

# Thermophysical Properties of Ionic Liquid, 1-Pentyl-3-methylimidazolium Chloride in Water at Different Temperatures

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**Abstract** Osmotic coefficients,  $\phi$ , electrical conductance data,  $\Lambda$ , and refractive indices,  $n_D$ , of aqueous solutions of the ionic liquid, 1-pentyl-3-methylimidazolium chloride [PnMIm]Cl have been measured at  $T = (298.15, 308.15, 318.15, \text{ and } 328.15) \text{ K}$ . Measurements of osmotic coefficients were carried out by the vapor-pressure osmometry method (VPO). Osmotic coefficient values show that ion–solvent interactions are stronger at lower temperature. The osmotic coefficients were correlated to the Pitzer-ion interaction and modified NRTL (MNRTL) models. From these data, mean molal activity coefficients,  $\gamma_{\pm}$ , and excess Gibbs free energies,  $G^E$ , have been calculated. Electrical conductance data have been applied for determination of association constants,  $K_a$ , and limiting molar conductances,  $\Lambda_0$ , using the low concentration chemical model (lcCM). Calculated ion-association constant,  $K_a$ , values show that ion-association effects increase at high temperatures which is in agreement with osmotic coefficient results. Experimental results of refractive indices for the binary system are reported, and have been fitted by a polynomial expansion.

**Keywords** Electrical conductance · Ionic liquids · Osmotic coefficients · 1-Pentyl-3-methylimidazolium chloride · Refractive index · Vapor pressure osmometry

## 1 Introduction

Recently, room-temperature ionic liquids (RTILs) as alternative solvents and reaction media have become an intense research area, because of their important advantages such as negligible vapor pressure, a wide liquid range, high conductivity, excellent

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dissolution ability for organic, inorganic, and polymeric compounds, ease of recycling, and nonflammability [1–3]. Therefore, they can replace toxic, flammable traditional volatile organic solvents in many research and industrial applications [4–7]. Ionic liquids comprise entirely of ions with a large organic cation such as 1-alkyl-3-methylimidazolium cation and an inorganic or organic anion such as  $\text{Cl}^-$  or  $[\text{BF}_4]^-$  anions. Since a large number of cations and anions can be combined, there is virtually no limit in the number of feasible ionic liquids.

It was found that the thermophysical properties of ionic liquids are strongly dependent on the nature of the cation and anion. The potential advantages of ionic liquids depend on studies of thermophysical properties such as activity coefficients, vapor–liquid equilibria, liquid–liquid phase equilibria, gas solubility, surface tensions, viscosities, electrical conductivities, etc. Therefore, various research groups started with systematic measurements of thermophysical properties [8,9]. These types of data were also used to gain a better understanding of solute–solvent interactions between ionic liquids and molecular solvents. Earlier, several authors investigated a series of imidazolium-based ionic liquids. For example, systematic measurements of density, viscosity, speed of sound, surface tension, thermal conductivity, and phase equilibria were reported [10–32].

This article is a continuation of our other studies on the systematic measurement of thermophysical properties of systems containing ionic liquids,  $[\text{BMIm}]\text{Br}$ ,  $[\text{HMIm}]\text{Br}$ ,  $[\text{Bmim}][\text{BF}_4]$ , and  $[\text{Bmim}][\text{PF}_6]$  in water or a molecular solvent [33,34]. The main objective of this study is the measurement of experimental osmotic coefficients, electrical conductance data, and refractive indices of aqueous solutions of the ionic liquid  $[\text{PnMIm}]\text{Cl}$ . Experimental osmotic coefficients have been measured using the vapor-pressure osmometry (VPO) method at temperatures  $T = (298.15 \text{ to } 328.15) \text{ K}$  at increments of 10 K. These data have been correlated with the Pitzer-ion interaction model [35] and one local composition model, the modified NRTL (MNRTL) electrolyte model [36]. These models have been successfully used for correlation of osmotic coefficients for electrolyte solutions. Experimental osmotic coefficients have been used for calculation of vapor-pressure depressions of these solutions. Using Pitzer-ion interaction parameters, mean molal activity coefficients and excess Gibbs free energies of the studied ionic liquid were obtained. Molar conductances of this system have been correlated with the low concentration chemical model (lcCM) of the conductance, and ion-association constants have been obtained at different temperatures. Experimental results of refractive indices for these studied systems are reported and have been fitted by a polynomial expansion.

## 2 Experimental

### 2.1 Materials

*N*-methylimidazole (>99 % mass fraction), 1-chloropropan (>99 % mass fraction), ethyl acetate (>99 % mass fraction), and toluene (>99 % mass fraction) were supplied by Merck. These reagents were used without further purification. The doubly dis-

tilled water was used for preparation of solutions. The pure water had an electrical conductivity of less than  $1.3 \mu\text{S} \cdot \text{cm}^{-1}$ .

