CIBULKA CORRELATION FOR TERNARY EXCESS MOLAR VOLUMES FOR $[MOA]^+[Tf_2N]^-$ AT DIFFERENT TEMPERATURES

ZIKHONA TYWABI

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PREFACE

The work described herein was perfomed under the supervision of Professor N. Deenadayalu at the 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.

Signed: Date:

Zikhona Tywabi

Signed: Date:

Prof. N. Deenadayalu

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ABSTRACT

In this work, the binary and ternary excess molar volumes have been calculated from the density, ρ, measurements using an Anton Paar (DMA 38) vibrating tube digital densimeter. One component of the ternary systems studied was an ionic liquid. The ionic liquid used is methyl trioctylammonium bis(trifluoromethylsulfonyl)imide $[MOA]^+[Tf_2N]^-$. Binary excess molar volumes were obtained for (1-butanol + ethyl acetate) and (2-butanol + ethyl acetate) systems at T = (298.15, 303.15, and 313.15) K. Ternary excess molar volumes were obtained for the mixtures $\{[MOA]^+[Tf_2N]^-$ + 2-propanol or 1-butanol or 2-butanol + ethyl acetate$\}$ at T = (298.15, 303.15, and 313.15) K.

The Redlich-Kister equation was fitted to the calculated binary excess molar volume data to obtain the fitting parameters which were used to calculate the partial molar volumes at infinite dilution. The calculated partial molar volume was used to better understand the intermolecular interactions of each component at infinite dilution. The Redlich-Kister parameters were also used in the Cibulka equation and the Cibulka equation was used to correlate the ternary excess molar volume data to give the fitting parameters.

The binary excess molar volumes, V_{m}^{E}, for the (1-butanol + ethyl acetate) and (2-butanol + ethyl acetate) are positive at each temperature over the entire composition range. At high mole fractions of the alcohol for the binary systems (2-propanol or 1-butanol or 2-butanol + ethyl acetate), V_{m}^{E} is positive again, similar to the Cibulka ternary correlation. The positive V_{m}^{E} values are due to the breaking of intermolecular interactions in the pure components during the mixing process.

The ternary excess molar volume, V_{123}^{E}, values are negative for all mole fractions. The negative values are due to a more efficient packing and/ or attractive intermolecular interactions in the mixtures than in the pure liquid. There is also a contraction in volume which can be attributed to electron-donor-acceptor type interactions between the ionic liquid and 2-propanol or 1-butanol or 2-butanol as well as ethyl acetate.

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List of Symbols

V_{123}^{E} = ternary excess molar volume

V_{m}^{E} = binary excess molar volumes

ρ = density

x_1 = mole fraction of 1st component

x_2 = mole fraction of 2nd component

x_3 = mole fraction of 3rd component

T = Temperature

K = Kelvin

M_1 = molar mass of $[\mathrm{MOA}]^{+}[\mathrm{Tf_2N}]^{-}$

M_2 = molar mass of 2-propanol or 1-butanol or 2-butanol

M_3 = molar mass of ethyl acetate

A_i = polynomial coefficient

N = polynomial degree

n = number of experimental points

k = number of coefficients used in the Redlich- Kister equation

z = mole fraction ratio between the 1st and 3rd component of the ternary system

b_0 = Cibulka parameter

b_1 = Cibulka parameter

b_2 = Cibulka parameter

σ = standard deviation for the ternary excess molar volume

CHAPTER 1

INTRODUCTION

1.1 IMPORTANCE OF BINARY AND TERNARY EXCESS MOLAR VOLUMES

Extensive information on the thermodynamic and thermophysical properties of pure liquids and liquid mixtures is needed not only as their use is increasing in many industrial processes as a green solvent, but also for the advancement of theoretical developments through an understanding of the intermolecular forces, solution structure, property relationship (Oswal and Putta, 2001).

Excess thermodynamic properties are extensively used to study the deviation of the real liquid mixture from ideality. The excess functions may be positive or negative their sign and magnitude representing the deviations from ideality (Bahadur and Deenadayalu, 2010a).

The complexity of the molecular interactions present in the liquid phase makes the task of predicting thermodynamic quantities difficult. Thermophysical 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). The knowledge of thermophysical properties of the ionic liquids mixed with other organic solvents is useful for the development of specific chemical processes (Dupont *et al.* 2002; Anastas and Warner 1998; Cann and Connelly 2000).

Thermodynamic properties, including excess molar volumes are also useful for the development of reliable predictive models for systems containing ILs. To this end the database of ionic liquid cation, anion and thermophysical properties should be useful (Domanska and Pobudkowska 2006).

Excess molar volumes can be used for understanding some of the molecular interactions (such as dispersion forces, hydrogen bonding interactions) in both the binary and ternary mixtures (Zhong and Wang 2007).

The excess molar volume data is a helpful parameter in the design of technological processes of a reaction (Gómez and Gonzàlez 2006), and can be used to predict vapour liquid equilibria using appropriate equation of state models (Sen 2007).

The objective of studying thermodynamic properties of binary and ternary mixtures of ionic liquids (ILs) is to contribute to a data bank of thermodynamic properties containing ILs and to investigate the relationship between ionic structures of ionic liquid and density of the binary and ternary mixtures, in order to establish principles for the molecular design of suitable ionic liquids for chemical separation processes (Sibiya and Deenadayalu 2008).

To design any process containing an ionic liquid on an industrial scale, it is necessary to know the thermodynamic or physical-chemical properties such as density, speed of sound and activity coefficients at infinite dilution (Letcher 2005).

1.2 AREA OF RESEARCH COVERED IN THIS WORK

The experimental data of physical properties such as densities and excess molar volumes is required for a full understanding of the thermodynamic properties of liquid mixtures, as well as for practical chemical engineering work (Resa *et al.* 2004).

There is very little published data for the physical properties of pure ionic liquids and their binary mixtures, but taking into account the number of possible ionic liquids, the data is small. Published experimental data for physical properties of ternary systems are even scarcer (Calvar *et al.* 2006).

In this work, we present experimental densities and excess molar volumes of the binary mixtures (ethyl acetate + 1-butanol or 2-butanol) and of the ternary mixture ($[MOA]^+[Tf_2N]^-$ + 2-propanol or 1-butanol or 2-butanol + ethyl acetate) over the entire composition range and at T = (298.15, 303.15 and 313.15) K.

The Redlich-Kister smoothing equation (Redlich and Kister 1948, Redlich and Kister 1984) was fitted to the experimental and literature excess molar volume data to get the binary Redlich-Kister parameters.

Partial molar volumes 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). The $V_{\mathrm{m,i}}^{\infty}$, data provide useful information about the interactions occurring in infinitely dilute solutions. These studies are of great help in characterizing the structure and properties of solutions (Domanka and Pobudkowsa 2006).

The ternary data was correlated with the Cibulka equation (Cibulka 1982) using the binary parameters and the results were discussed in terms of intermolecular interactions.

The experimental and Cibulka correlated ternary excess molar volumes are used to understand the influence of the third component on the pair-wise interactions in the ternary mixtures and the change in nature and degree of interaction between pairs of molecules (Bahadur and Deenadayalu 2010a).

The structure of the ionic liquid used in this work is presented in figure 1.1.

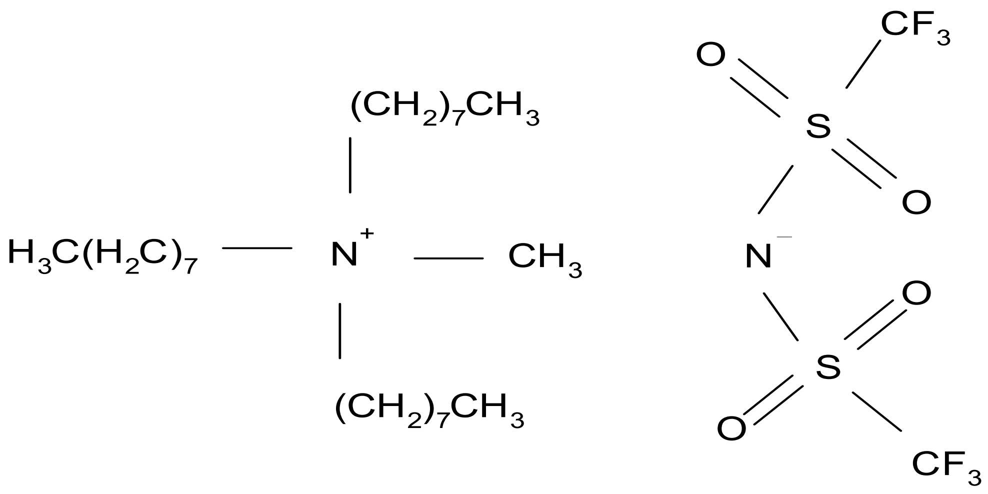


Figure 1.1 Methyl trioctylammonium bis(trifluoromethylsulfonyl)imide.

CHAPTER 2

IONIC LIQUIDS

2.1 INTRODUCTION

The investigations of thermophysical and thermodynamic properties of ionic liquids (ILs) are increasing rapidly (Sibiya and Deenadayalu 2008).
Ionic liquids have attracted considerable interest as environmentally friendly or "green" alternatives to conventional molecular organic solvents because they have extremely low vapour pressure, recyclable, low melting point, high thermal stability, non-flammability (Welton 1999; Rebelo *et al.* 2005; Wang *et al.* 2006; Zhang *et al.* 2006; Zafarani-Mottar and Shekaar 2006) and good dissolution properties (Baranyai *et al.* 2004) for most organic and inorganic compounds (Welton 1999; Sheldon 2001; Yang *et al.* 2005). They have an ionic character with thermophysical properties that are different from those of molecular liquids. Ionic liquids are defined as salts with a melting point temperature below the normal boiling point of water (100^{o} C) (Pereiro and Rodriguez 2006; Zafarani-Mottar and Shekaari 2005), if the salt's melting point is below room temperature, the IL is known as a room temperature ionic liquid (RTIL) (Berthod *et al.* 2008; Welton 1999).
Ionic liquids are composed of organic cations and various organic or inorganic anions. Numerous combinations of cations and anions are possible. They are considered as "designer solvents" since ionic liquid 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 Sheddon 2000).

The most common salts in use are those with alkylammonium, alkylphosphonium, alkylpyrrolidinium, N-alkylpyridinium, and N, N-dialkylimidazolium cations, and a variety of organic anions such as acetate, triflate, trifluoromethylsulphonate and trifluoroacetate or inorganic anions such as chloride, nitrite, bromide, chloroaluminate, hexafluorophosphates, perchlorate and tetrafluorophosphates (Zhang *et al.,* 2006).

2.1.1 Properties of ILs

ILs have widely tunable properties with regard to polarity, hydrophobicity and solvent miscibility through the appropriate selection of 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 for most organic and inorganic compounds (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 *et al.* 2004; Gutowki *et al.* 2003; Lachwa *et al.* 2005; Lachwa *et al.* 2006).

ILs has high stability to air and moisture, and wide electrochemical window. The ILs that are moisture and air stable at room temperature have potential uses for new chemical processes and technologies (Domanska and Pobudkowska 2006; Lozano and De Diego 2004). Some ionic liquids are highly hydroscopic and small quantities of water or other compounds in the ionic liquid cause considerable change in the physical properties (Calvar *et al.* 2006; González *et al.* 2006).

ILs has different chemical and physical properties in terms of its melting points, density, viscosity, surface tension, thermal stability, miscibility and vapor pressure, which makes it easy to characterize and identify its limitations in applications (Zhang *et al.* 2006).

2.2 IONIC LIQUID AS REPLACEMENT SOLVENT FOR VOLATILE ORGANIC COMPOUND (VOCs)

Ionic liquid research is increasing exponentially because of their use as a replacement solvent for volatile organic compound (VOCs)(Rogers and Seddon 2003). Ionic liquids are viewed as novel class of green, benign solvents or catalysts for a number of chemical processes such as separations, reactions, homogeneous two-phase catalysis and polymerization because of their negligible vapour pressure (Zafarani-Mottar and Shekaari 2006) which promise widespread application in industry (Wang *et al.*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).

Volatile organic compounds are organic compounds with a boiling point of ≤ 100˚ C and a vapour pressure >1 mmHg at 100˚ C. The VOCs are among the most common contaminants in the atmosphere. They are used extensively in chemical industries and occur in numerous products including fuels, solvents, paints, adhesives, deodorants, in combustion exhausts (Spyros *et al*. 2001).

VOCs are of great concern because, once such compounds are in a vapour state, they are much more mobile and therefore, more likely to be released to the environment, and they pose a public health risk as they contribute to a general increase in reactive hydrocarbons in the atmosphere, which can lead to the formation photochemical oxidants. When VOCs are oxidized in the presence of oxides in nitrogen, they lead to the formation of photochemical smog, harmful to humans, animals and vegetation. Even at very low concentrations, many of these materials are toxic, carcicogenic and thus represent a direct health risk to workers (Maria *et al*. 2000).

The use of these compounds in industrial processes has become a subject of much public concern and has led to active research into its replacements as solvents in inorganic sysnthesis and electrochemical applications (Verevkin *et al*. 2005).

The advantage of ionic liquids over VOCs as solvents for synthetic chemistry, chemical separation and for electrochemistry is the intrinsic lack of vapour pressure (Rogers and Seddon 2003). The large liquidus range and favourable solvation behaviour that room temperature ionic liquids possess, makes them suitable substituents for volatile organic compounds. Additionally, they can be used as catalysts (Welton 1999) while combining their power as solvents.

2.3 APPLICATION OF ILs

Due to their non-volatility, a major pathway for environmental release and contamination has been eliminated. ILs have been considered as having low impact on the environment and human health, and have been recognized as solvent for green Chemistry (Alonso *et al.* 2007).

An application of ILs is due to their distinctive properties and has been well documented by many researchers (Letcher and Reddy 2005). Ionic liquids can be used as an acid, base, ligand and also as a precursor salt in the preparations of carbenes. ILs have been used in reation rate enhancement, separations because of 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 Bart 2007).

ILs can be used as solvents for synthesis e.g. Diels-Alder cycloaddition reactions, Friedel-Craft acylation and alkylation, hydrogenation and oxidation reactions and Heck reactions; as biphasis system in combination with an organic solvent or water in extraction and separation technologies; as catalyst immobilizers for easy recycling of homogeneous catalysts; as electrolytes in electrochemistry (Zhong and Wang 2007).

ILs has been applied successfully or have great potential for application in the industrial processes (Welton 1999), can be used in the Biphase acid scavenging utilising IL process (BASIL) (Plechkova and Seddon 2008), in the cellulose processing (Rogers *et al.* 2002; Rogers *et al.* 2003), dimersol process, as paint additives (Plechkova and Seddon 2008), in nuclear industry (Giridhar and Venkatesan 2007) and in separations (Brennecke 2001).

2.3.1 Applications of ionic liquids in separation technology

2.3.1.1 Ionic liquids as mobile phase additives in liquid chromatography

Basic compounds most often bear positively charged amine groups in low pH mobile phases. Consequently these compounds are retained by a combination of electrical (charge-charge) and hydrophobic interactions with the stationary phase and the ions of the mobile phase.

They are easily separated by reverse phase liquid chromatography (RPLC) with silica-based stationary phases because of the interaction between the cationic sites of the compounds and the anionic silanols of the stationary phase. In the aqueous mobile phases, the charges interactions are usually stronger and slower than the hydrophobic interaction, which produces peak tailing and long retention times.

ILs can be used as mobile phase additives in reversed phase chromatography when mixed with other solvents as methanol and acetonitrile. The addition of ILs as the mobile phase in HPLC decreases the band tailing, reduces the band broadening, and improves the resolution (Han and Row 2010).

2.3.1.2 Ionic liquids used as extraction solvents in sample preparation

Some ILs are suitable for conventional liquid-liquid extraction because of their immiscibility with water as well as the high solubility of the organic species in them (Han and Row 2010). The design of safe and environmentally benign separation processes plays an increasingly important role in the development of extraction technology.

In general, for ionisable compounds transfer from the aqueous phase to the room temperature ionic liquid is more efficient for the neutral form of the compound. Adjustment of the pH of the aqueous phase is an effective means of adjusting selectivity for extraction by ILs, as is the case for non-ionic solvents (Han and Row 2010).

2.3.1.3 Ionic liquids as surface-bonded stationary phases

Several new IL bonded-surface stationary phases have been synthesized and the columns obtained were used to separate a variety of solutes for linear salvation energy relationship (LSER). LSER is the model used to describe the retention for the limited set of solutes under normal phase condition.

Another successful use of the IL bonded-surface stationary phase was the separation of different analytes (Han and Row 2010).

2.3.2 Ionic liquids as engineering fluids

2.3.2.1 Heat transfer fluids

Heat transfer fluids have applications in various systems including refrigeration and solar energy collection systems. The latter application is receiving particular attention because of global energy concerns. Solar energy is one of the cleanest energy sources and is also inexhaustible. Solar energy is normally converted into thermal energy or electricity for storage, while storage as thermal energy is more economical.

Converting solar energy to thermal form requires the heat transfer fluid to have unique thermal and physical properties that are not always met by current commercial resources (Wu *et al.* 2003).

The special properties required for heat transfer fluids include storage density, freezing point, thermal stability, and ability to meet cost goals, required quantity for a solar plant, vapour pressure, material compatibility, and viscosity. Many properties of ILs are superior to those of current heat transfer fluids (Van Valkenburg *et al.* 2005). ILs can store considerable amounts of heat, and they have a large liquid range, low vapour pressure and high thermal stability. The challenges of employing ILs as heat transfer fluids for solar energy storage were explained by as IL availability, cost, purity, material compatibility, environmental safety/health issues, and issues of intellectual property (Zhao 2006).

2.3.2.2 Azeotrope-breaking liquids

The separation of azeotropic or close-boiling mixtures has been a challenging subject in distillation or membrane processes (Jork *et al*. 2004; Seiler *et al.* 2004). This engineering problem is often solved by using extraction agents or entrainers. ILs as non-volatile entrainers has more advantages than conventional entrainers (Jork *et al.* 2005). Since ILs have a high boiling point and are thermally stable, they cause minimum distillate contamination (however, potential contamination might be due to the decomposition of products themselves at high temperatures). When favourable entrainers such as ILs are used, the extractive distillation may be energy efficient by lowering reflux ratios.

Experimentally, ILs have exhibited the ability to separate close-boiling or azeotropic mixtures including ethanol/water, acetone/methanol, tetrohydrofuran/water, methylcyclohexane/ toluene and acetic/water mixtures. Two patent applications also indicated that ILs are advantageous for aezotropic mixture separation because of the cost-effectiveness and wide selection of ILs (Zhao 2006).

2.3.2.3 Lubricants

The oil-like (viscous) appearance of ILs makes them ideal candidates as lubricants. ILs have the properties of a good lubricant: low volatility, high thermal stability, and low temperature fluidity. Experimentally, it was found that ILs have excellent friction-reduction and antiwear properties: they use vane or gear pumps which do not permit the formation of the full fluid film lubrication to protect contacting surfaces. They were found to be superior to some commercial lubricants such as phosphazene and perfluoropolyether (Zhao 2006).

2.3.2.4 Electrolytes for electrochemical industry

ILs have many favourable properties for the electrochemical industry, such as wide electrochemical potential windows, good electrical conductivity and solvent transport properties, wide liquid range, and ability to solvate various organic, inorganic, and organometallic compounds.

ILs have been used as electrolytes in a variety of applications such as batteries, actuators,capacitors,solar cells, fuel cells, membrane-free microelectrode sensors and electrosynthesis(Zhao 2006) . There are other novel applications of ILs in electrochemistry such as IL/polymer electrolyte composites and polymer in IL electrolytes. These novel electrolytes have potential applications in emerging electrochemical devices such as sensors, actuators, and lithium cells. These new materials have reinforced mechanical strength and improved electrical conductivity, which allow them to have potential applications as components of electronic devices (Zhao 2006).

2.3.2.5 Supported ionic liquid membranes

Membranes are functional materials for many separation processes including bioseperations. These processes are energy efficient, can be operated under moderate temperature and pressure, and do not emit large amounts of waste solvents. A unique type of membranes, support liquid membranes (SLMs) are porous solids impregnated with the liquid. Conventional SLMs had two problems, i.e.: (a) the loss of liquid through vaporization or dissolution in contacting phases and their loading limits (Carlin et al., 1998). On the other hand, since ILs are non-volatile and are able to selectively modify the properties of the membrane solvent, they have been incorporated into the porous membranes to form so-called functional supported ionic liquid membranes (SILMs) (Zhao 2006).

SILMs are versatile in a number of applications, including the following:

(a) Gas separations
(b) Separations by organic/ bio molecules
(c) Membrane-based sensors
(d) Membrane reactors

2.3.3 New materials for GC, HPLC and CE

In analytical chemistry, ILs have been explored as functional stationary phases for gas chromatography (GC), additives for high pressure liquid chromatography (HPLC), and electrolytes for capillary electrophoresis (CE). ILs can be coated onto the silica capillaries of GC, the resulting IL stationary phase has a dual property, being a polar stationary phase with polar compounds and acting as low-polarity phase with nonpolar compounds, achieving a satisfactory separation of various organic compounds.

Chiral ILs have also been used as the stationary phase of GC for a successful separation of chiral compounds (Berthod et al. 2001; Ding et al. 2004). ILs were also used as solvents in headspace GC, as additives in the mobile phase of HPLC, as electrolytes in CE for separating a variety of compounds (Andre et al. 2006).

ILs are being used in other analytical devices as well, including matrixes for matrix-assisted laser desorption ionization (MALDI) –mass spectrometry, sensors, and vis/NIR and Raman spectroelectrochemistry (Zhao 2006).

2.3.4 Plasticizers

The dominant plasticizer in the market is dioctyl phathalate (DOP). Although DOP is generally considered safe in plastics, there are still some concerns about its health and environmental impact. Besides these concerns, there are also needs for new plasticizers that have enhanced thermal stability and volatility and can be used at low temperatures and cause less polymer photo-oxidation.

Several ILs (imidazolium, ammonium, and phosphonium based) were used as plasticizers for polyvinylchloride (PVC) with comparable or improved properties (e.g. flexibility, leaching of plasticizers, and thermal stability) (Zhao 2006).

2.4 STRUCTURE OF IONIC LIQUIDS

Ionic liquids are generally salts based on the substituted imidazolium, or pyridinium cation and an inorganic anion such as halides $[AlCl_4]^-$, $[BF_4]^-$, or $[PF_6]^-$ or organic cations such as 1-alkyl-3-methylimidazolium or 1-alkylpyridinium and are very often liquids at room temperature (Domanska 2005).

A room temperature ionic liquid consists of bulky and asymmetric organic cations such as 1-alkyl-3-methylimidazolium, 1-alkylpyridium, and N-methyl-N-alkylpyrrolidinium ions and is shown in figures 2.1-2.2.

A wide range of anions are used, from simple halides, which generally have high melting points, to inorganic anions such as tetrafluoroborate and hexafluorophosphate and to large organic anions like bistriflimide, triflate or tosylate (Heintz 2005).

The structure of possible ionic liquid cations and anions is shown in figures 2.1-2.4 (Heintz 2005).

Cations:

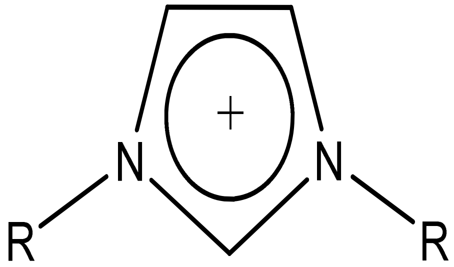


Figure 2.1 1,3-Dialkylimidazolium

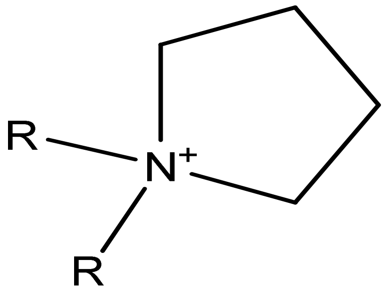


Figure 2.2 1,2-Dialkylpyrrolidinium

Anions:

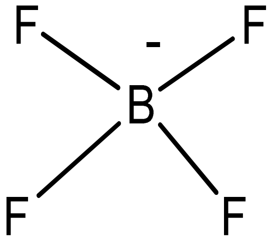


Figure 2.3 Tetrafluoroborate

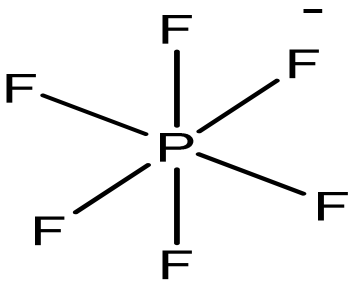


Figure 2.4 Hexafluorophosphate

CHAPTER 3

LITERATURE REVIEW

There is a paucity of experimental data for thermodynamic properties of solutions containing an ionic liquid (Sibiya *et al*. 2009).

The need for studying thermophysical properties of composite materials (or mixtures of pure substances) is often 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 interactions within those mixtures. (Sibiya *et al.*2009).

There are some experimental excess molar volume data of ionic liquids with alcohols in literature and only a few data on the ternary of ILs with alcohols and other organic solvents in the literature. These binary and ternary systems are given in tables 3.1 and 3.2.

The binary systems for the ternary system ({$[MOA]^+[Tf_2N]^-$ + 2-propanol or 1-butanol or 2-butanol + ethyl acetate}), are: ($[MOA]^+[Tf_2N]^-$ + 2-propranol), ($[MOA]^+[Tf_2N]^-$ + 1-butanol), ($[MOA]^+[Tf_2N]^-$ + 2-butanol), ($[MOA]^+[Tf_2N]^-$ + ethyl acetate), (2-propanol + ethyl acetate), (1-butanol + ethyl acetate) and (2-butanol + ethyl acetate). A summary of the binary V_m^E for the ternary studied in this work is given in table 3.1.

Table 3.1 Binary systems of the ternary systems ({$[MOA]^+[Tf_2N]^-$ + 2-propanol or 1-butanol or 2-butanol + ethyl acetate})

Author	**Systems**	V_m^E **/cm³·mol⁻¹**
Deenadayalu *et al*. 2010 a	$[MOA]^+[Tf_2N]^-$ + methyl/ethyl acetate	Negative V_m^E
Oswal *et al*. 2001	2-propanol + ethyl acetate	Positive V_m^E
Fermeglia *et al*. 1988	1-butanol + ethyl acetate	Positive and negative V_m^E
Resa *et al*. 2004	2-butanol + ethyl acetate	Positive V_m^E
Bahadur *et al*. 2011 (unpublished article)*	$[MOA]^+[Tf_2N]^-$ + 2-propanol or 1-butanol or 2-butanol	Negative V_m^E

* Unpublished data that is presented here in the results section.

Article in preparation J. Phys. ChemB Bahadur *et al*. 2011

Deenadayalu *et al*. (2010a) determined the densities and excess molar volume for the binary mixtures of ($[MOA]^+[Tf_2N]^-$ + methyl or ethyl acetate) at T = (298.15, 303.15 and 313.15) K. The excess molar volume V_m^E was found to be negative over the entire composition and the excess molar volume decreases with an increase in temperature except at T = 313.15 K.

Resa *et al*. (2004) reported the densities, refractive indices and speed of sound for the binary mixtures (2-butanol or 3-methyl-1-butanol + ethyl acetate) at T = (298.15, 303.15 and 308.15) K. The excess molar volume for the binary systems was calculated from the experimental densities and was then found to be positive over the entire composition, and it was also found that the excess molar volumes increases with an increase of temperature as well as with an increase in the size of the alcohol chain.

Fermeglia *et al*. (1988) determined the densities and kinematic viscosities at T = 298.15 K and at atmospheric pressure for the following binary systems (1-butanol + ethyl acetate). The excess molar volumes for the above systems show both positive and negative V_m^E values.

Oswal *et al*. (2001) determined the excess molar volumes for the binary mixtures of (ethyl acetate + methanol, or 1-propanol, or 2-propanol, or 1-hexanol) at T = (298.15, 303.15, 308.15, 313.15, 318.15 and 323.15) K. The excess molar volume for the binary systems was found to be both positive and negative for all the systems studied. It was also reported that the

V_m^E increase with an increase in temperature and also increase with increasing length of hydrocarbon chain of the alkanol.

Bahadur *et al.* (2011) determined the densities and excess molar volume for the binary mixtures of ($[MOA]^+[Tf_2N]^-$ + 2-propanol or 1-butanol or 2-butanol) at T = (298.15, 303.15 and 313.15) K. The excess molar volume was found to be negative at all temperatures over entire composition range.

Table 3.2 Summary of the binary data for other ILs systems taken from literature.

Author	**Systems**	V_m^E **/cm^3·mol^{-1}**
Heintz *et al.* 2005	$[OMIM]^+[BF_4]^-$ + 1-butanol or 1-pentanol	Positive and negative V_m^E
Arce *et al.* 2006	$[OMIM]^+[BF_4]^-$ + methanol	Negative V_m^E
Domanska *et al.* 2006	$[BMIM]^+[OcSO_4]^-$ + methanol or 1-butanol or 1-hexanol or 1-octanol or 1-decanol	Positive V_m^E
Sibiya *et al.* 2008	$[MOA]^+[Tf_2N]^-$ + methanol or ethanol or 1-propanol	Positive and negative V_m^E
Deenadayalu *et al.* 2009	$[EMIM]^+[EtSO_4]^-$ + methanol	Negative V_m^E

Sibiya *et al.* (2008) reported the densities for the binary systems of ($[MOA]^+[Tf_2N]^-$ + methanol or ethanol or 1-propanol) at T = (298.15, 303.15 and 313.15) K. The excess molar volume and isentropic compressibilities were then calculated from the experimental densities and the speed of sound respectively. The V_m^E values were both positive and negative.

Deenadayalu *et al.* (2009) determined the densities for the binary systems of ($[EMIM]^+[EtSO_4]^-$ + methanol or 1-propanol or 2-propanol) at T = (298.15, 303.15 and 313.15) K. The V_m^E values for the above systems were calculated from experimental density values for each temperature and were negative for all the systems over the entire composition range. V_m^E values increase with an increase in alcohol chain length and the increase in the alkyl group on the cation or anion. V_{m}^{E} was correlated with the pentic four parameter virial (PFV) equation of state (EoS) model.

Arce *et al.* (2006) determined the densities, refractive indices, speed of sound and dynamic viscosities of ($[\mathrm{OMIM}]^{+}[\mathrm{BF}_4]^{-}$ + methanol or ethanol or 1-propanol or 2-propanol) at T = 298.15 K and atmospheric pressure. V_{m}^{E} values were negative over the entire composition. The excess molar volume and molar refraction, isentropic compressibility and dynamic viscosity changes of mixing were calculated and then correlated by Redlich- Kister polynomial. The V_{m}^{E} for the above binary systems decreases as the chain length of alcohol decreases and is larger for the branched alcohol (2-propanol) than for linear alcohols.

Domanska *et al.* (2006) determined the solubility of ($[\mathrm{BMIM}]^{+}[\mathrm{OcSO}_4]^{-}$ + n-hexane or n-heptane or n-octane or n-decane), ($[\mathrm{BMIM}]^{+}[\mathrm{OcSO}_4]^{-}$ + methanol or 1-butanol or 1-hexanol or 1-octanol or 1-decanol). Domanska also reported the densities and excess molar volumes for the binary mixtures of ($[\mathrm{MMIM}]^{+}[\mathrm{CH}_3\mathrm{SO}_4]^{-}$ + methanol or ethanol or 1-butanol or 1-hexanol or 1-octanol or 1-decanol or water), ($[\mathrm{BMIM}]^{+}[\mathrm{OcSO}_4]^{-}$ + methanol or 1-butanol or 1-hexanol or 1-octanol or 1-decanol) at T = 298.15 K and atmospheric pressure. The V_{m}^{E} values for the above systems were very negative and positive as well as the values for the excess molar enthalpies as predicted by FBT model.

Heintz *et al.* (2005) reported the densities for the binary system ($[\mathrm{OMIM}]^{+}[\mathrm{BF}_4]^{-}$ + 1-butanol or 1-pentanol) at T = 298.15 K and ambient pressure. The V_{m}^{E} values were then calculated from the experimental densities and V_{m}^{E} values were negative in the alcohol rich range of mixture composition and positive in the alcohol poor range.

Bahadur *et al.* (2011) measured the densities for the binary system of ($[\mathrm{MOA}]^{+}[\mathrm{Tf}_2\mathrm{N}]^{-}$ + 2-propanol or 1-butanol or 2-butanol) at T = (298.15, 303.15 and 313.15) K. The V_{m}^{E} values were found to be negative for all the systems over the entire composition at all temperatures. The V_{m}^{E} values increase with an increase in temperature.

For the binary systems ([OMIM] $[\mathrm{BF}_4]$ + 1-butanol or 1-pentanol or methanol), V_{m}^{E} decreases as the chain length of the alcohol decreases and is bigger for the branched alcohols than for the linear alcohols.

Table 3.3 Summary of ternary systems containing an ionic liquid from the literature.

Author	Systems	V_m^E /cm^3·mol^{-1}
Calvar *et al.* 2007	$[C_8mim]^+[Cl]^-$ + ethanol + water EMISE + ethanol + water	Negative V_m^E
Deenadayalu *et al.* 2007	$[EMIM]^+[CH_3(OCH_2CH_2)_2OSO_3]^-$ + methanol + water	Positive and negative V_m^E
Bhujrajh and Deenadayalu 2008	$[EMIM]^+[BETI]^-$ + methanol + acetone	Negative V_m^E
Gonzalez *et al.* 2008	$[BMIM]^+[MeSO_4]^-$ + ethanol + water	Negative V_m^E
Andreatta *et al.* 2009	$[C_8mim]^+[NTf_2]^-$ + methanol + methyl acetate	Negative V_m^E
Andreatta *et al.* 2010	$[C_4mim]^+[NTf_2]^-$ + ethanol + ethyl acetate	Negative V_m^E
Deenadayalu *et al.* 2010a	$[MOA]^+[Tf_2N]^-$ + methanol + methyl acetate or ethyl acetate	Negative V_m^E
Deenadayalu *et al.* 2010b	$[MOA]^+[Tf_2N]^-$ + ethanol + methyl acetate or ethyl acetate	Negative V_m^E

Calvar *et al.* (2007) measured the densities, refractive indices, speeds of sound and dynamic viscosities of the ternary mixtures of (ethanol + water + EMISE) at $T = 298.15$ K and at atmospheric pressure. Excess molar volumes, refractive index deviation, isentropic compressibilities, molar isentropic compressibilities and excess free energies of activation of viscous flow have been calculated from experimental data. Excess molar volume showed negative deviations from ideal behaviour over the whole range of composition for all the systems studied. The Cibulka equation fitted and it gave smaller deviation for all studied excess properties.

Deenadayalu *et al.* (2007) evaluated the excess molar volumes for the ternary liquid system of ($[EMIM]^+[CH_3(OCH_2CH_2)_2OSO_3]^-$ + methanol + water) from the density measurements over the entire composition range at T = (298.15, 303.15 and 313.15) K. The excess molar volumes values were found to be negative at T = (298.15 and 303.15) K, and positive at T = 313.15 K. V_{123}^E become positive at higher mole fractions of ionic liquid, and at a corresponding decrease in mole fraction of water. The Redlich-Kister equation was used to fit the experimental data. The densities of pure liquid as well as of their system decreased with an increase in temperature.

