JOURNAL OF CHEMICAL & ENGINEERING DATA

ARTICLE

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Density, Refractive Index, and Excess Properties of 1-Butyl-3-methylimidazolium Tetrafluoroborate with Water and Monoethanolamine

Malyanah Mohd Taib and Thanapalan Murugesan*

Chemical Engineering Department, Universiti Teknologi PETRONAS, Tronoh-31750, Perak, Malaysia

ABSTRACT: The densities and refractive indices of binary mixtures containing 1-butyl-3-methylimidazolium tetrafluoroborate with water and monoethanolamine are measured at a temperature range of (293.15 to 353.15) K and within the whole range of composition. Excess molar volumes are deduced from the measured physical properties and correlated using Redlich−Kister polynomial equations. The excess molar volumes are positive for the entire mole fraction range, and the details are discussed. The thermal expansion coefficients are also derived from the measured density values.

INTRODUCTION

Natural gas, which is an important source of clean fuel and also a starting material for the synthesis of various petrochemical products, usually contains CO_2 and H_2S (acid gases). The presence of CO_2 lowers the heating value of natural gas, whereas H_2S increases the toxicity and corrosiveness.[1] Currently, common solvents like aqueous methyl diethanolamine (MDEA), monoethanolamine (MEA), and diethanolamine (DEA) are being used in commercial natural gas processing units. Even though the absorption process using amine solvents involes high energy consumption, their effectiveness in capturing CO_2 is relatively high.[2] In recent years, interest in the application of ionic liquids (ILs) as novel solvents has increased significantly due to their advantages over other volatile organic solvents.[3−6] The successful application of ILs as solvents have been demonstrated for a wide range of chemical reactions and industrial processess,[7−9] namely, electrolyte in solvent-free fuel system,[10] polymer electrolytes membranes,[11] fuel cells,[12] and solvent for carbon dioxide absorption.[13,14] Thus, ILs are currently considered as a replacement for the conventional volatile organic solvents because of their environmentally benign properties.[15] Recently, some researchers have studied and concluded that a few classes of ILs have an effective and high capability for CO_2 capture, and among the available ionic liquids, imidazolium based ionic liquids are found to be more ideal for CO_2 removal.[16−19] Because the basic physical properties are essential for the design, scale up, and sizing of the equipments for commercial applications, the information related to the thermodynamic and thermophysical properties of pure ILs as well as their mixtures with other compounds is essential.

A considerable amount of experimental data have been measured and reported for imidazolium based pure ILs. Jacquemin et al.[20] reported the physical properties of imidazolium based pure ILs containing 1-alkyl-3-methylimidazolium (alkyl = 2,4,6,8) as cation and bis{(trifluoromethyl)sulfonyl}imide ($[NTf_2]^-$), trifluoromethanesulfonate ($[OTF]^-$), tetrafluoroboarte ($[BF_4]^-$), and hexafluorophosphate ($[PF_6]^-$) as anions, whereas Soriano et al.[21] reported the density and refractive index data for pure 1-*n*-butyl-3-methylimidazolium-based ionic liquids. On the other hand, Tekin et al.[22] reported the properties of pure 1-butyl-3-methylimidazolium tetrafluoroborate and 1-butyl-3-methylimidazolium hexafluorophosphate at T = (298.15 to 398.15) K and pressures up to P = 40 MPa, whereas Kim et al.[23] reported the physical and electrochemical properties of pure 1-butyl-3-methylimidazolium bromide, 1-butyl-3-methylimidazolium iodide, and 1-butyl-3-methylimidazolium tetrafluoroborate. Only a very few researchers reported the physical and excess properties of a binary mixture of ILs. Malham et al.[9] reported the viscosities and refractive indices of binary mixtures of 1-butyl-3-methylimidazolium tetrafluoroborate and 1-butyl-2,3-dimethylimidazolium tetrafluoroborate with water at 298 K, whereas Iglesias-Otero et al.[24] reported the densities and refractive indices for the mixtures of IL and organic solvents. Recently our group has also reported the physical properties of binary mixtures of bis(2-hydroxyethyl)ammonium acetate with water and monoethanolamine at temperatures (303.15 to 353.15) K.[2]

On the basis of our preliminary experiments, 1-butyl-3-methylimidazolium tetrafluoroborate ($[Bmim][BF_4]$) has been found to be totally miscible with water and MEA at all proportions. Hence, in the present study, it is proposed to measure the physical properties (density and refractive index) of the binary mixtures of ($[Bmim][BF_4]$) with water and MEA in the temperature range from (293.15 to 353.15) K and at atmospheric pressure over the whole composition range and to estimate their excess properties for their potential application in industrial processess especially for the effective capture of CO_2. On the basis of the measured density, excess molar volumes, V^E were calculated and fitted using Redlich−Kister polynomial equation.

