-3}$	$u/\text{m.s}^{-1}$	n_D	x_1	$\rho/\text{g.cm}^{-3}$	$u/\text{m.s}^{-1}$	n_D
293.15K							
0.0000	1.05749	1158	1.37775	0.6078	1.02408	1353	1.49040
0.0502	1.05526	1186	1.39104	0.7001	1.02268	1371	1.49923
0.1064	1.05267	1214	1.40442	0.7938	1.02085	1386	1.50751
0.2005	1.04890	1266	1.42876	0.8958	1.01693	1402	1.51600
0.3083	1.04657	1322	1.45404	0.9562	1.01322	1414	1.52044
0.4069	1.04477	1365	1.47297	1.0000	1.01043	1423	1.52335
0.5064	1.04308	1399	1.48709				
0.6078	1.04108	1422	1.49851				
0.7001	1.03901	1442	1.50779	0.0000	1.02482	1061	1.36553
0.7938	1.03607	1456	1.51642	0.0502	1.02375	1088	1.37954
0.8958	1.03241	1474	1.52506	0.1064	1.02235	1118	1.39314
0.9562	1.02966	1487	1.52981	0.2005	1.02021	1168	1.41784
1.0000	1.02789	1497	1.53296	0.3083	1.01897	1223	1.44306
				0.4069	1.01780	1263	1.46109
				0.5064	1.01693	1297	1.47516
				0.6078	1.01575	1320	1.48652
				0.7001	1.01433	1337	1.49525
				0.7938	1.01263	1354	1.50369
				0.8958	1.00929	1368	1.51188
				0.9562	1.00550	1378	1.51585
				1.0000	1.00167	1387	1.51857
303.15K							
0.0000	1.04673	1124	1.37374	0.6078	1.01575	1320	1.48652
0.0502	1.04477	1151	1.38719	0.7001	1.01433	1337	1.49525
0.1064	1.04227	1180	1.40083	0.7938	1.01263	1354	1.50369
0.2005	1.03948	1233	1.42485	0.8958	1.00929	1368	1.51188
0.3083	1.03754	1288	1.45044	0.9562	1.00550	1378	1.51585
0.4069	1.03591	1329	1.46907	1.0000	1.00167	1387	1.51857
0.5064	1.03426	1364	1.48320				
0.6078	1.03305	1387	1.49453				
0.7001	1.03135	1406	1.50348				
0.7938	1.02908	1420	1.51198	0.0000	1.00648	1033	1.36252
0.8958	1.02531	1438	1.52050	0.0502	1.00651	1059	1.37655
0.9562	1.02205	1451	1.52510	0.1064	1.00636	1089	1.38977
1.0000	1.01917	1460	1.52811	0.2005	1.00612	1139	1.41416
				0.3083	1.00603	1192	1.43908
				0.4069	1.00579	1232	1.45705
				0.5064	1.00551	1265	1.47100
				0.6078	1.00531	1291	1.48225
				0.7001	1.00500	1309	1.49119
				0.7938	1.00447	1321	1.49951
				0.8958	1.00145	1337	1.50722
				0.9562	0.99819	1346	1.51128
				1.0000	0.99281	1352	1.51369
313.15K							
0.0000	1.03526	1092	1.36821	0.5064	1.00551	1265	1.47100
0.0502	1.03377	1119	1.38205	0.6078	1.00531	1291	1.48225
0.1064	1.03186	1148	1.39566	0.7001	1.00500	1309	1.49119
0.2005	1.02955	1199	1.42024	0.7938	1.00447	1321	1.49951
0.3083	1.02784	1255	1.44590	0.8958	1.00145	1337	1.50722
0.4069	1.02662	1296	1.46434	0.9562	0.99819	1346	1.51128
0.5064	1.02519	1330	1.47877	1.0000	0.99281	1352	1.51369

Standard uncertainties u are; $u(T) = 0.02$ K, $u(p) = 0.04$ MPa and the combined expanded uncertainty Uc in mole fraction, density, sound velocity and refractive index were $Uc(x) = 0.0008$, $Uc(\rho) = 0.02$ g.cm⁻³, $Uc(u) = 4$ m. s⁻¹ and $Uc(n) = 0.006$ respectively, (0.95 level of confidence).

Table 5.3D: Mole fraction of acetophenone (x_1), density (ρ), sound velocity (u), refractive index (n_D) for the binary mixtures of {acetophenone (x_1) + propionic acid (x_2)} (mix_{10}) at T = 293.15 - 333.15 K and pressure, $p = 0.1$ MPa.

x_1	$\rho/\text{g.cm}^{-3}$	$u/\text{m.s}^{-1}$	n_D	x_1	$\rho/\text{g.cm}^{-3}$	$u/\text{m.s}^{-1}$	n_D
293.15K							
0.0000	0.99824	1171	1.38715	0.6014	1.00313	1341	1.48276
0.0520	1.00423	1190	1.40621	0.6959	1.00409	1367	1.49383
0.1032	1.00983	1209	1.41929	0.7942	1.00513	1388	1.50437
0.2003	1.01352	1250	1.43788	0.9002	1.00725	1408	1.51468
0.2898	1.01483	1290	1.45179	0.9508	1.00883	1415	1.51904
0.4305	1.01603	1352	1.47167	1.0000	1.01043	1423	1.52335
0.4939	1.01704	1377	1.47978	323.15K			
0.6014	1.01829	1413	1.49302	0.0000	0.96612	1060	1.37414
0.6959	1.01946	1439	1.50395	0.0520	0.97685	1080	1.39066
0.7942	1.02098	1460	1.51439	0.1032	0.98163	1101	1.40258
0.9002	1.02330	1479	1.52457	0.2003	0.98724	1141	1.42063
0.9508	1.02482	1486	1.52899	0.2898	0.98956	1180	1.43506
1.0000	1.02789	1497	1.53296	0.4305	0.99198	1242	1.45579
303.15K				0.4939	0.99311	1266	1.46428
0.0000	0.98763	1134	1.38282	0.6014	0.99508	1305	1.47788
0.0520	0.99445	1153	1.40058	0.6959	0.99609	1332	1.48894
0.1032	1.00000	1172	1.41351	0.7942	0.99766	1352	1.49952
0.2003	1.00475	1213	1.43209	0.9002	0.99906	1372	1.50985
0.2898	1.00625	1253	1.44672	0.9508	1.00022	1381	1.51425
0.4305	1.00755	1314	1.46654	1.0000	1.00167	1387	1.51857
0.4939	1.00852	1340	1.47455	333.15K			
0.6014	1.00949	1377	1.48774	0.0000	0.95538	1025	1.36979
0.6959	1.01089	1402	1.49873	0.0520	0.96700	1046	1.38457
0.7942	1.01289	1425	1.50925	0.1032	0.97305	1065	1.39617
0.9002	1.01525	1443	1.51949	0.2003	0.97977	1106	1.41470
0.9508	1.01709	1452	1.52392	0.2898	0.98279	1145	1.42943
1.0000	1.01917	1460	1.52811	0.4305	0.98489	1206	1.45031
313.15K				0.4939	0.98549	1231	1.45888
0.0000	0.97682	1097	1.37850	0.6014	0.98679	1269	1.47249
0.0520	0.98566	1116	1.39572	0.6959	0.98886	1297	1.48349
0.1032	0.99027	1136	1.40825	0.7942	0.99001	1319	1.49423
0.2003	0.99575	1177	1.42657	0.9002	0.99072	1339	1.50478
0.2898	0.99785	1216	1.44075	0.9508	0.99142	1346	1.50929
0.4305	1.00008	1278	1.46105	1.0000	0.99281	1352	1.51369
0.4939	1.00119	1303	1.46938				

Standard uncertainties u are; $u(T) = 0.02$ K, $u(p) = 0.04$ MPa and the combined expanded uncertainty Uc in mole fraction, density, sound velocity and refractive index were $Uc(x) = 0.0008$, $Uc(\rho) = 0.02$ g.cm⁻³, $Uc(u) = 4$ m. s⁻¹ and $Uc(n) = 0.006$ respectively, (0.95 level of confidence).

Table 5.4D: Mole fraction (x_1) and surface tension (γ) for the binary mixture of {acetophenone (x_1) + acetic acid (x_2)} (mix_9) and {acetophenone (x_1) + propionic acid (x_2)} (mix_{10}) at $T = 298.15$ and pressure, $p = 0.1$ MPa.

x_1	$\gamma/(\text{mN.m}^{-1})$	x_1	$\gamma/(\text{mN.m}^{-1})$
{Acetophenone (x_1) + acetic acid (x_2)}		{Acetophenone (x_1) + propionic acid (x_2)}	
0.0000	27.21	0.0000	26.20
0.0502	27.48	0.0520	26.48
0.1064	27.94	0.1032	26.78
0.2005	28.45	0.2003	27.42
0.3083	29.15	0.2898	28.01
0.4069	29.92	0.4305	29.17
0.5064	30.90	0.4939	29.81
0.6078	31.95	0.6014	30.93
0.7001	33.06	0.6959	32.03
0.7938	34.32	0.7942	33.24
0.8958	36.10	0.9002	35.18
0.9562	37.58	0.9508	36.52
1.0000	38.77	1.0000	38.77

Standard uncertainties u are; $u(T) = 0.02$ K, $u(p) = 0.04$ MPa and the combined expanded uncertainty Uc in mole fraction and surface tension were $Uc(x) = 0.0008$ and $Uc(\gamma) = 1.11 \text{ mN.m}^{-1}$ respectively, (0.95 level of confidence).

Table 5.5D: Mole fraction of acetophenone (x_1), excess molar volume (V_m^E), isentropic compressibility (k_s), excess isentropic compressibility (k_s^E), excess sound velocity (u^E), intermolecular free-length (L_f) and deviation in refractive index (Δn_D) for the binary mixtures of {acetophenone (x_1) + acetic acid (x_2)} (*mix9*) T = 293.15 - 333.15 K and pressure, $p = 0.1$ MPa.

x_1	$V_m^E / \text{cm}^3 \cdot \text{mol}^{-1}$	$10^9 k_s / \text{TPa}^{-1}$	k_s^E / TPa^{-1}	$u^E / 10^1 \text{ m} \cdot \text{s}^{-1}$	$L_f / 10^9 \text{ m}$	$10^2 \Delta n_D$
293.15 K						
0.0000	0.000	705	0.00	0.0	1.711	0.000
0.0502	-0.037	674	-4.67	37.2	1.673	-0.182
0.1064	-0.059	645	-7.13	61.0	1.637	-0.369
0.2005	-0.095	595	-18.25	181.2	1.572	-0.157
0.3083	-0.230	546	-29.45	322.9	1.507	0.231
0.4069	-0.355	514	-32.83	387.0	1.461	0.465
0.5064	-0.472	490	-31.56	393.0	1.427	0.426
0.6078	-0.547	475	-23.94	304.5	1.405	0.281
0.7001	-0.571	463	-17.87	229.3	1.387	0.173
0.7938	-0.489	455	-9.42	114.5	1.375	0.098
0.8958	-0.314	446	-2.95	27.6	1.361	0.047
0.9562	-0.124	439	-0.78	5.0	1.351	0.026
1.0000	0.000	434	0.00	0.0	1.343	0.000
303.15 K						
0.0000	0.000	756	0.00	0.00	1.805	0.000
0.0502	-0.042	722	-5.02	35.8	1.764	-0.156
0.1064	-0.057	689	-9.24	73.1	1.723	-0.307
0.2005	-0.140	633	-22.88	204.7	1.652	-0.113
0.3083	-0.290	581	-34.34	340.8	1.582	0.319
0.4069	-0.417	547	-37.11	396.7	1.534	0.531
0.5064	-0.527	520	-36.40	414.5	1.496	0.500
0.6078	-0.662	503	-28.30	326.8	1.472	0.352
0.7001	-0.716	491	-20.96	241.3	1.454	0.216
0.7938	-0.696	482	-11.64	121.9	1.441	0.132
0.8958	-0.506	472	-4.62	37.3	1.425	0.072
0.9562	-0.256	465	-2.02	15.4	1.415	0.038
1.0000	0.000	460	0.00	0.00	1.408	0.000
313.15 K						
0.0000	0.000	810	0.00	0.0	1.902	0.000
0.0502	-0.055	773	-6.35	40.7	1.857	-0.121
0.1064	-0.090	735	-12.46	88.2	1.812	-0.280
0.2005	-0.183	675	-26.17	210.4	1.737	-0.038
0.3083	-0.329	618	-39.36	355.4	1.661	0.390

0.4069	-0.471	580	-42.73	416.7	1.610	0.575
0.5064	-0.584	552	-41.18	427.9	1.569	0.566
0.6078	-0.713	534	-32.60	345.8	1.543	0.440
0.7001	-0.781	520	-24.46	259.2	1.524	0.285
0.7938	-0.793	510	-15.45	154.3	1.509	0.173
0.8958	-0.571	500	-6.11	49.5	1.494	0.104
0.9562	-0.257	494	-1.94	12.0	1.485	0.050
1.0000	0.000	489	0.00	0.0	1.477	0.000
323.15 K						
0.0000	0.000	866	0.00	0.0	2.001	0.000
0.0502	-0.071	825	-7.37	42.1	1.953	-0.082
0.1064	-0.130	783	-15.66	99.2	1.903	-0.219
0.2005	-0.224	719	-30.34	221.0	1.823	0.066
0.3083	-0.393	656	-44.73	366.4	1.742	0.480
0.4069	-0.532	615	-48.49	431.3	1.687	0.646
0.5064	-0.686	584	-47.21	446.4	1.644	0.620
0.6078	-0.803	565	-37.92	368.4	1.616	0.484
0.7001	-0.865	551	-28.07	272.1	1.597	0.333
0.7938	-0.884	539	-19.71	186.1	1.578	0.247
0.8958	-0.716	529	-8.58	66.6	1.564	0.158
0.9562	-0.387	523	-3.17	18.9	1.556	0.065
1.0000	0.000	519	0.00	0.0	1.549	0.000
333.15 K						
0.0000	0.000	931	0.00	0.00	2.112	0.000
0.0502	-0.084	885	-9.31	48.3	2.059	-0.050
0.1064	-0.167	839	-19.19	108.9	2.004	-0.197
0.2005	-0.303	766	-37.69	246.9	1.915	0.093
0.3083	-0.472	700	-51.75	383.1	1.830	0.506
0.4069	-0.611	655	-56.20	454.5	1.770	0.685
0.5064	-0.745	621	-53.79	464.5	1.725	0.661
0.6078	-0.887	597	-46.08	413.5	1.691	0.525
0.7001	-1.001	581	-36.63	331.6	1.668	0.402
0.7938	-1.090	571	-23.99	203.8	1.653	0.310
0.8958	-0.904	559	-12.96	99.9	1.636	0.178
0.9562	-0.602	553	-6.40	43.1	1.627	0.095
1.0000	0.000	551	0.00	0.00	1.624	0.000

Standard uncertainties u are; $u(T) = 0.02$ K, $u(p) = 0.04$ MPa and the combined expanded uncertainty Uc in mole fraction, density, sound velocity and refractive index were $Uc(x) = 0.0008$, $Uc(\rho) = 0.02$ g.cm⁻³, $Uc(u) = 4$ m. s⁻¹ and $Uc(n) = 0.006$ respectively, (0.95 level of confidence).

