（ ※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。 ）

MLF Experimental Report	提出日 Date of Report July 10 (2014)
課題番号 Project No. 2014A0233 実験課題名 Title of experiment Surface structures of a mixture of water / antagonistic salts 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 Apr 25 to Apr 27 (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) Null water (H2O + D2O) + $NaBPh_4$ ($C_{24}H_{20}BNa$), $NaBPh_4$ = 30 mM

(2) Null water + $NaBPh_4$, $NaBPh_4$ = 85 mM

(3) Null water + $NaBPh_4$, $NaBPh_4$ = 150 mM

(4) Null water + $NaBPh_4$, $NaBPh_4$ = 500 mM

(5) Null water + stearic d-35 acid (saturated solution)

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 nanostructures in a binary mixture of water / salt, which is assumed to be formed on the surface of water.

So far, we discovered that an antagonistic salt, which is composed of hydrophilic cation and hydrophobic anion, can induce ordered structures (e.g., lamellar structure) although no surfactants or polymers are contained [1]. These experimental observations can be understood in the framework of the theory proposed by Onuki and Kitamura [2]. In their model, hydrophilic and hydrophobic ions tend to strongly adsorb to the interface between water and organic solvent. These ions reduce the interfacial tension between the solvents, and mesoscopic structures are induced [2]. In this manner, antagonistic salts behave as surfactants in some cases.

Here, it is known that surfactants forms monolayers (so-called Gibbs monolayers) on the surface of water.

Since pairs of hydrophilic cation and hydrophobic anion 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 antagonistic salts.

2-2 The results of the previous study

On the basis of this assumption, we investigated the surface tension and the nanostructures on the water containing

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

antagonistic salt, $NaBPh_4$ (Na^+ is hydrophilic, and BPh_4^- is hydrophobic). As shown in Fig. 1(a), surface tension of water decreases by adding $NaBPh_4$. Additionally, the results of neutron reflectometry study (BL16, Project No. 2012B0087) suggest that some kind of nanostructure is formed in these mixtures.

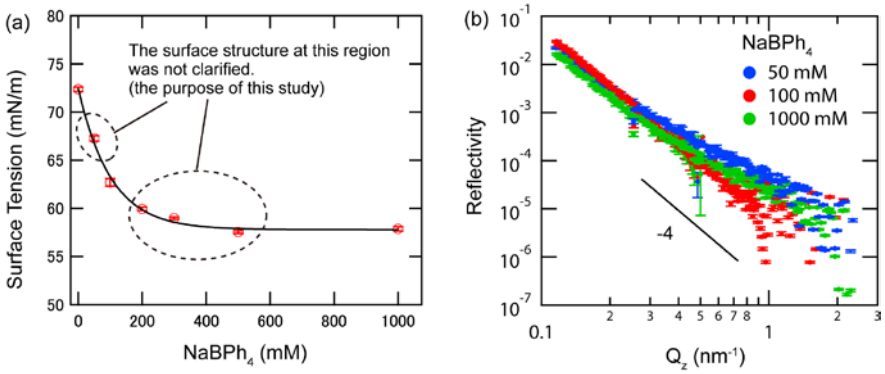

Figure 1: (a) The surface tension of null water (H_2O+D_2O) / $NaBPh_4$. (b) The neutron reflectivity from the mixture of null water / $NaBPh_4$.

2-3 The Results of this study

The successive results shown in Fig. 1 suggest that pairs of Na^+ and BPh_4^- ion behave as surfactant molecules; they aggregates on the surface of water, and decrease the surface tension. In the present study, we further investigated the surface structure of null water by adding $NaBPh_4$ by means of neutron reflectometry. For comparison, a mixture of null water / stearic d-35 acid (steric acid forms Gibbs monolayer on the surface) was also measured. Figure 2 shows the example of the results. When the concentration of $NaBPh_4$ is 30 mM, the reflectivity follows the power law, Q_z^{-2}. This profile is analogous to that of steric acid solution. Therefore, we consider that Na^+ and BPh_4^- forms monolayer-like structure on the surface of water. On the other hand, the feflectivity follows Q_z^{-4} when the concentration of NaBPh4 is 500 mM. In this case, Na^+ and BPh_4^- ions may distribute homogeneously. Now we are analyzing these data to clarify the surface structure in detail.

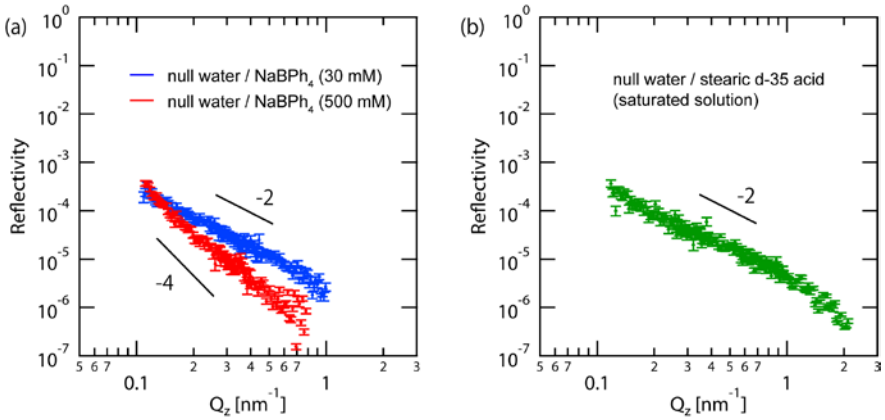

Figure 2: (a) The neutron reflectivity from the mixture of null water (H_2O+D_2O) / $NaBPh_4$ (30 mM and 500 mM). (b) The neutron reflectivity from the mixture of null water / stearic d-35 acid (saturated solution).

[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).