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X-ray absorption fine structure of bromide ions attracted by cationic surfactants at the heptane-water interface

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Abstract. The total-reflection X-ray spectroscopic technique was applied to an interfacial species at the liquid-liquid interface. The XAFS spectrum of bromide ions at the heptane-water interface was successfully obtained in the fluorescence mode. A slight change in the spectra was observed in the presence of the cationic surfactants, dimethyldilaurylammonium and stearyltrimethylammonium ions. This suggested that the hydrated structure of bromide ions attracted by the cationic surfactants at the heptane-water interface is different from neat interfaces or bulk aqueous phases.

1. Introduction

The liquid-liquid interface between two immiscible solutions is a two-dimensional specific reaction field. The interface is used in separation science, the synthesis of thin-layer materials, and biomembrane models [1, 2]. The distribution and structural analyses of interfacial species at a molecular level is crucial for understanding mass-transfer, adsorption, and heterogeneous reaction mechanisms at the interface. Interfacial species have been characterized by surface sensitive techniques such as total-internal reflection fluorometry [3] and surface second harmonic generation [4]. The coordination structure of the interfacial species including metal ions represents the key element of a super lattice structure and a chelate complex. However, such coordination structures cannot be studied directly by the previous surface sensitive techniques. Recently, X-ray reflectivity measurements [5] and theoretical simulations [6, 7] of the liquid-liquid interface have analyzed the interfacial charge distribution. This approach could provide a structural profile of the interface, which has remained difficult to investigate. The concentration profile and coordination structure of the interfacial species, however, has not been studied in detail because of the lack of a suitable technique to overcome the interface between the organic and aqueous phases.

XAFS is widely used to analyze the molecular structure in various chemical states. The fluorescence X-ray intensity is proportional to the concentration of the target species and the XANES is sensitive to the solvation structure of the anion [8, 9]. In particular, the total-reflection XAFS (TR-

XAFS) method has high sensitivity and selectivity to the species at the air-water interface [10]. Further applications of TR-XAFS combined with a linearly polarized X-ray and a fluorescence detection system has achieved structural analysis of the coordination and molecular orientation of a metal complex at the air-water interface [11, 12, 13]. In the previous report [14], we have developed a new TR-XAFS technique to study the interfacial species at the liquid-liquid interface.

Dimethyldilaurylammonium bromide (DMDLABr) and stearyltrimethylammonium bromide (STABr) are insoluble and slightly water-soluble cationic surfactants, respectively. The counter ion, Br⁻, is known to be attracted to the interface where the anion plays an important role in the formation of an electric double layer and participation in chemical synthesis at the interface. We have applied our new TR-XAFS technique to the bromide anion attracted by cationic alkylammonium surfactants adsorbed at the heptane-water interface.

2. Experiment

The liquid-liquid system was composed of heptane as an upper phase and a 10 mM NaBr or 0.10 mM STABr aqueous solution as a lower phase. DMDLABr was dissolved in chloroform and spread to form a monolayer on the 10 mM NaBr aqueous phase. After the formation of the monolayer, the heptane phase was carefully placed on the aqueous phase. The heptane, which was HPLC grade from Nacalai Tesque, was used as received. The aqueous solution was prepared with water purified by a Milli-Q system. All other reagents were of the highest commercially available grade.

The experiment was performed at BL39XU of SPring-8 in Hyogo, Japan. X-rays from an undulator in the storage ring were monochromatized by a diamond (111) double-crystal monochromator, and the higher harmonics were removed by an Rh-coated mirror. The stored current was 100 mA at 8 GeV. The X-ray beam was tilted downward using a 330 mm long mirror of silicon. In this study the critical angle around the Br K-edge for the heptane-water interface was 0.8 mrad, and the angle of incidence to the interface was 0.5 mrad. This ensured that the total reflection conditions through the energy range of a spectrum were maintained. The incident X-ray beam was shaped by a slit with vertical and horizontal sizes of 0.02 and 2 mm, respectively. An interface of 80 mm long and 40 mm wide was irradiated with a 20×2 mm² footprint. The cell windows for the X-ray and a detector were 0.050 mm thick polyimide films and 0.025 mm thick PTFE film, respectively.

