Fluid Phase Equilibria 375 (2014) 161–167

Contents lists available at ScienceDirect

Fluid Phase Equilibria

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

Impact of the cation symmetry on the mutual solubilities between water and imidazolium-based ionic liquids

Mónia A.R. Martins[a], Catarina M.S.S. Neves[a], Kiki A. Kurnia[a], Andreia Luís[a], Luís M.N.B.F. Santos[b], Mara G. Freire[a], Simão P. Pinho[c,d], João A.P. Coutinho[a,*]

[a] Departamento de Química, CICECO, Universidade de Aveiro, 3810-193 Aveiro, Portugal
[b] Centro de Investigação em Química, Departamento de Química e Bioquímica, Faculdade de Ciências da Universidade do Porto, R. Campo Alegre 687, P-4169-007 Porto, Portugal
[c] Associate Laboratory LSRE/LCM, Departamento de Tecnologia Química e Biológica, Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5301-857 Bragança, Portugal
[d] UNIFACS-Universidade de Salvador, Rua Dr. José Peroba 251, CEP 41770-235 Salvador, Brazil

ARTICLE INFO

Article history:
Received 19 February 2014
Received in revised form 8 May 2014
Accepted 12 May 2014
Available online 21 May 2014

Keywords:
Mutual solubilities
Ionic liquids
Water
Cation symmetry
COSMO-RS

ABSTRACT

Aiming at the evaluation of the impact of the ionic liquids (ILs) cation symmetry on their phase behaviour, in this work, novel mutual solubilities with water of the symmetric series of $[C_nC_n\text{im}][NTf_2]$ (with $n = 1–5$) were determined and compared with their isomeric forms of the asymmetric $[C_nC_1\text{im}][NTf_2]$ group. While the solubility of isomeric ILs in water was found to be similar, the solubility of water in ILs follows the same trend up to a maximum cation alkyl side chain length. For $n \geq 4$ in $[C_nC_n\text{im}][NTf_2]$ the solubility of water in the asymmetric ILs is slightly higher than that observed in the symmetric counterparts. The thermodynamic properties of solution and solvation derived from the experimental solubility data of ILs in water at infinite dilution, namely the Gibbs energy, enthalpy and entropy were used to evaluate the cation symmetry effect on the ILs solvation. It is shown that the solubility of ILs in water is entropically driven and highly influenced by the cation size. Accordingly, it was found that the ILs solubility in water of both symmetric and asymmetric series depends on their molecular volume. Based on these findings, a linear correlation between the logarithm of the solubility of ILs in water and their molar volume is here proposed for the $[NTf_2]$-based ILs at a fixed temperature.

1. Introduction

Ionic liquids (ILs) are salts composed of a large organic cation and an organic or inorganic anion that, unlike conventional salts, are liquid at or close to room temperature, and which make them attractive as alternative solvents for many chemical reactions and separation processes [1]. An important feature of ILs arises from their tunability, as their thermophysical properties such as density, viscosity, heat capacity, thermal conductivity, as well as their solvation ability, can be finely tuned by properly selecting a cation–anion combination [1,2]. In what concerns the IL-water miscibilities, the IL anion plays a major role although the cation also influences the hydrophobicity or hydrogen-bonding ability of the IL and can be further used to fine tune this property [3–12]. For instance, the 1-butyl-3-methylimidazolium cation, $[C_4C_1\text{im}]^+$, in combination with anions like Cl^-, Br^-, $[CF_3SO_3]^-$ or $[BF_4]^-$ are totally miscible with water at room temperature; yet, combined with $[C(CN)_3]^-$, $[PF_6]^-$ or $[NTf_2]^-$ they tend to phase separate at the same temperature [5]. However, if the alkyl side chain of the IL cation is sufficiently long, the IL-water system also display two phases, as happens with the $[C_{6-10}C_1\text{im}][BF_4]$ ILs [9,10]. Therefore, the wide array of possible cation-anion combinations permits flexibility in designing new ionic fluids and in optimizing their physical/chemical properties for particular applications. For this reason, ILs are generally referred as “designer solvents” [1,2,13].

The application of hydrophobic or non-water miscible ILs has shown promising results in the liquid–liquid extraction of value-added organic compounds from aqueous solutions [14–17]. They may also play an important role in the recovery of biofuels from fermentation broths [18–20]. The phase separation achieved at low temperatures with these systems facilitates the extraction processes at room temperature and thus represents an economic benefit. In this context, to design any process involving ILs at an industrial scale, it is necessary to know a wide range of thermophysical

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* Corresponding author. Tel.: +351 234 370200; fax: +351 234 370084.
E-mail address: jcoutinho@ua.pt (J.A.P. Coutinho).

http://dx.doi.org/10.1016/j.fluid.2014.05.013

Table 1
Investigated ionic liquids: name, abbreviation, source, molecular mass (*M*), and purity.

Chemical name	Abbreviation	Source	M (g mol^{-1})	Purity (mass %)
1,3-Dimethylimidazolium bis((trifluoromethyl)sulfonyl)imide	$[C_1C_1im][NTf_2]$	Iolitec	377.29	>99
1,3-Diethylimidazolium bis((trifluoromethyl)sulfonyl)imide	$[C_2C_2im][NTf_2]$	Iolitec	405.34	>99
1,3-Dipropylimidazolium bis((trifluoromethyl)sulfonyl)imide	$[C_3C_3im][NTf_2]$	Iolitec	433.39	>99
1,3-Dibutylimidazolium bis((trifluoromethyl)sulfonyl)imide	$[C_4C_4im][NTf_2]$	Iolitec	461.45	>99
1,3-Dipenthylimidazolium bis((trifluoromethyl)sulfonyl)imide	$[C_5C_5im][NTf_2]$	Iolitec	489.50	>99

properties and thermodynamic data, such as solid–liquid, liquid–liquid (LLE), and vapour–liquid equilibrium. Thermophysical properties along with the equilibrium data are also important to get a better understanding on the physical–chemical behaviour of ILs and to develop related thermodynamic models [21–24]. In addition, the impact of the water content on the ILs thermophysical properties is highly relevant [25–28], particularly in transport properties such as viscosity. On the other hand, the knowledge of the ILs solubility in water can also provide relevant information on their toxicity and bioaccumulation behaviour [29–31].

