Articles

Liquid interfaces related to lanthanide and actinide chemistry studied using vibrational sum frequency generation spectroscopy

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Vibrational sum frequency generation (VSFG) spectroscopy offers unique information about the molecular structure at liquid interfaces (gas/liquid, liquid/liquid, and solid/liquid) in the interfacial region, which is as thin as 1 nm. This paper presents some recent VSFG studies on liquid interfaces related to solvent extractions of lanthanide and actinide. In these studies, the organic phase of solvent extractions was excluded to prevent the transfer of lanthanide and actinide from the interface into the organic phase, and their complexes with extractants were attempted to observe at the air/aqueous solution interfaces using VSFG spectroscopy. For the Eu extraction system with the di-(2-ethylhexyl)phosphate (HDEHP) extractant, an interfacial Eu-HDEHP complex was observed, and Eu^{3+} existed between HDEHP and water molecules, whereas for U extraction with the tributyl phosphate (TBP) extractant, no U-TBP interfacial complexes were observed. These results suggest that the two ions transfer into the organic phase from the aqueous phase via different phase transfer mechanisms. This paper demonstrates that VSFG spectroscopy is a powerful technique to obtain unique information about liquid interfaces pertaining to lanthanide and actinide chemistry.

1. Introduction

Liquid interfaces, such as gas/liquid, liquid/liquid, and solid/liquid interfaces, are ubiquitous and play important roles in chemistry. For chemical reactions at interfaces, the interfacial region at a ~1-nm depth is important because this thin interfacial region corresponds to the scale of the sizes of molecules. However, it is generally difficult to observe this very thin region of liquid interfaces by conventional methods. For example, photoelectron spectroscopy requires a vacuum to detect electrons ejected from sample surfaces; thus, it is not appropriate for liquid interfaces. X-ray scattering methods are generally used to study liquid interfaces. However, high brightness X-rays are prepared by synchrotrons, and experiments for radioactive species are difficult in such facilities.

Vibrational sum frequency generation (VSFG) spectroscopy is one of the vibrational spectroscopic techniques besides FT-IR and Raman spectroscopy. VSFG spectroscopy is interface-specific and offers unique information on the molecular structure in the very thin interfacial region (~1 nm) of liquid interfaces.[1-3] Although many interfacial studies by VSFG spectroscopy have been published thus far, application to lanthanides and actinides has been very limited because previous studies have paid considerable attention to interface chemistry relating to light elements, such as interface chemistry in the cell membrane. Some metal complexes have been observed at air/aqueous interfaces using VSFG spectroscopy;[4-7] however, there have been no reports on actinides because special techniques and facilities for the management and treatment of actinides are required. Recently, we constructed an optical experimental setup for VSFG spectroscopy in a radiation management area in the Japan Atomic Energy Agency (JAEA), enabling us to study actinide chemistry by VSFG spectroscopy.

In this paper, the focus is on liquid interfaces of solvent extraction of lanthanides and actinides studied using VSFG spectroscopy. In solvent extraction [Figure 1(a)], extractants are dissolved in an organic phase, and some extractant molecules come to the liquid/liquid interface and cover the interface because of the surface activity of the extractants. Metal ions in the aqueous phase come to the interface and form complexes with extractants (ligands) to subsequently transfer to the organic phase. However, it is unknown what occurs at the interface and how water and extractant molecules are bonded to metals at the interface to transfer into the organic phase. This is because of the experimental difficulty related to the organic/aqueous interface, and one reason for the difficulty is that metal complexes at the interface transfer into the organic phase after complex formation at the interface and are difficult to observe at the interface. Therefore, we trapped metal com-
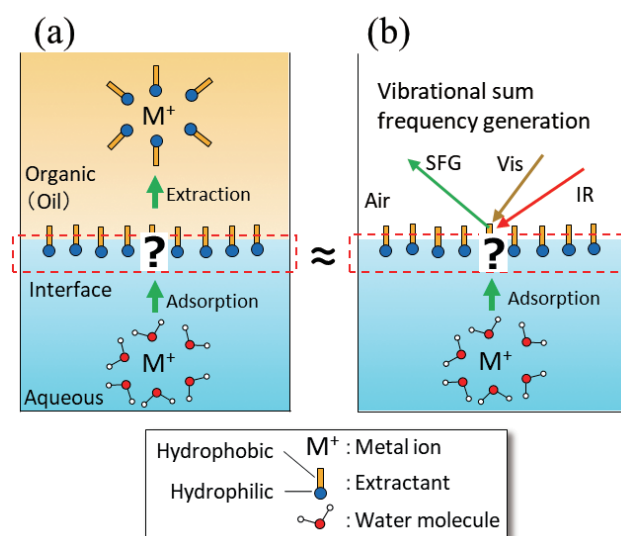
Figure 1. (a) A general model of solvent extraction, and (b) a sketch of an air/aqueous-extractant interface studied by VSFG spectroscopy.