Bhujrajh and Deenadayalu (2008) measured the densities for the binary and ternary mixtures for the system ($[EMIM]^+[BETI]^-$ + methanol + acetone) at T = (298.15, 303.15 and 313.15) K, and the speed of sound of data for the binary of ($[EMIM]^+[CH_3(OCH_2CH_2)_2OSO_3]^-$ + methanol) at T = 298.15 K. The excess molar volumes were calculated and fitted to the Redlich- Kister equation for the binary system. The excess molar volumes for the binary system of $[EMIM]^+[BETI]^-$ + methanol for low fractions of methanol, and for the binary system $[EMIM]^+[BETI]^-$ + methanol , excess molar volumes were negative throughout the whole composition range. The ternary excess molar volumes were negative for all three temperatures. The excess molar volume increases with an increase in temperature.

Gomez *et al.* (2008) reported the experimental densities, refractive indices and dynamic viscosities and their derived properties of the ternary system ($[MMIM]^+[MeSO_4]^-$ + ethanol + water) at T = 298.15 K and its binary systems at T = (298.15, 303.15 and 313.15) K. The physical properties were measured over the whole composition range and at 0.01 MPa. Excess molar volumes, viscosity deviations and excess free energy of activation for the above mentioned temperatures, were calculated and fitted to the Redlich- Kister equation to determine the fitting parameters and the root-mean squared deviations and for the ternary systems were calculated and correlated by the Cibulka equation. The excess molar volumes were found to be negative for the ternary system and the Cibulka equation gave the lowest deviations for all the studied excess properties.

Andreatta *et al.* (2009) reported the densities, dynamic viscosities, and refractive indices of the ternary system (methanol + methyl acetate and $[C_8mim]^+[NTf_2N]^-$) and the binary combinations of these constituents at T = 298.15 K. The excess molar volumes as well as molar refraction and viscosity changes of mixing were calculated and fitted by the Redlich-Kister equation to determine the fitting parameters and the root-mean-square deviations. The excess molar volumes for the binary systems were negative over the entire composition range and the ternary system also gave negative values indicating a negative deviation from the ideal behaviour.

Andreatta *et al.* (2010) measured the densities, viscosities, and refractive indices for the binary and ternary mixtures (ethanol + ethyl acetate and $[C_4mim]^+[NTf_2]^-$) and the binary combinations of these constituents at $T = 298.15$ K and at atmospheric pressure. The excess properties were calculated from the experimental data and fitted by the Redlich-Kister polynomial equation. The excess molar volume values were found to be negative for the binary systems over the whole composition range. The ternary system showed relatively large and negative excess molar volumes over the entire range of homogeneous mixtures.

Deenadayalu *et al.* (2010a) reported the densities and excess molar volume for the ternary mixture ($[MOA]^+[Tf_2N]^-$ + methanol + methyl acetate or ethyl acetate) at T = (298.15, 303.15 and 313.15) K. The ternary excess molar volumes were calculated from the experimental densities at each temperature and the V_{123}^E values were negative for all mole fractions of ionic liquid. The Cibulka equation was used for correlating the ternary data from the Redlich-Kister parameters and a good correlation was reported.

Deenadayalu *et al.* (2010b) measured the densities and excess molar volume for the ternary mixtures ($[MOA]^+[Tf_2N]^-$ + ethanol + methyl acetate or ethyl acetate) at T = (298.15, 303.15 and 313.15) K. The ternary excess molar volumes were calculated from the experimental densities at each temperature and the V_{123}^E values were negative for all mole fractions of ionic liquid. The Cibulka equation was again used for correlating the ternary data. Based on the chain length of the alcohol, the V_{123}^E values are more negative for the ternary system ($[MOA]^+[Tf_2N]^-$ + ethanol + ethyl acetate) than the ($[MOA]^+[Tf_2N]^-$ + methanol + ethyl acetate) system at all temperatures, because of the additional CH_2 group on the ethanol molecule (Deenadayalu 2010b), and also decrease for both the ternary systems with an increase in the temperature

From the ternary systems ($[C_8mim]^+[NTf_2]^-$ + methanol + methyl acetate) and ($[C_4mim]^+[NTf_2]^-$ + ethanol + ethyl acetate) it can be concluded that increasing alkyl chain length decreases as the V_{123}^E decreases.

CHAPTER 4
THEORY

4.1 EXCESS MOLAR VOLUME THEORY

Excess molar volume of mixing (V^E) is defined as the difference between the volume of mixing of the real mixture and the value corresponding to an ideal mixture at the same conditions of temperature, pressure and composition, which is given by the equation 4.1:

$$V^E = V^M_{real} - V^M_{ideal} \tag{4.1}$$

The change in volume can be attributed to a number of factors:

i. The difference in size and shape of the compounds
ii. The difference in the intermolecular interaction energy between like and unlike molecules
iii. The formation of new chemical species
iv. The hydrogen bonding and,
v. The structural changes due to molecular orientations

Excess molar volume data of liquid mixtures are utilised to understand the departure of the real system from ideal and, the nature of the specific interactions between the molecules of the components. Excess molar volumes are also useful in conversion of the excess thermodynamics functions determined at constant pressure, to the conditions of mixing at constant volume.

The excess molar volume (V^E_{m}) is defined as (McGlashan 1979; Walas 1985; Letcher 1975):

$$V^E_{\mathrm{m}} = V_{mix} - \sum_{i=1}^{N} x_i V_i^0 \tag{4.2}$$

where x_i is the mole fraction of component *i*, $V_{\mathrm{mix}} = V_{\mathrm{real}}$ and V_{i}^0 are the molar volumes of the mixture and pure component *i*, respectively. For a binary mixture:

$$V^E_m = V_{mix} - (x_1 V_1^0 + x_2 V_2^0) \tag{4.3}$$

The change in volume on mixing two liquids, 1 and 2 can be attributed to a number of processes (Letcher 1975):

i. The breakdown of 1-1 and 2-2 intermolecular interactions, which have a positive effect on the volume,
ii. The formation of 1-2 intermolecular interactions, which results in a decrease of the volume of the mixture,
iii. The packing effect caused by the difference in the size and shape of the component species and which may have a positive or negative effect on the particular species involved, and
iv. The 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).

The volume change of mixing of binary mixtures 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).

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

$$V = V(T, P, n_1, n_2, n_3, \ldots\ldots\, n_f) \tag{4.4}$$

At constant temperature and pressure this is:

$$\mathrm{V} = V(n_1, n_2, n_3, \ldots\ldots\, n_f) \tag{4.5}$$

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

$$V_{\mathrm{m,unmix}} = \sum_{\mathrm{i=1}}^{\mathrm{N}} x_{\mathrm{i}} V_{\mathrm{m,i}}^{0} = V_{\mathrm{m,ideal}} \tag{4.6}$$

where V^0 is the molar volume of the pure species i.

Once the liquids have been mixed together, the volume of the mixture is not normally the sum of the volumes of the pure liquids but given by:

$$V_{\mathrm{m,mix}} = (V_{\mathrm{m,real}}) = x_1 V_{\mathrm{m,1}} + x_2 V_{\mathrm{m,2}} \cdots\cdots x_{\mathrm{i}} V_{\mathrm{m,i}} = \sum_{\mathrm{i=1}}^{\mathrm{N}} x_{\mathrm{i}} V_{\mathrm{m,i}} \tag{4.7}$$

Where $V_{\mathrm{m,i}}$ is the partial molar volumes which is discussed under Section 4.3.1.

The excess molar volume of binary, V_{m}^{E} , and the ternary, V_{123}^{E} is given by:

$$V_{m}^{\mathrm{E}} = V_{m,mix} - V_{m,unmix} = V_{m,real} - V_{m,ideal} = \sum_{i=1}^{N} x_i (V_{m,i} - V_{m,i}^{0}) \tag{4.8}$$

where $V_{\mathrm{m}}^{\mathrm{E}}$ is the excess molar volume of the binary and V_{123}^{E} for the ternary system at constant temperature and pressure (Smith and Pagni 1998)

4.2 CORRELATION AND PREDICTION THEORIES OF EXCESS MOLAR VOLUMES

Ternary excess molar volumes can be calculated using the predictive expressions proposed by (Redlich-Kister 1948; Kohler 1960; Tsao-Smith 1953; Jacob-Fitzner 1977; Cibulka 1982).

i. Redlich-Kister equation

$$V_{123}^{\mathrm{E}} = \sum_{\mathrm{j>i}} V_{\mathrm{m,ij}}^{\mathrm{E}} (x_{\mathrm{i}}, x_{\mathrm{j}}) \tag{4.9}$$

and

$$V_{ij}^{E} = x_i x_j \sum_{s=0}^{N} {}_{ij}A_i (x_i - x_j)^{z} \tag{4.10}$$

where

A_{i} are the coefficients of expansion of the Redlich-Kister polynomial, N is the polynomial degree, x_{i} and x_{j} are the mole fractions of the component in the binary mixture, and s is the number of parameters.

ii. Cibulka equation

$$V_{123}^{E} = \sum_{\mathrm{i,j=1.2;1.3;2.3}} V_{\mathrm{ij}}^{\mathrm{E}} (x_{\mathrm{i}}, x_{\mathrm{j}}) - x_1 x_2 x_3 (b_0 - b_1 x_1 - b_2 x_2) \tag{4.11}$$

where x_1, x_2 and x_3 are the mole fractions of ($[MOA]^+[Tf_2N]^-$, 2-propanol, or 1-butanol or 2-butanol and ethyl acetate), respectively, and it contains the three parameters (b_0, b_1, b_2), which is a correlation over the binary contributions. The values of (b_0, b_1, b_2) were adjusted to the experimental ternary excess molar volumes and the distinctive function was in the form of the sum squares of the residuals (Deenadayalu 2010b). The correlation coefficients and the standard deviations values are listed in Table 7.1 for all the ternary systems. The graphs obtained from using the Cibulka parameters are given in Figures, 7.4-7.12.

Where V_{ij}^E is the binary excess molar volume at composition ($x_i^{'}, x_j^{'}$), such that $x_i^{'} + x_j^{'} = 1$, $x_i^{'}$ and $x_j^{'}$ can be obtained as projections in the triangle diagram as normal, direct and parallel projections.

In this work the Cibulka equation was used to correlate ternary systems {$[MOA]^+[Tf_2N]^-$ + 2-propanol or 1-butanol or 2-butanol + ethyl acetate} at T = (298.15, 303.15, and 313.15) K.

a. Normal projection

$$x_i^{'} = \frac{(1 + x_i - x_j)}{2}, x_j^{'} = \frac{(1 + x_j - x_i)}{2} \tag{4.12}$$

and $$V_{123}^E = \sum_{i<j} \frac{4 x_i x_j}{1 - (x_i - x_j)^2} V_{ij}^E (x_i^{'}, x_j^{'}) \tag{4.13}$$

The relation is similar to the Redlich-Kister expression.

b. Direct projection

$$x_i^{'} = \frac{x_i}{x_i + x_j}, x_j^{'} = \frac{x_j}{x_i + x_j} \tag{4.14}$$

and $V_{123}^E = \sum_{i<j} (x_i - x_j)^2 V_{ij}^E (x_i^{'}, x_j^{'})$

c. Parallel projection

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

$x_i^{'}(1) = x_i, x_j^{'}(1) = 1 - x_i$

and

$$x_{\mathrm{j}}^{'}(2) = 1 - x_{\mathrm{j}}, x_{\mathrm{j}}^{'}(2) = x_{\mathrm{j}}$$

This yields the relation:

$$V_{123}^{\mathrm{E}} = \frac{1}{2}\sum_{\mathrm{i<j}} \frac{x_{\mathrm{j}}}{1 - x_{\mathrm{i}}} V_{\mathrm{ij}}^{\mathrm{E}}(x_{\mathrm{i}}, 1 - x_{\mathrm{j}}) + \frac{x_{\mathrm{i}}}{1 - x_{\mathrm{j}}} V_{\mathrm{ij}}^{\mathrm{E}}(1 - x_{\mathrm{j}}, x_{\mathrm{i}}) \tag{4.15}$$

4.3 PARTIAL MOLAR PROPERTIES

4.3.1 Excess partial molar properties at infinite dilution

The excess 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 the solute and solvent are not identifiable through space occupancy, instead volumetric properties of a solution can be interpreted in terms of excess 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 4.16 at constant pressure, temperature and composition and it relates the experimentally obtained solution density derived from the densitometer experimental data, and mole fraction of solvent and solute.

$$V^{E}{}_{m} = \frac{x_1 M_1}{\rho_1} + \frac{x_2 M_2}{\rho_2} \tag{4.16}$$

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

$$\mathrm{d}V = \left(\frac{\partial V}{\partial T}\right)_{P,n} \mathrm{d}T + \left(\frac{\partial V}{\partial P}\right)_{T,n} \partial P + \left(\frac{\partial V}{\partial n_1}\right)_{P,n2,\mathrm{T}} \mathrm{d}n_1 + \left(\frac{\partial V}{\partial n_2}\right)_{P,n1,\mathrm{T}} \mathrm{d}n_2 \tag{4.17}$$

$$V^{E}{}_{m,1} = \left(\frac{\partial V}{\partial n_1}\right)_{T,P,n_2} = \left(\frac{\partial_n V^{m}}{\partial n_1}\right)_{T,P,n_2} \tag{4.18}$$

$$V^{E}{}_{m,2} = \left(\frac{\partial V}{\partial n_2}\right)_{T,P,n_1} = \left(\frac{\partial n V^{m}}{\partial n_1}\right)_{T,P,n_1} \tag{4.19}$$

Using the partial molar volumes defined in equation 4.18 and 4.19, ∂V from the equation 4.20 then becomes:

$$\partial V = \left(\frac{\partial V}{\partial T}\right)_{P,n} \partial T = \frac{1}{\partial T}\left(\frac{\partial V}{\partial P}\right)_{T,n} \partial P \tag{4.20}$$

Equation 4.19 describes how the change in the volume is related to the partial molar volume of the individual component.

The excess partial molar volumes can be obtained mathematically using Rosenboom's method. In this work the partial molar volumes were obtained from using the Redlich-Kister parameters.
The equations for $V_{m,1}$, equation 4.21 which is for component 2 and 4.22 which is for component 1:

$$V^{E}{}_{m,1} = [A_0 + A_1 + A_2 + A_3 + ...] \tag{4.21}$$

and

$$V^{E}{}_{m,2} = [A_0 - A_1 + A_2 - A_3 + ...] \tag{4.22}$$

where A_1 are the coefficients of expansion of the Redlich- Kister polynomial. The Redlich-Kister equation was fitted to the experimental data for the (1-butanol or 2-butanol + ethyl acetate) systems at the temperatures (298.15, 303.15 and 313.15) K. The binary parameters with the standard deviations, and partial molar volumes at infinite dilutions calculated from the Redlich- Kister equation are listed in table 6.6.

CHAPTER 5

EXPERIMENTAL

5.1 DIFFERENT EXPERIMENTAL METHODS USED FOR MEASURING EXCESS MOLAR VOLUMES

The binary excess molar volume, V_{m}^{E} , at constant concentration of x_1 of component 1 and x_2 of component 2 are defined as:

$$V_m^E = V_{mix} - (x_1 V_1^0 + x_2 V_2^0) \tag{5.1}$$

Where $\mathrm{V}_{\mathrm{i}}^{0}$ is the molar volume of the mixture pure components. The excess molar volumes, $V_{\mathrm{m}}^{\mathrm{E}}$ upon mixing two liquids may be measured either directly or indirectly.

The direct measurements involve mixing the two liquids and determining the volume change (dilatometric method).

The indirect measurement involves measuring the density of pure liquid and the density of the mixture by pycnometer or densitometer and the latter method was used in this work, using equations 5.2 and 5.3., respectively.

$$V_m^E = \frac{x_1 M_1 + x_2 M_2}{\rho} - \frac{x_1 M_1}{\rho_1} - \frac{x_2 M_2}{\rho_2} \tag{5.2}$$

$$V_{123}^E = \frac{x_1 M_1 + x_2 M_2 + x_3 M_3}{\rho} - \frac{x_1 M_1}{\rho_1} - \frac{x_2 M_2}{\rho_2} - \frac{x_3 M_3}{\rho_3} \tag{5.3}$$

(Battino 1971; Letcher 1975; Handa and Benson 1979; Beath and McGlashan 1977; Govender 1996; Nevines 1997; Redhi 2003).

The summary of the different techniques (direct and indirect) are given below:

5.1.1 DIRECT DETERMINATION

The direct method measures the volume change that occurs when the liquids are mixed. Direct methods of measurement of excess molar volumes; include the batch dilatometer and continuous dilution dilatometer.

The batch dilatometer is characterized by the determination of a single point per loading of the apparatus and the continuous dilatometer is characterized by the determination of many data points per loading of the apparatus (Handa and Benson 1979; Nevines 1997; Redhi 2003).

5.1.1.1 Batch dilatometer

The dilatometer is filled with known masses of pure liquids, which are separated by mercury. The height of the 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. Figure 5.1 shows a diagram of the typical batch dilatometer

The V_m^E, is determined from the volume change and the masses of the components. It was reported that by using this technique, one could achieve a precision of ± 0.003 $cm^3.mol^{-1}$ in the excess molar volume over the temperature range of (280-350) K (Keyes and Hildebrand 1971; Nevines 1997; Redhi 2003).The disadvantage of this apparatus is that it is difficult to fill the dilatometer and this is usually accomplished using the syringe. A major source of error in this method is the determination of the composition as it is 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 quite significant (Keyes and Hildebrand 1971; Nevines 1997; Redhi 2003).

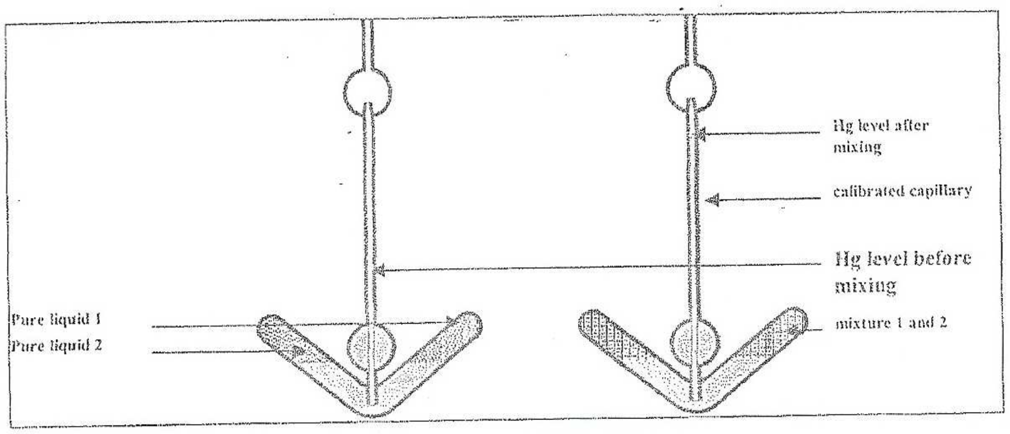


Figure 5.1 Batch dilatometer

5.1.1.2 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 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) recorded a precision of 0.0003cm^3.mol^{-1}, in the excess molar volume for their apparatus.

The continuous dilatometer apparatus is shown in figure 5.2

A measurement is made by filling the burette (e) with one of the pure liquids and the bulb (d) with the other liquid. As the dilatometer is tilted, some of the mercury is displaced into the burette through the capillary (c) and collects at the bottom of the burette. The 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 liquid that is displaced is determined from the height of the mercury in the burette. The capillary pressure effect is possible because mercury is used, and the compressibility of mercury has to be considered when determining the excess molar volume.

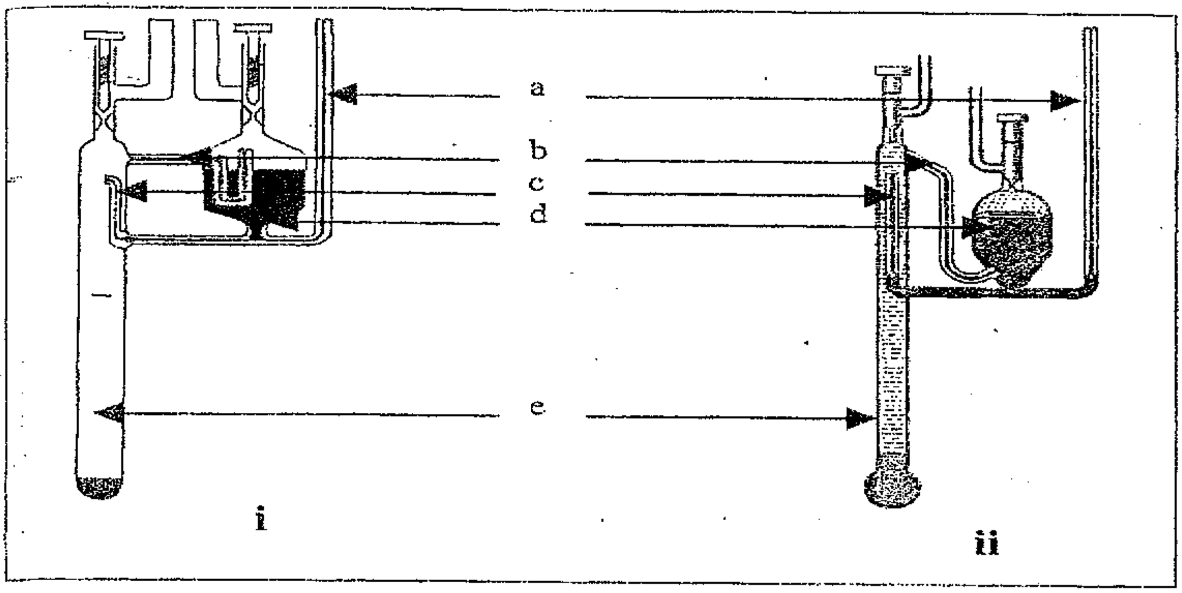


Figure 5.2 Continuous dilatometer (i) the design of Bottomly and Scott (ii) the design of Kumaran and McGlashan

- **(a) Calibrated capillary from which the volume change is determined**
- **(b) Liquid capillary**
- **(c) Mercury capillary**
- **(d) Bulb that contains mercury**
- **(e) Burette liquid**

5.1.2 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 excess molar volume. However, the development of highly accurate vibrating tube densitometers has made it possible to determine the excess molar volume with acceptable accuracy from the density measurements. This method is also simple.

The excess molar volumes for binary V_{m}^{E} and V_{123}^{E} ternary mixtures are determined from the density measurements using the following equations, respectively:

$$V_m^E = \frac{x_1 M_1 + x_2 M_2}{\rho} - \frac{x_1 M_1}{\rho_1} - \frac{x_2 M_2}{\rho_2} \qquad (5.2)$$

$$V_{123}^E = \frac{x_1 M_1 + x_2 M_2 + x_3 M_3}{\rho} - \frac{x_1 M_1}{\rho_1} - \frac{x_2 M_2}{\rho_2} - \frac{x_3 M_3}{\rho_3} \qquad (5.3)$$

where x_1, x_2 and x_3 are the mole fractions, M_1, M_2 and M_3 are the molar masses, ρ_1, ρ_2, ρ_3 and ρ are the densities where 1,2, and 3 refers to the component 1,2 and 3, respectively and ρ is the density of the mixture (Govender 1996; Nevines 1997; Redhi 2003).

5.1.2.1 Pycnometer

Pycnometry involves the determination of the mass for a fixed volume. A vessel with a known volume is filled with a liquid mixture of known composition. It is then weighed and this mass, together with the composition and volume is used to determine the excess molar volume.

A pycnometer is capable of a precision of 5 x 10^{-6} g·cm^{-3} for the density measurement, and to 0.001 cm^{3}·mol^{-1} for the excess molar volumes reported by (Wood and Bruisie 1943). The pycnometer apparatus is shown in figure 5.3.

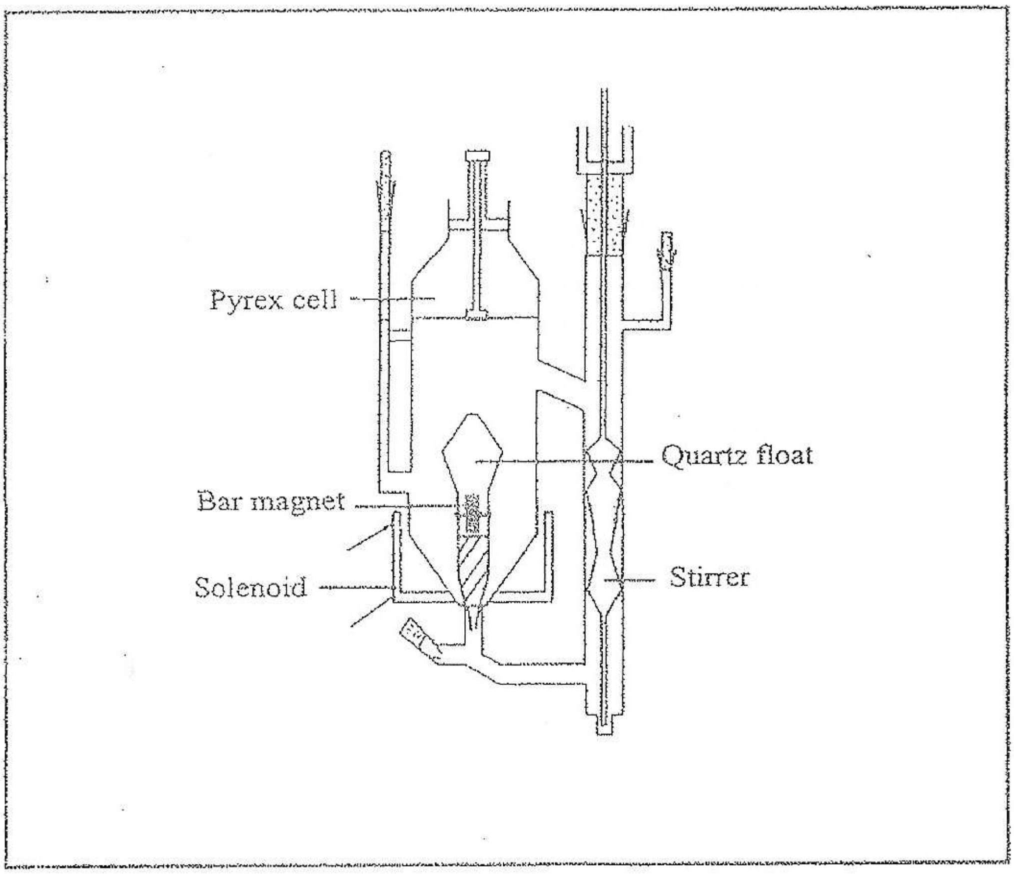
Figure 5.3: A typical pycnometer (a) empty pycnometer (b) filled pycnometer

5.1.2.2 Magnetic float densimeter

The mode of operation of a magnetic float densimeter is based on the determination of the height of a magnetic float in a liquid mixture. The height of this magnetic float in the presence of a known magnetic field is a function of the buoyancy of the liquid. The buoyancy of the liquid is related to the density of the liquid.

The magnetic float densimeter is shown in figure 5.4.

An instrument with a precision of 3 x 10^{-6} g·cm^{-3} has been reported which translates to a precision of 0.0008 cm^3·mol^{-1}, in of excess molar volume (Franks and Smith 1967).



5.4 Magnetic float densimeter

5.1.2.1 Mechanical oscillating densitometer

Mechanical oscillating (vibrating tube) densimeters coupled to digital output displays are widely used in the chemical industry, and in research laboratories to measure the densities of pure liquids and liquid mixtures.

The frequency of the vibrating tube containing a liquid that is subjected to a constant electric stimulation is related to the density of the liquid. According to Handa and Benson (1979), the frequency of a vibration of an undamped oscillator (e.g. tube containing a liquid) connected by a spring with constant elasticity,c, is related to the mass of oscillator,M, by using the following equation:

$$2\pi v = \left(\frac{c}{M}\right)^{\frac{1}{2}} \tag{5.4}$$

Since the oscillator is a hollow tube, M, is the total 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:

$$M = M_0 + \rho V \tag{5.5}$$

This mass, together with the composition and the volume of the vessel is used to determine the excess molar volume. The pycnometer apparatus is shown in figure 5.3.

Substitution of equation (5.5) into equation (5.4) and solving for ρ:

$$\rho = -\frac{M_0}{V} + \left(\frac{c}{4\pi^2}\right)\left(\frac{1}{V^2}\right) \tag{5.6}$$

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

$$\rho = A + B\left(\frac{1}{v}\right)^2 \tag{5.7}$$

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

$$\rho = A + B\tau^2 \tag{5.8}$$

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:

$$\rho - \rho_0 = B(\tau^2 - \tau_0^2) \tag{5.9}$$

Commercially available vibrating tube denismeters with a precision of 0.001% are available. This implies that a precision of 0.003 $\mathrm{cm^3 \cdot mol^{-1}}$ in the measurement of excess molar volume (Nevines 1997).

The Anton Paar (DMA 38) vibrating densitometer was used in this work to measure the densities of the binary and ternary mixtures.

5.2 EXPERIMENTAL APPARATUS

5.2.1 Vibrating tube densitometer

In this work the excess molar volume was determined by densimetry using the Anton Paar DMA 38 vibrating tube densitometer which is shown in figure 5.5.

Figure 5.5 DMA 38 densitometer

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 τ and the density ρ of a mixture is given by:

$$\rho = A + B\tau^2 \qquad (5.10)$$

The constants *A* and *B* are the 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.

5.2.2 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 v.

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

As the frequency is a function of mass, so when mass increases the frequency decreases, in other words the period of oscillation τ increases and is related by the following equation:

$$v = \frac{1}{\tau} \qquad (5.11)$$

A magnet is fixed to the measurement 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:

$$\tau = 2\pi \sqrt{\frac{(\rho V_c + m_c)}{K}} \qquad (5.12)$$

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

It follows that:

$$\rho = \frac{K\tau^2}{4\pi^2 V_c} - \frac{m_c}{V_c} \qquad (5.13)$$

The density and the period oscillation are related as follows:

$$\rho = A\tau^2 + B \tag{5.14}$$

$$\rho = \frac{K\tau^2}{4\pi^2 V_c} \text{ and } B = -\frac{m_c}{V_c}$$

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.

5.2.3 Materials

The IL used in this work is the {methyl trioctylammonium bis (trifluoromethylsulfonyl imide)} ($[MOA]^+[Tf_2N]^-$) which was used without any further purification.

The water content in all chemicals was determined by the Karl Fischer coulometer (Metrohm 831) which is shown in figure 5.6.

Figure 5.6 Karl Fischer coulometer (Metrohm 831) apparatus used for determining the water content

The mass % of water was found to be 0.0400% in $[MOA]^+[Tf_2N]^-$, 0.006% in ethyl acetate 0.0041% in 2-propanol, 0037% 1-butanol and 0.0038% 2-butanol. Ethyl acetate, 2-propanol, 1-butanol and 2-butanol were used without any further purification.

The information about the pure components, their suppliers and % mass purities used in this work is given in Table 5.1.

The literature and experimental density value of the pure compounds are reported in Table 5.2.

Table 5.1 Pure compounds, suppliers name and mass % purity.

Compound	**Purity %**	**Supplier**
$[MOA]^+[Tf_2N]^-$	99.0	Sigma-Aldrich
2-propanol	99.7	BHD chemicals
1-butanol	99.8	Hipersoir chemicals
2-butanol	99.5	Fluka
Ethyl acetate	99.7	Sigma-Aldrich

Table 5.2 Literature and experimental densities of the pure compounds at T = (298.15, 303.15, and 313.15) K.

Compounds	Purity %	$\rho/(\mathrm{g.cm}^3)$			
		Literature	Experimental		
		T= 298.15/K	T= 298.15/K	T= 303.15/K	T= 313.15/K
$[\mathrm{MOA}]^+[\mathrm{Tf_2N}]^-$	99.0	1.1069 [a]	1.1070	1.1022	1.0956
2-Propanol	99.7	0.7812 [b]	0.7814	0.7771	0.7688
1-Butanol	99.8	0.8055 [c]	0.8056	0.8035	0.7964
2-Butanol	99.5	0.8024 [d]	0.8026	0.7982	0.7905
Ethyl acetate	99.7	0.8947 [d]	0.8948	0.8886	0.8752

[a] Deenadayalu and Bahadur 2010a

[b] Oswal and Putta 2001

[c] Maurlzlo *et al*. 1998

[d] Resa *et al*. 2004

5.2.4 Preparation of binary and ternary mixtures

To obtain the exact mass of each component added, an OHAUS mass balance which has a precision of 0.0001 g was used. Binary data for (1-butanol + ethyl acetate) and (2-butanol + ethyl acetate) was only found at *T* = (298.15 and 303.15) K in literature. Therefore, the density measurements were determined at *T* = (298.15, 303.15 and 303.15) K, for (1-butanol or 2-butanol + ethyl acetate) systems. The binary mixtures were prepared by, first tarring the empty glass vials before the 1-butanol or 2-butanol was added. After tarring the mass balance, the first component (1-butanol or 2-butanol) was transferred into the stoppered bottles to prevent evaporation, then tarred again prior to adding the second component (ethyl acetate).

Before each ternary system was prepared, the mass of each component in the ternary mixture was calculated over the entire mole fraction range using an Excel spreadsheet, and a ternary plot was used to verify that the entire composition range was covered. The ternary mixture composition was calculated for a fixed z value covering the entire mole fraction range using the formula $z = x_3/ x_1$, where x_1 is the mole fraction of the ionic liquid and x_3 is the mole fraction of ethyl acetate. The z values were 7.57, 3.36, 1.26, 0.84, 0.42, 0.25 and 0.08. The calculated ternary composition plots can be found in Appendix 1.

The ternary mixtures were prepared by first tarring the glass vial before the IL was added. After the empty glass vial was tarred, the first calculated mass component (IL) was accurately transferred via a syringe into the air tight stoppered glass vial and weighed. The mass balance was tarred again, the mass of the second component (2-propanol or 1-butanol or 2-butanol) was obtained and the third component (ethyl acetate) was also accurately transferred into the same vial and weighed.

The mixtures were then shaken in stoppered bottles or vials in order to ensure complete homogeneity of the compounds, since the ionic liquid is slightly viscous. The injection of the solution into the densimeter was done slowly to avoid the formation of bubbles inside the vibrating tube of the densimeter.

The uncertainty for the binary and ternary mole fraction is 0.0006.

5.2.5 Experimental procedure for the instrument

Anton Paar DMA 38 vibrating U-tube densimeter was used for measuring the densities. The densitometer consists of a built-in thermostat controller which is capable of maintaining the temperature precisely to ± 0.01 K and measuring the density to ± 0.0001 $g\cdot cm^{-3}$.

Before each experimental run, the cell was first flushed with ethanol, and then dried with compressed dry air using a built-in pump. Ultra pure water supplied by SH Calibration Service GmbH Graz (used as calibration standard) was then introduced into the cell by means of a glass syringe. Calibration was done to eliminate instrumental errors. To verify that the instrument was working fine, we measured the density of the pure $[MOA]^+[Tf_2N]^-$, 2-propanol, 1-butanol, 2-butanol and ethyl acetate liquids and compared them with literature, and we found that the experimental and literarure excess molar volumes were within the experimental error (Deenadayalu and Bahadur 2010 b; Oswal and Putta 2001; Maurlzlo *et al.*1998 and Resa *et al.*2004).

