

4-4 Toward Elucidation of Solvent Extraction Mechanism — Observation of Metal Ions at an Interface Using a Laser —

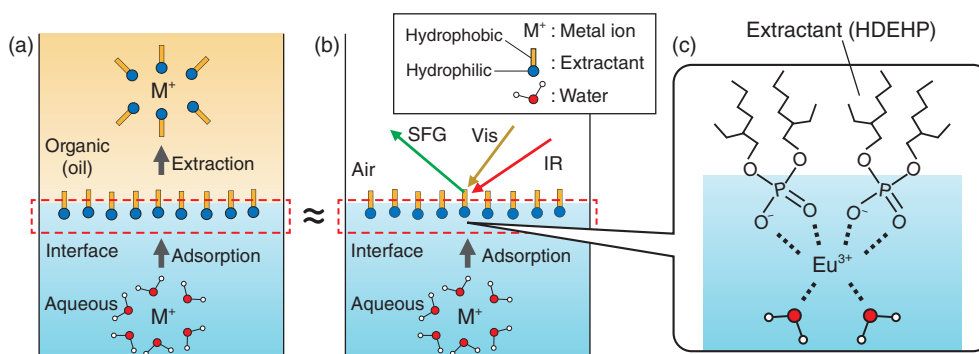


Fig.4-8 (a) Schematic of solvent extraction; (b) Diagram of the present research method; (c) Structure of a metal ion (Eu^{3+}) at the interface clarified in this study

Unlike the actual solvent extraction system (a), in the system without an organic phase (b), metal ions adsorbed to the interface are likely to stay there because no extraction takes place. The metal ions trapped at the interface were observed using sum frequency generation (SFG \rightarrow) spectroscopy with visible (Vis \rightarrow) and infrared (IR \rightarrow) pulse lasers, and the structure of the metal ions present at the interface were revealed (c).

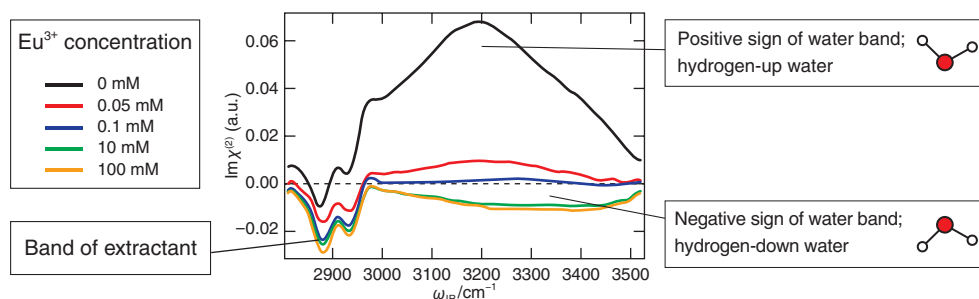


Fig.4-9 Vibrational spectra of the interface obtained by advanced laser spectroscopy: heterodyne-detected vibrational sum frequency generation spectroscopy

As the concentration of Eu^{3+} increases, the sign of the water band inverts from positive to negative. The sign of the water band corresponds to the direction of the water molecule present at the interface, and the interfacial water molecules showing negative sign point their hydrogen atoms downward. The hydrogen-down orientation of the interfacial water molecules is due to the bonding to Eu^{3+} , which adsorbs to the extractant (HDEHP) at the interface (Fig.4-8(c)).

Solvent extraction is a method for separation of metals. In solvent extraction, an aqueous phase dissolving metal ions and an organic phase dissolving a chemical called the extractant are brought into contact with each other, and metal ions are transferred from the aqueous phase to the organic phase (Fig.4-8(a)). Solvent extraction is one of the most important methods of treating radioactive waste generated by nuclear-power generation. Improving solvent-extraction technology is an important research topic.

In order to improve solvent extraction technology, fundamental research has conventionally focused upon the structure of metal ions in the aqueous and organic phases. On the other hand, the phase transfer mechanism of metals from the aqueous phase to the organic phase through the organic/aqueous interface remains poorly understood. Therefore, if the phase transfer mechanism occurring at the interface can be revealed, it is expected that new clues will be obtained for improvement of solvent extraction technology. However, it is generally difficult to observe metal ions at the interface.

In order to observe metal ions just before transfer from the interface to the organic phase, metal ions adsorbed to the interface between air and water (surface of the aqueous solution) were observed by advanced laser spectroscopy (Fig.4-8(b)). In the present study, extraction of europium ions (Eu^{3+}) using di-2-ethylhexyl phosphate extractant (HDEHP)

was selected as a representative example of common solvent extractions, and the interface vibrational spectra of the system were obtained (Fig.4-9). As the concentration of Eu^{3+} increases, the positive sign of the water signal becomes negative. This indicates that interfacial water molecules pointing upward (hydrogen-up) change to a downward (hydrogen-down) orientation as Eu^{3+} is adsorbed to the interface. That is, interfacial water molecules are bonded to Eu^{3+} with hydrogen-down orientation (Fig.4-8(c)). The structure of Eu^{3+} sandwiched between HDEHP and water molecules has not been reported so far in the organic or aqueous phases, so that the Eu^{3+} structure at the interface is unique.

Based on the findings mentioned above, we proposed a reaction model for solvent extraction of Eu^{3+} using HDEHP as follows. In the aqueous phase, Eu^{3+} is surrounded by water molecules, but Eu^{3+} is sandwiched between HDEHP and water molecules at the interface; subsequently, Eu^{3+} is extracted in the organic phase and surrounded by HDEHP.

In future work, we will conduct studies that lead to improvement of the extraction rate, separation efficiency, etc., by clarifying what is happening at the interface in actual solvent extractions of radioactive waste.

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Reference

Kusaka, R. et al., The Structure of a Lanthanide Complex at an Extractant/Water Interface Studied Using Heterodyne-Detected Vibrational Sum Frequency Generation, *Physical Chemistry Chemical Physics*, vol.20, issue 4, 2018, p.2809–2813.