Chemistry

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Bromide ions at the air/aqueous solution interface of dodecyltrimethylammonium bromide observed by total-reflection XAFS

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Introduction

Dodecyltrimethylammonium ion (DTA^+) consists of a hydrophobic group, a twelve-carbon chain, and a hydrophilic group, a trimethylammonium group. When DTA-Br is dissolved in water, DTA^+ ions come to the air/solution interface and the hydrophobic part of DTA^+ orients to the air phase. Br^- ions also come to the surface due to the electrostatic attraction from DTA^+. The aim of this study is to understand the solvation structure of Br^- ions at the surface.

Experiments

Total-reflection XAFS is surface sensitive. By this method, Br^- only within 10nm from the surface can be detected. At BL-7C station, we obtained the total-reflection XAFS spectra at Br K-edge for DTAB solutions at various concentrations.

Results and Discussion

Fig. 1 shows the surface densities of DTAB determined by measuring the surface tension and the total-reflection XAFS. They behave similarly.

Fig.2 shows the EXAFS χ spectra of DTAB solutions at various concentrations, starting from a 0mM DTAB (i.e. 0.1M KBr solution) which in Fig.2 exhibits the largest oscillation amplitude to 27.5mM DTAB with the smallest amplitude. The presence of isosbestic points indicates that these χ spectra consist of two components, one for free Br^- and the other for bound Br^- (to DTA^+ at the surface). The corresponding two spectra are extracted from the χ spectra of various concentrations by using the factor analysis. The EXAFS analysis on these spectra resulted in the bond distances of 0.32nm for Br-O (in Br-H-O-H) for both free and bound Br^- ions. By assuming the hydration number of six for the free Br^-, that for the bound Br^- is estimated to be around 3.5.

Fig.3 shows the fractions of the free and bound Br^- at the surface. The fractions of these ions vary almost linearly with the surface density of Br^-.

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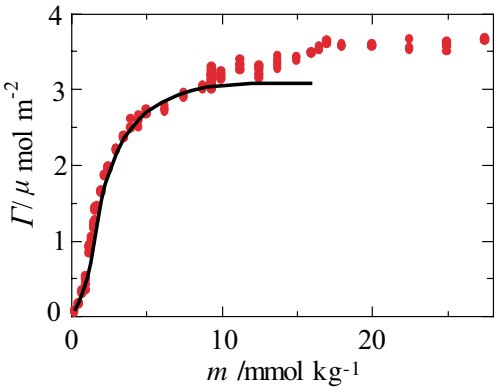

Fig.1 Surface density of Br^- by TR-XAFS (•) and by surface tention (——).

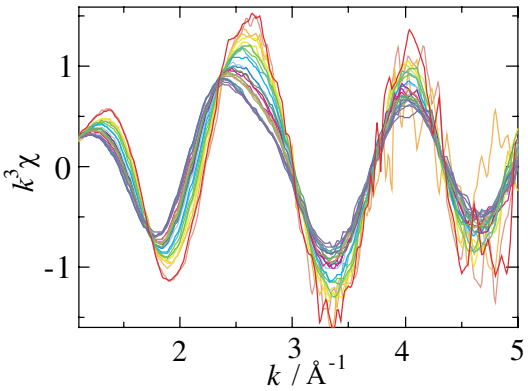

Fig.2 EXAFS spectra for solution surfaces with different DTAB concentrations.

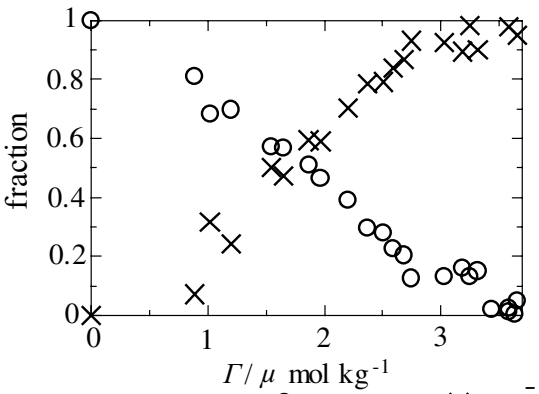

Fig.3 Fractions of free (O) and bound (×) Br^- at the surface.