Thermo-physical Properties and Activity Coefficients at Infinite Dilution for Ionic Liquid Systems at Several Temperatures

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PREFACE

The work described in this thesis was performed by the author under the supervision of Professor G. G. Redhi and Professor D. Ramjugernath at Durban University of Technology, Durban, South Africa, from 2013-2017. The study presents original work by the author and has not been submitted in any form to another tertiary institution or university. Where use is made of the work of others, it has been clearly stated in the text.

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DEDICATION

To the late **Mangla Prasad**, my father in law. I attribute all my success in life to the moral, intellectual and physical education I received from him.

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APPENDIX 1

List of publications from this work

1. **S. Singh**, I. Bahadur, G. G. Redhi, E. E. Ebenso, D. Ramjugernath **(2014)** “Density and speed of sound of 1-ethyl-3-methylimidazolium ethyl sulphate with acetic or propionic acid at different temperatures” **Journal of Molecular Liquids, 199: 518-523.**
2. **S. Singh**, I. Bahadur, G. G. Redhi, D. Ramjugernath, E. E. Ebenso, **(2014)** “Density and speed of sound measurements of imidazolium-based ionic liquids with acetonitrile at various temperatures” **Journal of Molecular Liquids, 200: 160-167.**
3. I. Bahadur, T. M. Letcher, **S. Singh**, P. Venkatesu, G. Redhi, D. Ramjugernath **(2015)** “Excess molar volumes of binary mixtures (an ionic liquid + water): a review” **Journal of Chemical Thermodynamics, 82: 34-46.**
4. **S. Singh**, I. Bahadur, G. G. Redhi, Eno E. Ebenso, D. Ramjugernath **(2015)** “Influence of alkyl group and temperature on thermophysical properties of carboxylic acid in ionic liquid mixtures” **Journal of Chemical Thermodynamics, 89: 104-11.**
5. **S. Singh**, I. Bahadur, P. Naidoo, G. Redhi, D. Ramjugernath (**2016**) “Application of 1-butyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide ionic liquid for the different types of separations problem: Activity coefficients at infinite dilution measurements using gas-liquid chromatography technique” **Journal of Molecular Liquids, 220:33-40.**
6. **S. Singh**, I. Bahadur, G. G. Redhi, D. Ramjugernath, E. E. Ebenso (**2016**) “Influence of alkyl group on interactions between carboxylic acid and acetonitrile at different temperatures” **Journal of Chemical Thermodynamics, 98:102-110.**
7. **S Singh**, I. Bahadur, G. G. Redhi, S Karlapudi, D Ramjugernath, T. Hofman, E. E. Ebenso **(2017)** Cibulka correlation for ternary excess/deviation properties of {[C_2MIM][$EtSO_4$] (x_1) + acetic or propionic acid (x_2) + acetonitrile (x_3)}systems at different temperatures.” **Journal of Chemical Thermodynamics, 107: 153-162.**
8. **S Singh**, I. Bahadur, G. G. Redhi, D. Ramjugernath, T. Hofman, **(2017)** Ternary excess/deviation properties of {[BMIM][SCN] (x_1) + acetic or propionic acid (x_2) + acetonitrile (x_3) }systems at different temperatures.” **Journal of Chemical Thermodynamics, under review.**

ABSTRACT

The thermodynamic properties of mixtures involving ionic liquids (ILs) with organic acid (acetic acid or propanoic acid) or acetonitrile at different temperatures were determined. The ILs used were imidazolium-based: 1-ethyl-3-methylimidazolium ethyl sulphate $[EMIM]^+[EtSO_4]^-$, 1-butyl-3-methylimidazolium thiocyanate $[BMIM]^+[SCN]^-$ and 1-butyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide ($[BMIM]^+[Tf_2N]^-$.

The ternary excess molar volume (V_{123}^E), isentropic compressibility (k_s) and deviation in isentropic compressibility (Δk_{s123}) were determined for four ternary liquid mixtures of {$[EMIM]^+[EtSO_4]^-$ or $[BMIM]^+[SCN]^-$ + acetic or propionic acid + acetonitrile} at different temperatures (293.15, 298.15, 303.15, 308.15 and 313.15) K and at a pressure of 0.1 MPa with aid of the experimental density (ρ), speed of sound (u) data. The calculated data were correlated by using the Cibulka equation with the help of Redlich–Kister parameters obtained from fitting the Redlich–Kister equation for the corresponding binary systems.

Furthermore, the density and speed of sound were also measured for eight corresponding binary systems at the same experimental conditions. The binary excess molar volume, isentropic compressibility and deviation in isentropic compressibility were also calculated for measured systems and fitted to the Redlich–Kister equation to obtain the Redlich–Kister parameters as well as to check the accuracy of measured data which were used to correlated experimental data using Cibulka equation. These results were discussed, in terms of how the sign and magnitude of thermodynamic functions were influenced by the addition of a third component to liquid systems. Also, the possible molecular and pair-wise interactions between component molecules and the effect of temperature on the thermophysical and thermodynamic properties were predicted.

In addition, the work focussed on application of ($[BMIM]^+[Tf_2N]^-$) ionic liquid for the separations of (alkane/aromatic), (alkane/alk-1-ene), (cycloalkane/aromatic) and (water/alkan-1-ol) using gas-liquid chromatography (GLC) technique. The activity coefficients at infinite dilution, γ_{13}^{∞}, for 31 organic solutes (alkanes, cycloalkanes, alkenes, alkynes, aromatics, alkanol and ketones) and water in ionic liquid were measured at temperatures of (323.15, 333.15, 343.15, 353.15 and 363.15) K. Stationary phase loadings of (42.83 and 68.66) % by mass were used to ensure repeatability of measurements. Partial molar excess enthalpies at infinite dilution, $\Delta H_1^{E,\infty}$, were also determined. The selectivities, S_{ij}^{∞}, and capacities, k_j^{∞}, were determined for the above separations. The separating ability of the investigated ionic liquid was compared with previously investigated ionic liquids and industrial solvents such as sulfolane, *n*-methyl-2-pyrrolidine (NMP) and *n*-formylmorpholine (NFM). The results obtained suggested that in general, the $[BMIM]^+[Tf_2N]^-$ had outperformed the conventional solvents such as sulfolane, NMP and NFM in terms of selectivity, while the $[BMIM][Tf_2N]$ had in general, performed better overall when the performance index was used for comparison.

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List of Symbols

ρ	density.
$V_{\mathrm{m}}^{\mathrm{E}}$, $V_{i,\mathrm{j}}^{\mathrm{E}}$	binary excess molar volume.
$V_{\mathrm{min}}^{\mathrm{E}}$	minimum binary excess molar volume.
V_{123}^{E}	ternary excess molar volume.
$V_{123\ \mathrm{min}}^{\mathrm{E}}$	minimum ternary excess molar volume.
z	mole fractions ratio between the 3rd and 1^{s} component of the ternary system.
(b_0, b_1, b_2)	Cibulka parameters.
T	temperature.
K	Kelvin.
x_1	mole fraction of the 1st component.
x_2	mole fraction of the 2nd component.
x_3	mole fraction of the 3rd component.
σ	standard deviation of ternary excess molar volume.
σ_{v}	standard deviation of apparent molar volume.
σ_{κ}	standard deviation of apparent molar isentropic compressibility.
M_1	molar mass of ionic liquid.
M_2	molar mass of alcohol.
M_3	molar mass of alkyl acetate or nitromethane.
A_{i}	polynomial coefficient.
N	polynomial degree.
n	number of experimental point.
k	number of coefficients used in the Redlich –Kister correlation.

V_ϕ	apparent molar volume.
V_ϕ^0	apparent molar volume at infinite dilution.
E_ϕ^0	infinite dilution apparent molar expansibility.
S_v	empirical parameter for apparent molar volume.
B_v	empirical parameter for apparent molar volume .
u	speed of sound.
κ_s	isentropic compressibility of mixture.
$\kappa_{\mathrm{s}0}$	isentropic compressibility of pure solvent.
κ_ϕ	apparent molar isentropic compressibility.
κ_ϕ^0	apparent molar isentropic compressibility at infinite dilution.
S_k	empirical parameter for apparent molar isentropic compressibility.
B_k	empirical parameter for apparent molar isentropic compressibility.
m	molality.

Ionic Liquid Abbreviations

$[BMIM]^+[BF_4]^-$	1-butyl-3-methylimidazolium tetrafluoroborate.
$[BMIM]^+[Br]^-$	1-butyl-3-methylimidazolium bromide.
$[BMIM]^+[CF_3SO_3]^-$	1-butyl-3-methylimidazolium trifluoromethanesulfonate.
$[BMIM]^+[CH_3(OCH_2CH_2)_2OSO_3]^-$	1-butyl-3-methyl-imidazolium diethyleneglycol monomethylether sulphate.
$[BMIM]^+[Cl]^-$	1-butyl-3-methylimidazolium chloride.
$[BMIM]^+[MeSO_4]^-$	1-butyl-3-methylimidazolium methyl sulfate.
$[BMIM]^+[OcSO_4]^-$	1-butyl-3-methylimidazolium octyl sulphate.
$[BMIM]^+[PF_6]^-$	1-butyl-3-methylimidazolium hexafluorophosphate.
$[BMIM]^+[Tf_2N]^-$	1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide.
$[BDMIM]^+[BF_4]^-$	1-Butyl-2, 3-dimethyl tetrafluoroborate.
$[BDMIM]^+[PF_6]^-$	1-Butyl-2, 3-dimethyl hexafluorophosphate.
$[BMPy]^+[BF_4]^-$	4-Butyl-4-methylpyridinium tetrafluoroborate.
$[EMIM]^+[Br]^-$	1-ethyl-3-methylimidazolium bromide.
$[EMIM]^+[BETI]^-$	1-ethyl-3-methylimidazolium bis(perfluoroethylsulphonyl)imide.
$[EMI]^+[Cl]^-$	1-ethyl-3-methylimidazolium chloride.
$[EMIM]^+[CH_3(OCH_2CH_2)_2OSO_3]^-$	1-ethyl-3-methylimidazolium diethyleneglycol monomethylether sulphate.
$[EMIM]^+[EtSO_4]^-$	1-ethyl-3-methylimidazolium ethylsulfate.
$[EMMIM]^+[Tf_2N]^-$	2, 3-Dimethyl-1-ethylimidazolium bis(trifluoromethylsulfonyl)imide.

$[HMIM]^+[Cl]^-$	1-hexyl-3-methylimidazolium chloride.
$[HMIM]^+[PF_6]^-$	1-hexyl-3-methylimidazolium hexafluorophosphate.
$[HMIM]^+[Tf_2N]^-$	1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide.
$[MMIM]^+[MeSO_4]^-$	1,3-dimethylimidazolium methyl sulphate.
$[MOA]^+[Tf_2N]^-$	methyl trioctylammonium bis(trifluoromethylsulfonyl)imide.
$[MOIM]^+[BF_4]^-$	1-methyl-3-octylimidazolium tetrafluoroborate.
$[MOIM]^+[Cl]^-$	1- methyl-3-octylimidazolium chloride.
$[MOIM]^+[CH_3(OCH_2CH_2)_2OSO_3]^-$	1-methyl-3-octyl-imidazolium diethyleneglycol monomethylether sulphate.
$[MOIM]^+[PF_6]^-$	1-methyl-3-octylimidazolium hexafluorophosphate.
$[MOIM]^+[Tf_2N]^-$	1- methyl-3-octylimidazolium bis(trifluoromethylsulfonyl)imide.
$[PMMIM]^+[Tf_2N]^-$	2, 3-Dimethyl-1-propylimidazolium bis(trifluoromethylsulfonyl)imide.
$[PMIM]^+[BF_4]^-$	1-methyl-3-pentylimidazolium tetrafluoroborate.
$[RMIM]^+[Br]^-$	1-alkyl-3-methylimidazolium bromide.

CHAPTER 1

INTRODUCTION

The need for accurate thermodynamic data is becoming increasingly important for industrial applications. However, the knowledge of thermophysical data of binary or ternary liquid mixtures of ILs and other organic solvents is essential for development of specific chemical processes (Dupont *et al.,* 2002; Anastas and Warner 1998; Cann and Connelly 2000). Furthermore, the thermophysical/thermodynamic properties are a key parameter to predict the intermolecular interactions between component molecules in liquid mixtures. Moreover, many principles of separation and transport processes hinge on the basis of such measurements (Narasigadu, 2006), most commonly used on processes such as distillation and solvent extraction (also called liquid-liquid extraction or extraction) (Henley *et al.*, 2011).

1.1 Ionic Liquids

1.1.1 Brief history of ionic liquid

Volatile organic compounds (VOCs) have traditionally been used in industry for such separations as extraction and in enhanced distillation. These chemicals however are hazardous to the environment and to human health due to the vapours released from related processes, and accounts for nearly 67% of all industrial emissions (Ram, 2013). Thus there is much imperative to seek safer and environmentally friendly alternatives. In this context, an ideal replacement would be characterized by very low volatility, high chemical and physical stability and high potential for recycling. Ionic liquids are considered as the potential greener replacement for commonly used volatile organic compounds. Ionic liquids (ILs) as “green” solvents have received a great deal of attention in recent times, due to their non-volatility and potential in the chemical industry as a whole. It is also nearly impossible to synthesise every possible kind of ionic liquid, and measure its properties. Ionic liquids are defined as liquids consisting entirely or almost entirely of ions, including molten or fused salts (Freemantle, 2010). More recently however, have they been generalized to cases where the melting points fail to exceed 100^{o}C, with higher melting ionic compounds termed as molten salts (Keskin *et al.,* 2007, Wasserscheid and Keim, 2000).

Ionic liquids have been documented since the late nineteenth century, during Friedel-Crafts reactions, when it was noted, but not investigated further (Freemantle, 2010), albeit the first purposeful synthesis of an ionic liquid occurred in 1914 (Wasserscheid and Keim, 2000) in which the salt ethylammonium nitrate $[EtNH_3][NO_3]$ appeared to be liquid at room temperature. Despite room temperature ILs (RTILs) being around for almost a century, interest has only been considerable within the last three decades. Freemantle (2010) and Tumba (2010) both summarise the list of significant events in the chemicals' history, and the reader is referred to their texts for further enlightenment.

1.1.2 Chemical composition and the structure of ionic liquids

Like most ionic compounds, an ionic liquid is typically composed of a cation electrostatically bonded to an anion. However, while most solid salts are composed entirely of inorganic elements, ionic liquids usually consist of nitrogen containing hetero-cyclic organic cations and inorganic or organic anions (Swapnil, 2012, Revelli *et al.*, 2009). The ionic structure and possibilities for the anion and cation combination also mean that ILs are incredibly tunable (Tumba, 2010) and would allow for more than 1014 anion and cation combinations (Chiappe and Pieraccini, 2003). Thus the name "designer solvent" has also been coined. Figure 1.2.1 includes some of the common cations and anions that have been studied.

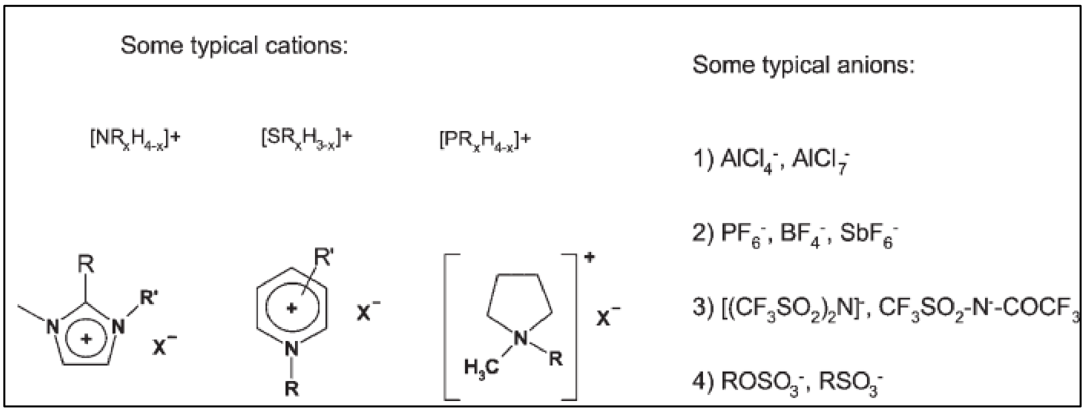


Figure 1.1.1 Typical cations and anions for ionic liquids (Chiappe and Pieraccini, 2003)

1.1.3 Common properties of ionic liquids

ILs are most well known for their wide liquid range and high thermal stability. Carmichael and Seddon (2000) state a range starting as low as -96^{o}C and terminating at about 400^{o}C. In contrast, typical salts such as sodium chloride (NaCl) have to be heated to temperatures in excess of 800 ^{o}C before melting occurs. The next prominent attribute is the negligible vapour pressures of ionic liquids, which has for the most part been the reason behind the name "green" chemical, and has exhaustively been mentioned by almost all authors dealing with ionic liquids. While this may be so at ambient temperatures, at higher temperatures of 100-120 ^{o}C the vapour pressure is still low, but detectable. The ionic liquid $[EMIM]^+[EtSO_4]^-$, for example, experiences a vapour pressure of 2.0 Pa at 120^{o}C. The reader is referred to appendix A for further enlightenment. The newly green synthesized ILs are used in fundamental knowledge of many disciplines of science and industries due to their unwonted properties *viz*. chemical stability, high ionic mobility, nonflammability, low vapour pressure, better solubility in various solvents and more potential for recycling (Domanska *et al.*, 2015, Welton, 1999, Kumar and Venkatesu, 2012, Kurnia *et al.*, 2014, Sendowski *et al.*, 2010, Pernak *et al.*, 2011, Keskin *et al.*, 2007, Zhao and Malhotra, 2002, Khupse and Kumar, 2010, Wlazło and Marciniak, 2012 & Aschenbrenner *et al.*, 2009)

Other common properties shared by most ILs are their high solvating power (Khupse and Kumar, 2010), high thermal and electrochemical stability (Wasserscheid and Keim, 2000), higher viscosity (Tumba, 2010), and while not a property, recyclability is also key characteristic (Galan *et al.*, 2011). Generally ILs have densities higher than that of molecular solvents. The viscosities are in many cases several hundreds of times higher; but are also highly dependent on temperature.

As previously stated, ILs are entirely tunable. Solvents can be created with specialised properties simply by varying the anion and cation combination. Unfortunately, a great deal of properties have yet to be quantified, as ILs is expanding extentively expecially with imidazolium cations (Chiappe and Pieraccini, 2003)

1.1.4 Relationship between structure and properties

Room-temperature ionic liquids (RTILs) have recently shown an elevated interest from both industrial and academic communities due to their distinct properties such as low volatility, large liquidus range, and good electrical conductivity. Even though the first RTILs was discovered in 1914, the huge interest in their application emerged rapidly in 1980's and since then their rapid significant growing interest have not yet been exhausted. Their unique character to possess enormous potentially interesting properties, both physical and chemical, make them of fundamental significance to researchers and have already attracted great attention as a media of green chemistry.

The asymmetric structures result in reduced lattice energies which allow free movement of ions in the liquid phase, while the high coulombic interactions account for the higher viscosities and low vapour pressures encountered. An IL's anion charge distribution, hydrogen bonding ability, dispersive interactions and polarity are some of the main factors which influence its physical properties (Revelli *et al.*, 2009).

Of particular interest to chemical engineers and the chemical process industry is the solvating power of ILs. ILs have the ability to selectively dissolve a wide range of chemicals; from fats and proteins, to plastics and even DNA (Renner, 2001).

1.1.5 The solvating ability of ionic liquids

The polarity of a liquid has been most commonly used to determine its solvating ability, and in the case of ionic liquids, it is governed by the ionic combination. Freemantle (2010) notes that as the coordinating ability of the anion is lowered, the hydrophobicity increases, for example, $[BMIM]^+[PF_6]^-$ is only about 1.88 g/100mL soluble in water at room temperature while $[BMIM]^+[BF_4]^-$ is completely miscible. It has been described that the solubility of tosylate ILs in oct-1-ene increases when the polarity of the cation is decreased (e.g. by increasing the chain length of any alkyl substituents) (Wasserscheid and Welton, 2008).Wassercheid and Keim (2000) have observed links between the dieletric constant of a compound and its ability to be dissolved by an ionic liquid.

1.1.6 Limitations of ionic liquids

There is a lack of information and data:

- A large proportion of all investigations on ionic liquids have focussed on, *n*-alkylpyridinium, *n*-alkylthiazolium, *n*-alkylimidazolium, tetraalkylammonium, and *n,n*-dialkylpyrazolium cations (Shamsuri and Abdullah, 2010).
- The description of ILs as designer solvents will only be realised once it is known what exactly to design and how flexible the different combinations are (Crowhurst et al., 2003).

Safety and toxicology has not been dealt with in sufficient detail:

- Toxilogical information on IL's is extremely limited.
- Most of the ILs that have been investigated are water soluble and can contaminate marine environments.
- Many halogen containing anions (e.g. $[Tf_2N]^-$, $[PF_6]^-$, $[CF_3SO_3]^-$, $[BF_4]^-$ or $[AlCl_4]^-$) have a weak hydrolysis stability (Swapnil, 2012), and could release toxic hydrogen halides (HF or HCl) into aquatic systems.

Availability is a problem and ionic liquids are still expensive:

- The biggest barrier to implementing ionic liquids is the extremely high cost (Shamsuri and Abdullah, 2010, Aschenbrenner *et al.*, 2009).
- Most ILs are available in low quantities not suitable for commercial applications.
- Impurities (especially moisture) have a large influence on the physical properties.
- It is not easy to synthesise and because of its low volatility, it is also difficult to purify (Rogers *et al.*, 2003).

1.1.7 Applications of ionic liquids

The focus of ILs has been, until recently, linked to research (Ram, 2013). Keskin *et al.* (2007) list some of the possible applications of ILs:

- Electrolyte in batteries
- Lubricants
- Plasticisers
- Solvents
- Catalysis in synthesis
- Matrices for mass spectroscopy
- Solvents to manufacture nano-materials
- Extraction
- Gas absorption agents

Freemantle (2010) reviewed some of the commercial applications of ILs:

- As of 1998, the DIFASOL process had commercially implemented ILs for the production of iso-octenes from butenes.
- By 2002 BASF had used ionic liquids for its “Biphasic Acid Scavenging” process, termed the BASIL process in Germany.
- In 2005, Air Products (situated in the USA) made public the use of ILs in the storage and transportation of phosphine and boron trifluoride.
- The Linde Company has experimented with ionic liquid-compressors for storage of hydrogen gas for use in fuel cells.
- Friedel-Crafts applications have been proposed to use chlorinated ionic liquids on a 10-ton scale - the largest proposed thus far (Rogers and Seddon, 2003).
- Particular separations of water-ethanol, thiophene from aliphatic hydrocarbons and methanol from aliphatic hydrocarbons have used ionic liquids on a small scale through extractive distillation (Revelli *et al.*, 2009).

However, the imidazolium based ILs and some organic liquids chosen in the present investigation have various industrial applications, Imidazolium based ILs especially have been meritoriously used in chemical synthesis, electrochemical technology, extraction process, bio-catalysis and separation science (Keshapolla *et al.*, 2014, Yan *et al.*, 2012, Swatloski *et al.*, 2002, Sun *et al.*, 2014, Dupont *et al.*, 2002). In addition, these ILs are vastly used in the related protein−DNA, liquid crystals, nano-materials, chromatography, mass spectrometry and materials for embalming (Dupont and Braz, 2004, Jones *et al.*, 1999, Svintradze *et al.,* 2008).

On the other hand, acetic acid and propionic acid are solvents, which have extensive applications in various industries, especially used in chemical industries as an intermediate for the production of different chemicals and in polymer, plastic and cosmetics industries (Kondaiah *et al.*, 2013). Similarly, a wide range of application of acetonitrile is due to its good properties such as superior UV absorbance, unmatched solubilizing properties amongst other solvents, relatively high dielectric constant, ability to dissolve electrolytes, miscibility with varieties of other solvents, acute toxicity, low viscosity and low chemical reactivity. Although the world is seriously working on ways to reduce over reliance on acetonitrile for industrial, pharmaceutical and academic purposes, acetonitrile still remains a versatile organic solvent with diverse application areas. These include its uses in analytical and purification methods in the laboratory settings, purification in refineries, in battery applications, in cyclic voltammetry, in the manufacture of DNA oligonucleotides synthesis and manufacturing of drug substances and products, photographic films, amongst others (Singh *et al.*, 2016).

1.2 Significance of thermophysical and thermodynamic properties

The thermophysical properties of ILs are basically useful to understand the fundamental knowledge of significant aspects in the solution chemistry. Generally, thermophysical properties can be modified by the addition of a suitable co-solvent to an ionic liquid due to a small change in the cationic or anionic part of the IL (Kavitha *et al.*, 2012, Govinda *et al.*, 2015, Greaves and Drummond, 2008, Govinda *et al.*, 2013, Gomez *et al.*, 2008). Moreover, ILs can be glaringly attributed as solvents for chemical reactions and separation processes from an industrial point of view, due to the various assemblies of ions in IL mixtures with organic solvent. The features of liquid mixtures are compulsory requirements for many industrial applications such as surface facilities, pipeline systems, heat transfer, mass transfer, fluid flow and biomedical research (Govinda *et al.*, 2011, Tokuda *et al.*, 2005, Blanchard *et al.*, 2001).

Furthermore, the thermophysical properties and its studies are essential in all aspects of applied research as these are the cores in screening, in order to establish a suitable material for a certain application or in developing/modifying their unique physiochemical properties which will enhance and provide the material’s usefulness in certain aspects of research or industrial application. Apparently, thermophysical data of systems are used to calculate the thermodynamic properties which are paramount to designing future processes and equipment involving these systems. However, the knowledge of thermodynamic properties is essential tools for microscopic level interactions of liquid mixtures because they provide valuable information about intermolecular interactions which occurs between unlike molecules (Pal *et al.*, 2015, Dragoescu, 2015, Teodorescu, 2015).

In addition, the thermodynamic properties also consent for new correlations and or analytical models to test the solution theories for their binary mixtures as well as to afford information about molecular interactions such as structural breaking or making properties and nature/characterization behavior of the compounds in their mixtures (Deenadayalu *et al.,* 2010).

Similarly, thermophysical and thermodynamic properties of ILs are very interesting to understand the intra- and intermolecular interactions that take place between component molecules in the mixtures and are also useful to unveil solvent-solvent, solute-solute and solute-solvent interactions between the ions of ILs and solvent molecules of binary and ternary liquid mixtures which is required for the scientific community (Behroozi and Zarei, 2012, Rajagopal and Chenthilnath, 2010, Altuwaim *et al.,* 2012, Venkatesu, 2010, S. Karlapudi *et al.,* (2014). Also, these properties are also important to investigate the nature of intermolecular interactions that can occur in liquid mixtures and that are dependent on the charge distribution and molecular geometry of the liquids. Furthermore, the thermodynamic properties of liquid mixtures having components capable of undergoing specific interactions, geometrical effects, molecular arrangements and molecular modeling (Radhamma, 2008, S. Karlapudi *et al.*, 2013, Janardhanaiah *et al.*, 2015, Sreenivasulu *et al.,* 2014).

1.3 Infinite dilution activity coefficients

Infinite dilution is described as a single (solute) molecule completely surrounded by other (solvent) molecules, exhibiting only solute-solvent interactions. This is graphically represented in figure 1.9.1.

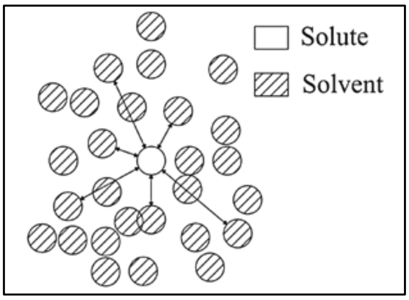


Figure 1.3.1 Graphical representation of infinite dilution for a binary mixture

In a binary mixture, the concept of infinite dilution can be represented mathematically as the concentration at which the solute concentration approaches zero, or the solvent concentration approaches one.

The activity coefficient γ_i of a component *i* in a mixture is given by:

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

where $\hat{f}_i$ is the fugacity of component *i* in solution, f_i the pure component fugacity and x_i the liquid phase mole fraction. For a further derivation of this property (and related terms) the reader is referred to Smith *et al.* (2005) or any other introductory text on phase equilibria.
The activity coefficient at infinite dilution (γ_i^∞) describes the case of maximum non-ideality. This value will present the most accurate information regarding the interaction between the solute and solvent (McMillan and Mayer, 1945).

In the practical sense, it would be nearly impossible to achieve true infinite dilution (by the definition stated). Kojima et al. (1997) explains that for a measurement to be valid there would have to be a range for the value of x_i. For example, for the ethanol in hexadecane system, a molar concentration of 1% would adequately approximate infinite dilution, however for highly associated compounds; this region may be as low as 10^{-7}. In such cases, one would have to consider the accuracy in measuring such systems over the extrapolation of modelled or simulated phase equilibria (Kojima *et al.,* 1997).

From an industrial point of view, γ_i^∞ values enable us to determine the phase equilibria for a very dilute solution. This can be used for:

- Developing processes for high purity extraction.
- Azeotropic distillation (Kojima *et al.,* 1997).
- Specialty chemical separation.
- Environmental separations and water purification.
- Evaluation of Henry's law constants
- Predicting azeotropes
- Solvent screening
- Determining partial excess enthalpies

For the purposes of this investigation, only the last two mentioned points were incorporated.

1.4 Scope of the present study

The thesis mainly contains three parts:

(a) Excess/deviation properties of binary ionic liquid mixtures

In this regards, the density (*ρ*), speed of sound (*u*), excess molar volume (V_m^E), isentropic compressibility (k_S) and deviation in isentropic compressibility (Δk_s) for binary liquid mixtures of [EMIM]$^+$[EtSO$_4$]$^-$ + Acetonitrile, [BMIM]$^+$[SCN]$^-$ + Acetonitrile, [EMIM]$^+$[EtSO$_4$]$^-$ + acetic acid or propionic acid, [BMIM]$^+$[SCN]$^-$ + acetic acid or propionic acid, Acetonitrile + acetic acid or propionic acid at temperature ranging from 293.15 K to 313.15 K in steps of 5 °C and at 0.1 MPa. The calculated properties $(V_m^E, \Delta k_s)$ were correlated with the Redlich-Kister polynomial equation to confirm the accuracy of experimental data. As well as the calculated excess properties were discussed interms of possible molecular interactions between component molecules.

(b) Excess/deviation properties ternary ionic liquids mixtures

In this perspective, Excess molar volume (V_{123}^E), isentropic compressibility (k_S) and deviation in isentropic compressibility (Δk_{s123}) were determined for four ternary liquid mixtures of {[EMIM]$^+$[EtSO$_4$]$^-$ + acetic Acid + acetonitrile}, {[EMIM]$^+$[EtSO$_4$]$^-$ + propionic acid + Acetonitrile}, {[BMIM]$^+$[SCN]$^-$ + acetic acid + acetonitrile} and {[BMIM]$^+$[SCN]$^-$ + propionic acid + Acetonitrile} at different temperatures (293.15, 298.15, 303.15, 308.15 and 313.15) K and at a pressure of 0.1 MPa with aid of the experimental measurements of density (*ρ*) and speed of sound (*u*). In this ternary systems ILs {[EMIM]$^+$[EtSO$_4$]$^-$ and [BMIM]$^+$[SCN]$^-$}, acetonitrile are considered as common components and acetic acid or propionic acid is non-common component. The calculated data were correlated by using the Cibulka equation with the help of Redlich–Kister parameters obtained from fitting the Redlich–Kister equation for the binary systems obtained from literature. Furthermore, how the sign and magnitude of thermodynamic functions were influenced by the addition of a third component to liquid systems was also studied, prediction of the possible molecular and pair-wise interactions between component molecules was attempted and the effect of temperature on the thermophysical and thermodynamic properties was correlated.

The following factors are significantlly a molecular interactions in binary/ternary liquid mixtures

[a] Difference in their size, shape and structure of the components.

[b] rupturing of hydrogen bonds in hydrogen bonded aggregates of components.
[c] decreasing the dipolar association in the polar components
[d] intra- and intermolecular interactions between like and unlike molecules
[e] interstitial accommodation of the smaller components into the larger components

(c) Activity coefficients at infinite dilution measurements of ionic liquid

The present work focussed on application of the environmental friendly, 1–butyl–3–methylimidazolium bis (trifluoromethylsulfonyl) imide ($[BMIM]^+[Tf_2N]^-$) ionic liquid for the separations of (alkane/aromatic), (alkane/alk-1-ene), (cycloalkane/aromatic) and (water/alkan-1-ol) using gas-liquid chromatography (GLC) technique. In this reason the activity coefficients at infinite dilution, γ_{13}^{∞}, for 31 organic solutes (alkanes, cycloalkanes, alkenes, alkynes, aromatics, alkanol and ketones) and water in ionic liquid were measured at temperatures of (323.15, 333.15, 343.15, 353.15 and 363.15) K. Stationary phase loadings of (42.83 and 68.66) % by mass were used to ensure repeatability of measurements.

Density and viscosity values were measured to confirm the purity of ionic liquid. Partial molar excess enthalpies at infinite dilution, $\Delta H_1^{E,\infty}$, were also determined. The selectivities, S_{1j}^{∞}, and capacities, k_j^{∞}, were determined for the above separations. The separating ability of the investigated ionic liquid was compared with previously investigated ionic liquids and industrial solvents such as sulfolane, *n*-methyl-2-pyrrolidine (NMP) and *n*-formylmorpholine (NFM).

The structures of the ILs used in this work are presented in Figures 1.4.1 - 1.4.3.

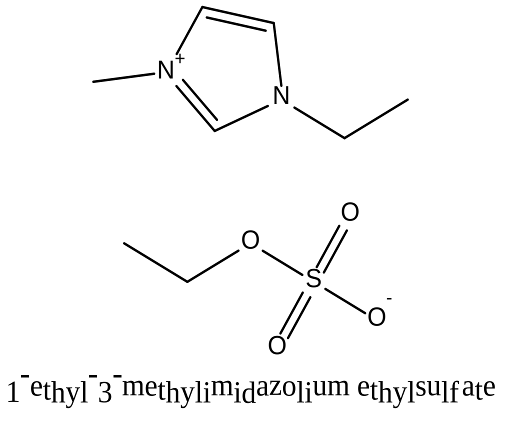


Figure 1.4.1 Structure of 1-ethyl-3-methylimidazolium ethylsulfate {$[EMIM]^+[EtSO_4]^-$ IL.

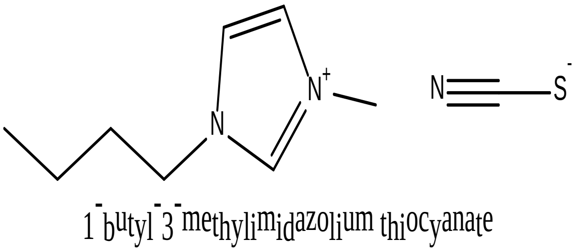


Figure 1.4.2 Structure of 1-butyl-3-methylimidazolium thiocyanate [BMIM]$^+$[SCN]$^-$ IL.

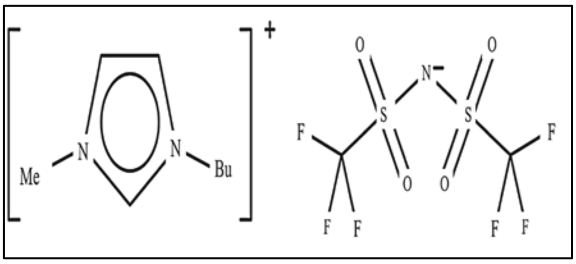


Figure 1.4.3 Structure of 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [BMIM][Tf$_2$N] IL.

CHAPTER 2

LITERATURE REVIEW

2.1 Binary imidazolium based ionic liquids systems

Ionic liquids are relatively newly found solvents and ascthey interest's chemists and researchers, their thermophysical properties of binary mixtures of organic salt or inorganic salt are important (Freemantle, 2010). These thermophysical properties of pure ionic liquids and their binary mixtures are with other organic solvents are of impotency in the designing of the future technological processes and equipment's (Maia, 2013). The study of thermophysical and thermodynamic properties of the ionic liquids is increasing since the last 20 years (and their binary mixtures with molecular organic solvents) (Freemantle, 2010). Some of the studied binary mixtures are listed below

Bahadur *et al*. (2016) studied densities, sound velocities, viscosities, and refractive indices of a series of alkyl imidazolium-based ionic liquids (ILs): 1-butyl-3-methylimidazolium tetrafluoroborate $[BMIM]^+[BF_4]^-$, 1-butyl-3-methylimidazolium hexafluorophosphate $[BMIM]^+[PF_6]^-$, 1-ethyl-3-methylimidazoium ethyl sulphate $[EMIM]^+[EtSO_4]^-$ and 1-ethyl-3-methylimidazolium tetrafluoroborate $[EMIM]^+[BF_4]^-$, with acetophenone binary mixtures over the extensive range of composition and at temperature ranging from (293.15- 333.15) K under atmospheric pressure. The excess molar volumes, deviation in isentropic compressibilities, deviation in viscosities and deviation in refractive indices were derived from experimental results. The obtained results of excess molar volume, isentropic compressibilities, deviation in viscosities were found to be both negative and positive while for deviation in refractive index were negative under the same experimental conditions. Redlich-Kister polynomial equation was used to check the accuracy of the experimental results. Both results of experimental and measured were intermolecular interfaces and structural effects

Lehmann *et al.* (2010) reported densities of $[EMIM]^+[EtSO_4]^-$ with its binary mixtures of different organic solvents which were: acetone, propylene carbonate, acetonitrile, methanol, ethanol, dichloromethane and water. the results of the excess molar volume for all binary mixtures determined from the density were negative indicating denser molecular packing than in the pure liquids.

Letcher *et al.* (2003) determined by gas-liquid chromatography at *T)* (298.15 K and 323.15 K) the activity coefficients at infinite dilution, γ_{13}^{∞} for both polar and nonpolar solutes in an ionic liquid, 1-hexyl-3-methylimidazolium tetrafluoroborate ($[HMIM^+][BF_4^-]$). The partial molar excess enthalpy values at infinite dilution have also been determined at T = 298.15 K. The result showed the magnitude of the large positive enthalpy due to the dissociation of the hydrogen bonds of methanol. In the alkane and cycloalkane series, the $\Delta H_1^{E,\infty}$ values increase with increasing carbon number.

Rao *et al.* (2016) determined density, refractive index and sound velocity for the binary mixtures of 1-butyl-3-methylimidazolium tetrafluoroborate and 2-pyrrolidone at temperature ranging from (298.15 to 323.15) K under atmospheric pressure. FT-IR was used to understand molecular interactions occurring in the binary mixture and its results showed ion-dipole interactions of IL and 2-pyrrolidone. Results of density were used obtain excess molar volumes and its results displayed an inversion in the sign from negative to positive deviation

Pal *et al.* (2016) studied ILs which were 1 -butyl-3-methylimidazolium tetrafluoroborate, 1- butyl-3-methylimidazolium methylsulfate and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide with 1,2-propanediol. Density and sound velocity for those ILs were determined over the temperature range of (293.15 to 318.15) K. The thermodynamic properties studies indicated a positive deviation from the ideality and spectroscopic results revealed that the multiple hydrogen bonding interactions of the studied systems transpired at microscopic level.

Reddy *et al.* (2016) studied density, sound velocity and refractive index of $[EMIM]^+$ $[BF_4]^-$ and 2-methoxyethanol. The thermophysical properties of pure and binary mixtures were determined at an atmospheric pressure at temperature ranging from (298.15 to 328.15) K. the results showed a strong intermolecular interactions between those mixtures and Infrared spectroscopy was used to confirm it.

Reddy *et al.* (2016) determined density, sound velocity and refractive index of $[EMIM]^+$ $[EtSO_4]^-$ pure component and its binary mixture with 2-ethoxyethanol under atmospheric temperature in a temperature ranging from (298.15 to 328.15) K. Few properties determined such as excess molar volume, excess values of partial molar volumes, free volume, isothermal compressibility and isobaric thermal expansion coefficient showed a negative results whereas speed of sound, refractive index, internal pressure gave a positive results which showed dominance of strong attractive forces.

Krishna *et al.* (2016) measured densities, ultrasonic speeds, and refractive index for 1 -butyl-3-methylimidazolium hexafluorophosphate $[BMIM]^+[PF_6]^-$ of pure and binary mixtures with 2-propoxyethanol at atmospheric pressure at a temperature ranging from (298.15-323.15) K. The results showed the formation of strong ion–dipole and hydrogen bonding interactions occurring between ILs $[BMIM]^+[PF_6]^-$ and 2-propoxyethanol molecules additionally the geometrical effect due to interstitial fitting of 2-propoxyethanol molecules into the interstices of ionic liquids. The FT-IR spectra were also conducted at room temperatures (298.15K) and examined in terms of the molecular interactions.

Fan *et al*. (2016) measured density and viscosity of 1-ethyl-3-methylimidazolium tetrafluoroborate with dimethyl sulfoxide, dimethylformamide and dimethylacetamide binary mixtures at temperatures ranging from (303.15 to 333.15) K under atmospheric pressure. Negative results of calculated excess molar volume and deviations in viscosity were obtained.

Krishna *et al*. (2015) determined densities and sound velocity for $[BMIM]^+[BF_4]^-$ pure and binary systems with alkanediol at temperature range of (298.15 to 323.15) and the results of excess molar volume were found to be negative.

Rao *et al.* (2015) studied density, refractive index and sound velocity of the $[BMIM]^+[BF_4]^-$ ionic liquid with NOP binary mixtures at temperature range from (298.15 - 323.15) K under atmospheric pressure. The results of excess isentropic compressibility, excess molar isentropic compressibility and excess intermolecular free length were negative from mole fraction of 0 to 0.2 and thus were due to solvation of the ions in the mixture, accredited to the strong attractive interactions and the remaining mole fractions were positive at all temperatures. Excess molar volume data were positive which indicated that there is a volume expansion upon mixing of the IL. The FT-IR spectrum which was conducted at room temperature gave more information about the molecular interactions, and revealed the presence of ion-dipole interactions between NOP and the IL ($[BMIM]^+[BF_4]^-$).

Rao *et al*. (2015) determined densities, refractive indexes and sound velocity of $[BMIM]^+[BF_4]^-$ with its binary mixtures of vinyl- 2-pyrrolidinone [NVP] at temperatures ranging from (298.15 to 323.15) K under atmospheric pressure. The excess isentropic compressibility, excess intermolecular free length, and excess molar volume data are negative over the whole complete composition range at all evaluated temperatures. The FT-IR spectrum for the binary mixtures was run to give information about molecular interactions and its results showed ion-dipole interactions between these mixtures.

Rao *et al.* (2015) determined density, sound velocity and refractive index as well as FT-IR spectra of $[BMIM]^+[BF_4]^-$ and its binary mixtures with N-methyl-2-pyrrolidinone [NMP] over the whole range of mole fraction, at temperatures ranging from (298.15 to323.15) K. The results for excess isentropic compressibility were negative values, and these values show strong attractive interactions, structural readjustments, and efficient packing upon mixing of the liquids. Furthermore, the FT-IR spectrum indicated ion-dipole interactions of $[BMIM]^+[BF_4]^-$ with [NMP].

Wu *et al*. (2015) measured densities and viscosities of binary mixtures of 1-butyl-3-methylimidazolium tetrafluoroborate with N,N-dimethylacetamide, acetonitrile, methanol and N-methyl-2-pyrrolidone in a mole fraction ranging from 0.1 to 0.9, at temperature of (303.15 to 333.15) K under atmospheric pressure. Excess molar volumes and deviation in viscosity results were found to be negative.

Vercher *et al*. (2015) measured thermophysical properties which were densities, sound velocity, viscosities and refractive indeces of pure compounds and binary mixture of $[BMIM]^+[BF_4]^-$ or $[EMIM]^+[BF_4]^-$ with methanol at temperature ranging from (278.15 to 318.15) K and under atmospheric pressure. Results of excess isentropic compressibility and excess molar volume obtained were negative, furthermore they became more negative as temperature increases due to changes in free volume. Deviation in refractive index showed positive results at all temperatures and across the entire composition range whereas deviation in viscosity gave negative results at all temperatures and entire composition range.

Rafiee and Frouzesh (2015) conducted measurements of thee binary and ternary mixtures of $[EMIM]^+[EtSO_4]^-$ with alkyl alcohol and 1,3-dichloro-2-propanol at temperature range (298.15–318.15) K and under pressure of 0.087 MPa. Negative results of excess molar volume of the binary mixtures IL with an alkyl alcohol were obtained while positive results of the excess molar volume of the binary mixtures IL with 1,3-dichloro-2-propanol were obtained additionally excess molar volume it deacreases with increasing temperature and thus were due to intermolecular interaction and steric effects. Thermal expansion coefficients were also calculated and the results were negative for all binary mixtures studied, moreover its values increased by increasing temperature.

Vaid *et al.* (2015) determined densities, sound velocity, and refractive indices for tetrahydrofuran binary mixtures with 3 types of imidazolium based ILs which were 1 -butyl-3-methylimidazolium hexafluorophosphate, 1-hexyl-3-methyl imidazolium hexafluorophosphate and 1-octyl-3-methylimidazolium hexafluorophosphate with. Those systems were evaluated at T = (293.15 to 323.15) K under atmospheric pressure. The excess properties calculated which were: excess molar volume and excess molar isentropic compressibility which were found to be negative and its negativitly increased as temperature increases while deviations in refractive index showed positive trend.

Vaid *et al.* (2015) determined densities, sound velocity, and refractive indices of binary mixtures of propylamine with various ILs which were: 1-butyl-3-methylimidazolium hexafluorophosphate, 1 -hexyl-3-methylimidazolium hexafluorophosphate and 1 -octyl-3-methylimidazolium hexafluorophosphate and their binary mixtures at T= (293.15 to 313.15) K and under the pressure of 0.1 MPa. Results of excess properties (excess molar volumes and excess molar isentropic compressibility's) were found to be negative furthermore as temperature increases they decrease while deviation in refractive index were positive and increases as temperature increases for all investigate systems.

Wua *et al.* (2014) evaluated densities and viscosities of binary mixtures of $[BMIM]^+[BF_4]^-$ with organic solvents which were: N,N-dimethylformamide, acetone and methyl ethyl ketone at temperature of (303.15 - 333.15) K. The results of calculated excess molar volume as well as deviations in viscosity were negative in all the studied systems.

Chaudhary *et al.* (2014) evaluated density, sound velocity, refractive index and specific conductivity for binary mixtures of 1-butyl-3 methylimidazolium tetrafluoroborate $[BMIM]^+[BF_4]^-$ with water at T = (293.15–323.15) K over the full composition range. Molecular spectroscopy including NMR and FTIR were used to understand the nature of molecular interactions occuring between $[BMIM]^+[BF_4]^-$ and water, and also to find the moieties in which the interactions are taking place. Results of density, sound velocity and refractive index demonstrated the existence of dispersion forces between $[BMIM]^+[BF_4]^-$ with water and the strength of dispersion force is more prominant at higher temperatures. The spectroscopic results showed the breaking of ion-pair interactions of the IL and hydrogen bonded network of water are taking dominant.

Ciocirlan *et al.* (2014) determined density and refractive index of 1-butyl-3-methylimidazolium tetrafluoroborate, $[BMIM]^+[BF_4]^-$ with its binary mixture of 1,4-dioxane, and 1-ethyl-3-methylimidazolium tetrafluoroborate, $[BMIM]^+[BF_4]^-$ with its binary mixture of 1,4-dioxane and ethylene glycol. ethylene glycol thermophysical properties were determined over the complete composition range at T = (293.15 to 353.15) K for densities and from T = (298.15 to 323.15) K for refractive indices. For all systems containing 1,4-dioxane excess molar volume were negative, while positive for systems having ethylene glycol were positive as well as the refractive index deviations were negative.

Bhagour *et al.* (2013) measured densities and sound velocity of 1-ethyl-3-methylimidazolium tetrafluoroborate $[BMIM]^+[BF_4]^-$ with its binary mixtures of acetone or dimethylsulphoxide at T= (293.15-308.15) K. The nature and extent of interactions existing in of ionic liquid mixtures in their pure and mixed state were calculated using the graph theory.

Iulian and Ciocirlan (2012) evaluated densities for the binary systems of 1-ethyl-3-methylimidazolium tetrafluoroborate $[EMIM]^+[BF_4]^-$ and 1-hexyl- 3methylimidazolium tetrafluoroborate $[HMIM]^+[BF_4]^-$, with organic solvents which were: dimethyl sulfoxide and acetonitrile over the entire range of composition at T= (298.15 to 353.15) K. Values of densities were used to calculated excess molar volume and its data were negative for all the composition range at all evaluated temperatures.

Rilo *et al.* (2012) evaluated densities of the IL 1-ethyl-3-methylimidazolium alkyl sulphate family, with the alkyl group being ethyl, butyl, hexyl and octyl ($[alkylMIM]^+[alkylS]^-$) and their binary mixtures with water and ethanol over the entire composition range, at *T*= (288-318) K at atmospheric pressure. The results of the excess molar volume for all the measured systems were very small magnitude.

Pal and Kumar (2012) measured densities and sound velocities for binary mixtures of IL $[BMIM]^+[BF_4]^-$ in diethylene glycol monomethyl ether, ethylene glycol monomethyl ether and triethylene glycol monomethyl ether over the entire composition range at *T*= (288.15 - 318.15) K. The results of excess molar volume were negative over the whole composition range.

Taib and Murugesan (2012) evaluated densities and refractive indexes IL 1-butyl-3-methylimidazolium tetrafluoroborate with its binary mixtures of water and monoethanol amine at *T*= (293.15 to 353.15) K over the complete range of composition. The results of excess molar volumes and thermal expansion coefficient were reduced from new experimental density. The resulting excess molar volume data were positive.

Bhattacharjee *et al.* (2012) determined densities and viscosities 1-alkyl-3-methylimidazolium alkyl sulphates with its binary mixtures of water at *T* = (278 - 343) K at atmospheric pressure. alkyl group substituents were: butyl and ethyl while the sulphates types were: hydrogen sulphate ($[HSO_4]^-$), methyl sulphate ($[MeSO_4]^-$), ethyl sulphate ($[EtSO_4]^-$). The densities and viscosities of the pure IL have had higher values, but the values of the mixtures strongly depend on the mole fraction of water, as mole fraction of water increases the density and viscosity of the IL decreases furthermore the thermophysical properties of the binary mixtures also decreased when the alkyl side chain of the cation and anion of the IL increased. The thermodynamic properties calculated show were negative which showed that denser molecular packing than in pure liquids. Both excess molar volume and deviations in viscosities decreases by increasing temperature additionally the deviation in viscosity increases when the cation alkyl chain length increases whereas anion had minimal effect.

Chaudhary *et al.* (2012) evaluated density, sound velocity and specific conductivity of IL 1-butyl-3-methylimidazolium hexafluorophosphate $[BMIM]^+[BF_4]^-$ with its binary mixtures of Triton X-45 and Triton X-100 for whole mole fraction at temperature ranging from (293.15 to 323.15) K. thermodynamic properties including excess molar volume, deviation in isentropic compressibility, partial molar excess volume, deviation in partial molar isentropic compressibility and deviation in specific conductivity were calculated furthermore spectroscopic measurements were made including FT-IR, hydgen and carbon 13 NMR to further understand the structural and interactional behavior of the mixtures.

Ciocirlan *et al.* (2011) measured densities and the dynamic viscosities for the ionic liquid $[BMIM]^+[BF_4]^-$ with selected binary mixtures of polar solvents which were dimethyl sulfoxide, and ethylene glycol, in the temperature ranging from (293.15 to 353.15) K. the results of excess molar volume of the system of $[BMIM]^+[BF_4]^-$ with dimethyl sulfoxide were negative while for $[BMIM]^+[BF_4]^-$ with ethylene glycol were positive for the investigated temperature and mole fraction complete range.

Li *et al.* (2010) measured densities of IL 1-butyl-3-methylimidazolium tetrafluoroborate, $[BMIM]^+[BF_4]^-$, with its binary mixture of aniline at T= (298.15 to 313.15) K and atmospheric pressure over the complete composition range. Partial molar volumes and apparent molar volumes were calculated. Excess molar volume were found to be negative which shows that the effects due to ion-dipole interactions and to packing between $[BMIM]^+[BF_4]^-$ and aniline dominate over disruption of dipolar orders.

Singh and Kumar (2010) reported density and refractive index for IL 1-butyl-3-methylimidazolium hexafluorophosphate $[BMIM]^+[PF_6]^-$ and its binary mixtures with ethylene glycol derivatives (diethylene glycol monomethyl ether, triethylene glycol monomethyl ether, triethylene glycol dimethyl ether and tetraethylene glycol dimethyl ether) over the complete composition range. The calculated properties were: excess molar volumes, apparent molar volumes, partial molar volumes and excess partial molar volumes. The density data were used to calculate their limiting values at infinite dilution respectively. The calculated excess molar volume shifted to more negative from an alkoxyalkanol to poly ether. Furthermore as temperature increases it decreases. The deviations in refractive index deviation from additivity on volume fraction basis was positive

Pal *et al.* (2010) studied density, sound velocity and refractive index for the binary mixtures of $[BMIM]^+[PF_6]^-$ with diethylene glycol monomethyl ether, propylene glycol monomethyl ether and propylene glycol monoethyl ether. Density data were used to calculate excess molar volume and changes in isentropic compressibility's and together with the sound velocity and the results of refractive index were used to calculate deviations in refractive index and molar fraction. Apparent molar volume and apparent molar compressibilities at infinite dilution data were used to calculate solute-solvent interactions.

Han *et al*. (2009) evaluated densities for IL 1-butyl-3-methylimidazolium tetrafluoroborate, $[BMIM]^+[BF_4]^-$, pure and binary mixture with benzene, ethanol and acetonitrile at T = (313.2 to 473.2) K. Excess molar volume data obtained were negative which shows more efficient packing or attractive interactions between IL $[BMIM]^+[BF4]^-$ with mixtures of organic solvents: benzene, ethanol and acetonitrile.

Fan *et. al* (2009) measured densities and viscosities for IL 1-butyl-3-methylimidazolium hexafluorophosphate ,$[BMIM]^+[PF_6]^-$, and methyl methacrylate (MMA) at T = (283.15 to 353.15) K under atmospheric pressure. All excess molar volumes were negative and became more negative as temperature increases. The density data was also fitted to the Redlich-Kister type equation

Gao *et al*. (2009) reported densities of the binary mixture of 1-butyl-3-methylimidazolium tetrafluoroborate,$[BMIM]^+[BF_4]^-$, with benzaldehyde over the varied range of compositions at T = (298.15 to 313.15) K and under atmospheric pressure. Density data was used to calculate excess molar volumes which were negative and this showed that the effects due to the ion-dipole interactions and packing between $[BMIM]^+[BF_4]^-$ and benzaldehyde are dominating over the disruption of dipole orders of benzaldehyde.

Tian *et al*. (2008) measured densities and viscosities of IL $[BMIM]^+[BF_4]^-$ with its binary mixtures of methyl formate or methyl acetate or ethyl formate or acetone at 298.15 K. The results of excess molar volume were negative for all investigated systems and thus may be due to the ion-dipole interactions that dominate. Results of the deviation in viscosity were negatively large due to the variance of viscosity differences between the IL and the organic solvent.

Malham and Turmine (2008) measured viscosity and refractive index of ILs 1-butyl-3-methylimidazolium tetrafluoroborate, $[BMIM]^+[BF_4]^-$, and 1-butyl-2,3-dimethylimidazolium tetrafluoroborate , $[BMMIm]^+[BF_4]^-$, with their binary mixtures of with water at T = 298.15 K over the complete composition range. The prediction of refractive indexes of pure and binary mixtures of the ILs was done by using Lorentz–Lorenz, Wiener, and Gladstone–Dale type of equations. Positive values were obtained for refractive index deviation, while negative values were obtained for viscosity deviation.

Domanska and Laskowska (2008) measured densities of IL 1-ethyl-3-methylimidazolium ethyl sulphate, $[EMIM]^+[EtSO_4]^-$, with alcohols: propanol or 1-butanol or 1-pentanol or 1-hexanol or 1-heptanol or 1-octanol or 1-nonanol or 1-decanol at T= 298.15 K under ambient pressure. The excess molar volume were both negative and positive, nonetheless the one for 1-propanol and 1-butanol were negative and thus were due to hydrogen bonding occurring between the short chain alcohols and IL, and high packing effects.

González *et al*. (2007) reported densities, sound velocity and viscosities of 1-ethyl-3-methylimidazolium ethyl sulphate, $[EMIM]^+[EtSO_4]^-$, with its binary mixtures with methanol, 1-propanol, and 2 propanol, at temperature ranging from (298.15 to 328.15) K, furthermore the refractive index measurements of the binary mixtures were conducted at T= 298.15 K, and excess molar volume of the studied systems were negative as well as excess molar isentropic compressions due to ion-dipole interactions. The deviation in viscosities were negative and as the temperature increases the values became less negative although the deviations of refractive indeces were found to be positive

Huo *et al*. (2007) determined densities of ILs 1-butyl-3-methylimidazolium hexafluorophosphate, $[BMIM]^+[PF_6]^-$, and 1-butyl-3-methylimidazolium tetrafluoroborate, $[BMIM]^+[BF_4]^-$, with benzene, 1-propanol and acetonitrile at temperature ranging from T = (293.15 to 343.15) K. The results of calculated excess molar volume were found to be negative for all investigated systems; furthermore benzene systems were the most negative ones. The effect of increasing temperature of the systems their thermodynamic values became more negative.

Iglesias-Otero *et al.* (2007) reported density and refractive index for IL $[BMIM]^+[BF_4]^-$ and its binary mixtures with methanol or 1,3-dichloropropane or dimethyl carbonate at temperature ranging from (293.15 to 318.15) K over the complete composition range. Results for excess molar volume were found to be negative as well as isobaric thermal expansivity for all examined systems. Thermodynamic data for all properties became more negative with increasing temperature.

Zafarani-Moattar and Majdan-Cegincara (2007) measured viscosity and refractive index for the pure components and binary systems of IL 1-butyl-3-methylimidazolium hexafluorophosphate, $[BMIM]^+[PF_6]^-$ with dimethylsulfoxide, tetrahydrofuran, acetonitrile and methanol, as well as density and sound velocity for solutions of $[BMIM]^+[PF_6]^-$ with tetrahydrofuran or dimethylsulfoxide were measured over the whole composition range at temperature of 298.15 K. All evaluated thermophysical properties and calculated thermodynamic properties from thermophysical data were estimated, individually. All of the estimated results were negative. The Redlich-Kister equation was applied successfully to correlate thermodynamic properties data which were: deviation in viscosity, deviation in refractive index, excess molar volume, and isentropic compressibility deviation.

Zhong *et al*. (2007) evaluated densities for binary mixtures of IL $[BMIM]^+[PF_6]^-$ with benzyl alcohol or benzaldehyde over the complete range of composition at temperature ranging from (298.15 K to 313.15) K at atmospheric pressure. Density data were utilised to calculate excess molar volumes and results obtained were negative, additionally it increase slightly with an increase in temperature, furthermore the fourth-order Redlich-Kister equation was used to correlate the data. The results indicated that the effects due to the ion–dipole interactions and packing between organic molecular liquids benzyl alcohol or benzaldehyde and $[BMIM]^+[PF_6]^-$ are dominating over the disruption of dipolar orders in benzyl alcohol or benzaldehyde.

Gómez *et al*. (2006) determined the density, sound velocity and refractive index for pure and binary mixtures of 1-ethyl-3-methylimidazolium ethyl sulphate $[EMIM]^+[EtSO_4]^-$ with water and ethanol at temperature of 298.15 and 313.15 K. Calculated results of deviation on refractive index are positive for both systems while the one for excess molar volumes and deviation in viscosity are negative, and as temperature increases they decrease.

Arce *et al*. (2006) measured densities, viscosities, refractive indices, and sound velocity for binary mixtures of IL 1-ethyl-3-methylimidazolium ethyl sulphate $[EMIM]^+[EtSO_4]^–$ with ethanol or 2-ethoxy-2-methylpropane and ternary mixture of $[EMIM]^+[EtSO_4]^–$ with ethanol and 2-ethoxy-2-methylpropane at temperature of 298.15 K and under atmospheric pressure. The excess molar volume results of both binary and ternary mixtures were found to be negative as well as the deviations of viscosity were negative for all the investigated systems. This is because of the great difference occurring between $[EMIM]^+[EtSO_4]^–$ and the viscosity of organic solvents. Density and velocity data were used to calculate isentropic compressibility values and was found to be negative.

Zhou *et al*. (2006) evaluated densities and viscosities of 1-butyl-3-methylimidazolium tetrafluoroborate $[BMIM]^+[BF_4]^-$ with water $[H_2O]$ binary mixtures , at T=(303.15 to 353.15) K. The results for density was utilised to calculate excess molar volumes and for viscosity was used to calculate deviation in viscosity. Thermophysical and derived properties showed a strong dependency on water content.

Zafarani-Moattar and Shekaari (2006) determined density and sound velocity of two types of ILs 1-*n*-butyl-3-methylimidazolium hexafluorophosphate and tetrabutylammonium hexafluorophosphate and their binary mixtures with organic solvents: methanol, acetonitrile, tetrahydrofuran, *N*,*N*-dimethylacetamide, and dimethylsulfoxide. The limiting apparent molar volumes for 1-*n*-butyl- 3-methyimidazolium were calculated and used to obtain data regarding ion-solvent interactions in the investigated systems.

Zafarani-Moattar and Shekaari (2006) measured sound velocity of ILs of 1-n-butyl-3-methylimidazolium hexafluorophosphate $[BMIM]^+[PF_6]^-$ or 1-n-butyl-3-methylimidazolium tetrafluoroborate $[BMIM]^+[BF_4]^-$ and their binary mixtures with acetonitrile and methanol at atmospheric pressure and temperature range of (298.15 to 318.15) K. Results of speed of sound were then used to calculate isentropic compressibility and excess isentropic compressibility data.

Zafarani-Moattar and Shekaari (2005) reported densities and sound velocity for $[BMIM]^+[PF_6]^-$ with its binary mixtures of methanol or acetonitrile over the complete composition range at T = (298.15 to 318.15) K. Density data was used to obtained excess molar volume and sound velocity was used to obtain isentropic compressibility deviations for all systems and their results were negative with the binary system containing methanol more negative than the one containing acetonitrile.

Zhang *et al*. (2004) evaluated the densities and viscosities of pure and binary mixtures of IL 1-ethyl-3-methylimidazolium tetrafluoroborate $[EMIM]^+[BF_4]^-$ with water at temperature ranging from (293.15 to 323.15) K. The results showed that both density and viscosity rely on water mole fraction as well as temperature and viscosity deviations are more profound to temperature in comparison to the excess molar volume this indicates that physical and derived properties of $[EMIM]^+[BF_4]^-$ strongly depend on the amount of water content

Zubeir *et al.* (2016) evaluated density, viscosity, surface tension, electrical conductivity and self-diffusion coefficient of 1-alkyl-3-methylimidazolium tricyanomethanide $[C_n mim][TCM]$ with n = 2, 4 and 6–8 ILs series at the temperature of 288 to 363 K. The obtained experimental values of thermophysical properties were used to calculate thermodynamic valuesand the results of the density studies revealed that for the cyano-based ILs densities decrease with increasing molar mass.

Zhang *et al.* (2016) investigated density, refractive index and dynamic viscosity for binary mixtures of ionic liquids 1-alkyl-3-methylimidazolium, $[C_n mim]X$ with n = 6, 8 and X = Cl, Br, and ethylene glycol (EG) as a second component of the mixtures at temperatures range of 288.15–333.15 K in addition at ambient pressure. Excess molar volume was correlated using the Redlich–Kister polynomial equation. Polynomial equations were used to investigate the variation of density, refractive index, and viscosity. The obtained experimental results were used to evaluate the influence of carbon chain-length and the anion of the ionic liquids as well as the influence of the temperature on the physicochemical properties of the binary systems.

Reddy *et al.* (2017) reported density, speed of sound and refractive index measurements of binary mixture of 1-ethyl-3-methylimidazolium trifluoromethanesulphonate+1-butanol, over the whole composition range at temperature range between 298.15 and 328.15 K under atmospheric pressure. Experimental results were used to obtain excess/deviation properties such as molar volumes, partial molar volumes, partial molar volumes at infinite dilution, isentropic compressibility, free length, speeds of sound, refractive index and isobaric thermal expansion coefficient. The thermodynamic properties results showed an existence of strong molecular interactions between the studied systems. Themophysical properties data were fitted into the Redlich–Kister type equation to obtain the binary coefficients and the standard deviations. IR-spectroscopy was utilised to understand molecular interactions taking place between those two components of the mixture.

Vatašcin, and Dohnal (2015) Thermophysical: density, viscosity, and refractive index of the binary mixture of water + 1-ethyl-3-methylimidazolium tricyanomethanide, [EMIM][TCM], IL were investigated at the temperature range from (288.15 to 318.15) K. Thermophysical properties results were used to obtain excess thermodynamic properties: Gibbs free energy, enthalpy, heat capacity, and volume and property deviations. Results for excess molar volume were found to be positive and deviation in viscosity were found to be negative as well as deviation is refractive index.

Vaid *et al.* (2016) evaluated thermophysical properties: density, speed of sound and refractive indices of the binary mixtures of 1-octyl-3-methylimidazolium tetrafluoroborate [C_8mim][BF_4] with isomers of butanol (1-butanol, 2-methyl-1-propanol, and 2-methyl-2-propanol). Excess and deviation results were calculated from experimental results and fitted into Redlich-Kister polynomial equation. The obtained results were interpreted in terms of interstitial accommodation, formation of the hydrogen bonds, ion–dipole interactions and structural factors occurring in the mixture, furthermore the data of excess molar volume were analysed over the Prigogine–Flory–Patterson (PFP) model and the extended real associated solution (ERAS) model.

