



Thermodynamic properties of the mixtures of some ionic liquids with alcohols using a simple equation of state

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ABSTRACT

In the present work, we have used a simple equation of state called the GMA EoS to calculate the density of three ionic liquid mixtures including 1-butyl-3-methylimidazolium hexafluorophosphate, [BMIM] [PF₆] + methanol, 1-butyl-3-methylimidazolium tetrafluoroborate, [BMIM] [BF₄] + methanol, and [BMIM] [BF₄] + ethanol at different temperatures, pressures, and compositions. The isothermal compressibility, excess molar volumes, and excess Gibbs molar energy of these mixtures have been computed using this equation of state. The values of statistical parameters show that the GMA EoS can predict these thermodynamic properties very well within the experimental errors. The results show that isothermal compressibility of ionic liquids is lower than alcohols and the effect of temperature and pressure on the isothermal compressibility of ionic liquids is lower than alcohols. The excess molar volumes and excess molar Gibbs energy for these ionic liquid mixtures with alcohols are all negative at various temperatures and pressures over the whole composition range. The results have been interpreted in terms of intermolecular interactions and structural factors of the ionic liquids and alcohols.

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1. Introduction

Ionic liquids (ILs) are defined as pure compounds, consisting only of cations and anions, which melt at or below 100 °C [1]. They have attracted an increasing number of scientific investigations because of their unique physical and chemical properties such as nonvolatility, high thermal stability, large liquid range, high ionic conductivity, non-flammability, wide electrochemical windows, and excellent solubility in many organic and inorganic substances [2–4]. These special characteristics make them suitable for many applications. They are often used as a medium for clean liquid–liquid extraction processes [5], as recyclable alternatives to organic solvents, as catalysts for organic and organometallic synthesis [1,2], as green solvents [1,3], and as media for analytical and physical chemistry [5]. In fact, they have been successfully employed in separation procedures, membrane technology, and as thermal fluids. Some of them have been used as lubricants and in biocatalysis with great advantages [2].

Binary mixtures of ILs with other fluids have been used for electrochemical applications (solar cells) [6]. The IL mixtures can also improve the thermodynamic and transport properties of working fluids as well as the efficiency of the chemical equipments such as batteries, photoelectrical cells, and other electrochemical apparatus. The use of the mixtures of ILs with other compounds such as alcohols

allows change and control of the properties of the mixtures to suit a given situation [6].

Thermodynamic properties of mixtures containing ionic liquids and alcohols are important for both the design of many technological processes and an understanding of the solute–solvent interactions in mixtures. These properties are required in the development of models for process design, energy efficiency, and in the evaluation of possible environmental impacts [7]. Volumetric properties of IL mixtures such as density and excess volume are some of the most important thermodynamic properties. The densities of a binary mixture containing ionic liquids are important from the theoretical viewpoint since these values can help to understand the theory of these liquids. The values of excess volume provide very useful information on the structural and intermolecular interactions between the ILs and alcohols [8]. Introduction of an alcohol to an IL alters the thermodynamic properties of ILs. The interpretation of the property changes and the ability to understand the fundamental mechanism at the molecular level are very difficult due to the complexity of the interactions between the ILs and alcohol molecules. In spite of the interest and practical importance of the mixtures of ILs with alcohols, there is a little work devoted to study their thermodynamic properties [4,6–8].

To exploit the potential of these new substances, it would be of great value to have prediction methods that can reliably predict the thermodynamic properties of ionic liquids and their mixtures with other compounds. This would help us to find a suitable ionic liquid for a certain task or to design new ionic liquids for special applications.

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Equations of states have been widely used for the calculation and prediction of thermodynamic properties needed in many technological theoretical processes. The purpose of the present paper is to reproduce and predict the volumetric properties such as density, isothermal compressibility, excess molar volume, and excess molar Gibbs energy of three ionic liquid mixtures, namely, [BMIM] [PF₆] + methanol, [BMIM] [BF₄] + methanol, and [BMIM] [BF₄] + ethanol at various temperatures, pressures, and compositions using the GMA equation of state and compare the results with the experimental data. A general equation of state has been derived for liquids by Goharshadi et al. [9] (Goharshadi–Morsali–Abbaspour “GMA EoS”). It has been used to calculate the different thermodynamic and volumetric properties such as density, isobaric expansion coefficient, and isothermal compressibility for a wide range of fluids including polar, nonpolar, and hydrogen-bonded fluids [9–13]. The GMA equation of state has been also applied for calculating the thermodynamic properties of liquid mixtures [13–18]. The equation of state is based on the average potential energy and is given as:

$$(2Z - 1)V_m^3 = A(T, X) + B(T, X)\rho \quad (1)$$

where Z , V_m , and ρ are compressibility factor, molar volume, and molar density, respectively. The intercept and slope of this equation depend on temperature via the equations:

$$A(T, X) = A_0 - 2A_1/RT + 2A_2 \ln T/R \quad (2)$$

$$B(T, X) = B_0 - 2B_1/RT + 2B_2 \ln T/R \quad (3)$$

where $A_0 - A_2$ and $B_0 - B_2$ are constants. To use the equation of state for a liquid, the A and B parameters must be known. To find these parameters, we may plot $(2Z - 1)V_m^3$ against ρ for different isotherms. The slope and intercept of the straight lines can be fitted with Eqs. (2) and (3) from which $A_0 - A_2$ and $B_0 - B_2$ can be found, respectively.

2. Results and discussion

2.1. Experimental test of the GMA EoS

Table 1 summarizes the formula and the temperature and pressure ranges of the ionic liquid mixtures of studied. The experimental PVT data of some ionic liquid mixtures at various temperatures and compositions have been used to examine the linearity of $(2Z - 1)V_m^3$ versus ρ (Eq. (1)). Figs. 1 and 2 show the isotherms of $(2Z - 1)V_m^3$ versus ρ for [BMIM] [BF₄] + ethanol at 298.15 K for different mole fractions and for [BMIM] [BF₄] + ethanol at $x = 0.5384$ at different temperatures, respectively. Table 2 shows the intercept (A), slope (B) of the fitted straight line (Eq. (1)), and the square of the correlation coefficient (R^2) for binary ionic liquid mixtures with methanol and ethanol at each temperature and composition. The values of the square of correlation coefficient confirm the linearity of Eq. (1) for all mixtures. Moreover, the density of three ionic liquid mixtures can be

Table 1

Formula and temperature and pressure ranges of the mixtures.

