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Determination of Surface Composition of Counter Ions of Cationic Surfactant Mixture at Air/Water Interface by Total-Reflection XAFS

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Introduction

In our previous study [1], the Br *K*-edge jump in the total reflection total conversion He^+ ion-yield x-ray absorption fine structure (TRTCY-XAFS) was utilized for estimating the surface density Γ values of dodecyltrimethylammonium bromide (DTAB) at the air/water interface. We found that (1) the coincidence between the Γ values calculated from the surface tension data and those from the jump J values was very good below the critical micelle concentration (cmc) and (2) TRTCY-XAFS method enables us to estimate the Br^- concentration in the surface region above the cmc. The aims of this study are to detect bromide ions selectively in the Br^- and Cl^- mixtures and then to estimate the mole fraction of bromide ion in the surface region of the DTAB and dodecyltrimethylammonium chloride (DTAC) mixtures. This experiment was applied to justify the criterion for ideal mixing in the adsorbed film derived for the ionic surfactant mixture with common ion [2].

Experimental

The TRTCY-XAFS experiment [3,4] was performed 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 total surfactant concentration m and mole fraction $X_{(bulk)}$ of DTAC in the mixture at 298 K. The mole fraction of chloride ions in the surface region $X_{(surface)}$ values were calculated by using $X_{(surface)} = (\Gamma - J)/\Gamma$. Here Γ is the total surface density evaluated from the surface tension measurement and J is the jump value converted into the surface density of Br^-.

Results and Discussion

Figure 1 shows the $X_{(surface)}$ in the DTAB-DTAC mixtures demonstrated as the m vs $X_{(surface)}$ plot together with the m vs $X_{(bulk)}$ plot at a given surface tension. This figure is called the phase diagram of adsorption that gives the equilibrium composition relation between the bulk solution and surface. It is clear that the surface region abounds in bromide ions compared to the bulk solution. The most important is that the m vs $X_{(surface)}$ plots do not give a linear relation between the m and $X_{(surface)}$ values, which has been adopted as a criterion of ideal mixing of molecules in the adsorbed film by many researchers. Instead, the plots are convex upward and the m vs $(X_{(surface)})^{1/2}$ is actually almost linear. This proves our idea that ideal mixing in the surface region for an ionic surfactant mixture with common surfactant ion is given by the linear relation of m^2 to $X_{(surface)}$ at a given surface tension [2].

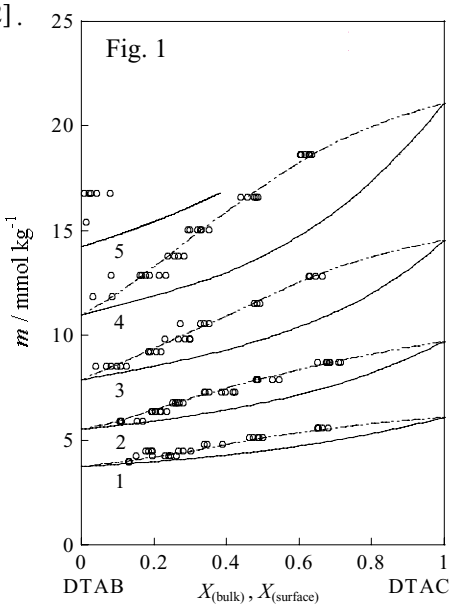

Fig. 1 Phase diagram of adsorption of the DTAB and DTAC mixture. Circles; m vs $X_{(surface)}$ plots from XAFS, Solid curve; m vs $X_{(bulk)}$ curves from surface tension measurements. (1) γ= 60 mN m^{-1}, (2) 55, (3) 50, (4) 45, (5) 41.

References

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