



Osmotic properties of binary mixtures of 1-butyl-1-methylpyrrolidinium iodide and water



Sayed Ashique Ahmed, Aninda Chatterjee, Banibrata Maity, Debabrata Seth *

Department of Chemistry, Indian Institute of Technology Patna, Patna 800013, Bihar, India

ARTICLE INFO

Article history:

Received 24 July 2014

Received in revised form 12 October 2014

Accepted 17 October 2014

Available online 4 November 2014

Keywords:

Vapour pressure osmometry

Osmotic coefficient

Activity

Ionic liquids

Critical micellar concentration

ABSTRACT

In this work the osmotic properties of the binary mixture of an ionic liquid (IL) and water were reported, by using the vapour pressure osmometry (VPO) technique. We have used 1-butyl-1-methylpyrrolidinium iodide as ionic liquid. We have measured the osmotic coefficients of the above IL–water binary mixture at three different temperatures: 313.15, 323.15 and 328.15 K. We have calculated several parameters related to vapour–liquid equilibria, such as the activity of water in the IL–water binary mixture and the depression of vapour pressure of water in the mixture. The Archer extension of Pitzer model was used to correlate the experimental osmotic coefficients with molality of the solution. The parameter of this Archer extension of Pitzer model was estimated from this correlation. We have used the pseudophase separation model on the experimental osmotic coefficient value to estimate the critical micellar concentration (cmc) of 1-butyl-1-methylpyrrolidinium iodide in water.

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1. Introduction

Ionic liquids (ILs) are important for different processes, which can be used as alternatives to the organic solvents for the design and control of industrial processes. Other important properties of ILs are: ability to solubilize a variety of compounds, very low vapour pressure, thermally high stability, wide liquid range and inflammable [1–3]. The IL is composed of ions; they have negligible vapour pressures at normal temperature and pressure conditions. Due to high viscosity, solubility of some organic solute in IL is less; which can be overcome by using some co-solvent. Activity and osmotic coefficients of electrolyte solutions are the basic thermodynamic parameters, which show the deviation of solution from ideality. It is needed to develop thermodynamic models of the mixture in different processes for understanding their thermodynamic behaviour. For this the knowledge of the non-ideality of the mixture as well as experimental phase equilibrium data are required. Hence, to understand the vapour–liquid equilibria (VLE) for the different system, the knowledge on osmotic and activity coefficients is of high importance. There are several methods available for the determination of these thermodynamic parameters such as headspace chromatography, direct vapour measurement, isopiestic method and vapour pressure osmometry (VPO). Among all these methods we preferred the vapour pressure osmometry (VPO) technique due to its high accuracy, less time consumption and small amount of sample is enough for doing the experiment. The purpose of this work is to present the variation experimental osmotic coefficient (ϕ) data as well as the other

thermodynamic parameters such as activity (a), the change of vapour pressure (Δp), and critical micelle concentration (cmc) of the binary aqueous mixtures containing 1-Butyl-1-methylpyrrolidinium iodide (IL) with temperature $T = 313.15, 323.15$ and 328.15 K, by using the VPO technique. The experimental osmotic coefficient data have been successfully correlated by using the Archer extension of Pitzer ion interaction model. There are several models developed, such as local composition, hyper-netted chain and mean spherical approximation models. In this study, the extended ion interaction Pitzer model modified by Archer is applied to correlate the experimental osmotic coefficient [4–6]. In this modified model, parameter C^ϕ is replaced by two different parameter functions, which are dependent on the ionic strength as well as one local composition model [7]. Several research groups have studied the osmotic properties of binary mixtures containing different ILs [8–29].

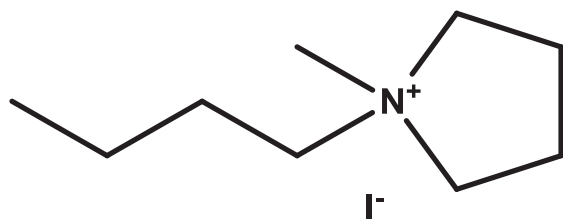
2. Experimental section

2.1. Materials

1-Butyl-1-methylpyrrolidinium iodide (Fig. 1) was purchased from Sigma Aldrich with high purity grade. 1-Butyl-1-methylpyrrolidinium iodide was dried under vacuum for 10 h before used. We have determined the moisture content in 1-butyl-1-methylpyrrolidinium iodide by using Karl Fischer titration methods (Model: Metrohm 831 KF Coulometer) and care has been taken during calculation of molality of the solution. The water content in the IL is 0.3%. In this experiment we used doubly distilled water for the preparation of binary solutions of the ionic liquid for analysis. The weighing of ionic liquid is carried out in a

* Corresponding author.

E-mail address: debabrata@iitp.ac.in (D. Seth).



1-Butyl-1-methylpyrrolidinium Iodide



Fig. 1. Molecular structure of the studied ionic liquid.

sealed vial inside the Glove box under nitrogen atmosphere, since ionic liquids are moisture sensitive. Each vial was weighted very carefully by an analytical balance (Mettler Toledo) with a precision of 10^{-4} g. All the solutions were kept tightly sealed by using a parafilm for minimization of absorption of atmospheric moisture. In each case, the measurements were executed quickly after the preparation of solutions to keep away from variations in composition due to absorption of water by the solution.

