

Miscibility and Distribution of Counterions of Different Valences in Surfactant Adsorbed Films

Yosuke Imai and Hiroki Matsubara*

Department of Chemistry, Kyushu University, Fukuoka 812-8581, Japan

1 Introduction

Electrical double layer is generally composed of the Stern layer and diffused double layer. In the Stern layer, the counterions bound to the oppositely charged surface, while those distributed in the diffused 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 amount and local chemical environment of surfactant counterions (Br^-) and found that the total amount of Br ions in electrical double layer and the ratio of Br⁻ ions in the Stern layer (bound-Br) and that in the diffused double layer (free-Br) can be deduced from Jump value analysis and EXAFS analysis, respectively [1,2].

We report here the application of TR-XAFS to the surface of dodecyltrimethylammonium bromide (DTAB) – bis-dodecyltrimethylammonium sulfate (DTA_2SO_4) binary aqueous solution. In this study, the effect of counterion valences on the counterion distribution was 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 13391 to 13633 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 13560 eV. The penetration depth of the evanescent wave was estimated to be around 9 nm; therefore, TR-XAFS 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 TR-XAFS were measured for the mixed DTAB – DTA_2SO_4 aqueous solution with varying the total molality \hat{m} and the composition of DTA_2SO_4 in the bulk solution \hat{X}_2 at 298.15 K under atmospheric pressure.

In order to investigate the miscibility of counterions, the compositions of DTA_2SO_4 in the adsorbed film evaluated by the jump value XAFS analysis (\hat{X}_2^{XAFS}) is shown in Fig. 1 together with that evaluated by the thermodynamic analysis of surface tension data (\hat{X}_2^{H}). The reasonable coincidence between the surface compositions obtained by two methods supports the reliability of the present experiment and analysis. Fig. 1 is the phase diagram of adsorption which expresses the relation between \hat{X}_2^{H} and \hat{X}_2 at constant surface tension. At 55 mN m^{-1} , \hat{X}_2^{H} is larger than \hat{X}_2 and smaller than \hat{X}_2^{H} of ideal mixing at all the bulk composition, which means that the SO_4^{2-} ions have higher affinity to the surface than Br^- ions and that the mixing of two components is advantageous in the adsorbed film. At 45.5 mN m^{-1} , the above mentioned tendency is greatly enhanced and the phase diagram changes from a cigar type to an azeotrope type.

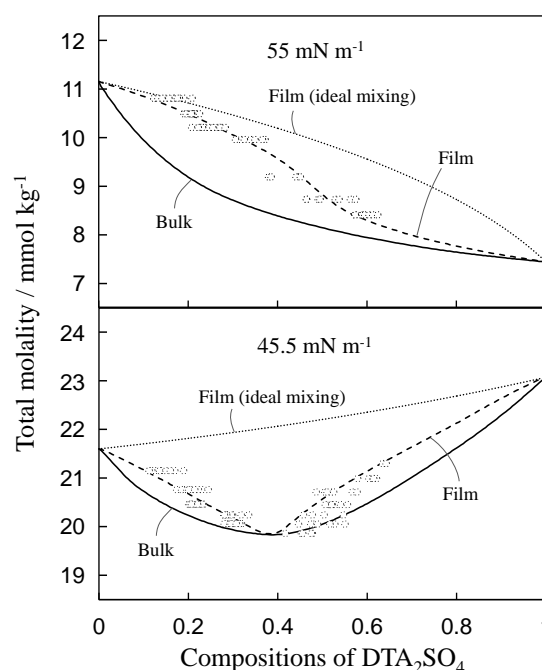


Fig. 1 Phase diagram of adsorption at constant surface tension. Solid, dashed and dotted curves represent \hat{m} vs. \hat{X}_2 , \hat{m} vs. \hat{X}_2^{H} and \hat{m} vs. \hat{X}_2^{H} of ideal mixing, respectively. Open circles represent \hat{X}_2^{XAFS} .

In order to investigate the counterion distribution, the ratio of bound Br α_2 was estimated. The EXAFS spectrum obtained can be expressed as,

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

where k is the photo electron wave vector, χ_1 and χ_2 the specific EXAFS spectra for free-Br and bound-Br, and α_1 and α_2 the weight of each spectrum, respectively. The α_2 determined by least-square fitting of the measured EXAFS spectrum is plotted in Fig. 2 against the surface composition.

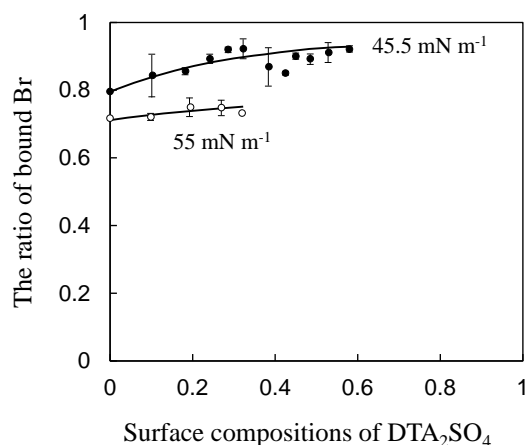


Fig. 2 The ratio of bound Br vs. surface composition of DTA₂SO₄ curves at constant surface tension.

The α_2 value increases monotonically with increasing \hat{X}_2^H from that of the DTAB pure system. This means that Br⁻ ion could occupy the Stern layer more preferentially to SO₄²⁻ ion as the surface composition of DTA₂SO₄ increases. This tendency is more remarkable when surface tension becomes lower, i.e., surface density becomes higher. From these data, it could be reasonably concluded that SO₄²⁻ ions are firmly hydrated and interact with DTA⁺ ions through electric attraction due to their high ionic valence, while Br⁻ ions are relatively easily dehydrated and preferentially bound to DTA⁺ ions.

The applicability of TR-XAFS method to the counterion distribution in the adsorbed film would be extended to the relevant topics in colloidal systems in near future. One of such examples is the preferential adsorption of BF₄⁻ ion over Br⁻ ion to the adsorbed film of DTA⁺ ion [3] where the difference between counterion distribution was discussed in terms of the adsorption energy, ion size, and hydrogen bond capability. We are now examining the obtained results based on the theoretical models for Hofmeister's specific ion effects theoretically.

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References

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* h.matsubarascc@chem.kyushu-univ.jp