CROSS TOKAI **Experimental Report** J-PARC	承認日 Date of Approval 2013/11/23 承認者 Approver Junichi SUZUKI 提出日 Date of Report 2013/02/28
課題番号 Project No. 2012B0001 実験課題名 Title of experiment Hierarchy Structure in Hydrogen Bonding Assisted System: Room Temperature Ionic Liquids-Water 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 Instrument scientist Junichi SUZUKI 装置名 Name of Instrument/（BL No.） TAIKAN/ BL15 実施日 Date of Experiment Feb. 18-19, 2013 48 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.

1. 試料 Name of sample(s) and chemical formula, or compositions including physical form.

[DEME][NO_3]: *N*, *N*-diethyl-*N*-methyl-*N*-2-methoxyethyl ammonium nitrate, $C_8H_{20}N_2O_4$
[DEME][NO_3]-80, 90 and 99 mol% D_2O

[bmim][NO_3]: 1-butyl-3-methylimidazolium nitrate, $C_8H_{15}N_3O_3$
[bmim][NO_3]-70, 75, 77.5, 80, 85, 90 and 95 mol% D_2O

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.

(i) Experimental methods

Quartz sample holders, whose thickness is 1 mm or 2 mm, were utilized to reduce the background at the small angle region. At temperature range from 25 down to 5 ^oC, data of [DEME][NO_3]- and [bmim][NO_3]-D_2O mixtures were collected using the cooling system.

(ii) Experimental results

In small angle X-ray scattering (SAXS), increments at SAXS intensities were observed in [bmim][NO_3]-80 and 93 mol% D_2O (Fig. 1). To determine the relative positions and size of water pool (D_2O) the small angle neutron scattering (SANS) experiments were carried out in TAIKAN (BL15). 2 dimensional (2D) scattering data were reduced into one dimensional (1D) patterns with corrections of $I(\lambda)$, discrimination, masking and solid angle of detectors. SANS of pure D_2O was measured for background estimation. As a function of D_2O concentrations, SANS intensities of [bmim][NO_3]-D_2O at room temperature are shown in Fig. 2. An apparent peak at around 0.3 $Å^{-1}$ develops above 90 mol% D_2O. Moreover, the peak intensity increased at 5 ^oC. The distinct aggregation was promoted at low temperate. A significant finding is that the peak is derived from the

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

D_2O aggregations inside the [bmim][NO_3]. This is because there is no specific peak in SAXS of [bmim][NO_3]-80 mol% D_2O as shown in Fig. 1. Density fluctuations of [bmim][NO_3] contribute to the gradient of the SAXS part. One of reasons is that H_2O/D_2O is not probed by the conventional X-ray. The maximum position of the peak in SANS corresponds to the size of ~19 Å. This is in good agreement with the previously predicted size of an “aggregated water” (water pool) [1]. In the literature [1], we have already predicted that partially refolded lysozyme in the [bmim][NO_3]-80 mol% D_2O depends extensively on the virtually introduced water pool.

In case of [DEME] based-water system, hierarchy structure is predominant at water-rich region by UV-vis absorption spectra, SAXS and prepeak of X-ray diffraction [2]. In SANS experiments, the water pool also exists in [DEME][NO_3]-80 mol% D_2O. Two peaks at the small angle region appeared at 0.2 and 0.4 $Å^{-1}$, respectively. One peak at the smaller *q* position increased with decreasing temperature. The software for data analysis at wide angle region is not accomplished so far. The quantitative data analysis at the medium angle rage will be carried out within one year after well-established data processing, since data in the detector bank at medium range has been stored.

Combined with SAXS, quantitative analysis and simulations will be performed by RMC++ to enhance a proof of the water pool. We confirm that D_2O sensitive neutron and insensitive X-ray can distinguish the specific D_2O water pool, which controls the secondary/tertiary structures of protein.

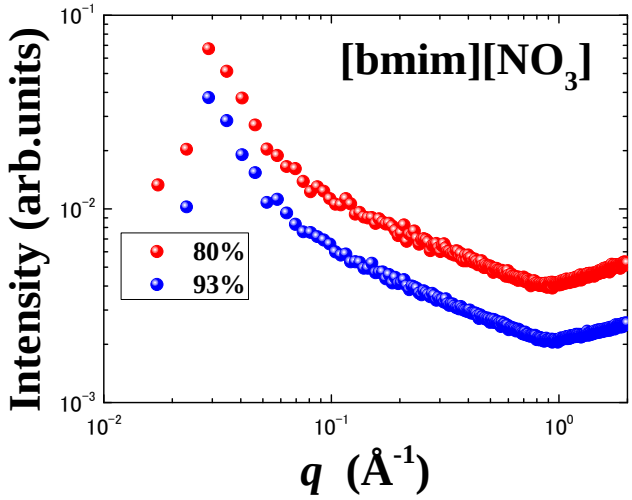

Fig. 1 SAXS of [bmim][NO_3]-80 and 93 mol% D_2O.

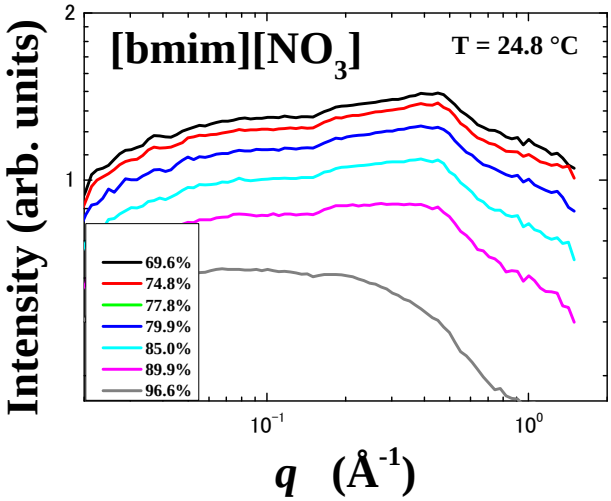

Fig. 2 SANS of [bmim][NO_3]-70~97 mol% D_2O at room temperature.

[1] T. Takekiyo, K. Yamazaki, E. Yamaguchi, H. Abe and Y. Yoshimura, *J. Phys. Chem. B* **116** (2012) 11092−11097.

[2] M. Aono, Y. Imai, Y. Ogata, H. Abe, T. Goto, Y. Yoshimura, T. Takekiyo, H. Matsumoto T. Arai, *Metal. Mater. Trans.* **42**A (2011) 37-40.