

4-6 Mechanism of Actinide Transfer Between Water and Oil

— Studies of the Molecular Structure of Solvent Extraction Interfaces Using Vibrational Sum Frequency Generation Spectroscopy —

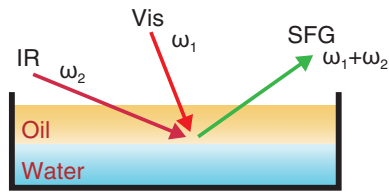


Fig.1 Vibrational sum frequency generation (VSGF) spectroscopy measurement

Visible (Vis) pulse light (with frequency ω_1) and infrared (IR) pulse light (with frequency ω_2) are incident at the interface between the oil and water phases, and the generated sum-frequency light (with frequency $\omega_1 + \omega_2$) is detected.

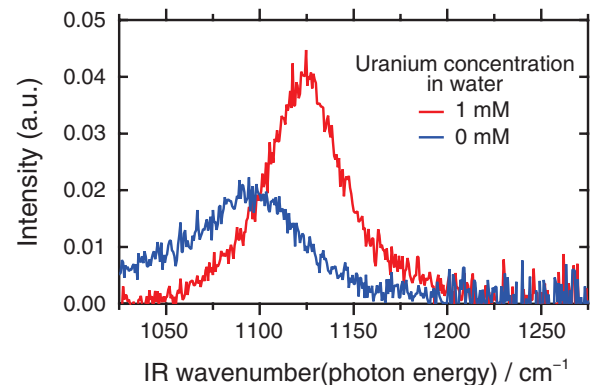


Fig.2 VSGF spectral data

The measurement results at the interface between the oil phase containing the extraction reagent (di(2-ethylhexyl)phosphoric acid) and the water phase containing uranium (uranyl ion) are shown. Signals originate from the symmetric stretching vibration of the two P–O bonds of the POO^- functional group in the extraction reagent. These results indicate that uranium is bound to the extraction reagent at the interface.

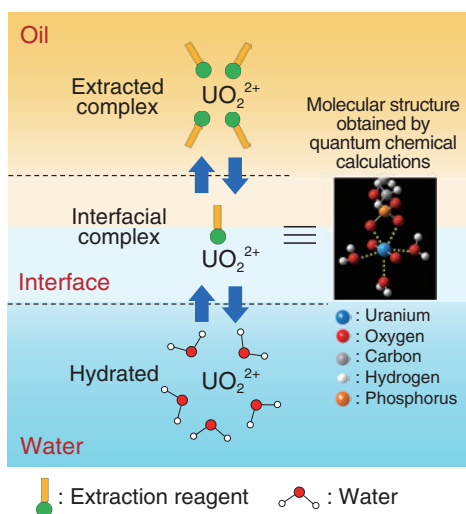


Fig.3 Model of uranium phase-transfer reaction

Uranium exists in different chemical states in the aqueous and organic phases. However, uranium can pass through the interface by undergoing a transformation into an intermediate chemical state at the interface, allowing it to move freely between the organic and aqueous phases.

Vibrational sum frequency generation (VSGF) spectroscopy is an advanced laser spectroscopy method that provides insights into the molecular structure at boundary regions (interfaces) where two different phases are in contact. As yet, there is a lack of research institutions capable of measuring nuclear fuel materials and radioactive isotopes using VSGF spectroscopy. In this study, we built a VSGF spectroscopy apparatus within our radiation-controlled area. Using this setup, we examined the mechanism of uranium transfer between the water and oil phases at the oil–water interface of the solvent extraction separation method for uranium.

In the VSGF spectroscopy measurement (Fig.1), visible and infrared lights were incident on the oil–water interface, and the light generated from the interface (i.e., sum-frequency light) was detected. Fig.2 shows the VSGF spectroscopy data obtained. When uranium was dissolved in either the water phase or the oil phase, the signal peak position shifted from 1100 cm^{-1} (—) to 1125 cm^{-1} (—). Analysis using the quantum chemical calculation program (Gaussian) confirmed that this shift can be attributed to the binding of two oxygen atoms of the POO^- group

in the extraction reagent to the uranium atom of the uranyl ion (UO_2^{2+}) at the interface (Fig.3).

It is well-known that uranium exists in different chemical states in the two phases—it exists as hydrated ions in the aqueous phase and as extraction complexes in the organic phase (Fig.3). However, the mechanism of how uranium passes through the interface is unknown. The findings of this study indicate that uranium moves between the two phases by forming a molecular structure as shown in Fig.3 with the extraction reagent at the interface.

Evidently, uranium has to pass through the oil–water interface to complete the extraction process, implying that the interface is the crucial reaction zone in solvent extraction. Further elucidation of the reactions occurring at the interface has potential for promoting the development of innovative uranium solvent extraction methods by using interfaces.

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Reference

Kusaka, R. et al., Development of Heavy Element Chemistry at Interfaces: Observing Actinide Complexes at the Oil/Water Interface in Solvent Extraction by Nonlinear Vibrational Spectroscopy, *The Journal of Physical Chemistry Letters*, vol.13, issue 30, 2022, p.7065–7071.