

Densities and Excess Molar Volume for the Ternary Systems (1-Butyl-3-methylimidazolium methyl sulphate + Nitromethane + Methanol or Ethanol or 1-Propanol) at $T = (303.15 \text{ and } 313.15) \text{ K}$

Indra Bahadur and Nirmala Deenadayalu*

Department of Chemistry, Durban University of Technology, Steve Biko Campus, P.O. Box 1334, Durban 4000, South Africa.

Received 10 September 2012, revised 16 May 2013, accepted 7 June 2013.

ABSTRACT

The densities of the ternary systems containing the ionic liquid 1-butyl-3-methylimidazolium methyl sulphate ($[\text{BMIM}]^+[\text{MeSO}_4]^-$) were determined. The ternary systems studied were ($[\text{BMIM}]^+[\text{MeSO}_4]^-$ + nitromethane + methanol or ethanol or 1-propanol) at the temperatures (303.15 and 313.15) K. The ternary excess molar volumes were calculated from the experimental densities at each temperature, being negative for all mole fractions of the ionic liquid. The minimum ternary excess molar volumes increase with an increase in temperature for the systems ($[\text{BMIM}]^+[\text{MeSO}_4]^-$ + nitromethane + methanol or ethanol), and decrease for the system ($[\text{BMIM}]^+[\text{MeSO}_4]^-$ + nitromethane + 1-propanol). The results are interpreted in terms of the alcohol chain length and the intermolecular interactions.

KEYWORDS

Density, excess molar volume, ionic liquid, alcohol, nitromethane.

1. Introduction

Ionic liquids (ILs) are low-melting molten salts which are composed of organic cations, and inorganic anions and their properties depend on the type of cation and anion.¹ ILs are studied as 'green solvents' for organic reactions, combined with a catalyst to extend its life span, and as reagents for nanomaterials.^{2,3} The physical properties of ILs such as density, viscosity, melting point, polarity and miscibility with water or molecular solvents, can be finely tuned by changing either the anion or the cation.²⁻⁶ ILs have other properties such as very low vapour pressure, wide electrochemical window, high recyclability, good ionic conductivities, thermal stability and nonflammability^{7,8} making them useful solvents for a wide range of applications.^{9,10} The applications of ILs are rapidly increasing in all modern scientific fields such as, separations,¹¹ organic synthesis,¹² homogeneous two-phase catalysis,¹³ extractions,¹⁴ electrochemistry,¹⁵ and polymerization processes.¹⁶

Thermophysical properties of mixtures of ILs with different solvents are useful for the design of chemical separation processes.^{17,18}

Ternary excess molar volumes, V_{123}^E , for IL systems have been reported by various researchers.¹⁹⁻²⁸ In this paper the densities were measured for the ternary systems ($[\text{BMIM}]^+[\text{MeSO}_4]^-$ + nitromethane + methanol or ethanol or 1-propanol) over the entire composition range at $T = (303.15 \text{ and } 313.15) \text{ K}$ and at atmospheric pressure. V_{123}^E data were calculated at $T = (303.15 \text{ and } 313.15) \text{ K}$ and at atmospheric pressure for IL systems by using the experimental density values. The results are interpreted in terms of intermolecular interactions and the alcohol chain length. This work is a continuation of our research group's work on thermodynamic properties of ILs.^{21-26, 29-35}

2. Experimental

2.1. Materials

The chemicals were purchased from Aldrich or Merck or Fluka and used without further purification. The chemicals, supplier, purity and the literature and experimental density (ρ) are given in Table 1. The density of the pure chemicals was determined at $T = (303.15 \text{ and } 313.15) \text{ K}$ and at atmospheric pressure. The water content in the IL was determined by using a Karl-Fischer coulometer (Metrohm797, Herisau, Switzerland) and the mass percent water content was found to be <0.0024 . The purity of the pure chemicals was assessed by a comparison of the experimental density values with the literature density values where available.^{31,36} The structure of the IL used in this work is given in Fig. 1.

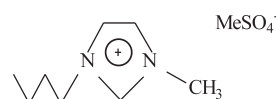


Figure 1 Structure of 1-butyl-3-methylimidazolium methyl sulphate $[\text{BMIM}]^+[\text{MeSO}_4]^-$.

2.2. Apparatus and Procedure

The ternary mixtures were prepared by transferring the pure liquids into stoppered bottles to prevent evaporation. The IL was first filled into the air-tight glass stoppered 5 cm³ glass vial and weighed. An OHAUS (Pine Brook, NJ, USA) mass balance was used to determine the mass of each component of the mixture. The mass balance has a precision of 0.0001 g. The uncertainty in the mole fraction was estimated to be 0.0006. The ternary mixtures were prepared from a spreadsheet calculation to obtain a constant z ratio ($z = x_2/x_1$) where x_1 and x_2 are the mole fractions of the ionic liquid and nitromethane, respectively, with varying mole fractions of methanol or ethanol or 1-propanol (x_3). The densities were measured with an Anton Paar (Graz, Austria)

* To whom correspondence should be addressed. E-mail: nirmalad@dut.ac.za

Table 1 Pure compound specifications: supplier, purity, literature and experimental density at $T = (303.15 \text{ and } 313.15) \text{ K}$.

Chemical	Supplier	Purity/mole fraction	$\rho/\text{g cm}^{-3}$		
			Literature	Experimental	
			$T = 303.15 \text{ K}$	$T = 303.15 \text{ K}$	$T = 303.15 \text{ K}$
Methanol	Sigma-Aldrich	0.998	0.7836 ^a	0.783	0.775
Ethanol	Sigma-Aldrich	0.998	0.7821 ^a	0.782	0.773
1-Propanol	Merck	0.995	0.7962 ^a	0.796	0.788
Nitromethane	Sigma-Aldrich	0.990	1.12439 ^b	1.124	1.112
[BMIM] ⁺ [MeSO ₄] ⁻	Sigma-Aldrich	0.970	1.20448 ^b	1.205	1.199

^a Reference 31. ^b Reference 36.

