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Osmotic Coefficients and Refractive Indices of Aqueous Solutions of Ionic Liquids Containing 1-Butyl-3-methylimidazolium Halide at T = (298.15 to 328.15) K

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Experimental results of the osmotic coefficients and refractive indices of aqueous solutions of ionic liquids containing 1-butyl-3-methylimidazolium chloride, [BMIm]Cl, and 1-butyl-3-methylimidazolium iodide, [BMIm]I, have been measured over the composition range of 3 mol·kg^{-1} at T = (298.15 to 328.15) K. The determination of experimental osmotic coefficients was performed by the vapor pressure osmometry method. The results show that osmotic coefficients increase when the concentration of ionic liquid and temperature increase. The osmotic coefficients were correlated to the Pitzer ion interaction and modified NRTL (MNRTL) models. From these data, mean activity coefficients and excess Gibbs free energies have been calculated. The results have been interpreted in terms of ion−solvent and ion−ion interactions and structural factors of the ionic liquid. Experimental results of refractive indices for the binary system are reported and have been fitted by a polynomial expansion.

Introduction

One of the most important types of organic salts is ionic liquids (ILs), which are liquids at or near room temperature in their pure state. They have been widely used in a number of fields in both academia and industry and exhibit many advantages such as a low melting point (< 373 K), a wide liquid range, suitable viscosity, thermal stability, the ability to dissolve a variety of materials, and most important, negligible vapor pressure.[1−3] ILs have been suggested as green and benign replacements for traditional volatile organic solvents, and a growing number of applications in the field of catalysis, chemical reactions, separations, electrochemistry and nanoscience investigations have been studied.[4−6] These developments demand reliable reference data on the thermophysical properties of their mixtures with other compounds. Measurements reveal ion−solvent and ion−ion interactions. Thermophysical properties of ILs are receiving increasing interest and are being studied more systematically. Aqueous solutions of ILs have been used in many processes, mainly for the synthesis of other ILs and extractive processes involving ILs on an industrial scale. To date, a number of papers have measured some physical properties of systems containing ILs such as the density, viscosity, speed of sound, surface tension, thermal conductivity, and phase equilibria. These papers mainly report these quantities over the whole composition range of ILs in water, and only some other works have been performed for dilute region solution of ILs.[7−17]

This Article is a continuation of a systematic study on the thermophysical properties of ILs and mixtures with ordinary molecular solvents.[18] In this work, we have measured osmotic coefficients, and refractive indices of aqueous solutions of ILs containing 1-butyl-3-methylimidazolium chloride, [BMIm]Cl, and 1-butyl-3-methylimidazolium iodide, [BMIm]I, at temperatures of T = (298.15 to 328.15) K. Experimental osmotic coefficients have been correlated with the Pitzer ion interaction model and one local composition model, the modified NRTL (MNRTL) electrolyte model.[19,20] By using Pitzer ion interaction parameters, also, mean activity coefficients and excess Gibbs energies of the studied ILs were obtained. The experimental results of refractive indices for theses studied systems are reported and have been fitted by a polynomial expansion.

Experimental Section

Chemicals. *N*-Methylimidazole (> 99 % mass fraction), 1-iodobutane (> 99 % mass fraction), 1-chlorobutane (> 99 % mass fraction), acetonitrile (GR, > 99.8 % mass fraction), and toluene (> 99 % mass fraction) were obtained from Merck. These reagents were used without further purification. Doubly distilled water with a specific conductivity of less than 1.3 μS·cm^{-1} was used for the preparation of solutions.

Synthesis of Ionic Liquids. [BMIm]Cl and [BMIm]I were synthesized and purified according to standard procedures described elsewhere.[21−23] Briefly, these ILs were synthesized by direct alkylation of *N*-methylimidazole (freshly distilled) with an excess of 1-cholobutane and 1-iodobutane in a round-bottomed flask at T = 353.15 K for 72 h under a nitrogen atmosphere. The crude product was dissolved in toluene, and the equilibrium was reached. The product was concentrated at T = 333.15 K using a rotary evaporator for at least 4 h under 0.7 kPa. These ILs were further dried under high vacuum at 353.15 K for 24 h to remove trace moisture. Water contents found by the Karl Fischer method in ILs was less than mass fraction 0.03 %. The obtained IL had a purity greater than mass fraction 0.98 %. We analyzed ILs by ^{1}H NMR (Brucker Av-300) and IR (Buck Scientific) spectra to confirm the absence of any major impurities, and they were found to be in good agreement with those reported in the literature.[24,25]

Experimental Procedure. We prepared the samples by filling glass vials with IL and doubly distilled water. Vials were closed tightly. The sample was taken from the vial with a syringe through a silicone septum and was immediately injected into the apparatus. The mass of chemicals was determined using a Sartrious analytical balance (AG TE214S Germany) with a precision of ± 1·10^{-4} g.

