

Determination and Modeling the Activity Coefficients of 1-Propyl-3-methylimidazolium Bromide in the Ethanol + Water Mixtures at T = (298.2, 308.2 and 318.2) K

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In this work, the results of the mean activity coefficient measurements for ionic liquid of 1-propyl-3-methylimidazolium bromide, [PrMim]Br, in ethanol + water mixtures have been reported using potentiometric measurements at $T = (298.2, 308.2 \text{ and } 318.2) \text{ K}$. The electromotive force (emf) measurements were performed on the galvanic cell of the type: Br-ISE | [PrMim] (m) ethanol (wt%), H₂O (1 - wt)% | [PrMim] - ISE, in mixed solvent system containing 0, 10, 20, 30% mass fractions of ethanol over ionic strength ranging from 0.0010-2.0000 mol kg⁻¹. The Pitzer ion-interaction model was used to analyze the activity coefficients for the studied system. The Pitzer ion-interaction parameters ($\beta^{(0)}$, $\beta^{(1)}$ and C^ϕ) were determined and employed to calculate the mean activity coefficients, the osmotic coefficients, and excess Gibbs free energies for the whole series of the studied system.

Keywords: Potentiometry, Activity coefficient, 1-Propyl-3-methylimidazolium bromide, Pitzer model

INTRODUCTION

The anhydrous ethanol is generally used as an intermediate and raw material in synthesis of chemical compounds such as esters. Production of anhydrous ethanol is very difficult and requires a lot of cost and energy in order to separate it from aqueous solution. Ionic liquids (ILs) are the salts with low melting point, low toxicity, good biodegradability, negligible vapor pressure, high conductivity and thermal stability that can facilitate the separation of alcohols [1]. Due to variety in structure and design of ionic liquids, they have the potential to be used in different compounds such as alcohols from fermentation broth [2], aromatic compounds [3], synthesis pharmaceuticals [5], catalysis [4,6] and electrolyte materials for Li/Na ion batteries, Li-sulfur batteries, and Li-oxygen batteries [7]. Thermodynamic, optical and transitional properties of ionic liquids are needed to study in water + alcohols mixtures for understanding the interactions concerning water, ionic

liquid and alcohols. In addition, alcohols play a critical role for the operation of many industrial processes involving ionic liquids. Activity and osmotic coefficients are the most useful thermodynamic data to describe the deviation of electrolyte solutions from ideality [8,9].

Regarding the importance of the ionic liquid mixtures, many research activities have been performed on the activity and osmotic coefficients [10-12]. E. Amado-Gonzalez, *et al.* determined the mean activity coefficient for NaCl in the mixture solvents (1-ethyl-3-methyl-imidazolium methane sulfonate, 1-ethyl-3-methyl-imidazolium ethyl sulfate + water) by potentiometric method at $T = 298.15 \text{ K}$, and calculated the ion interaction parameters $\beta^{(0)}$, $\beta^{(1)}$ and C^ϕ of Pitzer model [13]. B. Ghalami-Choobar, *et al.* reported the mean activity coefficient of 1-ethyl-3-methylimidazolium chloride in the mixed solvent of (formamide + water) using potentiometric method in different concentrations at $T = 298.2 \text{ K}$. They determined the Pitzer ion-interaction parameters β^0 , β^1 and C^ϕ and calculated the values of the mean activity coefficients, the osmotic coefficients, the excess Gibbs free energy and the

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solvent activity [14]. Due to the simplicity and rapidity of potentiometric measurements, this technique is generally used to measure the thermodynamic properties of electrolyte solutions.

In this study, the mean activity coefficient for 1-propyl-3-methyl imidazolium bromide ([PrMIm]Br) in ethanol + water mixtures have been reported using the potentiometric method at $T = (298.2, 308.2, 318.2)$ K. The galvanic cell containing ionic liquid ion selective electrode (IL-ISE) and bromide ion-selective electrode (Br-ISE) were used for potentiometric measurements. Exclusive ionophore was used to make the electrodes in our laboratory. The mean activity coefficients for ionic liquid in different mass fractions of ethanol in water + ethanol mixtures ($w_{\text{ethanol}}/w_{\text{mixture}}\% = 0, 10, 20$ and 30) were measured and the Pitzer model was used to analyze the experimental data. The Pitzer ion-interaction parameters β^0 , β^1 and C^ϕ were determined and utilized to calculate the mean activity coefficients, osmotic coefficients, and excess Gibbs free energy for the studied system.

EXPERIMENTAL

Materials Used

The organic solvents used were ethanol (reagent grade, Merck, >0.99 mass fraction), N-methylimidazole (reagent grade, Merck, >0.99 mass fraction) and 1-bromopropane (reagent grade, Merck, >0.99 mass fraction). The doubly distilled deionized water was used with a specific conductivity of approximately $0.9 \mu\text{S cm}^{-1}$ at $T = 298.2$ K.

Synthesis of Ionic Liquid

The [PrMIm]Br was prepared and purified using the procedure described in the literature [15-16]. Direct alkylation of imidazole was made to synthesize halide and halide-free ionic liquids. Ionic liquid based on imidazole and its derivative was produced in the presence an ester [17]. An excess of 1-bromopropane diluted with ethyl acetate was added as drop wise to round bottom flask contains N-methylimidazole in ice bath. Then, the obtained mixture was refluxed under a nitrogen atmosphere at $T = 353.2$ K for 72 h. The crude product was washed twice with ethyl acetate in a separator funnel. The obtained product was dried at least 5 h at $T = 345.2$ K and reduced the

pressure by a rotary evaporator. Trace amount of moisture was removed by the high vacuum desiccated for at least 24 h. The moisture (water) content in [PrMIm]Br was found by Karl Fischer method which was less than 0.02 mass fractions. The product was checked by ^1H NMR (Bruker Av-300) and FT-IR (PerkinElmer, Spectrum RXI) spectra to confirm the absence of any major impurities (see Figs. S1 and S2 in Supporting Information).

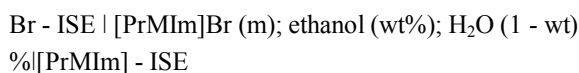
Preparation of Electrodes

The 1-propyl-3-methyl imidazolium ion selective electrode (IL-ISE) was prepared using the procedure described in the literature [12]. This ion selective electrode responded to 1-propyl-3-methyl imidazolium ion, so, it was used to measure the 1-propyl-3-methyl imidazolium ion in ethanol + water mixtures. In a glass dish of 2 cm diameter, 32 mg of PVC powder, 60 mg of plasticizer DBP, 5.1 mg of additive KTPCIPB, and 6 mg of polyanetholesulfonic acid sodium salt, as the ionophore, were mixed in 2 ml of tetrahydrofuran (THF) to provide cationic ion selective electrode. In another glass dish of 2 cm diameter, 32 mg of PVC powder, 65 mg of plasticizer DBP, and 3 mg of tridodecyl methyl ammonium chloride, as the ionophore, were mixed in 2 ml of THF to provide the bromide ion selective electrode (Br-ISE). The resulting mixtures were exposed to air to evaporate the solvent at the room temperature. The polymer membrane was removed from the plate after with PVC-THF viscose solution was attached the transparent PVC membrane on a glass tube with a diameter of 1 cm and a height of 6 cm. The Ag-AgCl wire electrodes were prepared using the procedure described in the literature [18] and applied as internal electrode on the ion selective electrodes.