Papovic *et al.* (2016) evaluated densities and viscosities of γ-butyrolactone (GBL) with 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ionic liquids (where alkyl = ethyl, hexyl, octyl) binary mixtures under the entire composition range at pressure of 0.1MPa. the calculated excess molar volume as well as were fitted into the Redlich–Kister's polynomial equation. The calculated results were used to obtain information about interactions between GBL and ionic liquids studied.

Patel *et al.* (2016) reported densities, speeds of sound and refractive indices of pure 1-alkyl-3-methylimidazolium bromide [$C_n$mim][Br] where (n = 4, 6 and 8) with poly ethylene glycol 400 binary mixtures at a pressure of 0.1 MPa, over the whole compositions range and temperature ranging from (293.15-323.15) K. Excess molar volumes, excess molar isentropic compressibilities and deviation in refractive indices were calculated from experimental results and then fitted to Redlich–Kister polynomial equation to evaluate the binary coefficients. Excess molar volume and excess molar isentropic compressibilities were largely negative and found to decrease with increasing temperature and size of alkyl chain of ionic liquid whereas deviations of refractive index were negative.

2.2 Ternary imidazolium based ionic liquids systems

Deenadayalu (2007) conducted densities of the ternary mixtures of ($[EMIM]^+[CH_3(OCH_2CH_2)_2OSO_3]^-$ + methanol + water) over the complete composition range at temperature range of (298.15 to 313.15) K. Excess molar volume was calculated from density results and its results were found to be negative at *T* = (298.15 and 303.15) K and positive at *T* = 313.15 K at a higher mole fraction of ILs and at a corresponding decrease in mole fraction of water.

Deenadayalu and Bhujrajh (2008) studied densities of ($[EMIM]^+[BETI]^-$ + methanol or acetone) binary system and ternary system of ($[EMIM]^+[BETI]^-$ + methanol + acetone) at temperature ranging from (298.15, 303.15 and 313.15) K. The speed of sound for the binary systems ($[EMIM]^+[CH_3]^-[(OCH_2CH_2)_2OSO_3]^-$ + methanol) at *T* = 298.15 K was also evaluated. Results of the excess molar volume for ($[EMIM]^+[BETI]^-$ + methanol) binary mixtures were positive at low mole fraction of methanol, whereas ($[EMIM]^+[BETI]^-$ + acetone) binary system were negative for the entire composition range. The excess molar volumes of the ternary system were negative for all temperatures. Isentropic compressibility for system ($[EMIM][CH_3]^+[(OCH_2CH_2)_2OSO_3]^-$ + methanol) was negative throughout the entire mole fraction investigated.

González *et al.* (2008) evaluated densities, dynamic viscosities, and refractive indices of ($[BMIM]^+[MeSO_4]^-$ + ethanol + water) ternary mixture at temperature of 298.15 K as well as ($[BMIM]^+[MeSO_4]^-$ ethanol or water) binary mixture at temperature ranging from (298.15, 313.15, 328.15) K. Thermophysical properties of both ternary and binary systems were measured over the complete range of composition under pressure of 0.1 MPa. Excess molar volumes for both binary and ternary systems over the whole composition range were found to be negative.

González *et al.* (2007) measured densities, refractive indices and dynamic viscosities of (1-propanol + water + $[EMIM]^+[EtSO_4]^-$) and (2-propanol + water + $[EMIM]^+[EtSO_4]^-$) ternary systems at *T* =298.15 K over the entire composition range under atmospheric pressure. Cibulka, Nagata and Sakura equations were used for the correlation of derived properties: Excess molar volumes, deviations of refractive index, deviations of viscosity, and excess free energies of activation of viscous flow. The results of excess molar volume for both ternary systems gave negative values; additionally the excess properties were used to test several prediction models.

Gomez *et al.* (2008) measured densities, dynamic viscosities and refractive indices of (ethanol + water + $[MMIM]^+[MeSO_4]^-$) ternary system at temperature of 298.15 K, and also measured similar properties for the ($[MMIM]^+[MeSO_4]^-$ + ethanol or water) binary system at temperature ranging from (298.15, 313.15, 328.15) K at pressure of 0.1MPa. Thermodynamic properties: Excess molar volumes, viscosity deviations, refractive index deviations and excess free energy of activation, were calculated and correlated using Cibulka equations, and fitted to the ternary data. Excess molar volumes for both binary and ternary systems were negative over the entire composition range. Excess properties of the ternary systems were predicted from binary contributions using geometrical solution models.

Andreatta *et al.* (2009) evaluated densities, dynamic viscosities, and refractive indices of (methyl acetate + methanol + $[C_8MIM]^+[Tf_2N]^-$) ternary system and its binary systems as well at T = 298.15 K. Various calculations were made which include: Excess molar volumes as well as molar refraction and viscosity changes of mixing. Excess molar volume results for both binary and ternary systems were negative over the total composition range.

Andreatta *et al.* (2010) measured densities, dynamic viscosities, and refractive indices of (ethyl acetate + ethanol + $[BMIM]^+[Tf_2N]^-$) ternary mixture and its binary mixtures at temperature of 298.15 K. Various calculations were made which include: Excess molar volumes as well as molar refraction and viscosity changes of mixing, were calculated. Excess molar volume results for both binary and ternary systems were negative over the total composition range.

Sharma *et al.* (2013) determined densities and speeds of sound for the ternary mixtures of 1-ethyl-3-methylimidazolium tetrafluoroborate + 1-methyl pyrrolidin-2-one or pyrrolidin-2-one + water over the complete mole fraction range at temperature ranging from (293.15 to 308.15) K. Differential scanning calorimeter as employed to measure heat capacity of the mixtures at same temperatures. Excess molar volumes and excess isentropic compressibility's were calculated using obtained results of densities and speeds of sounds respectively and were found to be both negative over the complete composition range, furthermore those calculated data were fitted into Redlich–Kister equation to calculate ternary adjustable parameters and standard deviations.

Sharma *et al.* (2015) determined densities and speeds of sound of {1-ethyl-3-methylimidazolium tetrafluoroborate + pyrrolidin-2-one or 1-methylpyrrolidin-2-one + cyclopentanone or cyclohexanone} ternary mixtures at temperatures (293.15 - 308.15) K. Results of excess molar volume and excess isentropic compressibility calculated from obtained results of physical properties were fitted to Redlich–Kister equation to determine ternary adjustable parameters together with their standard deviations. The resultant results from calculations were negative over the entire composition range and they deacreses with an increase in temperature, which suggested strong molecular interactions in the mixed state as compared to the pure state.

Sharma *et al.* (2014) measured densities and speeds of sound of ternary mixture of 1-ethyl-3-methylimidazolium tetrafluoroborate + 2-methylaniline + pyridine or α-, β- or γ-picoline over the entire mole fraction at temperature range of (293.15 to 308.15) K. Differential scanning calorimeter was employed to measure heat capacity of the mixtures. Excess molar volumes and excess isentropic compressibilities were calculated from the results of densities and speeds of sounds respectively then fitted in Redlich−Kister equation to obtain ternary adjustable parameters as well as standard deviations. The calculated thermodynamic results were found to be negative.

Sharma *et al.* (2013) measured densities, speed of sound and heat capacities of pure and ternary mixtures of 1-ethyl-3-methylimidazolium tetrafluoroborate + 1-methyl pyrrolidin-2-one or pyrrolidin-2-one + pyridine and their binary mixtures of 1-methyl pyrrolidin-2-one or pyrrolidin-2- one + pyridine at T = (293.15, 298.15, 303.15, and 308.15) K under atmospheric pressure. Results of measured densities, speeds of sound were used to calculate excess molar volumes and excess isentropic compressibilities and their results were negative over the complete range of composition, which suggested occurance of molecular packing among the constituents of the mixtures.

Arce *et al.* (2006) determined densities, speeds of sound, viscosities and refractive indices of ternary mixtures of 2-Ethoxy-2-methylpropane, Ethanol, and 1-Ethyl-3-methylimidazolium ethylsulfate at temperature of 298.15 K, under atmospheric pressure. Results of thermophysical properties were used to calculate excess molar volumes, deviation in viscosity, molar refraction, and isentropic compressibility. The results of excess molar volumes were negative, deviation in viscosity results were negative and hold large negative values due to differences of the components viscosity, isentropic compressibility results were also negative and the results of molar refraction was changes was very small. All of the calculated thermodynamic properties were fitted to the Redlich-Kister equation.

Calvar *et al.* (2007) reported densities, speeds of sound dynamic viscosities and refractive indices of two ternary systems consists of (ethanol + water with 1-octyl-3-methylimidazolium chloride ([C8mim] [Cl])) and (ethanol + water with 1-ethyl-3-methylimidazoliu methylsulfate (EMISE)) at T = 298.15 K and under atmospheric pressure. Obtained physical properties results were further used to calculate excess molar volumes, isentropic compressibilities, molar isentropic compressibilities, isentropic compressibility deviations, excess molar isentropic compressibilities, deviations of viscosity, deviations of refractive index and excess free energies of activation of viscous flow, furthermore they were fitted to Cibulka and Singh et al. equations for correlation. Excess molar volumes and deviations of viscosity of both studied systems were negative over the whole composition range, whereas for deviations of refractive index and excess free energies of activation of viscous flow are positive.

Riyazuddeen (2017) measured densities, speeds of sound and dynamic viscosities of pure, binary and ternary mixtures of 1-ethyl-3-methylimidazolium ethylsulfate, ($[EMIM]^+[ES]^-$), with solvents: 1-butanol and methanol at T = (298.15-323.15) K, with an interval of 5 K under pressure of 0.1 MPa. Experimental results were used to calculate: excess molar volumes, isentropic compressibilities, molar isentropic compressibilities, excess molar isentropic compressibility and deviations of viscosity and the results were discussed in terms of hydrogen bonding, ion-dipole interactions and structural effects on mixing of ILs and solvents. In addition the results of excess molar isentropic compressibility and deviations of viscosity were found to be negative for the ternary system [EMIM][ES] + 1-butanol + methanol.

Andreatta *et al.* (2010) measured densities, viscosities and refractive indices of binary and ternary mixtures of ethanol, ethyl acetate and 1-butyl-3-methyl-imidazolium bis trifluoromethylsulfonyl imide $[C_4MIM][NTF_2]$ at temperature of 298.15 K and under atmospheric pressure. The corresponding excess and deviation properties were calculated from obtained experimental results and were found to be negative moreover results of calculated properties were fitted in Redlich-Kister polynomial equation for correlations.

Rodrigues & Francesconi (2011) determined densities of both binary and ternary systems consists of water + (1,2-ethanediol or 1,2-propanediol or 1,3-propanediol or 1,2-butanediol) + (1-n-butyl-3-methylimidazolium bromide at mole fraction of 0.01) at temperature of 298.15 K and under atmospheric pressure. The calculated excess molar volumes for all systems investigated were found to be negative over the whole composition range and fitted in Redlich-Kister polynomial equation for all investigated systems.

2.3 Gas liquid chromatography

Heintz *et al.* (2005) measured activity coefficients at infinite dilution γ_i^{∞} of alkanes, alkenes, and alkyl benzenes and linear and branched C_1-C_6 alcohols, esters, and aldehydes in the ionic liquid 1-methyl-3-octyl-imidazolium tetrafluoroborate by gas chromatography. The measurements were carried out at different temperatures between 302 K and 396 K. Values of $\Delta H_1^{E,\infty}$ are positive and also increase slightly with increasing chain length of the linear alkanols.

Mutelet *et al.* (2007) determined activity coefficients at infinite dilution of 31 organic compounds in 1-hexadecyl-3-methylimidazolium tetrafluoroborate $[C_{16}MIM]^+[BF_4]^-$ using inverse gas chromatography at temperatures T = (323.15, 333.15, and 343.15) K. At infinite dilution for hydrocarbons it appears that activity coefficients decreased with the increasing of chain length of the cation. The high γ^{∞} values of alkanes denote a low solubility of non-polar compounds in ILs. And again, associating, polar and polarizable compounds present high affinity as indicated by the low γ^{∞} values.

Krummen *et al.* (2002) measured activity coefficients at infinite dilution using the dilutor technique for 20 solutes (alkanes, alkenes, cyclic hydrocarbons, aromatic hydrocarbons, ketones, alcohols, and water) in the ionic liquids 1-methyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide, 1-ethyl-3-methylimidazolium bis-(trifluoromethylsulfonyl) imide, 1-butyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide, and 1-ethyl-3-methylimidazolium ethylsulfate. The measurements were carried out over the temperature range 293.15 K and 333.15 K.

Ge *et al.* (2008) The activity coefficients at infinite dilution, γ_i^{∞} , for 25 organic solutes, alkanes, alkenes, alkyl benzenes, acetonitrile, acetone, 1,4-dioxane, tetrahydrofuran, ethyl acetate, and chloromethane, in the ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM][BF_4]) have been measured by the gas-liquid chromatographic method at temperatures from (303.15 to 363.15) K.

Deenadayalu *et al.* (2005) the activity coefficients at infinite dilution γ_{13}^{∞} for 14 solutes: alkanes, alkenes, an alkyne, cycloalkanes, benzene, and methanol in the ionic liquid 1-methyl-3-octyl-imidazolium diethyleneglycolmonomethylethersulfate were determined by gas + liquid chromatography at the temperatures (288.15, 298.15, and 313.15) K.

Zhou *et al.* (2006) determined activity coefficients at infinite dilution γ_i^{∞} of 17 alkanes, alkenes, and alkyl benzenes in the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate by gas chromatography using the ionic liquid as the stationary phase. The measurements were carried out at different temperatures between 303.15 K and 343.15 K.

Kato *et al.* (2004) measured infinite dilution activity coefficients γ_i^{∞} for various solutes (alkanes, alkenes, cycloalkanes, cycloalkenes, aromatics alcohols, ketones, esters, ethers, and water) in the five ionic liquids 1-methyl-3-methyl-imidazolium methylsulfate $[MMIM]^+$ $[CH_3SO_4]^-$,1-methyl 3-methylimidazolium methoxy ethylsulfate$[MMIM]^+[CH_3OC_2H_4SO_4]^-$, 1-methyl 3-methyl-imidazolium dimethylphosphate $[MMIM]^+[(CH_3)2PO_4]^-$, *n*-ethylpyridinium bis(trifluoromethylsulfonyl) imide $[C_5H_5NC_2H_5]^+[(CF_3SO_2)_2N]^-$ with an temperature range from 303.15 to 373.15 K.

David *et al.* (2003) measured activity coefficients for hydrocarbon solutes at infinite dilution in 1-methyl-3-octylimidazoliumchloride using the medium pressure gas–liquid chromatography method. The hydrocarbon solutes used were n-pentane, n-hexane, n-heptane, n-octane, 1-hexene, 1-heptene, 1-octene, 1-hexyne, 1-heptyne, 1-octyne, cyclopentane, cyclohexane, cycloheptane, benzene, and toluene. At the following three temperatures (298.15, 308.15, and 318.15) K activity coefficients at infinite dilution were determined. The results indicate that 1-methyl-3-octyl-imidazolium chloride is a reasonable solvent for the separation of an alkane or an alkene from benzene.

Blahut *et al*. (2010) determined infinite dilution activity coefficients γ_1^{∞} and gas–liquid partition coefficients K_L of 30 selected hydrocarbons, alcohols, ketones, ethers, esters, halo alkanes, nitrogen- and sulphur-containing compounds in the ionic liquid (IL) 1-ethyl-3-methylimidazolium methanesulfonate [EMIM][$MeSO_3$] were determined by gas–liquid chromatography at five temperatures ranging from 318.15 to 353.15 K. sample size and IL loading in the column, was found negligible.

Revelli *et al.* (2010) measured activity coefficients of 52 organic compounds in four ionic liquids (ILs), 1,3-dimethoxyimidazolium bis((trifluoromethyl)sulfonyl)imide, 1-(methylethylether)-3-methylimidazolium bis((trifluoromethyl)sulfonyl) imide, 1-ethanol-3-methylimidazolium bis((trifluoromethyl)-sulfonyl)imide, and 1-(3-cyanopropyl)-3-methylimidazolium dicyanamide, using inverse gas chromatography at temperature ranges from (312 to 353) K. ILs are commonly used as stationary phases in gas chromatographic separations, and there is a growing need to predict log *K*L values at higher temperatures. In this regard, Revelli *et al.,* (2010) showed that the Abraham model, with ion-specific equation coefficients, can be used to predict the enthalpy of solvation of organic gases and gaseous solutes, Δ*H*solv, into several ILs.

Yoo *et al.* (2013) reported Henry's constants and activity coefficients at infinite dilution using a customized capillary gas–liquid chromatography column for benzene, toluene, ethyl acetate, 1,4-dioxane, 1,2-dimethoxyethane, acetonitrile, nitromethane, tetrahydrofuran, chloroform, methanol, ethanol, and 1-propanol in ionic liquids 1-butyl,3-methylimidazolium hydrogen sulfate [BMIM][HSO_4] and 1-methyl,3-trimethylsilylmethylimidazolium [SiMIM][Cl] chloride from 313 to 413 K temperature. TGA for [BMIM][HSO4] and [SiMIM][Cl] indicates a degradation onset temperature near 550 and 473 K, respectively. Density data for [BMIM][HSO4] are and [SiMIM][Cl] are reported from 298 to 363 K.

Olivier *et al.* (2010) determined activity coefficients at infinite dilution for 24 solutes (n-alkanes, alk-1-enes, alk-1-ynes, cycloalkanes, alkylbenzenes, and alcohols) in the ionic liquid 1-ethyl-3-methylimidazolium trifluoromethanesulfonate at three different temperatures *T* = (313.15, 323.15, 333.15) K by using gas-liquid chromatography. Over the same temperature range the partial molar excess enthalpy values at infinite dilution were calculated from the experimental results. At T = (313.15, 323.15, 333.15) temperature range, 24 solutes have been investigated and the [EMIM][CF_3SO_3] appears to be a reasonable solvent for separation of aromatics/aliphatics.

Shevelyova *et al.* (2006) determined activity coefficients at infinite dilution γ_i^{∞} by gas chromatography using the IL as the stationary phase of 46 solutes like alkanes, alkenes, alkylbenzenes, linear and branched C_1-C_6 alcohols, esters, aldehydes, cyclohexanone oxime, and $\in$ -caprolactam in the ionic liquid (IL) 1-ethyl-3-methylimidazolium ethyl sulfate or [EMIM][$EtSO_4$] at temperature ranging from (302 and 396) K. Partial molar excess enthalpies at infinite dilution $\Delta H_1^{E,\infty}$ of the solutes in the ILs have been derived.

Rosenboom *et al.* (2012) measured infinite-dilution activity coefficients and Henry's constants for several organic solutes in 1-ethyl-3-methylimidazolium acetate [EMIM][Ac]. Two types of gas–liquid chromatography columns: packed columns and an open tubular wall-coated (OTWC) column were used at the temperature T = 313 to 413 K The organic solutes include n-hexane, 1-hexene, cyclohexane, heptane, benzene, toluene, ethyl acetate, tetrahydrofuran, 1,4-dioxane, acetonitrile, nitromethane, 1,2-methoxyethane, 1-propanol, 2-propanol, t-butanol and t-amyl alcohol. Results using packed columns are in good agreement with those using the OTWC column. However, there is a useful advantage associated with an OTWC column: for solutes such as alcohols, that have strong interactions with the stationary phase, measurements are faster due to their shorter retention time compared to those in packed columns. It appears that the OTWC column is more convenient than a packed column for measuring retention times of highly soluble solutes. Comparison between experimental data and COSMO-RS predictions shows only qualitative agreement.

Ge Ming-Lan *et al.* (2012) measured the activity coefficients at infinite dilution, γ_i^{∞} for 16 organic solutes, alkanes, alkenes, and alkyl benzenes in the ionic liquid 1-butyl-3-methylimidazolium dibutylphosphate ([BMIM][DBP]), by the gas−liquid chromatographic method. The measurements were carried out in the temperature range of (313.15 to 363.15) K.

Yan *et al.* (2010) determined the activity coefficients at infinite dilution, γ_i^{∞}, for both polar and non-polar solutes in the ionic liquid 1-ethyl-3-methylimidazolium tetracyanoborate [EMIM][TCB] by using gas–liquid chromatography at the temperatures from (303 to 343) K. The partial molar excess enthalpies at infinite dilution $\Delta H_1^{E,\infty}$ of the solutes in the ionic liquid were also calculated from the temperature dependence of the γ_i^{∞} values. It was found that the IL investigated shows lower selectivity at infinite dilution than the ionic liquids with the same cation in the separation process of aliphatic compounds from aromatic hydrocarbons by extraction.

Kozlova *et al.* (2009) determined activity coefficients at infinite dilution γ_i^{∞} of alkanes, alkenes, and alkylbenzenes as well as of the linear C1–C6 alcohols in the paramagnetic ionic liquid 1-butyl-3-methyl-imidazolium tetrachloridoferrate(III) by using gas chromatography using the ionic liquids as stationary phase between (305 and 403) K. At 298 K Activity coefficients at infinite dilution γ_i^{∞} of ionic liquid with the ionic liquids containing 1-butyl-3-methyl-imidazolium cation and different non-magnetic have been compared with results for 1-butyl-3-methyl-imidazolium tetrachloridoferrate (III). Anions have been compared at 298 K with No significant effects caused by the paramagnetic anion have been observed.

Domansaka *et al.* (2012) determined the activity coefficients at infinite dilution, γ_{13}^{∞}, for 59 solutes, including alkanes, cycloalkanes, alkenes, alkynes, aromatic hydrocarbons, alcohols, water, acetic acid, thiophene, ethers, ketones, esters, butanal, and acetonitrile in the ionic liquid hexyl-3-methylimidazolium tetracyanoborate, [HMIM][TCB], by gas–liquid chromatography at the temperature of (318.15 to 368.15) K. The selectivities at infinite dilution of the [HMIM][TCB] was found on average to be lower than those for the [EMIM][TCB] but higher than the generally used organic solvent such as NMP or sulfolane. The capacity for benzene was T = 328.15 K. The separation of aromatic from aliphatic hydrocarbons, as well as sulphur or nitrogen compounds from aliphatic hydrocarbons, was also on an average level.

Domanska *et al.* (2010) determined activity coefficients at infinite dilution γ_{13}^{∞} by using gas-liquid chromatography over temperature range from (298.15 to 368.15) K for 34 solutes: alkanes, alkenes, alkynes, cycloalkanes, aromatic hydrocarbons, alcohols, thiophene, ethers, acetone, and water in the ionic liquid 1-hexyl-3-methylimidazolium thiocyanate ([HMIM][SCN]). The partial molar excess enthalpies at infinite dilution values $\Delta H_1^{E,\infty}$ were calculated from the experimental γ_{13}^{∞} values, obtained over the temperature range. At infinite dilution it was found that [HMIM][SCN] ionic liquid shows much higher selectivity than the generally used organic solvents such as NMP[16] or sulfolane and other ionic liquids based on the $[HMIM]^+$ cation in the separation process of aliphatic/aromatic hydrocarbons.

Domanska *et al.* (2010) measured the activity coefficients at infinite dilution γ_{13}^{∞} and gas-liquid partition coefficients K_L for 43 solutes alkanes, alkenes, alkynes, cycloalkanes, aromatic hydrocarbons, alcohols, carboxylic acids, thiophene, ethers, ketones, and waters in the ionic liquid 1-decyl-3-methylimidazolium tetracyanoborate ([DMIM][TCB]) by gas-liquid chromatography from the temperatures ranging 318.15 to 378.15 K. It was found that the investigated [dmim][TCB] ionic liquid shows much higher capacity than NMP and sulfolane and selectivity on the same level as NMP and lower than that for sulfolane for the separation of aliphatic hydrocarbons from aromatic hydrocarbons.

Heintz *et al.* (2006) determined activity coefficients at infinite dilution γ_i^{∞} of alkanes, alkenes, and alkylbenzenes as well as of the linear and branched C_1-C_6 alcohols, esters, and aldehydes in the ionic liquids 1-hexyl-3-methylimidazolium bis-(trifluoromethylsulfonyl) imide by gas chromatography using the ionic liquids as stationary phase, at temperatures ranging from between 301 K and 396 K. From the temperature dependence of the limiting activity coefficients, partial molar excess enthalpies at infinite dilution $\Delta H_1^{E,\infty}$ of the solutes in the ionic liquids have been derived.

Heintz *et al.*(2002) determined activity coefficients at infinite dilution γ_i^{∞} by gas chromatography using the ionic liquids as the stationary phase of alkanes, alkenes, and alkylbenzenes as well as of the linear and branched C_1-C_6 alcohols, acetone, acetonitrile, ethyl acetate, alkyl ethers, and chloromethane in the ionic liquids 1-methyl-3-ethyl-imidazolium bis(trifluoromethyl-sulfonyl) amide and 1,2-dimethyl-3-ethyl-imidazolium bis(trifluoromethyl-sulfonyl). The measurements were carried out at different temperatures between 313 K and 363 K.

Heintz *et al.* (2005) measured activity coefficients at infinite dilution γ_i^{∞} of alkanes, alkenes, and alkylbenzenes as well as of the linear and branched C_1-C_7 alcohols, esters, and aldehydes in the ionic liquids 1-methyl-3-butylimidazolium bis(trifluoromethyl-sulfonyl) imide by using the gas chromatography technique using the ionic liquid as stationary phase, temperatures were ranging between 302 K and 385 K.

Mutelet *et al.* (2008) inverse gas chromatography was used to determined activity coefficients at infinite dilution, γ^{∞} using, of organic compounds in two new room-temperature ionic liquids (*n*-methacryloyloxyhexyl-*N*-methylimidazolium bromide ($C_{10}H_{17}O_2$MIM)(Br) at 313.15 and 323.15 K and *n*-acryloyloxypropyl-*N*-methylimidazolium bromide($C_6H_{11}O_2$MIM)(Br)). It was found that most of the solutes were retained largely by partition with a small contribution from adsorption and that *n*-alkanes were retained predominantly by interfacial adsorption on ionic liquids studied in this work. Abraham solvation parameter model was used for the solvation characteristics of the two ionic liquids for evaluation. It appeared in the results that the introduction of polar substituents to the cation of imidazolium ionic liquids affects strongly the behaviour of organic compounds in mixtures with the ionic liquids. In the separation of aliphatic hydrocarbons from aromatic hydrocarbons, the ionic liquid used shows a higher selectivity than that found by previous workers using classical organic solvents.

Mutelet *et al.* (2006) determined at 323.15 K, activity coefficients at infinite dilution γ^{∞} of 28 organic compounds in eight room-temperature ionic liquids of the family of 1-propyl boronic acid-3-alkylimidazolium bromide and 1-propenyl-3-alkylimidazolium bromide (with alkyl) methyl, octyl, decyl, or dodecyl) using inverse gas chromatography. Using all the available γ^{∞} data, the selectivities at infinite dilution S_{12}^{∞} were determined. It has been observed that γ^{∞} values of polar and nonpolar solutes decrease with increasing alkyl chain length of the ionic liquid. It was also found that there is a linear relationship between γ^{∞} values and the logarithm of the carbon number of the alkyl chain of ionic liquids.

Foco *et al.* (2006) measured by gas-liquid chromatography at (303, 323, and 343) K the infinite dilution activity coefficients of a series of polar and nonpolar solutes (alkanes, alcohols, ketones, ethers, aromatic hydrocarbons, halogenated compounds) in 1-ethyl-, 1-butyl-, 1-hexyl-, and 1-octyl-3-methylimidazolium tetrafluoroborate ionic liquids. The high γ^{∞} values of alkanes denote a very low solubility of these compounds in ILs. It appeared that the γ^{∞} values decrease as the length of the IL alkyl chain increases.

Anthony *et al.* (2001) measured vapor-liquid equilibrium using a gravimetric microbalance, which was designed to measure adsorption on solids of the vapour-liquid equilibrium and the liquid-liquid equilibrium phase behaviour and associated thermodynamic properties of water with three ionic liquids: 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF_6]), 1-*n*-octyl-3-methylimidazolium hexafluorophosphate ([C_8MIM][PF_6]), and 1-*n*-octyl-3-methylimidazolium tetrafluoroborate ([C_8MIM][BF4]). It appeared that the vapor-liquid and liquid-liquid equilibria of [BMIM][PF_6], [C_8MIM][PF_6], and [C_8MIM][BF_4] with water indicate that affinity for water is greater for ILs with [BF_4] as the anion than [PF_6], and that water affinity decreases with increasing alkyl chain length.

Sobota *et al.* (2009) determined infinite dilution activity coefficients γ_1^∞ and gas-liquid partition coefficients K_L of 30 selected hydrocarbons, alcohols, ketones, ethers, esters, haloalkanes, nitrogen- and sulfur-containing compounds in the ionic liquid(IL) 1-ethyl-3-methylimidazolium nitrate [EMIM][NO_3] by gas-liquid chromatography at five temperatures in the range from 318.15 to 353.15 K. Partial molar excess enthalpies and entropies at infinite dilution were derived from the temperature dependence of the γ_1^∞ values. In the hydrogen bonding, [EMIM]-[NO_3] has been found to act always as a proton acceptor lacking the proton donating capability.

Ge *et al.* (2007) measured activity coefficients at infinite dilution γ_i^∞ by the gas-liquid chromatographic method with the ionic liquid as the stationary phase for 17 organic solutes alkanes, alkenes, and alkyl benzenes in the ionic liquid 1-butyl-3-methylimidazolium trifluoromethanesulfonate ([BMIM][CF_3SO_3]). The measurements were carried out from (303.15 to 363.15) K. The partial molar excess enthalpies at infinite dilution $\Delta H_1^{E,\infty}$ of the solutes in the ionic liquid were also derived from the temperature dependence of the γ_i^∞ values.

Deenadayalu *et al.* (2006) determined the activity coefficients at infinite dilution γ_{13}^∞ for 14 solutes: alkanes, alkenes, an alkyne, cycloalkanes, benzene, and methanol in the ionic liquid 1-methyl-3-octyl-imidazolium diethyleneglycolmonomethylethersulfate by using gas + liquid chromatography technic at the temperatures (288.15, 298.15, and 313.15) K. An alkyl-substituted pyridinium ring with a SO_4 group present in the anion has higher selectivity values than one without the SO_4 group present in the anion.

Domanska *et al.* (2007) measured the activity coefficients at infinite dilution, γ_{13}^{∞} by gas-liquid chromatography at temperatures from 298.15-368.15 K for 29 solutes, alkanes, alkenes, alkynes, cycloalkanes, aromatic hydrocarbons, alcohols and water in the ionic liquid 1-ethyl-3-methylimidazolium trifluoroacetate ([EMIM][TFA]). The partial molar excess enthalpies at infinite dilution $\Delta H_1^{E,\infty}$ values were calculated from the experimental γ_{13}^{∞} values obtained over the temperature range. With respect to the separation of aliphatic hydrocarbons from aromatic hydrocarbons, the ionic liquid used shows a higher selectivity than that found by previous workers using organic solvents such as *N*-methyl-2-pyrrolidinone (NMP) [35]. Many of ILs based on 1-alkyl-3-methyl-imidazolium cation show higher selectivity than conventionally used entrainers, but in many cases the capacity for NMP and sulfolane is larger.

Domanska *et al.* (2008) determined the activity coefficients at infinite dilution, γ_{13}^{∞} for 32 solutes: alkanes, alkenes, alkynes, cycloalkanes, aromatic hydrocarbons, alcohols, thiophene, tetrahydrofurane, *tert*-butyl methyl ether, and water in the ionic liquid 1-butyl-3-methylimidazolium trifluoromethanesulfonate [BMIM][CF_3SO_3] by using gas-liquid chromatography method at the temperatures ranging from 298.15 to 368.15 K. The selectivities for the hexane/benzene, cyclohexane/benzene, *n*-hexane/thiophene, *n*-decane/thiophene, cyclohexane/thiophene, toluene/thiophene, and oct-1-ene/thiophene separation problems were calculated from the γ_{13}^{∞}. It is shown that ILs demonstrates a significant influence of the anion on the γ_{13}^{∞} values. It appeared that the values were very much higher than for entrainers such as NMP[40] or sulfolane[41] which are used in separation processes of aliphatic compounds from aromatic hydrocarbons by extraction in industry.

Letcher *et al.* (2003) determined the activity coefficients at infinite dilution, γ_{13}^{∞} for both polar and nonpolar solutes in the ionic liquid 1-hexyl-3-methylimidazolium hexafluorophosphate by gas-liquid chromatography at three temperatures viz. (298.15, 313.15, and 323.15) K. The partial molar excess enthalpies at infinite dilution and the selectivity values were calculated from the γ_{13}^{∞} values obtained over the temperature range. The selectivity values have been determined and are used to predict the solvent potential of the ionic liquid for the separation of liquid mixtures by extractive distillation. The γ_{13}^{∞} and S_{12}^{∞} data presented in this work indicated that

$[HMIM^+][PF_6^-]$ is a potentially useful solvent for separating benzene (and probably other aromatic hydrocarbons) from alkanes.

Letcher *et al.* (2005) determined by using the gas–liquid chromatography method the activity coefficients at infinite dilution, γ_{13}^{∞} (where 1 refers to the solute and 3 to the solvent), for both polar and non-polar solutes (alkanes, alk-1-enes, alk-1-ynes, cycloalkanes, benzene, carbon tetrachloride, and methanol) in the ionic liquid 1-hexyl 3-methyl-imidazolium bis(trifluoromethylsulfonyl)-imide $[HMIM][Tf_2N]$ at the temperatures T = (298.15, 313.15, and 333.15) K have been determined. The partial molar excess enthalpies at infinite dilution values $\Delta H_1^{E,\infty}$ were calculated from the experimental γ_{13}^{∞} values obtained over the temperature range. It appeared that the activity coefficients and intermolecular interactions of different solutes in IL are very much dependent on the chemical structure of the ionic liquid.

Bahadur *et al*. (2016) measured the activity coefficients at infinite dilution, γ_{13}^{∞} for 29 organic solutes (alkanes, cycloalkanes, alkenes, alkynes, aromatics, alkanols and ketones) and water in ionic liquid 1-ethyl-3-methylimidazolium n-octylsulphate $[EMIM]^+[OS]^-$ at temperatures of (318.15, 333.15, 348.15 and 358.15) K using (gas + liquid) chromatography (GLC) technique. It seemed unlikely that $[EMIM]^+[OS]^-$ would be used for the chosen hydrocarbon separations in industrial processes. The experimental data reported in this study can be used to fine-tune parameters of existing models and test the validity of new thermodynamic models applicable to imidazolium-based ILs.

Ayad *et al.* (2016) determined by inverse gas chromatography in the temperature range of 313 K to 353 K the infinite dilution activity coefficients and gas-to-liquid partition coefficients for 47 and 45 organic probe molecules dissolved in 1-hexylquinuclidinium bis(trifluoromethylsulfonyl)imide ($[Quin6]^+[Tf_2N]^-$) and 1-octylquinuclidinium bis(trifluoromethylsulfonyl)imide ($[Quin8]^+[Tf_2N]^-$).

Wlazlo *et al.* (2016) determined activity coefficients γ_{13}^{∞} at infinite dilution for 64 solutes of polar and non-polar solutes as alkanes, alkenes and alkynes as well as aromatic hydrocarbons, alcohols, water, ethers, ketones, acetonitrile, pyridine, 1-nitropropane, thiophene, and esters. The effect of interaction between organic solvents or water on the interfacial and bulk properties of 1-allyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}imide ([AMIM][NTf$_2$]) by gas-liquid chromatography at six temperatures in range of (318.15–368.15) K. It showed that the solvation properties are dependent on the cation and on the anion of the IL. The results reported show the average values of selectivity and capacity for [AMIM][NTf$_2$] ionic liquid as a separation agent.

Domanska *et al.* (2016) determined the activity coefficients at infinite dilution, γ_{13}^{∞} of several solutes in ionic liquid of 1-butyl-3-methylimidazolium dicyanamide, [BMIM][DCA] by gas liquid chromatography. The values of γ_{13}^{∞} for 64 solutes, including alkanes, cycloalkanes, alkenes, alkynes, aromatic hydrocarbons, alcohols, water, ethers, ketones, acetonitrile, pyridine, 1-nitropropane, thiophene, and esters in [BMIM][DCA at six temperatures in range of (318.15-368.15) K. The gas liquid partition coefficients were calculated for all solutes. The partial molar excess Gibbs energy, enthalpy and entropy at infinite dilution were calculated from the experimental γ_{13}^{∞} values. It was observed and concluded that the hydrogen bonding between polar organic solutes and an anion of an ionic liquid has a significant impact on the interaction between a solute and an IL. It determines the enthalpic behaviour of the binary mixture as well.

Wlazlo *et al.* (2015) determined activity coefficients at infinite dilution, γ_{13}^{∞} for 65 different solutes including alkanes, alkenes, alkynes, cycloalkanes, aromatic hydrocarbons, alcohols, thiophene, ethers, ketones, aldehydes, esters and water in the ionic liquid 1-ethyl-3-methylimidazolium trifluorotris(perfluoroethyl)phosphate using inverse gas chromatography within the temperature range from 318.15 to 368.15 K. The γ_{13}^{∞} values were used to calculate thermodynamic functions such as partial molar excess Gibbs energies $\Delta G_1^{E,\infty}$, enthalpies $\Delta H_1^{E,\infty}$ and entropies $\Delta S_1^{E,\infty}$ as well as gas–liquid partition coefficients of the solutes, K_L. The selectivity values calculated in this work from γ_{13}^{∞} are higher than for [hmim][FAP], which is to be expected for ILs with other anions, while the selectivities calculated using γ_{13}^{∞} from the Yan et al. work are lower than for [hmim][FAP].

Marcinkowski *et al.* (2014) determined activity coefficients at infinite dilution of 39 different solutes in the ionic liquid 1-hexyl-1,4-diaza[2.2.2]bicyclooctanium bis(trifluoromethylsulfonyl) imide ([HDABCO][NTf$_2$]) on gas–liquid chromatography (GLC) of organic solutes including alkanes, alcohols, ketones, benzene derivatives and McReynold's compounds. Activity coefficients were measured over the temperature range (331.15–363.15) K. The partial molar excess enthalpies of mixing at infinite dilution were determined based on Gibbs Helmholtz relationship. Selectivity at infinite dilution values have been also calculated for exemplary separation processes in the systems hexane/benzene and cyclohexane/benzene. A comparison between the determined selectivity values and pertinent literature data showed that the studied ionic liquid can become an alternative to presently used solvents in cases when mixture separation poses a problem.

Martins *et al.* (2015) measured the activity coefficients at infinite dilution, γ_{13}^{∞} of 55 organic solutes and water in three ionic liquids with the common cation 1-butyl-3-methylimidazolium and the polar anions Cl$^-$, [CH$_3$SO$_3$]$^-$ and [(CH$_3$)$_2$PO$_4$]$^-$ by using (gas + liquid) chromatography method measured at temperatures ranging from (358.15 to 388.15) K for alcohols and water, and T = (398.15 to 428.15) K for the other organic solutes including alkanes, cycloalkanes, alkenes, cycloalkanes, alkynes, ketones, ethers, cyclic ethers, aromatic hydrocarbons, esters, butyraldehyde, acetonitrile, pyridine, 1-nitropropane and thiophene. It appeared that the hydrogen bonding between organic solutes and the ILs anion plays a significant role on the interaction of the ILs with organic solutes, and determines the enthalpic behaviour of the binary mixtures. The selectivities achieved were quite high and, thus, these ILs could be used as an alternative separating agent for some typical separations.

Kurnia *et al.* (2014) determined activity coefficient at infinite dilution, γ_w^{∞} of water in several classes of ILs using COSMO-RS. The global average relative deviation was found to be 27.2%, indicating that the model presents a satisfactory prediction ability to estimate γ_w^{∞} in a broad range of ILs. It showed that the basicity of the ILs anions plays an important role in their interaction with water, and determines the enthalpic behaviour of the binary mixtures composed by ILs and water. And again it was observed that γ_w^{∞} increases with the cation size, but it are shown that the cation−anion interaction strength is also important and is strongly correlated to the anion ability to interact with water. The COSMO-RS method proved to be a useful tool for explaining the impact of ILs structural variations on their interaction with water so as to screen potential ILs with improved water interactions.

Bahadur *et al.* (2014) using gas + liquid chromatography determined activity coefficients at infinite dilution γ_{13}^{∞} for 28 polar and non-polar organic solutes (alkanes, cycloalkanes, alkenes, alkynes, aromatic compounds, alcohols, and ketones) in 1-ethyl-3-methylimidazolium 2-(2-methoxyethoxy) ethylsulfate of the interactions between volatile organic compounds and the ionic liquid (IL) 1-ethyl-3- methylimidazolium 2-(2-methoxyethoxy) ethylsulfate $[EMIM]^+[MDEGSO_4]^-$ at four temperature in the range T = (308.15, 313.15, 323.15 and 333.15) K. The IL $[EMIM]^+[MDEGSO_4]^-$ showed higher S_{ij}^{∞} values than $[BMIM]^+[\text{-}MDEGSO_4]^-$ and $[OMIM]^+[MDEGSO_4]^-$ and other conventional solvents such as NMP, NFM, and sulfolane for hexane/benzene separation.

Domanska *et al.* (2014) determined the activity coefficients at infinite dilution, γ_{13}^{∞}, for 63 solutes, including alkanes, cycloalkanes, alkenes, alkynes, aromatic hydrocarbons, alcohols, water, thiophene, ethers, ketones, esters, aldehyde, acetonitrile, pyridine and 1-nitropropane and 6 diols in the ionic liquid (IL) choline bis(trifluoromethylsulfonyl)imide, $[N_{1112OH}][NTf_2]$ by using (gas + liquid) chromatography at six temperatures in range of (318.15 to 368.15) K and at three temperatures for diols in the range of (388.15 to 418.15) K. The activity coefficients at infinite dilution uniformly decrease with increasing temperatures for most of the systems. It was shown that the γ_{13}^{∞} values depend on the kind of substance and polar group, alkane chain length and the relative position of the hydroxyl group in diols.

CHAPTER 3

THEORETICAL FRAMEWORK

3.1 Density (*ρ*)

Density is defined as mass per unit volume. Generally, the density of a substance (*ρ*) is calculated by the ratio of its mass to its volume.

$$\rho = \frac{\mathrm{m}}{v} \tag{3.1}$$

where both mass (*m*) and volume (*v*) are extensive properties.

Densities (*ρ*) and related volumetric properties of liquid mixtures are required for many industrial applications as well as for theoretical calculations. Nevertheless, density of the pure solvent and their mixtures are especially valuable in distillation processes, liquid-liquid extraction, mass and heat transfer etc. (Lazaro et al., 2015, Wang et al., 2105, Karlapudi et al., 2013). Density is a function of temperature for pure liquids and it can be expressed as:

$$\rho = kT + m' \tag{3.2}$$

where ρ is the density, *k* and m' are constants and *T* is temperature.

3.2 Excess molar volume (V_m^E)

The excess molar volume is one of the fundamental thermodynamic properties of liquid mixtures. The excess molar volume V_m^E is defined as (Walas 1985, McGlashan 1979, Letcher, 1975):

$$V_\mathrm{m}^\mathrm{E} = V_\mathrm{mixture} - \sum x_\mathrm{i} V_\mathrm{i}^0 \tag{3.3}$$

where x_i is the mole fraction of component *i*, V_mixture and V_i^0 are the molar volumes of the mixture and component *i*, respectively. However, the excess molar volumes of the solutions for binary liquid mixtures were calculated from the densities of pure liquids and their mixtures by using the following equation:

$$V^E = \frac{\sum_i^n = x_i M_i}{\rho m} - \sum_i^n = 1 \frac{x_i M_i}{\rho i} \tag{3.4}$$

where *x*, *M* and *ρ* are mole fraction, molar mass and density, respectively. *i* and *m* represent pure components and mixtures, respectively.

In addition, the excess molar volume (V_{123}^E) were calculated from the experimental densities of ternary liquid mixtures by using the following equation:

$$V_{123}^E = \frac{\sum_{i=1}^n x_i M_i}{\rho_m} - \sum_{i=1}^n \frac{x_i M_i}{\rho_i} \tag{3.5}$$

where x_i, M_i and ρ_i are represent the mole fraction, molar mass and pure densities of IL, acetonitrile and acetic acid or propionic acid respectively, n is number of components in the mixture and ρ_m indicates density of the ternary mixture. The excess molar volumes for binary or ternary liquid mixtures are derived from experimental density results which are very valuable to obtain the information about intermolecular interactions and geometrical effects between the component molecules. Likewise, the excess molar volume of liquid mixtures play a significant role in helping to specific interactions such as differences in the molecular size, shape, structural effects arising from interstitial accommodations and the continuation of solution theories because they depend on the intermolecular interactions such as hydrogen donor or acceptor specifically in liquid mixtures, dipole-dipole and van der Waal interactions.

Computation of binary excess molar volumes from different predictive expression

Binary excess volumes V_{AB}^{E} can be calculated using the predictive expressions proposed by (Redlich and Kister 1948).

According to Redlich-Kister

$$V_{AB}^{E} = \sum_{i<j} V_{ij}^{E}\,(x_i x_j)$$

$$V_{AB}^{E} = \left[\frac{x_A M_A + x_B M_B}{\rho_{mix}} - \left(\frac{x_A M_A}{\rho_A} + \frac{x_B M_B}{\rho_B}\right)\right] \tag{3.6}$$

where $V_{AB}^{E} = x_A\, x_B \sum_{i=0}^{n} (A_s)_{AB}(x_A - x_B)^s$ and $x_{A,}x_B$ are the mole fractions and M_A, M_B are molar masses of the components in a binary mixture.

Correlation of excess molar volumes by the Lorentz-Lorenz approximation

Correlation of the excess molar volume of liquid mixtures can be obtained using the refractive index obtained for the binary mixtures by the Lorentz-Lorenz approximation. Within the framework of the Lorentz-Lorenz approximation, $V_{\mathrm{m}}^{\mathrm{E}}$ can be correlated via the change in reduced free volume, namely:

$$\Delta\left(\frac{V_{\mathrm{m,f}}}{R}\right) = \frac{V_{\mathrm{m,f}}}{R} - \left(\frac{V_{\mathrm{m,f}}}{R}\right)^{\mathrm{id}} \tag{3.7}$$

where:

Application of the Lorentz-Lorenz equation allows this expression to be reduced to:

$$\Delta\left(\frac{V_{\mathrm{m,f}}}{R}\right)=\frac{3}{n^2-1}-\frac{3}{\left(n^{\mathrm{id}}\right)^2-1} \qquad (3.8)$$

The assumption $R = R^{\mathrm{id}}$, is most often a highly accurate approximation. The following expression can then be obtained from equation (3.8).

$$\Delta\left(\frac{V_{\mathrm{m,f}}}{R}\right)=\frac{V_{\mathrm{m}}^{\mathrm{E}}}{R} \qquad (3.9)$$

Therefore,

$$V_{\mathrm{m}}^{\mathrm{E}}=(-\Delta n)\frac{3R\left(n^{\mathrm{id}}+n\right)}{\left(n^2-1\right)\left(\left(n^{\mathrm{id}}\right)^2-1\right)}=(-\Delta n)f\left(R,n^{\mathrm{id}},n\right) \qquad (3.10)$$

Computation of ternary excess molar volumes from different predictive expressions

Excess molar volumes of ternary liquid mixtures can be calculated using the predictive expressions proposed by (Tsao-Smith., 1953), (Kohler., 1960), (Jacob-Fitzner., 1977), (Redlich-Kister., 1948) and (Cibulka., 1982).

(a) Tsao-Smith equation

$$V_{123}^{\mathrm{E}}=x_2(1-x_1)^{-1}\,V_{12}^{\mathrm{E}}+x_3(1-x_1)^{-1}\,V_{13}^{\mathrm{E}}+(1-x_1) \qquad (3.11)$$

where V_{12}^{E}, V_{13}^{E} and V_{23}^{E} are the excess molar volumes of binary liquid mixtures at composition $(x_{\mathrm{i}}', x_{\mathrm{j}}')$, such that $x_{\mathrm{i}}' = x_1$ for 1,2 and 1,3 binary systems and $x_2' = x_2/(x_2+x_3)$ for 2, 3 binary system.

(b) Kohler's equation

$$V_{123}^{\mathrm{E}}=(x_1+x_2)^2\,V_{12}^{\mathrm{E}}+(x_1+x_3)^2\,V_{13}^{\mathrm{E}}+(x_2+x_3)^2\,V_{23}^{\mathrm{E}} \qquad (3.12)$$

where

$$V_{\mathrm{ij}}^{\mathrm{E}}=x_{\mathrm{i}}'x_{\mathrm{j}}'\sum_{\mathrm{s}=0}^{\mathrm{n}}(A_{\mathrm{s}})_{\mathrm{i\,j}}\,\left(x_{\mathrm{i}}'-x_{\mathrm{j}}'\right)^{\mathrm{s}}$$

at composition $(x_{\mathrm{i}}', x_{\mathrm{j}}')$, such that

$$x_{\mathrm{i}}'=1-x_{\mathrm{j}}'=x_i/(x_i+x_j)$$

where x_{i} and x_{j} are the ternary mole fractions.

(c) Acob-Fitzner equation

$$V_{123}^{\mathrm{E}} = \frac{x_1 x_2 V_{12}^{\mathrm{E}}}{(x_1 + x_3/2)(x_2 + x_3/2)} + \frac{x_1 x_3 V_{13}^{\mathrm{E}}}{(x_1 + x_2/2)(x_3 + x_2/2)} + \frac{x_2 x_3 V_{23}^{\mathrm{E}}}{(x_2 + x_1/2)(x_3 + x_1/2)} \qquad (3.13)$$

where V_{12}^{E}, V_{13}^{E} and V_{23}^{E} are the binary excess molar volumes at composition $(x_{\mathrm{i}}', x_{\mathrm{j}}')$, such that $x_{\mathrm{i}} - x_{\mathrm{j}} = x_{\mathrm{i}}' - x_{\mathrm{j}}'$.

(d) Redlich-Kister equation

$$V_{123}^{\mathrm{E}} = \sum_{\mathrm{j}>i} V_{\mathrm{m,ij}}^{\mathrm{E}} \left(x_{\mathrm{i}}, x_{\mathrm{j}}\right), \qquad (3.14)$$

where

$$V_{\mathrm{ij}}^{\mathrm{E}} = x_{\mathrm{i}} x_{\mathrm{j}} \sum_{\mathrm{s}=0}^{\mathrm{n}} (A_{\mathrm{s}})_{\mathrm{i\,j}} \left(x_{\mathrm{i}} - x_{\mathrm{j}}\right)^{\mathrm{s}}$$

x_{i} and x_{j} are the mole fractions of the component in ternary liquid mixture and *s* is the number of parameters.

(e) Cibulka's equation

$$V_{123}^{\mathrm{E}} = \sum \frac{x_{\mathrm{i}} x_{\mathrm{j}}}{x_{\mathrm{i}}' x_{\mathrm{j}}'} V_{\mathrm{i\,j}}^{\mathrm{E}} \left(x_{\mathrm{i}}', x_{\mathrm{j}}'\right) \qquad (3.15)$$

where $V_{\mathrm{i\,j}}^{\mathrm{E}}$ is the binary excess molar volume at $(x_{\mathrm{i}}', x_{\mathrm{j}}')$ composition, such that $x_{\mathrm{i}}' + x_{\mathrm{j}}' = 1$. x_{i}' and x_{j}' can be obtained as projections in the triangle vector diagram as normal, direct and parallel projections.

(i) For normal projection

$$x_{\mathrm{i}}' = \frac{(1 + x_{\mathrm{i}} - x_{\mathrm{j}})}{2}, \quad x_{\mathrm{j}}' = \frac{(1 + x_{\mathrm{j}} - x_{\mathrm{i}})}{2},$$

and $$V_{123}^{E} = \sum\nolimits_{\mathrm{i}<\mathrm{j}} \frac{4 x_{\mathrm{i}} x_{\mathrm{j}}}{1 - (x_{\mathrm{i}} - x_{\mathrm{j}})^2} V_{\mathrm{ij}}^{\mathrm{E}}\left(x_{\mathrm{i}}', x_{\mathrm{j}}'\right) \qquad (3.16)$$

This relation is the similar to Redlich- Kister expression.

(ii) For direct projection

$$x_{\mathrm{i}}' = \frac{x_{\mathrm{i}}}{x_{\mathrm{i}} + x_{\mathrm{j}}}, \quad x_{\mathrm{j}}' = \frac{x_{\mathrm{j}}}{x_{\mathrm{i}} + x_{\mathrm{j}}}$$

and $$V_{123}^{E} = \sum\nolimits_{\mathrm{i}<\mathrm{j}} (x_{\mathrm{i}} - x_{\mathrm{j}})^2 V_{ij}^{\mathrm{E}}\left(x_{\mathrm{i}}', x_{\mathrm{j}}'\right) \qquad (3.17)$$

This is similar to Kohler's expression.

(iii) For parallel projection

The binary contributions can be written as the arithmetic mean contribution of the points of ternary compositions.

$x_{\mathrm{i}}'(1) = x_{\mathrm{I}}, x_{\mathrm{j}}'(1) = 1 - x_{\mathrm{I}}$ and $x_i'(2) = 1 - x_j,\ x_j'(2) = x_j$

This yields the relation

$$V_{123}^{\mathrm{E}} = \frac{1}{2} \sum_{\mathrm{i}<j} \frac{x_{\mathrm{j}}}{1-x_{\mathrm{i}}} V_{\mathrm{ij}}^{\mathrm{E}}\left(x_{\mathrm{i}}, 1 - x_{\mathrm{j}}\right) + \frac{x_{\mathrm{i}}}{1-x_{\mathrm{j}}} V_{\mathrm{ij}}^{\mathrm{E}}\left(1 - x_{\mathrm{j}},\ x_{\mathrm{i}}\right) \tag{3.18}$$

In the present study, the ternary excess molar volumes of liquid mixtures are correlated by using the binary excess molar volume parameters with aid of the Cibulka equation.

3. 3 Sound velocity

The sound velocity is another essential property of liquids (ILs or organic solvents) and their mixtures to detect the molecular interactions. The measurement of sound velocity in liquids provides a means for obtaining some equilibrium thermodynamic data which are not readily obtained by other experimental methods. The sound velocity was recognized as a very useful physicochemical research tool in 1930. From that time, the development and application of sound velocity techniques have increased rapidly and attained a level of precision that has prompted wide spread investigations concerning the theoretical aspects of thermodynamic and kinetic properties of solutions and binary mixtures. According to Langeman and Correy (1942) sound velocity in liquids is defined as the sum of ‘bond velocities’. Samal and Misra (1972), Aziz *et al.* (1972), Auslander and Onitiu (1971), Poole and Aziz (1972) and Younglove (1965), showed that there is a close relation between sound velocity and deviation or excess thermodynamic properties in liquid mixtures. Eyring and Hirschfelder (1937), Hirschfelder *et al.* (1937), Kincaid and Eyring (1937) states that molecules in the liquid state are loosely packed so as to leave some free space in between them. The sound velocity of liquids u_{liq} can be calculated from the free volume (*V*). However, free volume depends upon the model of liquid assumed and the calculation of *V* gives different values. Kittel (1946) derived a simpler relation for u_{liq} using Tonk’s equation (1936) as,

$$u_{\mathrm{liq}} = \left(\frac{V}{V_{\mathrm{a}}}\right)\left(\frac{3\gamma_{\mathrm{lib}}}{\gamma_{\mathrm{gas}}}\right)^{1/2} u_{\mathrm{gas}} \tag{3.19}$$

The relation gives a satisfactory estimate of sound velocity in some liquids.

Correlation of sound velocity of liquid mixtures from different theories of sound

The sound velocity of liquid mixtures can be calculated by using the different predictive expressions by Free Length Theory (FLT), Collision Factor Theory (CFT), Nomoto relation (NM) and Impedance Dependence Relation (IDR).

(a) Free length theory (FLT)

The main concept of intermolecular free length is the distance between surfaces of two molecules. Jacobson (1951) introduced free length theory to explain the sound velocity in pure liquids and their liquid mixtures. According to Jacobson

$$u_{\mathrm{lib}} = \frac{K}{L_{\mathrm{f}}\,\rho^{1/2}} \tag{3.20}$$

where *K* is a temperature dependent constant, ρ is the density and L_f is the free length in the liquid. Free length theory (FLT) of Jacobson was used by different investigators (Rai *et al.* 1989, Savaroglu and E. Aral 2005; 2006, Mahajan et al., 2012, Altuwaim et al., 2012 and Prakash *et al.* 1975) to evaluate the sound velocities in the liquid mixtures. In a mixtures (binary or ternary):

$$u_{\mathrm{mix}}\, L_{\mathrm{mix}}\, \rho_{\mathrm{mix}}^{1/2} = K \tag{3.21}$$

where u_{mix} and ρ_{mix} are sound velocity and density of liquid mixtures respectively. L_{mix} is the free length in the mixture. Free length (L_{f}) of pure liquids is calculated using the relation:

$$L_{\mathrm{f}} = \frac{K}{u_{\mathrm{exp}}\, \rho_{\mathrm{exp}}^{1/2}} \tag{3.22}$$

where u_{exp} and ρ_{exp} are experimentally determined sound velocity and density of liquid mixtures respectively. The surface area *Y*, per mole for the pure component is calculated using the following expression:

$$Y = \frac{2V_{\mathrm{a}}}{L_{\mathrm{f}}} \tag{3.23}$$

and $V_{\mathrm{a}} = V_{\mathrm{T}} - V_0$, where V_{a} is the available volume per mole, and V_0 and V_{T} are the molar volumes at absolute zero and at absolute temperature *T*, respectively. The values of V_0 were obtained using critical temperature as shown below (next page):

$$V_0 = V_{\mathrm{T}}\left(1 - \frac{T}{T_{\mathrm{C}}}\right)^{0.3} \tag{3.24}$$

L_{mix} is calculated employing the expression:

$$L_{\mathrm{mix}} = \frac{2[V - \sum_{i=1}^{3} x_{\mathrm{i}} V_0^{\mathrm{i}}]}{\sum_{\mathrm{i}=1}^{3} x_{\mathrm{i}} y_{\mathrm{i}}} \tag{3.25}$$

where x_{i} and V_0^{i} represents mole fraction and molar volume at absolute zero of component *i*, respectively, and *V* represents the molar volume of mixture.

(b) Collision Factor Theory (CFT)

Schaaffs (1940; 1974) developed the following formula for sound velocity in pure liquids on the basis of collision factor theory (CFT)

$$u = u_{\infty}\, S\, r_{\mathrm{f}} = u_{\infty}\, S\, \frac{\mathrm{B}}{\mathrm{V}} \tag{3.26}$$

where u_{∞} = 1600 m.s^{-1}, *S* is the collision factor, $r_{\mathrm{f}} = B/V$ is the space filling factor, *B* is the actual volume of the molecules per mole of liquid. Nutsch-Kuhnkies (1965) extended this concept to the binary liquid mixtures and showed that:

$$u_{\mathrm{mix}} = u_{\infty}\, S_{\mathrm{mix}}\, r_{\mathrm{f\,mix}} \tag{3.27}$$

This may be written as:

$$u_{\mathrm{mix}} = u_{\infty}[x_1 S_1 + x_2 S_2]\, \frac{[x_1 B_1 + x_2 B_2]}{V} \tag{3.28}$$

Rai *et al.* (1989) extended such studies to the ternary liquid mixtures to show that:

$$u_{\mathrm{mix}} = u_{\infty}[x_1 S_1 + x_2 S_2 + x_3 S_3]\, \frac{[x_1 B_1 + x_2 B_2 + x_3 B_3]}{V} \tag{3.29}$$

The suffixes 1, 2 and 3 denote the components 1, 2 and 3, respectively. The actual volume of the molecule per mole for the pure components is given by *B* and is calculated using the following equation:

$$B = \frac{4\pi}{3} r_{\mathrm{m}}^3\, N \tag{3.30}$$

where r_{m} is the molecular radius and *N* is the Avogadro number. The value of r_{m} has been obtained from Schaaff `s semi-empirical formula (3.31) and expression (3.32) suggested by Rao and Venkataseshaiah (1969).

$$\mathrm{r_m} = \sqrt[3]{a\left[1 - b\,\left(\sqrt{1 + 1/3b - 1}\right)\right]} \tag{3.31}$$

$\mathrm{r_m} =$

$$\sqrt[3]{a\left[1-b\left(\sqrt{1+\ 1/b-1}\right)\right]} \tag{3.32}$$

a and *b* of the above equations are given by

$$a = \frac{3V}{16\pi N} \ \ and \ \ b = \frac{\gamma RT}{MU^2} \tag{3.33}$$

where γ and *M* are specific heat ratio and molecular weight, respectively and other symbols have their usual meanings. The molecular diameter d, ($d = 2r_\mathrm{m}$) of pure liquids can also be computed from the data of surface tension (σ) and critical temperature (T_c) of pure liquids using the equation (Chaturvedi *et al.* 1979).

$$d^{5/2} = \frac{1}{7.21\times10^{19}} \cdot \frac{V\sigma^{1/4}}{T_\mathrm{C}^{1/4}} \tag{3.34}$$

(c) Nomoto relation

For sound velocity in binary liquid mixtures the following relation is developed by Nomoto (1956; 1958):

$$u = \left[\frac{x_1R_1+x_2R_2}{x_1V_1+x_2V_2}\right]^3 \tag{3.35}$$

Rai *et al.* (1989) extended the above equation for sound velocity to ternary liquid mixtures:

$$u = \left[\frac{x_1R_1+x_2R_2+x_3R_3}{x_1V_1+x_2V_2+x_3V_3}\right]^3 \tag{3.36}$$

where *x* and *V* are the mole fraction and molar volume respectively, *R* is molecular sound velocity and is related to molecular weight (M_i) sound velocity (*u*) and density (ρ_i) of the component *i*, as follows:

$$R_i = \frac{M_i}{\rho_i}\ u_i^{1/3} \tag{3.37}$$

The experimental and computed sound speed data of all the liquid mixtures were compared by calculating the relative root mean square deviation (Altuwaim et al., 2012).

$$\mathrm{RMSD} = \left[\frac{1}{n}\sum_{i=1}^{n}\left[\frac{y_{exp}-y_{pred}}{y_{exp}}\right]^2\right]^{1/2} \tag{3.38}$$

3.4 Isentropic compressibility

Isentropic compressibility (κ_S) is another thermodynamic property which influences the interactions between the molecules in the binary or ternary liquid mixtures, which can be defined as

$$\kappa_S = \frac{-1}{V}\left(\frac{\partial V}{\partial P}\right) \tag{3.39}$$

The isentropic compressibilities (k_s) were calculated by the indirect method from the Newton-Laplace equation given below for binary or ternary liquid mixtures:

$$k_s = \frac{1}{u^2 \rho} \tag{3.40}$$

where ρ is the density and u is the speed of sound of the binary mixtures.

$$k_{s123} = \frac{1}{u_{123}^2 \rho_{m123}} \tag{3.41}$$

where ρ_{m123} and u_{123} represents the density and speed of sound of the ternary mixtures.

The above equations was used in this work for the calculation of the deviation in isentropic compressibility for the binary/ternary liquid mixtures. Rao and Naidu (1974) defined a quantity $\Delta\kappa_S$ for binary or ternary liquid mixtures:

$$\Delta\kappa_S = \kappa_s - \kappa_s^{id} \tag{3.42}$$

where $\Delta\kappa_S$ is the deviation in isentropic compressibilities, κ_s and κ_s^{id} are the isentropic compressibilities for the real and ideal mixtures, respectively.

The ideal isentropic compressibility is calculated using the relation:

$$\kappa_s^{id} = \sum_{i=1}^{n} \Phi_i \kappa_{si} \tag{3.43}$$

where Φ_i and κ_{si} are volume fraction and isentropic compressibility of pure component i, respectively. In this perspective, have been calculated from deviations in isentropic compressibility for binary or ternary liquid mixtures, however deviation in isentropic compressibilities ($\Delta\kappa_S$) are also used to study the departure of a real mixtures from ideality and to understand the nature and strength of interactions between molecules in a liquid mixture.

The difference between the compressibility of a real solution and that of an ideal solution is called excess or deviation in isentropic compressibility. Unlike excess volume and excess enthalpy, excess compressibility is a complicated function expressed by:

$$\kappa^{\mathrm{E}} = -\frac{1}{V}\left(\frac{\partial \mathrm{V}}{\partial \mathrm{P}}\right)_{\mathrm{T}} + \left[\frac{1}{x_1V_1 + x_2V_2 + x_3V_3}\right]\left[\frac{\partial\,(x_1V_1 + x_2V_2 + x_3V_3)}{\partial P}\right]_{\mathrm{T}} \tag{3.44}$$

where V_1, V_2 and V_3 are molar volumes of pure components 1, 2 and 3, respectively at constant pressure and temperature. By introducing excess volume of the solutions equation (3.44) can be converted into the form:

$$\kappa^{\mathrm{E}} = -\frac{1}{V}\left(\frac{\partial \mathrm{V}}{\partial \mathrm{P}}\right)_{\mathrm{T}} + \left[\frac{V^{\mathrm{E}}}{x_1V_1 + x_2V_2 + x_3V_3}\right]\left[\frac{(\kappa_1x_1V_1 + \kappa_2x_2V_2 + \kappa_3x_3V_3)}{(x_1V_1 + x_2V_2 + x_3V_3)}\right] \tag{3.45}$$

where κ^{E} is made up of two terms: one is proportional to V^{E} and other to $\left(\frac{\partial \mathrm{V}}{\partial \mathrm{P}}\right)$. An attempt to formulate a theoretical expression for compressibility was made after the publication of the average potential model (Prigogine and Garikian 1950, Prigogine and Mathot 1952). Compressibility data relating to many liquid mixtures were used to test this theory. The agreement between theoretical and experimental values was found to be good (Reddy *et al.* 1964; Jeener 1956; Sackmann and Boczek 1961; Holder and Whalley 1962).