The process of injection was carried out slowly, to enable 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 out for the calibration. The solution mixtures were introduced into the sample cell in exactly the same manner as for the ultra pure water. The density values of water, pure solvents and air were determined after a series of density measurements to permit a continuous check on sample purity and operation of densitometer,

This was further verified by repeated measurements of the same solution at different times. Using the density and the composition of the mixtures, the excess molar volume was calculated using equations 5.15 for binary mixtures and 5.16 for ternary mixtures.

$$V_m^E = \frac{x_1 M_1 + x_2 M_2}{\rho} - \frac{x_1 M_1}{\rho_1} - \frac{x_2 M_2}{\rho_2} \tag{5.15}$$

and

$$V_{123}^E = \frac{x_1 M_1 + x_2 M_2 + x_3 M_3}{\rho} - \frac{x_1 M_1}{\rho_1} - \frac{x_2 M_2}{\rho_2} - \frac{x_3 M_3}{\rho_3} \tag{5.16}$$

5.2.6 Specifications of the instrument

Accuracy : 1 x 10^{-4} g·cm^{-3}

Min. sample volume : 2 cm^3

Measuring range : 0-3 g·cm^{-3}

Temperature range : 288 – 313 K

Pressure range : 10 bar (145 psi)

5.2.7 Validation of experimental technique

To test the experimental technique the excess molar volumes of the test system (octane + toluene) at $T = 298.15$ K was obtained and compared with the values in literature (Moravkova and Linek 2008). It was then found that the difference between the experimental and literature V_{m}^{E} values for the binary test system was within the experimental error. For binary, V_{m}^{E} the root mean square deviation (RMSD) was found to be ± 0.007 cm^{-3}·mol^{-1} for the binary excess molar volumes.

An equation for the literature data polynomial was obtained. For each experimental mole fractions, the polynomial was used to calculate the “expected” excess molar volumes. From the difference between the literature V_{m}^{E} and the experimental V_{m}^{E}, the experimental uncertainty was obtained.

The comparison of the experimental and literature binary data is presented in Table 5.3 and shown in figure 5.7.

Table 5.3 Experimental and literature binary data of the test system (toluene + octane) at T = 298.15 K.

x_1	x_2	$V^E_{\mathrm{m,lit}}$ / cm^3·mol^{-1}	$V^E_{\mathrm{m,exp}}$ / cm^3·mol^{-1}	$V^E_{\mathrm{m,lit}}$ - $V^E_{\mathrm{m,exp}}$ / cm^3·mol^{-1}
0.0653	0.9347	0.074	0.075	- 0.001
0.1274	0.8726	0.133	0.122	0.011
0.1940	0.8060	0.180	0.188	- 0.008
0.2515	0.7485	0.211	0.208	0.003
0.3935	0.6065	0.256	0.247	0.009
0.5404	0.4596	0.259	0.257	0.002
0.6736	0.3264	0.224	0.216	0.008
0.7207	0.2793	0.203	0.202	0.001
0.8724	0.1276	0.109	0.106	0.003
0.9323	0.0677	0.062	0.050	0.012
σV^E_{m}				**0.007** cm^3·mol^{-1}

Root mean square deviation (RMSD) given by the formula:

$$\sigma = \sqrt{\sum_{i=1}^{N} \frac{(x_i - x)^2}{N}} = \underline{\mathbf{0.007}}\ \mathrm{cm^{-3}{\cdot}mol^{-1}} \text{ where } x_{\mathrm{i}} = V^E_{\mathrm{m,exp}}$$

$x = V^E_{\mathrm{m}}$ mean

N = number of degrees of freedom

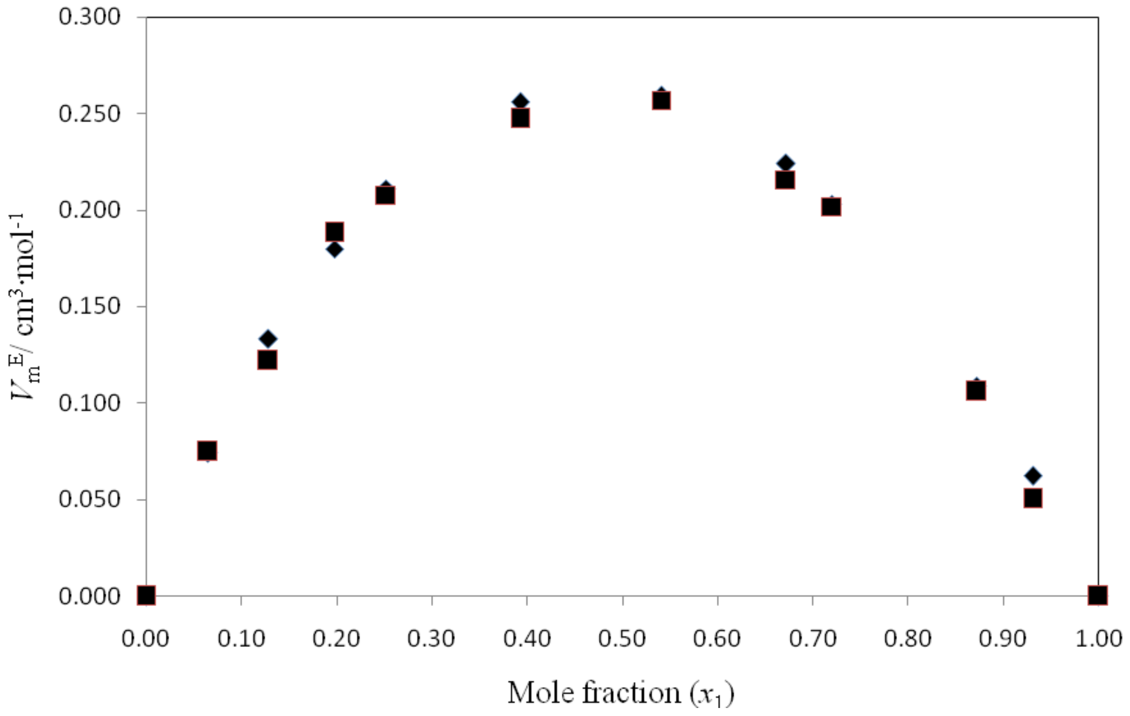


Figure 5.7 Comparison of the experimental, (■), and literature, (♦), excess molar volume values of octane + toluene at *T* = 298.15 K

CHAPTER 6

RESULTS

A. BINARY SYSTEMS

The excess molar volumes of binary mixtures (1-butanol + ethyl acetate) and (2-butanol + ethyl acetate) were measured at T = (298.15, 303.15 and 313.15) K and compared with the previously measured binary data published by (Fermeglia *et al.* 1988 and Resa *et al.* 2004). The reason for measuring the excess molar volumes of the above binary systems at T = (298.15, 303.15 and 313.15) K was because the excess molar volume of the binary systems (1-butanol + ethyl acetate) (Fermeglia *et al.* 1988) system was published only at T = 298.15 K, and the binary excess molar volume for the system (2-butanol+ ethyl acetate) (Resa *et al.* 2004) was only published at T = (298.15 and 303.15) K. The binary data for (2-propanol + ethyl acetate) has been published at T = (298.15, 303.15 and 313.15) K by (Oswal *et al.* 2001). The binary excess molar volume for the (2-propanol or 1-butanol or 2-butanol + IL) systems is work done by our research group (Bahadur *et al.* 2011). The data for these binary systems have not been presented before, but is presented here. The binary data for the (IL + ethyl acetate) system at T = (298.15, 303.15 and 313.15) K has been published (Bahadur *et al.* 2011). The excess molar volumes of the binary systems (1-butanol + ethyl acetate) and (2-butanol + ethyl acetate) were calculated from the experimental densities at T = (298.15, 303.15 and 313.15) K using equation (6.1).

$$V_m^{\mathrm{E}} = \frac{x_1 M_1 + x_2 M_2}{\rho} - \frac{x_1 M_1}{\rho_1} - \frac{x_2 M_2}{\rho_2} \qquad (6.1)$$

where x_1, and x_2 are mole fractions, M_1, and M_2 are the molar masses, ρ_1, and ρ_2 are the density of pure components: where '1' refers to 1-butanol or 2-butanol and '2' refers to ethyl acetate, and ρ is the density of the binary mixture. The measured density, ρ, and binary excess molar volume for the binary mixtures (1-butanol or 2-butanol + ethyl acetate) systems are presented in Tables 6.1 and 6.2, respectively. The binary curves for the experimental data are shown in figures 6.1-6.3 for (1-butanol + ethyl acetate) and for (2-butanol + ethyl acetate) in figures 6.4- 6.6, respectively.

The density and excess molar volume for the binary mixtures ($[\mathrm{MOA}]^+[\mathrm{Tf_2N}]^-$ + 2-propanol or 1-butanol or 2-butanol) at T = (298.15, 303.15 and 313.15) K, is given in Tables 6.3-6.5, respectively (article in preparation, Bahadur *et al.* 2011).

Table 6.1 Density, ρ, and excess molar volume, V_m^E for 1-Butanol (x_1) + Ethyl acetate (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})
	T = 298.15 K	
0.0904	0.8865	0.0794
0.1337	0.8823	0.1393
0.2525	0.8715	0.2111
0.3723	0.8607	0.2556
0.4807	0.8510	0.2719
0.5955	0.8409	0.2530
0.7032	0.8315	0.2097
0.8009	0.8230	0.1524
0.8916	0.8151	0.0881
0.9641	0.8086	0.0482
0.9795	0.8073	0.0293
	T = 303.15 K	
0.0904	0.8804	0.1318
0.1337	0.8768	0.1445
0.2525	0.8667	0.1910
0.3723	0.8566	0.2098
0.4807	0.8475	0.2061
0.5955	0.8380	0.1693
0.7032	0.8288	0.1500
0.8009	0.8206	0.1007
0.8916	0.8130	0.0413
0.9641	0.8067	0.0099
0.9795	0.8053	0.0067

Table 6.1 continued....

	T = 313.15 K	
0.0904	0.8696	0.0693
0.1337	0.8660	0.1056
0.2525	0.8566	0.1369
0.3723	0.8468	0.1864
0.4807	0.8380	0.2068
0.5955	0.8288	0.1968
0.7032	0.8201	0.1777
0.8009	0.8123	0.1341
0.8916	0.8050	0.0880
0.9641	0.7994	0.0138
0.9795	0.7981	0.0097

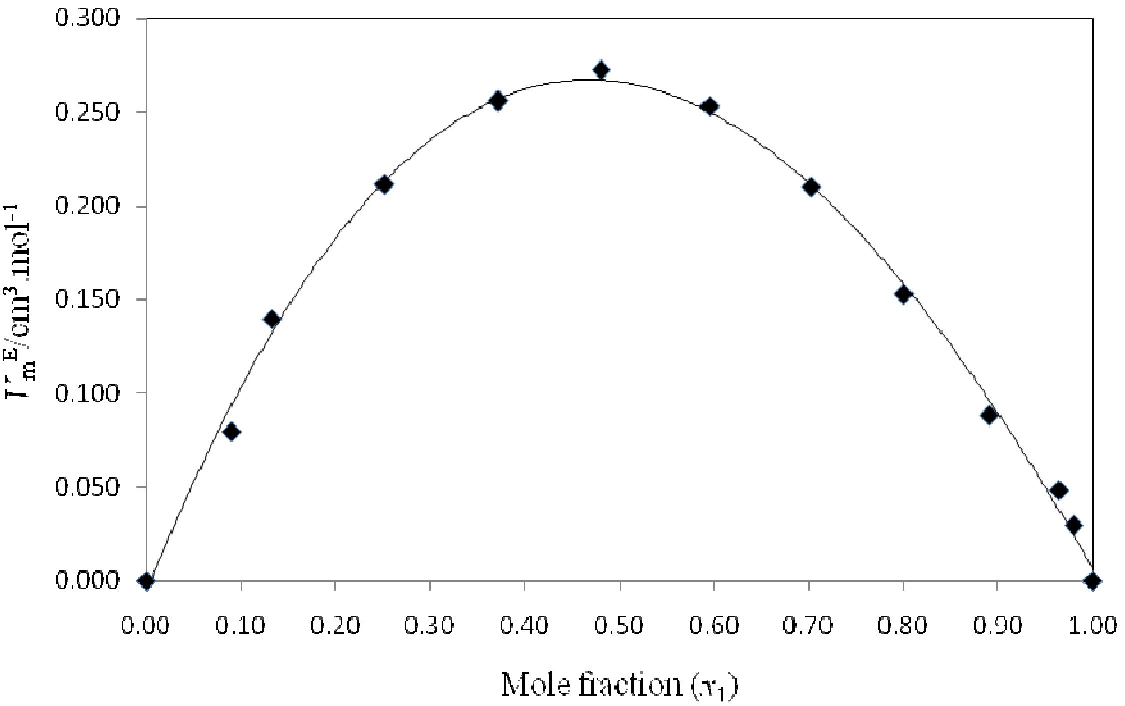


Figure 6.1 Plot of excess molar volume for the binary mixture of [1-butanol (x_1) + ethyl acetate (x_2)] at T = 298.15 K. Experimental points, (■), Redlich-Kister polynomials (-).

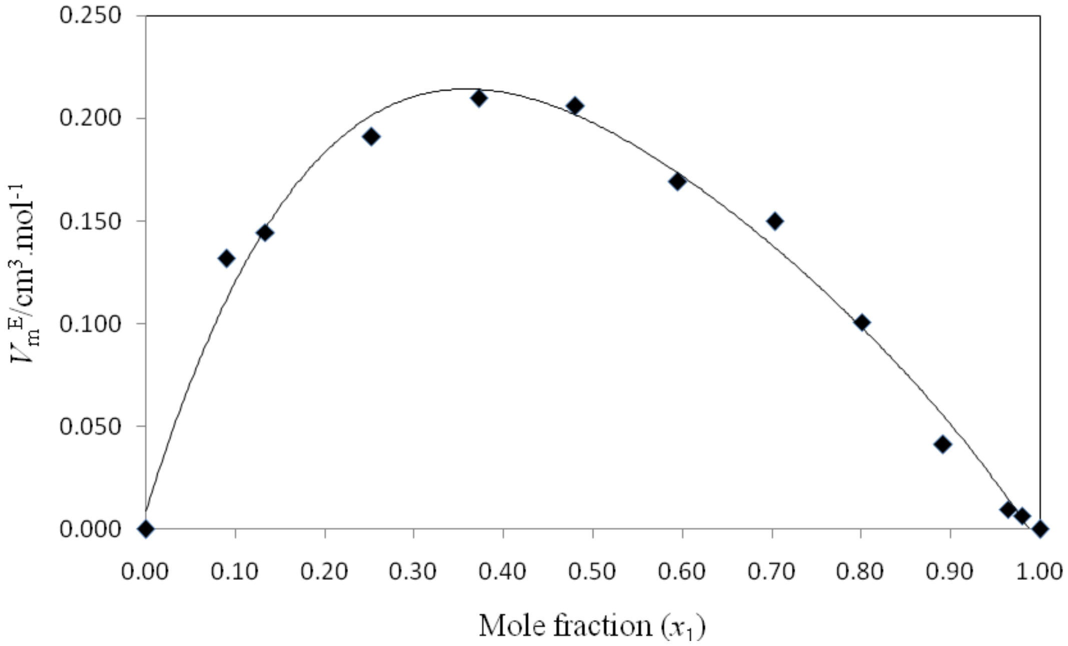


Figure 6.2 Plot of excess molar volumes for the binary mixture of [1-butanol (x_1) + ethyl acetate (x_2)] at T = 303.15 K. Experimental points, (■), Redlich-Kister polynomials (**-**).

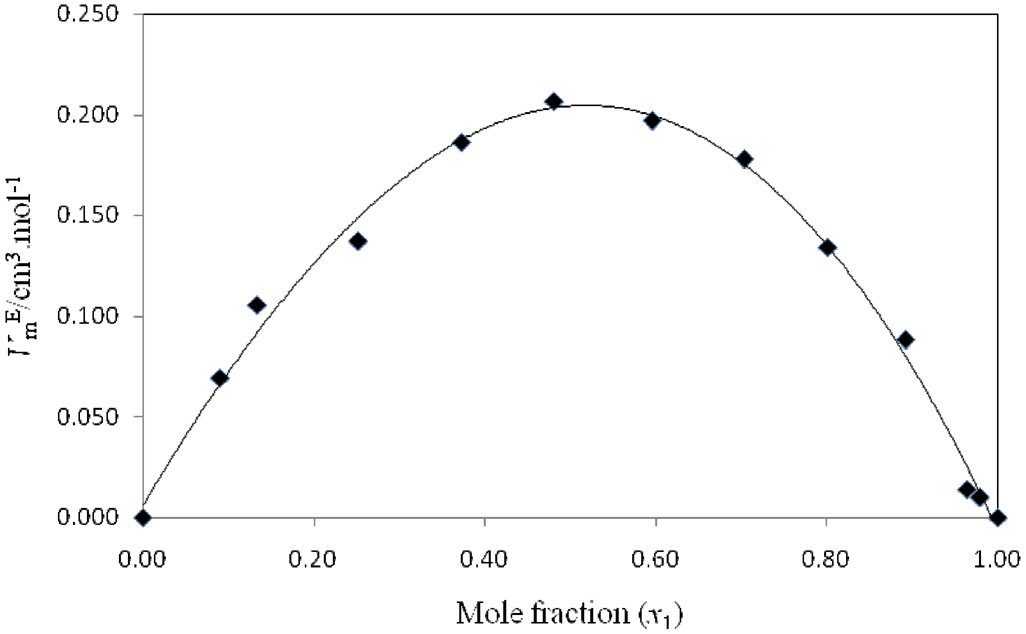


Figure 6.3 Plot of excess molar volumes for the binary mixture of [1-butanol (x_1) + ethyl acetate (x_2)] at T = 313.15 K. Experimental points, (■), Redlich-Kister polynomials (-).

Table 6.2 Density, ρ, and excess molar volume, V_{m}^{E} for 2-Butanol (x_1) + Ethyl acetate (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})
	T = 298.15 K	
0.0603	0.8885	0.1178
0.1109	0.8832	0.2147
0.1511	0.8789	0.3004
0.1998	0.8738	0.3896
0.2502	0.8688	0.4484
0.3020	0.8636	0.5130
0.3489	0.8589	0.5679
0.3988	0.8541	0.6005
0.4506	0.8494	0.5987
0.5011	0.8446	0.6182
0.5631	0.8390	0.6053
0.6010	0.8356	0.5919
0.6501	0.8311	0.5821
0.7032	0.8265	0.5376
0.7520	0.8225	0.4657
0.8012	0.8184	0.3983
0.8498	0.8146	0.2996
0.9028	0.8103	0.2061
0.9519	0.8067	0.0706
	T = 303.15 K	
0.0603	0.8825	0.1092
0.1109	0.8776	0.1728
0.1511	0.8732	0.2790
0.1998	0.8686	0.3226
0.2502	0.8635	0.4037
0.3020	0.8584	0.4682
0.3489	0.8539	0.5103

Table 6.2 continued....

0.3988	0.8492	0.5420
0.4506	0.8444	0.5621
0.5011	0.8399	0.5576
0.5631	0.8343	0.5572
0.6010	0.8309	0.5513
0.6501	0.8268	0.5052
0.7032	0.8224	0.4478
0.7520	0.8183	0.3967
0.8012	0.8140	0.3618
0.8498	0.8101	0.2836
0.9028	0.8058	0.2000
0.9519	0.8024	0.0498
	T = 313.15 K	
0.0603	0.8702	0.0258
0.1109	0.8656	0.0901
0.1511	0.8614	0.2027
0.1998	0.8571	0.2450
0.2502	0.8525	0.3034
0.3020	0.8475	0.3922
0.3489	0.8432	0.4431
0.3988	0.8387	0.4852
0.4506	0.8343	0.4933
0.5011	0.8299	0.5105
0.5631	0.8245	0.5276
0.6010	0.8212	0.5350
0.6501	0.8173	0.4968
0.7032	0.8129	0.4734
0.7520	0.8089	0.4418
0.8012	0.8051	0.3797
0.8498	0.8014	0.3083
0.9028	0.7974	0.2225
0.9519	0.7944	0.0545

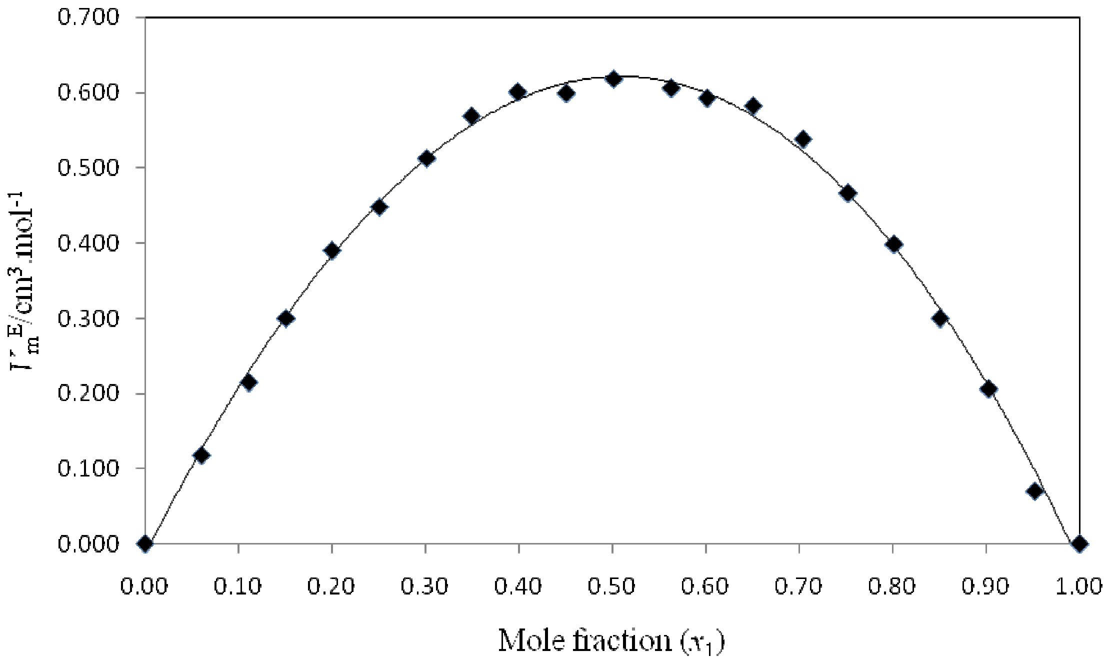


Figure 6.4 Plot of excess molar volumes for the binary mixture of [2-butanol (x_1) + ethyl acetate (x_2)] at T = 298.15 K. Experimental points, (■), Redlich-Kister polynomials (-).

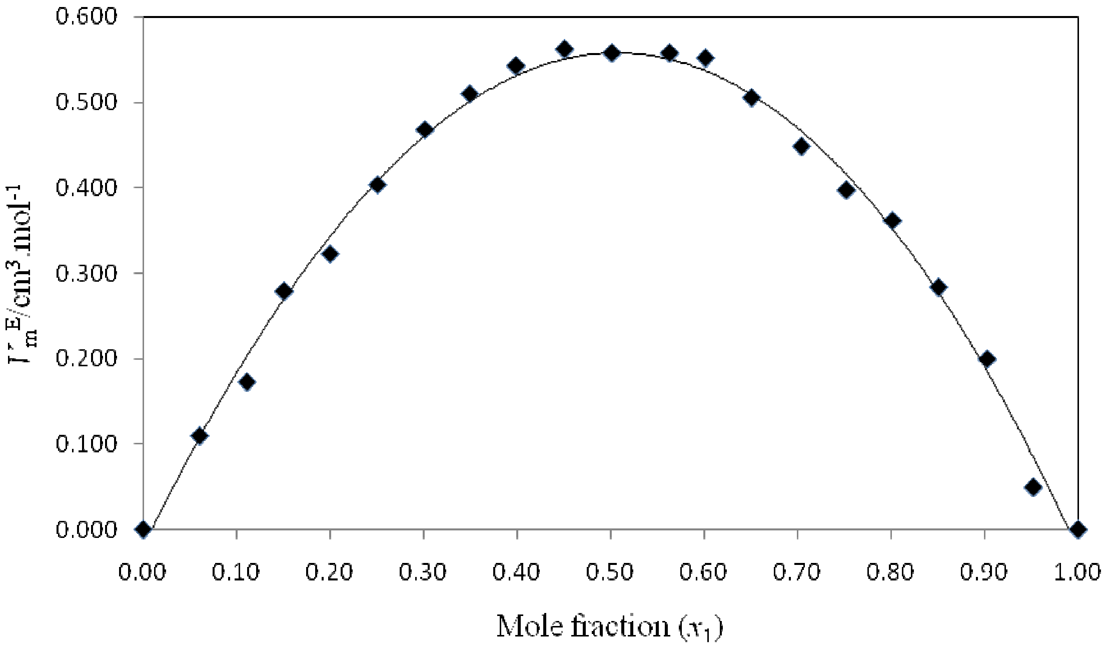


Figure 6.5 Plot of excess molar volumes for the binary mixture of [2-butanol (x_1) + ethyl acetate (x_2)] at T = 303.15 K. Experimental points, (■), Redlich-Kister polynomials (-).

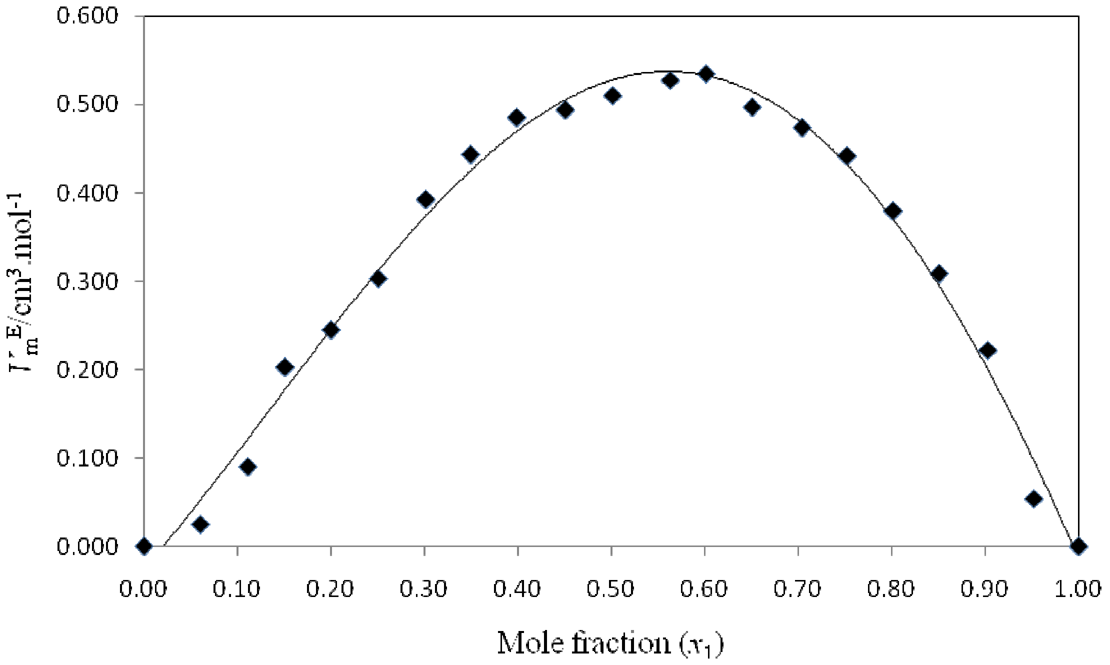


Figure 6.6 Plot of excess molar volumes for the binary mixture of [2-butanol (x_1) + ethyl acetate (x_2)] at T = 313.15 K. Experimental points, (■), Redlich-Kister polynomials (-).

Table 6.3 Density, ρ, and excess molar volume, V_m^E for $[MOA]^+[Tf_2N]^-$ (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})
	T = 298.15 K	
0.0530	0.8769	0.190
0.1000	0.9326	-0.279
0.2045	1.0049	-1.456
0.2841	1.0338	-1.681
0.3934	1.0562	-1.079
0.4824	1.0676	-0.271
0.5896	1.0789	0.257
0.7066	1.0890	0.429
0.7967	1.0952	0.505
0.8960	1.1005	0.734
	T = 303.15 K	
0.0530	0.8730	0.177
0.1000	0.9289	-0.324
0.2045	1.0015	-1.564
0.2841	1.0303	-1.776
0.3934	1.0526	-1.148
0.4824	1.0639	-0.304
0.5896	1.0752	0.234
0.7066	1.0854	0.374
0.7967	1.0916	0.452
0.8960	1.0969	0.683

Table 6.3 continued....

	T = 313.15 K	
0.0530	0.8651	0.176
0.1000	0.9213	-0.376
0.2045	0.9947	-1.778
0.2841	1.0233	-1.971
0.3934	1.0451	-1.218
0.4824	1.0566	-0.417
0.5896	1.0681	0.056
0.7066	1.0783	0.188
0.7967	1.0844	0.304
0.8960	1.0895	0.633

* Article in preparation J Phys Chem B. Bahadur *et al.* 2011

Table 6.4 Density, ρ, and excess molar volume, V_m^E for $[MOA]^+[Tf_2N]^-$ (x_1) + 1-Butanol (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})
	T = 298.15 K	
0.0654	0.8981	0.201
0.1421	0.9620	-0.147
0.2623	1.0180	-0.618
0.3284	1.0373	-0.777
0.4437	1.0604	-0.805
0.5343	1.0728	-0.641
0.6385	1.0834	-0.352
0.7397	1.0910	0.096
0.8432	1.0979	0.235
0.9195	1.1021	0.368
	T = 303.15 K	
0.0654	0.8943	0.248
0.1421	0.9586	-0.175
0.2623	1.0146	-0.672
0.3284	1.0339	-0.843
0.4437	1.0568	-0.829
0.5343	1.0691	-0.637
0.6385	1.0798	-0.387
0.7397	1.0874	0.058
0.8432	1.0942	0.239
0.9195	1.0986	0.272

Table 6.4 continued....

	T = 313.15 K	
0.0654	0.8872	0.227
0.1421	0.9518	-0.281
0.2623	1.0076	-0.786
0.3284	1.0269	-0.976
0.4437	1.0497	-0.960
0.5343	1.0621	-0.815
0.6385	1.0727	-0.546
0.7397	1.0805	-0.199
0.8432	1.0872	0.005
0.9195	1.0916	0.022

* Article in preparation J Phys Chem B. Bahadur *et al.* 2011

Table 6.5 Density, ρ, and excess molar volume, V_m^E for $[MOA]^+[Tf_2N]^-$ (x_1) + 2-Butanol (x_2) at T = (298.15, 303.15 and 313.15) K.*

x_1	$\rho/(g\cdot cm^{-3})$	$V_m^E/(cm^{-3}\cdot mol^{-1})$
	T = 298.15 K	
0.0654	0.8942	0.293
0.1397	0.9562	0.166
0.2623	1.0138	-0.057
0.3282	1.0334	-0.159
0.4054	1.0506	-0.213
0.5045	1.0667	-0.171
0.6051	1.0785	0.021
0.7046	1.0873	0.308
0.8080	1.0946	0.596
0.9067	1.1008	0.612
	T = 303.15 K	
0.0654	0.8903	0.280
0.1397	0.9527	0.087
0.2623	1.0102	-0.123
0.3282	1.0297	-0.202
0.4054	1.0469	-0.252
0.5045	1.0630	-0.204
0.6051	1.0748	-0.005
0.7046	1.0837	0.249
0.8080	1.0910	0.542
0.9067	1.0972	0.560

Table 6.5 continued....

	T = 313.15 K	
0.0654	0.8826	0.267
0.1397	0.9453	0.016
0.2623	1.0031	-0.270
0.3282	1.0225	-0.333
0.4054	1.0397	-0.389
0.5045	1.0557	-0.314
0.6051	1.0676	-0.150
0.7046	1.0765	0.103
0.8080	1.0839	0.349
0.9067	1.0900	0.409

* Article in preparation J Phys Chem B. Bahadur *et al.* 2011

The Redlich-Kister equation was fitted to all binary data to obtain the Redlich-Kister parameters. The Redlich-Kister equation is given as:

$$V_m^E = x_1 x_2 \sum_{i=1}^{N} A_i (2x_1 - 1)^{i-1} \tag{6.3}$$

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

The excess partial molar volumes at infinite dilution, $V_{\mathrm{m},1}^{\infty}$, are obtained from equation 6.4 which is for component 1 and 6.5 for component 2:

$$V_{m,2}^{E\infty} = [A_0 - A_1 + A_2 - A_3 + ...] \tag{6.4}$$

and

$$V_{m,1}^{E\infty} = [A_0 + A_1 + A_2 + A_3 + ...] \tag{6.5}$$

where A_1 are the coefficients of expansion of the Redlich- Kister polynomial. The Redlich-Kister equation was fitted to the experimental data for the (1-butanol or 2-butanol + ethyl acetate) systems at the temperatures (298.15, 303.15 and 313.15) K The binary parameters with the standard deviations, and partial molar volumes at infinite dilutions calculated from the Redlich- Kister equation are listed in table 6.6.

Table 6.6 also lists the correlation parameters obtained from the Redlich-Kister equation for (IL + 2-propanol or 1-butanol or 2-butanol) which is taken from unpublished data (Bahadur *et al.* 2011) and for (IL or 2-propanol + ethyl acetate) which was taken from literature (Deenadayalu 2010b; Oswal *et al.* 2001).

Table 6.6 Redlich-Kister fitting parameters for the binary systems (IL + 2-propanol or 1-butanol or 2-butanol) and for (IL, 2-propanol or 1-butanol or 2-butanol + ethyl acetate) systems at T = (298.15, 303.15, and 313.15) K.

T /K	A_0	A_1	A_2	A_3	A_4	$V_{m,1}^{E\infty}$/ $cm^3 \cdot mol^{-1}$	$V_{m,2}^{E\infty}$/ $cm^3 \cdot mol^{-1}$	σ/ $cm^3 \cdot mol^{-1}$
				2-Propanol + ethyl acetate[a]				
298.15	1.89	0.04	0.09	0.14	-	2.16	1.90	0.002
303.15	2.07	0.10	0.08	-	-	2.25	1.89	0.002
313.15	2.41	0.08	0.16	-	-	2.65	2.17	0.002
				1-Butanol + ethyl acetate[b]				
298.15	1.06	-1.15	-	-	-	-0.08	2.21	0.008
303.15	7.94	-4.55	2.37	-	-	5.75	14.85	0.011
313.15	8.18	-	-	-	-	8.18	8.18	0.009
				2-Butanol + ethyl acetate[b]				
298.15	2.30	-6.95	-2.96	-	-	-7.40	6.49	0.012
303.15	2.27	-5.15	-4.04	-	-	-6.93	3.38	0.015
313.15	2.11	-6.62	-5.57	-	-	10.08	3.16	0.021
				$[MOA]^+[Tf_2N]^-$ + 2-propanol[b]				
298.15	-0.69	14.05	-20.32	-10.97	49.76	31.83	-55.15	0.018
303.15	-0.81	14.47	-21.97	-11.61	41.41	21.49	-46.33	0.019
313.15	-1.22	14.19	-26.05	-10.66	47.50	23.76	-47.52	0.034

Table 6.6 continued....

$[MOA]^+[Tf_2N]^-$ + 1-butanol[b]								
298.15	-2.85	4.34	4.18	-3.77	6.19	8.09	-21.33	0.034
303.15	-2.92	4.86	3.86	-3.34	-5.31	-2.85	-9.67	0.052
313.15	-3.52	4.65	2.22	-7.00	6.16	2.51	-23.55	0.060
$[MOA]^+[Tf_2N]^-$ + 2-butanol[b]								
298.15	-0.75	1.56	4.18	1.69	7.63	14.31	-12.43	0.025
303.15	-0.86	1.71	3.18	1.40	8.13	13.56	-12.48	0.036
313.15	-1.34	1.98	1.85	-0.40	8.59	10.68	-14.16	0.038
$[MOA]^+[Tf_2N]^-$ + ethyl acetate[c]								
298.15	-6.00	1.64	-2.33	4.64	3.90	1.85	-4.52	0.030
303.15	-6.01	1.30	-0.29	2.83	0.18	-1.99	-4.37	0.060
313.15	-7.25	0.99	-0.21	4.18	1.81	-0.48	-5.66	0.040

[a] Reference Oswal and Putta *et al.* 2001

[b,] Article in preparation Bahadur *et al*. 2011 J. Phys Chem. B

[c] Reference Deenadayalu *et al.* 2010b

B. TERNARY SYSTEMS

The excess molar volumes for the ternary mixtures ($[MOA]^+[Tf_2N]^-$ + 2-propanol or 1-butanol or 2-butanol + ethyl acetate) at T = (298.15, 303.15 and 313.15) K was calculated from the experimental ternary densities using equation (6.6):

$$V_{123}^{E} = \frac{x_1 M_1 + x_2 M_2 + x_3 M_3}{\rho} - \frac{x_1 M_1}{\rho_1} - \frac{x_2 M_2}{\rho_2} - \frac{x_3 M_3}{\rho_3} \tag{6.6}$$

where x_1, x_2 and x_3 are mole fractions, M_1, M_2 and M_3 are the molar masses, ρ_1, ρ_2 and ρ_3 are the density of pure components:$[MOA]^+[Tf_2N]^-$, 2-propanol or 1-butanol or 2-butanol and ethyl acetate, respectively, and ρ is the density of the ternary mixture.

