EXCESS MOLAR VOLUMES, PARTIAL MOLAR VOLUMES AND ISENTROPIC COMPRESSIBILITIES OF BINARY SYSTEMS (IONIC LIQUID + ALKANOL).

by

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PREFACE

The work described herein was performed under the supervision of Professor N. Deenadayalu at Durban University of Technology, Durban, South Africa. The work is original unless stated in the text and has not been previously submitted for any other degree at any other university.

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Signed:
Prof. N. Deenadayalu (Supervisor) Date:

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ABSTRACT

The thermodynamic properties of binary liquid mixtures involving ionic liquids (ILs) with alcohols were determined. ILs are an important class of solvents since they are being investigated as environmentally benign solvents, because of their negligible vapour pressure, and as potential replacement solvents for volatile organic compounds (VOCs) currently used in industries. Alcohols were chosen for this study because they have hydrogen bonding and their interaction with ILs will help in understanding the intermolecular interactions. Also, their thermodynamic properties are used for the development of specific chemical processes.

The excess molar volumes of binary mixtures of {1-ethyl-3-methylimidazolium ethylsulfate + methanol or 1-propanol or 2-propanol}, {trioctylmethylammonium bis (trifluoromethyl-sulfonyl) imide + methanol or ethanol or 1-propanol}, {1-buty-3-methylimidazolium methylsulfate + methanol or ethanol or 1-propanol} were calculated from experimental density values, at T = (298.15, 303.15 and 313.15) K. The Redlich-Kister smoothing polynomial was fitted to the excess molar volume data.

The partial molar volumes of the binary mixtures {1-ethyl-3-methylimidazolium ethylsulfate + methanol or 1-propanol or 2-propanol}, {trioctylmethylammonium bis (trifluoromethyl-sulfonyl) imide + methanol or ethanol or 1-propanol}, {1-buty-3-methylimidazolium methylsulfate + methanol or ethanol or 1-propanol} were calculated from the Redlich-Kister coefficients, at T = (298.15, 303.15 and 313.15) K. This information was used to better understand the intermolecular interactions with each solvent at infinite dilution.

The isentropic compressibility of {trioctylmethylammonium bis (trifluoromethyl-sulfonyl) imide + methanol or ethanol or 1-propanol}, were calculated from the speed of sound data at T = 298.15 K.

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ρ = density

$V_{\mathrm{m}}^{\mathrm{E}}$ = excess molar volume

$V_{\mathrm{m,i}}^{\infty}$ = partial molar volume at infinite dilution

T = temperature

K = Kelvin

x_1 = mole fraction of the 1st component

x_2 = mole fraction of the 2nd component

σ = standard deviation

M_1 = molar mass of ionic liquid

M_2 = molar mass of alcohol

A_{i} = polynomial coefficient

N = polynomial degree

n = number of experimental points

k = number of coefficients used in the Redlich –Kister correlation

u = speed of sound

k_{s} = isentropic compressibility

Δk_{s} = isentropic compressibility deviation

CHAPTER 1

INTRODUCTION

1.1 THE IMPORTANCE OF IONIC LIQUIDS IN INDUSTRIES

Ionic liquids (ILs) are proving to be increasingly promising as a viable media for potentially green synthesis and separation operations, as well as, for novel applications, where the unique properties of the IL materials provides new options based upon different chemical and physical properties (Rogers and Seddon 2003). Ionic liquids are defined as salts with the melting temperature below the boiling point of water (Wilkes 2002). Most of the salts identified in the literature as ILs are liquid at room temperature, and often at substantially lower temperatures $< 100\ ^{o}C$ (Pereiro and Rodriguez 2006; Zafarani-Mottar and Shekaari 2005). ILs are composed of organic cations and various anions. As numerous combinations of cations and anions are possible, they are considered as "designer solvents" since the IL can be optimized for its physical properties for a specific application (Plechkova and Seddon 2008; Rogers *et al.* 2002; Wu and Marsh 2003; Carmichael and Seddon 2000)**.** ILs are being explored as possible environmentally benign solvents (Brennecke and Maginn 2001; Holbrey and Seddon1999; Seddon *et al.* 2000) because of their negligible vapour pressure (Earle *et al.* 2006; Zaitsau *et al.* 2006; Anthony *et al.* 2001; Dupont *et al.* 2002, Zafarani-Mottar and Shekaari 2006) and as potential replacement solvents for volatile organic compounds (VOCs) (Kaar *et al.* 2003; Poole 2004; Freemantle 1998) currently used in industry (Heintz and Lehman 2003; Bhujrajh and Deenadayalu 2006). Implementation of ionic liquids in industry could lead to a reduction in VOC emission and to a more cost-effective use of starting materials because ionic liquids are recyclable (Pereiro and

Rodriguez 2006; Zafarani-Mottar and Shekaari 2005; Domanska and Pobudkowska 2006; Seddon 1997).

VOCs are compounds that impact negatively on the environment. VOCs are released to the environment from indoor activities (example cooking and tobacco smoke) and outdoor activities (example combustion of fuel, emissions from petrochemical and chemical facilities) (Cohen 1996). VOCs are of particular concern since they readily volatilize into the atmosphere and are distributed over large regions leading to a population wide exposure to these chemicals. VOCs are present in liquid and solid processes and waste streams, in consumer products and in fossil fuels. VOCs in the environment present problems that are associated with a) human health problems, b) formation of ozone and urban precursors aerosol and c) odor. In most urban regions the concentration of VOCs contribute significantly to the total cancer risk associated with toxic air pollutants. The potential health risk associated with VOCs and their role in the formation of photochemical smog have led to increasing public concern regarding the presence of VOCs in the environment (Cohen 1996).

ILs are advanced, technological solvents that can be designed to fit a particular application. One regularly suggested advantage of ILs over VOCs as solvents, for both synthetic chemistry and for electrochemistry, is the intrinsic lack of vapour pressure (Rogers and Seddon 2003).

ILs have widely tunable properties with regard to polarity, hydrophobicity and solvent miscibility through the appropriate selection of the anion and cation. They are important because of their unique physical properties, such as low melting point, high thermal stability, non-flammability, no measurable vapour pressure (Rebelo *et al.* 2005) and good dissolution properties (Baranyai *et al.* 2004) for most organic and inorganic compounds (Welton 1999;

Sheldon 2001; Yang *et al.* 2005) and a very rich and complex behaviour as solvents which can be modified by changing the nature of the cation or anion (Scurto *at al.* 2004; Gutowki *et al.* 2003; Lachwa *et al.* 2005; Lachwa *et al.* 2006). The other main benefits of ILs are favourable solvation behaviour, high stability to air and moisture, and a wide electrochemical window. The ILs that are moisture and air stable (e.g. with $[Tf_2N]^-$ anion) at room temperature have potential uses for new chemical processes and technologies (Domanska and Pobudkowska 2006; Lozano and De Diego 2004).

They have been used in reaction rate enhancement, higher selectivities, higher yields in organic synthesis and in the optimization of compound characteristics through a broad choice of anion and cation combination (Brown *et al.* 1973; Pikkarainen 1982; Chakraborty and Hans-Jörg 2007). They can be used as solvents for synthetic purposes, e.g. Diels-Alder cycloaddition reactions (Fischer *et al.* 1999), Friedel-Craft acylation and alkylation, hydrogenation and oxidation reactions and Heck reactions; as biphasic system in combination with an organic solvent or water in extraction and separation technologies; as catalyst immobilizers for the easy recycling of homogeneous catalysts; as electrolytes in electrochemistry (Zhong and Wang 2007). Some ILs are highly hydroscopic and small quantities of water or other compounds in ionic liquids causes considerable changes in the physical properties (Seddon *et al.* 2000; Calvar *et al.* 2006; Gonzalenz *et al.* 2006).

Physical and thermodynamic properties of ionic liquids are unlimited because, the number of potential ILs are large (Yang *et al.* 2005, Najdanovic-Visak *et al.* 2002; Krummen *et al.* 2002; Arce *et al.* 2006; Jaquemin *et al.* 2006).

To design any process involving ILs on an industrial scale, it is necessary to know their thermodynamic or physico-chemical properties such as density, speed of sound through the liquid and activity coefficients at infinite dilution (Letcher *et al.* 2005). The precise numerical values of these properties are of significance in design and control of the chemical processes involving the ILs (Plechkova and Seddon 2008; Gómez and González 2006; Smith and Pagni 1989).

In solutions of ionic liquids, the structure and interaction of ions determine the unique properties of these solutions (Zafarani-Mottar and Shekaari 2005).

ILs have been applied successfully or have great potential for application in the following industrial processes given below (Welton 1999).

1. *The Biphosic Acid Scavenging utilising Ionic Liquids (BASIL) process*

The first major industrial application of ILs was the BASIL process by BASF, in which 1-methylimidazol was used to scavenge the acid from an existing process. This led to the formation of an IL which can easily be removed from the reaction mixture. But the easy removal of an unwanted side-product (as an IL rather then as a solid salt) is not the only advantage of this IL based process. By the formation of an IL it was possible to increase the space/time yield by a factor of 80,000. It should also be kept in mind that improvements on such scale are rare (Plechkova and Seddon 2008).

2. *Cellulose Processing*

Cellulose is the earth's most widespread natural organic compound and thus highly important as a bio-renewable resource. A more intensive exploitation of cellulose as a bio-renewable feedstock has to date been prevented by the lack of a suitable solvent that can be used in chemical processes (Rogers *et al.* 2003). Rogers found that by the addition of ILs, solutions of cellulose can now be produced for the first time at technically useful concentrations (Rogers *et al.* 2002). This new technology therefore opens up great potential for cellulose processing.

3. *Dimersol – Difasol*

The dimersol process is a traditional way to dimerise short chain alkenes into branched alkenes of higher molecular weight. Nobel laureate Yves Chauvin developed an IL –based process called the Difasol process. It is yet to be tested industrially (Plechkova and Seddon 2008).

4. P*aint additives*

ILs can enhance the finish, appearance and drying properties of paints. Degussa are marketing such ILs under the name of TEGO Dispers. These products are also added to a pliolite paint range (Plechkova and Seddon 2008).

5. *Air products – ILs as a transport medium for reactive gases*

Air products make use of ILs as a medium to transport reactive gases. Reactive gases such as trifluoroborane, phosphine or arsine, are stored in suitable ILs at sub-ambient pressure. This is a significant improvement over pressurized cylinders. The gases are withdrawn from the containers by applying a vacuum (Plechkova and Seddon 2008).

6. *Linde's IL 'piston'*

Air Product's Gasguard system relies on the solubility of some gases in ILs. Linde (1996) and his group are exploiting other gases insolubility in ILs. The solubility of hydrogen in ILs is very low. Linde uses the solubility of hydrogen in IL to compress hydrogen in filling stations (Plechkova and Seddon 2008).

7. *Nuclear industry*

ILs are extensively explored for various innovative applications in the nuclear industry, including the application of an IL as an extractant/diluent in a solvent extraction system and as an alternative electrolyte media for high temperature pyrochemical processing (Giridhar and Venkatesan 2007).

1.2 THE IMPORTANCE OF THERMODYNAMIC PHYSICAL PROPERTIES

During the last few years, investigations of thermophysical and thermodynamic properties have increased remarkably, but they are by no means exhausted (Marsh and Boxall 2004; Heintz 2005; Zhang *et al.* 2006; Fredlake 2004; Tokuda *et al.* 2004; Tokuda *et al.* 2005; Tokuda *et al.* 2006; Azevedo *et al.* 2005; Azevedo *et al.* 2005; Esperancia *et al.* 2006; Domanska 2005; Domanska 2006; Pereiro *et al.* 2007; Pereiro and Rodriguez 2007; Greaves *et al.* 2006).

The complexity of the molecular interactions present in the liquid phase makes the task of predicting thermodynamic quantities difficult. Thermo physical data are useful industrially, for the optimization of the design of various industrial processes (Bhujrajh and Deenadayalu 2006; Marsh and Boxal 2004; Domanska and Marciniak 2005). Knowledge of thermo physical properties of the ILs mixed with other organic solvents is useful for development of specific chemical processes (Dupont and de Souza 2002; Anastas and Warner 1998; Cann and Connelly 2000).

Thermodynamic properties, including activity coefficients at infinite dilution and excess molar volumes, $V_{\mathrm{m}}^{\mathrm{E}}$, are also useful for the development of reliable predictive models for systems containing ionic liquids. To this end, a database of IL cation, anion and thermo physical properties should be useful (Domanska and Pobudkowska 2006).

Excess molar volumes, $V_{\mathrm{m}}^{\mathrm{E}}$, and partial molar volumes, $V_{\mathrm{m,i}}^{\infty}$, can be used as a basis for understanding some of the molecular interactions (such as dispersion forces, hydrogen-bonding interactions) in binary mixtures (Zhong and Wang 2007). Excess molar volume data is a helpful parameter in the design of the technological processes of a reaction (Gómez and González 2006), and can be used to predict vapour liquid equilibria using appropriate equation of state (EoS) models (Sen 2007).

Partial molar volume at infinite dilution, $V_{\mathrm{m,i}}^{\infty}$, of a substance in a mixture is the change in volume per mole of added substance to a large volume of the first component (Atkins 1990). $V_{\mathrm{m,i}}^{\infty}$, data provide useful information about interactions occurring in infinitely dilute solutions. These studies are of great help in characterizing the structure and properties of solutions (Domanska and Pobudkowska 2006).

Measurement of the speed of sound, *u*, in liquids is a powerful source of information (e.g. the effects of small concentrations changes) about the thermo physical properties of chemical substances and their mixtures (Azevedo and Szydlowski 2004).

The objective of studying thermophysical properties of binary mixtures is to contribute to a data bank of thermodynamic properties of binary mixtures of ILs and to investigate the relationship between ionic structures of IL and density of the binary mixture, in order to establish principles for the molecular design of suitable ILs for chemical separation processes (Azevedo and Szydlowski 2004).

1.3 AREA OF RESEARCH COVERED IN THIS WORK

In this work the $V_{\mathrm{m}}^{\mathrm{E}}$ were determined for the binary system {1-ethyl-3-methylimidazolium ethylsulfate $[\mathrm{EMIM}]^{+}[\mathrm{EtSO_4}]^{-}$ + methanol or 1-propanol or 2-propanol}, {trioctylmethylammonium bis (trifluoromethyl-sulfonyl) imide $[\mathrm{OMA}]^{+}[\mathrm{Tf_2N}]^{-}$ + methanol or ethanol or 1-propanol}, {1-buty-3-methylimidazolium methylsulfate $[\mathrm{BMIM}]^{+}[\mathrm{MeSO_4}]^{-}$ + methanol or ethanol or 1-propanol}, over the entire composition range at T = (298.15, 303.15 and 313.15) K and the speed of sound u at T = 298.15 K and 1MHz for {$[\mathrm{OMA}]^{+}[\mathrm{Tf_2N}]^{-}$ + methanol or ethanol or 1-propanol}system. The Redlich-Kister smoothing equation was fitted to the excess molar volume and isentropic compressibilities data and the partial molar volumes were determined from the Redlich-Kister coefficients. The results are discussed in terms of intermolecular interaction.

Structures of the ILs used in this work are presented in figures 1.1 -1.3.

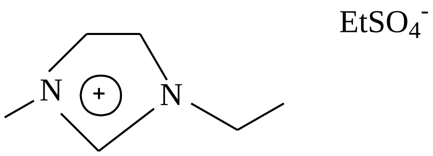

Figure 1.1 1-Ethyl-3-methylimidazolium ethylsulfate

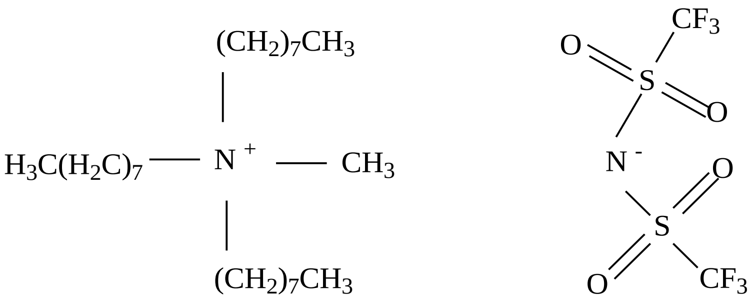

Figure 1.2 Trioctylmethylammonium bis (trifluoromethylsulfonyl) imide

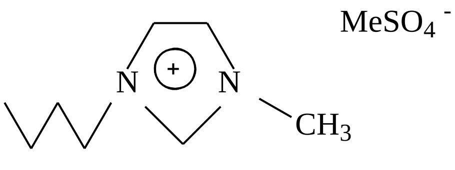

Figure 1.3 1-Butyl-3-methylimidazolium methylsulfate

CHAPTER 2

LITERATURE REVIEW

There is only a paucity of experimental data for thermodynamic properties of solutions containing an ionic liquid (Barbosa 2003).

The need for studying thermophysical properties of composite materials (or mixtures of pure substances) is often due to the deviation from ideality due to mixing, or a specific application for the required property (Blandamer 1973; Franks and Reid 1973; Millero 1971; Millero 1980; Hoiland 1986).

The composition dependence of the excess molar volume is used to understand the nature of the molecular scale processes within those mixtures.

There are some experimental V_m^E data of ionic liquids with alcohols and other organic solvents in the literature. These systems together with the V_m^E values are given in table 2.1.

Pereiro and Rodriguez (2006) determined experimental densities, speeds of sound and refractive indices of the binary mixtures of ethanol with (1,3-dimethyl imidazolium methyl sulfate) $[MMIM]^+[MeSO_4]^-$, 1-butyl-3-methyl imidazolium methyl sulfate $[BMIM]^+[MeSO_4]$, 1-butyl-3-methylimidazonium hexafluorophosphate $[BMIM]^+[PF_6]^-$, 1-hexyl-3-methylimidazonium hexafluorophosphate $[HMIM]^+[PF_6]^-$ and 1-methyl-3-octylimidazonium hexafluorophosphate $[OMIM]^+[PF_6]^-$ at T = (293.15 to 303.15) K. The excess molar volumes, changes of refractive index on mixing and deviation in isentropic compressibility for the above systems were calculated. Pereiro's results showed that the excess molar volumes and deviations in isentropic compressibilities decrease when the temperature in increased for the systems studied.

Zhong and Wang (2007) determined the density of the two binary mixtures formed by1-butyl-3-methylimidazonium hexafluorophosphate $[BMIM]^+ [PF_6]^-$ with aromatic compound (benzyl alcohol or benzaldehyde) over a full range of composition over the temperature range from (293.15 to 303.15) K and at atmospheric pressure. Zhong's results showed that, V_m^E, decreases slightly when temperature increases in the system studied.

Pereiro and Tojo (2006) determined the densities and refractive indices of the pure ionic liquid $[HMIM]^+ [PF_6]^-$ at temperature range from T = (278.15 to 318.15) K for density and from T = (288.15 to 318.15) K for refractive index. The coefficient of thermal expansion of $[HMIM]^+ [PF_6]^-$ was calculated from the experimental values of density. The densities and refractive indices of the binary mixtures involving dimethyl carbonate, (DMC), diethyl carbonate, (DEC), acetone, 2-butanone, 2-pentanone were measured at T = 298.15 K and atmospheric pressure. The excess molar volumes and changes of refractive index on mixing for the binary system were calculated.

Hofman *et al.* (2008) measured the densities of pure 1-ethyl-3-methylimidazolium ethylsulfate $[C_2mim][EtSO_4]$, with methanol over the temperature range (283.15 to 333.15), K and pressure range (0.1-35) MPa. The excess molar volumes have been calculated directly from experimental densities.

Singh and Kumar (2008) measured the densities and refractive indices for binary mixtures of 1-methyl-3-octylimidazolium tetrafluoroborate $[OMIM]^+[BF_4]^-$ with ethylene glycol monomethyl ether (EGMME, C_1E_1), diethylene glycol monomethyl ether (DEGMME, C_1E_2), and triethylene glycol monomethyl ether (TEGMME, C_1E_3), over the whole composition range. The experimental densities were used to estimate excess molar volumes, apparent molar volumes, partial molar volumes, excess partial molar volumes and their limiting values at infinite dilution.

Widegren and Magee (2007) measured the physical properties of 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide with water. Densities at temperature range

(258.15 to 373.15) K. Dynamic viscosity at (258.15 to 373.15) K. Kinetic viscosity at (293.15 to 298.15) K. Speed of sound through the mixture at (283.15 to 343.15) K.

Zafarani-Moattar and Shekaari (2005) reported the density, excess molar volumes, speed of sound data for 1-butyl-3-methylimidazolium hexafluorophosphate $[BMIM]^+[PF_6]^-$ + methanol and $[BMIM]^+[PF_6]^-$ + acetonitrile binary mixtures over the entire range of composition at

T = (298.15 to 318.15) K.