Flory and Abe (1965) defined excess compressibility as:

$$\kappa^{\mathrm{E}} = -\frac{1}{V}\left(\frac{\partial V^{E}}{\partial P}\right)_{T} = -\frac{1}{V}\left(\frac{\partial \bar{V}^{E}}{\partial P}\right)_{T} \tag{3.46}$$

where

$$\bar{V} - \bar{V}^{0} = \bar{V}^{\mathrm{E}} = \frac{V^{\mathrm{E}}}{x_1V_1^* + x_2V_2^*} \quad \text{and} \quad \bar{V}^{0} = \Phi_1\bar{V}_1 + \Phi_2\bar{V}_2$$

Φ_1 and Φ_1 are segment fractions, V_1^* and V_2^* are characteristic volumes.

The equation (3.47) can be expressed as:

$$\kappa^{\mathrm{E}} = \kappa - \left(\Phi_1\bar{V}_1\kappa_1 + \Phi_2\bar{V}_2\kappa_2\right)\bar{V}^{-1} \tag{3.47}$$

The compressibility,κ, is evaluated from an equation of state. The equation for excess compressibility setting P = 0 may be written in the form:

$$\kappa^{\mathrm{E}} = \frac{3\bar{V}^{2}}{P^{*}}\left(\left[(i^{\frac{1}{3}}-1)^{-1}-3\right]^{-1} - \left[\Phi_1\bar{V}_1\kappa_1 + \Phi_2\bar{V}_2\kappa_2\right]\bar{V}^{-1}\right) \tag{3.48}$$

The excess compressibilities predicted by the above equation were compared with experimental results for a number of binary liquid mixtures by Flory and Abe (1965).

Furthermore, the values of excess isentropic compressibilities (k_s^E) were calculated from the following relations recommended by (Benson and Kiyohara 1979, Douheret and Moreau 1985).

$$k_s^E = k_S - k_s^{id} \tag{3.49}$$

$$k_S^{id} = \sum_{\mathrm{i=1}}^{2}\phi_{\mathrm{i}}\left[\kappa_{\mathrm{s},i} + TV_i\left(\alpha_i^{2}\right)/\,C_{p,i}\right] - \left\{T\left(\sum_{i=1}^{2}x_iV_i\right)\left(\sum_{i=1}^{2}\phi_i\alpha_i\right)^{2}/\sum_{i=1}^{2}x_iC_{p,i}\right\} \tag{3.50}$$

here, $C_{\mathrm{p,i}}$ and α_i are the molar heat capacity and the thermal expansion coefficient of the ith component, respectively. The values α_i of have been calculated from the equation $\alpha_i = \left(\partial \mathrm{V}/\partial T\right)_P/V = -1/\rho\left(\partial\rho^{-1}/\partial \mathrm{T}\right)_P$.The volume fraction ϕ_i was calculated using equation given below:

$$\phi_i = x_iV_i \Big/ \Sigma_{i=1}^{n}x_iV_i \tag{3.51}$$

3.5 Methods of determining activity coefficients at infinite dilution

3.5.1 Predictive methods of determining the infinite dilution activity coefficient

It would be nearly impossible to synthesise and characterise every property of all possible combinations of cations and anions. Chiappe and Pieraccini (2003) suggest that in order to take full advantage of these relatively new chemicals, correlations and predictive models must be made between the various properties and molecular structures. Two commonly used models will be described briefly.

3.5.1.1 UNIFAC

The Universal Quasichemical Functional Group Activity Coefficients (UNIFAC) (Fredenslund et al., 1975) is probably the most used predictive tool for determining phase equilibria, especially vapour liquid equilibria (VLE). The model was originally designed for molecular mixtures, but with improvements such as those by Wang et al. (2008) have extended this to certain ionic groups including ionic liquids. This method is still in development for activity coefficients at infinite dilution in ionic liquids, and this current study could be used to improve the model in future.

3.5.1.2 COSMO

The conductor-like screening model for real solvents (COSMO-RS) and the variation called the segment activity coefficient model (COSMO-SAC) uses intermolecular quantum-mechanics to predict thermodynamic information (Constantinescu et al., 2005) . While this method is very powerful and does not rely heavily on experimental data, it is still in early development for ionic liquids and profiles required by the model have not been evaluated as yet.

3.5.2 Determination of partial excess enthalpies at infinite dilution

From the Gibbs-Helmholtz equation, the partial excess enthalpy ($H_i^{E,\infty}$) of a solute at infinite dilution can be determined, using the relationship the activity coefficients of a solute have with temperature:

$$\frac{\partial(\ln\gamma_{is}^{\infty})}{\partial(1/T)}=\frac{\Delta H_i^{E,\infty}}{R} \tag{3.52}$$

where T is the absolute temperature and R the universal gas constant. $H_i^{E,\infty}$ can be determined from the linear regression of the natural logarithm of the IDACs with the inverse of temperature:

$$\ln\gamma_{is}^{\infty}=a+\frac{b}{T} \tag{3.53}$$

where a and b are constants from regression. Typically an R_c value (the correlation coefficient) is presented as a measure of the accuracy of the equation.

3.5.3 The theory behind gas-liquid chromatography

Gas-liquid chromatography was used to measure the activity coefficients at infinite dilution for all solutes in this study. This was especially suited to the non-volatile ionic liquid solvents being tested, and will be reviewed in the experimental section (**Gas-liquid chromatography).** In using this method, Tumba (2010) outlines 3 assumptions that are considered:

1. The vapour or gas phase, composed of a solute (1) in a carrier gas (2) forms an ideal mixture.
2. The stationary phase forms a real liquid mixture with the solute (1) and solvent (3).
3. The gas and liquid phases are in thermodynamic equilibrium.

The most widely accepted equation for determining the IDAC value of a solute (1) in a solvent (3) using the GLC technique has been that developed by Everett (1965) and Cruickshank et al. (1969):

$$\ln \gamma_{13}^{\infty} = \ln\left(\frac{n_3RT}{V_NP_1^*}\right) - \frac{P_1^*\left(B_{11}\text{-}v_1^*\right)}{RT} + \frac{P_oJ_2^3(2B_{12}\text{-}v_1^{\infty})}{RT} \qquad (3.54)$$

where $\ln \gamma_{13}^{\infty}$ is the natural logarithm of the infinite dilution activity coefficient of solute (1) in a solvent (3), n_3 the number of moles of solvent in the stationary phase, R the universal gas constant, V_N the retention volume of the solute given by equation (3.57), $P_1{}^*$ the saturated vapour pressure of the solute, B_{11} the second viral coefficient of pure solute, v_1^* the molar volume of solute, P_o the outlet pressure, $P_oJ_2^3$ the mean system pressure, B_{12} the second virial cross-coefficient between the solute and carrier gas, and v_1^{∞} the partial molar volume of the solute at infinite dilution. The value of v_1^{∞} can be approximated as equal to v_1^* in the absence of data or when it is insignificant to the value of B_{12} (Everett, 1965).

The retention volume is given by: $V_N = J_2^3(t_R\text{-}t_G)q_{ov}$ (3.55)

where t_R is the retention time of the solute in the stationary phase, t_G the non-retainable gas retention time (dead time) and q_{ov} the corrected carrier gas flow rate, given by equation (3.56) for a soap bubble column (see figure in experimental section: Schematic of the GLC apparatus)

$$q_{ov} = q_o\left(\frac{T}{T_f}\right)\left[1 - \frac{P_w^*}{P_o}\right] \qquad (3.56)$$

where q_o is the measured flow rate, T_f the flow-meter temperature and P_w^* the saturated vapour pressure of water at T_f.

The pressure correction term, J_2^3, is given by:

$$J\frac{2}{3} = \frac{2}{3}\left(\frac{P_i / P_o)^3 - 1}{(P_i / P_o)^2 - 1}\right) \qquad (3.57)$$

where P_i is the inlet pressure of the column.

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

$$\frac{BP_c}{RT_c} = \frac{B}{V^*} = f^{(0)} + \omega f^{(1)} + af^{(2)} + bf^{(3)} \tag{3.58}$$

where
$$f^{(0)} = 0.1445 - \frac{0.330}{T_r} - \frac{0.1385}{T_r^2} - \frac{0.0121}{T_r^3} - \frac{0.000607}{T_r^8} \tag{3.59}$$

$$f^{(1)} = 0.0637 + \frac{0.331}{T_r^{\,2}} - \frac{0.423}{T_r^{\,3}} - \frac{0.008}{T_r^{\,8}} \tag{3.60}$$

$$f^{(2)} = \frac{1}{T_r^{\,6}} \tag{3.61}$$

$$f^{(3)} = -\frac{1}{T_r^{\,8}} \tag{3.62}$$

$$T_r = \frac{T}{T_c} \tag{3.63}$$

B is the virial coefficient, P_c, the critical pressure, T_c, the critical temperature, V^*, the characteristic volume, ω, the accentric factor, and T_r the reduced temperature. For values of a and b, correlations were used from the work of Tsonopoulos and Heidman (1990), and Tsonopoulos and Dymond (1997).

The cross virial coefficient, B_{12}, is calculated by equation (3.58), with mixing rules of Tsonopoulos (1974):

$$T_{cij} = \left(T_{cii}T_{cjj}\right)^{1/2}\left(1 - k_{ij}\right) \tag{3.64}$$

$$V_{ij}^* = \frac{\left(V_{cii}^{1/3} + V_{cjj}^{1/3}\right)^3}{4(Z_{cii} + Z_{cjj})} \tag{3.65}$$

$$\omega_{ij} = (\omega_{ii} + \omega_{jj})/2 \tag{3.66}$$

$$a_{ij} = (a_{ii} + a_{jj})/2 \tag{3.67}$$

$$b_{ij} = (b_{ii} + b_{jj})/2 \tag{3.68}$$

where k_{ij} is the binary interaction parameter and V_c, the critical volume. An estimation of the binary interaction parameter is given by the relationship of Chueh and Prausnitz (1967) for a reduced dipole moment (μ_r) close to zero.

$$k_{ij} = 1 - \left[\frac{2\left(V_{cii}V_{cjj}\right)^{1/6}}{\left(V_{cii}^{1/3}+V_{cjj}^{1/3}\right)}\right]^3 \tag{3.69}$$

The molar volume can be estimated from the Yamada and Gunn (1973) modification of the Rackett (1970) model:

$$V_s = V_c(0.29056 - 0.08775\ \omega)^{(1-T_r)^{2/7}} \tag{3.70}$$

where V_s is the saturated liquid molar volume.

Saturated vapour pressures were estimated using the Antoine's equation. Critical properties (P_c, T_c, V_c), the accentric factor (ω), and Antoine's coefficients were taken from various literature sources, all available in appendix C.

3.5.4 Calculation of uncertainty

Uncertainties for all calculated values were obtained via the law of propagation of uncertainties, which incorporates the uncertainties inherent to measuring devices (accuracy, repeatability etc. of sensors), and amongst other contributions, the repeatability in measurement. This is fully explained by Taylor and Kuyatt (1994) and the reader is referred to this text for further enlightenment. The main equation used is given by:

$$\mathrm{u}(\theta)=\sqrt{\sum_{i=1}^{y}\left[\frac{\partial\theta}{\partial x_i}\ u(x_i)\right]^2} \tag{3.71}$$

where θ is the calculated variable (γ_{13}^{∞} for this work), y is the number of independent variables and x_i is an independent variable used in calculating θ. In taking account repeatability of type A distributions of q repetitions, the error (u_r) by is given by the standard deviation:

$$\mathrm{u}_r(\theta) = \sigma = \sqrt{\frac{1}{n-1}\sum_{j=1}^{q}\left(\theta_j - \bar{\theta}\right)^2} \tag{3.72}$$

where θ_j is j^{th} repetition and $\bar{\theta}$ is the mean value of θ.

3.6 Theory of solutions

The theories of solutions are related excess molar volumes of binary liquid mixtures have been reviewed and discussed by (Williamson and Scott, 1970, Rowlinson, 1970, Flory, 1970, Hijmans *et al.* 1969, Scott and Fenby, 1969, Henderson, 1974, Battino, 1971, Stokes and Marsh, 1972, Patterson and Bardin, 1970, Handa and Benson 1979, Kehiaian, 1972, Tager and Adamova, 1980, Sanchez and Lacombe, 1976).

Scatchard (1931; 1932; 1934; 1937) formulated an equation for excess volume according to the Hildebrand (1929) concept of regular solution.

$$V^{\mathrm{E}} = nkU_{\mathrm{V}}^{\mathrm{E}} = nkG^{\mathrm{E}} \tag{3.73}$$

where n is the ratio of the internal pressure to the cohesive energy assumed to be the same for the pure and mixed component and k is the bulk compressibility which is assumed to be strictly additive in terms of volume fraction

Longuet-Higgins (1951) suggested an equivalent equation using the first order conformal solution theory. The equation takes the form

$$V^{\mathrm{E}} = \frac{\propto TG^{\mathrm{E}}}{\delta^2} \tag{3.74}$$

where $\propto$ is the thermal expansion coefficient. It is assumed to be strictly additive in terms of volume fraction of the components, δ is the solubility parameter of the mixture and is assumed to be the simple average:

$$\delta = \frac{\delta_1 + \delta_2}{2} \tag{3.75}$$

where δ_1 and δ_2 are solubility parameters for component 1 and 2, respectively.

Eyring (1936) was introduced the first cell-model of the liquid state. Furthermore, this model was used by Lennard-Jones and Devonshire (1937; 1938) and Prigogine and Garikian (1950) to relate the thermodynamic properties of liquid mixtures to intermolecular energy parameters. This model was also developed by Prigogine and Mathhot (1952) to permit G^{E} and V^{E} to have opposite signs (Mathot *et al.* 1953; 1956). It was assumed that cells of two different sizes exist in the liquid mixtures, cells containing molecules of species 1 and 2. The ratio of the diameters of the cells is then chosen so as to minimize the free energy of mixture. It was shown that a relatively large positive excess volume would result from quite a small difference in molecular size. It follows from this that negative excess volume which should occur for mixtures of molecules of the same size would only rarely be observed. However, application of cell model theory to binary liquid mixtures showed that experimental excess functions are in poor agreement with those predicted by the model.

Leland *et al.* (1968; 1969) proposed a statistical theory of liquid state. These workers used an approximation for a mixture of the type originally suggested by van der Waals in regard to parameters of the equation of state. Hence the theory was designed as ‘one-liquid’ van der Waals approximation to a ‘two-liquid’ model, which took into account the departure from a random distribution induced by differences in intermolecular energy.

Prigogine *et al.* (1953) extended the corresponding states approach, on the basis of the cell model, to chain molecules. The chain molecule was considered as a series of quasi-spherical segments. Balescu and Bull (1955) extended Prigogine’s average potential model to the solutions which included molecules differing in size and polarity. The equation for an excess peoperty included the two terms (a) contribution of central forces and (b) contribution due to orientataional forces of dipolar origin. This equation failed to predict quantitavely excess volume and excess enthalpy.

Ohta *et al.* (1981) checked the ability of the UNIQUAC model to predict the liquid-vapour pressures of (ethanol + benzene), (ethanol + 2-butanone) and (benzene + 2-butanone) mixtures. However, this model failed to give a satisfactory estimation of vapour-liquid equilibrium data of highly non-ideal mixtures.

The theories of liquid mixtures of more than two components are based on the theories of binary mixtures. (Hildebrand and Scott 1950) and (Scatchard 1931; 1932; 1934; 1937) extended the improved van Laar theory to the liquid solutions containing more than two components with an additional assumption that the excess entropy of mixing is zero at constant temperature and pressure.

Furthermore, Ohta *et al.* (1981) compared the predictions of UNIQUAC model with experimental data for the mixture. (ethanol + benzene + 2-butanone) and concluded that the UNIQUAC model gave a reasonable estimate of multi-component properties. However, the UNIQUAC models fails to gives a satisfactory estimate of vapour-liquid equilibrium data for highly non-ideal systems. In an attempt to improve the predictive ability of UNIQUAC model, (Nagata and Katoh 1980) assumed the energy of mixing U_{12}^{M} for a binary mixture to be of the form:

$$U_{12}^{\mathrm{M}} = x_1\theta_{21}u_{21} + x_2\theta_{12}u_{12} \tag{3.76}$$

where $\theta_{i\,\mathrm{j}}$ is the local area fraction of molecule *i* about a central

$$\theta_{21} = \theta_2 \exp^{\left(\frac{-u_{21}}{CRT}\right)} \Big/ \left[\theta_1 + \theta_2 \exp\left(\frac{-u_{21}}{CRT}\right)\right] \tag{3.77a}$$

$$\theta_{12} = \theta_1 \exp^{\left(\frac{-u_{12}}{CRT}\right)} \Big/ \left[\theta_2 + \theta_1 \exp\left(\frac{-u_{12}}{CRT}\right)\right] \tag{3.78b}$$

u_{21} and u_{12} represent the binary interaction parameters and *C* is the proportionality constant. Thus, the excess Gibbs free energy is given by:

$$\frac{G_{12}^{E}}{RT} = x_1 \ln\left(\frac{\Phi_1}{x_1}\right) + x_2 \ln\left(\frac{\Phi_2}{x_2}\right) + \frac{1}{2Z}\left[x_1q_1 \ln\left(\frac{\theta_1}{\Phi_1}\right) + x_2q_2 \ln\left(\frac{\theta_2}{\Phi_2}\right)\right] - Cx_1 \ln(\theta_1 + \theta_2\tau'_{21}) - Cx_1 \ln(\theta_2 + \theta_1\tau'_{12}) \tag{3.79}$$

and

$$\tau'_{12} = exp\left(\frac{-u_{12}}{CRT}\right) = exp\left(\frac{-\propto_{12}}{CT}\right) \tag{3.80}$$

This excess Gibbs function equation, called effective UNIQUAC equation was extended to multicomponent mixtures with an additional assumption that the constant *C* is identical in all contributing binary systems. Hence, for a multicomponent mixture, the excess Gibbs free energy equation becomes:

$$\frac{G_{12..n}^{E}}{RT} = \sum_{i=1}^{n} x_i \ln\left(\frac{\Phi_i}{x_i}\right) + \frac{1}{2Z}\sum_{i=1}^{n} x_iq_i \ln\left(\frac{\theta_i}{\Phi_i}\right) - C\sum_{i=1}^{n} x_i \ln\left(\sum_j \theta_j\tau'_{j\,i}\right) \tag{3.81}$$

with the activity coefficient γ_i given by

$$\ln\gamma_i = \ln\left(\frac{\Phi_i}{x_i}\right) + 1/2\ zq_i \ln\left(\frac{\theta_i}{\Phi_i}\right) + l_i - \frac{\Phi_i}{x_i}\sum_j x_jl_j + C\left[-\ln\left(\sum_j x_jG_{ji}\right) + 1 - \sum_k \frac{x_kG_{i\,k}}{\sum_j x_jG_{j\,k}} - \ln\left(\frac{\theta_i}{x_i}\right) - 1 + \frac{\theta_i}{x_i}\right] \tag{3.82}$$

where $G_{j\,i} = \frac{q_j}{q_i}\tau'_{j\,i}$

The predictive abilities of UNIQUAC and Effective UNIQUAC models were checked by (Nagata and Katoh 1980) in respect of (acetonitrile + ethanol + cyclohexane) ternary mixture and showed that the latter gives a closed solubility curve. On the other hand, the UNIQUAC equation gives an erroneous prediction of phase separation for (ethanol + cyclohexane) system.

Bronsted and Koefoed (1946) proposed the Principle of Congruence and showed that activity coefficient depends on the average of the carbon atoms per molecule. This principle was applied to a number of binary mixtures by (Desmyter and van der Waals 1958), (Holleman 1963), (Pflug and Benson 1968), (Dantzler and Knobler 1969), (Diaz Pena and Martin 1963), (McGlashan 1961), (Handa *et al.* 1977). (Shana and Canfield 1968) analysed the V^{E} data of the ternary mixture (methane + ethane + propane) at -165 ^{0}C and found that the principle of congruence gives a good estimate of V^E for mixtures which include alkanes beyond n-butane. Vonka et al. (1982) predicted excess volumes of multicomponent mixtures using the expression developed for excess free energy as:

$$V^{\mathrm{E}}_{1\,2\,3} = \sum_{i<j} \frac{x_i x_j}{x'_i x'_j} V^E_{i\,j}\left(x'_i, x'_j\right) \tag{3.83}$$

where $x'_i$and x'_j are defined as $x'_i + x'_j = 1$ and $V^E_{i\,j}$ corresponding to binary excess volume at the composition (x'_i, x'_j) can be obtained by projection of ternary point composition on to the axis of respective binary system in a triangular diagram.

In the normal projection

$$x'_i = \frac{1 + x_i - x_j}{2}\ , \qquad x'_j = \frac{1 - x_j - x_i}{2}$$

and

$$V^{\mathrm{E}}_{123} = \sum_{i<j} \frac{4\,x_i\,x_j}{1-(x_i-x_j)^2} V^E_{i\,j}\left(x'_i,\ x'_j\right) \tag{3.84}$$

This relation is similar to that of (Redlich and Kister 1948) for binary mixtures.

Under direct projection:

$$x'_i = \frac{x_i}{x_i + x_j}\ , \qquad x'_j = \frac{x_j}{x_i + x_j}$$

and

$$V^{\mathrm{E}}_{123} = \sum_{i<j} (x_i + x_j)^2\, V^E_{i\,j}\left(x'_i,\ x'_j\right) \tag{3.85}$$

In parallel projection:

$$V_{123}^{\mathrm{E}} = 1/2 \sum_{i<j} \left[\frac{x_j}{1 - x_i} V_{i\,j}^{E} \left(x_i', x_j' \right) + \frac{x_i}{1 - x_j} V_{i\,j}^{E} \left(x_i', x_j' \right) \right] \tag{3.86}$$

Garcia et al. (1984) computed the ternary excess volumes using the aforesaid projection methods and found that the normal projection method gives the better estimates of ternary data. (Cibulka 1982) also applied these projection methods to a number of ternary mixtures and found that the normal projection method gives a better estimate.

CHAPTER 4

EXPERIMENTAL

4.1 Excess molar volumes ($V_{\mathrm{m}}^{\mathrm{E}}$)

The excess molar volume is defined, at a constant concentration for x_1 and x_2 of component 1 and 2 respectively, by the following equation:

$$V_m^E = V_{mix} - \left[x_1 V_1^0 + x_2 V_2^0\right] \tag{4.1}$$

where V_{mix} is the molar volume of the binary mixture and x_1, x_2 and V_1°, V_2° are the mole fraction or molar volumes of components 1 and 2 respectively.

According to Smith (Smith *et al.,* 1989) the excess molar volume of mixing defined at constant temperature and pressure is given by:

$$V_{\mathrm{m}}^{\mathrm{E}} = V_{\mathrm{m,mix}} - V_{\mathrm{m,pure}} = V_{\mathrm{m,real}} - V_{\mathrm{m,ideal}} = \sum x_{\mathrm{I}}\left(V_{\mathrm{m,i}} - V_{\mathrm{m,i}}^{0}\right) \tag{4.2}$$

$V_{\mathrm{m,i}}$ is the partial molar volume of the i^{th} component and $V_{\mathrm{m,i}}^{0}$ is the molar volume of the pure species *i*.

Generally, excess molar volume can be measured experimentally by following two methods.

(i) Direct methods
(ii) Indirect methods

4.1.1 Measurements of excess molar volume by direct methods

The excess molar volume of the liquid mixture can measured by direct methods with the aid a of batch dilatometer and continuous dilution dilatometer. Batch dilatometer is characterized by the determination of a single data point per loading of the apparatus and continuous dilatometer is characterized by the determination of many data points per loading of the apparatus (Redhi, 2003; Handa and Benson 1979; Nevines, 1997).

4.1.1.1 Batch dilatometer

Batch dilatometer is filled with known weight of pure liquids, which are isolated by mercury. Then, the height of mercury in the calibrated graduated section is noted. These liquids are then mixed by rotating the dilatometer, the volume change on mixing is shown by the adjustment in the height of the mercury in the calibrated capillary. Finally, the excess molar volume ($V_{\mathrm{m}}^{\mathrm{E}}$) is gained from the volume change and the masses of the segments. It was reported that an accuracy of ± 0.003 $\mathrm{cm}^3\cdot\mathrm{mol}^{-1}$ in the excess molar volume could be accomplished over the temperature range of (280 to 350) K utilizing this method. The main drawback of the batch dilatometer it is very hard to fill the dilatometer and which is typically refined utilizing a narrow needle. A key source of error in this method is the determination of the components as it is significant to measure the dilatometer since it contains mercury. This results in large errors in the measured mass. The error associated with taking a difference in large masses is usually quiet significant (Nevines, 1997; Keyes and Hildebrand, 1917; Redhi, 2003). The batch dilatometer is presented in Figure 4.1.

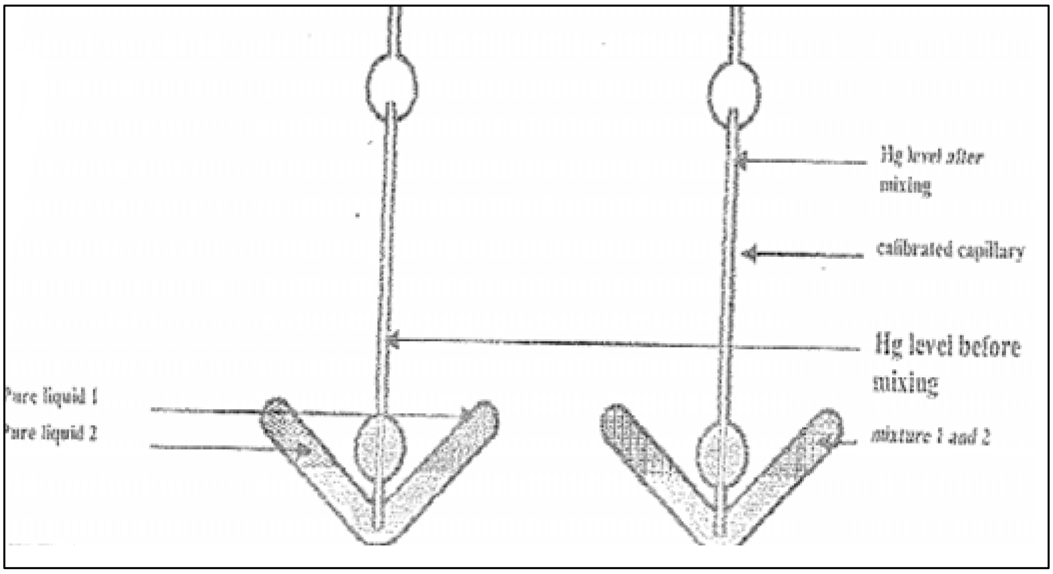


Figure 4.1. A typical batch dilatometer

4.1.1.2 Continuous dilatometer

A continuous dilatometer is a better tool than the batch dilatometer to measures the excess molar volume because less time is required for the measurement of ($V_{\mathrm{m}}^{\mathrm{E}}$) and more data is generated per loading. The mode of operation involves the successive addition of one liquid into the reservoir, which contains the other liquid and detecting the volume change that accompanies the addition. The dilatometer of Kumaran and McGlashan (1977) which is based on the design of Bottomly and

Scott (1974) is presented in Figure 4.2. Both are considered superior to other continuous dilatometers because mercury and the liquids do not pass through the greased gas. The instrument of Kumaran and McGlashan (1977) is considered an improvement on the one developed by Bottomly and Scott (1974) because it is easier to load. Kumaran and McGlashan (1977) reported a precision of 0.0003 $cm^3 \cdot mol^{-1}$ in V_m^E for their apparatus.

A measurement is made by filling the burette (e) with one of the pure liquids and the bulb (d) with the other pure liquid. As the dilatometer is tilted some of the mercury is displaced into the burette through a capillary (c) and collects at the bottom of the burette. This displaced mercury forces some of the pure liquid from the burette into the bulb through the higher capillary (b). After mixing, the change in volume is registered as a change in the level of the mercury in the calibrated capillary (a). The amount of pure liquid that is displaced is determined from the height of the mercury in the burette. Because mercury is used, a capillary pressure effect is possible and the compressibility of mercury has to be considered when determining the excess molar volume.

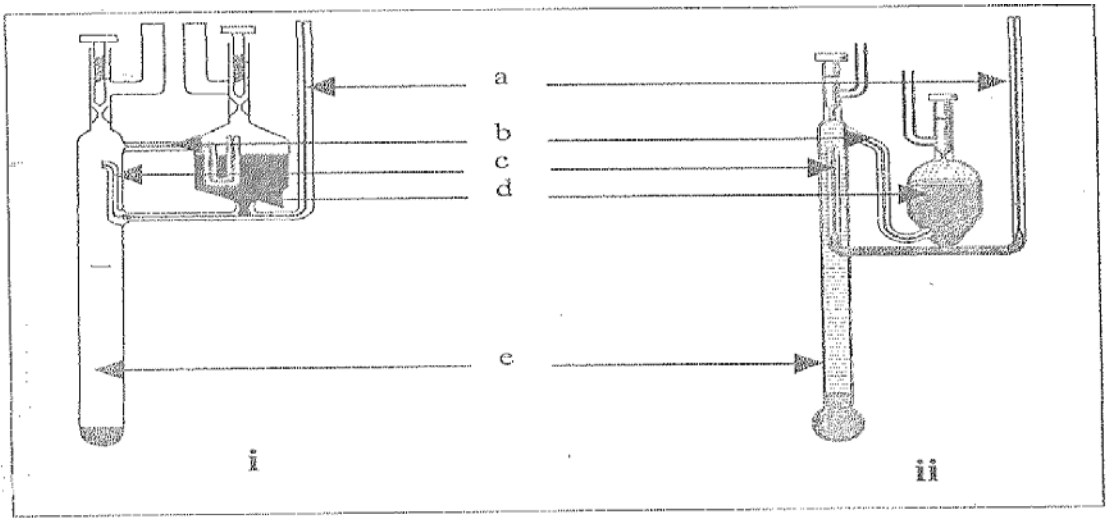


Figure 4.2. Continuous dilatometer (i) design of Bottomly and Scott, (ii) design of Kumaran and McGlashan. a; calibrated capillary from which the volume change is determined, b; liquid capillary, c; mercury capillary, d; bulb that contains mercury, e; burette liquid 2.

4.1.2 Measurement of excess molar volumes by indirect methods

The development of the dilatometer was accompanied by a higher accuracy from density measurement techniques and the earlier methods became less used for the determination of excess molar volume. Though, day to day more techniques were developed for the accurate measurement of the density, it is possible to determine V_m^E with acceptable accuracy from density measurements.

4.1.2.1 Pycnometry

Pycnometry involves the determination of the mass for a fixed volume. A vessel with a known volume is filled with a liquid mixture of known composition. It is then weighed and this mass, together with the composition and volume previously calibrated with a recommended standard liquid is used to determine V_m^E. A pycnometer capable of a precision of 5×10^{-6} g · cm^{-3} for density measurement translates into a precision of 0.001 cm^3·mol^{-1} for V_m^E, has been reported by (Wood and Brusie 1943). The pycnometer based on the design of (Wood and Brusie 1943) is shown in Figure 4.3.

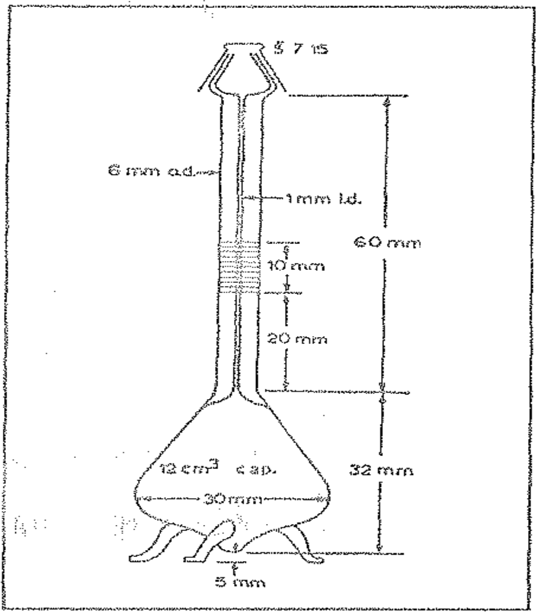


Figure 4.3. Schematic representation of the pycnometer based on the design of Wood and Brusie (1943).

4.1.2.2 Magnetic float densimeter

The mode of operation of a magnetic float densimeter is based on the determination of the height of a magnetic float in a liquid mixture. The height of this magnetic float in the presence of a known magnetic field is a function of the buoyancy of the liquid. The buoyancy of the liquid is related to the density of the liquid. An instrument with a precision 3×10^{-6} g·cm^{-3} has been reported and this translates to a precision of 0.0008 cm^3·mol^{-1} (Franks and Smith 1967). The magnetic float densitometer based on the design of (Franks and Smith 1967) is shown in Figure 4.4.

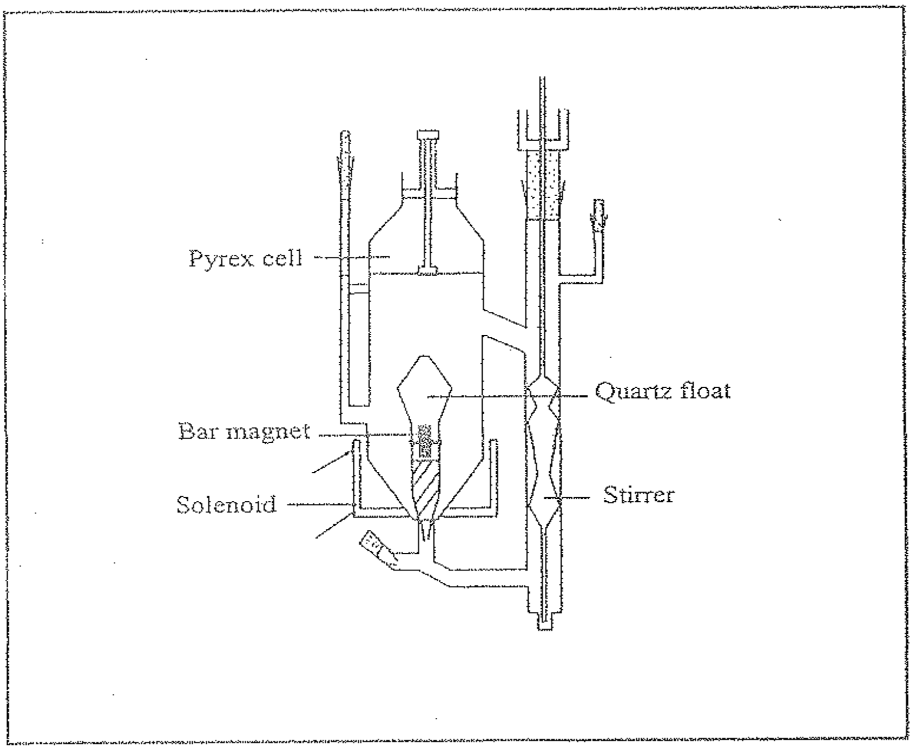


Figure 4.4. Schematic representation of a magnetic float densimeter of Franks & Smith (1967)

4.1.2.3 Mechanical oscillating densitometer

Mechanical oscillating (vibrating tube) densimeters linked to digital output displays are widely used in the chemical industry and in research laboratories to measure densities of pure liquids and liquid mixtures. The frequency of the vibrating tube containing a liquid that is subjected to a constant electric stimulation is related to the density of the liquid. According to Handa and Benson (1979), the frequency of vibration of an undamped oscillator (e.g. tube containing a liquid) connected by a spring with a constant elasticity, *c*, is related to the mass of the oscillator and the liquid, *M*, by the following equation:

$$2\pi v = \left(\frac{c}{M}\right)^{\frac{1}{2}} \tag{4.3}$$

where *M* is the mass of the contents in the tube and M_0 is the mass of the empty oscillator. Since the oscillator is a hollow tubes if a liquid with a density, ρ, fills the hollow tube occupying a volume *V,* then:

$$M = M_0 + \rho V \tag{4.4}$$

Substitution of equation (3.10) into equation (3.11) and solving for ρ:

$$\rho = -\frac{M_0}{V} + \left(\frac{c}{4\pi^2}\right)\left(\frac{1}{V^2}\right) \tag{4.5}$$

where $\frac{-M_0}{V}$ and $\frac{c}{4\pi^2 V}$ are constants. Therefore the following equation is valid:

$$\rho = A + B\left(\frac{1}{v}\right)^2 \tag{4.6}$$

The constants *A* and *B* are characteristics of the oscillator, τ is the period and density is given by the symbol, ρ, hence:

$$\rho = A + B\tau^2 \tag{4.7}$$

where *A* and *B* are determined by calibration. This involves determining the period for two pure substances of known density.

Since densities are measured relative to a reference material:

$$\rho - \rho_o = \mathrm{B}\left(\tau^2 - \tau_o^2\right) \tag{4.8}$$

Commercially available vibrating tube densimeters with a precision of 0.001 % are available. This implies a precision of 0.003 $\text{cm}^3\cdot\text{mol}^{-1}$ in the measurement of V_m^E (Nevines 1997).

4.2 Speed of sound and isentropic compressibility

The speed of sound is another essential property of pure liquids and their mixtures which results from the molecular interactions such as solvent–solvent, solute–solvent and solute–solute which occur in the liquid mixtures. Measurement of the speed of sound, *u*, in liquids is a useful source of information to detect small changes in gas composition or the effect of small concentration changes (Azevedo *et al* 2004). The isentropic compressibility (k_s) were calculated from the Newton-Laplace equation given below:

$$k_\text{s} = \frac{1}{\rho u^2} \tag{4.9}$$

where ρ is the density and *u* is the sound velocity in the binary mixture.

4.3 Experimental apparatus and method used in this work

4.3.1 Density and speed of sound measurements in the present work

In the present investigation, the density and speed of sound for pure liquids and their binary mixtures were measured using digital vibrating-tube densimeter and sound velocity analyzer Anton Paar (DSA 5000M) in the temperature range of 293.15 to 343.15 K, with an accuracy of ± 0.02 K and at atmospheric pressure. The uncertainty in density and speed of sound measurements were less than $\pm 9\times10^{-4}$ $g\cdot cm^{-3}$ and ± 0.8 $m\cdot s^{-1}$, respectively.

4.3.2 Mode of operation

For the density measurements, the vibrating U-shaped tube was kept inside a cavity of a metallic block with peltier devices which allow temperature and stability. The speed of sound cell was connected to one end of the U-shaped tube so that the same liquid can pass into it without loss and the same metallic block can control temperature. A diagram of the Anton Paar (DSA 5000M) apparatus used in this work is shown in Figure 4.5.

Figure 4.5 Anton Paar (DSA 5000M) density and speed of sound analyser.

4.3.2.1 Oscillating U-tube method

The sample is introduced into a U-shaped borosilicate glass tube that is excited to vibrate at its characteristic frequency electronically. The characteristic frequency changes depending on the density of the sample. Through a precise determination of the characteristic frequency and a mathematical conversion, the density of the sample can be measured. The density, ρ, is calculated from the quotient of the period of oscillation of the U-tube and the reference oscillator:

$$\rho = \mathrm{KA} \times \mathrm{Q}^2 \times \mathrm{f}_1 - \mathrm{KB} \times \mathrm{f}_2 \tag{4.10}$$

KA, KB	Apparatus constant
Q	Quotient for the period of oscillation of the U-tube divided by the period of oscillation for the reference oscillator
f_1, f_2	Correction terms for temperature, viscosity and non-linearity

The value of the density is displayed on the LCD screen. The DSA 5000 M is coupled with a computer which is loaded with a software that stores all the measured density values.

4.3.2.2 Sound velocity analyser

The sample is introduced into the sound velocity measuring cell that is bordered by an ultrasonic transmitter on the one side, and a receiver on the other side. The transmitter sends sound waves of a known period through the sample. The velocity of sound, u, can be calculated by using the period of the sound waves and the distance between the transmitter and receiver.

$$u = \frac{l \times (1 + 1.6 \times 10^{-5} \times \Delta T)}{\frac{\mathrm{P_s}}{512} - \mathrm{A} \times \mathrm{f}_3} \tag{4.11}$$

where l is the original path length of the sound waves, ΔT is the temperature deviation to 5 ^{o}C, P_S is the oscillation period of the received sound waves, A is apparatus constant for sound velocity, and f_3 is the correction term for temperature. Due to the high temperature dependency of the density and velocity of sound, the measuring cells are thermostated precisely, using the Peltier elements.

4.3.3 Features of DSA 5000 M

4.3.3.1 Accuracy

DSA 5000 M instrument is equipped with the world's most advanced digital density and sound velocity measurement technology where:

- The period of oscillation of the U-tube is measured by optical pickups.
- Two integrated Pt 100 platinum thermometers together with the Peltier elements provide an extremely precise thermostatting of the sample.

- There is a Thermo Balance which is an additional reference oscillator that provides long-term stability and enables precise measurements over the whole temperature range of the instrument with only one adjustment at 20 ^{o}C.

4.3.3.2 Error detection

A major source of measuring errors when using a density and sound velocity meter are gas bubbles in the measuring cells. To reduce the formation of gas bubbles Anton Paar introduced two new features:

Filling Check: The instrument automatically detects gas bubbles in the density measuring cell by an advanced analysis of its oscillation pattern and generates a warning message.

U-View: Using a real-time camera with zoom function the U-tube can be visually inspected for gas bubbles in the density measuring cell.

4.3.3.3 User interface

The touch screen user interface supports easy and intuitive operation in routine applications and in scientific research work. The user interface allows for:

- The measured density and/or sound velocity values to be automatically converted into concentration values for a large number of factory-programmed substances. The instrument can also be programmed special substances as required.
- Use under harsh industrial conditions, operate DSA 5000 M with the set of robust soft keys instead of the touch screen.
- The DSA 5000 M to be connected to an external keyboard, computer mouse or bar code reader.

4.3.3.4 Data management and safety

The DSA 5000 M offers up-to-date data management and safety features capable of storing 1000 data files with or without pictures. The instrument also has the following features:

- Print out reports.
- Export our data in the format of one’s choice (MS Excel, text or PDF).
- Choose between the interfaces: 4 × USB, Ethernet, RS-232, 2 × S-BUS and CAN BUS.
- Use the powerful audit trail function with tamper-proof data export.

4.3.3.5 Design

The tradition of the legendary previous DSA generations is continued in the M series:

- Compact design
- Sealed housing
- Robust housing materials: coated aluminium (top and sides), aluminium (base and back) and Polystyrene/Butadiene (front).

The Specifications for the DSA 5000 M are given in Table 4.1

Table 4.1 Specifications of the DSA 5000 M.

Measuring range density	0 to 3 g/cm^3
Measuring range sound velocity	1000 to 2000 m/s
Measuring range temperature	0 to 70 ^{o}C (32 to 158 ^{o}F)
Pressure range	0 to 3 bar (0 to 44 psi)
Repeatability density	0.000001 g/cm^3
Repeatability sound velocity	0.1 m/s
Repeatability temperatures	0.001 ^{o}C (0.002 ^{o}F)
Measuring time per sample	1 to 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

4.3.4 Materials

The water content of chemicals used in this work were measured by using a Metrohm 702 SM Titrino Metter. The Mass percent water content was found to be 0.05% in $[EMIM]^+[EtSO_4]^-$, 0.03% in acetic acid, 0.02% in propionic acid, 0.30% in diethyl carbonate, 0.36% in ethanol, 0.10 % in acetonitrile and 0.06 % in $[BMIM]^+[SCN]^-$. A summary of the pure chemicals their suppliers and purities used in this work is given in Table 4.2. The experimental and literature values of densities and speed of sound of the pure compound are given in Tables 4.3 and 4.4.

Table 4.2 Chemicals, their suppliers, mass fraction purity, molar mass and CAS No

Chemicals	Supplier	Mass fraction Purity (%)	Molar mass (g.mol)	CAS No
$[EMIM]^+[EtSO_4]^-$	Aldrich	99.0	236.29	342573-75-5
$[BMIM]^+[SCN]^-$	Aldrich	99.0	197.3	370865-89-7
Acetic acid	Aldrich	99.0	60.05	A6283
Propionic acid	Aldrich	99.5	74.08	79-09-4
Acetonitrile	Aldrich	99.0	41.05	271004

Table 4.3 Densities (ρ) of pure chemicals at T = 298.15 K.

Chemicals	Experimental	Literature
$[EMIM]^+[EtSO_4]^-$	1.23689	1.23763[a]
$[BMIM]^+[SCN]^-$	1.07034	1.06979[b]
Acetic acid	1.04413	1.04365[c]
Propionic acid	0.98794	0.98848[d]
Acetonitrile	0.77666	0.776533[e]

[a][Gomez *et al.* 2006], [b][Domanska and Krolikowska 2012], [c][Gonzalez *et al.* 2004]
[d][Bahadur *et al.* 2013], [e][Zafarani-Moattar and Shekaari 2005]

Table 4.4. Speed of sound (*u*) of pure chemicals at T = 298.15 K.

Chemicals	Experimental	Literature
$[EMIM]^+[EtSO_4]^-$	1680.8	1679.0[a]
$[BMIM]^+[SCN]^-$	1767.2	-
Acetic acid	1135.7	1132.0[b]
Propionic acid	1146.0	1146.7[c]
Acetonitrile	1279.0	1278.62[d]

[a][Gomez *et al.* 2006], [b][Gonzalez *et al.* 2004], [c][Bahadur *et al.* 2013], [d][Zafarani-Moattar and Shekaari 2005]

4.3.5 Preparation of binary liquid mixtures

Prior to making the experimental measurements, all the materials were degassed by ultrasound, kept out of the light over Fluka 0.3 nm molecular sieves for several days before the experiments were performed. The binary mixtures were prepared by transferring of the pure liquids into stoppered bottles using a syringe, to prevent loss of sample due to evaporation. The IL was first filled into the air-tight glass stoppered 10 cm^3 glass vial and weighed. An OHAUS analytical mass balance with a precision of ±0.0001 g was used to determine the mass of each component of the mixture. The estimated error in the mole fraction was ±0.0004.

Ultra-pure water supplied by SH Calibration Service GmbH Graz (used as the calibration standard) was then introduced into the cell by means of a glass syringe. The injection process was carried out slowly, enabling the liquid to properly wet the walls of the cell, and also to alleviate the risk of trapping air bubbles in the U-tube. The sample was always filled past its nodal points and the syringe was left in place at the nodal point during each measurement. The density of air and water was set for the calibration. The solution mixtures were introduced into the sample cell in exactly the same manner as for the ultra-pure water. Density or speed of sound values of water, pure solvents and air were determined after a series of density measurements to permit a continuous check on accuracy of the density determinations. This was further verified by repeated measurements of the same solution at different times. By using these densities, was calculated the excess molar volume for the binary or ternary liquid mixtures at different temperatures.

4.3.6 Systems studied in this work

In this perspective, the excess molar volumes (V_{123}^{E}), isentropic compressibilities (k_s) and deviation in isentropic compressibilities (Δk_{s123}) were determined for four ternary liquid mixtures of {$[EMIM]^+[EtSO_4]^-$ + acetonitrile + acetic acid or propionic acid} and {$[BMIM]^+[SCN]^-$ + acetonitrile + acetic acid or propionic acid} at different temperatures (293.15, 298.15, 303.15, 308.15 and 313.15) K and at a pressure of 0.1 MPa with aid of the experimental measurements of density (ρ), speed of sound (u). In these ternary systems $[EMIM]^+[EtSO_4]^-$, $[BMIM]^+[SCN]^-$ acetonitrile are considered as common components and acetic acid or propionic acid are non-common components.

4.3.6.1 Ternary liquid mixtures of (IL + acetonitrile + acetic acid or propionic acid)

1. (V_{123}^{E}) and (Δk_{s123}) data of {$[EMIM]^+[EtSO_4]^-$ + acetonitrile + acetic acid} at T = (293.15, 298.15, 303.15 and 313.15) K.
2. (V_{123}^{E}) and (Δk_{s123}) data of {$[EMIM]^+[EtSO_4]^-$ + acetonitrile + propionic acid} at T = (293.15, 298.15, 303.15 and 313.15) K.
3. (V_{123}^{E}) and (Δk_{s123}) data of {$[BMIM]^+[SCN]^-$ + acetonitrile + acetic acid} at T = (293.15, 298.15, 303.15 and 313.15) K.
4. (V_{123}^{E}) and (Δk_{s123}) data of {$[BMIM]^+[SCN]^-$ + acetonitrile + propionic acid} at T = (293.15, 298.15, 303.15 and 313.15) K.

4.3.6.2 Binary liquid mixtures of ($[EMIM]^+[EtSO_4]^-$ or $[BMIM]^+[SCN]^-$ + acetonitrile + acetic acid or propionic acid)

1. {$[EMIM]^+[EtSO_4]^-$} + acetonitrile at T = (293.15, 298.15, 303.15 and 313.15) K.
2. {$[EMIM]^+[EtSO_4]^-$} + acetic acid at T = (293.15, 298.15, 303.15 and 313.15) K.
3. {$[EMIM]^+[EtSO_4]^-$} + propionic acid at T = (293.15, 298.15, 303.15 and 313.15) K.
4. {$[BMIM]^+[SCN]^-$} + acetonitrile at T = (293.15, 298.15, 303.15 and 313.15) K.
5. {$[BMIM]^+[SCN]^-$} + acetic acid at T = (293.15, 298.15, 303.15 and 313.15) K.
6. {$[BMIM]^+[SCN]^-$} + propionic acid at T = (293.15, 298.15, 303.15 and 313.15) K.
7. Acetonitrile + acetic acid at T = (293.15, 298.15, 303.15 and 313.15) K.
8. Acetonitrile + propionic acid at T = (293.15, 298.15, 303.15 and 313.15) K.

4.4 Experimental techniques for determining infinite dilution activity coefficients (IDAC)

4.4.1 Differential ebulliometry method (DEM)

The linear relationship between the bubble point temperature and solute concentration can be used to determine the IDAC value (George., 2008). This method has been successful for numerous systems, however is not appropriate for highly non-ideal systems and should be used for compounds with similar relative volatilities (from 0.1 to 10) (George, 2008).

4.4.2 The inert gas stripping method (IGS)

An extremely dilute compound is stripped from a mixture by a flow of inert gas at a certain isotherm, within the confines of a cell. The exiting gas concentration is measured at set intervals, and observed should be an exponential decrement of solute concentration with the progress of time. The activity coefficient at infinite dilution is related to this phenomenon, and can thus be calculated. This method can be used for volatile solutes in non-volatile or volatile solvents with large relative volatilities (Tumba, 2010). This method is also referred to as the dilutor cell or continuous gas extraction technique (Tumba, 2010, Kojima *et al.*, 1997).

4.4.3 Gas-liquid chromatography (GLC)

This method was first proposed in 1956 (Kojima *et al.*, 1997) and has become the most popular method for the investigation of a wide range of thermo-physical properties at infinite dilution (Kojima *et al*., 1997). Most of this popularity has been in the measurement of IDACs for volatile solutes in non-volatile solvents. It is amongst the most rapid and reliable methods used for such measurements. Recent improvements and modification to techniques have allowed solvents with medium volatility to be characterised (Williams-Wynn *et al.*, 2013). Regardless of any modification, however, solvents to be tested are always coated on the inside of a column, and set in a temperature controlled environment. Many researchers have noted relative uncertainties in this method from 3 to 5% (Dallinga *et al.*, 1993, Bahadur *et al.*, 2014, Letcher *et al.*, 2005). The main disadvantage of this method, however, is that IDAC values cannot be determined for the investigated non-volatile solvent in a volatile solute (George, 2008).

While the GLC method used for measurements of IDACs remains similar, slight variations have been noted in literature. Letcher and Reddy (2007) used a pre-coiled stainless steel column and Domanska and Marciniak (2008) have used a pre-coiled glass column in order to prevent damage to the support material in the stationary phase. Tumba (2010) incorporated the aid of a vacuum to ensure a uniform distribution of the stationary phase, when working with ionic liquids.

The choice of an oven as part of a gas chromatograph over an oil or water bath has also become a preferred choice for control of the column temperature. Generally the oven is adequate at temperatures above 303.15 K, but if measurements are to be done at lower temperatures, a bath containing a suitable thermal fluid becomes the ideal choice as temperature control is improved. This is also chosen for when pre-saturation of a carrier gas with a solvent is necessary.

4.5 Experimental apparatus and procedure

The procedure necessary for the GLC technique is well established in many literature sources (Tumba, 2010, Bahadur *et al.*, 2014, Letcher *et al.*, 2005, Letcher and Deenadayalu, 2001). The procedure used, and any modifications will be comprehensively described.

4.5.1 Materials

The organic solutes and water used are summarised in the table below. These were analytical grade with purities ranging from 95.00 to 99.99 % mass purity, as stated by the manufacturer (see appendix D). As the GLC technique has the advantage that impurities are separated during measurements, no further purification of solutes was undertaken.

Table 4.5. List of solutes tested

	Solutes	
n-pentane	oct-1-ene	propan-1-ol
n-hexane	non-1-ene	propan-2-ol
n-heptane	pent-1-yne	acetone
n-octane	hex-1-yne	butan-2-one
n-nonane	hept-1-yne	butanol
cyclohexane	oct-1-yne	2-methylpropan-1-ol
cyclopentane	non-1-yne	water
cyclooctane	benzene	dichloromethane
methylcyclohexane	toluene	
pent-1-ene	ethylbenzene	
hex-1-ene	methanol	
hept-1-ene	ethanol	

The solvents, with manufacturer stated purities are given in table 4.6.

Table.4.6. List of solvents tested

Solvent	% purity
Hexadecane	99.0
1-ethyl-3-methylimidazolium n-octylsulphate [EMIM] OS	98
1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [BMIM][Tf_2N]	98

Chromosorb WHP 80/100 mesh supplied by SUPELCO was used as a support for the stationary phase in the column. Any moisture was removed through vacuum treating (described below).

4.5.2 Equipment description

The essential equipment used in the investigation was as follows (full specifications are included in appendix E):

1. SHIMADZU GC-2014 Gas-chromatograph with a thermal conductivity detector (TCD)
2. 1 m long, 4.1 mm inner diameter (ID) stainless steel (304) column
3. EDWARDS Vacuum pump
4. Ultrasonic bath with silicon oil (T_{max} = 75°C)
5. iLMAC Rotary evaporator with water bath
6. MKS 500 Karl Fischer titrator (10 ppm – 100% H_2O)
7. Soap bubble flow meter
8. Thermometer
9. Laboratory Barometer
10. OHAUS Mass balance (m_{max} = 210 g)

4.5.2.1. The gas-chromatograph

The main equipment used for measurements was the Gas-chromatograph (GC). This housed the 1 m long, 4.1 mm stainless steel column which was packed with the stationary phase prepared (see section 4.5.3.2). A temperature controlled oven regulated the temperature to an accuracy of ±0.1 K. A flow controller maintained an approximately constant flow rate of inert gas, and a near constant pressure during runs, to ±0.1 kPa. A schematic of this is shown in Figure 4.6. A key advantage of this apparatus was the attachment of an auto-sampler and an auto-injector; both fully programmable. This reliable system had enabled measurements with a high degree of reproducibility, and did not require constant attendance. It had also allowed for the efficient use of time as samples could be injected sequentially with a minimal delay. Data measured by the GC was transmitted to a computer where it was recorded. Conditions for approximately 4 – 6 hours at 313.15 K. This provided a sufficient amount of time for the support material to dry. The GC's built in flow transmitter was not calibrated accurately enough for reliable measurements. Hence the flow rate of the inert gas was measured using a soap bubble column (see figure 4.6). This had also required the use of a thermometer (accuracy ±0.5 K) and barometer (accuracy ±0.01 kPa) to measure the environmental temperature and pressure respectively.

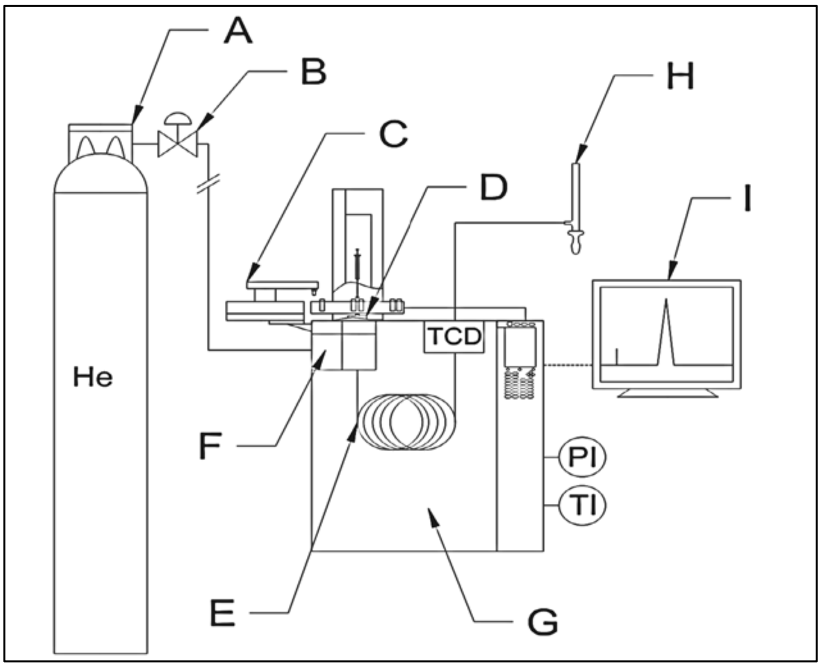


Figure 4.6. Schematic of the GLC apparatus. **A**-Helium carrier gas; **B**-flow regulator; **C**-Auto-injector arm; **D**-Injection port; **E**-Packed column; **F**-Flow controller; **G**-Temperature controlled oven; **H**-Soap bubble column flow meter; **I**-Recording computer.

4.5.3 Procedure

4.5.3.1 Solvent purification (step 1)

The ionic liquids tested were purified by degassing via a strong vacuum pump, and an ultra-sonic bath under heating. The solvents were housed in a 50 mL round bottom flask and connected by means of an adapter and valve to a vacuum pump. The flask was submerged in an ultra-sonic bath of silicon oil at 333.15 K for approximately 72 hours, with vibrations lasting for the initial 3 hours only. Immediately after removing the flask from the apparatus, it was sealed with a dual layer of parafilm and insulation tape, and stored in a covered beaker with silica gel crystals. This had ensured a minimal amount of water being drawn from the air during transport. During storage, the entire beaker and contents was placed in a desiccator. The moisture content of the ionic liquid was tested using Karl-Fischer titration, and ensured to be sufficiently low.

4.5.3.2 Preparation of the stationary phase (step 2)

A round bottom flask, supplied with the rotary evaporator used, was cleaned thoroughly before being dried and weighed on an accurate mass balance with a readability of ±0.0001 g. Chromosorb® support material was weighed into this. This was then carefully attached to the rotary evaporator coupled with a heated water bath. Drying commenced under vacuum.

The ionic liquid (or hexadecane) to be tested was then added to the support material within the flask, and then weighed. This was done quickly as to prevent significant absorption of moisture from the air. To ensure a uniform coating of solvent over the support material, dichloromethane as a solvent was mixed in. This solvent is especially suited because of its low boiling point (39.6 ^{o}C at 1 atm) and heat of vaporisation (28.6 kJ/mol); it could be removed easily. The flask was then attached once more to the drying apparatus until the dichloromethane was completely removed. The mixture was re-weighed to ensure the mass corresponded to what was originally weighed out.

The masses of the ionic liquids (or hexadecane) were ensured to be sufficiently high to prevent the effects of adsorption with the support material. Two different column loadings were also prepared for each solvent to ensure that no measurement depended on the concentration of solvent within the stationary phase and to ensure reproducibility of results.

4.5.3.3 Preparation of the column (step 3)

The specified column (4.1 mm-ID, 1 m long, stainless steel) was straightened manually using a bench vice and uncurling by hand. It was ensured visually that no kinks had formed during this process. The old content was removed by rapid and continuous beating using a ½ inch steel rod for approximately 10 minutes before compressed air was blown through. Thereafter, hot-soapy water was run gravitrimetrically for approximately 10 times through the column, using about 2 litres of fluid in each direction. This was followed by rinsing with hot de-ionised water in the same amount and an acetone flush to aid in the evaporation of remaining volatiles within the column. Compressed air was then blown through for about 5 minutes in short bursts.

4.5.3.4 Packing of the column (step4)

The prepared column was plugged on one end with inert glass wool, and covered with parafilm and sufficient backing to prevent any packing material from passing through during the insertion. This was then weighed as the mass of the empty column. The column was then clamped vertically using a stand, and a funnel attached to the open end with a rubber tube. The previously prepared stationary phase (of step 2) was then removed from the rotary evaporator and inserted through the funnel, once again beating the column with a steel rod to ensure a uniform and tightly packed stationary phase. A mass of inert glass wool was then weighed out, and a portion used to plug the open end of the column. The used mass was calculated by difference. The entire column was then weighed as the packed column mass, including the mass of the second inert glass wool plug. The step was done as quickly as possible to prevent the extremely dry materials from absorbing a significant amount of moisture from the air.

4.5.3.5 Installation and conditioning (step 5)

The column was manually coiled using the outside of a 70 mm outer diameter mild steel pipe. It was then installed into the GC and conditioned for about 12 hours at 363.15 K by allowing the helium carrier gas to flow through at 30 mL/min.

4.5.3.6 Measurements (step 6)

Measurements were undertaken at the temperatures of (313.15, 318.15, 323.15, 333.15, 343.15, 348.15, 353.15, 358.15 and 363.15) K or (313.15 to 363.15) K. Samples of solutes were injected from 1.5 mL vials by the auto-sampler and auto-injector, with an injection volume of 0.2 µL, to determine the solute retention time. Retention times were accurate to within ±0.001 min. The injected volume is within the range for an accurate representation of infinite dilution (Kojima et al., 1997). The retention times, temperature, and pressure drop of the column were measured by the GC’s internal sensors and recorded by a computer. The inert gas flow rate was measured using the exit stream from the GC by a soap bubble column, which varied from 0.42 to 0.53 mL/s. The effect of the water vapour pressure was accounted for by measuring the flow meter temperature (to ±0.5 K) and pressure (to ±0.01 kPa).

CHAPTER 5

RESULTS AND DISCUSSION

5.1 Excess molar volumes and deviation in isentropic compressibility for binary mixtures

In this work, density (ρ) and speed of sound (u) were measured for {$[EMIM]^+[EtSO_4]$}, {$[BMIM]^+[SCN]^-$}, acetic acid, propionic acid and acetonitrile and their binary systems {$[EMIM]^+[EtSO_4]$} with acetic acid or propionic acid, {$[BMIM]^+[SCN]^-$} with acetic acid or propionic acid, acetonitrile with acetic acid or propionic acid and acetonitrile with {$[EMIM]^+[EtSO_4]^-$} or {$[BMIM]^+[SCN]^-$} at 293.15, 298.15, 303.15, 308.15 and 313.15 K under atmospheric pressure. The derived properties such as excess molar volumes V_m^E, isentropic compressibility κ_s, and deviation in isentropic compressibility $\Delta\kappa_\mathrm{s}$, were calculated using experimental density and speed of sound data, respectively. Derived properties such as excess molar volumes V_m^E, and deviation in isentropic compressibility $\Delta\kappa_\mathrm{s}$, data were fitted to the Redlich–Kister polynomial equation. These results are useful for describing the intermolecular interactions, developing structure–property correlation, molecular modeling and structural effects that exist between component molecules in liquid mixtures.

5.1.1 Group 1: {$[EMIM]^+[EtSO_4]^-$} + acetic acid or propionic acid

Thermo physical properties of ILs and their binary mixtures with solvents are of fascinating and great practical importance in understanding the structural features of the pure ILs and its interactions when mixed with solvents. Obviously, studies on structural features of mixtures of IL with carboxylic acid are very interesting and sensitive to composition as well as the temperature. The data of ρ of pure carboxylic acid, IL and their binary mixtures were measured across the complete composition range at 293.15, 298.15, 303.15, 308.15 and 313.15 K, under atmospheric pressure and are given in Tables 5.1.1.1. The plots of density versus concentration of $[EMIM]^+[EtSO_4]^-$ at investigated temperatures are given in Fig. 5.1.1.1 (a) & (b). The ρ values for IL with acetic or propionic acid increase for the entire mole fraction, as shown in Fig. 5.1.1.1 (a) & (b) at all investigated temperatures. It can be observed that the ρ values decrease as temperature increases for both systems.

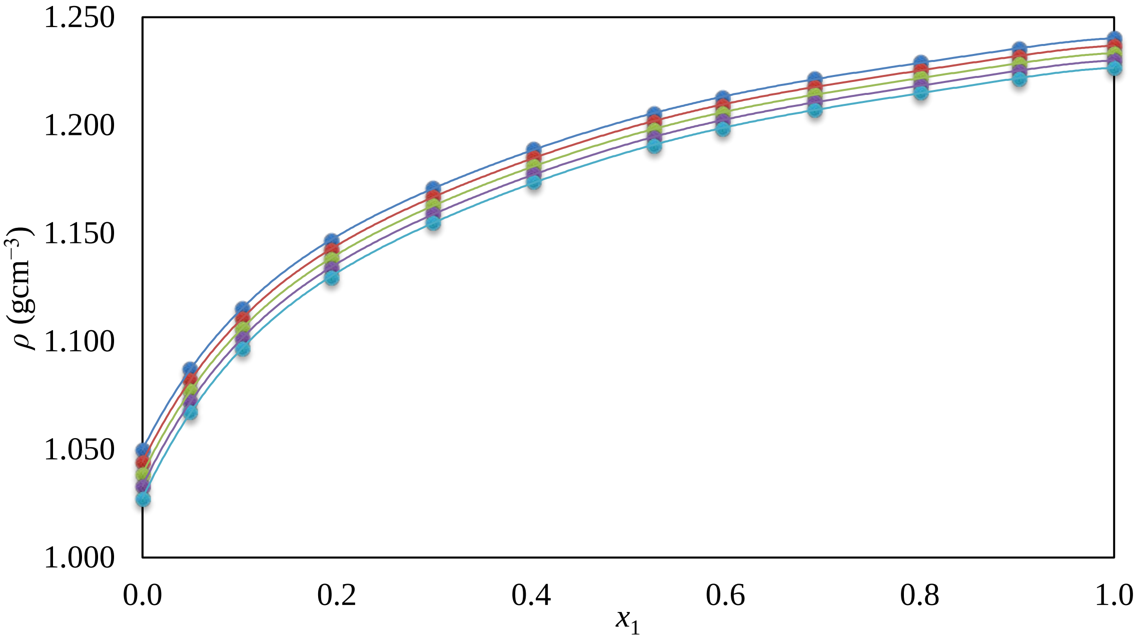


Fig. 5.1.1.1 (a) Density, ρ, for the mixtures of {[EMIM]$^+$[EtSO$_4$]$^-$ (x_1) + acetic acid (x_2)} as function of the composition expressed in the mole fraction of {[EMIM]$^+$[EtSO$_4$]$^-$ at 293.15 K (●), 298.15 K (●), 303.15 K (●), 308.15 K (●) and 313.15 K (●). The solid line represents the smoothness of these data.