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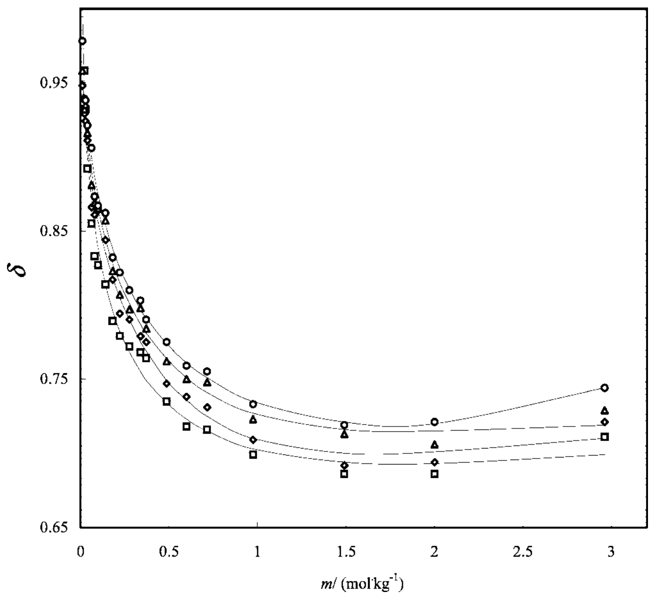

Figure 1. Osmotic coefficients of the ([BMIm]Cl + H_2O) system at experimental temperatures. Lines were generated using the MNRTL model. Data: □, 298.15 K; ◇, 308.15 K; △, 318.15 K; ○, 328.15 K.

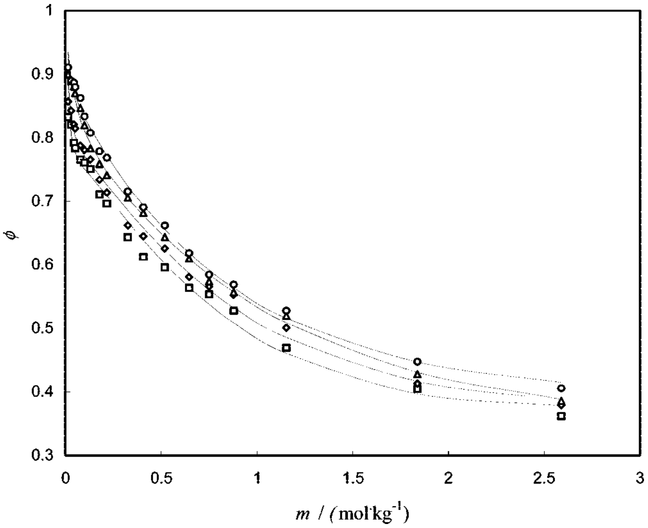

Figure 2. Osmotic coefficients of the ([BMIm]I + H_2O) system at experimental temperatures. Lines were generated using the MNRTL model. Data: □, 298.15 K; ◇, 308.15 K; △, 318.15 K; ○, 328.15 K.

Table 1. Experimental Osmotic Coefficients, ϕ, of Aqueous Solutions As a Function of Ionic Liquid Molality, m, at Different Temperature

	ϕ			
m/mol·kg^{-1}	T = 298.15 K	T = 308.15 K	T = 318.15 K	T = 328.15 K
		[BMIm]Cl + H_2O		
0.0105	1.004	0.948	0.958	0.978
0.0230	0.958	0.929	0.932	0.939
0.0289	0.932	0.924	0.935	0.938
0.0398	0.892	0.911	0.916	0.921
0.0621	0.855	0.866	0.881	0.906
0.0803	0.833	0.861	0.869	0.873
0.0986	0.827	0.864	0.865	0.867
0.1413	0.814	0.844	0.857	0.862
0.1816	0.789	0.817	0.823	0.832
0.2223	0.779	0.794	0.807	0.822
0.2764	0.772	0.790	0.797	0.810
0.3386	0.768	0.779	0.798	0.803
0.3710	0.764	0.775	0.784	0.790
0.4863	0.735	0.747	0.762	0.775
0.5990	0.718	0.738	0.750	0.759
0.7152	0.716	0.731	0.748	0.755
0.9754	0.699	0.709	0.723	0.733
1.4915	0.686	0.692	0.713	0.719
1.9999	0.686	0.694	0.706	0.721
2.9617	0.711	0.721	0.729	0.744
		[BMIm]I + H_2O		
0.0133	0.833	0.856	0.899	0.910
0.0293	0.821	0.843	0.888	0.889
0.0442	0.792	0.821	0.880	0.885
0.0505	0.784	0.814	0.869	0.878
0.0786	0.766	0.788	0.845	0.861
0.0995	0.761	0.780	0.819	0.833
0.1307	0.751	0.765	0.782	0.807
0.1782	0.711	0.734	0.758	0.778
0.2160	0.697	0.714	0.740	0.768
0.3257	0.644	0.662	0.706	0.715
0.4065	0.613	0.645	0.682	0.690
0.5184	0.596	0.626	0.644	0.662
0.6452	0.564	0.581	0.610	0.619
0.7509	0.554	0.566	0.574	0.586
0.8786	0.528	0.553	0.558	0.569
1.1538	0.470	0.501	0.521	0.528
1.8374	0.405	0.413	0.429	0.450
2.5889	0.362	0.380	0.387	0.408

