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Cation-cation interaction between $\text{Np}^{\text{VO}_2^+}$ and Li^+ in a concentrated LiCl solution

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Coordination circumstance of neptunyl ion in concentrated LiCl, CsCl, CaCl₂, and BaCl₂ solutions was analyzed by Raman spectrometry. The symmetric stretch (ν_1) mode of $\text{Np}^{\text{VO}_2^+}$ and $\text{Np}^{\text{VI}}\text{O}_2^{2+}$, and the asymmetric stretch (ν_3) mode of $\text{Np}^{\text{VO}_2^+}$ were found. The high Raman intensity of the ν_3 mode found for the concentrated LiCl system demonstrated that the cation-cation interaction (CCI) between $\text{Np}^{\text{VO}_2^+}$ and Li^+ occurs. The CCI was found to be stronger for the solvent alkali and alkaline earth cations having larger polarizing power.

Keywords: Raman spectrometry; neptunium; neptunyl; alkali; alkaline earth; chloride; cation-cation interaction

1. Introduction

Hydrated neptunyl ions of Np(V) and Np(VI) in aqueous solutions are known to have a pentagonal-bipyramidal geometry of $\text{NpO}_2(\text{H}_2\text{O})_5^{n+}$ (n : 1 or 2) [1]. Two axial oxygen atoms (O_{ax}) bound to Np to form NpO_2^{n+} and five oxygen atoms (O_{eq}) of hydrated water molecules are arranged in the equatorial plane. Neptunyl ion of Np(V), $\text{Np}^{\text{VO}_2^+}$, is possible to contact with co-existed cations in solutions. The cation-cation interaction (CCI), which is a mutual coordination of actinyl ions, was firstly found in a complexation of Np(V)-U(VI) [2]. Following the finding, the CCIs between $\text{Np}^{\text{VO}_2^+}$ and various cations or oxo-cations have been investigated (see references in [3]). These counter cations are multiply charged cations of heavy elements, and the CCI between Np(V) and monovalent light cations has not been reported. In the present study, we report the CCI between Li^+ and $\text{Np}^{\text{VO}_2^+}$ in a concentrated LiCl solution.

2. Experimental

Alkali and alkaline earth chlorides of analytical grade (Wako Pure Chemical Industries, Ltd. and Aldrich-APL L.L.C.) were used without purification. Weighed amounts of the chlorides and H₂O were mixed for preparing concentrated chloride solutions (~saturation solutions). A nitric acid solution containing ²³⁷Np was used as a starting material. A portion of the solution was once dried by heating, then HCl was added and dried by

heating (repeated twice). The dried salt, which is a mixture of Np(VI) and Np(V) chlorides, was dissolved in 1 mol dm⁻³ (M) HCl or the concentrated alkali chloride and alkaline earth chloride solutions. The concentration of Np was 0.01 M. The sample volume prepared was 50 μL (~6 kBq). The sample was taken in a quartz cell with 2 mm light path and the cell was sealed. By sealing, the redox equilibrium of Np was maintained during Raman spectrometry.

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 100 times. The experimental temperature was 298 K.

3. Results and discussion

3.1. CCI between $\text{Np}^{\text{VO}_2^+}$ and Li^+

The Raman spectra obtained are shown in **Figure 1**. The result of CaCl₂ system agreed well with our previous results [3]. Three Raman bands were found in the range of 680 to 920 cm⁻¹. The Raman bands are assigned to the symmetric stretch (ν_1) mode of $\text{Np}^{\text{VO}_2^+}$ and $\text{Np}^{\text{VI}}\text{O}_2^{2+}$, and the asymmetric stretch (ν_3) mode of $\text{Np}^{\text{VO}_2^+}$ [3].

The asymmetric stretch (ν_3) mode of linear YXY-($\text{D}_{\infty h}$) type molecules is infrared-active (not Raman-active), but it turns to Raman-active for linear YXZ-($\text{C}_{\infty v}$) type molecules [5]. The covalency of two

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Np-O_{ax} bonds of $\text{Np}^{\text{V}}\text{O}_2^+$ varies through the complexation of $\text{Np}^{\text{V}}\text{O}_2^+$ with solvent cations. In other words, the apparent masses of two O atoms become different resulting the $\text{YXZ-(C}_{\infty\text{v}})$ type molecule of $\text{Np}^{\text{V}}\text{O}_2^+$ in the concentrated systems. This indicates that the ν_3 mode appears in the Raman spectrum. The CCIs of Np(V)-Np(V) and/or Np(V)-Np(VI) would not occur due to the small Np concentration of 0.01 M [3,5]. The increase of Raman intensity for the ν_3 band of $\text{Np}^{\text{V}}\text{O}_2^+$ is hence attributable to the complexation of Np(V) with A^+ and AE^{2+} (A: Li or Cs, AE: Ca or Ba) via the oxo moiety of $\text{Np}^{\text{V}}\text{O}_2^+$.