Table 5.6D: Mole fraction of acetophenone (x_1), excess molar volume (V_m^E), isentropic compressibility (k_s), excess isentropic compressibility (k_s^E), excess sound velocity (u^E), intermolecular free-length (L_f) and deviation in refractive index (Δn_D) for the binary mixtures of {acetophenone (x_1) + propionic acid (x_2)} (mix_{10}) T = 293.15 - 333.15 K and pressure, p = 0.1 MPa.

x_1	$V_m^E / \text{cm}^3 \cdot \text{mol}^{-1}$	$10^9 k_s / \text{TPa}^{-1}$	k_s^E / TPa^{-1}	$u^E / 10^1 \text{ m} \cdot \text{s}^{-1}$	$L_f / 10^9 \text{ m}$	$10^2 \Delta n_D$
293.15 K						
0.0000	0.000	731	0.00	0.00	1.742	0.001
0.0520	-0.276	704	-3.65	9.2	1.710	0.746
0.1032	-0.548	677	-8.10	29.6	1.677	0.977
0.2003	-0.563	631	-15.55	108.9	1.619	0.948
0.2898	-0.426	592	-22.61	208.2	1.568	0.759
0.4305	-0.153	538	-31.13	363.7	1.496	0.528
0.4939	-0.079	518	-32.74	409.8	1.467	0.430
0.6014	0.080	492	-30.43	423.6	1.429	0.325
0.6959	0.203	474	-24.85	376.9	1.403	0.266
0.7942	0.288	459	-16.76	278.4	1.381	0.203
0.9002	0.290	447	-6.78	129.8	1.362	0.120
0.9508	0.238	442	-1.90	47.2	1.354	0.067
1.0000	0.000	434	0.00	0.00	1.343	0.000
303.15 K						
0.0000	0.000	788	0.00	0.00	1.843	0.000
0.0520	-0.335	757	-5.33	15.4	1.806	0.623
0.1032	-0.599	728	-10.16	36.8	1.771	0.844
0.2003	-0.683	676	-19.02	117.9	1.707	0.823
0.2898	-0.547	633	-26.88	219.2	1.651	0.714
0.4305	-0.260	575	-35.42	369.5	1.573	0.484
0.4939	-0.172	552	-37.69	423.8	1.542	0.379
0.6014	0.033	523	-34.76	438.1	1.501	0.273
0.6959	0.148	503	-28.50	390.6	1.472	0.222
0.7942	0.197	487	-20.16	298.8	1.448	0.170
0.9002	0.206	473	-8.54	141.3	1.428	0.096
0.9508	0.123	467	-4.14	71.6	1.418	0.044
1.0000	0.000	460	0.00	0.00	1.408	0.000
313.15 K						
0.0000	0.000	851	0.00	0.00	1.950	0.000
0.0520	-0.489	815	-7.91	18.9	1.907	0.575
0.1032	-0.674	782	-13.90	52.1	1.869	0.761
0.2003	-0.802	724	-24.69	140.3	1.798	0.722
0.2898	-0.701	678	-31.69	227.1	1.740	0.573
0.4305	-0.474	613	-42.13	386.8	1.654	0.399
0.4939	-0.392	588	-43.95	435.8	1.620	0.328

0.6014	-0.272	555	-41.91	462.3	1.574	0.245
0.6959	-0.103	533	-34.63	416.9	1.543	0.204
0.7942	0.059	516	-23.72	311.7	1.519	0.156
0.9002	0.110	501	-11.60	166.8	1.496	0.089
0.9508	0.061	495	-5.34	79.4	1.487	0.031
1.0000	0.000	489	0.00	0.00	1.477	0.000
323.15 K						
0.0000	0.000	920	0	0.00	2.063	0.000
0.0520	-0.640	877	-11.55	26.7	2.014	0.510
0.1032	-0.834	841	-18.38	62.0	1.972	0.641
0.2003	-0.961	778	-29.15	144.2	1.897	0.583
0.2898	-0.865	725	-38.67	246.5	1.832	0.464
0.4305	-0.634	654	-49.31	403.5	1.739	0.340
0.4939	-0.544	628	-49.75	439.5	1.704	0.288
0.6014	-0.412	590	-48.09	475.8	1.652	0.230
0.6959	-0.234	566	-40.61	439.5	1.618	0.190
0.7942	-0.115	548	-27.58	320.8	1.593	0.147
0.9002	0.030	531	-14.16	181.0	1.568	0.085
0.9508	0.037	524	-7.60	101.1	1.557	0.030
1.0000	0.000	519	0.00	0.00	1.549	0.000
333.15K						
0.0000	0.000	996	0.00	0.00	2.183	0.000
0.0520	-0.715	946	-14.68	33.4	2.128	0.343
0.1032	-1.009	905	-22.57	65.0	2.082	0.446
0.2003	-1.221	835	-36.21	154.9	1.999	0.447
0.2898	-1.178	776	-46.60	255.6	1.928	0.365
0.4305	-0.904	698	-56.79	407.5	1.828	0.264
0.4939	-0.755	670	-57.67	452.9	1.790	0.223
0.6014	-0.540	629	-54.69	486.5	1.735	0.169
0.6959	-0.462	601	-47.42	456.7	1.696	0.127
0.7942	-0.286	580	-34.02	354.1	1.667	0.102
0.9002	-0.046	563	-17.38	199.3	1.642	0.063
0.9508	0.022	556	-8.82	106.7	1.632	0.022
1.0000	0.000	551	0.00	0.00	1.624	0.000

Standard uncertainties u are; $u(T) = 0.02$ K, $u(p) = 0.04$ MPa and the combined expanded uncertainty Uc in mole fraction, density, sound velocity and refractive index were $Uc(x) = 0.0008$, $Uc(\rho) = 0.02$ g.cm⁻³, $Uc(u) = 4$ m. s⁻¹ and $Uc(n) = 0.006$ respectively, (0.95 level of confidence).

Table 5.7D: Mole fraction (x_1) and deviation in surface tension ($\Delta\gamma$) for the binary mixture of {acetophenone + acetic acid or propionic acid} (mix_9) and {acetophenone (x_1) + propionic acid (x_2)} (mix_{10}) at T = 298.15 K and pressure, $p = 0.1$ MPa.

x_1	$\Delta\gamma/(\text{mN.m}^{-1})$	x_1	$\Delta\gamma/(\text{mN.m}^{-1})$
{Acetophenone (x_1) + acetic acid (x_2)}		{Acetophenone (x_1) + acetic acid (x_2)}	
0.0000	0.000	0.0000	0.000
0.0502	-0.310	0.0520	-0.374
0.1064	-0.500	0.1032	-0.717
0.2005	-1.078	0.2003	-1.298
0.3083	-1.624	0.2898	-1.833
0.4069	-1.993	0.4305	-2.441
0.5064	-2.165	0.4939	-2.598
0.6078	-2.286	0.6014	-2.829
0.7001	-2.243	0.6959	-2.918
0.7938	-2.066	0.7942	-2.944
0.8958	-1.466	0.9002	-2.335
0.9562	-0.684	0.9508	-1.632
1.0000	0.000	1.0000	0.000

Standard uncertainties u are; $u(T) = 0.02$ K, $u(p) = 0.04$ MPa and the combined expanded uncertainty Uc in mole fraction and surface tension were $Uc(x) = 0.0008$ and $Uc(\gamma) = 1.11 \text{ mN.m}^{-1}$ respectively, (0.95 level of confidence).

Table 5.8D: Redlich-Kister coefficients (A_i) and standard deviation (σ) obtained for the binary mixtures of {acetophenone (x_1) + acetic acid (x_2)} (mix_9) and {acetophenone (x_1) + propionic acid (x_2)} (mix_{10}) at T = 293.15 - 333.15 K and pressure, $p = 0.1$ MPa.

	T/K	A_0	A_1	A_2	A_3	A_4	σ
{acetophenone (x_1) + acetic acid (x_2)}							
$V_m^E/\text{cm}^3\cdot\text{mol}^{-1}$	293.15	-1.867	2.256	0.194	-0.910	-4.229	0.011
	303.15	-2.136	2.557	-1.252	0.686	-0.294	0.011
	313.15	-2.323	2.727	-2.072	0.710	0.360	0.017
	323.15	-2.699	2.645	-1.214	2.067	-2.565	0.007
	333.15	-2.975	2.532	-2.408	4.378	-3.7135	0.025
k_s^E/TPa^{-1}	293.15	-127.96	-74.33	141.86	65.31	-53.09	1.01
	303.15	-143.12	-88.78	99.73	88.30	-0.09	0.78
	313.15	-164.92	-95.16	111.40	84.83	-8.36	0.55
	323.15	-186.32	-100.34	91.26	91.96	-3.12	0.91
	333.15	-217.54	-103.95	62.00	96.86	16.69	0.64
$u^E/10^1\text{ m}\cdot\text{s}^{-1}$	293.15	1561.2	616.9	-2004.4	-568.9	567.1	9.9
	303.15	1632.4	-652.4	-1968.0	-608.5	605.0	8.0
	313.15	1692.7	573.7	-1731.1	-511.7	363.9	6.9
	323.15	1757.9	518.6	-1607.7	-537.5	352.7	8.4
	333.15						
$10^2\Delta n_D$	293.15	0.012	-0.051	-0.068	0.050	0.058	0.0003
	303.15	1.565	-4.746	-7.237	4.506	6.972	0.0110
	313.15	1.811	-4.751	-6.748	4.222	6.565	0.0101
	323.15	2.173	-4.332	-7.103	3.286	7.599	0.0122
	333.15	2.292	-4.447	-6.906	3.193	8.121	0.0116
$\Delta\gamma$	298.15	-10.64	4.15	-1.89	12.50	-13.47	0.09
{acetophenone (x_1) + propionic acid (x_2)}							
$V_m^E/\text{cm}^3\cdot\text{mol}^{-1}$	293.15	-0.195	-2.999	-2.455	-4.057	1.791	0.028
	303.15	-0.540	-3.684	-2.731	-2.523	0.587	0.020
	313.15	-1.577	-2.792	-1.286	-4.317	-2.088	0.020
	323.15	-2.170	-2.599	-2.038	-5.543	-2.904	0.026
	333.15	-2.987	-3.364	-4.889	-5.176	0.392	0.035
k_s^E/TPa^{-1}	293.15	-129.81	12.33	94.21	-31.0	-19.62	0.38
	303.15	-148.56	8.45	98.56	-23.86	-44.60	0.36
	313.15	-175.75	14.60	106.90	-49.76	-78.53	0.39
	323.15	-202.83	11.66	115.75	-62.11	-125.87	0.54
	333.15	-232.18	6.83	72.89	-67.88	-92.55	0.58

$u^E/10^1 \text{ m.s}^{-1}$	293.15	1639	-1002.8	-1362.6	510.5	204.8	4.6
	303.15	1686.4	-1021.1	-1348.1	410.3	451.7	3.8
	313.15	1752.9	-1078.2	-1233.2	459.7	532.9	4.3
	323.15	1806.8	-1063.8	-1231.3	334.6	766.6	6.7
	333.15	1884.8	-527.7	-3186.5	284.1	2919.5	25.3
$10^2 \Delta n_D$	293.15	2.333	3.069	3.687	2.552	2.149	0.0064
	303.15	2.154	2.917	2.664	1.694	1.96	0.0119
	313.15	1.749	2.286	3.114	2.221	1.285	0.0078
	323.15	1.463	1.541	2.491	2.537	1.736	0.0071
	333.15	1.165	1.363	1.514	1.196	1.066	0.0058
$\Delta \gamma$	298.15	-8.71	3.25	-2.78	4.51	-0.30	0.042

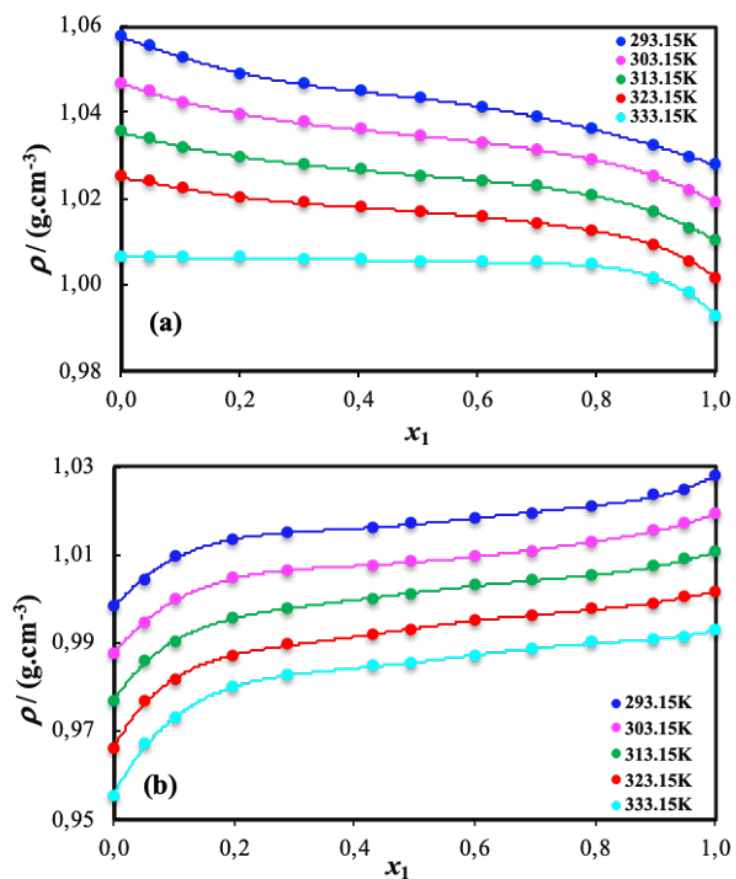


Figure 5.1D: Variations of density (ρ) with acetophenone mole fraction (x_1) for the binary mixtures of acetophenone with (a) acetic acid or (b) propionic acid at $T = 293.15 - 333.15$ K. The dotted lines show the smoothness of these data.

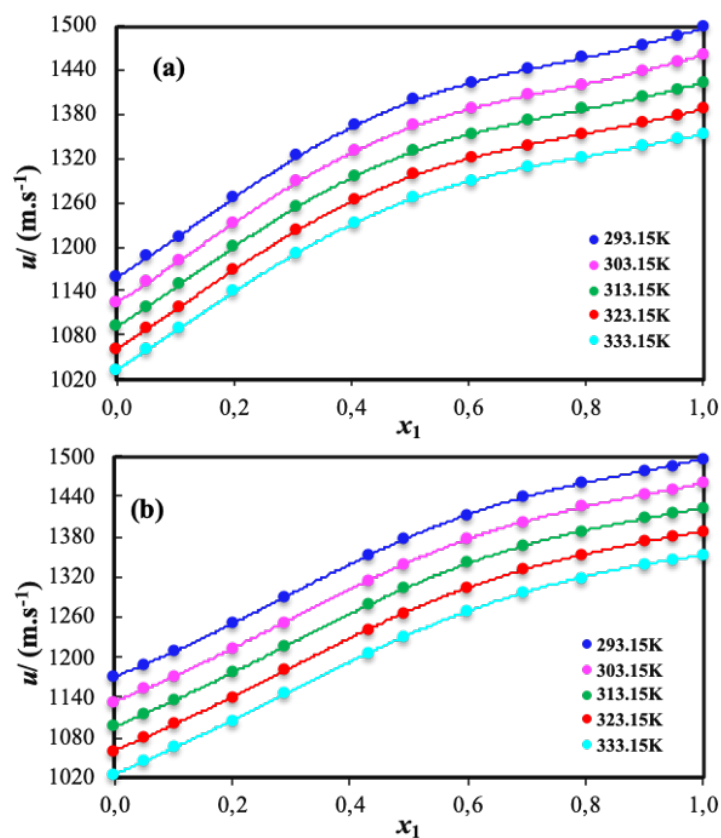


Figure 5.2D: Variations of sound velocity (u) with acetophenone mole fraction (x_1) for the binary mixtures of acetophenone with (a) acetic acid or (b) propionic acid} at $T = 293.15 - 333.15$ K. The dotted lines show the smoothness of these data.

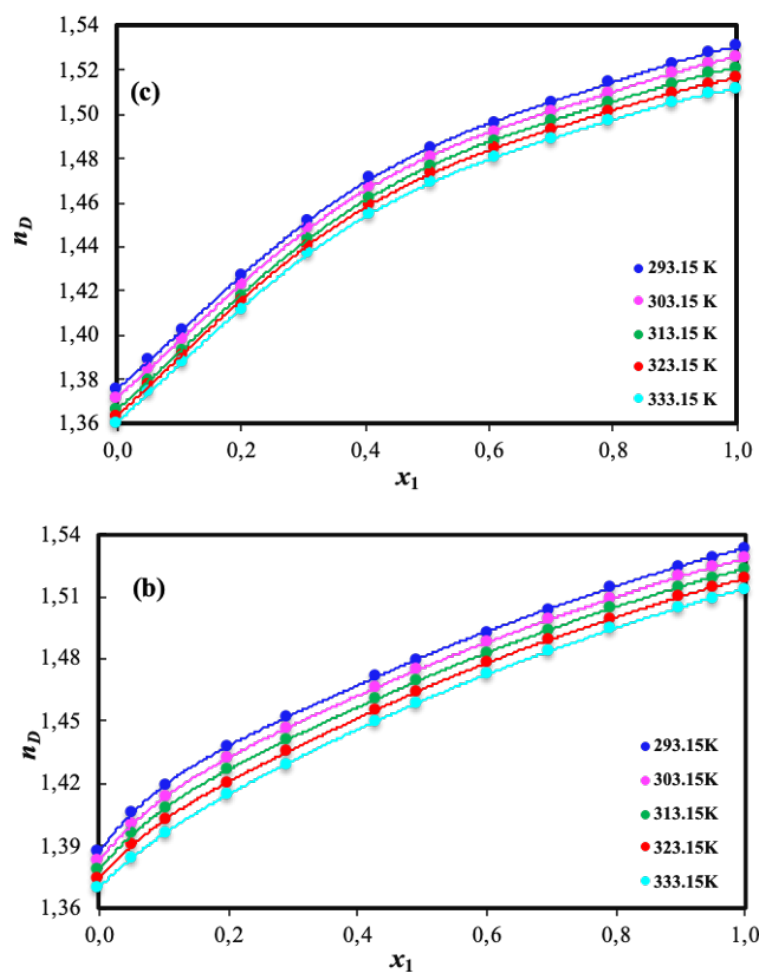


Figure 5.3D: Variations of refractive (n_D) with acetophenone mole fraction (x_1) for the binary mixtures of acetophenone with (a) acetic acid or (b) propionic acid at $T = 293.15 - 333.15$ K. The dotted lines show the smoothness of these data.