Compound	Formula	ΔT (k)	ΔP (MPa)	Ref.
[BMIM] [PF ₆] + methanol	C ₈ H ₁₅ N ₂ PF ₆ /CH ₃ OH	298.15–398.15	0.1–40	[23]
[BMIM] [BF ₄] + methanol	C ₈ H ₁₅ N ₂ BF ₄ /CH ₃ OH	298.15–398.15	0.1–40	[6]
[BMIM] [BF ₄] + ethanol	C ₈ H ₁₅ N ₂ BF ₄ /C ₂ H ₅ OH	298.15–398.15	0.1–40	[8]

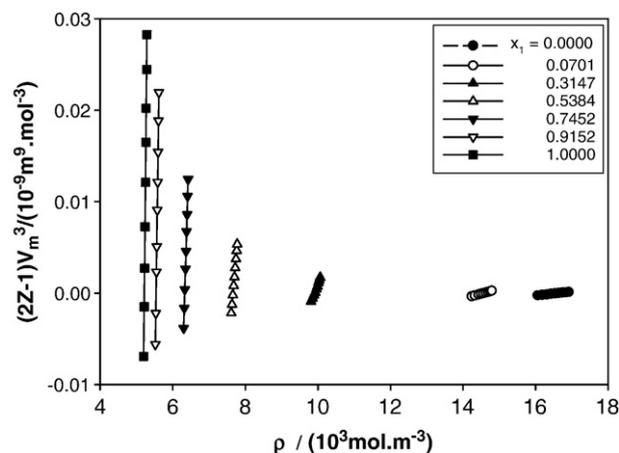


Fig. 1. $(2Z - 1)V_m^3$ versus ρ for [BMIM] [BF₄] (x) + ethanol ($1 - x$) mixtures at 298.15 K.

calculated based on the GMA EoS at different temperatures, pressures, and compositions by the following equation:

$$B(T, X)\rho^5 + A(T, X)\rho^4 + \rho - 2P/RT = 0 \quad (4)$$

The results have been compared with their corresponding experimental data using the statistical parameters, namely, the absolute average deviation (AAD) and the average percentile deviation (bias). They are defined as follows:

$$AAD = 1/N \sum_{i=1}^N 100 |Y_{\text{exp}} - Y_{\text{cal}} / Y_{\text{exp}}| \quad (5)$$

$$\text{bias} = 1/N \sum_{i=1}^N 100 (Y_{\text{exp}} - Y_{\text{cal}} / Y_{\text{exp}}) \quad (6)$$

where Y stands for each thermodynamic property.

The percent deviations between the experimental density data and those calculated based on the GMA EoS for pure methanol, pure [BMIM] [PF₆], and [BMIM] [PF₆] + methanol at different temperatures and compositions have been shown in Fig. 3. Table 3 presents the statistical parameters AAD, bias, and the number of data points for density of three ionic liquid mixtures. The values of AAD and bias show that the GMA EoS can reproduce the density with relatively high precision.

Isothermal compressibility coefficient, $\kappa_T = -(1/V)(\partial V/\partial P)_T$, for three ionic liquid mixtures with methanol and ethanol has been

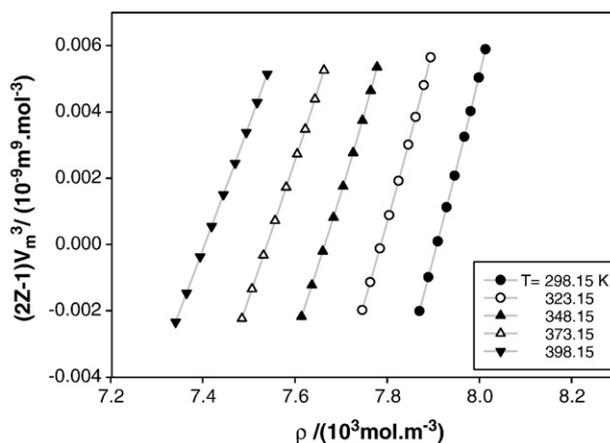


Fig. 2. $(2Z - 1)V_m^3$ versus ρ for [BMIM] [BF₄] (x) + ethanol ($1 - x$) at $x = 0.5384$.

Table 2
The intercept (*A*), slope (*B*), and square of correlation coefficient (*R*²) of Eq. (1) for three ionic liquid mixtures.

