MLF Experimental Report	提出日 Date of Report
課題番号 Project No. 2012B0087 実験課題名 Title of experiment Nanostructures composed of ions at the surface of water 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 Norifumi Yamada 装置名 Name of Instrument/(BL No.) BL 16 実施日 Date of Experiment Dec 16 to Dec 18 (2013)

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) D_2O
(2) D2O + $NaBPh_4$ ($C_{24}H_{20}BNa$), $NaBPh_4$ = 100 mM
(3) D2O + $NaBPh_4$, $NaBPh_4$ = 200 mM
(4) D2O + $NaBPh_4$, $NaBPh_4$ = 300 mM
(5) Null water (H2O + D2O) + $NaBPh_4$, $NaBPh_4$ = 100 mM
(6) Null water + $NaBPh_4$, $NaBPh_4$ = 200 mM
(7) Null water + $NaBPh_4$, $NaBPh_4$ = 300 mM
(8) Null water + NaCl, NaCl = 2 M

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 purpose of this research

The aim of this research is to observe the nanostructures in the binary mixture of water and salt, which is assumed to be formed at the surface of water.

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. Figure 1 shows the results of our recent research on a mixture of D_2O / 3-methylpyridine / $NaBPh_4$ (Na_+ is hydrophilic, and BPh_4^- is hydrophobic) [1]. In the optical microscope measurement, the formation of multi-lamellar vesicles with a scale of 10 μm is confirmed below 318 K since maltese cross patterns are seen under crossed Nicoles with polarized light. Furthermore, lamellar structures with a scale of 100 Å are observed by small-angle neutron scattering (SANS) measurement. These experimental observations can be understood in the framework of the theory proposed by Onuki and Kitamura [2,3]. 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 [2,3]. 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.

Here, it is known that surfactant molecules tend to adsorb to the surface of water because hydrophilic group prefers water, whereas hydrophobic group prefers air. Then, monolayer structures (so-called Langmuir - Blodgett film) is formed at the surface of water [4]. Since pairs of Na^+ and BPh_4^- have a feature of surfactant molecules, as mentioned above, it is expected that some kind of nanostructures are also formed at the surface of water in a binary mixture of water and $NaBPh_4$.

In order to confirm this idea, we observed the surface structure of water and $NaBPh_4$ mixture in this research. For comparison, the surface structure of water and hydrophilic salt, NaCl, was also observed. The measurements were done using neutron reflectometer, SOFIA (BL 16).

2-2 Results

Figure 1 shows the results obtained by this beam-time. As shown in Fig. 1(a), The reflectivity profile does not changed by adding $NaBPh_4$ into D_2O. On the other hand, the distinct difference is shown in case of the mixture of null water / salt; with increasing the amount of $NaBPh_4$, the reflectivity decreases. This may suggest that the roughness of the water surface increases due to the aggregation of $NaBPh_4$. It is noted that the roughness of water surface should be independent of the amount of NaCl since the power-low of the reflectivity shows -4, which corresponds to the power-low of flat surface.

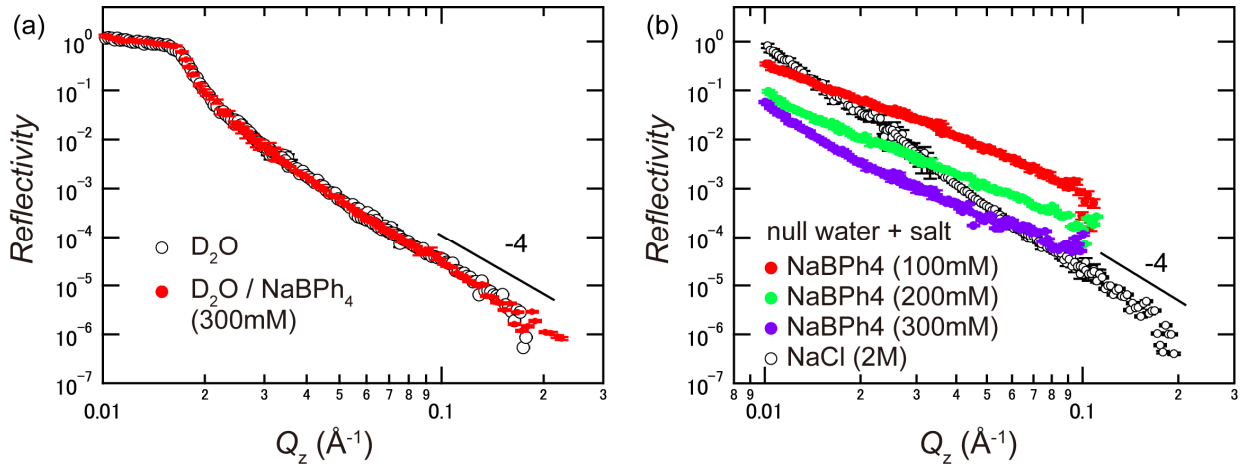

Figure 1: (a) The neutron reflectivity from the mixture of D_2O and D_2O / $NaBPh_4$ (300mM). (b) The neutron reflectivity from the mixture of null water (H_2O+D_2O) with $NaBPh_4$ (100mM, 200mM, 300mM) or NaCl (2M).

[1] K. Sadakane, A. Onuki, K. Nishida, S. Koizumi, and H. Seto, Phys. Rev. Lett., 103, 167803 (2009).

[2] A. Onuki and H. Kitamura, J. Chem. Phys., 121, 3143 (2004).

[3] A. Onuki, J. Chem. Phys., 128, 224704 (2008).

[4] P.G. de Gennes, "Capillarity and Wetting Phenomena: Drops, Bubbles, Pearls, Waves", Springer (2003).