Tables 6.7-6.9 list the measured ternary density and excess molar volume, V_{123}^{E}, for the ternary system of ($[MOA]^+[Tf_2N]^-$ + 2-propanol or 1-butanol or 2-butanol + ethyl acetate) at T = (298.15, 303.15 and 313.15) K, respectively. The V_{123}^{E} values are given at each temperature for decreasing z values where $z = x_3/x_1$, where x_1 is $[MOA]^+[Tf_2N]^-$, x_3 is ethyl acetate, respectively. The z values ranged from 7.57; 3.36; 1.26; 0.84; 0.42; 0.25 to 0.08.

Table 6.7 Density, ρ, and excess molar volume, V_{123}^{E} for ($[MOA]^{+}[Tf_2N]^{-}$ + 2-propanol+ ethyl acetate) at T = (298.15, 303.15 and 313.15) K.

x_1	x_2	x_3	ρ/ (g·cm^{-3})	V_{123}^{E} /cm^{-3}·mol^{-1}
		T = 298.15 K		
		z = 7.57		
0.0600	0.4856	0.4543	0.9234	-0.139
0.0281	0.7591	0.2127	0.9685	-0.416
0.0225	0.8077	0.1698	0.9838	-0.379
0.0946	0.2117	0.6938	0.9899	-0.266
0.1091	0.0653	0.8256	0.8619	-0.038
0.1167	0.0000	0.8833	0.8481	-0.052
		z = 3.36		
0.0939	0.5904	0.3156	0.9469	-0.337
0.1429	0.3764	0.4807	0.9896	-0.690
0.1847	0.1949	0.6204	1.0145	-0.783
0.2017	0.1193	0.6790	1.0230	-0.837
0.2291	0.0000	0.7709	1.0345	-0.840
		z = 1.26		
0.2304	0.4790	0.2906	1.0212	-0.844
0.3156	0.2854	0.3990	1.0488	-1.101
0.3523	0.2034	0.4443	1.0579	-1.249
0.3954	0.1064	0.4982	1.0670	-1.420
0.4417	0.0000	0.5583	1.0747	-1.421
		z = 0.84		
0.1100	0.7974	0.0926	0.9479	-0.459
0.1911	0.6482	0.1607	1.0018	-0.895
0.3356	0.3825	0.2819	1.0515	-1.311
0.4338	0.2018	0.3644	1.0712	-1.611
0.3759	0.4664	0.1578	1.0562	-1.110

Table 6.7 continued.....

$z = 0.42$				
0.5101	0.2753	0.2146	1.0780	-1.373
0.6157	0.1256	0.2587	1.0896	-1.523
0.6625	0.0596	0.2779	1.0938	-1.600
0.7037	0.0000	0.2963	1.0967	-1.496
$z = 0.25$				
0.2927	0.6337	0.0736	1.0322	-0.373
0.4909	0.3849	0.1242	1.0727	-0.866
0.6302	0.2105	0.1593	1.0888	-1.191
0.7088	0.1119	0.1794	1.0952	-1.221
0.7993	0.0000	0.2007	1.1013	-1.280
$z = 0.08$				
0.7867	0.1483	0.0650	1.0978	-0.606
0.8568	0.0733	0.0698	1.1020	-0.656
0.6371	0.3113	0.0516	1.0864	-0.537
0.4409	0.5232	0.0359	1.0623	-0.325
0.9209	0.0000	0.0791	1.1054	-0.703
$T = 303.15$ K				
$z = 7.57$				
0.0600	0.4856	0.4543	0.9184	-0.170
0.0281	0.7591	0.2127	0.8560	-0.157
0.0225	0.8077	0.1698	0.8424	-0.158
0.0946	0.2117	0.6938	0.9636	-0.514
0.1091	0.0653	0.8256	0.9788	-0.487
0.1167	0.0000	0.8833	0.9849	-0.383

Table 6.7 continued....

		$z = 3.36$		
0.0939	0.5904	0.3156	0.9429	-0.488
0.1429	0.3764	0.4807	0.9845	-0.720
0.1847	0.1949	0.6204	1.0098	-0.910
0.2017	0.1193	0.6790	1.0180	-0.919
0.2291	0.0000	0.7709	1.0295	-0.937
		$z = 1.26$		
0.2304	0.4790	0.2906	1.0183	-1.267
0.3156	0.2854	0.3990	1.0450	-1.410
0.3523	0.2034	0.4443	1.0535	-1.435
0.3954	0.1064	0.4982	1.0622	-1.517
0.4417	0.0000	0.5583	1.0696	-1.444
		$z = 0.84$		
0.1100	0.7974	0.0926	0.9457	-0.830
0.1911	0.6482	0.1607	0.9995	-1.362
0.3356	0.3825	0.2819	1.0478	-1.632
0.4338	0.2018	0.3644	1.0668	-1.801
0.5433	0.0000	0.4567	1.0803	-1.551
		$z = 0.42$		
0.3759	0.4664	0.1578	1.0514	-1.141
0.5101	0.2753	0.2146	1.0728	-1.292
0.6157	0.1256	0.2587	1.0843	-1.398
0.6625	0.0596	0.2779	1.0882	-1.353
0.7037	0.0000	0.2963	1.0915	-1.399
		$z = 0.25$		
0.2927	0.6337	0.0736	1.0295	-0.845
0.4909	0.3849	0.1242	1.0687	-1.138
0.6302	0.2105	0.1593	1.0840	-1.227
0.7088	0.1119	0.1794	1.0903	-1.221
0.7993	0.0000	0.2007	1.0962	-1.192

Table 6.7 continued....

$z = 0.08$

0.7867	0.1483	0.0650	1.0931	-0.666
0.8568	0.0733	0.0698	1.0973	-0.720
0.6371	0.3113	0.0516	1.0819	-0.670
0.4409	0.5232	0.0359	1.0580	-0.471
0.9209	0.0000	0.0791	1.1005	-0.673

$T = 313.15$ K

$z = 7.57$

0.0600	0.4856	0.4543	0.9090	-0.260
0.0281	0.7591	0.2127	0.8478	-0.034
0.0225	0.8077	0.1698	0.8339	-0.090
0.0946	0.2117	0.6938	0.9545	-0.741
0.1091	0.0653	0.8256	0.9693	-0.705
0.1167	0.0000	0.8833	0.9749	-0.539

$z = 3.36$

0.0939	0.5904	0.3156	0.9355	-0.751
0.1429	0.3764	0.4807	0.9769	-1.025
0.1847	0.1949	0.6204	1.0021	-1.252
0.2017	0.1193	0.6790	1.0099	-1.206
0.2291	0.0000	0.7709	1.0209	-1.148

$z = 1.26$

0.2304	0.4790	0.2906	1.0108	-1.439
0.3156	0.2854	0.3990	1.0380	-1.175
0.3523	0.2034	0.4443	1.0467	-1.802
0.3954	0.1064	0.4982	1.0548	-1.738
0.4417	0.0000	0.5583	1.0625	-1.758

Table 6.7 continued....

		$z = 0.84$		
0.1100	0.7974	0.0926	0.9373	-0.819
0.1911	0.6482	0.1607	0.9911	-1.323
0.3356	0.3825	0.2819	1.0405	-1.791
0.4338	0.2018	0.3644	1.0599	-2.073
0.5433	0.0000	0.4567	1.0734	-1.834
		$z = 0.42$		
0.3759	0.4664	0.1578	1.0445	-1.307
0.5101	0.2753	0.2146	1.0663	-1.575
0.6157	0.1256	0.2587	1.0776	-1.614
0.6625	0.0596	0.2779	1.0819	-1.724
0.7037	0.0000	0.2963	1.0850	-1.695
		$z = 0.25$		
0.2927	0.6337	0.0736	1.0223	-0.919
0.4909	0.3849	0.1242	1.0620	-1.308
0.6302	0.2105	0.1593	1.0773	-1.381
0.7088	0.1119	0.1794	1.0836	-1.365
0.7993	0.0000	0.2007	1.0896	-1.368
		$z = 0.08$		
0.7867	0.1483	0.0650	1.0108	-1.439
0.8568	0.0733	0.0698	1.0380	-1.715
0.6371	0.3113	0.0516	1.0467	-1.802
0.4409	0.5232	0.0359	1.0548	-1.738
0.9209	0.0000	0.0791	1.0625	-1.758

Table 6.8 Density, ρ, and excess molar volume, V_{123}^{E} for ([MOA]$^+$[Tf$_2$N]$^-$ + 1-butanol + ethyl acetate) at *T* = (298.15, 303.15 and 313.15) K.

x_1	x_2	x_3	ρ/ (g·cm^{-3})	V_{123}^{E} /cm^{-3}·mol^{-1}
		T = 298.15 K		
		z = 7.57		
0.0660	0.4347	0.4992	0.9372	-0.821
0.0328	0.7188	0.2484	0.8800	-0.202
0.0263	0.7746	0.1990	0.8669	-0.092
0.0957	0.1808	0.7235	0.9731	-0.850
0.1102	0.0560	0.8338	0.9857	-0.525
0.1167	0.0000	0.8833	0.9899	-0.266
		z = 3.36		
0.1058	0.5394	0.3548	0.9593	-0.754
0.1538	0.3299	0.5164	0.9968	-1.047
0.1912	0.1637	0.6452	1.0186	-1.116
0.2024	0.1182	0.6794	1.0254	-1.059
0.2291	0.0000	0.7709	1.0345	-0.840
		z = 1.26		
0.2512	0.4243	0.3245	1.0280	-1.150
0.3331	0.2457	0.4212	1.0520	-1.253
0.3657	0.1728	0.4615	1.0600	-1.352
0.4022	0.0901	0.5077	1.0677	-1.423
0.4417	0.0000	0.5583	1.0747	-1.421
		z = 0.84		
0.1295	0.7617	0.1087	0.9630	-0.857
0.2176	0.5993	0.1830	1.0117	-1.284
0.3614	0.3350	0.3036	1.0558	-1.563
0.4494	0.1701	0.3805	1.0725	-1.605
0.5433	0.0000	0.4567	1.0854	-1.559

Table 6.8 continued....

$z = 0.42$				
0.4124	0.4141	0.1735	1.0608	-1.342
0.5373	0.2396	0.2231	1.0800	-1.449
0.6280	0.1057	0.2664	1.0904	-1.545
0.6664	0.0527	0.2809	1.0941	-1.552
0.7037	0.0000	0.2963	1.0967	-1.496
$z = 0.25$				
0.3320	0.5814	0.0866	1.0399	-0.700
0.5288	0.3389	0.1323	1.0762	-1.142
0.6561	0.1775	0.1664	1.0900	-1.209
0.7246	0.0925	0.1829	1.0959	-1.306
0.7993	0.0000	0.2007	1.1013	-1.280
$z = 0.08$				
0.8087	0.1246	0.0667	1.0985	-0.866
0.8495	0.0617	0.0888	1.1025	-0.853
0.6693	0.2642	0.0664	1.0898	-1.005
0.4910	0.4715	0.0375	1.0681	-0.818
0.9209	0.0000	0.0791	1.1054	-0.703
$T = 303.13$ K				
$z = 7.57$				
0.0660	0.4347	0.4992	0.9327	-0.825
0.0328	0.7188	0.2484	0.8770	-0.254
0.0263	0.7746	0.1990	0.8634	-0.046
0.0957	0.1808	0.7235	0.9672	-0.762
0.1102	0.0560	0.8338	0.9805	-0.591

Table 6.8 continued....

		$z = 3.36$		
0.1058	0.5394	0.3548	0.9554	-0.803
0.1538	0.3299	0.5164	0.9918	-1.012
0.1912	0.1637	0.6452	1.0135	-1.133
0.2024	0.1182	0.6794	1.0205	-1.139
0.2291	0.0000	0.7709	1.0295	-0.937
		$z = 1.26$		
0.2512	0.4243	0.3245	1.0234	-1.138
0.3331	0.2457	0.4212	1.0477	-1.393
0.3657	0.1728	0.4615	1.0552	-1.396
0.4022	0.0901	0.5077	1.0625	-1.388
0.4417	0.0000	0.5583	1.0696	-1.442
		$z = 0.84$		
0.1295	0.7617	0.1087	0.9598	-0.926
0.2176	0.5993	0.1830	1.0080	-1.377
0.3614	0.3350	0.3036	1.0513	-1.615
0.4494	0.1701	0.3805	1.0679	-1.697
0.5433	0.0000	0.4567	1.0803	-1.551
		$z = 0.42$		
0.4124	0.4141	0.1735	1.0564	-1.412
0.5373	0.2396	0.2231	1.0756	-1.571
0.6280	0.1057	0.2664	1.0855	-1.539
0.6664	0.0527	0.2809	1.0890	-1.483
0.7037	0.0000	0.2963	1.0915	-1.399
		$z = 0.25$		
0.3320	0.5814	0.0866	1.0358	-0.733
0.5288	0.3389	0.1323	1.0715	-1.116
0.6561	0.1775	0.1664	1.0855	-1.316
0.7246	0.0925	0.1829	1.0910	-1.282
0.7993	0.0000	0.2007	1.0962	-1.192

Table 6.8 continued....

		$z = 0.08$		
0.8087	0.1246	0.0667	1.0941	-1.013
0.8495	0.0617	0.0888	1.0978	-0.895
0.6693	0.2642	0.0664	1.0854	-1.049
0.4910	0.4715	0.0375	1.0644	-0.944
0.9209	0.0000	0.0791	1.1005	-0.676
		$T = 313.13$ K		
		$z = 7.57$		
0.0660	0.4347	0.4992	0.9240	-0.973
0.0328	0.7188	0.2484	0.8680	-0.198
0.0263	0.7746	0.1990	0.8550	-0.037
0.0957	0.1808	0.7235	0.9573	-0.859
0.1102	0.0560	0.8338	0.97705	-0.727
0.1167	0.0000	0.8833	0.9749	-0.539
		$z = 3.36$		
0.1058	0.5394	0.3548	0.9474	-0.924
0.1538	0.3299	0.5164	0.9836	-1.189
0.1912	0.1637	0.6452	1.0046	-1.236
0.2024	0.1182	0.6794	1.0116	-1.263
0.2291	0.0000	0.7709	1.0209	-1.148
		$z = 1.26$		
0.2512	0.4243	0.3245	1.0179	-1.690
0.3331	0.2457	0.4212	1.0412	-1.790
0.3657	0.1728	0.4615	1.0487	-1.823
0.4022	0.0901	0.5077	1.0561	-1.849

Table 6.8 continued....

		$z = 0.84$		
0.1295	0.7617	0.1087	0.9532	-1.095
0.2176	0.5993	0.1830	1.0018	-1.680
0.3614	0.3350	0.3036	1.0448	-1.940
0.4494	0.1701	0.3805	1.0609	-1.920
0.5433	0.0000	0.4567	1.0734	-1.834
		$z = 0.42$		
0.4124	0.4141	0.1735	1.0493	-1.471
0.5373	0.2396	0.2231	1.0683	-1.561
0.6280	0.1057	0.2664	1.0785	-1.631
0.6664	0.0527	0.2809	1.0821	-1.611
0.7037	0.0000	0.2963	1.0850	-1.695
		$z = 0.25$		
0.3320	0.5814	0.0866	1.0295	-0.946
0.5288	0.3389	0.1323	1.0650	-1.307
0.6561	0.1775	0.1664	1.0790	-1.523
0.7246	0.0925	0.1829	1.0844	-1.456
0.7993	0.0000	0.2007	1.0896	-1.368
		$z = 0.08$		
0.8087	0.1246	0.0667	1.0873	-1.003
0.8495	0.0617	0.0888	1.0912	-0.970
0.6693	0.2642	0.0664	1.0788	-1.133
0.4910	0.4715	0.0375	1.0579	-1.059
0.9209	0.0000	0.0791	1.0941	-0.850

Table 6.9 Density, ρ, and excess molar volume, V_{123}^{E} for ($[MOA]^{+}[Tf_2N]^{-}$ + 2-butanol+ ethyl acetate) at *T* = (298.15, 303.15 and 313.15) K.

x_1	x_2	x_3	ρ/ (g·cm^{-3})	V_{123}^{E} /cm^{-3}·mol^{-1}
		T = 298.15 K		
		z = 7.57		
0.0660	0.4347	0.4992	0.9354	-0.733
0.0328	0.7188	0.2484	0.8790	-0.337
0.0263	0.7746	0.1990	0.8649	-0.154
0.0957	0.1808	0.7235	0.9714	-0.689
0.1102	0.0560	0.8338	0.9853	-0.521
0.1167	0.0000	0.8833	0.8481	-0.266
		z = 3.36		
0.1058	0.5394	0.3548	0.9583	-0.787
0.1538	0.3299	0.5164	0.9959	-1.021
0.1912	0.1637	0.6452	1.0180	-1.090
0.2024	0.1182	0.6794	1.0236	-1.109
0.2291	0.0000	0.7709	1.0345	-0.840
		z = 1.26		
0.2512	0.4243	0.3245	1.0264	-1.081
0.3331	0.2457	0.4212	1.0514	-1.220
0.3657	0.1728	0.4615	1.0596	-1.349
0.4022	0.0901	0.5077	1.0674	-1.401
0.4417	0.0000	0.5583	1.0747	-1.421

Table 6.9 continued....

$z = 0.84$				
0.1295	0.7617	0.1087	0.9610	-0.798
0.2176	0.5993	0.1830	1.0096	-1.091
0.3614	0.3350	0.3036	1.0546	-1.396
0.4494	0.1701	0.3805	1.0720	-1.543
0.5433	0.0000	0.4567	1.0854	-1.559
$z = 0.42$				
0.4124	0.4141	0.1735	1.0600	-1.307
0.5373	0.2396	0.2231	1.0795	-1.575
0.6280	0.1057	0.2664	1.0898	-1.614
0.6664	0.0527	0.2809	1.0935	-1.724
0.7037	0.0000	0.2963	1.0967	-1.496
$z = 0.25$				
0.3320	0.5814	0.0866	1.0395	-0.785
0.5288	0.3389	0.1323	1.0757	-1.117
0.6561	0.1775	0.1664	1.0898	-1.183
0.7246	0.0925	0.1829	1.0958	-1.247
0.7993	0.0000	0.2007	1.1013	-1.280
$z = 0.08$				
0.8087	0.1246	0.0667	1.0989	-0.828
0.8495	0.0617	0.0888	1.1017	-0.793
0.6693	0.2642	0.0664	1.0886	-0.944
0.4910	0.4715	0.0375	1.0676	-0.786
0.9209	0.0000	0.0791	1.1054	-0.703

Table 6.9 continued....

T = 303.13 K				
z = 7.57				
0.0660	0.4347	0.4992	0.9309	-0.851
0.0328	0.7188	0.2484	0.8769	-0.694
0.0263	0.7746	0.1990	0.8629	-0.506
0.0957	0.1808	0.7235	0.9661	-0.736
0.1102	0.0560	0.8338	0.9801	-0.601
0.1167	0.0000	0.8833	0.9849	-0.383
z = 3.36				
0.1058	0.5394	0.3548	0.9554	-1.133
0.1538	0.3299	0.5164	0.9912	-1.128
0.1912	0.1637	0.6452	1.0127	-1.112
0.2024	0.1182	0.6794	1.0179	-1.059
0.2291	0.0000	0.7709	1.0295	-0.937
z = 1.26				
0.2512	0.4243	0.3245	1.0225	-1.333
0.3331	0.2457	0.4212	1.0472	-1.450
0.3657	0.1728	0.4615	1.0551	-1.517
0.4022	0.0901	0.5077	1.0626	-1.500
0.4417	0.0000	0.5583	1.0696	-1.442
z = 0.84				
0.1295	0.7617	0.1087	0.9569	-0.922
0.2176	0.5993	0.1830	1.0052	-1.202
0.3614	0.3350	0.3036	1.0500	-1.509
0.4494	0.1701	0.3805	1.0672	-1.621
0.5433	0.0000	0.4567	1.0803	-1.551

Table 6.9 continued....

		$z = 0.42$		
0.4124	0.4141	0.1735	1.0551	-1.240
0.5373	0.2396	0.2231	1.0745	-1.394
0.6280	0.1057	0.2664	1.0846	-1.365
0.6664	0.0527	0.2809	1.0881	-1.327
0.7037	0.0000	0.2963	1.0915	-1.399
		$z = 0.25$		
0.3320	0.5814	0.0866	1.0358	-1.073
0.5288	0.3389	0.1323	1.0713	-1.280
0.6561	0.1775	0.1664	1.0852	-1.298
0.7246	0.0925	0.1829	1.0910	-1.290
0.7993	0.0000	0.2007	1.0962	-1.192
		$z = 0.08$		
0.8087	0.1246	0.0667	1.0940	-0.801
0.8495	0.0617	0.0888	1.0968	-0.768
0.6693	0.2642	0.0664	1.0838	-0.963
0.4910	0.4715	0.0375	1.0636	-1.047
0.9209	0.0000	0.0791	1.1005	-0.673
		$T = 313.13$ K		
		$z = 7.57$		
0.0660	0.4347	0.4992	0.9210	-0.559
0.0328	0.7188	0.2484	0.8681	-0.224
0.0263	0.7746	0.1990	0.8553	-0.116
0.0957	0.1808	0.7235	0.9558	-0.659
0.1102	0.0560	0.8338	0.9700	-0.685
0.1167	0.0000	0.8833	0.9749	-0.539

Table 6.9 continued....

$z = 3.36$				
0.1058	0.5394	0.3548	0.9473	-0.908
0.1538	0.3299	0.5164	0.9828	-1.063
0.1912	0.1637	0.6452	1.0042	-1.191
0.2024	0.1182	0.6794	1.0097	-1.237
0.2291	0.0000	0.7709	1.0209	-1.148
$z = 1.26$				
0.2512	0.4243	0.3245	1.0160	-1.277
0.3331	0.2457	0.4212	1.0400	-1.489
0.3657	0.1728	0.4615	1.0475	-1.505
0.4022	0.0901	0.5077	1.0554	-1.652
0.4417	0.0000	0.5583	1.0625	-1.758
$z = 0.84$				
0.1295	0.7617	0.1087	0.9521	-0.913
0.2176	0.5993	0.1830	0.9996	-1.237
0.3614	0.3350	0.3036	1.0434	-1.572
0.4494	0.1701	0.3805	1.0600	-1.649
0.5433	0.0000	0.4567	1.0734	-1.834
$z = 0.42$				
0.4112	0.4155	0.1734	1.0481	-1.130
0.5379	0.2355	0.2266	1.0676	-1.324
0.6312	0.1041	0.2648	1.0782	-1.517
0.6720	0.0495	0.2785	1.0820	-1.572
0.7037	0.0000	0.2963	1.0850	-1.695
$z = 0.25$				
0.3320	0.5814	0.0866	1.0293	-0.895
0.5288	0.3389	0.1323	1.0646	-1.172
0.6561	0.1775	0.1664	1.0784	-1.289
0.7246	0.0925	0.1829	1.0842	-1.372
0.7993	0.0000	0.2007	1.0896	-1.368

Table 6.9 continued....

		$z = 0.08$		
0.8087	0.1246	0.0667	1.0871	-0.913
0.8495	0.0617	0.0888	1.0910	-0.875
0.6693	0.2642	0.0664	1.0781	-0.868
0.4910	0.4715	0.0375	1.0571	-0.830
0.9209	0.0000	0.0791	1.0941	-0.850

CHAPTER 7

DISCUSSION

Excess molar properties represent deviations from ideality and provide an indication of the interaction between the components in a mixture.

The excess molar volume represents the difference between the molar volume of a real solution and the molar volume of an ideal solution. The values of excess properties depend on the type and extent of intermolecular interactions and on the difference in size and shape of unlike molecules (Oswal and Putta 2001). In the systems studied here, the following factors influence on the values of the excess molar volumes of the mixtures of ILs with alcohols:

a) expansion of an alcohol due to breaking of some hydrogen bonds of an alcohol during addition of the ILs.
b) contraction due to specific interactions of an alcohol molecule with an IL
c) size difference
d) expansion due to steric repulsion between alkyl chain of an alcohol and that of ILs.
e) formation of new ester-alkanol polymers.
f) ion-dipole or alcohol-ion interactions

The results obtained in this work for both binary and ternary excess molar volume are discussed in terms of the above intermolecular interactions.

When the small alcohol molecule fits into the interstices upon mixing with ILs, this filling effect and also the ion-dipole interactions between alcohol and the ammonium ring of the IL, all contribute to the negative values of the excess molar volumes (Abareshi *et al*. 2009; Oswal and Putta 2001).

The positive excess molar volumes values may be 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 IL (Gomez *et al.* 2006; Sibiya and Deenadayalu 2008). Alkanol molecules are protic and strongly self-associated through hydrogen-bonds in their pure state, with degrees of association depending on the chain length, position of OH group, temperature, and dilution by other substances. Due to the electron-donating inductive effect of the alkyl group, the strength of intermolecular or hydrogen bonding in alkanols are expected to decrease with an increase in their chain lengths (Deenadayalu and Bhujrajh 2006).

For the IL the cation and anion are capable of forming intermolecular bonds such as ion-dipole with negative and positive ends of molecules. Usually, it is assumed that in IL one kind of hydrogen bond occurs, probably linear bonds, whereas in alcohols two kinds of hydrogen bonds are present leading to cyclic dimers and linear higher polymers, depending on the length of the alcohol chain that is present. Weak intermolecular interactions occurring between the hydroxyl group and the IL lead to negative values of excess molar volumes.

The values of partial molar volumes, V_{m}^{∞} , provide useful information about various types of interactions occurring dilute in solutions. These studies are of great help in characterizing the structure of properties of solutions.

A. BINARY EXCESS MOLAR VOLUMES

a) 2-Propanol or 1-butanol or 2-butanol + ethyl acetate

The excess molar volumes for the binary systems (1-butanol + ethyl acetate) and (2-butanol + ethyl acetate) were previously published at $T = 298.15$ K by (Fermeglia *et al.* 1988) and at $T = (298.15$ and $303.15)$ K by (Resa *et al.* 2004), respectively. The maximum excess molar volume for this work for the the binary systems (1-butanol or 2-butanol + ethyl acetate) were found to be positive at all three temperatures which agree with the results of (Fermeglia 1988 and Resa 2004). The positive excess molar volume is due to the breakdown of the hydrogen bonding in the alcohol molecules (Gomez *et al.* 2006; Sibiya and Deenadayalu 2008). For the (2-propanol + ethyl acetate) system in the literature (Oswal *et al.* 2001) V_m^E is also positive. For the system (2-propanol + ethyl acetate) (Oswal *et al.* 2001) $V_{\mathrm{m,max}}^E = 0.4747\ \mathrm{cm^3{\cdot}mol^{-1}}$ at $T = 298.15$ K, $V_{\mathrm{m,max}}^E = 0.5196\ \mathrm{cm^3{\cdot}mol^{-1}}$ at $T = 303.15$ K, and $V_{\mathrm{m,max}}^E = 0.6052\ \mathrm{cm^3{\cdot}mol^{-1}}$ at $T = 313.15$ K. The maximum excess molar volume, $V_{\mathrm{m,max}}^E$ at $T = 298.15$ K obtained in this work is compared with the one obtained by Fermeglia (1988). For the binary system (1-butanol + ethyl acetate), $V_{\mathrm{m,max}}^E$ was found to be $= 0.2719\ \mathrm{cm^3{\cdot}mol^{-1}}$ for this work and $0.2703\ \mathrm{cm^3{\cdot}mol^{-1}}$ for Fermeglia (1988). The difference between the results of Fermeglia and this work is $0.0016\ \mathrm{cm^3{\cdot}mol^{-1}}$, so the results are in good agreement with each other. The comparison between this work and the literature binary data of (1-butanol + ethyl acetate) measured at $T = 298.15$ K is shown in figure 7.1.

For the binary system (2-butanol + ethyl acetate) at $T = 298.15$ K, $V_{\mathrm{m,max}}^E$ was found to be $= 0.6182\ \mathrm{cm^3{\cdot}mol^{-1}}$ for this work and $0.6400\ \mathrm{cm^3{\cdot}mol^{-1}}$ for Resa (2004), at $T = 303.15$ K $V_{\mathrm{m,max}}^E = 0.5621\ \mathrm{cm^3{\cdot}mol^{-1}}$ for this work and $0.6630\ \mathrm{cm^3{\cdot}mol^{-1}}$ obtained by Resa (2004). The difference between the results of Resa (2004) and this work is $0.0218\ \mathrm{cm^3{\cdot}mol^{-1}}$ at $T = 298.15$ K and $0.1009\ \mathrm{cm^3{\cdot}mol^{-1}}$ at $T = 303.15$ K. As it can be seen from figures 7.2 and 7.3, the results for this work are lower than those reported in literature, the difference between the experimental and literature results may be due to the volatility of the alcohol or due to the small amounts of water in the solvents as it is well known, that small addition of low molar mass solvent can dramatically increase or decrease (depending on the nature of the impurity) the thermodynamic properties relative to the properties of the pure solvents (Abdulagatov *et al.* 2008). The results for the excess molar volumes for the binary systems studied (1-butanol or 2-butanol + ethyl acetate) at $T = (298.15$, 303.15 and $313.15)$ K are given in tables 6.1-6.2, respectively.

For the other temperatures where V_{m}^{E} for the (1-butanol or 2-butanol + ethyl acetate) systems is not in the literature, this work gave $V_{\mathrm{m,max}}^{E}$ = 0.2098 $\mathrm{cm^3 \cdot mol^{-1}}$ for (1-butanol + ethyl acetate) system at T = 303.15 K, and $V_{\mathrm{m,max}}^{E}$ = 0.2068 $\mathrm{cm^3 \cdot mol^{-1}}$ at T = 313.15 K. For the system (2-butanol + ethyl acetate), this work gave $V_{\mathrm{m,max}}^{E}$ = 0.5350 $\mathrm{cm^3 \cdot mol^{-1}}$ at T = 313.15 K.

It can be seen that for (1-butanol or 2-butanol + ethyl acetate) binary systems at all temperatures, the excess molar volume values becomes less positive as temperature increases. In general, hydrogen bonding is more temperature dependent than Coulombic interactions. The hydrogen of the hydroxyl group on the alcohol molecule form hydrogen bonds with the oxygen of the ethyl acetate molecules. Hydrogen bond breaking results in a decrease in V_{m}^{E} with temperature (Bhujrajh and Deenadayalu 2007).

Table 6.6 list partial molar volumes at infinite dilution, $V_{\mathrm{m},1}^{\infty}$ and $V_{\mathrm{m},2}^{\infty}$ data for the binary systems (IL + 2-propanol or 1-butanol or 2-butanol) at T = 298.15, 303.15 and 313.15 K. For (2-propanol + ethyl acetate) system $V_{\mathrm{m},1}^{\infty}$ is positive at all temperatures. For (1-butanol or 2-butanol + ethyl acetate) systems, the partial molar volumes at infinite dilution $V_{\mathrm{m},1}^{\infty}$ are positive and negative. The $V_{\mathrm{m},1}^{\infty}$ trend is 2-butanol < 1-butanol < 2-propanol, except for 1-butanol at T = 303.15 K and for 2-butanol at T = 313.15 K where the trend is reversed. The partial molar volume at infinite dilution, $V_{\mathrm{m},1}^{\infty}$ increase as temperature increase. The values for $V_{\mathrm{m},2}^{\infty}$ are positive for all three temperatures.

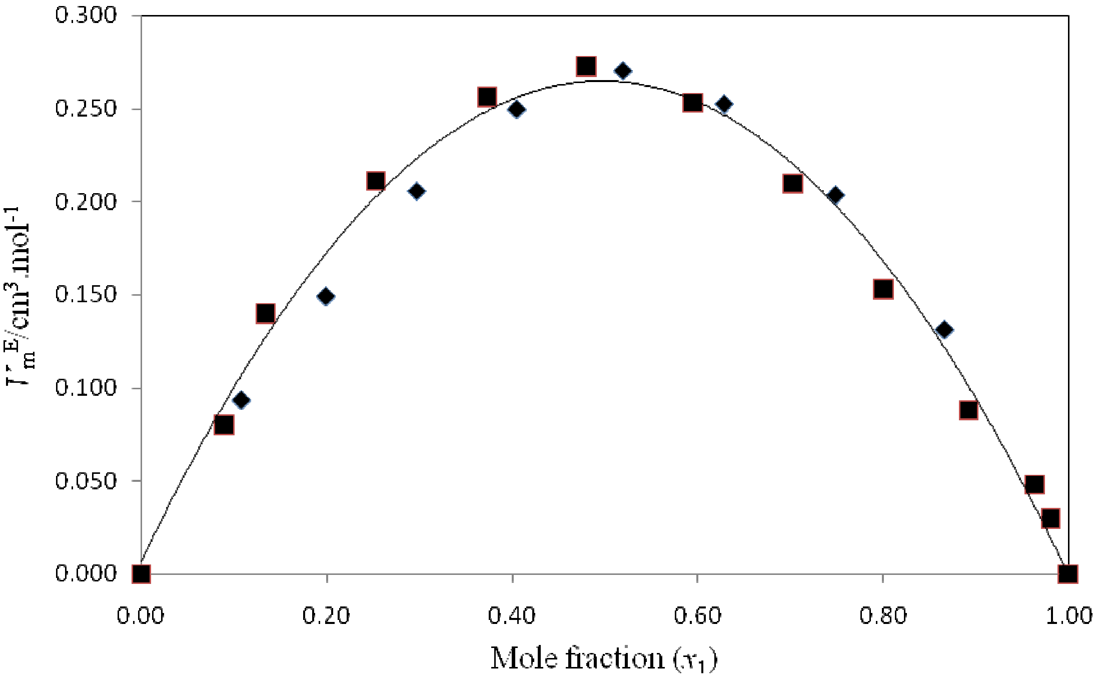


Figure 7.1 Plot of excess molar volumes of binary mixture of 1-butanol (x_1) + ethyl acetate (x_2) at T = 298.15 K. Experimental points, (■), literature points, (♦),Redlich-Kister polynomials (-).

