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|  MLF Experimental Report | 提出日 Date of Report |
| 課題番号 Project No. 2014A0277 実験課題名 Title of experiment CO ₂ absorption and surface structure of room temperature ionic liquid-based mixtures 実験責任者名 Name of principal investigator Hiroshi ABE 所属 Affiliation National Defense Academy | 装置責任者 Name of responsible person Norifumi YAMADA 装置名 Name of Instrument/(BL No.) SOFIA/ BL-16 実施日 Date of Experiment May 18-20, 2014 71.5 hours |

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.

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| 1. 試料 Name of sample(s) and chemical formula, or compositions including physical form. |
| <p>[N3111][TFSI]: <i>N, N, N</i>-trimethyl-<i>N</i>-propylammonium bis(trifluoromethylsulfonyl)imide [N4111][TFSI]: Butyltrimethylammonium bis(trifluoromethylsulfonyl)imide [N4441][TFSI]: Tributylmethylammonium bis(trifluoromethylsulfonyl)imide [DEME][TFSI]: <i>N, N</i>-Diethyl-<i>N</i>-methyl-<i>N</i>-(2-methoxyethyl)ammonium bis(trifluoromethylsulfonyl)imide</p> |

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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. |
| <p>(i) Experimental methods Neutron reflectivity was carried out in order to obtain surface condition of room temperature ionic liquids (RTILs) with/without CO₂. Sample changer, which is filled with CO₂, can cover temperature range from 15 to 35 °C. Chemically stable polytetrafluoroethylene is used for sample containers.</p> <p>(ii) Experimental results Hydrophobic RTILs used in this study are quaternary ammonium cation, where TFSI anion is commonly selected. In the RTILs, [N4111][TFSI] is the RTIL possessing high CO₂ absorption efficiency. Temperature dependence of neutron reflectivity of pure [N4111][TFSI] was observed in atmospheric circumstance (Fig. 1). Neutron reflectivity has little temperature dependence, although the reflectivity is modulated at around $3.5 \cdot 10^{-2} \text{ \AA}^{-1}$. As well as other RTILs, the observed neutron reflectivity in pure [N4111][TFSI] obeys Q^{-4}-dependence. A significant finding is that higher neutron reflectivity is induced at 16.0 °C by CO₂ filled circumstance (Fig. 2(b)). The enhancement is suppressed sensitively at higher temperature (Fig. 2(a)). Thus, we deduce that the CO₂ effect in neutron reflectivity is directly connected with high CO₂ absorption efficiency.</p> |

2. 実験方法及び結果(つづき) Experimental method and results (continued)

In order to clarify CO₂ effect of pure [N4111][TFSI], we examine other quaternary RTILs. Figures 3(a)-(c) reveal neutron reflectivity at 21.0 °C of pure [N3111][TFSI], [N4441][TFSI] and [DEME][TFSI], respectively. In contrast to [N4111][TFSI], rough surface is formed by CO₂ circumstance in other RTILs. At least, less CO₂ absorption efficiency might be caused by the surface fluctuations.

In propanol-based mixtures, we cannot measure neutron reflectivity due to negative curvature on the free surface. Some idea is necessary to resolve the above problem. Now, we are analyzing the observed data and simulating using software for neutron reflectivity. Density profile near the surface is indispensable to clarify the mechanism of CO₂ absorption process into the RTILs.

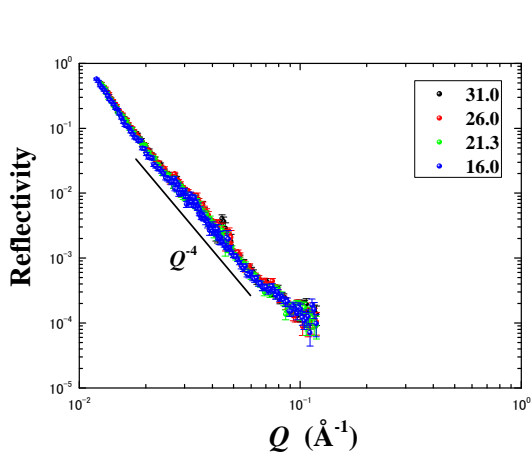


Fig. 1 Temperature dependence of neutron reflectivity of pure [N4111][TFSI].