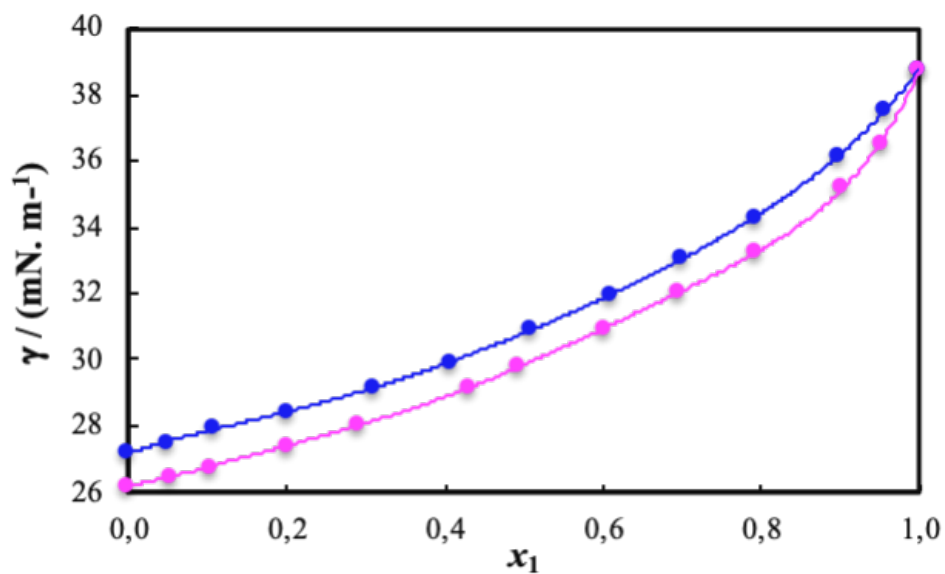


Figure 5.4D: Variations of surface tension (γ) with acetophenone mole fraction (x_1) for the binary mixtures of (•){acetophenone (x_1) + acetic acid (x_2)} and (•){acetophenone (x_1) + propionic acid (x_2)} binary mixtures at $T = 298.15$ K. The dotted lines show the smoothness of these data.

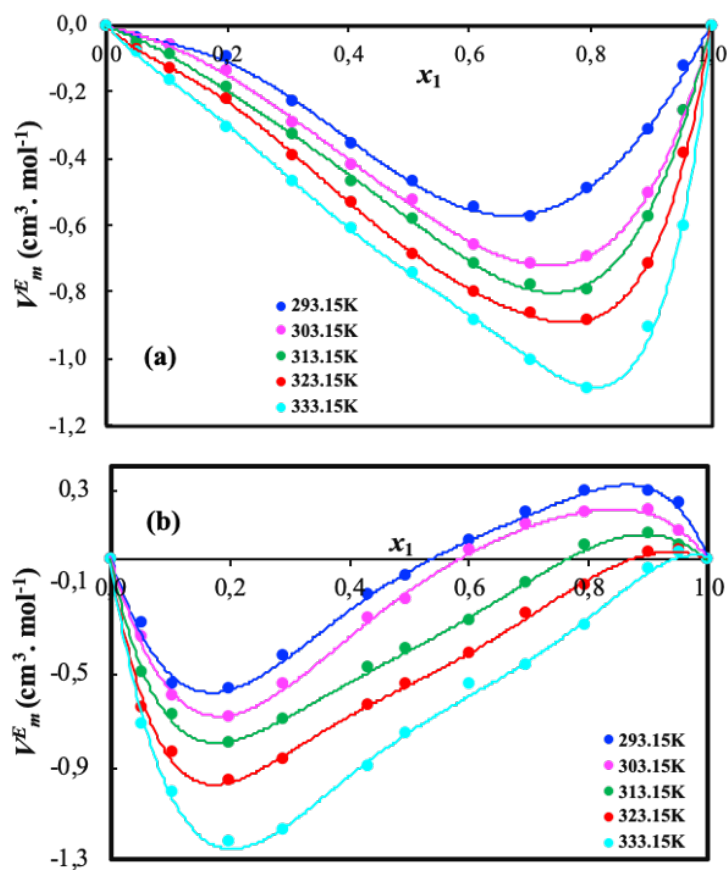


Figure 5.5D: Variations of excess molar volume (V_m^E) with acetophenone mole fraction (x_1) for the binary mixtures of acetophenone with (a) acetic acid or (b) propionic acid at $T = 293.15$ - 333.15 K. The solid lines were generated using the Redlich-Kister curve-fitting.

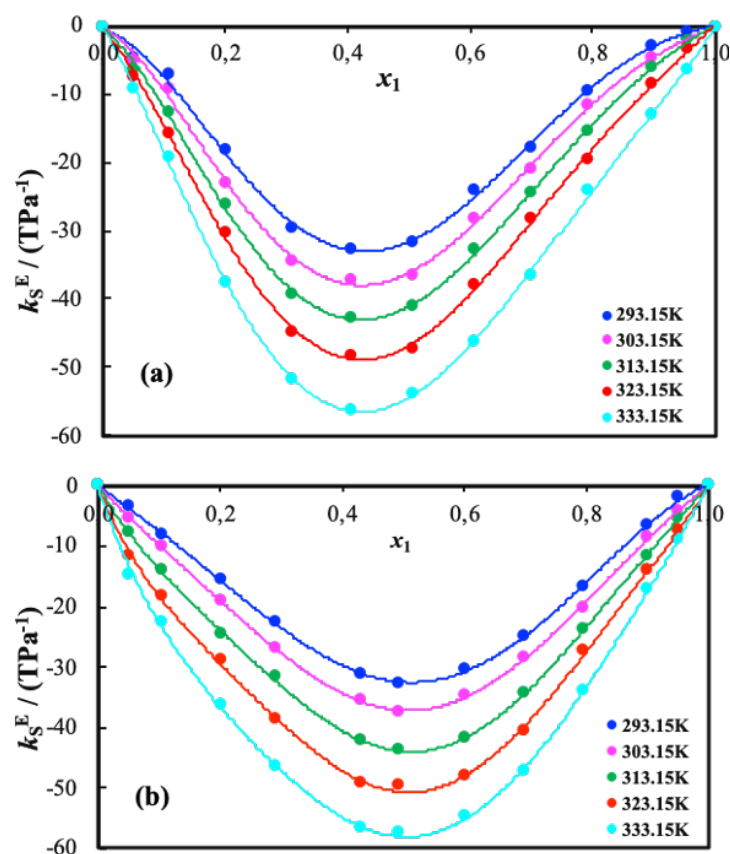


Figure 5.6D: Variations of excess isentropic compressibility (k_s^E) with acetophenone mole fraction (x_1) for the binary mixtures of acetophenone with (a) acetic acid or (b) propionic acid at $T = 293.15 - 333.15$ K. The solid lines were generated using the Redlich-Kister curve-fitting.

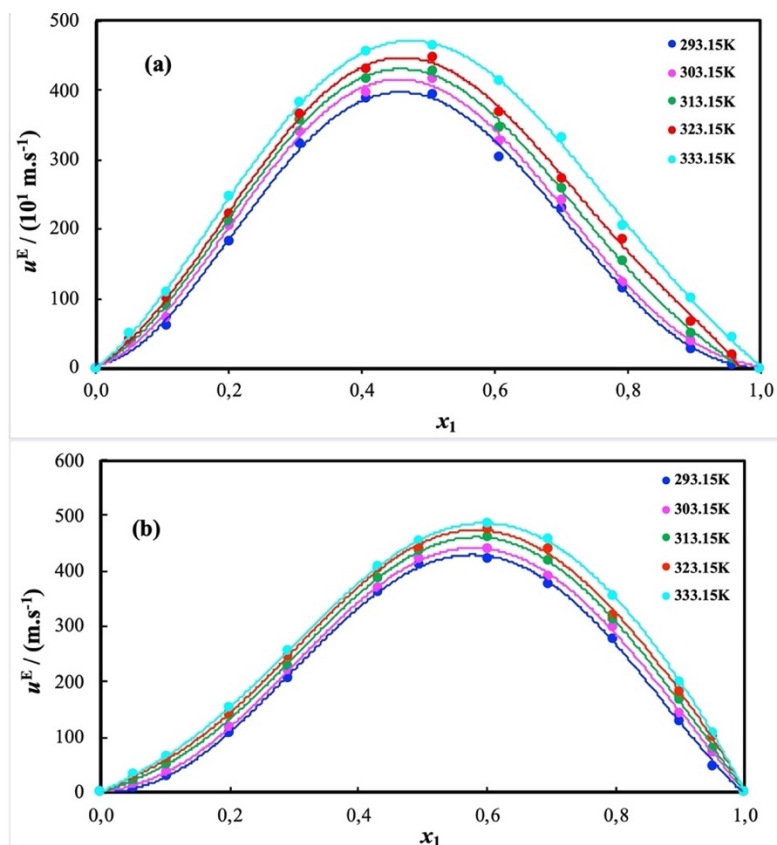


Figure 5.7D: Variations of excess sound velocity (u^E) with acetophenone mole fraction (x_1) for the binary mixtures of acetophenone with (a) acetic acid or (b) propionic acid at $T = 293.15$ - 333.15 K. The solid lines were generated using the Redlich-Kister curve-fitting.

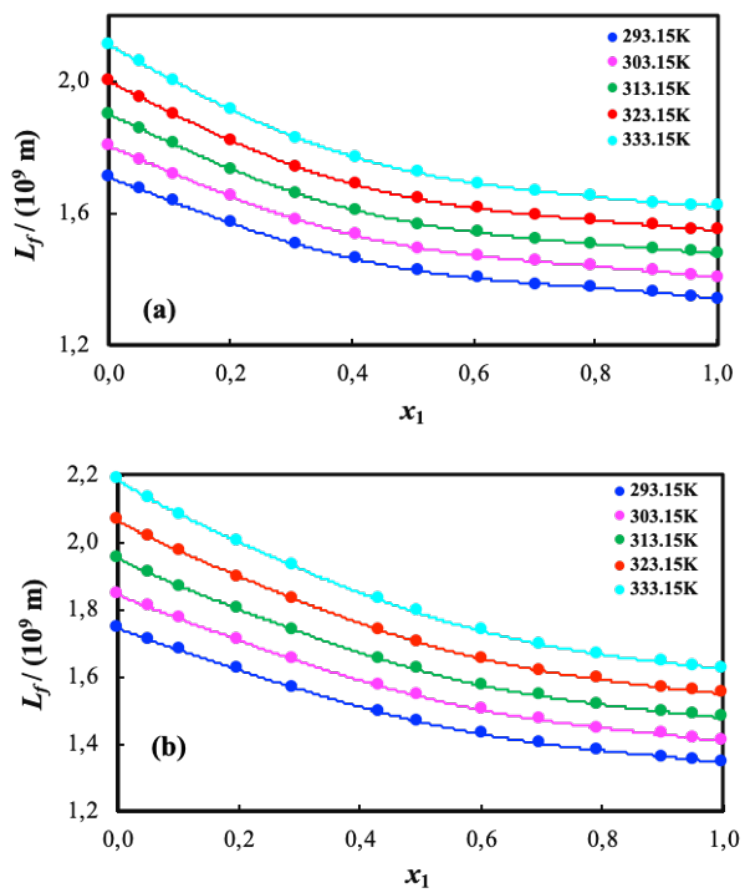


Figure 5.8D: Variations of intermolecular free-length (L_f) with acetophenone mole fraction (x_1) for the binary mixtures of acetophenone with (a) acetic acid or (b) propionic acid at $T = 293.15 - 333.15$ K.

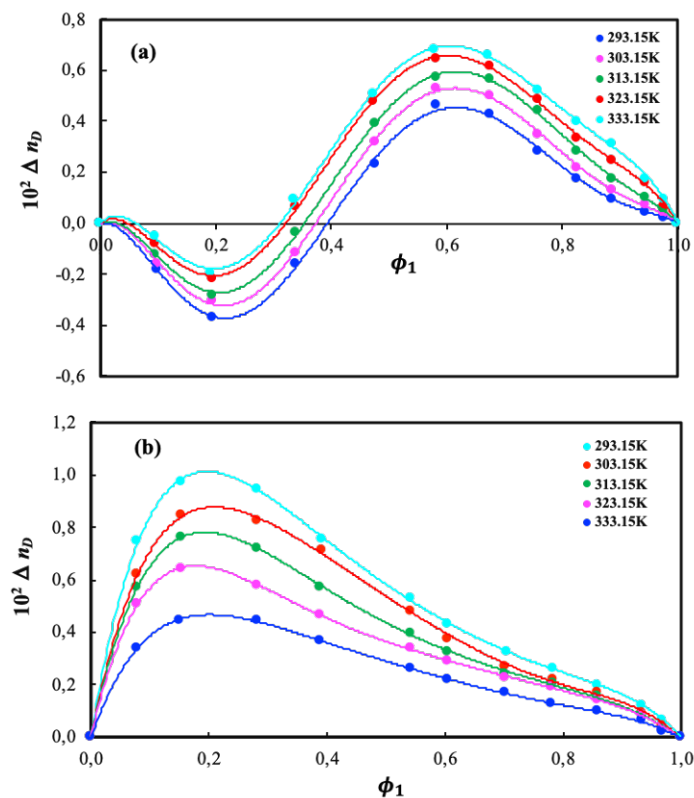


Figure 5.9D: Variations of deviation in refractive index (Δn_D) with acetophenone volume fraction (ϕ_1) for the binary mixtures of acetophenone with (a) acetic acid or (b) propionic acid at $T = 293.15 - 333.15$ K. The solid lines were generated using the Redlich-Kister curve-fitting.

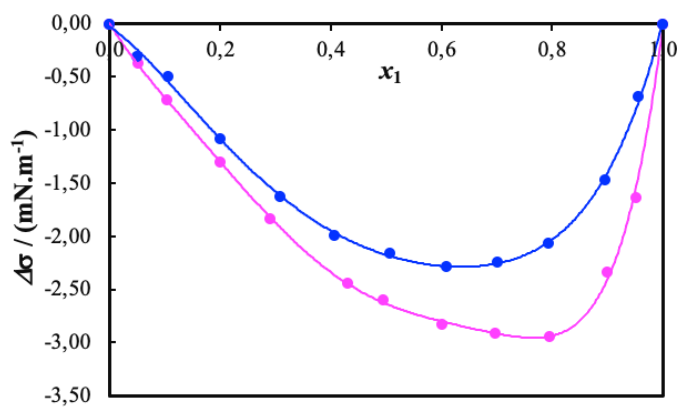


Figure 5.10D: Variations of deviation in surface tension ($\Delta\gamma$) with acetophenone mole fraction (x_1) for (●){acetophenone (x_1) + acetic acid (x_2)} and (●){acetophenone (x_1) + propionic acid (x_2)} binary mixtures at $T = 298.15$ K. The solid lines were generated using the Redlich-Kister curve-fitting.