Osmotic Coefficient Measurements. Osmotic coefficients were measured with the help of the vapor pressure osmometery method (VPO) K-7000 (Knauer). With this method, osmotic coefficients were indirectly determined by using voltage changes of thermistors caused by changes in the temperature. This type of osmometer, its principle of operation, and its application to the estimation of osmotic coefficients of IL solutions have been described in an earlier study.[26] Briefly, in the beginning, a droplet of pure solvent was attached to each thermistor, and after 5 min of equilibration, the reading was adjusted to zero. Then, the pure solvent on one of the thermistors was replaced by the IL solution. A change in temperature changed the resistance of the thermistors. As long as changes in the temperature were small, the resistance was proportional to ΔT. For aqueous solutions, the instrument was calibrated using NaCl reference solutions with known osmotic coefficients in the proper concentration range, yielding a function that correlated the panel readings to the corresponding concentrations of the reference solutions and their osmotic coefficients; then, under the same conditions, the panel readings were measured for the studied IL solutions. The standard uncertainty in the output of instrument was ± 1 Ω, and the maximum variation was within ± 2 % of the measured value. The cell temperature, which was electronically controlled, had a standard uncertainty of $\pm 1 \cdot 10^{-3}$ K. Special care was taken to keep the drop size and shape as constant as possible and equal on both thermistors. For each solution, at least five measurements (zero point adjustment and new solution) were performed, and the mean value was reported. Osmotic coefficients of aqueous solutions of NaCl were calculated with the help of the equation developed by Colin.[27] This equipment has been widely applied in measuring osmotic coefficients of electrolyte and nonelectrolyte solutions, especially for the dilute region, and has given good agreement in comparison with direct vapor pressure lowering. The uncertainty for the experimental osmotic coefficient was $< \pm 6 \cdot 10^{-3}$, and that for the calculated activity coefficient was $< \pm 2 \cdot 10^{-2}$.[28−30]

Refractive Index Measurements. Refractive indices of the studied systems at different temperature were determined using a digital refractometer (ATAGO-DRA1 Japan) with an uncertainty of $\pm 1 \cdot 10^{-4}$. The instrument was calibrated with doubly distilled water and tetrachloroethylene before each series of measurements according to the manual instruction. Calibration was checked with pure liquids with a known refractive index.

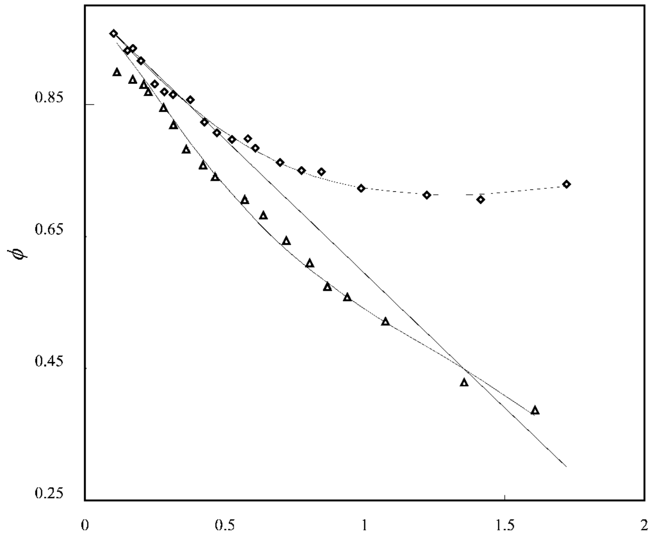

Figure 3. Comparison of osmotic coefficients of aqueous solutions of the studied ionic liquids system at $T = 328.15$ K: ◇, [BMIm]Cl; △, [BMIm]I.