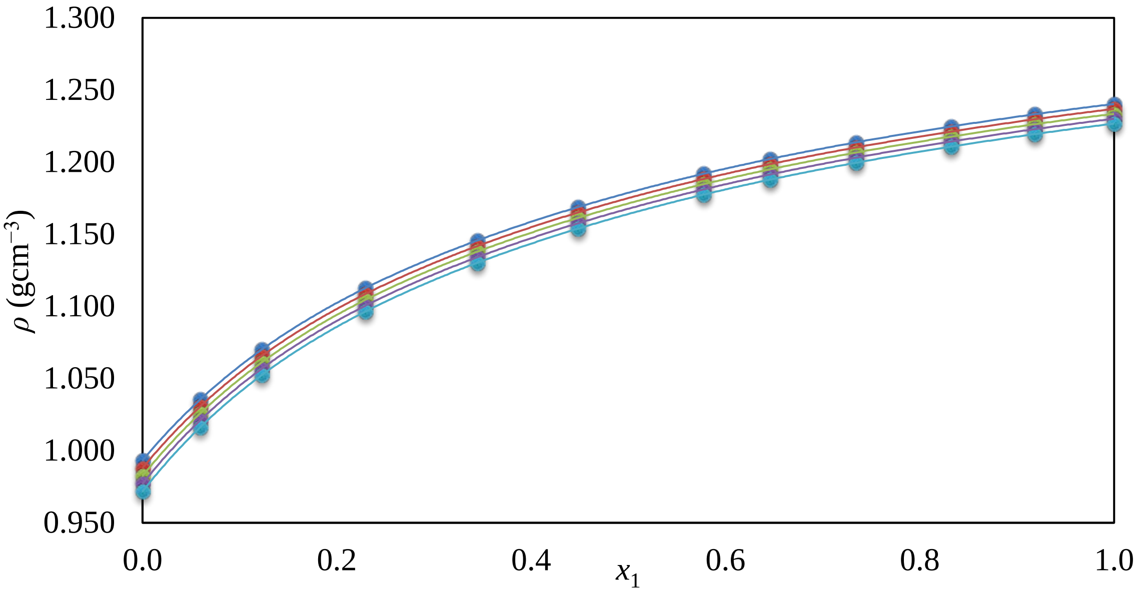


Fig. 5.1.1.1 (b) Density, ρ, for the mixtures of {[EMIM]$^+$[EtSO$_4$]$^-$ (x_1) + propionic acid (x_2)} as function of the composition expressed in the mole fraction of {[EMIM]$^+$[EtSO$_4$]$^-$ at 293.15 K (●), 298.15 K (●), 303.15 K (●), 308.15 K (●) and 313.15 K (●). The solid line represents the smoothness of these data.

Speed of sound is also an important property which describes the solvent–solvent, solute–solvent and solute–solute interactions which occur in the mixture (Roy. 2011) In this regard, the speeds of sound, u, were also measured at 293.15, 298.15, 303.15, 308.15 and 313.15 K, under atmospheric pressure and are given in Table 5.1.1.1. Fig. 5.1.1.2 (a) and (b) shows the temperature-dependent of u values for mixtures of $[EMIM]^+[EtSO4]^-$ with acetic or propionic acid at investigated temperatures. The u values were found to increase sharply with increasing mole fraction of $[EMIM]^+[EtSO4]^-$ at investigated temperatures. The experimental results reveal that u values decrease as temperature increases for both systems.

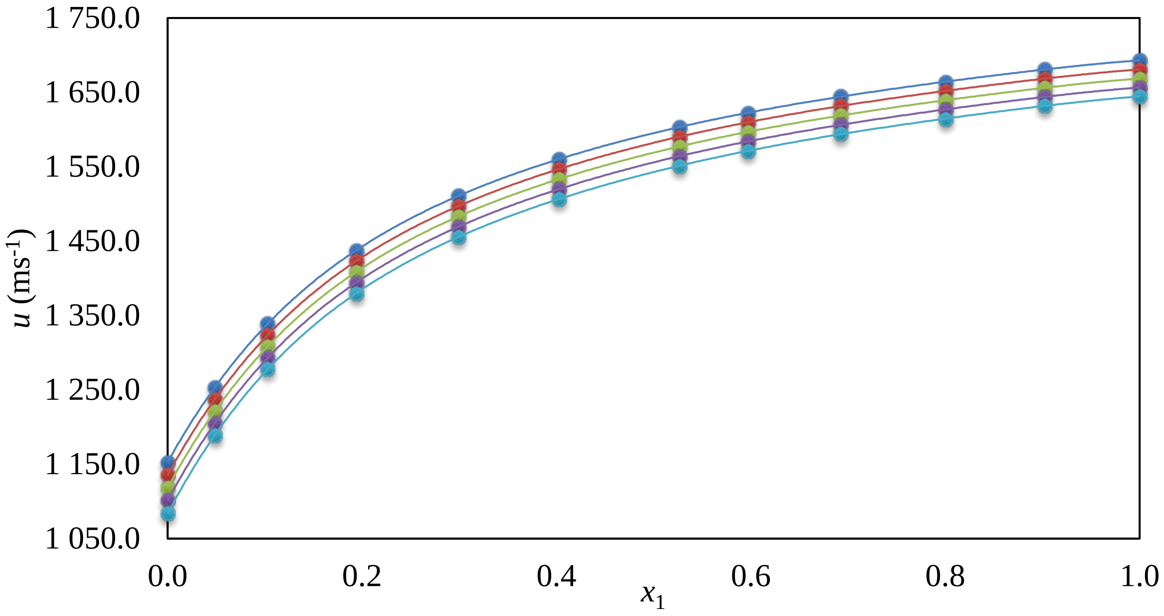


Fig. 5.1.1.2 (a) Speed of sound velocity, *u*, for the mixtures of (a) $\{[EMIM]^+[EtSO_4]^-$ (x_1) + acetic acid $(x_2)\}$ as function of the composition expressed in the mole fraction of $\{[EMIM]^+[EtSO_4]^-$ at 293.15 K (●), 298.15 K (●), 303.15 K (●), 308.15 K (●) and 313.15 K (●). The solid line represents the smoothness of these data.

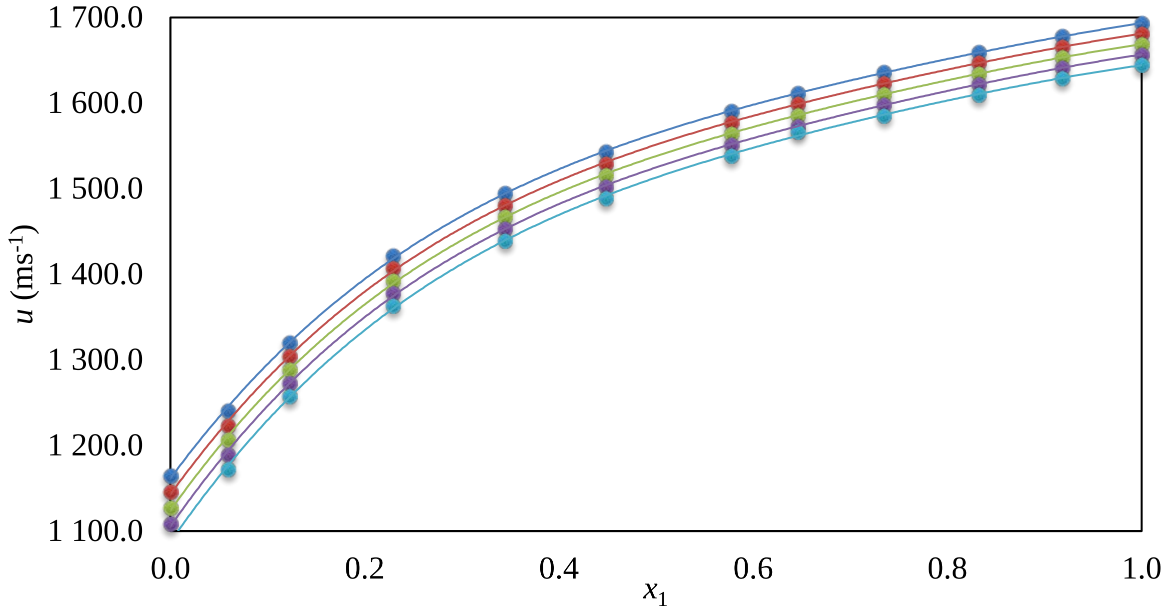


Fig. 5.1.1.1 (b) Speed of sound velocity, *u*, for the mixtures of {$[EMIM]^+[EtSO_4]^-$ (x_1) + propionic acid (x_2)} as function of the composition expressed in the mole fraction of {$[EMIM]^+[EtSO_4]^-$} at 293.15 K (●), 298.15 K (●), 303.15 K (●), 308.15 K (●) and 313.15 K (●). The solid line represents the smoothness of these data.

Table 5.1.1.1 report the results of excess molar volume V_m^E, for the $[EMIM]^+[EtSO_4]^-$ (x_1) + acetic or propionic acid (x_2) systems and are also plotted in Fig. 5.1.1.3 (a) and (b).

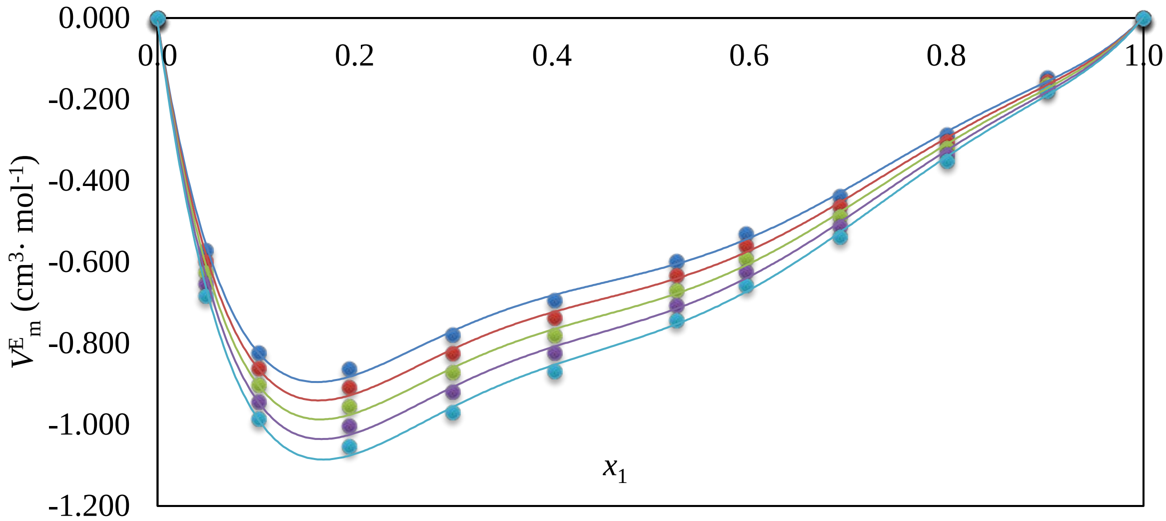


Fig. 5.1.1.3 (a) Excess molar volumes, V_m^E, of binary mixtures of (a) {$[EMIM]^+[EtSO_4]^-$ (x_1) + acetic acid (x_2)} as function of the composition expressed in the mole fraction of {$[EMIM]^+[EtSO_4]^-$ at 293.15 K (●), 298.15 K (●), 303.15 K (●), 308.15 K (●) and 313.15 K (●). The solid lines were generated using Redlich-Kister curve-fitting.

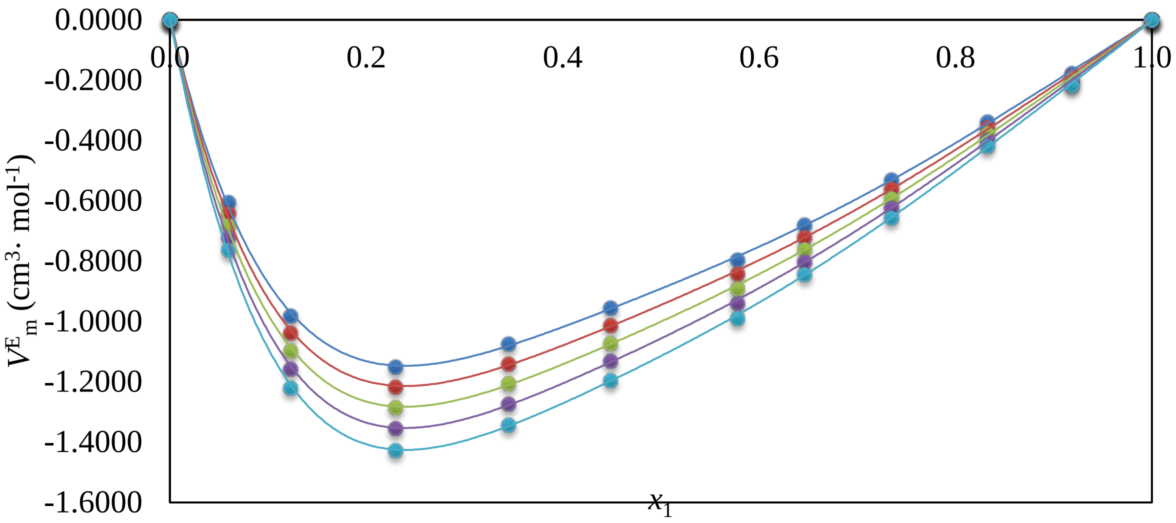


Fig. 5.1.1.3 (b) Excess molar volumes, V^{E}_{m}, of binary mixtures of $[EMIM]^{+}[EtSO_4]^{-}$ (x_1) + propionic acid (x_2)} as function of the composition expressed in the mole fraction of {$[EMIM]^{+}[EtSO_4]^{-}$ at 293.15 K (●), 298.15 K (●), 303.15 K (●), 308.15 K (●) and 313.15 K (●). The solid lines were generated using Redlich-Kister curve-fitting.

As seen from results reported in Table 5.1.1.1 the V^{E}_{m} values for $[EMIM]^{+}[EtSO_4]^{-}$ with acetic or propionic acid are negative throughout the whole range of composition at all investigated temperatures for both systems. ILs are complex solvents, and have a capability to interact with acetic or propionic acid molecules simultaneously through, dispersive, ionic, hydrogen bonding, and dipolar interaction (Deenadayalu. 2006) The negative contribution reveals that interactions between unlike molecules such as formation of hydrogen bonds and charge transfer complexes. In this study, when acetic or propionic acid is mixed with $[EMIM]^{+}[EtSO_4]^{-}$, ion–dipole interactions between acetic or propionic acid molecules and imidazolium ring of IL lead to the negative V^{E}_{m} values. The packing/filling effect of acetic or propionic acid molecules in the interstices of IL, ion–dipole interactions between acetic or propionic acid and imidazolium ring of IL, all contribute to the negative values of V^{E}_{m} (Deenadayalu. 2006) The V^{E}_{m} minimum values decrease with an increase in temperature for both the systems. The negative values of {$[EMIM]^{+}[EtSO_4]^{-}$ (x_1) + propionic acid (x_2)} > {[EMIM]+[EtSO4]– (x_1) + acetic acid (x_2)} are an indication of the presence of stronger interactions in the mixtures. These results indicate that the interaction of $[EMIM]^{+}[EtSO_4]^{-}$ with propionic acid is stronger than $[EMIM]^{+}[EtSO_4]^{-}$ with acetic acid due to the addition of an alkyl group on propionic acid. The $V^{E}_{m,\,min}$ values were −1.053 cm^{3} mol^{-1}, and −1.427 cm^{3}.mol^{-1} occurring at x_1 = 0.1943 and 0.2293, respectively for the systems {$[EMIM]^{+}[EtSO_4]^{-}$ (x_1) + acetic or propionic acid (x_2)} at all temperatures.

Moreover, The results of isentropic compressibility κ_S, and deviation in isentropic compressibility, $\Delta\kappa_S$, for {$[EMIM]^+[EtSO_4]^-$ (x_1) + acetic or propionic acid (x_2)} systems at different temperatures also given in Table 5.1.1.1.

Table 5.1.1.1 Densities, ρ, excess molar volume, V_m^E, speed of sound, u, isentropic compressibility, κ_S, and deviation in isentropic compressibility, $\Delta\kappa_S$, for the binary system {$[EMIM]^+[EtSO_4]^-$ (x_1) + acetic acid or propionic acid (x_2)} at 293.15, 298.15, 303.15, 308.15 and 313.15 K.

x_1	ρ/gcm^{-3}	V_m^E /cm^{3}mol^{-1}	u/ms^{-1}	κ_S/10^8×Pa^{-1}	$\Delta\kappa_S$ /10^8×Pa^{-1}
{$[EMIM]^+[EtSO_4]^-$ + acetic acid					
T = 293.15 K					
0.0000	1.04975	0.000	1152.7	72	0.0
0.0488	1.08732	-0.572	1253.3	59	-11.0
0.1027	1.11529	-0.823	1339.1	50	-17.2
0.1943	1.14654	-0.863	1437.5	42	-21.0
0.2990	1.17099	-0.779	1510.8	37	-21.3
0.4025	1.18902	-0.695	1560.5	35	-19.6
0.5263	1.20543	-0.598	1603.2	32	-16.5
0.5969	1.21290	-0.530	1622.3	31	-14.4
0.6920	1.22144	-0.438	1644.8	30	-11.3
0.8007	1.22923	-0.288	1663.9	29	-7.4
0.9022	1.23534	-0.147	1681.0	29	-3.7
1.0000	1.24032	0.000	1693.1	28	0.0
T = 298.15 K					
0.0000	1.04413	0.000	1135.7	74	0.0
0.0488	1.08230	-0.598	1237.2	60	-11.7
0.1027	1.11066	-0.862	1324.0	51	-18.2
0.1943	1.14228	-0.908	1423.1	43	-22.2
0.2990	1.16701	-0.824	1497.0	38	-22.4
0.4025	1.18520	-0.737	1547.1	35	-20.6
0.5263	1.20174	-0.633	1590.2	33	-17.3
0.5969	1.20926	-0.561	1609.6	32	-15.1

0.6920	1.21787	-0.463	1632.2	31	-11.9
0.8007	1.22571	-0.303	1651.5	30	-7.8
0.9022	1.23187	-0.155	1668.7	29	-3.9
1.0000	1.23689	0.000	1680.8	29	0.0
T = 303.15 K					
0.0000	1.03848	0.000	1118.4	77	0.0
0.0488	1.07727	-0.625	1221.0	62	-12.4
0.1027	1.10602	-0.902	1308.6	53	-19.3
0.1943	1.13803	-0.955	1408.6	44	-23.4
0.2990	1.16302	-0.871	1483.1	39	-23.6
0.4025	1.18138	-0.780	1533.6	36	-21.7
0.5263	1.19806	-0.669	1577.1	34	-18.2
0.5969	1.20563	-0.592	1596.6	33	-15.9
0.6920	1.21431	-0.488	1619.5	31	-12.5
0.8007	1.22220	-0.319	1639.0	30	-8.2
0.9022	1.22841	-0.163	1656.4	30	-4.1
1.0000	1.23346	0.000	1668.5	29	0.0
T = 308.15 K					
0.0000	1.03283	0.000	1101.2	80	0.0
0.0488	1.07225	-0.654	1204.9	64	-13.2
0.1027	1.10140	-0.943	1293.3	54	-20.4
0.1943	1.13380	-1.003	1394.1	45	-24.7
0.2990	1.15905	-0.919	1469.2	40	-24.9
0.4025	1.17757	-0.824	1520.1	37	-22.9
0.5263	1.19439	-0.706	1564.0	34	-19.2
0.5969	1.20202	-0.624	1583.8	33	-16.7
0.6920	1.21076	-0.512	1606.9	32	-13.1
0.8007	1.21871	-0.335	1626.6	31	-8.6
0.9022	1.22497	-0.171	1644.2	30	-4.3
1.0000	1.23006	0.000	1656.4	30	0.0
T = 313.15 K					
0.0000	1.02718	0.000	1084.0	83	0.0
0.0488	1.06723	-0.683	1188.8	66	-14.0

0.1027	1.09677	-0.986	1278.0	56	-21.6
0.1943	1.12957	-1.053	1379.8	47	-26.1
0.2990	1.15509	-0.969	1455.5	41	-26.2
0.4025	1.17378	-0.869	1506.8	38	-24.1
0.5263	1.19073	-0.743	1551.1	35	-20.2
0.5969	1.19842	-0.656	1571.0	34	-17.6
0.6920	1.20722	-0.538	1594.4	33	-13.8
0.8007	1.21523	-0.351	1614.3	32	-9.1
0.9022	1.22154	-0.179	1632.0	31	-4.6
1.0000	1.22667	0.000	1644.4	30	0.0

{$[EMIM]^+[EtSO_4]^-$ + propionic acid

T = 293.15 K

0.0000	0.99333	0.000	1164.7	74	0.0
0.0595	1.03538	-0.604	1240.4	63	-8.7
0.1226	1.07014	-0.981	1320.2	54	-15.0
0.2293	1.11264	-1.150	1421.7	44	-19.2
0.3444	1.14563	-1.075	1494.8	39	-19.3
0.4484	1.16885	-0.954	1542.7	36	-17.6
0.5776	1.19205	-0.796	1590.3	33	-14.4
0.6461	1.20218	-0.680	1611.6	32	-12.4
0.7345	1.21374	-0.530	1635.9	31	-9.6
0.8322	1.22467	-0.338	1659.4	30	-6.2
0.9182	1.23321	-0.177	1678.0	29	-3.1
1.0000	1.24032	0.000	1693.1	28	0.0

T = 298.15 K

0.0000	0.98794	0.000	1146.0	77	0.0
0.0595	1.03059	-0.642	1223.4	65	-9.4
0.1226	1.06571	-1.038	1304.5	55	-16.0
0.2293	1.10856	-1.216	1407.2	46	-20.4
0.3444	1.14175	-1.139	1481.0	40	-20.5
0.4484	1.16511	-1.012	1529.4	37	-18.7
0.5776	1.18841	-0.843	1577.4	34	-15.3
0.6461	1.19858	-0.720	1598.8	33	-13.1
0.7345	1.21019	-0.561	1623.3	31	-10.1

0.8322	1.22116	-0.357	1647.0	30	-6.6
0.9182	1.22974	-0.187	1665.8	29	-3.3
1.0000	1.23689	0.000	1680.8	29	0.0

T = 303.15 K

0.0000	0.98254	0.000	1127.1	80	0.0
0.0595	1.02579	-0.681	1206.2	67	-10.1
0.1226	1.06129	-1.097	1288.6	57	-17.1
0.2293	1.10448	-1.285	1392.4	47	-21.7
0.3444	1.13788	-1.205	1467.0	41	-21.7
0.4484	1.16137	-1.071	1515.9	37	-19.8
0.5776	1.18479	-0.891	1564.4	34	-16.2
0.6461	1.19500	-0.761	1585.9	33	-13.9
0.7345	1.20666	-0.592	1610.7	32	-10.7
0.8322	1.21768	-0.377	1634.6	31	-6.9
0.9182	1.22629	-0.197	1653.5	30	-3.5
1.0000	1.23346	0.000	1668.5	29	0.0

T = 308.15 K

0.0000	0.97714	0.000	1108.3	83	0.0
0.0595	1.02100	-0.721	1189.2	69	-10.9
0.1226	1.05687	-1.157	1272.8	58	-18.3
0.2293	1.10041	-1.355	1377.8	48	-23.1
0.3444	1.13403	-1.273	1453.1	42	-23.1
0.4484	1.15763	-1.131	1502.5	38	-21.0
0.5776	1.18117	-0.939	1551.4	35	-17.1
0.6461	1.19143	-0.802	1573.2	34	-14.7
0.7345	1.20314	-0.623	1598.1	33	-11.3
0.8322	1.21420	-0.397	1622.2	31	-7.3
0.9182	1.22286	-0.207	1641.2	30	-3.7
1.0000	1.23006	0.000	1656.4	30	0.0

T = 313.15 K

0.0000	0.97175	0.000	1089.6	87	0.0
0.0595	1.01621	-0.763	1172.3	72	-11.7
0.1226	1.05246	-1.219	1257.1	60	-19.6

0.2293	1.09635	-1.427	1363.3	49	-24.6
0.3444	1.13019	-1.342	1439.4	43	-24.5
0.4484	1.15393	-1.194	1489.2	39	-22.3
0.5776	1.17756	-0.989	1538.5	36	-18.2
0.6461	1.18787	-0.844	1566.5	34	-15.8
0.7345	1.19963	-0.655	1585.6	33	-12.0
0.8322	1.21074	-0.417	1609.9	32	-7.8
0.9182	1.21944	-0.217	1629.1	31	-3.9
1.0000	1.22667	0.000	1644.4	30	0.0

It is evident from the results reported in Table 5.1.1.1 that in general, the κ_S values increase as temperature increases at a fixed composition for both systems due to an increase in thermal agitation, making the solution more compressible (Zafarani-Moattar. 2005) The κ_S value decreases with concentration of $[EMIM]^+[EtSO_4]^-$ at a fixed temperature for both systems. The interactions between the binary mixtures lead to the decrease in the free-space, thereby contributing to the negative deviation in isentropic compressibility (Gowrisankar. 2013) Fig. 5.1.1.4 (a) & (b) shows that the $\Delta\kappa S$ values of $[EMIM]^+[EtSO_4]^-$ with acetic or propionic acid are negative over the entire composition range of $[EMIM]^+[EtSO_4]^-$ at all temperatures. The $\Delta\kappa_{S,min}$ values were −26.2 and −24.6 occurring at x_1 = 0.2990 and 0.2293, respectively for each system. The behaviour of $\Delta\kappa_S$ implies that these mixtures are less compressible than the ideal mixture. This is due to the closer approach of unlike molecules and a stronger interaction between acetic or propionic acid and $[EMIM]^+[EtSO_4]^-$ mixtures that leads to a decrease in compressibility. In general, the $\Delta\kappa_S$ values decrease with an increase in temperature for both systems at a fixed composition of $[EMIM]^+[EtSO_4]^-$ as shown in Fig. 5.1.1.4 (a) and (b).

The $\Delta\kappa_S$ values for $\{[EMIM]^+[EtSO4]^-$ (x_1) + propionic acid (x_2)} > $\{[EMIM]^+[EtSO4]^-$ (x_1) + acetic acid (x_2)} indicating that there is a decrease in compressibility from the ideal mixture in order of propionic acid > acetic acid due to the addition of an alkyl group. The decrease in compressibility is due to stronger interaction between components of mixtures due to the proximity of unlike molecules (Zafarani-Moattar. 2005) The excess/deviation functions have been correlated by the Redlich–Kister equation. These results are summarized in Table 5.1.1.2, together with the corresponding standard deviations (σ).

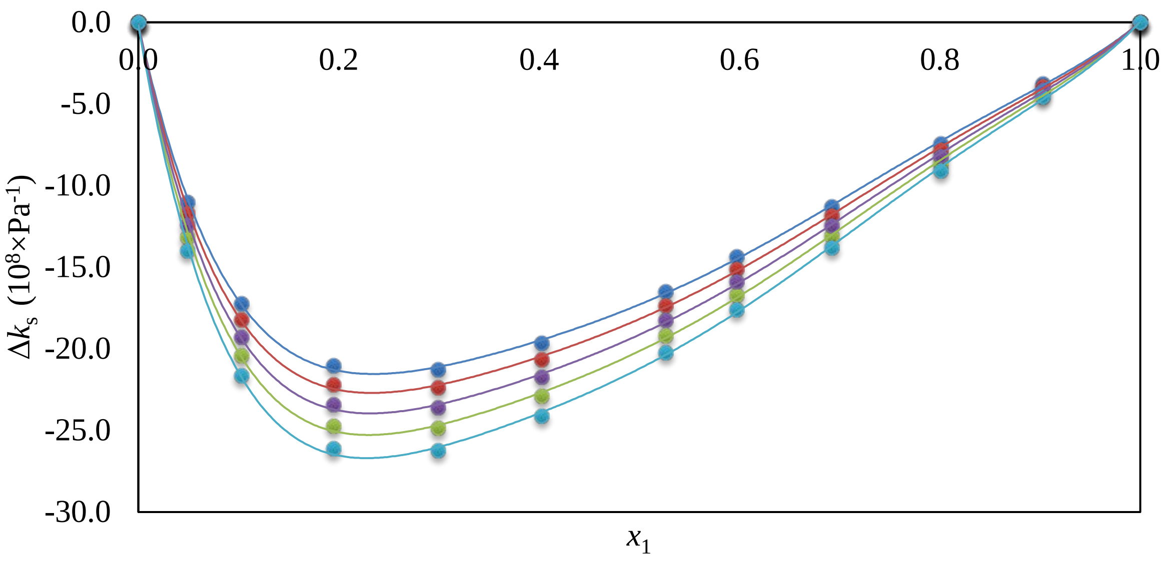


Fig. 5.1.1.4 (a) Deviation in isentropic compressibility, $\Delta\kappa_S$, of binary mixtures of {$[EMIM]^+[EtSO_4]^-$ (x_1) + acetic acid (x_2)} as function of the composition expressed in the mole fraction of {$[EMIM]^+[EtSO_4]^-$ at 293.15 K (●), 298.15 K (●), 303.15 K (●), 308.15 K (●) and 313.15 K (●). The solid lines were generated using Redlich-Kister curve-fitting.

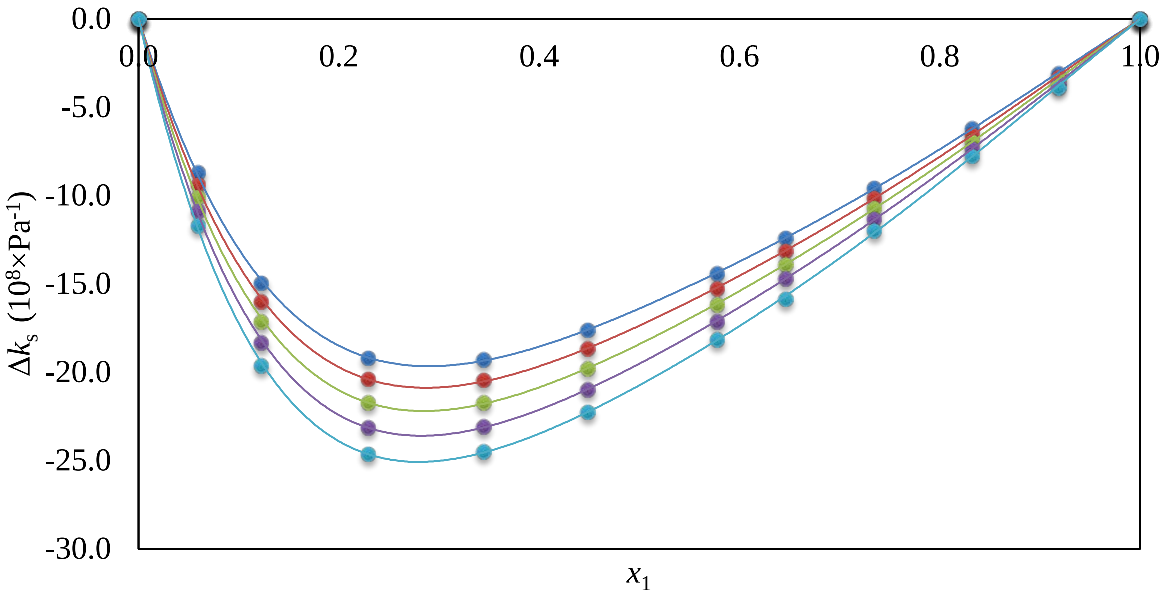


Fig. 5.1.1.4 (b) Deviation in isentropic compressibility, $\Delta\kappa_S$, of binary mixtures of {$[EMIM]^+[EtSO_4]^-$ (x_1) + propionic acid (x_2)} as function of the composition expressed in the mole fraction of {$[EMIM]^+[EtSO_4]^-$ at 293.15 K (●), 298.15 K (●), 303.15 K (●), 308.15 K (●) and 313.15 K (●). The solid lines were generated using Redlich-Kister curve-fitting.

Table 5.1.1.2 Coefficients A_i, and standard deviations, σ, obtained for the binary systems {[EMIM]$^+$[EtSO$_4$]$^-$ (x_1) + acetic or propionic acid (x_2)} at different temperatures for the Redlich-Kister equation.

	T /K	A_0	A_1	A_2	A_3	A_4	σ
		{[EMIM]$^+$[EtSO$_4$]$^-$ (x_1) + acetic acid (x_2)}					
V_m^E /cm^{3}mol^{-1}	293.15	-2.492	-1.255	-1.253	-5.185	-5.208	0.015
	298.15	-2.641	-1.352	-1.298	-5.364	-5.411	0.016
	303.15	-2.792	-1.458	-1.364	-5.538	-5.597	0.017
	308.15	-2.948	-1.571	-1.396	-5.716	-5.849	0.018
	313.15	-3.105	-1.687	-1.477	-5.908	-6.037	0.019
$\Delta\kappa_S$ /10^8×Pa^{-1}	293.15	-69.2	-50.3	-34.0	-64.0	-61.9	0.2
	298.15	-72.6	-52.7	-37.2	-68.9	-65.4	0.2
	303.15	-76.5	-55.5	-38.4	-73.8	-71.5	0.2
	308.15	-80.7	-59.0	-38.7	-78.0	-79.2	0.3
	313.15	-84.9	-61.8	-41.0	-83.1	-85.6	0.3
		{[EMIM]$^+$[EtSO$_4$]$^-$ (x_1) + propionic acid (x_2)}					
V_m^E /cm^{3}mol^{-1}	293.15	-3.566	-2.659	-3.044	-3.068	-1.176	0.010
	298.15	-3.782	-2.813	-3.145	-3.260	-1.357	0.009
	303.15	-4.002	-2.978	-3.275	-3.452	-1.511	0.009
	308.15	-4.226	-3.154	-3.404	-3.636	-1.674	0.009
	313.15	-4.458	-3.330	-3.503	-3.843	-1.890	0.009
$\Delta\kappa_S$ /10^8×Pa^{-1}	293.15	-65.5	-49.4	-42.9	-23.9	-0.5	0.1
	298.15	-69.7	-52.7	-43.1	-26.0	-6.3	0.1
	303.15	-73.9	-55.6	-45.4	-30.1	-8.8	0.1
	308.15	-78.2	-59.6	-48.5	-33.0	-11.5	0.1
	313.15	-83.2	-62.1	-51.9	-38.7	-13.1	0.1

5.1.2 Group 2: {$[BMIM]^+[SCN]^-$} + acetic acid or propionic acid

The density, ρ, was measured at 293.15, 298.15, 303.15, 308.15 and 313.15 K, and at p = 0.1 MPa for the $[BMIM]^+[SCN]^-$, acetic acid, propionic acid, and their binary systems {$[BMIM]^+[SCN]^-$ (x_1) + acetic or propionic acid (x_2)}, and are given in Table 5.1.2.3. The plots of density versus concentration of $[BMIM]^+[SCN]^-$ at investigated temperatures are given in Fig. 5.1.2.5 a & b. It is evident from the results reported in Table 5.1.2.3 that the ρ values decreases with an increase in temperature for both systems. The ρ values increases with an increase in concentration of IL for both systems except at higher concentration of IL for the system {$[BMIM]^+[SCN]^-$ (x_1) + acetic acid (x_2)} where it is decreases. The ρ values increased with an increase in concentration of IL which is due to strengthening of $[BMIM]^+[SCN]^-$ and acetic or propionic acid interactions and densities decreased with increase in concentration which may be due to the weakening of $[BMIM]^+[SCN]^-$ and acetic acid interactions, when the $[BMIM]^+[SCN]^-$ and acetic or propionic acid were mixed (Deosarkar. 2013)

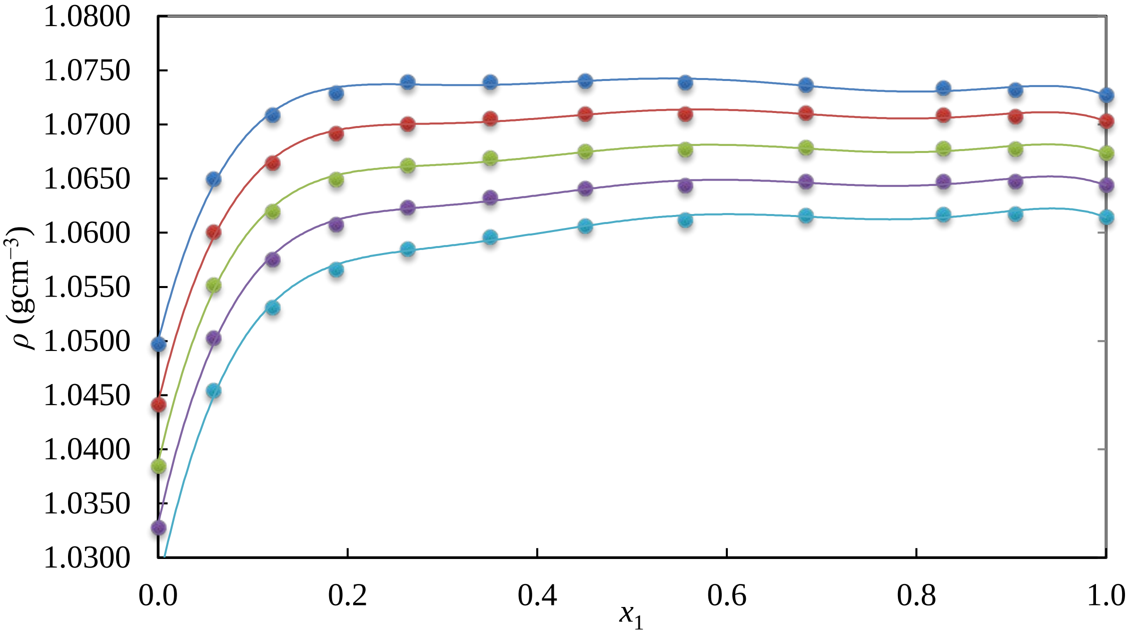


Fig. 5.1.2.5 (a) Density, ρ, for the mixtures of (a) {[BMIM]$^+$[SCN]$^-$ (x_1) + acetic acid (x_2)} as function of the composition expressed in the mole fraction of {[BMIM]$^+$[SCN]$^-$ at 293.15 K (●), 298.15 K (●), 303.15 K (●), 308.15 K (●) and 313.15 K (●). The dotted line represents the smoothness of these data.

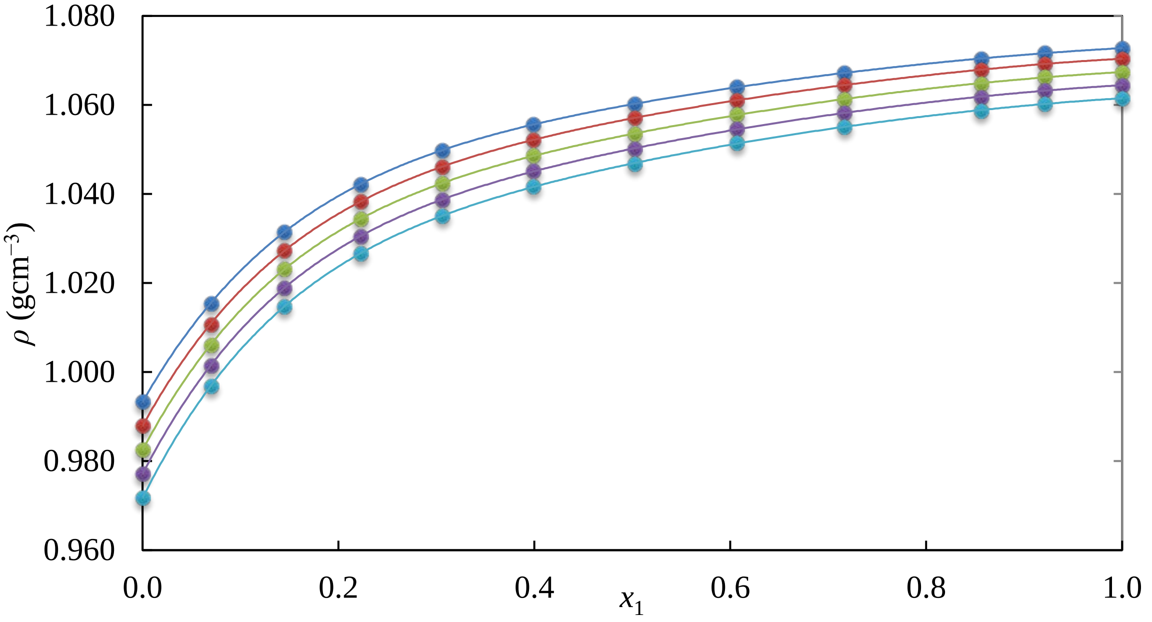


Fig. 5.1.2.5 (b) Density, ρ, for the mixtures of {[BMIM]$^+$[SCN]$^-$ (x_1) + propionic acid (x_2)} as function of the composition expressed in the mole fraction of {[BMIM]$^+$[SCN]$^-$ at 293.15 K (●), 298.15 K (●), 303.15 K (●), 308.15 K (●) and 313.15 K (●). The dotted line represents the smoothness of these data.

Sound velocity is also an important property which describes the solvent-solvent, solute-solvent and solute-solute interactions which occur in the mixture (Roy. 2011) In this regards, the sound velocity data, *u*, were also measured at 293.15, 298.15, 303.15, 308.15 and 313.15 K, and at p = 0.1 MPa, and are given in Table 5.1.2.3. The plots of sound velocity versus concentration of $[BMIM]^+[SCN]^-$, at investigated temperatures, are given in Fig. 5.1.2.6 (a) and (b). It is evident from the results reported in Table 5.1.2.3 that the *u* values also decreases with an increase in temperature and increases with an increase the concentration of $[BMIM]^+[SCN]^-$ for both systems.

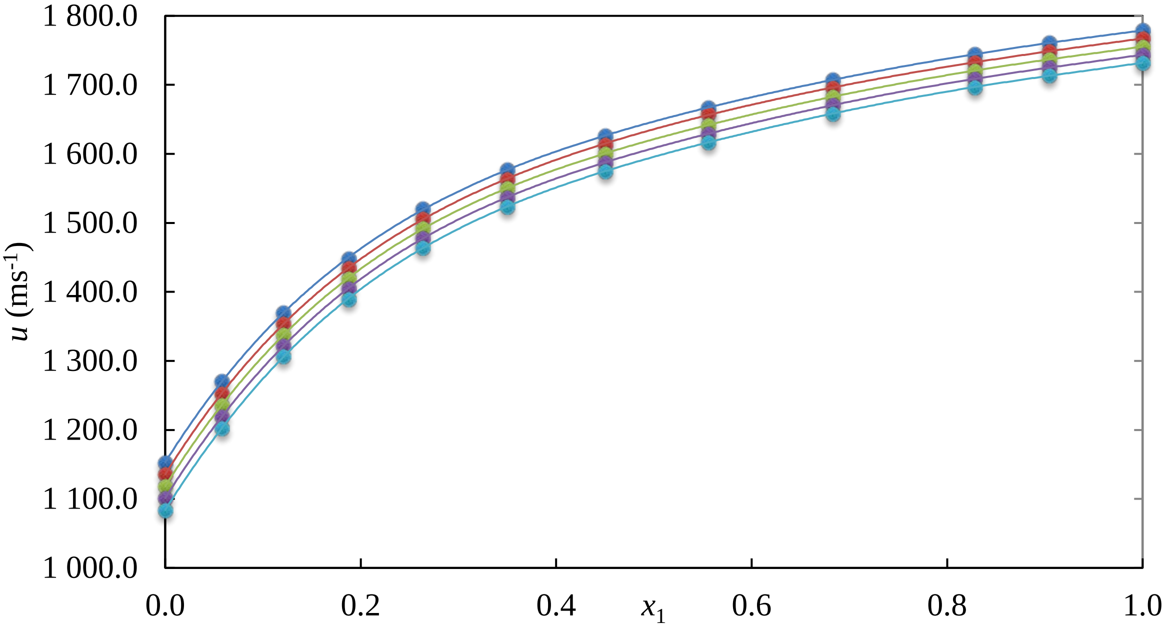


Fig. 5.1.2.6 (a) Sound velocity, *u*, for the mixtures of {$[BMIM]^+[SCN]^-$ (x_1) + acetic acid (x_2)} as function of the composition expressed in the mole fraction of {$[BMIM]^+[SCN]^-$ at 293.15 K (●), 298.15 K (●), 303.15 K (●), 308.15 K (●) and 313.15 K (●). The dotted line represents the smoothness of these data.

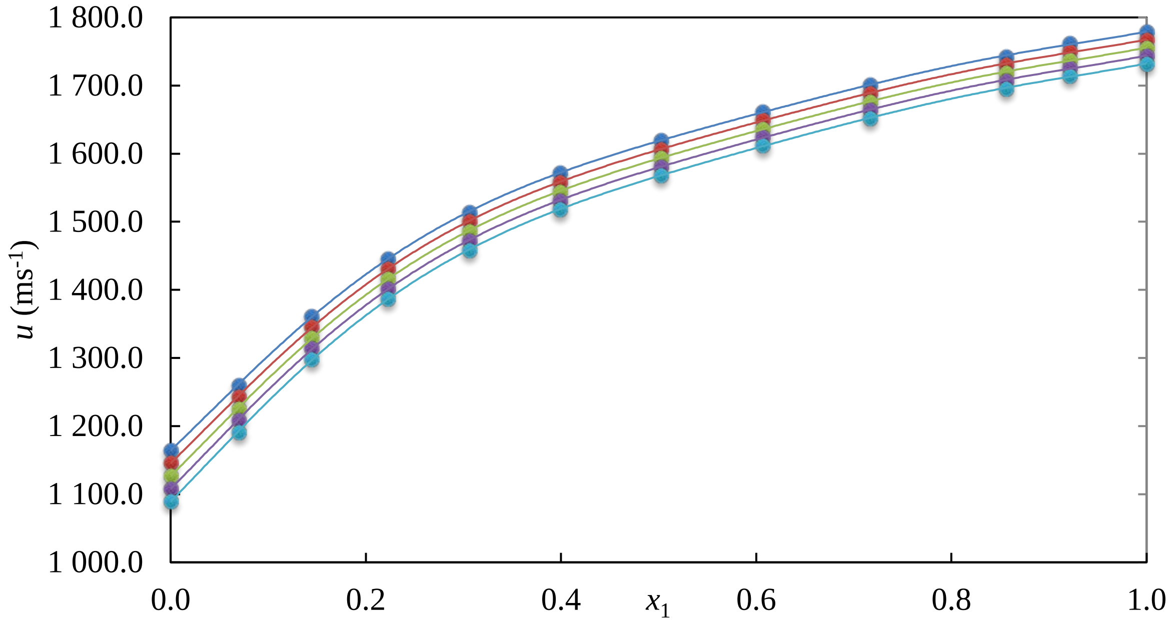


Fig. 5.1.2.6 (b) Sound velocity, *u*, for the mixtures of {[BMIM]$^+$[SCN]$^-$ (x_1) + propionic acid (x_2)} as function of the composition expressed in the mole fraction of {[BMIM]$^+$[SCN]$^-$ at 293.15 K (●), 298.15 K (●), 303.15 K (●), 308.15 K (●) and 313.15 K (●). The dotted line represents the smoothness of these data.

Table 5.1.2.3, report the results of excess molar volume, V_m^E, for the {[BMIM]$^+$[SCN]$^-$ (x_1) + acetic or propionic acid (x_2)} systems and are also plotted in Fig. 5.1.2.7 (a) and (b).

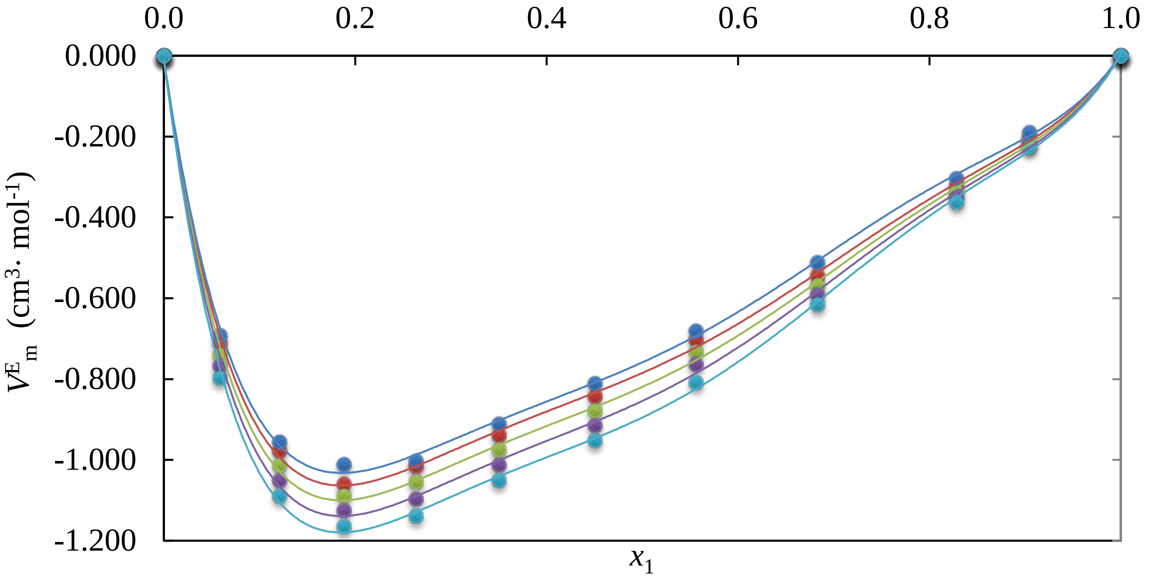


Fig. 5.1.2.7 (a) Excess molar volumes, V_m^E, of binary mixtures of {[BMIM]$^+$[SCN]$^-$ (x_1) + acetic acid (x_2)} as function of the composition expressed in the mole fraction of {[BMIM]$^+$[SCN]$^-$ at 293.15 K (●), 298.15 K (●), 303.15 K (●), 308.15 K (●) and 313.15 K (●). The dotted lines were generated using Redlich-Kister curve-fitting.

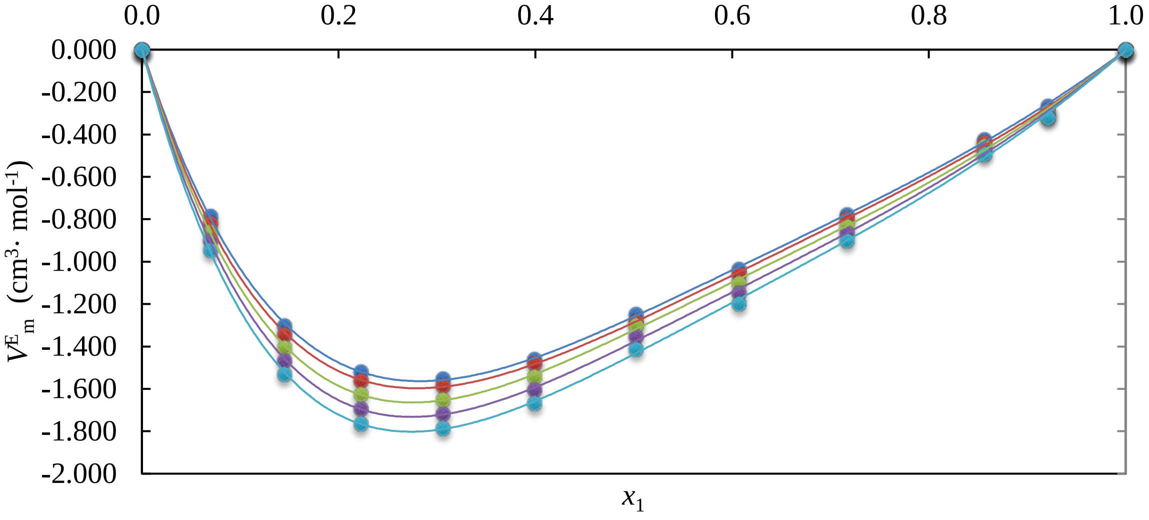


Fig. 5.1.2.7 (b) Excess molar volumes, V_m^E, of binary mixtures of {[BMIM]$^+$[SCN]$^-$ (x_1) + propionic acid (x_2)} as function of the composition expressed in the mole fraction of {[BMIM]$^+$[SCN]$^-$ at 293.15 K (●), 298.15 K (●), 303.15 K (●), 308.15 K (●) and 313.15 K (●). The dotted lines were generated using Redlich-Kister curve-fitting.

It is evident from the results reported in Table 5.1.2.3, that the V_m^E values are negative for both systems. ILs are complex solvents, and have a capability to interact with acetic or propionic acid molecules simultaneously through, dispersive, ionic, hydrogen bonding, and dipolar interaction (Deenadayalu. 2006) The negative V_m^E values for the binary system suggest that a more efficient packing and/or attractive interaction occurred when the [BMIM]$^+$[SCN]$^-$ and acetic or propionic acid were mixed (Deenadayalu. 2006) The acetic or propionic acid tends to fill the interstices of [BMIM]$^+$[SCN]$^-$, and the ion–dipole interaction between the acetic or propionic acid and the [BMIM]$^+$[SCN]$^-$, all contribute to the negative values of excess molar volumes.

The negative values of {[BMIM]$^+$[SCN]$^-$ (x_1) + propionic acid (x_2)} > {[BMIM]$^+$[SCN]$^-$ (x_1) + acetic acid (x_2)} are an indication of the presence of stronger interaction in the mixtures. These results indicate that the interaction of [BMIM]$^+$[SCN]$^-$ with propionic acid is stronger than [BMIM]$^+$[SCN]$^-$ with acetic acid due to the addition alkyl group on propionic acid. The $V_{m,\min}^E$ values were -1.164 cm^{3}mol^{-1} and -1.786 cm^{3}mol^{-1} and occurs at x_1 = 0.1878 and 0.3060, respectively for the systems {[BMIM]$^+$[SCN]$^-$ (x_1) + acetic or propionic acid (x_2)} at all temperatures. The V_m^E minimum values decrease with an increase in temperature for both the systems.

Furthermore, the results of isentropic compressibility, κ_S, and deviation in isentropic compressibility, $\Delta\kappa_S$, for {[BMIM]$^+$[SCN]$^-$ (x_1) + acetic or propionic acid (x_2)} systems at 293.15, 298.15, 303.15, 308.15 and 313.15 K are also given in Table 5.1.2.3.

Table 5.1.2.3 Densities, ρ, excess molar volume, V_m^E, sound velocity, u, isentropic compressibility, κ_S, and deviation in isentropic compressibility, $\Delta\kappa_S$, for the binary system {[BMIM]$^+$[SCN]$^-$ (x_1) + acetic acid or propionic acid (x_2)} at 293.15, 298.15, 303.15, 308.15 and 313.15 K and at pressure p = 0.1 MPa.

x_1	ρ/g·cm^{-3}	V_m^E /cm^3·mol^{-1}	u/m·s^{-1}	$10^8 \times \kappa_S$ /Pa^{-1}	$10^8 \times \Delta\kappa_S$ /Pa^{-1}
		{[BMIM]$^+$[SCN]$^-$ (x_1) + acetic acid			
		T = 293.15 K			
0.0000	1.04975	0.000	1152.7	72	0.0
0.0580	1.06497	-0.692	1270.5	58	-6.5
0.1206	1.07089	-0.955	1369.6	50	-8.8
0.1878	1.07293	-1.010	1448.3	44	-9.0
0.2632	1.07393	-1.002	1520.0	40	-8.6
0.3498	1.07395	-0.910	1576.8	37	-7.2
0.4503	1.07404	-0.811	1626.5	35	-5.7
0.5559	1.07389	-0.681	1667.0	34	-4.2
0.6831	1.07366	-0.511	1707.6	32	-2.7
0.8282	1.07335	-0.303	1744.3	31	-1.3
0.9042	1.07319	-0.189	1760.7	30	-0.7
1.0000	1.07274	0.000	1778.8	29	0.0
		T = 298.15 K			
0.0000	1.04413	0.000	1135.7	74	0.0
0.0580	1.06008	-0.712	1252.4	60	-6.7
0.1206	1.06645	-0.977	1353.9	51	-9.4
0.1878	1.06920	-1.058	1433.8	45	-9.6
0.2632	1.07007	-1.015	1506.3	41	-9.1
0.3498	1.07059	-0.939	1563.6	38	-7.7
0.4503	1.07098	-0.842	1613.6	36	-6.1
0.5559	1.07099	-0.702	1658.3	34	-4.6
0.6831	1.07108	-0.545	1695.4	32	-2.9

0.8282	1.07087	-0.322	1732.4	31	-1.4
0.9042	1.07077	-0.203	1749.0	31	-0.8
1.0000	1.07034	0.000	1767.2	30	0.0
T = 303.15 K					
0.0000	1.03848	0.000	1118.4	77	0.0
0.0580	1.05520	-0.739	1235.9	62	-7.2
0.1206	1.06200	-1.013	1338.0	53	-10.0
0.1878	1.06496	-1.089	1419.0	47	-10.3
0.2632	1.06621	-1.054	1492.2	42	-9.7
0.3498	1.06692	-0.975	1550.1	39	-8.2
0.4503	1.06753	-0.878	1600.6	37	-6.5
0.5559	1.06768	-0.732	1641.9	35	-4.8
0.6831	1.06790	-0.568	1683.1	33	-3.1
0.8282	1.06781	-0.335	1720.3	32	-1.5
0.9042	1.06774	-0.210	1737.0	31	-0.8
1.0000	1.06737	0.000	1755.4	30	0.0
T = 308.15 K					
0.0000	1.0328	0.000	1101.2	80	0.0
0.0580	1.05032	-0.767	1218.7	64	-7.6
0.1206	1.05756	-1.050	1322.1	54	-10.6
0.1878	1.06077	-1.124	1404.2	48	-11.0
0.2632	1.06235	-1.096	1478.1	43	-10.4
0.3498	1.06327	-1.012	1536.6	40	-8.8
0.4503	1.06410	-0.914	1587.6	37	-6.9
0.5559	1.06439	-0.763	1629.3	35	-5.1
0.6831	1.06474	-0.591	1670.8	34	-3.3
0.8282	1.06475	-0.348	1708.4	32	-1.6
0.9042	1.06474	-0.218	1725.2	32	-0.9
1.0000	1.06442	0.000	1743.7	31	0.0
T = 313.15 K					
0.0000	1.02718	0.000	1084.0	83	0.0
0.0580	1.04544	-0.797	1202.0	66	-8.1
0.1206	1.05312	-1.088	1306.4	56	-11.4
0.1878	1.05664	-1.164	1389.4	49	-11.7

0.2632	1.05851	-1.138	1464.2	44	-11.1
0.3498	1.05963	-1.050	1523.3	41	-9.4
0.4503	1.06067	-0.952	1574.8	38	-7.4
0.5559	1.06121	-0.807	1616.9	36	-5.4
0.6831	1.06159	-0.615	1658.6	34	-3.5
0.8282	1.06171	-0.361	1696.4	33	-1.7
0.9042	1.06175	-0.225	1713.4	32	-0.9
1.0000	1.06147	0.000	1732.1	31	0.0

{[BMIM]$^+$[SCN]$^-$ (x_1) + propionic acid

T = 293.15 K

0.0000	0.99333	0.000	1164.7	74	0.0
0.0698	1.01542	-0.784	1260.2	62	-5.1
0.1444	1.03152	-1.301	1361.3	52	-8.6
0.2223	1.04218	-1.519	1445.8	46	-9.5
0.3060	1.04978	-1.551	1514.4	42	-9.0
0.3989	1.05566	-1.460	1571.4	38	-7.7
0.5022	1.06019	-1.248	1619.3	36	-6.0
0.6068	1.06402	-1.033	1662.0	34	-4.5
0.7166	1.06720	-0.778	1700.9	32	-3.1
0.8561	1.07036	-0.422	1742.8	31	-1.5
0.9209	1.07170	-0.267	1761.8	30	-0.8
1.0000	1.07274	0.000	1778.8	29	0.0

T = 298.15 K

0.0000	0.98794	0.000	1146.0	77	0.0
0.0698	1.01077	-0.817	1243.0	64	-5.6
0.1444	1.02732	-1.345	1345.7	54	-9.3
0.2223	1.03827	-1.561	1431.2	47	-10.3
0.3060	1.04609	-1.584	1500.5	42	-9.7
0.3989	1.05215	-1.480	1558.1	39	-8.3
0.5022	1.05709	-1.281	1606.6	37	-6.5
0.6068	1.06109	-1.058	1649.6	35	-4.8
0.7166	1.06446	-0.797	1688.8	33	-3.3
0.8561	1.06784	-0.437	1730.9	31	-1.6

0.9209	1.06930	-0.285	1750.0	31	-0.9
1.0000	1.07034	0.000	1767.2	30	0.0
T = 303.15 K					
0.0000	0.98254	0.000	1127.1	80	0.0
0.0698	1.00613	-0.858	1225.7	66	-6.1
0.1444	1.02313	-1.405	1329.8	55	-10.1
0.2223	1.03437	-1.626	1416.3	48	-11.1
0.3060	1.04240	-1.650	1486.3	43	-10.5
0.3989	1.04865	-1.541	1544.6	40	-9.0
0.5022	1.05343	-1.298	1593.7	37	-7.0
0.6068	1.05785	-1.102	1637.0	35	-5.2
0.7166	1.06132	-0.831	1676.4	34	-3.6
0.8561	1.06479	-0.455	1718.9	32	-1.7
0.9209	1.06630	-0.296	1738.1	31	-1.0
1.0000	1.06737	0.000	1755.4	30	0.0
T = 308.15 K					
0.0000	0.97714	0.000	1108.3	83	0.0
0.0698	1.00149	-0.901	1208.3	68	-6.7
0.1444	1.01895	-1.466	1313.9	57	-10.9
0.2223	1.03048	-1.694	1401.5	49	-12.0
0.3060	1.03873	-1.717	1472.3	44	-11.3
0.3989	1.04517	-1.604	1531.1	41	-9.6
0.5022	1.05009	-1.352	1580.8	38	-7.5
0.6068	1.05464	-1.148	1624.6	36	-5.6
0.7166	1.05820	-0.865	1664.2	34	-3.8
0.8561	1.06176	-0.473	1707.0	32	-1.8
0.9209	1.06330	-0.307	1726.3	32	-1.0
1.0000	1.06442	0.000	1743.7	31	0.0
T = 313.15 K					
0.0000	0.97175	0.000	1089.6	87	0.0
0.0698	0.99686	-0.945	1191.0	71	-7.3
0.1444	1.01478	-1.530	1298.1	58	-11.8
0.2223	1.02660	-1.764	1386.8	51	-12.9
0.3060	1.03507	-1.786	1458.3	45	-12.1

0.3989	1.04169	-1.668	1517.8	42	-10.4
0.5022	1.04679	-1.411	1568.1	39	-8.1
0.6068	1.05144	-1.196	1612.2	37	-6.0
0.7166	1.05509	-0.900	1652.1	35	-4.1
0.8561	1.05874	-0.491	1695.1	33	-1.9
0.9209	1.06033	-0.319	1714.6	32	-1.1
1.0000	1.06147	0.000	1732.1	31	0.0

Standard uncertainties u are $u(T) = \pm 0.02$ K, $u(p) = \pm 0.04$ MPa and the combined expanded uncertainty Uc in mole fractions, density and sound velocity measurements were less than $U_c(x) = \pm\ 0.0004$, $U_c(\rho) = \pm\ 2 \times 10^{-5}$ g·cm^{-3} and $U_c(u) = \pm\ 0.8$ m·s^{-1}, respectively (0.95 level of confidence).

It is evident from the results reported in Table 5.1.2.3 that in general, the isentropic compressibility, κ_s, values increases with an increase in temperature at a fixed composition for both systems due to an increase in thermal agitation, making the solution more compressible (Zafarani-Moattar. 2005) The κ_s value decreases with concentration of [BMIM]$^+$[SCN]$^-$ at a fixed temperature for both systems.

The interactions between the binary mixtures lead to the decrease in the free-space, thereby contributing to the negative deviation in isentropic compressibility (Gowrisankar. 2013) The deviation in isentropic compressibility, $\Delta\kappa_s$, over the entire composition range of [BMIM]$^+$[SCN]$^-$ for both systems is plotted in Fig. 5.1.2.8 (a) and (b).