<i>x</i>	<i>T</i> (K)	<i>A</i> (10 ⁻⁹ m ⁹ mol ⁻³)	<i>B</i> (10 ⁻¹² m ¹² mol ⁻⁴)	<i>R</i> ²	<i>x</i>	<i>T</i> (K)	<i>A</i> (10 ⁻⁹ m ⁹ mol ⁻³)	<i>B</i> (10 ⁻¹² m ¹² mol ⁻⁴)	<i>R</i> ²
[BMIM][PF₆] (<i>x</i>) + Methanol (1–<i>x</i>)					[BMIM][BF₄] (<i>x</i>) + Methanol (1–<i>x</i>)				
0.00000	298.15	–0.002038	0.000080	0.9999	0.0000	298.15	–0.002033	0.000080	1.0000
	323.15	–0.001840	0.000074	0.9999		323.15	–0.001838	0.000074	1.0000
	348.15	–0.001669	0.000069	1.0000		348.15	–0.001666	0.000069	1.0000
	373.15	–0.001516	0.000064	1.0000		373.15	–0.001516	0.000064	1.0000
	398.15	–0.001373	0.000060	1.0000		398.15	–0.001396	0.000061	0.9986
0.02297	298.15	–0.003273	0.000141	0.9993	0.0088	298.15	–0.002404	0.000098	0.9999
	323.15	–0.002989	0.000132	0.9982		323.15	–0.002180	0.000091	0.9997
	348.15	–0.002790	0.000126	0.9985		348.15	–0.001961	0.000084	0.9999
	373.15	–0.002468	0.000114	0.9988		373.15	–0.001798	0.000079	0.9997
	398.15	–0.002120	0.000100	0.9981		398.15	–0.001646	0.000074	0.9991
0.08317	298.15	–0.008711	0.000460	0.9994	0.0433	298.15	–0.004501	0.000205	0.9996
	323.15	–0.007930	0.000428	0.9993		323.15	–0.003910	0.000182	0.9993
	348.15	–0.007284	0.000402	0.9993		348.15	–0.003450	0.000164	0.9993
	373.15	–0.006457	0.000363	0.9994		373.15	–0.003248	0.000158	0.9985
	398.15	–0.005705	0.000326	0.9996		398.15	–0.002958	0.000147	0.9979
0.26147	298.15	–0.065889	0.005461	0.9999	0.1302	298.15	–0.014679	0.000850	0.9984
	323.15	–0.058999	0.004974	1.0000		323.15	–0.012083	0.000714	1.0000
	348.15	–0.052188	0.004477	1.0000		348.15	–0.010927	0.000657	0.9987
	373.15	–0.046184	0.004034	0.9999		373.15	–0.010039	0.000616	0.9997
	398.15	–0.040947	0.003644	1.0000		398.15	–0.009298	0.000582	0.9999
0.49343	298.15	–0.365031	0.044550	0.9999	0.2626	298.15	–0.053950	0.004163	0.9983
	323.15	–0.318367	0.039499	1.0000		323.15	–0.046109	0.003618	0.9997
	348.15	–0.283189	0.035718	1.0000		348.15	–0.040073	0.003200	1.0000
	373.15	–0.255906	0.032823	0.9999		373.15	–0.035504	0.002884	0.9998
	398.15	–0.222178	0.029021	1.0000		398.15	–0.031769	0.002628	0.9997
0.75255	298.15	–1.356650	0.225027	0.9998	0.4988	298.15	–0.282354	0.031602	0.9995
	323.15	–1.183250	0.199540	0.9998		323.15	–0.250303	0.028468	0.9992
	348.15	–1.056150	0.180999	1.0000		348.15	–0.216666	0.025027	0.9999
	373.15	–0.959603	0.167139	1.0000		373.15	–0.187226	0.021977	1.0000
	398.15	–0.828461	0.146853	1.0000		398.15	–0.161138	0.019216	0.9998
0.90612	298.15	–2.518980	0.483298	0.9997	0.7501	298.15	–1.022710	0.152494	1.0000
	323.15	–2.192050	0.427642	0.9997		323.15	–0.883787	0.133806	1.0000
	348.15	–1.956310	0.387804	1.0000		348.15	–0.766054	0.117746	1.0000
	373.15	–1.779900	0.358519	1.0000		373.15	–0.671522	0.104774	0.9999
	398.15	–1.533190	0.314198	1.0000		398.15	–0.594846	0.094189	1.0000
1.00000	298.15	–3.587950	0.745325	0.9999	0.9102	298.15	–1.937320	0.334786	0.9999
	323.15	–3.063390	0.647209	0.9997		323.15	–1.694550	0.297319	1.0000
	348.15	–2.721990	0.584324	0.9997		348.15	–1.459580	0.259934	0.9999
	373.15	–2.494660	0.544024	1.0000		373.15	–1.297670	0.234470	1.0000
	398.15	–2.320350	0.513741	0.9999		398.15	–1.154010	0.211506	1.0000
1.0000	298.15	–2.685190	0.499891	0.9996	0.5384	298.15	–0.429126	0.054283	0.9996
	323.15	–2.329620	0.440245	1.0000		323.15	–0.392040	0.050366	0.9994
	348.15	–2.015670	0.386536	0.9993		348.15	–0.344282	0.044932	0.9990
	373.15	–1.794520	0.349101	0.9999		373.15	–0.313930	0.041653	0.9999
	398.15	–1.610020	0.317623	0.9993		398.15	–0.276098	0.037302	0.9999
[BMIM][BF₄] (<i>x</i>) + Ethanol (1–<i>x</i>)									
0.0000	298.15	–0.009323	0.000535	0.9999	0.7452	298.15	–1.061720	0.162698	0.9997
	323.15	–0.008199	0.000481	1.0000		323.15	–0.947957	0.147491	0.9998
	348.15	–0.007227	0.000435	0.9999		348.15	–0.828191	0.130844	0.9995
	373.15	–0.006377	0.000394	0.9999		373.15	–0.751106	0.120480	0.9995
	398.15	–0.005627	0.000359	1.0000		398.15	–0.659846	0.107547	0.9999
0.0701	298.15	–0.018980	0.001251	0.9997	0.9152	298.15	–2.002370	0.350821	0.9999
	323.15	–0.017485	0.001175	0.9991		323.15	–1.754470	0.312055	0.9999
	348.15	–0.015934	0.001094	0.9980		348.15	–1.537960	0.277641	0.9999
	373.15	–0.013949	0.000981	0.9998		373.15	–1.373350	0.251627	0.9999
	398.15	–0.012607	0.000907	0.9974		398.15	–1.230150	0.228654	1.0000
0.3147	298.15	–0.016046	0.001484	0.9998	1.0000	298.15	–2.656960	0.494635	0.9997
	323.15	–0.015559	0.001456	0.9994		323.15	–2.329620	0.440245	1.0000
	348.15	–0.014626	0.001382	0.9988		348.15	–2.015610	0.386525	0.9993
	373.15	–0.013587	0.001296	0.9997		373.15	–1.794510	0.349099	0.9999
	398.15	–0.012792	0.001233	0.9999		398.15	–1.610000	0.317619	0.9993

calculated at different temperatures, pressures, and compositions based on the GMA EoS using the following equation:

$$\kappa_T = \frac{2}{\rho RT + 4\rho^4(RTA_0 - 2A_1 + 2TA_2 \ln T) + 5\rho^5(B_0RT - 2B_1 + 2B_2T \ln T)} \quad (7)$$