DMA 38 vibrating U-tube densimeter. Ultra-pure water supplied by SH Calibration Service GmbH Graz, Austria and dried air were used for the calibration of the densimeter at $T = 298.15 \text{ K}$.²⁹ The temperature maintenance and control were regulated by a built-in thermostat controller with a temperature uncertainty of $\pm 0.02 \text{ K}$. The repeatability and accuracy in experimental measurements was (± 0.0002 and ± 0.001) g cm^{-3} for density. The uncertainty in density for the ternary system was $\pm 0.001 \text{ g cm}^{-3}$. The ternary excess molar volumes V_{123}^E were calculated from the experimental density. The experimental uncertainty in V_{123}^E was $\pm 0.2 \text{ cm}^3 \text{ mol}^{-1}$. The experimental technique was validated by measuring the density for the test system (octane + toluene) at $T = 298.15 \text{ K}$ and comparing it with the literature density.³⁷ The difference between experimental and literature density for the test system was within the experimental error.

3. Results and Discussion

Densities, ρ , and ternary excess molar volumes, V_{123}^E , for the (IL + nitromethane + methanol or ethanol or 1-propanol) systems as a function of composition at $T = (303.15 \text{ and } 313.15) \text{ K}$ are given in Tables 2–4. The V_{123}^E was calculated by using Equation (1):

$$V_{123}^E = \frac{x_1 M_1 + x_2 M_2 + x_3 M_3}{\rho} - \frac{x_1 M_1}{\rho_1} - \frac{x_2 M_2}{\rho_2} - \frac{x_3 M_3}{\rho_3} \quad (1)$$

where M_1 , M_2 and M_3 are the molecular masses, ρ_1 , ρ_2 , and ρ_3 are the densities of pure components 1, 2, or 3, respectively, where '1' refers to the IL, '2' to nitromethane and '3' to methanol or ethanol or 1-propanol and ρ is the density of the mixture.

The binary V_m^E data for (IL + methanol)³¹, (IL + ethanol)³¹, (IL + 1-propanol)³¹, (IL + nitromethane)³⁶, (methanol + nitromethane)³⁸, (ethanol + nitromethane)³⁸ and (1-propanol + nitromethane)³⁸ were published in the literature. For each ternary system there are three sets of binary data: (i) (IL + an alcohol) (ii) (IL + nitromethane) and (iii) (an alcohol + nitromethane).

(i) (IL + nitromethane + methanol)

The binary V_m^E data for (IL + methanol) at the temperatures (303.15 and 313.15) K are negative for all mole fractions of the IL due to the more efficient packing and/or attractive interaction between the IL and the methanol molecules.³¹ The V_m^E values at the temperatures (303.15 and 313.15) K are $-1.444 \text{ cm}^3 \text{ mol}^{-1}$ at $x_1 = 0.4386$ and $-1.531 \text{ cm}^3 \text{ mol}^{-1}$ at $x_1 = 0.5589$, respectively.³¹

For the system (IL + nitromethane) V_m^E are negative at the temperatures (303.15 and 313.15) K, and at all mole fractions of the IL.²⁵ The $V_{m,\min}^E$ values at the temperatures (303.15 and 313.15) K are $-0.602 \text{ cm}^3 \text{ mol}^{-1}$ and $-0.667 \text{ cm}^3 \text{ mol}^{-1}$, respectively, both occurring at $x_1 = 0.2998$.³⁶

For the binary system (methanol + nitromethane) V_m^E is negative at the temperature 303.15 K, and both positive and negative at the temperature 313.15 K due to the hydrogen bond rupture and dispersive interactions between unlike molecules (positive

contributions) and dipole–dipole interactions and geometrical fitting of the nitromethane into the methanol structure (negative contributions).³⁸ The $V_{m,\min}^E$ values at the temperatures (303.15 and 313.15) K are $-0.1687 \text{ cm}^3 \text{ mol}^{-1}$ at $x_1 = 0.6500$ and $-0.1523 \text{ cm}^3 \text{ mol}^{-1}$ at $x_1 = 0.7500$, respectively.³⁸

Figures 2 and 3 are the plots of V_{123}^E vs. mole fraction of methanol for the ternary system (IL + nitromethane + methanol). V_{123}^E values are negative for the ternary composition curves, as can be

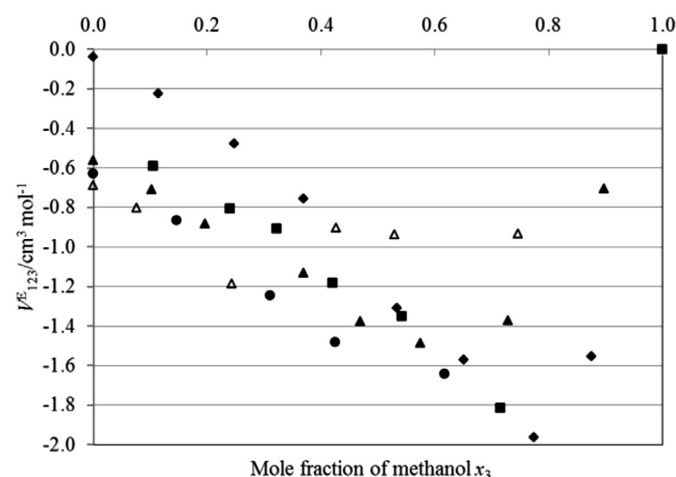


Figure 2 Graph of excess molar volumes, V_{123}^E , for the ternary mixture [BMIM]⁺[MeSO₄]⁻ (x_1) + nitromethane (x_2) + methanol (x_3) against mole fraction of methanol at $T = 303.15 \text{ K}$ at constant $z = x_2/x_1$. The symbols represent experimental results: Δ , $z = 4.21$; \bullet , $z = 1.87$; \blacktriangle , $z = 0.70$; \blacksquare , $z = 0.23$; \blacklozenge , $z = 0.04$.