Apparatus and Procedure

To check the electrodes, the responses of the IL-ISE and Br-ISE electrodes were evaluated against saturated calomel reference electrode. The stock electrolyte solution was prepared by adding weighted amounts of ionic liquid using an analytical balance (A & D) with accuracy 0.1 mg into the proportion volume of ethanol and double-distilled water. The cell potentials of the mixed ternary system (ionic liquid + water + ethanol) were measured and the results were then used to determine the activity coefficients. The standard

addition method was applied to measure the emf of the solutions with the following galvanic cell:



where m and w are the molality of $[\text{PrMIm}]\text{Br}$ and the mass fraction of ethanol in the mixed solvent system, respectively. The concentrated solutions of $[\text{PrMIm}]\text{Br}$ were added into a specified volume of mixed solvent (ethanol + water). Proper Pipette and suitable Hamilton syringes (CH-7402 Bonaduz) were used to perform the standard addition steps. A multimeter (Martini instruments Mi 180) connected to the computer was used to collect data every 10 s with 15 min time interval for all solutions. The water from a thermostatically regulated bath (Model GFL) was circled around the sample holder with a double-wall container to keep constant of solutions at $T = (298.2, 308.2$ and $318.2 \pm 0.1)$ K.

THERMODYNAMICS MODEL

To correlate the experimental data and determination of thermodynamic properties, was performed using the Pitzer ion interaction model [19, 20]. The mean molal activity coefficient (γ_{\pm}) based on the Pitzer model for ionic liquid can be given as follow:

$$\ln \gamma_{\pm(\text{ionic liquid})} = f^{\gamma} + B^{\gamma}_{(\text{ionic liquid})} I + 1.5 C^{\phi}_{(\text{ionic liquid})} I^2 \quad (1)$$

where

$$f^{\gamma} = -A_{\phi} \left[\frac{\sqrt{I}}{1 + b\sqrt{I}} + \left(\frac{2}{b} \right) \ln \left(1 + b\sqrt{I} \right) \right] \quad (2)$$

$$B^{\gamma}_{(\text{ionic liquid})} = 2\beta^{(0)}_{(\text{ionic liquid})} + \frac{2\beta^{(1)}_{(\text{ionic liquid})}}{\alpha^2 I} \left[1 - \left(1 + \alpha\sqrt{I} - \frac{\alpha^2 I}{2} \right) e^{-\alpha\sqrt{I}} \right] \quad (3)$$

where α and b are presumed to be constant with values of 2.0 and 1.2 $\text{kg}^{1/2} \text{mol}^{-1/2}$, respectively. The I symbol stands for the total ionic strength on a molality scale in ethanol + water mixtures. $\beta^{(0)}$, $\beta^{(1)}$ and C^{ϕ} are attributed to solute-

specific interaction Pitzer parameters for electrolyte solution that their values should be determined for ionic liquid in solvent mixtures. A_{ϕ} shows the Debye-Hückel parameter for the osmotic coefficients defined by:

$$A_{\phi} = \frac{1.4006 \times 10^6 \rho^{1/2}}{(\epsilon_r T)^{3/2}} \text{kg}^{1/2} \text{mol}^{-1/2} \quad (4)$$

where ρ , ϵ_r and T are solvent density (kg m^{-3}), solvent relative permittivity and the Kelvin temperature, respectively. The values of density (ρ), molar mass, relative permittivity (ϵ_r), Debye-Hückel constants (A_{ϕ}) of the pure water, and the mixture (ethanol-water) were reported in Table 1 [21-24].

RESULTS AND DISCUSSION

Calibration of PrMIm-ISE and Br-ISE Electrode Pairs

To check the electrode answer, before start any experiment, IL-ISE and Br-ISE were applied separately versus the calomel electrode, and standard $[\text{PrMIm}]\text{Br}$ solutions were made to measure the emf of cell (A) with concentration range from 0.0001-1.0000 mol kg^{-1} . The Nernst equation for cell (A) is:

$$E_A = E' + k \log(m^{\gamma_{\pm([\text{PrMIm}]\text{Br})}}) = E^0 + s \log \phi_{\pm} m \quad (5)$$

where $k = (\ln 10)RT/ZF$ demonstrates Nernst slope. Z is the charge of ion that is equal to one in this work, and R , F and T are universal gas constant, Faraday constant, and absolute temperature, respectively. The γ_{\pm} , E_0 and s terms are the mean activity coefficient of ionic liquid in pure water, the experimental standard potential of cell (A), and Nernst slope, respectively. The calibration of electrode pair was performed according to literature [12]. The potentials were measured and drawn against $\log(\gamma^{\circ}(\pm[\text{PrMIm}]\text{Br}) I)$ for the cell containing $[\text{PrMIm}]\text{Br}$ electrolyte in water at $T = 298.2$ K. Figure 1 indicates that the electrode pair is suitable for thermodynamic measurements because of a good Nernst slope (s) and a high linear correlation coefficient ($R^2 = 0.9999$).

Table 1. The Values of Density (ρ), Molar Mass, Relative Permittivity (ϵ_r), and Debye-Hückel Constants (A_ϕ), as the Functions of the Mass Fraction of Ethanol in Ethanol-water Mixtures at 298.2, 308.2 and 318.2 K

wt%	ρ^a (g cm ⁻³)	M (g mol ⁻¹)	$\epsilon_r^{b,c}$	A_ϕ (kg ^{1/2} mol ^{-1/2})
T = 298.2 K				
0	0.9972	18.015	78.38	0.3915
10	0.9804	19.791	72.31	0.4337
20	0.9686	20.524	66.71	0.4913
30	0.9506	21.991	61.11	0.5550
T = 308.2 K				
0	0.9941	18.015	74.83	0.3985
10	0.9768	19.674	68.85	0.4478
20	0.9613	20.501	63.46	0.5020
30	0.9440	22.015	55.46	0.6090
T = 318.2 K				
0	0.9902	18.015	71.51	0.4060
10	0.9752	19.159	65.42	0.4605
20	0.9560	20.010	60.25	0.5159
30	0.9354	21.232	47.08	0.7388

Determination of the Mean Activity Coefficients and Pitzer Parameters

The determined mean activity coefficients for the solutions of [PrMIm]Br in the ethanol mass fractions of 10%, 20% and 30% in accordance to Eq. (5) by standard addition method were given at T = (298.2, 308.2 and 318.2) K in Table 2. The Pitzer ion-interaction parameters, E^0 and s were obtained using Eqs. (1) and (5) by an iteration minimization procedure employing the Microsoft Excel (solver) program. Table 3 shows the obtained values of Pitzer parameter $\beta^{(0)}$, $\beta^{(1)}$, $C\phi$, slope, s and the cell constant potential, E^0 , for [PrMIm]Br in mass fractions 0%, 10%, 20% and 30% of ethanol in (water + ethanol) mixtures at

different temperatures. Figure 2 shows the obtained values of $\beta^{(0)}$ and $\beta^{(1)}$ versus the reverse value of the relative permittivity of the ethanol-water mixture and pure water that were found to show the similar trends with the literature [25,26].