This work represents an extension of our previous investigations towards the understanding of the ILs structural variation, such as cation alkyl side chain length [3], type of anion [4,5], structural isomerism [6], and cation core [5,7], and the respective impact on their mutual solubilities with water. All the systems previously examined showed upper critical solution (UCST) behaviour, with a very low solubility of ILs in the water-rich phase and significant water solubility in the IL-rich phase (in mole fraction). Here, the effect of the cation symmetry on the mutual solubilities with water is investigated for the first time. The ILs studied are composed of the bis(trifluoromethylsulfonyl)imide anion combined with the symmetric series of 1,3-dialkylimidazolium cations, $[C_nC_nim]^+$ (with $n = 1–5$). The LLE data were measured in the temperature range between 288.15 K and 318.15 K. The experimental data were then compared with predictive results from the COnductor like Screening MOdel for Real Solvents (COSMO-RS) [32,33]. Along with our previous work [3], the results obtained here provide a general picture on the impact of the cation symmetry and of the alkyl side chain length on the mutual solubilities between ILs and water. Moreover, from the temperature-dependence solubility data, the thermodynamic properties of solution were also derived and discussed (at the water-rich phase).

2. Experimental

2.1. Chemicals

The experimental mutual solubilities with water were carried out for the 5 ILs presented in Table 1. The chemical structures of the studied compounds are presented in Fig. 1. To reduce their impurities, individual samples of ILs were dried under vacuum at 0.1 Pa and 353.15 K, under constant stirring, and for a minimum period of 48 h. After, the purity of each IL was checked by ^{1}H, ^{13}C, and ^{19}F NMR. The water content of the dried ILs was determined using a Metrohm 831 Karl Fischer (KF) coulometer, with the analyte Hydranal® – Coulomat AG from Riedel-de Haën, and was found to be below 100 ppm for all samples. Ultrapure water, double distilled, passed by a reverse osmosis system and further treated with a MilliQ plus 185 water purification apparatus, was used throughout the mutual solubility experiments (M (H_2O) = 18.01 g mol^{-1}). The water used presents a resistivity of 18.2 MΩ cm, a TOC smaller than 5 µg dm^{-3} and is free of particles > 0.22 µm.

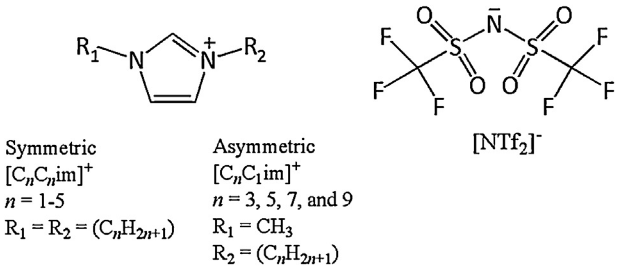

Fig. 1. Chemical structures of the studied imidazolium-based ILs.

2.2. Apparatus and procedure

The mutual solubilities between water and ILs were determined in the temperature range from (288.15 to 318.15) K and at atmospheric pressure using a LLE method previously detailed [3,5,6]. The ionic liquid and water phases were initially vigorously stirred and allowed to settle and equilibrate for at least 48 h [25]. This period of time proved to be enough to guarantee a complete separation of the two phases, as well as their saturation. The samples, in tightly-closed glass vials with a septum cap, were put inside an aluminium block specially designed for this purpose, as schematically depicted in Fig. 2. The isolated air bath is capable of maintaining the temperature within ± 0.01 K. The temperature control was achieved with a PID temperature controller driven by a calibrated Pt100 (class 1/10) temperature sensor inserted in the aluminium block. A Julabo (model F25-HD) refrigerated bath and circulator was used as the cooling source of the thermostatized aluminium block. The temperature accuracy was ±0.01 K. Both phases were sampled at each temperature from the equilibrium vials using glass syringes maintained dry and kept at the same temperature of the measurements. The solubility of water in the IL-rich phase was measured by KF titration, whereas the solubility of IL in the water-rich phase was measured by UV–vis spectroscopy, using a SHIMADZU UV-1700 PharmaSpec Spectrometer, and at a wavelength of 211 nm. This wavelength was found to be the maximum UV absorption wavelength for the imidazolium-based ILs investigated here. Approximately 0.1 g of the IL-rich phase was sampled and directly injected in the KF coulometric titrator to determine the water content. For the water-rich phase, ca. 0.5 g of each sample was taken and diluted in (250–500) cm^3 of ultrapure water. At each temperature, each measurement was repeated at least 5 times, and the results are reported as the average solubility value along with the respective standard deviations.

2.3. COSMO-RS

COSMO-RS is a predictive method developed by Klamt and coworkers for providing the thermodynamic equilibrium of fluids and mixtures and that uses a statistical thermodynamic approach based on the results of unimolecular quantum chemical calculations [32,34]. The model can be used to predict the phase behaviour of binary mixtures and subsequently the concentration of each component in a given phase [35,36]. Previously we used COSMO-RS to predict the equilibrium behaviour of ILs and water and confirmed its high capability as a predictive tool [5,37].

The standard procedure of COSMO-RS calculations employed in this work consisted essentially in two steps: (*i*) the continuum