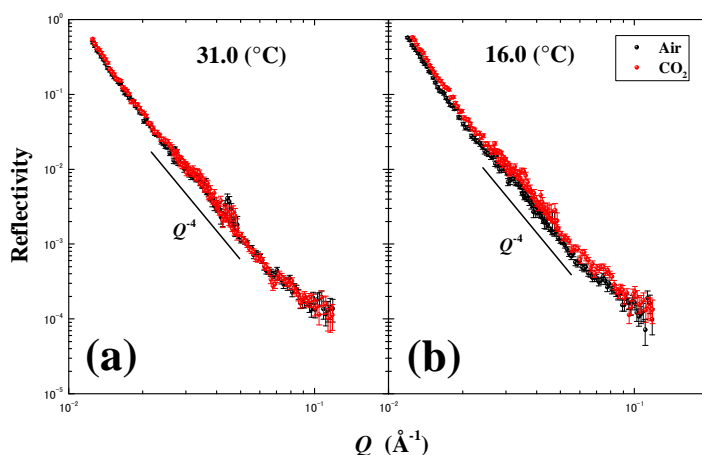


Fig. 2 CO₂ effect at (a) 31.0 °C and (b) 16.0 °C.

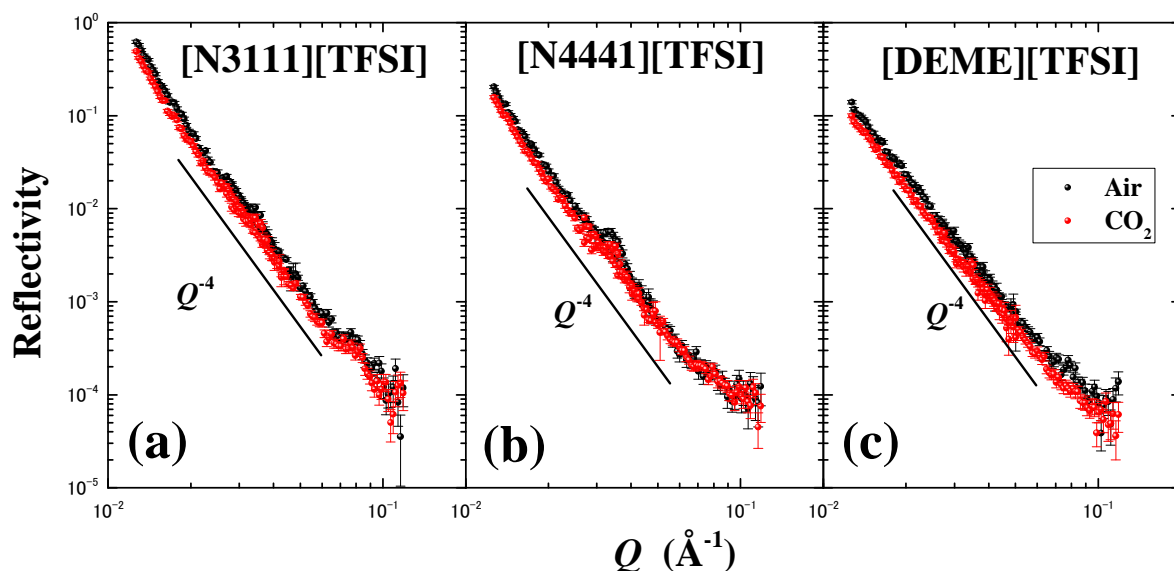


Fig. 3 Neutron reflectivity at 21.0 °C of (a) pure [N3111][TFSI], (b) pure [N4441][TFSI] and (c) pure [DEME][TFSI]. CO₂ enable it to reduce the reflectivity except for that of [N4111][TFSI].