The experimental cell has been reported in detail [14]. A glass frame with only the top face coated by dimethylsilane was placed in between two phases to form a smooth and flat-top convex meniscus which was not contacted with Teflon made cell walls. The delivery of the aqueous phase volume was controlled by a syringe and was injected from the bottom of the cell to achieve appropriate levels of the interface and the meniscus shape. The cell was placed on a remote-controlled elevation stage to allow adjustment of the interface level to the X-ray beam path. The reflected beam at the interface was monitored by a CCD camera downstream of the cell, and the angle of incidence was continuously monitored. The distance between the detector window and the interface was within a few mm. The attenuation length, at which the intensity dropped to 1/e around the energy of the Br K-edge, was estimated to be about 18 mm. In this study, the incident X-ray was absorbed by the heptane phase, and the intensity dropped by about 30 % when compared with the previous air-water studies [10, 15]. The fluorescence intensity from the interfacial region was detected perpendicularly to the interface by a 7-element silicon drift detector (SDD) from Oursstex Co., Japan. The penetration depth of evanescent waves at the heptane-water interface under total reflection conditions was calculated to be less than 9 nm, if the absorption effect was neglected. In contrast, the penetration depth of evanescent waves at the air-water interface was experimentally estimated to be less than 10 nm [10].

3. Results and Discussion

The Br K-edge TR-XAFS spectra from Br⁻ at the heptane-water interface were successfully obtained in the presence of the cationic surfactants, DMDLA⁺ and STA⁺. The spectra were normalized and are shown in Figures 1 and 2. The EXAFS χ spectra in the restricted region are inserted in the figures. The experimental configurations must be optimized for each run in order to detect the

fluorescence signal with a high efficiency. Thus the quantitative analysis for intensity of XAFS spectra could not be achieved at the present work. It is difficult to obtain the spectra at the higher energy region over 13500 eV because of the weak signal intensity in this study. The baseline modulation in Figures 1 and 2 was found as a systematic error in the measurement system. The water sub-phase is 10 mM NaBr of DMDLABr system and 0.1 mM STABr in Figures 1 and 2, respectively. The concentration of Br⁻ at the interface in Figure 1 is expected to be larger than Figure 2, and the detector may be saturated with the intense signal around 13475 eV in Figure 1. Br⁻, in general, is highly soluble in a polar solvent but not in a non-polar solvent such as heptane. We confirmed that no fluorescence signal was detected from Br⁻ in the bulk heptane phase (Figure 1 (e)). Although the fluorescence X-ray was possibly emitted from Br⁻ in the bulk aqueous phase, a fluorescence signal was not detected. This is because of the low Br⁻ concentration in the aqueous phase. As a result, only the Br⁻ located at the interface was observed in the spectra. As shown in Figures 1 (a) and 2 (a), the TR-XAFS spectra of Br⁻, attracted by surfactants DMDLA⁺ and STA⁺, at the heptane-water interface resemble the spectra at the air-water interface as shown in Figures 1 (b) and 2 (b).

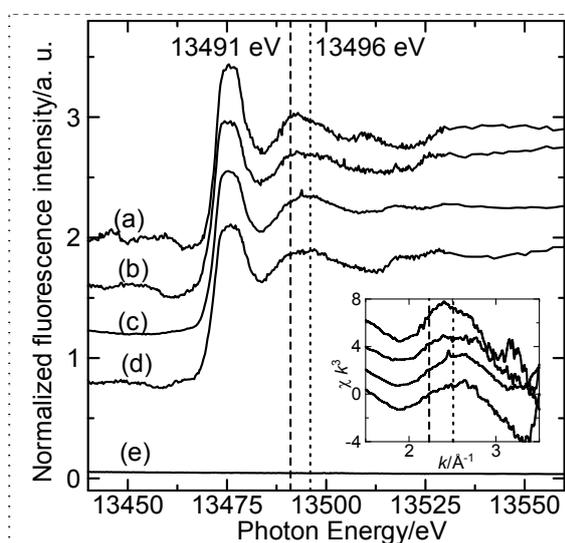


Figure 1. XAFS spectra at Br K-edge measured at the air-water and heptane-water interface of NaBr aqueous solution with and without DMDLA⁺ monolayer.

