J. Chem. Thermodynamics 40 (2008) 1087–1094

Contents lists available at ScienceDirect

J. Chem. Thermodynamics

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

Mixing thermodynamic properties of 1-butyl-4-methylpyridinium tetrafluoroborate [b4mpy][BF$_4$] with water and with an alkan-1ol (methanol to pentanol)

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ARTICLE INFO

Article history:
Received 9 December 2007
Received in revised form 25 February 2008
Accepted 27 February 2008
Available online 5 March 2008

Keywords:
Excess enthalpies
Excess volumes
LLE
[b4mpy][BF$_4$]
Alkanol
Water

ABSTRACT

This article presents a study of the behaviour in solution of 1-butyl-4-methylpyridinium tetrafluoroborate [b4mpy][BF$_4$] in water and in the first five alkanols of the series methanol to pentan-1-ol. The excess enthalpies, H^E_m and volumes, V^E_m were determined at the temperatures (298.15 and 318.15) K. At these temperatures, the [b4mpy][BF$_4$] was completely miscible in water, methanol, and ethanol, but only partially miscible in the other alkanols. A solubility study was carried out and the (liquid + liquid) equilibria of the ([b4mpy][BF$_4$] + alkanol) systems were experimentally determined, evaluating zones of complete miscibility and determining the UCST in each case. The mixtures with water gave positive values of H^E_m and V^E_m, being also positive the changes of these quantities with temperature. The mixtures with alkanols gave values of $H^E_m > 0$ and $V^E_m < 0$, and for these binary mixtures $(dH^E_m/dT)_p > 0$ and $(dV^E_m/dT)_p < 0$. For all cases, results were interpreted and compared with data obtained in mixtures with another isomer [b3mpy][BF$_4$]. Excess properties were correlated with a suitable equation and the area and volume parameters were calculated for [b4mpy][BF$_4$].

1. Introduction

Ionic liquids (IL) and their mixtures with different types of substances are still receiving considerable attention from researchers and there is an increasing wealth of publications about the properties and applications of these materials. One of their most striking characteristics is their almost negligible vapour pressures, which has especially influenced the direction of much of the research [1,2]. In spite of the difficulty in their handling new applications are constantly being discovered and analysed. However, there is still insufficient basic knowledge about these substances and the full range of their potential is unknown. One of the least known aspects of their behaviour is their affinity for different groups of compounds with which they show either total or partial miscibility, such as the alkanols. Contrarily to this, in most cases they are insoluble in relatively inert solvents, such as the alkanes, and to a lesser extent in aromatic derivatives [3,4]. The alkanols are an interesting group of solvents and our research team is currently undertaking a project to systematically study the structural influence of pyridinium ILs with alkanols. We are attempting to establish the dependence of physical and chemical properties on cation and anion type and structure. Cation and anion changes have already been demonstrated to have an important effect on the solubility, density, and viscosity.

In a previous work [5], the behaviour in solution of 1-butyl-3-methylpyridinium tetrafluoroborate [b3mpy][BF$_4$] was studied, and in this work we report the results of research carried out on 1-butyl-4-methylpyridinium tetrafluoroborate [b4mpy][BF$_4$]. Other isomers will be studied in the future.

In the present study, we analyse (liquid + liquid) equilibria (LLE) and other properties of binary mixtures of [b4mpy][BF$_4$] with water and with several alkanols, in order to establish the influence of hydrogen bonds and other intermolecular interactions in solutions with IL. On the one hand, the effect of the alkanol chain is studied and, on the other, the position of the methyl group in the cation [bmpy]. There has been very little research into [b4mpy][BF$_4$] in spite of the fact that it is one of the most reported pyridinium-based ILs regarding applications [6–10]. We are interested in knowing the different interactional effects between the (IL + alkanol) systems and also the (IL + water) mixing process, owing to the hydrophilic nature of the IL. For the mixtures {[b4mpy][BF$_4$] + alkanol} (methanol to pentanol), studies were carried out on the LLE in the temperature range (275 to 330) K, in order to determine the miscibility zones in which the mixing properties, V^E_m and H^E_m, can be determined. For the binary systems

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0021-9614/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jct.2008.02.019

in this work, the literature [8] presents data of densities and V_m^E for {[b4mpy][BF_4] + methanol} at several temperatures, which will be used for purposes of comparison. With the information obtained here and in future works a better understanding of the molecular interactions can be achieved, and the effect of different cation structures on the thermophysical properties can be established. Other works [9,10] on different properties for the same IL are also considered for discussion.

2. Experimental section

2.1. Materials

The alkanols used in this work were supplied by Fluka and Aldrich and were of maximum commercial purity, verified with a GC, HP6890 model, equipped with FID, and gave values very similar to manufacturer's values. The IL, [b4mpy][BF_4], was supplied by Solvent Innovation and had a commercial purity of 99% and a water contents of 710 ppm, which was contrasted with Mettler Karl Fischer DHL-48 titrator, and fluoride of 514 ppm. Nonetheless, the IL was dried under high vacuum at 343 K using a semi-micro-distiller with slow heating to remove impurities, mainly water, resulting a final water content slightly lower than that of the commercial product. To prevent contact with the ambient air, the IL was kept in a sealed dessicator and placed in a room with constant dehumidification. Both the IL and alkanols were degassed before use in an ultrasound bath for several hours and the alkanols were stored above previously-activated molecular sieves of 0.3 nm. During the experiments, the purity of the IL was verified with density measurements. The water used in the experiments was bidistilled in our laboratory and had an electrical conductance of <2 μS.