Esperanca *et al.* (2006) determined the speed of propagation of ultrasound waves and densities in pure ionic liquids (1-propyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide $[C_3mim]^+$ $[Tf_2N]^-$ and (1-pentyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide $[C_5mim]^+[Tf_2N]^-$. Speed of sound measurements have been carried over a range of temperature ($298 < T / K > 338$)

and pressure ($0.1 < p$ / MPa < 200). Density measurements have been performed over a broad range of temperature ($298 < T$ / K > 333) and pressure ($0.1 < p$ / MPa < 60).

Gomez *et al.* (2006) determined the experimental densities, dynamic viscosities, excess molar volumes, speed of sound and isentropic compressibilities over the whole composition range for (1-ethyl-3-methylimidazolium ethylsulphate $[EMIM]^+[EtSO_4]^-$+ ethanol) and (1-ethyl-3-methylimidazolium ethylsulphate $[EMIM]^+ [EtSO_4]^-$ + water) binary systems at T = (268.15, 313.15 and 328.15) K and atmospheric pressure. The Redlich-Kister equation was fitted to the excess molar volume, viscosity deviation and the deviation in isentropic compressibility data for the binary systems to determine the fitting parameters and the root mean square deviations.

Domanska *et al.* (2006) determined the solubility of 1-butyl-3-methylimidazolium octylsulphate $[BMIM]^+ [OcSO_4]^-$ in hydrocarbon (n-hexane, n-heptane, n-octane or n-decane) solutions and alcohols (methanol, 1-butanol, 1-hexanol, 1-octanol or 1-decanol) solutions. Densities and excess molar volumes have been determined for 1- methyl-3-methylimidazolium methylsulphate $[MMIM]^+[MeSO_4]^-$ with alcohols (methanol, ethanol or 1-butanol) and with water, for 1-butyl-3-methylimidazolium methylsulphate $[BMIM]^+ [MeSO_4]^-$ with an alcohol (methanol, ethanol, 1-butanol, 1-hexanol, 1-octanol or 1-decanol) and with water and for 1-butyl-3-methylimidazolium octylsulphate $[BMIM]^+ [OcSO_4]^-$ with an alcohol (methanol, 1-butanol, 1-hexanol, 1-octanol or 1-decanol) at T = 298.15 K and atmospheric pressure.

Pereiro and Rodriguez (2006) determined the experimental densities, speed of sound through the mixtures and refractive indices of binary mixtures of 1,3-dimethylimidazolium methylsulphate $[MMIM]^+ [MeSO_4]^-$, 1-butyl-3-methylimidazolium methylsulphate $[BMIM]^+ [MeSO_4]^-$, 1-hexyl-3-methylimidazolium hexafluorophosphate $[HMIM]^+ [PF_6]^-$ and 1-methyl-3-octylimidazolium hexafluorophosphate $[OMIM]^+ [PF_6]^-$ with ethanol from T = (293.15 to 303.15) K. Excess molar volumes, changes of refractive index on mixing and deviation in isentropic compressibility for the above systems were calculated.

Yang *et al.* (2005) measured the densities of aqueous solutions of 1-methyl-3-ethylimidazolium ethylsulphate [EMISE] at T = (278.15 to 333.15) K. The values of the apparent and partial molar volume were determined and apparent molar expansibilities of [EMISE] and the coefficients of thermal expansion of the solutions were calculated.

Yang *et al.* (2005) measured the densities of 1-methyl-3-ethylimidazolium ethylsulphate [EMISE] in a temperature range at T = (278.2 to 338.2) K. Values of the apparent molar volume were also calculated.

Heintz *et al.* (2002) presented the experimental data of densities and viscosities for the system 4-methyl-N-butylpyridinium tetrafluoroborate + methanol at T = (25, 40, 50 and 323.15) K and ambient pressure. Excess molar volumes and excess logarithm viscosities have been determined. Kumelan *et al.* (2008) presented experimental results for the solubility of tetrafluoromethane in the ionic liquid 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([hmim][Tf_2N]) for temperature between (293.3 and 413.3) K, at pressures up to 9.6 MPa.

Jin *et al.* (2008) reported physical properties for 4 room temperature ionic liquids consisting of the 1-butyl-3-methylimidazolioum cation with various perfluorinated anions and the bis(trifluoromethylsulfonyl)imide $[Tf_2N]^-$ with 12 pyrolidinium, ammonium, and hydroxyl containing cations.

Seddon *et al.* (2000) published the excess molar volumes data for the binary systems $[BMIM]^+$ $[BF_4]^-$ with water at T = (313.15 and 353.15) K.

Rebelo *et al.* (2004) conducted an extensive thermodynamic analysis of the $[BMIM]^+$ $[BF_4]^-$ with water at T = (278.15 – 333.15) K which included, V_m^E, H_m^E and C_p^m.

Zhang *et al.* (2004) published V_m^E, data together with the Redlich-Kister correlation parameters for the binary system $[EMIM]^+$ $[BF_4]^-$ with water at several temperatures.

Wang *et al.* (2003) utilized the Redlich-Kister equation with four parameters for the description of V_m^E data for $[BMIM]^+$ $[BF_4]^-$ with acetonitrile or dichloromethane or 2-butanoneor N,N-dimethylformamide at T =298.15 K.

Lopes *et al.* (2005) reported, V_m^E, data of six binary mixtures composed of two different ionic liquids with a common anion $[Tf_2N]^-$ $\{[C_mMIM]^-$ $[Tf_2N]^-$ $+\{[C_nMIM]^-$ $[Tf_2N]^-)$ with n and m ranging from 2 to 10} at T = (298.15 and 333.15) K, as well, V_m^E, data of three binary systems containing $[BMIM]^-$ as a common cation: {($[BMIM]^+$ $[Tf_2N]^-$ + $[BMIM]^-$ $[PF_6]^-$), ($[BMIM]^+$ $[Tf_2N]^-$ + $[BMIM]^-$ $[PF_4]^-$) and ($[BMIM]^+$ $[BF_4]^-$ + $[BMIM]^-$ $[PF_6]^-$)}.

Bhujrajh and Deenadayalu (2007) evaluated $V_{\mathrm{m}}^{\mathrm{E}}$ from density measurements over the entire composition range for ternary systems of ionic liquids {1-ethyl-3-methyl-imidazolium diethyleneglycol monomethylether sulphate $[EMIM][CH_3]^+[(OCH_2CH_2)_2OSO_3]^-$ + methanol + water}at T = (298.15, 303.15 and 313.15) K.

Bhujrajh and Deenadayalu (2008) measured the densities of binary system{1-ethyl-3-methyl-imidazolium bis(perfluoroethylsulphonyl)imide $[EMIM]^-$ $[BETI]^-$ + methanol or acetone and ternary system {$[EMIM]^-$ $[BETI]^-$ + methanol + acetone} respectively at T = (298.15, 303.15 and 313.15) K and the speed of sound data for the binary systems 1-ethyl-3-methyl-imidazolium diethyleneglycol monomethylether sulphate {$[EMIM][CH_3]^+[(OCH_2CH_2)_2OSO_3]^-$ + methanol} at T = 298.15 K. The excess molar volumes were calculated from the experimental densities. Redlich-Kister equation was fitted to the calculated excess molar volumes.

Table 2.1 $V^{E}_{m,min}$ results for ILs and alcohols systems in the literature

Author	**Systems**	**$V^{E}_{m,min}$** **($cm^{3\cdot}\ mol^{-1}$)**
Pereiro and Rodriguez 2006	$[MMIM]^{+}$ [.$MeSO_4]^{-}$ + ethanol	
	At T =293.15 K	-1.095
	At T =298.15 K	-1.142
	At T =303.15 K	-1.191
	$[BMIM]^{+}$ [$MeSO_4]^{-}$ + ethanol	
	At T =293.15 K	-0.659
	At T =298.15 K	-0.706
	At T =303.15 K	-0.714
	$[BMIM^{+}]$ $[PF_6]^{-}$ + ethanol	
	At T =293.15 K	-0.499
	At T =298.15 K	-0.502
	At T =303.15 K	-0.529
	$[HMIM]^{+}$ [$PF_6]^{-}$ + ethanol	
	At T =293.15 K	-0.505
	At T =298.15 K	-0.556
	At T =303.15 K	-0.476
	$[OMIM]^{+}$ [$PF_6]^{-}$ + ethanol	
	At T =293.15 K	-0.475
	At T =293.15 K	-0.494
	At T =303.15 K	-0.512

Gomez *et al.* 2006	$[EMIM]^+[EtSO_4]^-$ + ethanol	
	At *T* =298.15 K	-0.672
	At *T* =313.15 K	-0.825
	At *T* =328.15 K	-0.984
Zhong *et al.* 2007	$[BMIM]^+ [PF_6]^-$ + benzyl alcohol	-0.989
	$[BMIM]^+ [PF_6]^-$ + benzyl alcohol	-1.351
Domanska *et al.* 2006	$[MMIM]^+[MeSO_4]^-$ + methanol	-1.242
	$[MMIM]^+[MeSO_4]^-$ + ethanol	-1.177
	$[MMIM]^+[MeSO_4]^-$ + butanol	-0.753
	$[BMIM]^+[MeSO_4]^-$ + methanol	-0.176
	$[BMIM]^+[MeSO_4]^-$ + ethanol	-0.662
	$[BMIM]^+[MeSO_4]^-$ + 1-butanol	-0.154
	$[BMIM]^+[MeSO_4]^-$ + 1-hexanol	0.052
	$[BMIM]^+[MeSO_4]^-$ + 1-octanol	0.049
	$[BMIM]^+[MeSO_4]^-$ + 1- decanol	0.104
	$[BMIM]^+[OcSO_4]^-$ + methanol	-1.024
	$[BMIM]^+[OcSO_4]^-$ + 1-butanol	0.016
	$[BMIM]^+[OcSO_4]^-$ + 1-hexanol	0.037
	$[BMIM]^+[OcSO_4]^-$ + 1-octanol	0.087
	$[BMIM]^+[OcSO_4]^-$ + 1-decanol	0.059
Hofman *et al* 2008	$[C_2mim][EtSO_4]$ + methanol	
	At *T* =283.15 K	-0.850
	At *T* =293.15 K	-0.890

	At *T* =298.15 K	-0.950
	At *T* =303.15 K	-0.980
	At *T* =313.15 K	-1.070
	At *T* =323.15 K	-1.160
	At *T* =333.15 K	-1.250
Bhujrajh and Deenadayalu 2007	$[EMIM][CH_3]^+[(OCH_2CH_2)_2 OSO_3]^-$ + methanol + water	
	At *T* =298.15 K	-0.998
	At *T* =303.15 K	-0.888
	At *T* =313.15 K	-0.630
Bhujrajh and Deenadayalu 2008	$[EMIM]^- [BETI]^-$ + methanol	
	At *T* =298.15 K	-0.040
	At *T* =303.15 K	-0.050
	At *T* =313.15 K	-0.080

CHAPTER 3

EXCESS MOLAR VOLUMES

3.1 INTRODUCTION

The excess molar volume $V_{\mathrm{m}}^{\mathrm{E}}$ is defined as (McGlashan 1979, Walas 1985, Letcher 1975):

$$V_{\mathrm{m}}^{\mathrm{E}} = V_{\mathrm{mixture}} - \sum x_{\mathrm{i}} V_{\mathrm{i}}^{0} \tag{3.1}$$

where x_i is the mole fraction of component *i*, V_{mixture} and V_i^o are the molar volumes of the mixture component I, respectively. For a binary mixture,

$$V_{\mathrm{m}}^{\mathrm{E}} = V_{\mathrm{mixture}} - (x_1 V_1^0 + x_2 V_2^0) \tag{3.2}$$

The change in volume on mixing two liquids, 1 and 2 can be attributed to a number of processes (Letcher 1975): a) the breakdown of 1-1 and 2-2 intermolecular interaction which have a positive effect on the volume, b) the formation of 1-2 intermolecular interaction which results in a decrease of the volume of the mixture, c) packing effect caused by the difference in the size and shape of the component species and which may have positive or negative effect on the particular species involved and d) formation of new chemical species (Redhi 2003).

There is no volume change upon mixing two liquids to form a thermodynamically ideal solution at constant temperature and pressure, but a volume change may occur when two real liquids are mixed (Battino 1971).

Volume change on mixing of binary liquid mixtures, $\mathrm{V}_{\mathrm{m}}^{\mathrm{E}}$, at constant pressure and temperature is of interest to chemists and chemical engineers, and is an indicator of the non-idealities present in real mixtures. It is also important to thermochemists because it serves as a sensitive indicator for the applicability of liquid theories to liquid mixtures [Redhi 2003].

In reality it is impossible to apportion with any strong conviction the contributing effects of the intermolecular interactions of the dissimilar molecules, because of the packing effect (Deenadayalu 2000).

3.2 DETERMINATION OF EXCESS MOLAR VOLUMES

The volume, (V), of a mixture is a function of temperature, (T), pressure, (P), and number of moles, (n), i.e:

$$V = V(T, P, n_1, n_2, n_3 \ldots n_f) \tag{3.3}$$

At constant temperature and pressure this is:

$$V = V(n_1, n_2, n_3 \ldots n_f) \tag{3.4}$$

The volume of the unmixed component liquids V_{unmix} at the constant temperature and pressure may be written as:

$$V_{\mathrm{m,unmix}} = \sum x_1 V^0_{\mathrm{m,i}} = V_{\mathrm{m,ideal}} \tag{3.5}$$

where $V^0_{\mathrm{m,i}}$ is the molar volume of the pure species i.

Once the liquids have been mixed together the volume of the mixture $V_{\mathrm{m,mix}}$ is not normally the sum of the volumes of the pure liquids but is given by:

$$V_{\mathrm{m,mix}} = (V_{\mathrm{m,real}}) \neq x_1 V_{\mathrm{m,1}} + x_2 V_{\mathrm{m,2}} + \ldots\ldots x_i V_{\mathrm{m,i}} = \sum x_i V_{\mathrm{m,i}} \tag{3.6}$$

where V_m^E is the excess molar volume at constant temperature and pressure (Smith and Pagni 1998).

The excess molar volume of mixing, V_m^E, is given by:

$$V_m^E = V_{m,mix} - V_{m,unmix} = V_{m,real} - V_{m,ideal} = \sum x_I \left(V_{m,i} - V_{m,i}^0 \right) \qquad (3.7)$$

3.3 EXPERIMENTAL METHODS FOR MEASUREMENT OF EXCESS MOLAR VOLUMES

The excess molar volume, V_m^E, at a constant concentration of x_1 of component 1 is defined as

$$V_m^E = V_{\text{mixture}} - \left(x_1 V_1^0 + x_2 V_2^0 \right) \qquad (3.8)$$

where sum of the last two terms is the ideal molar volume of the mixture.

The excess molar volume, V_m^E, upon mixing two liquids may be measured either directly or indirectly. The direct measurements involve mixing the liquids and determining the volume change (dilatometric method) and the indirect measurements involve measuring the density of the pure liquid as well as the density of the mixture and calculating, V_m^E, from these values, (pycnometer or densitometer) (Battino 1971; Letcher 1975; Handa and Benson 1979, Beath *et al.* 1969; Pflug and Benson 1968; Stokes and Marsh 1972; Marsh 1980, 1984; Kumaran and Mcglashan 1977; Govender 1996; Nevines 1997; Redhi 2003). The later method was used in this work. The details for this instrument is given in chapter 3, page 33. Summary of the various techniques (direct and indirect methods) are given here.

3.3.1 Direct determination

The direct method measures the volume change that occurs when the liquids are mixed. Direct methods of measurement of, V_m^E , include 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 [Handa and Benson 1979; Nevines 1997; Redhi 2003).

3.3.1.1 Batch dilatometer

An example of a batch dilatometer is shown in figure 3.1.

The dilatometer is filled with known masses of pure liquids, which are separated by mercury. The height of mercury in the calibrated graduated column is noted. The liquids are mixed by rotating the dilatometer and the volume change on mixing is indicated by the change in the height of the mercury in the calibrated capillary. The, V_m^E , is determined from the volume change and the masses of the components. It was reported that a precision of ± 0.003 $cm^3 \cdot mol^{-1}$ in the, V_m^E , could be achieved over the temperature range of (280 to 350) K using this technique. A disadvantage of this apparatus is that it is difficult to fill the dilatometer and this is usually accomplished using a syringe. A major source of error in this method is the determination of the composition as is it necessary to weigh the dilatometer as 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 (Keyes and Hildebrand 1917; Nevines 1997; Redhi 2003).

3.3.1.2 Continuous dilatometer

This technique has become more popular than the batch technique because it is less time consuming 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 is presented in figure 3.2 (Bottomly and Scott 1974). Both are considered superior to other continuous dilatometer because mercury and the liquids do not pass through 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) report a precision of $\forall$ 0.0003 cm$^{3}\cdot$ mol^{-1} in V_{m}^{E} for their apparatus (Nevines 1997).

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.

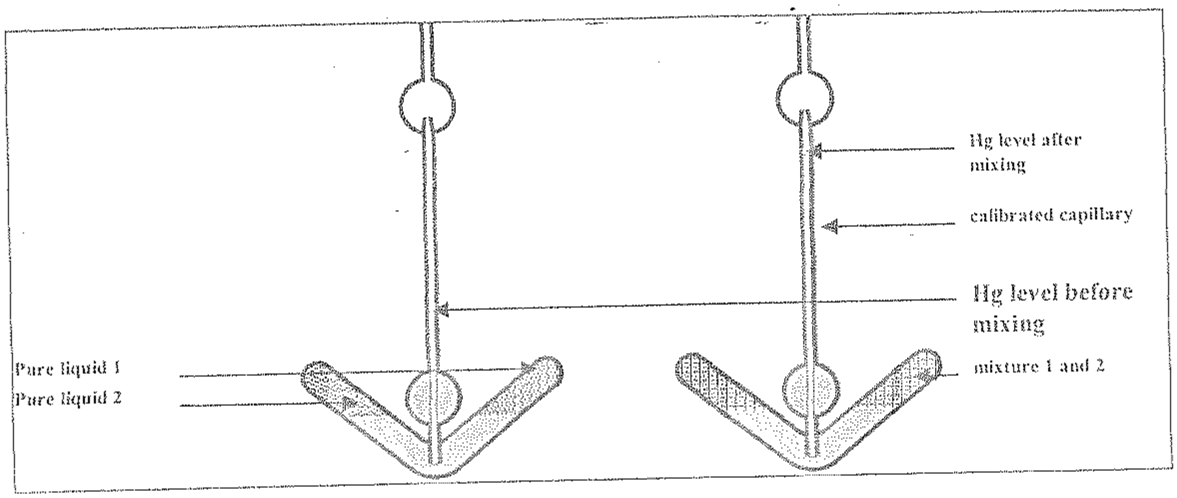

Figure 3.1 A typical batch dilatometer

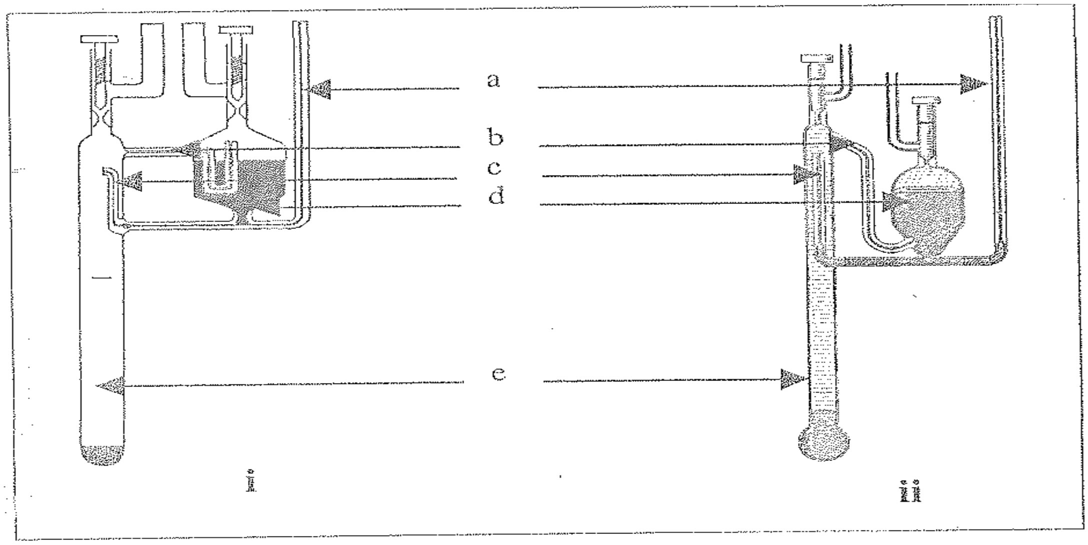

Figure 3.2 Continuous dilatometer (i) design of Bottomly and Scott, (ii) design of Kumaran and McGlashan. a; calibrated capillary from which the volume change is determined, b; liquid capillary, c; mercury capillary, d; bulb that contains mercury, e; burette liquid 2

3.3.2 Indirect determination

As the development of the dilatometer was accompanied by a greater accuracy than was possible from density measurement techniques, the latter method became less popular for determination of V_m^E. However the development of highly accurate vibrating tube densitometers has made it possible to determine, V_m^E, with acceptable accuracy from density measurements. This method is also very simple.

