

Solvation structures of bromide ions at the air/solution interface and in the bulk

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Introduction

Many solution chemists are now making efforts to know whether halide anions come to the top layer of the aqueous solution on the contrary to the classical electrostatic model which predicts that the ions are repelled from the surface. If the halide anions prefer the solution surface, their solvation structure at the surface may not be the same as that in the bulk. This issue can be studied by the XAFS experiment.

Total-reflection XAFS (TR-XAFS) spectroscopy applied to the solution surface provides detailed information about the solvation structure of the substances at the air/solution interface. A study on hydration structures of Br⁻ ions at the air/dodecyltrimethylammonium bromide (DTA-Br) aqueous solution interface has been reported [1]. In the present report, the difference in the solvation structure of Br⁻ ions is discussed by comparing the XAFS results from the TR-XAFS and the normal transmission XAFS.

Experiments

The Br-K edge XAFS spectrum of a 100mmol kg⁻¹ NaBr solution was recorded at BL12C by using the transmission method. The TR-XAFS was performed at BL7C for the surface of the same solution.

Results and Discussion

Fig. 1 shows the χ spectra for Br⁻ ions in the bulk of a 100mM kg⁻¹ NaBr solution (B-Br) (red line) and at its solution surface (S-Br) (black line). The curve fitting analyses on the χ spectra indicate that the Br-O (in Br⁻...H-O-H) bond length is shorter for S-Br. The hydration numbers are similar each other or that for S-Br is slightly smaller. It is usually observed that smaller coordination number results in shorter coordination distance.

Since the BL7C station provides a horizontally-polarized X-ray, the TR-XAFS method detects the coordinating atoms on the horizontal plane strongly but not the vertically coordinating atoms. Fig.1 also shows one of the χ spectra obtained from Br K-edge TR-XAFS for the DTA-Br aqueous solution surface (green line). As reported previously [1], there are two kinds of Br⁻ ions at the surface of surface active DTA-Br solution, one strongly contacting with the DTA⁺ positive head and having smaller hydration number (DTA-Bound Br⁻), and the other weakly contacting to the cation head and having larger hydration number similar to the bulk value of 6

(Free Br⁻). The green line pertains to the Free Br⁻. The bond length for Free Br⁻ is shorter than that for S-Br and its hydration number is larger. This result is in accordance with a model in which Free Br⁻ is surrounded by water molecules on the horizontal plane fixed by neighbour DTA⁺ head groups at side, thus the hydration number detected by the TR-XAFS becomes large, but due to the loss of some of hydration water molecules, possibly on the top position of Br⁻ anion, the bond length becomes short.

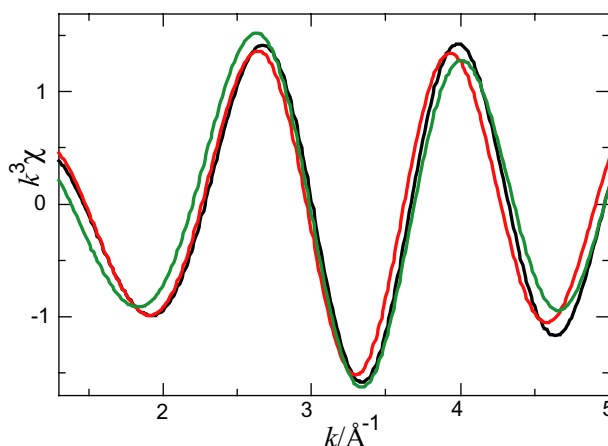


Fig.1 EXAFS χ spectra.

Br ⁻ ions	$r_{\text{Br-O}}/\text{nm}$	hydration number
in the NaBr bulk solution	0.327	6.0
on the NaBr solution surface	0.323	5.6
on the DTA-Br solution surface [#]	0.318	7.2

Table 1. The results of EXAFS analysis. [#]Br⁻ ions weakly bound to DTA⁺ cation at the surface.

Reference

[1] *P F Activity Report 2004 #22 Part B (2005)*

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