EXPERIMENTAL SECTION

All samples were prepared freshly and retained at room temperature for 24 h, to ensure their solubility at the desired temperature. Samples were kept in airtight glass vials and sealed with parafilm to prevent any possible humid effects on the samples. The samples were prepared based on mass fraction using an analytical balance (model AS120S, Mettler Toledo)

Received: July 31, 2011
Accepted: October 4, 2011
Published: November 04, 2011

dx.doi.org/10.1021/je2007204 | *J. Chem. Eng. Data* 2012, 57, 120–126

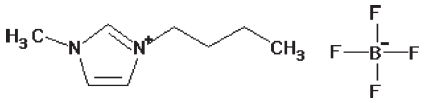

Figure 1. Structure of [Bmim][BF_4] studied in the present work.

Table 1. Comparison of Measured Density ρ for Pure Components with Literature Values at Temperature from (293.15 to 353.15) K

		MEA		[Bmim][BF_4]	
properties	T/K	this work	lit.	this work	lit.
ρ/g.cm^{-3}	293.15	1.01643		1.20416	1.2049[20]
	298.15	1.01301		1.20057	1.200297[7]
					1.2011[20]
					1201[21]
	303.15	1.00970	1.0091[27]	1.19698	1.1974[20]
	313.15	1.00247	1.00021[27]	1.18986	N/A
	323.15	0.99480	0.994[26]	1.18281	1.1827[20]
			0.9934[26]		
	333.15	0.98675	0.9850[25]	1.17583	1.1753[20]
	343.15	0.97862	0.9773[25]	1.16890	1.1680[20]
	353.15	0.97040	0.9696[25]	1.16204	N/A
n_D	293.15	1.45601	1.4539[28]	1.42592	
	298.15	1.45432	1.4521[28]	1.42475	1.422[9]
					1.4218[21]
					1.4227[23]
	303.15	1.45273	1.4503[28]	1.42369	1.4206[21]
					1.4214[23]
	313.15	1.44913	N/A	1.42128	1.4192[23]
	323.15	1.44561	N/A	1.41900	1.4172[23]
	333.15	1.44213	N/A	1.41656	N/A
	343.15	1.43862	N/A	1.41388	N/A
	353.15	1.43472	N/A	1.41135	N/A

with a precision of ± 0.0001 g and later were converted to mole fraction.

Chemicals. The IL 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF_4]) used in this study was obtained from Merck (< 99 % purity). The sample was dried for 24 h under vacuum at 373.15 K to remove any possible traces of water before being used. The structure of ([Bmim][BF_4]) is shown in Figure 1. Monoethanolamine (AR grade, Aldrich with 99 % purity) and double distilled deionized water were used for the preparation of the binary mixtures with ([Bmim][BF_4]). Millipore quality water with known density and refactive index was used for the calibration of the analytical instruments. The properties of the pure chemicals used in the present work are presented in Table 1 along with the available literature values,[20−28] for comparison purposes. The results show a minor deviation from the reported data, which might be due to the difference in the purity of samples.

Density. The densities of the binary mixtures including pure MEA and [Bmim][BF_4] were measured using an oscillating U-tube densimeter (model DMA-5000 M, Anton Paar) at temperatures from (293.15 to 353.15) K with a built-in platinum resistance thermometer with an uncertainty of ± 0.01 K . The apparatus was calibrated frequently, by measuring the density of Millipore quality water and dry air as instructed by the supplier

Table 2. Density ρ (g·cm^{-3}), Refractive Index n_D, and Excess Molar Volume V^E (cm^3·mol^{-1}) for the [Bmim][BF_4] (1) − Water (2) Binary Mixture at Temperature from (293.15 to 353.15) K