Table 1 shows the density values measured, ρ, and the refraction indices, n_D, for the pure compounds at two temperatures (298.15 and 318.15) K. Values for the alkanols, methanol, and butanol are not shown since these were almost identical to those recorded in a previous work [5]. Density values for the same IL at three temperatures are recorded in the literature [8–10], with two somewhat different values recorded at 298.15 K, although by applying a simple correlation we could estimate the values presented in table 1 together with those measured for this work. However, the water contents of the [b4mpy][BF_4] are not given in the cited references. Since viscosity is sensitive to water contents, this property was measured at 298.15 K for the IL, giving a value of 214 mPa·s *vs* the value of 196 mPa·s recorded in the literature [8].

2.2. Equipment and procedures

To measure the total or partial solubility zones of the binary systems {x_{IL}[b4mpy][BF_4] + (1 − x_{IL}) alkan-1-ol} (methanol to pentanol) a continuous dilution procedure was used, with visual detection of turbidity changes, until a homogeneous phase was formed. Measurements were made in the interval (275 to 335) K and at atmospheric pressure, using a glass cell, with a precision of ±0.02 K, by circulation of water thermostatically controlled by a Haake Phoenix II external waterbath. The transition temperature was measured with an ASL-F25 digital thermometer with a reading error of ±1 mK, using a submerged PT100 probe, with a reading error of ±0.02 K. Measurements were made at the start of the experiment with a known quantity of IL, that was introduced into a sealed equilibrium cell, to which known quantities of alkanol were added using a 1001-TLL Hamilton syringe screwed onto a stainless steel needle, with a stopper valve to prevent contamination of the IL. After the mixture has formed in the LLE cell, the magnetic stirrer is operated in continuous mode, while heating/cooling the cell slowly until the solution homogenizes. The error in the molar fraction in the IL calculated in each step of the continuous process increases systematically with each experiment, and in a quasi-linear way, giving a total uncertainty of ±0.001 U in the calculation of x_{IL}. The process is repeated in the opposite direction, adding known quantities of IL to an also known quantity of alkanol.

TABLE 1
Physical properties of pure compounds.

Compound	T/K	$\rho/(\text{kg}\cdot\text{m}^{-3})$		n_D	
		Experimental	Literature	Experimental	Literature
$[\text{b4mpy}]^+[F_4B]^-$	298.15	1183.49	1181.10[a] 1184.24[b]	1.4517	
	318.15	1169.12	1168.67[c]	1.4470	
Pentan-1-ol	298.15		811.50[d]	1.4078	1.4079[d]
	318.15	796.10	795.97[e]	1.4003	1.3997[e]

[a] Reference [8].
[b] Reference [9].
[c] Interpolated reference [8].
[d] Reference [11].
[e] Reference [12].

The density measurements were made with an Anton Paar/Austria DMA-58 vibrating tube densimeter equipped with its own Peltier effect temperature control system, which maintained the temperature of the apparatus at ±0.01 K. Nonetheless, to improve the temperature control, the densimeter was connected to a thermostatic bath with a temperature fixed at (T − 0.5) K, where T is the working temperature selected, from (298.15 to 318.15) K, in this work. At each temperature, the densimeter was calibrated with bidistilled and degassed water and with nonane (74252, Fluka) also previously degassed, using the densities reported in a previous work [12].

The viscosity was measured with a Selecta ST-1000 rotational viscosimeter, equipped with a small-volume cell with a reading error of ±1% at the bottom of the scale, the reproducibility was 0.2%. It was calibrated with a reference substance provided by Brookfield Engineering Laboratories at a temperature of 298.15 K. Thermostatization with a temperature control of ±0.01 K was carried out in the previously described thermostatic bath.

Binary mixtures (IL + alkanol, or + water) were prepared by weighing quantities in sealed 5 ml glass vials and the mixture was homogenized with a magnetic stirrer for 10–20 min before being introduced into the densimeter, to prevent contact between the IL solution and the ambient air. The imprecision of the molar fractions in the IL of the freshly prepared synthetic mixtures x_{IL} was estimated to be ±0.0002. The excess volumes V_m^E were estimated from the density values of each of the mixtures and those of the pure compounds, obtaining the paired values (x_{IL}, V_m^E). The uncertainty of the V_m^E was $\pm 2\cdot 10^{-9}\ \text{m}^3\cdot\text{mol}^{-1}$.

The n_D of the pure compounds were measured in an Abbe 320 refractometer, from Zuzi, at a wavelength of 5893 Å and with a reading error of ±0.0002 U. The temperature, controlled to ±0.02 K, was achieved with the Haake external circulation bath described previously. The measurements were compared first with values measured for pure water at each working temperature. The values found are shown in table 1 although no values were found in the literature for the IL, while values for pentan-1-ol were considered to be acceptable.

Mixing enthalpies, H_m^E, were determined by directly measuring the caloric energy generated in the mixing process. The miscibility diagram of the binary systems (IL + alkanol) clearly show the zones where the measurements can be made, both of H_m^E and of V_m^E, at temperatures of (298.15 and 318.15) K. A Setaram MS80 Calvet calorimeter was used, which was first calibrated at each temperature with a cell provided by the manufacturer applying a Joule effect and using different values of electrical power with the EJ2 unit, also from Setaram. Electrical calibration of the apparatus was checked