## 2.2 Synthesis of Ionic Liquid

[PnMIm]Cl was prepared and purified by using the procedure described in the literature [37,38]. In brief, [PnMIm]Cl was synthesized by direct alkylation of *N*-methylimidazole (freshly distilled) with an excess of 1-chloropentane (10 mol%) in a two-necked round bottom flask fitted with a water condenser and a gas inlet and provided with a Teflon-coated magnetic spin bar charged with  $\text{N}_2$  at  $T = 353.15 \text{ K}$  for 72 h with continuous magnetic stirring until two phases were formed. The resulting viscous liquid was cooled and dissolved in ethyl acetate, and after equilibrium, was decanted, and the procedure was repeated three times using fresh ethyl acetate. The yellowish product was concentrated at around of  $T = 333 \text{ K}$  using a rotary evaporator for at least 4 h at 0.7 kPa. These ionic liquids were further dried under high vacuum at around 353 K for 24 h to remove trace amounts of water. The ionic liquid was analyzed by  $^1\text{H}$  NMR (Bruker 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 [39,40].

## 2.3 Apparatus and Procedures

The samples were prepared by filling glass vials with the ionic liquid and doubly distilled water. Vials were closed tightly. The sample was taken from the vial with a syringe through a silicone septum and transferred immediately into the apparatus. The mass of chemicals was determined using a Sartorius analytical balance with a precision of  $\pm 1 \times 10^{-4} \text{ g}$ . Osmotic coefficient measurements were performed with the help of a vapor-pressure osmometer (VPO) K-7000 (Knauer Inc). With this method, osmotic coefficients were determined indirectly by using voltage changes of thermistors caused by changes in temperature. This type of osmometer, its principle of operation, and its application to the estimation of osmotic coefficients of ionic liquid solutions have been described in an earlier study [41]. In brief, in the beginning, a droplet of pure solvent is attached to each thermistor, and after 5 min of equilibration, the reading is adjusted to zero. Then the pure solvent on one of the thermistors is replaced by the ionic liquid solution. The change in temperature changes the resistance of the thermistors. As long as changes in temperature are small, the resistance is proportional to  $\Delta T$ .

For aqueous solutions, the instrument was calibrated using NaCl reference solutions with known osmotic coefficients in the proper concentration range, yielding a function that correlates the panel readings to the corresponding concentrations of the reference solutions and their osmotic coefficients. Then at the same conditions, the panel readings were measured for the studied ionic liquid solutions. The standard uncertainty in the output of the instrument was  $1 \Omega$ , and the maximum variation was within  $\pm 2\%$  of the measured value. The cell temperature, which is electronically controlled, has a standard uncertainty of  $1 \times 10^{-3} \text{ K}$ . 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 is reported. Osmotic coefficients of aqueous solutions of NaCl were calculated with the help of the equation developed by Colin [42]. This equipment has been widely applied for measuring osmotic coefficients of electrolyte and nonelectrolyte solutions, especially for the dilute region, and shows good agreement in comparison with the direct vapor-pressure lowering [43–45] method.

Refractive indices of the studied systems at different temperatures were determined using a digital refractometer (ATAGO-DRA1 Japan) with an uncertainty of  $1 \times 10^{-4}$  calibrated with doubly distilled water and tetrachloroethylene before each series of measurements. Calibration was checked with pure liquids of known refractive index. The temperature was controlled with a circulating bath Julabo NP (Germany) thermostat with a temperature stability of  $\pm 0.01$  K. Electrical-conductance measurements were carried out on a digital conductivity meter (Meterohm 712) with a sensitivity of 0.1 % and a dipping-type conductivity cell with platinized electrodes with a cell constant of  $0.824 \text{ cm}^{-1}$  under a nitrogen atmosphere and at a frequency of 1 MHz. The total uncertainty for this property is  $1 \text{ S} \cdot \text{cm}^2 \cdot \text{mol}^{-3}$ . The cell constant was calibrated with aqueous KCl solutions. About 50 ml of pure solvent was placed in the conductivity cell, and the cell was closed. A weighed pure ionic liquid was added with a syringe to the cell containing the solvent. Circulating water from a thermostatically regulated bath surrounded the sample holder with a double wall to maintain the temperature within a precision of 0.02 K. The conductivity cell was purged with nitrogen during each run. The conductivities of ionic liquid solutions were always corrected for the contribution of the pure water. The osmotic coefficients,  $\phi$ , of the studied aqueous solutions of ionic liquid with molality,  $m$ , in equilibrium were obtained according to