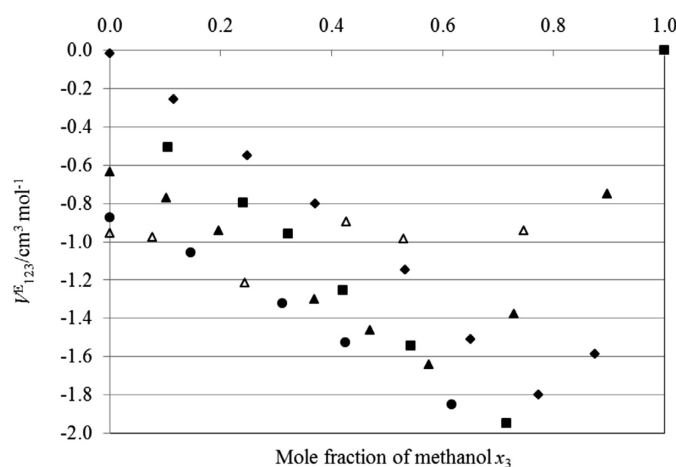


Figure 3 Graph of excess molar volumes, V_{123}^E , for the ternary mixture [BMIM]⁺[MeSO₄]⁻ (x_1) + nitromethane (x_2) + methanol (x_3) against mole fraction of methanol at $T = 313.15 \text{ K}$ at constant $z = x_2/x_1$. The symbols represent experimental results: Δ , $z = 4.21$; \bullet , $z = 1.87$; \blacktriangle , $z = 0.70$; \blacksquare , $z = 0.23$; \blacklozenge , $z = 0.04$.

Table 2 Densities and excess molar volume for ionic liquid (x_1) + nitromethane (x_2) + methanol (x_3) at $T = (303.15$ and $313.15)$ K.

x_1	x_3	$\rho/\text{g cm}^{-3}$	$V_{123}^E/\text{cm}^3\text{mol}^{-1}$
[BMIM] ⁺ [MeSO ₄] ⁻ (x_1) + nitromethane (x_2) + methanol (x_3)			
$T = 303.15\text{K}$ $z = 4.21$			
0.0485	0.7471	0.956	-0.9
0.0903	0.5290	1.044	-0.9
0.1099	0.4269	1.076	-0.9
0.1452	0.2429	1.130	-1.2
0.1771	0.0765	1.159	-0.8
0.1917	0.0000	1.172	-0.7
$z = 1.87$			
0.1332	0.6173	1.054	-1.6
0.1998	0.4256	1.112	-1.5
0.2390	0.3114	1.137	-1.2
0.2971	0.1467	1.164	-0.9
0.3482	0.0000	1.185	-0.6
$z = 0.70$			
0.0603	0.8974	0.914	-0.7
0.1591	0.7290	1.036	-1.4
0.2494	0.5752	1.098	-1.5
0.3119	0.4692	1.127	-1.4
0.3705	0.3690	1.146	-1.1
0.4720	0.1965	1.174	-0.9
0.5271	0.1026	1.186	-0.7
0.5875	0.0000	1.197	-0.6
$z = 0.23$			
0.2301	0.7162	1.072	-1.8
0.3706	0.5428	1.126	-1.4
0.4692	0.4211	1.152	-1.2
0.5494	0.3222	1.167	-0.9
0.6151	0.2409	1.178	-0.8
0.7242	0.1053	1.193	-0.6
0.8106	0.0000	1.203	-0.4
$z = 0.04$			
0.8468	0.1150	1.194	-0.2
0.4466	0.5333	1.137	-1.3
0.3340	0.6509	1.106	-1.6
0.7200	0.2475	1.181	-0.5
0.6031	0.3697	1.165	-0.8
0.9568	0.0000	1.204	-0.1
0.2165	0.7737	1.058	-2.0
$T = 313.15\text{K}$ $z = 4.21$			
0.1197	0.8749	0.982	-1.5
0.0485	0.7471	0.946	-0.9
0.0903	0.5290	1.035	-1.0
0.1099	0.4269	1.066	-0.9
0.1452	0.2429	1.120	-1.2
0.1771	0.0765	1.152	-1.0
0.1917	0.0000	1.166	-1.0
$z = 1.87$			
0.1332	0.6173	1.048	-1.8
0.1998	0.4256	1.104	-1.5
0.2390	0.3114	1.129	-1.3
0.2971	0.1467	1.158	-1.1
0.3482	0.0000	1.179	-0.9