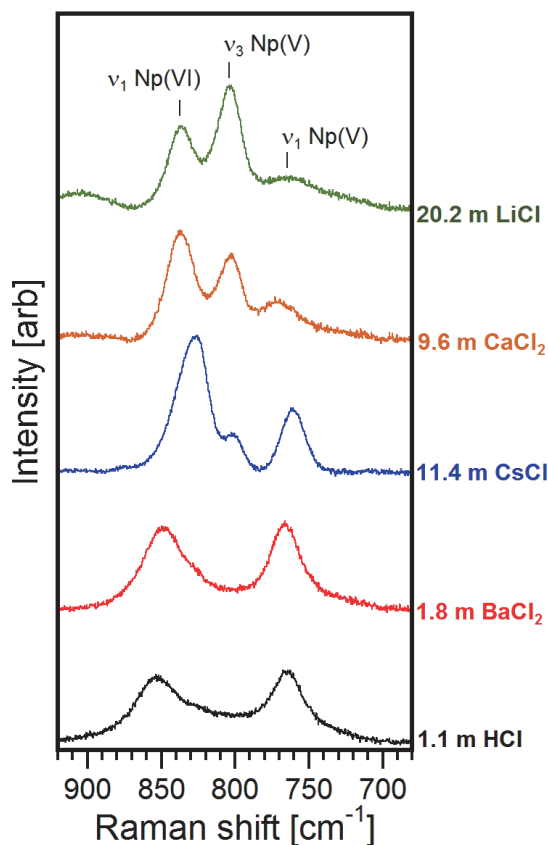


Figure 1. Raman spectra of 0.01 M Np in HCl and concentrated ACl and AECl_2 (A: Li or Cs, AE: Ca or Ba) solutions. Background spectrum was subtracted. Raman intensity was normalized by sum of peak areas. Molal concentrations (m : mol kg^{-1}) of ACl and AECl_2 are shown together.

Deconvolution analysis of the Raman spectra shown in Figure 1 was performed by fitting the Gaussian/Lorentzian sum function, and then, the ratio of Raman bands, ν_3/ν_1 , for $\text{Np}^{\text{V}}\text{O}_2^+$ were evaluated (Figure 2).

The CCI was found to be stronger for the solvent alkali and alkaline earth cations having larger polarizing power, Z/r^2 , where Z and r are valence and ionic radius, respectively. The high ν_3/ν_1 ratio of the concentrated LiCl system demonstrated that the CCI between $\text{Np}^{\text{V}}\text{O}_2^+$ and Li^+ occurs.

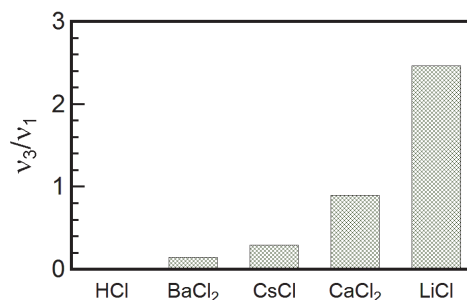


Figure 2. Intensity ratio of the Raman bands, ν_3/ν_1 , for $\text{Np}^{\text{V}}\text{O}_2^+$.

3.2. ν_1 shift of $\text{Np}^{\text{V}}\text{O}_2^+$ and $\text{Np}^{\text{VI}}\text{O}_2^{2+}$

The ν_1 shift of uranyl is known as a probe to understand the substitution reaction of ligands in the equatorial plane. In concentrated chloride systems, the ν_1 frequency decreases with the increase of Cl concentration [9]. This suggests that the bond strength of U-O_{ax} decreases via the substitution of water molecules in the equatorial plane by Cl^- ions. The same trend was found for $\text{Np}^{\text{VI}}\text{O}_2^{2+}$ [9]. It is of interest that the correlation could find in $\text{Np}^{\text{V}}\text{O}_2^+$.