x_1	ρ	V^E	n_D	ρ	V^E	n_D
		293.15 K			323.15 K	
0.0000	0.99822	0.00000	1.33693	0.98810	0.00000	1.33264
0.1000	1.10369	0.15621	1.38272	1.08338	0.31035	1.37539
0.2000	1.14095	0.27311	1.39910	1.11948	0.44993	1.39171
0.2950	1.15958	0.35765	1.40761	1.13793	0.53014	1.39962
0.4016	1.17298	0.39435	1.41358	1.15147	0.53999	1.40524
0.5002	1.18160	0.39267	1.41743	1.15987	0.54036	1.40933
0.5963	1.18801	0.35761	1.42022	1.16622	0.49652	1.41195
0.6997	1.19337	0.30080	1.42207	1.17168	0.41150	1.41433
0.8014	1.19782	0.19899	1.42370	1.17635	0.26214	1.41642
0.8988	1.20132	0.09094	1.42561	1.17992	0.12107	1.41763
1.0000	1.20416	0.00000	1.42592	1.18281	0.00000	1.41900
		298.15 K			333.15 K	
0.0000	0.99705	0.00000	1.33607	0.98320	0.00000	1.33085
0.1000	1.10040	0.18594	1.38145	1.07605	0.35905	1.37300
0.2000	1.13732	0.31081	1.39788	1.11233	0.49240	1.38880
0.2950	1.15586	0.39758	1.40608	1.13080	0.57126	1.39679
0.4016	1.16924	0.43289	1.41195	1.14435	0.57843	1.40255
0.5002	1.17793	0.42324	1.41595	1.15277	0.57554	1.40661
0.5963	1.18435	0.38422	1.41855	1.15903	0.53916	1.40958
0.6997	1.18970	0.32442	1.42070	1.16461	0.43819	1.41180
0.8014	1.19422	0.21024	1.42246	1.16929	0.28163	1.41396
0.8988	1.19772	0.09690	1.42423	1.17291	0.13027	1.41509
1.0000	1.20057	0.00000	1.42475	1.17583	0.00000	1.41656
		303.15 K			343.15 K	
0.0000	0.99570	0.00000	1.33549	0.97780	0.00000	1.32881
0.1000	1.09703	0.21579	1.38027	1.06866	0.40362	1.37053
0.2000	1.13342	0.35839	1.39671	1.10512	0.53326	1.38600
0.2950	1.15211	0.43685	1.40456	1.12382	0.59995	1.39386
0.4016	1.16547	0.47201	1.41044	1.13732	0.60921	1.39999
0.5002	1.17425	0.45300	1.41460	1.14579	0.60056	1.40400
0.5963	1.18072	0.40550	1.41703	1.15206	0.56062	1.40693
0.6997	1.18607	0.34242	1.41934	1.15755	0.46729	1.40930
0.8014	1.19061	0.22044	1.42120	1.16229	0.30041	1.41123
0.8988	1.19412	0.10115	1.42291	1.16595	0.13981	1.41244
1.0000	1.19698	0.00000	1.42369	1.16890	0.00000	1.41388
		313.15 K			353.15 K	
0.0000	0.99220	0.00000	1.33422	0.97180	0.00000	1.32665
0.1000	1.09058	0.25479	1.37772	1.06140	0.43539	1.36796
0.2000	1.12658	0.40077	1.39427	1.09786	0.57075	1.38301
0.2950	1.14511	0.47991	1.40199	1.11677	0.62836	1.39093
0.4016	1.15853	0.50220	1.40774	1.13024	0.64156	1.39746
0.5002	1.16710	0.49289	1.41185	1.13872	0.63345	1.40138
0.5963	1.17345	0.45120	1.41448	1.14499	0.59478	1.40435
0.6997	1.17890	0.37144	1.41686	1.15052	0.49745	1.40688
0.8014	1.18345	0.24150	1.41879	1.15534	0.31919	1.40884
0.8988	1.18699	0.11105	1.42027	1.15904	0.14920	1.41003
1.0000	1.18986	0.00000	1.42128	1.16204	0.00000	1.41135

dx.doi.org/10.1021/je2007204 |J. Chem. Eng. Data 2012, 57, 120–126

Table 3. Density ρ ($g \cdot cm^{-3}$), Refractive Index n_D, and Excess Molar Volume V^E ($cm^3 \cdot mol^{-1}$) for the [Bmim][BF_4] (1) − MEA (2) Binary Mixture at Temperature from (293.15 to 353.15) K

x_1	ρ	V^E	n_D	ρ	V^E	n_D
		293.15 K			323.15 K	
0.0000	1.01643	0.00000	1.45601	0.99480	0.00000	1.44561
0.0999	1.06467	1.73305	1.44991	1.04111	1.87202	1.43978
0.2001	1.09643	2.65560	1.44389	1.07278	2.86868	1.43437
0.2994	1.12225	2.93138	1.43940	1.09887	3.16921	1.43020
0.4004	1.14193	2.92730	1.43589	1.11905	3.15372	1.42717
0.4999	1.15655	2.78837	1.43332	1.13347	3.04964	1.42445
0.5994	1.16902	2.45519	1.43129	1.14585	2.73833	1.42292
0.7005	1.17949	2.01679	1.42954	1.15634	2.30605	1.42148
0.7992	1.18810	1.51373	1.42820	1.16525	1.76932	1.42032
0.9002	1.19652	0.81344	1.42712	1.17492	0.87890	1.41932
1.0000	1.20416	0.00000	1.42592	1.18281	0.00000	1.41900
		298.15 K			333.15 K	
0.0000	1.01301	0.00000	1.45432	0.98675	0.00000	1.44213
0.0999	1.06078	1.75658	1.44855	1.03318	1.91174	1.43631
0.2001	1.09238	2.69720	1.44225	1.06489	2.93535	1.43077
0.2994	1.11837	2.96938	1.43802	1.09118	3.24106	1.42750
0.4004	1.13810	2.96516	1.43458	1.11156	3.22017	1.42422
0.4999	1.15255	2.84381	1.43184	1.12618	3.10567	1.42184
0.5994	1.16495	2.52068	1.42990	1.13840	2.81403	1.42014
0.7005	1.17554	2.07198	1.42799	1.14882	2.39355	1.41880
0.7992	1.18412	1.57360	1.42688	1.15795	1.83024	1.41775
0.9002	1.19289	0.82453	1.42585	1.16785	0.89917	1.41707
1.0000	1.20057	0.00000	1.42475	1.17583	0.00000	1.41656
		303.15 K			343.15 K	
0.0000	1.00970	0.00000	1.45273	0.97862	0.00000	1.43862
0.0999	1.05687	1.78308	1.44655	1.02521	1.95356	1.43291
0.2001	1.08849	2.73249	1.44075	1.05698	3.00493	1.42766
0.2994	1.11447	3.01041	1.43648	1.08358	3.30954	1.42410
0.4004	1.13429	3.00266	1.43322	1.10401	3.29706	1.42130
0.4999	1.14867	2.88958	1.43027	1.11883	3.17159	1.41904
0.5994	1.16091	2.58481	1.42855	1.13100	2.89024	1.41739
0.7005	1.17148	2.14031	1.42689	1.14137	2.48161	1.41605
0.7992	1.18017	1.63174	1.42559	1.15051	1.91822	1.41530
0.9002	1.18925	0.83509	1.42429	1.16085	0.91919	1.41397
1.0000	1.19698	0.00000	1.42369	1.16890	0.00000	1.41388
		313.15 K			353.15 K	
0.0000	1.00247	0.00000	1.44913	0.97040	0.00000	1.43472
0.0999	1.04901	1.82944	1.44309	1.01717	1.99797	1.42970
0.2001	1.08064	2.80170	1.43765	1.04906	3.07785	1.42456
0.2994	1.10667	3.09035	1.43333	1.07591	3.38672	1.42104
0.4004	1.12656	3.08653	1.43025	1.09667	3.36001	1.41839
0.4999	1.14100	2.97436	1.42753	1.11153	3.23900	1.41617
0.5994	1.15335	2.66195	1.42573	1.12365	2.96836	1.41490
0.7005	1.16393	2.21763	1.42416	1.13416	2.54613	1.41357
0.7992	1.17272	1.69427	1.42296	1.14322	1.99450	1.41267
0.9002	1.18205	0.85771	1.42206	1.15390	0.93970	1.41202
1.0000	1.18986	0.00000	1.42128	1.16204	0.00000	1.41135