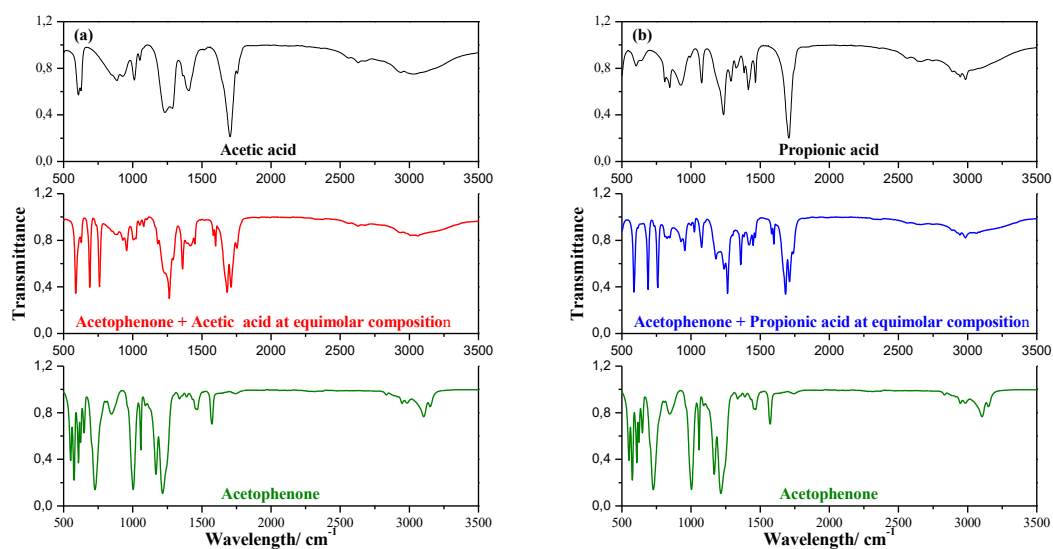


Figure 5.11D: FTIR spectrums of pure acetophenone, acetic acid, propionic acid and their binary mixtures at an equimolar composition

Appendix E: This section presents the results obtained for ternary mixtures of IL [BMIM][BF₄] or [BMIM][PF₆] with acetophenone and acetic or propionic acid.

Table 5.1E: Mole fraction (x_1, x_2, x_3), density (ρ_{123}) and sound velocity (u_{123}) for the ternary mixture of {[BMIM][BF₄] (x_1) + acetic acid (x_2) + acetophenone (x_3)} (mix_1) at T = 293.15 - 333.15 K and pressure, $p = 0.1$ MPa.

x_1	x_2	x_3	$\rho/\text{g.cm}^{-3}$	$u/\text{m.s}^{-1}$	$V_{m123}^E/\text{cm}^{-3}\cdot\text{mol}^{-1}$	$\Delta k_{s123}/\text{TPa}^{-1}$
293.15K						
0.2441	0.5454	0.2105	1.118	-	-0.087	-
0.3466	0.3559	0.2975	1.137	1502	-0.812	168420
0.4011	0.2534	0.3455	1.131	1529	0.331	162224
0.1158	0.8459	0.0383	1.091	-	0.570	-
0.2808	0.6258	0.0933	1.135	1424	-0.204	207348
0.4082	0.4527	0.1391	1.152	1484	-0.287	190045
0.4734	0.3746	0.1519	1.149	1526	0.760	241934
0.5528	0.2652	0.1820	1.162	1525	0.014	124134
0.6550	0.1326	0.2124	1.161	1565	1.164	124235
0.3826	0.5760	0.0414	1.137	1475	1.583	301239
0.5511	0.3896	0.0593	-	1510	-	-
0.6485	0.2802	0.0712	1.166	1552	1.619	213455
0.7731	0.1443	0.0826	1.175	1566	1.734	125205
0.8472	0.0594	0.0934	1.177	1569	2.094	61407
0.0398	0.5885	0.3717	1.060	1375	-0.313	144864
0.0438	0.5468	0.4093	1.055	1375	0.024	115323
0.0545	0.4356	0.5098	1.057	1420	-0.251	131292
0.0650	0.3257	0.6093	1.041	1432	1.336	94331
0.0744	0.2308	0.6948	1.057	-	-0.237	-
0.0861	0.1090	0.8050	1.041	1482	1.485	40294
0.0964	0.7164	0.1871	1.054	1310	2.188	112160
0.1733	0.4900	0.3367	1.075	1425	1.747	173847
0.2064	0.3948	0.3987	1.082	1479	1.618	227053
0.2676	0.2162	0.5162	1.089	1503	1.661	121381
303.15K						
0.2441	0.5454	0.2105	1.108	-	0.056	-
0.3466	0.3559	0.2975	1.129	1474	-0.853	172514
0.4011	0.2534	0.3455	1.123	1501	0.307	169299
0.1158	0.8459	0.0383	1.081	-	0.587	-
0.2808	0.6258	0.0933	1.127	1395	-0.223	210149
0.4082	0.4527	0.1391	1.144	1456	-0.309	193541
0.4734	0.3746	0.1519	1.141	1501	0.809	248702
0.5528	0.2652	0.1820	1.155	1498	-0.004	126623
0.6550	0.1326	0.2124	1.153	1541	1.158	131043

0.3826	0.5760	0.0414	-	1444	-	-
0.5511	0.3896	0.0593	-	1483	-	-
0.6485	0.2802	0.0712	-	1528	-	-
0.7731	0.1443	0.0826	1.167	1542	-	128669
0.8472	0.0594	0.0934	1.170	1545	2.082	63160
0.0398	0.5885	0.3717	1.050	1340	-0.318	142443
0.0438	0.5468	0.4093	1.045	1340	0.032	112197
0.0545	0.4356	0.5098	1.049	1386	-0.258	129467
0.0650	0.3257	0.6093	1.032	1396	1.374	89837
0.0744	0.2308	0.6948	1.046	-	-0.006	-
0.0861	0.1090	0.8050	1.032	1446	1.516	38280
0.0964	0.7164	0.1871	1.044	1279	2.288	115968
0.1733	0.4900	0.3367	1.066	1393	1.819	175270
0.2064	0.3948	0.3987	1.072	1449	1.716	231817
0.2676	0.2162	0.5162	1.080	1473	1.708	127490
313.15K						
0.2441	0.5454	0.2105	1.098	-	0.160	-
0.3466	0.3559	0.2975	1.121	1445	-0.913	174479
0.4011	0.2534	0.3455	1.114	1475	0.393	178308
0.1158	0.8459	0.0383	1.071	-	0.570	-
0.2808	0.6258	0.0933	1.118	1367	-0.271	209778
0.4082	0.4527	0.1391	1.135	1429	-0.353	194838
0.4734	0.3746	0.1519	1.131	1479	0.982	264114
0.5528	0.2652	0.1820	1.147	1472	-0.034	128345
0.6550	0.1326	0.2124	1.145	1517	1.227	138668
0.3826	0.5760	0.0414	-	1415	-	-
0.5511	0.3896	0.0593	-	1457	-	-
0.6485	0.2802	0.0712	1.151	1504	1.650	223191
0.7731	0.1443	0.0826	1.160	1518	1.735	131087
0.8472	0.0594	0.0934	1.162	1522	2.110	67477
0.0398	0.5885	0.3717	1.040	1306	-0.348	136804
0.0438	0.5468	0.4093	1.036	1305	0.019	106390
0.0545	0.4356	0.5098	1.039	1351	-0.284	125265
0.0650	0.3257	0.6093	1.023	1360	1.400	83614
0.0744	0.2308	0.6948	1.035	-	0.224	-
0.0861	0.1090	0.8050	1.023	1411	1.547	36078
0.0964	0.7164	0.1871	1.033	1247	2.369	113435
0.1733	0.4900	0.3367	1.056	1362	1.913	175095
0.2064	0.3948	0.3987	1.062	1420	1.842	235893
0.2676	0.2162	0.5162	1.069	1442	1.999	133854
323.15K						
0.2441	0.5454	0.2105	1.087	-	0.301	-
0.3466	0.3559	0.2975	1.113	1417	-0.957	175669
0.4011	0.2534	0.3455	1.105	1449	0.549	187133
0.1158	0.8459	0.0383	1.061	-	0.599	-
0.2808	0.6258	0.0933	1.109	1339	-0.287	208066
0.4082	0.4527	0.1391	1.128	1403	-0.377	195178
0.4734	0.3746	0.1519	1.123	1457	1.020	274289
0.5528	0.2652	0.1820	1.139	1446	-0.049	129515

0.6550	0.1326	0.2124	1.137	1493	1.367	146579
0.3826	0.5760	0.0414	-	1387	-	-
0.5511	0.3896	0.0593	-	1431	-	-
0.6485	0.2802	0.0712	1.143	1481	1.653	225533
0.7731	0.1443	0.0826	1.152	1495	1.804	134065
0.8472	0.0594	0.0934	1.155	1498	2.181	67145
0.0398	0.5885	0.3717	1.031	1271	-0.345	129655
0.0438	0.5468	0.4093	1.027	1270	0.037	99132
0.0545	0.4356	0.5098	1.030	1317	-0.286	119956
0.0650	0.3257	0.6093	1.014	1324	1.446	76638
0.0744	0.2308	0.6948	1.023	-	0.477	-
0.0861	0.1090	0.8050	1.015	1376	1.590	33716
0.0964	0.7164	0.1871	1.023	1214	2.500	107382
0.1733	0.4900	0.3367	1.046	1331	2.049	173097
0.2064	0.3948	0.3987	1.053	1390	1.926	237384
0.2676	0.2162	0.5162	1.059	1412	2.283	137746
333.15K						
0.2441	0.5454	0.2105	1.077	-	0.204	-
0.3466	0.3559	0.2975	1.105	1390	-1.176	172429
0.4011	0.2534	0.3455	1.096	1423	0.496	187459
0.1158	0.8459	0.0383	1.052	1147	0.234	66607
0.2808	0.6258	0.0933	1.101	1311	-0.601	199018
0.4082	0.4527	0.1391	1.120	1377	-0.617	190138
0.4734	0.3746	0.1519	1.115	-	0.893	-
0.5528	0.2652	0.1820	1.132	1420	-0.194	127374
0.6550	0.1326	0.2124	1.128	1470	1.473	152552
0.3826	0.5760	0.0414	-	1359	-	-
0.5511	0.3896	0.0593	-	1406	-	-
0.6485	0.2802	0.0712	1.135	1457	1.609	224281
0.7731	0.1443	0.0826	1.145	1472	1.822	134962
0.8472	0.0594	0.0934	1.147	1474	2.249	68052
0.0398	0.5885	0.3717	1.022	1237	-0.618	114953
0.0438	0.5468	0.4093	1.017	1235	-0.203	84795
0.0545	0.4356	0.5098	1.021	1283	-0.495	108933
0.0650	0.3257	0.6093	1.004	1289	1.338	65356
0.0744	0.2308	0.6948	1.012	-	0.630	-
0.0861	0.1090	0.8050	1.006	1341	1.580	29442
0.0964	0.7164	0.1871	1.013	1181	2.305	91832
0.1733	0.4900	0.3367	1.037	1301	1.935	167606
0.2064	0.3948	0.3987	1.044	1361	1.892	235284
0.2676	0.2162	0.5162	1.050	1382	2.320	135985

Standard uncertainties u are; $u(T) = 0.02$ K, $u(p) = 0.04$ MPa and the combined expanded uncertainty Uc in mole fraction, density and sound velocity were $Uc(x) = 0.0006$, $Uc(\rho) = 0.006$ g.cm⁻³ and $Uc(u) = 1$ m.s⁻¹, respectively, (0.95 level of confidence).

Table 5.2E: Mole fraction (x_1, x_2, x_3), density(ρ_{123}) and sound velocity(u_{123}) for the ternary mixture of {[BMIM][BF₄] (x_1) + propionic acid (x_2) + acetophenone (x_3)} (*mix₂*) at T = 293.15 - 333.15 K and pressure, $p = 0.1$ MPa.

x_1	x_2	x_3	$\rho/\text{g.cm}^{-3}$	$u/\text{m.s}^{-1}$	$V_{m123}^E/\text{cm}^{-3}\cdot\text{mol}^{-1}$	$\Delta k_{s123}/\text{TPa}^{-1}$
293.15K						
0.2712	0.4940	0.2349	1.099	1430	-0.229	109599
0.3720	0.3085	0.3196	1.126	1498	-0.901	104670
0.4214	0.2157	0.3629	1.118	1531	1.023	138949
0.1377	0.8164	0.0459	1.053	1376	0.421	292615
0.3201	0.5730	0.1068	1.116	1420	-0.676	124741
0.4459	0.4018	0.1523	1.118	-	1.925	-
0.5107	0.3258	0.1635	1.150	1503	-0.640	103567
0.5815	0.2256	0.1929	1.139	1529	2.021	119239
0.6722	0.1106	0.2172	1.145	1564	2.932	119226
0.4305	0.5233	0.0461	1.136	1444	-0.282	125771
0.5951	0.3412	0.0637	1.157	1495	0.317	92421
0.6843	0.2408	0.0749	1.161	1550	1.438	161669
0.7903	0.1200	0.0897	1.162	1565	3.012	112066
0.8572	0.0485	0.0943	1.191	-	-0.161	-
0.0378	0.6101	0.3521	1.014	1363	1.164	147282
0.0485	0.4975	0.4540	1.036	-	-0.223	-
0.0593	0.3848	0.5558	1.020	1369	-3.120	-25059
0.0692	0.2816	0.6493	1.032	1423	1.222	18374
0.0782	0.1901	0.7317	1.031	1436	1.744	-17384
0.0877	0.0898	0.8225	1.047	1492	0.435	30362
0.1117	0.6723	0.2160	1.019	1375	3.063	231183
0.1912	0.4374	0.3714	1.048	1478	2.977	278537
0.2245	0.3408	0.4347	1.065	1513	2.155	269598
0.2747	0.1802	0.5451	1.099	1528	-0.319	123185
303.15K						
0.2712	0.4940	0.2349	1.091	1400	-0.276	115449
0.3720	0.3085	0.3196	1.118	1469	-0.960	111446
0.4214	0.2157	0.3629	1.109	1504	1.133	148797
0.1377	0.8164	0.0459	1.035	1348	1.221	319034
0.3201	0.5730	0.1068	1.108	1392	-0.743	133183
0.4459	0.4018	0.1523	1.108	-	2.106	-
0.5107	0.3258	0.1635	1.142	1476	-0.693	110186
0.5815	0.2256	0.1929	1.131	1503	2.151	127131
0.6722	0.1106	0.2172	1.137	1538	3.082	125824
0.4305	0.5233	0.0461	1.128	1417	-0.337	133986
0.5951	0.3412	0.0637	1.147	1466	0.586	94949
0.6843	0.2408	0.0749	1.153	1526	1.407	168183
0.7903	0.1200	0.0897	1.154	1541	3.090	117274
0.8572	0.0485	0.0943	1.184	-	-0.163	-
0.0378	0.6101	0.3521	1.005	1327	1.215	146802

