Thermodynamic properties of aqueous solutions of ionic liquids 1-alkyl-3-methylimidazolium bromide at $T=(298.15 \text{ to } 328.15) \text{ K}$

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Introduction

Ionic liquids (ILs) are organic salts, which are liquids at ambient temperatures, with extremely low vapor pressure. These compounds are known as solvents for a variety of applications, including organic and inorganic synthesis, battery applications, chromatographic stationary phases, and separation science [1-2]. In spite of their importance and interest, a detailed knowledge on the thermodynamic properties such as activity coefficients, excess thermodynamic properties of ionic liquids + molecular solvents are very limited. Vapor pressure osmometry (VPO) has been used for determination of activity or osmotic coefficient data [3]. VPO is one of the simplest techniques because of reliability, performance at ambient pressure, easier and cheaper, shorter time measurements and using over the wide concentration ranges, provided that the solutions are not too viscous and that there are thermodynamic reference data for solutions in this solvent.

The osmotic coefficients of aqueous solutions of ionic liquids, 1-propyl-3-methylimidazolium bromide [PMIm]Br, 1-hexyl-3-methylimidazolium bromide [HMIm]Br were determined by the vapor pressure osmometry method Osmomat K-7000 (Knauer) at temperatures 298.15 K to 328.15 K and reliably correlated by 3-parameter Pitzer model. The parameters for these equations, along with the corresponding standard deviations are presented for these systems. The obtained parameters were used to calculate the mean molal activity coefficients. By using mean molal activity coefficients and osmotic coefficients data, excess Gibbs energy, excess enthalpy and excess entropy of the studied ionic liquids were calculated.

Keywords: Osmotic coefficients; Ionic liquids; Vapor pressure osmometry; Excess thermodynamics functions.
Experimental

[HMIm]Br and [PMIm] Br were prepared and purified by using the procedure described in the literature. Ionic liquid was analysed 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. The osmotic coefficients $\phi$ of aqueous solutions of ionic liquids with molality $m$ were obtained according to $\phi = \nu_r m_r \phi_r / \nu m$, where $\phi_r$, $m_r$ and $\nu_r$ are referred to reference electrolyte.

Results and discussion

The 3-parameter Pitzer model has the following form for a binary 1:1 electrolyte solution,

$$\phi - 1 = \frac{\phi_r}{1 + \frac{b m}{2} \exp(-\alpha I^2)} + \frac{1}{1 + \frac{b m}{2}} + m(\beta(0) + \beta(1) \exp(-\alpha I^2)) + m^2 C \phi$$

Using $\phi$ values and second virial coefficients of water, vapor pressure of the studied solutions could be calculated. These data were correlated using 3-parameters Pitzer model with good accuracy. Also, mean molal activity coefficients $\gamma_{\pm}$ and excess Gibbs energy may be calculated using each set of the model parameters [5].

$$\ln \gamma_{\pm} = -A_0 \phi + bm \ln(1 + bm \phi) + m(2\beta + A_1 + A_2) + m^2 \left(3C + A_3\right)$$

$$G^E = RT \left(1 - \phi + \ln \gamma_{\pm}\right)$$

Knowing $G^E$ values for different temperatures, it is possible to calculate the excess enthalpy and excess entropy functions [6]

$$[\partial G^E / \partial T]_p = -S^E \quad H^E = -T \left[\partial(G^E / T) / \partial T\right]$$
The vapor pressure of solvent, $p$ can be calculated from the measured activity with help of the relations

\[
\Delta = -\ln \frac{a}{s} \quad \text{and} \quad \ln a = \ln p + (B - V') \left( p - p^* \right),
\]

\[
m\nu M_S \left( \frac{\Delta}{p^*} - \frac{\Delta}{p} \right) = RT
\]
It is interesting to compare the behaviour of [PMIm] Br in solution with [HMIm] Br. The calculated vapor pressure data show that the vapor pressure depression for [PMIm] Br solutions more than the corresponding [HMIm] Br solutions. It was concluded that the interaction between [PMIm] Br and water is stronger than [HMIm] Br. This conclusion is due to the stronger interaction and high charge density of [PMIm]$^+$ cation vs. [HMIm]$^+$ cation (anions are same). Therefore, in these compounds the alkyl group on cation plays an important role in the thermophysical behaviour in solution. Negative values of $G^E$ indicate that there is a great compatibility between ion liquid and water.
Figure 1. (a) Calculated values of vapor pressure for [PMIm] Br)+H2O (■) and [HMIm] Br)+H2O (K) at 318.15 K and (b) Calculated Excess thermodynamic functions for [PMIm] Br)+H2O system at 318.15 K.

References