Hydrophobic Ionic Liquids and Water Mutual Solubilities

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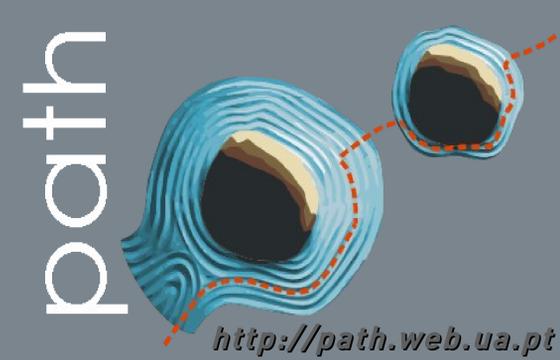
1. Introduction

In recent years ionic liquids (ILs) have gathered special attention from the scientific community and an exponential increase of studies involving different features, properties and applications of ILs have been presented in literature. Their particular physicochemical characteristics such as high solvation ability and coordination properties, non flammability, wide liquidus range, wide electrochemical window, high thermal stability and negligible vapor pressures make of them suitable candidates for a large range of applications [1]. Moreover, the possibility of controlling their polar/apolar characteristics by correctly choosing the cation and/or the anion allows them to present selective solubilities for particular components in fluid mixtures. This characteristic, coupled with their negligible vapor pressures, has transformed ILs into excellent alternatives as potential green solvents with an obviously high industrial interest. While ILs cannot contribute to air pollution due to their negligible vapour pressures, they may have in fact a significant solubility in water (even the ones known as "hydrophobics") and, as a result, this is the most likely medium through which ILs will enter and pollute the environment [2, 3]. In addition, their release to aquatic environments could cause water contamination because of their potential toxicity and limited biodegradability. The ILs toxicity is directly related and mainly controlled by their lipophilicity [4]. This kind of studies have demonstrated that the ILs toxicity is primordially determined by the cation nature and it is essentially driven by the cation alkyl side chain length [4]. Therefore, the ILs bioaccumulation is directly proportional to their hydrophobicity and thus, the knowledge of their water solubility can be a way of predicting the toxicity and bioaccumulation impact of an ionic liquid in the ecosystem. Some contributions dealing with experimental solubilities between ILs and water have already been reported [5].

2. Experimental

The mutual solubilities measurements were performed at temperatures from (288.15 to 318.15) K and at atmospheric pressure. The two phases were vigorously agitated and allowed to reach equilibrium for a minimum of 48 h. The vials were thermostated on an aluminum block, immersed in an isolated air bath. The solubility of water in the IL-rich phase was determined with a Metrohm 831 Karl-Fischer (KF) coulometer. The solubility of ILs in the water-rich phase was determined by UV-spectroscopy using a SHIMADZU UV-1700, Pharma-Spec Spectrometer.
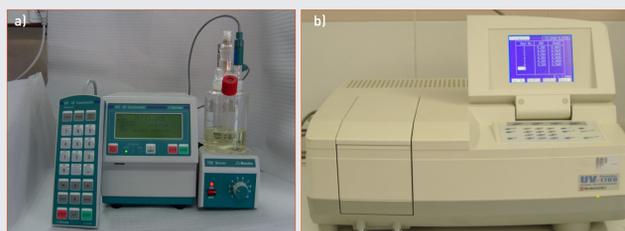