The, V_m^E, for a binary mixture is determined from density measurements using the following equation:

$$V_m^E = \frac{x_1 M_1 + x_2 M_2}{\rho} - \frac{x_1 M_1}{\rho_1} - \frac{x_2 M_2}{\rho_2} \tag{3.9}$$

where x_1 and x_2 are the mole fractions, M_1 and M_2 are molar masses, ρ_1, ρ_2 and ρ are the densities where 1 and 2 refers to the component 1 and 2 respectively and ρ is the density of the mixture (Govender 1996; Nevines 1997; Redhi 2003).

3.3.2.1 Pycnometry

Pycnometry involves the determination of 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 of the vessel 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 Bruisie 1943). The pycnometer based on the design of (Wood and Bruisie 1943) is shown in figure 3.3.

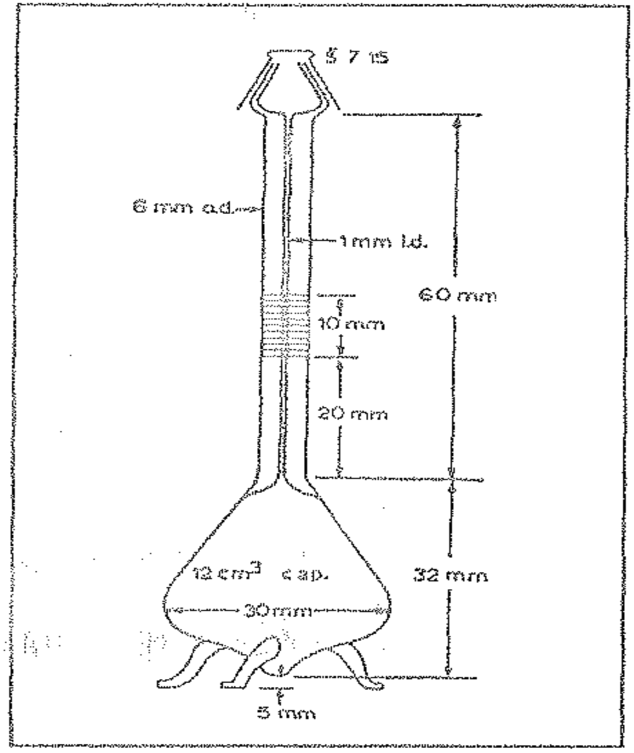

Figure 3.3 The pycnometer based on the design of Wood and Bruisie

3.3.2.2 Magnetic Float densimeter

The mode of operation of 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 $\mathrm{cm}^{3}\cdot$ mol^{-1} Franks and Smith (1967). The magnetic float densitometer based on the design of (Franks and Smith 1967) is shown in figure 3.4.

3.3.2.2 Mechanical Oscillating densitometer

Mechanical oscillating (vibrating tube) densimeters coupled to digital output displays are being widely used in the chemical industry, and in research laboratories to measure densities of liquid 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 a 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, *M*, by using the following equation

$$2\pi\nu = \left(\frac{c}{M}\right)^{\frac{1}{2}} \tag{3.10}$$

Since the oscillator is a hollow tube, *M* is the sum of the contents in the tube and the true mass, M_0. If a liquid with a density, ρ, fills the hollow which has a volume *V,* then:

$$M = M_0 + \rho V \tag{3.11}$$

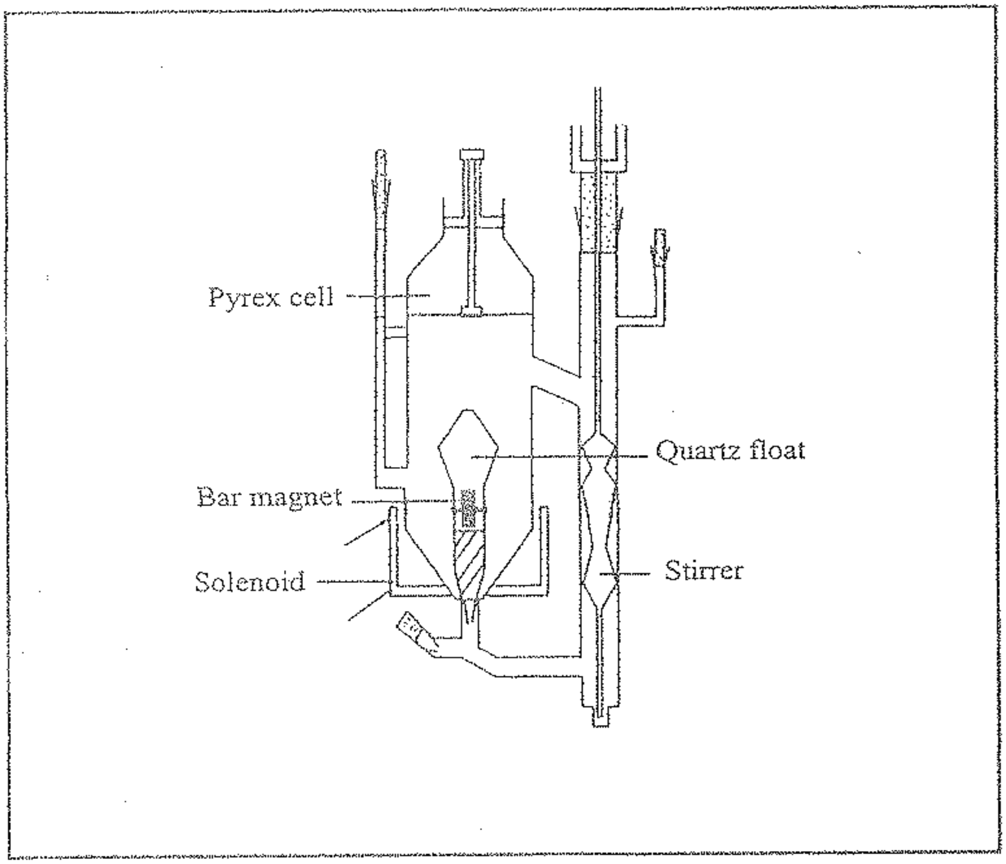

Figure 3.4 Magnetic float densitometer

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

$$\rho = -\frac{M_0}{V} + \left(\frac{c}{4\pi^2}\right)\left(\frac{1}{V^2}\right) \tag{3.12}$$

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

$$\rho = A + B\left(\frac{1}{\nu}\right)^{2} \tag{3.13}$$

where $\frac{-M_0}{V}$ and $\frac{c}{4\pi V^2}$

The constants *A* and *B* are characteristics of the oscillator. 1/< is termed the period and is given the symbol, ρ, hence :

$$\rho = A + B\tau^2 \tag{3.14}$$

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

Since densities are measured relative to a reference material:

$$\rho - \rho_o = B(\tau^2 - \tau_o^2) \tag{3.15}$$

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

In this work the Anton Paar DMA 38 vibrating tube densitometer was used to measure the excess molar volumes.

CHAPTER 4

EXPERIMENTAL

4.1 EXPERIMENTAL APPARATUS AND TECHNIQUE

A. EXCESS MOLAR VOLUMES

4.1.1 Experimental apparatus

In this work $V_{\mathrm{m}}^{\mathrm{E}}$ was determined by densimetry using the Anton Paar DMA 38 vibrating tube densitometer.

4.1.2 The Vibrating Tube Densitomer (Anton Paar DMA 38)

The density determination is based on the measurement of the oscillations of a vibrating U-shaped sample tube. This tube is filled with the liquid sample mixture and the relationship between the period ϑ and the density ρ of the mixture is given by:

$$\rho = \mathrm{A} + \mathrm{B}\,\tau^2 \tag{4.1}$$

The constants A and B are instrument constants for each individual oscillator and can be determined by two calibration measurements with samples of known density, e.g. dry air and deionised water.

A diagram of the density measuring apparatus used in this work is shown in figure 4.1.

4.1.3 Mode of Operation

The density measurements are based on the electromagnetically induced oscillation of the glass U-tube. One complete back and forth movement of a vibration is a period, its duration is the period of oscillation τ. The number of periods per second is the frequency ν.

Figure 4.1 DMA 38 Densitometer

Each glass tube vibrates at a characteristic or natural frequency. this changes when the tube is filled with the substance.

As the frequency is a function of mass. when the mass increases, the frequency decreases in other words the period of oscillation τ increases

$$\nu = \frac{1}{\tau} \tag{4.2}$$

A magnet is fixed to the measurements tube which is made to oscillate by a transmitter. A sensor measures the period of oscillation τ.

The period of oscillation is obtained from the equation:

$$\tau = 2\pi\sqrt{\frac{(\rho V_c + \mathrm{mc})}{\mathrm{K}}} \tag{4.3}$$

where ρ is the density of the sample in measurement, V_c is the volume of sample (capacity of tube), mc is the mass of the measured tube, K is the measurement tube constant.

It follows that

$$\rho = \frac{\mathrm{K}\,\tau^2}{4\pi^2 V_c} - \frac{\mathrm{mc}}{V_c} \tag{4.4}$$

The density and the period oscillation ϑ are related as follows:

$$\rho = \mathrm{A}\,\tau^2 + \mathrm{B} \tag{4.5}$$

$$\mathrm{A} = \frac{\mathrm{K}\,\tau^2}{4\pi^2 \mathrm{V_c}} \quad \text{and} \quad \mathrm{B} = -\frac{\mathrm{mc}}{\mathrm{V_c}}$$

A and B are constants which are determined by the elasticity, structure and mass of the measurement tube. In this work the density was given as the output from the DMA 38 densitometer.

4.1.4 Materials

The water content in all chemicals was determined by a Karl Fischer Coulometer [Metrohm 831]. Mass percent water content was found to be 0.0024 % in $[BMIM]^+$ $[MeSO_4]^-$, 0.0400 % in $[OMA]^+$ $[Tf_2N]^-$, 0.0400 % in $[EMIM]^+$ $[EtSO_4]^-$, 0.0016 % in methanol, 0.0061 % in ethanol, 0.0023 % in 1-propanol and 0.0041 % in 2-propanol.

The ionic liquids were used without any further purification. Methanol was first dried with potassium carbonate and then distilled before being used. Ethanol, 1-propanol and 2-propanol were first dried with magnesium turnings and then distilled before being used (Riddick and Bunger 1986).

A summary of the compounds their suppliers and purities used in this work is given in table 4.1. Tables 4.2 gives the experimental and literature values for densities of the pure compound.

Three density values for $[EMIM]^+$ $[EtSO_4]^-$ were obtained 1.2317, 1.2357 and 1.2373 because different bottles of the same chemical were used.

Table 4.1 Compound, their suppliers and mass % purity

Compound	**Supplier**	**Purity Mass %**
Methanol	Sigma Aldrich	99.9
Ethanol	Riedel-de Haën	99.8
1 Propanol	Merck	99.5
2 - Propanol	BDH Chemicals	99.7
BMIM]$^+$ [MeSO$_4$]$^-$	Sigma Aldrich	99.9
[EMIM]$^+$ [EtSO$_4$]$^-$	Solvent Innovation	99
[OMA]$^+$[Tf$_2$N]$^-$	Solvent Innovation	98

Table 4.2 Densities, ρ, of pure components at *T* = (298.15, 303.15, and 313.15) K

Chemical	ρ / (g·cm $^{-3}$)			
	Literature		**Experimental**	
	T/K 298.15	T/K 298.15	T/K 303.15	T/K 313.15
Methanol	0.78637[a]	0.7862	0.7836	0.7748
Ethanol	0.7852[a]	0.7854	0.7821	0.7739
1 Propanol	0.79960[a]	0.7994	0.7962	0.7884
2 - Propanol	0.78126[a]	0.7818	0.7777	0.7690
$[BMIM]^+ [MeSO_4]^-$	1.2124[b]	1.2120	1.2023	1.1975
$[EMIM]^+ [EtSO_4]^-$	1.2296[b]	1.2317	1.2284	1.2216
	1.2373[c]	1.2357	1.2322	1.2259
		1.2373	1.2339	1.2278
$[OMA]^+ [Tf_2N]^-$		1.1093	1.1051	1.0983

[a] (Riddick and Bunger 1986)

[b] (Domanska and Pobudkowska 2006)

[c] (González and González 2007)

4.1.5 Preparation of mixtures

Mixtures with composition spanning the entire mole fraction   range were prepared. The binary mixtures were prepared by transferring, via syringe, the pure liquids into stoppered bottles to prevent evaporation, using an OHAUS mass balance for the determination of masses of each component. The mass balance has a precision of 0.0001 g. The mixtures were shaken in order to ensure complete homogeneity of the two compounds, since the ionic liquid is slightly viscous. To avoid formation of bubbles inside the vibrating tube of the densimeter, injections were done slowly.

4.1.6 Experimental procedure for instrument

The densities were measured using an Anton Paar DMA 38 vibrating U-tube densimeter. The densimeter consists of a built-in thermostat controller capable of maintaining temperature precisely to ± 0.01 K and measuring density to ± 0.0001 $g \cdot cm^{-3}$.

Prior to each experimental run, the cell was first flushed with ethanol. After flushing compressed dry air was blown through the cell. 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 values of water, pure solvents and air were determined between each solution injection, to permit a continuous check on both sample purity and densitometer operation.

The precision of ρ, was judged by repeated measurements of the same solution at different times. Using the density and the composition of the mixtures $V_{\mathrm{m}}^{\mathrm{E}}$ was calculated according to equation 3.9.

4.1.7 Specifications of the instrument

Accuracy : 1×10^{-3} g / cm^3

Min. Sample Volume : I cm^3

Measuring Range : 0 -3 g / cm^3

Temperature Range : 15 – 40 $^{\mathrm{o}}$C

Pressure Range : 10 bar (145 psi)

4.1.8 Validation of experimental technique

The experimental technique was assessed by determination of the excess molar volumes for the test system (toluene + cyclohexane) at T = 298.15 K and comparing it with the literature values (Oswal and Maisuria 2004). The difference between experimental and literature $V_{\mathrm{m}}^{\mathrm{E}}$ were within the experimental error. The maximum uncertainty in $V_{\mathrm{m}}^{\mathrm{E}}$ is ± 0.007 cm$^{3}\cdot$ mol^{-1}

The comparison between this work and the literature data is shown in table 4.3 and graphed in figure 4.2

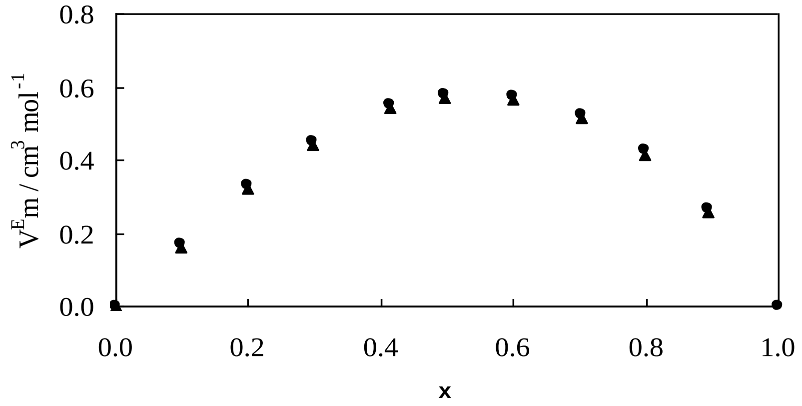

Figure 4.2 Comparison of the V_m^E from this work with the literature results for the mixtures $\{C_6H_{12}(x_1) + C_6H_5CH_3(x_2)\}$ at T = 298.15 K, ●, literature results; ▲, this work

4.2 PARTIAL MOLAR PROPERTIES

4.2.1 Partial molar volumes at infinite dilution

The partial molar volumes at infinite dilution have been used to study interactions at infinite dilution.

The thermodynamic approach, based on the concept of partial properties was proposed in order to determine the effect of each component (solute and solvent) and solute concentration on volumetric thermodynamic properties of binary solutions.

When a solute is introduced into a solvent it usually responds in some way resulting in changes in its molar volume. The contribution made by solute and solvent are not promptly identifiable through space occupancy, instead volumetric properties of a solution can be interpreted in terms of partial molar properties from solution density or specific volume (Barbosa 2003).

The volume of a binary solution, a dependent variable, is described by a set of independent variables given by two intensive variables, pressure and temperature, and the composition variable, expressed in terms of, for example, mole fraction. The procedure starts by defining the molar volume, and given by equation 4.6 at constant pressure, temperature and composition and relates the experimentally obtained solution density, ρ, derived from ultrasonic experimental data, and mole fraction of solvent and solute.

$$V^{\infty}_{\mathrm{m,i}} = \frac{1}{\rho \left(x_1 M_1 + x_2 M_2 \right)} \qquad (4.6)$$

The partial molar volume of each component, $V_{\mathrm{m,i}}$, in solution is defined as a partial derivative of solution volume and consequently depend on the variables temperature , pressure and the amount of each component, and could be expressed in terms of either number of moles, n_i or mole fraction x_i.

$$dV = \left(\frac{\partial V}{\partial T}\right)_{P,n} dT + \left(\frac{\partial V}{\partial P}\right)_{T,n} + \left(\frac{\partial V}{\partial n_1}\right)_{P,n_2} dn_1 + \left(\frac{\partial V}{\partial n_2}\right)_{P,n_1} dn_2 \tag{4.7}$$

$$V_{m,1} = \left(\frac{\partial V}{\partial n_1}\right)_{T,P,n_2} = \left(\frac{\partial n V^m}{\partial n_1}\right)_{T,P,n_2} \tag{4.8}$$

$$V_{m,2} = \left(\frac{\partial V}{\partial n_2}\right)_{T,P,n_1} = \left(\frac{\partial n V^m}{\partial n_2}\right)_{T,P,n_1} \tag{4.9}$$

Using the partial molar volumes defined in equations 4.8 and 4.9 dV from equation 4.7 becomes

$$dV = \left(\frac{\partial V}{\partial T}\right)_{P,m} = dT \left(\frac{\partial V}{\partial P}\right)_{T,n} dP + \sum V_i d n_i \tag{4.10}$$

Equation 4.9 describes how change in the volume is related to the partial molar volumes of the individual components.

4.3 EXCESS MOLAR VOLUMES MEASURED IN THIS STUDY

4.3.1 Systems Studied in this Work

In this work the excess molar volumes of mixing were determined at T = (298.15, 303.15 and 313.15) K for the three ILs over the entire composition range. The follow (IL + an alkanol) binary system was studied:

1. {1-ethyl-3-methylimidazolium ethylsulfate + methanol or 1-propanol or 2-propanol}
2. {trioctylmethylammonium bis (trifluoromethyl-sulfonyl) imide + methanol or ethanol or 1- propanol}
3. {1-buty-3-methylimidazolium methylsulfate + methanol or ethanol or 1-propanol}

B. ISENTROPIC COMPRESSIBILITY

4.4 Introduction

Measurement of the speed of sound, *u*, in liquids is a powerful source of information (e.g. to detect small changes in gas composition or the effects of small concentrations changes) about the thermophysical properties of chemical substances and their mixtures (Azevedo and Szydlowski 2004).

Speed of sound and density, are used to calculate isentropic compressibility by means of the

Newton-Laplace eqn. $k_s = \frac{1}{\rho u^2}$. (4.11)

Therefore, a number of thermodynamic functions can be derived by measuring the speed of sound over a range of pressures and temperatures. By measuring u(P,T), one can obtain ρ(P,T), V(P,T), which allows calculation of many thermodynamic functions (Barbosa 2003).

4.4.1 Ultrasonic interferometer

The instrument used in this work is a Mittal multrifrequency interferometer. It is a simple and direct device to determine the ultrasonic velocity in liquids with a high degree of accuracy.