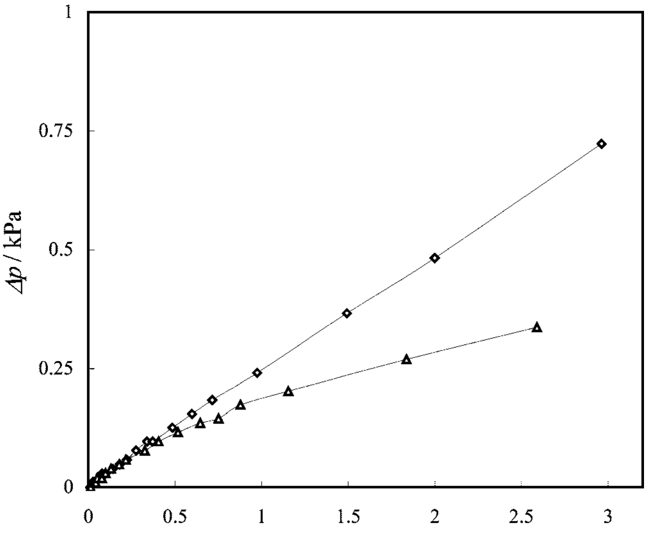

Figure 4. Vapor pressure depression of aqueous solutions of the studied ionic liquids system at $T = 328.15$ K: ◇, [BMIm]Cl; △, [BMIm]I.

Table 2. Second Virial Coefficient, B_s, Molar Volume, V_s, Density, d_s, Relative Permittivity, ε, Debye−Hückel Constant for the Osmotic Coefficient, A_ϕ, and Vapor Pressure of Pure Water, p^*, at the Experimental Temperatures

T	$10^6 \cdot B_s$	$10^6 \cdot V_s$	d_s	A_ϕ	p^*	
K	$m^3 \cdot mol^{-1}$	$m^3 \cdot mol^{-1}$	$kg \cdot m^{-3}$	$(kg \cdot mol^{-1})^{1/2}$	kPa	ε
298.15	−3272.9	18.07	997.043	0.39145	3.170	78.38
308.15	−1604.6	18.12	994.029	0.39849	5.629	74.86
318.15	−1421.1	18.19	990.168	0.40620	9.595	71.50
328.15	−1249.3	18.28	985.650	0.41456	15.763	68.29

Table 3. Parameters of the Pitzer Model for ([BMIm]X + H_2O) at Different Temperature

T/K	$\beta^{(0)}$	$\beta^{(1)}$	$C^{(\phi)}$	$\sigma(\phi)$
		[BMIm]Cl + H_2O		
298.15	0.04733	−1.20989	−0.01159	0.019
308.15	0.00362	−0.87037	0.00145	0.009
318.15	0.00307	−0.71597	0.00143	0.007
328.15	−0.01446	−0.53625	0.00796	0.007
		[BMIm]I + H_2O		
298.15	0.10814	−2.61306	−0.06777	0.043
308.15	0.04990	−2.15516	−0.04883	0.034
318.15	−0.08711	−1.35370	−0.00488	0.016
328.15	−0.13732	−1.01537	0.01395	0.012

Temperature was controlled with a circulating bath Julabo MP (Germany) thermostat with ± 0.02 K uncertainty in temperature.

Results and Discussion

The experimental osmotic coefficients ϕ of the aqueous solutions of ILs with molality, m, in equilibrium were obtained according to

$$\phi = (\nu_r m_r \phi_r)/(\nu m) \tag{1}$$

where ϕ_r, m_r, and ν_r are the osmotic coefficient, the molality, and the stoichiometric number of references electrolyte (NaCl), which are set to be equal to 2, respectively, showing the same instrument reading as the IL solution, which means that the vapor pressure (and therefore the solvent activity) is equal in both solutions.[19]

Table 1 gives the experimental osmotic coefficients, ϕ, of the aqueous solutions of ILs containing [BMIm]Cl and [BMIm]I at $T = (298.15$ to $328.15)$ K at intervals of 10 K using eq 1.

Figures 1 and 2 show the molal concentration dependence of the experimental osmotic coefficients for aqueous solutions of [BMIm]Cl and [BMIm]I at experimental temperatures of $T = (298.15$ to $328.15)$ K, respectively. As shown in these Figures, the osmotic coefficients increase only slightly when the temperature increases from (298.15 to 328.15) K. The behavior of the osmotic coefficients can be interpreted in terms of ion-solvation and ion-association interactions. Upon examination of these Figures, it is noted that the osmotic coefficients in the dilute region decrease with increasing concentration of ILs, showing the presence of nonideality due to ion-association interactions. Figure 3 shows that the osmotic coefficients of studied ILs vary versus the Debye−Hückel limiting law (DHLL) as follows: [BMIm]Cl > [BMIm]I at a temperature of 328.15 K. This indicates the effect of anion attached to imidazolium cation in the studied ILs. This Figure shows that there is a larger deviation from DHLL in aqueous solution [BMIm]Cl than in [BMIm]I. Negative deviations from DHLL for aqueous solutions of IL may be an indication of ion association, and positive deviations from DHLL may be an indication of ion-solvation interactions, that is, the stronger the ion solvation, the higher the osmotic coefficient.[31,32]