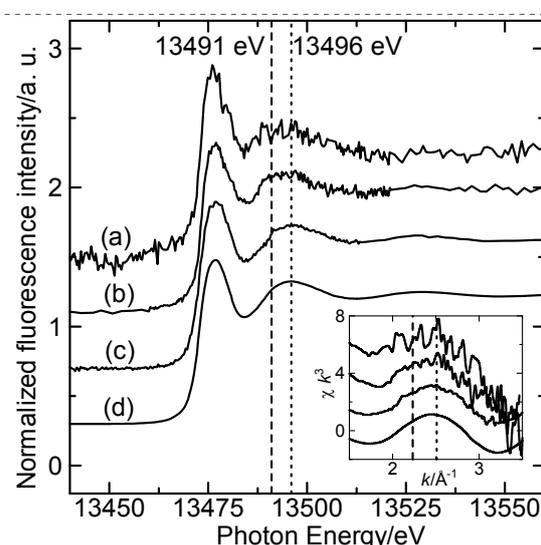


Figure 2. XAFS spectra at Br K-edge measured at the air-water and heptane-water interface in the presence of STABr.

The TR-XAFS spectra of Br⁻ without the DMDLA⁺ are presented in Figures 1 (c) and 1 (d) for the heptane-water and air-water interfaces, respectively. The peaks around 13496 eV in Figures 1 (c) and 1 (d) are broaden and slightly shifted to around 13491 eV in Figure 1 (b). The feature in the spectrum represents the combination of the different molecular structures [8]. Br⁻ adsorbed on ion-exchange resins in protic and aprotic solvents has been reported [16] and on a surfactant monolayer at the air-water interface [17]. In reference 15, soaking quaternary ammonium resins in water led to the broadened feature in EXAFS spectra of Br⁻. Solvated and bound Br⁻ have been suggested to coexist in the resins, and the spectra of the Br⁻ are reproduced by the combination of spectra for the bound and fully hydrated Br⁻. In reference 16, Br⁻ directly bound to the ammonium groups in the surfactant monolayer was detected at the air-water interface. The spectra in Figures 1 (c) and 1 (d) are from the fully hydrated Br⁻. The slightly lower peak shift and intensity in the spectra in Figures 1 (a) and 1 (b) indicates the presence of the solvated structure of the bound Br⁻.

The distribution and coordination structure of surfactants at the heptane-water interface is expected to be different from those at the air-water interface because of the interaction of the surfactants with

the organic phase. The DMDLA⁺ is expected to be differently assembled at the heptane-water interface than the air-water, and the solvation behavior of Br⁻ will be affected by the counter ion such as the DMDLA⁺ monolayer. However, no significant change was observed in Figures 1 (a) and 1 (b). The coordination structure of the Br⁻ observed at the heptane-water interface will be similar to that at the air-water interface. The assembled structure of the DMDLA⁺ monolayer at the heptane-water interface will be same as the air-water and not affect the hydrated structure of Br⁻.

Similar spectral changes in the STABr solution were also observed as shown in Figures 2. The fluorescence XAFS spectra of Br⁻ in the presence of STA⁺ in the bulk water phase were obtained with a 19 element solid state detector (SSD) from Canberra Co. (Figure 2 (c)). The spectrum in Figure 2 (d) represents a 0.1 M NaBr aqueous solution recorded in transmission mode. The Br⁻ ion bound to the STA⁺ ion at the interface of the STABr aqueous solution will be partially dehydrated at both the air-water and the heptane-water interfaces as shown in Figures 3 (a) and (b), respectively. As for the Br⁻ ion bound to the DMDLA⁺ monolayer, the Br⁻ ion at the interface in the presence of the STA⁺ monolayer is dehydrated and bound to the quaternary ammonium group in the STA⁺ molecule.

4. Conclusions

The selective TR-XAFS spectra of the interfacial species at the liquid-liquid interface could be measured in situ. The hydration structure of Br⁻ at the interface was observed to be different from that in the bulk aqueous phase. The strong interaction of Br⁻ with a quaternary ammonium moiety leads to the dehydration of the Br⁻ ion. The adsorption structures of the Br⁻ ion attracted by the DMDLA⁺ and STA⁺ ions at the heptane-water interface resemble those at the air-water interface. Further improvement of the experimental setup and EXAFS analyses of the high quality TR-XAFS spectra will enable us to reveal the coordination structure of the interfacial species.

Acknowledgments

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