The statistical parameters for isothermal compressibility coefficient of the three ionic liquid mixtures have been given in Table 4. The values of

statistical parameters confirm the reliability of the GMA EoS in predicting and reproducing the isothermal compressibility of the ionic liquid mixtures. Fig. 4 shows isothermal compressibility coefficient as a function of pressure for different temperatures for methanol, ethanol, [BMIM][PF₆], and [BMIM][BF₄]. The isothermal compressibility coefficient of studied alcohols and ionic liquids increases with increasing temperature and decreases with increasing pressure (Fig. 4). When a fluid is pressurized, the molecular distance decreases, resulting in a less compressible fluid. Raising temperature increases the molecular motions due to a larger free

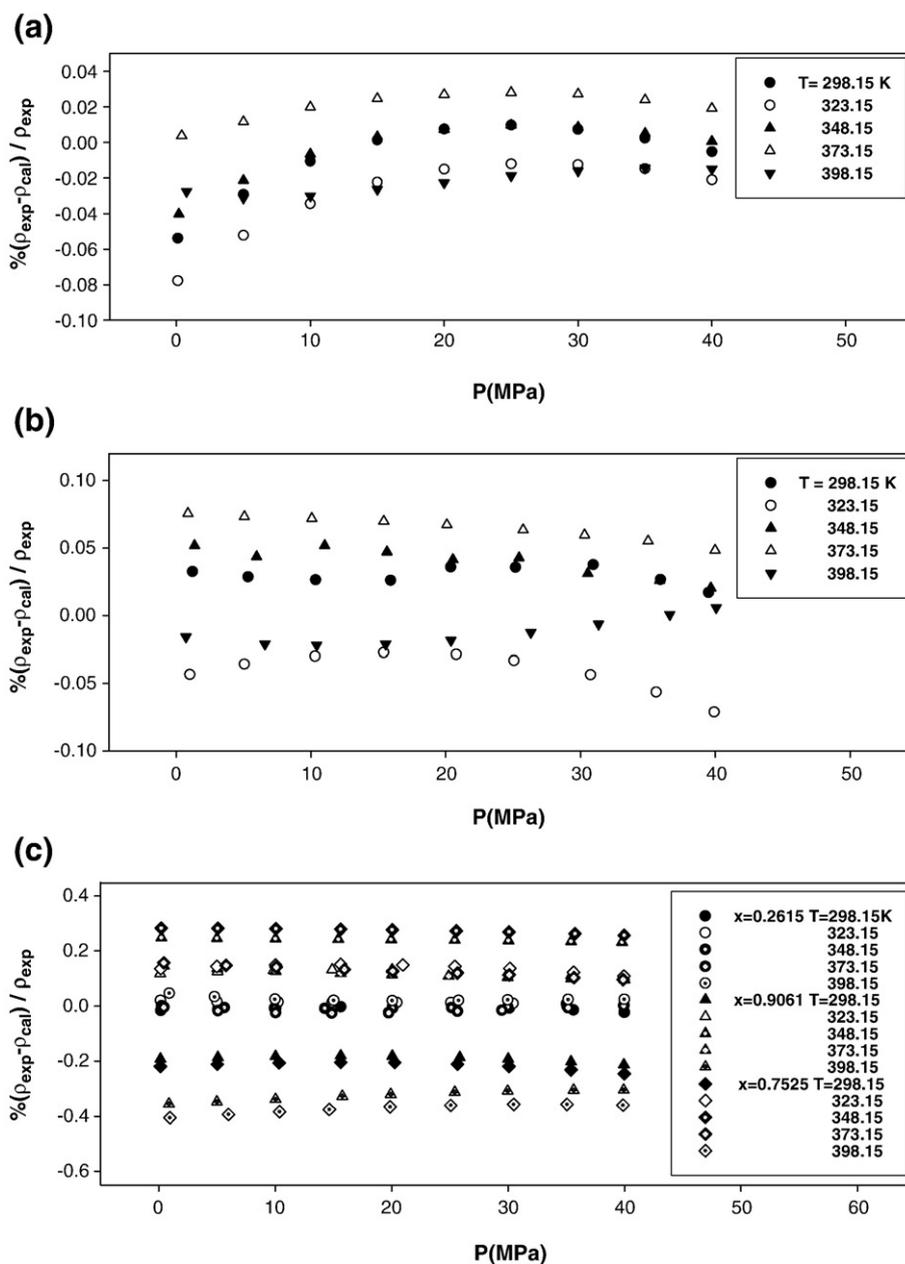


Fig. 3. Percent deviation between the calculated and experimental data for density (a) pure methanol (b) pure BMIMPF₆ (c) [BMIM] [PF₆] + methanol at different temperatures and compositions.

Table 3
The statistical parameters of density for ionic liquid mixtures.

x	Bias	AAD	NP	x	Bias	AAD	NP
[BMIM] [PF ₆] (x) + methanol (1-x)				0.1302	-0.0188	0.0795	45
0.00000	-0.0085	0.0196	45	0.2626	-0.0106	0.0248	45
0.02297	-0.0254	0.0738	45	0.4988	0.0052	0.0204	45
0.08317	-0.0378	0.0497	45	0.7501	-0.0013	0.0047	45
0.26147	0.0017	0.0136	45	0.9102	-0.0049	0.0081	45
0.49343	0.0018	0.0185	45	1.0000	-0.1923	0.1923	45
0.75255	-0.0075	0.1989	45	[BMIM] [BF ₄] (x) + ethanol (1-x)			
0.90612	-0.0106	0.2257	45	0.0000	0.5570	0.5570	45
1.00000	0.0162	0.0378	45	0.0701	-0.0380	0.0653	45
[BMIM] [BF ₄] (x) + methanol (1-x)				0.5384	0.1864	0.1864	45
0.0000	0.0080	0.0515	45	0.7452	-0.6646	0.6646	45
0.0088	-0.0269	0.0351	45	0.9152	-0.4524	0.4524	45
0.0433	-0.0449	0.0634	45	1.0000	-0.1252	0.1252	45