Activities, a_s, and vapor pressures, p, of aqueous solutions of ILs for the studied IL as a function of the molality of ILs, m, were calculated from the measured quantities of osmotic coefficients using the equations

$$\ln(a_s) = -\phi \nu m M_s \tag{2}$$

and

$$\ln a_s = \ln\left(\frac{p}{p^*}\right) + \frac{(B - V_s^*)(p - p^*)}{RT} \tag{3}$$

In the preceding equations, a_s is the activity of the solvent, T is the absolute temperature, p is the vapor pressure of the solution, and p^* is that of the pure solvent. B_s is the second virial coefficient, and V_s is the molar volume of pure solvent. The second virial coefficients and the molar volumes of pure water at $T = (298.15$ to $328.15)$ K are presented in Table 2.[33,34]

As can be seen from Figure 4, the calculated vapor pressure depression ($\Delta p = p^* - p$) values for the [BMIm]X + H_2O

Table 4. Parameters of the MNRTL Model for ([BMIm]X + H_2O) at Different Temperatures

T/K	$\tau_{ca,s}$	$\tau_{s,ca}$	$\omega_{ca,s}$	$\omega_{s,ca}$	$\sigma(\phi)$
		[BMIm]Cl + H_2O			
298.15	0.00022	0.53133	4.80666	−3.37357	0.007
308.15	0.00042	0.59739	5.58835	−3.61128	0.007
318.15	0.00054	0.50912	5.21572	−3.59603	0.007
328.15	−0.00047	0.62967	3.24265	−3.82272	0.008
		[BMIm]I + H_2O			
298.15	0.00865	2.11507	6.40646	−2.44467	0.015
308.15	0.19279	0.42059	2.25812	−6.89201	0.013
318.15	0.23336	0.25806	2.06739	−5.99583	0.011
328.15	0.17149	0.16106	2.27586	−7.08587	0.009

mixtures have the following order at 328.15 K: [BMIm]Cl + H_2O > [BMIm]I + H_2O. The extent of vapor pressure depression is related to ion−solvent interactions between IL and H_2O. This means that ion−solvent interactions occur more often in the [BMIm]Cl + H_2O system than in the other studied systems.

Pitzer Ion Interaction and MNRTL Models. Several models are available in the literature for the correlation of osmotic coefficients as a function of molalities. The three-parameters Pitzer-ion interaction model has been successfully used for aqueous electrolyte solutions and has the following form for a binary 1:1 electrolyte solution[19]

$$\phi - 1 = f^{\phi} + mB^{\phi} + m^2C^{\phi} \tag{4a}$$

where

$$f^{\phi} = \frac{-A_{\phi}I^{1/2}}{1 + bI^{1/2}} \tag{4b}$$

$$B^{\phi} = \beta^{(0)} + \beta^{(1)}\exp(-\alpha I^{1/2}) \tag{4c}$$

$$A_{\phi} = \left(\frac{1}{3}\right)\sqrt{2\pi N_A d_0}\left(\frac{e^2}{2\pi\varepsilon_0 D_e kT}\right)^{\frac{3}{2}} \tag{4d}$$

In these equations, $\beta^{(0)}$, $\beta^{(1)}$ and C^{ϕ} are ion-interaction parameters of the Pitzer model that are dependent on temperature and pressure, and A_{ϕ} is the Debye−Hückel constant for the osmotic coefficient on the molal scale. In eq 4d, N_A is Avogadro's number, e is the proton charge, ε_0 is the permittivity of vacuum, and k is the Boltzman constant. A_{ϕ} values calculated from eq 4d for water are given in Table 2 at temperatures of T = (298.15 to 328.15) K.[35] The term I is the ionic strength in molality, $I = (1/2)\Sigma m_i z_i^2$, where m_i is the molality of the ith ion and z_i is the absolute value for ith ionic charge. The remaining symbols have their usual meanings. The other constants were b = 1.2 $kg^{1/2}\cdot mol^{-1/2}$ and α = 2 $kg^{1/2}\cdot mol^{-1/2}$, which yield reliable fits for some aqueous electrolyte solutions. The Pitzer ion interaction model parameters of the studied systems are given in Table 3 using the nonlinear least-squares method.