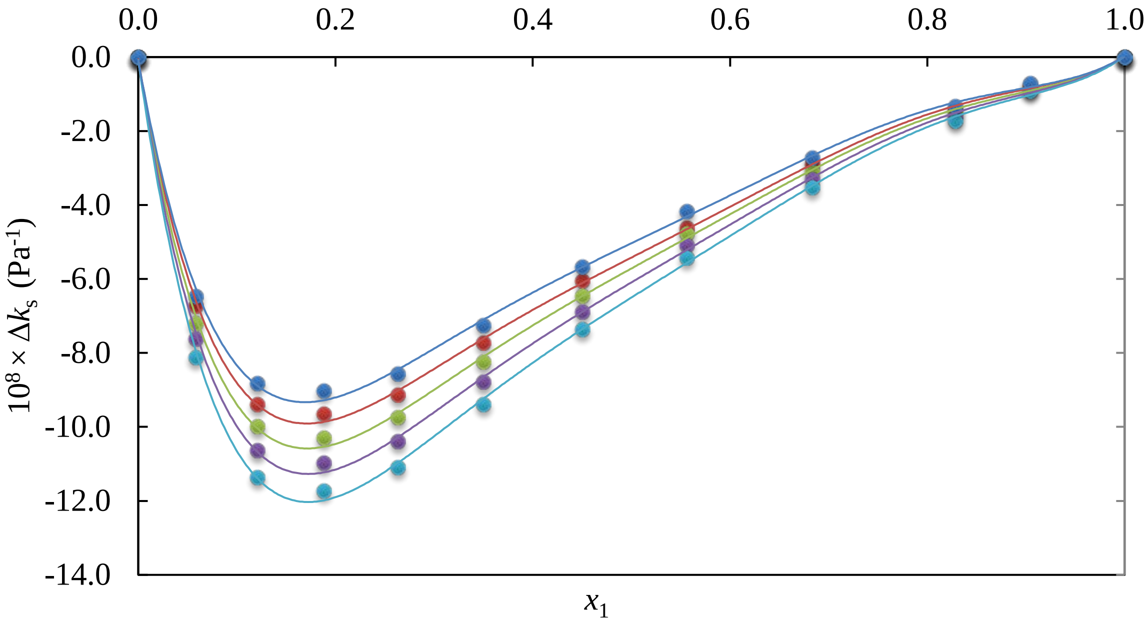


Fig. 5.1.2.8 (a) Deviation of isentropic compressibility, $\Delta\kappa_S$, of binary mixtures of {[BMIM]$^+$[SCN]$^-$ (x_1) + acetic acid (x_2)} as function of the composition expressed in the mole fraction of {[BMIM]$^+$[SCN]$^-$ at 293.15 K (●), 298.15 K (●), 303.15 K (●), 308.15 K (●) and 313.15 K (●).The dotted lines were generated using Redlich-Kister curve-fitting.

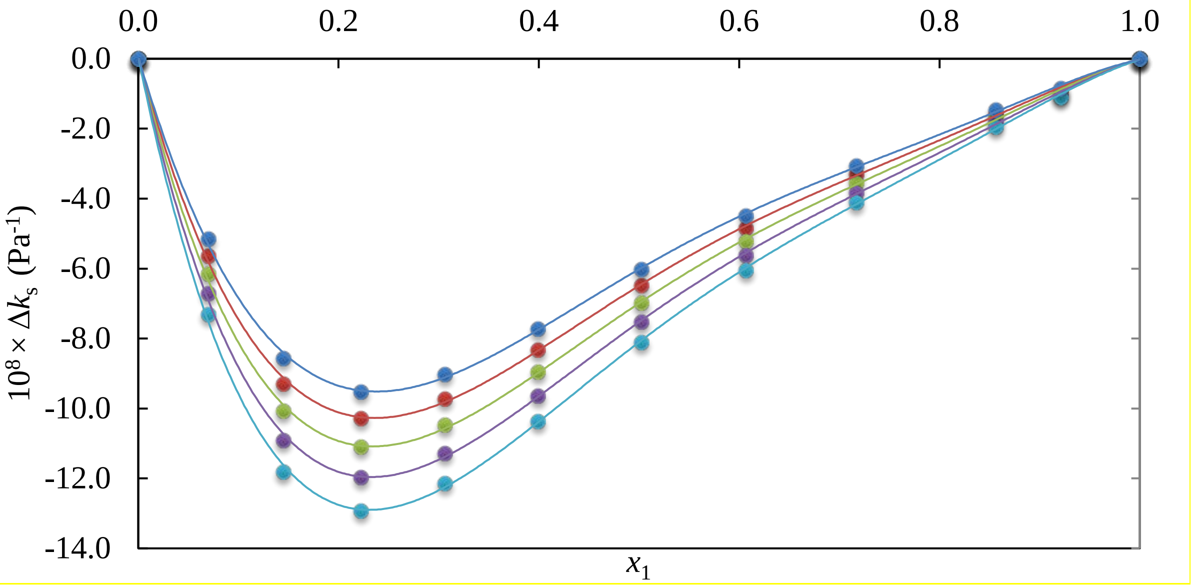


Fig. 5.1.2.8 (b). Deviation of isentropic compressibility, $\Delta\kappa_S$, of binary mixtures of {[BMIM]$^+$[SCN]$^-$ (x_1) + propionic acid (x_2)} as function of the composition expressed in the mole fraction of {[BMIM]$^+$[SCN]$^-$ at 293.15 K (●), 298.15 K (●), 303.15 K (●), 308.15 K (●) and 313.15 K (●).The dotted lines were generated using Redlich-Kister curve-fitting.

It evident from these figures that the values of $\Delta\kappa_S$ are negative for both systems indicating that these mixtures are less compressible than the ideal mixture. This is most likely due to closer approach of unlike molecules as well as a stronger interaction between acetic or propionic acid and $[BMIM]^+[SCN]^-$ mixtures, that leads to a decrease in the compressibility of mixtures. These concluding remarks are in good agreement with those obtained from the volumetric studies. In general, the $\Delta\kappa_S$ values decrease with an increase in temperature for both systems at a fixed composition of $[BMIM]^+[SCN]^-$ as shown in Fig. 5.1.2.8 (a) and (b). The $\Delta\kappa_S$ values for $\{[BMIM]^+[SCN]^- (x_1)$ + acetic acid $(x_2)\} > \{[BMIM]^+[SCN]^- (x_1)$ + propionic acid $(x_2)\}$ indicating that there is a decrease compressibility from the ideal mixture in the order acetic acid > propionic acid, due to the addition of alkyl group. The decrease in compressibility is due to stronger interaction between components of mixtures due to the proximity of unlike molecules (Zafarani-Moattar. 2005) The $\Delta\kappa_{S,min}$ values were -11.7×10^{-8} Pa^{-1} and -12.9×10^{-8} Pa^{-1} and occurs at $x_1 = 0.1878$ and 0.2223, respectively, for each system at all temperatures. The excess/deviation functions have been correlated by the Redlich–Kister equation. These results are summarized in Table 5.1.2.4, together with the corresponding standard deviations (σ).

Table 5.1.2.4 Coefficients A_i, and standard deviations, σ, obtained for the binary systems {[BMIM]$^+$[SCN]$^-$ (x_1) + acetic or propionic acid (x_2)} at different temperatures and at pressure p = 0.1 MPa for the Redlich-Kister equation

	T (K)	A_0	A_1	A_2	A_3	A_4	σ
	{[BMIM]$^+$[SCN]$^-$ (x_1) + acetic acid (x_2)}						
V_m^E /cm^3·mol^{-1}	293.15	-3.038	-2.128	-1.468	-4.230	-5.287	0.016
	298.15	-3.142	-2.075	-1.663	-4.467	-5.272	0.015
	303.15	-3.280	-2.134	-1.589	-4.638	-5.614	0.017
	308.15	-3.418	-2.207	-1.557	-4.803	-5.917	0.018
	313.15	-3.582	-2.247	-1.414	-5.067	-6.353	0.018
$10^8 \times \Delta\kappa_S$ /Pa^{-1}	293.15	-65.4	-49.6	-33.5	-49.5	-46.3	0.2
	298.15	-69.6	-51.0	-33.2	-54.6	-49.7	0.2
	303.15	-72.6	-55.8	-40.0	-54.0	-47.7	0.2
	308.15	-76.5	-58.8	-43.3	-57.6	-48.3	0.2
	313.15	-80.9	-61.9	-44.6	-62.3	-53.6	0.2
	{[BMIM]$^+$[SCN]$^-$ (x_1) + propionic acid (x_2)}						
V_m^E /cm^3·mol^{-1}	293.15	-5.041	-4.257	-3.847	-1.50	0.026	0.011
	298.15	-5.081	-4.295	-4.395	-1.353	0.226	0.016
	303.15	-5.294	-4.442	-4.550	-1.531	0.122	0.016
	308.15	-5.515	-4.600	-4.673	-1.709	-0.040	0.017
	313.15	-5.748	-4.760	-4.753	-1.904	-0.275	0.017
$10^8 \times \Delta\kappa_S$ /Pa^{-1}	293.15	-24.0	-32.7	-38.2	-12.3	12.1	0.1
	298.15	-67.0	-53.5	-46.6	-16.2	8.2	0.1
	303.15	-71.3	-56.5	-50.5	-18.9	8.3	0.1
	308.15	-75.7	-60.9	-52.5	-20.8	5.7	0.1
	313.15	-80.5	-64.6	-54.7	-22.9	2.8	0.1

Standard uncertainties u are $u(T)$ = ±0.02 K, $u(p)$ = ±0.04 MPa and the combined expanded uncertainty Uc in mole fractions, density and sound velocity measurements were less than $U_c(x)$ = ± 0.0004, $U_c(\rho)$ = ± 2 x 10^{-5} g·cm^{-3} and $U_c(u)$ = ± 0.8 m·s^{-1}, respectively (0.95 level of confidence).

5.1.3 Group 3: Acetonitrile with acetic acid or propionic acid

The density, ρ, was measured for the acetic acid, propionic acid, acetonitrile, and their binary systems {acetic acid or propionic acid (x_1) + acetonitrile (x_2)}at 293.15, 298.15, 303.15, 308.15 and 313.15 K, and at p = 0.1 MPa and are given in Tables 5.1.3.5 and 6. The plots of density of studied systems versus concentration of acetic acid or propionic acid, respectively, at investigated temperatures together with literature values reported by (Ahluwalia *et al*. 1995) at 298.15 K (●) and 308.15 K (●) for both systems are given in Figs. 5.1.3.9 (a) and (b).

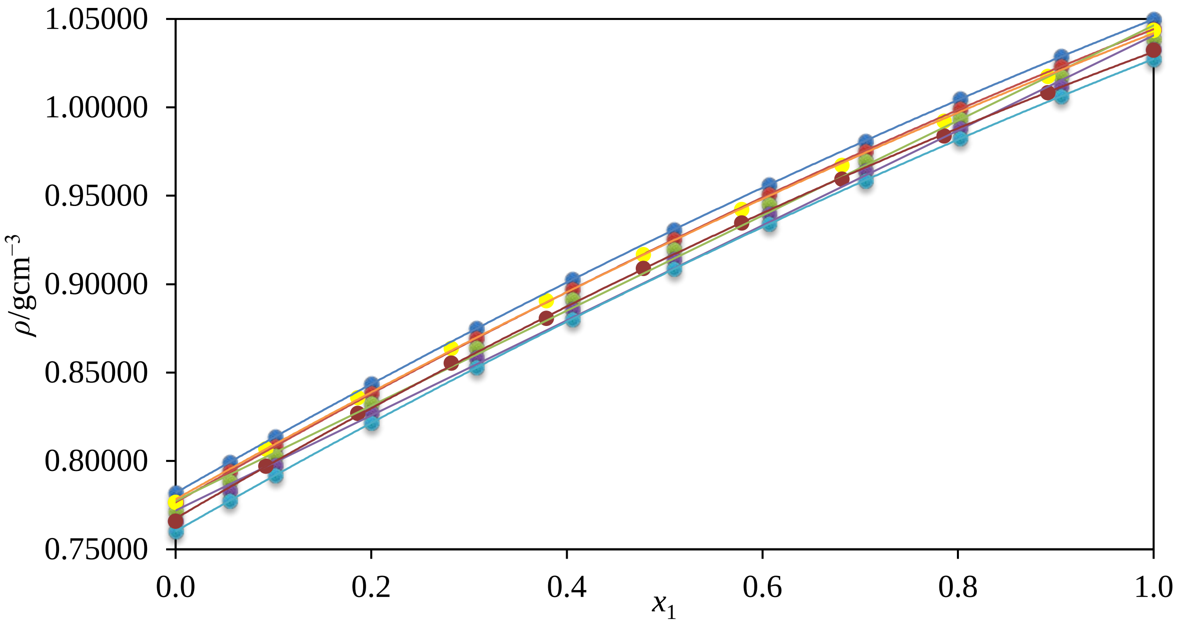


Fig. 5.1.3.9 (a) Density, ρ, of binary mixtures of {acetic acid (x_1) + acetonitrile(x_2)} at 293.15 K (●), 298.15 K (●), 303.15 K (●), 308.15 K (●) and 313.15 K (●) together with literature values reported by Ahluwalia et al. [31] at 298.15 K (●) and 308.15 K (●) for both systems. The solid line represents the smoothness of these data.

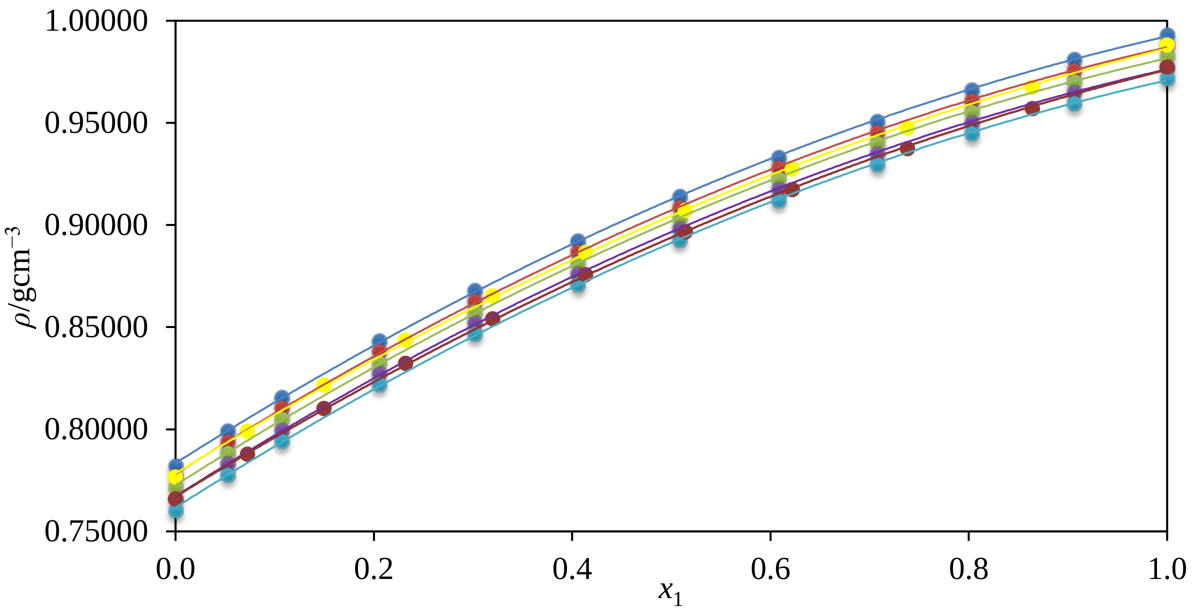


Fig. 5.1.3.9 (b) Density, ρ, of binary mixtures of {propionic acid (x_1) + acetonitrile(x_2)} at 293.15 K (●), 298.15 K (●), 303.15 K (●), 308.15 K (●) and 313.15 K (●) together with literature values reported by Ahluwalia *et al*. (1995) at 298.15 K (●) and 308.15 K (●) for both systems. The solid line represents the smoothness of these data.

From the Figs. 5.1.3.9 (a) and (b), it appears that experimental density values for both systems have a similar trend for concentration and temperature with (Ahluwalia *et al*. 1995) but there is a deviation in density values 0.005 g.cm^{-3} between the experimental density values and those reported by (Ahluwalia *et al*. 1995) This may be attributed due to the purity of the chemicals, accuracy of the solution preparation as well as the accuracy of the instrument. In the present work, the measurement was done on resent advance instrument as compared to those reported by Ahluwalia et al. It is evident from the results reported in Tables 5.1.3.5 and 6 that the ρ values decreases with an increase in temperature. Increasing the temperature of the mixtures, the thermal agitation taking place and causes molecules in the mixture to speed up and spread slightly further apart, occupying a larger volume due to this density decreases. The ρ values increases with an increase in concentration for both systems.

Solvent-solvent, solute-solvent and solute-solute interactions which occur in the liquid mixtures can be described by speed of sound data (Roy. 2011) In this regards, the speed of sound, u, were also measured at 293.15, 298.15, 303.15, 308.15 and 313.15 K, and at p = 0.1 MPa, and are given in Tables 5.1.3.5 and 6. The plots of speed of sound versus concentration of acetic or propionic acid, respectively, at investigated temperatures together with literature values reported by Marczal et al. (Marczak. 2008) at 293.47 K (●) and 308.77 K (●) for {propionic acid (x_1) + acetonitrile (x_2)} system are given in Figs. 5.1.3.10 (a) and (b), respectively.

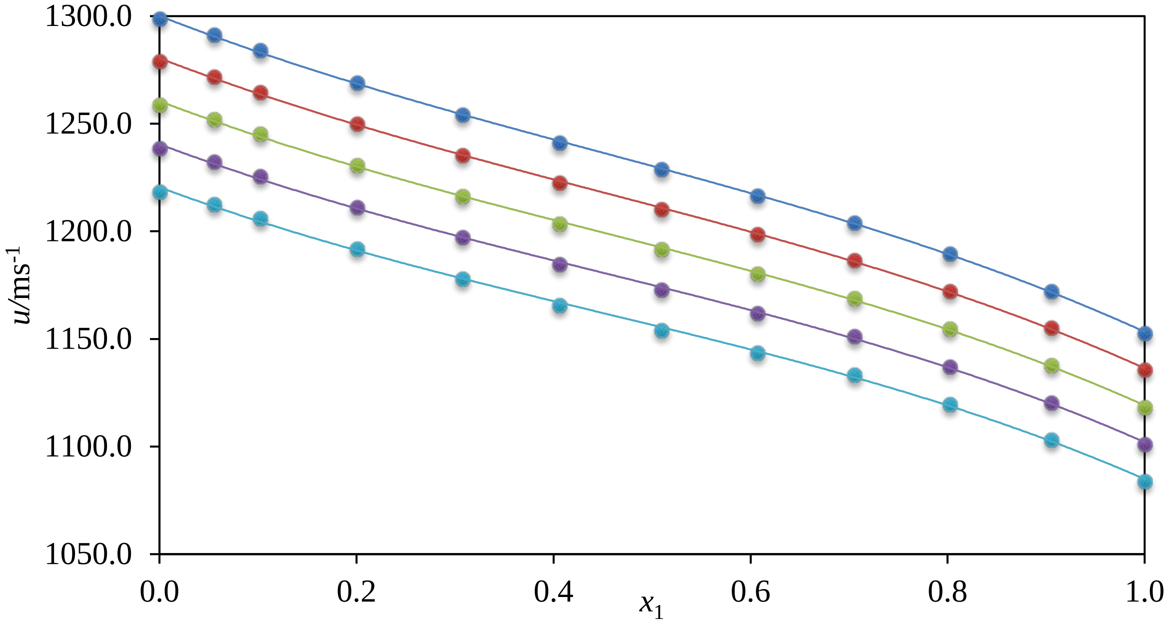
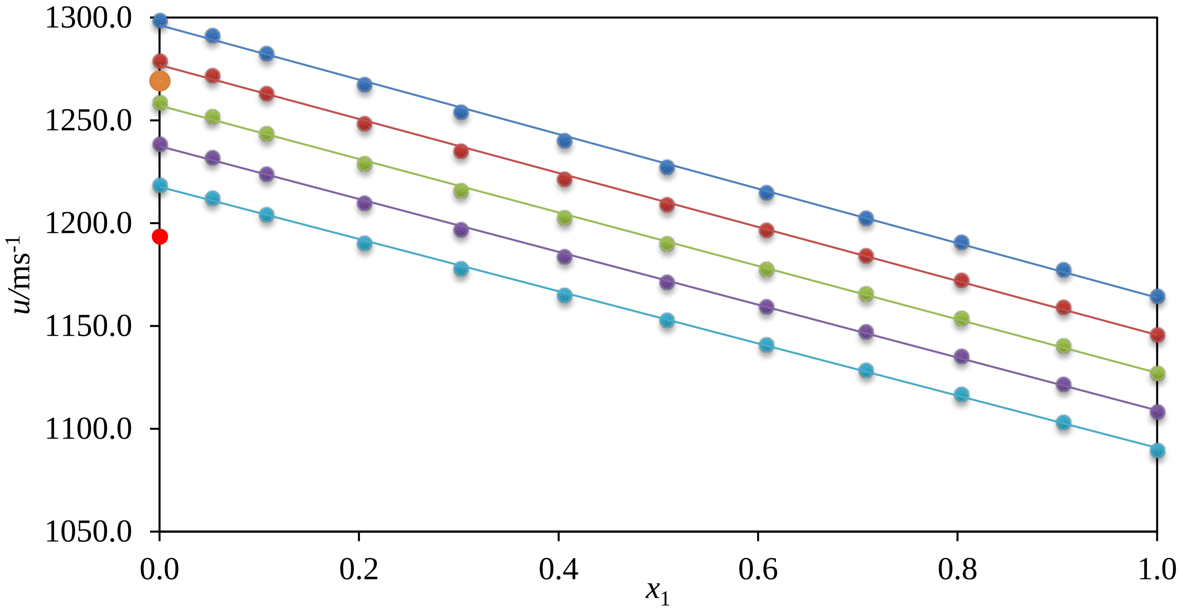


Fig. 5.1.3.10 (a) Sound velocity, *u*, of binary mixtures of {acetic acid (x_1) + acetonitrile (x_2)} at 293.15 K (●), 298.15 K (●), 303.15 K (●), 308.15 K (●) and 313.15 K (●) together with literature values reported by (Marczak. 2008) at 293.47 K (●) and 308.77 K (●) for {propionic acid (x_1) + acetonitrile (x_2)} system. The solid line represents the smoothness of these data.



Figs. 5.1.3.10 (b). Sound velocity, *u*, of binary mixtures of {propionic acid (x_1) + acetonitrile (x_2)} at 293.15 K (●), 298.15 K (●), 303.15 K (●), 308.15 K (●) and 313.15 K (●) together with literature values reported by (Marczak. 2008). at 293.47 K (●) and 308.77 K (●) for {propionic acid (x_1) + acetonitrile (x_2)} system. The solid line represents the smoothness of these data.

It is evident from the results reported in Tables 5.1.3.5 and 6 that the *u* values also decreases with an increase in temperature and concentration for both systems. Speed of sound is mainly depend on the density, increasing the temperature of the mixtures, the thermal agitation taking place and causes molecules in the mixture to speed up and spread slightly further apart, occupying a larger volume due to this density decreases as speed of velocity also decreases. From the Fig. 5.1.3.10 (b), it appears that experimental speed of sound values for {propionic acid (x_1) + acetonitrile (x_2)} system have a similar trend for concentration and temperature with (Marczak *et al*. 2008) but there is a deviation in speed of sound values 30 m.s^{-1} between the experimental speed of sound values and those reported by (Marczak. 2008). Probably, it is due to some calibration problem in (Marczak. 2008). It is also suspected that the data reported in (Marczak. 2008) are erroneous, since the pure component data for speed of sound (acetonitrile) deviate from numerous literatures (Chen *et al*. 2015, Shukla *et al*. 2013, Grande *et al*. 2013) data by 30 m.s^{-1} but experimental data of present work is good agreement with numerous literatures (Chen *et al*. 2015, Shukla *et al*. 2013, Grande *et al*. 2013) data. In the present work, the measurement was also done on resent advance instrument as compared to those reported by (Marczak. 2008)

The excess molar volumes, $V_{\mathrm{m}}^{\mathrm{E}}$, for studied systems were calculated using equation given (Singh *et al*. 2014, Singh *et al*. 2014, Singh *et al*. 2016, Bahadur *et al*. 2014, Bahadur e*t al*. 2014, Bahadur *et al*. 2014, Bahadur *et al*. 2016) and are reported in Tables 5.1.3.5 and 6, and also for the sake of clarity and comparison, plotted experimental values together with literature values reported by Letcher and Redhi (2000) at 298.15 K (●) and Lark and Banipal (1985) at 298.15 K (●) and 308.15 K (●) for both systems in Fig. 5.1.3.11 (a) and (b), respectively.

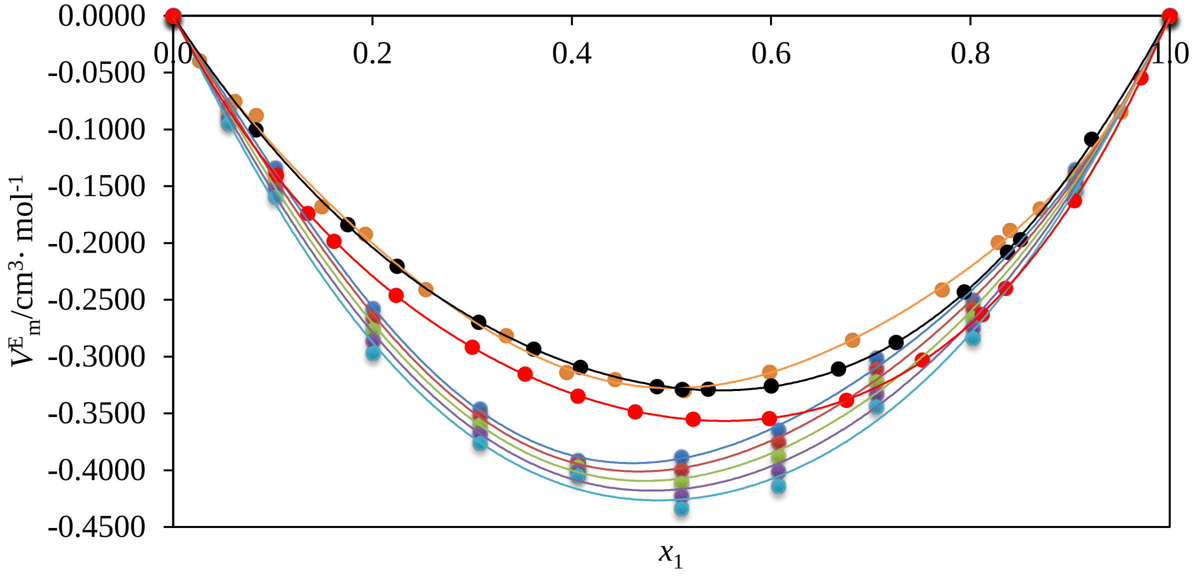


Fig. 5.1.3.11 (a). Excess molar volume, V^E_m, of binary mixtures of {acetic acid (x_1) + acetonitrile (x_2)} at 293.15 K (●), 298.15 K (●), 303.15 K (●),308.15 K (●) and 313.15 K (●) together with literature values reported by Letcher and Redhi at 298.15 K (●) and Lark and Banipal at 298.15 K (●) and 308.15 K (●) for both systems. The solid lines were generated using Redlich-Kister curve-fitting.

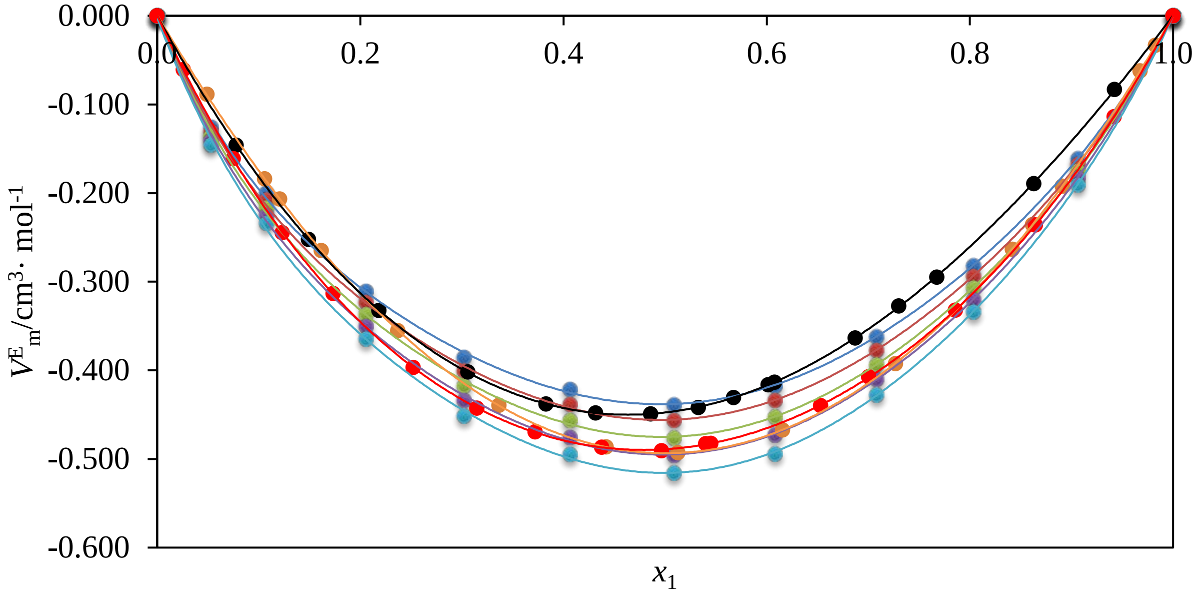


Fig. 5.1.3.11 (b) Excess molar volume, V^E_m, of binary mixtures of {propionic acid (x_1) + acetonitrile (x_2)} at 293.15 K (●), 298.15 K (●), 303.15 K (●),308.15 K (●) and 313.15 K (●) together with literature values reported by Letcher and Redhi at 298.15 K (●) and Lark and Banipal at 298.15 K (●) and 308.15 K (●) for both systems. The solid lines were generated using Redlich-Kister curve-fitting.

From the Fig. 5.1.3.11 (a) and (b), it appears that the negative experimental $V_{\mathrm{m}}^{\mathrm{E}}$ values are quite consistent with Letcher and Redhi and Lark and Banipal for both systems and also follow the tends with temperature for the system {propionic acid (x_1) + acetonitrile (x_2)} with Lark and Banipal but it does not follow the trends with temperature for the systems {acetic or propionic acid (x_1) + acetonitrile (x_2)} with Letcher and Redhi and for the system {acetic acid (x_1) + acetonitrile (x_2)} with Lark and Banipal. This may be attributed to the purity of the chemicals, accuracy of the solution preparation as well as the accuracy of the instrument. To the best of our knowledge, there are no suitable data available in the literature for any of the mixtures considered here to compare our results. From The $V_{\mathrm{m}}^{\mathrm{E}}$ values were negative and decrease with an increase in temperature over the entire range of solvents composition at the studied temperature for both systems as shown in Fig. 5.1.3.11 (a) and (b).The negative $V_{\mathrm{m}}^{\mathrm{E}}$ values attributed mainly to the association between the organic acid and acetonitrile through dipole-dipole interactions. The negative $V_{\mathrm{m}}^{\mathrm{E}}$ values for the binary systems also suggest that a more efficient packing and/or attractive interactions occurred when the acetic or propionic acid and acetonitrile were mixed (Deenadayalu. 2006) The magnitudes of the negative $V_{\mathrm{m}}^{\mathrm{E}}$ were in the order: propionic acid<acetic acid for the binary mixtures with the acetonitrile indicating that the interactions of propionic acid with acetonitrile is stronger than acetic acid with acetonitrile due to mainly addition of alkyl group on propionic acid. The $V_{\mathrm{m,\,min}}^{\mathrm{E}}$ values were -0.434 $\mathrm{cm^3.mol^{-1}}$, and -0.513 $\mathrm{cm^3.mol^{-1}}$occurs at $x_1 = 0.5096$ and 0.5084, respectively for the systems {acetic or propionic acid(x_1) + acetonitrile (x_2)} at all temperatures. The $V_{\mathrm{m,\,min}}^{\mathrm{E}}$ values were also occurring at almost equimolar concentration for both systems. The $V_{\mathrm{m,\,min}}^{\mathrm{E}}$ values decrease with an increase in temperature for both systems. As suggested by Treszczanowicz et al, Roux & Desnoyers and Vijayalakshmi et al. the variation of excess molar volumes, $V_{\mathrm{m}}^{\mathrm{E}}$, is the resultant contribution from several effects. These may be divided into different types, (i) chemical, (ii) physical and (iii) structural. Structural contributions arising from geometrical fitting of one component into the other due to the differences in the free volume and molar volume between components which lead to a negative contribution to $V_{\mathrm{m}}^{\mathrm{E}}$. In this present study, the structural contributions are predominantly evident in the binary systems. The composition and temperature dependence of $V_{\mathrm{m}}^{\mathrm{E}}$ for the studied mixtures may be explained based on structural contributions arising from interstitial accommodation and changes of free volume.

The Newton-Laplace equation is the starting point for the calculation of isentropic compressibility, κ_S, of solutions (Rowlinson .1970, Hirschfelder *et al.* 1937). The deviations in isentropic compressibility, $\Delta\kappa$s, were calculated using the equation given the previous publication (Singh *et al.* 2014, Singh *et al.* 2014, Singh *et al.* 2016, Roy *et al.* 2011, Bahadur *et al.* 2014, Bahadur e*t al.* 2014, Bahadur *et al.* 2014, Bahadur *et al.* 2016). The results for isentropic compressibility, κ_S, and deviation in isentropic compressibility, $\Delta\kappa$s, for studied systems are also given in Tables 5.1.3.5 and 6. Tables 5.1.3.5 and 6, shows that the κ_S values increases with an increase in temperature at a fixed composition for both systems due to an increase in thermal agitation, making acetic or propionic acid with acetonitrile solution more compressible Zafarani-Moattar (2005).

Table 5.1.3.5 Densities, ρ, excess molar volume, V_m^E, sound velocity, u, isentropic compressibility, κ_S, and deviation in isentropic compressibility, $\Delta\kappa_s$, for the binary system{acetic acid (x_1) + acetonitrile (x_2)} at 293.15, 298.15, 303.15, 308.15 and 313.15 K and at pressure p = 0.1 MPa.

x_1	ρ/gcm^{-3}	V_m^E /cm^{3}mol^{-1}	u/ms^{-1}	κ_S /10^8×Pa^{-1}	$\Delta\kappa_S$ /10^8×Pa^{-1}
			T = 293.15 K		
0.0000	0.78204	0.000	1298.8	76	0.0
0.0555	0.79934	-0.079	1291.4	75	-0.6
0.1023	0.81366	-0.134	1284.0	75	-0.8
0.2005	0.84356	-0.258	1269.0	74	-1.4
0.3077	0.87500	-0.346	1254.2	73	-1.9
0.4059	0.90280	-0.391	1241.1	72	-2.2
0.5096	0.93080	-0.388	1228.8	71	-2.6
0.6069	0.95624	-0.364	1216.5	71	-2.6
0.7052	0.98084	-0.301	1204.1	70	-2.6
0.8022	1.00482	-0.250	1189.6	70	-2.2
0.9054	1.02878	-0.135	1172.3	71	-1.4
1.0000	1.04975	0.000	1152.7	72	0.0
			T = 298.15 K		
0.0000	0.77666	0.000	1279.0	79	0.0
0.0555	0.79396	-0.082	1271.9	78	-0.6
0.1023	0.80827	-0.139	1264.8	77	-0.9

0.2005	0.83814	-0.266	1250.0	76	-1.5
0.3077	0.86948	-0.352	1235.5	75	-2.0
0.4059	0.89717	-0.393	1222.5	75	-2.3
0.5096	0.92530	-0.400	1210.1	74	-2.6
0.6069	0.95073	-0.375	1198.5	73	-2.8
0.7052	0.97530	-0.311	1186.6	73	-2.8
0.8022	0.99926	-0.257	1172.2	73	-2.3
0.9054	1.02318	-0.139	1155.1	73	-1.4
1.0000	1.04413	0.000	1135.7	74	0.0
T = 303.15 K					
0.0000	0.77124	0.000	1258.8	82	0.0
0.0555	0.78854	-0.086	1252.2	81	-0.7
0.1023	0.80285	-0.146	1245.3	80	-1.0
0.2005	0.83269	-0.276	1230.6	79	-1.6
0.3077	0.86394	-0.359	1216.3	78	-2.1
0.4059	0.89152	-0.397	1203.5	77	-2.4
0.5096	0.91977	-0.411	1191.6	77	-2.8
0.6069	0.94520	-0.388	1180.3	76	-3.0
0.7052	0.96976	-0.322	1168.9	75	-2.9
0.8022	0.99368	-0.266	1154.7	75	-2.5
0.9054	1.01758	-0.144	1137.8	76	-1.5
1.0000	1.03848	0.000	1118.4	77	0.0
T = 308.15 K					
0.0000	0.76578	0.000	1238.6	85	0.0
0.0555	0.78309	-0.090	1232.4	84	-0.7
0.1023	0.79739	-0.152	1225.6	83	-1.1
0.2005	0.82722	-0.286	1211.3	82	-1.7
0.3077	0.85837	-0.367	1197.2	81	-2.2
0.4059	0.88586	-0.400	1184.7	80	-2.5
0.5096	0.91420	-0.423	1172.9	80	-2.9
0.6069	0.93966	-0.401	1162.0	79	-3.1
0.7052	0.96419	-0.332	1151.1	78	-3.1
0.8022	0.98810	-0.274	1137.2	78	-2.6
0.9054	1.01197	-0.148	1120.4	79	-1.6

1.0000	1.03283	0.000	1101.2	80	0.0
T = 313.15 K					
0.0000	0.76029	0.000]	1218.5	89	0.0
0.0555	0.77760	-0.094	1212.5	87	-0.8
0.1023	0.79191	-0.159	1206.0	87	-1.2
0.2005	0.82171	-0.296	1191.9	86	-1.8
0.3077	0.85279	-0.376	1178.1	84	-2.3
0.4059	0.88016	-0.404	1165.8	84	-2.7
0.5096	0.90860	-0.434	1154.2	83	-3.0
0.6069	0.93410	-0.414	1143.6	82	-3.3
0.7052	0.95862	-0.344	1133.4	81	-3.3
0.8022	0.98250	-0.283	1119.6	81	-2.8
0.9054	1.00634	-0.153	1103.1	82	-1.7
1.0000	1.02718	0.000	1084.0	83	0.0

Standard uncertainties u are $u(T) = \pm 0.02$ K, $u(p) = \pm 0.04$ MPa and the combined expanded uncertainty Uc in mole fractions, density and sound velocity measurements were less than $U_c(x) = \pm 0.0004$, $U_c(\rho) = \pm 9\times10^{-4}$ g·cm^{-3} and $U_c(u) = \pm 0.8$ m·s^{-1}, respectively (0.95 level of confidence).

Table 5.1.3.6 Densities, ρ, excess molar volume, $V_{\mathrm{m}}^{\mathrm{E}}$, sound velocity, u, isentropic compressibility, κ_{S}, and deviation in isentropic compressibility, $\Delta\kappa_{\mathrm{S}}$, for the binary system {propionic acid (x_1) + acetonitrile (x_2)}at 293.15, 298.15, 303.15, 308.15 and 313.15 K and at pressure p = 0.1 MPa.

x_1	ρ/gcm^{-3}	$V_{\mathrm{m}}^{\mathrm{E}}$ /cm^{3}mol^{-1}	u/ms^{-1}	κ_{S}/10^8×Pa^{-1}	$\Delta\kappa_{\mathrm{S}}$ /10^8×Pa^{-1}
		T = 293.15 K			
0.0000	0.78204	0.000	1298.8	76	0.0
0.0524	0.79931	-0.125	1291.4	75	-0.7
0.1072	0.81580	-0.199	1282.6	75	-1.1
0.2054	0.84339	-0.311	1267.5	74	-1.7
0.3018	0.86807	-0.385	1254.0	73	-2.1
0.4059	0.89222	-0.421	1240.2	73	-2.3
0.5084	0.91405	-0.439	1227.4	73	-2.4
0.6081	0.93330	-0.417	1215.0	73	-2.3
0.7080	0.95084	-0.362	1202.6	73	-2.0
0.8033	0.96614	-0.282	1190.8	73	-1.5
0.9062	0.98115	-0.161	1177.6	73	-0.9
1.0000	0.99333	0.000	1164.7	74	0.0
		T = 298.15 K			
0.0000	0.77666	0.000	1279.0	79	0.0
0.0524	0.79395	-0.130	1271.9	78	-0.8
0.1072	0.81046	-0.207	1263.2	77	-1.2
0.2054	0.83808	-0.323	1248.5	77	-1.8
0.3018	0.86277	-0.400	1235.2	76	-2.3
0.4059	0.88694	-0.438	1221.7	76	-2.5
0.5084	0.90877	-0.456	1209.0	75	-2.6
0.6081	0.92801	-0.434	1196.8	75	-2.5
0.7080	0.94555	-0.377	1184.2	75	-2.1
0.8033	0.96083	-0.294	1172.4	76	-1.7
0.9062	0.97580	-0.167	1159.1	76	-1.0
1.0000	0.98794	0.000	1146.0	77	0.0
		T = 303.15 K			

0.0000	0.77124	0.000	1258.8	82	0.0
0.0524	0.78856	-0.135	1252.0	81	-0.8
0.1072	0.80508	-0.216	1243.6	80	-1.3
0.2054	0.83273	-0.336	1229.1	79	-2.0
0.3018	0.85745	-0.417	1216.1	79	-2.5
0.4059	0.88163	-0.457	1202.8	78	-2.7
0.5084	0.90348	-0.476	1190.3	78	-2.8
0.6081	0.92273	-0.452	1177.8	78	-2.7
0.7080	0.94026	-0.393	1165.7	78	-2.4
0.8033	0.95552	-0.307	1153.9	79	-1.8
0.9062	0.97046	-0.175	1140.5	79	-1.1
1.0000	0.98254	0.000	1127.1	80	0.0
		T = 308.15 K			
0.0000	0.76578	0.000	1238.6	85	0.0
0.0524	0.78313	-0.140	1232.1	84	-0.9
0.1072	0.79968	-0.225	1223.9	83	-1.4
0.2054	0.82735	-0.350	1209.8	83	-2.2
0.3018	0.85210	-0.434	1197.0	82	-2.7
0.4059	0.87630	-0.475	1183.9	81	-3.0
0.5084	0.89817	-0.495	1171.5	81	-3.1
0.6081	0.91744	-0.472	1159.5	81	-2.9
0.7080	0.93495	-0.410	1147.2	81	-2.6
0.8033	0.95020	-0.320	1135.3	82	-2.0
0.9062	0.96511	-0.182	1121.8	82	-1.2
1.0000	0.97715	0.000	1108.3	83	0.0
		T = 313.15 K			
0.0000	0.76029	0.000	1218.5	89	0.0
0.0524	0.77767	-0.145	1212.3	87	-1.0
0.1072	0.79424	-0.234	1204.3	87	-1.6
0.2054	0.82195	-0.364	1190.4	86	-2.3
0.3018	0.84672	-0.451	1177.8	85	-2.9
0.4059	0.87095	-0.495	1165.0	85	-3.2
0.5084	0.89284	-0.515	1152.8	84	-3.3
0.6081	0.91215	-0.494	1141.0	84	-3.2

0.7080	0.92963	-0.427	1128.6	84	-2.8
0.8033	0.94488	-0.334	1116.8	85	-2.2
0.9062	0.95976	-0.190	1103.3	86	-1.3
1.0000	0.97175	0.000	1089.6	87	0.0

Standard uncertainties u are $u(T) = \pm 0.02$ K, $u(p) = \pm 0.04$ MPa and the combined expanded uncertainty Uc in mole fractions, density and sound velocity measurements were less than $U_c(x) = \pm 0.0004$, $U_c(\rho) = \pm 9\times10^{-4}$ $g\cdot cm^{-3}$ and $U_c(u) = \pm 0.8$ $m\cdot s^{-1}$, respectively (0.95 level of confidence).

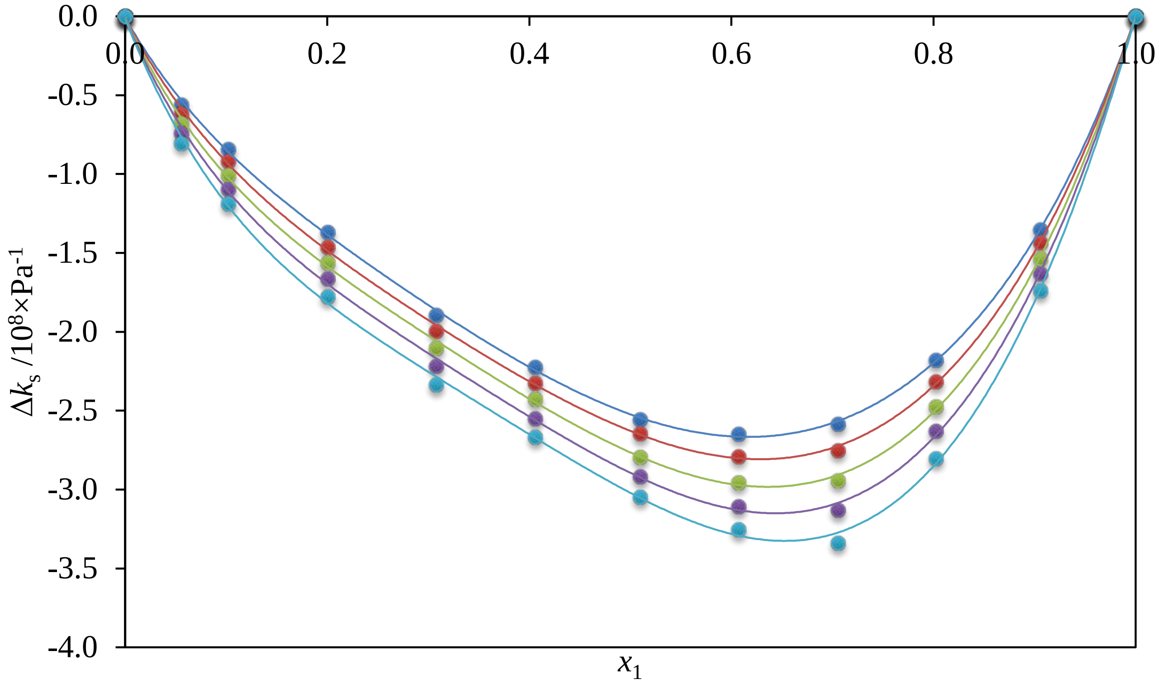


Fig. 5.1.3.12 (a) Deviation of isentropic compressibility, $\Delta\kappa_S$, of binary mixtures of {acetic acid (x_1) + acetonitrile (x_2)} at 293.15 K (●), 298.15 K (●), 303.15 K (●),308.15 K (●) and 313.15 K (●).The solid lines were generated using Redlich-Kister curve-fitting.

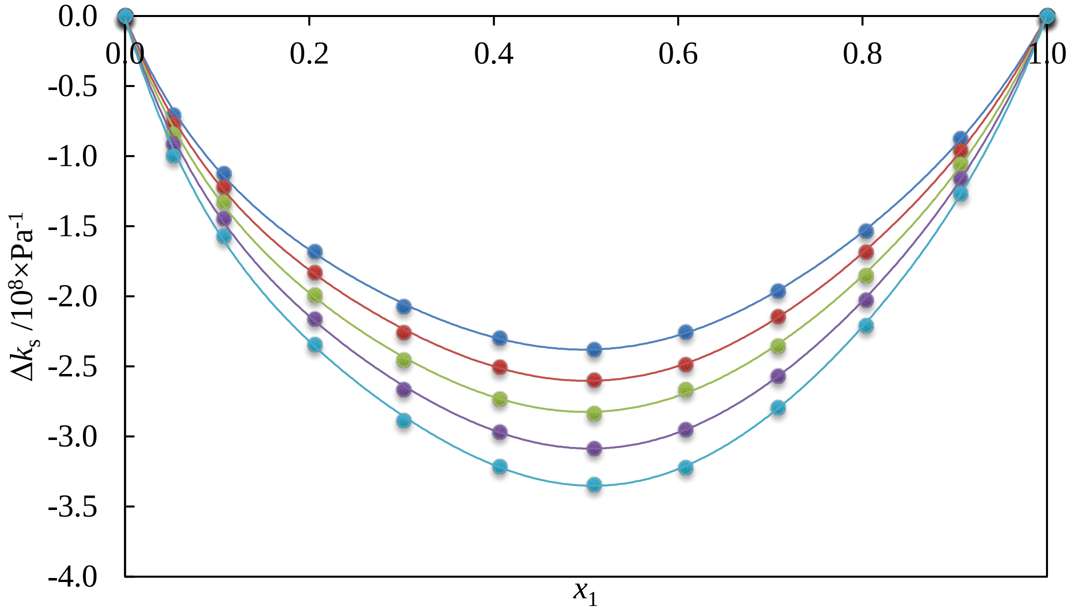


Fig. 5.1.3.12 (b) Deviation of isentropic compressibility, $\Delta\kappa_S$, of binary mixtures of {propionic acid (x_1) + acetonitrile (x_2)}at 293.15 K (●), 298.15 K (●), 303.15 K (●),308.15 K (●) and 313.15 K (●).The solid lines were generated using Redlich-Kister curve-fitting.

In general, the κ_s value decreases with composition at a fixed temperature for both systems. The interactions between organic acid and acetonitrile mixtures lead to the decrease in the free-space, thereby contributing to the negative deviations in isentropic compressibility Gowrisankar. The diagram of Figs. 5.1.3.12 (a) and (b) shows the deviation in isentropic compressibility, $\Delta\kappa_s$, over the entire composition range at studied temperature for both systems.

Figs. 5.1.3.12 (a) and (b) show that the $\Delta\kappa_s$ values are negative for both systems; this is an indication that these mixtures are less compressible than the ideal mixtures. This is due to closer approach of unlike molecules and stronger interactions between acetic or propionic acid and acetonitrile mixtures that subsequently leads to a decrease in the compressibility of the mixtures. These results are in good agreement with those obtained from the volumetric studies. The $\Delta\kappa_s$ values decrease with an increase in temperature for both systems at a fixed composition. The $\Delta\kappa_{s,\text{min}}$ values were the same for both systems but different composition such as $-3.3\times10^{-8}\times\text{Pa}^{-1}$ and $-3.3\times10^{-8}\times\text{Pa}^{-1}$which occurs at $x_1 = 0.7052$ and 0.5084, respectively. The excess/derived properties calculated from the thermophysical properties such as density and speed of sound for {acetic acid or propionic acid (x_1) + acetonitrile (x_2)} systems and were correlated using the Redlich–Kister equation. The values of the fitting parameters have been determined using a least-square method. These results are summarized in Table 5.1.3.7, together with the corresponding standard deviations (σ).

Table 5.1.3.7 Coefficients $A_{i,}$ and standard deviations, σ, obtained for the binary systems {acetic or propionic acid (x_1) + acetonitrile (x_2)} at different temperatures and at pressure p = 0.1 MPa for the Redlich-Kister equation.

	T/K	A_0	A_1	A_2	A_3	A_4	Σ
	{acetic acid (x_1) + acetonitrile (x_2)}						
V_m^E /cm^{3}mol^{-1}	293.15	-5.019	-2.972	-1.711	-4.099	-2.266	0.020
	298.15	-5.229	-3.118	-1.833	-4.237	-2.372	0.022
	303.15	-5.447	-3.258	-1.978	-4.420	-2.470	0.023
	308.15	-5.675	-3.416	-2.087	-4.594	-2.645	0.024
	313.15	-5.913	-3.581	-2.211	-4.791	-2.793	0.025
$\Delta\kappa_S$ /10^8×Pa^{-1}	293.15	-71.6	-49.9	-38.0	-41.3	-26.8	0.2
	298.15	-75.7	-52.9	-39.2	-43.8	-32.0	0.2
	303.15	-80.1	-56.8	-41.1	-46.2	-34.5	0.2
	308.15	-84.7	-59.9	-44.0	-50.7	-36.6	0.2
	313.15	-89.6	-63.9	-45.3	-54.1	-43.3	0.2
	{propionic acid (x_1) + acetonitrile (x_2)}						
V_m^E /cm^{3}mol^{-1}	293.15	-5.062	-2.550	-1.251	-2.816	-3.248	0.016
	298.15	-5.055	-2.889	-1.465	-2.707	-3.362	0.016
	303.15	-5.276	-3.029	-1.533	-2.888	-3.570	0.017
	308.15	-5.507	-3.190	-1.606	-3.041	-3.794	0.018
	313.15	-5.745	-3.348	-1.746	-3.239	-3.928	0.019
$\Delta\kappa_S$ /10^8×Pa^{-1}	293.15	-70.5	-48.4	-28.0	-43.2	-42.6	0.2
	298.15	-74.4	-51.3	-32.7	-46.5	-41.8	0.2
	303.15	-78.6	-54.8	-34.4	-49.7	-45.4	0.2
	308.15	-83.5	-58.2	-35.0	-53.1	-51.8	0.2
	313.15	-88.4	-62.1	-37.5	-56.6	-56.1	0.2

Standard uncertainties u are $u(T)$ = ±0.02 K, $u(p)$ = ±0.04 MPa and the combined expanded uncertainty Uc in mole fractions, density and sound velocity measurements were less than $U_c(x)$ = ± 0.0004, $U_c(\rho)$ = ± 9×10^{-4} g·cm^{-3} and $U_c(u)$ = ± 0.8 m·s^{-1}, respectively (0.95 level of confidence).

5.1.4 Group 4: {$[EMIM]^+[EtSO_4]^-$} or {$[BMIM]^+[SCN]^-$ + Acetonitrile }

The density, ρ, were measured at 293.15, 298.15, 303.15, 308.15 and 313.15 K, and at p = 0.1 MPa for the $[EMIM]^+[EtSO_4]^-$, $[BMIM]^+[SCN]^-$, acetonitrile, and their binary systems {$[EMIM]^+[EtSO_4]^-$ or $[BMIM]^+[SCN]^-$ (x_1) + acetonitrile (x_2)} and are given in Table 5.1.4.8 and 9. The plots of density versus concentration of $[EMIM]^+[EtSO_4]^-$ or $[BMIM]^+[SCN]^-$, respectively, at investigated temperatures are given in Figs. 5.1.4.13 (a) and (b), respectively. It is evident from the results reported in Table 3 and 4 that the ρ values decreases with an increase in temperature and increase with concentration for both systems.

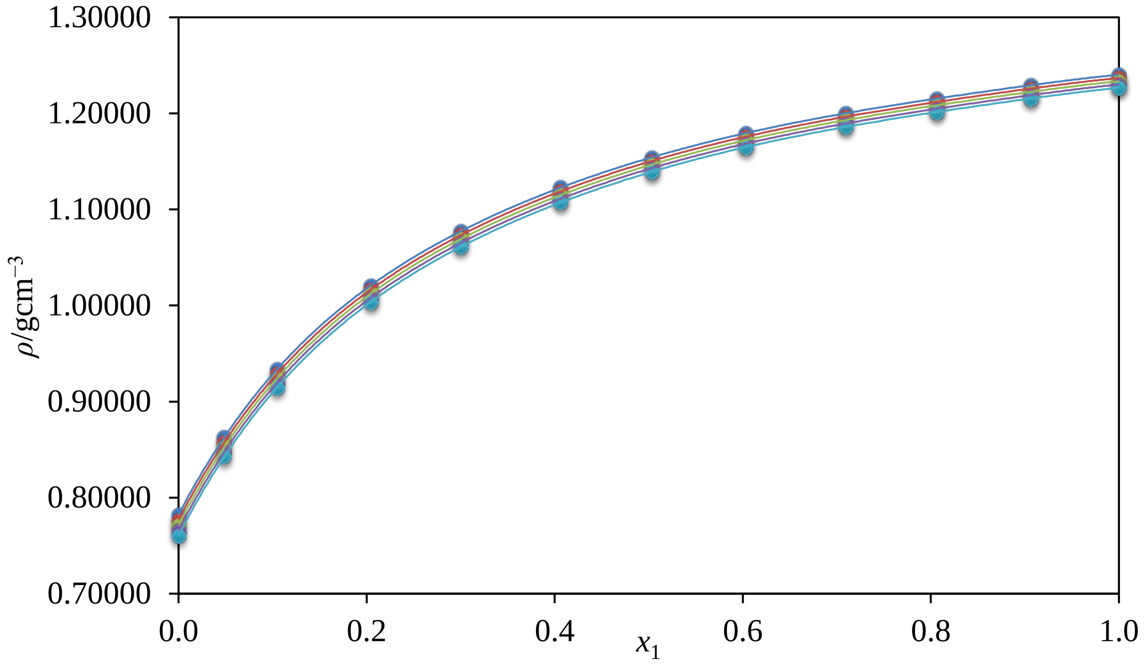


Fig. 5.1.4.13 (a) Density, ρ, for the mixtures of {$[EMIM]^+[EtSO_4]^-$ (x_1) + acetonitrile (x_2)} at 293.15 K (●), 298.15 K (●), 303.15 K (●), 308.15 K (●) and 313.15 K (●). The dotted line represents the smoothness of these data.

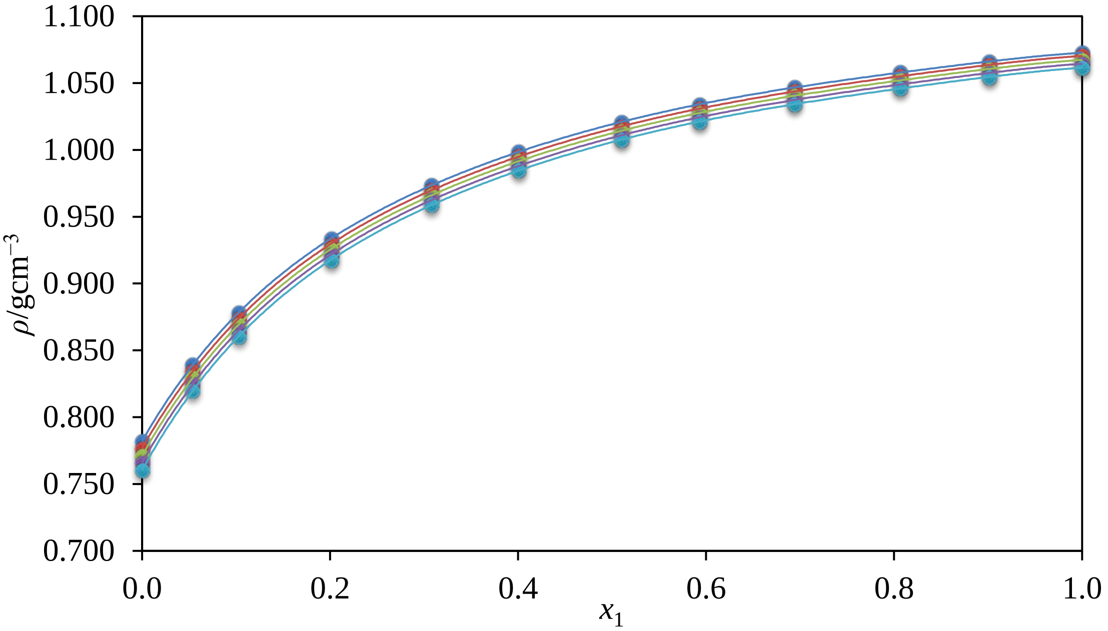


Fig 5.1.4.13 (b) Density, ρ, for the mixtures of {$[BMIM]^+[SCN]^-$ (x_1) + acetonitrile (x_2)} at 293.15 K (●), 298.15 K (●), 303.15 K (●), 308.15 K (●) and 313.15 K (●). The dotted line represents the smoothness of these data.

The speed of sound is also an important property which describes interactions such as solvent-solvent, solute-solvent and solute-solute which occur in the liquid mixtures (Roy. 2011) In this regards, the speed of sound, *u*, were also measured at 293.15, 298.15, 303.15, 308.15 and 313.15 K, and at p = 0.1 MPa and are given in Table 5.1.4.8 and 9. The plots of speed of sound concentration of $[EMIM]^+[EtSO_4]^-$ or $[BMIM]^+[SCN]^-$, respectively, at investigated temperatures, are given in Figs. 5.1.4.14 (a) and (b), respectively. It is evident from the results reported in Table 3 and 4 that the *u* values also decreases with an increase in temperature and increase with concentration for both systems. It can be also seen from Figs. 5.1.4.14 (a) and (b) that the temperature effects of speed of sound are more prominent than density for both systems.

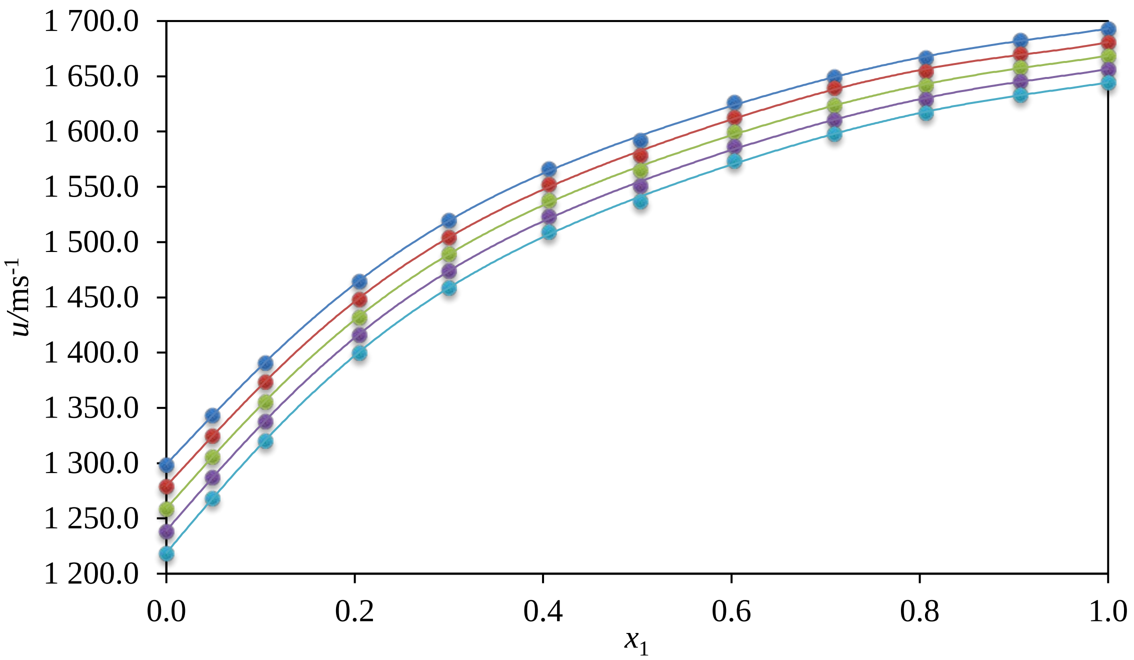


Fig. 5.1.4.14 (a) Speed of sound, *u*, for the mixtures of {$[EMIM]^+[EtSO_4]^-$ (x_1) + acetonitrile (x_2)} at 293.15 K (●), 298.15 K (●), 303.15 K (●), 308.15 K (●) and 313.15 K (●). The dotted line represents the smoothness of these data.

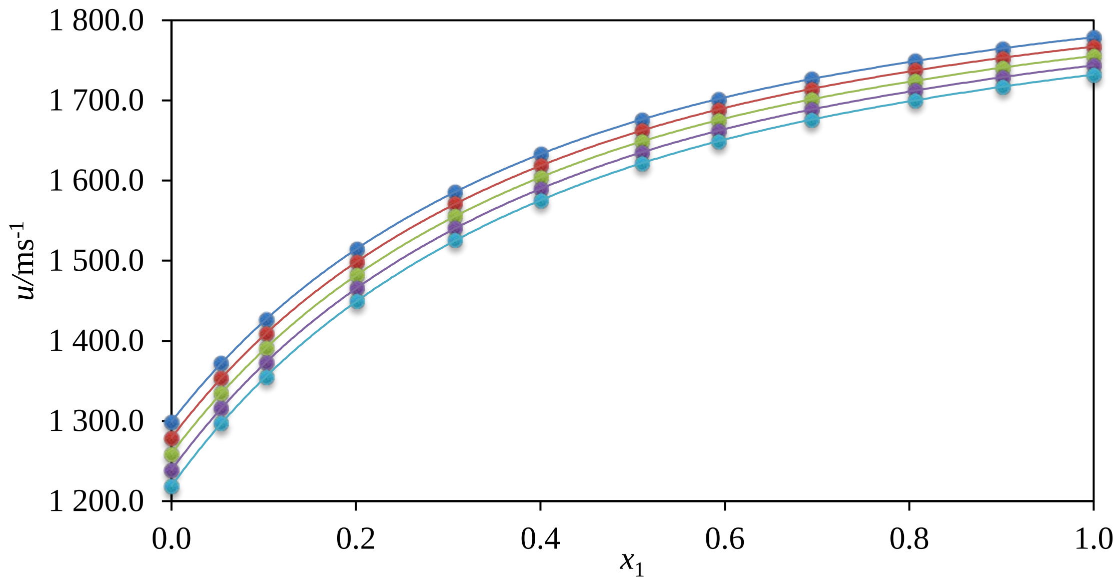


Fig. 5.1.4.14 (b) Speed of sound, *u*, for the mixtures of {$[BMIM]^+[SCN]^-$ (x_1) + acetonitrile (x_2)} at 293.15 K (●), 298.15 K (●), 303.15 K (●), 308.15 K (●) and 313.15 K (●). The dotted line represents the smoothness of these data.

The excess molar volume, V_m^E, calculated from density data at experimental condition for the $\{[EMIM]^+[EtSO_4]^-$ or $[BMIM]^+[SCN]^-$ (x_1) + acetonitrile $(x_2)\}$ systems are reported in Table 5.1.4.8 and 9, and also plotted in Figs. 5.1.4.15 (a) & (b), respectively.