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plexes at the air/aqueous interface after the adsorption of metal ions to the interface [Figure 1(b)], and the complexes formed at the interface were observed by VSFG spectroscopy.[8,9] When surface-active molecules cover interfaces, as shown in Figure 1, the air/aqueous interface and organic/aqueous interface have similar molecular structures[10] so that the air/aqueous interface is an appropriate model for the organic/aqueous interface to study the molecular structure of interfacial complexes.

2. Experimental

2.1. Materials and samples. High-purity water (18.2 MΩ·cm resistivity, Millipore, Milli-Q), di-(2-ethylhexyl)phosphate (HDEHP, ~100%, Tokyo Chemical Industry), europium(III) nitrate hexahydrate (Eu(NO$_3$)$_3$·6H$_2$O, >99.95%, Kanto Chemical), tri-n-butyl phosphate (TBP, >98.0%, Kanto Chemical), nitric acid (1.42) (for Ultratrace Analysis, Wako), and uranyl nitrate were used to prepare the sample aqueous solutions. Uranyl nitrate was obtained by evaporating the aqueous solution dissolving uranium metal using the nitric acid. For the study of the solvent extraction of europium by the HDEHP extractant, the sample aqueous solutions dissolved a small amount of HDEHP and europium nitrate. The sample solutions were prepared by mixing an aqueous solution saturated with HDEHP and an aqueous solution to dissolve the europium nitrate in a 1:3 volume ratio, and the Eu^{3+} concentration of the solution was 10 mM. For the study of the solvent extraction of uranium by the TBP extractant, the concentrations of TBP and nitric acid in the sample solutions were 10^{-4} M and 3 M, respectively. The concentration of uranyl nitrate in the samples was 0.9 M.

2.2. Vibrational sum frequency generation (VSFG) spectroscopy. The experimental setup was described previously.[8,9] Briefly, a Ti:Sapphire regenerative amplifier (795 nm, 5.7 mJ, 95 fs, 1 kHz) was used as the light source. One part of the output was spectrally narrowed by a bandpass filter (center wavelength: 794.7 nm, bandwidth: 1.5 nm) and used as the ω$_1$ light. The other part of the output was converted to a tunable and broadband infrared beam by an optical parametric amplifier (TOPAS-prime) with a difference frequency generation unit and used as the ω$_2$ light. The ω$_1$ and ω$_2$ beams were focused onto the sample surface of the aqueous solution to generate sum frequency light (ω$_3$) from the sample surface. When the two pulses were spatially and temporally overlapped at the interface, sum frequency light was generated from the interface through the second-order nonlinear optical effect. Under electric dipole approximation, sum frequency light is only generated from anisotropic interfaces where the inversion symmetry is broken and is not generated from isotropic media (i.e., bulk). The interfacial region where sum frequency generation occurs is typically considered to be ~1 nm in depth so that interface-specific information can be obtained by detecting the sum frequency light. The incident angles and the polarization directions were ~50° and s for ω$_1$ and ~60° and p for ω$_2$, respectively. The s-polarized component of ω$_3$ was isolated using a Glan–Taylor prism, introduced into a polychromator, and detected using a charge-coupled device. For the VSFG spectroscopy with the heterodyne detection mode for the Eu-HDEHP study,[8] the ω$_1$ and ω$_2$ beams were focused into a thin y-cut quartz crystal (10-mm thickness) before the sample to generate sum frequency light (ω$_{LO}$). The ω$_{LO}$ light was passed through a glass plate to delay ω$_{LO}$ with respect to the ω$_1$ and ω$_2$ pulses, and the ω$_3$ and ω$_{LO}$ lights were introduced to a polychromator and detected by a CCD. The y-cut quartz crystal absorbs light of a wavenumber less than ~1300 cm^{-1}; thus, heterodyne detection cannot be performed in the i.e., region of the P=O stretch of TBP at approximately 1250 cm^{-1} in the current experimental setup; thus, the P=O stretch of TBP was

