Chemistry

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Hydration structure of iodide ions adsorbed to micelles in octyltrimethyl-ammonium iodide aqueous solution

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Introduction

Alkyltrimethylammonium halide forms micelles in aqueous solution above critical micelle concentration [cmc]. At cmc, the properties of solution change in various points of view.

Focusing on the interaction between cationic surfactant and anion in aqueous solution, the aim of the present study is to know whether micelle adsorbed I^- has the same hydration structure as that of free I^- by using EXAFS.

Experiments

Octyltrimethylammonium iodide (C_8TAI) was synthesized and was purified by recrystallizing with pure water. The electric conductivity experiments were performed in our laboratory. The fluorescence XAFS spectra at the I L_{III} edge were obtained at BL-9A station. The incident and fluorescent X-ray intensities were measured by an ionization chamber and a Lytle detector, respectively, at room temperature. All the X-ray paths, I_0 chamber and a sample cell were purged with He gas. The detection gas for Lytle detector was N_2.

Results and Discussion

Fig.1 shows spectra of C_8TAI aqueous solutions at various concentrations. It is clear that they have isosbestic points, thus they should consist of two components, i.e. free I^- and micelle adsorbed I^-. The corresponding two spectra are extracted from spectra of various concentrations of C_8TAI by using the factor analysis.

Fig.2 shows the ratios of the two components calculated, and also those from the electric conductivity measurements. It should be noted here that though the ratios are given from two different methods, their dependences on concentration are quite similar. If there were no aggregates in the solution, the ratio of free I^- should remain one at pre-micelle concentrations. Fig.2 shows the presence of cationic surfactant-I^- aggregates even in the range of concentration less than cmc.

The EXAFS analysis indicates that if the hydration number of six for free I^- ions is assumed, that of micelle adsorbed I^- ions would be about four. The I-O distances (in I···H-O-H) are 0.330nm and 0.323nm, for free and micelle adsorbed I^- ions, respectively. It is concluded, therefore, that micelle adsorbed I^- ions have fewer hydration number and shorter coordination distance.

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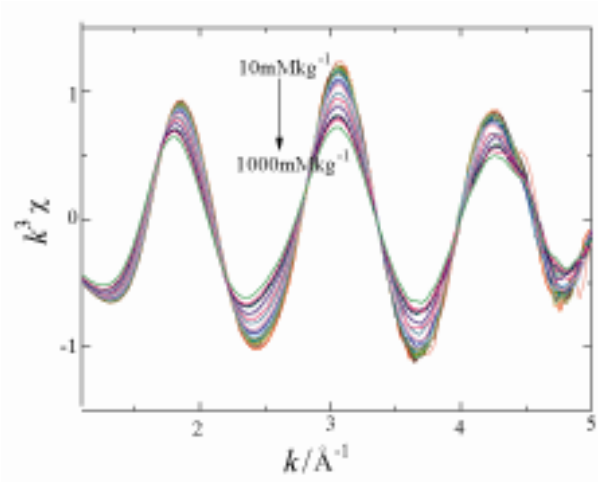

Fig.1 spectra of C_8TAI aqueous solutions at various concentrations.

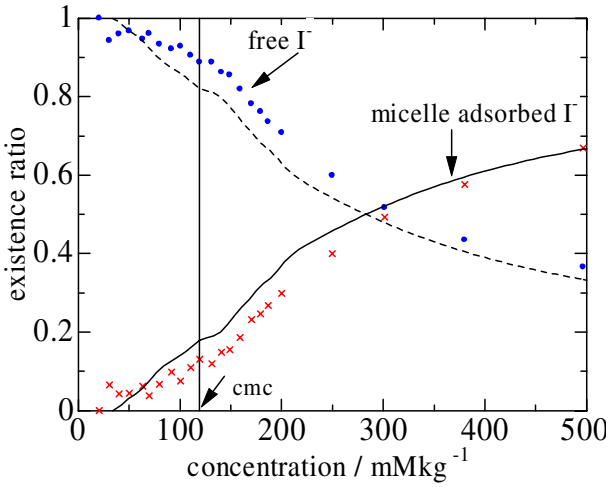

Fig.2 The existence ratio of two components from the electric conductivity measurement (solid and dashed line) and from the XAFS with factor analysis (crosses and circles).