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

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In this work, the results of the mean activity coefficient measurements for ionic liquid of 1-propyl-3-methylimidazolium bromide, \([\text{PrMIm}]\text{Br}\), 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: \( \text{Br-ISE} \mid \text{[PrMIm]}(m) \text{ ethanol (wt%)}, \text{H}_2\text{O (1-wt)}\% \mid \text{[PrMIm]} - \text{ISE} \), 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 \( C^\phi \)) 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 pharmaceutics [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 \( C^\phi \) 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 \( \beta^0, \beta^1 \) and \( C^\phi \) 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 $\beta^0$, $\beta^1$ and $C^0$ 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 $\mu$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 $^1$H NMR (Brucker 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 ionic 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 polyethylenesulfonic 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. 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:

\[ \text{Br} - \text{ISE} \mid [\text{PrMIm}]\text{Br} \ (m); \text{ethanol (wt%)}; \text{H}_2\text{O} \ (1 \ - \ wt\%) \ %[\text{PrMIm}] - \text{ISE} \]

where \( m \) and \( w \) are the molality of \([\text{PrMIm}]\text{Br}\) and the mass fraction of ethanol in the mixed solvent, 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 (\( \gamma \)) based on the Pitzer model for ionic liquid can be given as follows:

\[
\ln A_T(\text{ionic liquid}) = f^2 + B_{ionic \ liquid} + 1.5C_{ionic \ liquid} T^2
\]

where

\[
f^2 = A_0\left[\frac{\sqrt{T}}{1 + b\sqrt{T}} + \left(\frac{2}{b}\right)ln\left(1 + b\sqrt{T}\right)\right]
\]

\[
B_{ionic \ liquid} = 2\beta^{(0)}_{ionic \ liquid} - \frac{2\beta^{(0)}_{ionic \ liquid}}{a^2T}\left[1 - \left(1 + a\sqrt{T} - \frac{a^2T}{2}\right)e^{-\gamma}\right]
\]

where \( a \) and \( b \) are presumed to be constant with values of 2.0 and 1.2 kg\(^{1/2}\) mol\(^{-1/2}\), respectively. The I symbol stands for the total ionic strength on a molality scale in ethanol + water mixtures. \( \beta^{(0)} \) and \( C^b \) are attributed to solute-specific interaction Pitzer parameters for electrolyte solution that their values should be determined for ionic liquid in solvent mixtures. \( A_0 \) shows the Debye–Hückel parameter for the osmotic coefficients defined by:

\[
A_0 = \frac{1.4006 \times 10^6 \rho^{-1/2}}{(e_\gamma T)^{3/2}} kg^{1/2} mol^{-1/2}
\]

where \( \rho, e_\gamma \) and \( T \) are solvent density (kg m\(^{-3}\)), solvent relative permittivity and the Kelvin temperature, respectively. The values of density (\( \rho \)), molar mass, relative permittivity (\( e_\gamma \)), Debye–Hückel constants (\( A_0 \)) of the pure water, and the mixture (ethanol-water) were reported in Table I [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:

\[
E_A = E^r_A + k \cdot \log(m \gamma_{[\text{PrMIm}]\text{Br}}) = E^r_A + s \log(f_{\gamma} m)
\]

where \( k = (\ln10)RT/ZF \) 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 \( \gamma \), \( E^r_a \) 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 \( \log(\gamma^{r}_A([\text{PrMIm}]\text{Br} I)) \) 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 (\( R^2 = 0.9999 \)).
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 $1/\varepsilon$. 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

Table 1. The Values of Density ($\rho$), Molar Mass, Relative Permittivity ($\varepsilon_r$), and Debye-Hückel Constants ($A_\phi$), as the Functions of the Mass Fraction of Ethanol in Ethanol-water Mixtures at 298.2, 308.2 and 318.2 K

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<th>$M$ (g mol$^{-1}$)</th>
<th>$\varepsilon_r$</th>
<th>$A_\phi$ (kg$^{1/2}$ mol$^{-1/2}$)</th>
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$^a$ Values of density ($\rho$) at T = 298.2 K

$^b$ Values of density ($\rho$) at T = 308.2 K

$^c$ Values of density ($\rho$) at T = 318.2 K
Fig. 1. The cell (A) emf as a function of log(γ± I) to calibrate the IL-ISE and Br-ISE electrode pair at 298.2 K.