measured by homodyne detection. All VSFG measurements were performed immediately after place a sample solution on a container made of Teflon. The experimental room temperature was 19°C–22°C. The intensity of sum frequency light increases when the wavelength of the infrared light introduced onto an interface is resonant with the energy levels of the vibrational modes of the chemical species at the interface. Thus, vibrational spectra are obtained by monitoring the intensity of the sum frequency light as a function of the wavenumber of the infrared light (cm^{-1}) in VSFG spectroscopy.

3. Results and Discussion

Trivalent europium ion (Eu^{3+}) is extracted into an organic phase with the extractant of di-(2-ethylhexyl)phosphate (HDEHP), and Eu^{3+} is extracted as Eu(DEHP · HDEHP)$_3$ in an organic phase.[11] The HDEHP extractant dissolved in aqueous solutions spontaneously come to the surfaces of aqueous solutions and form air/aqueous-HDEHP interface; thus, the VSFG measurement was performed on the surface. Figure 2 shows the vibrational spectra of the air/aqueous-HDEHP interfaces observed by VSFG spectroscopy in the CH and OH stretch frequency region.[8] The vertical axis shows the imaginary part of second-order nonlinear susceptibility, Imχ$^{(2)}$, and was measured by heterodyne-detected VSFG spectroscopy.[12,13] The absolute value of Imχ$^{(2)}$ increases when the IR wavenumber is resonant with the energy levels of the chemical species at the interface, and the sign of Imχ$^{(2)}$ corresponds to the orientation of chemical species at the interface. The CH stretch bands of HDEHP at approximately 2900 cm^{-1} show the existence of HDEHP at the interface. When the europium ions are dissolved in the aqueous phase, a large change in the band of the OH stretching vibration of water (3000−3500 