The experimental osmotic coefficients in the studied ILs from the VPO method are also described formally by using the local composition MNRTL equation.[20] The MNRTL equation gives the best empirical description and has real physical meaning for the correlation of osmotic and activity coefficients. In the MNRTL model, the excess Gibbs free energy of an electrolyte solution and, consequently, the activity coefficients of solvent have been written as the sum of long-range (LR) and short-range (SR) contributions

$$\ln(\gamma_S) = \ln(\gamma_S^{LR}) + \ln(\gamma_S^{SR}) \tag{5}$$

where subscript s refers to solvent.

The LR contribution is represented by the Pitzer−Debye−Huckel (PDH) equation. The PDH equation for activity coefficient of component i is

$$\ln(\gamma_i^{PDH}) = -\left(\frac{1}{M_s}\right)^{\frac{1}{2}}A_{\phi}\left\{\frac{2z^2\ln(1+\rho I_x^{1/2})}{\rho} + \frac{z_i^2 I_x^{1/2} - 2I_x^{3/2}}{1+\rho I_x^{1/2}}\right\} \tag{6}$$

where I_x is the ionic strength on a mole fraction basis ($I_x = (1/2)\Sigma z_i^2 x_i$) and ρ is the closest distance parameter, and its value is 14.9 for aqueous solutions.

The MNRTL model represents the SR contribution for the solvent activity coefficient. In this equation there are four fitting parameters

$$\ln\gamma_{s,MNRTL} = 4X_c[\tau_{ca}W_{ca,s}/(X_s + 2\ \ W_{ca,s}X_c)^2 + \tau_{s,ca}(W_{s,ca} - 1)/(X_c + X_sW_{ca,s})^2] \tag{7}$$

in which $\tau_{ca,s}$ (salt-solvent parameter) and $\tau_{s,ca}$ (solvent-salt parameter) are the model parameters, and the following definition has been carried out

$$W_i = \exp(-\alpha\tau_i + \omega_i) \tag{8}$$

where the $\omega_{ca,s}$ and $\omega_{s,ca}$ are also adjustable parameters and α is the nonrandomness factor equal to 0.2, and $X_c = z_c x_c$, $X_a = z_a x_a$, and $X_s = x_s$.

The activity coefficient equation was converted to the osmotic coefficient ϕ via the following equation

$$\phi = -\ [\ln(\gamma_S^{LR}) + \ln(\gamma_S^{SR}) + \ln(x_s)]/\nu m M_s \tag{9}$$

In the preceding equation ν is the stoichiometric number of the IL, M_s ($kg\cdot mol^{-1}$) is the molar mass of the solvent, and x_s is the mole fraction of the solvent. The standard deviations obtained for the fit in the osmotic coefficients are defined as

$$\sigma(\phi) = \left(\sum_i(\phi_{exptl} - \phi_{calcd})^2/(N - m)\right)^{1/2} \tag{10}$$

where ϕ_{exptl}, ϕ_{calcd}, N, and m show experimental osmotic coefficients data, calculated osmotic coefficients values, the number of data, and the number of model parameters, respectively. The MNRTL model parameters of the studied systems are given in Table 4.

These values show that the Pitzer ion interaction and MNRTL models satisfactorily correlate with the experimental osmotic coefficients of aqueous solutions of studied ILs.

Determination of Mean Molal Activity Coefficient. The osmotic coefficients can be used in the calculation of the mean molal activity coefficients of the ILs. Application of the Gibbs−Dühem equation for eq 4a and the use of Pitzer model parameters gives

$$\ln\gamma_{\pm} = f^{\gamma} + mB^{\gamma} + m^2C^{\gamma} \tag{11a}$$

where

$$f^{\gamma} = -A_{\phi}\left[\frac{I^{1/2}}{1+bI^{1/2}} + \frac{2}{b}(1+bI^{1/2})\right] \tag{11b}$$

$$B^{\gamma} = 2\beta^{(0)} + \frac{2\beta^{(1)}}{\alpha^2 I}\left[1 - \left(1 + \alpha I^{1/2} - \frac{\alpha^2 I}{2}\right)\exp(-\alpha I^{1/2})\right] \tag{11c}$$

$$C^{\gamma} = \frac{3}{2}C^{\phi} \tag{11d}$$

The accuracy of the calculated $\gamma_{\pm}$ values depends on how well the model correlates with the osmotic coefficients data for the

