

Short Communication

Raman Spectroscopic Study on NpO_2^+ - Ca^{2+} Interaction in Highly Concentrated Calcium Chloride

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Abstract

Coordination circumstance of neptunyl ion in concentrated CaCl_2 solutions was analyzed by Raman spectrometry. Besides the symmetric stretch (ν_1) mode of NpO_2^+ and NpO_2^{2+} , the asymmetric stretch (ν_3) mode of NpO_2^+ was found. The Raman intensity of the ν_3 mode increased with the concentration of CaCl_2 in the system. This would be attributable to the cation-cation interaction between Np(V) and Ca(II) .

Keywords

Raman spectrometry, neptunium, neptunyl, calcium chloride, cation-cation interaction

Introduction

The mutual coordination of actinyl ions especially in oxidation state (V) [1] is known as "cation-cation interaction (CCI)". The first evidence of CCI has been found in a complexation of Np(V)-U(VI) [1]. Following it, the CCIs of Np(V) with various cations in aqueous solutions have been found [2-17]. Multiply charged cations [2-8] or oxo-cations [1,9-17] contact with Np(V) dissolved in aqueous solutions as neptunyl ion, NpO_2^+ .

Absorption spectrophotometry is the possible analytical method for finding the CCI of Np(V) complexes [1-10,13-15,17]. This technique is effective for the systems containing Np(V) and cations with valence (III) or higher. As divalent cations, only CCIs of Np(V)-Hg(II) and Np(V)-Pb(II) are reported, in which the CCI was not clearly distinguished in absorption spectra [2]. To our knowledge, the CCI between Np(V) and divalent alkaline earth cations has not been found yet.

Another analytical method, Raman spectrometry, is effective for finding the CCI of Np(V) complexes via stretching vibrations of NpO_2^+ [9,12,13]. This method was applied for the pairs of actinyl cations, that is, $\text{NpO}_2^+ - \text{UO}_2^{2+}$, $\text{NpO}_2^+ - \text{NpO}_2^+$, and $\text{NpO}_2^+ - \text{NpO}_2^{2+}$.

Calcium chloride hexahydrate, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, possesses a low melting point, 303 K. The melt is identical with 6.9 mol dm⁻³ (M) and 9.6 mol kg⁻¹ (m) CaCl_2 aqueous solution. Cations, anions, and water molecules in molten hydrate salts, so-called hydrate melts, contact each other continuously by forming a quasi-lattice structure [18]. The coordination circumstance of solute ions dissolved in the media is different from that in water abundant systems, and hence chemical behavior of actinides in concentrated CaCl_2 systems is of interest [19,20]. In the present study, we investigated the stretching vibrations of NpO_2^+ in highly concentrated CaCl_2 solutions by Raman spectrometry.

The possibility of the CCI between Np(V) and Ca(II) is discussed.

Experimental

Calcium chloride dihydrate, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, of analytical grade (Wako Pure Chemical Industries, Ltd.) was used without purification. Weighed amounts of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and H_2O were mixed for preparing solutions with various concentrations of CaCl_2 . In order to analyze Np(VI) and Np(V) in the same sample, a nitric acid solution containing ^{237}Np was used as a starting material. A portion of the solution was once dried by heating, where the dried salt is a nitrate of Np(VI) and Np(V), and then the CaCl_2 solution prepared was added. The concentration of Np was 0.01 M. The sample volume prepared was 0.2 mL. The sample was taken in a quartz cell with 2 mm light path and the cell was sealed. Electronic absorption spectra of the samples were measured in the wavelength range from 340 to 1350 nm at 0.5 nm intervals by using an UV/Vis/NIR spectrophotometer (Shimadzu, UV-3100PC).

Raman spectra were measured by using a Raman spectrophotometer (NRS-3100, JASCO). A green laser with the wavelength of 531.9 nm was used at the output power of 57.6 mW. The measurement interval of a charge-coupled device (CCD) detector was set to be every 0.3 cm^{-1} . The operations of each 3-seconds measurement were accumulated by 300 times. The experimental temperature was 298 K.

It should be noted that the water activity in hydrate melts is extremely small [19], and the solubility of oxygen in the media is very low [21]. The redox reaction of solutes in the media is hence deeply suppressed [20]. The Raman spectra and absorption spectra of the sealed samples remained the same throughout the experiment. The molar ratio of Np(VI)/Np(V) in our system estimated by using molar absorptivities [22] was 3.