$$\phi = (v_r m_r \phi_r) / (vm) \quad (1)$$

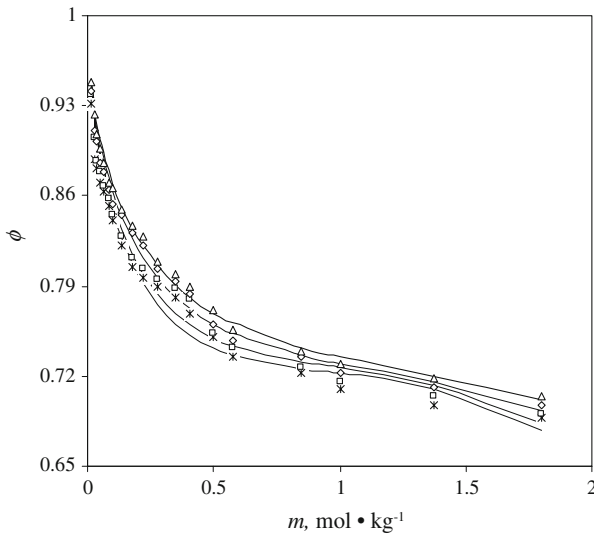
where  $\phi_r$ ,  $m_r$ , and  $v_r$  are, respectively, the osmotic coefficient, the molality, and the stoichiometric number of the reference electrolyte which are set equal to two. At this molality, the vapor pressure of the aqueous solution of ionic liquid and reference electrolyte are the same.

### 3 Results and Discussion

Table 1 gives the experimental osmotic coefficients,  $\phi$ , of the aqueous solutions of [PnMIm]Cl, at  $T = (298.15 \text{ to } 328.15) \text{ K}$  at increments of 10 K using Eq. 1. Figure 1 shows the molal concentration dependence of the experimental osmotic coefficients for aqueous solutions of [PnMIm]Cl, at  $T = (298.15 \text{ to } 328.15) \text{ K}$ . The behavior of the osmotic coefficients can be interpreted in terms of ion-solvation and ion-association interactions. On examination of Fig. 1, it is noted that the osmotic coefficient decreases with increasing concentration of ionic liquid showing the presence of nonideality due to ion-association interactions. This figure shows that  $\phi$  values of the [PnMIm]Cl solutions are less sensitive to variations in temperature. With increasing temperature, the  $\phi$  values increased showing nonideality behavior at low temperature. Our previous studies showed that the ion-association constants of aqueous solutions of [HMIm]Br

**Table 1** Experimental osmotic coefficient data,  $\phi^{\text{exp}}$ , of ([PnMIm]Cl + H<sub>2</sub>O) at different temperatures

$m$ (mol · kg <sup>-1</sup> )	$T = 298.15$ K	$T = 308.15$ K	$T = 318.15$ K	$T = 328.15$ K
0.0140	0.931	0.938	0.941	0.949
0.0263	0.889	0.905	0.911	0.923
0.0391	0.882	0.887	0.903	0.908
0.0518	0.871	0.878	0.885	0.897
0.0634	0.863	0.868	0.878	0.886
0.0840	0.852	0.858	0.865	0.870
0.1007	0.841	0.845	0.854	0.866
0.1369	0.821	0.829	0.845	0.849
0.1784	0.805	0.812	0.831	0.837
0.2198	0.797	0.803	0.822	0.828
0.2765	0.790	0.795	0.803	0.809
0.3517	0.781	0.788	0.794	0.799
0.4043	0.768	0.780	0.784	0.790
0.5014	0.750	0.753	0.760	0.771
0.5758	0.735	0.742	0.748	0.756
0.8464	0.722	0.726	0.735	0.739
1.0016	0.710	0.715	0.723	0.730
1.3758	0.697	0.704	0.711	0.718
1.7972	0.687	0.691	0.697	0.704



**Fig. 1** Plot of osmotic coefficients of [PnMIm] Cl + H<sub>2</sub>O mixture versus molality of ionic liquid: lines were generated using MNRTL model; data: \*, 298.15 K; □, 308.15 K; △, 318.15 K; ◇, 328.15 K

**Table 2** Second virial coefficient  $B_s$ , molar volume  $V_s$ , density  $d_s$ , relative permittivity  $\epsilon$ , Debye–Hückel constant for the osmotic coefficient  $A_\phi$ , and vapor pressure of pure water  $p^*$ , at the experimental temperatures

$T$ (K)	$B_s \times 10^6$ ( $\text{m}^3 \cdot \text{mol}^{-1}$ )	$V_s \times 10^6$ ( $\text{m}^3 \cdot \text{mol}^{-1}$ )	$d_s$ ( $\text{kg} \cdot \text{m}^{-3}$ )	$A_\phi$ ( $\text{kg} \cdot \text{mol}^{-1}$ ) <sup>1/2</sup>	$p^*$ (kPa)	$\epsilon$
298.15	−3272.93	18.07	997.043	0.39145	3.1698	78.38
308.15	−1604.58	18.12	994.029	0.39849	5.6291	74.86
318.15	−1420.97	18.19	990.168	0.40620	9.5953	71.50
328.15	−1249.25	18.28	985.650	0.41456	15.7630	68.29

have larger values at higher temperatures [34]. This means that the concentration of an ion pair in an ionic liquid increases at higher temperatures, resulting in a decrease of osmotic coefficients. Similar behavior was observed for some ionic liquids in different organic solvents [46].