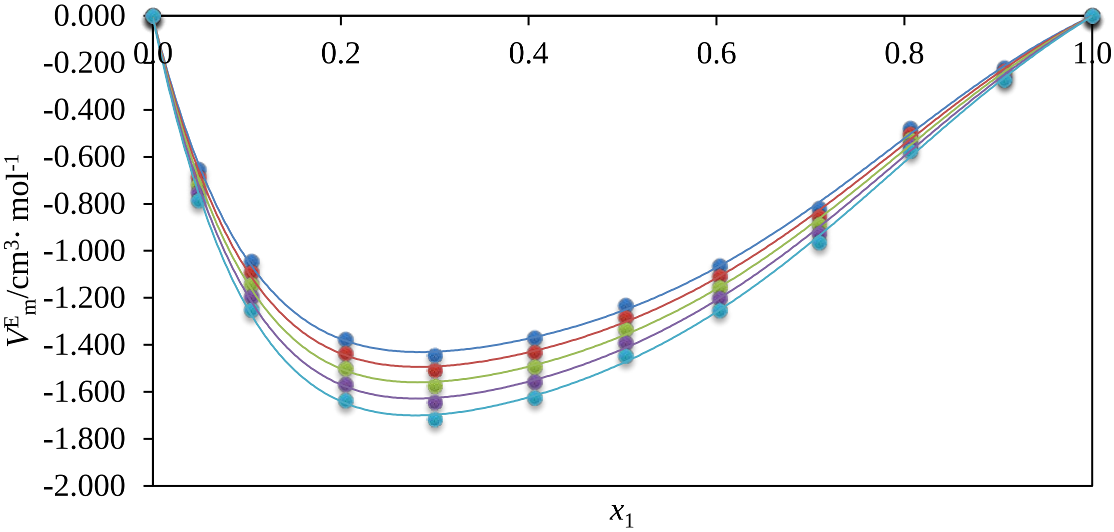
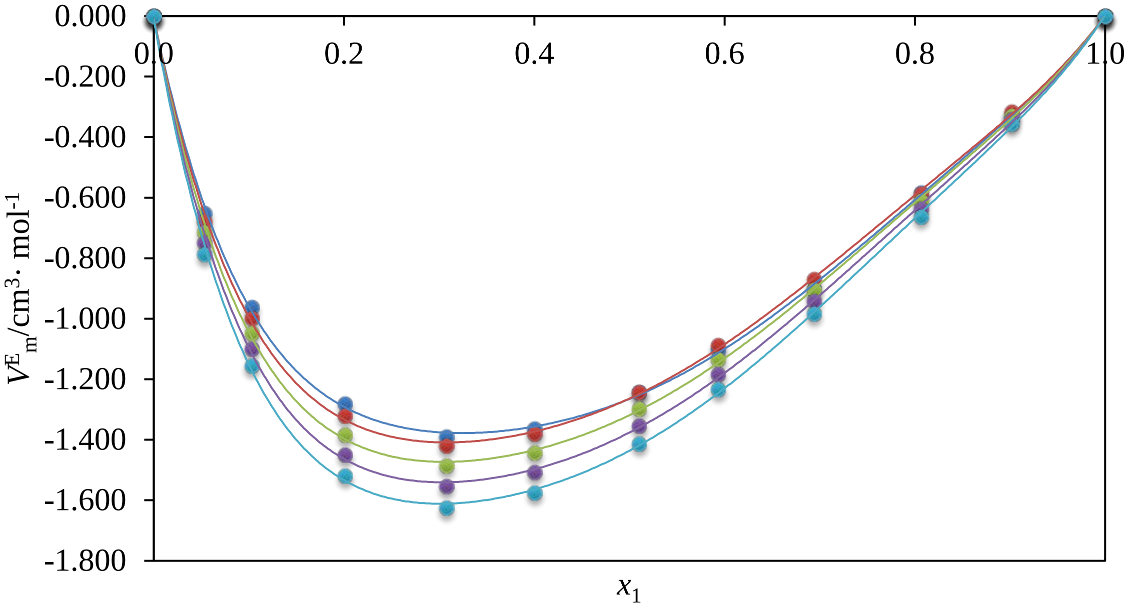


Fig. 5.1.4.15 (a) Excess molar volumes, V_m^E, of binary mixtures of $\{[EMIM]^+[EtSO_4]^-$ (x_1) + acetonitrile $(x_2)\}$ at 293.15 K (●), 298.15 K (●), 303.15 K (●), 308.15 K (●) and 313.15 K (●). The dotted lines were generated using Redlich-Kister curve-fitting.



Figs. 5.1.4.15 (b). Excess molar volumes, V_m^E, of binary mixtures of $\{[BMIM]^+[SCN]^-$ (x_1) + acetonitrile $(x_2)\}$ at 293.15 K (●), 298.15 K (●), 303.15 K (●), 308.15 K (●) and 313.15 K (●). The dotted lines were generated using Redlich-Kister curve-fitting.

It is evident from the results reported in Table 5.1.4.8 and 9, that the $V_{\mathrm{m}}^{\mathrm{E}}$ values are negative for both systems. The ILs $[\mathrm{EMIM}]^+[\mathrm{EtSO_4}]^-$ or $[\mathrm{BMIM}]^+[\mathrm{SCN}]^-$ are complex solvents, and have a capability to interact with organic solvent such as acetonitrile molecules simultaneously through, interactions such as dispersive, ionic, hydrogen bonding, and dipolar (Deenadayalu. 2011). The negative $V_{\mathrm{m}}^{\mathrm{E}}$ values for the binary system suggest that a more efficient packing and or attractive interactions occurred when the $[\mathrm{EMIM}]^+[\mathrm{EtSO_4}]^-$ or $[\mathrm{BMIM}]^+[\mathrm{SCN}]^-$ and acetonitrile were mixed (Deenadayalu. 2011). The acetonitrile tends to fill the interstices of $[\mathrm{EMIM}]^+[\mathrm{EtSO_4}]^-$ or $[\mathrm{BMIM}]^+[\mathrm{SCN}]^-$, and the ion–dipole interaction between the acetonitrile and $[\mathrm{EMIM}]^+[\mathrm{EtSO_4}]^-$ or $[\mathrm{BMIM}]^+[\mathrm{SCN}]^-$, all contribute to the negative values of $V_{\mathrm{m}}^{\mathrm{E}}$ (Deenadayalu. 2006)

The negative $V_{\mathrm{m}}^{\mathrm{E}}$ values of $\{[\mathrm{EMIM}]^+[\mathrm{EtSO_4}]^-$ (x_1) + acetonitrile (x_2)} > $\{[\mathrm{BMIM}]^+[\mathrm{SCN}]^-$ (x_1) + acetonitrile (x_2)} are indication of the interactions of $\{[\mathrm{EMIM}]^+[\mathrm{EtSO_4}]^-$ with acetonitrile is stronger than $[\mathrm{BMIM}]^+[\mathrm{SCN}]^-$ with acetonitrile. The $V_{\mathrm{m,\,min}}^{\mathrm{E}}$ values were -1.716, and -1.625 occurs at $x_1 = 0.2999$ and 0.3075, respectively for the systems $\{[\mathrm{EMIM}]^+[\mathrm{EtSO_4}]^-$ or $[\mathrm{BMIM}]^+[\mathrm{SCN}]^-$ (x_1) + acetonitrile (x_2)} at all temperatures. The $V_{\mathrm{m,\,min}}^{\mathrm{E}}$ values were also occurs at almost equimolar concentration. The $V_{\mathrm{m,\,min}}^{\mathrm{E}}$ values decrease with an increase in temperature for both the systems.

The isentropic compressibility, κ_s, and deviation in isentropic compressibility, $\Delta\kappa\mathrm{s}$, calculated from density and speed of sound for $\{\{[\mathrm{EMIM}]^+[\mathrm{EtSO_4}]^-$ or $[\mathrm{BMIM}]^+[\mathrm{SCN}]^-$ (x_1) + acetonitrile (x_2)} systems at experimental condition are also given in Table 5.1.4.8 and 9.

Table 5.1.4.8 Densities, ρ, excess molar volume, $V_{\mathrm{m}}^{\mathrm{E}}$, speed of sound, u, isentropic compressibility, κ_{s}, and deviation in isentropic compressibility, $\Delta\kappa_{\mathrm{s}}$, for the binary system {$[\mathrm{EMIM}]^+[\mathrm{EtSO_4}]^-$ (x_1) + acetonitrile (x_2)} at 293.15, 298.15, 303.15, 308.15 and 313.15 K.

x_1	$\rho/\mathrm{gcm^{-3}}$	$V_{\mathrm{m}}^{\mathrm{E}}/\mathrm{cm^3mol^{-1}}$	$u/\mathrm{ms^{-1}}$	$\kappa_{\mathrm{s}}/10^8\times\mathrm{Pa^{-1}}$	$\Delta\kappa_{\mathrm{s}}/10^8\times\mathrm{Pa^{-1}}$
		T = 293.15 K			
0.0000	0.78204	0.000	1298.8	76	0.0
0.0484	0.86302	-0.654	1343.4	64	-9.3
0.1049	0.93338	-1.045	1390.8	55	-15.4
0.2047	1.02076	-1.375	1464.6	46	-20.4
0.2999	1.07753	-1.445	1519.6	40	-21.3
0.4062	1.12292	-1.370	1566.5	36	-20.1
0.5033	1.15401	-1.233	1592.4	34	-17.6
0.6030	1.17919	-1.063	1626.4	32	-15.0
0.7094	1.20037	-0.818	1649.5	31	-11.4
0.8064	1.21543	-0.478	1667.0	30	-7.8
0.9066	1.22921	-0.223	1682.6	29	-3.8
1.0000	1.24032	0.000	1693.1	28	0.0
		T = 298.15 K			
0.0000	0.77666	0.000	1279.0	79	0.0
0.0484	0.85802	-0.684	1324.8	66	-9.9
0.1049	0.92868	-1.092	1373.4	57	-16.4
0.2047	1.01645	-1.436	1448.5	47	-21.6
0.2999	1.07346	-1.508	1504.5	41	-22.5
0.4062	1.11905	-1.431	1552.3	37	-21.3
0.5033	1.15023	-1.282	1578.7	35	-18.6
0.6030	1.17554	-1.108	1613.3	33	-15.8
0.7094	1.19680	-0.852	1639.7	31	-12.1
0.8064	1.21191	-0.501	1654.5	30	-8.2
0.9066	1.22575	-0.235	1670.3	29	-4.1
1.0000	1.23689	0.000	1680.8	29	0.0
		T = 303.15 K			
0.0000	0.77124	0.000	1258.8	82	0.0

0.0484	0.85298	-0.716	1306.0	69	-10.5
0.1049	0.92397	-1.143	1355.6	59	-17.4
0.2047	1.01213	-1.500	1432.3	48	-22.9
0.2999	1.06939	-1.575	1489.3	42	-23.9
0.4062	1.11516	-1.492	1537.9	38	-22.5
0.5033	1.14645	-1.335	1564.7	36	-19.7
0.6030	1.17189	-1.155	1599.9	33	-16.7
0.7094	1.19323	-0.888	1623.8	32	-12.7
0.8064	1.20841	-0.526	1641.9	31	-8.6
0.9066	1.22229	-0.247	1657.9	30	-4.3
1.0000	1.23346	0.000	1668.5	29	0.0
T = 308.15 K					
0.0000	0.76578	0.000	1238.6	85	0.0
0.0484	0.84793	-0.750	1287.1	71	-11.2
0.1049	0.91925	-1.196	1337.9	61	-18.5
0.2047	1.00782	-1.567	1416.0	49	-24.3
0.2999	1.06533	-1.643	1474.1	43	-25.3
0.4062	1.11130	-1.557	1523.5	39	-23.8
0.5033	1.14268	-1.390	1550.8	36	-20.8
0.6030	1.16824	-1.202	1586.6	34	-17.7
0.7094	1.18968	-0.925	1610.9	32	-13.4
0.8064	1.20491	-0.550	1629.3	31	-9.1
0.9066	1.21885	-0.260	1645.6	30	-4.5
1.0000	1.23006	0.000	1656.4	30	0.0
T = 313.15 K					
0.0000	0.76029	0.000	1218.5	89	0.0
0.0484	0.84286	-0.786	1268.3	74	-12.0
0.1049	0.91451	-1.251	1320.2	63	-19.7
0.2047	1.00349	-1.637	1399.8	51	-25.8
0.2999	1.06127	-1.716	1458.9	44	-26.8
0.4062	1.10743	-1.624	1509.3	40	-25.2
0.5033	1.13893	-1.447	1537.0	37	-22.0
0.6030	1.16462	-1.253	1573.5	35	-18.7
0.7094	1.18613	-0.962	1598.1	33	-14.1

0.8064	1.20142	-0.575	1616.8	32	-9.6
0.9066	1.21542	-0.272	1633.5	31	-4.8
1.0000	1.22667	0.000	1644.4	30	0.0

Table 5.1.4.9 Densities, ρ, excess molar volume, V_m^E, speed of sound, u, isentropic compressibility, κ_s , and deviation in isentropic compressibility, $\Delta\kappa_s$, for the binary system {[BMIM]$^+$[SCN]$^-$ (x_1) + acetonitrile (x_2)} at 293.15, 298.15, 303.15, 308.15 and 313.15 K.

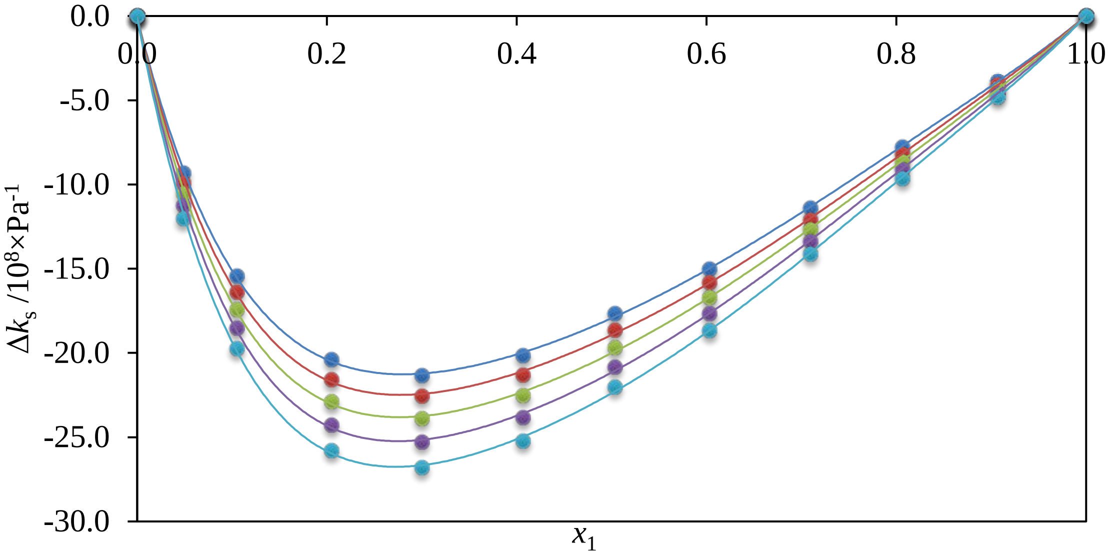
x_1	ρ/gcm^{-3}	V_m^E /cm^{3}mol^{-1}	u/ms^{-1}	κ_s/10^8×Pa^{-1}	$\Delta\kappa_s$ /10^8×Pa^{-1}
T = 293.15 K					
0.0000	0.78204	0.000	1298.8	76	0.0
0.0535	0.83928	-0.653	1372.3	63	-10.1
0.1029	0.87819	-0.962	1426.5	56	-15.1
0.2012	0.93348	-1.281	1514.7	47	-19.8
0.3075	0.97357	-1.389	1586.2	41	-20.7
0.4006	0.99869	-1.363	1633.3	38	-19.7
0.5101	1.02081	-1.242	1676.1	35	-17.3
0.5932	1.03389	-1.103	1701.6	33	-14.9
0.6939	1.04682	-0.903	1726.8	32	-11.6
0.8064	1.05801	-0.584	1749.3	31	-7.5
0.9016	1.06601	-0.329	1764.8	30	-3.9
1.0000	1.07274	0.000	1778.8	29	0.0
		T = 298.15 K			
0.0000	0.77666	0.000	1278.8	79	0.0
0.0535	0.83448	-0.679	1353.6	65	-10.7
0.1029	0.87373	-0.998	1408.9	58	-16.1
0.2012	0.92948	-1.321	1498.6	48	-21.0
0.3075	0.96989	-1.420	1571.2	42	-22.0
0.4006	0.99519	-1.381	1618.7	38	-20.8
0.5101	1.01748	-1.243	1662.5	36	-18.3
0.5932	1.03065	-1.088	1688.5	34	-15.7
0.6939	1.04367	-0.869	1714.1	33	-12.3
0.8064	1.05533	-0.587	1737.8	31	-8.0

0.9016	1.06339	-0.316	1752.9	31	-4.1
1.0000	1.07034	0.000	1767.2	30	0.0
		T = 303.15 K			
0.0000	0.77124	0.000	1258.8	82	0.0
0.0535	0.82964	-0.714	1334.8	68	-11.4
0.1029	0.86925	-1.048	1391.0	59	-17.1
0.2012	0.92548	-1.383	1482.1	49	-22.3
0.3075	0.96621	-1.485	1556.0	43	-23.3
0.4006	0.99170	-1.442	1604.2	39	-22.0
0.5101	1.01415	-1.297	1648.8	36	-19.3
0.5932	1.02741	-1.135	1675.3	35	-16.6
0.6939	1.04052	-0.905	1701.4	33	-12.9
0.8064	1.05227	-0.611	1724.7	32	-8.4
0.9016	1.06037	-0.328	1740.8	31	-4.3
1.0000	1.06737	0.000	1755.4	30	0.0
		T = 308.15 K			
0.0000	0.76578	0.000	1238.6	85	0.0
0.0535	0.82479	-0.750	1316.0	70	-12.2
0.1029	0.86477	-1.100	1373.1	61	-18.2
0.2012	0.92148	-1.449	1465.7	51	-23.7
0.3075	0.96253	-1.553	1540.8	44	-24.7
0.4006	0.98821	-1.507	1589.7	40	-23.4
0.5101	1.01083	-1.354	1635.2	37	-20.5
0.5932	1.02418	-1.183	1662.1	35	-17.6
0.6939	1.03738	-0.943	1688.7	34	-13.7
0.8064	1.04921	-0.636	1712.5	33	-8.9
0.9016	1.05737	-0.342	1728.9	32	-4.6
1.0000	1.06442	0.000	1743.7	31	0.0
		T = 313.15 K			
0.0000	0.76029	0.000	1218.5	89	0.0
0.0535	0.81992	-0.788	1297.2	72	-13.0
0.1029	0.86027	-1.155	1355.2	63	-19.4
0.2012	0.91747	-1.519	1449.4	52	-25.2
0.3075	0.95885	-1.625	1525.7	45	-26.2

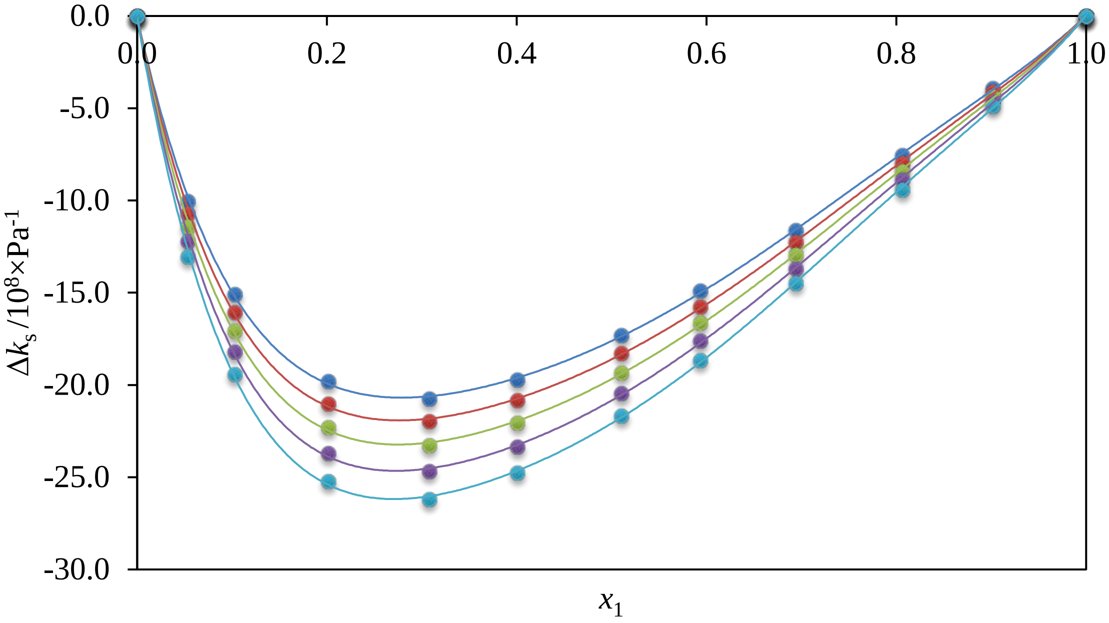
0.4006	0.98473	-1.574	1575.4	41	-24.8
0.5101	1.00751	-1.412	1621.7	38	-21.7
0.5932	1.02097	-1.234	1649.0	36	-18.6
0.6939	1.03426	-0.983	1676.1	34	-14.5
0.8064	1.04617	-0.663	1700.3	33	-9.4
0.9016	1.05438	-0.355	1717.0	32	-4.9
1.0000	1.06147	0.000	1732.1	31	0.0

It is evident from the results reported in Table 5.1.4.8 and 9 that in general the κ_S values increases with an increase in temperature at a fixed composition for both systems due to an increase in thermal agitation, making the $[EMIM]^+[EtSO_4]^-$ or $[BMIM]^+[SCN]^-$ with acetonitrile solution more compressible (Zafarani-Moattar and Shekaari. 2005 and 2006) . The κ_S value decreases with concentration at a fixed temperature for both systems.

The interactions between the liquid mixtures lead to the decrease in the free-space, thereby contributing to the negative deviation in isentropic compressibility (Gowrisankar. 2013). The deviation in isentropic compressibility, $\Delta\kappa_S$, over the entire composition range for both systems is plotted in Figs. 5.1.4.16 (a) and (b).



Figs. 5.1.4.16 (a). Deviation of isentropic compressibility, $\Delta\kappa_S$, of binary mixtures of {[EMIM]$^+$[EtSO$_4$]$^-$ (x_1) + acetonitrile (x_2)} at 293.15 K (●), 298.15 K (●), 303.15 K (●), 308.15 K (●) and 313.15 K (●). The dotted lines were generated using Redlich-Kister curve-fitting.



Figs. 5.1.4.16 (b). Deviation of isentropic compressibility, $\Delta\kappa_S$, of binary mixtures of {[BMIM]$^+$[SCN]$^-$ (x_1) + acetonitrile (x_2)} at 293.15 K (●), 298.15 K (●), 303.15 K (●), 308.15 K (●) and 313.15 K (●). The dotted lines were generated using Redlich-Kister curve-fitting.

It evident from these figures that the $\Delta\kappa_s$ values are negative for both systems indicating that these mixtures are less compressible than the ideal mixture. This is due to closer approach of unlike molecules and a stronger interaction between $[EMIM]^+[EtSO_4]^-$ or $[BMIM]^+[SCN]^-$ and acetonitrile mixtures that leads to a decrease in the compressibility of mixtures. These concluding remarks are in good agreement with those obtained from the volumetric studies. The $\Delta\kappa_s$ values decrease with an increase in temperature for both systems at a fixed composition as shown in Figs. 5.1.4.16 (a) and (b). The $\Delta\kappa_s$ values for $\{[BMIM]^+[SCN]^-$ (x_1) + acetonitrile (x_2)$\}$ > $\{[EMIM]^+[EtSO_4]^-$ (x_1) + acetonitrile (x_2)$\}$ indicating that there is a decrease compressibility from the ideal mixture in the order: $[BMIM]^+[SCN]^-$ > $\{[EMIM]^+[EtSO_4]^-$. The decrease in compressibility is due to stronger interaction between $\{[EMIM]^+[EtSO_4]^-$ or $\{[BMIM]^+[SCN]^-$ with acetonitrile mixtures due to the proximity of unlike molecules Zafarani-Moattar. The $\Delta\kappa_{s\,,\mathrm{min}}$ values were -26.8 and -26.2 occurs at $x_1 = 0.2999$ and 0.3075, respectively for each system at all temperatures. The $V^{E}_{m,\,\mathrm{min}}$ and $\Delta\kappa_{s,\,\mathrm{min}}$ values were occurs at same composition for both systems, respectively. The excess/deviation properties calculated from density and speed of sound data for $\{[EMIM]^+[EtSO_4]^-$ or $[BMIM]^+[SCN]^-$ (x_1) + acetonitrile (x_2)$\}$ systems were fitted to the Redlich–Kister equation [39]. The values of the fitting parameters A_i have been determined using a least-square method. These results are summarized in Table 5.1.4.10, together with the corresponding standard deviations (σ).

Table 5.1.4.10. Coefficients A_i, and standard deviations, σ, obtained for the binary systems {[EMIM]$^+$[EtSO$_4$]$^-$ or [BMIM]$^+$[SCN]$^-$ (x_1) + acetonitrile (x_2)} at different temperatures for the Redlich-Kister equation.

	T/K	A_0	A_1	A_2	A_3	A_4	σ
	{[EMIM]$^+$[EtSO$_4$]$^-$ (x_1) + acetonitrile (x_2)}						
V_m^E /cm^{3}mol^{-1}	293.15	-3.038	-2.128	-1.468	-4.230	-5.287	0.016
	298.15	-3.142	-2.075	-1.663	-4.467	-5.272	0.015
	303.15	-3.280	-2.134	-1.589	-4.638	-5.614	0.017
	308.15	-3.418	-2.207	-1.557	-4.803	-5.917	0.018
	313.15	-3.582	-2.247	-1.414	-5.067	-6.353	0.018
$\Delta\kappa_S$ /10^8×Pa^{-1}	293.15	-65.4	-49.6	-33.5	-49.5	-46.3	0.2
	298.15	-69.6	-51.0	-33.2	-54.6	-49.7	0.2
	303.15	-72.6	-55.8	-40.0	-54.0	-47.7	0.2
	308.15	-76.5	-58.8	-43.3	-57.6	-48.3	0.2
	313.15	-80.9	-61.9	-44.6	-62.3	-53.6	0.2
	{[BMIM]$^+$[SCN]$^-$ (x_1) + acetonitrile (x_2)}						
V_m^E /cm^{3}mol^{-1}	293.15	-5.076	-3.925	-4.545	-1.138	0.387	0.016
	298.15	-5.081	-4.295	-4.395	-1.353	0.226	0.016
	303.15	-5.294	-4.442	-4.550	-1.531	0.122	0.016
	308.15	-5.515	-4.600	-4.673	-1.709	-0.040	0.017
	313.15	-5.748	-4.760	-4.753	-1.904	-0.275	0.017
$\Delta\kappa_S$ /10^8×Pa^{-1}	293.15	-63.2	-50.1	-44.9	-13.8	11.0	0.1
	298.15	-67.0	-53.5	-46.6	-16.2	8.2	0.1
	303.15	-71.3	-56.5	-50.5	-18.9	8.3	0.1
	308.15	-75.7	-60.9	-52.5	-20.8	5.7	0.1
	313.15	-80.5	-64.6	-54.7	-22.9	2.8	0.1

5.2 Excess molar volumes and deviation in isentropic compressibility for ternary mixtures

In this perspective, the main intention is to be revealed the possible intra and inter molecular interactions among the component molecules in liquid mixtures by the addition of third component (acetic acid or propionic acid) on IL + acetonitrile binary system. Excess molar volume (V_{123}^{E}), isentropic compressibility (k_s) and deviation in isentropic compressibility (Δk_{s123}) were determined for two ternary liquid mixtures of {[EMIM]$^+$[EtSO$_4$]$^-$ + acetonitrile + acetic acid or propionic acid} and {[BMIM]$^+$[SCN]$^-$ + acetonitrile + acetic acid or propionic acid} at different temperatures (293.15, 298.15, 303.15, 308.15 and 313.15) K and at a pressure of 0.1 MPa with aid of the experimental measurements of density (ρ), speed of sound (u). The calculated ternary excess volume and deviation in isentropic compressibility data were correlated by using the Cibulka equation with the aid of Redlich–Kister parameters fitted to the five binary systems obtained from literature. Furthermore, the measured thermodynamic properties were discussed interms of molecular interactions between component molecules in liquid mixtures.

5.2.1 Group 5: {[EMIM]$^+$[EtSO$_4$]$^-$ + acetonitrile + acetic acid or propionic acid

The values of density (ρ), speed of sound (u), excess molar volume (V_{123}^{E}), isentropic compressibility (k_s) and deviation in isentropic compressibility (Δk_{s123}) for ternary liquid mixtures of {[EMIM]$^+$[EtSO$_4$]$^-$ + acetic acid + acetonitrile} and {[EMIM]$^+$[EtSO$_4$]$^-$ + propionic acid + acetonitrile} at all the investigated temperatures are listed in Table 5.2.1.11.

Table 5.2.1.11. Density (ρ), speed of sound (u), excess volume (V_{123}^{E}), isentropic compressibility (k_S) and deviation in isentropic compressibility (Δk_{s123}) for {$[EMIM]^+[EtSO_4]^-$ (1) + acetic acid or propionic acid (2) + acetonitrile (3)} at (293.15, 298.15, 303.15, 308.15 and 313.15) K.

x_1	x_2	ρ/gcm^{-3}	V_{123}^{E}/cm^{3}mol^{-1}	u/ms^{-1}	κ_S /10^8×Pa^{-1}	(Δk_{s123})/10^8×Pa^{-1}
{$[EMIM]^+[EtSO_4]^-$ + acetic acid + acetonitrile}						
T = 293.15 K						
0.0680	0.5284	1.01469	-0.933	1336.7	55	-15.2
0.1009	0.2975	0.99452	-1.052	1382.8	53	-17.2
0.1126	0.2205	0.98910	-1.104	1395.8	52	-17.6
0.1290	0.1085	0.98111	-1.197	1411.4	51	-18.0
0.1672	0.3906	1.06174	-1.010	1432.3	46	-20.3
0.2126	0.2277	1.06194	-1.089	1470.8	44	-21.2
0.2325	0.1539	1.06205	-1.161	1484.5	43	-21.4
0.1038	0.7936	1.09557	-0.828	1355.8	50	-17.9
0.2309	0.5332	1.11957	-0.889	1479.1	41	-21.8
0.3114	0.3618	1.13002	-0.961	1527.5	38	-21.5
0.3560	0.2933	1.13814	-0.974	1548.0	37	-21.0
0.3980	0.1998	1.14191	-1.041	1566.8	36	-20.3
0.4538	0.0964	1.14820	-1.065	1588.9	34	-19.3
0.3450	0.5414	1.16434	-0.716	1541.4	36	-21.0
0.4835	0.3567	1.18325	-0.703	1594.3	33	-18.0
0.5604	0.2535	1.18992	-0.535	1619.7	32	-16.0
0.6545	0.1295	1.19819	-0.471	1643.1	31	-13.2
0.7078	0.0525	1.20237	-0.524	1652.1	30	-11.4
0.7527	0.0000	1.20511	-0.367	1662.4	30	-9.9
0.8825	0.0606	1.22942	-0.101	1678.5	29	-4.6
0.6002	0.3617	1.20906	-0.475	1624.7	31	-14.4
0.4887	0.4803	1.19712	-0.586	1594.2	33	-17.7
0.8075	0.1402	1.22505	-0.223	1666.6	29	-7.3
0.7287	0.2257	1.21984	-0.329	1652.7	30	-10.1
0.3492	0.6287	1.17464	-0.491	1532.9	36	-20.3
0.2108	0.7759	1.14861	-0.836	1456.7	41	-21.5

T = 298.15 K						
0.0680	0.5284	1.00984	-0.973	1320.4	57	-16.2
0.1009	0.2975	0.98985	-1.100	1366.3	54	-18.2
0.1126	0.2205	0.98449	-1.155	1379.3	53	-18.7
0.1290	0.1085	0.97653	-1.249	1394.7	53	-19.1
0.1672	0.3906	1.05743	-1.068	1416.2	47	-21.5
0.2126	0.2277	1.05768	-1.146	1455.5	45	-22.4
0.2325	0.1539	1.05783	-1.219	1469.3	44	-22.6
0.1038	0.7936	1.09092	-0.868	1340.5	51	-19.0
0.2309	0.5332	1.11539	-0.939	1464.6	42	-23.0
0.3114	0.3618	1.12601	-1.013	1513.4	39	-22.7
0.3560	0.2933	1.13420	-1.026	1533.8	37	-22.1
0.3980	0.1998	1.13802	-1.092	1552.8	36	-21.4
0.4538	0.0964	1.14439	-1.117	1575.4	35	-20.3
0.3450	0.5414	1.16047	-0.766	1527.7	37	-22.1
0.4835	0.3567	1.17949	-0.743	1581.0	34	-19.0
0.5604	0.2535	1.18622	-0.570	1606.6	33	-16.9
0.6545	0.1295	1.19456	-0.502	1630.2	32	-13.8
0.7078	0.0525	1.19878	-0.552	1639.3	31	-12.0
0.7527	0.0000	1.20155	-0.393	1649.7	31	-10.4
0.8825	0.0606	1.22592	-0.109	1666.1	29	-4.8
0.6002	0.3617	1.20541	-0.503	1611.8	32	-15.1
0.4887	0.4803	1.19337	-0.622	1581.0	34	-18.6
0.8075	0.1402	1.22151	-0.236	1654.1	30	-7.7
0.7287	0.2257	1.21627	-0.348	1640.1	31	-10.6
0.3492	0.6287	1.17070	-0.530	1519.2	37	-21.4
0.2108	0.7759	1.14440	-0.881	1442.6	42	-22.7
T = 303.15 K						
0.0680	0.5284	1.00498	-1.017	1303.9	59	-17.2
0.1009	0.2975	0.98518	-1.152	1349.6	56	-19.3
0.1126	0.2205	0.97985	-1.208	1362.6	55	-19.9
0.1290	0.1085	0.97195	-1.305	1377.9	54	-20.3
0.1672	0.3906	1.05307	-1.126	1400.5	48	-22.7
0.2126	0.2277	1.05342	-1.206	1440.0	46	-23.7

0.2325	0.1539	1.05362	-1.280	1453.8	45	-23.9
0.1038	0.7936	1.08629	-0.910	1325.1	52	-20.1
0.2309	0.5332	1.11123	-0.993	1450.0	43	-24.3
0.3114	0.3618	1.12202	-1.070	1499.0	40	-24.0
0.3560	0.2933	1.13028	-1.082	1519.6	38	-23.3
0.3980	0.1998	1.13416	-1.148	1538.5	37	-22.6
0.4538	0.0964	1.14058	-1.171	1561.5	36	-21.5
0.3450	0.5414	1.15654	-0.814	1513.9	38	-23.3
0.4835	0.3567	1.17574	-0.786	1567.6	35	-20.0
0.5604	0.2535	1.18253	-0.608	1593.4	33	-17.8
0.6545	0.1295	1.19095	-0.534	1617.2	32	-14.6
0.7078	0.0525	1.19519	-0.583	1626.4	32	-12.6
0.7527	0.0000	1.19799	-0.420	1636.9	31	-11.0
0.8825	0.0606	1.22244	-0.119	1653.7	30	-5.1
0.6002	0.3617	1.20176	-0.534	1598.9	33	-15.9
0.4887	0.4803	1.18964	-0.660	1567.7	34	-19.5
0.8075	0.1402	1.21799	-0.252	1641.5	30	-8.1
0.7287	0.2257	1.21271	-0.370	1627.4	31	-11.2
0.3492	0.6287	1.16677	-0.572	1505.3	38	-22.6
0.2108	0.7759	1.14019	-0.928	1428.3	43	-24.0
			T = 308.15 K			
0.0680	0.5284	1.00012	-1.062	1287.5	60	-18.2
0.1009	0.2975	0.98050	-1.206	1333.1	57	-20.6
0.1126	0.2205	0.97522	-1.265	1346.0	57	-21.1
0.1290	0.1085	0.96736	-1.365	1361.1	56	-21.6
0.1672	0.3906	1.04871	-1.185	1384.8	50	-24.1
0.2126	0.2277	1.04917	-1.268	1424.5	47	-25.2
0.2325	0.1539	1.04940	-1.344	1438.4	46	-25.3
0.1038	0.7936	1.08165	-0.954	1309.6	54	-21.3
0.2309	0.5332	1.10708	-1.049	1435.4	44	-25.7
0.3114	0.3618	1.11803	-1.127	1484.6	41	-25.3
0.3560	0.2933	1.12636	-1.138	1505.6	39	-24.6
0.3980	0.1998	1.13029	-1.206	1524.4	38	-23.9
0.4538	0.0964	1.13677	-1.226	1547.5	37	-22.7

0.3450	0.5414	1.15262	-0.861	1500.2	39	-24.6
0.4835	0.3567	1.17200	-0.830	1554.2	35	-21.1
0.5604	0.2535	1.17886	-0.646	1580.3	34	-18.7
0.6545	0.1295	1.18734	-0.567	1604.3	33	-15.4
0.7078	0.0525	1.19163	-0.614	1613.7	32	-13.3
0.7527	0.0000	1.19446	-0.448	1624.2	32	-11.6
0.8825	0.0606	1.21897	-0.128	1641.4	30	-5.4
0.6002	0.3617	1.19814	-0.565	1586.1	33	-16.7
0.4887	0.4803	1.18592	-0.698	1554.7	35	-20.6
0.8075	0.1402	1.21449	-0.266	1629.1	31	-8.5
0.7287	0.2257	1.20917	-0.391	1614.9	32	-11.8
0.3492	0.6287	1.16285	-0.615	1491.4	39	-23.8
0.2108	0.7759	1.13600	-0.976	1414.0	44	-25.3
T = 313.15 K						
0.0680	0.5284	0.99526	-1.109	1271.2	62	-19.4
0.1009	0.2975	0.97582	-1.263	1316.7	59	-21.9
0.1126	0.2205	0.97059	-1.324	1329.4	58	-22.4
0.1290	0.1085	0.96278	-1.427	1344.4	57	-23.0
0.1672	0.3906	1.04435	-1.247	1369.3	51	-25.5
0.2126	0.2277	1.04491	-1.333	1409.2	48	-26.7
0.2325	0.1539	1.04519	-1.411	1423.0	47	-26.9
0.1038	0.7936	1.07702	-0.999	1294.2	55	-22.5
0.2309	0.5332	1.10293	-1.106	1420.9	45	-27.1
0.3114	0.3618	1.11404	-1.187	1470.3	42	-26.8
0.3560	0.2933	1.12245	-1.197	1491.5	40	-26.1
0.3980	0.1998	1.12644	-1.265	1510.4	39	-25.3
0.4538	0.0964	1.13297	-1.285	1533.7	38	-24.0
0.3450	0.5414	1.14870	-0.911	1486.7	39	-25.9
0.4835	0.3567	1.16827	-0.875	1539.7	36	-22.2
0.5604	0.2535	1.17520	-0.687	1566.7	35	-19.7
0.6545	0.1295	1.18375	-0.602	1591.5	33	-16.2
0.7078	0.0525	1.18807	-0.647	1600.9	33	-14.1
0.7527	0.0000	1.19093	-0.478	1611.6	32	-12.3
0.8825	0.0606	1.21552	-0.139	1629.3	31	-5.7

0.6002	0.3617	1.19453	-0.598	1573.4	34	-17.6
0.4887	0.4803	1.18221	-0.739	1541.7	36	-21.7
0.8075	0.1402	1.21100	-0.283	1616.8	32	-9.0
0.7287	0.2257	1.20564	-0.414	1602.4	32	-12.4
0.3492	0.6287	1.15896	-0.659	1477.7	40	-25.1
0.2108	0.7759	1.13183	-1.027	1399.9	45	-26.7

{$[\text{Emim}]^+[\text{EtSO}_4]^-$ + propionic acid + acetonitrile}

T = 293.15 K

0.0756	0.4765	0.99010	-1.184	1336.6	57	-14.9
0.1074	0.2567	0.98284	-1.253	1384.2	53	-17.2
0.1175	0.1866	0.98007	-1.246	1396.4	52	-17.6
0.1316	0.0898	0.97659	-1.256	1411.9	51	-18.0
0.1812	0.3427	1.04493	-1.094	1437.4	46	-20.3
0.2223	0.1931	1.05184	-1.085	1472.9	44	-21.1
0.2398	0.1274	1.05473	-1.102	1487.2	43	-21.3
0.1240	0.7536	1.05760	-1.011	1347.4	52	-16.6
0.2593	0.4850	1.09929	-1.024	1474.3	42	-20.8
0.3416	0.3217	1.11876	-0.939	1527.4	38	-20.7
0.3844	0.2380	1.12762	-0.870	1552.4	37	-20.3
0.4180	0.1700	1.13585	-1.003	1567.4	36	-19.8
0.4638	0.0791	1.14472	-1.003	1589.8	35	-19.0
0.3833	0.4907	1.14520	-0.886	1527.9	37	-19.3
0.5191	0.3109	1.17248	-0.792	1587.9	34	-16.7
0.6388	0.3114	1.19662	-0.405	1619.8	32	-13.0
0.5364	0.4297	1.18128	-0.594	1582.3	34	-15.7
0.3965	0.5787	1.15461	-0.842	1527.2	37	-18.9
0.2472	0.7373	1.11689	-1.124	1440.0	43	-18.5

T = 298.15 K

0.0756	0.4765	0.98540	-1.236	1319.7	58	-15.9
0.1074	0.2567	0.97825	-1.309	1367.3	55	-18.2
0.1175	0.1866	0.97550	-1.301	1379.8	54	-18.7
0.1316	0.0898	0.97204	-1.311	1395.2	53	-19.1
0.1812	0.3427	1.04061	-1.154	1422.0	48	-21.5
0.2223	0.1931	1.04761	-1.144	1457.7	45	-22.3

0.2398	0.1274	1.05052	-1.161	1471.7	44	-22.5
0.1240	0.7536	1.05315	-1.067	1331.5	54	-17.7
0.2593	0.4850	1.09520	-1.086	1459.5	43	-22.1
0.3416	0.3217	1.11480	-0.997	1513.2	39	-21.9
0.3844	0.2380	1.12372	-0.926	1538.5	38	-21.5
0.4180	0.1700	1.13199	-1.059	1553.5	37	-20.9
0.4638	0.0791	1.14091	-1.055	1576.1	35	-20.1
0.3833	0.4907	1.14135	-0.944	1514.2	38	-20.5
0.5191	0.3109	1.16876	-0.841	1574.7	35	-17.7
0.6388	0.3114	1.19300	-0.442	1607.1	32	-13.7
0.5364	0.4297	1.17759	-0.640	1569.3	34	-16.7
0.3965	0.5787	1.15078	-0.900	1513.7	38	-20.0
0.2472	0.7373	1.11282	-1.188	1425.7	44	-20.9
T = 303.15 K						
0.0756	0.4765	0.98070	-1.291	1302.7	60	-16.9
0.1074	0.2567	0.97365	-1.368	1350.4	56	-19.4
0.1175	0.1866	0.97093	-1.361	1362.9	55	-19.9
0.1316	0.0898	0.96749	-1.370	1378.3	54	-20.3
0.1812	0.3427	1.03629	-1.216	1406.3	49	-22.9
0.2223	0.1931	1.04337	-1.207	1442.2	46	-23.7
0.2398	0.1274	1.04631	-1.224	1456.2	45	-23.9
0.1240	0.7536	1.04870	-1.126	1315.7	55	-18.9
0.2593	0.4850	1.09112	-1.151	1444.7	44	-23.4
0.3416	0.3217	1.11086	-1.060	1498.8	40	-23.2
0.3844	0.2380	1.11983	-0.985	1524.2	38	-22.7
0.4180	0.1700	1.12815	-1.117	1539.4	37	-22.1
0.4638	0.0791	1.13712	-1.111	1562.1	36	-21.2
0.3833	0.4907	1.13750	-1.006	1500.4	39	-21.7
0.5191	0.3109	1.16506	-0.893	1561.4	35	-18.7
0.6388	0.3114	1.18940	-0.481	1594.3	33	-14.5
0.5364	0.4297	1.17391	-0.690	1556.1	35	-17.6
0.3965	0.5787	1.14697	-0.961	1500.1	39	-21.2
0.2472	0.7373	1.10877	-1.256	1411.2	45	-22.3
T = 308.15 K						

0.0756	0.4765	0.97599	-1.347	1285.7	62	-18.1
0.1074	0.2567	0.96905	-1.429	1333.8	58	-20.7
0.1175	0.1866	0.96635	-1.422	1346.0	57	-21.1
0.1316	0.0898	0.96293	-1.432	1361.4	56	-21.6
0.1812	0.3427	1.03197	-1.281	1390.6	50	-24.3
0.2223	0.1931	1.03914	-1.273	1426.7	47	-25.2
0.2398	0.1274	1.04211	-1.289	1440.7	46	-25.3
0.1240	0.7536	1.04426	-1.186	1299.9	57	-20.2
0.2593	0.4850	1.08704	-1.217	1430.0	45	-24.9
0.3416	0.3217	1.10692	-1.123	1484.5	41	-24.6
0.3844	0.2380	1.11594	-1.046	1509.9	39	-24.1
0.4180	0.1700	1.12430	-1.177	1525.3	38	-23.4
0.4638	0.0791	1.13332	-1.168	1548.1	37	-22.4
0.3833	0.4907	1.13366	-1.068	1486.6	40	-23.1
0.5191	0.3109	1.16137	-0.945	1548.1	36	-19.8
0.6388	0.3114	1.18581	-0.520	1581.4	34	-15.4
0.5364	0.4297	1.17025	-0.739	1543.0	36	-18.7
0.3965	0.5787	1.14316	-1.022	1486.5	40	-22.5
0.2472	0.7373	1.10473	-1.325	1396.7	46	-23.7
T = 313.15 K						
0.0756	0.4765	0.97128	-1.406	1268.9	64	-19.3
0.1074	0.2567	0.96445	-1.493	1317.0	60	-22.0
0.1175	0.1866	0.96177	-1.487	1329.2	59	-22.5
0.1316	0.0898	0.95837	-1.496	1344.5	58	-23.0
0.1812	0.3427	1.02765	-1.348	1375.0	51	-25.9
0.2223	0.1931	1.03490	-1.340	1411.3	49	-26.7
0.2398	0.1274	1.03790	-1.356	1425.3	47	-26.9
0.1240	0.7536	1.03982	-1.248	1284.2	58	-21.6
0.2593	0.4850	1.08297	-1.285	1415.4	46	-26.4
0.3416	0.3217	1.10298	-1.188	1470.2	42	-26.1
0.3844	0.2380	1.11206	-1.108	1495.8	40	-25.5
0.4180	0.1700	1.12047	-1.239	1511.3	39	-24.8
0.4638	0.0791	1.12954	-1.227	1534.2	38	-23.7
0.3833	0.4907	1.12984	-1.132	1472.9	41	-24.5

0.5191	0.3109	1.15768	-0.998	1534.9	37	-21.0
0.6388	0.3114	1.18223	-0.560	1568.7	34	-16.3
0.5364	0.4297	1.16660	-0.789	1529.9	37	-19.8
0.3965	0.5787	1.13937	-1.085	1473.1	40	-23.9
0.2472	0.7373	1.10070	-1.396	1382.3	48	-25.2

The V^E or Δk_{s123} data for different pairs of the binary systems were studied previously at different temperatures by our research group. The Redlich-Kister parameters along with the standard deviations σ (V^E) and Δk_{s123} for the following binary systems {[EMIM]$^+$[EtSO$_4$]$^-$ + acetic acid or propionic acid} (Singh *et al*. 2014) {[EMIM]$^+$[EtSO$_4$]$^-$ + acetonitrile} (Singh *et al*. 2014) and acetonitrile + acetic acid or propionic acid (Singh *et al*. 2014) are given in Table 5.2.1.12. The ternary data were correlated by using the Cibulka equation.

Table 5.2.1.12. The Redlich–Kister parameters fitted to experimental excess volumes and deviation in isentropic compressibilities for binary systems composing the ternary systems: {IL + acetonitrile + {acetic acid or propionic acid}} at T = (293.15, 298.15, 303.15, 308.15 and 313.15) K and at pressure p = 0.1 MPa along with coefficients standard deviations σ (V^E) or (Δk_{s123}) of the fit.

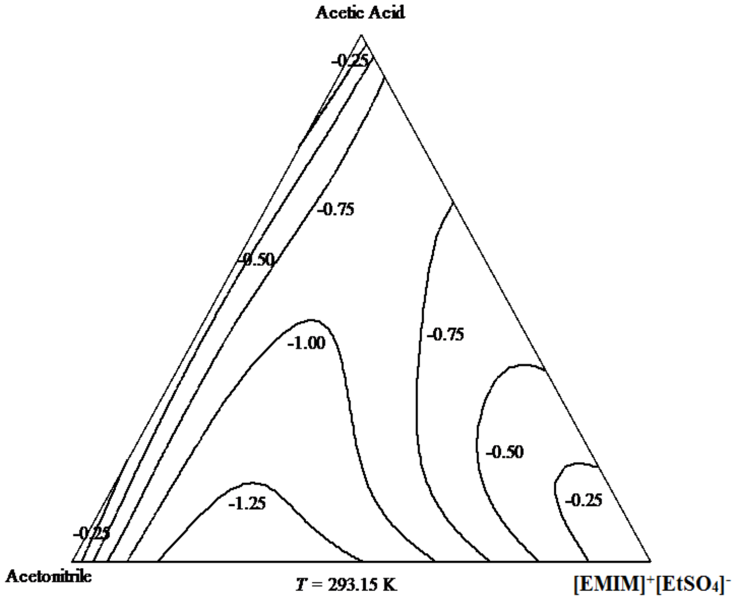
	T /K	A_0	A_1	A_2	A_3	A_4	Σ
	{[EMIM]$^+$[EtSO$_4$]$^-$ (x_1) + acetic acid (x_2)}						
V_m^E /cm^{3}mol^{-1}	293.15	-2.492	-1.255	-1.253	-5.185	-5.208	0.015
	298.15	-2.641	-1.352	-1.298	-5.364	-5.411	0.016
	303.15	-2.792	-1.458	-1.364	-5.538	-5.597	0.017
	308.15	-2.948	-1.571	-1.396	-5.716	-5.849	0.018
	313.15	-3.105	-1.687	-1.477	-5.908	-6.037	0.019
$\Delta\kappa_S$ /10^8×Pa^{-1}	293.15	-69.2	-50.3	-34.0	-64.0	-61.9	0.2
	298.15	-72.6	-52.7	-37.2	-68.9	-65.4	0.2
	303.15	-76.5	-55.5	-38.4	-73.8	-71.5	0.2
	308.15	-80.7	-59.0	-38.7	-78.0	-79.2	0.3
	313.15	-84.9	-61.8	-41.0	-83.1	-85.6	0.3
	{[EMIM]$^+$[EtSO$_4$]$^-$ (x_1) + propionic acid (x_2)}						
V_m^E /cm^{3}mol^{-1}	293.15	-3.566	-2.659	-3.044	-3.068	-1.176	0.010
	298.15	-3.782	-2.813	-3.145	-3.260	-1.357	0.009
	303.15	-4.002	-2.978	-3.275	-3.452	-1.511	0.009
	308.15	-4.226	-3.154	-3.404	-3.636	-1.674	0.009
	313.15	-4.458	-3.330	-3.503	-3.843	-1.890	0.009
$\Delta\kappa_S$ /10^8×Pa^{-1}	293.15	-65.5	-49.4	-42.9	-23.9	-0.5	0.1
	298.15	-69.7	-52.7	-43.1	-26.0	-6.3	0.1
	303.15	-73.9	-55.6	-45.4	-30.1	-8.8	0.1
	308.15	-78.2	-59.6	-48.5	-33.0	-11.5	0.1
	313.15	-83.2	-62.1	-51.9	-38.7	-13.1	0.1
	{acetic acid (x_1) + acetonitrile (x_2)}						

V_m^E /cm^{3}mol^{-1}	293.15	-5.019	-2.972	-1.711	-4.099	-2.266	0.020
	298.15	-5.229	-3.118	-1.833	-4.237	-2.372	0.022
	303.15	-5.447	-3.258	-1.978	-4.420	-2.470	0.023
	308.15	-5.675	-3.416	-2.087	-4.594	-2.645	0.024
	313.15	-5.913	-3.581	-2.211	-4.791	-2.793	0.025
$\Delta\kappa_S$ /10^8×Pa^{-1}	293.15	-71.6	-49.9	-38.0	-41.3	-26.8	0.2
	298.15	-75.7	-52.9	-39.2	-43.8	-32.0	0.2
	303.15	-80.1	-56.8	-41.1	-46.2	-34.5	0.2
	308.15	-84.7	-59.9	-44.0	-50.7	-36.6	0.2
	313.15	-89.6	-63.9	-45.3	-54.1	-43.3	0.2
{propionic acid (x_1) + acetonitrile (x_2)}							
V_m^E /cm^{3}mol^{-1}	293.15	-5.062	-2.550	-1.251	-2.816	-3.248	0.016
	298.15	-5.055	-2.889	-1.465	-2.707	-3.362	0.016
	303.15	-5.276	-3.029	-1.533	-2.888	-3.570	0.017
	308.15	-5.507	-3.190	-1.606	-3.041	-3.794	0.018
	313.15	-5.745	-3.348	-1.746	-3.239	-3.928	0.019
$\Delta\kappa_S$ /10^8×Pa^{-1}	293.15	-70.5	-48.4	-28.0	-43.2	-42.6	0.2
	298.15	-74.4	-51.3	-32.7	-46.5	-41.8	0.2
	303.15	-78.6	-54.8	-34.4	-49.7	-45.4	0.2
	308.15	-83.5	-58.2	-35.0	-53.1	-51.8	0.2
	313.15	-88.4	-62.1	-37.5	-56.6	-56.1	0.2

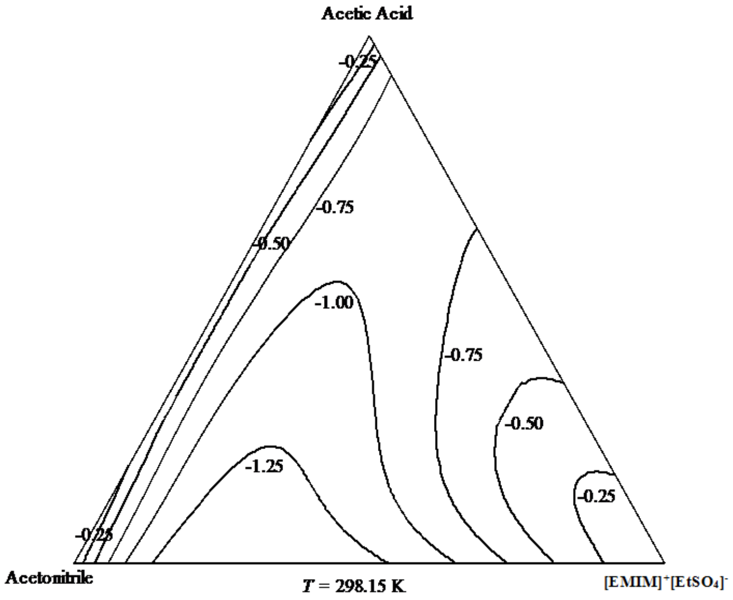
	{[EMIM]$^+$[EtSO$_4$]$^-$ (x_1) + acetonitrile (x_2)}						
V_m^E /cm^{3}mol^{-1}	293.15	-3.038	-2.128	-1.468	-4.230	-5.287	0.016
	298.15	-3.142	-2.075	-1.663	-4.467	-5.272	0.015
	303.15	-3.280	-2.134	-1.589	-4.638	-5.614	0.017
	308.15	-3.418	-2.207	-1.557	-4.803	-5.917	0.018
	313.15	-3.582	-2.247	-1.414	-5.067	-6.353	0.018
$\Delta\kappa_S$ /10^8×Pa^{-1}	293.15	-65.4	-49.6	-33.5	-49.5	-46.3	0.2
	298.15	-69.6	-51.0	-33.2	-54.6	-49.7	0.2
	303.15	-72.6	-55.8	-40.0	-54.0	-47.7	0.2
	308.15	-76.5	-58.8	-43.3	-57.6	-48.3	0.2
	313.15	-80.9	-61.9	-44.6	-62.3	-53.6	0.2

Standard uncertainties u are $u(T)$ = ±0.02 K, $u(p)$ = ±0.04 MPa and the combined expanded uncertainty Uc in mole fractions, density and sound velocity measurements were less than $U_c(x)$ = ± 0.0004, $U_c(\rho)$ = ± 9×10^{-4} g·cm^{-3} and $U_c(u)$ = ± 0.8 m·s^{-1}, respectively (0.95 level of confidence).

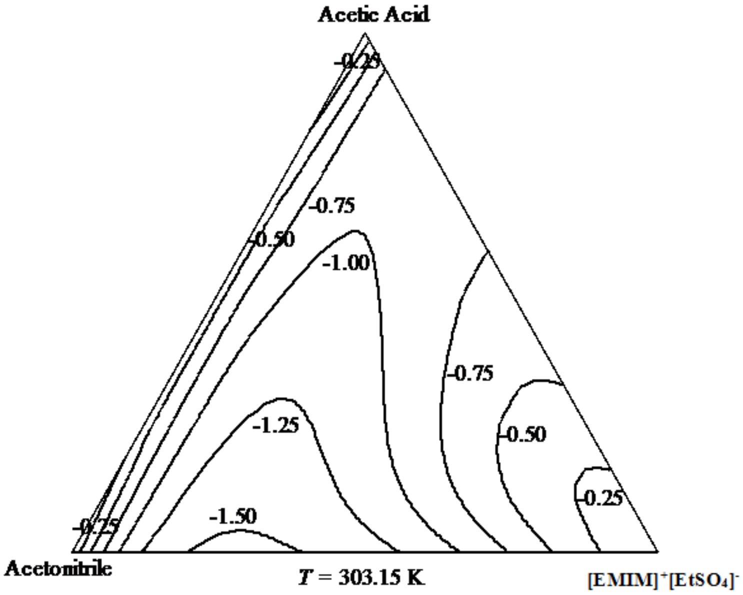
The excess molar volume data for the ternary liquid mixtures of {[EMIM]$^+$[EtSO$_4$]$^-$ + acetic acid + acetonitrile} and {[EMIM]$^+$[EtSO$_4$]$^-$ + propionic acid + acetonitrile}were plotted in Figs. 5.1.4.17 and 18.



a


Acetic Acid
-0.25
-0.75
-0.50
-1.00
-0.75
-0.50
-1.25
-0.25
-0.25
Acetonitrile
T = 298.15 K
[EMIM]+[EtSO4]-

b


Acetic Acid
-0.25
-0.75
-0.50
-1.00
-0.75
-0.50
-1.25
-0.25
-1.50
-0.25
Acetonitrile
T = 303.15 K
[EMIM]+[EtSO4]-

c

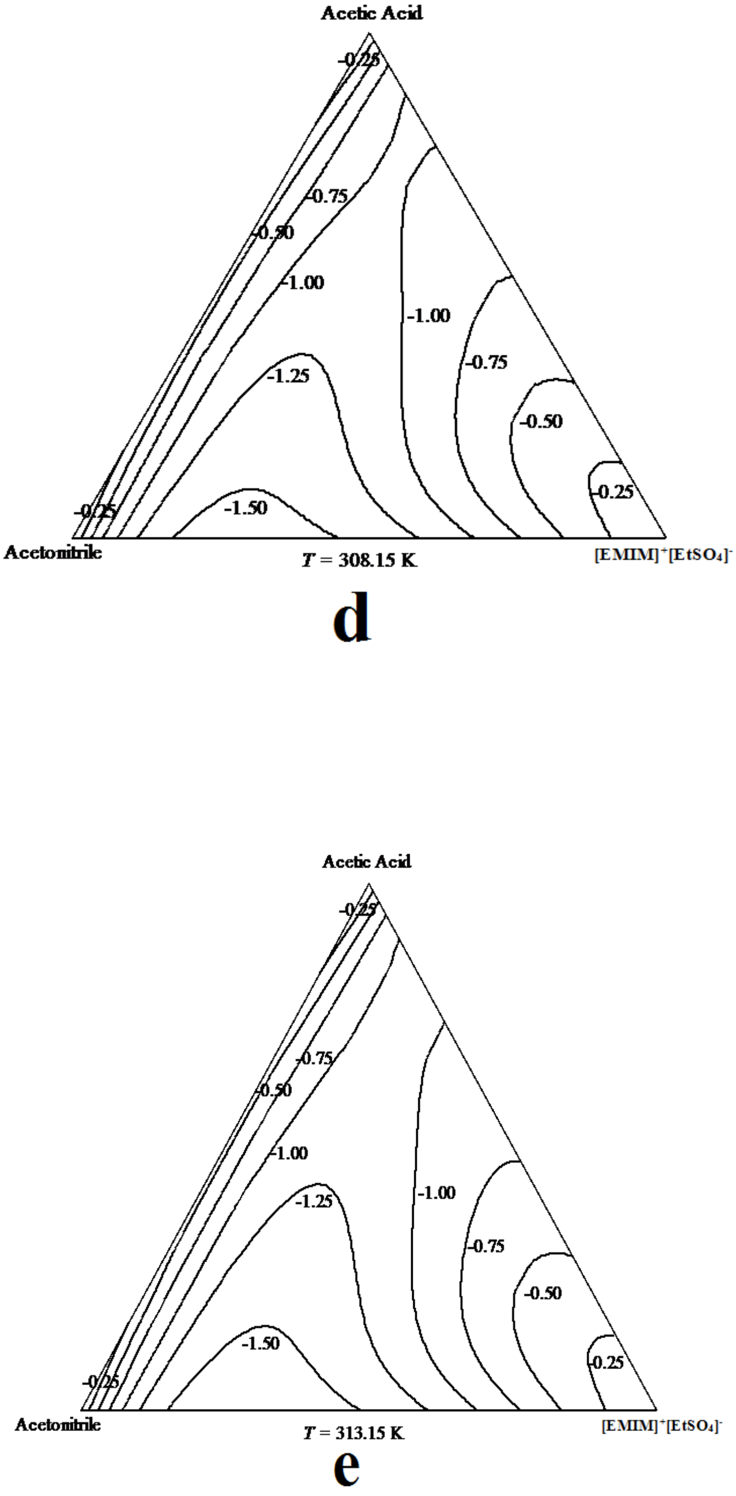
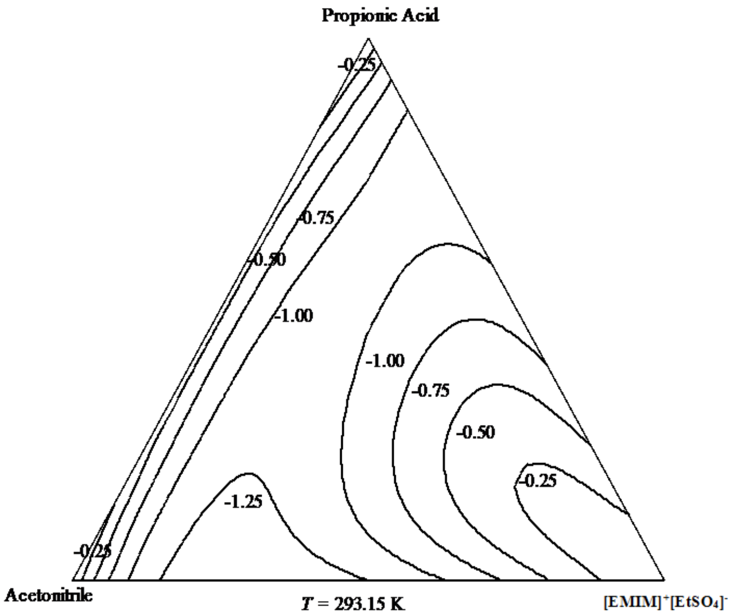
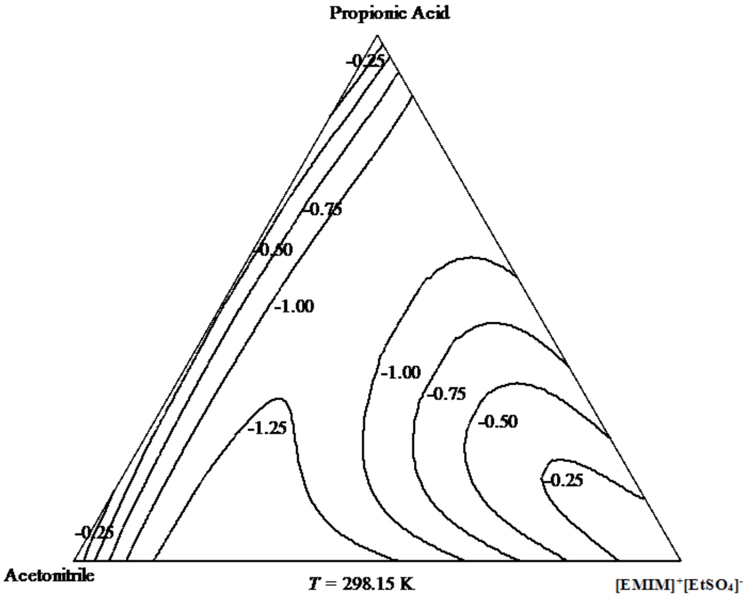


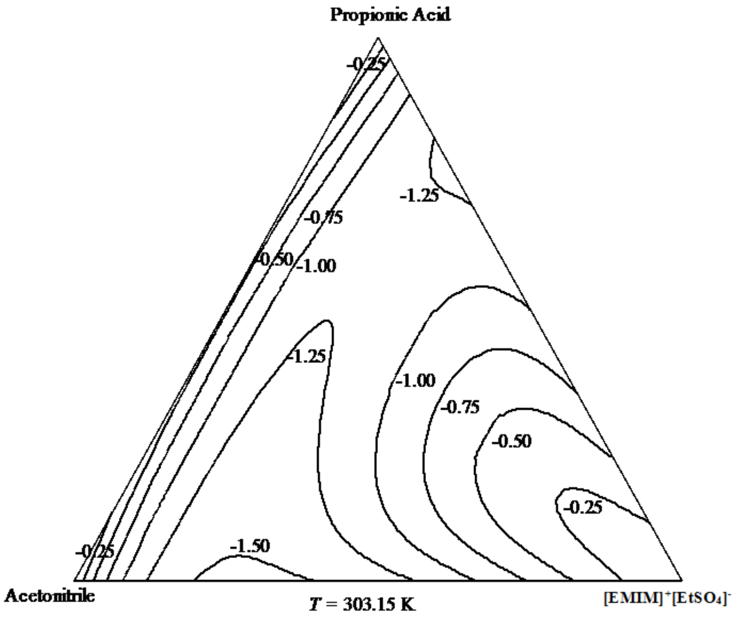
Fig. 5.1.4.17 Plots of excess volume (V_{123}^{E}) calculated by the Cibulka equation for ternary liquid mixtures of {$[EMIM]^+$ $[EtSO_4]^-$ + acetic acid + acetonitrile} at (a) 293.15 K, (b) 298.15 K, (c) 303.15 K, (d) 308.15 K, (e) 313.15 K.