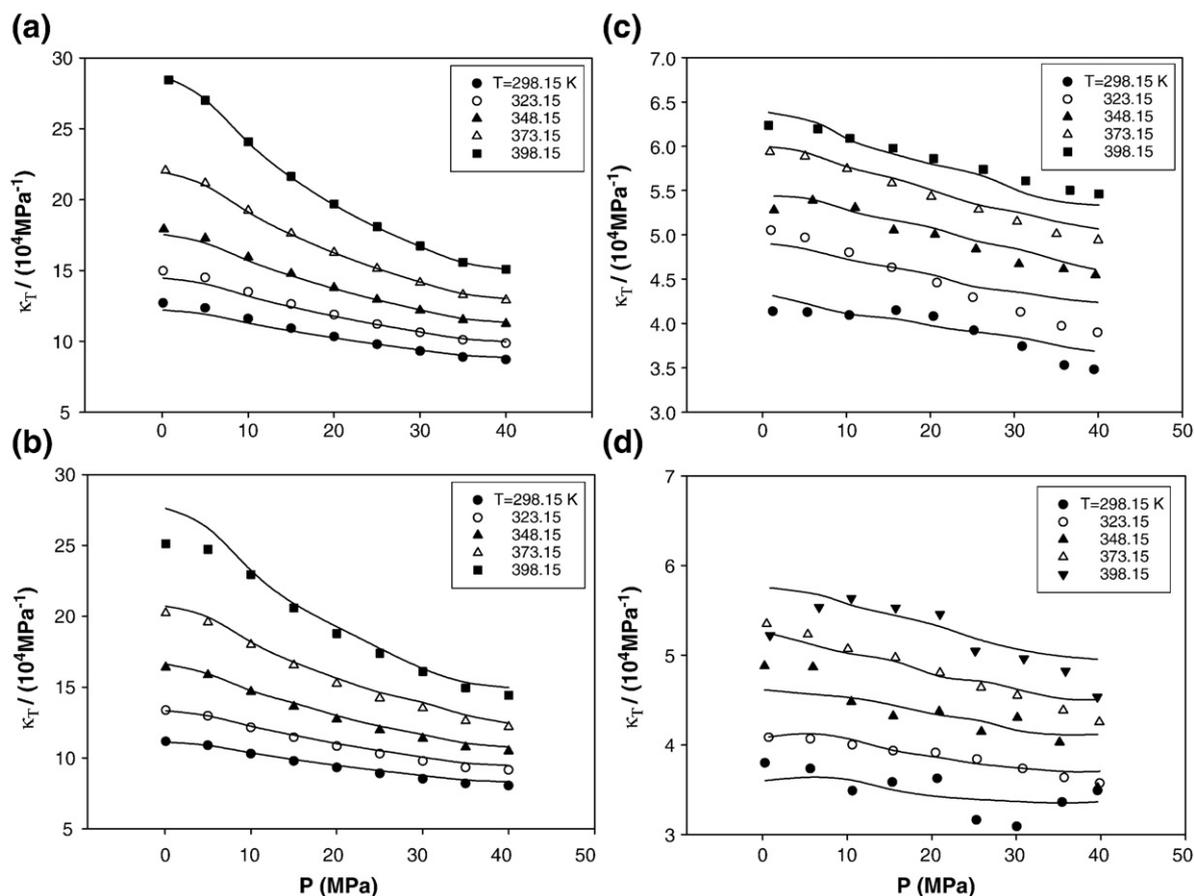


Fig. 4. Isothermal compressibility coefficient versus pressure for (a) methanol (b) ethanol (c) [BMIM] [PF₆] (d) [BMIM] [BF₄] at different temperatures.

volume and molecular distance, resulting in a more compressible fluid. The values of isothermal compressibility of [BMIM] [PF₆] and [BMIM] [BF₄] for temperatures 298.15 to 398.15 K at 0.1 MPa vary from 4.1 to 6.3 (10^{-4} MPa⁻¹) and 3.7 to 5.2 (10^{-4} MPa⁻¹), respectively. The values of isothermal compressibility of methanol and ethanol at the same ranges of temperatures and at 0.1 MPa vary from 12 to 28 (10^{-4} MPa⁻¹) and 11 to 25 (10^{-4} MPa⁻¹), respectively. The values of isothermal compressibility of ionic liquids are significantly lower than those of alcohols. It is plausible to say that the intermolecular interactions of ILs are stronger than those of alcohols. The same behavior was observed for 1-ethyl-3-methylimidazolium ethylsulfate, [C₂mim] [EtSO₄] [19]. The effect of temperature and pressure on the isothermal compressibility of ILs is lower compared with alcohols. Fig. 5 displays the isothermal compressibility coefficient versus pressure for the mixtures [BMIM] [PF₆] + methanol ($x=0.75255$) and

[BMIM] [BF₄] + methanol ($x=0.7501$) at different temperatures. The values of isothermal compressibility of ILs mixtures with alcohols are near those of pure ionic liquids for the same temperature and pressure. It seems that ILs play the key role in the isothermal compressibility of these mixtures. This may be explained by stronger molecular interactions of ILs as compared with alcohols. Fig. 6 shows the isothermal compressibility versus mole fractions for [BMIM] [PF₆] + methanol and [BMIM] [BF₄] + methanol at different temperatures. Both mixtures follow the same trend for the dependency of isothermal compressibility on mole fraction. As Fig. 6 shows moving along the ionic liquid-rich phase, the compressibility falls from a high value for pure methanol to the considerably lower value for ionic liquids. This decrease is strongly nonlinear being very steep at low concentrations of the ionic liquid. Therefore, a solution acquires the volumetric properties typical for the

Table 4

AAD and bias of calculated and experimental isothermal compressibility for ionic liquid mixtures.

x	Bias	AAD	x	Bias	AAD
[BMIM] [PF ₆] (x) + methanol (1-x)			[BMIM][BF ₄] (x) + ethanol (1-x)		
0.00000	0.5629	1.0230	0.0000	-2.1604	2.1940
0.02297	0.7183	4.2791	0.0701	-1.2727	5.3130
0.08317	1.1342	4.4540	0.5384	-2.7607	3.9453
0.26147	-0.2167	1.2468	0.7452	1.4775	3.4608
0.49343	-0.0369	1.2815	0.9152	1.0156	2.2573
0.75255	-0.7036	2.0294	1.0000	-1.0152	3.2358
0.90612	-1.4445	2.8947			
1.00000	-1.2021	2.3146			
[BMIM] [BF ₄] (x) + methanol (1-x)					
0.0000	0.5281	1.5239			
0.0088	0.3104	1.6274			
0.0433	0.7656	5.0241			