x_1	x_3	$\rho/\text{g cm}^{-3}$	$V_{123}^E/\text{cm}^3\text{mol}^{-1}$
$z = 0.70$			
0.0603	0.8974	0.906	-0.7
0.1591	0.7290	1.028	-1.4
0.2494	0.5752	1.092	-1.6
0.3119	0.4692	1.120	-1.5
0.3705	0.3690	1.140	-1.3
0.4720	0.1965	1.167	-0.9
0.5271	0.1026	1.179	-0.8
0.5875	0.0000	1.190	-0.6
$z = 0.23$			
0.2301	0.7162	1.066	-1.9
0.3706	0.5428	1.120	-1.5
0.4692	0.4211	1.145	-1.2
0.5494	0.3222	1.161	-1.0
0.6151	0.2409	1.171	-0.8
0.7242	0.1053	1.186	-0.5
0.8106	0.0000	1.196	-0.4
$z = 0.04$			
0.8468	0.1150	1.188	-0.3
0.4466	0.5333	1.129	-1.1
0.3340	0.6509	1.098	-1.5
0.7200	0.2475	1.175	-0.6
0.6031	0.3697	1.159	-0.8
0.9568	0.0000	1.198	-0.0
0.2165	0.7737	1.048	-1.8
0.1197	0.8749	0.974	-1.6

expected, since the three binary $V_{m,\min}^E$ values are all negative. The negative values of V_{123}^E for (IL + nitromethane + methanol) show that the (ion-dipole) interactions and packing effect between methanol, nitromethane and the IL are dominating over the dissociation of any intermolecular hydrogen bonds in methanol and nitromethane.²⁷

From Table 2, it can be seen that for the system ([BMIM]⁺[MeSO₄]⁻ + nitromethane + methanol) $V_{123,\min}^E$ decreases with a decreasing z values (increasing mole fractions of IL) except at $z = 0.70$ at the temperatures (303.15 and 313.15) K and also at $z = 0.04$ for the temperature 313.15 K.

From Table 2, it can also be seen that the $V_{123,\min}^E$ increases with an increase in temperature for the system ([BMIM]⁺[MeSO₄]⁻ + nitromethane + methanol). The $V_{123,\min}^E$ values of (-2.0 and -1.9) cm³ mol⁻¹ at each temperature are similar in magnitude to the V_m^E values for the ([BMIM]⁺[MeSO₄]⁻ + methanol) binary system.³¹

(ii) (IL + nitromethane + ethanol)

The binary V_m^E data for (IL + ethanol) at the temperatures (303.15 and 313.15) K are negative for all mole fractions of the IL due to the same effects that occur in the binary system (IL + methanol). The $V_{m,\min}^E$ values at the temperatures (303.15 and 313.15) K both occur at $x_1 = 0.4056$ and are -0.775 cm³ mol⁻¹ and -0.869 cm³ mol⁻¹, respectively.³¹ The binary excess molar volumes of (IL + ethanol) are greater than for the (IL + methanol) systems.³¹

For the binary system (ethanol + nitromethane) V_m^E are both positive and negative at the temperatures (303.15 and 313.15) K due to the same effects that occur in the binary system (methanol + nitromethane).³⁸ The $V_{m,\min}^E$ values at the temperatures (303.15 and 313.15) K are -0.0292 cm³ mol⁻¹ at $x_1 = 0.8500$ and -0.0040 cm³ mol⁻¹ at $x_1 = 0.9500$, respectively.³⁸ The binary excess molar volumes of (ethanol + nitromethane) are greater

Table 3 Densities and excess molar volume for ionic liquid (x_1) + nitromethane (x_2) + ethanol (x_3) at $T = (303.15$ and $313.15)$ K.

x_1	x_3	$\rho/\text{g cm}^{-3}$	$V_{123}^E/\text{cm}^3\text{mol}^{-1}$
[BMIM] ⁺ [MeSO ₄] ⁻ (x_1) + nitromethane (x_2) + ethanol (x_3)			
$T = 303.15\text{K}$ $z = 4.21$			
0.0628	0.6726	0.949	-0.8
0.1076	0.4385	1.038	-0.8
0.1263	0.3412	1.071	-0.7
0.1568	0.1824	1.124	-0.9
0.1813	0.0545	1.159	-0.8
0.1917	0.0000	1.172	-0.7
$z = 1.87$			
0.1640	0.5288	1.049	-1.7
0.2297	0.3403	1.106	-1.2
0.2898	0.1676	1.149	-0.9
0.3109	0.1070	1.163	-0.8
0.3481	0.0000	1.186	-0.7
$z = 0.70$			
0.0829	0.8588	0.911	-0.9
0.2045	0.6517	1.035	-1.8
0.3024	0.4850	1.094	-1.5
0.3638	0.3807	1.121	-1.1
0.4175	0.2891	1.143	-1.0
0.5020	0.1454	1.172	-0.7
0.5875	0.0000	1.197	-0.5
$z = 0.23$			
0.2942	0.6370	1.063	-1.6
0.4439	0.4523	1.123	-1.3
0.5383	0.3359	1.149	-1.0
0.6637	0.1808	1.176	-0.6
0.7482	0.0757	1.192	-0.5
0.8106	0.0000	1.202	-0.3
$z = 0.04$			
0.8775	0.0829	1.193	-0.1
0.5332	0.4428	1.132	-1.0
0.4166	0.5646	1.100	-1.4
0.7787	0.1862	1.179	-0.3
0.6796	0.2898	1.164	-0.7
0.9568	0.0000	1.204	-0.0
0.2833	0.7039	1.045	-1.4
$T = 313.15\text{K}$ $z = 4.21$			
0.1632	0.8294	0.967	-1.0
0.0628	0.6726	0.940	-0.8
0.1076	0.4385	1.029	-0.8
0.1263	0.3412	1.062	-0.8
0.1568	0.1824	1.112	-0.7
0.1813	0.0545	1.148	-0.7
0.1917	0.0000	1.162	-0.6
$z = 1.87$			
0.1640	0.5288	1.040	-1.7
0.2297	0.3403	1.099	-1.4
0.2898	0.1676	1.141	-0.9
0.3109	0.1070	1.154	-0.7
0.3481	0.0000	1.176	-0.6
$z = 0.70$			
0.0829	0.8588	0.903	-1.0
0.2045	0.6517	1.025	-1.7

