Chemistry

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Hydration Structure of Bromide Ion Adsorbed to Micelles in Octyltrimethylammonium Bromide Aqueous Solution

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Introduction

Alkyltrimethylammonium halide forms cationic micelles above critical miceller concentration [cmc]. At cmc, the property of solution changes in various manners.

Above cmc, there are two kinds of bromide ions in octyltrimethylammonium bromide [C_8TAB] aqueous solution. Some of the bromide ions adhere to the micelles because of their charges (Micelle Adsorbed Br^-: MAB) and others are in the bulk solution (Free Br^-: FB). Focusing on the interaction between cationic surfactant and bromide ions, the aim of this study is to know whether the MAB has the same hydration structure as the FB.

The hydration structure of iodide ions in octyltrimethylammonium iodide [C_8TAI] aqueous solution has been reported [1] and the present report is its extension.

Experimental

C_8TAB was purified three times with ethanol and acetone. The electric conductivity measurements were performed in our laboratory. The Br-K edge XAFS spectra were obtained at BL10B station by using the transmittion method.

Results and discussion

Fig. 1 shows χ spectra obtained at various concentrations. Amplitude and period of the χ oscillation change with concentration. Since the χ spectra have isosbestic points, they are divided into two spectra by using the factor analysis. These two spectra pertain to FB and MAB.

The dots in Fig. 2 show the existence ratios of the two kinds of Br^- by the factor analysis performed on the χ spectra. The cmc of C_8TAB aqueous solution is approximately 225mMkg^{-1} [2]. It is clear, however, that C_8TAB forms a kind of aggregates even before the cmc. The crosses in Fig.2 indicate the ratios obtained from conductivity measurement. The two totally different methods, X-ray spectrometry and electrical conductivity, give almost the same values for the existence ratios. The breakpoint of electric conductivity curve corresponding to the cmc is obscure and far less clear for C_8TAB compared to that for C_8TAI.

The EXAFS analyses conclude that the Br—O distances (in Br^-···H-O-H) are 0.325nm and 0.321nm for FB and MAB, respectively. By taking the standard hydration number of six for FB [3], that for MAB is estimated to be about four. The results of the shorter distance and the smaller hydration number for the micelle adsorbed anion are in accord with those for I^- in C_8TAI aqueous solution.

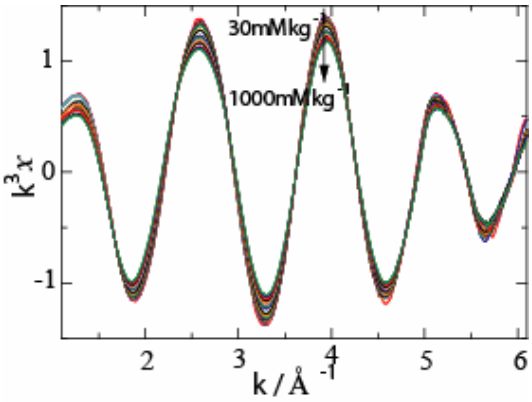

Fig. 1 the χ spectra of C_8TAB aqueous solutions at various concentrations

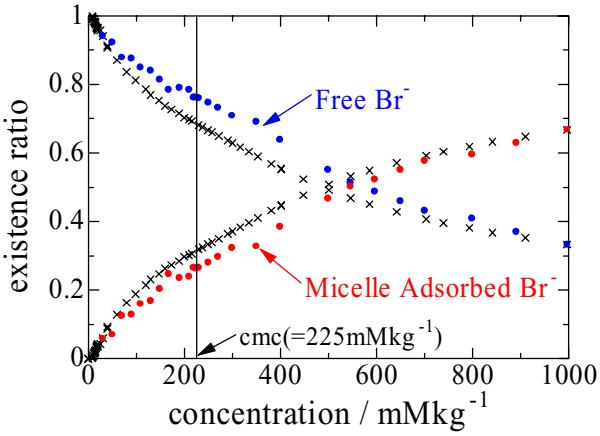

Fig. 2 the existence ratios of Free Br^- and Micelle Adsorbed Br^- by the factor analysis (blue and red dots) and by the conductivity measurement (crosses)

References

[1] *PF Activity Report 2004, B*, 20 (2005).
[2] G. D'Errico *et al., Phys.Chem.Chem.Phys.*, **4**, 5317 (2002).
[3] Hitoshi Otaki *et al., Chem. Rev.* 93, 1157 (1993).

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