Results and discussion

The literature data of CCIs found for Np(V) are summarized in Table 1. It is clear that absorption spectrophotometry is a powerful tool for finding the CCI of Np(V). The absorption band of NpO_2^+ at *ca.* 980 nm is sensitive to the CCI, which results in a shoulder peak at higher wavelength of the absorption band. Clear increase of absorbance of the shoulder peak has been found for the complexation of NpO_2^+ with VO_2^+ [9], UO_2^{2+} [1,5,10,17], or NpO_2^{2+} [15]. For the CCIs between Np(V) and divalent cations (Hg^{2+} and Pb^{2+}), the two distinct absorption bands were not observed [2]. In the present CaCl_2 systems, no shoulder peak was found for the Np(V) absorption band, but a red shift from 985.2 nm to 987.6 nm was found with the increase of CaCl_2 concentration.

The Raman spectra obtained are shown in Fig. 1. Three Raman bands were found in the range of 680 to 900 cm^{-1} . Since it was confirmed by absorption spectrophotometry that the samples contain both Np(V) and Np(VI), these Raman bands are assigned to vibrational modes of NpO_2^+ and NpO_2^{2+} species. The Raman frequency of the symmetric stretch (ν_1) mode of hydrated NpO_2^+ is reported to be 766-767 cm^{-1} [9,12,23,24], while that of hydrated NpO_2^{2+} 854-863 cm^{-1} [23-25]. In Fig. 1, the Raman bands at 766-768 cm^{-1} and 835-839 cm^{-1} obtained are assigned to be ν_1 modes of hydrated neptunyl chlorides of Np(V) and Np(VI), respectively.

The complexation of Np(V) with trivalent metal cations via the oxo moiety of NpO_2^+ has been reported in a pioneering work of CCI [2]. The Raman intensity of the band at 802-805 cm^{-1} shown in Fig. 1 clearly increases with the concentration of CaCl_2 . This suggests that Ca^{2+} contacts with O of NpO_2^+ . It is of interest that, in Raman spectroscopic studies on CCI of Np(V)-V(IV) [9] and Np(V)-Np(V) [12,13], the ν_3 band of NpO_2^+ which is not Raman-active was observed. Similar phenomenon may

have occurred in the present study.

The symmetric stretch (ν_1) mode of linear $YXY-(D_{\infty h})$ type molecules is Raman-active while the asymmetric stretch (ν_3) mode of them is infrared-active (not Raman-active) [26]. The ν_3 mode turns to Raman-active for linear $YXZ-(C_{\infty v})$ type molecules [26]. NpO_2^+ possesses two $Np=O$ bonds. If the covalency of two $Np=O$ bonds and/or the apparent mass of two O atoms vary through the complexation of NpO_2^+ with Ca^{2+} , NpO_2^+ would act as a $YXZ-(C_{\infty v})$ type molecule. This means that the ν_3 mode appears in the Raman spectrum. The ν_3 frequency of NpO_2^+ found for the CCI of $Np(V)$ - $Np(V)$ is 37 cm^{-1} larger than its ν_1 frequency [12]. In the present study, the Raman band at $802\text{-}805\text{ cm}^{-1}$ is *ca.* 37 cm^{-1} larger than the ν_1 band of NpO_2^+ ($766\text{-}768\text{ cm}^{-1}$). The Np concentration of 0.01 M may be too small to found the CCIs of $Np(V)$ - $Np(V)$ [10-14] and/or $Np(V)$ - $Np(VI)$ [1,15,16]. The Raman band found at $802\text{-}805\text{ cm}^{-1}$ would hence be the ν_3 band of NpO_2^+ and the increase of its Raman intensity would be attributable to the complexation of $Np(V)$ with Ca^{2+} via the oxo moiety of NpO_2^+ .

Conclusions

A Raman band corresponding to the ν_3 mode of NpO_2^+ was found for the highly concentrated $CaCl_2$ system. This would be attributable to the complexation of $Np(V)$ with Ca^{2+} via the oxo moiety of NpO_2^+ . Absorption spectrophotometry is not effective for studying the $Np(V)$ - $Ca(II)$ interaction, while Raman spectrometry is useful to find the CCI.

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168 **Table 1** Cations for CCIs of Np(V) in aqueous solutions.