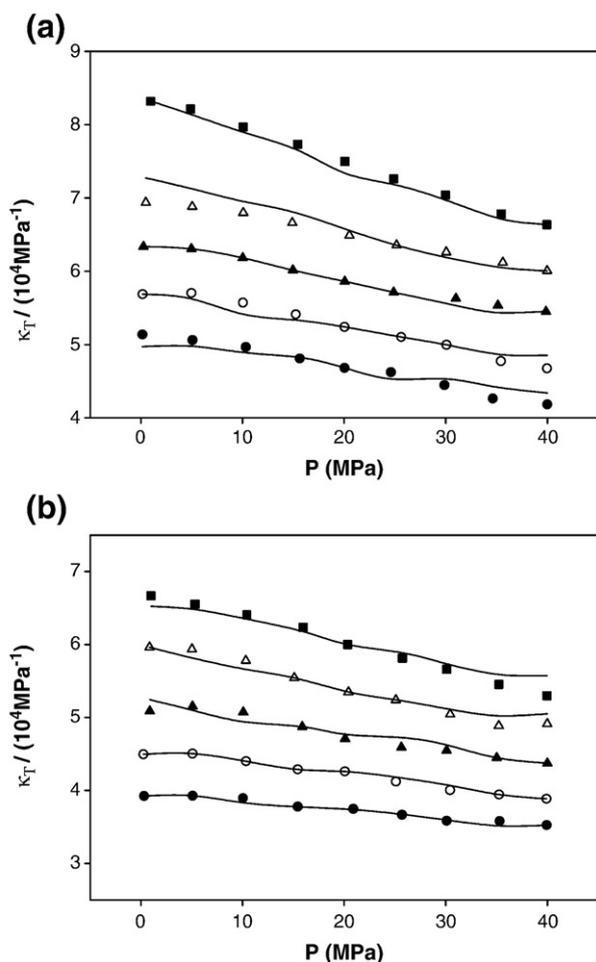


Fig. 5. Isothermal compressibility coefficient versus pressure for (a) methanol + [BMIM] [PF₆] at $x = 0.75255$ and (b) methanol + [BMIM] [BF₄] at $x = 0.7501$ for 298.15 K (●), 323.15 K (○), 348.15 K (▲), 373.15 K (△), 398.15 K (■). The symbols are experimental data and the solid curves are calculated data.

ionic liquid very quickly, beginning from $x = 0.2$. Hence, even in such diluted solutions, the peculiar structure of ionic liquids is preserved. Similar results for [C₂mim] [EtSO₄] + methanol were reported by Hofman et al. [19].

The following equations are used for calculating the excess molar volume and excess molar Gibbs energy, respectively.

$$V_m^E(P, T, x) = V_m(P, T, x) - x_1 V_{m,1}(P, T) - x_2 V_{m,2}(P, T) \quad (8)$$

$$\Delta G_m^E = \int_{P_0}^P V_m^E dp \quad (9)$$

where $V_m(P, T, x)$ is the molar volume of the mixture at concentration x for a given temperature T and pressure P , and $V_{m,1}(P, T)$ and $V_{m,2}(P, T)$ are the molar volumes of the pure components at the same temperature and pressure. The values of excess Gibbs energy are calculated by integration from excess volume.

Figs. 7 and 8 show the experimental and calculated values of excess molar volumes. Fig. 7(a) displays the value of excess molar volumes for the [BMIM] [PF₆] + methanol system at 30 MPa and Fig. 7 (b) shows the value of excess molar volumes for the same mixture at 373.15 K. Fig. 8 shows the excess molar volumes against mole fraction at 10 and 30 MPa for [BMIM] [PF₆] + methanol and [BMIM] [BF₄] + methanol at 298.15 K. There is a good agreement between the calculated and experimental values of excess molar volumes for these mixtures.

It is evident that the excess molar volumes for the mixtures of [BMIM] [PF₆] + methanol and [BMIM] [BF₄] + methanol are all negative at different temperatures and pressures over the whole composition range. Therefore, these mixtures are members of a class often called “attractive” mixtures. Similar behaviors were observed for the mixture of [C₄mim] [PF₆] + acetone, [C₄mim] [PF₆] + 2-butanone, [C₄mim] [PF₆] + pentanone [2], and [C₂mim] [EtSO₄] + methanol [19]. The negative values of excess molar volumes indicate that there are strong attractive attractions between ILs and alcohols. Hence, the strength of the intermolecular hydrogen bonding is not only one factor influencing the excess molar volume. The molecular size and shape of the components and the packing effect are equally important factors. Four opposing sets of factors influence on the values of excess molar volumes of the mixtures of ILs with alcohols: expansion of an alcohol due to breaking of some of the hydrogen bonds of an alcohol during addition of the ILs, contraction due to specific interactions of an alcohol molecule with an IL, size difference, and expansion due to steric repulsion between alkyl chain of an alcohol and that of ILs. The molar volume for [BMIM] [PF₆] is $207.94 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$, which is greater than that of methanol ($40.74 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$) at 298.15 K at atmospheric pressure. This difference causes a relatively small alcohol molecule fits into the interstices upon mixing with ILs. This filling effect and also the ion-dipole interactions between alcohol and the imidazolium ring of the ionic liquids, all contribute to the negative values of the molar excess volumes.

