Development of the total-reflection XAFS method for the liquid-liquid interface

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Abstract. A total-reflection X-ray absorption fine structure (TR-XAFS) method was successfully extended to the liquid-liquid interface that allowed the investigation of the ‘buried’ interface by fluorescence detection. The first X-ray absorption spectrum at the Br K-edge for bromide ions concentrated at the heptane-water interface was observed in the presence of dimethyldipalmitylammonium ions.

1. Introduction
The liquid-liquid interface between two immiscible solutions composed of organic and aqueous phases is a two-dimensional specific reaction field used in separation science, the synthesis of thin-layer materials, and also in biomembrane models. The structure analysis of interfacial species at a molecular level is crucial to understand mass-transfer, adsorption, and heterogeneous reaction mechanisms at the interface. The coordination structure of the interfacial species, however, has not been studied in detail because of lack of a suitable technique to overcome the ‘buried’ interface between the organic and aqueous phases.

The interfacial species have been characterized by surface sensitive techniques such as total-internal reflection fluorometry [1] and surface second harmonic generation [2]. The coordination structure of the interfacial species including metal ions, which are the keys of a super lattice structure and a chelate complex, however, cannot be studied directly by these methods. Recently, X-ray reflectivity of the liquid-liquid interface has been studied to analyze the charge distribution of the interface [3]. The method might provide a structural profile of the interface, but it is still difficult to investigate the coordination structure of the interfacial species.

X-ray absorption fine structure (XAFS) is widely used to analyze the molecular structure at various chemical states. In particular, the total-reflection XAFS (TR-XAFS) method has high sensitivity and selectivity to the species at the air-water interface [4]. Further application of TR-XAFS combined with a linearly polarized X-ray and fluorescence detection has achieved the structure analysis of the coordination and the molecular orientation of the metal complex at the air-water interface [5, 6].
this study, we applied the TR-XAFS technique to study the interfacial species at the heptane-water interface.

2. Experimental

2.1. Materials
The liquid-liquid system was composed of heptane as an upper phase and a 1 mM KBr aqueous solution as a lower phase. The heptane, which was HPLC grade from Nacala 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 available grade. A cationic surfactant, dimethyldipalmitylammonium bromide (DMDPABr), was dissolved in chloroform and spread to form a monolayer on the aqueous phase. After the formation of the monolayer, the heptane phase was carefully placed on the aqueous phase.

2.2. Measurement
The experimental setup is shown in Figure 1. 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 double crystal monochromator with a diamond (111) surface, and the higher harmonics was removed by an Rh-coated mirror. The stored current was 100 mA at 8 GeV. The X-ray beam was tilted downward with a 330 mm long mirror of silicon, as shown in Figure 1. In this study the critical angle around the Br K-edge for the heptane-water interface was 0.8 mrad, and the angle of incident to the interface was 0.5 mrad to maintain the total reflection conditions through the energy range of a spectrum. The penetration depth of evanescent waves at the interface under total reflection conditions was estimated around 90 nm near the energy of the Br K-edge. 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 40-mm long and 20-mm wide was irradiated with a 20×2 mm² footprint. Cell windows for the X-ray and a detector are 50-μm thick Kapton films.

![Experimental setup for TR-XAFS at the liquid-liquid interface.](image)

The most important point for the TR-XAFS method at the liquid-liquid interface is to keep a flat and smooth interface. The interface appears in a plateau of a convex meniscus of the aqueous phase with respect to the organic phase. A glass frame with only the top face coated by alkylsilane was placed in between two phases to form a smooth meniscus separated from the cell walls. The aqueous
phase volume was controlled by a syringe pouring the aqueous solution from the bottom of the cell to achieve appropriate levels of the interface and the meniscus shape. The cell was also put on an elevation stage to adjust the interface level to the X-ray beam path. The reflected beam at the interface was monitored by a CCD camera downstream on the cell, and the angle of incidence was continuously confirmed by monitor. The adjustable detector window height was within a few mm of the interface. The attenuation length at which the intensity dropped to 1/e around the energy at Br K-edge was estimated to be about 18 mm. In this study, the incident X-ray was absorbed by the organic phase, and the intensity dropped to about 30% in comparison with previous air-water studies [4]. The fluorescence signal was detected perpendicularly to the interface by a 7-element silicon drift detector (SDD) from Ourstex Co., Japan.

3. Results and Discussion

In the presence of cationic surfactant, DMDPA\(^+\), the Br K-edge TR-XAFS spectrum from Br\(^-\) concentrated at heptane-water interface was successfully obtained, as shown in Figure 2(a). When the level of the interface was adjusted to the lower level, X-ray beam did not irradiate the interface and passed through the bulk organic phase at a few mm from the interface. Br\(^-\), in general, is highly soluble in a polar solvent but not in a non-polar solvent such as heptane. The fluorescence signal from Br\(^-\) in the bulk heptane phase was significantly smaller than the signal from the interface. (Figure 2(b)). For the case in which Br\(^-\) is not concentrated at the interface in the absence of DMDPABr, fluorescence signals corresponding to Br\(^-\) were hardly observed (Figure 2(c)). Although the fluorescence X-ray was possibly emitted from Br\(^-\) in the bulk aqueous phase within the penetration depth of the evanescent wave, the fluorescence signal could not be detected in the present condition of the low concentration in the aqueous phase. As a result, the spectrum was only observed from the interface. The TR-XAFS spectrum of the concentrated Br\(^-\) at the heptane-water interface (Figure 2(a)) seemed to resemble the hydrated Br\(^-\) in previous results [4]. A further study will clearly reveal the coordination structure of the interfacial species.

![Figure 2](image)

**Figure 2.** XAFS spectra at Br K-edge measured: (a) at heptane-water interface with DMDPA\(^+\); (b) in heptane phase; (c) at heptane-water interface without DMDPA\(^+\). Aqueous phase was 1 mM KBr aqueous solution. Fluorescence X-ray intensity \(I_f\) was normalized by incident X-ray intensity \(I_0\).

4. Conclusion
We developed the TR-XAFS method for the liquid-liquid interface and demonstrated high potential to study the interfacial species. The new method will lead to in situ study the interfacial concentration profile and the coordination structure of interfacial species. Further improvements and applications to metal ions and metal complexes in various liquid-liquid systems are also going on.

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