and validated using several ILs for which the data were already established.[2,13,15,29] The apparatus is precise to within 1×10^{-5} $g \cdot cm^{-3}$ and the uncertainty of the measurements was better than 4×10^{-5} $g \cdot cm^{-3}$. The density measurements for the binary mixture samples were made in triplicate and the average values are reported for further analysis.

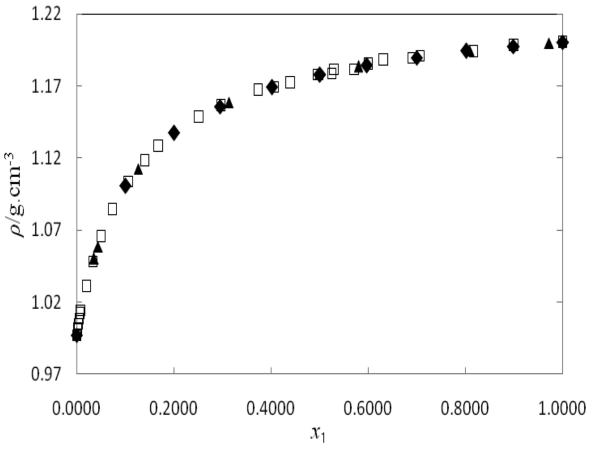

Figure 2. Comparison of present density data for pure [Bmim][BF_4] with published data at T = 298.15 K: ♦, this work; □, Rilo et al.;[30] ▲, Malham and Turmine.[31]

Refractive Index. The refractive indices of the binary mixtures including the pure MEA and [Bmim][BF_4] were measured using the digital refractometer (model ATAGO RX-5000) with precision to within 2×10^{-5}, and the uncertainty of the measurements was better than 4×10^{-5} in the temperature range of (293.15 to 353.15) K. The temperature of the apparatus was controlled to within ± 0.05 °C. The apparatus was calibrated by measuring the refractive index of Millipore quality water and again validated using several ILs for which the data were established.[2,13,15,29] All the measurements were made in triplicate and the average values are considered for further analaysis.

RESULTS AND DISCUSSION

Density. The densities of [Bmim][BF_4]−water and [Bmim][BF_4]−MEA were measured over the temperature range from T = (293.15 to 353.15) K and reported in Tables 2 and 3, respectively. The present data obtained for [Bmim][BF_4]−water systems are compared with those of the available literature[30−32] and a satisfactory agreement was found (Figures 2 and 3). The densities of both binary systems decreased with increasing temperature and decreasing mole fraction of IL. The variation of density with respect to temperature for both mixtures are shown in Figures 4 and 5. In general this expected behavior is a general physical phenomenon and common for most of fluids including ILs. A careful analysis of residuals showed that the density and temperature relationship is not exactly linear, and hence to improve the accuracy for the representation of data and further predictions, a second order polynomial of the following form was used to correlate the variation of density with temperature

$$\rho = A_0 + A_1 T + A_2 T^2 \quad (1)$$

where T is the temperature and A_0, A_1, and A_2 are the optimized coefficients. The optimized coefficients were estimated using the least-squares method, and the values are listed in Table 4.

