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Determination of Surface Excess Concentration of Cationic Surfactants at Air/Water Interface by Total-Reflection XAFS

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Introduction

Surface excess concentration Γ of a surfactant is usually calculated from the dependence of surface tension on the bulk concentration by using the Gibbs adsorption equation. Although this method is very convenient, it has some shortcomings as follows: it does not give Γ values directly and is not applicable to the surface being equilibrium with micellar solution. Recently, the Br *K*-edge jump in the total reflection total conversion He$^+$ ion-yield x-ray absorption fine structure (TRTCY-XAFS) is correlated to the Γ values of a cationic surfactant having bromide ion as its counter ion at the air/aqueous solution surface [1]. In this study, this method was utilized for estimating Γ values of dodecyltrimethylammonium bromide (DTAB). It was shown that this TRTCY-XAFS method surmounted the shortcomings mentioned above, at least partly, and also was applicable to the surfactant mixtures [3].

Experimental

The TRTCY-XAFS experiment was performed according to the methods of Watanabe et al [1,2] at the BL-7C of Photon Factory, High Energy Accelerator Research Organization in Tsukuba. The Br *K*-edge jump J was measured as a function of the DTAB concentration m at 298 K. To convert J into Γ values, the DTAB solution at 9.35 mmol kg^{-1} was adopted as a calibration standard.

Results and Discussion

Figure 1 shows the J values converted into surface excess concentrations (circles) and Γ values calculated from the surface tension data (solid line) for the DTAB solution. The coincidence between them is pretty good at concentrations below about 10 mmol kg^{-1}, although some scatters in J values were observed. Thus the TRTCY-XAFS method was proved to give reliable Γ values. The discrepancy at higher concentrations, but below the critical micelle concentration (cmc), may offer important information on a structural change of adsorbed film, the distribution of ions in the electrical double layer, and so on, which are not extracted only from surface tension data. This point is under consideration. It is more important that this method enables us to estimate the J values at concentrations even above the cmc, where Γ values cannot be estimated from the surface tension data. This data gives new insight on the adsorbed films being equilibrium with micelle particles in the solution. By combining the Br *K*-edge jump J values employed here and XAFS information, the structure of adsorbed film, especially electrical double layer and solvation state of bromide ions, will be elucidated.

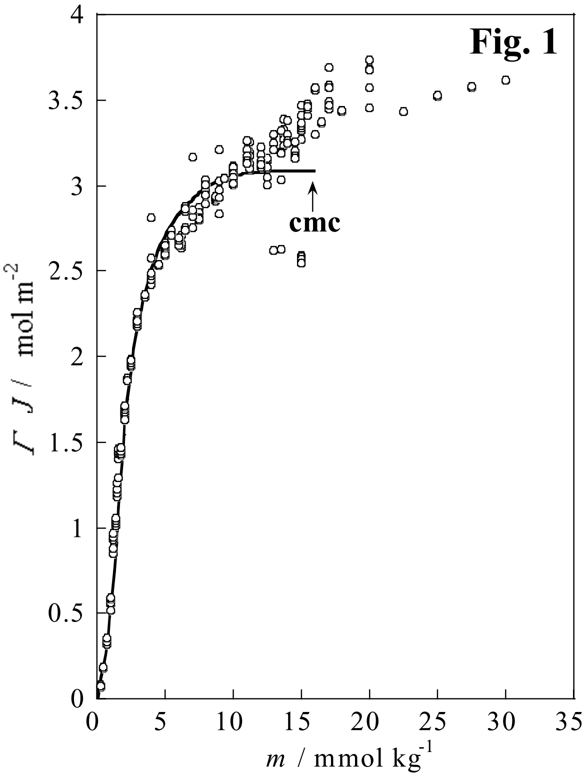

Fig. 1 Surface excess concentration of DTAB at the air/water interface. Cicles; J values from XAFS, Solid curve; Γ vs m curve from surface tension measurements.

References

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