0.0485	0.4975	0.4540	1.026	-	-0.243	-
0.0593	0.3848	0.5558	1.010	1335	2.021	-18480
0.0692	0.2816	0.6493	1.023	1387	1.243	16045
0.0782	0.1901	0.7317	1.022	1399	1.789	-21815
0.0877	0.0898	0.8225	1.038	1457	0.430	31103
0.1117	0.6723	0.2160	1.009	1346	3.183	244582
0.1912	0.4374	0.3714	1.039	1450	3.048	291597
0.2245	0.3408	0.4347	1.056	1480	2.301	269401
0.2747	0.1802	0.5451	1.089	1501	-0.200	139946
313.15K						
0.2712	0.4940	0.2349	1.0821	-	-0.324	-
0.3720	0.3085	0.3196	1.1096	1441	-1.027	117164
0.4214	0.2157	0.3629	1.0988	1481	1.417	172360
0.1377	0.8164	0.0459	1.0272	1319	1.036	325267
0.3201	0.5730	0.1068	1.0995	1364	-0.825	141228
0.4459	0.4018	0.1523	1.0970	1452	2.48	241879
0.5107	0.3258	0.1635	1.1346	1450	-0.754	116815
0.5815	0.2256	0.1929	1.1213	1476	2.383	133221
0.6722	0.1106	0.2172	1.1292	1515	3.131	135259
0.4305	0.5233	0.0461	1.1197	1391	-0.403	142460
0.5951	0.3412	0.0637	1.1370	-	0.864	-
0.6843	0.2408	0.0749	1.1455	1502	1.405	174973
0.7903	0.1200	0.0897	1.1465	1518	3.198	124684
0.8572	0.0485	0.0943	1.1762	1517	-0.162	18320
0.0378	0.6101	0.3521	0.9945	1290	1.263	141643
0.0485	0.4975	0.4540	1.0171	-	-0.27	-
0.0593	0.3848	0.5558	1.0001	1296	2.148	-25893
0.0692	0.2816	0.6493	1.0138	1350	1.263	14276
0.0782	0.1901	0.7317	1.0133	1362	1.841	-23640
0.0877	0.0898	0.8225	1.0297	1422	0.423	31872
0.1117	0.6723	0.2160	0.9981	1313	3.326	246296
0.1912	0.4374	0.3714	1.0294	1413	3.192	279586
0.2245	0.3408	0.4347	1.0464	1457	2.393	295098
0.2747	0.1802	0.5451	1.0780	1472	0.11	155027
323.15K						
0.2712	0.4940	0.2349	1.074	1341	-0.369	126976
0.3720	0.3085	0.3196	1.102	1413	-1.100	122890
0.4214	0.2157	0.3629	1.088	1457	1.769	191679
0.1377	0.8164	0.0459	1.017	1288	1.105	327763
0.3201	0.5730	0.1068	1.091	1337	-0.910	148605
0.4459	0.4018	0.1523	1.085	-	3.032	-
0.5107	0.3258	0.1635	1.127	1424	-0.817	123061
0.5815	0.2256	0.1929	1.111	1451	2.683	141591
0.6722	0.1106	0.2172	1.120	1491	3.342	144163
0.4305	0.5233	0.0461	1.112	1365	-0.469	150516
0.5951	0.3412	0.0637	1.128	1406	1.018	87148
0.6843	0.2408	0.0749	1.138	1478	1.353	178643
0.7903	0.1200	0.0897	1.139	1492	3.213	122329
0.8572	0.0485	0.0943	1.169	-	-0.160	-

0.0378	0.6101	0.3521	0.984	1254	1.327	137826
0.0485	0.4975	0.4540	1.008	1272	-0.292	60559
0.0593	0.3848	0.5558	0.990	1260	2.310	153148
0.0692	0.2816	0.6493	1.005	1315	1.291	12607
0.0782	0.1901	0.7317	1.004	1327	1.910	-25148
0.0877	0.0898	0.8225	1.021	1388	0.419	32477
0.1117	0.6723	0.2160	0.988	1279	3.493	243432
0.1912	0.4374	0.3714	1.019	1383	3.362	285528
0.2245	0.3408	0.4347	1.036	1429	2.650	306722
0.2747	0.1802	0.5451	1.068	1443	0.326	164905
333.15K						
0.2712	0.4940	0.2349	1.065	1312	-0.408	131534
0.3720	0.3085	0.3196	1.094	1385	-1.188	127813
0.4214	0.2157	0.3629	1.079	1435	1.950	210661
0.1377	0.8164	0.0459	1.003	1261	1.539	343906
0.3201	0.5730	0.1068	1.083	1310	-1.004	155012
0.4459	0.4018	0.1523	1.072	-	3.643	-
0.5107	0.3258	0.1635	1.119	1399	-0.889	128544
0.5815	0.2256	0.1929	1.102	1428	3.021	154912
0.6722	0.1106	0.2172	1.112	1467	3.483	150028
0.4305	0.5233	0.0461	1.104	1340	-0.541	157708
0.5951	0.3412	0.0637	1.117	1376	1.432	230568
0.6843	0.2408	0.0749	1.131	1456	1.386	185021
0.7903	0.1200	0.0897	1.131	1470	3.332	128317
0.8572	0.0485	0.0943	1.162	-	-0.163	-
0.0378	0.6101	0.3521	0.974	1219	1.392	134276
0.0485	0.4975	0.4540	0.999	1237	-0.314	58530
0.0593	0.3848	0.5558	0.979	1223	2.489	-31329
0.0692	0.2816	0.6493	0.996	1280	1.321	10401
0.0782	0.1901	0.7317	0.995	1292	1.997	-26763
0.0877	0.0898	0.8225	1.013	1354	0.407	31790
0.1117	0.6723	0.2160	0.977	1252	3.661	255933
0.1912	0.4374	0.3714	1.010	1351	3.519	283351
0.2245	0.3408	0.4347	1.026	1400	2.849	312311
0.2747	0.1802	0.5451	1.058	1415	0.525	173314

Standard uncertainties u are; $u(T) = 0.02$ K, $u(p) = 0.04$ MPa and the combined expanded uncertainty U_c in mole fraction, density and sound velocity were $U_c(x) = 0.0006$, $U_c(\rho) = 0.006$ g.cm⁻³ and $U_c(u) = 1$ m.s⁻¹, respectively, (0.95 level of confidence).

Table 5.3E Mole fraction (x_1, x_2, x_3), density (ρ_{123}) and sound velocity (u_{123}) for the ternary mixture of {[BMIM][PF₆] (x_1)+ acetic acid (x_2) + acetophenone (x_3)} (mix_3) at T = 293.15 - 333.15 K and pressure, $p = 0.1$ MPa.

x_1	x_2	x_3	$\rho/\text{g}\cdot\text{cm}^{-3}$	$u/\text{m}\cdot\text{s}^{-1}$	$V_{m123}^E/\text{cm}^3\cdot\text{mol}^{-1}$	$\Delta k_{s123}/\text{TPa}^{-1}$
293.15K						
0.2697	0.4953	0.2350	1.210	-	-0.266	-
0.3710	0.3099	0.3191	-	1429	-	-
0.4203	0.2165	0.3632	1.270	1445	-3.190	-73720
0.1378	0.8170	0.0452	1.096	1232	5.226	37535
0.3202	0.5734	0.1064	1.199	1338	3.885	37417
0.4456	0.4021	0.1523	1.290	1407	-1.881	2179
0.5108	0.3257	0.1636	1.307	1420	-2.422	-18597
0.5802	0.2258	0.1940	1.315	1434	-2.320	-44234
0.6720	0.1111	0.2169	1.340	1456	-3.947	-73272
0.4304	0.5232	0.0464	1.230	-	5.235	-
0.5952	0.3418	0.0630	1.325	1403	-1.281	-8883
0.6845	0.2407	0.0749	1.360	1423	-3.951	-40331
0.7895	0.1199	0.0906	1.389	1442	-6.198	-74720
0.8559	0.0495	0.0946	1.397	1452	-6.872	-87210
0.0374	0.6095	0.3531	1.069	1334	0.258	64393
0.0485	0.4975	0.4540	1.108	1373	-2.760	4147
0.0593	0.3848	0.5558	1.112	1438	-3.120	53086
0.0692	0.2821	0.6487	1.061	-	1.790	-
0.0779	0.1906	0.7315	1.058	1464	2.360	69729
0.0877	0.0895	0.8228	1.094	1479	-1.372	-42566
0.1117	0.6723	0.2160	1.147	1326	-1.044	36690
0.1912	0.4374	0.3714	1.180	1401	-1.781	2024
0.2256	0.3425	0.4319	1.167	1409	0.355	-24320
0.2795	0.1819	0.5386	1.205	1459	-2.558	-72904
303.15K						
0.2697	0.4953	0.2350	1.203	-	-0.476	-
0.3710	0.3099	0.3191	-	1401	-	-
0.4203	0.2165	0.3632	1.261	1416	-3.194	-63403
0.1378	0.8170	0.0452	1.086	1200	5.321	39039
0.3202	0.5734	0.1064	1.190	1309	3.961	42440
0.4456	0.4021	0.1523	1.280	1379	-1.887	9026
0.5108	0.3257	0.1636	1.298	1393	-2.429	-9130
0.5802	0.2258	0.1940	1.306	1408	-2.314	-34819
0.6720	0.1111	0.2169	1.331	1430	-3.966	-63247
0.4304	0.5232	0.0464	1.218	-	5.528	-
0.5952	0.3418	0.0630	1.315	1377	-1.202	-946
0.6845	0.2407	0.0749	1.351	1398	-3.964	-31574
0.7895	0.1199	0.0906	1.378	1417	-6.214	-66258

0.8559	0.0495	0.0946	1.388	1428	-6.898	-79694
0.0374	0.6095	0.3531	1.059	1299	0.279	63303
0.0485	0.4975	0.4540	1.098	1337	-2.736	5061
0.0593	0.3848	0.5558	1.102	1402	-3.134	67687
0.0692	0.2821	0.6487	1.052	-	1.845	-
0.0779	0.1906	0.7315	1.049	1428	2.416	67198
0.0877	0.0895	0.8228	1.085	1444	-1.355	-37831
0.1117	0.6723	0.2160	1.136	1294	-1.034	42418
0.1912	0.4374	0.3714	1.171	1370	-1.793	11220
0.2256	0.3425	0.4319	1.155	1376	0.641	-18012
0.2795	0.1819	0.5386	1.196	1427	-2.539	-64816
313.15						
0.2697	0.4953	0.2350	1.188	-	0.105	-
0.3710	0.3099	0.3191	-	1373	-	-
0.4203	0.2165	0.3632	1.251	1388	-3.210	-54921
0.1378	0.8170	0.0452	1.075	1167	5.439	33965
0.3202	0.5734	0.1064	1.180	1281	4.043	46938
0.4456	0.4021	0.1523	1.271	1351	-1.909	14305
0.5108	0.3257	0.1636	1.289	1367	-2.462	-2186
0.5802	0.2258	0.1940	-	1382	-	-
0.6720	0.1111	0.2169	-	1405	-	-
0.4304	0.5232	0.0464	1.205	-	5.999	-
0.5952	0.3418	0.0630	1.305	1351	-1.113	5116
0.6845	0.2407	0.0749	1.342	1373	-4.031	-25467
0.7895	0.1199	0.0906	1.369	1394	-6.243	-59240
0.8559	0.0495	0.0946	1.379	1404	-6.935	-73165
0.0374	0.6095	0.3531	1.049	1264	0.278	58678
0.0485	0.4975	0.4540	1.088	1302	-2.733	2955
0.0593	0.3848	0.5558	1.093	1366	-3.205	63359
0.0692	0.2821	0.6487	1.042	-	1.890	-
0.0779	0.1906	0.7315	1.040	1392	2.465	63230
0.0877	0.0895	0.8228	1.076	1410	-1.342	-34009
0.1117	0.6723	0.2160	1.127	1262	-1.064	43611
0.1912	0.4374	0.3714	1.161	1340	-1.831	17108
0.2256	0.3425	0.4319	1.143	1342	0.898	-16580
0.2795	0.1819	0.5386	1.186	1395	-2.486	-57411
323.15K						
0.2697	0.4953	0.2350	1.176	1278	0.334	8353
0.3710	0.3099	0.3191	-	-	-	-
0.4203	0.2165	0.3632	1.242	1360	-3.211	-47307
0.1378	0.8170	0.0452	1.065	1130	5.586	17508
0.3202	0.5734	0.1064	1.170	1253	4.144	48661
0.4456	0.4021	0.1523	1.262	1324	-1.914	19056
0.5108	0.3257	0.1636	1.280	1341	-2.502	2801
0.5802	0.2258	0.1940	-	1356	-	-
0.6720	0.1111	0.2169	-	1381	-	-
0.4304	0.5232	0.0464	1.193	-	6.414	-
0.5952	0.3418	0.0630	1.295	1326	-0.985	10678
0.6845	0.2407	0.0749	1.334	1349	-4.232	-21632

0.7895	0.1199	0.0906	1.360	1370	-6.267	-52879
0.8559	0.0495	0.0946	1.370	1381	-6.973	-67160
0.0374	0.6095	0.3531	1.039	1229	0.314	52127
0.0485	0.4975	0.4540	1.077	1266	-2.700	-755
0.0593	0.3848	0.5558	1.084	1331	-3.258	58056
0.0692	0.2821	0.6487	1.033	-	1.956	-
0.0779	0.1906	0.7315	1.030	1356	2.530	58832
0.0877	0.0895	0.8228	1.066	1375	-1.322	-32752
0.1117	0.6723	0.2160	1.117	1217	-1.067	12377
0.1912	0.4374	0.3714	1.152	1309	-1.851	20492
0.2256	0.3425	0.4319	1.133	1308	1.093	-17424
0.2795	0.1819	0.5386	1.176	1364	-2.440	-51265
333.15K						
0.2697	0.4953	0.2350	1.167	1247	0.116	400
0.3710	0.3099	0.3191	-	-	-	-
0.4203	0.2165	0.3632	1.233	1332	-3.291	-42709
0.1378	0.8170	0.0452	1.056	1102	5.244	9750
0.3202	0.5734	0.1064	1.161	1225	3.931	43213
0.4456	0.4021	0.1523	1.253	1299	-2.127	19370
0.5108	0.3257	0.1636	1.272	1315	-2.818	1915
0.5802	0.2258	0.1940	1.279	1331	-2.409	-17222
0.6720	0.1111	0.2169	1.304	1356	-4.104	-41109
0.4304	0.5232	0.0464	1.186	-	6.056	-
0.5952	0.3418	0.0630	1.286	1302	-1.037	12122
0.6845	0.2407	0.0749	1.329	1325	-4.763	-23281
0.7895	0.1199	0.0906	1.351	1347	-6.348	-48368
0.8559	0.0495	0.0946	1.362	1358	-7.033	-62217
0.0374	0.6095	0.3531	1.029	1194	0.054	36947
0.0485	0.4975	0.4540	1.067	1231	-2.915	-11698
0.0593	0.3848	0.5558	1.075	1295	-3.532	47078
0.0692	0.2821	0.6487	1.023	-	1.889	-
0.0779	0.1906	0.7315	1.021	1321	2.503	51386
0.0877	0.0895	0.8228	1.057	1340	-1.349	-33647
0.1117	0.6723	0.2160	1.109	1179	-1.541	-12147
0.1912	0.4374	0.3714	1.144	1272	-2.233	-507
0.2256	0.3425	0.4319	1.122	1275	1.116	-23993
0.2795	0.1819	0.5386	1.167	1334	-2.482	-48180

Standard uncertainties u are; $u(T) = 0.02$ K, $u(p) = 0.04$ MPa and the combined expanded uncertainty U_c in mole fraction, density and sound velocity were $U_c(x) = 0.0006$, $U_c(\rho) = 0.006$ g.cm⁻³ and $U_c(u) = 1$ m.s⁻¹, respectively, (0.95 level of confidence).

Table 5.4E: Redlich-Kister coefficients (A_i) and standard deviations (σ) obtained for the binary mixtures of {[BMIM][BF₄] or [BMIM][PF₆] + acetophenone} at T = 293.15 - 333.15 K and pressure, $p = 0.1$ MPa [367].

	T/K	A_0	A_1	A_2	A_3	A_4	σ
{[BMIM][BF₄] (x_1) + acetophenone (x_2)}							
$V_m^E / \text{cm}^3 \cdot \text{mol}^{-1}$	293.15	18.852	-0.637	-3.972	-1.029	0.131	0.106
	303.15	19.631	-0.803	-4.373	-3.110	3.022	0.103
	313.15	20.449	-1.587	-6.059	-4.431	8.210	0.113
	323.15	21.333	-1.755	-6.516	-7.050	11.654	0.119
	333.15	22.574	-2.933	-13.007	-9.821	22.630	0.170
$\Delta k_s / \text{TPa}^{-1}$	293.15	237330	-22924	37085	89050	44842	543
	303.15	233685	-20053	24521	99867	11297	411
	313.15	225243	-18744	25051	111467	-44855	831
	323.15	214378	-32887	34326	146457	-104398	644
	333.15	203168	-320638	217978	1486978	-1228338	1373
{[BMIM][PF₆] (x_1) + acetophenone (x_2)}							
$V_m^E / \text{cm}^3 \cdot \text{mol}^{-1}$	293.15	25.867	-19.539	-13.925	-5.802	17.259	0.058
	303.15	26.252	-19.848	-14.239	-6.323	18.098	0.060
	313.15	26.668	-20.117	-14.717	-7.167	19.465	0.062
	323.15	27.111	-20.513	-14.953	-7.661	20.216	0.065
	333.15	27.629	-20.878	-15.365	-8.669	21.732	0.069
$\Delta k_s / \text{TPa}^{-1}$	293.15	169167	-254159	-217659	-58317	92919	656
	303.15	138325	-290681	-137488	57475	-64931	610
	313.15	115907	-259106	-185707	-213	-50674	998
	323.15	87080	-306315	-225102	151424	-95946	983
	333.15	58272	-285865	-282296	114651	4623	

Table 5.5E: Redlich-Kister coefficients (A_i) and standard deviation (σ) obtained for the binary mixtures of {[BMIM][BF₄] (x_1) or [BMIM][PF₆] (x_1) + acetic acid (x_2)} and {[BMIM][BF₄] (x_1) + propionic acid (x_2)} at T = 293.15 - 333.15 K and pressure, $p = 0.1$ MPa.