Fig. 1 – a) Karl-Fischer (KF) coulometer; b) SHIMADZU UV-1700, Pharma-Spec Spectrometer
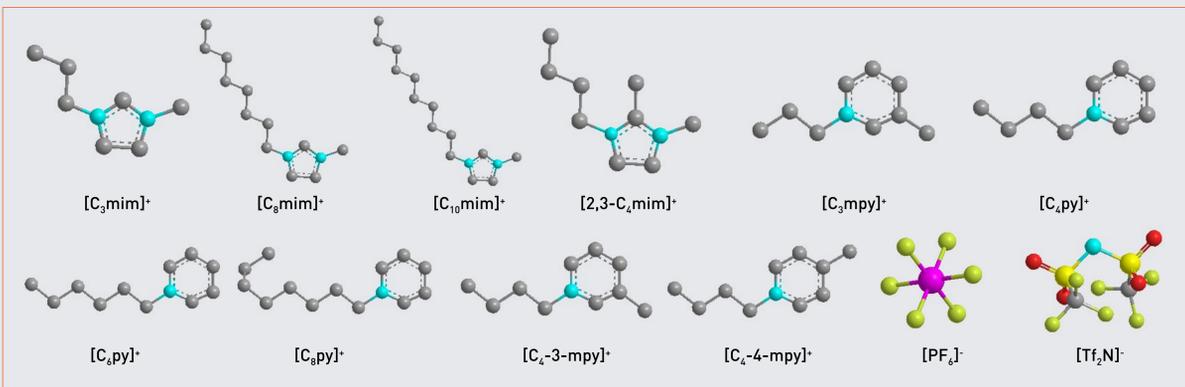

$[C_3mim]^+$ $[C_8mim]^+$ $[C_{10}mim]^+$ $[2,3-C_4mim]^+$ $[C_3mpy]^+$ $[C_4py]^+$

$[C_4py]^+$ $[C_8py]^+$ $[C_4-3-mpy]^+$ $[C_4-4-mpy]^+$ $[PF_6]^-$ $[Tf_2N]^-$

Fig. 2 – Cation and anion structures of the studied ILs

3. Results

The mutual solubilities between the imidazolium and pyridinium-based ILs and water were measured in the temperature range from (288.15 to 318.15) K and at atmospheric pressure. Due to its high melting point, the solubility of water in $[C_3mpy][PF_6]$ was only measured for temperatures above 303.15 K.
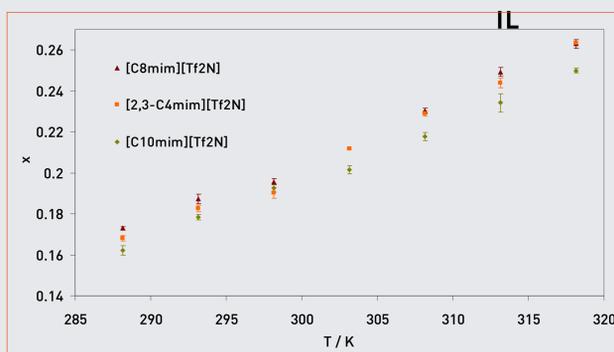
Water Solubility in IL

Fig. 3 – Water molar fraction (x) experimental data as function of temperature (T) in ILs $[C_{10}mim][Tf_2N]$, $[2,3-C_4mim][Tf_2N]$ and $[C_8mim][Tf_2N]$

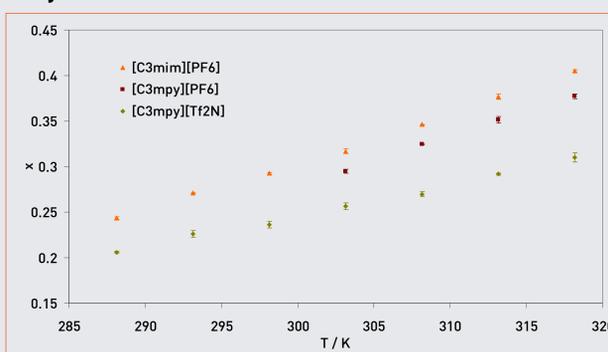$[C_{10}mim][Tf_2N] < [2,3-C_4mim][Tf_2N] < [C_8mim][Tf_2N]$