It consists of: i) high frequency generator, which is designed to excite the quartz plate fixed at the bottom of the measuring cell at its resonant frequency to generate ultrasonic waves in the experimental liquid in the measuring cell. A macro-ammeter to observe the changes in the current and two controls for the purpose of sensitivity regulation and initial adjustments of micro-ammeter are provided on the high frequency generator.

ii) Measuring cell, which is a specially designed double walled cell for maintaining the temperature of the liquid constant during the experiment. A fine micrometer screw is provided at the top, which can lower or raise the reflector plate in the cell through a known distance. It has a quartz plate fixed at the bottom.

A diagram showing the ultrasonic interferometer is shown in figure 4.3.

4.4.2 Working Principle

The principle used in the measurement of velocity, (ν), is based on the accurate determination of the wavelength, (λ), in the medium. Ultrasonic waves of known frequency (ν) are produced by a quartz plate cell. A movable plate kept parallel to the quartz plate reflects the waves. If the separation between these plates is exactly a whole multiple of the sound wavelength, standing waves are formed in the medium. The acoustic resonance give rise to an electrical reaction on the generator driving the quartz plate and the anode current of the generator becomes maximum.

If the distance between the reflector and crystal is increased or decreased and the variation is exactly one half wavelength, ($\lambda/2$) or multiple of it, anode current again becomes maximum.

From the knowledge of wavelength, (λ), the velocity, (V), can be obtained by the relation:

Velocity =Wavelength × frequency

$$V = \lambda \times \nu \tag{4.12}$$

4.4.3 Systems Studied in this Work

In this work the speed of sound was measured over the entire composition range at T = 298.15 K, the isentropic compressibility was then calculated from the speed of sound experimental values. The systems studied are $\{[\mathrm{OMA}]^{+}[\mathrm{Tf_2N}]^{-}$ + methanol or ethanol or 1-propanol$\}$ at T = 298 K, using a multifrequency ultrasonic interferometer M-81G at 1 MHz.

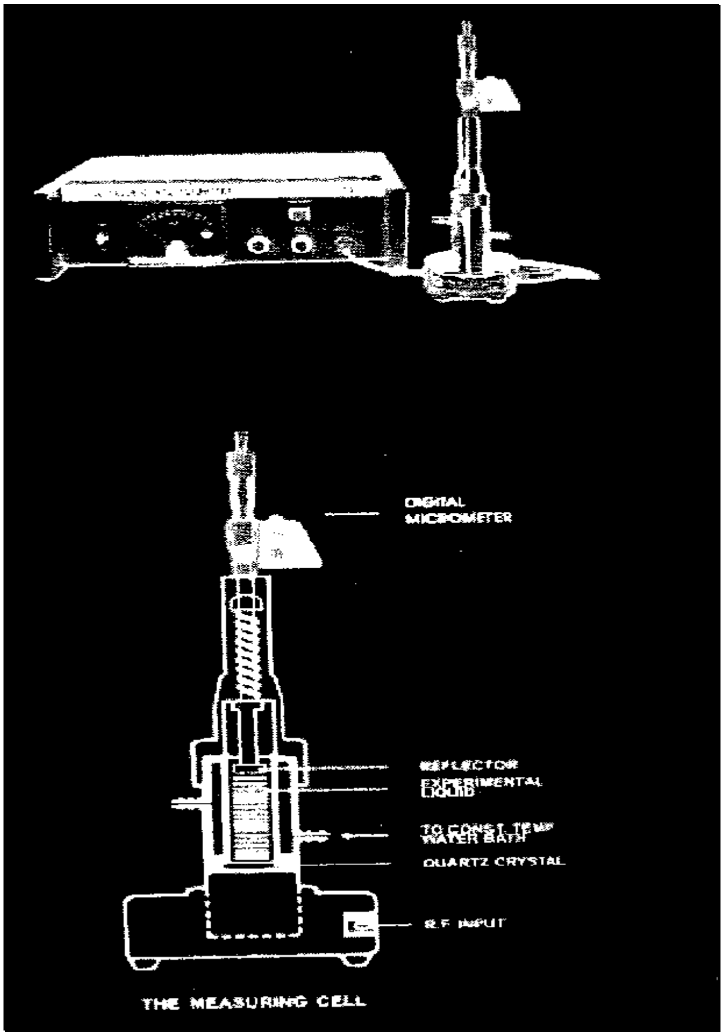

Figure 4.3 Diagram of Interferometer

CHAPTER 5

RESULTS

INTRODUCTION

The excess molar volumes of the studied systems {1-ethyl-3-methylimidazolium ethylsulfate $[EMIM]^+[EtSO_4]^-$ + methanol or 1-propanol or 2-propanol}, {trioctylmethylammonium bis (trifluoromethyl-sulfonyl) imide $[OMA]^+[Tf_2N]^-$ + methanol or ethanol or 1-propanol}, {1-buty-3-methylimidazolium methylsulfate $[BMIM]^+[MeSO_4]^-$ + methanol or ethanol or 1-propanol}were calculated from the experimental density values, using equation (5.1)

$$V_m^E = \frac{x_1 M_1 + x_2 M_2}{\rho} - \frac{x_1 M_1}{\rho_1} - \frac{x_2 M_2}{\rho_2} \tag{5.1}$$

where x_1 and x_2 are mole fractions, M_1 and M_2 are molecular masses, ρ_1 and ρ_2 are densities of the pure components, where “1” and “2” refer to the IL and alcohol, respectively, and ρ is density of the mixture.

Redlich-Kister polynomial (a smoothing equation) was fitted to the calculated excess molar volumes equation (5.2), using a commercial software programme (MathCAD).

$$V_m^E/(\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}) = x(1-x)\sum_{i=0}^{N} A_i (2x-1)^i \tag{5.2}$$

where A_i is the polynomial coefficient and N is the polynomial degree.

The error between the experimental and the calculated excess molar volume values were obtained by using equation (5.3).

The standard deviations σ (V_m^E) is defined as:

$$\sigma(V_m^E) = [(V_m^E \exp - V_m^E \mathrm{cal})^2 / n - k]^{1/2} \quad (5.3)$$

where n is the number of experimental points and k is the number of coefficients used in the Redlich –Kister correlation.

The partial molar volumes at infinite dilution, $V_{m,i}^{\infty}$, are obtained from:

$$V_{m,1}^{\infty} = [A_0 + A_1 + A_2 + A_3 \ldots] \quad (5.4)$$

And

$$V_{m,2}^{\infty} = [A_0 - A_1 + A_2 - A_3 + \ldots] \quad (5.5)$$

where A_1 are the coefficients of expansion of the Redlich -Kister polynomial.

The speed of sound for the systems {$[OMA]^+[Tf_2N]^-$ + methanol or ethanol or 1-propanol} studied were measured at T = 298.15 K and at 1 MHz. The isentropic compressibility, $k_{s,}$ was calculated from the Newton-Laplace equation:

$$k_S = \frac{1}{\rho u^2} \quad (5.6)$$

The experimental isentropic compressibility deviations, Δk_S, were obtained from the equation:

$$\Delta k_S = k_S - \sum_i^N x_i k_{S,i} \quad (5.7)$$

where $k_{s,i}$ is the isentropic compressibility of the pure component i. Redlich-Kister equation was also fitted to the Δk_S values.

(i) Excess Molar Volumes and Partial Molar Volumes

The excess molar volumes were calculated using equation (5.1).

The excess molar volumes for all the systems were obtained at three temperatures namely (298.15, 303.15 and 313.15) K.

The results for densities, ρ, and excess molar volumes, $V_{\mathrm{m}}^{\mathrm{E}}$ for {1-ethyl-3-methylimidazolium ethylsulfate $[\mathrm{EMIM}]^+$ $[\mathrm{EtSO_4}]^-$ + methanol or 1- propanol or 2-propanol}, {trioctylmethylammonium bis (trifluoromethyl-sulfonyl) imide $[\mathrm{OMA}]^+[\mathrm{Tf_2N}]^-$ + methanol or ethanol or 1-propanol} and {1-buty-3-methylimidazolium methylsulfate $[\mathrm{BMIM}]^+[\mathrm{MeSO_4}]^-$ + methanol or ethanol or 1-propanol} systems studied are given in tables 5.1 – 5.9 and plotted in figures 5.1 – 5.9

(ii) Partial Molar Volumes at infinite dilution

The partial molar volume at infinite dilution, $V_{\mathrm{m,i}}^{\infty}$, was obtained from Redlich-Kister coefficients, using equations 5.4 and 5.5.

The coefficients A_{i}, partial molar volumes at infinite dilution, $V_{\mathrm{m,i}}^{\infty}$, and standard deviations, σ obtained for all the system studied are given in tables 5.10 - 5.12

(iii) Isentropic Compressibility

The isentropic compressibilities, k_{s}, were calculated from the Newton-Laplace equation (3.6), and the experimental isentropic compressibility deviations, Δk_{S}, were obtained from equation (3.7). Redlich-Kister equation was also fitted to the Δk_{S}, values.

The results for speed of sound, u, isentropic compressibility, k_{s}, deviation in isentropic compressibility for the binary system {$[\mathrm{OMA}]^+$ $[\mathrm{Tf_2N}]^-$ + methanol or ethanol or 1-propanol} at T = 298.15 K are presented in tables 5.13 - 5.15 and plotted in figures 5.10 – 5.12.

Table 5.1 Densities, ρ, and excess molar volumes, V_m^E, for {$[EMIM]^+[EtSO_4]^-$ (x_1) + methanol (x_2)} at T = (298.15, 303.15 and 313.15) K

x_1	ρ /(g · cm^{-3})	V_m^E /(cm^3· mol^{-1})	x_1	ρ /(g · cm^{-3})	V_m^E /(cm^3· mol^{-1})
$[EMIM]^+[EtSO_4]^-$ (x_1) + Methanol (x_2)					
T = 298.15 K					
0.0338	0.8583	-0.432	0.4449	1.1510	-1.153
0.0353	0.8601	-0.398	0.4707	1.1579	-1.138
0.1229	0.9795	-0.931	0.5619	1.1787	-1.073
0.1234	0.9798	-0.922	0.5665	1.1794	-1.046
0.2522	1.0757	-1.144	0.7601	1.2086	-0.616
0.3582	1.1232	-1.171			
T = 303.15 K					
0.0338	0.8537	-0.411	0.3582	1.1195	-1.183
0.0353	0.8556	-0.382	0.4707	1.1542	-1.138
0.1229	0.9753	-0.929	0.5619	1.1747	-1.032
0.1234	0.9756	-0.921	0.5665	1.1755	-1.014
0.2026	1.0420	-1.130	0.6105	1.1830	-0.878
0.2522	1.0719	-1.157			
T = 313.15 K					
0.0338	0.8451	-0.438	0.4453	1.1406	-1.255
0.0353	0.8472	-0.419	0.4917	1.1529	-1.238
0.1234	0.9672	-0.955	0.6083	1.1771	-1.098
0.1805	1.0163	-1.021	0.8753	1.2096	-0.177
0.2771	1.0761	-1.142			
0.3582	1.1117	-1.209			

Table 5.2 Densities, ρ, and excess molar volumes, V_m^E, for {$[EMIM]^+[EtSO_4]^-$ (x_1) + 1-propanol (x_2) } at T = (298.15, 303.15 and 313.15) K

x_1	ρ /(g·cm^{-3})	V_m^E /(cm^3· mol^{-1})	x_1	ρ /(g · cm^{-3})	V_m^E /(cm^3· mol^{-1})
		$[EMIM]^+[EtSO_4]^-$ (x_1) + 1-Propanol (x_2)			
		T = 298.15 K			
0.0648	0.8683	-0.214	0.5114	1.1213	-0.569
0.1142	0.9111	-0.375	0.5814	1.1436	-0.519
0.1579	0.9447	-0.435	0.7276	1.1821	-0.347
0.2832	1.0237	-0.593	0.8789	1.2143	-0.148
0.4697	1.1067	-0.599	0.9519	1.2274	-0.029
		T = 303.15 K			
0.0648	0.8626	-0.173	0.5114	1.1181	-0.628
0.1142	0.9066	-0.336	0.5814	1.1405	-0.603
0.1579	0.9404	-0.406	0.7276	1.1794	-0.451
0.2832	1.0194	-0.558	0.8789	1.2111	-0.202
0.4697	1.1032	-0.640	0.9519	1.2242	-0.078
		T = 313.15 K			
0.0648	0.8561	-0.235	0.5114	1.1115	-0.677
0.1142	0.8998	-0.374	0.5814	1.1338	-0.614
0.1579	0.9335	-0.435	0.7276	1.1728	-0.452
0.2832	1.0129	-0.625	0.8789	1.2046	-0.192
0.4697	1.0967	-0.691	0.9519	1.2179	-0.086

Table 5.3 Densities, ρ, and excess molar volume, V_m^E, for {$[EMIM]^+[EtSO_4]^-$ (x_1) + 2-propanol (x_2)} at T = (298.15, 303.15 and 313.15) K

x_1	ρ /(g · cm^{-3})	V_m^E /(cm^3· mol^{-1})	x_1	ρ /(g · cm^{-3})	V_m^E /(cm^3· mol^{-1})
$[EMIM]^+[EtSO_4]^-$ (x_1) + 2-Propanol (x_2)					
T = 298.15 K					
0.0665	0.8522	-0.192	0.5203	1.1172	-0.388
0.1114	0.8926	-0.286	0.5882	1.1378	-0.340
0.2553	0.9954	-0.438	0.7084	1.1744	-0.246
0.3374	1.0403	-0.452	0.8825	1.2147	-0.082
0.4452	1.0889	-0.440	0.9545	1.2289	-0.026
T = 303.15 K					
0.0665	0.8483	-0.218	0.5203	1.1146	-0.539
0.1114	0.8890	-0.323	0.5882	1.1371	-0.468
0.2553	0.9924	-0.555	0.7084	1.1714	-0.334
0.3374	1.0378	-0.622	0.8825	1.2115	-0.125
0.4452	1.0864	-0.606	0.9545	1.2258	-0.046
T = 313.15 K					
0.0665	0.8396	-0.220	0.5203	1.1078	-0.617
0.1114	0.8810	-0.392	0.5882	1.1302	-0.509
0.2553	0.9851	-0.664	0.7084	1.1642	-0.330
0.3374	1.0306	-0.717	0.8825	1.2051	-0.129
0.4452	1.0794	-0.687	0.9545	1.2193	-0.032

Table 5.4 Densities, ρ, and excess molar volumes, V_m^E, for {$[BMIM]^+[MeSO_4]^-$ (x_1) + methanol (x_2)} at T = (298.15, 303.15 and 313.15) K

x_1	ρ /(g · cm^{-3})	V_m^E /(cm^3· mol^{-1})	x_1	ρ /(g . cm^{-3})	V_m^E /(cm^3· mol^{-1})
		$[BMIM]^+[MeSO_4]^-$ (x_1) + Methanol (x_2)			
		T = 298.15 K			
0.0533	0.8905	-0.308	0.5589	1.1628	-0.936
0.1131	0.9638	-0.644	0.6518	1.1775	-0.771
0.1936	1.0329	-0.914	0.7169	1.1858	-0.617
0.2651	1.0748	-1.057	0.7935	1.1944	-0.432
0.3228	1.1002	-1.100	0.8510	1.1997	-0.291
0.4386	1.1371	-1.094	0.9206	1.2058	-0.147
		T = 303.15 K			
0.0533	0.8841	-0.407	0.5589	1.1575	-1.321
0.1131	0.9596	-0.695	0.6518	1.1717	-1.171
0.1936	1.0294	-1.101	0.7169	1.1794	-0.987
0.2651	1.0713	-1.318	0.7935	1.1871	-0.754
0.3228	1.0964	-1.406	0.8510	1.1921	-0.571
0.4386	1.1325	-1.444	0.9206	1.1975	-0.353
		T = 313.15 K			
0.0533	0.8740	-0.321	0.5589	1.1535	-1.531
0.1131	0.9504	-0.629	0.6518	1.1680	-1.405
0.1936	1.0207	-1.022	0.7169	1.1758	-1.227
0.2651	1.0630	-1.225	0.7935	1.11833	-0.957
0.3228	1.0890	-1.355	0.8510	1.1880	-0.720
0.4386	1.1270	-1.520	0.9206	1.1930	-0.424

Table 5.5 Densities, ρ, and excess molar volumes, V_m^E, for {$[BMIM]^+[MeSO_4]^-$ (x_1) + ethanol (x_2)} at T = (298.15, 303.15 and 313.15) K

x_1	ρ /(g · cm^{-3})	V_m^E /(cm^3· mol^{-1})	x_1	ρ /(g · cm^{-3})	V_m^E /(cm^3· mol^{-1})
$[BMIM]^+[MeSO_4]^-$ (x_1) + Ethanol (x_2)					
		T = 298.15 K			
0.0738	0.8814	-0.202	0.6223	1.1533	-0.524
0.1547	0.9573	-0.403	0.7231	1.1731	-0.415
0.2046	0.9950	-0.508	0.8249	1.1896	-0.281
0.3165	1.0560	-0.615	0.8877	1.1983	-0.173
0.4056	1.0926	-0.647	0.9424	1.2052	-0.079
0.5095	1.1256	-0.619			
		T = 303.15 K			
0.0738	0.8771	-0.214	0.6223	1.1460	-0.698
0.1547	0.9520	-0.418	0.7231	1.1652	-0.568
0.2046	0.9893	-0.537	0.8249	1.1810	-0.385
0.3165	1.0500	-0.713	0.8877	1.1895	-0.276
0.4056	1.0862	-0.775	0.9424	1.1960	-0.141
0.5095	1.1187	-0.767			
		T = 313.15 K			
0.0738	0.8694	-0.236	0.6223	1.1414	-0.844
0.1547	0.9445	-0.427	0.7231	1.1609	-0.729
0.2046	0.9819	-0.533	0.8249	1.1768	-0.535
0.3165	1.0437	-0.767	0.8877	1.1851	-0.377
0.4056	1.0806	-0.869	0.9424	1.1915	-0.210
0.5095	1.1134	-0.859			

Table 5.6 Densities, ρ, and excess molar volumes, V_{m}^{E}, for {$[BMIM]^{+}[MeSO_4]^{-}$ (x_1) + 1-propanol (x_2)} at T = (298.15, 303.15 and 313.15 K

x_1	ρ /(g · cm^{-3})	V_{m}^{E} /(cm^{3}· mol^{-1})	x_1	ρ /(g · cm^{-3})	V_{m}^{E} /(cm^{3}· mol^{-1})
$[BMIM]^{+}[MeSO_4]^{-}$ (x_1) + 1-Propanol (x_2)					
T = 298.15 K					
0.1011	0.8978	-0.099	0.5862	1.1293	-0.223
0.1258	0.9175	-0.121	0.6708	1.1508	-0.190
0.2100	0.9752	-0.176	0.7775	1.1740	-0.139
0.2639	1.0060	-0.205	0.8542	1.1885	-0.100
0.3556	1.0500	-0.230	0.9168	1.1897	-0.064
0.4756	1.0957	-0.235	0.9600	1.1992	-0.059
T = 303.15 K					
0.1011	0.8930	-0.094	0.5862	1.1121	-0.227
0.1258	0.9128	-0.124	0.6708	1.1423	-0.193
0.2100	0.9698	-0.194	0.7775	1.1650	-0.133
0.2639	1.0001	-0.221	0.8542	1.1792	-0.090
0.3556	1.0434	-0.248	0.9168	1.1897	-0.055
0.4756	1.0883	-0.251	0.9600	1.1964	-0.023
T = 313.15 K					
0.1011	0.8858	-0.097	0.5862	1.1156	-0.257
0.1258	0.9054	-0.129	0.6708	1.1371	-0.248
0.2100	0.9626	-0.187	0.7775	1.1600	-0.179
0.2639	0.9931	-0.213	0.8542	1.1743	-0.124
0.3556	1.0368	-0.246	0.9168	1.1848	-0.067
0.4756	1.0822	-0.260	0.9600	1.1916	-0.037