The activities,  $a_s$ , and vapor pressure,  $p$ , of water for the studied systems ([PnMIm]Cl + H<sub>2</sub>O) as a function of the molality of ionic liquid,  $m$ , were calculated from osmotic coefficient data using the following equations:

$$\ln(a_s) = -\phi \nu m M_s \quad (2)$$

and

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

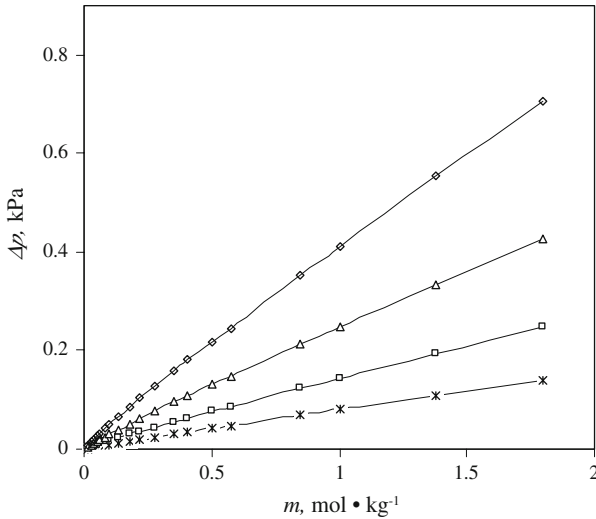
In these equations,  $M_s$  is the molar mass of the solvent,  $\nu$  is the stoichiometric numbers of ionic liquid,  $T$  is the absolute temperature,  $p$  is the vapor pressure of the solution, and  $p^*$  is that of the pure solvent.  $B_s$  is the second virial coefficient, and  $V_s^*$  is the molar volume of the pure solvent.  $B_s$  and  $V_s^*$  values of the pure water at  $T = (298.15 \text{ to } 328.15) \text{ K}$  are presented in Table 2 [47].

The effect of temperature on the calculated vapor-pressure depression ( $\Delta p = p^* - p$ ) values for the [PnMIm]Br + H<sub>2</sub>O mixtures has been shown in Fig. 2. The extent of  $\Delta p$  values is related to ion–solvent interactions between the ionic liquid and H<sub>2</sub>O.

### 3.1 Correlation of Osmotic Coefficient Data

Several models are available in the literature for correlation of the concentration dependence of osmotic coefficients. The Pitzer-ion interaction model has been widely used for aqueous electrolyte solutions and has the following form for a binary 1:1 electrolyte solution;

$$\phi - 1 = f^\phi + mB^\phi + m^2C^\phi \quad (4a)$$



**Fig. 2** Plot of vapor-pressure depressions of [PnMIm]Cl + H<sub>2</sub>O mixture versus molality of ionic liquid: \*, 298.15 K; □, 308.15 K; △, 318.15 K; ◇, 328.15 K

**Table 3** Parameters of the Pitzer model for [PnMIm]Cl + H<sub>2</sub>O system at different temperatures

<i>T</i> (K)	$\beta^{(0)}$	$\beta^{(1)}$	$C^\phi$	$\sigma(\phi)$
298.15	0.18445	-1.47888	-0.08389	0.015
308.15	0.14927	-1.27887	-0.06888	0.012
318.15	0.08614	-0.95993	-0.04178	0.009
328.15	0.04744	-0.74104	-0.02450	0.006

where

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

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

In these equations,  $\beta^{(0)}$ ,  $\beta^{(1)}$ , and  $C^\phi$  are the ion interaction parameters of the Pitzer model that are dependent on temperature and pressure and  $A_\phi$  is the Debye–Hückel constant for the osmotic coefficient on the molal scale.  $A_\phi$  values for water are given in Table 2 at temperatures  $T = (298.15 \text{ to } 328.15) \text{ K}$  [48]. The term,  $I$ , is the ionic strength in molality,  $I = (1/2)\sum m_i z_i^2$  where  $m_i$  is the molality of the  $i$ th ion and  $z_i$  is the absolute value for the  $i$ th ionic charge. The other constants were  $b = 1.2 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$  and  $\alpha = 2 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$  which yield reliable fits for some aqueous electrolyte solutions. The Pitzer-ion interaction model parameters of the studied system are given in Table 3 using a nonlinear least-squares method.