The coefficient of thermal expansion (α), which is the measure of the changes in volume of the solution with temperature, can

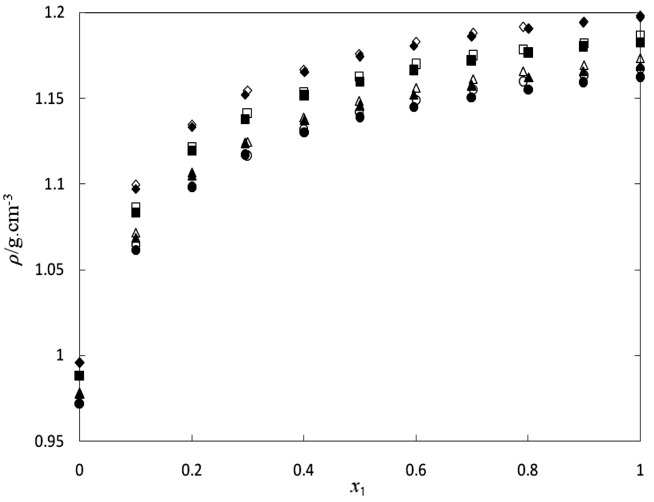

Figure 3. Comparison of present data for [Bmim][BF_4] + water system with published data. Present data: ◆, T = 303.15 K; ■, T = 323.15 K; ▲, T = 343.15 K; ●, T = 353.15 K. Zhou et al.:[32] ◇, T = 303.15 K; □, T = 323.15 K; △, T = 343.15 K; ○, T = 353.15 K.

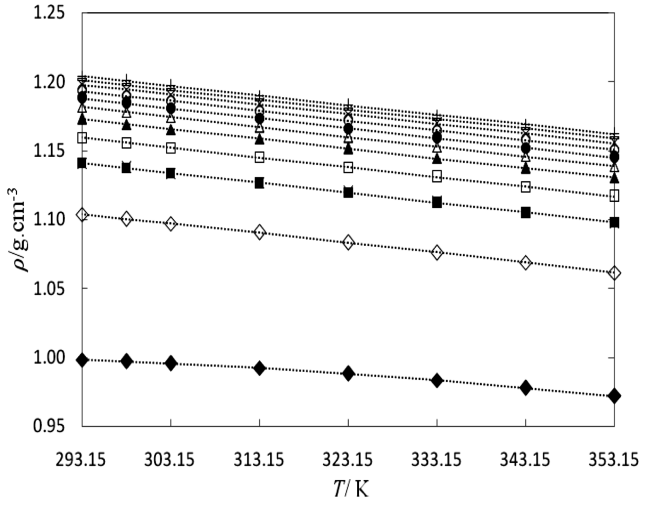

Figure 4. Plot of experimental values of density ρ against temperature T and fitted curve (----) for [Bmim][BF_4] (1) + water (2) binary mixture: ♦, 0.0000; ◇, 0.1000; ■, 0.2000; □, 0.2950; ▲, 0.4016; △, 0.5002; ●, 0.5963; ○,0.6997; ×, 0.8014; —, 0.8988 ; +, 1.000.

further be estimated using the following expression

$$\alpha/(K^{-1}) = -\frac{1}{\rho}\left(\frac{\partial\rho}{\partial T}\right) \tag{2}$$

where α is the thermal expansion coefficient, ρ is the density of the mixture, and T is the temperature. For this purpose, the partial derivative of eq 1 was evaluated, and the coefficients of thermal expansion were calculated. For the case of [Bmim][BF_4]−water syatems the variation of thermal expansion coefficients with temperature is not significant which is in good agreement with the observations of Kumar et al.[33] But the variations with the concentration of [Bmim][BF_4] is relatively high. The α values for [Bmim][BF_4]−MEA systems decreased with increasing mole fraction of [Bmim][BF_4].

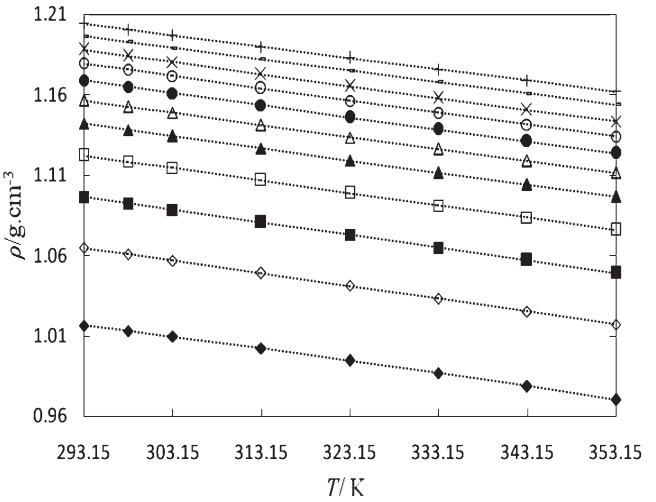

Figure 5. Plot of experimental values of density ρ against temperature T and fitted curve (----) for [Bmim][BF_4] (1) + MEA (2) binary mixture: ♦, 0.0000; ◇, 0.0999; ■, 0.2001; □, 0.2994; ▲, 0.4004; △, 0.4999; ●, 0.5994; ○, 0.7005; ×, 0.7992; —, 0.9002 ; +, 1.000.