	T/K	A_0	A_1	A_2	A_3	A_4	σ
{[BMIM][BF₄] (x_1) + acetic acid (x_2)}							
$V_m^E / \text{cm}^3 \cdot \text{mol}^{-1}$	293.15	-1.046	-3.532	-3.321	-2.252	4.024	0.049
	303.15	-1.202	-3.408	-3.387	-2.535	3.523	0.045
	313.15	-1.416	-3.716	-2.733	-2.532	1.275	0.041
	323.15	-1.533	-3.624	-2.682	-2.848	0.452	0.027
	333.15	-2.479	-5.037	-4.356	-3.999	1.016	0.084
$\Delta k_s / \text{TPa}^{-1}$	293.15	955668	593081	746626	277051	349111	8756
	303.15	972551	611000	760185	265773	352403	8630
	313.15	980131	601113	753480	287942	398590	8875
	323.15	982097	597613	757577	294330	423295	8738
	333.15	997722	609335	763111	335270	462208	8544
{[BMIM][BF₄] (x_1) + propionic acid (x_2)}							
$V_m^E / \text{cm}^3 \cdot \text{mol}^{-1}$	293.15	-3.598	-4.464	-10.371	-40.169	-8.474	-
	303.15	-3.925	-4.336	-13.334	-41.235	-8.371	0.144
	313.15	-4.756	-5.220	-16.047	-36.757	-11.081	0.087
	323.15	-5.058	-5.529	-17.229	-36.393	-12.189	0.123
	333.15	-5.550	-5.698	-21.437	-37.931	-8.676	0.108
$\Delta k_s / \text{TPa}^{-1}$	293.15	623529.	439591.	197737.	-916354.	-942650	
	303.15	696472.	397207.	343506.	-756019.	-1245591	
	313.15	756901.	416762.	369213.	-527788.	-1243595	
	323.15	805714.	430132.	372150.	-398466.	-1170684	
	333.15	871402.	511091.	292666.	-294285.	-978230	
{[BMIM][PF₆] (x_1) + acetic acid (x_2)}							
$V_m^E / \text{cm}^3 \cdot \text{mol}^{-1}$	293.15	2.799	-6.231	-4.602	0.805	-1.583	0.048
	303.15	3.346	-7.730	-3.702	2.526	-3.348	-
	313.15	3.525	-8.539	-0.657	3.186	-6.205	0.045
	323.15	4.316	-8.877	-3.804	3.916	-2.254	0.052
	333.15	5.210	-10.358	-2.772	4.844	-2.975	0.090
$\Delta k_s / \text{TPa}^{-1}$	293.15	455993	198085	181882	-47897	-237290	
	303.15	475359	228493	290691	-27348	-350571	
	313.15	502485	203230	222083	140326	-139997	
	323.15	531744	211663	27832	219708	216663	
	333.15	568184	257728	4235	176408	253831	

Table 5.6E: Redlich-Kister coefficients (A_i) and standard deviation (σ) obtained for the binary mixtures of {acetic acid (x_1) + acetophenone (x_2)} and {propionic acid (x_1) + acetophenone (x_2)} at T = 293.15 - 333.15 K and pressure, $p = 0.1$ MPa.

	T/K	A_0	A_1	A_2	A_3	A_4	σ
{acetic acid (x_1) + acetophenone (x_2)}							
$V_m^E / \text{cm}^3 \cdot \text{mol}^{-1}$	293.15	-1.867	-2.256	0.194	0.910	-0.423	
	303.15	-2.136	-2.557	-1.252	-0.686	-0.294	
	313.15	-2.323	-2.727	-2.072	-0.710	0.360	
	323.15	-2.699	-2.645	-1.214	-2.067	-2.564	
	333.15	-2.972	-2.522	-2.474	-4.421	-3.563	0.024
$\Delta k_s / \text{TPa}^{-1}$	293.15	471335	259308	-896699	123144	78432	
	303.15	463197	290965	-991881	79473	193297	
	313.15	448665	245746	-717816	116032	-210565	
	323.15	428678	229466	-648638	132531	-313939	
	333.15	431625	404400	-1141189	-523507	845053	
{acetic acid (x_1) + acetophenone (x_2)}							
$V_m^E / \text{cm}^3 \cdot \text{mol}^{-1}$	293.15	-0.194	2.999	-2.454	4.060	1.785	0.028
	303.15	-0.539	3.679	-2.746	2.533	0.607	0.020
	313.15	-1.577	2.789	-1.284	4.323	-2.081	0.020
	323.15	-2.170	2.599	-2.038	5.543	-2.904	0.026
	333.15	-2.987	3.366	-4.890	5.174	0.392	0.035
$\Delta k_s / \text{TPa}^{-1}$	293.15	380243	378855	-450168	-106661	163745	
	303.15	364532	387411	-446456	-104363	215851	
	313.15	340606	376516	-369640	-79506	175660	
	323.15	323032	358767	-375127	-21656	227989	
	333.15	296452	380468	-320701	-22817	208442	

Table 5.7E: Parameters for the model 1 (Redlich-Kister) + 4 (5p-model) for the ternary mixture of {[BMIM][BF₄] (*x*₁) + acetic acid (*x*₂) + acetophenone (*x*₃)}(*mix*₁).

$Y_{123} = V_{m123}^E$, parameters in $cm^3 \cdot mol^{-1}$						
T / K	A_0	A_1	A_2	A_3	A_4	σ
293.15	-40.9	97.5	8.13	218	169	0.87
303.15	-42.6	130	57.2	230	116	0.80
313.15	-40.4	123	57.5	231	153	0.89
323.15	-39.3	136	72.7	238	176	0.90
333.15	-41.5	141	85.4	227	218	0.93
$Y_{123} = \Delta k_{s123}$, parameters in $10^5 \cdot TPa^{-1}$						
T / K	A_0	A_1	A_2	A_3	A_4	σ
293.15	-1.26	-	-	-	-	0.28
303.15	0.32	-	-	-	-	0.29
313.15	1.28	-	-	-	-	0.31
323.15	2.79	-	-	-	-	0.33
333.15	4.85	-	-	-	-	0.36

For Δk_{s123} with parameters A_1 to A_4 equal to 0, the model is equivalent to 1 (Redlich-Kister) + 2 (1p-Cibulka).

Table 5.8E: Parameters for the model 9 (“average”) + 7 (11p-model) for the ternary mixture of {[BMIM][BF₄] (*x*₁) + propionic acid (*x*₂) + acetophenone (*x*₃)}(*mix*₂).

$Y_{123} = V_{m123}^E$, parameters in $cm^3 \cdot mol^{-1}$												
T / K	A_0	A_1	A_2	A_3	A_4	A_5	A_6	A_7	A_8	A_9	A_{10}	σ
293.15	-30.1	189	99.7	803	-141	-	-	-	-	-	-	0.84
303.15	-31.9	197	107	861	-108	-	-	-	-	-	-	0.92
313.15	-28.1	175	110	843	-56.6	-	-	-	-	-	-	1.05
323.15	-25.2	184	127	885	-56.7	-	-	-	-	-	-	1.12
333.15	-23.2	198	143	951	-32.6	-	-	-	-	-	-	1.24
$Y_{123} = \Delta k_{s123}$, parameters in $10^5 \cdot TPa^{-1}$												
T / K	A_0	A_1	A_2	A_3	A_4	A_5	A_6	A_7	A_8	A_9	A_{10}	σ
293.15	53.7	29	29.0	-993	-139	-1362	-901	3465	35.7	4685	1495	0.36
303.15	4.95	-71.0	-80.1	-411	258	-522	289	2085	-385	2812	-526	0.34
313.15	-13.6	-237	-13.3	-694	467	-290	-614	2751	-719	2997	819	0.49
323.15	66.2	36.6	75.8	-914	-245	-1162	-1109	3104	308	3894	1508	0.36
333.15	67.1	-14.6	23.8	-1127	-78.5	-1527	-1042	3794	-78.0	5132	1653	0.58

For V_{m123}^E with parameters A_5 to A_{10} equal to 0, the model is equivalent to 9 (“average”) + 4 (5p-model).

Table 5.9E: Parameters for the model 9 (“average”) + 7 (11p-model) for the ternary mixture of {[BMIM][PF₆] (x_1) + acetic acid (x_2) + acetophenone (x_3)}(mix_3).

$Y_{123} = V_{m123}^E$, parameters in $cm^3 \cdot mol^{-1}$												
T / K	A_0	A_1	A_2	A_3	A_4	A_5	A_6	A_7	A_8	A_9	A_{10}	σ
293.15	-103	556	126	-942	618	-4746	-1103	529	254	11314	-312	1.8
303.15	-103	574	170	-897	593	-4699	-1342	370	375	11126	-32.8	1.8
313.15	-89.5	649	165	-1589	717	-4494	-1401	1746	41.1	10796	128	1.9
323.15	-87.6	673	176	-1665	732	-4599	-1480	1893	56.8	10994	226	2.0
333.15	-86.5	756	196	-1239	641	-5383	-1460	655	469	12861	192	2.0
$Y_{123} = \Delta k_{s123}$, parameters in $10^5 \cdot TPa^{-1}$												
T / K	A_0	A_1	A_2	A_3	A_4	A_5	A_6	A_7	A_8	A_9	A_{10}	σ
293.15	-27.62	17.32	-22.4	-83.75	9.577	185.2	12.02	-	-	-	-	0.33
303.15	-25.08	17.11	-23.18	-72.39	10.34	169.1	22.11	-	-	-	-	0.32
313.15	-22.66	15.04	-24.29	-77.02	7.631	139.7	29.15	-	-	-	-	0.31
323.15	-31.92	19.42	-12.64	64.66	82.09	22.56	7.762	-388.3	-118.6	-	-	0.25
333.15	-30.07	27.59	-34.11	-43.01	95	-301.7	288.6	-92.04	-164.6	707	-499.1	0.24

For Δk_{s123} with parameters A_7 to A_{10} equal to 0, the model is equivalent to 9 (“average”) + 5 (7p-model) and with parameters A_9 and A_{10} equal to 0, the model is equivalent to 9 (“average”) + 6 (9p-model).

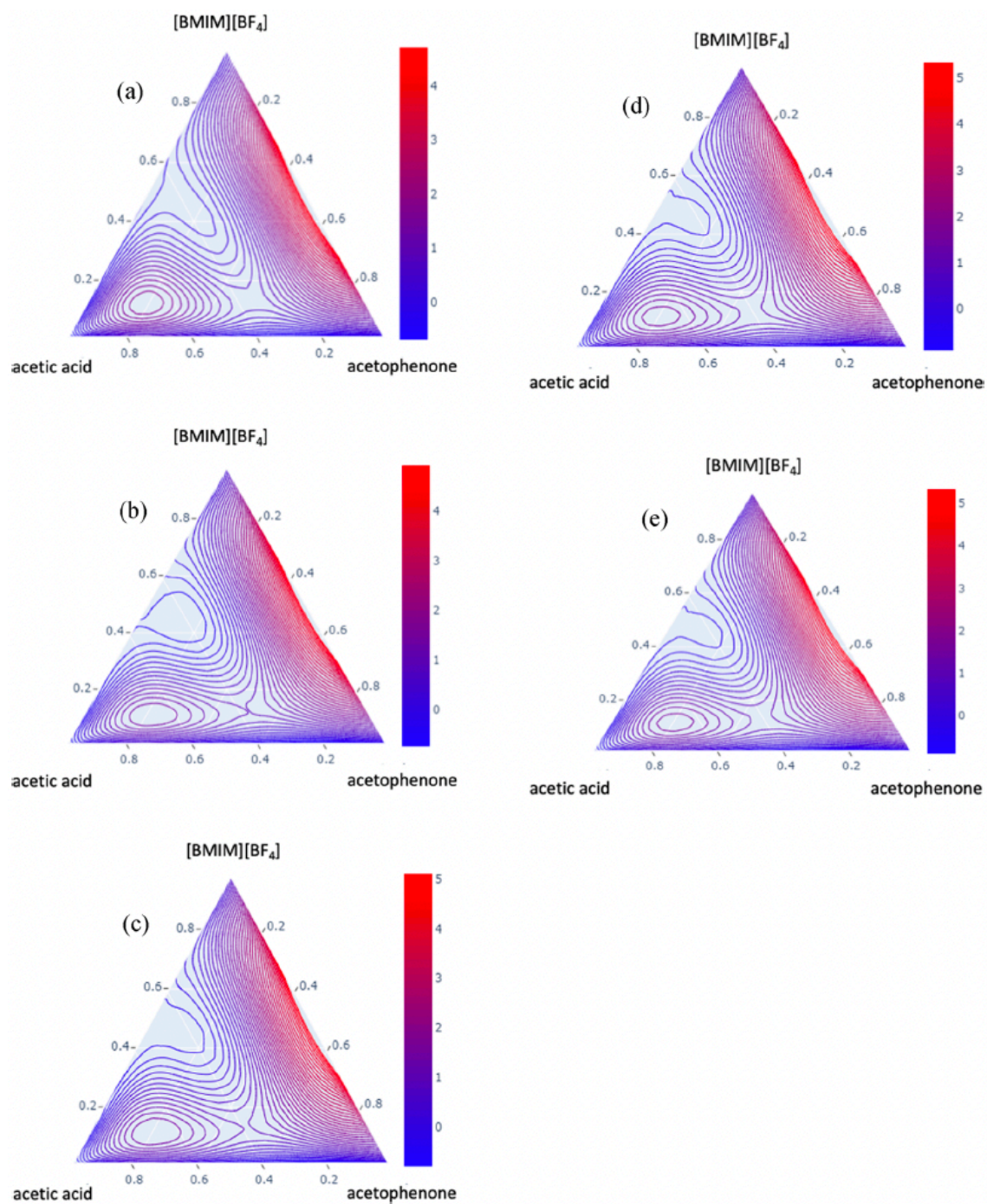


Figure 5.1E: Variations of excess molar volume (V_{m123}^E) with IL mole fraction (x_1) for the ternary mixtures of $\{[\text{BMIM}][\text{BF}_4](x_1) + \text{acetic acid}(x_2) + \text{acetophenone}(x_3)\}$ at (a) 293.15 K, (b) 303.15 K, (c) 313.15 K, (d) 323.15 K and (e) 333.15 K.