Table 5.7 Densities, ρ, and excess molar volumes, $V_{\mathrm{m}}^{\mathrm{E}}$, for $\{[\mathrm{OMA}]^+[\mathrm{Tf_2N}]^-$ (x_1) + methanol (x_2)} at T = (298.15 , 303.15 and 313.15) K

x_1	ρ /(g · cm^{-3})	$V_{\mathrm{m}}^{\mathrm{E}}$ /(cm^3· mol^{-1})	x_1	ρ /(g · cm^{-3})	$V_{\mathrm{m}}^{\mathrm{E}}$ /(cm^3· mol^{-1})
		{$[\mathrm{OMA}]^+[\mathrm{Tf_2N}]^-$ (x_1) + Methanol (x_2)}			
		T = 298.15 K			
0.0781	0.9578	0.600	0.5362	1.0887	0.652
0.1291	0.9990	0.860	0.6529	1.0966	0.356
0.2125	1.0370	0.965	0.7084	1.0995	0.229
0.3500	1.0679	0.972	0.8522	1.1057	-0.234
0.4172	1.0770	0.910	0.9345	1.1079	-0.224
		T = 303.15 K			
0.0781	0.9535	0.546	0.5362	1.0826	1.180
0.1291	0.9941	0.877	0.6529	1.0915	0.626
0.2125	1.0311	1.164	0.7084	1.0950	0.288
0.3500	1.0615	1.396	0.8522	1.1015	-0.292
0.4172	1.0707	1.380	0.9345	1.1037	-0.280
		T = 313.15 K			
0.0781	0.9400	1.050	0.5362	1.0761	1.096
0.1291	0.9818	1.423	0.6529	1.0845	0.730
0.2125	1.0217	1.503	0.7084	1.0877	0.526
0.3500	1.0545	1.409	0.8522	1.0947	-0.224
0.4172	1.0640	1.339	0.9345	1.0972	-0.344

Table 5.8 Densities, ρ, and excess molar volumes, V_m^E, for {[OMA]$^+$[Tf$_2$N]$^-$ (x_1) + ethanol (x_2)} at T = (298.15, 303.15 and 313.15) K

x_1	ρ /(g · cm^{-3})	V_m^E /(cm^3· mol^{-1})	x_1	ρ /(g · cm^{-3})	V_m^E /(cm^3· mol^{-1})
{[OMA]$^+$[Tf$_2$N]$^-$ (x_1) + Ethanol (x_2)}					
		T = 298.15 K			
0.0484	0.8955	-0.043	0.5145	1.0802	0.360
0.1731	1.0050	-0.042	0.6307	1.0900	0.498
0.2728	1.0410	0.037	0.7338	1.0965	0.594
0.3353	1.0552	0.123	0.7774	1.0989	0.590
0.4286	1.0704	0.217	0.9393	1.1071	0.241
		T = 303.15 K			
0.0484	0.8956	-0.467	0.5145	1.0715	1.736
0.1731	1.0034	-0.455	0.6307	1.0818	1.940
0.2728	1.0361	0.153	0.7338	1.0896	1.697
0.3353	1.0495	0.440	0.7774	1.0922	1.663
0.4286	1.0625	1.194	0.9493	1.1027	0.342
		T = 313.15 K			
0.0484	0.8833	-0.074	0.5145	1.0680	0.649
0.1731	0.9935	-0.113	0.6307	1.0779	0.840
0.2728	1.0293	0.044	0.7338	1.0847	0.886
0.3353	1.0436	0.138	0.7774	1.0872	0.864
0.4286	1.0584	0.385	0.9493	1.0959	0.338

Table 5.9 Densities, ρ, and excess molar volumes, V_m^E, for {$[OMA]^+[Tf_2N]^-$ (x_1) + 1-propanol (x_2)} at T = (298.15, 303.15 and 313.15) K

x_1	ρ /(g · cm^{-3})	V_m^E /(cm^3· mol^{-1})	x_1	ρ /(g · cm^{-3})	V_m^E /(cm^3· mol^{-1})
{$[OMA]^+[Tf_2N]^-$ (x_1) + 1-Propanol (x_2)}					
T = 298.15 K					
0.0736	0.9191	-0.032	0.5240	1.0762	0.285
0.1146	0.9560	-0.025	0.6882	1.0915	0.371
0.2152	1.0109	0.014	0.7833	1.0979	0.357
0.3303	1.0452	0.101	0.8439	1.1015	0.296
0.4033	1.0594	0.183	0.9533	1.1070	0.138
T = 303.15 K					
0.0736	0.9145	-0.032	0.5240	1.0717	0.352
0.1146	0.9515	-0.032	0.6882	1.0871	0.393
0.2152	1.0063	0.040	0.7833	1.0937	0.346
0.3303	1.0406	0.153	0.8439	1.0973	0.288
0.4033	1.0548	0.253	0.9533	1.1030	0.084
T = 313.15 K					
0.0736	0.9072	-0.081	0.5240	1.0637	0.678
0.1146	0.9441	-0.059	0.6882	1.0796	0.631
0.2152	0.9987	0.085	0.7833	1.0866	0.450
0.3303	1.0325	0.371	0.8439	1.0904	0.315
0.4033	1.0467	0.524	0.9533	1.0962	0.079

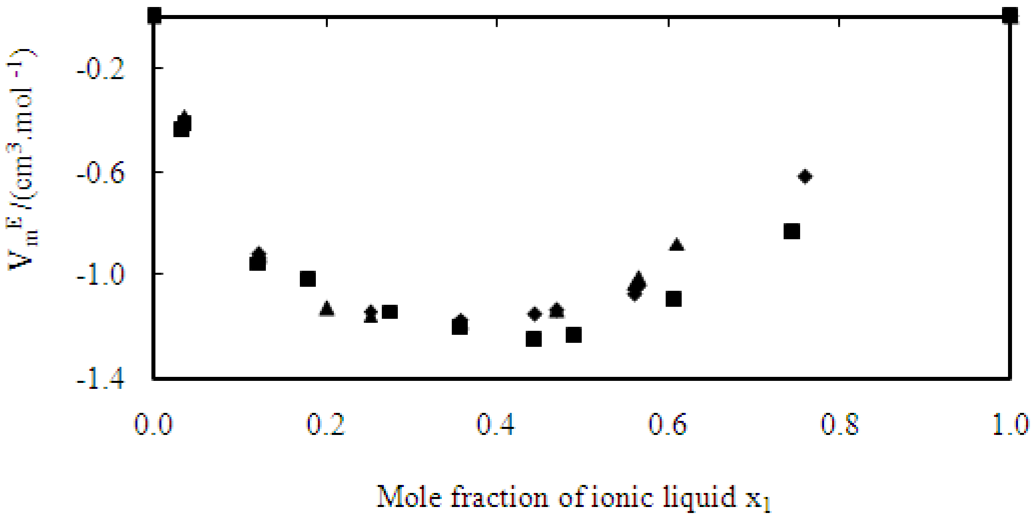

Figure 5.1 **Plot of excess molar volumes, V_m^E, of binary mixtures of {$[EMIM]^+[EtSO_4]^-$ (x_1) + Methanol (x_2)} against mole fraction of ionic liquid ♦ at T = 298.15 K, ▲ at T = 303.15 K, ■ at T = 313 K**

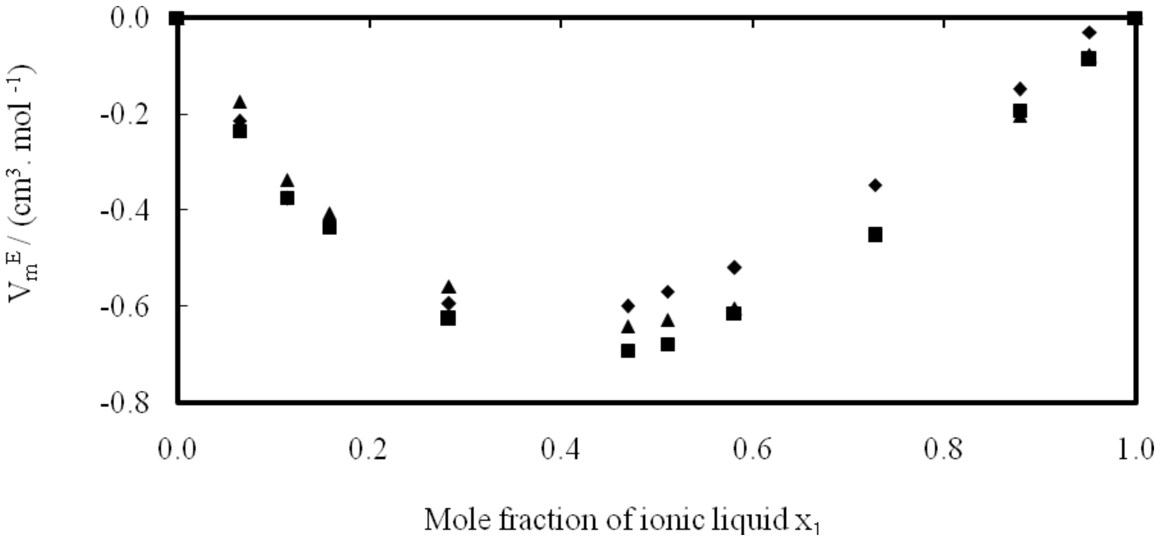

Figure 5.2 **Plot excess molar volumes, V_m^E, of binary mixtures of {EMIM]$^+$[EtSO$_4$]$^-$ (x_1) + 1-propanol (x_2)} against mole fraction of ionic liquid ♦ at T = 298.15 K, ▲ at T = 303.15 K, ■ at T = 313.15 K**

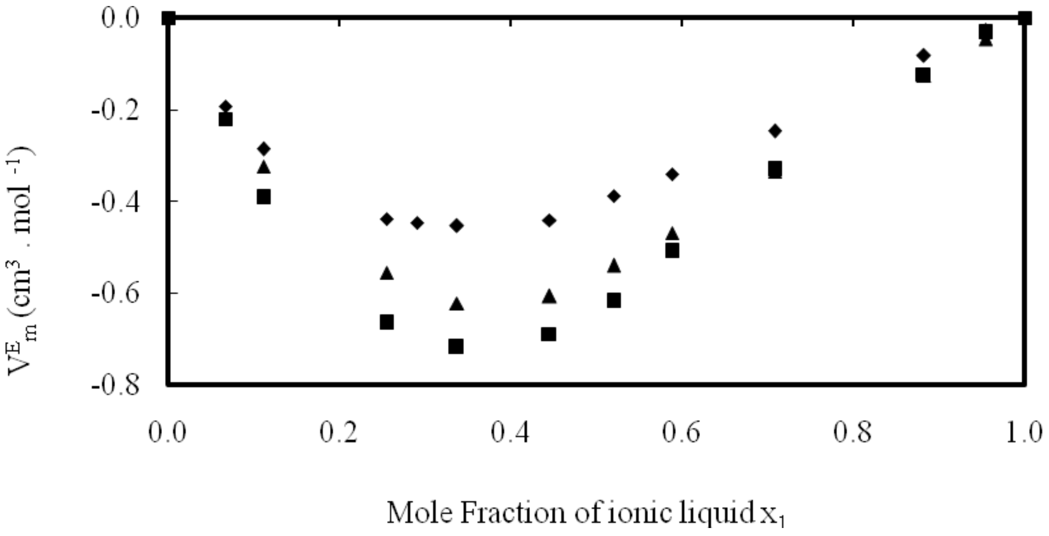

Figure 5.3 **Plot excess molar volumes, V^E_m, of binary mixtures of {$[EMIM]^+[EtSO_4]^-$ (x_1) + 2-Propanol (x_2)} against mole fraction of ionic liquid ♦ at T = 298.15 K, ▲ at T = 303.15 K, ■ at T = 313 K**

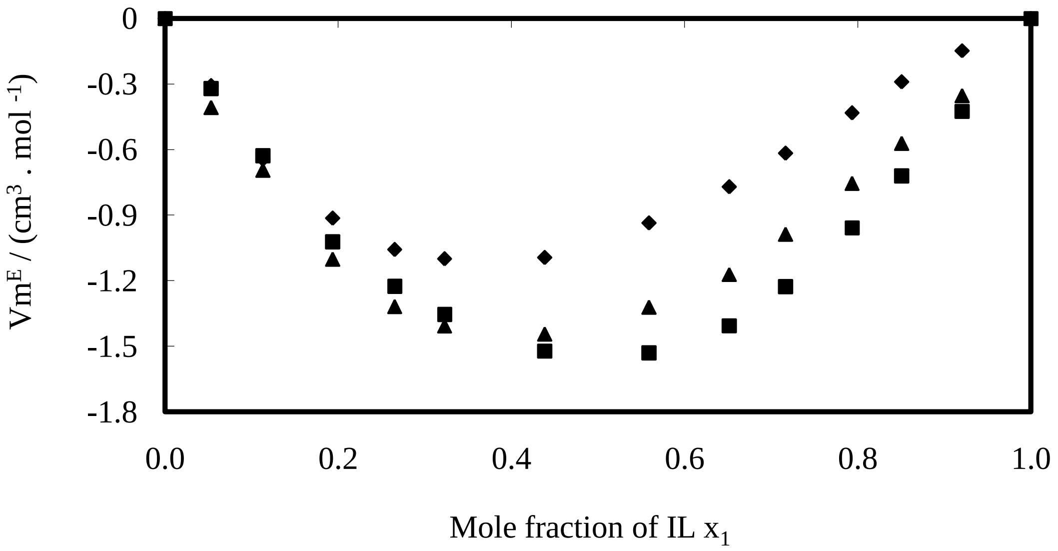

Figure 5.4 **Plot of excess molar volumes, V_m^E, of binary mixtures of {$[BMIM]^+[MeSO_4]^-$ (x_1) + Methanol (x_2)} against mole fraction of ionic liquid ♦ at *T* = 298.15 K, ▲ at *T* = 303.15 K, ■ at *T* = 313.15 K**

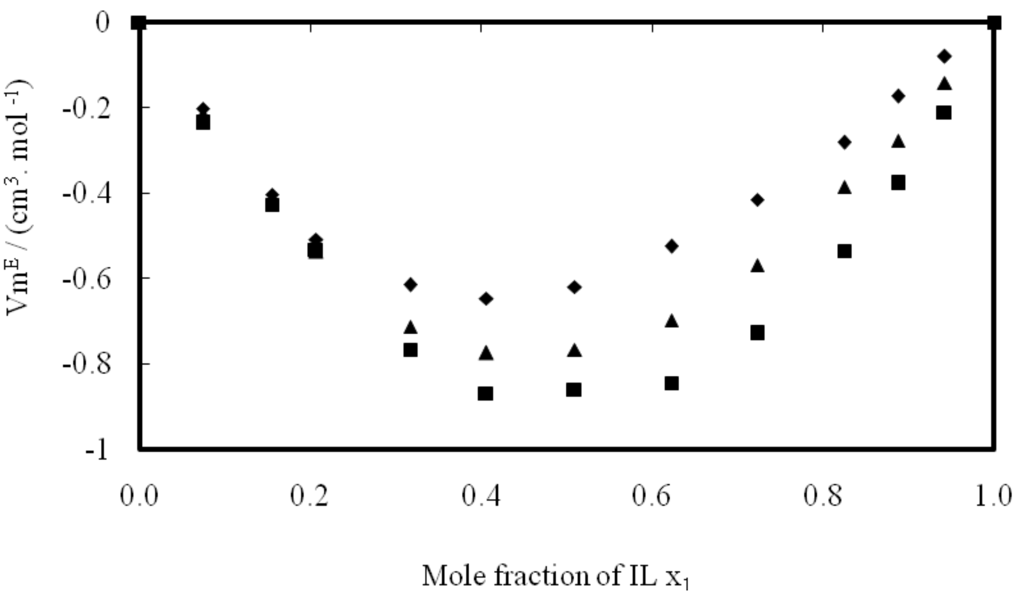

Figure 5.5 Plot excess molar volumes, V_m^E, of binary mixtures of {$[BMIM]^+[MeSO_4]^-$ (x_1) + Ethanol (x_2)} against mole fraction of ionic liquid ♦ at T = 298.15 K, ▲ at T = 303.15 K, ■ at T = 313.15 K

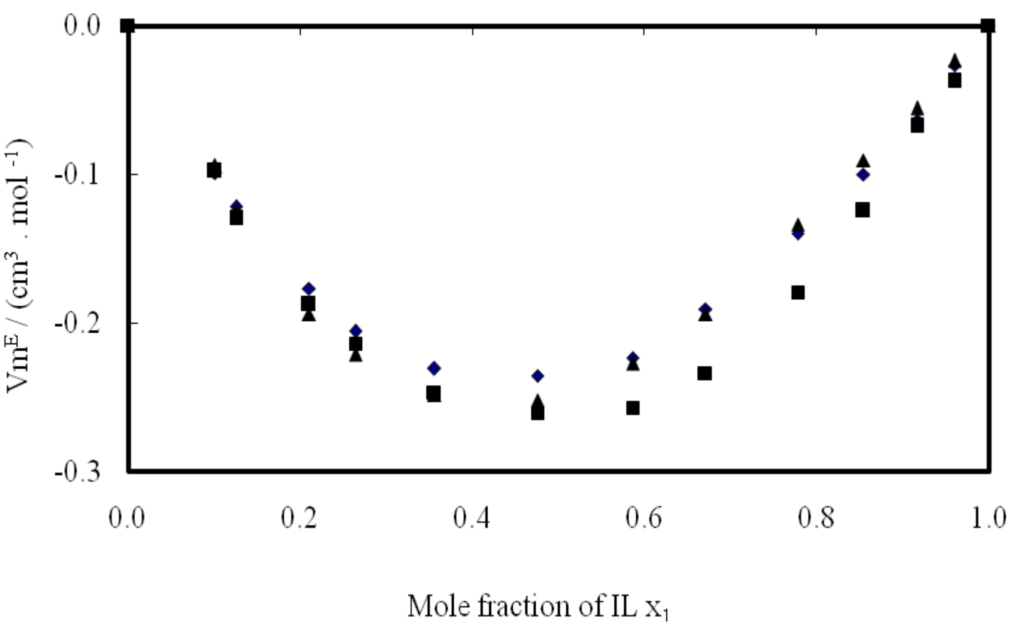

Figure 5.6 **Plot excess molar volumes, V_m^E, of binary mixtures of {$[BMIM]^+[MeSO_4]^-$ (x_1) + 1-Propanol (x_2)} against mole fraction of ionic liquid ♦ at T = 298.15 K, ▲ at T = 303.15 K, ■ at T = 313.15 K**

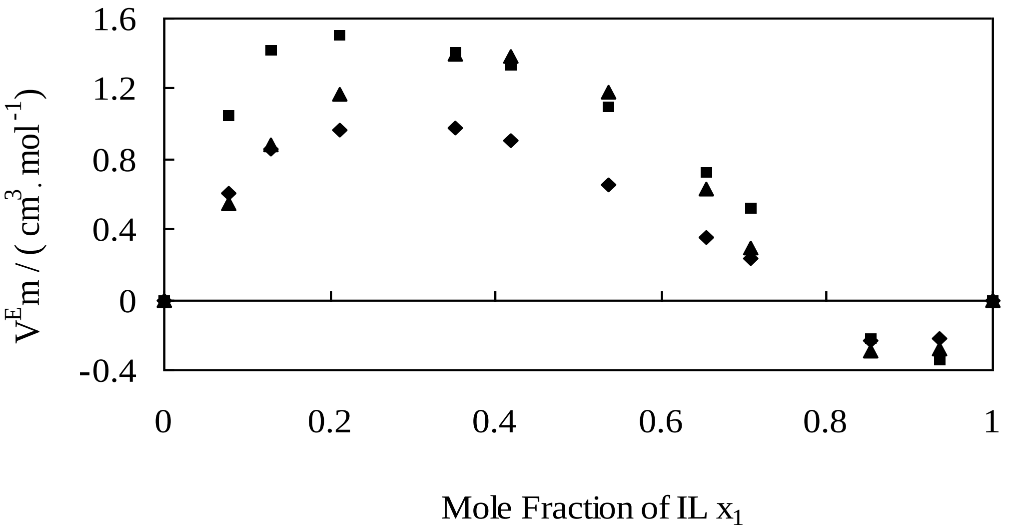

Figure 5.7 Plot of excess molar volumes, V_m^E, of binary mixtures of {$[OMA]^+ [Tf_2N]^-$ (x_1) + methanol (x_2)} against mole fraction of ionic liquid ♦ at T = 298.15 K, ▲ at T = 303.15 K, ■ at T = 313 K