x_1	x_3	$\rho/\text{g cm}^{-3}$	$V_{123}^E/\text{cm}^3\text{mol}^{-1}$
0.3024	0.4850	1.087	-1.6
0.3638	0.3807	1.115	-1.3
0.4175	0.2891	1.136	-1.1
0.5020	0.1454	1.165	-0.8
0.5875	0.0000	1.188	-0.4
$z = 0.23$			
0.2942	0.6370	1.055	-1.5
0.4439	0.4523	1.116	-1.4
0.5383	0.3359	1.143	-1.1
0.6637	0.1808	1.170	-0.6
0.7482	0.0757	1.184	-0.3
0.8106	0.0000	1.194	-0.1
$z = 0.04$			
0.8775	0.0829	1.187	-0.1
0.5332	0.4428	1.127	-1.1
0.4166	0.5646	1.093	-1.4
0.7787	0.1862	1.173	-0.3
0.6796	0.2898	1.158	-0.7
0.9568	0.0000	1.198	-0.0
0.2833	0.7039	1.036	-1.2
0.1632	0.8294	0.958	-0.9

than those for the binary system (methanol + nitromethane).

Figures 4 and 5 are the plots of V_{123}^E versus mole fraction of ethanol for the ternary system (IL + nitromethane + ethanol). V_{123}^E values are negative for the ternary composition curves. The negative values of V_{123}^E for the ternary system (IL + nitromethane + ethanol) are due to the same effects that occur in the ternary (IL + nitromethane + methanol) system.

From Table 2, it is evident that for the system ([BMIM]⁺[MeSO₄]⁻ + nitromethane + ethanol) $V_{m,\min}^E$ decreases with a decreasing z value except at $z = 0.23$ and 0.04 for both the temperatures (303.15 and 313.15) K. Also, $V_{m,\min}^E$ increases with an increase in temperature for the system ([BMIM]⁺[MeSO₄]⁻ + nitromethane + ethanol). The $V_{m,\min}^E$ values of (-1.8 and -1.7) cm³ mol⁻¹ at each temperature are similar in magnitude to the $V_{m,\min}^E$ values for the ([BMIM]⁺[MeSO₄]⁻ + ethanol) binary system.³¹ The $V_{123,\min}^E$ of (IL + nitromethane + ethanol) is greater than (IL + nitromethane + methanol) for each temperature.

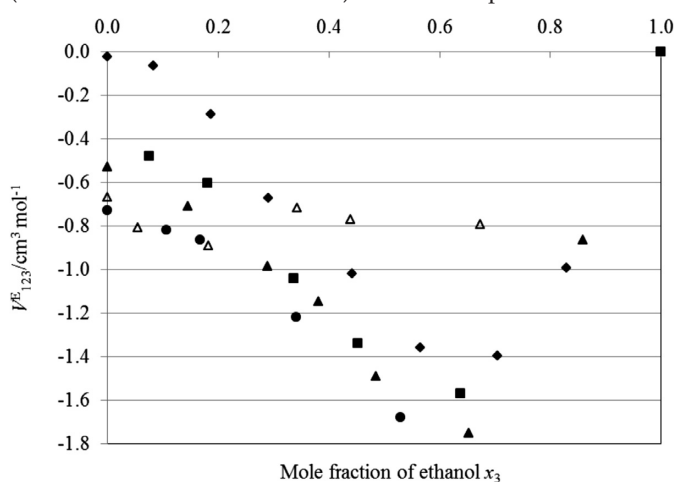


Figure 4 Graph of excess molar volumes, V_{123}^E , for the ternary mixture [BMIM]⁺[MeSO₄]⁻ (x_1) + nitromethane (x_2) + ethanol (x_3) against mole fraction of ethanol at $T = 303.15$ K at constant $z = x_2/x_1$. The symbols represent experimental results: Δ , $z = 4.21$; \bullet , $z = 1.87$; \blacktriangle , $z = 0.70$; \blacksquare , $z = 0.23$; \blacklozenge , $z = 0.04$.

Table 4 Densities and excess molar volume for ionic liquid (x_1) + nitromethane (x_2) + 1-propanol (x_3) at $T = (303.15$ and $313.15)$ K.