As observed, $\beta^{(0)}$ can indicate the total binary ionic interactions, and $\beta^{(1)}$ can present the interactions between unlike-charged ions which almost change linearly with $1/\epsilon$. The linear dependence displayed in this work is reasonable. This behavior can be seen in the other electrolytes in different aqueous mixtures of organic solvents [8]. Figure 3 shows the dependence of the mean activity coefficient on the molality of [PrMIm]Br in ternary mixtures ([PrMIm]Br

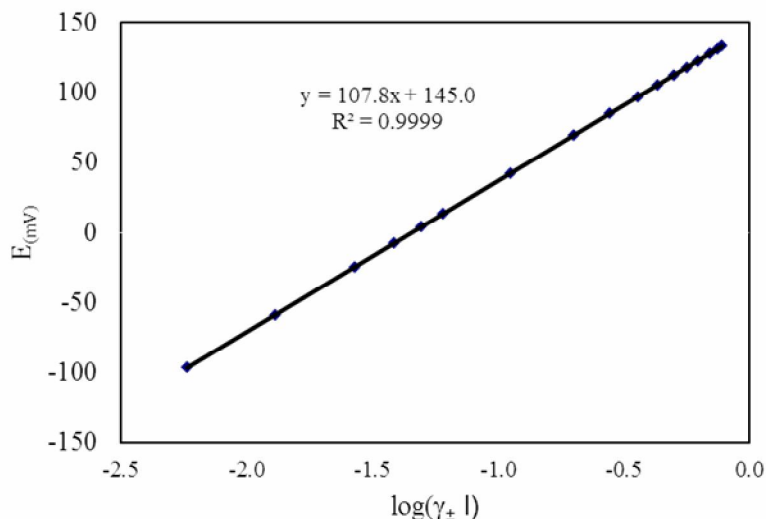


Fig. 1. The cell (A) emf as a function of $\log(\gamma_{\pm})$ to calibrate the IL-ISE and Br-ISE electrode pair at 298.2 K.

Table 2. The [PrMIm]Br molalities ($m_{[\text{PrMIm}]\text{Br}}$), the Mean Activity Coefficients (γ_{\pm} , PrMImBr), and emf Data (E/mV) in Mass Fractions 0%, 10%, 20% and 30% of Ethanol in (Water + Ethanol) Mixtures at 298.2, 308.2 and 318.2K

$m_{[\text{PrMIm}]\text{Br}}$ (mol kg ⁻¹)	E (mV)	$\gamma_{\pm[\text{PrMIm}]\text{Br}}$	$m_{[\text{PrMIm}]\text{Br}}$ (mol kg ⁻¹)	E (mV)	$\gamma_{\pm[\text{PrMIm}]\text{Br}}$	$m_{[\text{PrMIm}]\text{Br}}$ (mol kg ⁻¹)	E (mV)	$\gamma_{\pm[\text{PrMIm}]\text{Br}}$
T/K = 298.2			T/K = 308.2			T/K = 318.2		
wt% = 0								
0.0118	-88.8	0.8891	0.0118	-75.8	0.8904	0.0118	-80.7	0.9299
0.0235	-57.8	0.8467	0.0236	-46.3	0.8776	0.0235	-51.7	0.8851
0.0399	-34.0	0.8189	0.0399	-24.9	0.8469	0.0397	-29.6	0.8521
0.0560	-18.8	0.7981	0.0561	-10.2	0.8440	0.0558	-14.6	0.8443
0.0721	-8.5	0.7681	0.0722	-0.3	0.8235	0.0718	-5.2	0.8080
0.0902	0.9	0.7454	0.1395	25.1	0.7629	0.1388	22.6	0.7726
0.1568	24.0	0.6924	0.2044	37.9	0.7210	0.2035	37.1	0.7265
0.3429	55.0	0.6016	0.3862	62.1	0.6592	0.3846	63.9	0.6941
0.5288	71.4	0.5477	0.5679	77.0	0.6220	0.5657	80.2	0.6769
0.6957	80.2	0.4994	0.7314	84.9	0.5764	0.7289	90.8	0.6644
0.8750	87.8	0.4652	0.9072	92.6	0.5484	0.9044	99.6	0.6501

Table 2. Continued

1.0598	95.6	0.4508	1.0887	99.9	0.5354	1.0857	106.6	0.6328
1.2445	100.4	0.4245	1.2703	104.9	0.5188	1.2673	112.1	0.6117
1.4340	105.3	0.4074	1.4569	109.0	0.5019	1.4542	116.4	0.5861
1.6292	109.4	0.3908	1.6494	113.6	0.4937	1.6470	119.6	0.5553
1.8277	114.2	0.3845	1.8454	117.3	0.4874	1.8435	121.7	0.5201
2.0303	118.7	0.3798	2.0458	120.7	0.4852	2.0446	122.9	0.4806
wt% = 10								
0.0123	-100.1	0.8494	0.0123	-87.4	0.8567	0.0059	-96.1	0.9914
0.0244	-65.7	0.8244	0.0245	-54.7	0.8376	0.0146	-58.4	0.8882
0.0414	-39.5	0.8053	0.0415	-32.7	0.7754	0.0321	-24.5	0.8350
0.0582	-24.2	0.7683	0.0583	-17.0	0.7599	0.0495	-7.3	0.7823
0.0748	-12.8	0.7434	0.0797	-3.1	0.7380	0.0667	4.4	0.7445
0.0937	-3.1	0.7152	0.0962	4.5	0.7139	0.0839	13.7	0.7223
0.3772	56.2	0.5543	0.1881	33.9	0.6655	0.1682	42.6	0.6675
0.5325	68.9	0.5016	0.3596	60.0	0.5928	0.3295	69.7	0.6081
0.6923	78.0	0.4591	0.5355	75.2	0.5430	0.4819	85.0	0.5764
0.8539	84.8	0.4240	0.7125	85.6	0.5049	0.6494	97.0	0.5518
1.0147	90.0	0.3948	0.8879	93.3	0.4744	0.8066	105.5	0.5330
1.1852	94.6	0.3687	1.0732	99.8	0.4477	0.9751	112.7	0.5146
1.3599	98.4	0.3461	1.2442	104.7	0.4269	1.1326	118.2	0.4976
1.5341	101.8	0.3269	1.4340	109.3	0.4071	1.2981	122.8	0.4793
1.7125	104.7	0.3102	1.6273	113.4	0.3900	1.5494	128.1	0.4496
1.8676	108.6	0.3064	1.8327	117.2	0.3745	1.7742	131.3	0.4209
2.0351	111.7	0.2984	2.0383	120.7	0.3614	1.9767	133.2	0.3932
wt% = 20								
0.0143	-89.3	0.8988	0.0142	-86.9	0.8526	0.0084	-101.4	0.8641
0.0285	-57.1	0.7995	0.0283	-56.3	0.7968	0.0168	-67.2	0.8337
0.0454	-32.5	0.7767	0.0452	-35.5	0.7628	0.0308	-38.6	0.7891
0.0622	-18.8	0.7232	0.0619	-22.1	0.7310	0.0474	-19.0	0.7458
0.0790	-6.8	0.7058	0.0786	-12.0	0.7076	0.0639	-5.3	0.7191
0.0956	3.3	0.6979	0.0951	-4.3	0.6837	0.0803	5.2	0.6998