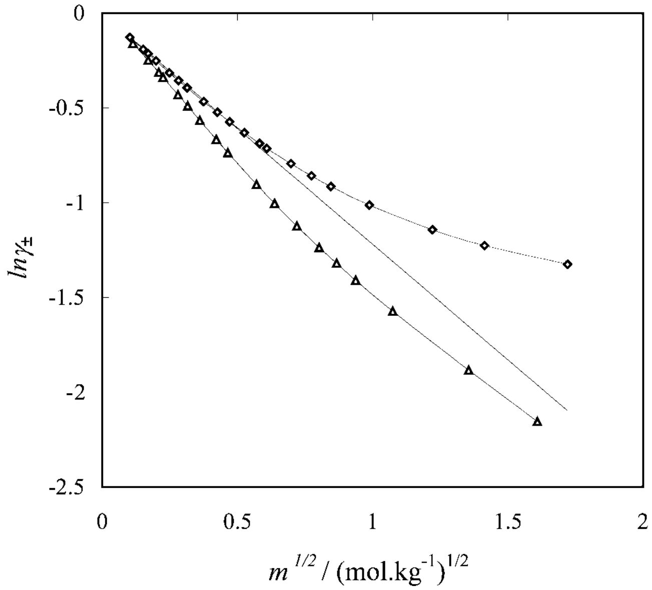

Figure 5. Activity coefficients of ([BMIm]X + H_2O) systems at 318.15 K. Straight line is related to DHLL. ◇, [BMIm]Cl; △, [BMIm]I.

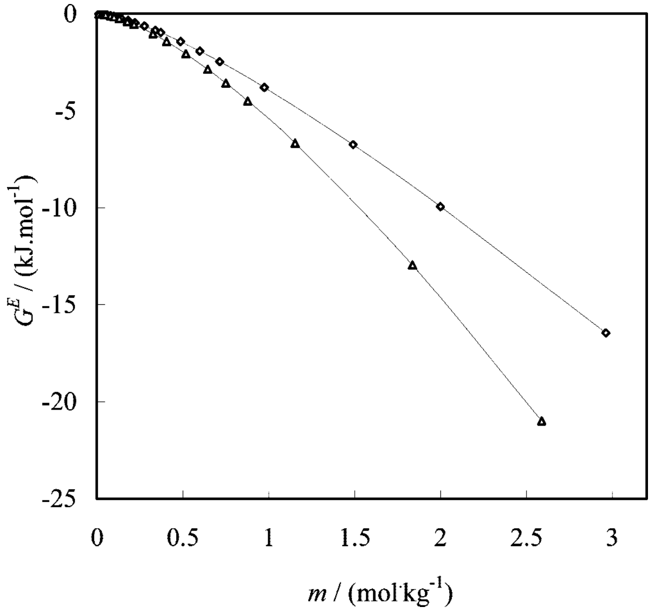

Figure 6. Excess Gibbs free energy of aqueous solutions of the studied ionic liquids system at T = 318.15 K: ◇, [BMIm]Cl; △, [BMIm]I.

studied systems.[36] The dependence of the mean molal activity coefficient data on the IL concentration is shown in Figure 5 for aqueous solutions of studied ILs at T = 318.15 K. This Figure shows that the solutions of [BMIm]Cl deviate from DHLL behavior more than do the other investigated IL solutions. This means that ion−solvent interactions in [BMIm]Cl solutions are stronger than those in [BMIm]I and because of the influence of the halide anion on the water structure.

Excess Gibbs Free Energy. Nonidealities can be conveniently presented in terms of the total excess thermodynamic functions. The principal free-energy function involved in the excess Gibbs free energy, G^E is given in terms of osmotic and activity coefficients by

$$G^E = \nu n_{IL} RT[\ln(\gamma_{\pm}) + 1 - \phi] \qquad (12)$$

where n_{IL} is the number of moles of IL. Figure 6 shows the excess Gibbs free energy for investigated systems calculated from the osmotic coefficient and the mean molal activity coefficient data at 318.15 K. In all composition ranges for a given temperature, the excess Gibbs free energies of the ([BMIm]Cl + H_2O) system are a larger deviation from DHLL than are those of ([BMIm]I + H_2O). These phenomena can be attributed to the stronger interactions between water and [BMIm]Cl, which decrease the excess Gibbs free energy. [32]