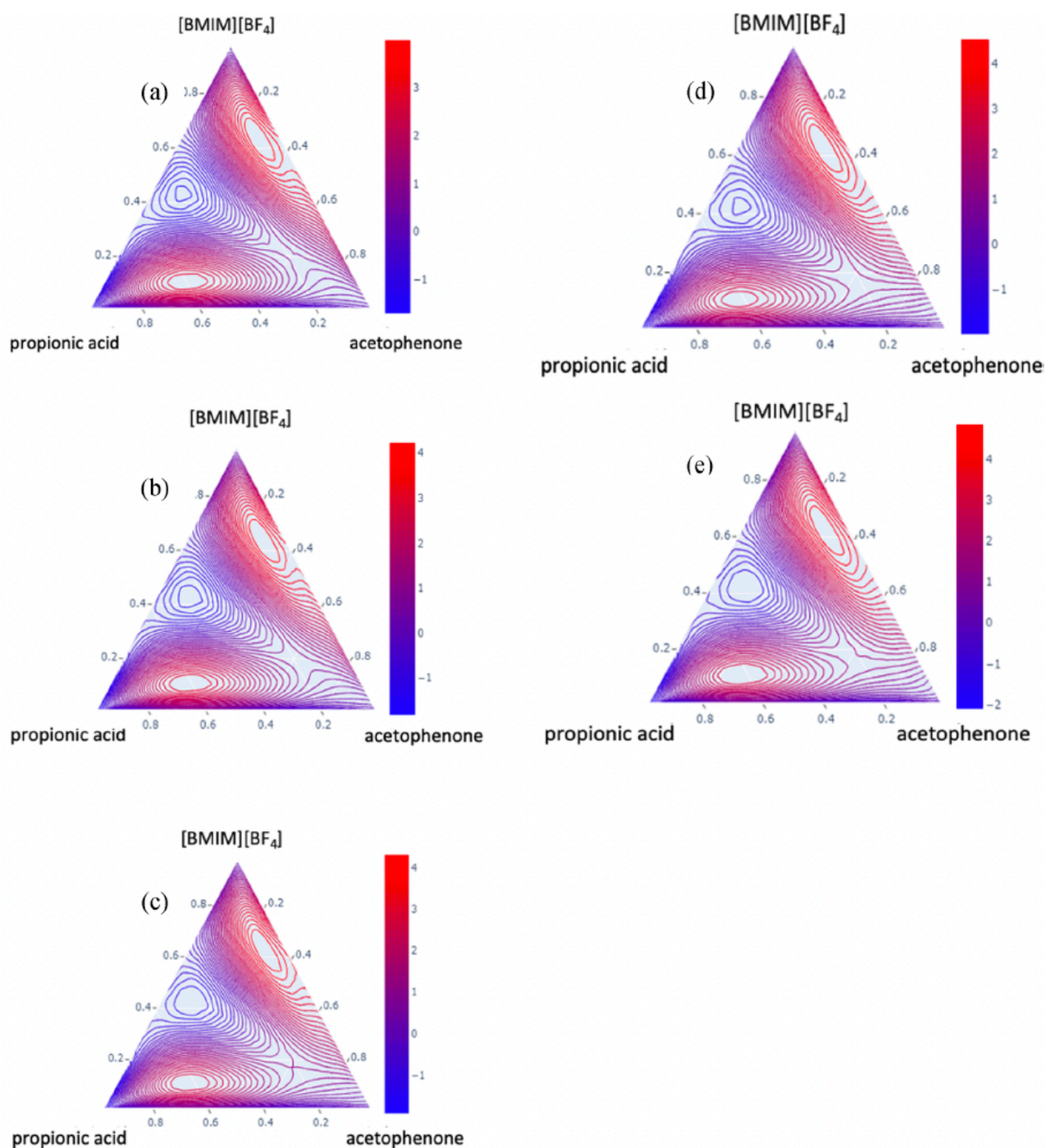


Figure 5.2E: Variations of excess molar volume (V_{m123}^E) with IL mole fraction (x_1) for the ternary mixtures of $\{[\text{BMIM}][\text{BF}_4] (x_1) + \text{propionic acid} (x_2) + \text{acetophenone} (x_3)\}$ at (a) 293.15 K, (b) 303.15 K, (c) 313.15 K, (d) 323.15 K and (e) 333.15 K.

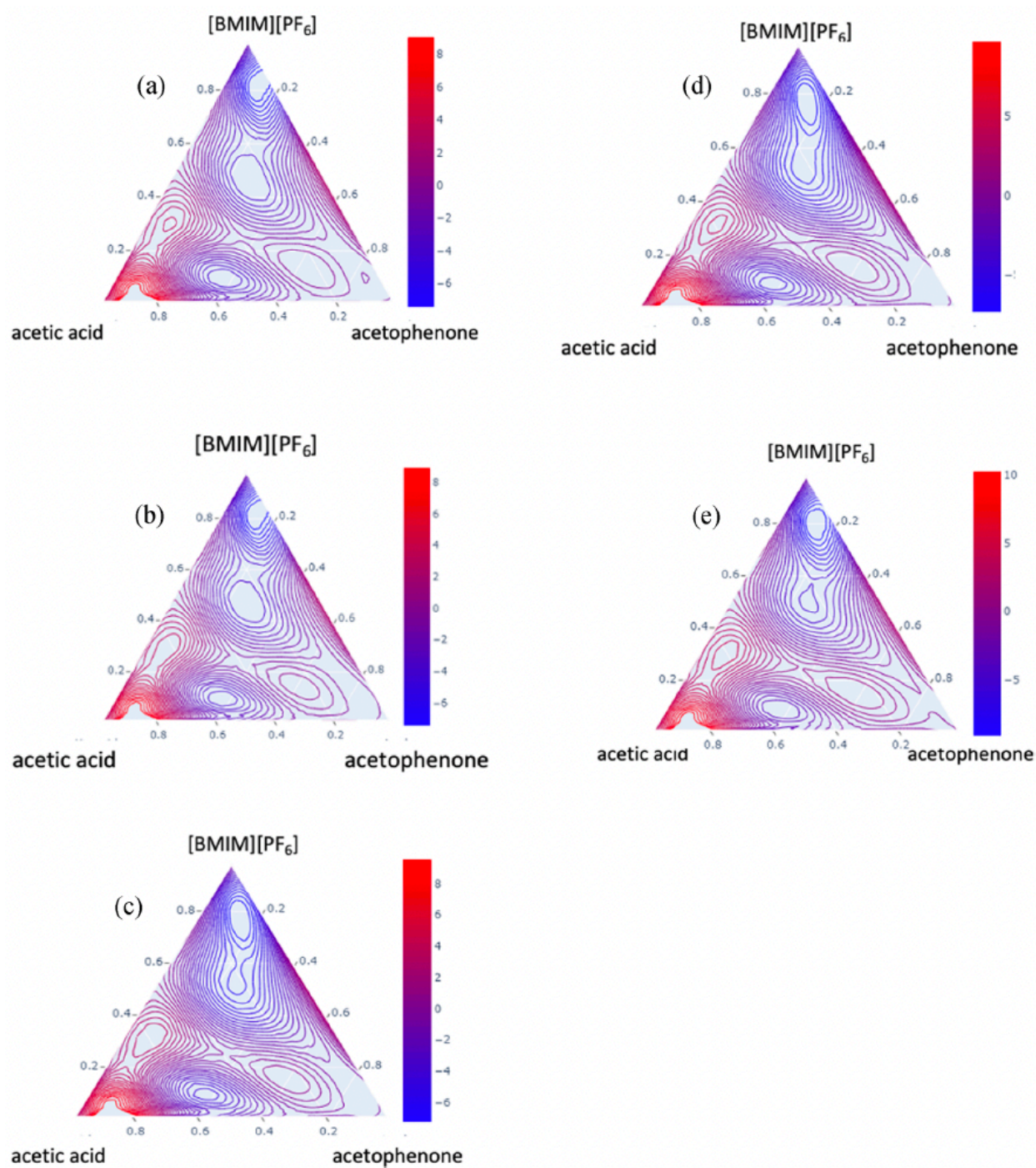


Figure 5.3E: Variations of excess molar volume (V_{m123}^E) with IL mole fraction (x_1) for the ternary mixtures of $\{[\text{BMIM}][\text{PF}_6] (x_1) + \text{acetic acid} (x_2) + \text{acetophenone} (x_3)\}$ at (a) 293.15 K, (b) 303.15 K, (c) 313.15 K, (d) 323.15 K and (e) 333.15 K.

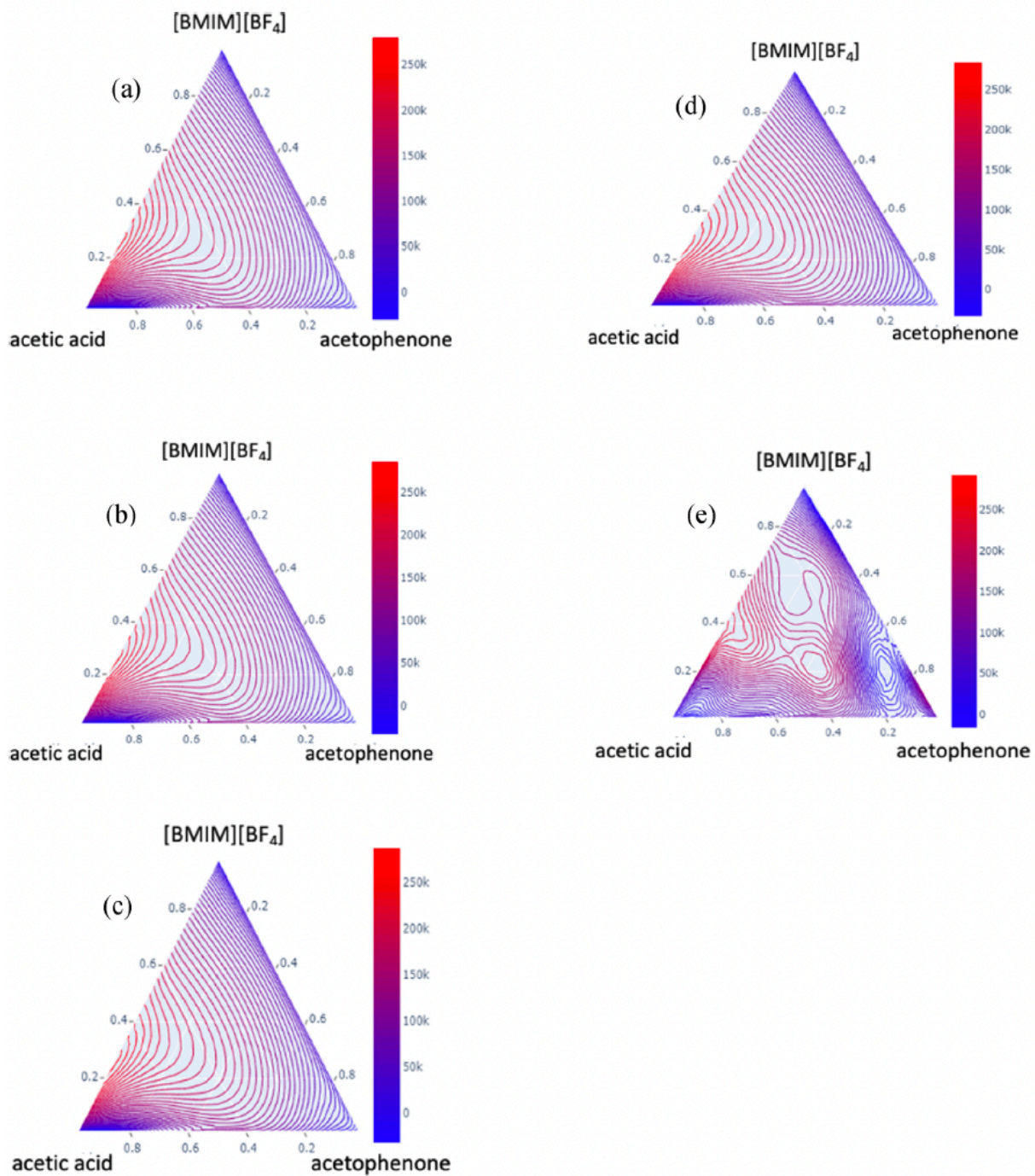


Figure 5.4E: Variations of deviation in isentropic compressibility (Δk_{s123}) with IL mole fraction (x_1) for the ternary mixtures of {[BMIM][BF₄] (x_1) + acetic acid (x_2) + acetophenone (x_3)} at (a) 293.15 K, (b) 303.15 K, (c) 313.15 K, (d) 323.15 K and (e) 333.15 K.

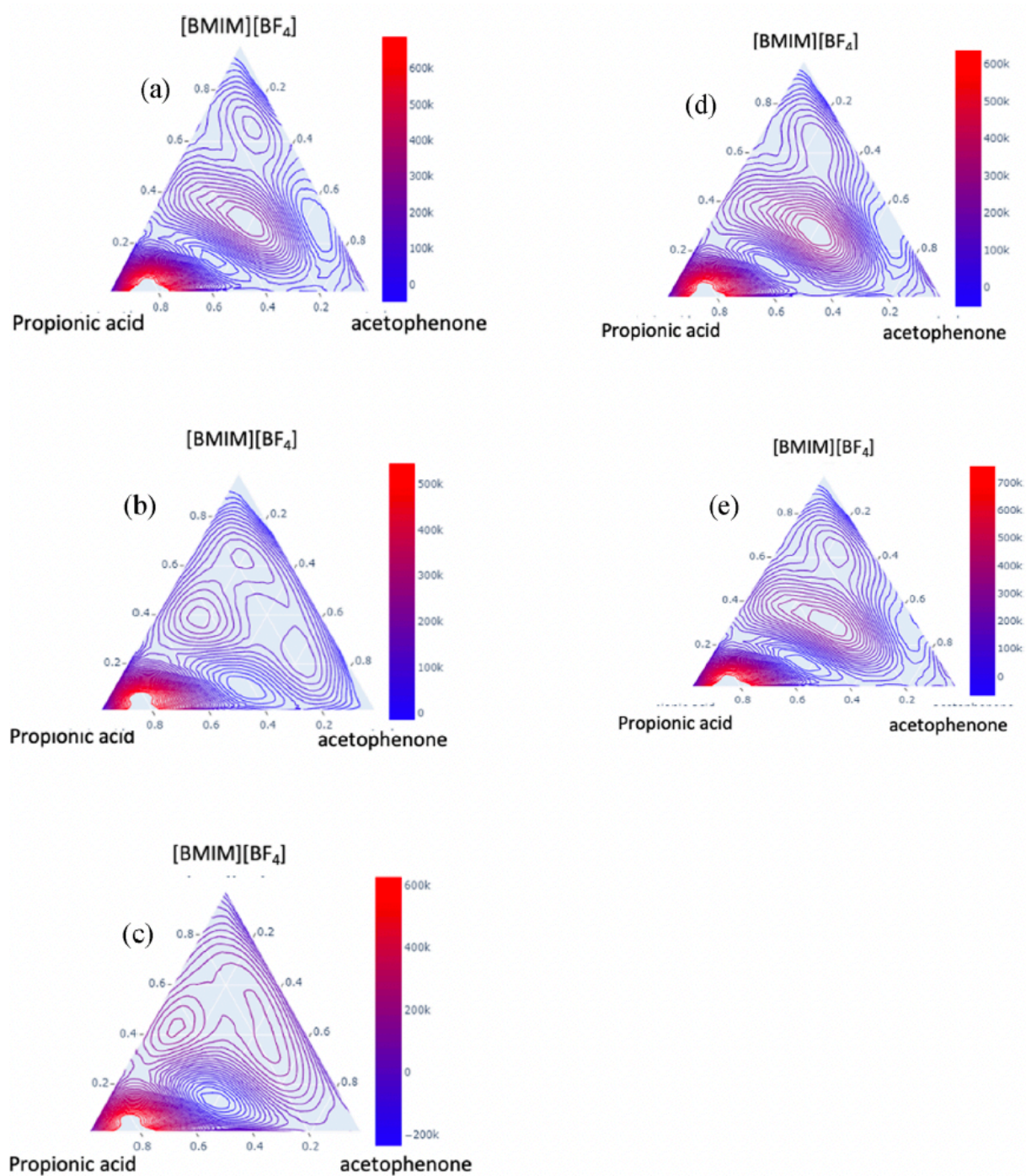


Figure 5.5E: Variations of deviation in isentropic compressibility (Δk_{s123}) with IL mole fraction (x_1) for the ternary mixtures of $\{[\text{BMIM}][\text{BF}_4] (x_1) + \text{propionic acid} (x_2) + \text{acetophenone} (x_3)\}$ at (a) 293.15 K, (b) 303.15 K, (c) 313.15 K, (d) 323.15 K and (e) 333.15 K.