Table 2. Continued

0.1773	32.7	0.6355	0.1764	21.7	0.6264	0.1872	42.8	0.6172
0.3334	60.1	0.5505	0.3318	46.1	0.5471	0.3396	68.3	0.5554
0.5044	76.3	0.4856	0.5020	61.1	0.4907	0.4832	83.2	0.5195
0.6865	87.2	0.4327	0.6834	71.7	0.4470	0.6406	95.0	0.4908
0.8559	94.1	0.3929	0.8521	79.0	0.4156	0.8084	104.5	0.4663
1.0328	99.5	0.3583	1.0284	85.0	0.3893	0.9645	111.4	0.4465
1.2142	103.7	0.3286	1.2093	90.1	0.3675	1.1278	117.3	0.4274
1.3976	107.1	0.3032	1.3762	94.2	0.3510	1.2954	122.1	0.4085
1.5806	109.9	0.2816	1.5601	98.2	0.3360	1.4501	125.8	0.3914
1.7746	112.3	0.2621	1.7551	102.1	0.3234	1.6208	129.0	0.3724
1.9623	114.4	0.2460	1.9437	105.7	0.3138	1.8140	131.7	0.3507
wt% = 30								
0.0088	-101.3	0.8965	0.0147	-66.9	0.8015	0.0089	-67.0	0.8008
0.0176	-70.5	0.8225	0.0235	-46.2	0.7736	0.0266	-17.4	0.7096
0.0351	-39.9	0.7529	0.0410	-22.2	0.7325	0.0442	4.6	0.6588
0.0524	-21.3	0.7257	0.0584	-7.9	0.6936	0.0617	19.5	0.6231
0.0697	-9.0	0.6953	0.0757	2.0	0.6583	0.0791	27.1	0.5956
0.0869	0.3	0.6698	0.0929	9.9	0.6328	0.0964	37.1	0.5731
0.1712	28.1	0.5870	0.1773	36.1	0.5731	0.2640	78.4	0.4719
0.3327	51.9	0.4824	0.3390	58.9	0.4836	0.3966	93.4	0.4219
0.5098	64.7	0.4048	0.4919	70.9	0.4281	0.5478	104.8	0.3824
0.6989	72.6	0.3448	0.6599	79.7	0.3833	0.6910	112.7	0.3542
0.8750	77.4	0.3027	0.8177	85.7	0.3509	0.8489	119.5	0.3293
1.0395	80.7	0.2720	0.9868	90.8	0.3236	1.0181	125.2	0.3074
1.2304	83.8	0.2443	1.1641	95.3	0.3012	1.1766	129.6	0.2899
1.4067	86.4	0.2248	1.3290	98.9	0.2847	1.3610	133.1	0.2721
1.5701	88.7	0.2108	1.4993	102.4	0.2714	1.5319	136.4	0.2576
1.7219	90.9	0.2007	1.6573	105.5	0.2620	1.6905	139.1	0.2455
1.8904	93.5	0.1925	1.8741	109.3	0.2508	1.8778	141.4	0.2323

Uncertainties: $u(T) = \pm 0.1$ K; $u(m) = \pm 0.0001$ mol kg⁻¹, $u(E) = \pm 0.2$ mV, $u(\gamma_{\pm}) = \pm 0.0047$, $u(\text{wt}\%) = \pm 0.03$.

Table 3. The Values Obtained of Pitzer Parameter $\beta^{(0)}$, $\beta^{(1)}$, C^ϕ , Slope and the Cell Constant Potential for [PrMIm]Br Electrolyte in Mass Fractions 0%, 10%, 20% and 30% of Ethanol in (Water + Ethanol) Mixtures at Different Temperatures

wt%	$\beta^{(0)}$ (kg mol ⁻¹)	$\beta^{(1)}$ (kg mol ⁻¹)	C^ϕ (kg ² mol ⁻²)	s	E^0 (mv)
T/K = 298.2					
0%	-0.1360	0.2093	0.0536	111.2	131.2
10%	-0.1923	0.3252	0.0561	119.9	137.7
20%	-0.2415	0.5840	0.0559	119.3	155.3
30%	-0.4583	0.5900	0.1578	117.1	145.0
T/K = 308.2					
0%	0.0200	0.1867	-0.0081	100.4	122.8
10%	-0.0379	0.1955	0.0021	112.8	135.6
20%	-0.1213	0.3022	0.0434	113.1	130.0
30%	-0.1545	0.3846	0.0587	110.1	145.4
T/K = 318.2					
0%	0.2150	0.0810	-0.1228	104.21	123.6
10%	0.0880	0.1096	-0.0552	107.9	145.0
20%	0.0428	0.1108	-0.0309	120.1	155.3
30%	0.0122	0.3047	-0.0147	117.0	184.2

Uncertainties: $u(T) = \pm 0.1$ K; $u(\text{wt}\%) = \pm 0.03$.

+ water + ethanol) with 0%, 10%, 20% and 30% ethanol mass fractions at $T = 298.2$ K. A similar trend was observed at $T = (308.2$ and $318.2)$ K (see Figs. S3-S4 in Supporting Information file). It can be seen that the mean activity coefficients of [PrMIm]Br decrease by increasing the ethanol mass fraction in mixtures at the same molality concentration of [PrMIm]Br. In addition, the mean activity coefficients of [PrMIm]Br decrease by addition of [PrMIm]Br molality concentration at the same ethanol mass fraction in mixture. Since the values of activity coefficients

are less than unity, it can be concluded that the ion-ion interactions are more significant than the ion-solvent interactions. Figure 4 displays the mean activity coefficient on the molality concentration of IL in ternary mixtures ([PrMIm]Br + water + ethanol) with 10% ethanol mass fraction at $T = (298.2, 308.2$ and $318.2)$ K. Generally, a similar trend was observed with 0, 20 and 30% ethanol mass fraction (see Figs. S5-S7 in Supporting Information). It was observed the mean activity coefficient increases with increasing the temperature.

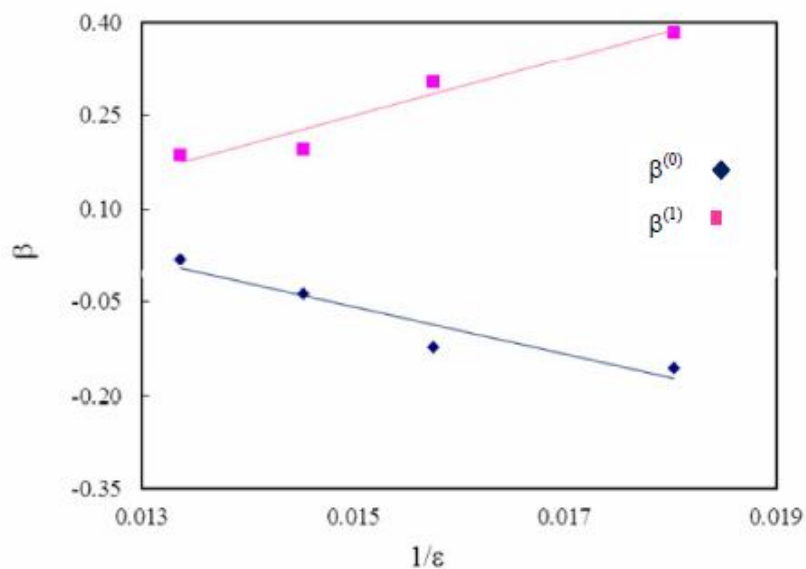


Fig. 2. Variation of Pitzer parameters $\beta^{(0)}$ (♦) and $\beta^{(1)}$ (■) for [PrMIm]Br against the reverse value of relative permittivity of the ethanol-water mixtures at 308.2 K.

