MLF Experimental Report	提出日 Date of Report September 18 (2014)
課題番号 Project No. 2014A0206 実験課題名 Title of experiment Hierarchical structures in a mixture of water / organic solvent / antagonistic salt 実験責任者名 Name of principal investigator Koichiro Sadakane 所属 Affiliation Ritsumeikan University	装置責任者 Name of responsible person Toshiya Otomo 装置名 Name of Instrument/（BL No.） BL 21 実施日 Date of Experiment May 16 to May 18 (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) Deuterium Oxide (D_2O)

(2) Deuterium Oxide (D_2O) + 3-methylpyridine (C_6H_7N) + $NaBPh_4$ ($C_{24}H_{20}BNa$), $NaBPh_4$ = 0 ～ 200 mM

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.

2-1 The background of this research

The aim of this research is to observe the hierarchical structures in a mixture of water / organic solvent / antagonistic salt with a scale of 1 Å to 100 Å.

So far, we investigated the effect of an antagonistic salt, which is composed of hydrophilic cation and hydrophobic anion, on a mixture of water and organic solvent. For example, a lamellar structure with a scale of 100 Å was observed in a mixture of water / 3-methylpyridine / $NaBPh_4$ by small-angle neutron scattering (SANS) measurement although no surfactant is contained (KS, et al., 2009). Such an experimental observation can be understood in the framework of the theory proposed by Onuki and Kitamura (A. Onuki and H. Kitamura, 2008). In their model, hydrophilic and hydrophobic ions can be adsorbed to the interface between water and organic solvent. These ions reduce the interfacial tension between the solvents, and mesoscopic structures are induced. Therefore, it is assumed that pairs of hydrophilic cation (Na^+) and hydrophobic anion (BPh_4^-) play roles of surface-active agent in a mixture of water and 3-methylpyridine. However, the details of how a salt-induced ordered structure is formed are not understood completely.

In this study, we observed the distribution of D_2O, 3-methylpyridine, Na^+, and BPh_4^- by means of High Intensity Total Diffractometer at BL21 (NOVA) to clarify the driving force of the ordered structure in the mixture.

2-2 Experiments

D_2O (99.9% purity, Pure Chemical Industries), 3-methylpyridine-d7 (deuterated 3-methylpyridine, 98% purity,

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

Cambridge Isotope Aldrich), and $NaBPh_4$ (sodium tetraphenylborate, 99.5% purity, DOJINDO) were mixed without further purification. The volume fraction of 3-methylpyridine, $\phi_{3MP} = V_{3MP}/(V_{water} + V_{3MP} + V_{salt})$, was set at 0.09, 0.10, 0.12, and 0.13 (V_{water}, V_{3MP}, and V_{salt} denote the volumes of D_2O, 3-methylpyridine-d7, and $NaBPh_4$, respectively). The concentration of $NaBPh_4$ in the mixture, C_{salt}, was varied between 0 mmol/L and 200 mmol/L. The neutron diffraction measurements were performed at BL21, NOVA. The samples were kept in titanium–vanadium cells with a diameter of 6 mm. The sample temperature was controlled between 303 K and 333 K with an accuracy of ± 0.1 K. The observed data were corrected for transmission, background scattering, and the sample thickness to obtain absolute intensities. Then, the pair correlation function, $g(r)$, was also evaluated.

2-3 Results

Figure 1 (a) shows the diffraction data ($I(Q)$ vs Q) for a mixture of D_2O / 3-methylpyridine-d7 / $NaBPh_4$. Several peaks, which reflect the distribution of D_2O, 3-methylpyridine-7, Na^+, and BPh_4^-, are confirmed. Using these data, we also evaluated the pair-correlation function, $g(r)$ (see Fig. 1 (b)). Now we are discussing how to interpret these results with our collaborator, Professor. Kameda in Yamagata University.

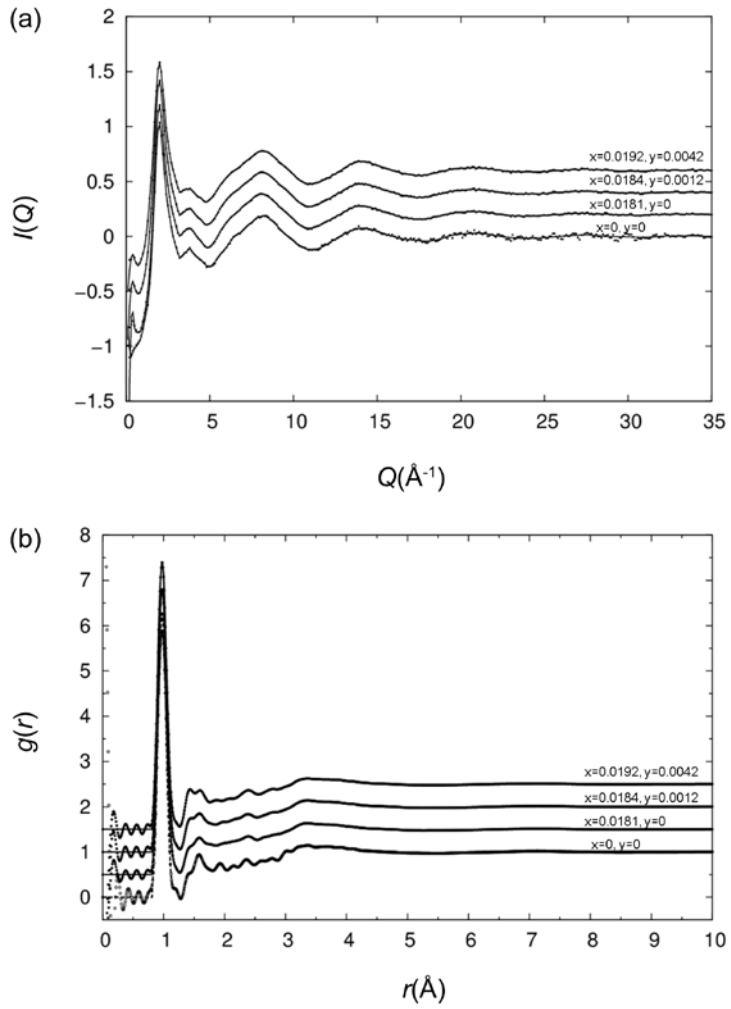

Figure 1: (a) The neutron diffraction profile ($I(Q)$ vs Q) for the mixture D_2O / 3-methylpyridine-d7 / $NaBPh_4$.Here, X and Y denote the molar fraction of 3-methylpyridine-d7 and NaBPh4, respectively. (b) The pare-correlation function, $g(r)$ for the same mixtures as Fig. 1 (a).