x_1	x_3	$\rho/\text{g cm}^{-3}$	$V_{123}^E/\text{cm}^3\text{mol}^{-1}$
[BMIM] ⁺ [MeSO ₄] ⁻ (x_1) + nitromethane (x_2) + 1-propanol (x_3)			
$T = 303.15\text{K}$ $z = 4.21$			
0.0979	0.4893	1.001	-0.7
0.1372	0.2842	1.075	-0.7
0.1637	0.1460	1.122	-0.6
0.1836	0.0423	1.157	-0.6
0.1913	0.0000	1.171	-0.6
0.0745	0.6116	0.955	-0.6
0.1199	0.3745	1.043	-0.7
0.0539	0.7187	0.913	-0.5
0.0350	0.8172	0.872	-0.3
$z = 1.87$			
0.1871	0.4625	1.046	-1.1
0.2495	0.2834	1.105	-0.8
0.2803	0.1947	1.131	-0.7
0.3188	0.0841	1.162	-0.6
0.3481	0.0000	1.185	-0.6
0.1454	0.5823	1.002	-1.1
$z = 0.70$			
0.1639	0.7208	0.975	-1.0
0.1037	0.8234	0.920	-0.8
0.2412	0.5892	1.033	-1.0
0.3410	0.4193	1.093	-1.0
0.3993	0.3203	1.122	-0.8
0.4477	0.2377	1.143	-0.7
0.5197	0.1153	1.171	-0.5
0.5875	0.0000	1.195	-0.3
$z = 0.23$			
0.3456	0.5736	1.062	-0.9
0.4964	0.3876	1.122	-0.8
0.5841	0.2794	1.148	-0.7
0.6930	0.1447	1.176	-0.4
0.8106	0.0000	1.201	-0.1
$z = 0.04$			
0.8948	0.0648	1.194	-0.1
0.5946	0.3786	1.133	-0.7
0.4798	0.4985	1.099	-0.8
0.8141	0.1492	1.180	-0.2
0.7289	0.2382	1.164	-0.4
0.9568	0.0000	1.204	-0.0
0.3390	0.6457	1.045	-0.8
0.2024	0.7885	0.971	-0.6
$T = 313.15\text{K}$ $z = 4.21$			
0.0979	0.4893	0.992	-0.7
0.1372	0.2842	1.066	-0.7
0.1637	0.1460	1.113	-0.7
0.1836	0.0423	1.148	-0.7
0.1913	0.0000	1.162	-0.7
0.0745	0.6116	0.946	-0.6
0.1199	0.3745	1.034	-0.7
0.0539	0.7187	0.905	-0.5
0.0350	0.8172	0.866	-0.4
$z = 1.87$			
0.1871	0.4625	1.039	-1.1
0.2495	0.2834	1.097	-0.9

x_1	x_3	$\rho/\text{g cm}^{-3}$	$V_{123}^E/\text{cm}^3\text{mol}^{-1}$
0.2803	0.1947	1.124	-0.8
0.3188	0.0841	1.155	-0.7
0.3481	0.0000	1.177	-0.7
0.1454	0.5823	0.995	-1.2
$z = 0.70$			
0.1639	0.7208	0.969	-1.2
0.1037	0.8234	0.914	-1.1
0.2412	0.5892	1.026	-1.2
0.3410	0.4193	1.086	-1.0
0.3993	0.3203	1.115	-0.9
0.4477	0.2377	1.136	-0.8
0.5197	0.1153	1.165	-0.6
0.5875	0.0000	1.189	-0.5
$z = 0.23$			
0.3456	0.5736	1.055	-1.0
0.4964	0.3876	1.115	-0.9
0.5841	0.2794	1.142	-0.8
0.6930	0.1447	1.170	-0.4
0.8106	0.0000	1.195	-0.2
$z = 0.04$			
0.8948	0.0648	1.188	-0.1
0.5946	0.3786	1.127	-0.8
0.4798	0.4985	1.093	-0.9
0.8141	0.1492	1.174	-0.2
0.7289	0.2382	1.158	-0.5
0.9568	0.0000	1.198	-0.0
0.3390	0.6457	1.038	-0.8
0.2024	0.7885	0.964	-0.6

(iii) (IL + nitromethane + 1-propanol)

The binary V_m^E data for (IL + 1-propanol) at the temperatures (303.15 and 313.15) K are negative for all mole fractions of the IL due to the same effects that occur in the binary systems (IL + methanol or ethanol). The $V_{m,\min}^E$ values at the temperatures (303.15 and 313.15) K both occur at $x_1 = 0.4756$ are $-0.251\text{ cm}^3\text{mol}^{-1}$ and $-0.260\text{ cm}^3\text{mol}^{-1}$, respectively.³¹ The binary excess molar volumes of (IL + 1-propanol) are greater than (IL + ethanol) that are greater than the (IL + methanol) system due to the increase in the alcohol chain length.³¹

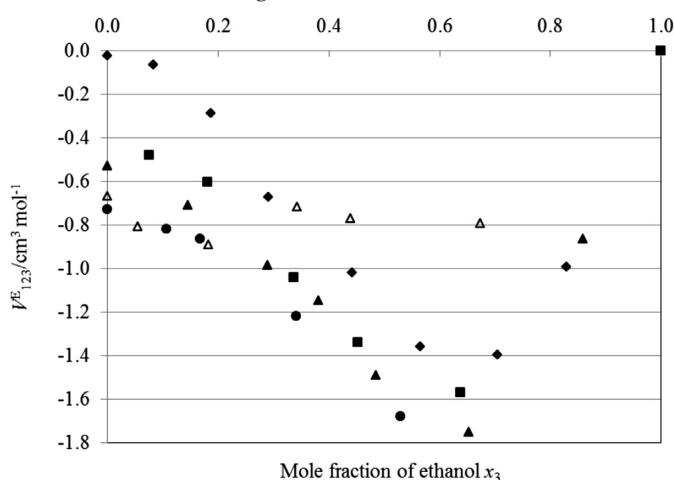


Figure 5 Graph of excess molar volumes, V_{123}^E , for the ternary mixture [BMIM]⁺[MeSO₄]⁻ (x_1) + nitromethane (x_2) + ethanol (x_3) against mole fraction of ethanol at $T = 313.15\text{ K}$ at constant $z = x_2/x_1$. The symbols represent experimental results: Δ , $z = 4.21$; \bullet , $z = 1.87$; \blacktriangle , $z = 0.70$; \blacksquare , $z = 0.23$; \blacklozenge , $z = 0.04$.