Excess molar volume of mixtures are commonly related to the differences and changes of structure undergone by the pure component when mixed with other compounds.[2] The excess molar volume V^E for the binary mixtures were obtained using the following relation:

$$V^E = \frac{x_1M_1 + x_2M_2}{\rho_m} - \frac{x_1M_1}{\rho_1} - \frac{x_2M_2}{\rho_2} \tag{3}$$

where ρ_m is the density of the mixture, x_1 and x_2 are the mole fraction of pure component 1 and 2, respectively, and M_1 and M_2 are the molecular weight of pure component 1 and 2, respectively. The calculated excess molar volumes for the binary systems are presented in Tables 2 and 3 and shown plotted in Figures 6 and 7. The figures show that the binary mixtures of [Bmim][BF_4] with water and MEA exibit positive deviation from ideality, with the highest value at $x_{[Bmim][BF4]}$ = 0.4016 for the [Bmim][BF_4]−water system and $x_{[Bmim][BF4]}$ = 0.2994 for the [Bmim][BF_4]−MEA system. The magnitude of the excess volume increases with increasing temperatures. The increase in the magnitude of the positive V^E values with temperature might be attributed to the decreasing importance of hydrogen bonding effect with increasing temperature. The positive value indicate that there is a volume expansion on mixing. The interaction between unlike molecules are weaker and insufficient to cause volume contraction. The dependence of V^E on temperature and composition for the mixtures can also be explained by the variation in intermolecular forces between the compounds or the variation in the molecular packing, which are due to the differences in size and shape of the molecules forming a binary mixture with other compound.

The estimated values of V^E for each mixtures were correlated using the Redlich−Kister polynomial equation[34]

$$\Delta Q = x_1x_2\sum_{k=0}^{5} A_k(x_1 - x_2)^k \tag{4}$$

where ΔQ and x are the excess properties and the mole fraction respectively. The order (k) and the coefficients (A_k) of the Redlich−Kister polynomial equation were obtained using the

method of least-squares. The parameters of the Redlich−Kister equation for representing excess molar volumes for the [Bmim][BF_4]−water and [Bmim][BF_4]−MEA systems are found to be the function of temperatures. Hence the following form of polynomial is used to represent the coefficients as a function of temperature and the optimized coefficients are presented in Table 5

$$A_k = B_0 + B_1T + B_2T^2 + B_3T^3 + B_4T^4 \quad (5)$$

The rms errors estimated according to the following equation were found to be ≤ 0.01

$$\mathrm{RMS} = \left[\sum\left(\frac{x_{\mathrm{exp}} - x_{\mathrm{calc}}}{x_{\mathrm{exp}}}\right)^2\right]^{1/2} \quad (6)$$

Table 4. Fitting Parameters of eq 1 and Errors for the Correlation of Density for [Bmim][BF_4] (1) − Water and [Bmim][BF_4] (1) − MEA Binary Mixtures

x_1	A_0	A_1	A_2	rms
		[Bmim][BF_4]−Water		
0.0000	0.77723	1.74810×10^{-3}	-3.39049×10^{-6}	2.14928×10^{-4}
0.1000	1.21206	-8.92449×10^{-5}	-9.56382×10^{-7}	3.35913×10^{-4}
0.2000	1.34450	-6.77816×10^{-4}	-5.78618×10^{-8}	2.92416×10^{-4}
0.2950	1.39630	-8.87507×10^{-4}	2.71958×10^{-7}	1.55083×10^{-4}
0.4016	1.39957	-8.26424×10^{-4}	1.80966×10^{-7}	2.13472×10^{-4}
0.5002	1.42165	-9.06223×10^{-4}	2.97703×10^{-7}	7.56068×10^{-5}
0.5963	1.43087	-9.20768×10^{-4}	3.15047×10^{-7}	2.14928×10^{-4}
0.6997	1.41837	-8.14132×10^{-4}	1.57482×10^{-7}	9.85750×10^{-5}
0.8014	1.43225	-8.75679×10^{-4}	2.59262×10^{-7}	7.40726×10^{-6}
0.8988	1.43756	-8.89972×10^{-4}	2.86841×10^{-7}	7.53360×10^{-6}
1.0000	1.44333	-9.10294×10^{-4}	3.22186×10^{-7}	1.06178×10^{-5}
		[Bmim][BF_4]−MEA		
0.0000	1.08420	2.20000×10^{-4}	-1.53000×10^{-6}	3.29835×10^{-4}
0.0999	1.27453	-6.52969×10^{-4}	-2.14541×10^{-7}	1.33446×10^{-5}
0.2001	1.32292	-7.59920×10^{-4}	-4.39604×10^{-8}	8.68002×10^{-5}
0.2994	1.37127	-9.13058×10^{-4}	2.17297×10^{-7}	7.08154×10^{-5}
0.4004	1.39379	-9.45556×10^{-4}	2.94953×10^{-7}	9.10470×10^{-5}
0.4999	1.43629	-1.12574×10^{-3}	5.84118×10^{-7}	1.41158×10^{-4}
0.5994	1.44719	-1.11231×10^{-3}	5.55926×10^{-7}	2.10562×10^{-4}
0.7005	1.45800	-1.11234×10^{-3}	5.52985×10^{-7}	1.39065×10^{-4}
0.7992	1.45034	-1.01919×10^{-3}	4.23773×10^{-7}	1.93219×10^{-4}
0.9002	1.43861	-9.21795×10^{-4}	3.27344×10^{-7}	1.04766×10^{-5}