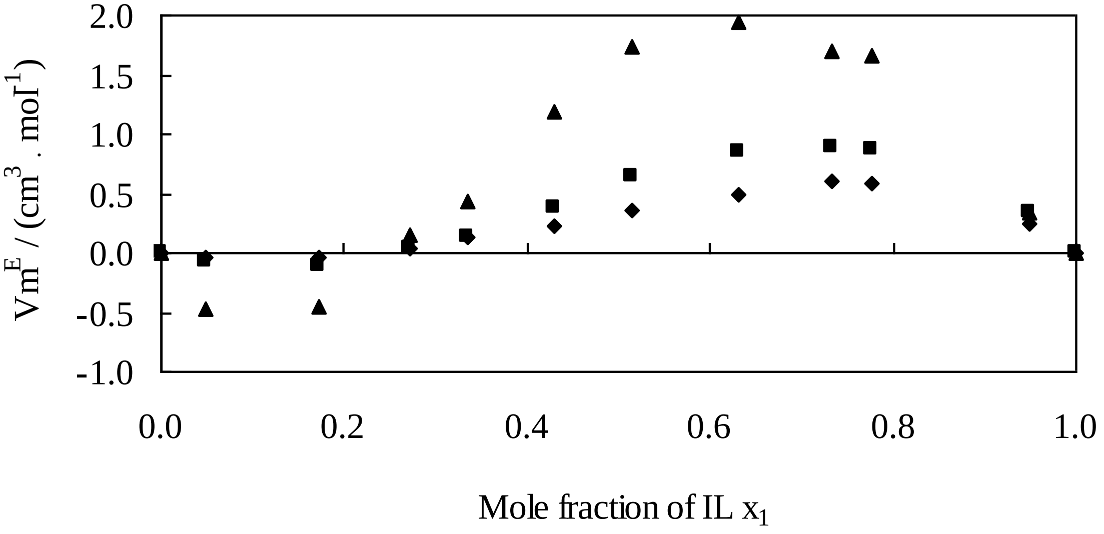

Figure 5.8 Plot excess molar volumes, V_m^E, of binary mixtures of {$[OMA]^+ [Tf_2N]^-$ (x_1) + ethanol (x_2)} against mole fraction of ionic liquid ♦ at T = 298.15 K, ▲ at T = 303.15 K, ■ at T = 313 K

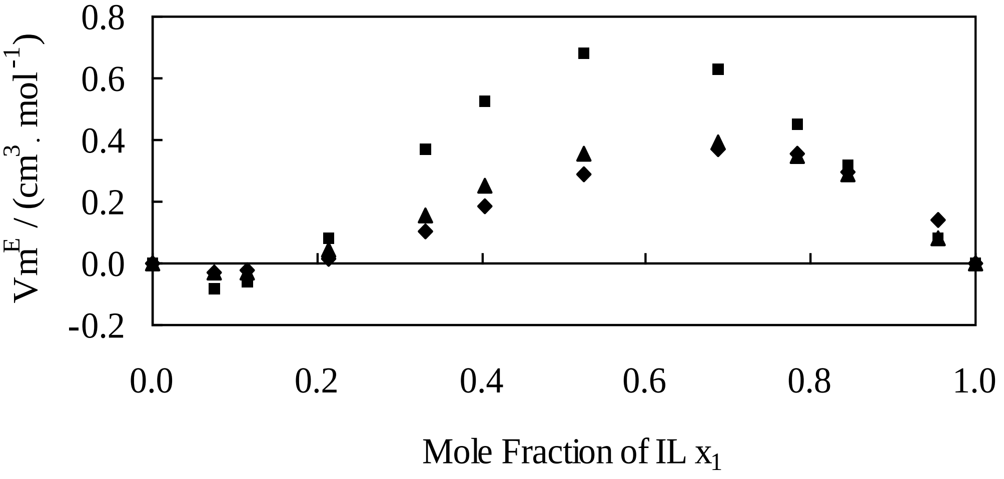

Figure 5.9 **Plot excess molar volumes, V_m^E, of binary mixtures of {[OMA]$^+$ [Tf$_2$N]$^-$ (x_1) + 1-Propanol (x_2)} against mole fraction of ionic liquid ♦ at T = 298.15 K, ▲ at T = 303.15 K, ■ at T = 313.15 K**

Table 5.10 The coefficients A_i, partial molar volumes at infinite dilution, $V_{m,i}^{\infty}$, and standard deviations, σ, obtained for [EMIM]$^+$[EtSO$_4$]$^-$ + methanol or 1-propanol or 1- propanol} at T = (298.15, 303.15 and 313.15) K

T / K	A_0	A_1	A_2	A_3	A_4	$V_{m,1}^{\infty}$ (cm^3 · mol^{-1})	$V_{m,2}^{\infty}$ (cm^3 · mol^{-1})	σ (cm^3 · mol^{-1})
{[EMIM]$^+$[EtSO$_4$]$^-$ (x_1) + Methanol (x_2)}								
298.15	-4.527	-1.704	0.317	-3.608	-4.585	-10.499	-3.483	0.017
303.15	-4.752	-4.206	4.349	-1.771	-7.187	-13.567	-1.613	0.092
313.15	-5.049	-2.990	8.622	-3.554	-14.493	-17.464	-4.376	0.081
{[EMIM]$^+$[EtSO$_4$]$^-$ (x_1) + 1-Propanol (x_2)}								
298.15	-2.317	-1.229	-0.309	-0.410	0.336	-3.929	-0.651	0.012
303.15	-2.533	-0.455	-0.144	-0.571	0.296	-3.407	-1.355	0.012
313.15	-2.720	-0.824	0.467	-0.486	0.802	-4.365	-1.745	0.010
{[EMIM]$^+$[EtSO$_4$]$^-$ (x_1) + 2-Propanol (x_2)}								
298.15	-1.615	-1.138	-0.357	-0.350	0.006	-3.476	-0.491	0.004
303.15	-2.251	-1.613	0.160	0.482	-0.264	-3.540	-1.170	0.007
313.15	2.530	-2.286	0.101	0.898	0.087	-3.730	-0.954	0.010

Table 5.11 The coefficients $A_{i,}$ partial molar volumes at infinite dilution, $V^{\infty}_{\mathrm{m,i}}$ and standard deviations, σ obtained for {$[\mathrm{BMIM}]^{+}[\mathrm{MeSO_4}]^{-}$ + methanol or ethanol or 2-propanol} at T = (298.15, 303.15 and 313.15) K

T / K	A_0	A_1	A_2	A_3	A_4	$V^{\infty}_{\mathrm{m,1}}$ ($\mathrm{cm^3 \cdot mol^{-1}}$)	$V^{\infty}_{\mathrm{m,2}}$ ($\mathrm{cm^3 \cdot mol^{-1}}$)	σ ($\mathrm{cm^3 \cdot mol^{-1}}$)
{$[\mathrm{BMIM}]^{+}[\mathrm{MeSO_4}]^{-}$ (x_1) + Methanol (x_2)}								
298.15	-4.104	-2.585	-0.545	-0.152	0.663	-6.723	-1.249	0.011
303.15	-5.647	-2.158	-0.452	0.681	-0.084	-7.66	-4.706	0.021
313.15	-6.200	-0.154	0.103	-0.572	0.267	-6.556	-5.104	0.017
{$[\mathrm{BMIM}]^{+}[\mathrm{MeSO_4}]^{-}$ (x_1) + Ethanol (x_2)}								
298.15	-2.473	-1.035	-0.475	-0.306	0.993	-2.684	-1.226	0.005
303.15	-3.108	-0.619	0.197	0.512	0.164	-2.854	-2.64	0.006
313.15	-3.551	0.095	0.146	0.427	-0.193	-3.076	-4.12	0.017
{$[\mathrm{BMIM}]^{+}[\mathrm{MeSO_4}]^{-}$ (x_1) + 1-Propanol (x_2)}								
298.15	-0.908	-0.099	-0.676	-0.399	1.424	-0.658	0.338	0.025
303.15	-0.975	-0.309	-0.368	-0.030	1.035	-0.647	0.031	0.013
313.15	-1.028	0.149	-0.844	-0.637	1.697	-0.663	0.313	0.018

Table 5.12 The coefficients A_i, partial molar volumes at infinite dilution, $V_{m,i}^{\infty}$ and standard deviation, σ obtained for ionic liquid {$[OMA]^+ [Tf_2N]^-$ (x_1) + a) methanol or ethanol or 1-propanol at T = (298.15, 303.15 and 313.15) K

T / K	A_0	A_1	A_2	A_3	A_4	$V_{m,1}^{\infty}$ ($cm^3 \cdot mol^{-1}$)	$V_{m,2}^{\infty}$ ($cm^3 \cdot mol^{-1}$)	σ ($cm^3 \cdot mol^{-1}$)
			{$[OMA]^+[Tf_2N]^-$ (x_1) + Methanol (x_2)}					
298.15	3.007	3.916	-0.520	4.536	-0.273	10.666	-6.238	0.026
303.15	5.047	5.462	-6.581	2.777	3.011	9.716	-6.762	0.028
313.15	4.378	3.741	0.362	11.313	-0.082	20.072	-10.036	0.026
			{$[OMA]^+[Tf_2N]^-$ (x_1) + Ethanol (x_2)}					
298.15	1.319	-2.893	1.444	-0.630	-0.727	-1.487	5.559	0.009
303.15	6.409	-9.592	-7.420	0.389	-2.197	-12.411	6.773	0.069
313.15	2.364	-4.915	-0.547	0.272	1.245	-1.581	-7.705	0.010
			{$[OMA]^+[Tf_2N]^-$ (x_1) + 1-Propanol (x_2)}					
298.15	1.077	-1.698	-0.113	-0.220	0.338	-0.636	3.22	0.007
303.15	1.339	-1.606	-0.524	0.051	-0.293	-0.293	-1.03	0.008
313.15	2.666	-1.902	-3.327	0.128	0.237	-2.198	1.35	0.006

Table 5.13 Speed of sound, *u*, isentropic compressibility, k_s, deviations in isentropic compressibility, Δk_s, standard deviation, σ, Redlich-Kister parameters, A_i, for the binary system $\{[OMA]^+ [Tf_2N]^- (x_1) + \text{methanol } (x_2)\}$ at T = 298.15 K

x_1	ρ /(g·cm^{-3})	u / (m·s^{-1})	k_s / (T Pa^{-1})	Δk_S / (T Pa^{-1})
		$\{[OMA]^+[Tf_2N]^- (x_1) + \text{Methanol } (x_2)\}$		
0.0336	0.8945	1097.8	1043.4	- 1.8
0.1291	0.9990	1085.4	1034.6	- 83.6
0.2125	1.0370	1074.5	1026.8	- 138.7
0.4172	1.0770	1047.9	1008.0	- 146.2
0.5362	1.0887	1032.4	997.0	- 96.5
0.6611	1.0949	1016.1	985.4	- 53.6
0.7084	1.0993	1010.0	981.1	- 22.2
0.8522	1.1057	991.2	967.8	30.1

Δk_s / (T Pa^{-1})	A_0	A_1	A_2	A_3	A_4	$\sigma(\Delta k_s)$/T Pa^{-1}
	-452.5	-844.5	-366.2	261.9	1535.0	4.6

Table 5.14 Speed of sound, *u*, isentropic compressibility, k_s, deviations in isentropic compressibility, Δk_s, standard deviation, σ, and Redlich-Kister parameters, A_i, for the binary system {$[OMA]^+ [Tf_2N]^-$ (x_1) + ethanol (x_2)} at *T* = 298.15 K

x_1	ρ /(g·cm^{-3})	*u* /(m·s^{-1})	k_s / (T Pa^{-1})	Δk_S / (T Pa^{-1})
		{$[OMA]^+[Tf_2N]^-$ (x_1) + Ethanol (x_2)}		
0.1731	1.0050	1116.1	965.2	- 89.6
0.2728	1.0410	1098.8	963.9	- 121.7
0.3353	1.0552	1087.9	963.0	- 122.8
0.4286	1.0704	1071.6	961.8	- 107.9
0.5145	1.0802	1056.6	960.6	- 108.0
0.6307	1.0900	1036.4	959.1	- 59.7
0.7338	1.0965	1018.4	957.7	- 30.9
0.7774	1.0989	1010.8	957.1	- 13.5
0.9493	1.1071	980.8	954.8	46.0

Δks / (TPa^{-1})	A_0	A_1	A_2	A_3	A_4	$\sigma(\Delta k_s)$/T Pa^{-1}
	-399.4	-405.8	-219.5	-374.9	1304	4.6

Table 5.15 Speed of sound, *u*, isentropic compressibility, k_s, deviations in isentropic compressibility, Δk_s, standard deviation, σ, and Redlich-Kister parameters, A_i, for the binary system $\{[OMA]^+ [Tf_2N]^- (x_1) + \text{1-propanol} (x_2)\}$ at *T* = 298.15 K

x_1	ρ /(g·cm^{-3})	u / (m·s^{-1})	k_s / (T Pa^{-1})	Δk_S / (T Pa^{-1})
$\{[OMA]^+[Tf_2N]^- (x_1) + \text{1-Propanol} (x_2)\}$				
0.0736	0.9191	1187.7	868.4	21.1
0.1146	0.9560	1178.1	872.2	5.0
0.2152	1.0109	1154.7	881.5	- 14.2
0.3303	1.0452	1127.9	892.2	- 27.7
0.4033	1.0594	1110.9	898.9	- 42.7
0.5240	1.0762	1082.8	910.1	- 41.0
0.6682	1.0915	1049.2	923.4	- 28.9
0.7833	1.0970	1022.4	934.1	- 7.8
0.8439	1.1015	1008.3	939.7	9.5
0.9533	1.1071	982.9	949.8	42.6

Δks / (TPa^{-1})	A_0	A_1	A_2	A_3	A_4	$\sigma(\Delta k_s)$/T Pa^{-1}
	-154.0	52.22	-158.7	-317.8	1296.0	4.6

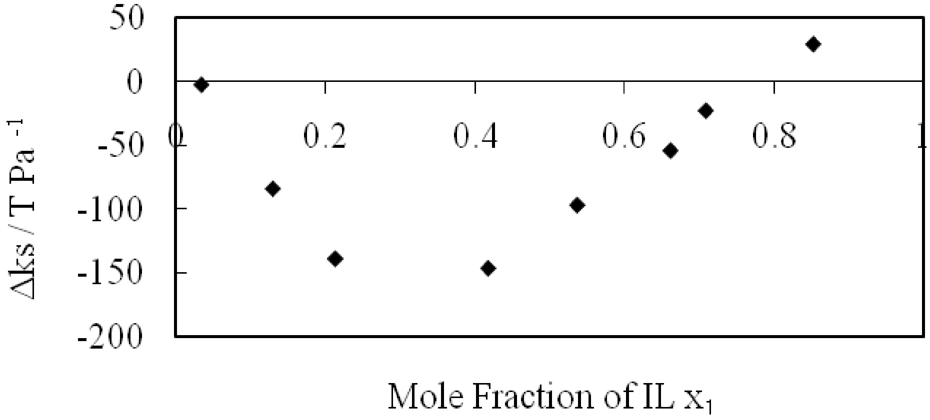

Figure 5.10. Plot of deviation in isentropic compressibilities against mole fraction of IL at *T* = 298.15 K for {trioctylmethylammonium bis (trifluoromethylsulfonyl) imide $[OMA]^+ [Tf_2N]^-$ (x_1) + methanol (x_2)}

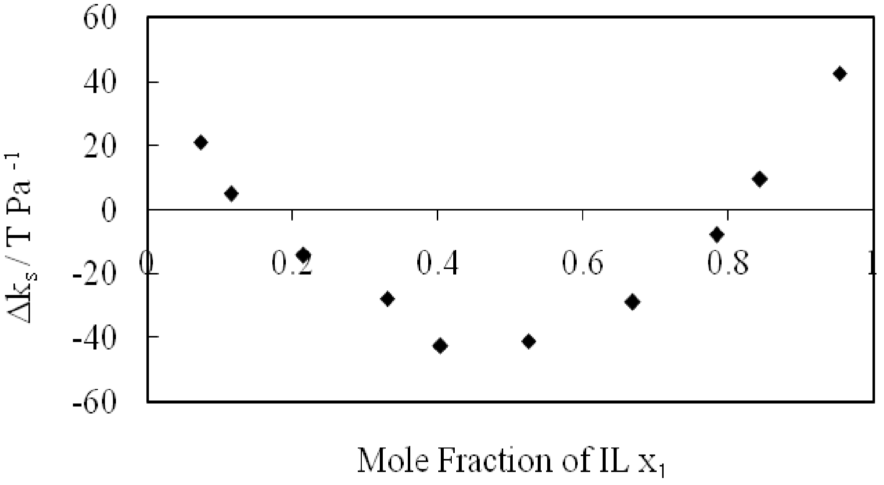

Figure 5.11. Plot of deviation in isentropic compressibilities against mole fraction of IL at T = 298.15 K for { trioctylmethylammonium bis (trifluoromethylsulfonyl) imide $[OMA]^+ [Tf_2N]^-$ (x_1) + ethanol (x_2)}

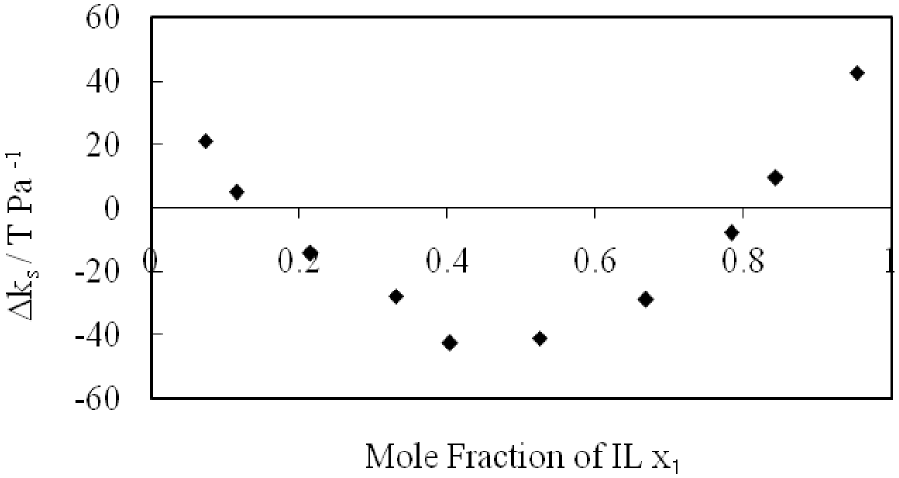

Figure 5.12. Plot of deviation in isentropic compressibilities against mole fraction of IL at T =298.15 K for {trioctylmethylammonium bis (trifluoromethylsulfonyl) imide $[OMA]^+$ $[Tf_2N]^-$ (x_1) + 1-propanol (x_2)}

CHAPTER 6

DISCUSSION

The results obtained in this work for the binary systems {$[EMIM]^+$ $[EtSO_4]^-$ + methanol or 1-propanol or 2-propanol}, {$[OMA]^+[Tf_2N]^-$ + methanol or ethanol or 1-propanol}, {$[BMIM]^+[MeSO_4]^-$ + methanol or ethanol or 1-propanol}, over the entire composition range at T = (298.15, 303.15 and 313.15) K and the speed of sound, u, at T = 298.15 K and 1MHz for {$[OMA]^+[Tf_2N]^-$ + methanol or ethanol or 1-propanol} system are discussed. Similar systems available in the literature are compared with our results.

Excess molar volumes are the results of the intermolecular interactions that are due to the difference between the real and the ideal molar volumes. Positive excess molar volumes are the result of intermolecular dissociation effect ‘bond breaking’ of the pure solvents. The negative excess molar volumes are due to association between the solutes molecules and a packing.

For the imidazolium cation two different alkyl groups attached to the IL $[EMIM]^+$ $[EtSO_4]^-$ and $[BMIM]^+$[$MeSO_4]^-$ were studied. This was to study the effect of the ethyl and butyl groups on the $V_{\mathrm{m}}^{\mathrm{E}}$ values. For both of the (IL + methanol or 1-propanol) the $V_{\mathrm{m,\,min}}^{\mathrm{E}}$ results decrease with an increase in temperature and increase with an increase in alcohol chain length. The $V_{\mathrm{m,\,min}}^{\mathrm{E}}$, $V_{\mathrm{m},1}^{\infty}$ and $V_{\mathrm{m},2}^{\infty}$ results for ($[EMIM]^+$ $[EtSO_4]^-$ + methanol or 1-propanol) are more negative then for ($[BMIM]^+$ $[MeSO_4]^-$ + methanol or 1-propanol).

The minimum excess molar volumes, $V_{\mathrm{m,\,min}}^{\mathrm{E}}$, at T = (298.15 and 303.15) K, and the comparison of the results obtained in this work with those obtained by Pereiro and by Domanska are shown in table 6.4. For ($[BMIM]^+$[$MeSO_4]^-$ + ethanol) system at T = 298.15 K Pereiro obtained results $V_{\mathrm{m,\,min}}^{\mathrm{E}}$ -0.706 $cm^3 \cdot mol^{-1}$, Domanska -0.662 $cm^3 \cdot mol^{-1}$ and for this work -0.674

$cm^{3} \cdot mol^{-1}$. The difference between the results of Domanska and this work is 0.02 $cm^{3} \cdot mol^{-1}$ and the difference with Pereiro is 0.06 $cm^{3} \cdot mol^{-1}$. At T= 303.15 K Pereiro obtained $V_{m,\min}^{E}$ -0.746 $cm^{3} \cdot mol^{-1}$ and for this work -0.775 $cm^{3} \cdot mol^{-1}$, the difference is 0.03 $cm^{3} \cdot mol^{-1}$. For {$[BMIM]^{+}$[$MeSO_4]^{-}$ + methanol} system at T = 298.15 K Domanska obtained $V_{m,\min}^{E}$ -1.133 $cm^{3} \cdot mol^{-1}$, and for this work -1.100 $cm^{3} \cdot mol^{-1}$, the difference is 0.03 $cm^{3} \cdot mol^{-1}$. The results are in good agreement and they decrease with an increase in temperature and increase with an increase in alcohol chain length.