Fig. 4 – Water molar fraction (x) experimental data as function of temperature (T) in ILs $[C_3mpy][Tf_2N]$, $[C_3mpy][PF_6]$ and $[C_3mim][PF_6]$
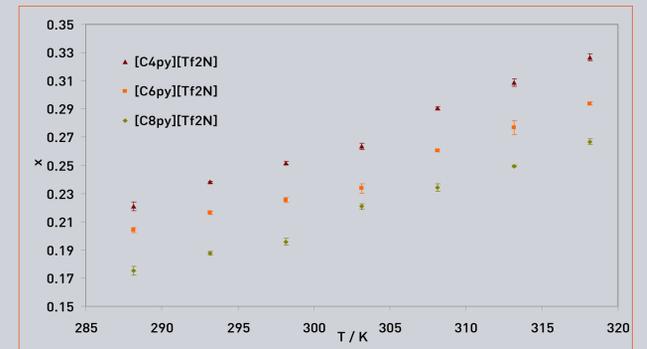
$[C_3mpy][Tf_2N] < [C_3mpy][PF_6] < [C_3mim][PF_6]$

Fig. 5 – Water molar fraction (x) experimental data as function of temperature (T) in ILs $[C_6py][Tf_2N]$, $[C_4py][Tf_2N]$ and $[C_4py][Tf_2N]$
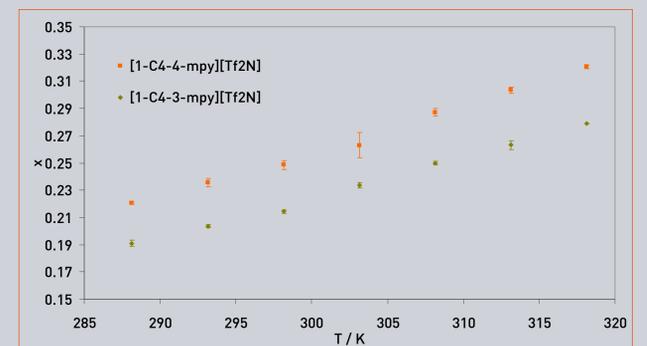
$[C_8py][Tf_2N] < [C_6py][Tf_2N] < [C_4py][Tf_2N]$

Fig. 6 – Water molar fraction (x) experimental data as function of temperature (T) in ILs $[C_4-3-mpy][Tf_2N]$ and $[C_4-3-mpy][Tf_2N]$

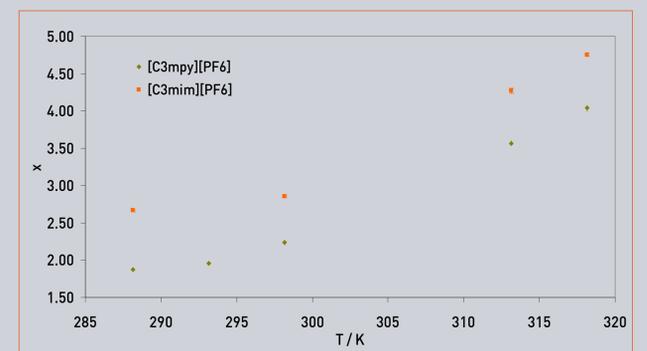$[C_4-3-mpy][Tf_2N] < [C_4-3-mpy][Tf_2N]$

ILs Solubility in water

Fig. 7 – ILs ($[C_3mpy][PF_6]$ and $[C_3mim][PF_6]$) molar fraction (x) experimental data as function of temperature (T) in water

$[C_3mpy][PF_6] < [C_3mim][PF_6]$

4. Conclusions

The hydrophobic tendency of the cation family increases from imidazolium to pyridinium-based ILs and with the alkyl chain length increase within the same cation family. On the other hand, the anion hydrophobic tendency increases from hexafluorophosphate to bis(trifluoromethylsulfonyl)imide-based anions ILs. In addition, the results depicting the ILs amphiphilic character can be used to fine tune the ILs mutual solubilities with water and to manage their ecotoxicity impact.

References

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