Refractive Index. The refractive indices of IL [Bmim][BF_4]−water and [Bmim][BF_4]−MEA mixtures were measured over the range from T = (293.15 to 353.15) K. The experimental data for [Bmim][BF_4]−water are reported in Table 2 whereas for [Bmim][BF_4]−MEA, the data are presented in Table 3. The refractive index values for [Bmim][BF_4]−water mixtures increase with increasing composition of IL and decrease with temperature, which are in good agreement with the observations of Malham et al.[9] The dependency of refractive index of these binary mixture follow the second order polynomial (similar to eq 3), whereas on the other hand, the refractive index for [Bmim][BF_4]−MEA mixtures decreases with increasing composition of IL and temperature. This is due to the fact that the refractive index for pure MEA is higher than that for the pure [Bmim][BF_4]. The refractive index of liquid mixtures can be predicted with the prior knowledge of its density together with the refractive index and densities of the pure components. For the prediction of the refractive index of binary mixtures, $n_{\mathrm{Dm,calc.}}$, the following expressions were used:

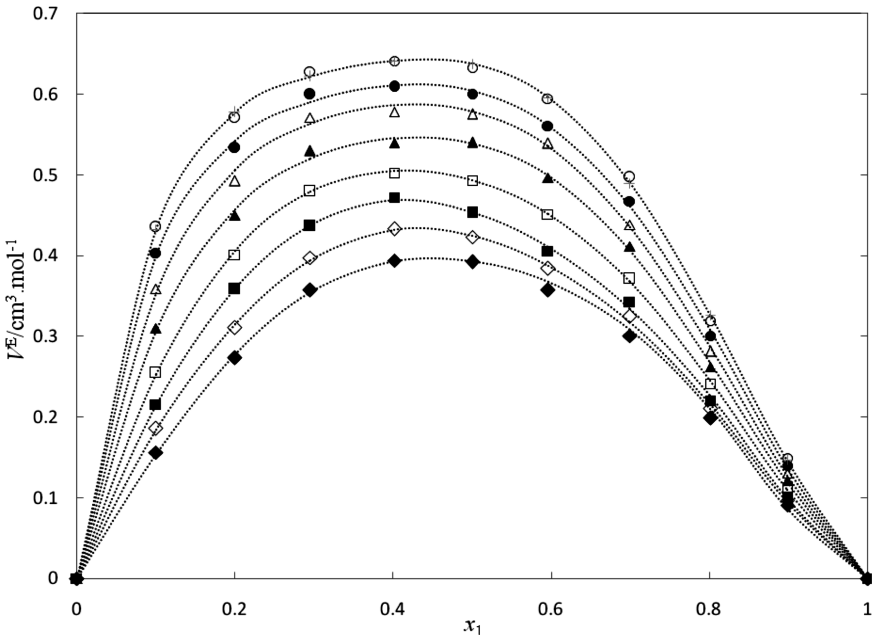

Figure 6. Excess molar volume V^E vs mole fraction x_1 for [Bmim][BF_4] (1) + water (2) binary mixture at different mole fraction with the Redlich−Kister equation at different temperatures: ♦, 293.15 K; ◇, 298.15 K; ▲, 303.15 K; △, 313.15 K; ■, 323.15 K; □, 333.15 K, ●, 343.15 K; ○, 353.15 K.

