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Phase Transition of Alkane Wetting Film on Surfactant Solution and Structural Change in Electrical Double Layer

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1 Introduction

Electrical double layer is generally composed of the Stern layer and diffusion double layer. In the Stern layer, the counterions bound to the oppositely charged surface, while those distributed in the diffusion double layer more loosely interacting with the charged surface. The adsorbed film formed by ionic surfactants necessarily associates with the electrical double layer, however, the detail structure of them has never determined due to a lack of proper experimental techniques.

Recently, we have utilized total-reflection XAFS to investigate the local chemical environment of surfactant counterions (Br^-) and found that the ratio of Br^- ions in the diffused double layer (free-Br) and in the Stern layer (bound-Br) can be deduced from EXAFS analysis [1,2].

We report here the application of TR-XAFS to the hexadecane wetting film on hexadecyl-trimethylammonium bromide (HTAB) aqueous solution surface. In this case, hexadecane molecules penetrate into the surfactant adsorbed film then gives rise to the surface phase transition between liquid- and solid-monolayers upon cooling [3]. Therefore, the effect of surface phase transition to the structure of electrical double layer can be discussed.

2 Experiment

The XAFS experiments were performed by using the synchrotron radiation at beamline 7C of the Photon Factory of the National Laboratory for High Energy Accelerator Research Organization (Tsukuba, Japan). The XAFS method was applied to the air/water surface under the total-reflection condition. The X-ray beam monochromatized by a double-crystal monochromator [Si-(111)] hits the solution surface at about 1 mrad. The incident beam intensity I_0 was measured by a gas ionization chamber filled with nitrogen, the signal intensity I was detected by the total-conversion helium ion yield method, and I/I_0 versus photon energy plots were obtained. In the present study, the photon energy was scanned from 13 391 to 13 633 eV, which was enough to obtain the jump values at the K absorption edge and to extract the solvation structure because the oscillation of the spectra was greatly diminished at photon energies above 13 560 eV. The depth of the evanescent wave was estimated to be around 7 nm; therefore, TRXAFS is surface-selective. Details of the principle, procedures, and schematic views of the methods were fully described in our previous papers [1, 2].

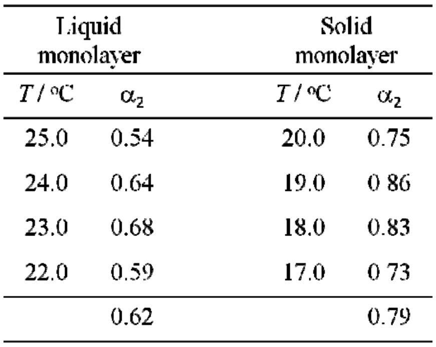
3 Results and Discussion

The surfactant concentration was fixed at m = 0.1 mmol kg^{-1}. Hexadecane dissolved in chloroform was placed onto the HTAB solution surface to spread hexadecane molecules in the adsorbed film. The EXAFS spectrum obtained can be expressed as follows,

$$k^3\chi = \alpha_1 k^3\chi_1 + \alpha_2 k^3\chi_2 \qquad (1)$$

where k is the photo electron wave vector. χ_1 and χ_2 indicate the specific EXAFS spectra for free-Br and bound-Br, and α_1 and α_2 the weight of each spectrum. The α_2 determined by least-square fitting of the measured EXAFS spectrum is summarized in Table. 1 as a function of temperature. The surface phase transition temperature determined by ellipsometry is around 21.0 °C. From these data, we have concluded that the ratio of Br^- ion in the Stern layer increases accompanied with the liquid-solid phase transition of the mixed adsorbed film of surfactant and oil. In other words, the compression of electrical double layer occurs by the surface phase transition. This idea would be potentially of relevance to a wide range of industrial processes, including foaming and emulsification. Our latest paper concerning thin-thick transition of foam film induced by surface phase transition is one of such examples [4].

Table 1: Ratio of bound Br^- in the adsorbed film



Liquid monolayer		Solid monolayer	
T / °C	α_2	T / °C	α_2
25.0	0.54	20.0	0.75
24.0	0.64	19.0	0.86
23.0	0.68	18.0	0.83
22.0	0.59	17.0	0.73
	0.62		0.79

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References

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