The experimental osmotic coefficients in the studied ionic liquid are described formally by using the local composition modified NRTL (MNRTL) equation. 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,  $\gamma_s$ , have been expressed as the sum of long-range (LR) and short-range (SR) contributions;

$$\ln(\gamma_s) = \ln(\gamma_s^{\text{LR}}) + \ln(\gamma_s^{\text{SR}}) \quad (5)$$

where subscript,  $s$ , refers to the solvent.

The long-range contribution is represented by the Pitzer–Debye–Hückel (PDH) equation. The PDH equation for the solvent activity coefficient has the following form:

$$\ln(\gamma_s^{\text{PDH}}) = - \left( \frac{1}{M_s} \right)^{\frac{1}{2}} A_\phi \left\{ \frac{2z_i^2 \ln(1 + \rho I_x^{\frac{1}{2}})}{\rho} + \frac{z_i^2 I_x^{\frac{1}{2}} - 2I_x^{\frac{3}{2}}}{1 + \rho I_x^{\frac{1}{2}}} \right\} \quad (6)$$

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

The MNRTL model that represents the short-range contribution for the solvent activity coefficient has been developed by Jaretum and Aly [10]. This model is expressed in the following form where there are four fitting parameters:

$$\begin{aligned} \ln \gamma_{s,\text{MNRTL}} \\ = 4X_c^2 \left[ \tau_{\text{ca},s} W_{\text{ca},s} / (X_s + 2W_{\text{ca},s} X_c)^2 + \tau_{s,\text{ca}} (W_{s,\text{ca}} - 1) / (X_c + X_s W_{\text{ca},s})^2 \right] \end{aligned} \quad (7)$$

for which  $\tau_{\text{ca},s}$  (salt–solvent parameter) and  $\tau_{s,\text{ca}}$  (solvent–salt parameter) are the model parameters, and the following definition have been carried out:

$$W_i = \exp(-\alpha \tau_i + \omega_i) \quad (8)$$

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

The activity coefficient equation was converted to the osmotic coefficient,  $\phi$ , via the following equation:

$$\phi = - \left[ \ln(\gamma_s^{\text{LR}}) + \ln(\gamma_s^{\text{SR}}) + \ln(x_s) \right] / \nu m M_s \quad (9)$$

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

$$\sigma(\phi) = \left( \sum_i (\phi^{\text{exp}} - \phi^{\text{cal}})^2 / (N - m) \right)^{1/2} \quad (10)$$



**Table 4** Parameters of the MNRTL model for the [PnMIm]Cl + H<sub>2</sub>O system at different temperatures

<i>T</i> (K)	$\tau_{s,ca}$	$\tau_{ca,s}$	$\omega_{s,ca}$	$\omega_{ca,s}$	$\sigma(\phi)$
298.15	0.00057	0.62879	5.94743	−3.33258	0.005
308.15	0.00071	0.63671	5.71695	−3.22733	0.004
318.15	0.00059	0.64235	2.23788	−3.94052	0.017
328.15	0.03500	0.14782	2.81891	−6.34772	0.003

where  $\phi^{exp}$ ,  $\phi^{cal}$ ,  $N$ , and  $m$  are the experimental osmotic coefficients, calculated osmotic coefficients, number of experimental data, and number of model parameters, respectively. The MNRTL model parameters of the investigated system are given in Table 4.

These values show that the Pitzer-ion interaction and MNRTL models can be used for satisfactory correlation of the experimental osmotic coefficients of aqueous solutions of the studied ionic liquid. But the standard deviation values for the MNRTL model are better than for the other model.

### 3.2 Determination of Mean Molal Activity Coefficient and Excess Gibbs Free Energy

The osmotic coefficients can be used for calculation of the mean molal activity coefficients of the ionic liquid. Applications of the Gibbs–Dühem equation for Eq. 4a and using Pitzer model parameters, give

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

where

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

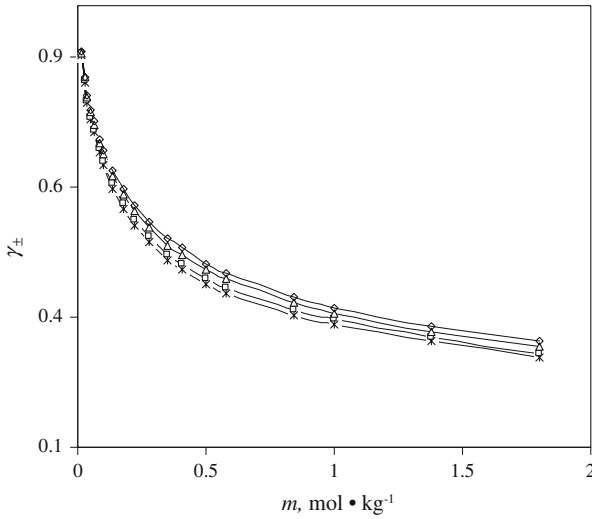
$$B^{\gamma} = 2\beta^{(0)} + \frac{2\beta^{(1)}}{\alpha^2 I} \left[ 1 - \left( 1 + \alpha I^{\frac{1}{2}} - \frac{\alpha^2 I}{2} \right) \exp \left( -\alpha I^{\frac{1}{2}} \right) \right] \tag{11c}$$