A relatively strong pressure and temperature influence on the values of excess volumes of the mixtures of ILs with alcohols is observed. The

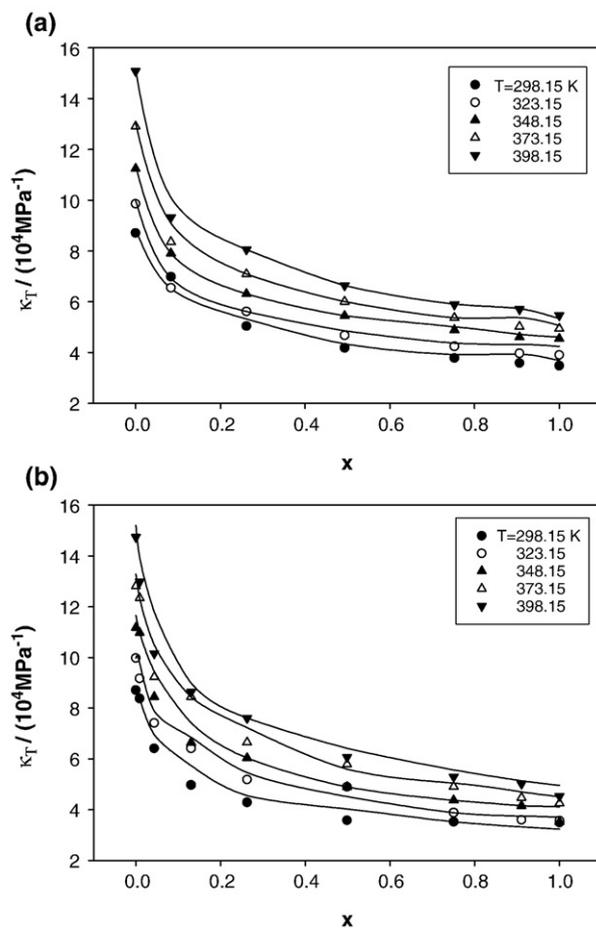


Fig. 6. Isothermal compressibility of (a) [BMIM] [PF₆] + methanol and (b) [BMIM] [BF₄] + methanol versus mole fraction at $P = 40$ MPa. The symbols are experimental data and the solid curves are calculated data.

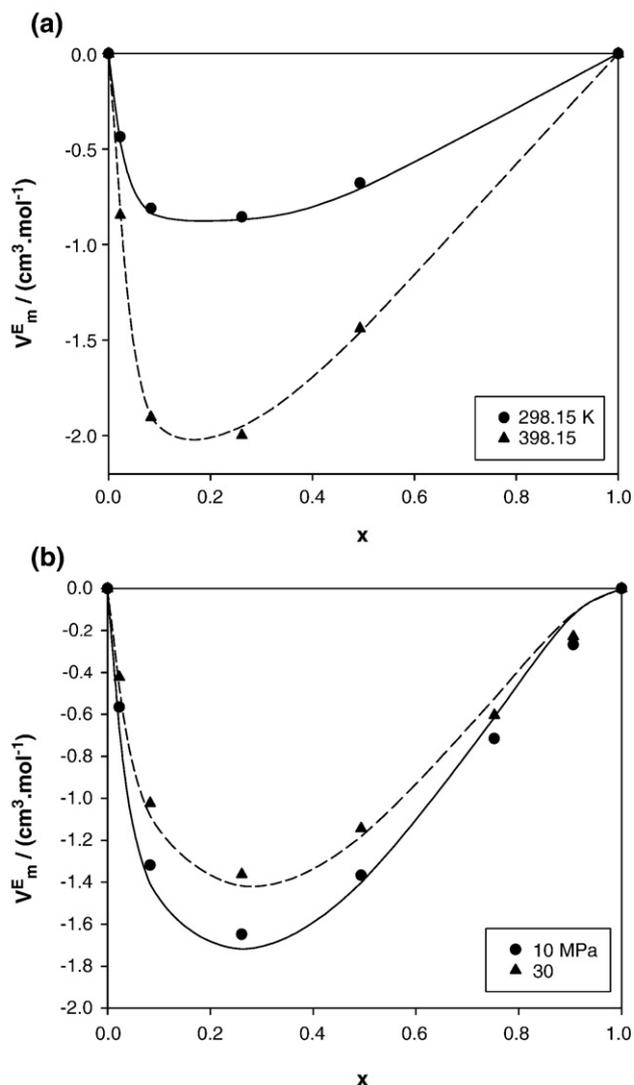


Fig. 7. Experimental (symbols) and calculated (solid lines) excess molar volumes for the [BMIM] [PF₆] (*x*) + methanol (1 – *x*) system versus mole fraction (a) at 30 MPa for two temperatures (b) at 373.15 K for two pressures.

excess molar volume becomes more negative with increasing the temperature and decreasing the pressure (Fig. 7(a) and (b)). As figures show, the curves of excess molar volumes of methanol + [BMIM] [PF₆] and methanol + [BMIM] [BF₄] mixtures are noticeably skewed towards low mole fraction of [BMIM] [PF₆] and [BMIM] [BF₄], respectively. It is more interesting that the minimum of excess molar volume occurs approximately between 0.2 and 0.3 mole fraction of ILs. The same behavior was observed for other ILs mixtures containing alcohols [2,19–21]. This can be attributed partly to the large differences between the size of the ionic liquids and alcohol molecules and also to the specific interactions between highly associated (H-bonding) neutral molecules of alcohol and IL ions ([BF₄][−], [PF₆][−], and [BMIM]⁺) [19]. From these observations, it is plausible to suggest that an unusual structure appears in the vicinity of this particular composition (*x* ≈ 0.3) of the mixtures of ILs with alcohols.

As Fig. 8 shows, the values of excess molar volume for the mixtures of [BMIM] [BF₄] + methanol are more negative than those for the mixtures of [BMIM] [PF₆] + methanol in the ionic liquid-rich phase. The anion [BF₄][−] is smaller than [PF₆][−] and thus has high charge density. This means that [BMIM] [BF₄] interacts stronger than [BMIM] [PF₆] with methanol leading to more negative excess molar volume in [BMIM] [BF₄] + methanol mixture. The relative affinity of [BF₄][−] is greater than [PF₆][−] with alcohols. This trend is the same as was

observed by Jacob et al. [22]. Thus, the choice of anion has a dramatic effect on the excess molar volume of imidazolium-based ionic liquids with alcohols.

The excess molar Gibbs energy of these mixtures is negative at the whole concentration range (Fig. 9). This means that the mixtures of ILs with alcohols are miscible because of strong interactions between them. Again, similar to the excess molar volume the minimum of the Gibbs molar energy curve versus mole fraction occurs at *x* = 0.3.