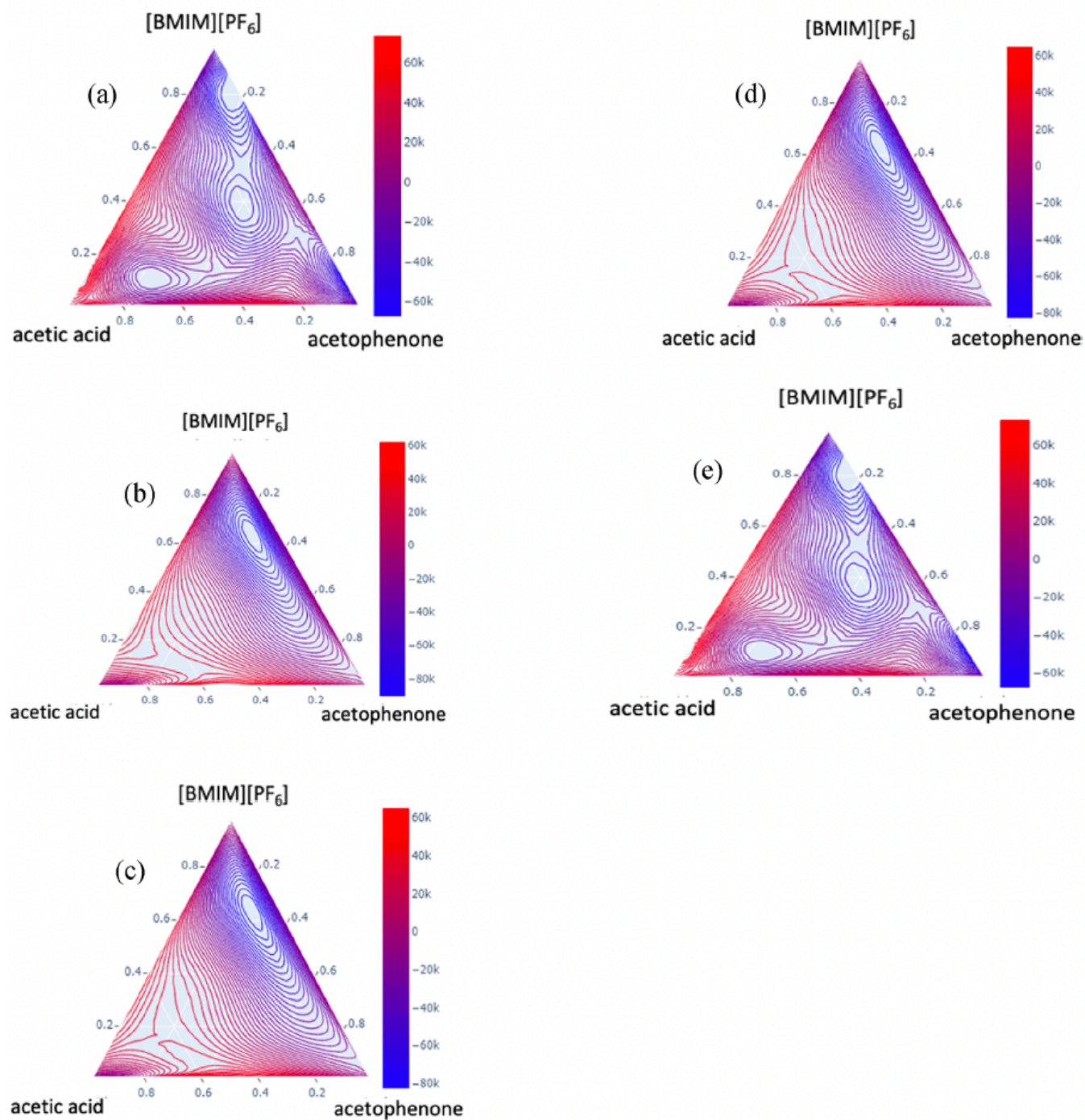


Figure 5.6E: Variations of deviation in isentropic compressibility (Δk_{s123}) with IL mole fraction (x_1) for the ternary mixtures of {[BMIM][PF₆] (x_1) + acetic acid (x_2) + acetophenone (x_3)} at (a) 293.15 K, (b) 303.15 K, (c) 313.15 K, (d) 323.15 K and (e) 333.15 K.

Appendix F: This section presents the title pages of the research articles produced under this study.

1st Publication

Intermolecular Interactions between 1-Ethyl-3-methylimidazolium-Based Ionic Liquids with Carboxylic Acid at Different Temperatures via Thermodynamic and Spectroscopic Studies

Kgomotso Masilo and Indra Bahadur*



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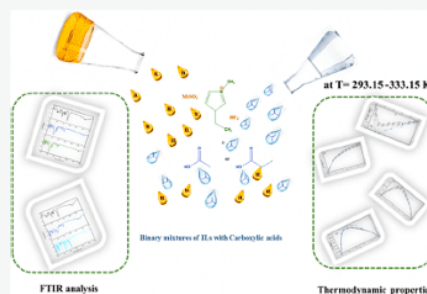
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ABSTRACT: In this work, we studied the intermolecular interactions of binary mixtures of 1-ethyl-3-methylimidazolium-based ionic liquids (ILs) with acetic or propionic acid. The physicochemical behavior of the binary mixtures was investigated by measuring the thermophysical properties, including the density (ρ), sound velocity (u), and refractive index (n_D), over the complete range of the IL mole fraction at $T = 293.15$ – 333.15 K and $p = 0.1$ MPa. The surface tension (γ) of the binary mixtures was also measured at $T = 298.15$ K but not determined under other studied temperatures due to the lack of a temperature controller. The excess molar volumes (V_m^E), excess isentropic compressibilities (k_s^E), excess sound velocity (u^E), intermolecular free length (L_f), deviation in the refractive index (Δn_D), and deviation in the surface tension ($\Delta \gamma$) were determined from experimental results. These parameters were further fitted to the Redlich–Kister polynomial equation. FTIR studies of pure components and binary systems at an equimolar composition were conducted to clarify results from thermodynamic properties and also analyze the intermolecular interactions occurring in the mixture. A survey on available literature data was carried out to compare with our experimental data. The selected ILs allowed us to compare the influence of the anion on the thermophysical and thermodynamic properties the mixtures.



1. INTRODUCTION

The thermophysical and thermodynamic properties of solvent systems are studied for various reasons; one of the most important reasons is that these properties give information about the solute–solute, solute–solvent, and solvent–solvent interactions of mixtures under various conditions. The sign and magnitude are key factors that determine the type of interactions between components^{1,2} of various sizes, shapes, and types of chemical nature. Understanding the thermodynamic parameters is directly useful in design and separation processes in fields of food, pharmaceutical, and chemical industries, which include gas and oil refinery industries for flow assurance and refining of oils.³

Ionic liquids (ILs) have gained interest as a greener replacement for conventional organic solvent with the aim of implementing environmentally friendly chemistry practices. ILs have also gained recognition as neoteric solvents from the scientific community due to their distinctive properties such as an extremely low vapor pressure,⁴ non-volatility, non-flammability,⁵ high thermal stability, and high selectivity and liquid temperature ranges.^{6,7} They are also stable on exposure to air and moisture,⁸ easily recyclable, and highly polar and have an extensive range of miscibility with compounds varying in polarities.^{9,10} These properties can be controlled to adapt to a specific application by structural modifications in which the

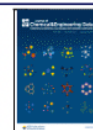
different combinations of the cation and anion are formed.¹¹ The flexibility of IL and experiences gathered thus far give substantial evidence that they can be the core of enhanced engineering, chemical, biological, and separation processes.¹² One of the most studied ILs contains the imidazolium cation with varying heteroatom functionalities. In this study, we have used ILs formed by a 1-ethyl-3-methylimidazolium cation (EMIM⁺) and tetrafluoroborate (BF₄[−]) and methylsulphate (MeSO₄[−]) anions shown in Figure 1.

Carboxylic acids are weak acids comprising two functional groups, a hydroxyl and a carbonyl group, which define their physicochemical behavior. Carboxylic acids are polar and capable of self-associating through hydrogen bonding¹³ as shown in Figure 2. They have remarkable application in the food and pharmaceutical industries. In food production, they are used as an acidulant to preserve food and beverages, flouring agent,¹⁴ and natural pigment for food and nutraceuticals.¹⁵ In pharmaceutical industries, the acids are

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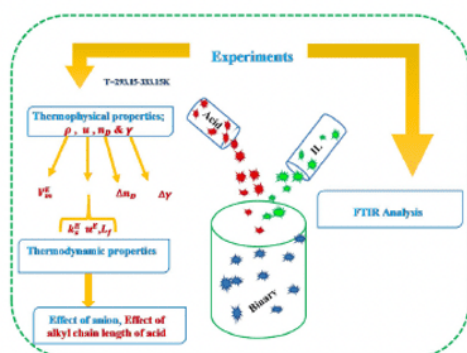
Colloids and Surfaces A: Physicochemical and Engineering Aspects

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Interactions between 1-butyl-3-methylimidazolium cation with various anions and carboxylic acids: Physicochemical and spectroscopic aspects

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GRAPHICAL ABSTRACT



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Excess sound velocity
Intermolecular free length
Refractive index
Surface tension

ABSTRACT

In this work, the intermolecular interactions for binary mixtures of ionic liquids, 1-butyl-3-methylimidazolium tetrafluoroborate, 1-butyl-3-methylimidazolium hexafluorophosphate with acetic and propionic acid were evaluated through the measurement of thermophysical properties, density (ρ), sound velocity (u), refractive index (n_D) and surface tension (γ) at $T = (293.15 - 333.15)$ K and $p = 0.1$ MPa. The experimental results were used to compute the thermodynamic properties of the binary mixtures, which were then fitted to the Redlich–Kister polynomial equation. The FTIR spectra of the pure components and the binary mixtures at an equimolar composition were recorded to confirm results from thermodynamic properties. The variations of the thermodynamic properties with IL mole fraction and temperature and the effect of the IL anion and alkyl length of the carboxylic acid on the thermodynamic properties have been discussed.

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Investigation on the molecular interaction of binary mixtures of acetophenone with carboxylic acids at various temperature: Thermodynamic and spectroscopic aspects

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ABSTRACT

In the present work, the molecular interactions of binary mixtures of acetophenone with carboxylic acids such as acetic and propionic acid were investigated through the measurement of thermophysical properties including, density (ρ), sound velocity (u), refractive index (n_D) and surface tension (γ) at temperature ranges of (293.15–333.15) K and pressure, $p = 0.1$ MPa. The thermodynamic properties of the binary mixtures were calculated from the experimental thermophysical properties as a function of acetophenone mole fraction, which were in turn used to give an understanding about the molecular interactions existing in the binary mixtures. The thermodynamic properties were correlated with the Redlich-Kister polynomial. The FT-IR spectrums of pure acetophenone and carboxylic acids and their binary mixtures at an equimolar composition were measured. The variations of the thermodynamic properties with acetophenone mole fraction and temperature have been discussed.

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1. Introduction

Thermodynamic and transport studies of liquid mixtures provide information about the kind of intermolecular interactions that exist between various mixing components which are then utilized in the development of molecular models defining the thermodynamic behaviour of mixtures [1–4]. Intermolecular interactions play a vital role in liquid mixtures in that they influence the arrangement, orientation, and conformations of the molecules in solutions. Generally, in chemical design and chemical process industries, material is treated in fluid form, and as a result, knowledge of the thermodynamic and transport properties are required. These properties are further important in understanding engineering applications regarding heat transfer, mass transfer, and fluid flow.

In the present work we have studied thermodynamic properties of liquid mixtures including acetophenone (as a common compound) and different carboxylic acids. Acetophenone is a methyl ketone which is capable of acting as intermediate in the synthesis of many other compounds such as alkoxides, hydroxy alkynes, phosphine oxides and cyanohydrins [5–7]. The major uses of ace-

tophenone are as a catalyst for the polymerization of olefins; in organic synthesis and as a specialty solvent for plastics and resins. It is also used in the manufacture of rubber, dyestuffs, corrosion inhibitors, pharmaceuticals and agrochemicals. In addition, it has been widely used as an ingredient that creates fragrances and flavour producing smells like jasmine [5], almond, cherry, orange-blossom or other fruits [8] in non-alcoholic beverages, soaps, detergents, cosmetics and perfumes [9–11]. Acetophenone occurs naturally in several foodstuff such as essential oil of cloves, filbert nuts, honey, nectarines, sweet corn or can be obtained as a by-product in the Hock phenol synthesis, and it further purified from the high-boiling residue by distillation. Considering acetophenone's natural presence in certain foods, it would be ideal to categorize it as a nontoxic compound to some living organisms. Carboxylic acids on the other hand occur widely in nature and have been applied in many industrial processes. Acetic acid has been used as raw material in the manufacture of polyester resins, biodegradable plastics, cellulose, and esters soap, while propionic acid can be utilized as in the food and beverages industry, where it serves as acidulant, food preservative as well as flavouring agents [12–17]. The structure of carboxylic acids contains a hydroxyl ($-\text{OH}$) and carbonyl group ($\text{C}=\text{O}$). The $-\text{OH}$ group is bonded to a ($\text{C}=\text{O}$) group making up a carboxyl group ($-\text{COOH}$), which defines their physicochemical behaviour. The favourable properties and

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Measurement and Modeling of Thermodynamic Properties for Ternary Mixtures Containing 1-Butyl-3-methylimidazolium-Based Ionic Liquids with Acetophenone and Acetic or Propionic Acid

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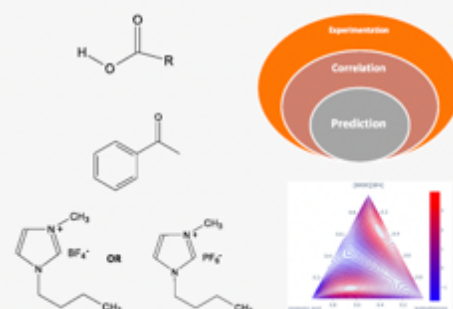
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ABSTRACT: In the present work, we obtained density (ρ_{123}), speed of sound (u_{123}), excess molar volume (V_{m123}^E), and deviation in isentropic compressibility (Δk_{123}) for ternary mixtures of {[BMIM][BF₄] (x_1) + acetic acid (x_2) + acetophenone (x_3)} (mixture 1), {[BMIM][BF₄] (x_1) + propionic acid (x_2) + acetophenone (x_3)} (mixture 2), and {[BMIM][PF₆] (x_1) + acetic acid (x_2) + acetophenone (x_3)} (mixture 3) at temperatures ranging between 293.15 and 333.15 K and at a pressure of 0.1 MPa. V_{m123}^E and Δk_{123} values of the ternary systems were modeled with 9 predictive (no estimated parameter) and 7 correlative terms, leading to a total of 63 evaluated models. Using a standardized deviation (σ), it was possible to estimate the optimal number of parameters in the correlation, which varied from 1 to 11. The average σ for V_{m123}^E mixture 3 was about twice the values for mixtures 1 and 2, even using more parameters for the last mixtures. For Δk_{123} , σ is in the same range for the three mixtures, even though only one parameter is used in each temperature for mixture 1 and up to 11 are used in mixtures 2 and 3. These results indicate that nonideality qualitatively is in the order mixture 3 > mixture 2 > mixture 1.



1. INTRODUCTION

Ionic liquids (ILs) are room-temperature molten salts that are made up of a combination of large organic cations and typically smaller organic/inorganic anions. Due to their low vapor pressure,¹ nonflammability,² high liquid temperature ranges, high thermal and electrochemical stability,³ tunability,⁴ ability to extract and dissolve many inorganic, organic, and polymeric compounds,⁵ high ionic conductivity, and reusability, ILs have been widely applied in various industrial processes.^{6–9} The two main drawbacks of ILs are that they are very costly and more viscous when compared to conventional organic solvents, which may hinder their use in other applications. To expand their uses and to better tune their chemical properties, mixtures of ILs with molecular organic solvents appear to be a promising solution. Mixing ILs and molecular organic solvents is one measure to minimize the expenses associated with ILs in order to reduce their viscosity without a major effect to their advantages as green solvents and save time preparing new ILs with the same desired properties. Mixtures of ILs and molecular organic solvents have gained the interest of researchers because the resulting liquid mixtures are advantageous over both ILs and molecular organic solvents considered individually.

The thermophysical and thermodynamic properties of liquid mixtures are effectively used in interpreting the nature of intermolecular interactions (i.e., solute–solute, solute–solvent, solvent–solvent interactions), molecular arrangements, geo-

metrical effects, and phase behavior of fluids between component molecules. The thermophysical and thermodynamic properties of IL ternary mixtures together with their dependency on temperature and concentration are important for use in chemical engineering design in applications that included surface facilities,¹⁰ pipeline systems,¹¹ heat transfer and mass transfer operations,^{12,13} fluid flow,¹⁴ and chemical separation/purification processes in the pharmaceutical¹⁵ industry. Also, the thermodynamic properties of IL ternary mixtures are of theoretical interest for the development of new correlation or prediction models, which are directly applied in the design of technological processes.^{16,17} Even when small quantities of a low molar mass molecular organic solvent are added to an IL, their thermodynamic properties can vary largely.

Among a variety of ILs, the imidazolium-based ILs are comparatively more versatile. The hydrogen atoms attached to an imidazolium ring can be substituted with another atom or compound to produce desired properties. The imidazolium-based ILs show promising applications in various fields and are

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