6.1 Experimental V_{m}^{E}

6.1.1. {1-ethyl-3-methylimidazolium ethylsulfate + methanol or 1-propanol or 2-propanol} binary system

The results for the excess molar volumes for the binary systems studied {$[EMIM]^{+}[EtSO_4]^{-}$ + methanol or 1-propanol or 2-propanol}are given in tables 5.1-5.3 and graphed in figures 5.1-5.3. The excess molar volumes for these systems are negative over the entire composition range which indicates that a more efficient packing and / or attractive interaction occurred when the ionic liquid and the alcohol were mixed (Zhong and Wang 2007). Ionic liquids are complex solvents, and capable of interacting simultaneously with other molecules via, dispersive, ionic, hydrogen bonding and dipolar interaction (Zhong and Wang 2007). The alkanol tends to fill the interstices of the ionic liquid, and the ion-dipole interaction between organic molecular liquid and the imidazolium ring of the ionic liquids, all contribute to the negative values of the excess molar volumes (Zhong and Wang 2007, Bhujrajh and Deenadayalu 2006, Pereiro and Rodreguez 2006).

From the results the, $V_{\mathrm{m}}^{\mathrm{E}}$, values increase with the increase in the alcohol chain length.

From figure 5.1 in can be seen that the curves are skewed to the alcohol-rich region. The skewing of the curves is due to the greater difference in the molar volume of the ionic liquid and the alcohol (Bhujrajh and Deenadayalu 2006), since methanol has a smaller molar volume, changes in $V_{\mathrm{m}}^{\mathrm{E}}$ is more pronounced.

The excess molar volumes become more negative as the temperature increases because the kinetic energy of molecules also increases with temperature, which leads to a decrease in interaction of the molecules (Zhong and Wang 2007). The ionic liquid with 1-propanol system has more negative, $V_{\mathrm{m}}^{\mathrm{E}}$, value for

T = (298.15 and 303.15) K than the 2-propanol due to favourable packing of the 1-propanol molecule. 2-Propanol is branched and bulky causing the packing effect to diminish (Bhujrajh and Deenadayalu 2006).

For T = 313.15 K 2-propanol, $V_{\mathrm{m}}^{\mathrm{E}}$, result is less than 1-propanol, probably due to the kinetic effect being greater than the unfavourable packing effect for 2-propanol.

Equimolar composition for {$[\mathrm{EMIM}]^+[\mathrm{EtSO_4}]^-$ + methanol or 1-propanol or 2-propanol} is shown in table 6.1 and graph 6.1.

Table 6.1 V_m^E at equimolar composition for binary system {$[EMIM]^+[EtSO_4]^-$ + methanol or 1-propanol or 2-propanol} at *T* = 298.15, 303.15 and 313.15) K

T / K	V_m^E cm$^3\cdot$ mol^{-1}		
	Methanol	1-propanol	2-propanol
298.15	-1.138	-0.569	-0.388
303.15	-1.138	-0.628	-0.539
313.15	-1.238	-0.677	-0.617

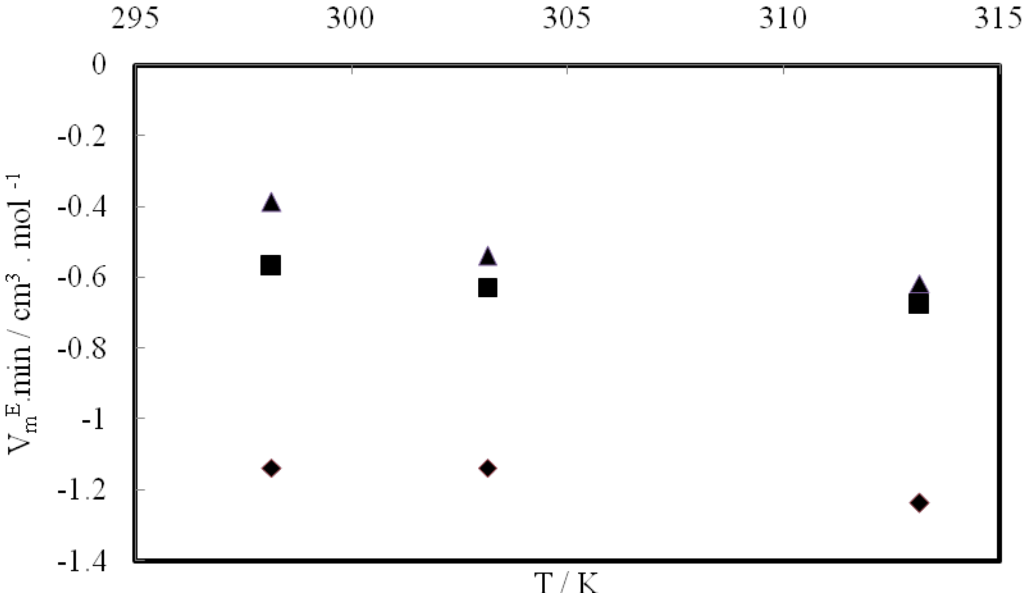

Figure 6.1 $\mathbf{V_m^E}$ **for equimolar composition of binary system {[EMIM]$^+$[EtSO$_4$]$^-$ + ♦, methanol or ■, 1-propanol or ▲, 2-propanol} against temperature at *T* = 298.15, 303.15 and 313.15) K**

6.1.2 {1-buty-3-methylimidazolium methylsulfate + methanol or ethanol or 1-propanol} binary system

The results for the excess molar volumes for the binary systems studied are given in table 5.2 and graphed in figures 5.4-5.6. The excess molar volumes for all the systems studied {$[\mathrm{BMIM}]^+[\mathrm{MeSO_4}]^-$ + methanol or ethanol or 1-propanol}are negative for the entire composition range and at all temperatures shown in figures 5.4-5.6.

The excess molar volume becomes less negative in the following order methanol < ethanol < 1-propanol. The interaction between IL and the alcohol are stronger interaction than of the pure components resulting in the {$[\mathrm{EMIM}]^+[\mathrm{EtSO_4}]^-$ + methanol or 1-propanol or 2-propanol}ion-dipole interactions and packing effect between the organic solvents to dominate over disrupted dipole order.

V_m^E, values increase with the increase in alcohol chain length and decrease with increase in temperature.

The $V_\mathrm{m,min}^\mathrm{E}$ values at T = 298.15 K at $x_1 = 0.3228$ is -1.100 $\mathrm{cm^3 \cdot mol^{-1}}$, $x_1 = 0.4056$ is -0.647 $\mathrm{cm^3 \cdot mol^{-1}}$, $x_1 = 0.4756$ is -0.235 $\mathrm{cm^3 \cdot mol^{-1}}$, for methanol, ethanol or 1-propanol, respectively. The minimum of the V_m^E, curve shifted for methanol $x_1 = 0.3228$ to 1-propanol $x_1 = 0.4756$. This trend in V_m^E values can be attributed to a decreased interaction between IL and alcohol and to a packing effect, both decrease with increase of alcohol chain length.

V_m^E values for equimolar compositions of {$[\mathrm{BMIM}]^+[\mathrm{MeSO_4}]^-$ + methanol or ethanol or 1-propanol} are shown in table 6.2 and graph 6.2.

Table 6.2 V_m^E at equimolar composition for binary system {[BMIM]$^+$[MeSO$_4$]$^-$ + methanol or ethanol or 1-propanol} at *T* = 298.15, 303.15 and 313.15) K

T / K	V_m^E cm$^3\cdot$ mol^{-1}		
	methanol	ethanol	1-propanol
298.15	-0.936	-0.619	-0.235
303.15	-1.321	-0.767	-0.251
313.15	-1.531	-0.859	-0.260

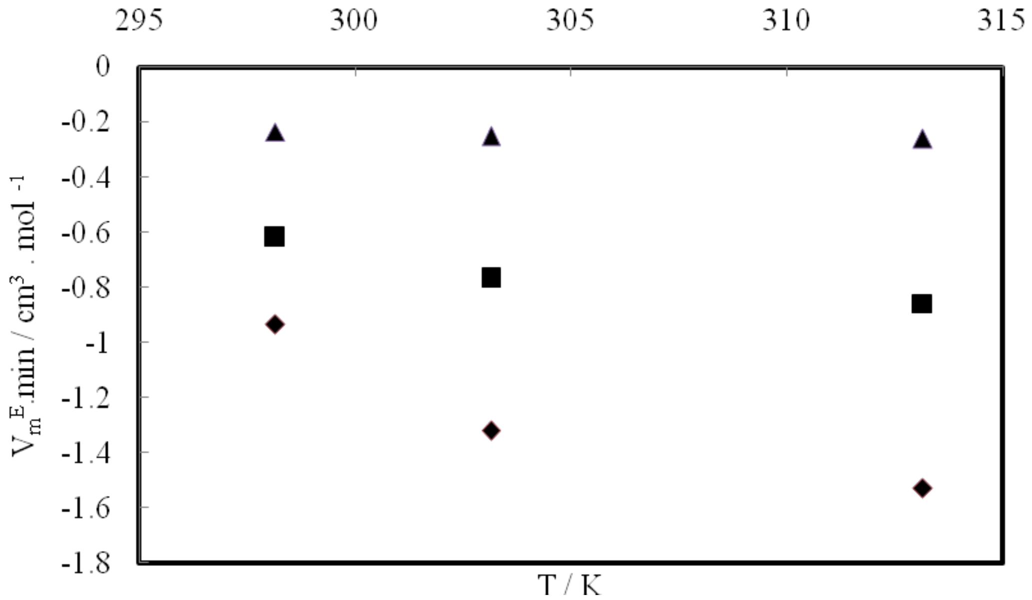

Figure 6.2 $\mathbf{V_m^E}$ **at equimolar composition for binary system {[BMIM]$^+$[MeSO$_4$]$^-$ + ♦, methanol or ■, ethanol or ▲, 1-propanol} against temperature at *T* = (298.15, 303.15 and 313.15) K**

6.1.3 {trioctylmethylammonium bis (trifluoromethyl-sulfonyl) imide + methanol or ethanol or 1-propanol} system.

The results for the excess molar volumes for the binary systems studied $\{[OMA]^+[Tf_2N]^-$ + methanol or ethanol or 1-propanol$\}$are given in tables 5.7-5.9 and graphed in figures 5.7-5.9. The excess molar volumes for these binary systems have both negative and positive values for each system. For the binary system $\{[OMA]^+[Tf_2N]^-$ + methanol$\}$ the V_m^E values are negative at high mole fraction and positive at low mole fraction of the IL. For the binary systems $\{[OMA]^+[Tf_2N]^-$ + ethanol or 1-propanol$\}$ V_m^E values are negative at low mole fraction and positive at high mole fraction of IL. Sigmoidal-shaped curves have been observed for this system, it has been suggested that this shape results from two opposing effects (Treszczanowics and Benson 1991; Paraskevopoulos and Missem 1962). The behaviour in the IL rich region may be attributed to the break down of the hydrogen bonded structure of alcohol. The behaviour in the alcohol rich region may be attributed to the accommodation of the IL interstitially in the hydrogen bonded structure of alcohol (Oswal and Ghael 2004).

The stronger interaction between the IL and alcohol mixture then in the pure liquids also contribute to the negative excess molar volume (Zafarani-Mottar and Shekaari 2006). The positive excess molar volume values are due to the dissociation of the hydrogen bonding in the alcohol being greater than intermolecular bond formation between the IL and the alkanol or due to the dissociation of the ion pairs forming the ionic liquid (Gómez and González 2006).

V_m^E, values for (IL + methanol) system are negative for mole fraction of IL > 0.7 for all temperatures. For (IL + ethanol) system, the V_m^E, values are negative for mole fraction of IL

< 0.27. For the (IL + 1-propanol) systems, the V_m^E, values are negative for mole fraction of IL < 0.21. The minimum and maximum V_m^E, values increases as the temperature increases for (IL + methanol or 1-propanol) system, while for (IL + ethanol) system minimum and maximum V_m^E, values did not increase as the temperature increased.

For the (IL + methanol) system the negative V_m^E, for mole fraction of IL > 0.7 is possibly due to the packing of the small methanol molecules into the IL matrices. For mole fraction of IL < 0.7 V_m^E, is positive possibly due to the break down of the hydrogen bonding in the methanol molecules. The reverse trend for (IL + ethanol or 1-propanol) system is possibly due to the alkanol having an additional CH_2 group/s that changes the intermolecular interactions, an opposite effect to that of (IL + methanol) system.

V_m^E, decreases as the alcohol chain length increases at T = (298.15 and 313.15) K, while at T = 303.15 K V_m^E, ethanol < 1-propanol < methanol. As the alkyl chain length of the alcohol increased it was observed that the minimum was shifted from high mole fraction of IL to low mole fraction of IL and vice versa.

V_m^E for equimolar composition for {$[OMA]^+[Tf_2N]^-$ + methanol or ethanol or 1-propanol} is shown in table 6.3 and graph 6.3.

Table 6.3 V_m^E at equimolar composition for binary system {$[OMA]^+[Tf_2N]^-$ + methanol or ethanol or 1-propanol} at *T* = 298.15, 303.15 and 313.15) K

T / K	V_m^E $cm^3 \cdot mol^{-1}$		
	methanol	ethanol	1-propanol
298.15	0.651	0.360	0.285
303.15	1.180	1.736	0.352
313.15	1.096	0.649	0.678

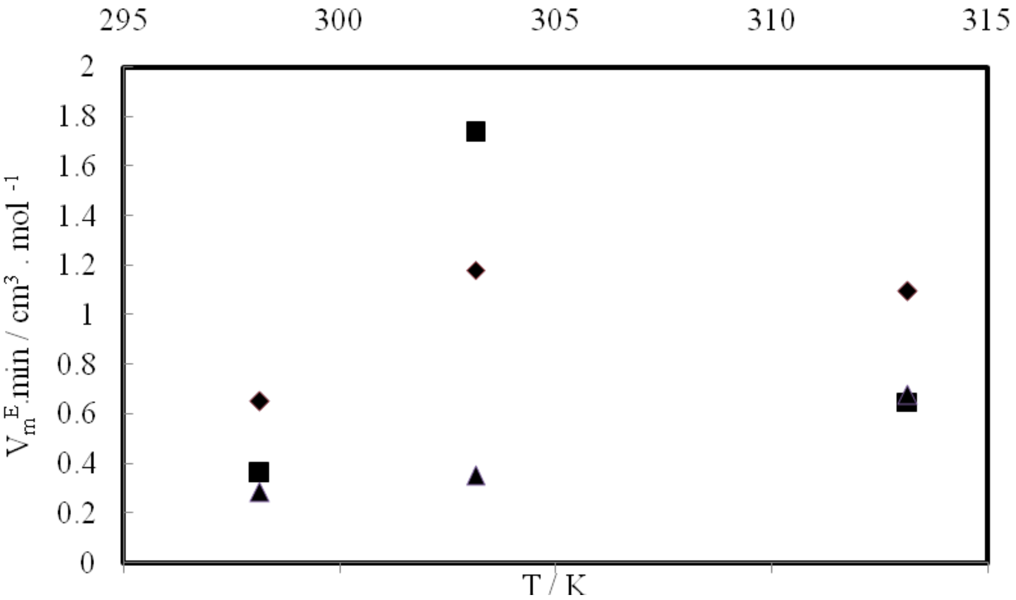

Figure 6.3 V_m^E at equimolar composition for binary system {[OMA]$^+$[Tf$_2$N]$^-$ + ♦, methanol or ■, ethanol or ▲, 1-propanol} against temperature at *T* = (298.15, 303.15 and 313.15) K

6.2. Partial Molar Volumes $\mathbf{V^{\infty}_{m,i}}$

6.2.1 {1-ethyl-3-methylimidazolium ethylsulfate + methanol or 1-propanol or 2-propanol} binary system

The results for the partial molar volumes for the binary systems studied are given in table 5.10 . The results obtained for $V^{\infty}_{\mathrm{m,i}}$, are all negative and the trend is methanol < 1-propanol < 2-propanol. In general the partial molar volumes at infinite dilution , $V^{\infty}_{\mathrm{m,1}}$, decrease as the temperature increases for the systems studied. $V^{\infty}_{\mathrm{m,1}}$, increases as the alcohol chain length increases except at 303.15 K.

The results for $V^{\infty}_{\mathrm{m,2}}$, are negative for all three temperatures for the binary system, they decrease with an increase in temperature and increase with an increase in alcohol chain length. The partial molar volumes at infinite dilution for IL $V^{\infty}_{\mathrm{m,1}}$, are more negative than the partial molar volumes at infinite dilution $V^{\infty}_{\mathrm{m,2}}$, of the alcohol for all the systems studied. This is because for more concentrated alcohol solution, not all the hydrogen bonds are broken (Domanska and Pobudkowska 2006).

6.2.2. {1-buty-3-methylimidazolium methylsulfate + methanol or ethanol or 1-propanol} binary systems

The results for the partial molar volumes for the binary systems studied are given in table 5.11. The partial molar volumes at infinite dilution, $V^{\infty}_{\mathrm{m,1}}$, increase as the alcohol chain length increases. The results obtained for $V^{\infty}_{\mathrm{m,1}}$, are all negative at all temperatures. Alkanol molecules are protic and strongly self-associated through hydrogen bonds in their pure state, with degrees of association depending on the chain length of alcohol (Bhujrajh and Deenadayalu 2006). The results obtained for $V_{\mathrm{m},2}^{\infty}$, are negative at all temperature for the ($[BMIM]^+[MeSO_4]^-$ + methanol or ethanol) system, and are positive at all temperatures for ($[BMIM]^+[MeSO_4]^-$ + 1-propanol) system. The partial molar volumes at infinite dilution for $[BMIM]^+[MeSO_4]^-$ IL $V_{\mathrm{m},1}^{\infty}$, are more negative than the partial molar volumes at infinite dilution $V_{\mathrm{m},2}^{\infty}$, of the alcohol, this is again because not all hydrogen bonds are broken with a small amount of IL present (Zafarani-Mottar, Shekaari 2005). For ($[BMIM]^+[MeSO_4]^-$ +1-propanol) system partial molar volume at infinite dilution for $V_{\mathrm{m},2}^{\infty}$, alcohol are positive at all temperatures, indicating that the dissociation effect is greater than any association effect, i.e the hydrogen bonding in pure state for 1-propanol is weaker than for methanol and ethanol.

6.2.3 {trioctylmethylammonium bis (trifluoromethyl-sulfonyl) imide + methanol or ethanol or 1-propanol} binary system.

The results for the partial molar volumes for the binary systems {$[OMA]^+[Tf_2N]^-$ + methanol or ethanol or 1-propanol}are given in table 5.12.

The results obtained for $V_{\mathrm{m},1}^{\infty}$, are negative for (IL + ethanol or 1-propanol) systems. For (IL + methanol) system the partial molar volume at infinite dilution for IL $V_{\mathrm{m},1}^{\infty}$, are positive, indicating that the dissociation effect is greater than any association effect. $V_{\mathrm{m},2}^{\infty}$ is negative indicating that methanol is probably incorporated into the IL matrix. The results for $V_{\mathrm{m},2}^{\infty}$, are positive for (IL + ethanol or 1-propanol) systems at all temperatures, while they are negative for (IL + methanol) system at all temperatures.

6.3 Previous Work

There is no literature data for the $[EMIM]^+$ $[EtSO_4]^-$ and {OMA]$^+$$[Tf_2N]^-$ ILs with the alcohols studied here.

Of the systems studied here at three temperatures, V_m^E**,** data for the ($[BMIM]^+[MeSO_4]^-$ + methanol or ethanol) at T = 298.15 K, was done by (Domanska and Pobudkowska 2006). The reported results showed a good agreement with the results obtained in this work at high mole fraction of IL. The V_m^E data are plotted in figures 6.1 and 6.2, with both the data tabulated in tables 6.1 and 6.2.

The V_m^E, for the mixtures {$[BMIM]^+[MeSO_4]^-$ + ethanol} at T = (298.15 and 303.15) K, was also done by (Pereiro 2006). The reported results also showed better agreement with the results obtained in this work at T = 298.15 K than at T = 303.15 K, again at high mole fraction of IL. The comparison of results is shown in figures 6.3 and 6.4, with the data in table 6.3 and 6.4.