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

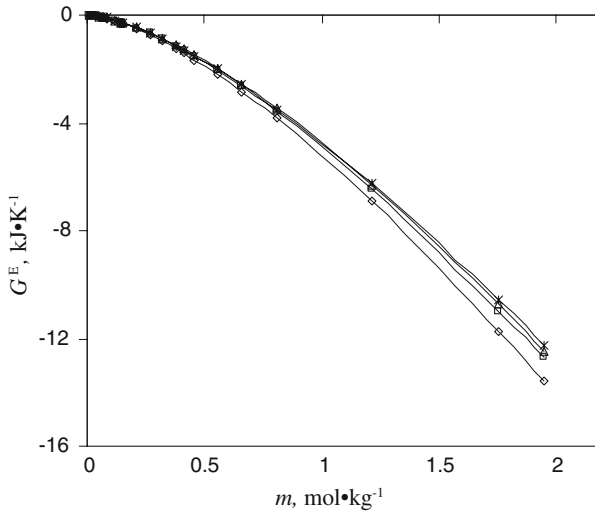
The accuracy of calculated  $\gamma_{\pm}$  values depends on how well the model correlates the osmotic coefficient data for the studied systems [49]. The dependence of the mean molal activity coefficient data on the ionic liquid concentration is shown in Fig. 3 for aqueous solutions of the studied ionic liquid.

Nonidealities can be conveniently presented in terms of 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

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



**Fig. 3** Plot of mean molal activity coefficients of [PnMim] Cl + H<sub>2</sub>O mixture versus molality of ionic liquid: \*, 298.15K; □, 308.15 K; △, 318.15 K; ◇, 328.15 K



**Fig. 4** Plot of excess Gibbs free energies of [PnMim] Cl + H<sub>2</sub>O mixture versus molality of ionic liquid: \*, 298.15K; □, 308.15 K; △, 318.15 K; ◇, 328.15 K

where  $n_{IL}$  is the number of moles of ionic liquid. Figure 4 shows the excess Gibbs free energy values for aqueous solutions of [PnMim]Cl calculated from osmotic coefficient and mean molal activity coefficient data at the experimental temperatures.

**Table 5** Molar concentrations  $c$  ( $\text{mol} \cdot \text{m}^{-3}$ ) and molar conductivities  $\Lambda$  ( $\text{S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$ ) of aqueous solutions of ([PnMIm]Cl + H<sub>2</sub>O) system at different temperatures

298.15 K		308.15 K		318.15 K		328.15 K	
$c$	$\Lambda$	$c$	$\Lambda$	$c$	$\Lambda$	$c$	$\Lambda$
0.6930	88.50	0.7520	99.32	0.2730	115.47	0.5880	118.70
1.4530	88.01	1.6430	97.49	0.5920	113.69	1.0760	117.62
2.0970	87.28	2.6860	96.35	1.2070	112.21	1.6120	116.75
2.7320	86.94	3.4700	95.61	2.0020	111.25	2.1090	116.41
4.6370	86.38	4.1910	95.95	2.7570	109.82	2.9490	115.95
6.2720	85.78	5.0810	95.32	3.4830	108.02	3.7210	115.57
7.7540	85.18	6.2150	94.45	4.4580	107.34	4.6080	114.63
10.2260	84.05	7.6460	93.70	5.6010	106.49	5.8970	113.41
12.8330	83.24	9.1720	92.68	7.3480	104.92	7.0870	111.27
17.7490	81.65	11.0210	91.68	8.9040	103.80	8.6320	109.73
21.8570	80.44	12.6850	91.16	10.5170	102.96	10.3430	107.84
27.0420	79.33	14.4700	90.62	12.4040	101.97	12.2920	105.69
32.0540	78.28	16.2500	90.17	14.7780	100.62	15.3870	104.78
		17.9940	89.50	16.6060	99.96	17.8760	103.59
		19.8590	88.95	19.5950	98.89	20.1130	102.93
		22.5340	88.06	22.4110	97.76	22.7300	101.07
		25.4910	87.30	25.4460	96.63		
		28.8450	86.30	28.9690	95.27		
		32.4530	85.58				