cm^{-1}) was observed. The positive band was observed at a concentration of 0 mM Eu^{3+}, and the negative band was observed at a concentration of 10 mM Eu^{3+}. This indicated that Eu^{3+} adsorbed on the interface and that the structure of water at the interface drastically changed upon Eu^{3+} adsorption. Furthermore, the positive and negative signs of Imχ$^{(2)}$ determine the orientation of the interfacial water.[14] Because the positive and negative signs of the OH stretching bands of water correspond to the OH-up and OH-down orientations of water, respectively, the water molecules at the interface were found to turn their OH groups downward when Eu^{3+} adsorbed to the interface, and the water molecules were bonded to Eu^{3+} using their oxygen atoms
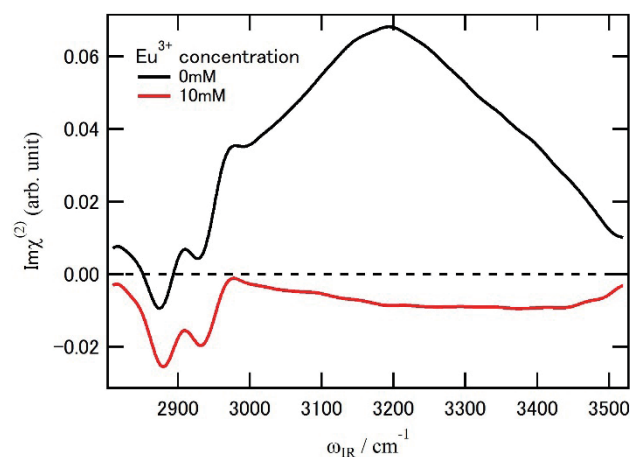
Figure 2. Vibrational spectra of the air/aqueous-HDEHP interfaces obtained by heterodyne-detected VSFG spectroscopy. The wavenumber region corresponds to that of CH and OH stretching vibrations. The concentration shown in the inset is the Eu^{3+} concentration in the aqueous solutions. This was reproduced from Ref. 8 with permission from the Royal Society of Chemistry.
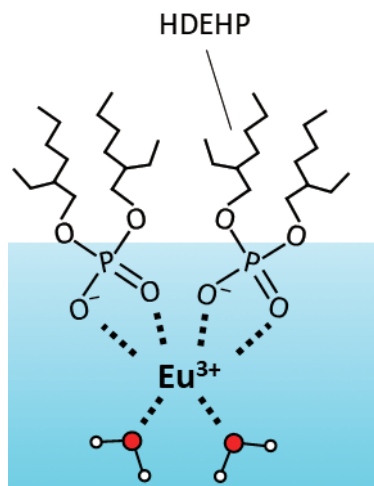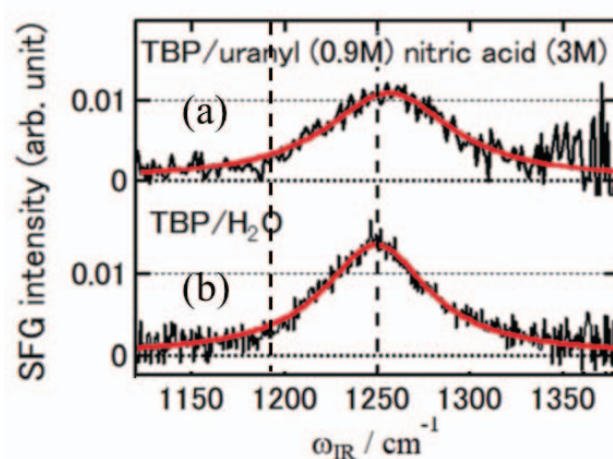
Figure 3. Structure of the Eu-HDEHP complex at the air/aqueous-HDEHP interface. This was reproduced from Ref. 8 with permission from the Royal Society of Chemistry.

Figure 4. Vibrational spectra of air/aqueous-TBP interfaces obtained by VSFG spectroscopy. The wavenumber region corresponds to the P=O stretching region of TBP. This was reproduced from Ref. 9 with permission from the Royal Society of Chemistry.

Figure 5. (a) Sketch showing uranyl nitrate not adsorbed to the air/aqueous-TBP interface and (b) Proposed model of the solvent extraction of uranium by TBP.

