Fluid Phase Equilibria 383 (2014) 72–77

Contents lists available at ScienceDirect

Fluid Phase Equilibria

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

Influence of the number, position and length of the alkyl-substituents on the solubility of water in pyridinium-based ionic liquids

Emilio J. González, Eugénia A. Macedo *

LSRE – Laboratory of Separation and Reaction Engineering, Associate laboratory *LSRE/LCM*, Department of Chemical Engineering, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, Porto 4200-465, Portugal

ARTICLE INFO

Article history:
Received 17 July 2014
Received in revised form 15 September 2014
Accepted 25 September 2014
Available online 8 October 2014

Keywords:
Solubility
Water
Ionic liquid
NRTL model

ABSTRACT

In this work, the solubility of water in eight pyridinium-based ionic liquids were experimentally determined at several temperatures and atmospheric pressure, and the temperature-composition phase diagrams are reported. From these data, the effect of the number, position (positional isomers) and length of the substituents of the cation was analyzed and discussed. The obtained results indicate that water content in the studied ionic liquids increases with temperature and, in general, it decreases as the number and length of the substituents increase. As regards the position of the alkyl groups, the solubility of water decreases with the proximity of the substituents. Finally, the miscibility of water in the studied ionic liquids was satisfactorily described with the Non-Random Two-Liquid (NRTL) thermodynamic model.

1. Introduction

Ionic liquids (ILs) are ionic compounds with a melting point lower than 100 °C. As is known, these solvents show interesting properties such as being at the liquid phase in a wide range of temperatures, having high thermal stability, and ability to dissolve a wide variety of materials. These characteristics make them attractive for a number of applications such as catalysis, chemical reactions, separations processes, electrochemistry, or nanoscience research [1].

Until recently, the presence of water in the ILs has been considered as a problem because small quantities of this compound significantly affect the properties of pure ILs. This is a common behavior which was observed in both hydrophobic and hydrophilic ILs due to ILs considered as “hydrophobic” are usually quite “hygroscopic”. Nevertheless, traces of water could improve the properties of ILs because water has a wide variety of properties that pure ILs do not possess [2]. For example, hydrated ILs show lower viscosity that enhance the flow and pumping in any industrial process; can increase the field of certain chemical reactions [3], or facilitate the dissolving and preserving proteins [4,5].

On the other hand, it is also known that hydrophobic ILs with certain anions such as bis(trifluoromethylsulfonyl)imide, $[NTf_2]^-$, or hexafluorophosphate, $[PF_6]^-$ lead to immiscible mixtures when they are mixed with an excess of water. These mixtures are formed by two phases (aqueous phase and ionic liquid-rich phase) and usually are presented as a novel medium in direct liquid–liquid extraction [6]. Some examples of uses of hydrophobic ILs in separation processes are the extraction of metals, including alkali, alkaline earth, heavy and radioactive metals, or biological molecules such as carbohydrates, organic acids and antibiotics [7,8].

For the potential application of ionic liquid/water mixtures in future liquid extraction processes, the knowledge of the phase behavior between hydrophobic ILs and water is of great practical relevance.

In this work, the solubility of water in eight pyridinium-based ILs with $[NTf_2]^-$ anion was experimentally determined as a function of temperature. Specifically, the studied ILs were 1-ethylpyridinium bis(trifluoromethylsulfonyl)imide; $[Epy][NTf_2]$; 1-ethyl-2-methylpyridinium bis(trifluoromethylsulfonyl)imide; $[^1E^2Mpy][NTF_2]$; 1-ethyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide; $[^1E^3Mpy][NTF_2]$; 1-ethyl-4-methylpyridinium bis(trifluoromethylsulfonyl)imide; $[^1E^4Mpy][NTF_2]$; 1-butylpyridinium bis(trifluoromethylsulfonyl)imide; $[Bpy][NTf_2]$; 1-butyl-2-methylpyridinium bis(trifluoromethylsulfonyl)imide; $[^1B^2Mpy][NTF_2]$; 1-butyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide; $[^1B^3Mpy][NTF_2]$; and 1-butyl-4-methylpyridinium bis(trifluoromethylsulfonyl)imide; $[^1B^4Mpy][NTF_2]$. This family of ILs was selected in order to evaluate the effect of the number, position and length of the alkyl substituents on the solubility of water in this kind of ILs. Moreover, pyridinium-cation ILs can be fully biodegraded and the metabolites of biodegradation are significantly less toxic to a common aquatic organism [9]. This, together with their specific properties such as being liquid in

---

* Corresponding author. Tel.: +351 225081653; fax: +351 225081674.
E-mail address: eamacedo@fe.up.pt (E.A. Macedo).

0378-3812/$ – see front matter © 2014 Published by Elsevier B.V.
http://dx.doi.org/10.1016/j.fluid.2014.09.028

wide temperature range or show stability against air and moisture, make them potentially useful in different processes [10].