Propionic Acid
-0.25
-0.75
-0.50
-1.00
-1.00
-0.75
-0.50
-0.25
-1.25
-0.25
Acetonitrile
T = 293.15 K
[EMIM]+[EtSO4]-

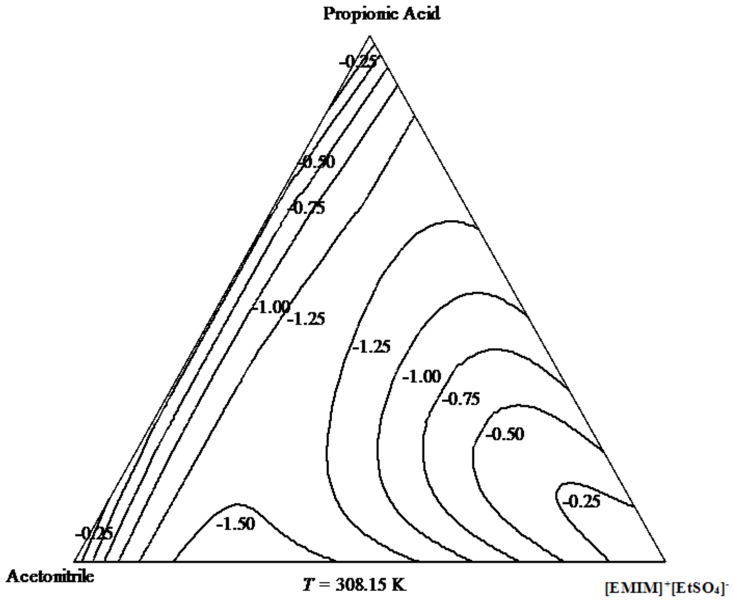
a


Propionic Acid
-0.25
-0.75
-0.50
-1.00
-1.00
-0.75
-0.50
-0.25
-1.25
-0.25
Acetonitrile
T = 298.15 K
[EMIM]+[EtSO4]-

b


Propionic Acid
-0.25
-1.25
-0.75
-0.50
-1.00
-1.25
-1.00
-0.75
-0.50
-0.25
-0.25
-1.50
Acetonitrile
T = 303.15 K
[EMIM]$^+$[EtSO$_4$]$^-$

c


Propionic Acid
-0.25
-0.50
-0.75
-1.00
-1.25
-1.25
-1.00
-0.75
-0.50
-0.25
-0.25
-1.50
Acetonitrile
T = 308.15 K
[EMIM]$^+$[EtSO$_4$]$^-$

d

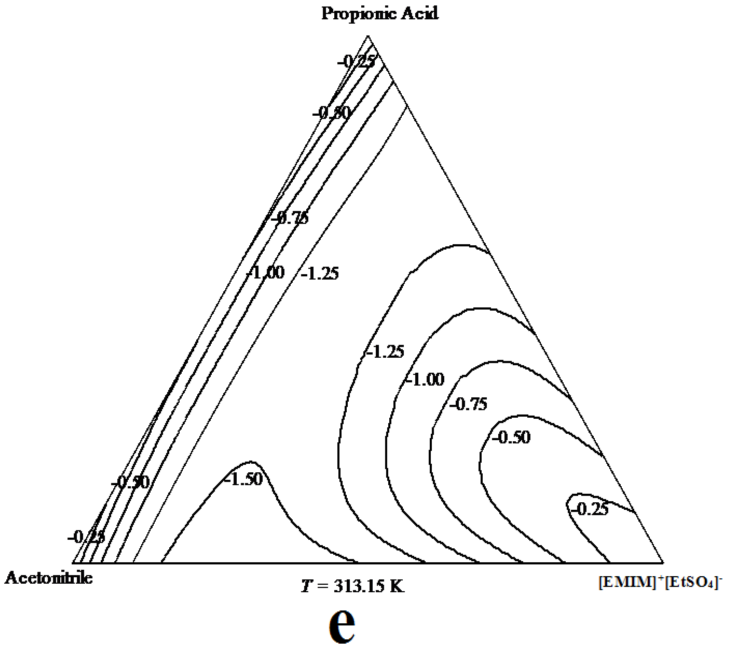
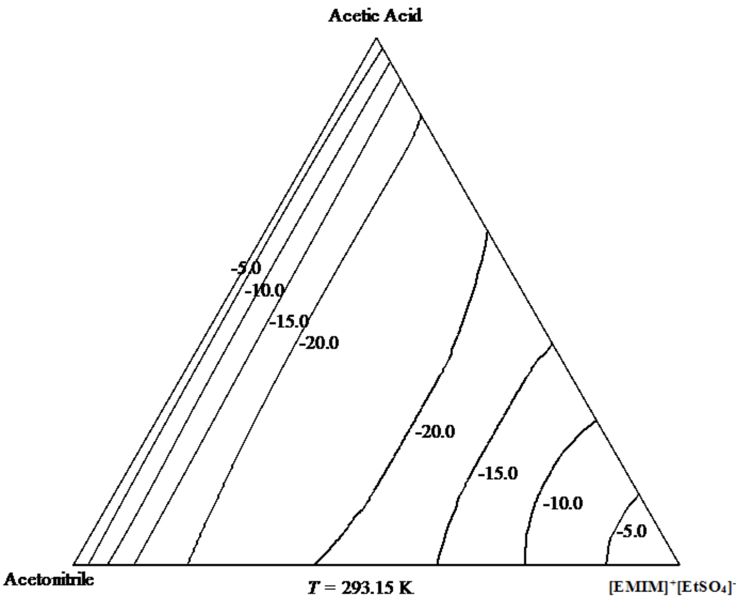
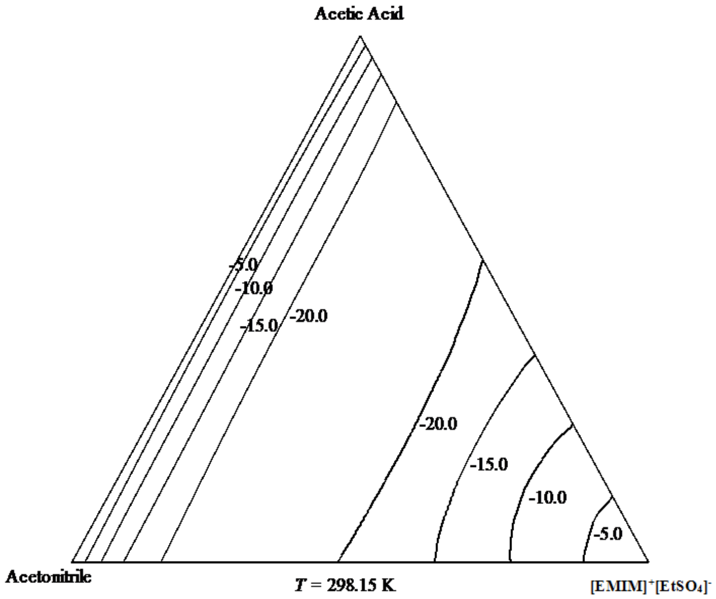


Fig. 5.1.4.18 Plots of excess volume (V^E_{123}) obtained from the Cibulka equation for ternary liquid mixtures {[EMIM]$^+$[EtSO$_4$]$^-$ + propionic acid + acetonitrile} at (a) 293.15 K, (b) 298.15 K, (c) 303.15 K, (d) 308.15 K, (e) 313.15 K.

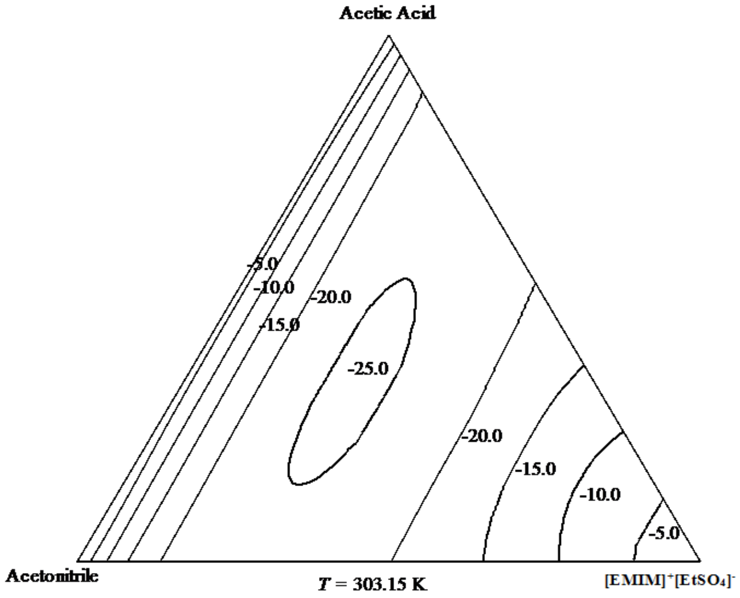
As seen from results, the (V^E_{123}) data is negative over the entire composition range at all the temperatures for both systems. According to J. DeRuiter, acids (acetic acid or propionic acid) have stronger dipoles and thus can form stronger H-bonds with other substances capable of H-bonding interactions. Addition of these acids (acetic acid or propionic acid) with IL + acetonitrile causes the breakage of hydrogen bonded complexes in pure acetic acid or propionic acid and acetonitrile molecules lose their dipolar association. Also, IL’s have the capability to interact with component molecules through ion–dipole, ion–pair and dipolar interactions in liquid mixtures (Venkatramana *et al.* 2015, Ali *et al.* 2004, Prasad *et al.* 2006). The more negative (V^E_{123}) values observed for propionic acid with IL + acetonitrile system compared acetic acid with IL + acetonitrile system due to the higher electron – donor capacity of propionic acid than acetic acid. The speed of sound is another essential property of pure liquids and their mixtures which results from the molecular interactions. The values deviation in isentropic compressibilities are plotted in Figs. 5.1.4.19 and 20 for the ternary mixtures {[EMIM]$^+$[EtSO$_4$]$^-$ + acetic acid + acetonitrile} and {[EMIM]$^+$[EtSO$_4$]$^-$ + propionic acid + acetonitrile} at different temperatures.


Acetic Acid
-5.0
-10.0
-15.0
-20.0
-20.0
-15.0
-10.0
-5.0
Acetonitrile
T = 293.15 K
[EMIM]$^+$[EtSO$_4$]$^-$

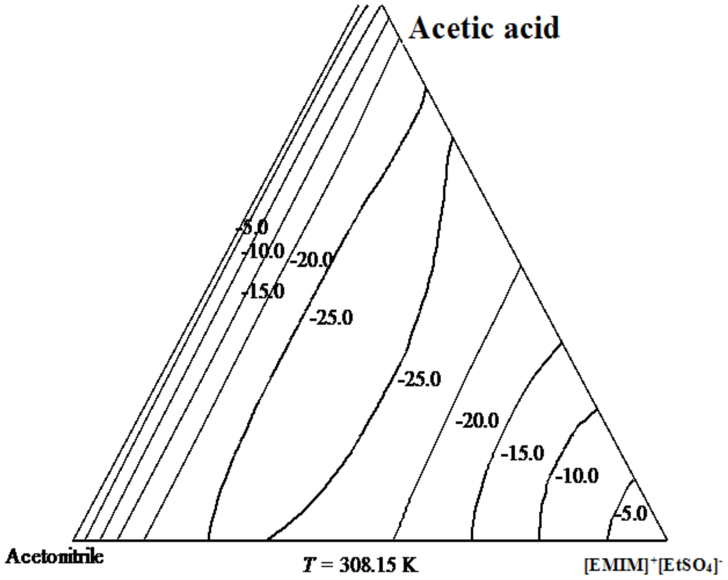
a


Acetic Acid
-5.0
-10.0
-15.0
-20.0
-20.0
-15.0
-10.0
-5.0
Acetonitrile
T = 298.15 K
[EMIM]$^+$[EtSO$_4$]$^-$

b


Acetic Acid
-5.0
-10.0
-15.0
-20.0
-25.0
-20.0
-15.0
-10.0
-5.0
Acetonitrile
T = 303.15 K
$[EMIM]^+[EtSO_4]^-$

c


Acetic acid
-5.0
-10.0
-20.0
-15.0
-25.0
-25.0
-20.0
-15.0
-10.0
-5.0
Acetonitrile
T = 308.15 K
$[EMIM]^+[EtSO_4]^-$

d

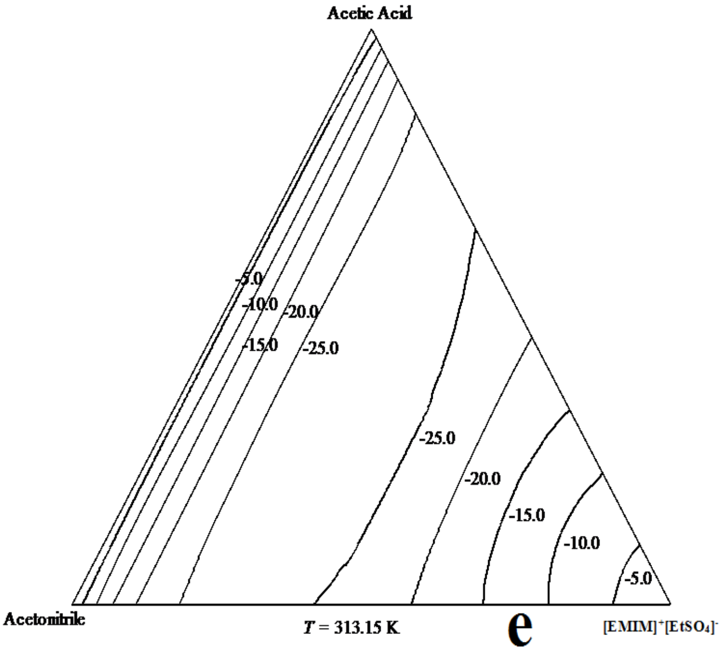
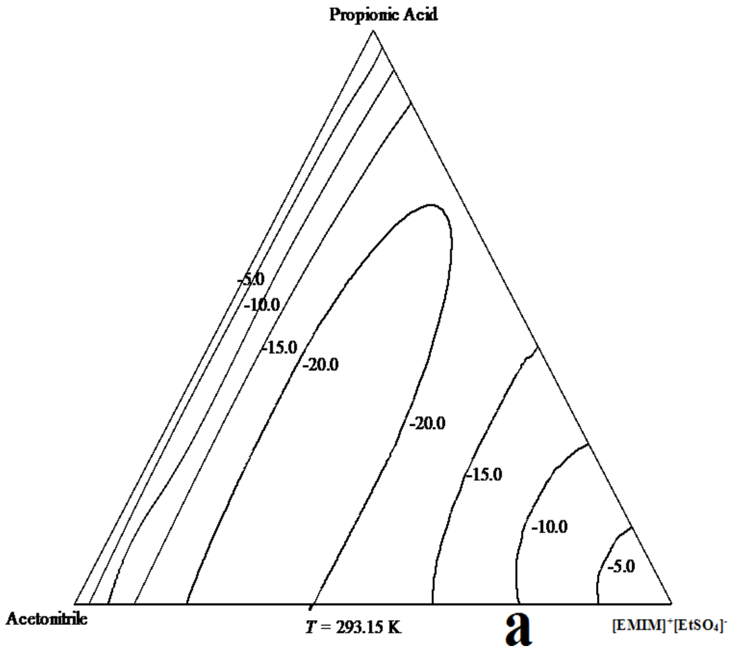
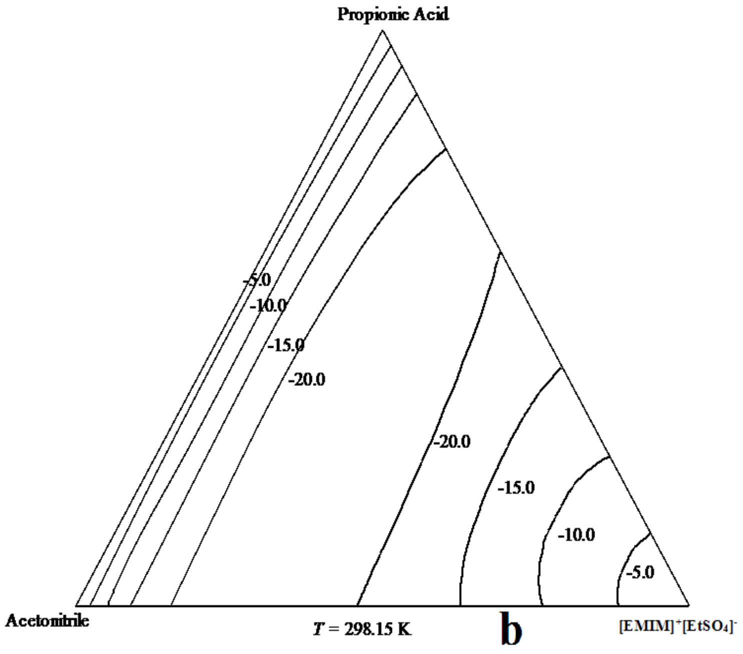
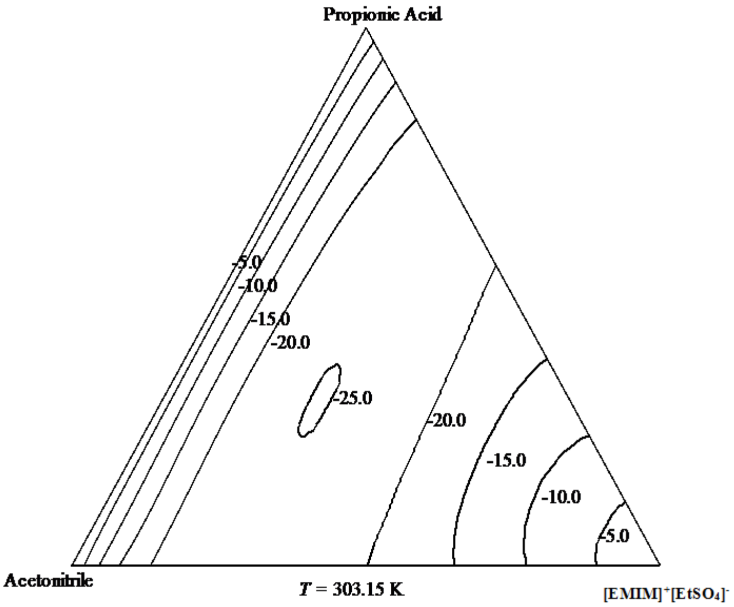


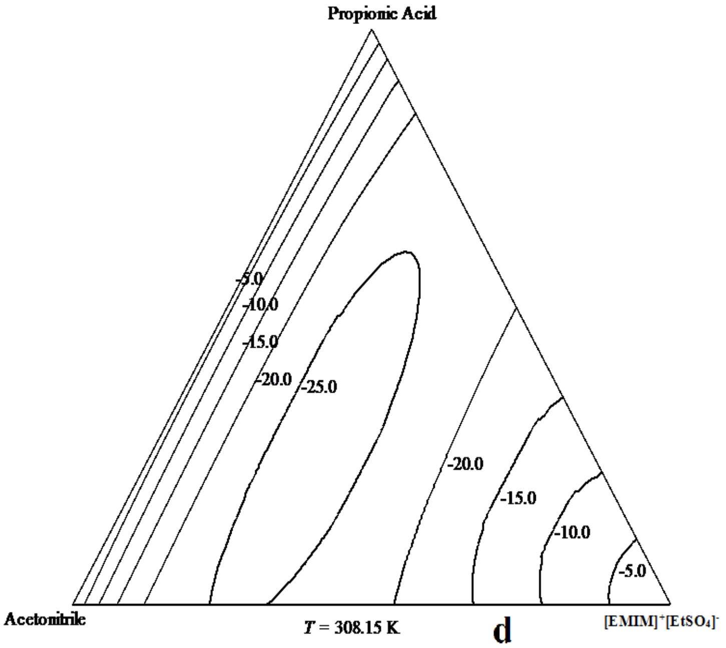
Fig. 5.1.4.19 Plots of deviations in isentropic compressibility (Δk_{s123}) obtained from the Cibulka equation for ternary liquid mixtures {[EMIM]$^+$[EtSO$_4$]$^-$ + acetic acid + acetonitrile} at (a) 293.15 K, (b) 298.15 K, (c) 303.15 K, (d) 308.15 K, (e) 313.15 K.


Propionic Acid
-5.0
-10.0
-15.0
-20.0
-20.0
-15.0
-10.0
-5.0
Acetonitrile
T = 293.15 K
a
$[EMIM]^+[EtSO_4]^-$


Propionic Acid
-5.0
-10.0
-15.0
-20.0
-20.0
-15.0
-10.0
-5.0
Acetonitrile
T = 298.15 K
b
$[EMIM]^+[EtSO_4]^-$


Propionic Acid
-5.0
-10.0
-15.0
-20.0
-25.0
-20.0
-15.0
-10.0
-5.0
Acetonitrile
T = 303.15 K
[EMIM]+[EtSO4]-

c


Propionic Acid
-5.0
-10.0
-15.0
-20.0
-25.0
-20.0
-15.0
-10.0
-5.0
Acetonitrile
T = 308.15 K
[EMIM]+[EtSO4]-

d

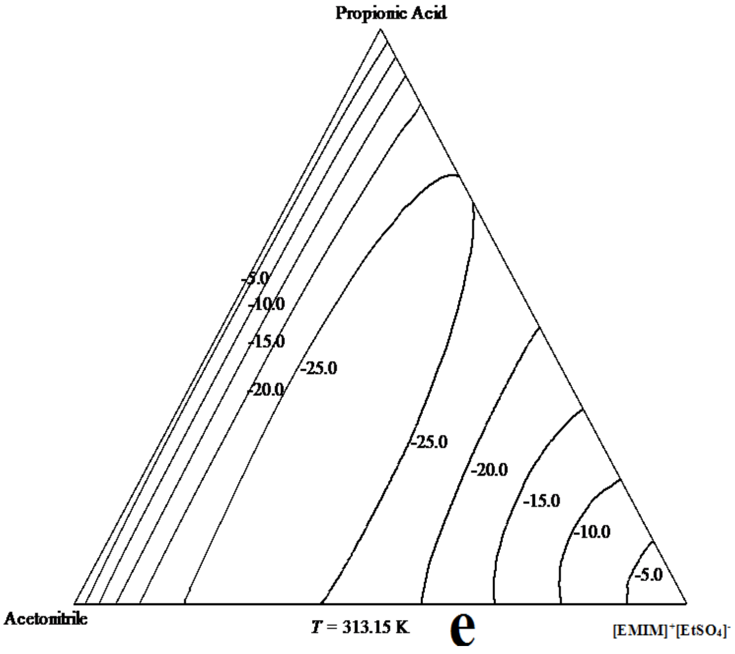


Fig. 5.1.4.20 Plots of deviations in isentropic compressibility (Δk_{s123}) obtained from the Cibulka equation for ternary liquid mixtures {$[EMIM]^+[EtSO_4]^-$ + propionic acid + acetonitrile} at (a) 293.15 K, (b) 298.15 K, (c) 303.15 K, (d) 308.15 K, (e) 313.15 K.

A probation of curves in Fig. 5.1.4.19 and 20 shows negative deviation over the entire composition range for all the ternary mixtures at all temperatures. The negative deviation in isentropic compressibility suggest the existence of charge – transfer complexes and decreasing the free – space between component molecules in ternary liquid mixtures. Furthermore, the (V_{123}^E) and (Δk_{s123}) values are decrease with increasing the temperature. The higher temperatures can be attributed to increased thermal motion of molecules may allow a more effective occupation of interstitials Lehmann et al. The values of the Cibulka coefficients (b_n) fitted to experimental excess molar volumes and deviation in isentropic compressibility of the {$[EMIM][EtSO_4]$ (x_1) or + acetic or propionic acid (x_2) + acetonitrile (x_3)} systems at temperature range from (293.15 to 313.15) K and at $p = 1 \times 10^5$ Pa together with the corresponding standard deviations of the fit (σ) are given in Table 5.2.1.13.

Table 5.2.1.13 The values of the Cibulka coefficients (b_n) fitted to experimental excess volumes of the {[EMIM][EtSO$_4$] (x_1) or + acetic or propionic acid (x_2) + acetonitrile (x_3)} systems at temperature range from (293.15 to 313.15) K and at $p = 1 \times 10^5$ Pa together with the corresponding standard deviations of the fit (σ).

T/K	b_0	b_1	b_2	σ
{[EMIM][EtSO$_4$] (x_1) + acetic acid (x_2) + acetonitrile (x_3)}				
V^E_{123}/cm^3 mol^{-1}				
293.15	−11.129	36.792	0.82328	0.05
298.15	−12.152	38.710	1.1002	0.06
303.15	−13.204	40.517	1.4517	0.05
308.15	−14.358	42.501	1.9388	0.05
313.15	−15.503	44.364	2.4169	0.06
{[EMIM][EtSO$_4$] (x_1) + propionic acid (x_2) + acetonitrile (x_3)}				
293.15	−16.109	63.661	3.1790	0.10
298.15	−16.852	65.410	3.3208	0.10
303.15	−17.586	67.040	3.4144	0.10
308.15	−18.450	68.913	3.6795	0.10
313.15	−19.328	70.941	3.9149	0.10
{[EMIM][EtSO$_4$] (x_1) + acetic acid (x_2) + acetonitrile (x_3)}				
(Δk_{s123}) (10^8 Pa)$^{-1}$				
293.15	−327.0	499.4	25.6	0.07
298.15	−348.4	539.5	20.5	0.08
303.15	−370.0	571.6	23.5	0.09
308.15	−398.7	617.4	29.8	0.10
313.15	−433.9	668.7	48.5	0.10
{[EMIM][EtSO$_4$] (x_1) + propionic acid (x_2) + acetonitrile (x_3)}				
293.15	−326.4	535.3	17.7	0.06
298.15	−339.6	563.8	2.1	0.06
303.15	−363.2	608.9	2.3	0.07
308.15	−383.7	644.7	−4.2	0.07
313.15	−418.8	721.2	−1.0	0.08

5.2.2 Group 6: {[BMIM]$^+$[SCN]$^-$ + acetonitrile + acetic acid or propionic acid

The experimental density (ρ), speed of sound (u), excess molar volume (V^E_{123}), isentropic compressibility (k_s) and deviation in isentropic compressibility (Δk_{s123}) for ternary liquid mixtures of {[BMIM]$^+$[SCN]$^-$ + acetic acid + acetonitrile} and {[BMIM]$^+$[SCN]$^-$ + propionic acid + acetonitrile} at all the investigated temperatures are listed in **Table 5.2.2.13**.

Table 5.2.2.13. Density (ρ), speed of sound (u), excess volume (V^E_{123}), isentropic compressibility (k_S) and deviation in isentropic compressibility (Δk_{s123}) for {[BMIM]$^+$[SCN]$^-$ (1) + acetic acid or propionic acid (2) + acetonitrile (3)} at (293.15, 298.15, 303.15, 308.15 and 313.15) K.

x_1	x_2	ρ/gcm^{-3}	V^E_{123}/cm^{3}mol^{-1}	u/ms^{-1}	κ_S /10^8×Pa^{-1}	(Δk_{s123})/10^8×Pa^{-1}
{[BMIM]$^+$[SCN]$^-$ + acetic acid + acetonitrile}						
T = 293.15 K						
0.0807	0.5208	0.98364	-0.940	1370.6	54	-15.8
0.1197	0.2937	0.92948	0.682	1464.6	50	-18.9
0.1318	0.2153	0.94212	-1.055	1443.1	51	-17.8
0.1505	0.1077	0.95148	-2.771	1424.7	52	-16.6
0.1947	0.3792	1.00060	-1.237	1495.0	45	-20.5
0.2444	0.2184	0.98894	-1.323	1536.6	43	-20.8
0.2659	0.1458	0.98428	-1.395	1554.7	42	-20.9
0.1237	0.7741	1.05251	-1.056	1406.3	48	-18.9
0.2666	0.5138	1.04106	-1.131	1541.0	40	-20.9
0.3581	0.3470	1.03553	-1.150	1598.1	38	-20.0
0.4065	0.2570	1.03278	-1.154	1624.3	37	-19.2
0.4466	0.1862	1.03147	-1.186	1644.7	36	-18.5
0.5000	0.0880	1.02937	-1.223	1670.2	35	-17.4
0.3870	0.5070	1.06075	-0.959	1604.8	37	-19.2
0.5223	0.3350	1.05905	-0.885	1664.6	34	-16.1
0.6059	0.2284	1.05810	-0.830	1694.2	33	-13.9
0.6946	0.1142	1.05535	-0.529	1715.0	32	-10.9
0.7494	0.0466	1.05579	-0.579	1733.3	32	-9.4
0.9024	0.0516	1.06984	-0.255	1756.2	30	-3.5
0.6430	0.3229	1.07055	-0.599	1684.8	33	-11.8
0.5330	0.4394	1.07114	-0.746	1658.6	34	-15.4
0.8329	0.1208	1.07010	-0.407	1748.2	31	-6.1
0.7615	0.1969	1.07009	-0.455	1729.5	31	-8.5
0.3907	0.5872	1.07136	-0.898	1604.0	36	-19.0

T = 298.15 K

0.0807	0.5208	0.97899	-0.971	1354.3	56	-16.8
0.1197	0.2937	0.92525	0.651	1448.3	52	-20.0
0.1318	0.2153	0.93780	-1.091	1426.9	52	-19.0
0.1505	0.1077	0.94707	-2.809	1408.5	53	-17.7
0.1947	0.3792	0.99656	-1.271	1480.1	46	-21.7
0.2444	0.2184	0.98507	-1.355	1521.7	44	-22.0
0.2659	0.1458	0.98047	-1.427	1540.0	43	-22.1
0.1237	0.7741	1.04813	-1.084	1390.8	49	-19.9
0.2666	0.5138	1.03723	-1.151	1526.9	41	-22.1
0.3581	0.3470	1.03192	-1.162	1584.4	39	-21.1
0.4065	0.2570	1.02926	-1.161	1610.8	37	-20.3
0.4466	0.1862	1.02803	-1.190	1631.3	37	-19.5
0.5000	0.0880	1.02601	-1.221	1656.9	36	-18.4
0.3870	0.5070	1.05719	-0.959	1591.6	37	-20.2
0.5223	0.3350	1.05569	-0.869	1651.8	35	-17.0
0.6059	0.2284	1.05484	-0.801	1681.6	34	-14.6
0.6946	0.1142	1.05216	-0.483	1702.5	33	-11.5
0.7494	0.0466	1.05265	-0.527	1721.0	32	-9.9
0.9024	0.0516	1.06679	-0.170	1744.3	31	-3.6
0.6430	0.3229	1.06730	-0.555	1672.2	34	-12.4
0.5330	0.4394	1.06779	-0.723	1645.7	35	-16.2
0.8329	0.1208	1.06701	-0.336	1736.1	31	-6.4
0.7615	0.1969	1.06695	-0.394	1717.4	32	-8.9
0.3907	0.5872	1.06779	-0.895	1591.0	37	-20.0

T = 303.15 K

0.0807	0.5208	0.97433	-1.013	1337.8	57	-17.8
0.1197	0.2937	0.92102	0.603	1431.7	53	-21.3
0.1318	0.2153	0.93348	-1.144	1410.4	54	-20.2
0.1505	0.1077	0.94265	-2.866	1392.0	55	-18.8
0.1947	0.3792	0.99251	-1.326	1464.8	47	-23.0
0.2444	0.2184	0.98121	-1.415	1506.7	45	-23.3
0.2659	0.1458	0.97667	-1.489	1524.9	44	-23.4
0.1237	0.7741	1.04374	-1.127	1375.2	51	-21.1

0.2666	0.5138	1.03341	-1.200	1512.6	42	-23.3
0.3581	0.3470	1.02833	-1.213	1570.6	39	-22.3
0.4065	0.2570	1.02576	-1.212	1597.1	38	-21.5
0.4466	0.1862	1.02459	-1.240	1617.6	37	-20.7
0.5000	0.0880	1.02265	-1.271	1643.4	36	-19.5
0.3870	0.5070	1.05363	-1.001	1578.3	38	-21.4
0.5223	0.3350	1.05236	-0.907	1638.9	35	-18.0
0.6059	0.2284	1.05159	-0.835	1668.8	34	-15.4
0.6946	0.1142	1.04897	-0.509	1689.8	33	-12.2
0.7494	0.0466	1.04953	-0.552	1708.5	33	-10.4
0.9024	0.0516	1.06375	-0.176	1732.3	31	-3.8
0.6430	0.3229	1.06406	-0.577	1659.6	34	-13.1
0.5330	0.4394	1.06445	-0.754	1633.2	35	-17.1
0.8329	0.1208	1.06394	-0.349	1724.0	32	-6.8
0.7615	0.1969	1.06382	-0.411	1705.1	32	-9.4
0.3907	0.5872	1.06424	-0.933	1577.7	38	-21.1
			T = 308.15 K			
0.0807	0.5208	0.96968	-1.057	1321.4	59	-18.9
0.1197	0.2937	0.91679	0.554	1415.2	54	-22.6
0.1318	0.2153	0.92915	-1.200	1394.0	55	-21.4
0.1505	0.1077	0.93823	-2.926	1375.6	56	-20.1
0.1947	0.3792	0.98847	-1.383	1449.6	48	-24.4
0.2444	0.2184	0.97735	-1.477	1491.6	46	-24.7
0.2659	0.1458	0.97288	-1.554	1509.9	45	-24.8
0.1237	0.7741	1.03937	-1.171	1359.7	52	-22.3
0.2666	0.5138	1.02959	-1.251	1498.4	43	-24.7
0.3581	0.3470	1.02474	-1.266	1556.8	40	-23.6
0.4065	0.2570	1.02226	-1.264	1583.4	39	-22.7
0.4466	0.1862	1.02116	-1.292	1604.0	38	-21.9
0.5000	0.0880	1.01929	-1.322	1629.9	37	-20.6
0.3870	0.5070	1.05009	-1.044	1564.9	39	-22.6
0.5223	0.3350	1.04903	-0.945	1626.1	36	-19.0
0.6059	0.2284	1.04836	-0.870	1656.0	35	-16.3
0.6946	0.1142	1.04580	-0.534	1677.2	34	-12.9

0.7494	0.0466	1.04641	-0.578	1696.0	33	-11.0
0.9024	0.0516	1.06072	-0.181	1720.3	32	-4.1
0.6430	0.3229	1.06083	-0.599	1647.4	35	-13.8
0.5330	0.4394	1.06112	-0.785	1620.5	36	-18.0
0.8329	0.1208	1.06089	-0.362	1711.9	32	-7.2
0.7615	0.1969	1.06071	-0.427	1692.9	33	-9.9
0.3907	0.5872	1.05717	-0.616	1551.4	39	-21.5

T = 313.15 K

0.0807	0.5208	0.96502	-1.103	1304.9	61	-20.1
0.1197	0.2937	0.91256	0.502	1398.7	56	-24.0
0.1318	0.2153	0.92482	-1.258	1377.6	57	-22.8
0.1505	0.1077	0.93382	-2.990	1359.2	58	-21.4
0.1947	0.3792	0.98444	-1.444	1434.4	49	-25.9
0.2444	0.2184	0.97349	-1.543	1476.7	47	-26.3
0.2659	0.1458	0.96909	-1.622	1494.9	46	-26.4
0.1237	0.7741	1.03500	-1.217	1344.3	53	-23.6
0.2666	0.5138	1.02579	-1.304	1484.2	44	-26.1
0.3581	0.3470	1.02117	-1.321	1543.0	41	-25.0
0.4065	0.2570	1.01877	-1.319	1569.6	40	-24.0
0.4466	0.1862	1.01774	-1.348	1590.6	39	-23.1
0.5000	0.0880	1.01595	-1.378	1616.5	38	-21.8
0.3870	0.5070	1.04655	-1.089	1551.7	40	-23.9
0.5223	0.3350	1.04571	-0.986	1613.3	37	-20.1
0.6059	0.2284	1.04513	-0.907	1643.5	35	-17.2
0.6946	0.1142	1.04264	-0.563	1664.6	35	-13.6
0.7494	0.0466	1.04331	-0.606	1683.6	34	-11.7
0.9024	0.0516	1.05771	-0.189	1708.4	32	-4.3
0.6430	0.3229	1.05761	-0.623	1635.1	35	-14.6
0.5330	0.4394	1.05780	-0.819	1608.0	37	-19.0
0.8329	0.1208	1.05784	-0.377	1700.0	33	-7.6
0.7615	0.1969	1.05760	-0.445	1680.9	33	-10.4
0.3907	0.5872	1.07163	-2.459	1503.7	41	-21.6

{[BMIM]$^+$[SCN]$^-$ + propionic acid + acetonitrile}

T = 293.15 K

0.0893	0.4698	0.96117	-1.236	1363.2	56	-14.9
0.1261	0.2516	0.94157	-1.271	1426.5	52	-17.4
0.1376	0.1824	0.93475	-1.243	1442.3	51	-17.7
0.1536	0.0875	0.92569	-1.219	1464.5	50	-18.2
0.2098	0.3319	0.98405	-1.226	1479.5	46	-19.1
0.2549	0.1852	0.97982	-1.295	1528.2	44	-20.0
0.2730	0.1210	0.97709	-1.285	1544.6	43	-20.1
0.1449	0.7359	1.01798	-1.346	1382.2	51	-16.5
0.2955	0.4618	1.02000	-1.062	1526.5	42	-19.3
0.3821	0.3031	1.02288	-1.118	1584.0	39	-18.6
0.4263	0.2218	1.02536	-1.276	1610.7	38	-18.1
0.4624	0.1564	1.02500	-1.143	1635.4	36	-17.7
0.5051	0.0753	1.02568	-1.146	1661.5	35	-17.0
0.4270	0.4528	1.03694	-0.260	1573.2	39	-16.3
0.5581	0.2791	1.05029	-1.118	1656.1	35	-14.8
0.6329	0.1944	1.05323	-1.002	1688.0	33	-12.8
0.7091	0.0944	1.05433	-0.795	1718.0	32	-10.7
0.7484	0.0457	1.05307	-0.404	1735.9	32	-9.5
0.9091	0.0425	1.06666	0.057	1764.4	30	-3.5
0.6793	0.2847	1.06245	-0.670	1693.7	33	-11.1
0.5823	0.3871	1.05998	-0.947	1657.8	34	-13.9
0.8534	0.1018	1.06826	-0.504	1744.1	31	-5.3
0.7932	0.1659	1.06689	-0.627	1727.1	31	-7.4
0.4402	0.5364	1.05508	-1.305	1594.3	37	-17.3
0.2821	0.7028	1.04625	-1.537	1499.5	43	-19.1
T = 298.15 K						
0.0893	0.4698	0.95667	-1.279	1346.2	58	-15.9
0.1261	0.2516	0.93725	-1.314	1409.9	54	-18.5
0.1376	0.1824	0.93048	-1.284	1425.8	53	-18.8
0.1536	0.0875	0.92149	-1.260	1448.1	52	-19.3
0.2098	0.3319	0.98003	-1.262	1463.9	48	-20.3
0.2549	0.1852	0.97594	-1.326	1513.0	45	-21.2
0.2730	0.1210	0.97328	-1.317	1529.4	44	-21.3
0.1449	0.7359	1.01376	-1.388	1366.0	53	-17.6

0.2955	0.4618	1.01515	-0.980	1512.0	43	-20.5
0.3821	0.3031	1.01912	-1.113	1570.0	40	-19.8
0.4263	0.2218	1.02186	-1.286	1596.9	38	-19.2
0.4624	0.1564	1.02156	-1.147	1621.8	37	-18.7
0.5051	0.0753	1.02229	-1.142	1648.0	36	-17.9
0.4270	0.4528	1.03402	-0.329	1559.3	40	-17.4
0.5581	0.2791	1.04697	-1.107	1643.2	35	-15.7
0.6329	0.1944	1.04999	-0.976	1675.3	34	-13.6
0.7091	0.0944	1.05116	-0.753	1705.5	33	-11.3
0.7484	0.0457	1.04987	-0.344	1723.7	32	-10.1
0.9091	0.0425	1.06357	0.151	1752.8	31	-3.7
0.6793	0.2847	1.05920	-0.627	1681.4	33	-11.7
0.5823	0.3871	1.05665	-0.926	1645.3	35	-14.7
0.8534	0.1018	1.06518	-0.433	1732.2	31	-5.6
0.7932	0.1659	1.06378	-0.568	1715.0	32	-7.8
0.4402	0.5364	1.05159	-1.311	1581.1	38	-18.3
0.2821	0.7028	1.04249	-1.571	1485.5	43	-20.3
T = 303.15 K						
0.0893	0.4698	0.95217	-1.334	1329.5	59	-17.0
0.1261	0.2516	0.93293	-1.373	1393.2	55	-19.7
0.1376	0.1824	0.92621	-1.343	1409.1	54	-20.1
0.1536	0.0875	0.91730	-1.320	1431.3	53	-20.6
0.2098	0.3319	0.97603	-1.322	1448.2	49	-21.6
0.2549	0.1852	0.97215	-1.393	1497.7	46	-22.5
0.2730	0.1210	0.96948	-1.379	1514.0	45	-22.6
0.1449	0.7359	1.00955	-1.448	1349.9	54	-18.8
0.2955	0.4618	1.01079	-0.976	1497.4	44	-21.7
0.3821	0.3031	1.01533	-1.146	1556.0	41	-21.0
0.4263	0.2218	1.01837	-1.341	1583.1	39	-20.3
0.4624	0.1564	1.01813	-1.199	1608.0	38	-19.8
0.5051	0.0753	1.01891	-1.190	1634.4	37	-19.0
0.4270	0.4528	1.02976	-0.288	1545.4	41	-18.4
0.5581	0.2791	1.04367	-1.153	1630.3	36	-16.6
0.6329	0.1944	1.04677	-1.016	1662.6	35	-14.4

0.7091	0.0944	1.04799	-0.783	1693.0	33	-11.9
0.7484	0.0457	1.04667	-0.360	1711.4	33	-10.6
0.9091	0.0425	1.06048	0.154	1740.9	31	-3.9
0.6793	0.2847	1.05597	-0.653	1669.2	34	-12.4
0.5823	0.3871	1.05333	-0.963	1632.7	36	-15.6
0.8534	0.1018	1.06212	-0.448	1720.0	32	-5.9
0.7932	0.1659	1.06067	-0.590	1702.9	33	-8.2
0.4402	0.5364	1.04811	-1.364	1567.9	39	-19.5
0.2821	0.7028	1.03873	-1.635	1471.2	44	-21.6
			T = 308.15 K			
0.0893	0.4698	0.94767	-1.391	1312.6	61	-18.2
0.1261	0.2516	0.92862	-1.434	1376.5	57	-21.0
0.1376	0.1824	0.92195	-1.405	1392.4	56	-21.4
0.1536	0.0875	0.91310	-1.383	1414.6	55	-21.9
0.2098	0.3319	0.97203	-1.383	1432.6	50	-23.0
0.2549	0.1852	0.96830	-1.458	1482.5	47	-24.0
0.2730	0.1210	0.96569	-1.444	1498.8	46	-24.0
0.1449	0.7359	1.00536	-1.510	1334.1	56	-20.1
0.2955	0.4618	1.00552	-0.881	1482.9	45	-23.0
0.3821	0.3031	1.01164	-1.189	1542.0	42	-22.3
0.4263	0.2218	1.01489	-1.399	1569.3	40	-21.6
0.4624	0.1564	1.01471	-1.254	1594.4	39	-21.0
0.5051	0.0753	1.01554	-1.240	1620.9	37	-20.1
0.4270	0.4528	1.02554	-0.251	1530.6	42	-19.5
0.5581	0.2791	1.04038	-1.200	1617.5	37	-17.6
0.6329	0.1944	1.04356	-1.057	1649.9	35	-15.3
0.7091	0.0944	1.04484	-0.814	1680.6	34	-12.6
0.7484	0.0457	1.04349	-0.375	1699.1	33	-11.3
0.9091	0.0425	1.05740	0.158	1729.2	32	-4.1
0.6793	0.2847	1.05274	-0.679	1657.0	35	-13.2
0.5823	0.3871	1.05003	-1.002	1620.3	36	-16.6
0.8534	0.1018	1.05907	-0.464	1708.1	32	-6.3
0.7932	0.1659	1.05759	-0.612	1690.8	33	-8.7
0.4402	0.5364	1.04464	-1.418	1554.9	40	-20.7

0.2821	0.7028	1.03498	-1.700	1456.9	46	-23.0
			T = 313.15 K			
0.0893	0.4698	0.94317	-1.450	1295.8	63	-19.4
0.1261	0.2516	0.92430	-1.498	1359.8	59	-22.4
0.1376	0.1824	0.91768	-1.470	1375.8	58	-22.8
0.1536	0.0875	0.90891	-1.449	1398.0	56	-23.3
0.2098	0.3319	0.96803	-1.448	1417.3	51	-24.5
0.2549	0.1852	0.96447	-1.527	1467.4	48	-25.5
0.2730	0.1210	0.96191	-1.513	1483.7	47	-25.5
0.1449	0.7359	1.00116	-1.574	1318.8	57	-21.5
0.2955	0.4618	1.00113	-0.875	1468.4	46	-24.5
0.3821	0.3031	1.00784	-1.223	1528.1	42	-23.7
0.4263	0.2218	1.01143	-1.460	1555.7	41	-22.9
0.4624	0.1564	1.01131	-1.313	1580.8	40	-22.3
0.5051	0.0753	1.01214	-1.290	1607.4	38	-21.3
0.4270	0.4528	1.02133	-0.215	1515.6	43	-20.7
0.5581	0.2791	1.03710	-1.250	1604.6	37	-18.7
0.6329	0.1944	1.04037	-1.101	1637.3	36	-16.2
0.7091	0.0944	1.04170	-0.849	1668.1	34	-13.4
0.7484	0.0457	1.04032	-0.394	1686.8	34	-11.9
0.9091	0.0425	1.05434	0.161	1717.4	32	-4.4
0.6793	0.2847	1.04953	-0.708	1644.8	35	-14.0
0.5823	0.3871	1.04674	-1.043	1607.9	37	-17.6
0.8534	0.1018	1.05605	-0.483	1696.2	33	-6.7
0.7932	0.1659	1.05451	-0.636	1678.9	34	-9.3
0.4402	0.5364	1.04119	-1.474	1541.9	40	-22.0
0.2821	0.7028	1.03124	-1.767	1442.7	47	-24.5

The V^E or Δk_{s123} data for the binary systems of {[BMIM]$^+$[SCN]$^-$ + acetic acid or propionic acid}, {[BMIM]$^+$[SCN]$^-$ + acetonitrile} and acetonitrile + acetic acid or propionic acid were studied previously at different temperatures by our research group. The Redlich-Kister parameters along with the standard deviations σ (V^E) and (Δk_{s123}) of five binary systems are given in Table 5.2.2.14. Also, the ternary data were correlated by using the Cibulka equation.

Table 5.2.2.14. The Redlich–Kister parameters fitted to experimental excess volumes for binary systems composing the ternary systems: {[BMIM]$^+$[SCN]$^-$ + acetonitrile + {acetic acid or propionic acid}} at T = (293.15, 298.15, 303.15, 308.15 and 313.15) K and at pressure p = 0.1 MPa along with coefficients standard deviations σ (V^E) of the fit.

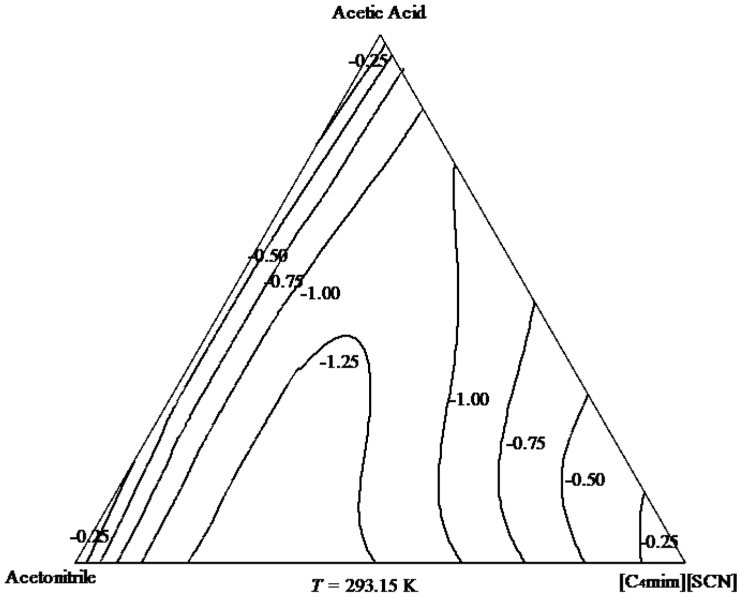
	T (K)	A_0	A_1	A_2	A_3	A_4	Σ
{[BMIM]$^+$[SCN]$^-$ (x_1) + acetic acid (x_2)}							
V_m^E /cm^3·mol^{-1}	293.15	-3.038	-2.128	-1.468	-4.230	-5.287	0.016
	298.15	-3.142	-2.075	-1.663	-4.467	-5.272	0.015
	303.15	-3.280	-2.134	-1.589	-4.638	-5.614	0.017
	308.15	-3.418	-2.207	-1.557	-4.803	-5.917	0.018
	313.15	-3.582	-2.247	-1.414	-5.067	-6.353	0.018
$10^8 \times \Delta\kappa_s$ /Pa^{-1}	293.15	-65.4	-49.6	-33.5	-49.5	-46.3	0.2
	298.15	-69.6	-51.0	-33.2	-54.6	-49.7	0.2
	303.15	-72.6	-55.8	-40.0	-54.0	-47.7	0.2
	308.15	-76.5	-58.8	-43.3	-57.6	-48.3	0.2
	313.15	-80.9	-61.9	-44.6	-62.3	-53.6	0.2
{[BMIM]$^+$[SCN]$^-$ (x_1) + propionic acid (x_2)}							
V_m^E /cm^3·mol^{-1}	293.15	-5.041	-4.257	-3.847	-1.50	0.026	0.011
	298.15	-5.081	-4.295	-4.395	-1.353	0.226	0.016
	303.15	-5.294	-4.442	-4.550	-1.531	0.122	0.016

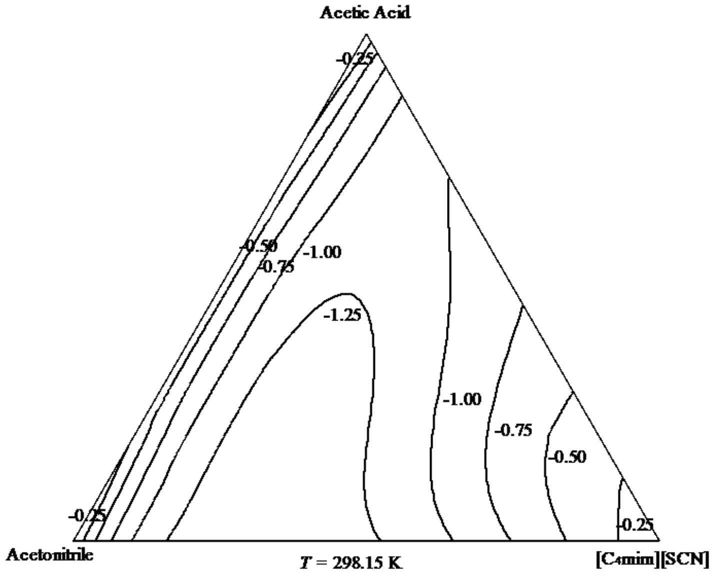
	308.15	-5.515	-4.600	-4.673	-1.709	-0.040	0.017
	313.15	-5.748	-4.760	-4.753	-1.904	-0.275	0.017
$10^8 \times \Delta\kappa_S$ /Pa^{-1}	293.15	-24.0	-32.7	-38.2	-12.3	12.1	0.1
	298.15	-67.0	-53.5	-46.6	-16.2	8.2	0.1
	303.15	-71.3	-56.5	-50.5	-18.9	8.3	0.1
	308.15	-75.7	-60.9	-52.5	-20.8	5.7	0.1
	313.15	-80.5	-64.6	-54.7	-22.9	2.8	0.1
{acetic acid (x_1) + acetonitrile (x_2)}							
V_m^E /cm^{3}mol^{-1}	293.15	-5.019	-2.972	-1.711	-4.099	-2.266	0.020
	298.15	-5.229	-3.118	-1.833	-4.237	-2.372	0.022
	303.15	-5.447	-3.258	-1.978	-4.420	-2.470	0.023
	308.15	-5.675	-3.416	-2.087	-4.594	-2.645	0.024
	313.15	-5.913	-3.581	-2.211	-4.791	-2.793	0.025
$\Delta\kappa_S$ /$10^8\times$Pa^{-1}	293.15	-71.6	-49.9	-38.0	-41.3	-26.8	0.2
	298.15	-75.7	-52.9	-39.2	-43.8	-32.0	0.2
	303.15	-80.1	-56.8	-41.1	-46.2	-34.5	0.2
	308.15	-84.7	-59.9	-44.0	-50.7	-36.6	0.2
	313.15	-89.6	-63.9	-45.3	-54.1	-43.3	0.2
{propionic acid (x_1) + acetonitrile (x_2)}							
V_m^E /cm^{3}mol^{-1}	293.15	-5.062	-2.550	-1.251	-2.816	-3.248	0.016
	298.15	-5.055	-2.889	-1.465	-2.707	-3.362	0.016
	303.15	-5.276	-3.029	-1.533	-2.888	-3.570	0.017

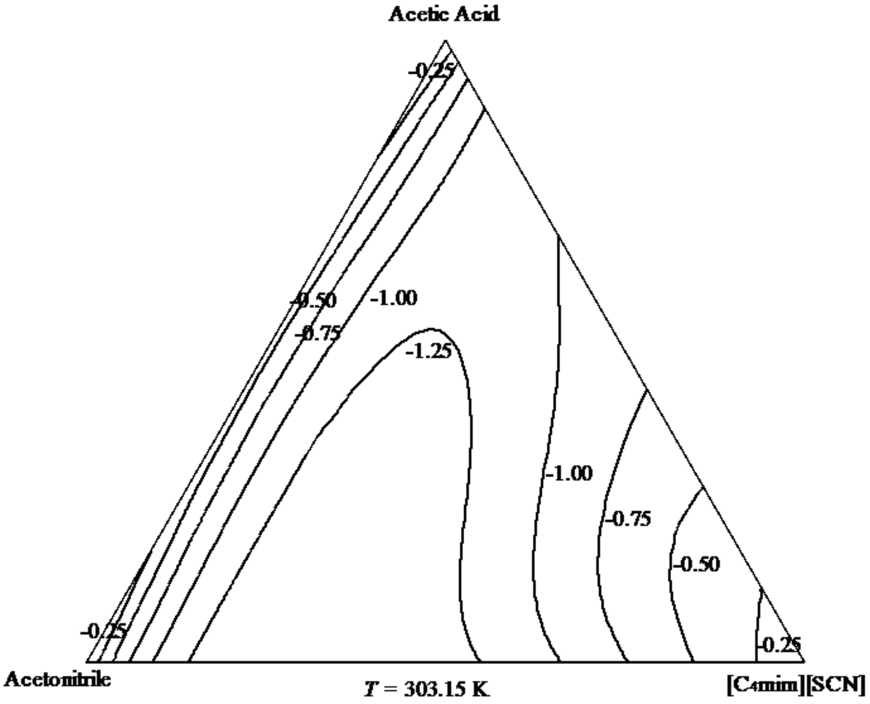
	308.15	-5.507	-3.190	-1.606	-3.041	-3.794	0.018
	313.15	-5.745	-3.348	-1.746	-3.239	-3.928	0.019
$\Delta\kappa_S$ /10^8×Pa^{-1}	293.15	-70.5	-48.4	-28.0	-43.2	-42.6	0.2
	298.15	-74.4	-51.3	-32.7	-46.5	-41.8	0.2
	303.15	-78.6	-54.8	-34.4	-49.7	-45.4	0.2
	308.15	-83.5	-58.2	-35.0	-53.1	-51.8	0.2
	313.15	-88.4	-62.1	-37.5	-56.6	-56.1	0.2
	{$[BMIM]^+[SCN]^-$ (x_1) + acetonitrile (x_2)}						
V_m^E /cm^3mol^{-1}	293.15	-5.076	-3.925	-4.545	-1.138	0.387	0.016
	298.15	-5.081	-4.295	-4.395	-1.353	0.226	0.016
	303.15	-5.294	-4.442	-4.550	-1.531	0.122	0.016
	308.15	-5.515	-4.600	-4.673	-1.709	-0.040	0.017
	313.15	-5.748	-4.760	-4.753	-1.904	-0.275	0.017
$\Delta\kappa_S$ /10^8×Pa^{-1}	293.15	-63.2	-50.1	-44.9	-13.8	11.0	0.1
	298.15	-67.0	-53.5	-46.6	-16.2	8.2	0.1
	303.15	-71.3	-56.5	-50.5	-18.9	8.3	0.1
	308.15	-75.7	-60.9	-52.5	-20.8	5.7	0.1
	313.15	-80.5	-64.6	-54.7	-22.9	2.8	0.1

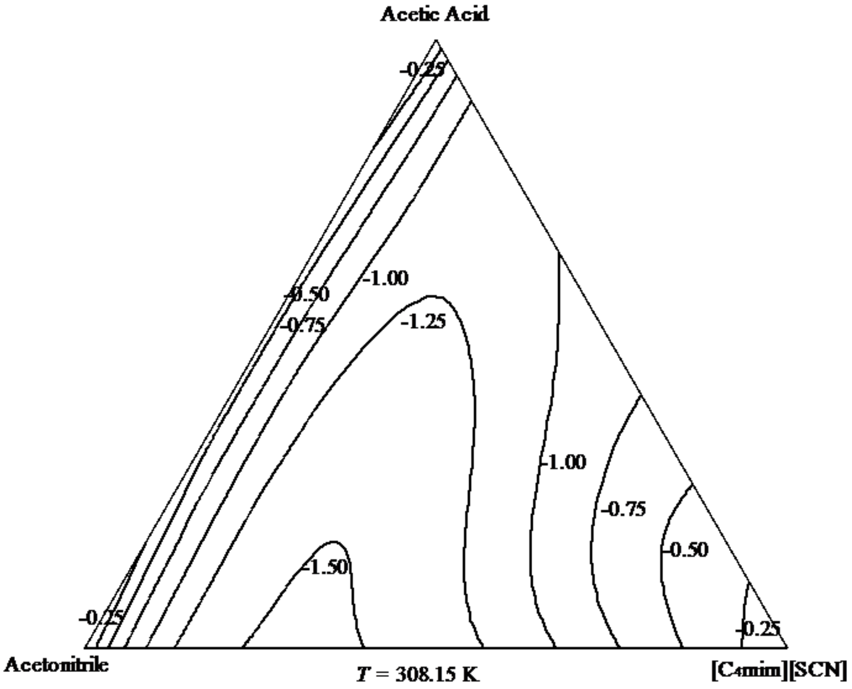
Standard uncertainties u are $u(T)$ = ±0.02 K, $u(p)$ = ±0.04 MPa and the combined expanded uncertainty Uc in mole fractions, density and sound velocity measurements were less than $U_c(x)$ = ± 0.0004, $U_c(\rho)$ = ± 9×10^{-4} $g\cdot cm^{-3}$ and $U_c(u)$ = ± 0.8 $m\cdot s^{-1}$, respectively (0.95 level of confidence).

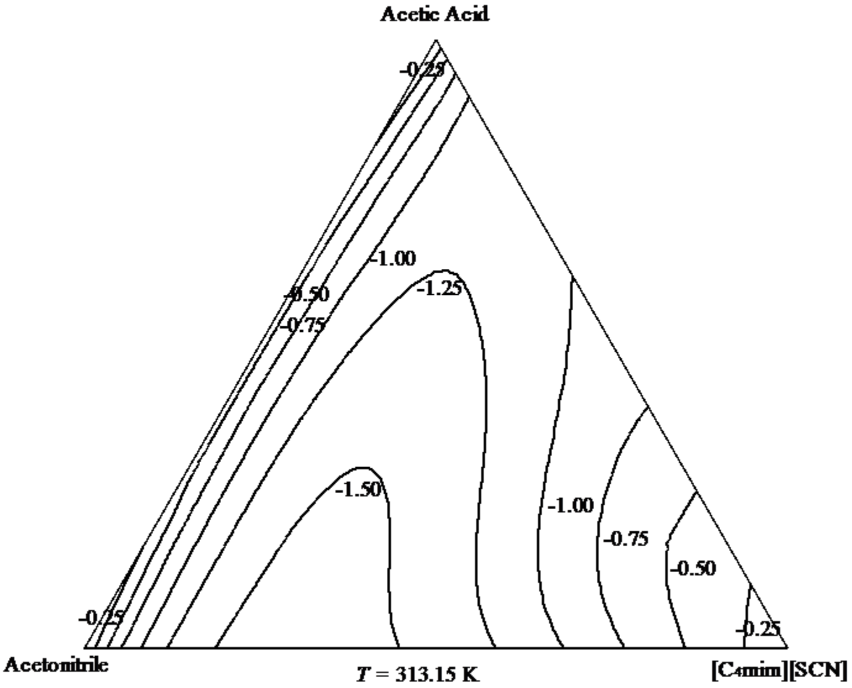
Figs. 5.2.2.21 and 22 shows the excess molar volume data for the ternary liquid mixtures of {[BMIM]$^+$[SCN]$^-$ + acetic acid + acetonitrile} and {[BMIM]$^+$[SCN]$^-$ + propionic acid + acetonitrile}.