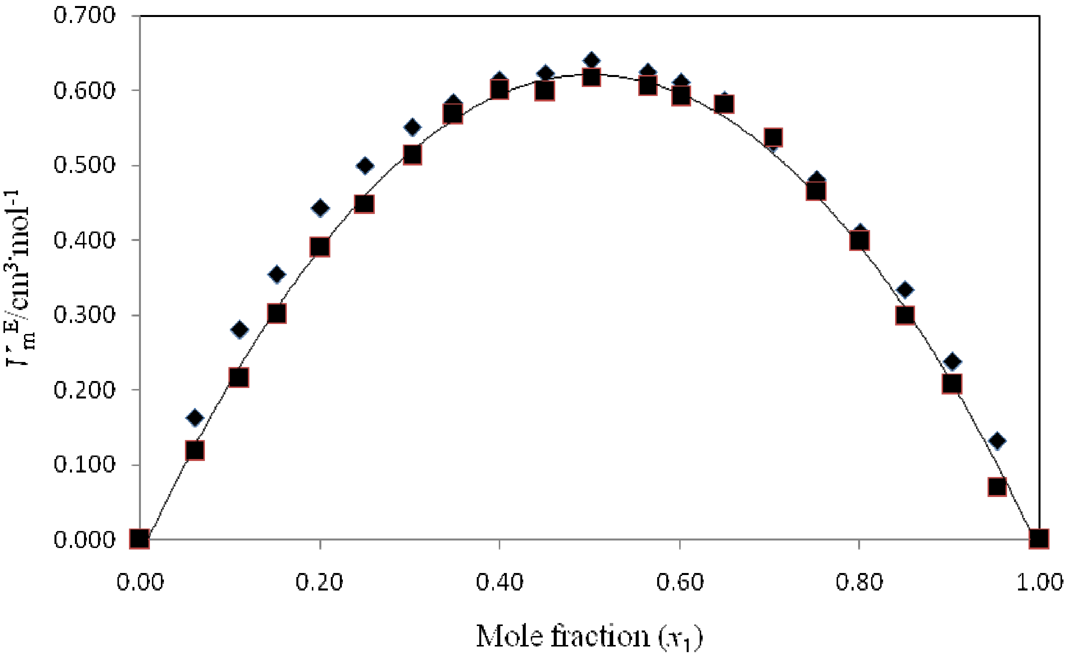


Figure 7.2 Plot of excess molar volumes of binary mixture of 2-butanol (x_1) + ethyl acetate (x_2) at T = 298.15 K. Experimental points, (■), literature points, (♦), Redlich-Kister polynomials (-).

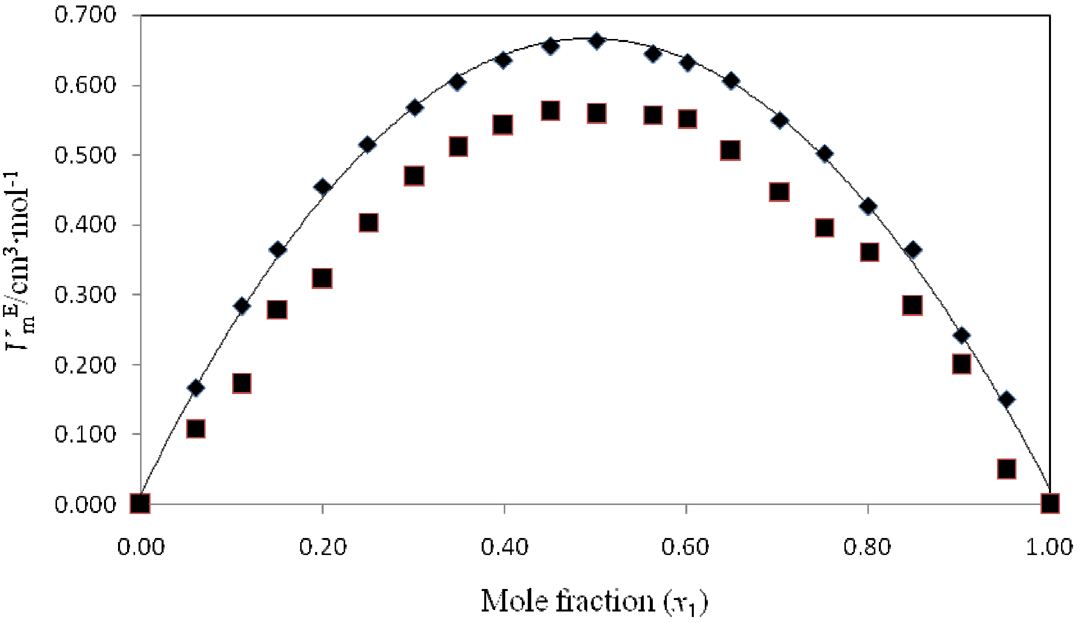


Figure 7.3 Plot of excess molar volumes of binary mixture of 2-butanol (x_1) + ethyl acetate (x_2) at T = 303.15 K. Experimental points, (■), literature points, (♦), Redlich-Kister polynomials (-).

(b) $[MOA]^+[Tf_2N]^-$+ 2-propanol or 1-butanol or 2-butanol *

The results for the excess molar volumes for the binary systems studied (IL + 2-propanol or 1-butanol or 2-butanol) are given in tables 6.3-6.5, respectively. The excess molar volumes for these systems are both negative and positive over the entire composition range.

V_m^E values for (IL + 2-propanol) for all temperatures are negative at $x_1 \geq 0.1000$ mole fraction and become positive at $x_1 > 0.4824$. V_m^E values for (IL + 1-butanol) at $T =$ (298.15 and 303.15) K are negative at $x_1 \geq 0.1421$ and become positive at $x_1 > 0.6385$. For the (IL + 1-butanol) at $T = 313.15$ K, V_m^E values become positive at $x_1 > 0.7397$. V_m^E values for (IL + 2-butanol) at $T =$ (298.15, 303.15 and 313.15) K are negative at $x_1 \geq 0.2623$ and become positive at $x_1 > 0.6051$, but at $T = 298.15$ K V_m^E values become positive at $x_1 > 0.5045$.

For the binary system (IL + 2-propanol), $V_{m,min}^E = -1.681$ cm^3·mol^{-1} at $T = 298.15$ K, $V_{m,min}^E = -1.776$ cm^3·mol^{-1} at $T = 303.15$ K and $V_{m,min}^E = -1.971$ cm^3·mol^{-1} at $T = 313.15$ K. For the binary system (IL +1-butanol), $V_{m,min}^E = -0.805$ cm^3·mol^{-1} at $T = 298.15$ K, $V_{m,min}^E = -0.843$ cm^3·mol^{-1} at $T = 303.15$ K and $V_{m,min}^E = -0.976$ cm^3·mol^{-1} at $T = 313.15$ K. For the binary system (IL +2-butanol), $V_{m,min}^E = -0.213$ cm^3·mol^{-1} at $T = 298.15$ K, $V_{m,min}^E = -0.252$ cm^3·mol^{-1} at $T = 303.15$ K and $V_{m,min}^E = -0.389$ cm^3·mol^{-1} at $T = 313.15$ K. It can be seen that for all three binary systems at all temperatures, the excess molar volume values become more negative as temperature increases, because the kinetic energy of molecules also increases with temperature, which leads to an increase in interaction of the different molecules. This effect is greater for the alkanols than for the ionic liquid, resulting in contraction in volume (Zhang and Wang 2007; Pereiro *et al.* 2006; Sibiya and Deenadayalu 2009).

The negative excess molar volume values indicate the that efficient packing and/or attractive interaction occurred when the IL and the alcohol were mixed (Bhujrajh and Deenadayalu 2007, Sibiya and Deenadayalu 2008). The alkanol tends to fill the interstices of the IL, and the ion-dipole interaction between the organic molecular liquid and the ILs, all contribute to the negative values of the excess molar volumes (Bhujrajh and Deenadayalu 2007).

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 alkonol due to the dissociation of the ion pairs forming the IL (Gomez *et al.* 2006). At high mole fractions of alcohol and at low mole fractions of alcohol positive V_{m}^{E} is due to the disruption of the hydrogen bonding in the alcohols.

For all temperatures $V_{\mathrm{m}}^{\mathrm{E}}$ values also increases as the alcohol chain length increases, because the relaxation time increases with an increase in chain length, and thereby lowers the interaction of the alkanol and IL (Zhang and Wang 2007; Sibiya and Deenadayalu 2009). For the system (IL + 2-butanol) at all temperatures, $V_{\mathrm{m,min}}^{\mathrm{E}}$ is more positive than 1-butanol and 2-propanol systems, due to favourable packing of the 2-butanol than for 1-butanol and 2-propanol. The 2-butanol is branched and bulky, which causes the packing effect to diminish (Deenadayalu and Bhujrajh 2007).

Table 6.6 list partial molar volumes at infinite dilution, $V_{\mathrm{m},1}^{\infty}$ and $V_{\mathrm{m},2}^{\infty}$ data for the binary systems (IL + 2-propanol or 1-butanol or 2-butanol) at T = 298.15, 303.15 and 313.15 K. For (IL + 2-propanol or 1-butanol or 2-butanol) systems the partial molar volume at infinite dilution for IL $V_{\mathrm{m},1}^{\infty}$ are positive at all temperatures except for (IL + 1-butanol) system at T = 303.15 K and the trend is 1-butanol < 2-butanol < 2-propanol indicating that the dissociation effect is greater than any association effect. In general the partial molar volume at infinite dilution for IL $V_{\mathrm{m},1}^{\infty}$ decreases as temperature increases for all the systems studied except at T = 313.15 K for the system (IL + 1-butanol). The values for $V_{\mathrm{m},2}^{\infty}$ are all negative and the trend is 2-butanol > 1-butanol > 2-propanol, except for 1-butanol at T = 303.15 K.

In general, the partial molar volumes at infinite dilutions for IL $V_{\mathrm{m},1}^{\infty}$ are less negative than the partial molar volumes at infinite dilutions $V_{\mathrm{m},2}^{\infty}$ of the alcohol for the (IL + 2-propanol or 1-butanol or 2-butanol) systems. It is postulated that for the more concentrated IL solution, the compensation effect between IL-alcohol intermolecular bond formation is greater than the alcohol-alcohol bond dissociation. Also, the smaller 2-propanol alcohol molecules can be accommodated into the interstices of the IL molecule.

(c) $[MOA]^+[Tf_2N]^-$+ ethyl acetate

The binary excess molar volume data for (IL + ethyl acetate) was published in the literature (Deenadayalu *et al.* 2010b). The excess molar volumes for the system are negative over the entire composition range, this is probably due to the packing of small ethyl acetate molecules into the ionic liquid matrices (Deenadayalu *et al.* 2010b).

The interactions between the IL ions with the ethyl acetate can occur through the cation of the lone pair of electrons on the ethyl acetate molecules (Deenadayalu and Bahadur 2010a). The excess molar volume decreases as temperature increases

For the system (IL + ethyl acetate) the $V^{\mathrm{E}}_{\mathrm{m,min}}$ was found to be -1.579 $\mathrm{cm^3 \cdot mol^{-1}}$ at

T = 298.15 K, -1.551 $\mathrm{cm^3 \cdot mol^{-1}}$ at T = 303.15 K and -1.834 $\mathrm{cm^3 \cdot mol^{-1}}$ at T = 313.15 K. It can be seen that for the binary system (IL + ethyl acetate), the excess molar volume values become more negative as temperature increases except at T = 303.15 K, because the kinetic energy molecules increase with temperature which leads to a decrease in interaction of molecules (Deenadayalu *et al*. 2009).

The negative excess molar volume values indicate that efficient packing and/or attractive interaction in the mixtures than in pure liquids (Bhujrajh and Deenadayalu 2007). Strong ion-dipole interactions between unlike molecules justify the negative values of this property (Andreatta *et al.* 2009).

$V^{\infty}_{\mathrm{m,1}}$ and $V^{\infty}_{\mathrm{m,2}}$ results are presented in table 6.6. For (IL + ethyl acetate) system the partial molar volume at infinite dilution for IL $V^{\infty}_{\mathrm{m,1}}$ are negative for all temperatures indicating that ethyl acetate is probably incorporated into the IL matrix (Sibiya and Deenadayalu 2008). The $V^{\infty}_{\mathrm{m,2}}$ values are positive at all temperatures.

B. TERNARY EXCESS MOLAR VOLUMES

The results obtained in this work for the ternary excess molar volumes for the systems ($[MOA]^+[Tf_2N]^-$ + 2-propanol or 1-butanol or 2-butanol + ethyl acetate), at T = (298.15, 303.15 and 313.15) K over the entire composition range are discussed in terms of the intermolecular interactions occurring in both the ternary and the binary systems.

The binary data was used for obtaining the Redlich-Kister parameters which were used in the ternary excess molar volume data correlation by the Cibulka equation (equation 7.1) which is given below:

$$V_{123}^{E} = \sum_{\mathrm{i,j=1,2;1,3;2,3}} V_{\mathrm{ij}}^{E}(x_{\mathrm{i}}, x_{\mathrm{j}}) + x_1 x_2 x_3 (b_0 + b_1 x_1 + b_2 x_2) \qquad (7.1)$$

where x_1, x_2 and x_3 are the mole fractions of $MOA]^+[Tf_2N]^-$, 2-propanol, or 1-butanol or 2-butanol and ethyl acetate, respectively, and it contains the three parameters (b_0, b_1, b_2), which is a correlation over the binary contributions. The values of (b_0, b_1, b_2) were adjusted to the experimental ternary excess molar volumes and the distinctive function was in the form of the sum squares of the residuals (Deenadayalu 2010b). The correlation coefficients and the standard deviations values are listed in Table 7.1 for all the ternary systems. The graphs obtained from using the Cibulka parameters are given in Figures, 7.4-7.12.

The standard deviation is defined by the following equation:

$$\sigma = \sum_{i=1}^{n} [(V_{123\exp}^{E} - V_{123calc}^{E})^2 \Big/ (n-k)]^{\frac{1}{2}} \qquad (7.2)$$

Where n is the number of the experimental points and k is the number of coefficients used in the Cibulka correlation. In this work k is 3.

Table 7.1 Smoothing coefficients and standard deviations for the Cibulka equation at T = (298.15, 303.15 and 313.15) K.

T /K	b_0	b_1	b_2	σ/ $cm^3 \cdot mol^{-1}$
		$[MOA]^+[Tf_2N]^-$ + 2-propanol + ethyl acetate		
298.15	-8.86	-53.76	26.14	0.17
303.15	-16.21	-40.21	12.56	0.18
313.15	-37.83	-2.46	31.02	0.14
		$[MOA]^+[Tf_2N]^-$ + 1-butanol + ethyl acetate		
298.15	-20.11	3.97	-1.19	0.20
303.15	-16.47	-9.57	-0.07	0.20
313.15	-23.40	11.70	-7.00	0.16
		$[MOA]^+[Tf_2N]^-$ + 2-butanol + ethyl acetate		
298.15	-26.93	13.31	-20.97	0.21
303.15	-22.78	9.61	-42.86	0.24
313.15	-28.03	22.73	-32.80	0.20

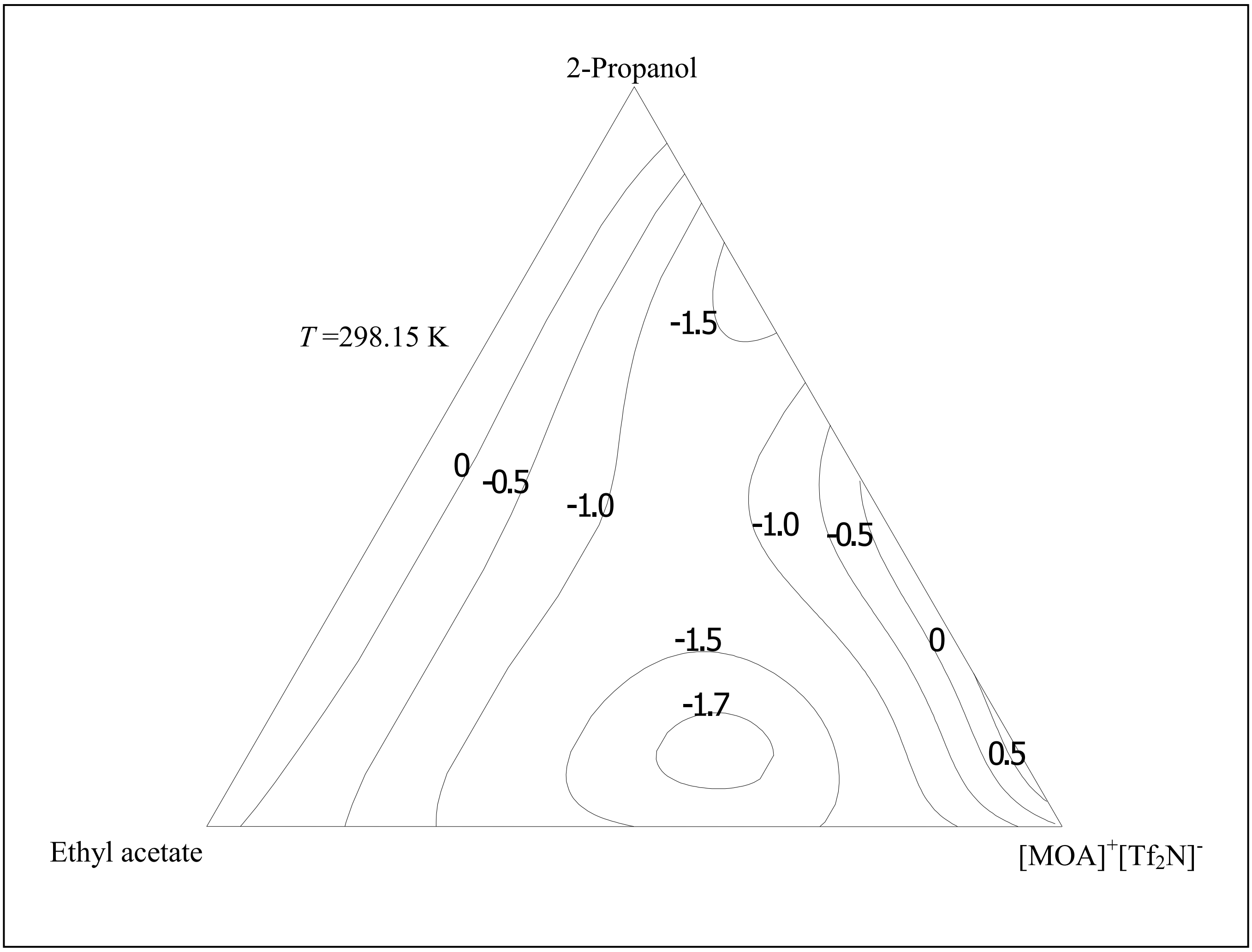


Figure 7.4 Graph of excess molar volumes for the ternary mixtures $\{[MOA]^+[Tf_2N]^-\}$ + 2-propanol + ethyl acetate at $T = 298.15$ K. The solid lines were calculated by the Cibulka equation with the values of the parameters fitted to the binary and ternary data.

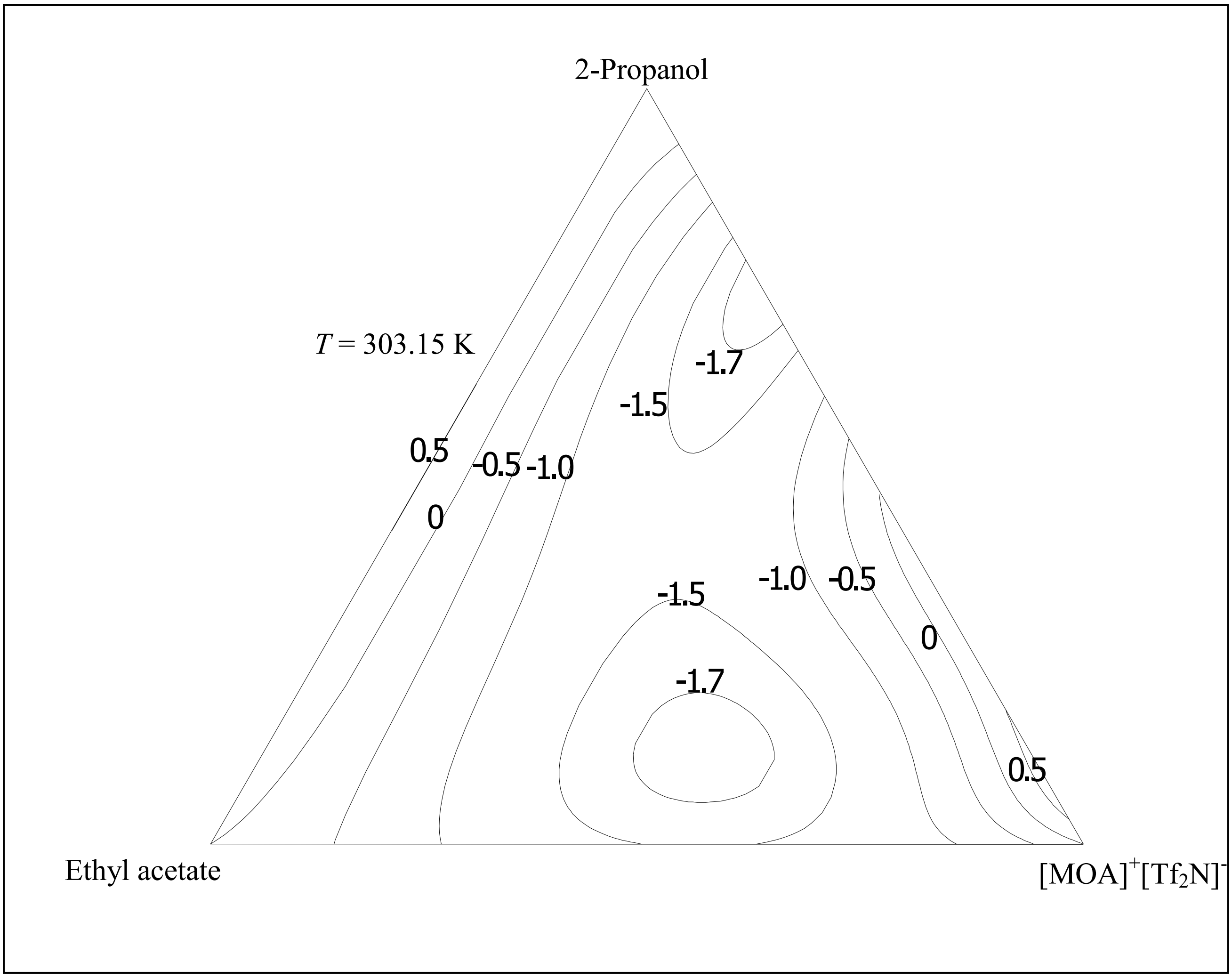


Figure 7.5 Graph of excess molar volumes for the ternary mixtures {$[MOA]^+[Tf_2N]^-$} + 2-propanol + ethyl acetate at T = 303.15 K. The solid lines were calculated by the Cibulka equation with the values of the parameters fitted to the binary and ternary data.

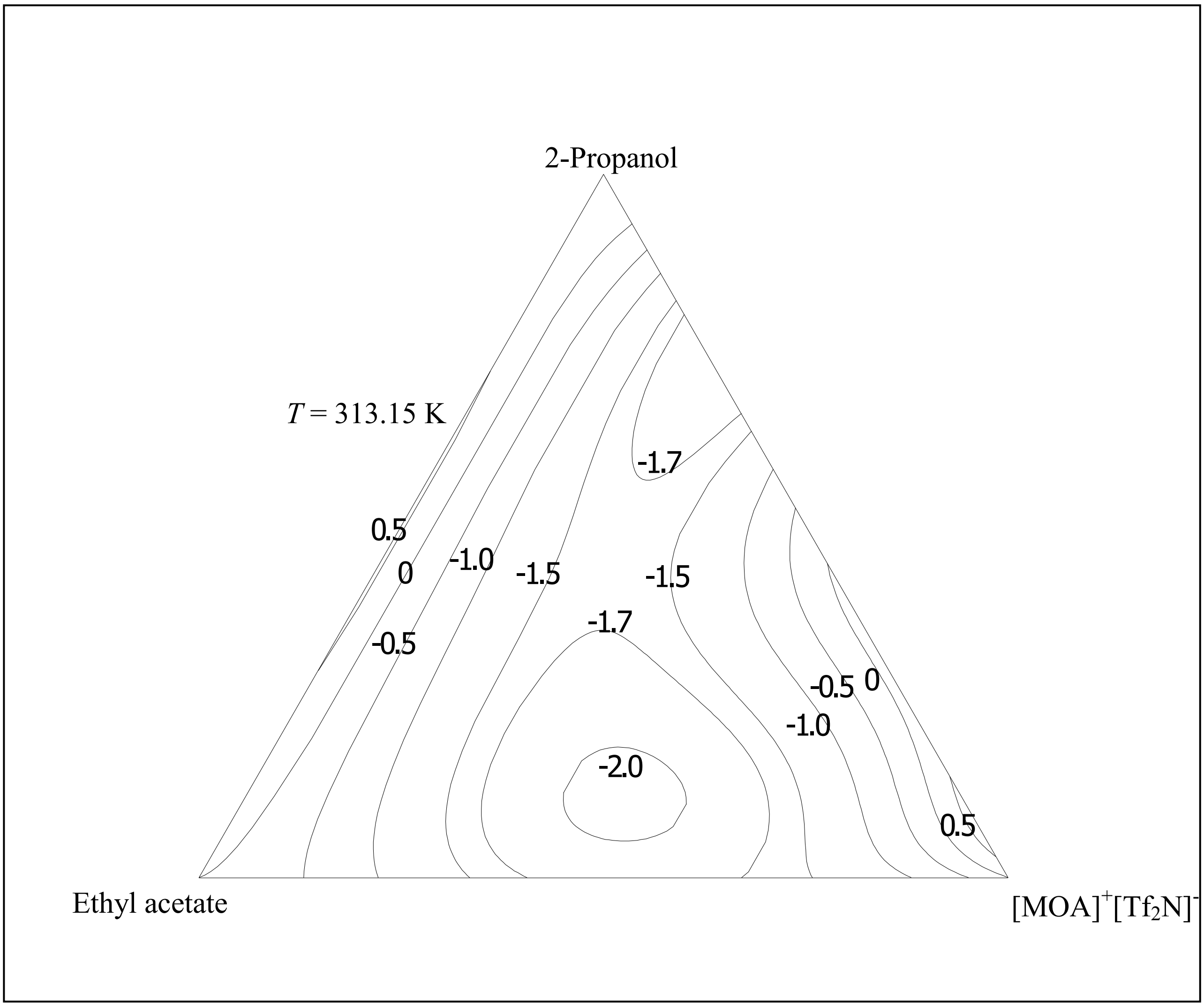


Figure 7.6 Graph of excess molar volumes for the ternary mixtures $[MOA]^+[Tf_2N]^-$ + 2-propanol + ethyl acetate at $T = 313.15$ K. The solid lines were calculated by the Cibulka equation with the values of the parameters fitted to the binary and ternary data.

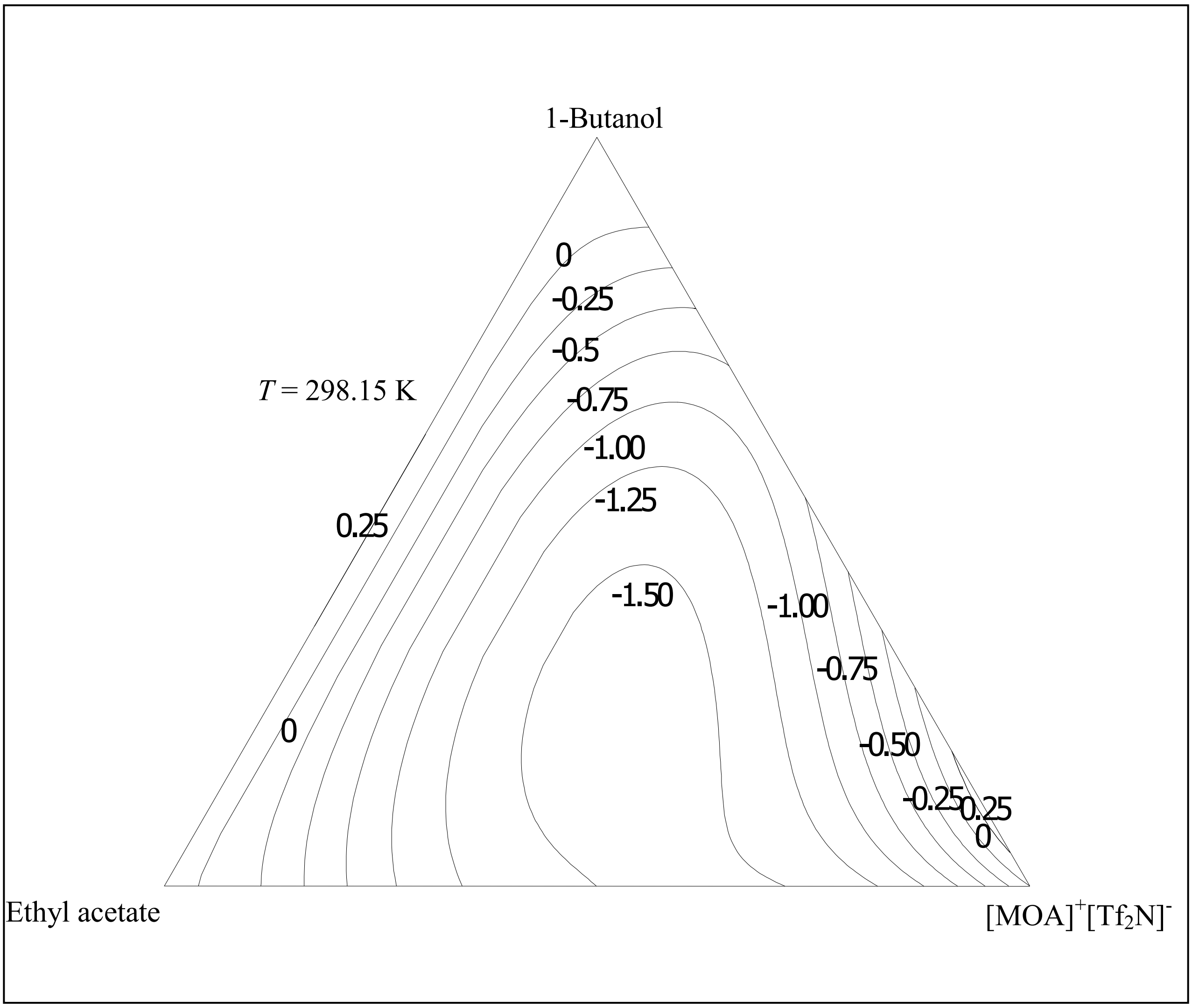


Figure 7.7 Graph of excess molar volumes for the ternary mixtures $[MOA]^+[Tf_2N]^-$ + 1-butanol + ethyl acetate at *T* = 298.15 K. The solid lines were calculated by the Cibulka equation with the values of the parameters fitted to the binary and ternary data.

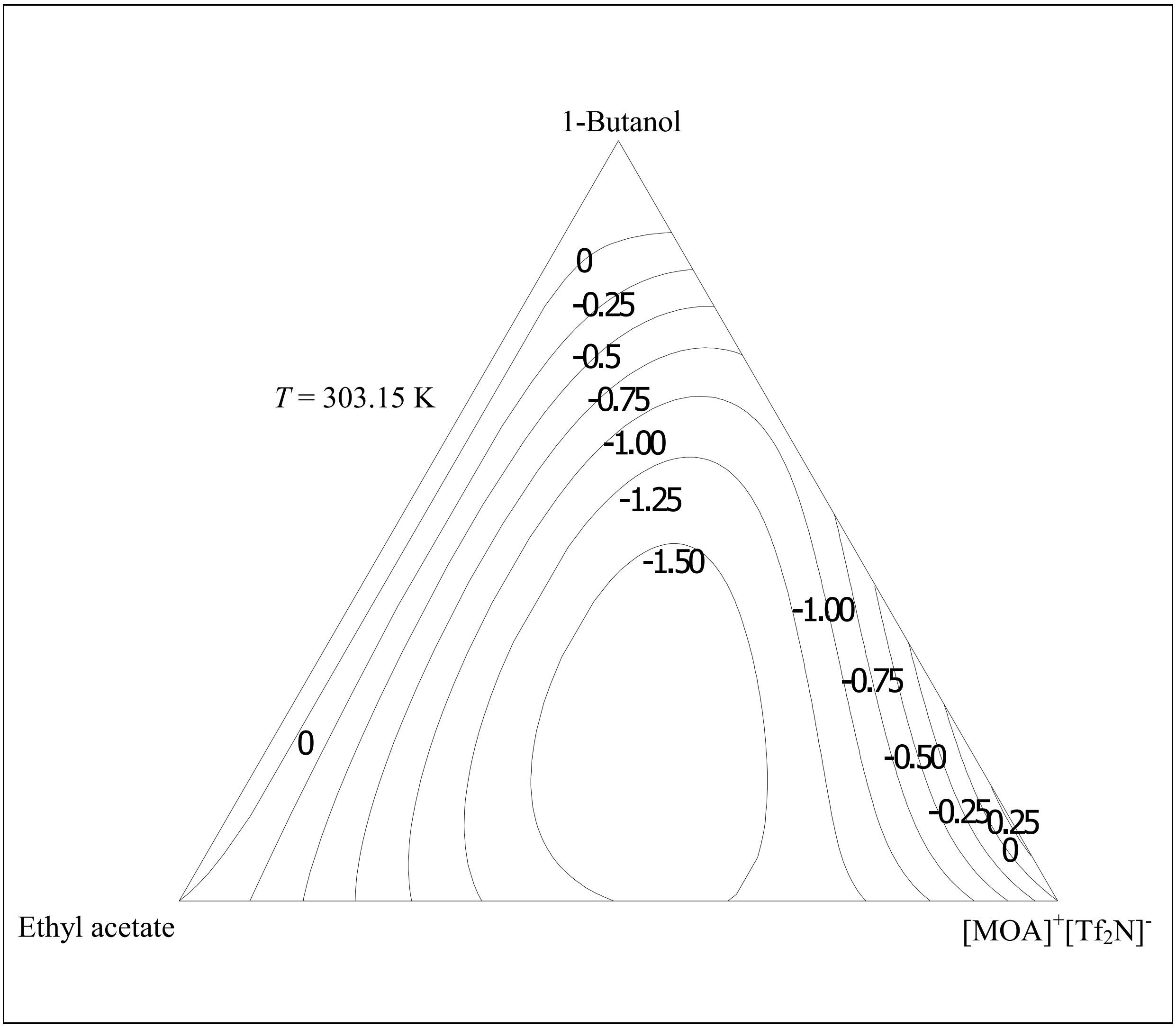


Figure 7.8 Graph of excess molar volumes for the ternary mixtures $[MOA]^+[Tf_2N]^-$ + 1-butanol + ethyl acetate at T = 303.15 K. The solid lines were calculated by the Cibulka equation with the values of the parameters fitted to the binary and ternary data.