(Figure 3). From this result, we proposed that Eu^{3+} extraction into the organic phase occurred after the formation of the complex at the interface.
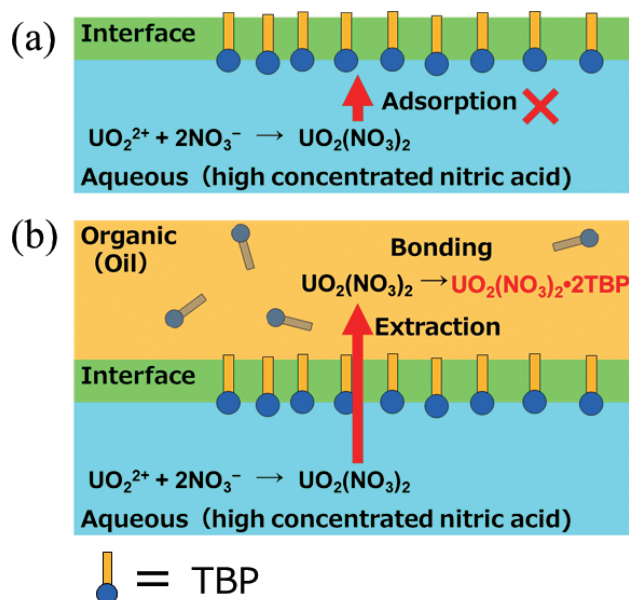
The extraction of uranyl ions by tributyl phosphate (TBP) is one of the most significant solvent extractions in the nuclear fuel cycle. TBP extractant dissolved in aqueous solution spontaneously comes to the surface of the aqueous solution and forms an air/aqueous-TBP interface, and a VSFG measurement was performed on this surface. In the aqueous phase of solvent extraction, uranyl ions exist as uranyl nitrate, $UO_2(NO_3)_2$, because of the high concentration of nitric acid. Some molecular dynamics simulation studies have suggested that many types of uranyl-TBP complexes, such as $UO_2(NO_3)_2(TBP)_2$, $UO_2(NO_3)_2(H_2O)(TBP)_2$, and $UO_2(NO_3)(TBP)_4$, are formed at the interface before extraction into the organic phase.[15-18] However, there have not been any experimental evidence of the complex formation at the interface. Figure 4 shows the vibrational spectra of the air/aqueous-TBP interface, and the bands observed are due to the P=O stretch of TBP,[9] indicating the existence of TBP at the interface. The wavenumber of P=O stretching is sensitive to whether the P=O group of TBP is bonded to uranyl; when TBP is bonded to uranyl, the band of the P=O group shifts from ~1250 cm^{-1} to ~1190 cm^{-1} [9,19], probably because of the weakening of the P=O bond upon complexation. However, at high concentrations of uranyl and nitric acid [Figure 4(a)], which is the condition that uranyl is well extracted into an organic phase, the P=O band was observed at ~1250 cm^{-1}, and the band position at ~1250 cm^{-1} was observed in the absence of uranyl and nitric acid [Figure 4(b)]. Therefore, uranyl was not adsorbed to the air/aqueous-TBP interface and did not form complexes with TBP at the interface [Figure 5(a)]. From the conclusion from Figure 5(a), as shown in Figure 5(b), it can be proposed that uranyl nitrate [$UO_2(NO_3)_2$] in the aqueous phase transfers into the organic phase without staying at the interface. After transfer into the organic phase, uranyl nitrate forms a complex with TBP, which is $UO_2(NO_3)_2 \cdot 2TBP$, and the extraction of uranium is completed.

4. Conclusions

VSFG spectroscopy has been applied to air/aqueous-extractant interfaces, where trivalent europium ions and uranyl ions are dissolved in the aqueous phase. At the air/aqueous-HDEHP interface, the Eu-HDEHP complex is formed at the interface, and Eu^{3+} is sandwiched between HDEHP and water molecules. Based on this result, it can be proposed that Eu^{3+} forms the Eu-HDEHP interfacial complex at the interface before phase transfer into the organic phase. On the other hand, uranyl nitrate is not adsorbed to the air/aqueous-TBP interface and does not form complexes with TBP at the interface. Thus, uranyl nitrate likely transfers into the organic phase without staying at the interface, and complex formation with TBP occurs in the organic phase. The two different results for europium and uranyl ions suggest that the extraction mechanism that occurs at the interface will depend on the type of solvent extraction. These studies demonstrate that VSFG spectroscopy is a powerful technique that can obtain unique information regarding the mechanism of solvent extractions of lanthanides and actinides. It is expected that lanthanide and actinide chemistry that occurs at many other interfaces will be revealed by VSFG spectroscopy.

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