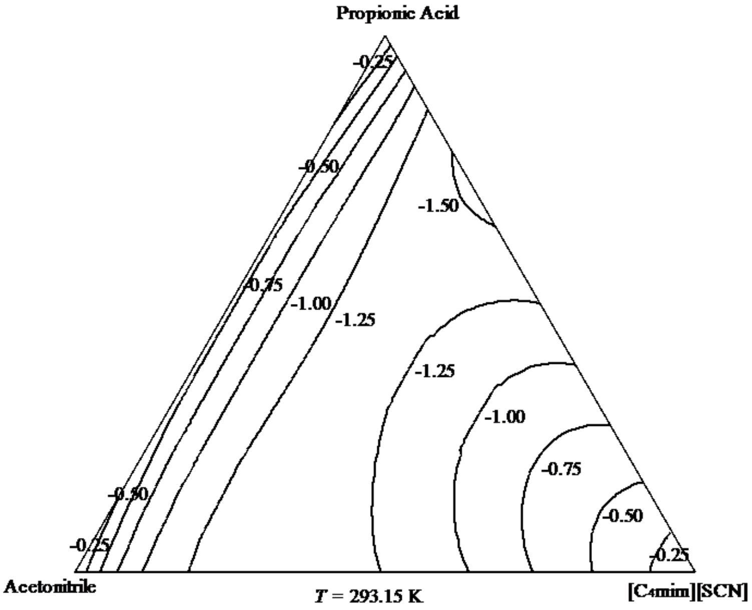


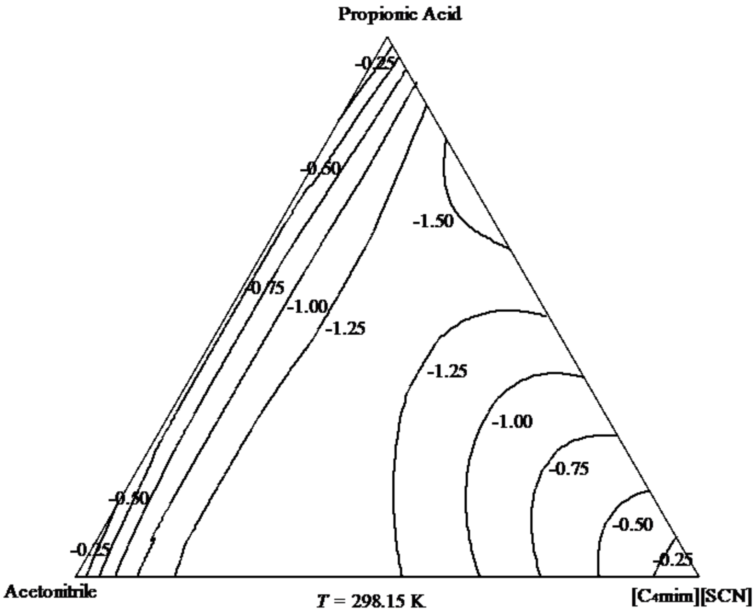

Acetic Acid
-0.25
-0.50
-0.75
-1.00
-1.25
-1.00
-0.75
-0.50
-0.25
-0.25
Acetonitrile
T = 303.15 K
[C4mim][SCN]

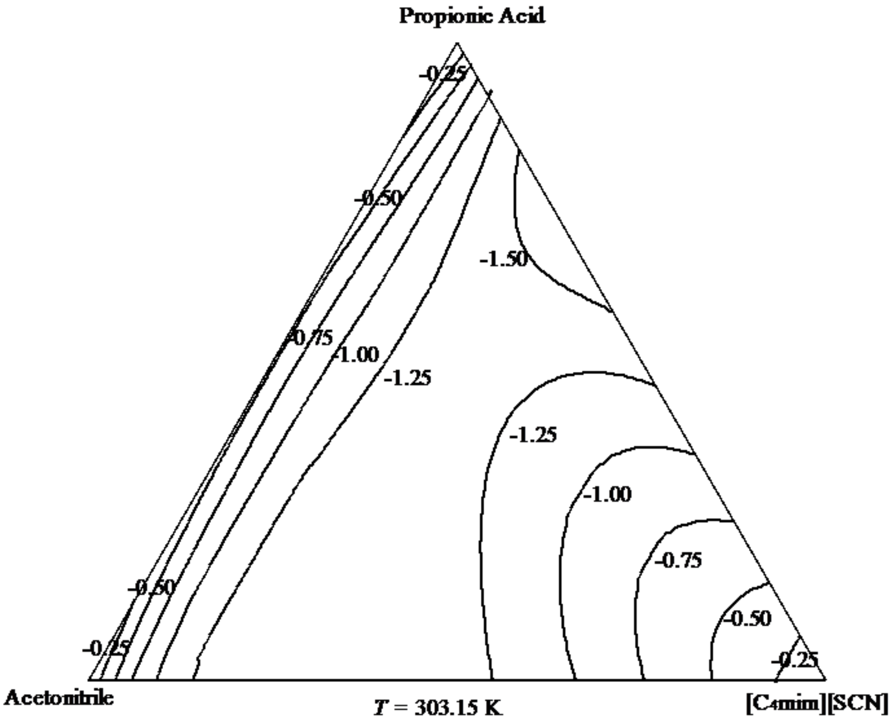

Acetic Acid
-0.25
-0.50
-0.75
-1.00
-1.25
-1.50
-1.00
-0.75
-0.50
-0.25
-0.25
Acetonitrile
T = 308.15 K
[C4mim][SCN]

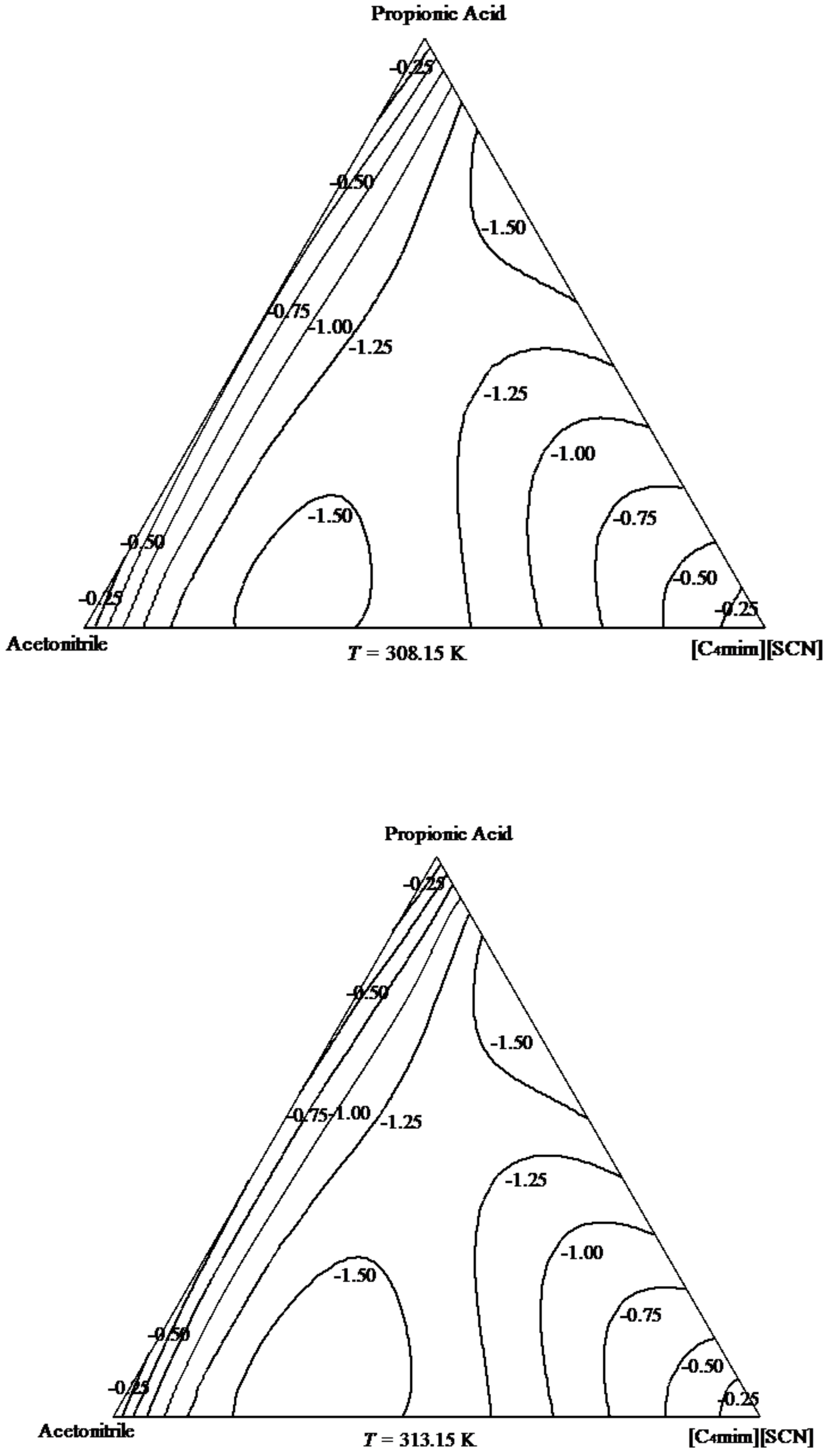


Figs. 5.2.2.21. Plots of excess volume (V_{123}^{E}) calculated by the Cibulka equation for ternary liquid mixtures of {$[BMIM]^{+}[SCN]^{-}$ + acetic acid + acetonitrile} at different temperatures.



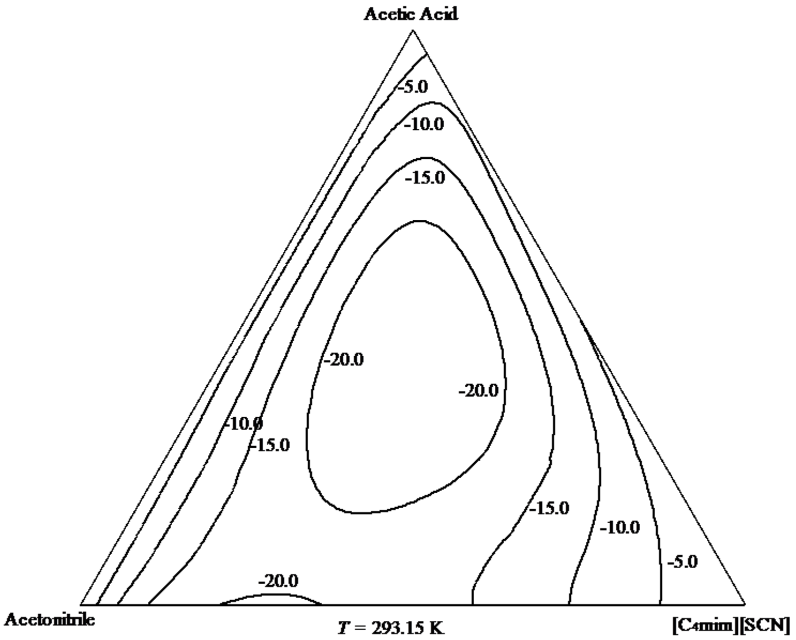

Propionic Acid
-0.25
-0.50
-0.75
-1.00
-1.25
-1.50
-1.25
-1.00
-0.75
-0.50
-0.25
-0.50
-0.25
Acetonitrile
T = 298.15 K
[C4mim][SCN]

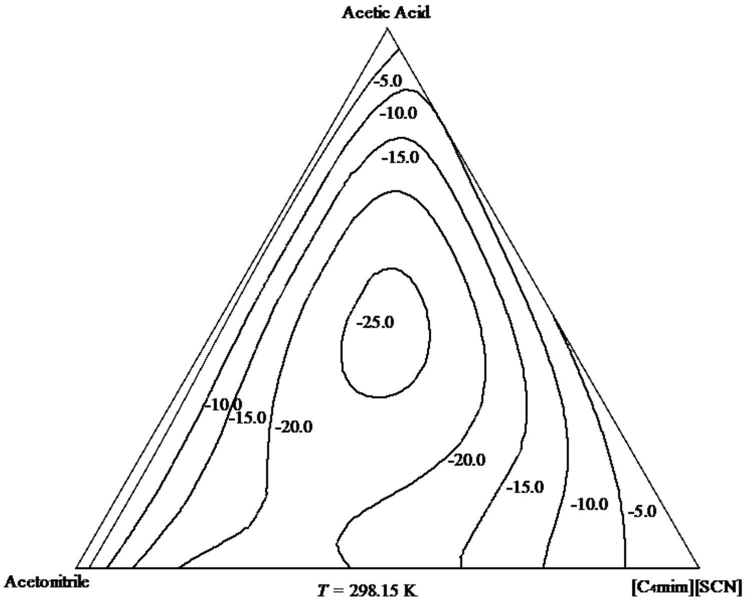

Propionic Acid
-0.25
-0.50
-0.75
-1.00
-1.25
-1.50
-1.25
-1.00
-0.75
-0.50
-0.25
-0.50
-0.25
Acetonitrile
T = 303.15 K
[C4mim][SCN]

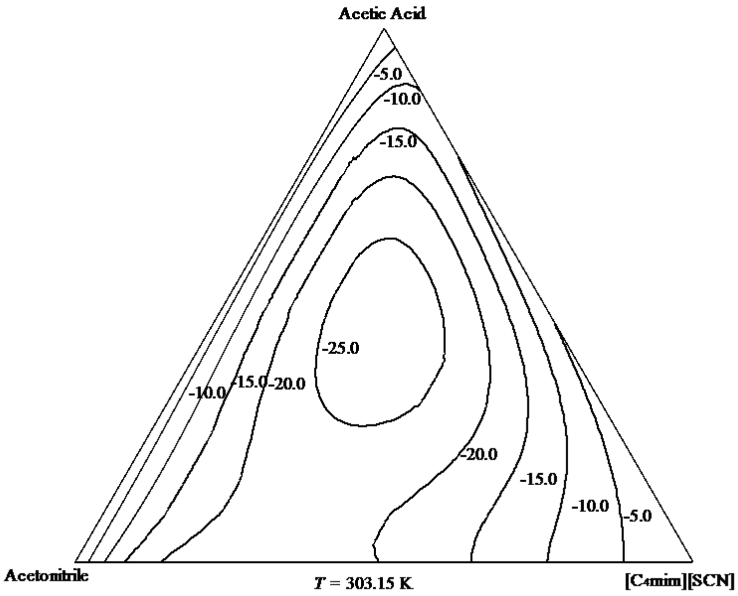


Figs. 5.2.2.22. Plots of excess volume (V_{123}^{E}) calculated by the Cibulka equation for ternary liquid mixtures of {$[BMIM]^{+}[SCN]^{-}$ + propionic acid + acetonitrile} at different temperatures.

The (V_{123}^{E}) data is negative over the entire composition range at all the temperatures for both systems. Acids (acetic acid or propionic acid) have stronger dipoles and thus can form stronger H-bonds with other substances capable of H-bonding interactions by DeRuiter (2005). Mixing of these acetic acid or propionic acid with [BMIM]$^+$[SCN]$^-$ + acetonitrile causes the breakage of hydrogen bonded complexes in pure acetic acid or propionic acid and acetonitrile molecules lose their dipolar association. Also, IL’s have the capability to interact with component molecules through ion–dipole, ion–pair and dipolar interactions in liquid mixtures Ali et al., Prasad et al. The more negative (V^E_{123}) values observed for propionic acid with [BMIM]$^+$[SCN]$^-$ + acetonitrile system compared acetic acid with [BMIM]$^+$[SCN]$^-$ + acetonitrile system due to the higher electron – donor capacity of propionic acid than acetic acid. The speed of sound is another essential property of pure liquids and their mixtures which results from the molecular interactions. The values deviation in isentropic compressibilities are plotted in Figs. 5.2.2.23 and 24, for the ternary mixtures {[BMIM]$^+$[SCN]$^-$ + acetic acid + acetonitrile} and {[BMIM]$^+$[SCN]$^-$ + propionic acid + acetonitrile} at 293.15 K, 298.15 K, 303.15 K, 308.15 K and 313.15 K.




Acetic Acid
-5.0
-10.0
-15.0
-25.0
-10.0
-15.0
-20.0
-20.0
-15.0
-10.0
-5.0
Acetonitrile
T = 298.15 K
[C4mim][SCN]


Acetic Acid
-5.0
-10.0
-15.0
-25.0
-10.0
-15.0
-20.0
-20.0
-15.0
-10.0
-5.0
Acetonitrile
T = 303.15 K
[C4mim][SCN]

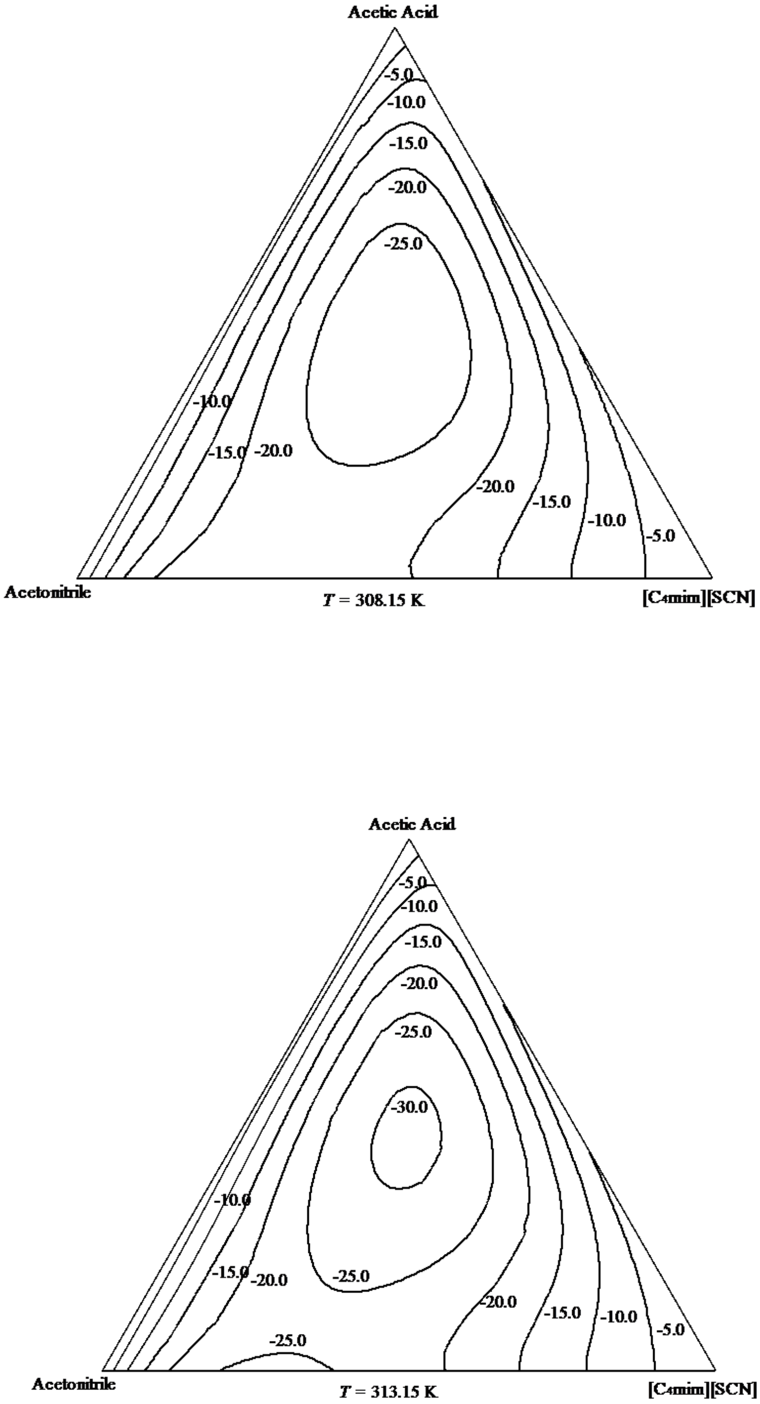
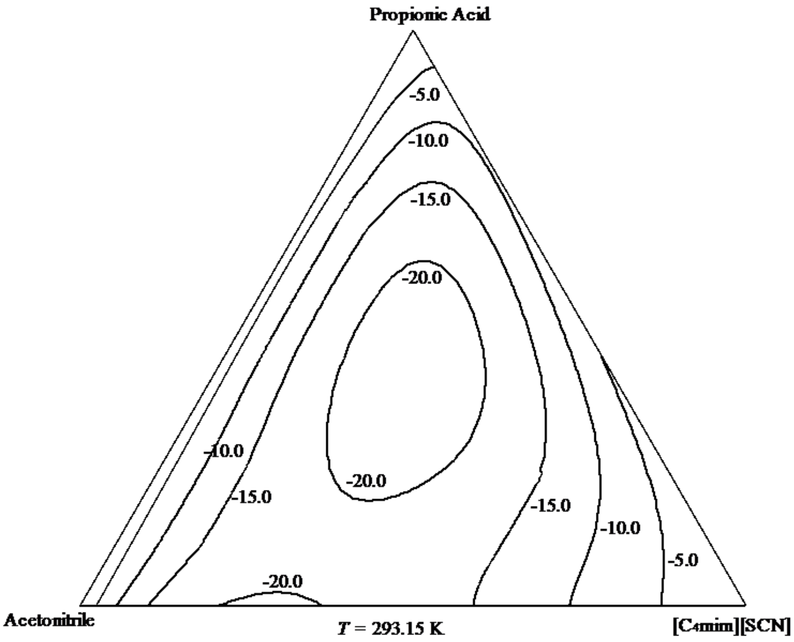
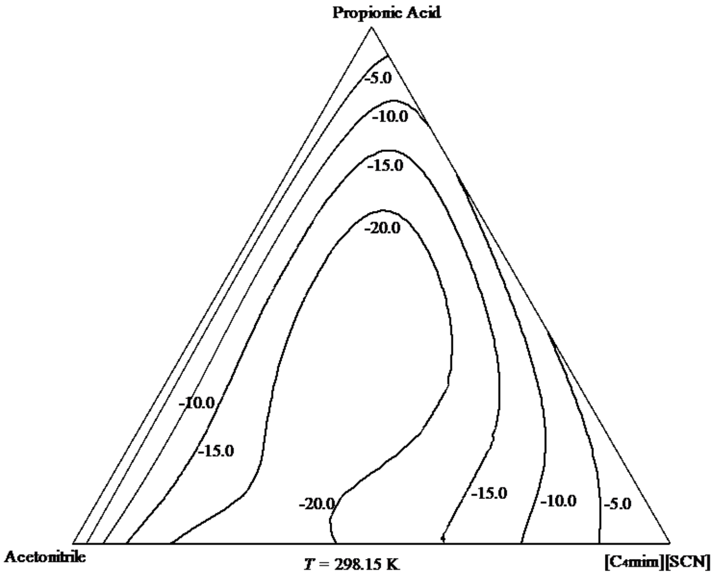
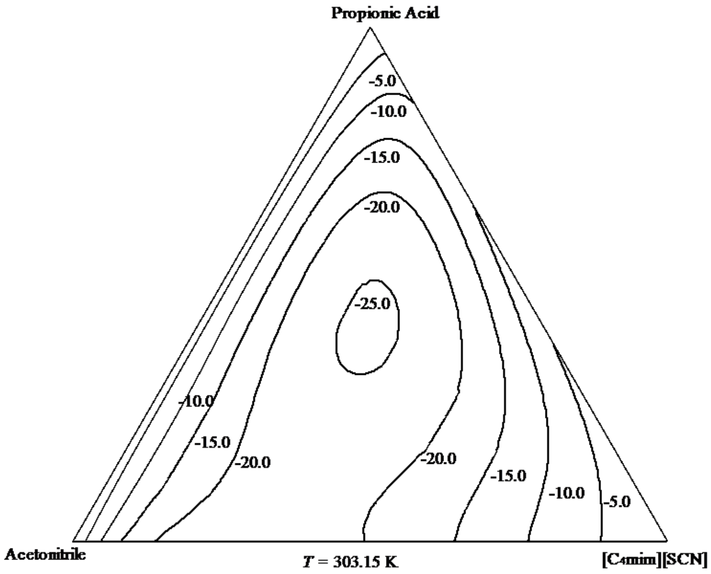
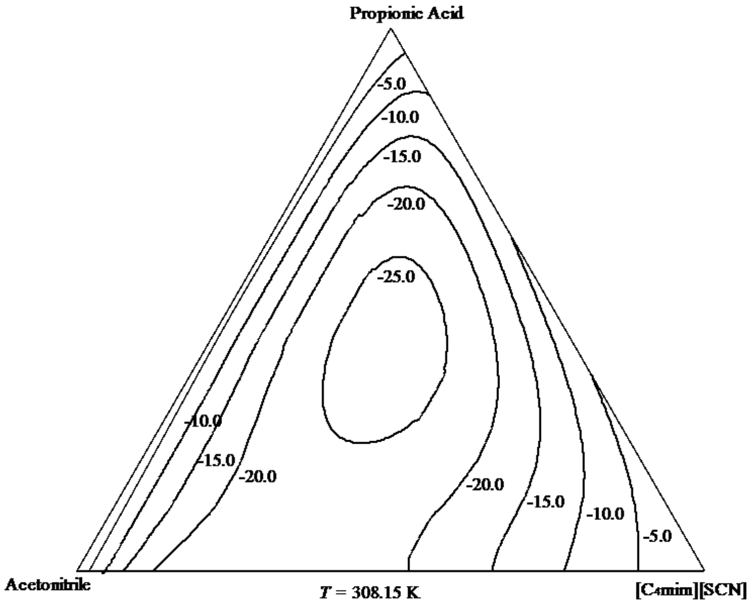


Fig. 5.2.2.23 Plots of deviations in isentropic compressibility (Δk_{s123}) obtained from the Cibulka equation for ternary liquid mixtures {$[BMIM]^{+}[SCN]^{-}$ + acetic acid + acetonitrile} at different temperatures.


Propionic Acid
-5.0
-10.0
-15.0
-20.0
-10.0
-15.0
-20.0
-15.0
-10.0
-5.0
-20.0
Acetonitrile
T = 293.15 K
[C4mim][SCN]


Propionic Acid
-5.0
-10.0
-15.0
-20.0
-10.0
-15.0
-20.0
-15.0
-10.0
-5.0
Acetonitrile
T = 298.15 K
[C4mim][SCN]


Propionic Acid
-5.0
-10.0
-15.0
-20.0
-25.0
-10.0
-15.0
-20.0
-20.0
-15.0
-10.0
-5.0
Acetonitrile
T = 303.15 K
[C4mim][SCN]


Propionic Acid
-5.0
-10.0
-15.0
-20.0
-25.0
-10.0
-15.0
-20.0
-20.0
-15.0
-10.0
-5.0
Acetonitrile
T = 308.15 K
[C4mim][SCN]

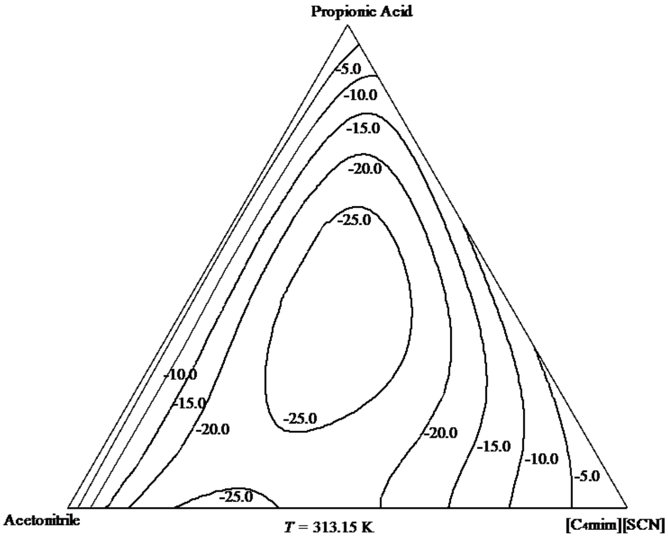


Fig. 5.2.2.24 Plots of deviations in isentropic compressibility (Δk_{s123}) obtained from the Cibulka equation for ternary liquid mixtures {$[BMIM]^+[SCN]^-$ + propionic acid + acetonitrile} at different temperatures.

As seen from results reported in Table 5.2.2.13, the $V_{\mathrm{m}}^{\mathrm{E}}$ values for $[BMIM]^+[SCN]^-$ with acetic or propionic acid are negative throughout the whole range of composition at all investigated temperatures for both systems. The negative deviation in isentropic compressibility suggest the existence of charge – transfer complexes and decreasing the free – space between component molecules in ternary liquid mixtures. Furthermore, the $\Delta\kappa_{\mathrm{S}}$ values for {$[BMIM]^+[SCN]^-$ (1) + propionic acid (2) + acetonitrile (3)} > {$[BMIM]^+[SCN]^-$ (1) + acetic acid (2) + acetonitrile (3)} indicating that there is a decrease deviation in isentropic compressibilities from the ideal mixture in order of propionic acid > acetic acid due to the addition of an alkyl group. Furthermore, the (V_{123}^{E}) and (Δk_{s123}) values are decrease with increasing the temperature. The higher temperatures can be attributed to increased thermal motion of molecules may allow a more effective occupation of interstitials Lehmann et al. The values of the Cibulka coefficients (b_n) fitted to experimental excess molar volumes and deviation in isentropic compressibility of the {[BMIM][SCN] (x_1) or + acetic or propionic acid (x_2) + acetonitrile (x_3)} systems at temperature range from (293.15 to 313.15) K and at $p = 1 \times 10^5$ Pa together with the corresponding standard deviations of the fit (σ) are given in Table 5.2.1.15.

Table 5.2.1.15. The values of the Cibulka coefficients (b_n) fitted to experimental excess volumes of the {[BMIM][SCN] (x_1) or + acetic or propionic acid (x_2) + acetonitrile (x_3)} systems at temperature range from (293.15 to 313.15) K and at $p = 1 \times 10^5$ Pa together with the corresponding standard deviations of the fit (σ).

T/K	b_0	b_1	b_2	σ
{[BMIM][SCN] (x_1) + acetic acid (x_2) + acetonitrile (x_3)}				
V^E_{123}/cm^3 mol^{-1}				
293.15	−11.028	22.266	-2.758	0.05
298.15	−14.486	31.050	-0.420	0.06
303.15	−15.383	32.688	-0.336	0.06
308.15	−17.937	36.248	3.503	0.10
313.15	−17.339	36.389	-0.107	0.06
{[BMIM][SCN] (x_1) + propionic acid (x_2) + acetonitrile (x_3)}				
293.15	−18.374	27.651	10.626	0.10
298.15	−15.360	35.287	16.179	0.16
303.15	−16.770	37.339	18.992	0.17
308.15	−19.253	40.236	26.189	0.19
313.15	−20.879	42.678	29.835	0.20
{[BMIM][SCN] (x_1) + acetic acid (x_2) + acetonitrile (x_3)}				
(Δk_{s123}) (10^8 Pa)$^{-1}$				
293.15	15.8	-153.1	-924.8	3.3
298.15	5.2	-137.8	-961.3	3.4
303.15	−0.1	-143.3	-1005.1	3.6
308.15	−9.0	-135.6	-1048.6	3.7
313.15	−24.5	-123.1	-1082.3	3.8
{[BMIM][SCN] (x_1) + propionic acid (x_2) + acetonitrile (x_3)}				
293.15	−6.5	-138.1	-698.8	3.1
298.15	−7.2	-143.5	-741.1	3.2
303.15	−16.8	-137.1	-768.0	3.4
308.15	−21.1	-139.5	−807.4	3.6
313.15	−27.6	-139.2	−849.6	3.8

5.3 Group 7: Application of 1-butyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide ionic liquid for the different types of separations problem: activity coefficients at infinite dilution measurements using gas-liquid chromatography technique

The present work focussed on application of the environmental friendly1–butyl–3–methylimidazolium bis(trifluoromethylsulfonyl) imide ($[BMIM]^+[Tf_2N]^-$) ionic liquid for the separations of (alkane/aromatic), (alkane/alk-1-ene), (cycloalkane/aromatic) and (water/alkan-1-ol) using gas-liquid chromatography (GLC) technique. In this reason the activity coefficients at infinite dilution, γ_{13}^{∞}, for 31 organic solutes (alkanes, cycloalkanes, alkenes, alkynes, aromatics, alkanol and ketones) and water in ionic liquid were measured at temperatures of (323.15, 333.15, 343.15, 353.15 and 363.15) K. Stationary phase loadings of (42.83 and 68.66) % by mass were used to ensure repeatability of measurements. Density and viscosity values were measured to confirm the purity of ionic liquid. Partial molar excess enthalpies at infinite dilution, $\Delta H_1^{E,\infty}$, were also determined. The selectivities, S_{ij}^{∞}, and capacities, k_j^{∞}, were determined for the above separations. The separating ability of the investigated ionic liquid was compared with previously investigated ionic liquids and industrial solvents such as sulfolane, *n*-methyl-2-pyrrolidine (NMP) and *n*-formylmorpholine (NFM).

The results of γ_{13}^{∞} for 31 solutes in the $[BMIM]^+[Tf_2N]^-$ ionic liquid are reported in Table 5.3.15, with uncertainty.

The natural logarithm of the γ_{13}^{∞} values as a function of the inverse absolute temperature for all solutes in $[BMIM]^+[Tf_2N]^-$ are shown in Figs. 5.3.25-32.

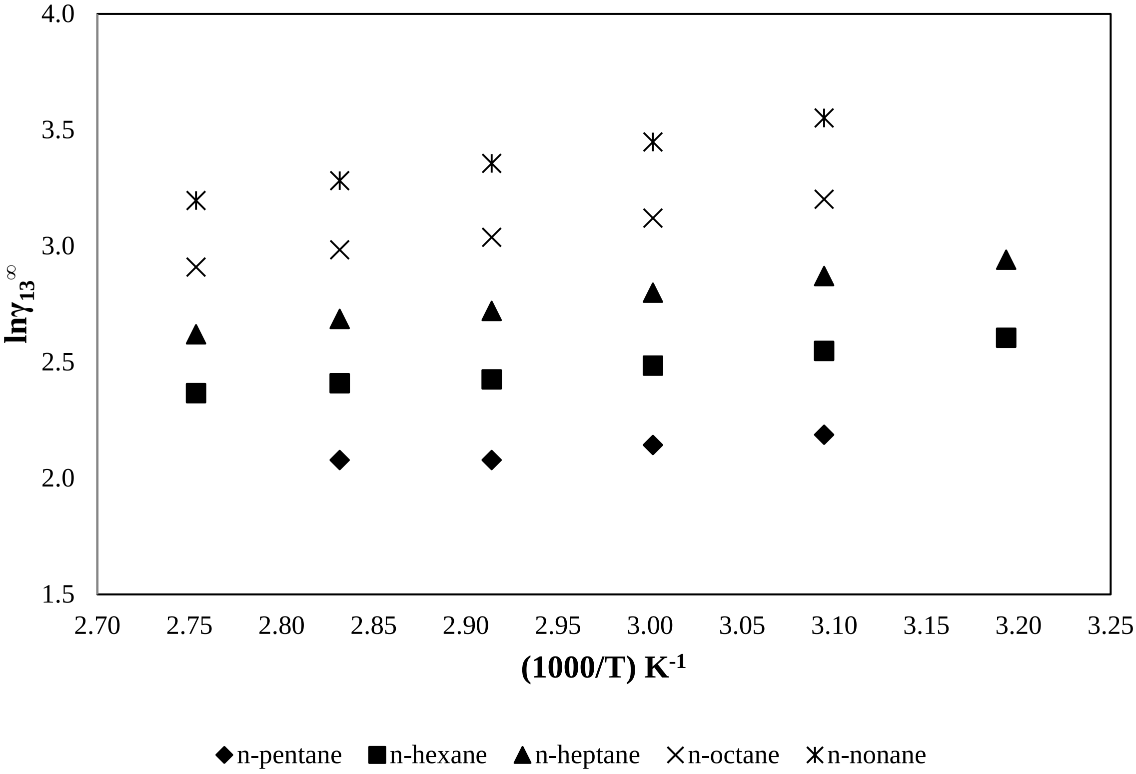


Fig. 5.3.25. Plot of $\ln\gamma_i^{\infty}$ for $[BMIM]^+[Tf_2N]^-$ versus 1000/*T* for various alkanes.

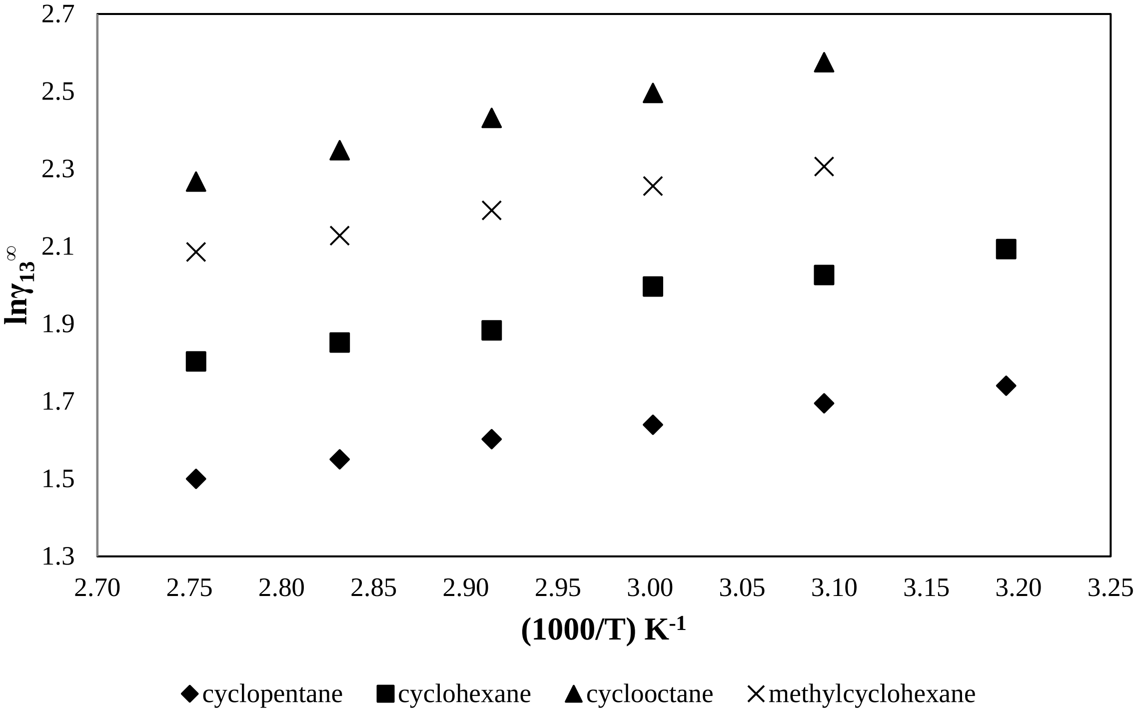


Fig. 5.3.26. Plot of $\ln\gamma_i^{\infty}$ for $[BMIM]^+[Tf_2N]^-$ versus 1000/*T* for various cycloalkanes.

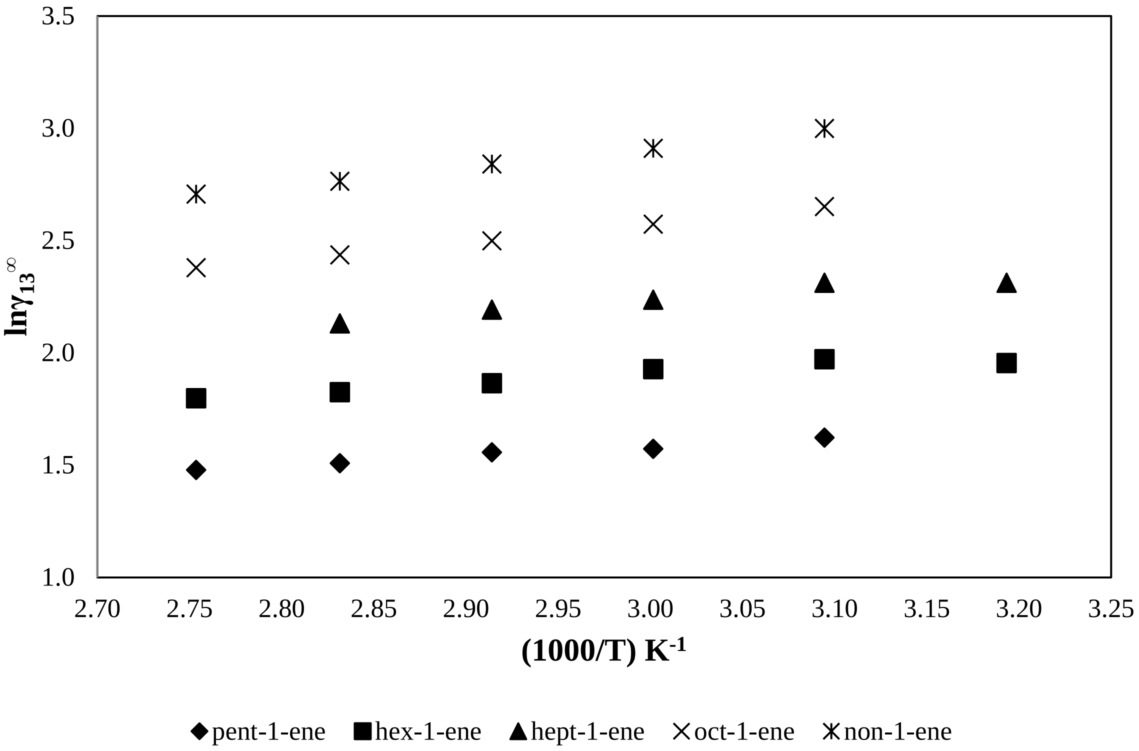


Fig. 5.3.27. Plot of lnγ_i^{∞} for $[BMIM]^+[Tf_2N]^-$ versus 1000/*T* for various alkenes.

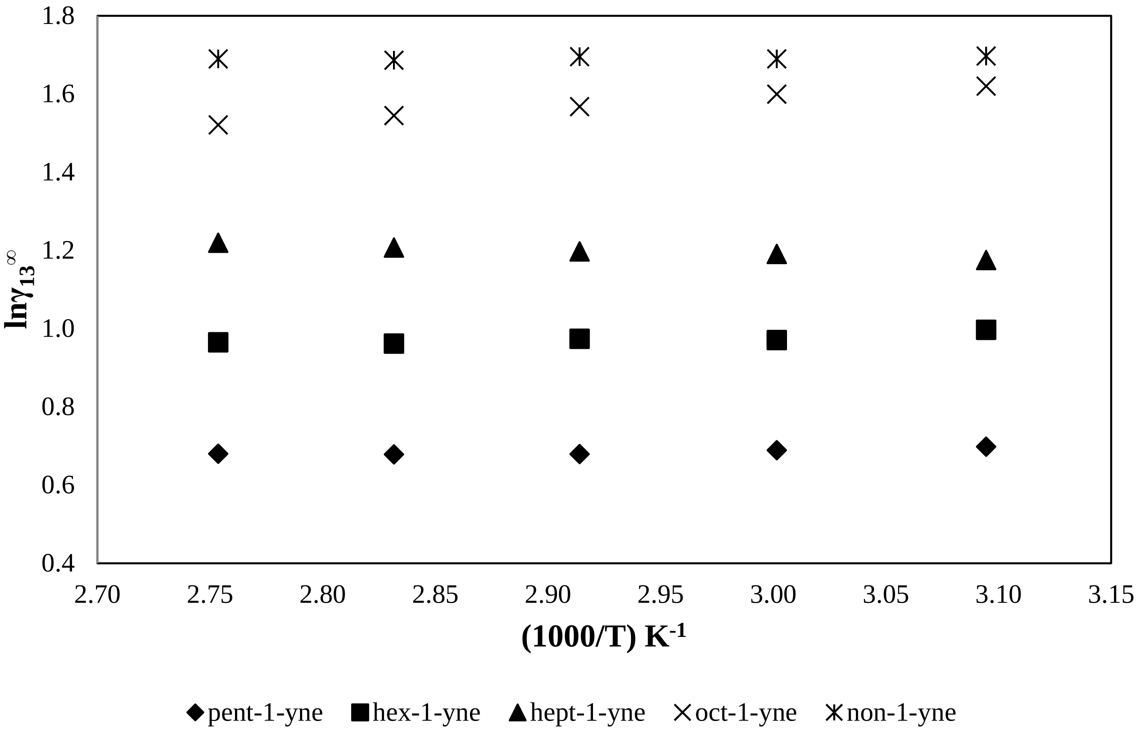


Fig. 5.3.28. Plot of lnγ_i^{∞} for $[BMIM]^+[Tf_2N]^-$ versus 1000/*T* for various alkynes.

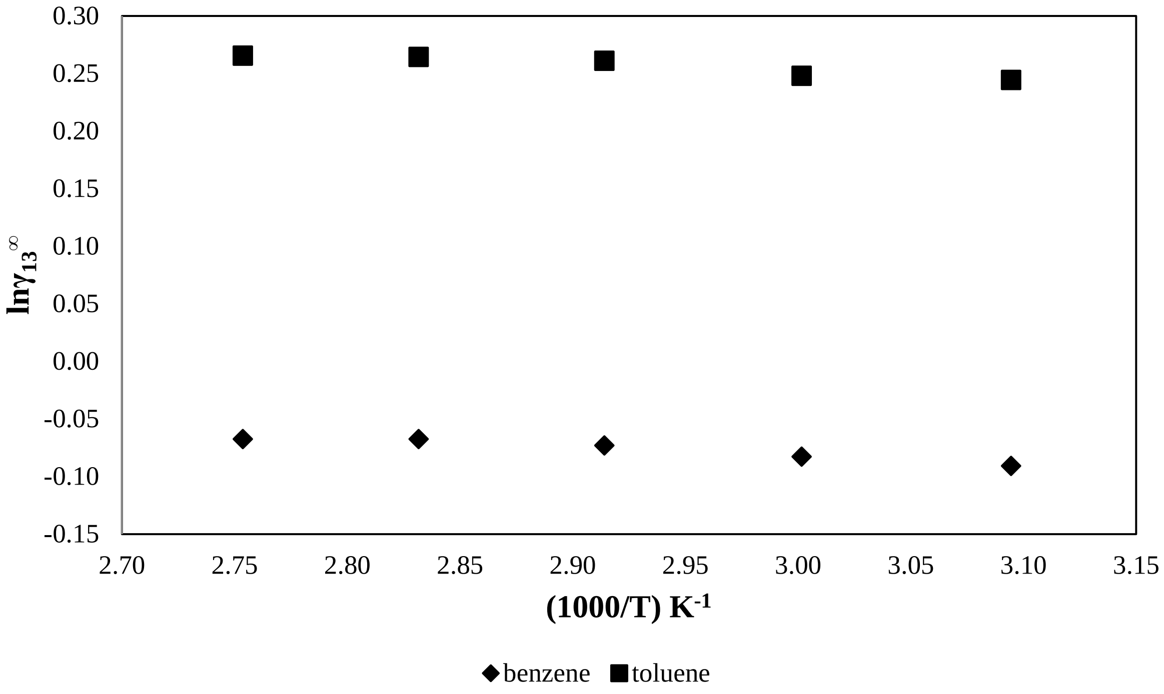


Fig. 5.3.29. Plot of $\ln\gamma_i^\infty$ for $[BMIM]^+[Tf_2N]^-$ versus 1000/*T* for various aromatics.

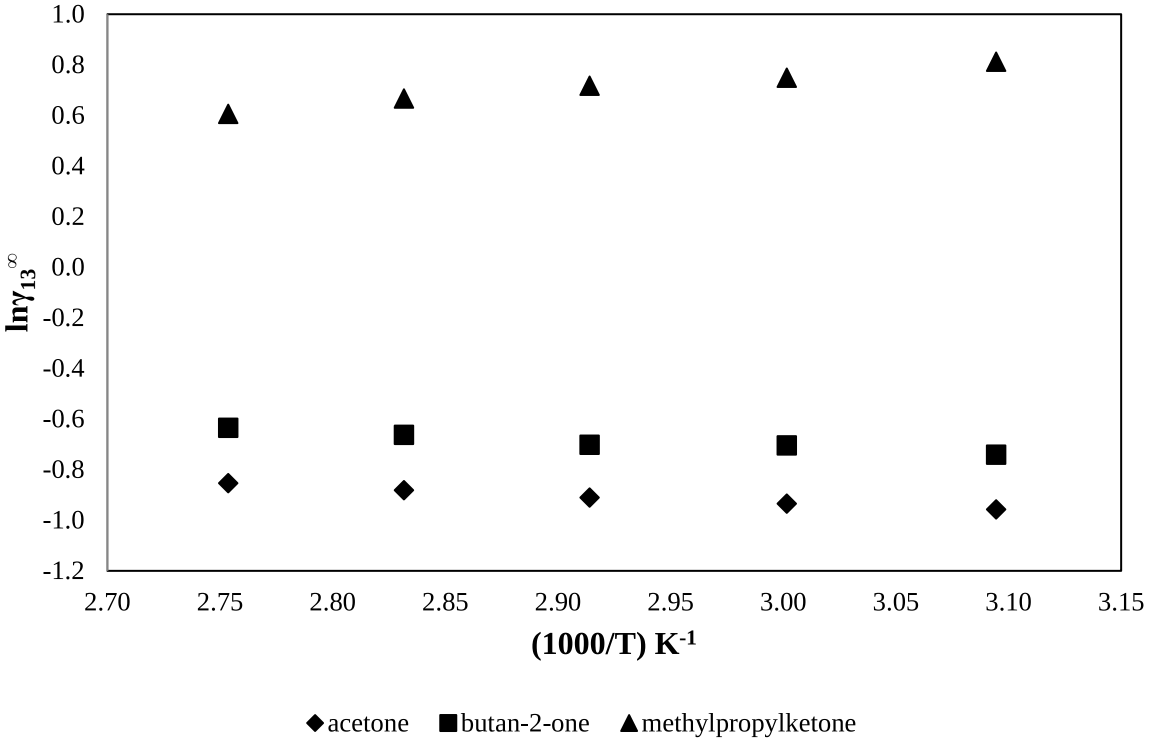


Fig. 5.3.30. Plot of $\ln\gamma_i^\infty$ for $[BMIM]^+[Tf_2N]^-$ versus 1000/*T* for various ketones.

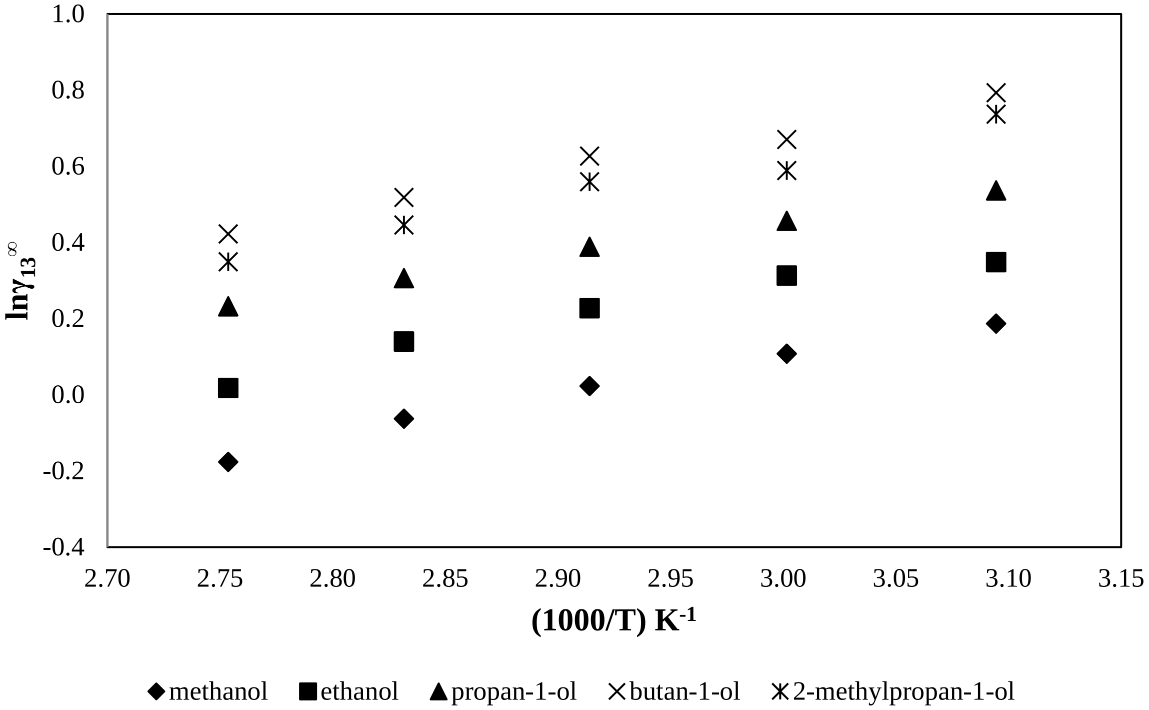


Fig. 5.3.31. Plot of $\ln\gamma_i^{\infty}$ for $[BMIM]^+[Tf_2N]^-$ versus 1000/*T* for various alkanol.

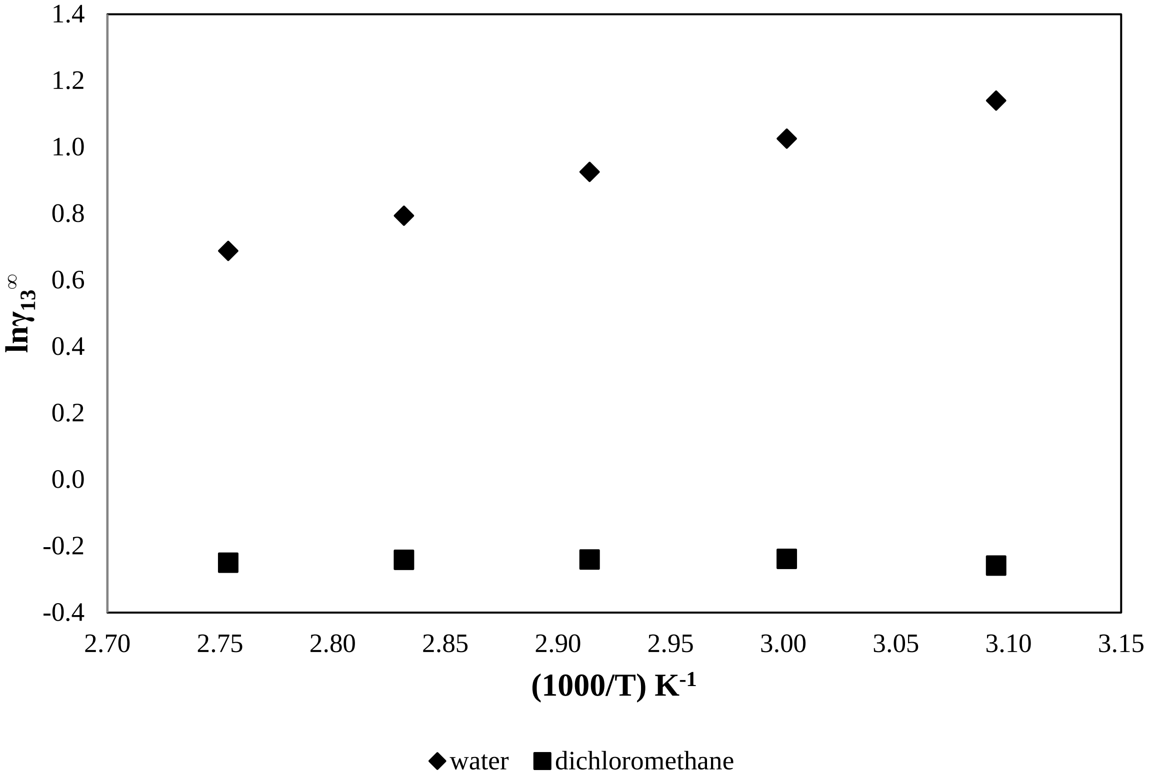


Fig. 5.3.32. Plot of $\ln\gamma_i^{\infty}$ for $[BMIM]^+[Tf_2N]^-$ versus 1000/*T* for water and dichloromethane.

The values of γ_{13}^{∞} increases by class of solute in the order: ketones < dichloromethane < aromatics < alkanols < alkynes < alkenes < cycloalkanes < alkanes. The lower value of γ_{13}^{∞} at all temperatures for water, followed by alkenes which indicate the strong IL-solute interactions due to the hydrogen bonding. The aromatics (benzene and toluene) have delocalised π-electrons which can increase the solute-solvent interactions profoundly with ILs despite this compound's electro-neutrality. Alkanes, cycloalkanes, alkenes and alkynes have higher γ_{13}^{∞} values as compared to other solutes due to the weaker solute-solvent interactions. From the above sequence it can been seen that more aliphatic compound, have higher γ_{13}^{∞} values. Cycloalkanes values of γ_{13}^{∞} have lower than the linear alkanes and indicates that strong interactions exists between the cyclic structure and the imidazolium ring. Alkenes have lower γ_{13}^{∞} values than alkanes with the same carbon number indicate the interactions of the double bond in alkenes with the IL. The alkynes have lower γ_{13}^{∞} values than the corresponding alkanes, alkenes and cycloalkanes with the same carbon number suggesting the stronger attractive interactions which are caused by the hydrogen atoms and π electrons of the triple bond in alkynes.

The values of $\frac{\Delta H_i^{E,\infty}}{R}$ were calculated from the γ_{13}^{∞} and its temperature dependence from the Gibbs–Helmholtz equation and are given in Table 5.3.15. The activity coefficients of alkanes, cycloalkanes, alkenes, alkynes, alkanol and water were displayed a positive relationship with the inverse of temperature except hept-1-yne. The positive values for the excess enthalpy at infinite dilution indicated that increase in solubility in IL of the respective solutes as the temperature was raised. There does exist, for rest solutes, negative gradients and hence negative excess enthalpies at infinite dilution with a decrease in solubility in the IL as the temperature was raised. The relation of the number of carbon atoms on an alkyl chain (or ring) for the solutes (alkanes, alkenes, alkynes, aromatics, cyclic hydrocarbons and alkanols) follow linear trends with the logarithm of the activity coefficient at (323.15 and 363.15) K (see Figs. 5.3.33 and 34). Figs. 5.3.33 and 34 displayed positive relationships which exist for all the aforementioned groups at all temperatures.

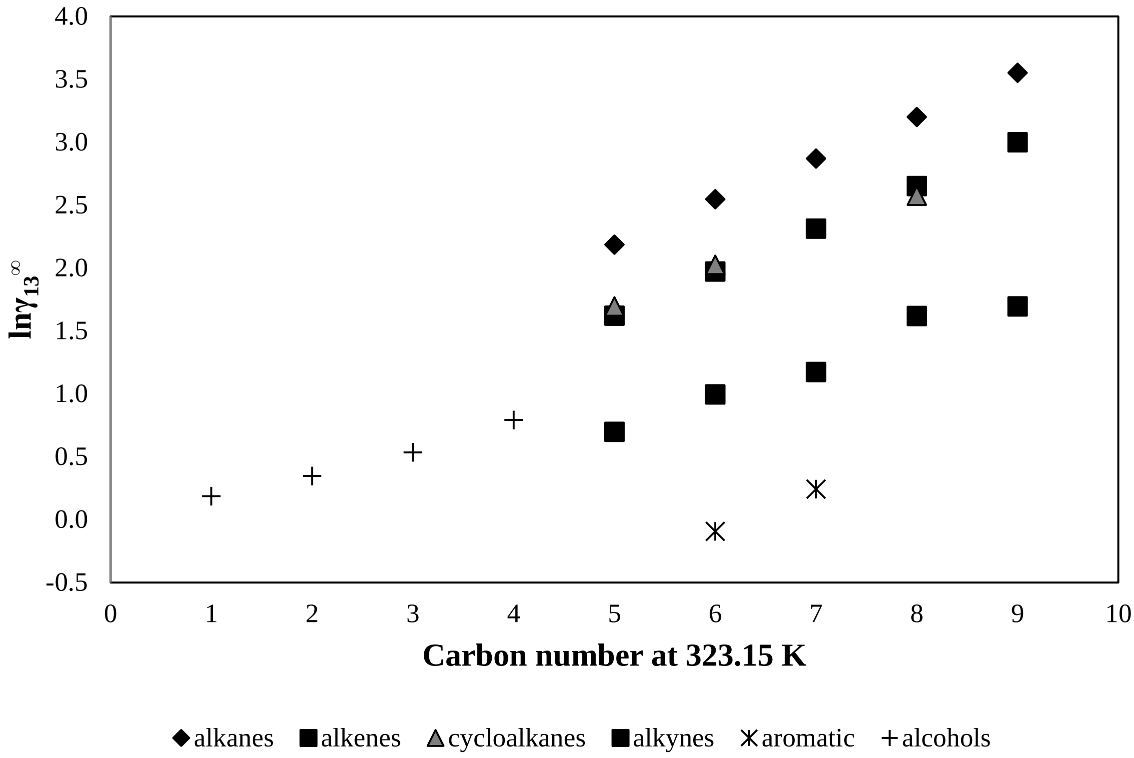


Fig. 5.3.33. Plot of lnγ_i^∞ as a function of the number of carbon atoms in an alkyl-chain, for different classes of solutes in $[BMIM]^+[Tf_2N]^-$ at 323.15 K.

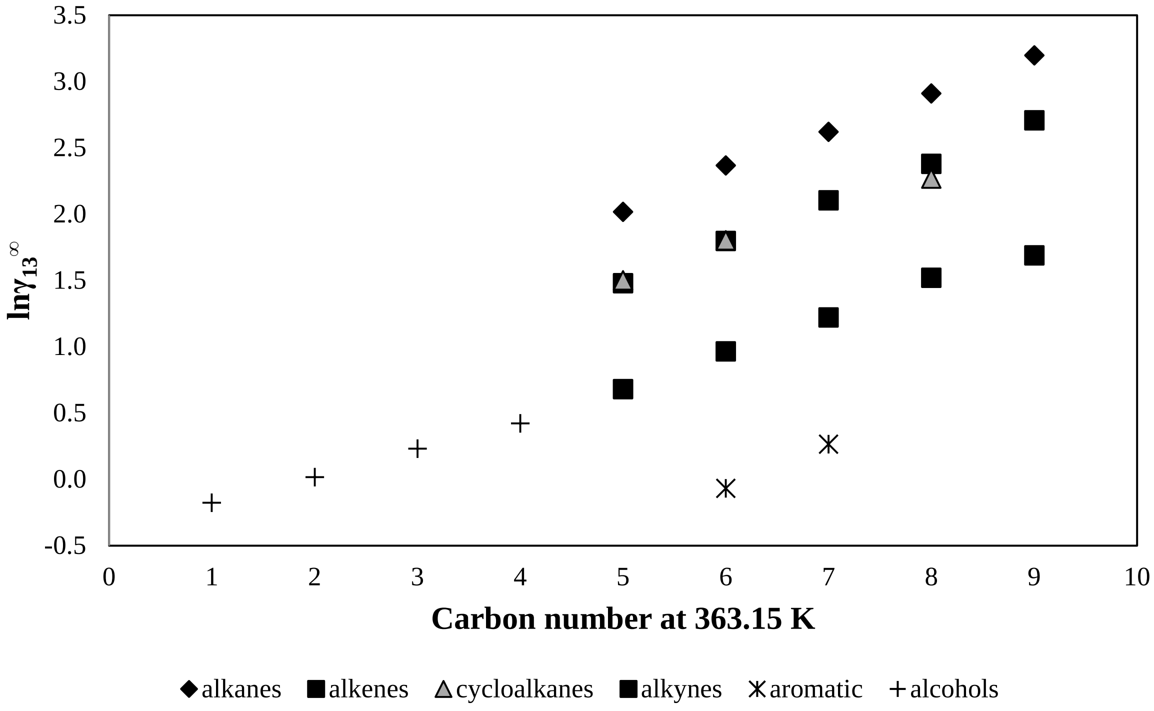


Fig. 5.3.34. Plot of lnγ_i^∞ as a function of the number of carbon atoms in an alkyl-chain, for different classes of solutes in $[BMIM]^+[Tf_2N]^-$ at 363.15 K.

The selectivities and capacities for the different separation such as *n*-hexane/benzene, *n*-cyclohexane/benzene, *n*-hexane/hex-1-ene and water/butan-1-ol separations at 313.15 K are given in Table 5.3.16**.**

Table 5.3.16 Selectivities and capacities of various ionic liquids and conventional solvents for different separation problems at 313.15 K.

Solvent	**Selectivity at infinite dilution (S_{ij}^{∞})**				**Limiting capacity (k_j^{∞})**		
	n-hexane/benzene	cyclohexane/benzene	n-hexane/hex-1-ene	water/butan-1-ol	benzene	hex-1-ene	butan-1-ol
$[BMIM]^+[Tf_2N]^-$	15.20	9.25	1.79	1.47	1.11	0.13	0.42
$[BMIM]^+[SbF_6]^-$ [Tumba 2010]	22.25	12.52	2.08	-	0.79	0.07	-
$[BMIM]^+[MDEGSO_4]^-$ [Letcher et. al. 2001]	32.85	14.00		-	0.50	-	-
$[BMIM]^+[SCN]^-$ [Domanska et. al. 2009]	82.45	23.24	3.39	-	0.46	0.02	-
$[BMIM]^+[OS]^-$ [Letcher et. al. 2001]	-	-	1.40	-	-	0.18	-
NFM [Williams-Wynn et. al. 2013]	14.75	8.28	1.79	-	0.51	0.06	-
NMP[Krummen et. al. 2000]	11.24	7.05	1.89	-	0.95	0.16	-
Sulfolane [Mollmann et al. 1997]	23.62	12.74	-	0.59	0.55	-	0.21

$\beta_{ij}^{\infty} = \frac{\gamma_{is}^{\infty}}{\gamma_{js}^{\infty}}$, $k_j^{\infty} = \frac{1}{\gamma_{js}^{\infty}}$; *i=interpolated; ex=extrapolated*

These selectivities and capacities values were compared with other ILs by Tumba (2010), Letcher *et al.* (2001), Domanska and Laskowska. (2009), containing the 1-bthyl-3-methylimidazolium $[BMIM]^+$ cation to describe the influence of the anion on these separations and also compared solvating ability of IL with the industrial solvents by Williams-Wynn *et al.* (2013), Krummen *et al.* (2002), Mollmann and Gmehling (1997), such as sulfolane, NMP and NFM. The selectivities values were 15.20, 9.25, 1.79, and 1.47 for the *n*-hexane/benzene, cyclohexane/benzene, n-hexane/hex-1-ene and water/butan-1-ol, respectively and are significantly less than the previously investigated ILs but higher than that for industrial solvents. The capacities for the same separations are however higher than the other solvents except NMP and $[BMIM]^+[OS]^-$. The trends observed here indicated that the $[Tf_2N]^-$ anion inhibits the separating efficiency of the imidazolium based IL with $[BMIM]^+$ except $[OS]^-$ anion for the separation of n-hexane/hex-1-ene, and thus the investigated IL would be used for industrial separations for the selected processes.

CHAPTER 6

CONCLUSIONS

In this chapter, the conclusion was made based on the investigation and is discussed.

The ternary excess molar volume (V_{123}^{E}), isentropic compressibility (k_S) and deviation in isentropic compressibility (Δk_{s123}) were determined for four ternary liquid mixtures of {$[EMIM]^+[EtSO_4]^-$ or $[BMIM]^+[SCN]^-$ + acetic or propionic acid + acetonitrile} at different temperatures (293.15, 298.15, 303.15, 308.15 and 313.15) K and at a pressure of 0.1 MPa. The calculated data were correlated by using the Cibulka equation. The results were discussed in terms of intermolecular interactions. The ternary excess/deviation properties values are negative for all compositions of IL. The smaller organic acid and acetonitrile molecules are probably incorporated into the vast IL matrix (a packing effect) which is further enhanced by intermolecular hydrogen bonding between the organic acid and acetonitrile molecules and ion–dipole interaction between the IL ions, organic acid, and acetonitrile molecules. The Cibulka equation was used to correlate the ternary data and indicated that the ternary contribution (three-body effect) is dominant.

Furthermore, the density and speed of sound were also measured for eight corresponding binary systems at same experimental condition. The binary excess molar volume, isentropic compressibility and deviation in isentropic compressibility were also calculated for measured system and fitted to the Redlich–Kister equation. Negative deviations were observed for both excess molar volume and deviation in isentropic compressibility for all investigated binary systems at all temperatures indicates that strong interaction between the studied binary mixtures molecules. The density, speed of sound, excess molar volume and deviation in isentropic compressibility show a detrimental effect while isentropic compressibility shows incremental effect with temperature.

In addition, the activity coefficients at infinite dilution, γ_{13}^{∞}, for 31 organic solutes (alkanes, cycloalkanes, alkenes, alkynes, aromatics, alkanol and ketones) and water in $[BMIM]^+[Tf_2N]^-$ were measured at temperatures of (323.15 to 363.15) K. The selectivities, S_{ij}^{∞}, and capacities, k_j^{∞}, were determined for the above separations. The separating ability of the investigated ionic liquid was compared with previously investigated ionic liquids and industrial solvents such as sulfolane, *n*-methyl-2-pyrrolidine (NMP) and *n*-formylmorpholine (NFM) and found that in general, the $[BMIM]^+[Tf_2N]^-$ had outperformed the conventional solvents such as sulfolane, NMP and NFM in terms of selectivity, while the $[BMIM][Tf_2N]$ had in general, performed better overall when the performance index was used for comparison. These results are useful to describe the intermolecular interactions; developing structure–property correlation and molecular modeling that exist between mixtures. These results provide better molecular interactions for the mixing of the solvents and better analysis of the solvation process.

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