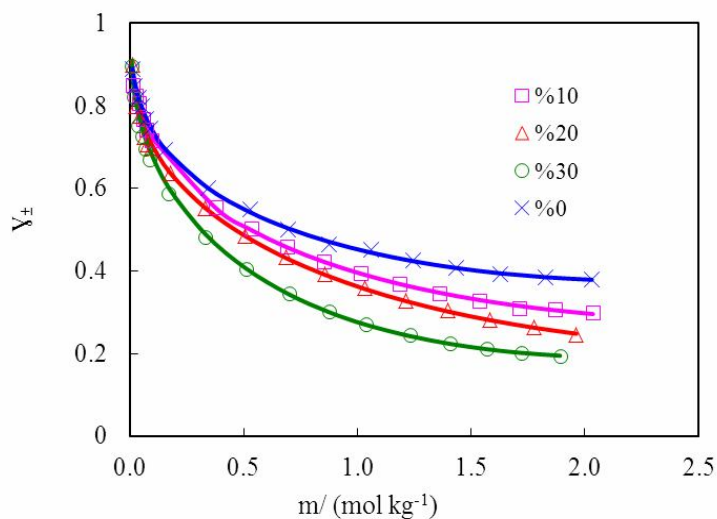


Fig. 3. The mean activity coefficient (γ_{\pm}) for [PrMIm]Br against the molality (m) of electrolyte in various ethanol-water mixed solvent systems containing 0, 10, 20 and 30% mass fractions of ethanol at 298.2 K. Lines represent Pitzer model according to Eq. (1).

Calculation of Thermodynamic Properties by the Pitzer Model

The Pitzer model was applied to predict the

thermodynamic properties of under investigation system using the obtained parameters. The osmotic coefficients (ϕ), the excess Gibbs free energy (G^E), and solvent activity

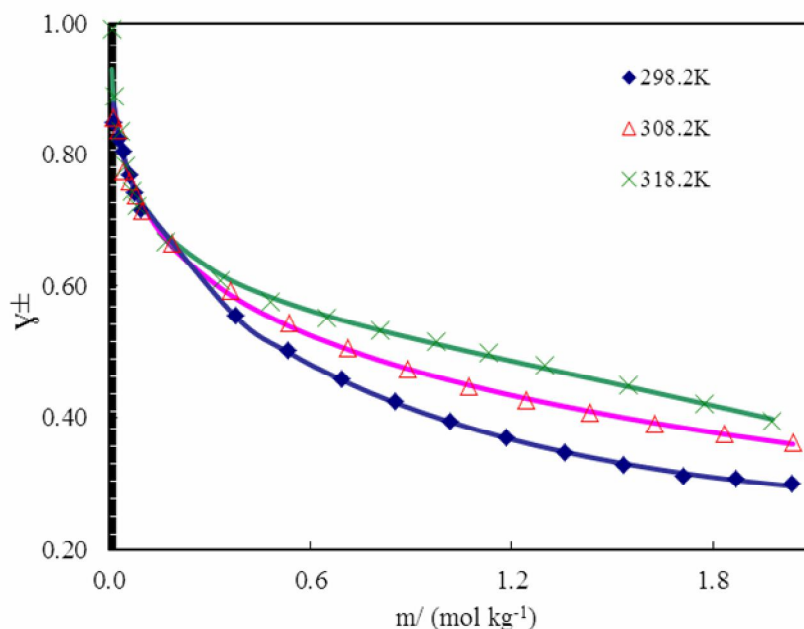


Fig. 4. Temperature comparison of the mean activity coefficient (γ_{\pm}) of [PrMIm]Br in the ethanol + water mixtures as a function molality concentration (m) of [PrMIm]Br in mass fraction 10% of ethanol. Solid lines were generated using Pitzer model.

Table 4. The Values Calculated of Osmotic Coefficients (ϕ), Solvent Activity (a_s) and Excess Gibbs Free Energies (G^E), as the Functions of [PrMIm]Br Molalities in Different Mass Fractions of Ethanol in (Water + Ethanol) Mixtures at 298.2, 308.2 and 318.2 K

m (mol kg ⁻¹)	ϕ	G^E/RT	a_s	m (mol kg ⁻¹)	ϕ	G^E/RT	a_s	M (mol kg ⁻¹)	ϕ	G^E/RT	a_s
T/K = 298.2				T/K = 308.2				T/K = 318.2			
wt% = 0											
0.0118	0.9628	-0.0019	0.9996	0.0118	0.9637	-0.0019	0.9996	0.0118	0.9643	-0.0009	0.9996
0.0235	0.9497	-0.0052	0.9992	0.0235	0.9520	-0.0051	0.9992	0.0235	0.9538	-0.0036	0.9992
0.0399	0.9372	-0.0111	0.9987	0.0397	0.9416	-0.0109	0.9986	0.0397	0.9452	-0.0084	0.9986
0.0560	0.9277	-0.0182	0.9981	0.0559	0.9341	-0.0177	0.9981	0.0558	0.9397	-0.0122	0.9981
0.0721	0.9198	-0.0261	0.9976	0.0719	0.9283	-0.0252	0.9976	0.0718	0.9359	-0.0214	0.9976
0.0902	0.9121	-0.0361	0.9970	0.1389	0.9122	-0.0634	0.9954	0.1388	0.9283	-0.0517	0.9954
0.1568	0.8898	-0.0798	0.9950	0.2035	0.9024	-0.1073	0.9934	0.2035	0.9265	-0.1001	0.9932