2.2. Apparatus and procedure

Several research groups reported a detailed procedure for the measurement of the osmotic coefficients of the binary mixture of ionic liquids and solvents [8–21]. The vapour pressure osmometry measurements were carried with the help of Knauer (Model: K-7000) vapour pressure osmometer, at three different temperatures, $T = 313.15$, 323.15 and 328.15 K. The instrument was calibrated by a standard solution of NaCl supplied with the instrument. The K-7000 instrument has a measuring chamber, which contains an air tight cell and consists of two thermistors, which are placed inside it. This measuring chamber contains a solvent reservoir, paper wicks and six microsyringes. Air tight cell is required for the saturation of gas phase with solvent vapour during the experiment. The basic principle of this instrument is based on variation of resistance differences (ΔR) due to the change of temperature (ΔT) in two thermistors respectively, in a Wheatstone bridge circuit. Initially, with the help of microsyringe solvent droplets are placed directly on two thermistors and after equilibration, the instrumental reading was adjusted to zero. After that one of the pure solvent droplets at the thermostat is replaced by the IL solution with the help of other four microsyringes. The vapour pressure of a pure solvent is greater than the vapour pressure of any solution containing solute. For this reason, replacing pure solvent drop by a drop of solution, causes vapour pressure difference between two droplets at thermostats. Due to vapour pressure differences between two droplets condensation processes take place from the thermistor containing the pure solvent to other thermistors having the ionic liquid solutions. This leads to an increase in temperature (ΔT) until vapour pressure of both droplets becomes equal, generally ~5 minute time is sufficient to get the steady state. This temperature difference (ΔT) is measured in terms of the resistance difference between the two thermistors (ΔR). Wheatstone bridge circuit measures the resistance difference (ΔR) between the thermistors. The standard uncertainty in instrumental reading was $\pm 1 \Omega$.

The experimental osmotic coefficients ϕ for ionic liquid solutions with molality m were obtained by using the following equation [12]

$$\phi = \frac{\nu_r m_r}{\nu m} \phi_r \quad (1)$$

where ϕ_r , ν_r and m_r are the osmotic coefficients, stoichiometric number of reference electrolyte and molality of reference electrolyte (molality

Table 1

Second virial coefficients, B_s , molar volumes, V_s , of water and the vapour pressure of the pure solvent, p^* , at the studied temperature.

T/K	$10^4 B_s/\text{m}^3 \text{mol}^{-1}$	$10^6 V_s^*/\text{m}^3 \text{mol}^{-1}$	p^*/kPa
313.15	−9.701	18.157	7.3814
323.15	−8.440	18.233	12.344
328.15	−12.492	18.280	15.763

showing the same instrumental reading as the ionic liquid solution, which implies that vapour pressure is equal in both solutions) respectively. In this experiment, we used aqueous NaCl as the reference solution. The value of stoichiometric numbers (ν_r) of the reference solution (NaCl) was set to be 2. Similarly ϕ , ν and m in Eq. (1) represent the osmotic coefficient of ionic liquid solution, stoichiometric number of investigated IL electrolyte and molality of IL solution respectively. For every solution, the average instrumental value is noted down. The total uncertainties in the experimental osmotic coefficient values are ± 0.006 .

3. Results and discussion

3.1. Osmotic coefficient & activity

The osmotic coefficient values for the binary aqueous solutions of ionic liquid have been calculated by using Eq. (1) at $T = 313.15$, 323.15 and 328.15 K (Table 2). The experimental osmotic coefficient values are shown in Table 1. Activity (a) and vapour pressures (p) of the solutions have been calculated by using the following correlations [20] (Table 3)

$$\phi = \frac{\ln(a_s)}{\nu m M_s} \quad (2)$$

$$\ln(a_s) = \ln(p/p^*) + (B_s - V_s^*)(p - p^*)/RT \quad (3)$$

$$\Delta p = p - p^* \quad (4)$$

where, a_s and M_s are the activity of the solvent and the molar mass of the solvent and p and p^* are the vapour pressure of the solution and the vapour pressure of the pure solvent, respectively. R is the universal gas constant and T is the absolute temperature. B_s and V_s are the second virial coefficient and molar volume of the pure solvent, respectively. On the right hand side of Eq. (3) the second term represents the deviation from ideal behaviour of solvent vapour. The values of B_s and V_s are

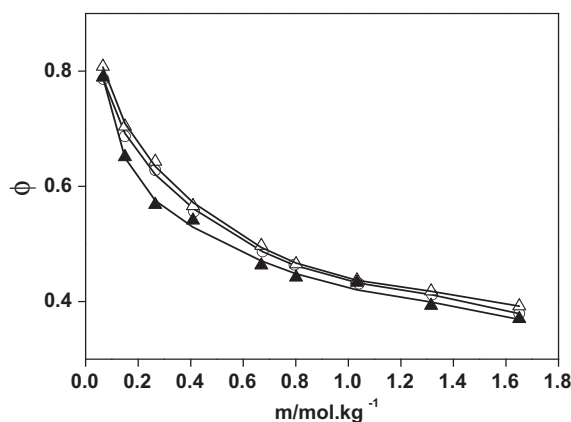


Fig. 2. The variation of experimental osmotic coefficients, ϕ , plotted against molality, m , for the binary mixtures of $[\text{BmPr}][\text{I}] + \text{water}$ and lines are generated by using the Archer extension of Pitzer model at $T = 313.15$ K (\blacktriangle); $T = 323.15$ K (\circ) and $T = 328.15$ K (\triangle).

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