

実験報告書様式(緊急課題)

(※本報告書は英語で記述してください。ただし、産業利用課題として採択されている方は日本語で記述していただいても結構です。)

 <b>Experimental Report</b> 	承認日 Date of Approval 2014/5/22 承認者 Approver Shibata Kaoru 提出日 Date of Report 2014/5/22
課題番号 Project No. 2014AU0201  実験課題名 Title of experiment  Dynamics in "ionic liquid"-water mixtures by quasi-elastic neutron scattering  実験責任者名 Name of principal investigator David L. Price 所属 Affiliation CNRS_CEMHTI Orleans, France	装置責任者 Name of Instrument scientist K. Shibata and T. Yamada 装置名 Name of Instrument/(BL No.) DNA (BL02) 実施日 Date of Experiment 3-6 May 2014

試料、実験方法、利用の結果得られた主なデータ、考察、結論等を、記述して下さい。(適宜、図表添付のこと)  
 Please report your samples, experimental method and results, discussion and conclusions. Please add figures and tables for better explanation.

1. 試料 Name of sample(s) and chemical formula, or compositions including physical form. 1-octyl-3-methylimidazolium tetrafluoroborate - water mixture, (C <sub>12</sub> H <sub>23</sub> N <sub>2</sub> BF <sub>4</sub> )(1-x)(H <sub>2</sub> O) <sub>x</sub> , x = 0, 0.15, 0.3, 0.5, 1 1-octyl-3-methylimidazolium tetrafluoroborate – heavy water mixture, (C <sub>12</sub> H <sub>23</sub> N <sub>2</sub> BF <sub>4</sub> )(1-x)(D <sub>2</sub> O) <sub>x</sub> , x = 0.15, 0.3, 0.5, 1 1-octyl-3-methylimidazolium chloride - water mixture, (C <sub>12</sub> H <sub>23</sub> N <sub>2</sub> Cl)(1-x)(H <sub>2</sub> O) <sub>x</sub> , x = 0, 0.5 1-octyl-3-methylimidazolium chloride – heavy water mixture, (C <sub>12</sub> H <sub>23</sub> N <sub>2</sub> Cl)(1-x)(D <sub>2</sub> O) <sub>x</sub> , x = 0.5
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2. 実験方法及び結果 (実験がうまくいかなかった場合、その理由を記述してください。) Experimental method and results. If you failed to conduct experiment as planned, please describe reasons.  Ionic liquids (ILs) are the focus of great interest due to their novelty, interesting properties and tuning possibilities. For application purposes, as well as for environmental reasons, it is of the utmost importance to understand how the structure and dynamics of ILs change when water is added to them, breaking the original ion network. Several studies have already been devoted to this question and they show some interesting features, as well as some puzzling issues. For example: <ul style="list-style-type: none"> <li>- It has been shown that water molecules absorbed from the air are present mostly in the non self-associated state, bound via H-bonding with anions forming complex: anion-HOH-anion.</li> </ul>
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Very small amounts of water have a dramatic effect on the rate of diffusion and it has been proposed that “wet” ILs may not be considered as homogeneous solvents but as “nanostructured” materials, through hydrogen bond interactions that can possess in some cases polar and nonpolar regions [1]. Also at those very low hydrations, a change in hydration regime has been proposed based on viscosity measurements [2].

- When larger quantities of water are added spontaneous self-organization is observed, at least in the case of long chain ILs. It has been even proposed the existence of regions of confined water and eventually of gelation [3].
- MD simulations on long chain ILs also indicate that the cations self-assemble to form aggregates with the alkyl tails buried inside. These simulations indicate that the cation diffusion decreases with increasing chain length and particularly that there is a dramatic change in the case of aqueous [C<sub>16</sub>mim][Br] due to the presence of larger aggregates [4]. Concerning the role of water, other simulation studies indicate that the most ordered nanostructure forms when the H-bonding ability of the anions is saturated by the water (at a water fraction of about 80%) [5].
- Other recent MD investigations comparing ILs with alkyl side chains of different lengths (4 vs 8 C atoms) confirm that increasing the length changes significantly the cation aggregation behavior. In the same work it is found that replacing the BF<sub>4</sub><sup>-</sup> anion by Cl<sup>-</sup> slows both the diffusion of cations and water molecules. They also conclude that water molecules are less likely to form clusters in C<sub>8</sub>mimCl water mixtures than in C<sub>8</sub>mimBF<sub>4</sub> water mixtures. Furthermore the interaction with water is greater for C<sub>4</sub>mim than for C<sub>8</sub>mim, causing a slower rotation of water [6].
- Changes in the activation energy for the rotational motion of water have also been observed by NMR [7]
- Finally MD studies on hydrophobic ILs (C<sub>4</sub>mimPF<sub>6</sub> and C<sub>8</sub>mimPF<sub>6</sub>) found that in the water rich region the diffusion of the water and the anion is larger in the IL with the longer chain [8], in contrast with the behavior found in [6] for C<sub>4</sub>mimBF<sub>4</sub> and C<sub>8</sub>mimBF<sub>4</sub> water mixtures.

As it can be appreciated most of the information concerning the behavior of IL-water mixtures comes from computer simulations. While they can provide a very detailed picture of both the structure and dynamics of such mixtures, the potentials employed and their results need to be validated experimentally. In this contest QENS provides an invaluable tool to determine the microscopic details of the diffusion mechanisms and compare them to the simulation results.

We have already started to explore in detail the structure of such mixtures using three prototypical ILs: C<sub>4</sub>mimBF<sub>4</sub>, C<sub>8</sub>mimBF<sub>4</sub> and C<sub>8</sub>mimCl. However, only QENS can provide the information needed to understand the microscopic mechanisms related to the long-range diffusion of the IL or the water, as well as those concerning local motions such as the rotation of the water molecules or the constrained motion of the alkyl chains. Our previous work on C<sub>2</sub>mimBr serves as an example of the power of combining QENS and MD simulations [9].

We have measured propose two different systems: C<sub>8</sub>mimBF<sub>4</sub> and C<sub>8</sub>mimCl and their solutions with H<sub>2</sub>O and D<sub>2</sub>O. By comparing solutions with H<sub>2</sub>O and D<sub>2</sub>O at the same composition we plan to separate the dynamics of the ionic liquid and water molecules. All samples except pure water were run with and without the pulse-shaping chopper to sort out the several processes involved. One composition was run at 5 temperatures over the range 270 - 315 K to determine the activation energies of the different processes. Immediately apparent is a significant speeding up of the translational diffusion and a slight increase in the rate of the local modes with the addition of water. Analysis is in progress to determine the detailed dynamics.

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