Table 4. Continued

0.3429	0.8473	-0.2445	0.9896	0.3845	0.8855	-0.2549	0.9878	0.3846	0.9292	-0.2264	0.9872
0.5288	0.8169	-0.4538	0.9846	0.5655	0.8746	-0.4273	0.9823	0.5657	0.9320	-0.3646	0.9812
0.6957	0.7956	-0.6710	0.9803	0.7284	0.8668	-0.5982	0.9774	0.7289	0.9310	-0.4955	0.9758
0.8750	0.7777	-0.9296	0.9758	0.9036	0.8596	-0.7954	0.9723	0.9044	0.9247	-0.6426	0.9703
1.0598	0.7640	-1.2190	0.9712	1.0844	0.8528	-1.0115	0.9671	1.0857	0.9117	-0.8021	0.9650
1.2445	0.7549	-1.5277	0.9667	1.2654	0.8464	-1.2392	0.9620	1.2673	0.8917	-0.9711	0.9601
1.4340	0.7501	-1.8612	0.9620	1.4515	0.8399	-1.4839	0.9569	1.4542	0.8635	-1.1572	0.9558
1.6292	0.7498	-2.2186	0.9569	1.6434	0.8333	-1.7468	0.9517	1.6470	0.8262	-1.3651	0.9522
1.8277	0.7541	-2.5932	0.9516	1.8388	0.8264	-2.0248	0.9465	1.8435	0.7794	-1.5970	0.9496
2.0303	0.7634	-2.9839	0.9457	2.0388	0.8192	-2.3195	0.9414	2.0446	0.7221	-1.8595	0.9482
wt% = 10											
0.0123	0.9585	-0.0030	0.9995	0.0123	0.9577	-0.0022	0.9995	0.0059	0.9687	-0.0005	0.9998
0.0244	0.9441	-0.0067	0.9991	0.0245	0.9436	-0.0061	0.9991	0.0146	0.9538	-0.0030	0.9995
0.0414	0.9302	-0.0121	0.9985	0.0415	0.9306	-0.0131	0.9985	0.0321	0.9372	-0.0093	0.9988
0.0582	0.9196	-0.0213	0.9980	0.0583	0.9210	-0.0214	0.9979	0.0495	0.9267	-0.0172	0.9982
0.0748	0.9107	-0.0310	0.9974	0.0797	0.9114	-0.0335	0.9971	0.0667	0.9190	-0.0263	0.9977
0.0937	0.9019	-0.0444	0.9968	0.0962	0.9053	-0.0437	0.9966	0.0839	0.9129	-0.0362	0.9971
0.3772	0.8180	-0.3079	0.9882	0.1881	0.8807	-0.1124	0.9935	0.1682	0.8945	-0.0952	0.9943
0.5325	0.7850	-0.5057	0.9841	0.3596	0.8517	-0.2770	0.9880	0.3295	0.8776	-0.2370	0.9890
0.6923	0.7558	-0.7399	0.9801	0.5355	0.8301	-0.4802	0.9827	0.4819	0.8680	-0.3932	0.9841
0.8539	0.7304	-1.0049	0.9764	0.7125	0.8120	-0.7116	0.9775	0.6494	0.8590	-0.5827	0.9789
1.0147	0.7088	-1.2950	0.9728	0.8879	0.7963	-0.9634	0.9726	0.8066	0.8502	-0.7747	0.9741
1.1852	0.6898	-1.6297	0.9691	1.0732	0.7814	-1.2502	0.9675	0.9751	0.8395	-0.9937	0.9691
1.3599	0.6743	-1.9999	0.9654	1.2442	0.7686	-1.5322	0.9631	1.1326	0.8279	-1.2106	0.9647
1.5341	0.6628	-2.3957	0.9617	1.4340	0.7555	-1.8627	0.9583	1.2981	0.8136	-1.4507	0.9603
1.7125	0.6550	-2.8275	0.9579	1.6273	0.7430	-2.2169	0.9535	1.5494	0.7875	-1.8404	0.9543
1.8676	0.6515	-3.1165	0.9544	1.8327	0.7305	-2.6116	0.9487	1.7742	0.7592	-2.2162	0.9497

Table 4. Continued

2.0351	0.6510	-3.5020	0.9505	2.0383	0.7187	-3.0239	0.9440	1.9767	0.7297	-2.5780	0.9462
wt% = 20											
0.0143	0.9518	-0.0030	0.9994	0.0142	0.9493	-0.0031	0.9994	0.0084	0.9577	-0.0015	0.9997
0.0285	0.9361	-0.0082	0.9989	0.0283	0.9324	-0.0085	0.9989	0.0168	0.9429	-0.0041	0.9994
0.0454	0.9231	-0.0161	0.9983	0.0452	0.9185	-0.0167	0.9983	0.0308	0.9268	-0.0099	0.9989
0.0622	0.9129	-0.0253	0.9977	0.0619	0.9078	-0.0263	0.9977	0.0474	0.9136	-0.0183	0.9983
0.0790	0.9043	-0.0355	0.9971	0.0786	0.8990	-0.0370	0.9971	0.0639	0.9037	-0.0281	0.9977
0.0956	0.8967	-0.0466	0.9965	0.0951	0.8914	-0.0486	0.9965	0.0803	0.8958	-0.0389	0.9971
0.1773	0.8661	-0.1122	0.9937	0.1764	0.8628	-0.1168	0.9938	0.1872	0.8658	-0.1274	0.9935
0.3334	0.8195	-0.2766	0.9888	0.3318	0.8252	-0.2847	0.9888	0.3396	0.8462	-0.2887	0.9885
0.5044	0.7752	-0.5026	0.9841	0.5020	0.7946	-0.5097	0.9838	0.4832	0.8355	-0.4658	0.9840
0.6865	0.7329	-0.7879	0.9796	0.6834	0.7686	-0.7859	0.9787	0.6406	0.8263	-0.6808	0.9791
0.8559	0.6974	-1.0897	0.9758	0.8521	0.7490	-1.0706	0.9742	0.8084	0.8166	-0.9297	0.9741
1.0328	0.6643	-1.4386	0.9722	1.0284	0.7324	-1.3924	0.9696	0.9645	0.8065	-1.1772	0.9696
1.2142	0.6343	-1.8292	0.9689	1.2093	0.7193	-1.7447	0.9650	1.1278	0.7939	-1.4508	0.9651
1.3976	0.6082	-2.2543	0.9657	1.3762	0.7105	-2.0870	0.9607	1.2954	0.7783	-1.7465	0.9607
1.5806	0.5864	-2.7062	0.9627	1.5601	0.7043	-2.4806	0.9559	1.4501	0.7613	-2.0323	0.9568
1.7746	0.5678	-3.2121	0.9595	1.7551	0.7015	-2.9135	0.9508	1.6208	0.7394	-2.3615	0.9528
1.9623	0.5542	-3.7252	0.9563	1.9437	0.7026	-3.3451	0.9455	1.8140	0.7103	-2.7519	0.9486
wt% = 30											
0.0088	0.9592	-0.0010	0.9996	0.0147	0.9377	-0.0040	0.9994	0.0089	0.9383	-0.0023	0.9996
0.0176	0.9442	-0.0042	0.9993	0.0235	0.9242	-0.0079	0.9990	0.0266	0.9018	-0.0114	0.9990
0.0351	0.9238	-0.0115	0.9986	0.0410	0.9051	-0.0176	0.9984	0.0442	0.8804	-0.0236	0.9983
0.0524	0.9084	-0.0208	0.9979	0.0584	0.8910	-0.0293	0.9977	0.0617	0.8648	-0.0379	0.9977
0.0697	0.8953	-0.0315	0.9973	0.0757	0.8795	-0.0425	0.9971	0.0791	0.8527	-0.0539	0.9971
0.0869	0.8836	-0.0435	0.9966	0.0929	0.8697	-0.0569	0.9965	0.0964	0.8427	-0.0712	0.9965
0.1712	0.8355	-0.1180	0.9937	0.1773	0.8335	-0.1425	0.9935	0.2640	0.7908	-0.2889	0.9911
0.3327	0.7607	-0.3172	0.9889	0.3390	0.7863	-0.3556	0.9883	0.3966	0.7711	-0.5036	0.9871