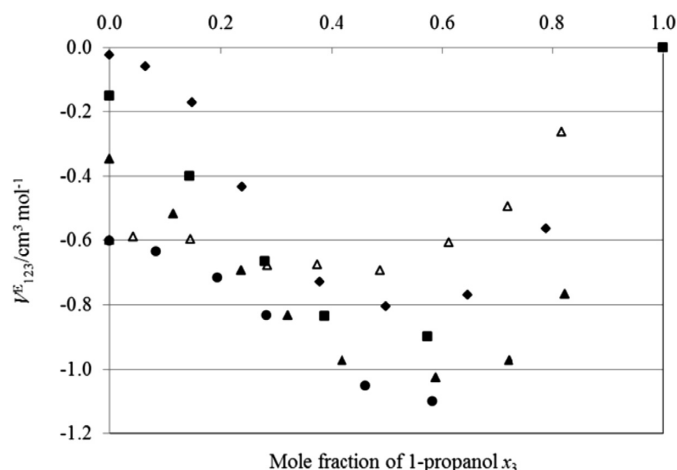


Figure 6 Graph of excess molar volumes, V_{123}^E , for the ternary mixture $[\text{BMIM}]^+[\text{MeSO}_4]^- (x_1) + \text{nitromethane} (x_2) + 1\text{-propanol} (x_3)$ against mole fraction of 1-propanol at $T = 303.15$ K at constant $z = x_2/x_1$. The symbols represent experimental results: Δ , $z = 4.21$; \bullet , $z = 1.87$; \blacksquare , $z = 0.70$; \blacklozenge , $z = 0.04$.

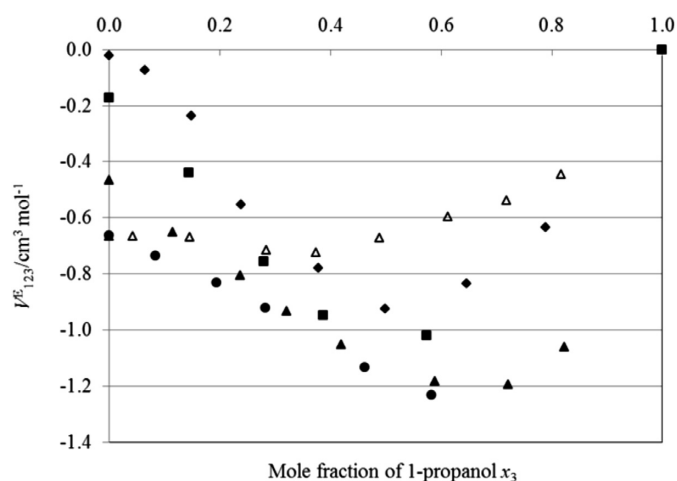


Figure 7 Graph of excess molar volumes, V_{123}^E , for the ternary mixture $[\text{BMIM}]^+[\text{MeSO}_4]^- (x_1) + \text{nitromethane} (x_2) + 1\text{-propanol} (x_3)$ against mole fraction of 1-propanol at $T = 313.15$ K at constant $z = x_2/x_1$. The symbols represent experimental results: Δ , $z = 4.21$; \bullet , $z = 1.87$; \blacksquare , $z = 0.70$; \blacklozenge , $z = 0.04$.

For the binary system (1-propanol + nitromethane) V_m^E is positive at the temperatures (303.15 and 313.15) K due to a decrease in the intermolecular interactions. The $V_{m,\min}^E$ values at the temperatures (303.15 and 313.15) K both occur at $x_1 = 0.9500$ and are $0.0374 \text{ cm}^3 \text{ mol}^{-1}$ and $0.0542 \text{ cm}^3 \text{ mol}^{-1}$, respectively.³⁸ The excess molar volumes of (1-propanol + nitromethane) are greater than (ethanol + nitromethane) are greater than (methanol + nitromethane) system due to the increase in the alcohol chain length.³⁸

Figures 6–7 are the plots of V_{123}^E versus mole fraction of 1-propanol for the ternary system (IL + nitromethane + 1-propanol). V_{123}^E values are negative for all ternary composition curves. The negative values of V_{123}^E for (IL + nitromethane + 1-propanol) are due to similar effects that occur in the ternary (IL + nitromethane + methanol or ethanol) systems.

From Table 4 it can be seen that for the ternary system ($[\text{BMIM}]^+[\text{MeSO}_4]^- + \text{nitromethane} + 1\text{-propanol}$) $V_{123,\min}^E$ increases with decreasing z values for both temperatures and decreases with an increase in temperature. The $V_{123,\min}^E$ of (IL + nitromethane + 1-propanol) is greater than (IL + nitromethane

+ ethanol) is greater than (IL + nitromethane + methanol) systems due to a decrease in intermolecular interactions among the three components and a less compact structure (a decrease in the packing effect) possibly due to the larger 1-propanol molecules. The $V_{123,\min}^E$ increases in the order (IL + nitromethane + 1-propanol) > (IL + nitromethane + ethanol) > (IL + nitromethane + methanol) at each temperature.

4. Conclusions

In this paper, the densities and V_{123}^E have been reported for the ternary systems (IL + nitromethane + methanol or ethanol or 1-propanol) at the temperatures (303.15 and 313.15) K. The V_{123}^E values are negative for all compositions of the IL and $V_{123,\min}^E$ increases with an increase in temperature for the systems (IL + nitromethane + methanol or ethanol) and decreases for the system (IL + nitromethane + 1-propanol). The negative V_{123}^E values are due to strong intermolecular interactions, as well as, a more efficient packing effect among the alcohol, nitromethane and the IL. The IL, an alcohol and/or the nitromethane are engaged in specific interactions, and the ability of the alcohol to form hydrogen bonds with the IL is increased by the presence of the nitromethane molecules. $V_{123,\min}^E$ values increase in the order (IL + nitromethane + 1-propanol) > (IL + nitromethane + ethanol) > (IL + nitromethane + methanol) at each temperature.

