（ ※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。）

J-PARC **MLF Experimental Report**	提出日 Date of Report
課題番号 Project No. 2014B0255 実験課題名 Title of experiment Structural characterization of adsorbed films of hair-conditioner surfactants at the solid/water interface using neutron reflectometry 実験責任者名 Name of principal investigator Ken-ichi Iimura 所属 Affiliation Utsunomiya University	装置責任者 Name of responsible person Dr. Norifumi Yamada 装置名 Name of Instrument/（BL No.） SOFIA (BL No.16) 実施日 Date of Experiment 27-28 February 2015, 1-4 March 2016

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.

・ Disciform silicon plate (75 mmφ × 8 mm)

・ Ureidopropyltriethoxysilane-modified silicon plate

・ Adsorbed films of docosyltrimethylammonium chloride, 1-octadecanol, 1-docosanol, and/or a copolymer of hydroxyethylacrylamide/acrylic acid

・ Deuterium water

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.

A highly polished surface of disciform silicon substrate was used for surfactant adsorption and neutron reflectivity (NR) measurement. The substrate surface was chemically modified with a self-assembled monolayer of ureidopropyltriethoxysilane (UPTES) beforehand. Surfactants used were docosyltrimethyl-ammonium chloride (DTAC), 1-octadecanol (C18OH), and 1-docosanol (C22OH). A hydroxylethylacryl-amide/acrylic acid (HEAA-AA) copolymer was also employed to evaluate its effect on film structures. The substrate was sandwiched between aluminum holders of a sealable sample cell through o-rings, and an aqueous surfactant solution was filled in the cell. After a few minutes for allowing adsorption of surfactant molecules at the solution/substrate interface, the content fluid in the cell (ca. 4 mL) was removed by sucking with a microsyringe, and then immediately the same amount of D_2O was injected to the interior space of cell with another microsyringe. The procedure of sucking-D_2O injection, which is called 'rinse' in this report, was repeated to replace H_2O by D_2O in the cell and also to remove non-adsorbed surfactant molecules from the cell interior. After rinsing with D_2O of a defined volume, the sample cell was tightly sealed, and then a NR measurement was performed. The measurements were also made for a bare silicon

substrate and a UPTES-modified silicon substrate to obtain reference data.

Figure 1 shows NR profiles measured for films adsorbed from a mixed surfactant solution of DTAC/C18OH/C22OH after rinse with D_2O of 8, 16, 24, and 48 mL. The interference fringes are obviously observed in these profiles, which is in contrast to cases for the bare silicon substrate and UPTES-modified silicon substrate (Figure 2 (a)) where the reflectivity was monotonously decreased with the increase of Q_z. In addition, the profile features including fringe positions seems to be very similar to each other irrespective of the quantity of D_2O for rinse. This observation indicates that the interior liquid was mostly replaced by D_2O through the rinse with 8 mL, and the adsorbed films are considerably stable against the D_2O rinse. Investigation of film structures through curve fitting analysis up to the present suggests that the adsorbed films are in multilayers, most probably stacked bilayers, at the liquid/solid interface.

In Figure 2, NR profiles for (a) UPTES-modified substrate and (b-d) adsorbed films from surfactant solutions of (b) DTAC/C18OH/C22OH, (c) DTAC/C18OH/C22OH/HEAA-AA, and (d) DTAC are compared. The quantity of D_2O used for rinse of adsorbed film systems was 24 mL. The profile (b) and (c) are very resemble, suggesting addition of HEAA-AA in the surfactant solution does not give significant changes in film structure at this condition and/or rinse stage. However, the notable difference is found between (b, c) and (d). The profile feature of (d) implies the formation of a thin bilayer film of DTAC, which is consistent with a common aspect for adsorbed films of long-chain quaternary ammonium salts at the interfaces of water or D_2O and hydrophilic solids. Thus, the comparison indicates the addition of long-chain alcohols in the DTAC solution induces the multilayer formation. In such films, the increase of adsorbed quantity of surfactant molecules is also expected.

Investigations of film structures and properties with other analytical techniques for the same adsorbed film systems, as well as careful fitting-analysis of the NR data to find precise parameters, have been in progress. Further studies will be continued to clarify film structures, effects of additives, and their correlation to film properties.
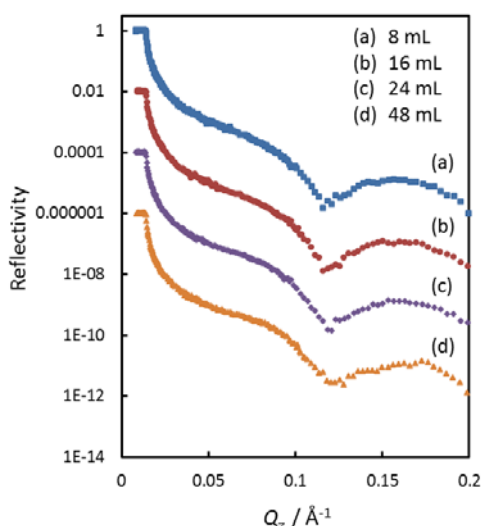

Figure 1   NR profiles for films adsorbed from a mixed surfactant solution of DTAC/C18OH/C22OH. The profile (b), (c), and (d) are shifted for clarity.
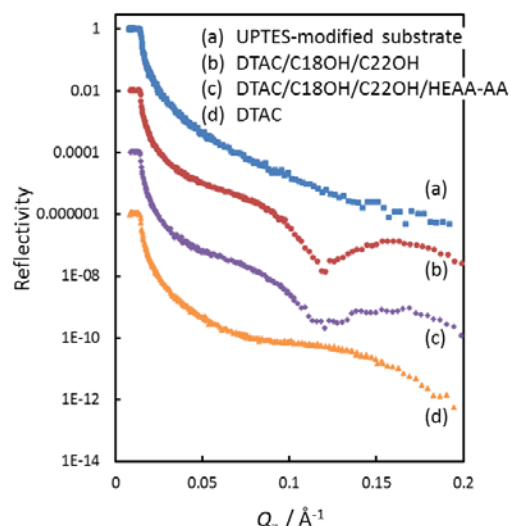
Figure 2 NR profiles for (a) UPTES-modified substrate and (b-d) adsorbed films from surfactant solutions after rinse with D_2O of 24 mL. The profile (b), (c), and (d) are shifted for clarity.