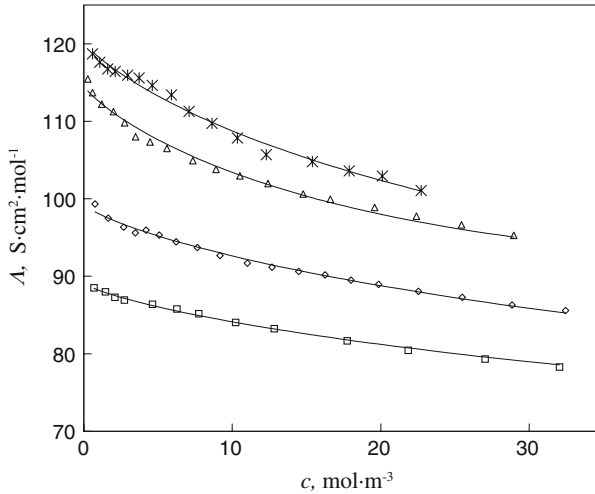
### 3.3 Determination of Ion-Association Constant

The calculated molar conductivities,  $\Lambda$ , using the measured specific conductivities in the aqueous solutions of the ionic liquid are given in Table 5. Figure 5 shows the dependence of the molar conductivity,  $\Lambda$ , on the molar concentration,  $c$ , of the ionic liquid for the investigated system at different experimental temperatures. It is shown that the molar conductivity,  $\Lambda$ , decreases with increasing ionic liquid concentration. An increase in the ionic liquid concentration causes the formation of ion-pairs in the dilute region and stronger ion association in the studied mixtures and then a decreasing molar conductivity.

There are many different equations for the treatment of conductance data [50]. The low concentration chemical model (lcCM) is recently applied widely for the correlation of conductance data in aqueous and nonaqueous electrolyte solutions [51].

Analysis of conductivity data in the framework of the low-concentration chemical model (lcCM) uses the set of equations,

$$\Lambda = \alpha \left[ \Lambda_0 - S(c\alpha)^{1/2} + E c \alpha \ln(c\alpha) + J_1 c \alpha + J_2 (c\alpha)^{3/2} \right] \quad (13)$$



**Fig. 5** Plot of molar conductivities of [PnMIm]Cl + H<sub>2</sub>O mixture versus molar concentrations of ionic liquid. Lines were generated using lcCM model; data: □, 298.15 K; △, 308.15 K; ◇, 318.15 K; \*, 328.15 K

where the ion-association constant,  $K_a$ , is defined as

$$K_a = \frac{1 - \alpha}{\alpha^2 c \gamma_{\pm}^2} \quad (14)$$

where

$$\ln \gamma_{\pm} = -\frac{\kappa q}{1 + \kappa R} \quad (15)$$

$$\kappa^2 = \frac{16 \times 10^3 N_A z^2 e^2 \alpha c}{\epsilon_0 \epsilon k_B T} \quad (16)$$

$$q = \frac{z^2 e^2}{8\pi \epsilon_0 \epsilon k_B T} \quad (17)$$

and  $\Lambda$  and  $\Lambda_0$  are the molar conductivities and limiting molar conductivity, respectively;  $\alpha$  is the fraction of oppositely charged ions acting as ion pairs,  $R$  is a distance parameter, and  $\gamma_{\pm}$  is the corresponding mean activity coefficient of the free ions. The coefficients  $E$ ,  $J_1$ , and  $J_2$  required for calculations were taken from Ref. [51]. The rest of the parameters have the usual meanings. Three-parameter fits of the molar conductivity data yields the ion-association constant,  $K_a$ , the limiting molar conductivity,  $\Lambda_0$ , and distance parameter,  $R$ , by nonlinear least-squares iteration.  $K_a$ ,  $\Lambda_0$ , and  $R$  parameters are summarized in Table 6.

Water promotes dissociation significantly due to its high dielectric constant and its ability to form strong hydrogen bonding with anions of the ionic liquid.

**Table 6** Ion-association constant  $K_a$ , limiting molar conductance  $\Lambda_0$ , distance parameter  $R$ , and standard deviation of molar conductance for  $([\text{PnMIm}]\text{Cl} + \text{H}_2\text{O}) \sigma(\Lambda)$  in low concentrations at different temperatures

$T$ (K)	$K_a$ ( $\text{dm}^3 \cdot \text{mol}^{-1}$ )	$\Lambda_0$ ( $\text{S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$ )	$R \times 10^{10}$ (m)	$\sigma(\Lambda)$
298.15	4.9	89.31	5.28	0.17
308.15	5.8	99.36	2.31	0.38
318.15	9.1	114.04	2.27	0.96
328.15	10.3	120.43	1.60	0.71

The standard deviation  $\sigma(\Lambda)$  of the measured molar conductivities  $\Lambda(\text{exp.})$  and the calculated value  $\Lambda(\text{calc.})$  was computed as follows:

$$\sigma(\Lambda) = \left( \sum [\Lambda(\text{exp.}) - \Lambda(\text{calc.})]^2 / (N - p) \right)^{1/2} \quad (18)$$

where  $N$  and  $p$  show the number of experimental data and model parameters, respectively.