Table 4. Continued

0.5098	0.6919	-0.6046	0.9846	0.4919	0.7528	-0.6000	0.9838	0.5478	0.7559	-0.7800	0.9827
0.6989	0.6307	-0.9778	0.9808	0.6599	0.7231	-0.9065	0.9792	0.6910	0.7443	-1.0666	0.9787
0.8750	0.5844	-1.3786	0.9778	0.8177	0.7004	-1.2244	0.9751	0.8489	0.7323	-1.4060	0.9745
1.0395	0.5503	-1.7927	0.9752	0.9868	0.6808	-1.5925	0.9709	1.0181	0.7189	-1.7939	0.9701
1.2304	0.5219	-2.3147	0.9722	1.1641	0.6651	-2.0045	0.9665	1.1766	0.7050	-2.1773	0.9663
1.4067	0.5063	-2.8298	0.9692	1.3290	0.6548	-2.4083	0.9624	1.3610	0.6865	-2.6458	0.9620
1.5701	0.5009	-3.3300	0.9660	1.4993	0.6482	-2.8429	0.9581	1.5319	0.6666	-3.0999	0.9583
1.7219	0.5038	-3.8103	0.9626	1.6573	0.6457	-3.2599	0.9540	1.6905	0.6456	-3.5379	0.9550
1.8904	0.5159	-4.3565	0.9580	1.9415	0.6498	-4.0360	0.9460	1.8778	0.6173	-4.0745	0.9514

Uncertainties: $u(T) = \pm 0.1$ K; $u(m) = \pm 0.0001$ mol kg⁻¹, $u(G^E/RT) = \pm 0.0015$, $u(\phi) = \pm 0.01$, $u(a_s) = \pm 0.0030$.

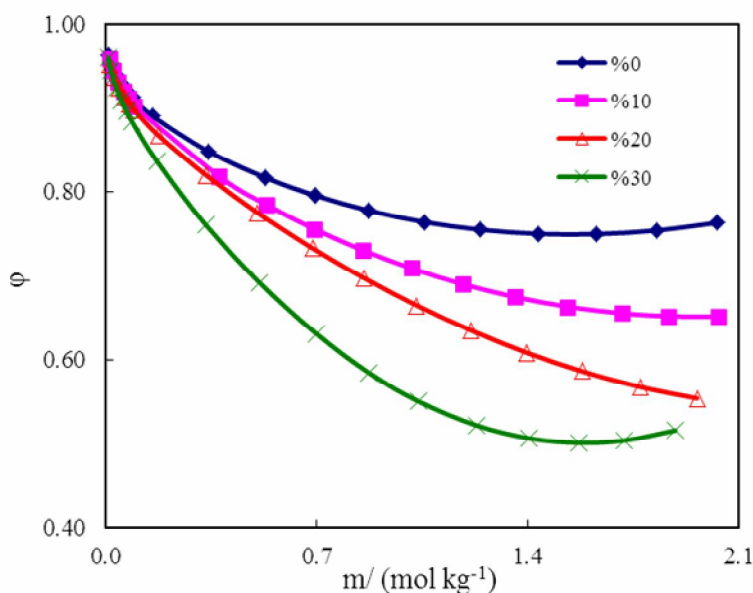


Fig. 5. The osmotic coefficient (ϕ) against the molality (m) of [PrMIm]Br ionic liquid in 0, 10, 20, and 30% mass fractions of ethanol in ethanol - water mixed solvent based on Pitzer model at 298.2 K.

(a_s) for [PrMIm]Br in ternary mixture ([PrMIm]Br + water + ethanol) and binary mixture ([PrMIm]Br + water) can be computed using Eqs. (6)-(9).

$$\phi = 1 - \frac{A_\phi \sqrt{I}}{1 + b\sqrt{I}} + B_{[\text{PrMIm}]\text{Br}}^\phi + C_{[\text{PrMIm}]\text{Br}}^\phi I^2 \quad (6)$$

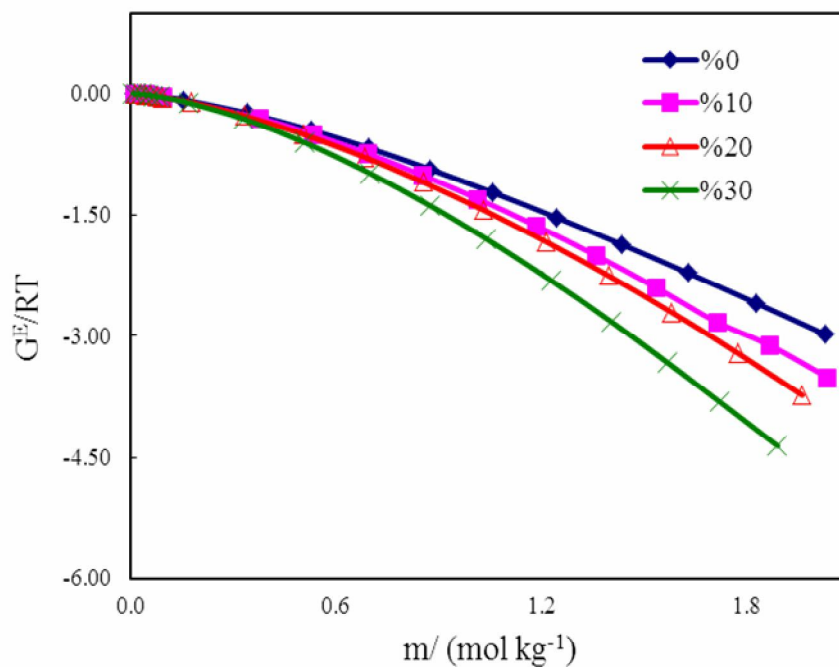


Fig. 6. The excess Gibbs free energy (G^E) against the molality (m) [PrMIm]Br ionic liquid in 0, 10, 20, and 30% mass fractions of ethanol in ethanol - water mixed based on Pitzer model at 298.2 K.

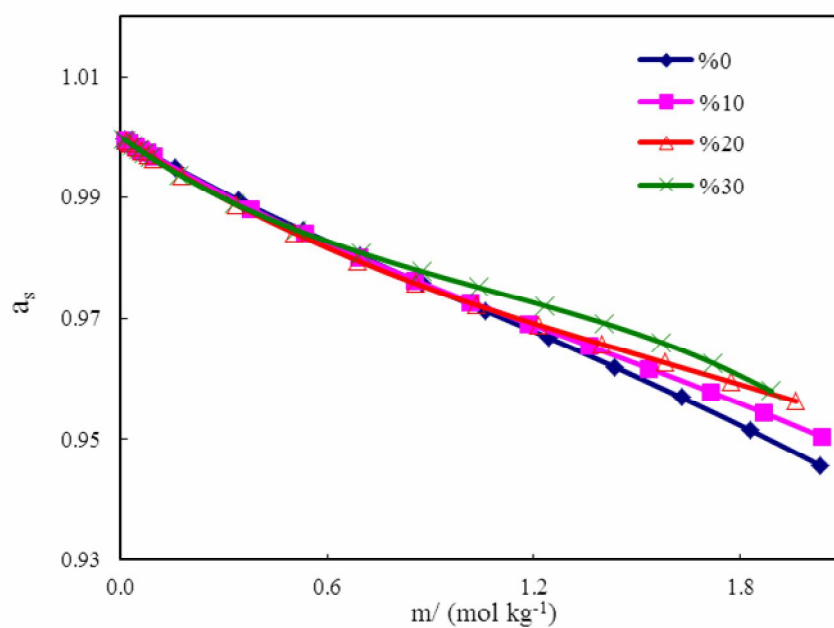


Fig. 7. The solvent activity (a_s) against the molality (m) of the [PrMIm]Br ionic liquid in 0, 10, 20, and 30% mass fractions of ethanol in ethanol - water mixed based on Pitzer model at 298.2 K.

