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Local Structure of Zwitterionic Surfactants and Bromide ion at Solution Surface

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Introduction

Zwitterionic surfactants, *N*-dodecyl-*N*,*N*-dimecyl-ammonio-butane-sulfonic acid (DDABS), are adsorbed at the aqueous solution surface. The anionic sulfoic group of DDABS interacts with an electrolyte added to the aqueous solution. The structure at the solution surface depends on the concentration and property of the electrolyte. Using $CuBr_2$ as the electrolyte, the local structures of DDABS and $CuBr_2$ were analyzed by the TRTEY-XAFS (Total-Reflection Total-Electron-Yield) method.

Experimental

TRTEY measurement was carried out by using an evanescent wave. When X-ray was introduced at a grazing angle to the solution surface (about 0.8 mrad), where the total reflection occurred, the evanescent wave was generated at the surface. Auger electrons and photoelectrons were ejected from the solution surface by the evanescent wave. The X-ray absorption intensity was estimated from the current intensity by their electrons. All XAFS spectra were recorded at BL-7C of Photon Factory, High Energy Accelerator Research Organization in Tsukuba.

Samples were aqueous solutions with 5mmol dm^{-3} DDABS and (a) 5, (b) 10, (c) 20, (d) 40 mmol dm^{-3} $CuBr_2$.

Results and Discussion

The fourier transformed XAFS spectra are shown in Fig. 1. XAFS parameters for DDABS and $CuBr_2$ aqueous solutions at Br *K*-edge were determined by curve-fitting. The Br-neighboring atom distance for (a) is 3.4 Å and that for (c) is 3.2 Å. The higher concentrations of $CuBr_2$, the shorter the distances between bromide ions and the neighboring atoms. This is due to the contributions of hydrated bromide ions in the bulk solution. According to the surface adsorption estimated from the edge jump at Br *K*-edge, the XAFS spectrum for (a) is mainly affected by bromide ions existing near the solution surface area, whereas the spectrum for (c) is almost the same as that obtained for hydrated bromide ion. The distance between the hydrated bromide ion in the bulk solution and coordinating atoms (six oxygen atoms of water molecules) is 3.2 Å. The XAFS spectra for (c) and (d) are dominantly affected by hydrated bromide ions.

The bromide ions electrostatically interact with hydrogen atoms of the methyl groups bonded to the quaternary nitrogen atom, as schematically illustrated in Fig. 2. The bromide ion may bridge two DDABS molecules. As a results, DDABS film at solution surface is stabilized by this Br bridge.

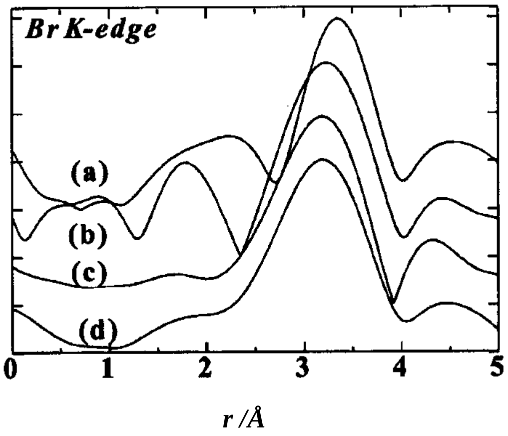

Fig. 1. Fourier transforms for aqueous solution samples with 5mmol dm^{-3} DDABS and (a) 5, (b) 10, (c) 20, (d) 40 mmol dm^{-3} $CuBr_2$ aq.

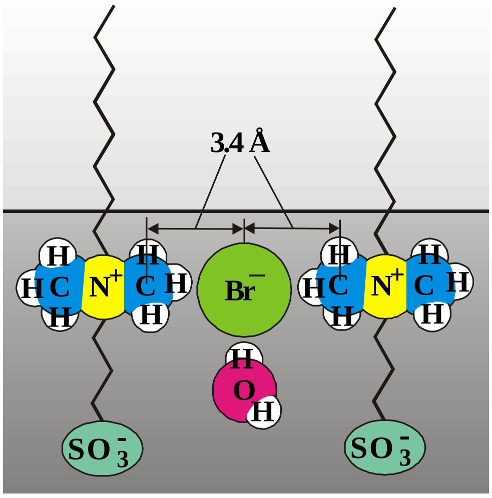

Fig. 2. The model for DDABS and bromide ion on the aqueous solution surface.

References

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