Acknowledgements

The authors acknowledge the National Research Foundation, South Africa, and Durban University of Technology for a post-doctoral scholarship for Dr I. Bahadur.

References

- 1 T. Welton, *Chem. Rev.*, 1999, 99, 2071–2083.
- 2 S. Baj, A. Chrobok and S. Derfla, *Green Chem.*, 2006, 8, 292–295.
- 3 K.R. Seddon, *J. Chem. Technol. Biotechnol.*, 1997, 68, 351–356.
- 4 P. Wasserscheid and W. Keim, *Angew. Chem., Int. Ed.*, 2000, 39, 3772–3789.
- 5 E.R. Cooper, C.D. Andrews, P.S. Wheatley, P.B. Webb, P. Wormald and R.E. Morris, *Nature*, 2004, 430, 1012–1016.
- 6 H.T. Karimata and N. Sugimoto, *Angew. Chem. Int. Ed.*, 2012, 51, 1416–1419.
- 7 T. Sato, G. Masuda and K. Takagi, *Electrochim. Act.*, 2004, 49, 3603–3611.
- 8 M.J. Earle, P. McCormac and K.R. Seddon, *Green Chem.*, 1999, 1, 23–25.
- 9 D. Kerle, R. Ludwig, A. Geiger and D. Paschek, *J. Phys. Chem. B.*, 2009, 113, 12727–12735.
- 10 M. Galiński, A. Lewandowski and I. Stępnik, *Electrochim. Act.*, 2006, 51, 5567–5580.
- 11 J.G. Huddleston, H.D. Williams, R.P. Swatloski, A.E. Visser and R.D. Rogers, *Chem. Commun.*, 1998, 16, 1765–1766.
- 12 R. Sheldon, *Chem. Commun.*, 2001, 23, 2399–2407.
- 13 S. Zhang, Q. Zhang and Z.C. Zhang, *Ind. Eng. Chem. Res.*, 2004, 43, 614–622.
- 14 J. Esser, P. Wasserscheid and A. Jess, *Green Chem.*, 2004, 6, 316–322.
- 15 M.V.B. Zanoni, E.I. Rogers, C. Hardacre and R.G. Compton, *Anal. Chim. Acta*, 2010, 659, 115–121.
- 16 P. Kubisa, *Prog. Polym. Sci.*, 2009, 34, 1333–1347.
- 17 M. Freemantle, *An Introduction to Ionic Liquids*, RSC Publishing, Cambridge, UK, 2010.
- 18 M.T. Zafarani-Mottar and H. Shekaari, *J. Chem. Thermodyn.*, 2005, 37, 1029–1035.
- 19 E. Gómez, B. González, N. Calvar and Á. Domínguez, *J. Chem. Thermodyn.*, 2008, 40, 1208–1216.
- 20 B. González, N. Calvar, E. Gómez and Á. Domínguez, *J. Chem. Thermodyn.*, 2008, 40, 1274–1281.
- 21 N. Deenadayalu, S. Kumar and P. Bhujrajh, *J. Chem. Thermodyn.*, 2007, 39, 1318–1324.

- 22 N. Deenadayalu and P. Bhujrajh, *J. Chem. Eng. Data*, 2008, **53**, 1098–1102.
- 23 N. Deenadayalu, I. Bahadur and T. Hofman, *J. Chem. Eng. Data*, 2010, **55**, 2636–2642.
- 24 N. Deenadayalu, I. Bahadur and T. Hofman, *J. Chem. Thermodyn.*, 2010, **42**, 726–733.
- 25 N. Deenadayalu, I. Bahadur and T. Hofman, *J. Chem. Eng. Data*, 2011, **56**, 1682–1686.
- 26 I. Bahadur, N. Deenadayalu, Z. Tywabi, S. Sen and T. Hofman, *J. Chem. Thermodyn.*, 2012, **49**, 24–38.
- 27 A.E. Andreatta, A. Arce, E. Rodil and A. Soto, *J. Chem. Thermodyn.*, 2009, **41**, 1317–1323.
- 28 A.E. Andreatta, A. Arce, E. Rodil and A. Soto, *J. Solution Chem.*, 2010, **39**, 371–383.
- 29 P.N. Sibiyi and N. Deenadayalu, *J. Chem. Thermodyn.*, 2008, **40**, 1041–1045.
- 30 N. Deenadayalu, S. Sen and P.N. Sibiyi, *J. Chem. Thermodyn.*, 2009, **41**, 538–548.
- 31 P.N. Sibiyi and N. Deenadayalu, *S. Afr. J. Chem.*, 2009, **62**, 20–25.
- 32 P. Bhujrajh and N. Deenadayalu, *J. Solution Chem.*, 2007, **36**, 631–642.
- 33 N. Deenadayalu, K.C. Ngcongco, T.M. Letcher and D. Ramjugernath, *J. Chem. Eng. Data*, 2006, **51**, 988–991.
- 34 N. Deenadayalu, S.H. Thango, T.M. Letcher and D. Ramjugernath, *J. Chem. Thermodyn.*, 2006, **38**, 542–546.
- 35 I. Bahadur and N. Deenadayalu, *J. Solution Chem.*, 2011, **40**, 1528–1543.
- 36 M.A. Iglesias-Otero, J. Troncoso, E. Carballo and L. Romani, *J. Chem. Eng. Data*, 2008, **53**, 1298–1301.
- 37 L. Moràvková and J. Linek, *J. Chem. Thermodyn.*, 2008, **40**, 671–676.
- 38 C-H. Tu, S-L. Lee and I-H. Peng, *J. Chem. Eng. Data*, 2001, **46**, 151–155.