Table 2. The [PrMIm]Br molalities (m_{[PrMIm]Br}), the Mean Activity Coefficients (γ±, 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

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Table 2. Continued

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

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+ 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.

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<th>β(1) (kg mol⁻¹)</th>
<th>C⁰ (kg² mol⁻²)</th>
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<th>E⁰ (mv)</th>
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Uncertainties: u(T) = ±0.1 K; u(wt%) = ±0.03.

Table 3. The Values Obtained of Pitzer Parameter β(0), β(1), C⁰, 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.
Calculation of Thermodynamic Properties by the Pitzer Model

The Pitzer model was applied to predict the thermodynamic properties of the under investigation system using the obtained parameters. The osmotic coefficients ($\phi$), the excess Gibbs free energy ($G^e$), and solvent activity...
Fig. 4. Temperature comparison of the mean activity coefficient ($\gamma_\pm$) 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 ($\phi$), 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

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<th>$a_s$</th>
<th>m (mol kg$^{-1}$)</th>
<th>$\phi$</th>
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Table 4. Continued

Table 4. Continued

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Uncertainties: u(T) = ±0.1 K; u(m) = ±0.0001 mol kg⁻¹, u(GE/RT) = ±0.0015, u(φ) = ±0.01, u(aₜ) = ±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.

(aₜ) for [PrMIm]Br in ternary mixture ([PrMIm]Br + water + ethanol) and binary mixture ([PrMIm]Br + water) can be computed using Eqs. (6)-(9).
Fig. 6. The excess Gibbs free energy (G°) against the molality (m) of [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 \((\varphi)\) \([\text{PrMIm}]\text{Br} + \text{ethanol} + \text{water}\) mixtures as a function of molality concentration \((m)\) of \([\text{PrMIm}]\text{Br}\) 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 \([\text{PrMIm}]\text{Br} + \text{ethanol} + \text{water}\) mixtures as a function of molality concentration \((m)\) of \([\text{PrMIm}]\text{Br}\) in mass fraction 10\% \((W_{\text{ethanol}}/W_{\text{mixture}})\) based on Pitzer model.
\[ B^i_{[\text{PrMIm}Br]} = \beta^{(1)}_{[\text{PrMIm}Br]} + \beta^{(2)}_{[\text{PrMIm}Br]} \exp(-\alpha \sqrt{T}) \]  
(7)

\[ G^s = 2m_{\text{IL}}RT(1 - \varphi + \ln\gamma_{s}) \]  
(8)

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

\[ a_s = \exp(-\varphi_{\text{MI}}) \]  
(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 \( T = (298.2, 308.2 \text{ and } 318.2) \) K.

In Figs 5-7, the osmotic coefficients (\( \varphi \)), the excess Gibbs free energy, and solvent activity versus the ternary systems water + [PrMIm]Br + ethanol were compared with various mass fractions at \( T = 298.2 \) 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 (\( \varphi \)), the excess Gibbs free energy on the molality concentration of IL in ternary mixtures ([PrMIm]Br + water + ethanol) with 10% ethanol mass fraction at \( T = (298.2, 308.2 \text{ and } 318.2) \) 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 \( T = (298.2, 308.2 \text{ and } 318.2) \) K. The Pitzer parameters (\( \beta^{(1)} \), \( \beta^{(2)} \) and \( C^b \)) 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.

**ACKNOWLEDGEMENTS**

The authors thank the University of Guilan for supporting of this work.

**REFERENCES**