6.4 Isentropic Compressibility

The results for the binary system {$[OMA]^+$ $[Tf_2N]^-$ + methanol or ethanol or 1-propanol} at T = 298.15 K are tabulated in tables 5.13-5.15 and plotted in figure s 5.10-5.12

The speed of sound increases with the increase in alcohol chain length due to higher nigidity (Pal *et al.* 2008). This may also be due to the IL, a large bulky compound, being unable to break the self association for the alcohol molecules (Pal *et al.* 2008).

Negative Δk_s values indicate that the mixture is less compressible than the corresponding ideal mixture (Pal *et al.* 2008, Zafarani-Moattar and Shekaari 2005). This is due to the closer approach of unlike molecules and stronger interaction between components of mixtures that lead to a decrease in compressibility (Victor P.J., Hazra D.K., 2002, Sahan et al. 1995).

The Δk_s values for 1-propanol > ethanol > methanol indicating that there is a decrease in compressibility from the ideal mixture in the order 1-propanol > ethanol > methanol (Barbosa 2003). The decrease in compressibility is due to stronger interaction between components of mixtures due to the proximity of unlike molecules (Zafarani-Moattar and Shekaari 2005). From the figure 5.10-5.12 the solution of IL is more compressible than the solution of (IL +ethanol or 1-propanol).

Data for k_s values against mole fraction of {$[OMA]^+ [Tf_2N]^-$ + methanol or ethanol or 1-propanol} at T = 298.15 K is shown in figure 6.8 and tabulated in table 6.7.

Table 6.4 Mole fraction, x_1, and excess molar volumes, V_m^E, for binary system $\{[BMIM]^+[MeSO_4]^-$ (x_1) + methanol (x_2)$\}$ results obtained in this work and those obtained by Domanska at T = 298.15 K

x_1	V_m^E / $cm^3 \cdot mol^{-1}$ (This work)	x_1	V_m^E / $cm^3 \cdot mol^{-1}$ (Domanska)
	T = 298.15 K		
0.0533	-0.3080	0.0507	-0.8725
0.1131	-0.6443	0.1550	-1.1339
0.1936	-0.9144	0.2346	-1.1238
0.2651	-1.0576	0.3427	-1.0936
0.3228	-1.1003	0.4338	-1.0146
0.4386	-1.0945	0.5365	-0.8774
0.5589	-0.9368	0.6332	-0.6868
0.6518	-0.7710	0.7371	-0.4942
0.7169	-0.6170	0.8223	-0.3665
0.7935	-0.4324	0.9308	-0.1760
0.8510	-0.2911		
0.9206	-0.1478		

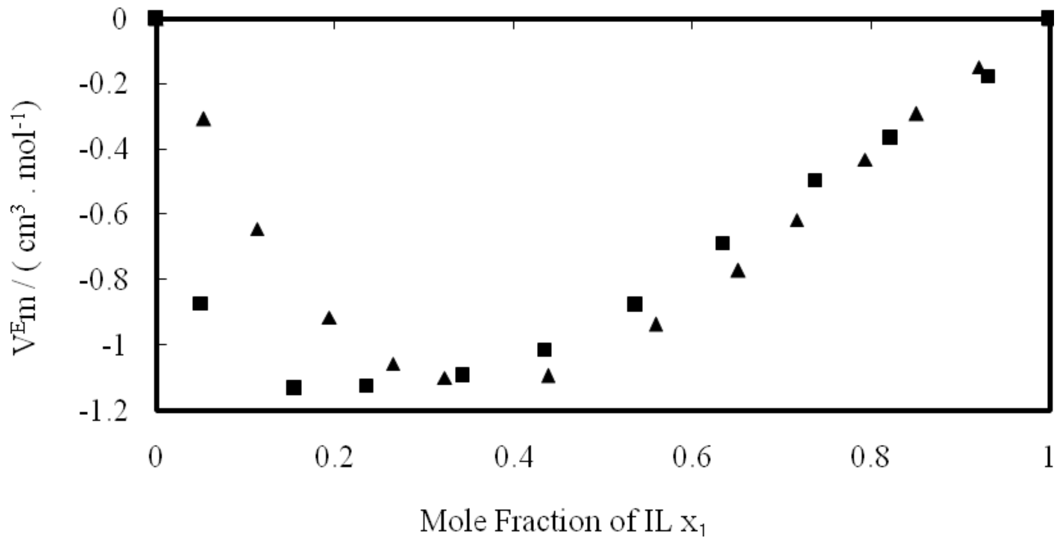

Figure 6.4 Plot excess molar volumes, V_m^E, of binary mixtures of {$[BMIM]^+[MeSO_4]^-$ (x_1) + methanol (x_2)} against mole fraction of ionic liquid at T = 298.15 K, ▲ this work, ♦ Domanska

Table 6.5 Mole fraction, x_{1}, and excess molar volumes, $\mathrm{V}_{\mathrm{m}}^{\mathrm{E}}$, for binary system $\{[\mathrm{BMIM}]^{+}[\ \mathrm{MeSO}_4]\ (x_1)^{-}$ + ethanol $(x_2)\}$ results obtained in this work and by Domanska and Pereiro at T = 298.15 K

x_1	$V_{\mathrm{m}}^{\mathrm{E}}$ /$\mathrm{cm}^{3}\cdot\mathrm{mol}^{1}$ (This work)	x_1	$V_{\mathrm{m}}^{\mathrm{E}}$ /$\mathrm{cm}^{3}\cdot\mathrm{mol}^{1}$ (Pereiro)	x_1	$V_{\mathrm{m}}^{\mathrm{E}}$ /$\mathrm{cm}^{3}\cdot\mathrm{mol}^{1}$ (Domanska)
	T = 298.15 K				
0.0738	-0.2022	0.0501	-0.3450	0.0713	-0.4150
0.1547	-0.4030	0.1015	-0.5230	0.1221	-0.5207
0.2064	-0.5082	0.1961	-0.6750	0.2349	-0.6323
0.3165	-0.6159	0.2990	-0.7060	0.3448	-0.6625
0.4056	-0.6475	0.3914	-0.6970	0.4588	-0.6193
0.5095	-0.6196	0.5025	-0.6240	0.5629	-0.5563
0.6223	-0.5248	0.6073	-0.5290	0.6403	-0.4403
0.7231	-0.4153	0.6982	-0.4180	0.7372	-0.3185
0.8249	-0.2814	0.8002	-0.2520	0.8406	-0.1907
0.8877	-0.1735	0.8992	-0.1070	0.9614	-0.0355
0.9424	-0.079	0.9498	-0.0340		

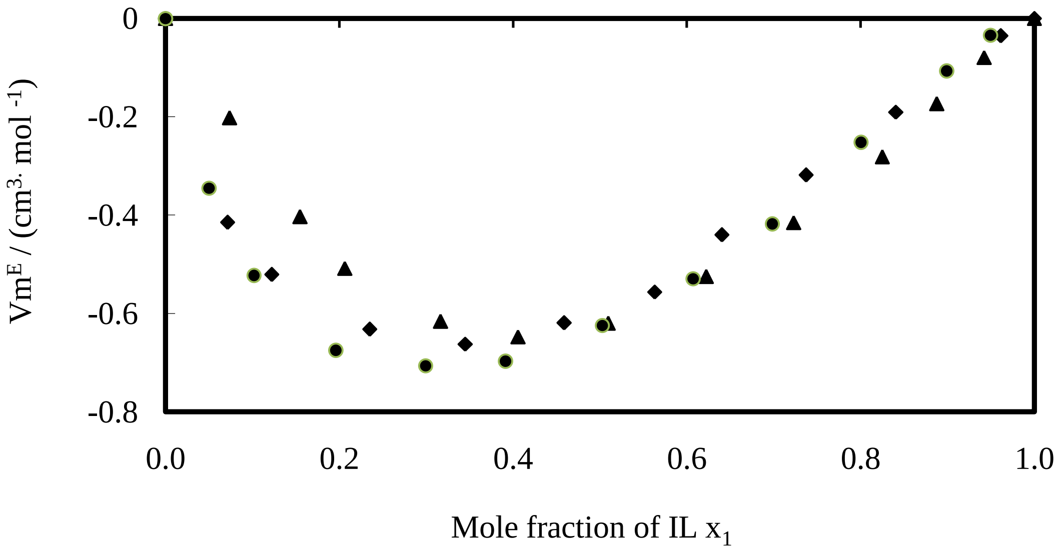

Figure 6.5 Plot excess molar volumes, V_m^E, of binary mixtures of {[BMIM]$^+$[MeSO$_4$]$^-$ (x_1) + ethanol (x_2)} against mole fraction of ionic liquid at T = 298.15 K, ▲ this work, ● Pereiro and ♦ Domanska

Table 6.6 Mole fraction, x_{1}, and excess molar volumes, V_{m}^{E}, for binary system {$[BMIM]^{+}[MeSO_{4}]^{-}$ (x_{1})+ ethanol (x_{2})} results obtained in this work with those obtained by Pereiro at T = 303.15 K

x_1	V_m^E / cm^3· mol^{-1} (This work)	x_1	V_m^E /cm^3·mol^{-1} (Pereiro)
	T = 303.15 K		
0.0501	-0.358	0.0738	-0.2143
0.1015	-0.551	0.1547	-0.4183
0.1961	-0.714	0.2064	-0.5377
0.2990	-0.746	0.3165	-0.7134
0.3914	-0.727	0.4056	-0.7752
0.5025	-0.653	0.5095	-0.7673
0.6073	-0.558	0.6223	-0.6987
0.6982	-0.438	0.7231	-0.5689
0.8002	-0.274	0.8249	-0.3859
0.8992	-0.119	0.8877	-0.2766
0.9498	-0.04	0.9424	-0.1414

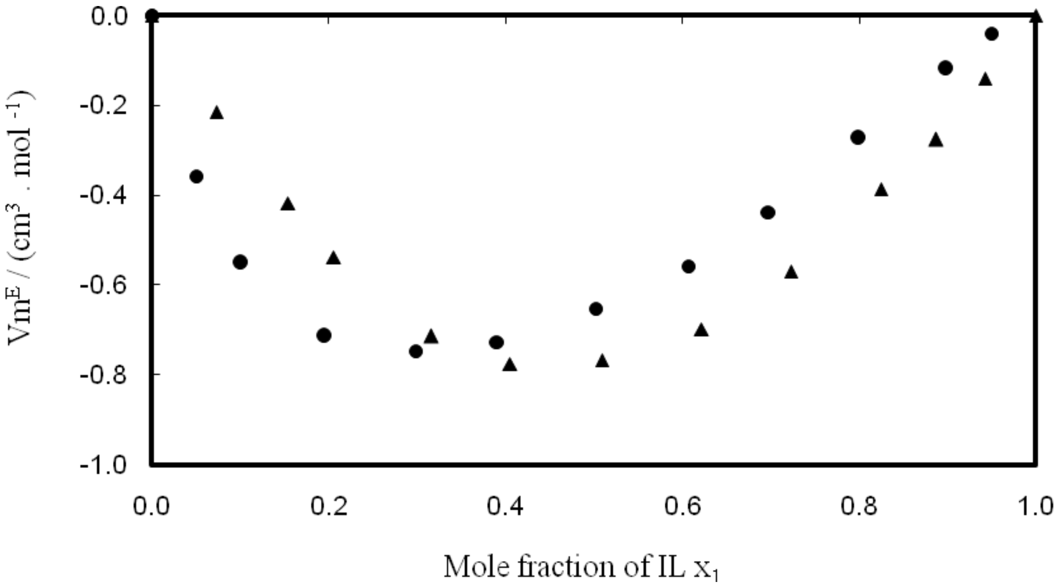

Figure 6.6 **Plot excess molar volumes, V_m^E, of binary mixtures of {[BMIM]$^+$[MeSO$_4$]$^-$ (x_1) + ethanol (x_2)} against mole fraction of ionic liquid at T = 303.15 K, ▲ this work, ● Pereiro**

Table 6.7 The minimum excess molar volumes, $V^{E}_{m,min}$ at T = (298.15, 303.15 and 313.15), from this work and by Pereiro and Domanska

	Systems	$V^{E}_{m,\min}$ /(cm^3·mol^{-1})		
		T = 298.15 K	T = 303.15 K	T = 313.15 K
A.B. Pereiro [a]	$[BMIM]^+[MeSO_4]^-$ + ethanol	-0.706	-0.746	
U. Domanska [b]	$[BMIM]^+[MeSO_4]^-$ + methanol	-1.133		
U. Domanska [b]	$[BMIM]^+[MeSO_4]^-$ + ethanol	-0.662		
This Work	$[BMIM]^+[MeSO_4]^-$ + methanol	-1.100	-1.444	-1.531
	$[BMIM]^+[MeSO_4]^-$ + ethanol	-0.647	-0.775	-0.869
	$[BMIM]^+[MeSO_4]^-$ + 1-propanol	-0.235	-0.251	-0.260

Table 6.8 k_s values against mole fraction of $\{[OMA]^+[Tf_2N]^-$ + methanol or ethanol or 1-propanol$\}$ against temperature at T = 298.15 K

x_1	k_s /T Pa $^{-1}$ methanol	x_1	k_s /T Pa $^{-1}$ ethanol	x_1	k_s /T Pa $^{-1}$ 1-propanol
	T = 298.15 K				
0.0336	1043.4	0.1731	965.2	0.0736	868.4
0.1291	1034.6	0.2728	963.9	0.1146	872.2
0.2125	1026.8	0.3353	963.0	0.2152	881.5
0.4172	1008.0	0.4286	961.8	0.3303	892.2
0.5362	997.0	0.5145	960.6	0.4033	898.9
0.6611	985.4	0.6307	959.1	0.5240	910.1
0.7084	981.1	0.7338	957.7	0.6682	923.4
0.8522	967.8	0.7774	957.1	0.7833	934.1
		0.9493	954.8	0.8439	939.7
				0.9533	949.8

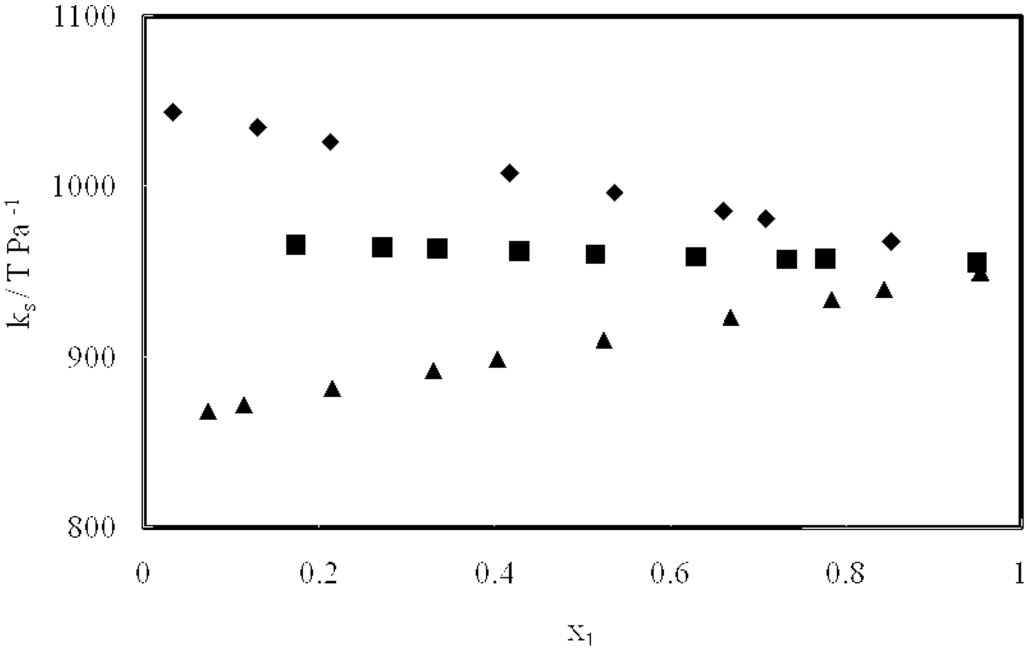

Figure 6.8 k_s values against mole fraction of {$[OMA]^+[Tf_2N]^-$ + ♦, methanol or ■, ethanol or ▲, 1-propanol} against temperature at T = 298.15 K

CHAPTER 7

CONCLUSION

The densities were measured at T = (298.15, 303.15 and 313.15) K, over the entire composition range for the binary systems (ionic liquid + alcohol). Redlich-Kister smoothing polynomial equation was fitted with the excess molar volume data, isentropic compressibility and the partial molar volumes were determined from the Redlich-Kister coefficients.

7.1 Excess Molar Volumes

7.1.1 {1-ethyl-3-methylimidazolium ethylsulfate + methanol or 1-propanol or 2-propanol}

The $V_{\mathrm{m}}^{\mathrm{E}}$, results were interpreted in terms of the alcohol chain length and, it was found that the $V_{\mathrm{m}}^{\mathrm{E}}$, increases as the alcohol chain length increases, and decreases slightly with the temperature increases.

7.1.2 {trioctylmethylammonium bis (trifluoromethyl-sulfonyl) imide + methanol or ethanol or 1-propanol}

The $V_{\mathrm{m}}^{\mathrm{E}}$, results were interpreted in terms of the alcohol chain length. It was found that the $V_{\mathrm{m}}^{\mathrm{E}}$, decreases as the alcohol chain length increases at (298.15 and 313.15) K, while at 303.15 K $V_{\mathrm{m}}^{\mathrm{E}}$, for ethanol < 1-propanol < methanol . It increases as the temperature increases for (IL + ethanol or 1-propanol) systems, while for (IL + ethanol) system it does not increase as the temperature increases.

7.1.3 {1-buty-3-methylimidazolium methylsulfate + methanol or ethanol or 1-propanol}

The V_m^E, results obtained from this study reveal that the negative values V_m^E, observed for the mixtures can be explained by the strong hydrogen bonding effects between unlike molecules. An increase in alcohol chain length resulted in an increase in the values of V_m^E, while the increase in temperature resulted in the decrease in V_m^E.

7.2 Partial Molar Volumes

7.2.1 {1-ethyl-3-methylimidazolium ethylsulfate + methanol or 1-propanol or 2-propanol}

The results obtained for $V_{m,i}^{\infty}$, are all negative and the trend is methanol < 1-propanol < 2-propanol. The partial molar volumes at infinite dilution $V_{m,1}^{\infty}$, decrease as the temperature increases for all the systems studied. $V_{m,1}^{\infty}$, increase as the alcohol chain length increase except at 303.15 K.

The results for $V_{m,2}^{\infty}$, are negative at all temperatures for this systems, increases with an increase in temperature and increase with the increase in alcohol chain length (Sen 2007). The partial molar volumes at infinite dilution for IL $V_{m,1}^{\infty}$, are more negative than the partial molar volumes at infinite dilution $V_{m,2}^{\infty}$, of the alcohol for all the systems

7.2.2 {trioctylmethylammonium bis (trifluoromethyl-sulfonyl) imide + methanol or ethanol or 1- propanol}

The partial molar volumes $V_{m,1}^{\infty}$, obtained for this system has no trend with the increase in temperature or the increase in alcohol chain length.

7.2.3 {1-buty-3-methylimidazolium methylsulfate + methanol or ethanol or 1-propanol}

The partial molar volume at infinite dilution $V_{\mathrm{m},1}^{\infty}$, and $V_{\mathrm{m},2}^{\infty}$, of ionic liquid and alcohol indicate the strength of pure component hydrogen bonds. The increase in $V_{\mathrm{m},1}^{\infty}$, values was observed with an increase in alcohol chain length.

7.3 Isentropic Compressibility

{trioctylmethylammonium bis (trifluoromethyl-sulfonyl) imide + methanol or ethanol or 1-propanol}

The negative $\Delta k_{\mathrm{S},}$ values indicate that there is a decrease in compressibility from the ideal mixture.

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APPENDICES

List of Publications

1. Excess molar volumes, and excess isentropic compressibilities of binary systems {trioctylmethylammonium bis (trifluoromethysulfonyl) imide + methanol or ethanol or 1-propanol} at different temperatures. (J. Chemical Thermodynamics 40, 2008, 1041-1045)

2. Excess molar volumes and Partial molar volumes of binary systems (1-buty-3-methylimidazolium methylsulfate + methanol or ethanol or 1-propanol) at T = (298.15, 303.15 and 313.15) K. (South African Journal of Chemistry) Submitted

3. Application of the PFV EoS correlation to excess molar volumes of (1-Ethyl-3-Methylimidazolium Ethylsulfate + Alkanols) at different temperatures. (Accepted for publication).