dx.doi.org/10.1021/je2007204 |J. Chem. Eng. Data 2012, 57, 120–126

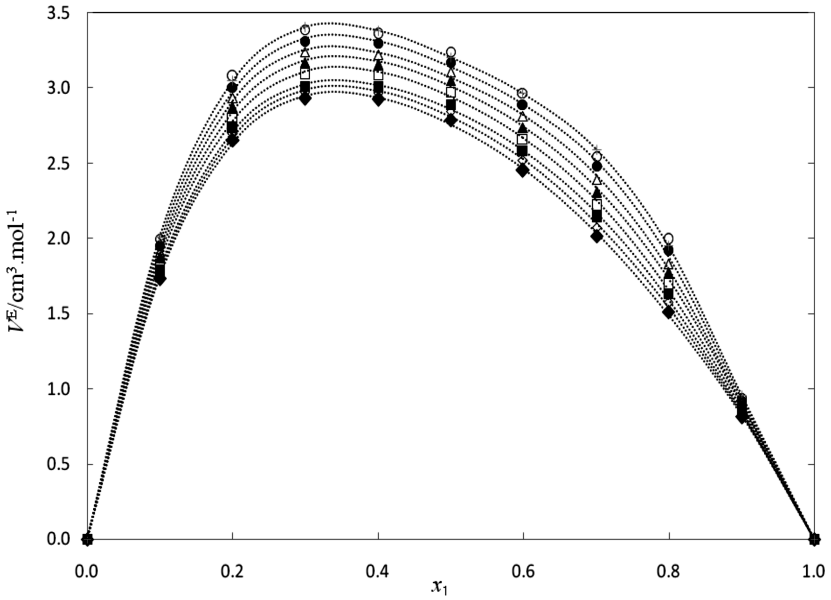

Figure 7. Excess molar volume V^E vs mole fraction x_1 for [Bmim][BF_4] (1) + MEA (2) binary mixture at different mole fraction with the Redlich−Kister equation at different temperatures: ♦, 293.15 K; ◇, 298.15 K; ▲, 303.15 K; △, 313.15 K; ■, 323.15 K; □, 333.15 K, ●, 343.15 K; ○, 353.15 K.

Table 5. Parameters of the Redlich Kister Equation (eq 4) for Excess Molar Volume V^E/cm^3·mol^{-1} as a Function of Temperature (eq 5)

	V^E/cm^3·mol^{-1}				
	B_0	B_1	B_2	B_3	B_4
	[BMIM][BF_4] + Water System				
A_0	−290.434	3.40995	−0.01507	2.9845×10^{-5}	-2.2260×10^{-8}
A_1	7960.11	−97.9047	0.45096	-9.2204×10^{-4}	7.0610×10^{-7}
A_2	2074.93	−25.9611	0.12156	-2.5249×10^{-4}	1.9630×10^{-7}
A_3	−28410.9	352.095	−1.63310	3.3602×10^{-3}	-2.5882×10^{-6}
A_4	−7933.50	99.2480	−0.46508	9.6721×10^{-4}	-7.5300×10^{-7}
A_5	30671.8	−382.484	1.78506	-3.6953×10^{-3}	2.8631×10^{-6}
	[BMIM][BF_4] + MEA System				
A_0	−246.425	2.71525	−0.01071	1.8688×10^{-5}	-1.1989×10^{-8}
A_1	−6823.79	83.8868	−0.38661	7.9115×10^{-4}	-6.0649×10^{-7}
A_2	−12262.8	152.466	−0.70986	1.4669×10^{-3}	-1.1346×10^{-6}
A_3	8394.45	−103.362	0.47660	-9.7602×10^{-4}	7.4917×10^{-7}
A_4	20268.6	−252.057	1.17426	-2.4282×10^{-3}	1.8797×10^{-6}
A_5	3232.38	−39.1885	0.17838	-3.6050×10^{-4}	2.7237×10^{-7}

The Lorentz−Lorenz equation[35]

$$\frac{{n_{\mathrm{Dm,cal.}}}^2 - 1}{{n_{\mathrm{Dm,calc.}}}^2 + 2} = \sum_{i=1}^{N}\left[\varphi_i\left(\frac{{n_{\mathrm{D}i}}^2 - 1}{{n_{\mathrm{D}i}}^2 + 2}\right)\right] \quad (7)$$

The Dale−Gladstone equation[36]

$$n_{\mathrm{Dm,calc.}} - 1 = \sum_{i=1}^{N}[\varphi_i(n_{\mathrm{D}i} - 1)] \quad (8)$$

where $n_{\mathrm{Dm,calc.}}$ is the refractive index of the mixture and $n_{\mathrm{D}i}$ and ϕ_i are the refractive index and the volumetric fraction of components i, respectively. Based on the analysis of the present refractive index data, it was found that the present refractive index data fits very well with the equation proposed by Dale-Gladstone (RMS of ≤0.002 and ≤0.003 for [Bmim][BF_4] − water and [Bmim][BF_4] − MEA mixture respectively) when compared with Lorentz−Lorenz equation (≤0.017 for both mixtures).

CONCLUSION

The densities and refractive indices of two binary mixtures of 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF_4]) with water and monoethanolamine were measured at a temperature range of (293.15 to 353.15) K over the whole range of composition. Excess molar volumes and the thermal expansion coefficients were deduced from the measured density values in order to explain the molecular interaction between the two components. Satisfactory correlations for the composition dependence of the excess molar volumes were obtained by fitting with fifth- order Redlich−Kister polynomials. The Dale−Gladstone equation was found to predict the present refractive index data well compared with Lorentz−Lorenz equation.

AUTHOR INFORMATION

Corresponding Author

*E-mail: murugesan@petronas.com.my; tmgesan_57@yahoo.com.

Funding Sources

The authors are grateful to the Ministry of Science, Technology, and Innovation (MOSTI), Malaysia for financial support (eScience Fund 03-02-02-SF0044).

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