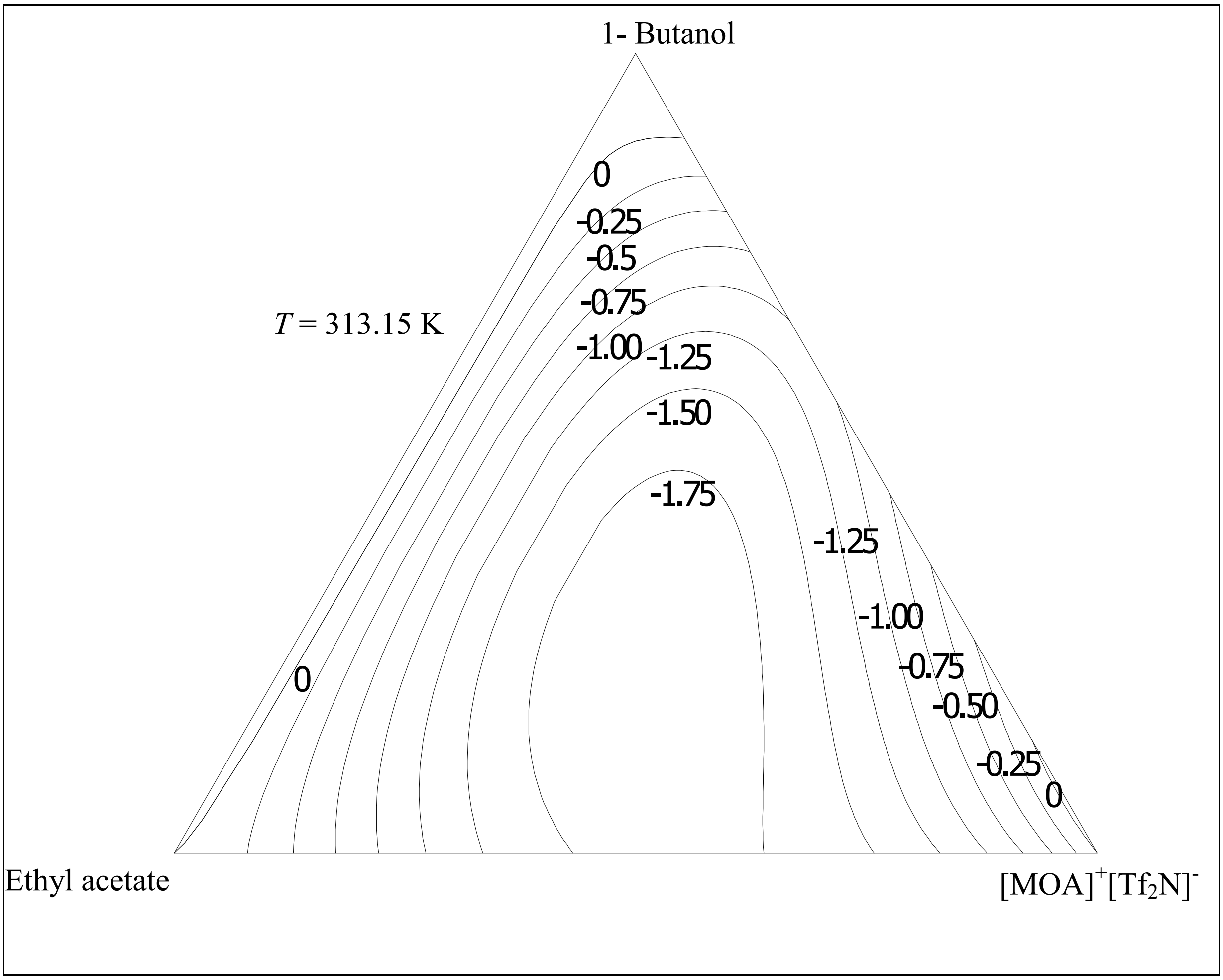


Figure 7.9 Graph of excess molar volumes for the ternary mixtures $[MOA]^+[Tf_2N]^-$ + 2-propanol + ethyl acetate at T = 313.15 K. The solid lines were calculated by the Cibulka equation with the values of the parameters fitted to the binary and ternary data.

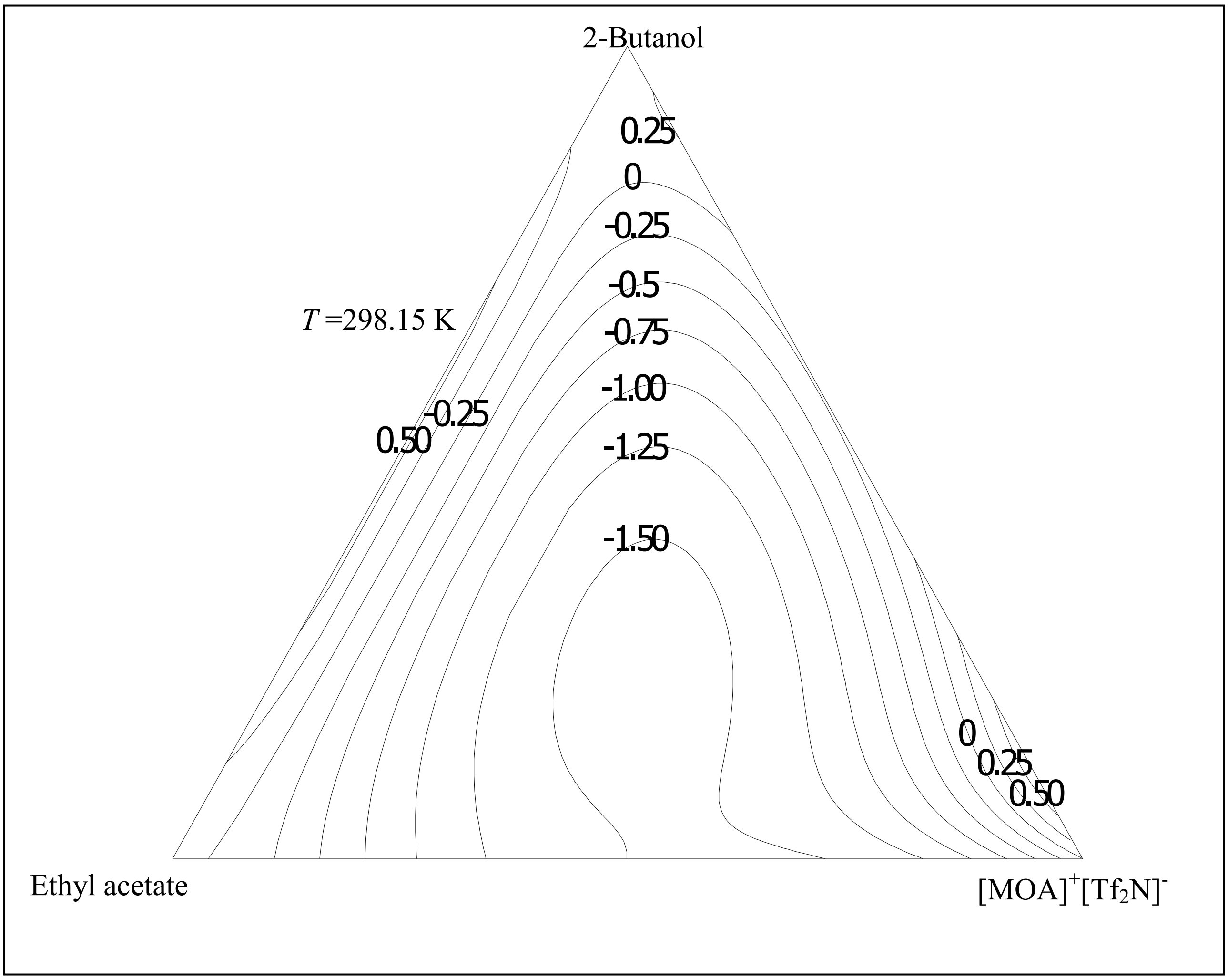


Figure 7.10 Graph of excess molar volumes for the ternary mixtures $[MOA]^+[Tf_2N]^-$ + 2-butanol+ ethyl acetate at $T = 298.15$ K. The solid lines were calculated by the Cibulka equation with the values of the parameters fitted to the binary and ternary data.

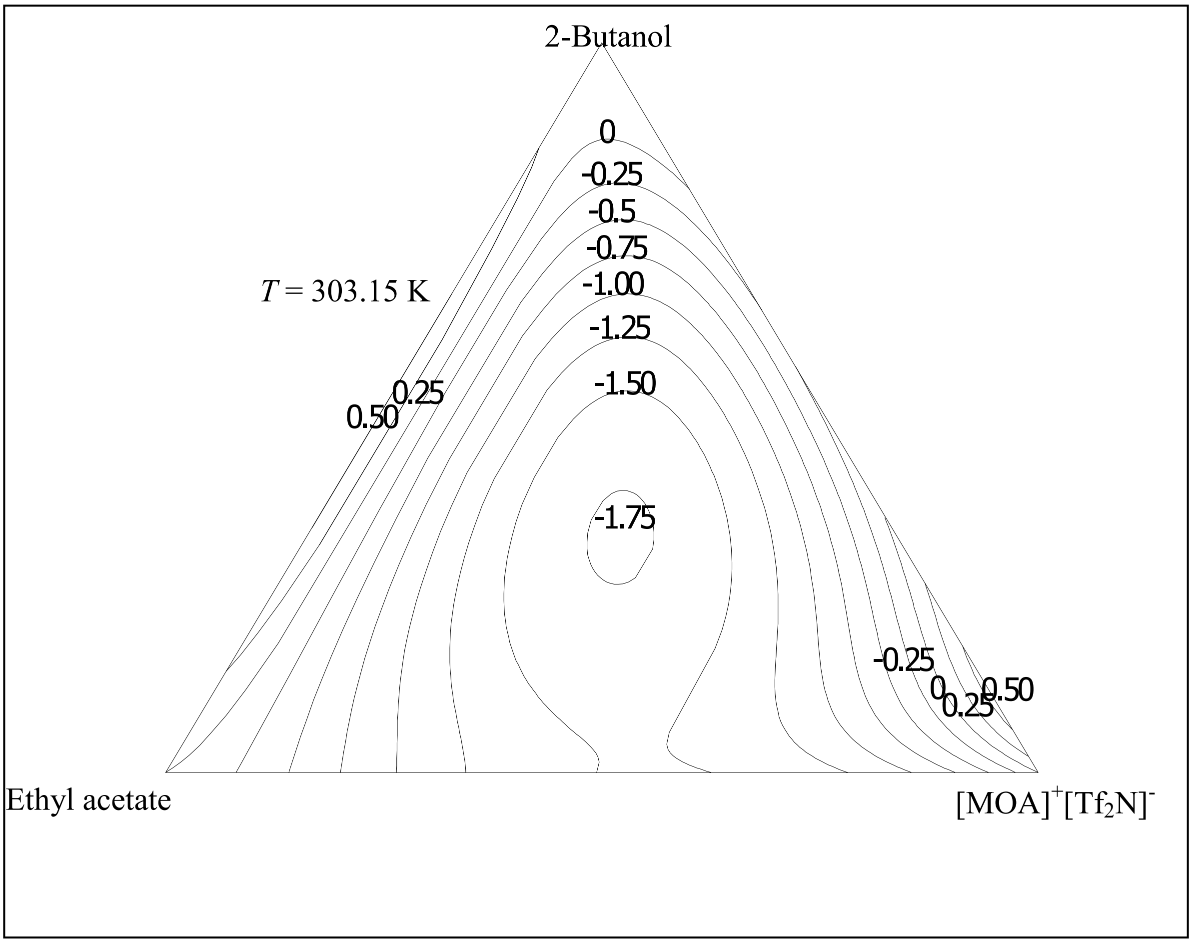


Figure 7.11 Graph of excess molar volumes for the ternary mixtures $[MOA]^+[Tf_2N]^-$ + 2-butanol+ ethyl acetate at *T* = 303.15 K. The solid lines were calculated by the Cibulka equation with the values of the parameters fitted to the binary and ternary data.

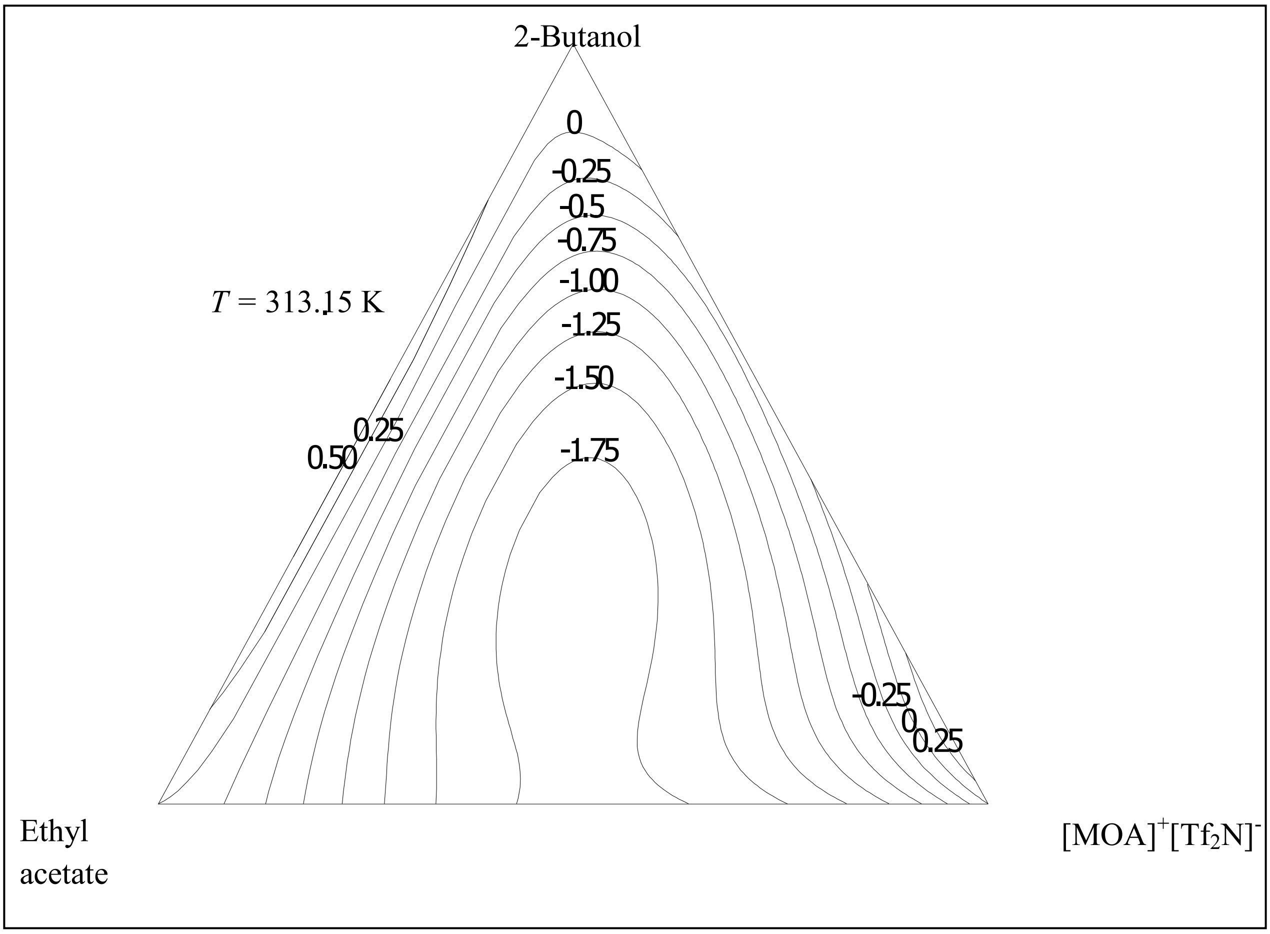


Figure 7.12 Graph of excess molar volumes for the ternary mixtures $[MOA]^+[Tf_2N]^-$ + 2-butanol+ ethyl acetate at T = 313.15 K. The solid lines were calculated by the Cibulka equation with the values of the parameters fitted to the binary and ternary data.

a) $[MOA]^+[Tf_2N]^-$ + 2-propanol + ethyl acetate

The ternary system ($[MOA]^+[Tf_2N]^-$ + 2-propanol + ethyl acetate), has three binary systems ($[MOA]^+[Tf_2N]^-$ + 2-propanol) (Bahadur *et al.* 2011), ($[MOA]^+[Tf_2N]^-$ + ethyl acetate) (Deenadayalu and Bahadur 2010a), and (2-propanol + ethyl acetate) (Oswal and Putta 2001).

The ternary V_{123}^E for ($[MOA]^+[Tf_2N]^-$ + 2-propanol + ethyl acetate) is presented in table 6.7. The V_{123}^E values are negative at all mole fractions of IL which is similar to the binary ($[MOA]^+[Tf_2N]^-$ + ethyl acetate) found in literature (Deenadayalu and Bahadur 2010a). V_{123}^E becomes more negative as the temperature increases because the kinetic energy of the molecules increases with temperature, which leads to the increase in the interaction of molecules (Deenadayalu and Sibiya 2009). Negative excess molar volumes may be due to the effect of ion dipole interactions between IL, 2-propanol and ethyl acetate and or the packing effect dominating over the dipolar orders in the alcohol and acetate (Deenadayalu *et al.* 2008). Interactions between the IL ions with 2-propanol and ethyl acetate can occur through the cation of the IL and lone pair of electrons on the 2-propanol and ethyl acetate as well as accommodation of smaller 2-propanol molecules into the interstices of IL (Deenadayalu *et al.* 2008, Bahadur 2010). V_{123}^E decreases with decreasing z values except at $z = 0.25$ and 0.08. V_{123}^E has the smallest value at $z = 0.84$ for all temperatures. Figures 7.4-7.6, shows the graphs of the ternary excess molar volumes obtained from using the Cibulka equation parameters. The Cibulka diagram for ternary system ($[MOA]^+[Tf_2N]^-$ + 2-propanol + ethyl acetate) shows that the $V_{\mathrm{m,min}}^E$ occurs at low mole fractions of 2-propanol at $T = 298.15$ K and at equimolar concentration for $T = (303.15$ and $313.15)$ K. From the graph, it can be seen that the excess molar volume is positive for (IL + 2-propanol) at high mole fractions of IL and (2-propanol + ethyl acetate) which is similar to the binary data ($[MOA]^+[Tf_2N]^-$ + 2-propanol) taken from unpublished work (Bahadur *et al.* 2011) and (2-propanol + ethyl acetate) (Oswal and Putta 2001) taken from previously published work.

b) $[MOA]^+[Tf_2N]^-$ + 1-butanol + ethyl acetate

The ternary system ($[MOA]^+[Tf_2N]^-$ + 1-butanol + ethyl acetate) has three binary systems: ($[MOA]^+[Tf_2N]^-$ + 1-butanol) (Bahadur et al. 2011), ($[MOA]^+[Tf_2N]^-$ + ethyl acetate) (Deenadayalu and Bahadur 2010a), and (1-butanol + ethyl acetate) (Fermeglia 1988).

For the ternary system of ($[MOA]^+[Tf_2N]^-$ + 1-butanol + ethyl acetate) is presented in table 6.8. The V_{123}^E values are negative at all mole fractions of IL which is similar to the binary of

($[MOA]^+[Tf_2N]^-$ + ethyl acetate) (Deenadayalu and Bahadur 2010a) which indicates that more efficient packing and/ or attractive interaction occurred when the IL alcohol and ethyl acetate were mixed (Deenadayalu *et al.* 2009). The negative values may be due to the same effects that occur in the ternary system (IL + 2-propanol + ethyl acetate) above.

V_{123}^{E} becomes more negative as the temperature increases because the kinetic energy of the molecules increases with temperature (Deenadayalu *et al.* 2009). $V_{123,\mathrm{min}}^{\mathrm{E}}$ decreases with decreasing z values for $z \geq 0.84$ and for $z \leq 0.42$. The $V_{123,}^{\mathrm{E}}$ value is the smallest at $z = 0.84$ for all temperatures. Figures 7.7-7.9, shows the graphs of the ternary excess molar volumes obtained from using the Cibulka equation parameters. The Cibulka diagram for ternary system ($[MOA]^+[Tf_2N]^-$ + 1-butanol + ethyl acetate) shows that the $V_{\mathrm{m,min}}^{\mathrm{E}}$ occurs at the mid-region of the ternary graph at all temperatures. From the graph, it can be seen that the excess molar volume is positive for (IL + 1-butanol) and (1-butanol + ethyl acetate) which corresponds to the binary data ($[MOA]^+[Tf_2N]^-$ + 1-butanol) taken from unpublished work (Bahadur *et al.* 2011) and (1-butanol + ethyl acetate) (Fermeglia 1988) taken from previously published work.

c) $[MOA]^+[Tf_2N]^-$ + 2-butanol + ethyl acetate

The ternary system ($[MOA]^+[Tf_2N]^-$ + 2-butanol + ethyl acetate) has three binary systems: ($[MOA]^+[Tf_2N]^-$ + 2-butanol) binary data is taken from unpublished work (Bahadur *et al.* 2011), the binary excess molar volume data for ($[MOA]^+[Tf_2N]^-$ + ethyl acetate) (Deenadayalu and Bahadur 2010 a), and (2-butanol + ethyl acetate) (Resa 2004) taken from previously published work.

For the ternary system of ($[MOA]^+[Tf_2N]^-$ + 1-butanol + ethyl acetate) is presented in table 6.9. The V_{123}^{E} values are negative at all mole fractions which may be due to the accommodation of the small 2-butanol and ethyl acetate molecules into the IL matrices and ion-dipole interactions.

The stronger interactions between the IL, alcohol and ethyl acetate mixture than in pure liquids also contribute to the negative excess molar volume (Zafarani-Mottarnd Shekaari 2006).

The negative values of the ternary excess molar volumes for (IL + 2-butanol + ethyl acetate) systems shows that the effect due to the (ion-dipole) interactions between 2-butanol, as well as, ethyl acetate + IL and the packing effect are dominating over the dipolar orders in the alcohol and ethyl acetate (Deenadayalu 2008). The negative values may be due to the same effects that occur in the ternary system (IL + 2-propanol + ethyl acetate) above. $V_{123,\mathrm{min}}^{\mathrm{E}}$ decreases for the $z \geq 0.84$ and for $z \leq 0.42$. The $V_{123,}^{\mathrm{E}}$ value is the smallest at $z = 0.84$ at $T = 298.15$ K, and at $z = 0.84$ at $T = 303.15$ K and at $z = 0.84$ at $T = 313.15$ K. Figures 7.9-7.12, shows the graphs of the ternary excess molar volumes obtained from using the Cibulka equation parameters. The Cibulka diagram for ternary system ($[\mathrm{MOA}]^+[\mathrm{Tf_2N}]^-$ + 2-butanol + ethyl acetate) shows that the $V_{123,}^{\mathrm{E}}$ increases as the mole fraction of 2-butanol increases at all temperatures. From the graph, it can be seen that the excess molar volume is positive for (IL + 2-butanol) at high mole fractions of IL and (2-butanol + ethyl acetate) at equimolar concentrations which is similar to the binary data ($[\mathrm{MOA}]^+[\mathrm{Tf_2N}]^-$ + 2-butanol) taken from unpublished work (Bahadur *et al.* 2011) and (2-butanol + ethyl acetate) (Resa 2004) taken from previously published work.

CHAPTER 8

CONCLUSION

The densities were measured for the binary systems (1-butanol or 2-butanol + ethyl acetate) and for the ternary systems ($[\mathrm{MOA}]^+[\mathrm{Tf_2N}]^-$ + 2-propanol or 1-butanol or 2-butanol + ethyl acetate) at T = (298.15, 303.15 and 313.15) K over the entire composition. For each ternary system, the corresponding binary systems not investigated here were obtained from the literature.

The binary data was used for obtaining the Redlich-Kister parameters whereas the ternary excess molar volume data was correlated by the Cibulka equation. The Redlich-Kister parameters from the binary data were used in the Cibulka correlation. For the binary systems (1-butanol or 2-butanol + ethyl acetate) the excess molar volumes were found to become less positive as the temperature increases, this may be due to the breakdown of hydrogen bonding in the alcohol molecules.

The results were interpreted in terms of alcohol chain length and, it was found that V_m^E decreases with alcohol chain length increases except for (1-butanol + ethyl acetate) at T = 303.15 K, and decreases slightly with temperature except for the (1-butanol + ethyl acetate) system at T = 303.15 K (Bahadur 2011).

For the ternary systems ($[\mathrm{MOA}]^+[\mathrm{Tf_2N}]^-$ + 2-propanol or 1-butanol or 2-butanol + ethyl acetate), V_m^E was found to be negative over the entire composition. V_{123}^E becomes more negative as the temperature increases for the (IL + 2-propanol or 1-butanol + ethyl acetate) systems. The negative V_m^E may be due to the packing of small alcohol molecules into the IL matrices.

The Cibulka equation gave a good qualitative correlation to the experimental V_{123}^E data.

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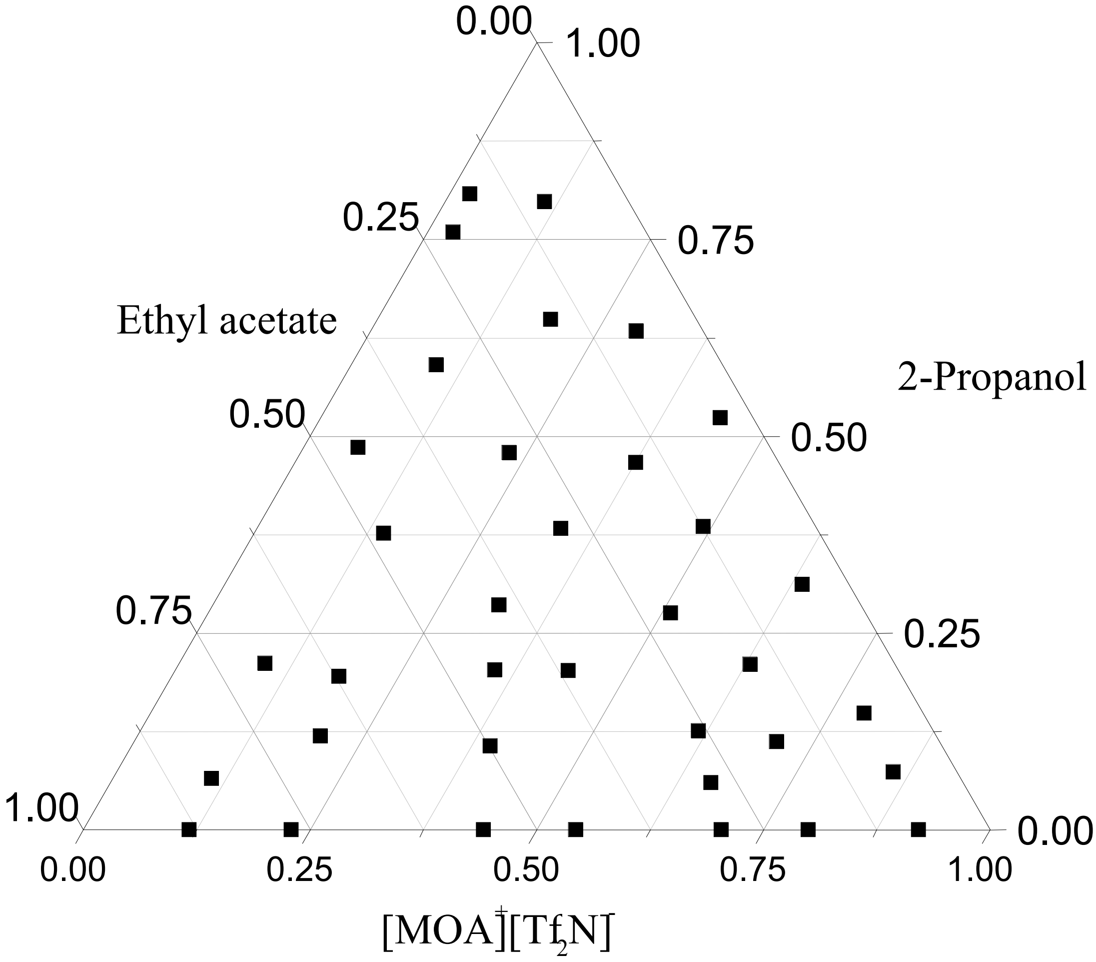
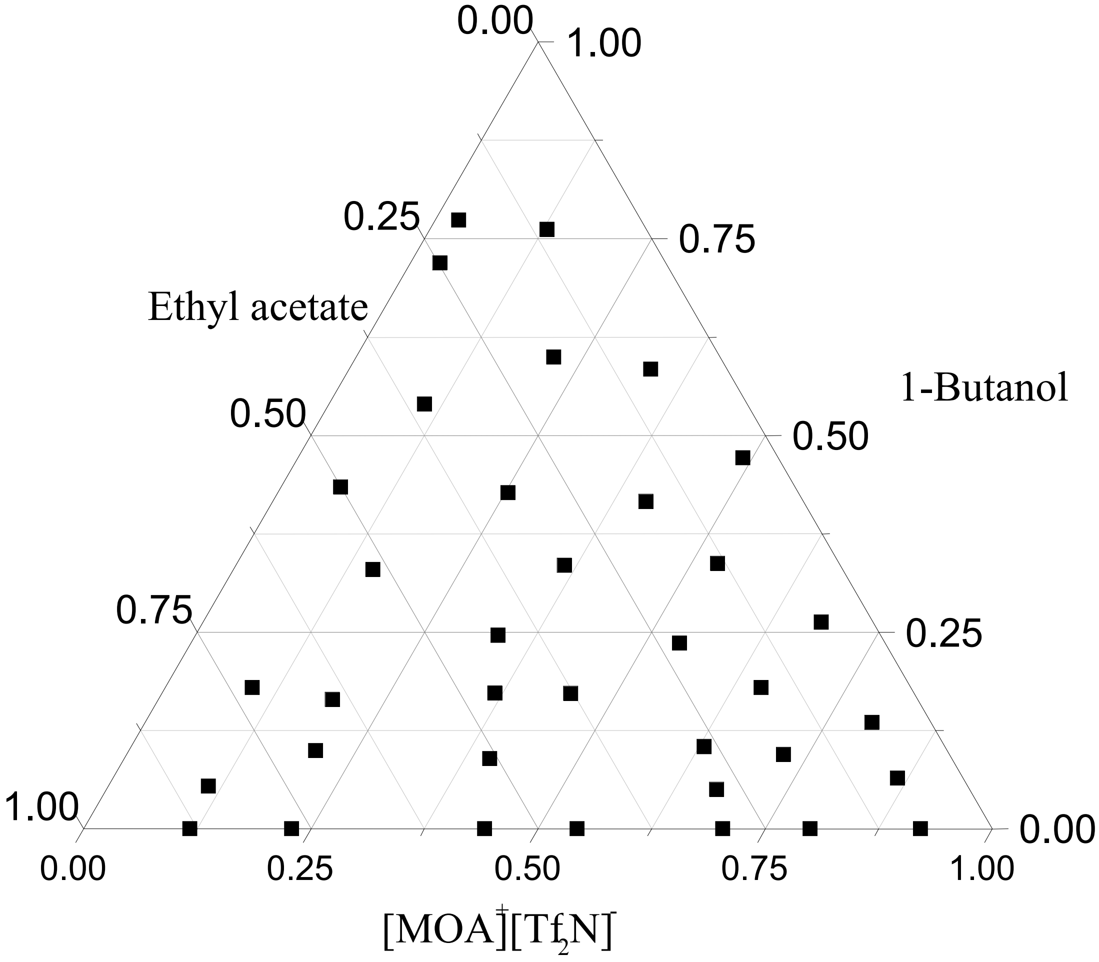
APPENDICES

Appendix 1: Ternary composition plots to verify coverage of the entire ternary composition for the system (IL + 2-propanol + ethyl acetate)



For the system (IL + 1-butanol + ethyl acetate)



For the system (IL + 2-butanol + ethyl acetate)

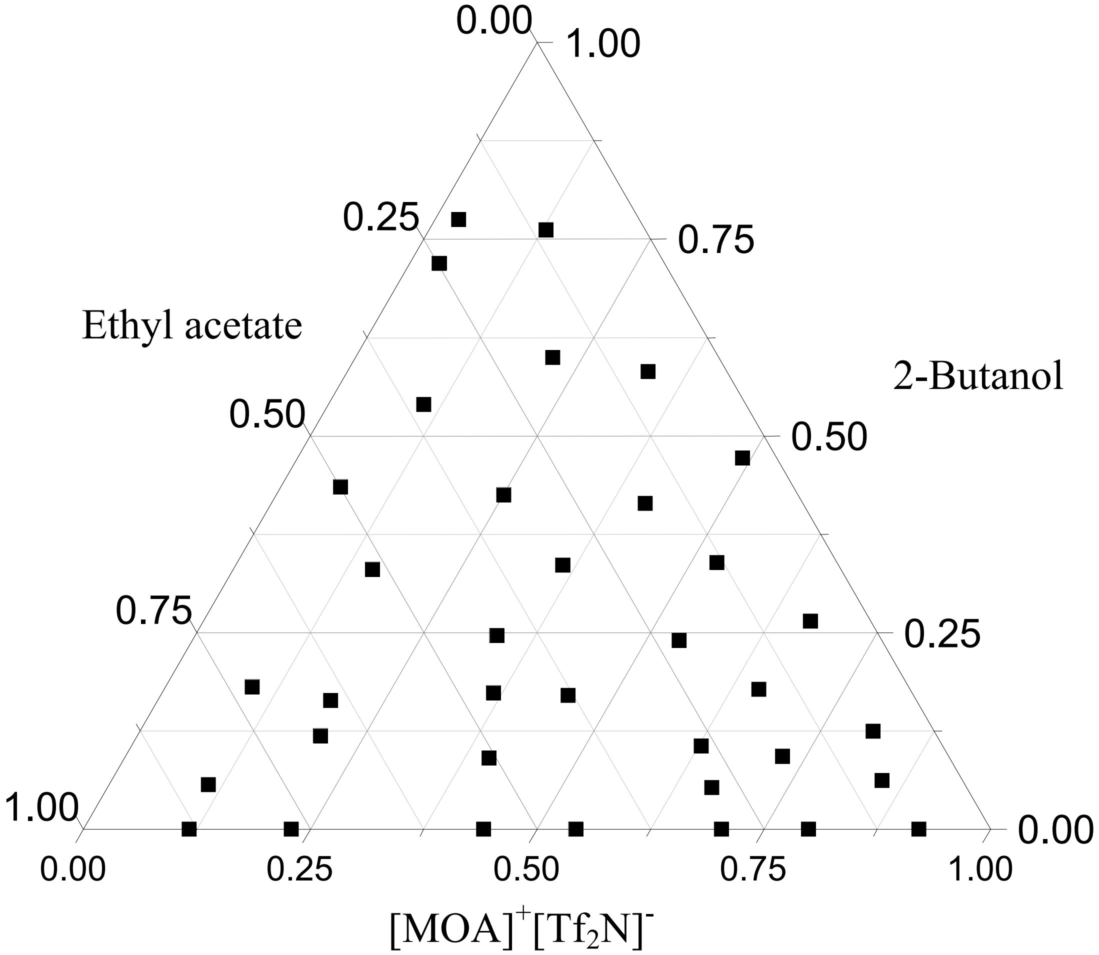


TABLE 1: Pure compound specifications: suppliers, purity, literature, and experimental densities at T = (298.15, 303.15, and 313.15) K.

Compound	Supplier	Mole fraction	$\rho/(\mathrm{g \cdot cm^{-3}})$			
			Literature	Experimental		
			Temperature /K			
			298.15	298.15	303.15	313.15
2-Propanol	BDH	0.997	0.78126[a]	0.7812	0.7772	0.7694
1-Butanol	BDH	0.998	0.80575[b]	0.8070	0.8037	0.7967
2-Butanol	Fulka	0.995	0.8024[c]	0.8028	0.7988	0.7911
$[\mathrm{MOA}]^+[\mathrm{Tf_2N}]^-$	Solvent Innovation	0.980	1.1093[d]	1.1069	1.1032	1.0957
Ethyl acetate	Fluka	0.997	0.8947	0.8948	0.8886	0.8752

[a] Reference [27].

[b] Reference [29]

[c] Reference [30].