A considerable amount of studies on the solubility between water and ILs formed by the NTf$_2$ anion can be found in the literature [10–27]. The results obtained hitherto show that mutual solubility of water–ionic liquid systems are mainly defined by the anion followed by the cation alkyl chain length. Nevertheless, the effect of the number and position (positional isomers) of the substituents has not been sufficiently studied. For pyridinium-based ILs containing the NTf$_2$ anion, two works were found in the literature [25,26] in which the effect of positional isomers of *N*-alkylpyridinium-based ILs on the mutual solubility of water/ionic liquid mixtures was analyzed. Specifically, Freire et al. [26] have studied the solubility of water in ILs with *meta* and *para* substitutions ([^{1}B^{3}Mpy][NTF$_2$] and [^{1}B^{4}Mpy][NTF$_2$] while Papaiconomou et al. [25] have compared the solubility of water in ILs with *ortho* and *para* substitutions (1-octyl-2-methylpyridinium bis(trifluoromethanesulfonyl)imide, [^{1}O^{2}Mpy][NTf$_2$], and 1-octyl-4-methylpyridinium bis(trifluoromethanesulfonyl)imide, [^{1}O^{4}Mpy][NTf$_2$]). Curiously, an opposite behavior was observed in both works. While Freire et al. [26] observed that the solubility of water in *N*-butylpyridinium-based ILs decreases with the proximity of the substituents, Papaiconomou et al. [25] concluded that the water content decrease for ILs containing the [NTf$_2$]$^-$ anion when the methyl group on the octylpyridinium cation changes from *ortho* to *para* position.

In order to better understand the behavior of this kind of ILs, the study is now extended to ethyl- and butyl-pyridinium-based ILs substituted in *ortho, meta* and *para* positions.

The liquid–liquid equilibrium (LLE) data found in the literature [10,26,27] for the binary mixtures {[Bpy][NTF$_2$], or [^{1}B^{3}Mpy][NTf$_2$], or [^{1}B^{4}Mpy][NTf$_2$] + water} were also included for comparison purpose. Finally, the solubility of water in the ILs reported in this work was satisfactorily modelled using the Non-Random Two-Liquid (NRTL) model [28].

2. Material and methods

2.1. Chemicals

The ILs used in this work (see structures in Fig. 1) were supplied by IOLITEC (Germany) with high purity. Since the objective of this work was to determine the maximum solubility of water in ILs by Karl Fischer Titration, a previous drying stage was not necessary and ILs were used as were received, without any other pre-treatment. The CAS number, purity, molar mass, *M*, water content, w_{w}, and halide content, w_{halide}, of the studied ILs are reported in Table 1.

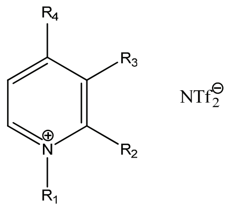
The experimental determination of the liquid–liquid equilibrium for the binary mixtures {water + ionic liquid} was carried out using Milli-Q water (Millipore).

The cathodic and anodic tritrants used to measure the water content by KF Titration were Coulomat CG and Coulomat AG (Sigma–Aldrich), respectively.

2.2. Solubility of water in the ILs

The solubility of water in the ILs was studied through the experimental determination of the LLE of binary mixtures {ionic liquid (1) + water (2)}. For this, an immiscible {ionic liquid + water} binary mixture was placed inside a glass cell sealed using a silicon cover. In order to ensure an intimate contact between both phases, the mixture was vigorously stirred for 8 h and then, it was left for 24 h in a thermostatic bath (PoliScience digital temperature controller, with a stability of ±0.01 K) to achieve thermodynamic equilibrium. The temperature was controlled using a digital thermometer (ASL model F200) with an uncertainty of ±0.01 K. Next, a sample from the IL-rich phase was withdrawn using a syringe and its water content was determined by Karl Fischer titration using a Mettler Toledo C20 Coulometric KF Titrator.

Binary mixtures were prepared in duplicate in order to estimate the uncertainty in the determination of the composition. The obtained results show that the error for the water content, in molar fraction, was less than 0.006.



R$_1$	R$_2$	R$_3$	R$_4$	Ionic liquid	Acronym
C$_2$H$_5$	H	H	H	1-ethylpyridinium bis(trifluoromethylsulfonyl)imide	[Epy][NTf$_2$]
C$_2$H$_5$	CH$_3$	H	H	1-ethyl-2-methylpyridinium bis(trifluoromethylsulfonyl)imide	[^{1}E^{2}Mpy][NTf$_2$]
C$_2$H$_5$	H	CH$_3$	H	1-ethyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide	[^{1}E^{3}Mpy][NTf$_2$]
C$_2$H$_5$	H	H	CH$_3$	1-ethyl-4-methylpyridinium bis(trifluoromethylsulfonyl)imide	[^{1}E^{4}Mpy][NTf$_2$]
C$_4$H$_9$	H	H	H	1-butylpyridinium bis(trifluoromethylsulfonyl)imide	[Bpy][NTf$_2$]
C$_4$H$_9$	CH$_3$	H	H	1-butyl-2-methylpyridinium bis(trifluoromethylsulfonyl)imide	[^{1}B^{2}Mpy][NTf$_2$]
C$_4$H$_9$	H	CH$_3$	H	1-butyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide	[^{1}B^{3}Mpy][NTf$_2$]
C$_4$H$_9$	H	H	CH$_3$	1-butyl-4-methylpyridinium bis(trifluoromethylsulfonyl)imide	[^{1}B^{4}Mpy][NTf$_2$]

Fig. 1. Structures of the pyridinium based-ILs.