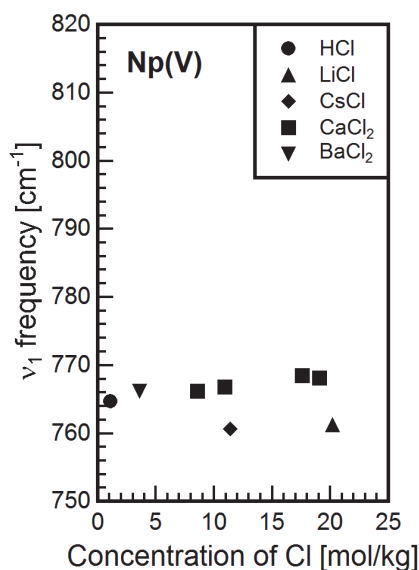


Figure 3. Raman shift of Np(V) complexes in chloride systems. ν_1 frequencies of $\text{Np}^{\text{V}}\text{O}_2^+$ are shown as functions of molal concentration of Cl in solvent alkali chlorides and alkaline earth chlorides. The data of concentrated CaCl_2 systems in our previous study [9] are shown together.

The ν_1 frequencies of $\text{Np}^{\text{V}}\text{O}_2^+$ are shown as functions of molal concentration of Cl in solvent ACl and AECl_2 (Figure 3). The ν_1 frequency of hydrated $\text{Np}^{\text{V}}\text{O}_2^+$, $\text{Np}^{\text{V}}\text{O}_2(\text{H}_2\text{O})_5^+$, has been reported to be 766–767 cm^{-1} [9 and references therein]. All the ν_1 frequencies of $\text{Np}^{\text{V}}\text{O}_2^+$ shown in Figure 3 showed similar values with a variety of $\sim 10 \text{ cm}^{-1}$. Though the formation constant of $\text{Np}^{\text{V}}\text{O}_2\text{Cl}^+$ is smaller than that of $\text{Np}^{\text{VI}}\text{O}_2\text{Cl}^+$ [10], in a recent study [11], the association of $\text{Np}^{\text{V}}\text{O}_2^+$ with Cl^- was found in a

concentrated NaCl-CaCl₂ system. In the same manner as our previous study [9], the ν_1 frequency change of Np^{VO}O₂ via the ligand exchange of H₂O by Cl⁻ was tested by using *ab initio* method. The association of Np^{VO}O₂⁺ with Cl⁻ depressed the ν_1 frequency of ~ 10 cm⁻¹. This magnitude of change was not distinguished in Fig. 3.

In **Figure 4**, the ν_1 frequencies of Np^{VI}O₂²⁺ are shown as functions of those of UO₂²⁺. Both the horizontal and vertical axes are scaled to be 40 cm⁻¹. It is clear that the ν_1 frequency of Np^{VI}O₂²⁺ varies widely about 30 cm⁻¹ and is proportional to that of UO₂²⁺. As well as the U(VI) case, the ν_1 shift of Np(VI) neptunyl is concluded to be a probe to understand the substitution reaction of ligands in the equatorial plane.

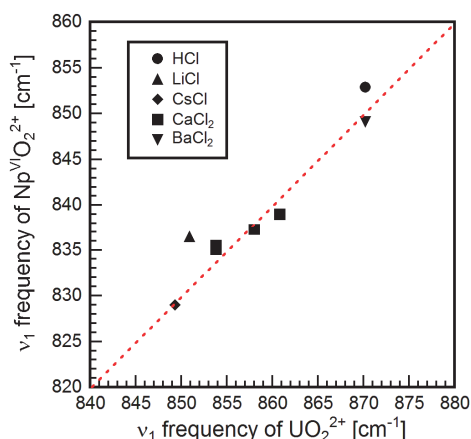


Figure 4. Correlation of ν_1 frequencies between Np^{VI}O₂²⁺ and UO₂²⁺. The ν_1 frequencies of UO₂²⁺ are reproduced from [9]. The data of concentrated CaCl₂ systems in our previous study [9] are shown together.

4. Conclusion

High Raman intensity of the ν_3 mode of Np^{VO}O₂⁺ was found for a concentrated LiCl system. This resulted from the CCI between Np^{VO}O₂⁺ and Li⁺ via the oxo moiety of Np^{VO}O₂⁺. The solvent alkali and alkaline earth cations having larger polarizing power induced the larger CCI. The ν_1 frequency of Np^{VI}O₂²⁺ decreased with the increase of Cl concentration of solvent, and was proportional to that of UO₂²⁺.

Acknowledgements

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