J. Chem. Thermodynamics 40 (2008) 1346–1351

Contents lists available at ScienceDirect

J. Chem. Thermodynamics

journal homepage: www.elsevier.com/locate/jct

Osmotic coefficients of aqueous solutions of four ionic liquids at $T = (313.15$ and $333.15)$ K

Begoña González [a], Noelia Calvar [b], Ángeles Domínguez [b], Eugénia A. Macedo [a,*]

[a] Laboratory of Separation and Reaction Engineering, Departamento de Engenharia Química, Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal
[b] Departamento de Ingeniería Química, Universidad de Vigo, 36200 Vigo, Spain

ARTICLE INFO

Article history:
Received 21 February 2008
Received in revised form 9 May 2008
Accepted 20 May 2008
Available online 28 May 2008

Keywords:
Osmotic coefficients
Activity
Vapour pressure osmometry
Ionic liquids

ABSTRACT

Measurements of osmotic coefficients of BmimCl (1-butyl-3-methylimidazolium chloride), HmimCl (1-hexyl-3-methylimidazolium chloride), $MmimMeSO_4$ (1,3-dimethylimidazolium methylsulfate), and $BmimMeSO_4$ (1-butyl-3-methylimidazolium methylsulfate) with water at $T = (313.15$ and $333.15)$ K are reported in this work. Vapour pressure and activity data of all the studied binary systems are obtained from experimental data. The osmotic coefficients data are correlated using the extended Pitzer model of Archer and the modified NRTL (MNRTL) model and standard deviations obtained with both models are given too. The parameters obtained with the extended Pitzer model of Archer are used to calculate the mean molal activity coefficients.

1. Introduction

Ionic liquids (ILs) are room temperature molten salts with interesting properties, such as their negligible vapour pressures. This and other properties, such as their ability to solubilize an enormous variety of compounds, good thermal stability which make them liquids over a large temperature range including ambient temperature, non-flammability, and facility to recycle, make the ILs a new alternative as solvents for different processes [1,2]. Nowadays, these salts have attracted world-wide scientific interest in academia and industry. Thermodynamic properties of binary electrolyte solutions are needed for the design and control of industrial processes.

Experimental phase equilibrium data are required to develop thermodynamic models and for the understanding of their thermodynamic behaviour. VLE {(vapour + liquid) equilibrium} data [3,4] permit checking the potential of models which are applied for the description of the real behaviour of systems with ionic liquids.

The aim of this work is to present experimental osmotic coefficients data of the aqueous binary mixtures containing the ionic liquids BmimCl, HmimCl, $MmimMeSO_4$, and $BmimMeSO_4$ at $T = (313.15$ and $333.15)$ K using for their determination the vapour pressure osmometry method (VPO). For the prediction of the VLE behaviour the activity and osmotic coefficients are of great interest. Osmotic coefficients of ionic liquids obtained with the vapour pressure osmometry are very scarce in the literature [5], in spite of the advantages of this technique, such as its accuracy, being less time-consuming, and the fact that small amounts are enough, saving ionic liquid, which, compared with organic solvents, is an expensive component.

During the 1970s of last century, Pitzer [6] established a new generation of theories using multiparameters to correlate the thermodynamic properties of electrolyte solutions, several models were developed namely MSA, HNC, and local composition (LC) models. In this study, a modified Pitzer equation, the extended Pitzer model of Archer [7,8] and one local composition model, the modified NRTL (MNRTL) [9] are applied to correlate the osmotic coefficient experimental data. The results indicate that both models describe the osmotic coefficients of the studied binary systems with acceptable accuracy. The parameters obtained with the extended Pitzer model of Archer were used to calculate the mean molal activity coefficients.

2. Experimental

2.1. Materials

1-Butyl-3-methylimidazolium chloride (BmimCl), 1-hexyl-3-methylimidazolium chloride (HmimCl), 1,3-Dimethylimidazolium methylsulfate ($MmimMeSO_4$), and 1-butyl-3-methylimidazolium methylsulfate ($BmimMeSO_4$) were synthesised in our laboratory, following the previously published procedure [10–12]. They were dried by heating {(343.15 to 353.15) K} and stirring under high

---

* Corresponding author.
E-mail address: eamacedo@fe.up.pt (E.A. Macedo).

0021-9614/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jct.2008.05.011

vacuum ($2 \cdot 10^{-1}$ Pa) for 48 h always prior to their use. To assure their purity, NMR were made and their pure densities were determined and compared with those reported by Gómez *et al.* [10] and Pereiro *et al.* [11,12]; no differences were found. The water contents were determined using a 756 Karl Fischer coulometer, and they were lower than 0.03% mass. Water used in this work was bidistilled and deionized.

2.2. Method

The vapour pressure osmometry measurements were carried out with a Knauer K-7000 vapour pressure osmometer (VPO) at (313.15 and 333.15) K [5]. The osmometer consists in two thermistors that are located in a cell where the gas phase is saturated with solvent vapour. These thermistors measure resistance changes caused by changes in the temperature. The cell temperature is electronically controlled and maintained with an uncertainty of ±0.01 K. At the beginning, a droplet of pure solvent is attached to each thermistor with the help of a microsyringe, and after 5 min of equilibration, the reading is adjusted to zero. The vapour pressure of any solution containing solutes is lower than the vapour pressure of a pure solvent. Hence, replacing one drop of pure solvent with one drop of a solution leads to a vapour pressure difference between the two droplets. The increasing vapour pressure of the solution droplet leads to an increase of temperature (ΔT). This ΔT is measured in terms of ΔR, the difference in the resistances of the two thermistors. A bridge circuit measures the resistance difference of both thermistors. Normally, about (4 to 6) min is enough to get steady state. 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 were performed and the mean value is reported. The uncertainty was ±1 Ω. In order to obtain the calibration factor k, NaCl solutions of different known molalities were studied, obtaining their ΔR. The factor k value is the intersection with the y-axis of the line resulting of the representation of molality *versus* ΔR. This procedure for determining of factor k was performed following the instructions given in the manual of the apparatus.