[d] Reference [26]

TABLE 2: Binary densities and excess molar volumes for {ionic liquid (x_1) + 2-propanol (x_2)} at T = (298.15, 303.15, and 313.15) K

x_1	$\rho/(\mathrm{g \cdot cm^{-3}})$	$V_{12}^{\mathrm{E}}/(\mathrm{cm^3 \cdot mol^{-1}})$	x_1	$\rho/(\mathrm{g \cdot cm^{-3}})$	$V_{12}^{\mathrm{E}}/(\mathrm{cm^3 \cdot mol^{-1}})$
		$[\mathrm{MOA}]^+[\mathrm{Tf_2N}]^-$ (x_1) + 2-propanol (x_2)			
		T = 298.15 K			
0.0530	0.8769	0.191	0.4824	1.0676	-0.271
0.1000	0.9326	-0.279	0.5896	1.0789	0.257
0.2045	1.0049	-1.456	0.7066	1.089	0.429
0.2841	1.0338	-1.681	0.7967	1.0952	0.505
0.3934	1.0562	-1.079	0.8960	1.1005	0.734
		T = 303.15 K			
0.0530	0.8730	0.177	0.4824	1.0639	-0.304
0.1000	0.9289	-0.324	0.5896	1.0752	0.234
0.2045	1.0015	-1.564	0.7066	1.0854	0.374
0.2841	1.0303	-1.776	0.7967	1.0916	0.452
0.3934	1.0526	-1.148	0.8960	1.0969	0.683
		T = 313.15 K			
0.0530	0.8651	0.176	0.4824	1.0566	-0.417
0.1000	0.9213	-0.376	0.5896	1.0681	0.056
0.2045	0.9947	-1.778	0.7066	1.0783	0.188
0.2841	1.0233	-1.971	0.7967	1.0844	0.304
0.3934	1.0451	-1.218	0.8960	1.0895	0.633

TABLE 3: Binary densities and excess molar volumes for {ionic liquid (x_1) + 1-butanol (x_2)} at T = (298.15, 303.15, and 313.15) K

x_1	$\rho/(\text{g} \cdot \text{cm}^{-3})$	$V_{12}^{E}/(\text{cm}^3 \cdot \text{mol}^{-1})$	x_1	$\rho/(\text{g} \cdot \text{cm}^{-3})$	$V_{12}^{E}/(\text{cm}^3 \cdot \text{mol}^{-1})$
		$[\text{MOA}]^+[\text{Tf}_2\text{N}]^-$ (x_1) + 1-butanol (x_2)			
		T = 298.15 K			
0.0654	0.8981	0.201	0.5343	1.0728	-0.641
0.1421	0.9620	-0.147	0.6385	1.0834	-0.352
0.2623	1.0180	-0.618	0.7397	1.0910	0.096
0.3284	1.0373	-0.777	0.8432	1.0979	0.235
0.4437	1.0604	-0.805	0.9195	1.1021	0.368
		T = 303.15 K			
0.0654	0.8943	0.248	0.5343	1.0691	-0.637
0.1421	0.9586	-0.175	0.6385	1.0798	-0.387
0.2623	1.0146	-0.672	0.7397	1.0874	0.058
0.3284	1.0339	-0.843	0.8432	1.0942	0.239
0.4437	1.0568	-0.829	0.9195	1.0986	0.272
		T = 313.15 K			
0.0654	0.8872	0.227	0.5343	1.0621	-0.815
0.1421	0.9518	-0.281	0.6385	1.0727	-0.546
0.2623	1.0076	-0.786	0.7397	1.0805	-0.199
0.3284	1.0269	-0.976	0.8432	1.0872	0.005
0.4437	1.0497	-0.960	0.9195	1.0916	0.022

TABLE 4: Binary densities and excess molar volumes for {ionic liquid (x_1) + 2-butanol (x_2)} at T = (298.15, 303.15, and 313.15) K

x_1	$\rho/(\mathrm{g \cdot cm^{-3}})$	$V_{12}^{E}/(\mathrm{cm^3 \cdot mol^{-1}})$	x_1	$\rho/(\mathrm{g \cdot cm^{-3}})$	$V_{12}^{E}/(\mathrm{cm^3 \cdot mol^{-1}})$
		$[\mathrm{MOA}]^+[\mathrm{Tf_2N}]^-$ (x_1) + 2-butanol (x_2)			
		T = 298.15 K			
0.0654	0.8942	0.293	0.5045	1.0667	-0.171
0.1397	0.9562	0.166	0.6051	1.0785	0.021
0.2623	1.0138	-0.057	0.7046	1.0873	0.308
0.3282	1.0334	-0.159	0.8080	1.0946	0.596
0.4054	1.0506	-0.213	0.9067	1.1008	0.612
		T = 303.15 K			
0.0654	0.8903	0.280	0.5045	1.0630	-0.204
0.1397	0.9527	0.087	0.6051	1.0748	-0.005
0.2623	1.0102	-0.123	0.7046	1.0837	0.249
0.3282	1.0297	-0.202	0.8080	1.0910	0.542
0.4054	1.0469	-0.252	0.9067	1.0972	0.560
		T = 313.15 K			
0.0654	0.8826	0.267	0.5045	1.0557	-0.314
0.1397	0.9453	0.016	0.6051	1.0676	-0.150
0.2623	1.0031	-0.270	0.7046	1.0765	0.103
0.3282	1.0225	-0.333	0.8080	1.0839	0.349
0.4054	1.0397	-0.389	0.9067	1.0900	0.409

TABLE 5: Binary densities and excess molar volumes for {1-butanol (x_1) + ethyl acetate (x_2)} at T = (298.15, 303.15 and 313.15) K

x_1	ρ/ (g·cm^{-3})	V_{12}^{E} / (cm^{-3}·mol^{-1})	x_1	ρ/ (g·cm^{-3})	V_{12}^{E} / (cm^{-3}·mol^{-1})
		T = 298.15 K			
0.0904	0.8865	0.079	0.7032	0.8315	0.210
0.1337	0.8823	0.139	0.8009	0.8230	0.152
0.2525	0.8715	0.211	0.8916	0.8151	0.088
0.3723	0.8607	0.256	0.9641	0.8086	0.048
0.4807	0.8510	0.272	0.9795	0.8073	0.029
0.5955	0.8409	0.253			
		T = 303.15 K			
0.0904	0.8804	0.131	0.7032	0.8288	0.150
0.1337	0.8768	0.145	0.8009	0.8206	0.101
0.2525	0.8667	0.191	0.8916	0.8130	0.041
0.3723	0.8566	0.210	0.9641	0.8067	0.010
0.4807	0.8475	0.206	0.9795	0.8053	0.007
0.5955	0.8380	0.169			
		T = 313.15 K			
0.0904	0.8696	0.069	0.7032	0.8201	0.178
0.1337	0.8660	0.106	0.8009	0.8123	0.134
0.2525	0.8566	0.137	0.8916	0.8050	0.088
0.3723	0.8468	0.186	0.9641	0.7994	0.014
0.4807	0.8380	0.207	0.9795	0.7981	0.010
0.5955	0.8288	0.197			

TABLE 6: Binary densities and excess molar volumes for {2-butanol (x_1) + ethyl acetate (x_2)} at T = (298.15, 303.15 and 313.15) K

x_1	ρ/ (g·cm^{-3})	V_{12}^{E} / (cm^{-3}·mol^{-1})	x_1	ρ/ (g·cm^{-3})	V_{12}^{E} / (cm^{-3}·mol^{-1})
T =298.15 K					
0.0603	0.8885	0.1178	0.5631	0.8390	0.6053
0.1109	0.8832	0.2147	0.6010	0.8356	0.5919
0.1511	0.8789	0.3004	0.6501	0.8311	0.5821
0.1998	0.8738	0.3896	0.7032	0.8265	0.5376
0.2502	0.8688	0.4484	0.7520	0.8225	0.4657
0.3020	0.8636	0.5130	0.8012	0.8184	0.3983
0.3489	0.8589	0.5679	0.8498	0.8146	0.2996
0.3988	0.8541	0.6005	0.9028	0.8103	0.2061
0.4506	0.8494	0.5987	0.9519	0.8067	0.0706
0.5011	0.8446	0.6182			
T =303.15 K					
0.0603	0.8702	0.0258	0.5631	0.8245	0.5276
0.1109	0.8656	0.0901	0.6010	0.8212	0.5350
0.1511	0.8614	0.2027	0.6501	0.8173	0.4968
0.1998	0.8571	0.2450	0.7032	0.8129	0.4734
0.2502	0.8525	0.3034	0.7520	0.8089	0.4418
0.3020	0.8475	0.3922	0.8012	0.8051	0.3797
0.3489	0.8432	0.4431	0.8498	0.8014	0.3083
0.3988	0.8387	0.4852	0.9028	0.7974	0.2225
0.4506	0.8343	0.4933	0.9519	0.7944	0.0545
0.5011	0.8299	0.5105			
T =303.15 K					
0.0603	0.8702	0.0258	0.5631	0.8245	0.5276
0.1109	0.8656	0.0901	0.6010	0.8212	0.5350
0.1511	0.8614	0.2027	0.6501	0.8173	0.4968
0.1998	0.8571	0.2450	0.7032	0.8129	0.4734
0.2502	0.8525	0.3034	0.7520	0.8089	0.4418

0.3020	0.8475	0.3922	0.8012	0.8051	0.3797
0.3489	0.8432	0.4431	0.8498	0.8014	0.3083
0.3988	0.8387	0.4852	0.9028	0.7974	0.2225
0.4506	0.8343	0.4933	0.9519	0.7944	0.0545
0.5011	0.8299	0.5105			

TABLE 7: The coefficients A_i, partial molar volumes at infinite dilution and relative mean standard deviations, σ, obtained for (a) $[MOA]^+[Tf_2N]^-$ + 2-propanol, (b) $[MOA]^+[Tf_2N]^-$ + 1-butanol, (c) $[MOA]^+[Tf_2N]^-$ + 2-butanol (d) 1-butanol + ethyl acetate (e) 2-butanol + ethyl acetate at T = (298.15, 303.15, and 313.15) K

T/K	A_o	A_1	A_2	A_3	A_4	$V_{m,1}^{\infty}$	$V_{m,2}^{\infty}$	$\sigma^{1)}$ /(cm^3 · mol^{-1}
(a)								
298.15	−0.694	−14.051	-20.319	10.972	39.795	15.703	21.861	0.018
303.15	−0.815	−14.472	-21.980	11.610	41.406	15.749	21.473	0.019
313.15	−1.220	−14.189	-26.050	10.661	47.498	16.700	23.756	0.034
(b)								
298.15	−2.702	−4.516	3.991	3.657	6.541	6.971	8.689	0.042
303.15	−2.921	−4.857	3.345	5.308	7.145	8.020	7.118	0.051
313.15	−3.519	−4.654	2.215	7.005	6.160	7.207	2.505	0.059
(c)								
298.15	−0.657	−2.468	5.656	−0.230	4.911	7.212	12.608	0.025
303.15	−0.757	−2.549	4.499	−0.085	5.681	6.789	12.057	0.036
313.15	−1.233	−2.690	2.808	1.402	6.814	7.101	9.677	0.038
(d)								
298.15	1.063	-1.146	-	-	-	-0.083	2.209	0.008
303.15	7.935	-4.553	2.365	-	-	5.747	14.853	0.011
313.15	8.175	-	-	-	-	8.175	8.175	0.009
(e)								
298.15	2.504	-6.946	-2.958	-	-	-7.400	6.492	0.012
303.15	2.269	-5.153	-4.044	-	-	-6.928	3.378	0.015
313.15	2.114	-6.617	-5.574	-	-	10.077	3.157	0.021

TABLE 8: Binary interaction parameters obtained from Virial Based Mixing Rule correlation and standard deviations obtained for {$[OMA]^+[Tf_2N]^-$ + a) 2-propanol, b) 1-butanol c) 2-butanol} d) 1-butanol + ethyl acetate e) 2-butanol + ethyl acetate at T = (298.15, 303.15 and 313.15) K.

T/ K	k_{12}	λ_{112}	η_{1122}	ξ_{11222}	
$[OMA]^+[Tf_2N]^-$ + 2-propanol					
298.15	0.002145	0.3008	-0.7299	0.7765	-0.3124
303.15	0.002665	0.3091	-0.7558	0.8070	-0.3246
313.15	0.003563	0.3394	-0.8444	0.9139	-0.3701
$[OMA]^+[Tf_2N]^-$ + 1-butanol					
298.15	0.001047	0.09466	-0.1586	0.1305	-0.05067
303.15	0.001142	0.1046	-0.1805	0.1514	-0.05785
313.15	0.002411	0.09560	-0.1649	0.1356	-0.04967
$[OMA]^+[Tf_2N]^-$ + 2-butanol					
298.15	-0.002338	0.07539	-0.1180	0.09578	-0.04013
303.15	-0.001846	0.07689	-0.1287	0.1107	-0.04623
313.15	-0.0009147	0.08417	-0.1505	0.1351	-0.05495
1-butanol + ethyl acetate					
2-butanol + ethyl acetate					

TABLE 9: The partial molar volumes at infinite dilution obtained from the Redlich –Kister (RK) parameters and that obtained from the VBMR parameters for (a) $[MOA]^+[Tf_2N]^-$ + 2-propanol, (b) $[MOA]^+[Tf_2N]^-$ + 1-butanol, (c) $[MOA]^+[Tf_2N]^-$ + 2-butanol (d) 1-butanol + ethyl acetate (e) 2-butanol + ethyl acetate at T = (298.15, 303.15, and 313.15) K

T/K	$V^{\infty}_{m,1}$ (RK)	$V^{\infty}_{m,2}$ (RK)	$V^{\infty}_{m,1}$ VBMR	$V^{\infty}_{m,2}$ VBMR
(a) 298.15	15.703	21.861	15.559	21.693
303.15	15.749	21.473	15.653	21.364
313.15	16.700	23.756	16.584	23.626
(b) 298.15	6.971	8.689	7.244	8.331
303.15	8.020	7.118	8.272	7.346
313.15	7.207	2.505	7.393	2.743
(c) 298.15	7.212	12.608	7.492	12.777
303.15	6.789	12.057	7.067	12.243
313.15	7.101	9.677	7.354	9.881
(d) 298.15	-7.400	6.492		
303.15	-6.928	3.378		
313.15	10.077	3.157		
(e) 298.15				
303.15				
313.15				

TABLE 10: Ternary density, ρ, and excess molar volume, V_{123}^{E} for (Ionic liquid + 2-propanol + ethyl acetate) at T = (298.15, 303.15 and 313.15) K.

x_1	x_2	x_3	ρ/ (g·cm^{-3})	V_{123}^{E}/ (cm^{-3}·mol^{-1})
T = 298.15 K				
z =7.57				
0.0600	0.4856	0.4543	0.9234	-0.139
0.0281	0.7591	0.2127	0.9685	-0.416
0.0225	0.8077	0.1698	0.9838	-0.379
0.0946	0.2117	0.6938	0.9899	-0.266
0.1091	0.0653	0.8256	0.8619	-0.038
0.1167	0.0000	0.8833	0.8481	-0.052
z =3.36				
0.0939	0.5904	0.3156	0.9469	-0.337
0.1429	0.3764	0.4807	0.9896	-0.690
0.1847	0.1949	0.6204	1.0145	-0.783
0.2017	0.1193	0.6790	1.0230	-0.837
0.2291	0.0000	0.7709	1.0345	-0.840
0.0939	0.5904	0.3156	0.9469	-0.337
z =1.26				
0.2304	0.4790	0.2906	1.0212	-0.844
0.3156	0.2854	0.3990	1.0488	-1.101
0.3523	0.2034	0.4443	1.0579	-1.249
0.3954	0.1064	0.4982	1.0670	-1.420
0.4417	0.0000	0.5583	1.0747	-1.421
z =0.84				
0.1100	0.7974	0.0926	0.9479	-0.459
0.1911	0.6482	0.1607	1.0018	-0.895
0.3356	0.3825	0.2819	1.0515	-1.311
0.4338	0.2018	0.3644	1.0712	-1.611
0.5433	0.0000	0.4567	1.0854	-1.560
z =0.42				
0.3759	0.4664	0.1578	1.0562	-1.110
0.5101	0.2753	0.2146	1.0780	-1.373
0.6157	0.1256	0.2587	1.0896	-1.523
0.6625	0.0596	0.2779	1.0938	-1.600
0.7037	0.0000	0.2963	1.0967	-1.496
z =0.25				
0.2927	0.6337	0.0736	1.0322	-0.373
0.4909	0.3849	0.1242	1.0727	-0.866
0.6302	0.2105	0.1593	1.0888	-1.191
0.7088	0.1119	0.1794	1.0952	-1.221
0.7993	0.0000	0.2007	1.1013	-1.280
z =0.08				
0.7867	0.1483	0.0650	1.0978	-0.606
0.8568	0.0733	0.0698	1.1020	-0.656

0.6371	0.3113	0.0516	1.0864	-0.537
0.4409	0.5232	0.0359	1.0623	-0.325

T =303.15 K

z =7.57

0.0600	0.4856	0.4543	0.9184	-0.170
0.0281	0.7591	0.2127	0.8560	-0.157
0.0225	0.8077	0.1698	0.8424	-0.158
0.0946	0.2117	0.6938	0.9636	-0.514
0.1091	0.0653	0.8256	0.9788	-0.487
0.1167	0.0000	0.8833	0.9849	-0.383

z =1.26

0.2304	0.4790	0.2906	1.0183	-1.267
0.3156	0.2854	0.3990	1.0450	-1.410
0.3523	0.2034	0.4443	1.0535	-1.435
0.3954	0.1064	0.4982	1.0622	-1.517
0.4417	0.0000	0.5583	1.0696	-1.444

z =0.84

0.1100	0.7974	0.0926	0.9457	-0.830
0.1911	0.6482	0.1607	0.9995	-1.362
0.3356	0.3825	0.2819	1.0478	-1.632
0.4338	0.2018	0.3644	1.0668	-1.801
0.5433	0.0000	0.4567	1.0803	-1.551

z =0.42

0.3759	0.4664	0.1578	1.0514	-1.141
0.5101	0.2753	0.2146	1.0728	-1.292
0.6157	0.1256	0.2587	1.0843	-1.398
0.6625	0.0596	0.2779	1.0882	-1.353
0.7037	0.0000	0.2963	1.0915	-1.399

z =0.25

0.2927	0.6337	0.0736	1.0295	-0.845
0.4909	0.3849	0.1242	1.0687	-1.138
0.6302	0.2105	0.1593	1.0840	-1.227
0.7088	0.1119	0.1794	1.0903	-1.221
0.7993	0.0000	0.2007	1.0962	-1.192

z =0.08

0.7867	0.1483	0.0650	1.0931	-0.666
0.8568	0.0733	0.0698	1.0973	-0.720
0.6371	0.3113	0.0516	1.0819	-0.670
0.4409	0.5232	0.0359	1.0580	-0.471
0.9209	0.0000	0.0791	1.1005	-0.673

$T = 313.15$ K

$z = 7.57$

0.0600	0.4856	0.4543	0.9090	-0.260
0.0281	0.7591	0.2127	0.8478	-0.034
0.0225	0.8077	0.1698	0.8339	-0.090
0.0946	0.2117	0.6938	0.9545	-0.741
0.1091	0.0653	0.8256	0.9693	-0.705
0.1167	0.0000	0.8833	0.9749	-0.539

$z = 3.36$

0.0939	0.5904	0.3156	0.9355	-0.751
0.1429	0.3764	0.4807	0.9769	-1.025
0.1847	0.1949	0.6204	1.0021	-1.252
0.2017	0.1193	0.6790	1.0099	-1.206
0.2291	0.0000	0.7709	1.0209	-1.148

$z = 1.26$

0.2304	0.4790	0.2906	1.0108	-1.439
0.3156	0.2854	0.3990	1.0380	-1.175
0.3523	0.2034	0.4443	1.0467	-1.802
0.3954	0.1064	0.4982	1.0548	-1.738
0.4417	0.0000	0.5583	1.0625	-1.758

$z = 0.84$

0.1100	0.7974	0.0926	0.9373	-0.819
0.1911	0.6482	0.1607	0.9911	-1.323
0.3356	0.3825	0.2819	1.0405	-1.791
0.4338	0.2018	0.3644	1.0599	-2.073
0.5433	0.0000	0.4567	1.0734	-1.834

$z = 0.42$

0.3759	0.4664	0.1578	1.0445	-1.307
0.5101	0.2753	0.2146	1.0663	-1.575
0.6157	0.1256	0.2587	1.0776	-1.614
0.6625	0.0596	0.2779	1.0819	-1.724
0.7037	0.0000	0.2963	1.0850	-1.695

$z = 0.25$

0.2927	0.6337	0.0736	1.0223	-0.919
0.4909	0.3849	0.1242	1.0620	-1.308
0.6302	0.2105	0.1593	1.0773	-1.381
0.7088	0.1119	0.1794	1.0836	-1.365
0.7993	0.0000	0.2007	1.0896	-1.368

$z = 0.08$

0.7867	0.1483	0.0650	1.0108	-1.439
0.8568	0.0733	0.0698	1.0380	-1.715
0.6371	0.3113	0.0516	1.0467	-1.802
0.4409	0.5232	0.0359	1.0548	-1.738
0.9209	0.0000	0.0791	1.0625	-1.758

TABLE 11: Ternary density, ρ, and excess molar volume, V_{123}^{E} for (Ionic liquid + 1-butanol + ethyl acetate) at T = (298.15, 303.15 and 313.15) K.

x_1	x_2	x_3	ρ/ (g·cm^{-3})	V_{123}^{E}/ (cm^{-3}·mol^{-1})
		T = 298.15 K		
		z =7.57		
0.0660	0.4347	0.4992	0.9372	-0.821
0.0328	0.7188	0.2484	0.8800	-0.202
0.0263	0.7746	0.1990	0.8669	-0.092
0.0957	0.1808	0.7235	0.9731	-0.850
0.1102	0.0560	0.8338	0.9857	-0.525
0.1167	0.0000	0.8833	0.9899	-0.266
		z =3.36		
0.1058	0.5394	0.3548	0.9593	-0.754
0.1538	0.3299	0.5164	0.9968	-1.047
0.1912	0.1637	0.6452	1.0186	-1.116
0.2024	0.1182	0.6794	1.0254	-1.059
0.2291	0.0000	0.7709	1.0345	-0.840
		z =1.26		
0.2512	0.4243	0.3245	1.0280	-1.150
0.3331	0.2457	0.4212	1.0520	-1.253
0.3657	0.1728	0.4615	1.0600	-1.352
0.4022	0.0901	0.5077	1.0677	-1.423
0.4417	0.0000	0.5583	1.0747	-1.421
		z =0.84		
0.1295	0.7617	0.1087	0.9630	-0.857
0.2176	0.5993	0.1830	1.0117	-1.284
0.3614	0.3350	0.3036	1.0558	-1.563
0.4494	0.1701	0.3805	1.0725	-1.605
0.5433	0.0000	0.4567	1.0854	-1.559
		z =0.42		
0.4124	0.4141	0.1735	1.0608	-1.342
0.5373	0.2396	0.2231	1.0800	-1.449
0.6280	0.1057	0.2664	1.0904	-1.545
0.6664	0.0527	0.2809	1.0941	-1.552
0.7037	0.0000	0.2963	1.0967	-1.496
		z =0.25		
0.3320	0.5814	0.0866	1.0399	-0.700
0.5288	0.3389	0.1323	1.0762	-1.142
0.6561	0.1775	0.1664	1.0900	-1.209
0.7246	0.0925	0.1829	1.0959	-1.306
0.7993	0.0000	0.2007	1.1013	-1.280
		z =0.08		
0.8087	0.1246	0.0667	1.0985	-0.866
0.8495	0.0617	0.0888	1.1025	-0.853
0.6693	0.2642	0.0664	1.0898	-1.005
0.4910	0.4715	0.0375	1.0681	-0.818
0.9209	0.0000	0.0791	1.1054	-0.703

		T = 303.15 K		
		z =7.57		
0.0660	0.4347	0.4992	0.9327	-0.825
0.0328	0.7188	0.2484	0.8770	-0.254
0.0263	0.7746	0.1990	0.8634	-0.046
0.0957	0.1808	0.7235	0.9672	-0.762
0.1102	0.0560	0.8338	0.9805	-0.591
0.1167	0.0000	0.8833	0.9849	-0.383
		z =3.36		
0.1058	0.5394	0.3548	0.9554	-0.803
0.1538	0.3299	0.5164	0.9918	-1.012
0.1912	0.1637	0.6452	1.0135	-1.133
0.2024	0.1182	0.6794	1.0205	-1.139
0.2291	0.0000	0.7709	1.0295	-0.937
		z =1.26		
0.2512	0.4243	0.3245	1.0234	-1.138
0.3331	0.2457	0.4212	1.0477	-1.393
0.3657	0.1728	0.4615	1.0552	-1.396
0.4022	0.0901	0.5077	1.0625	-1.388
0.4417	0.0000	0.5583	1.0696	-1.442
		z =0.84		
0.1295	0.7617	0.1087	0.9598	-0.926
0.2176	0.5993	0.1830	1.0080	-1.377
0.3614	0.3350	0.3036	1.0513	-1.615
0.4494	0.1701	0.3805	1.0679	-1.697
0.5433	0.0000	0.4567	1.0803	-1.551
		z =0.42		
0.4124	0.4141	0.1735	1.0564	-1.412
0.5373	0.2396	0.2231	1.0756	-1.571
0.6280	0.1057	0.2664	1.0855	-1.539
0.6664	0.0527	0.2809	1.0890	-1.483
0.7037	0.0000	0.2963	1.0915	-1.399
		z =0.25		
0.3320	0.5814	0.0866	1.0358	-0.733
0.5288	0.3389	0.1323	1.0715	-1.116
0.6561	0.1775	0.1664	1.0855	-1.316
0.7246	0.0925	0.1829	1.0910	-1.282
0.7993	0.0000	0.2007	1.0962	-1.192
		z =0.08		
0.8087	0.1246	0.0667	1.0941	-1.013
0.8495	0.0617	0.0888	1.0978	-0.895
0.6693	0.2642	0.0664	1.0854	-1.049
0.4910	0.4715	0.0375	1.0644	-0.944
0.9209	0.0000	0.0791	1.1005	-0.676

		T = 313.15 K		
		z =7.57		
0.0660	0.4347	0.4992	0.9240	-0.973
0.0328	0.7188	0.2484	0.8680	-0.198
0.0263	0.7746	0.1990	0.8550	-0.037
0.0957	0.1808	0.7235	0.9573	-0.859
0.1102	0.0560	0.8338	0.97705	-0.727
0.1167	0.0000	0.8833	0.9749	-0.539
		z =3.36		
0.1058	0.5394	0.3548	0.9474	-0.924
0.1538	0.3299	0.5164	0.9836	-1.189
0.1912	0.1637	0.6452	1.0046	-1.236
0.2024	0.1182	0.6794	1.0116	-1.263
0.2291	0.0000	0.7709	1.0209	-1.148
0.1058	0.5394	0.3548	0.9474	-0.924
		z =1.26		
0.2512	0.4243	0.3245	1.0179	-1.690
0.3331	0.2457	0.4212	1.0412	-1.790
0.3657	0.1728	0.4615	1.0487	-1.823
0.4022	0.0901	0.5077	1.0561	-1.849
0.4417	0.0000	0.5583	1.0625	-1.758
		z =0.84		
0.1295	0.7617	0.1087	0.9532	-1.095
0.2176	0.5993	0.1830	1.0018	-1.680
0.3614	0.3350	0.3036	1.0448	-1.940
0.4494	0.1701	0.3805	1.0609	-1.920
0.5433	0.0000	0.4567	1.0734	-1.834
		z =0.42		
0.4124	0.4141	0.1735	1.0493	-1.471
0.5373	0.2396	0.2231	1.0683	-1.561
0.6280	0.1057	0.2664	1.0785	-1.631
0.6664	0.0527	0.2809	1.0821	-1.611
0.7037	0.0000	0.2963	1.0850	-1.695
		z =0.25		
0.3320	0.5814	0.0866	1.0295	-0.946
0.5288	0.3389	0.1323	1.0650	-1.307
0.6561	0.1775	0.1664	1.0790	-1.523
0.7246	0.0925	0.1829	1.0844	-1.456
0.7993	0.0000	0.2007	1.0896	-1.368
		z =0.08		
0.8087	0.1246	0.0667	1.0873	-1.003
0.8495	0.0617	0.0888	1.0912	-0.970
0.6693	0.2642	0.0664	1.0788	-1.133
0.4910	0.4715	0.0375	1.0579	-1.059
0.9209	0.0000	0.0791	1.0941	-0.850

TABLE 12: Ternary density, ρ, and excess molar volume, V_{123}^{E} for (Ionic liquid + 2-butanol+ ethyl acetate) at T = (298.15, 303.15 and 313.15) K.

x_1	x_2	x_3	ρ/ (g·cm^{-3})	V_{123}^{E} / (cm^{-3}·mol^{-1})
		T = 298.15 K		
		z = 7.57		
0.0660	0.4347	0.4992	0.9354	-0.733
0.0328	0.7188	0.2484	0.8790	-0.337
0.0263	0.7746	0.1990	0.8649	-0.154
0.0957	0.1808	0.7235	0.9714	-0.689
0.1102	0.0560	0.8338	0.9853	-0.521
0.1167	0.0000	0.8833	0.8481	-0.266
0.0660	0.4347	0.4992	0.9354	-0.733
		z =3.36		
0.1058	0.5394	0.3548	0.9583	-0.787
0.1538	0.3299	0.5164	0.9959	-1.021
0.1912	0.1637	0.6452	1.0180	-1.090
0.2024	0.1182	0.6794	1.0236	-1.109
0.2291	0.0000	0.7709	1.0345	-0.840
		z =1.26		
0.2512	0.4243	0.3245	1.0264	-1.081
0.3331	0.2457	0.4212	1.0514	-1.220
0.3657	0.1728	0.4615	1.0596	-1.349
0.4022	0.0901	0.5077	1.0674	-1.401
0.4417	0.0000	0.5583	1.0747	-1.421
		z =0.84		
0.1295	0.7617	0.1087	0.9610	-0.798
0.2176	0.5993	0.1830	1.0096	-1.091
0.3614	0.3350	0.3036	1.0546	-1.396
0.4494	0.1701	0.3805	1.0720	-1.543
0.5433	0.0000	0.4567	1.0854	-1.559
		z =0.42		
0.4124	0.4141	0.1735	1.0600	-1.307
0.5373	0.2396	0.2231	1.0795	-1.575
0.6280	0.1057	0.2664	1.0898	-1.614
0.6664	0.0527	0.2809	1.0935	-1.724
0.7037	0.0000	0.2963	1.0967	-1.496
		z =0.25		
0.3320	0.5814	0.0866	1.0395	-0.785
0.5288	0.3389	0.1323	1.0757	-1.117
0.6561	0.1775	0.1664	1.0898	-1.183
0.7246	0.0925	0.1829	1.0958	-1.247
0.7993	0.0000	0.2007	1.1013	-1.280
		z =0.08		
0.8087	0.1246	0.0667	1.0989	-0.828
0.8495	0.0617	0.0888	1.1017	-0.793

0.6693	0.2642	0.0664	1.0886	-0.944
0.4910	0.4715	0.0375	1.0676	-0.786
0.9209	0.0000	0.0791	1.1054	-0.703
		T = 303.15 K		
		z = 7.57		
0.0660	0.4347	0.4992	0.9309	-0.851
0.0328	0.7188	0.2484	0.8769	-0.694
0.0263	0.7746	0.1990	0.8629	-0.506
0.0957	0.1808	0.7235	0.9661	-0.736
0.1102	0.0560	0.8338	0.9801	-0.601
0.1167	0.0000	0.8833	0.9849	-0.383
		z =3.36		
0.1058	0.5394	0.3548	0.9554	-1.133
0.1538	0.3299	0.5164	0.9912	-1.128
0.1912	0.1637	0.6452	1.0127	-1.112
0.2024	0.1182	0.6794	1.0179	-1.059
0.2291	0.0000	0.7709	1.0295	-0.937
		z =1.26		
0.2512	0.4243	0.3245	1.0225	-1.333
0.3331	0.2457	0.4212	1.0472	-1.450
0.3657	0.1728	0.4615	1.0551	-1.517
0.4022	0.0901	0.5077	1.0626	-1.500
0.4417	0.0000	0.5583	1.0696	-1.442
		z =0.84		
0.1295	0.7617	0.1087	0.9569	-0.922
0.2176	0.5993	0.1830	1.0052	-1.202
0.3614	0.3350	0.3036	1.0500	-1.509
0.4494	0.1701	0.3805	1.0672	-1.621
0.5433	0.0000	0.4567	1.0803	-1.551
		z =0.42		
0.4124	0.4141	0.1735	1.0551	-1.240
0.5373	0.2396	0.2231	1.0745	-1.394
0.6280	0.1057	0.2664	1.0846	-1.365
0.6664	0.0527	0.2809	1.0881	-1.327
0.7037	0.0000	0.2963	1.0915	-1.399
		z =0.25		
0.3320	0.5814	0.0866	1.0358	-1.073
0.5288	0.3389	0.1323	1.0713	-1.280
0.6561	0.1775	0.1664	1.0852	-1.298
0.7246	0.0925	0.1829	1.0910	-1.290
0.7993	0.0000	0.2007	1.0962	-1.192
		z =0.08		
0.8087	0.1246	0.0667	1.0940	-0.801
0.8495	0.0617	0.0888	1.0968	-0.768
0.6693	0.2642	0.0664	1.0838	-0.963

0.4910	0.4715	0.0375	1.0636	-1.047
0.9209	0.0000	0.0791	1.1005	-0.673
T = 313.15 K				
z = 7.57				
0.0660	0.4347	0.4992	0.9210	-0.559
0.0328	0.7188	0.2484	0.8681	-0.224
0.0263	0.7746	0.1990	0.8553	-0.116
0.0957	0.1808	0.7235	0.9558	-0.659
0.1102	0.0560	0.8338	0.9700	-0.685
0.1167	0.0000	0.8833	0.9749	-0.539
z =3.36				
0.1058	0.5394	0.3548	0.9473	-0.908
0.1538	0.3299	0.5164	0.9828	-1.063
0.1912	0.1637	0.6452	1.0042	-1.191
0.2024	0.1182	0.6794	1.0097	-1.237
0.2291	0.0000	0.7709	1.0209	-1.148
z =1.26				
0.2512	0.4243	0.3245	1.0160	-1.277
0.3331	0.2457	0.4212	1.0400	-1.489
0.3657	0.1728	0.4615	1.0475	-1.505
0.4022	0.0901	0.5077	1.0554	-1.652
0.4417	0.0000	0.5583	1.0625	-1.758
z =0.84				
0.1295	0.7617	0.1087	0.9521	-0.913
0.2176	0.5993	0.1830	0.9996	-1.237
0.3614	0.3350	0.3036	1.0434	-1.572
0.4494	0.1701	0.3805	1.0600	-1.649
0.5433	0.0000	0.4567	1.0734	-1.834
z =0.42				
0.4112	0.4155	0.1734	1.0481	-1.130
0.5379	0.2355	0.2266	1.0676	-1.324
0.6312	0.1041	0.2648	1.0782	-1.517
0.6720	0.0495	0.2785	1.0820	-1.572
0.7037	0.0000	0.2963	1.0850	-1.695
z =0.25				
0.3320	0.5814	0.0866	1.0293	-0.895
0.5288	0.3389	0.1323	1.0646	-1.172
0.6561	0.1775	0.1664	1.0784	-1.289
0.7246	0.0925	0.1829	1.0842	-1.372
0.7993	0.0000	0.2007	1.0896	-1.368
z =0.08				
0.8087	0.1246	0.0667	1.0871	-0.913
0.8495	0.0617	0.0888	1.0910	-0.875
0.6693	0.2642	0.0664	1.0781	-0.868
0.4910	0.4715	0.0375	1.0571	-0.830
0.9209	0.0000	0.0791	1.0941	-0.850

TABLE 13 : Smoothing Coefficients and Standard Deviation for Cibulka Equation at T = (298.15, 303.15 and 313.15) K

T/K	b_0	b_1	b_2	σ_S
	$[MOA]^+[Tf_2N]^-$ (x_1) + 2-propanol (x_2) + ethyl acetate (x_3)			
298.15	-8.85669	-53.75698	26.14328	0.17
303.15	-16.21188	-40.20545	12.56015	0.17
313.15	-37.82652	-2.462188	31.02055	0.13
	$[MOA]^+[Tf_2N]^-$ (x_1) + 1-butanol (x_2) + ethyl acetate (x_3)			
298.15	-20.11710	3.96595	-1.1856	0.20
303.15	-16.46755	-9.57106	-0.07346	0.20
313.15	-23.39665	11.69914	-6.99739	0.15
	$[MOA]^+[Tf_2N]^-$ (x_1) + 2-butanol (x_2) + ethyl acetate (x_3)			
298.15	-26.93157	13.31379	-20.96522	0.21
303.15	-22.78219	9.60763	-42.86072	0.24
313.15	-28.0324	22.73148	-32.80080	0.20

FIGURE 1. Structure of the IL, (methyl trioctylammonium bis(trifluoromethylsulfonyl)imide).