3. Conclusions

Knowledge of the impact of different factors on the thermodynamic and excess properties of ionic liquids with other liquids is useful for developing ionic liquids as designer solvents. In the present paper, a simple equation of state has been used to reproduce and predict density, isothermal compressibility, excess molar volume, and excess molar Gibbs energy for three ionic liquid mixtures with alcohols at different temperatures, pressures, and compositions. The results show that the GMA EoS can apply for these ionic liquid mixtures successfully.

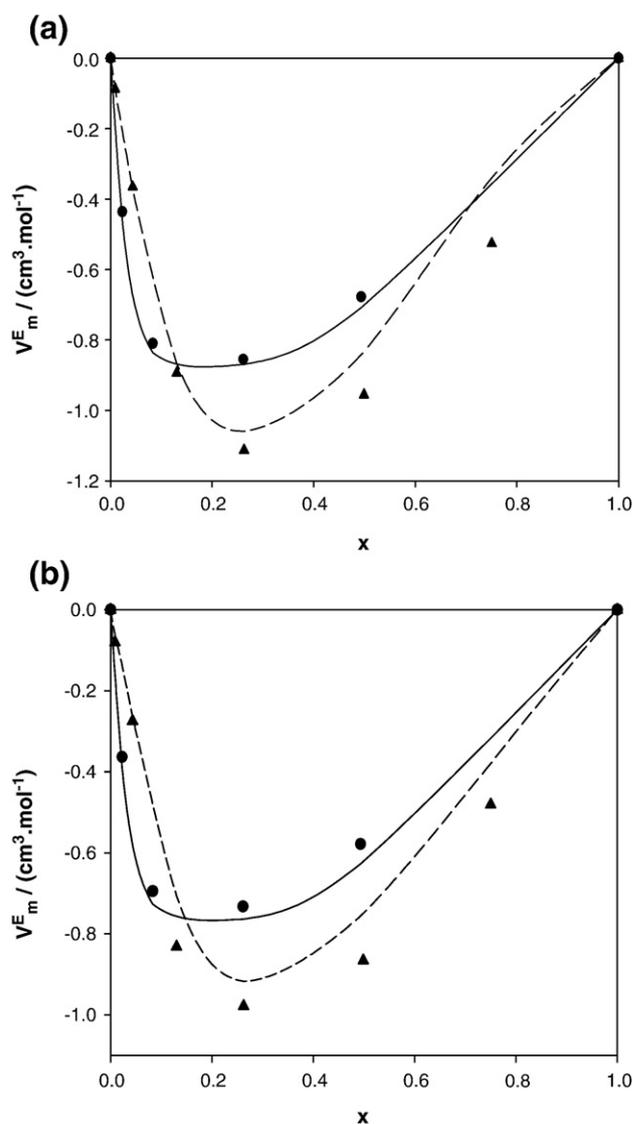


Fig. 8. Excess molar volume versus mole fraction for [BMIM] [PF₆] (*x*) + methanol (1 – *x*) (●) and [BMIM] [BF₄] (*x*) + methanol (1 – *x*) (▲) at 298.15 (a) 10 MPa and (b) 30 MPa. The symbols are the experimental values and the solid lines follow the calculated data.

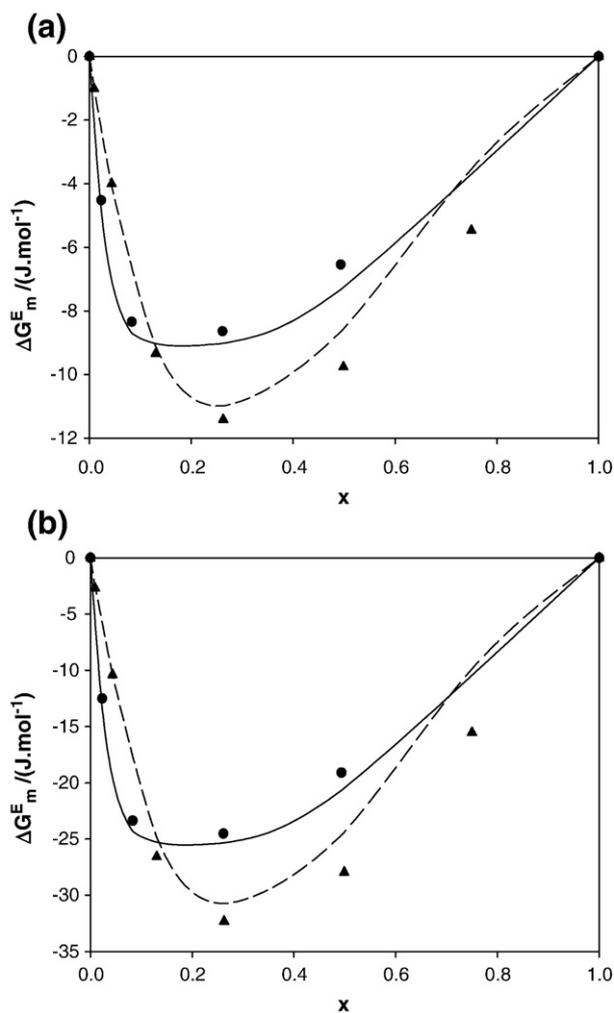


Fig. 9. Excess molar Gibbs energy versus mole fraction for [BMIM][PF₆](x) + methanol ($1-x$) (●) and [BMIM][BF₄](x) + methanol ($1-x$) (▲) at 298.15 (a) 10 MPa and (b) 30 MPa. The symbols are the experimental values and the solid lines follow the calculated data.

Isothermal compressibility falls from a high value for pure methanol to the considerably lower value for ionic liquids with

increasing the mole fraction of ionic liquid in the IL+alcohol mixtures. The negative excess molar volumes for these systems indicate that a more efficient packing and attractive interactions occur when the ionic liquid and alcohol are mixed. The minimum in the graphs of excess molar volumes and excess molar Gibbs energy versus mole fraction for these mixtures occurs at approximately a certain mole fraction. Changing [PF₆]⁻ with [BF₄]⁻, shifts the values of excess molar volume and excess molar Gibbs energy to the more negative values in the ionic liquid-rich phase. This shift is due to stronger attractive interactions becomes in the case of [BF₄]⁻.

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