3. Results and discussion

3.1. Experimental results

The osmotic coefficients, ϕ, of the solutions of molality m were calculated using the following equation:

$$\nu\phi m = k\Delta R, \tag{1}$$

where ν is the number of ions into which an electrolyte dissociates.

From the experimental osmotic coefficients it is possible to calculate the activity and vapour pressures of the different solutions using the following relations:

$$\phi = -\ln a_s / \nu m M_s, \tag{2}$$

$$\ln a_s = \ln(p/p^*) + (B_s - V_s^*)(p - p^*)/RT, \tag{3}$$

where a_s is the activity of the solvent, M_s is the molecular weight of the solvent, T is the absolute temperature, p is the vapour pressure of the solution, and p^* is the vapour pressure of the pure solvent. B_s and V_s^* are the second virial coefficient and molar volume of the pure solvent, respectively. The values for B_s are $-9.701 \cdot 10^{-4}\ \text{m}^3 \cdot \text{mol}^{-1}$ at 313.15 K and $-7.290 \cdot 10^{-4}\ \text{m}^3 \cdot \text{mol}^{-1}$ at 313.15 K [13] and for V_s^* are $18.157 \cdot 10^{-6}\ \text{m}^3 \cdot \text{mol}^{-1}$ at 313.15 K and $18.323 \cdot 10^{-6}\ \text{m}^3 \cdot \text{mol}^{-1}$ at 333.15 K [14]. The uncertainty for the experimental osmotic coefficients and for the calculated activity coefficients were < ± 0.006 and < ± 0.02, respectively.

TABLE 1
Osmotic coefficients, ϕ, activities, a, and vapour pressures, p, of {water (1) + 1-butyl-3-methylimidazolium chloride (BmimCl) (2)}

$m/(\text{mol} \cdot \text{kg}^{-1})$	ϕ_1	a_1	p/kPa
	T = 313.15 K		
0.0566	0.993	0.9980	7.362
0.3127	0.956	0.9893	7.298
0.6885	0.936	0.9770	7.207
1.0050	0.917	0.9673	7.136
1.2691	0.905	0.9595	7.078
1.4271	0.901	0.9547	7.043
1.7982	0.898	0.9435	6.959
1.9970	0.894	0.9377	6.916
2.2914	0.893	0.9289	6.852
2.6218	0.889	0.9194	6.782
2.9465	0.887	0.9101	6.712
3.1500	0.887	0.9042	6.669
3.5307	0.889	0.8931	6.586
4.0884	0.894	0.8766	6.465
	T = 333.15 K		
0.0566	0.948	0.9981	19.886
0.3127	0.902	0.9899	19.722
0.6885	0.862	0.9789	19.501
1.0050	0.846	0.9698	19.320
1.2691	0.824	0.9630	19.183
1.4271	0.821	0.9587	19.097
1.7982	0.809	0.9489	18.902
1.9970	0.805	0.9438	18.798
2.2914	0.801	0.9360	18.642
2.6218	0.802	0.9271	18.464
2.9465	0.801	0.9185	18.293
3.1500	0.800	0.9132	18.187
3.5307	0.800	0.9033	17.988
4.0884	0.806	0.8880	17.682

Tables 1–4 present the osmotic coefficients, activities, and vapour pressures for the different binary mixtures studied at the reported temperatures.

In figure 1 the vapour pressure depression, Δp, *versus* molality is presented for all studied aqueous mixtures at 313.15 K. Δp was calculated using the vapour pressures of the mixtures, p, and the pure solvent vapour pressure, p^*:

$$\Delta p = p^* - p. \tag{4}$$

The magnitude of vapour pressure depression is a property directly related to the solute–solvent interactions. From figure 1 it is possible to deduce that the solute–solvent interactions are as follows:

$$\text{H}_2\text{O} + \text{BmimCl} \approx \text{H}_2\text{O} + \text{MmimMeSO}_4 > \text{H}_2\text{O} + \text{BmimMeSO}_4 > \text{H}_2\text{O} + \text{HmimCl}$$

It is possible to observe that when the alkyl side-chain of the cation becomes longer then the solute–solvent interactions decrease. When the anion of the ionic liquid is Cl^- the interactions are higher than when the anion is MeSO_4^-. The behaviour of the Δp of studied binary systems at T = 313.15 K is similar to the behaviour of these systems at T = 333.15 K.

3.2. Thermodynamic modelling

3.2.1. Extended Pitzer model of Archer

For the correlation of the experimental osmotic coefficient data the extended Pitzer model modified by Archer [7,8] was used. For a binary 1:1 electrolyte solution, this model presents the following expression:

$$\phi - 1 = f^\phi + mB^\phi + m^2C^\phi, \tag{5}$$