FIGURE 2. Graph of excess molar volumes, V_{123}^{E}, of the ternary mixture for $\{[\mathrm{MOA}]^{+}[\mathrm{Tf_2N}]^{-}$ (x_1) + 2-propanol (x_2) + ethyl acetate (x_3) at: (a) T = 298.15 K, (b) T = 303.15 K, (c) T = 313.15 K. Solid lines calculated by the Cibulka equation using the values of the parameters fitted to the binary and ternary data.

FIGURE 3. Graph of excess molar volumes, V_{123}^{E}, of the ternary mixture for $\{[\mathrm{MOA}]^{+}[\mathrm{Tf_2N}]^{-}$ (x_1) + 1-butanol (x_2) + ethyl acetate (x_3) at: (a) T = 298.15 K, (b) T = 303.15 K, (c) T = 313.15 K. Solid lines calculated by the Cibulka equation using the values of the parameters fitted to the binary and ternary data.

FIGURE 4. Graph of excess molar volumes, V_{123}^{E}, of the ternary mixture for $\{[\mathrm{MOA}]^{+}[\mathrm{Tf_2N}]^{-}$ (x_1) + 2-butanol (x_2) + ethyl acetate (x_3): (a) T = 298.15 K, (b) T = 303.15 K, (c) T = 313.15 K. Solid lines calculated by the Cibulka equation using the values of the parameters fitted to the binary and ternary data.

FIGURE 1

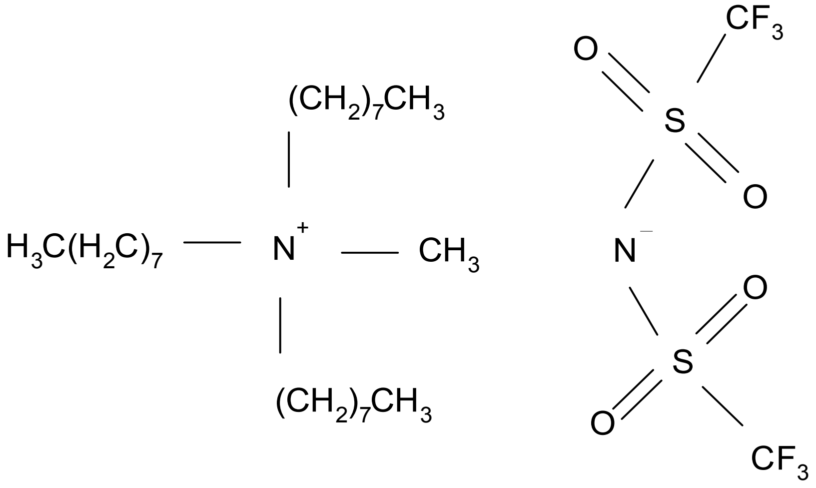
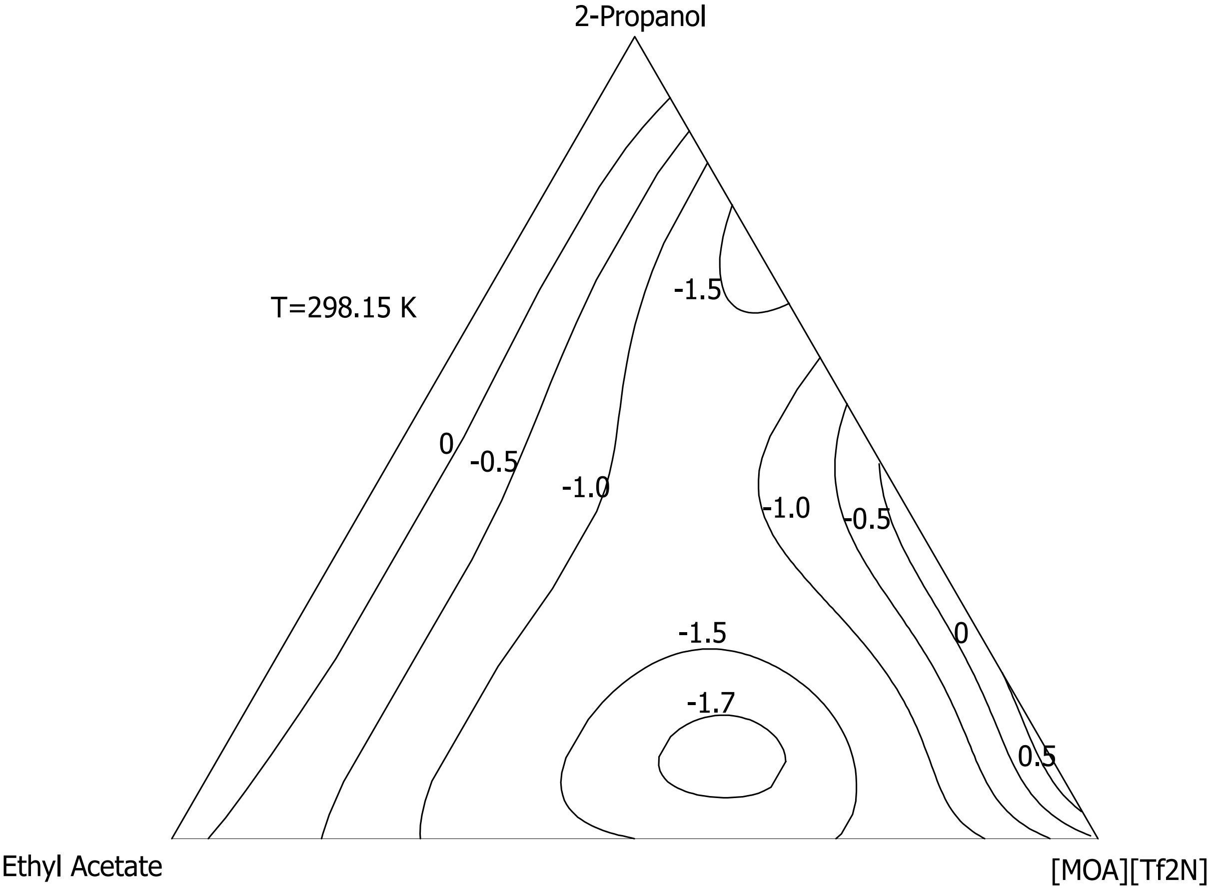
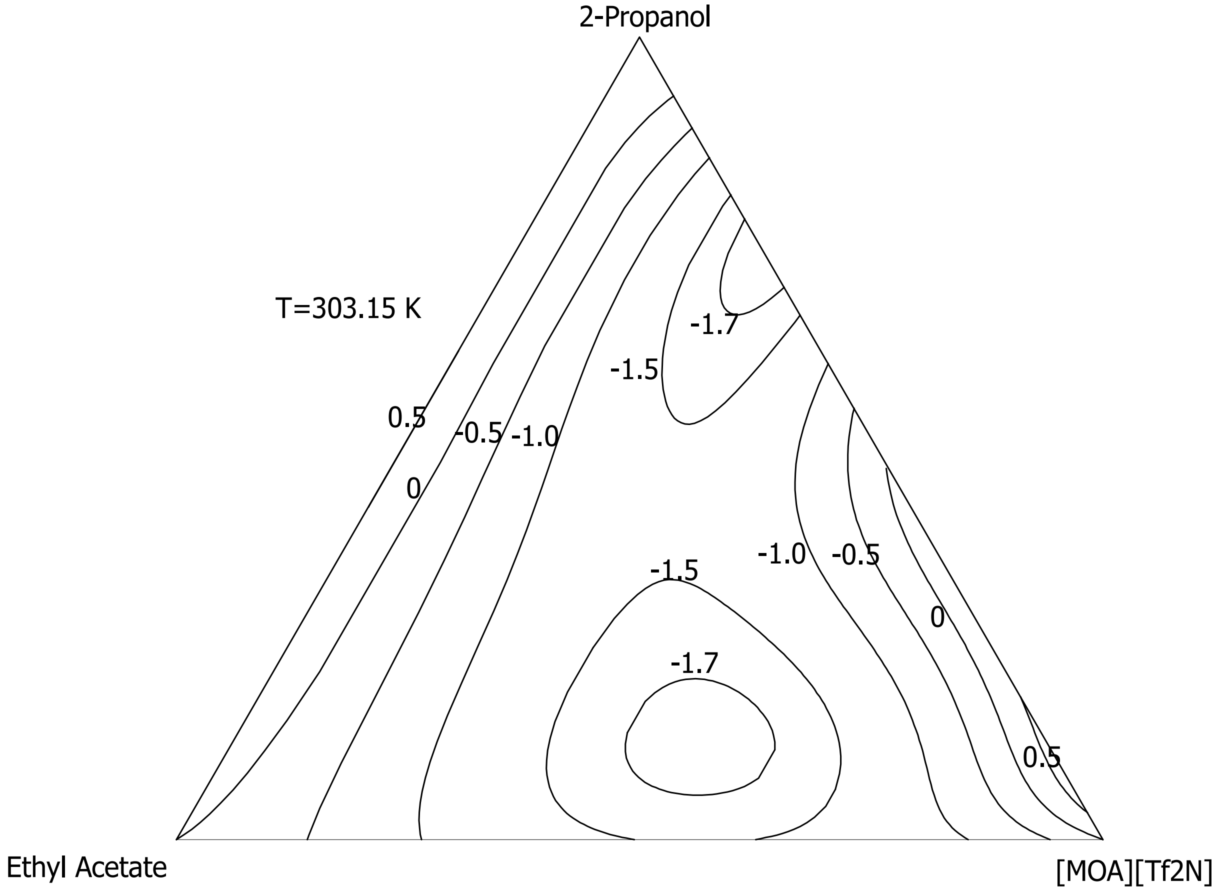


FIGURE 2


2-Propanol
T=298.15 K
-1.5
0
-0.5
-1.0
-1.0
-0.5
-1.5
0
-1.7
0.5
Ethyl Acetate
[MOA][Tf2N]


2-Propanol
T=303.15 K
-1.7
-1.5
0.5
-0.5
-1.0
0
-1.0
-0.5
-1.5
0
-1.7
0.5
Ethyl Acetate
[MOA][Tf2N]

(c)

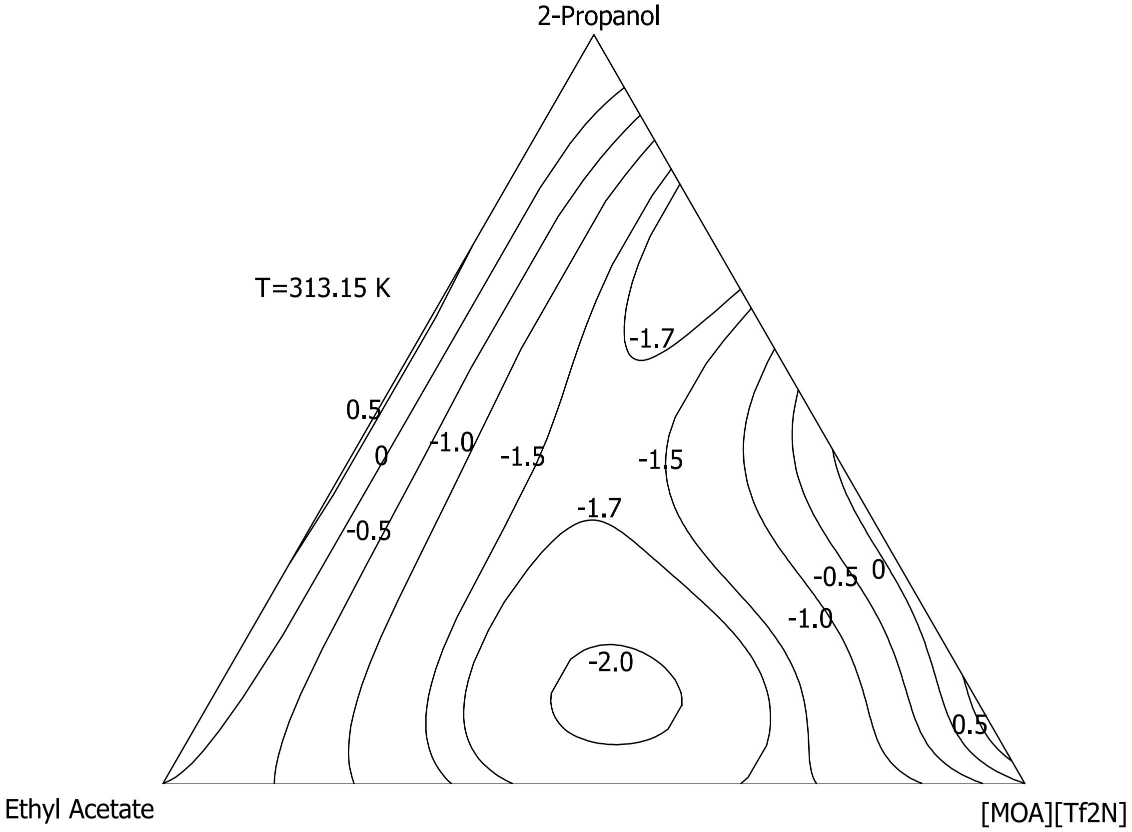
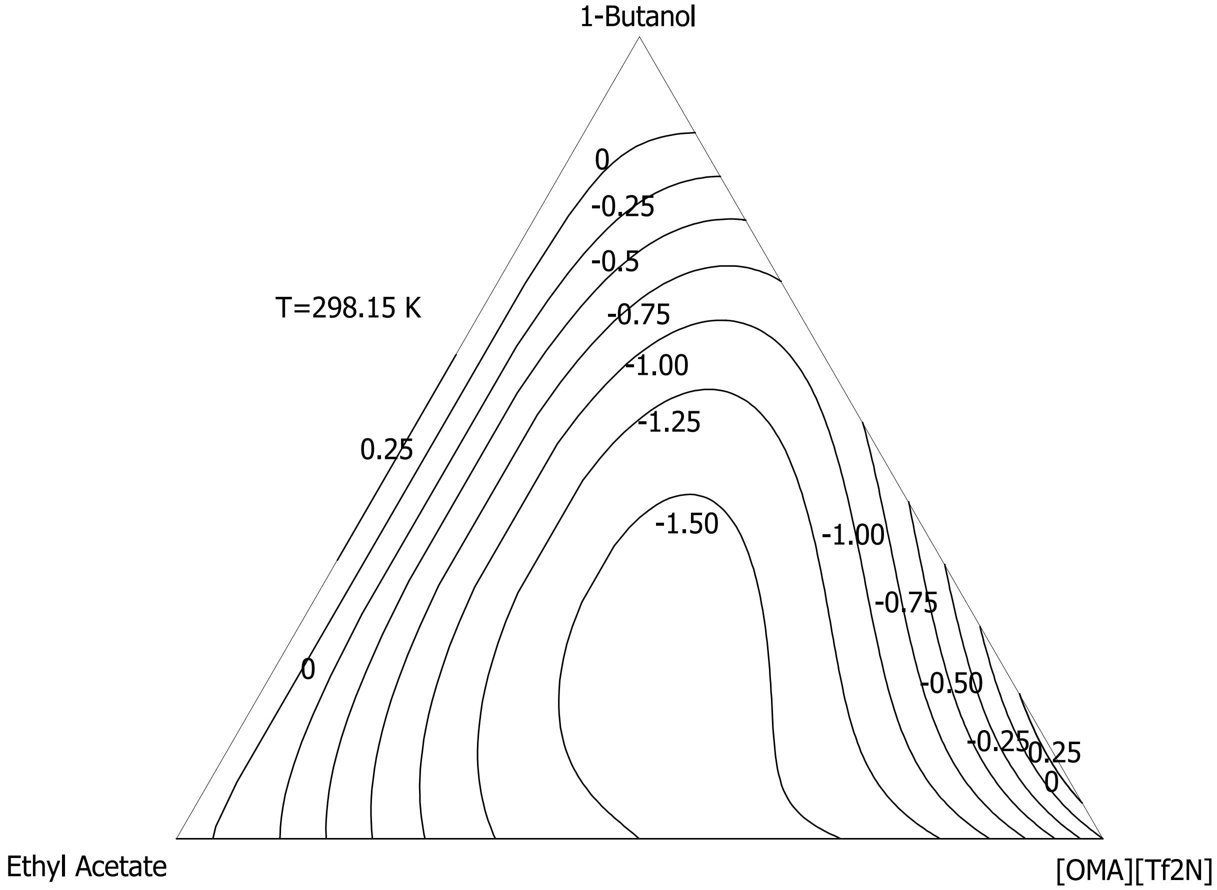
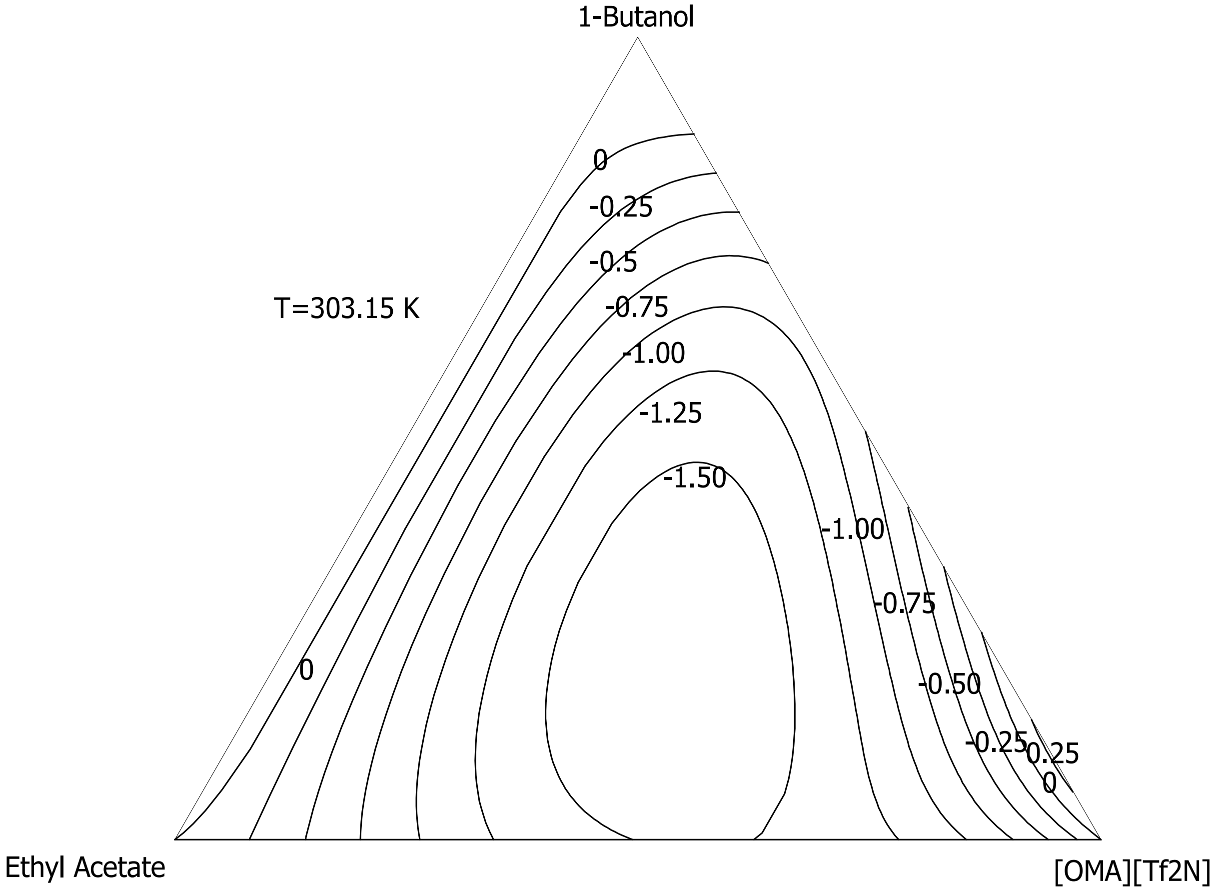

2-Propanol
T=313.15 K
0.5
0
-1.0
-1.5
-0.5
-1.7
-1.5
-1.7
-2.0
-0.5
0
-1.0
0.5
Ethyl Acetate
[MOA][Tf2N]

FIGURE 3

(a)


1-Butanol
T=298.15 K
0
-0.25
-0.5
-0.75
-1.00
-1.25
-1.50
0.25
0
-1.00
-0.75
-0.50
-0.25
0.25
0
Ethyl Acetate
[OMA][Tf2N]

(b)


1-Butanol
T=303.15 K
0
-0.25
-0.5
-0.75
-1.00
-1.25
-1.50
-1.00
-0.75
-0.50
-0.25
0.25
0
0
Ethyl Acetate
[OMA][Tf2N]

(c)

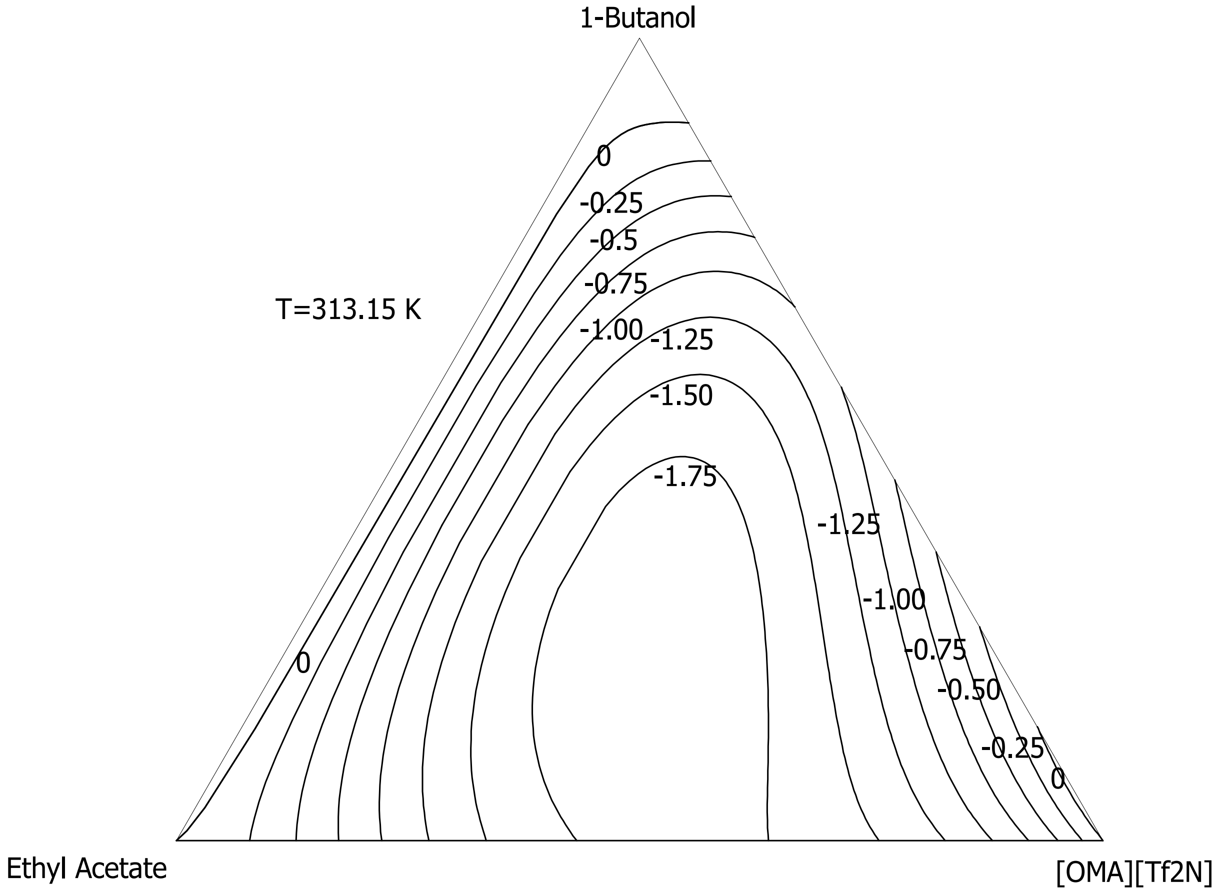
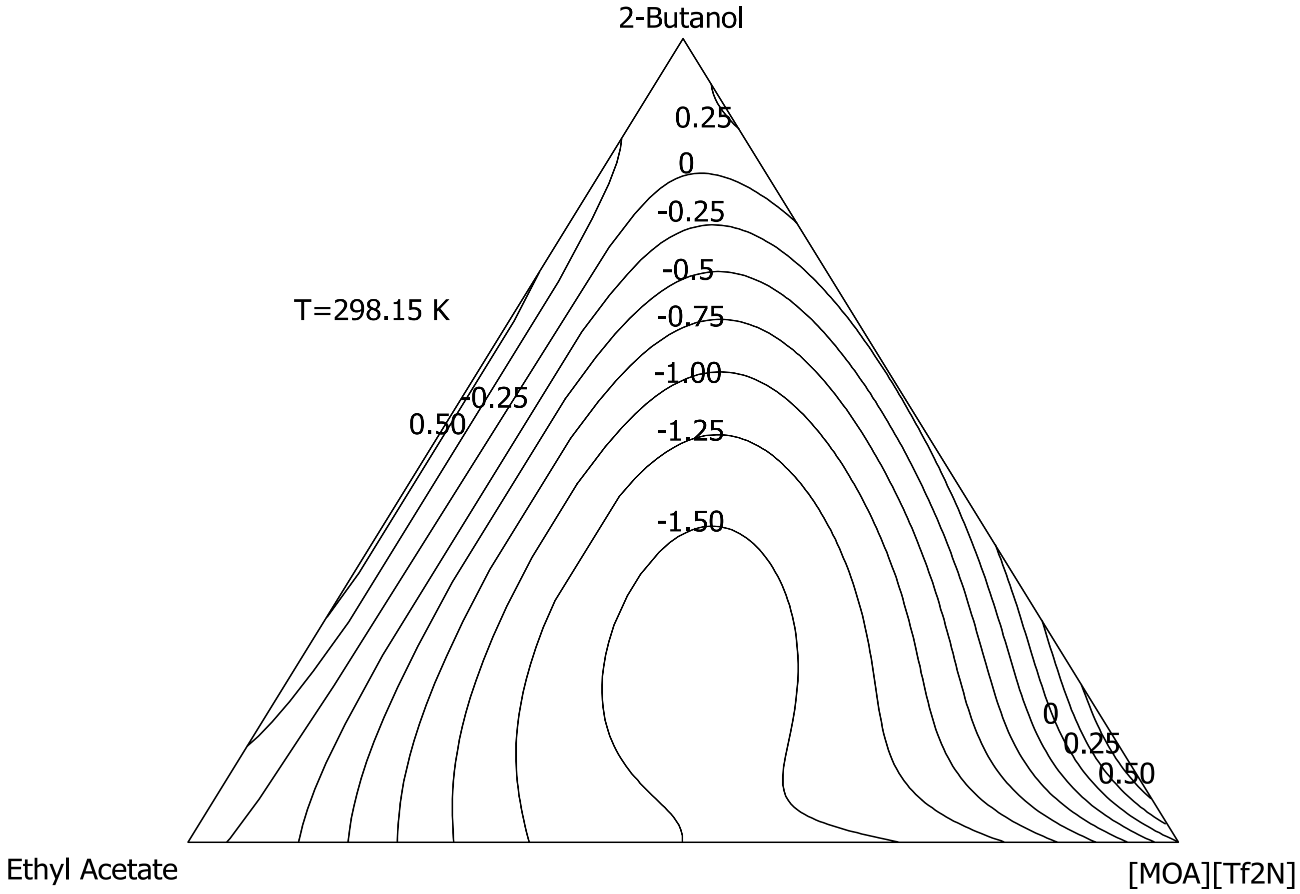
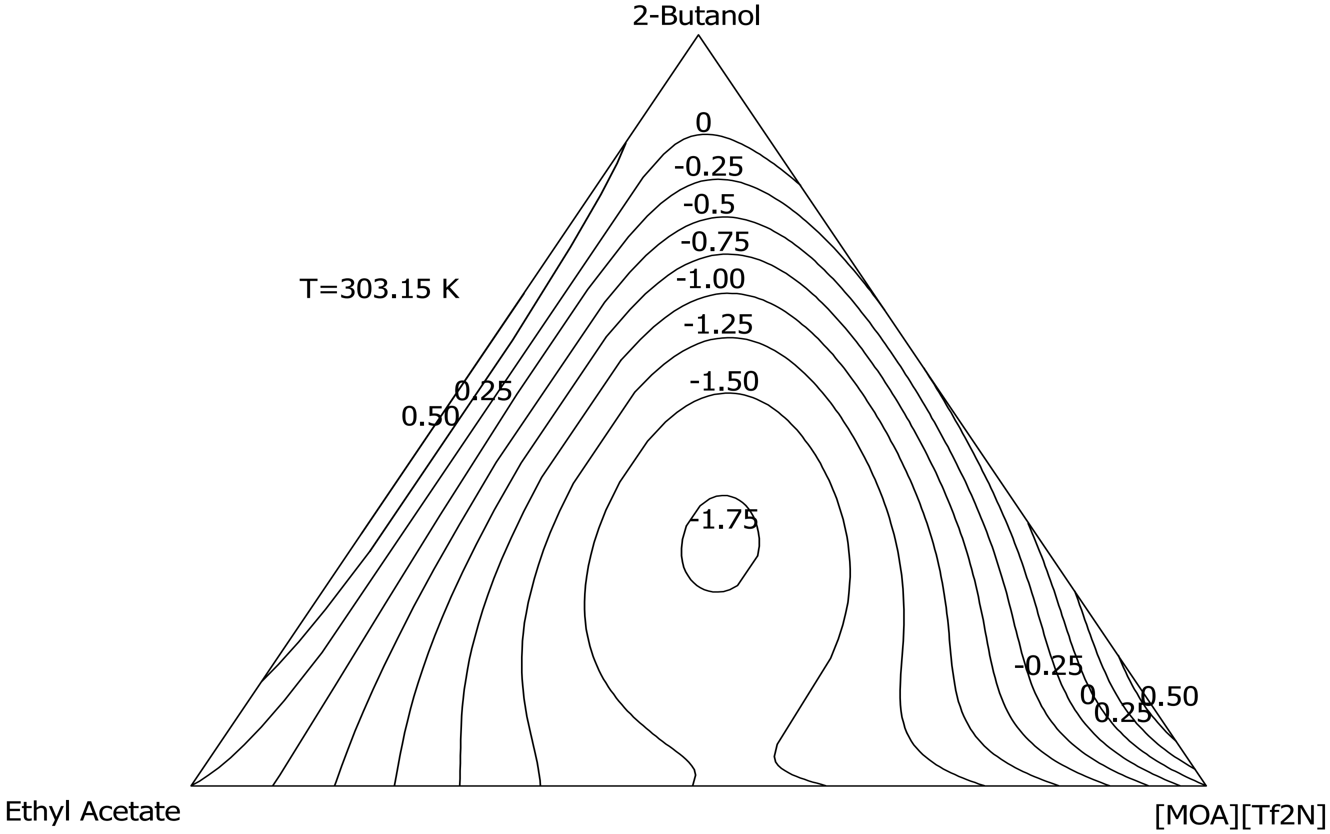

1-Butanol
T=313.15 K
0
-0.25
-0.5
-0.75
-1.00
-1.25
-1.50
-1.75
-1.25
-1.00
-0.75
-0.50
-0.25
0
0
Ethyl Acetate
[OMA][Tf2N]

FIGURE 4

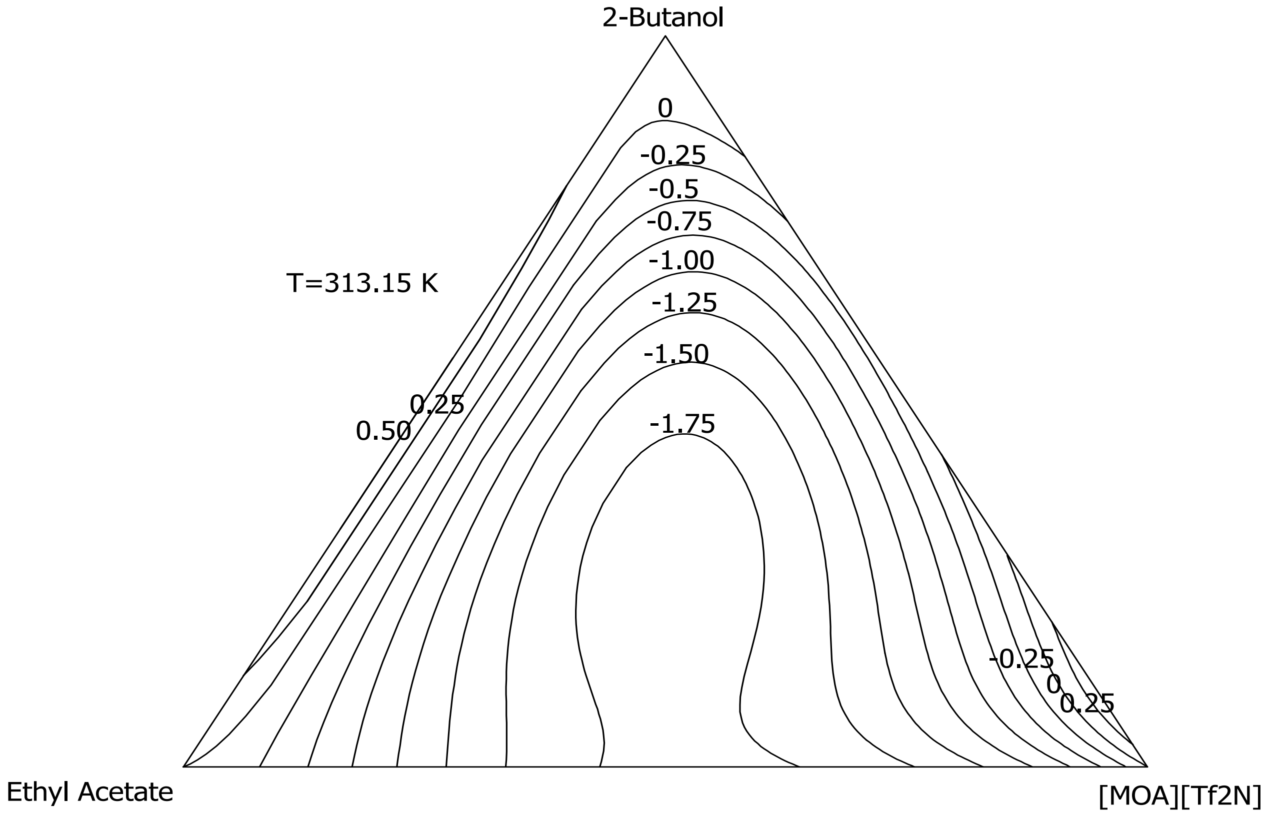
(a)


2-Butanol
0.25
0
-0.25
-0.5
-0.75
-1.00
-1.25
-1.50
T=298.15 K
-0.25
0.50
0
0.25
0.50
Ethyl Acetate
[MOA][Tf2N]

(b)


2-Butanol
0
-0.25
-0.5
-0.75
-1.00
T=303.15 K
-1.25
-1.50
0.25
0.50
-1.75
-0.25
0
0.25
0.50
Ethyl Acetate
[MOA][Tf2N]

(c)


2-Butanol
0
-0.25
-0.5
-0.75
-1.00
T=313.15 K
-1.25
-1.50
0.25
0.50
-1.75
-0.25
0
0.25
Ethyl Acetate
[MOA][Tf2N]