Valence	Cation	Medium	Analytical method ^a	Reference
(II)	Ca ²⁺	Chloride	Raman spectrometry	This study
	Hg ²⁺	Perchlorate	Absorption spectrophotometry	[2]
	Pb ²⁺	Perchlorate	Absorption spectrophotometry	[2]
(III)	Al ³⁺	Perchlorate	Absorption spectrophotometry	[2]
	Sc ³⁺	Perchlorate	Absorption spectrophotometry	[2]
	Cr ³⁺	Perchlorate	Absorption spectrophotometry	[2,3]
	Fe ³⁺	Perchlorate	Absorption spectrophotometry	[2,4,5]
	Ga ³⁺	Perchlorate	Absorption spectrophotometry	[2]
	Rh ³⁺	Perchlorate	Absorption spectrophotometry	[6]
			Infrared spectrometry	
	In ³⁺	Perchlorate	Absorption spectrophotometry	[2,7]
(IV)	BiO ⁺	Perchlorate	Absorption spectrophotometry	[2]
	VO ²⁺	Perchlorate	Absorption spectrophotometry	[9]
			Raman spectrometry	
	Th ⁴⁺	Perchlorate	Absorption spectrophotometry	[5,8]
(V)	NpO ₂ ⁺	Perchlorate	LIPAS	[8]
		Perchlorate	Absorption spectrophotometry	[10]
		Perchlorate	HEXS	[11]
		Perchlorate	Raman spectrometry	[12]
		Nitrate	Absorption spectrophotometry	[13,14]
		Nitrate	EXAFS	[14]
(VI)	UO ₂ ²⁺	Nitrate	Raman spectrometry	[13]
		Perchlorate	Absorption spectrophotometry	[1,5,10,15]
		Perchlorate	Potentiometric measurement	[1]
			Proton relaxation measurement	
		Perchlorate	LAXS	[16]
		Perchlorate	LIPAS	[8]
	NpO ₂ ²⁺	Perchlorate	Raman spectrometry	[12],
		Nitrate	Absorption spectrophotometry	[17]
			Microcalorimetry	
		Perchlorate	Absorption spectrophotometry	[1,15]
		Perchlorate	Potentiometric measurement	[1]
			Proton relaxation measurement	
		Perchlorate	LAXS	[16]

169 ^a EXAFS: Extended X-ray Absorption Fine Structure, HEXS: High-Energy X-ray Scattering, LAXS:
 170 Large-Angle X-ray Scattering, LIPAS: Laser -Induced PhotoAcoustic Spectroscopy.

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Figure Caption

Fig. 1 Raman spectra of 0.01 M Np in concentrated CaCl_2 solutions. Background spectrum was subtracted. Raman intensity was normalized by sum of peak areas.

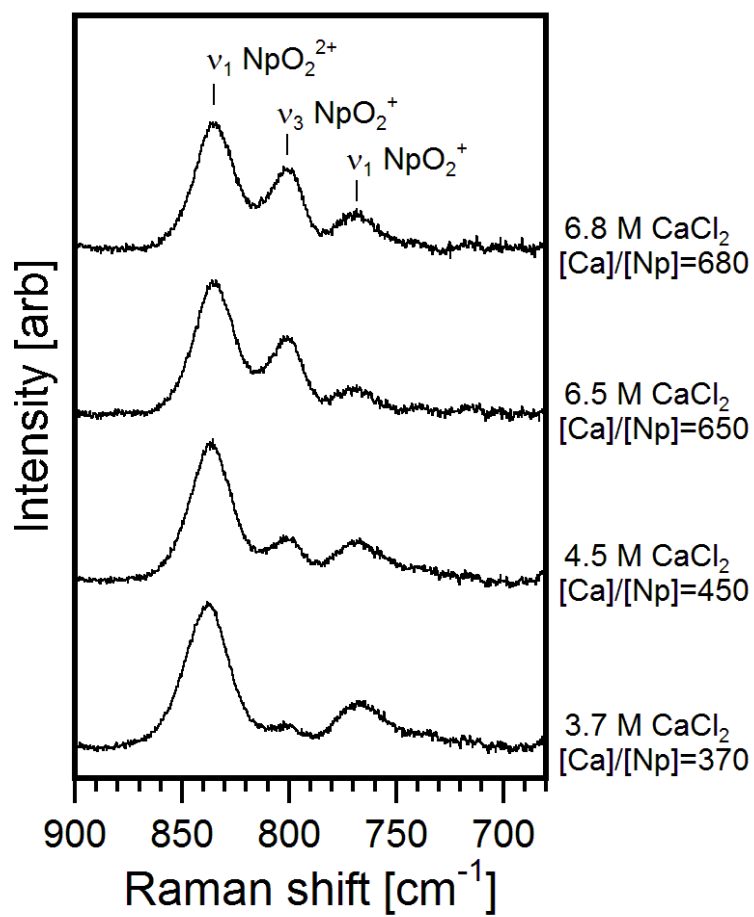


Fig. 1 (T. Fujii et al.)