Table 5. Refractive Indices, n_D, of Aqueous Solutions of [BMIm]X as a Function of Ionic Liquid Molality, m, at Different Temperature

m	n_D			
mol·kg^{-1}	T = 298.15 K	T = 308.15 K	T = 318.15 K	T = 328.15 K
	[BMIm]Cl + H_2O			
0.0105	1.3330	1.3317	1.3292	1.3273
0.0230	1.3334	1.3320	1.3295	1.3275
0.0289	1.3335	1.3323	1.3296	1.3277
0.0398	1.3340	1.3326	1.3300	1.3280
0.0621	1.3343	1.3330	1.3305	1.3288
0.0803	1.3349	1.3336	1.3310	1.3290
0.0986	1.3354	1.3341	1.3312	1.3297
0.1413	1.3366	1.3351	1.3325	1.3309
0.1816	1.3377	1.3363	1.3338	1.3319
0.2223	1.3388	1.3373	1.3346	1.3331
0.2764	1.3404	1.3389	1.3362	1.3343
0.3386	1.3419	1.3403	1.3377	1.3358
0.3710	1.3428	1.3416	1.3387	1.3369
0.4863	1.3457	1.3441	1.3415	1.3398
0.5990	1.3484	1.3469	1.3442	1.3422
0.7152	1.3512	1.3497	1.3467	1.3449
0.9754	1.3571	1.3562	1.3528	1.3508
1.4915	1.3679	1.3661	1.3631	1.3611
1.9999	1.3774	1.3754	1.3723	1.3703
2.9617	1.3923	1.3904	1.3872	1.3849
	[BMIm]I + H_2O			
0.0133	1.3331	1.3321	1.3305	1.3285
0.0293	1.3336	1.3325	1.3310	1.3289
0.0442	1.3343	1.3330	1.3316	1.3293
0.0505	1.3346	1.3334	1.3317	1.3298
0.0786	1.3356	1.3344	1.3328	1.3310
0.0995	1.3365	1.3353	1.3336	1.3315
0.1307	1.3376	1.3363	1.3347	1.3329
0.1782	1.3395	1.3381	1.3364	1.3347
0.2160	1.3410	1.3397	1.3380	1.3359
0.3257	1.3449	1.3435	1.3418	1.3404
0.4065	1.3478	1.3467	1.3447	1.3433
0.5184	1.3519	1.3503	1.3487	1.3464
0.6452	1.3560	1.3548	1.3529	1.3507
0.7509	1.3595	1.3580	1.3561	1.3541
0.8786	1.3635	1.3620	1.3600	1.3578
1.1538	1.3714	1.3701	1.3680	1.3657
1.8374	1.3893	1.3876	1.3853	1.3831
2.5889	1.4054	1.4035	1.4012	1.3986

Table 6. Parameters of Polynomial Fitting and Standard Deviations for Refractive Indices of System ([BMIm]X + H_2O) at Different Temperatures

T/K	n_D*	$10^4 \cdot A_1$	$10^4 \cdot A_2$	$10^4 \cdot A_3$	$10^4 \cdot \sigma(n_D - n_D^*)$
		[BMIm]Cl + H_2O			
298.15	1.3325	289.698	−40.1740	3.5645	1.475
308.15	1.3316	273.300	−29.7700	1.5092	2.439
318.15	1.3301	226.627	4.3049	−5.3638	7.898
328.15	1.3284	222.538	6.5968	−5.9004	8.649
		[BMIm]I + H_2O			
298.15	1.3325	401.567	−61.0920	5.7025	0.843
308.15	1.3316	385.983	−48.4930	2.5567	1.792
318.15	1.3301	378.306	−46.0910	2.3056	2.013
328.15	1.3284	370.490	−41.7210	1.2776	3.908

Refractive Index Measurements. Experimental results for the studied aqueous solutions of ILs are reported in Table 5. This table shows the refractive indices of aqueous solutions of ILs as a function of the molality of IL. As can be seen, the n_D values decrease as the temperature increases. However, refractive indices decrease when the size of the anion of IL increases; this behavior is similar to n_D values obtained by Liu et al. and Kim et al. for the other studied IL mixtures.[37,38]

The values of the refractive indices of the binary systems have been fitted by a polynomial expansion of the form

$$n_D - n_D^* = \sum_{i=1}^{3} A_i m^i \tag{13}$$

where m is the molality of the ILs, n_D^* is refractive index of pure water, and A_i values are the fitting parameters given in Table 6 together with corresponding standard deviation values.

Conclusions

The experimental osmotic coefficients of aqueous solutions of ILs 1-butyl-3-methylimidazolium chloride and 1-butyl-3-methylimidazolium iodide were determined by the vapor pressure osmometry method over the temperature range of $T = (298.15 \text{ to } 328.15)$ K. Experimental osmotic coefficients are reliably correlated by the Pitzer ion interaction and MNRTL models with good accuracy. From the comparison of osmotic coefficients, it is concluded that the aqueous solution of [BMIm]Cl shows a more pronounced deviation from DHLL and more vapor pressure depression than the [BMIm]I solution, which was interpreted in terms of ion−solvent interactions. Mean molal activity coefficients and excess Gibbs free energies of studied systems were calculated from the obtained Pitzer model parameters. Refractive index properties of ILs in water have been reported at temperatures of $T = (298.15 \text{ to } 328.15)$ K.

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