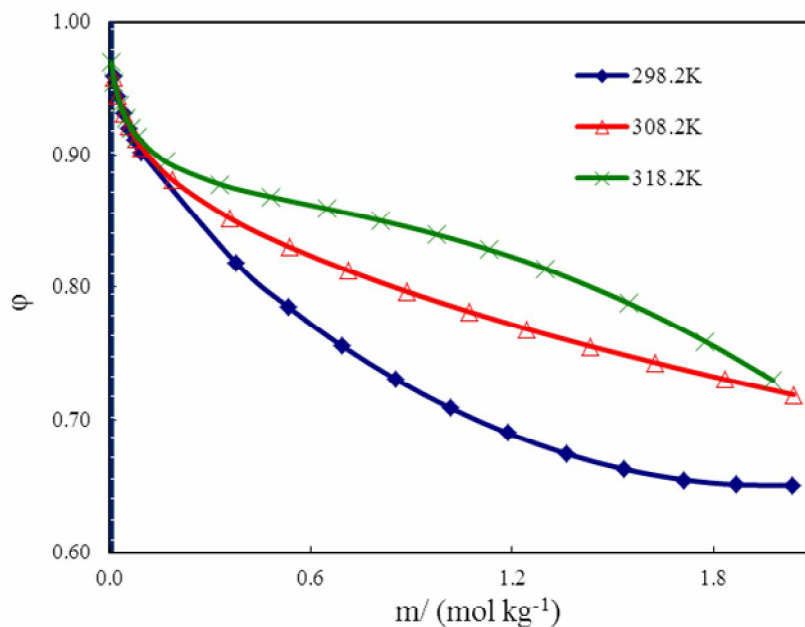


Fig. 8. The osmotic coefficient of (ϕ) [PrMIm]Br + ethanol + water mixtures as a function of molality concentration (m) of [PrMIm]Br in mass fraction 10% ($w_{\text{Ethanol}}/w_{\text{mixture}}$). Solid lines were generated using Pitzer model.

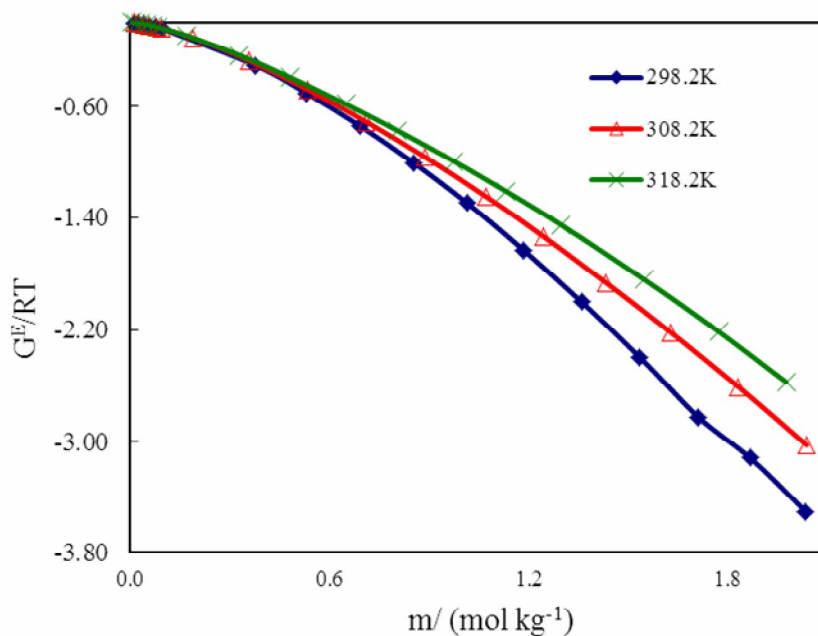


Fig. 9. The excess Gibbs free energy (G^E) of [PrMIm]Br + ethanol + water mixtures as a function of molality concentration (m) of [PrMIm]Br in mass fraction 10% ($w_{\text{Ethanol}}/w_{\text{mixture}}$) based on Pitzer model.

$$B_{[\text{PrMIm}]\text{Br}}^{\circ} = \beta_{[\text{PrMIm}]\text{Br}}^{(0)} + \beta_{[\text{PrMIm}]\text{Br}}^{(1)} \exp(-\alpha\sqrt{I}) \quad (7)$$

$$G^E = 2m_{\text{IL}}RT(1 - \phi + \ln\gamma_{\pm}) \quad (8)$$

where m_{IL} is the molality of ionic liquid of [PrMIm]Br.

$$a_s = \exp\left(\frac{-\phi MI}{500}\right) \quad (9)$$

The values of osmotic coefficients, the excess Gibbs free energy, and solvent activity are shown in Table 4 for different mass fractions of ethanol in (water + ethanol) mixtures at $T = (298.2, 308.2 \text{ and } 318.2) \text{ K}$.

In Figs 5-7, the osmotic coefficients (ϕ), the excess Gibbs free energy, and solvent activity versus the ternary systems water + [PrMIm]Br + ethanol were compared with various mass fractions at $T = 298.2 \text{ K}$. It is observed that with increasing mass fraction of ethanol in solvent mixture, the magnitude of the excess Gibbs free energy decreases.

Furthermore, the magnitude of excess Gibbs free energy decreases with increase in molality concentration of [PrMIm]Br for all of the studied electrolyte systems showing non-ideal behavior of excess Gibbs free energy in the solution at higher molality concentration. Figures 8 and 9 show the osmotic coefficients (ϕ), the excess Gibbs free energy on the molality concentration of IL in ternary mixtures ([PrMIm]Br + water + ethanol) with 10% ethanol mass fraction at $T = (298.2, 308.2 \text{ and } 318.2) \text{ K}$. It can be seen that the magnitude of excess Gibbs free energy decreases by increasing temperature at the same mass fraction of ethanol. The effect of temperature on the excess Gibbs free energy can be designated in terms of temperature dependency of solvent dielectric constant, long- range interactions, and short- range interactions in accordance to Eqs. (1)-(4).

CONCLUSIONS

The cell potentials were measured for [PrMIm]Br ionic liquid in water + ethanol mixed solvent containing 0, 10, 20, and 30% mass fractions of ethanol using self-made electrodes at $T = (298.2, 308.2 \text{ and } 318.2) \text{ K}$. The Pitzer

parameters ($\beta^{(0)}$, $\beta^{(1)}$ and C^{ϕ}) were determined for the studied system. Values of osmotic coefficient and excess Gibbs free energy were obtained using the experimental data relationship with Pitzer model. The excess Gibbs free energy decreased with increasing mass fraction of ethanol. The obtained results show that the adjustable parameters of Pitzer's model have the explicit relation. It can be concluded that the Pitzer model can be used to analyze the ternary system containing ionic liquid satisfactorily.

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