The increase in  $K_a$  values with increasing temperature in Table 6 show that the extent of ion association in  $[\text{PnMIm}]\text{Cl} + \text{H}_2\text{O}$  solutions increases with increasing temperature, resulting in decreases of ion–solvent interactions. Therefore, strong ion solvation was observed for  $[\text{PnMIm}]\text{Cl} + \text{H}_2\text{O}$  solutions at low temperature. Hydration of this ionic liquid is similar to tetraalkylammonium halide, which occurs by the occupation of intermolecular cavities of an ice-like water structure by organic chains of these ions [52]. However, it is known that the ionic liquids, particularly imidazolium chlorides, are very little hydrated (small hydration numbers as compared to usual alkali or alkaline earth metal halides), but  $[\text{PnMIm}]\text{Cl}$  is strongly hydrated in comparison with imidazolium chlorides with a small alkyl chain length.

### 3.4 Refractive Index Data Correlation

Experimental refractive index data,  $n_D$ , for the investigated aqueous solutions of ionic liquid are reported in Table 7. This table shows the refractive indices of aqueous solutions of ionic liquid as a function of the molality of the ionic liquid. As can be seen, the  $n_D$  values increase as the temperature increases. This behavior is similar to the  $n_D$  results obtained by Liu et al. [53] and Kim et al. [54] for the other studied ionic liquid mixtures.

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

$$n_D - n_D^* = \sum_{i=1}^3 A_i m^i \quad (19)$$

**Table 7** Refractive indices,  $n_D$ , of aqueous solutions of [PnMIm]Cl as a function of ionic liquid concentration at different temperatures

$m$ (mol · kg <sup>-1</sup> )	$n_D$			
	298.15 K	308.15 K	318.15 K	328.15 K
0.0140	1.3331	1.3318	1.3302	1.3282
0.0263	1.3334	1.3321	1.3305	1.3284
0.0391	1.3338	1.3324	1.3308	1.3288
0.0518	1.3342	1.3328	1.3313	1.3291
0.0634	1.3344	1.3331	1.3316	1.3294
0.0840	1.3351	1.3339	1.3322	1.3305
0.1007	1.3358	1.3344	1.3327	1.3309
0.1369	1.3367	1.3357	1.3336	1.3316
0.1784	1.3379	1.3367	1.3349	1.3328
0.2198	1.3392	1.3378	1.3359	1.3339
0.2765	1.3408	1.3397	1.3377	1.3356
0.3517	1.3430	1.3416	1.3397	1.3376
0.4043	1.3443	1.3430	1.3411	1.3389
0.5014	1.3470	1.3457	1.3437	1.3419
0.5758	1.3489	1.3475	1.3457	1.3440
0.8464	1.3558	1.3547	1.3523	1.3505
1.0016	1.3596	1.3579	1.3557	1.3537
1.3758	1.3679	1.3658	1.3639	1.3619
1.7972	1.3764	1.3745	1.3721	1.3697

**Table 8** Parameters of polynomial fits and standard deviations for refractive indices of ([PnMIm]Cl + H<sub>2</sub>O) system at different temperatures

$T$ (K)	$n_D^*$	$A_1 \times 10^4$	$A_2 \times 10^4$	$A_3 \times 10^4$	$\sigma(n_D - n_D^*) \times 10^4$
298.15	1.3325	312.1462	-47.1701	5.1871	0.8899
308.15	1.3316	296.7031	-35.5040	1.6582	2.3304
318.15	1.3301	277.4533	-16.6165	-4.18154	2.2127
328.15	1.3284	262.2036	3.56160	-11.5386	4.4008

where  $m$  is the molality of the ionic liquid,  $n_D^*$  is the refractive index of pure water, and  $A_i$ 's are fitting parameters given in Table 8 together with corresponding standard deviations.

#### 4 Conclusions

The experimental osmotic coefficients of aqueous solutions of the ionic liquid 1-pentyl-3-methylimidazolium chloride, were determined by the vapor-pressure

osmometry method at temperatures  $T = (298.15 \text{ to } 328.15) \text{ K}$  at intervals of 10 K. The obtained experimental osmotic coefficients have been reliably correlated by Pitzer–ion interaction and MNRTL models with good accuracy. Mean molal activity coefficients and excess Gibbs free energies of studied system were calculated from the obtained Pitzer model parameters. Refractive indices and electrical conductance properties of ionic liquids in water have been reported at temperatures  $T = (298.15 \text{ to } 328.15) \text{ K}$ . Ion-association constant values increase with increasing temperature and show that the extent of ion association increases with increasing temperature and the (ion + solvent) interactions decrease.

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