Cation-cation interaction between Np\(^{\text{V}}\)O\(_2^+\) and Li\(^+\) in a concentrated LiCl solution

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Coordination circumstance of neptunyl ion in concentrated LiCl, CsCl, CaCl\(_2\), and BaCl\(_2\) solutions was analyzed by Raman spectrometry. The symmetric stretch (\(\nu_1\)) mode of Np\(^{\text{V}}\)O\(_2^+\) and Np\(^{\text{V}}\)O\(_2^{2+}\), and the asymmetric stretch (\(\nu_3\)) mode of Np\(^{\text{V}}\)O\(_2^+\) were found. The high Raman intensity of the \(\nu_3\) mode found for the concentrated LiCl system demonstrated that the cation-cation interaction (CCI) between Np\(^{\text{V}}\)O\(_2^+\) 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 NpO\(_2\)(H\(_2\)O)\(_n^+\) (\(n\): 1 or 2) [1]. Two axial oxygen atoms (O\(_{ax}\)) bound to Np to form NpO\(_2^{2+}\) and five oxygen atoms (O\(_{eq}\)) of hydrated water molecules are arranged in the equatorial plane. Neptunyl ion of Np(V), Np\(^{\text{V}}\)O\(_2^+\), 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 Np\(^{\text{V}}\)O\(_2^+\) 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 Np\(^{\text{V}}\)O\(_2^+\) 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 H\(_2\)O were mixed for preparing concentrated chloride solutions (~saturation solutions). A nitric acid solution containing \(^{237}\)Np was used as a starting material. A portion of the solution was once 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 \(\mu\)L (~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 Np\(^{\text{V}}\)O\(_2^+\) and Li\(^+\)

The Raman spectra obtained are shown in Figure 1. The result of CaCl\(_2\) 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 (\(\nu_1\)) mode of Np\(^{\text{V}}\)O\(_2^+\) and Np\(^{\text{V}}\)O\(_2^{2+}\), and the asymmetric stretch (\(\nu_3\)) mode of Np\(^{\text{V}}\)O\(_2^+\) [3].

The asymmetric stretch (\(\nu_3\)) mode of linear YXY-(D\(_{\infty}\)) type molecules is infrared-active (not Raman-active), but it turns to Raman-active for linear YXZ-(C\(_{\infty}\)) type molecules [5]. The covalency of two
Np-O<sub>ax</sub> bonds of Np<sup>V</sup>O<sub>2</sub><sup>-</sup> varies through the complexation of Np<sup>V</sup>O<sub>2</sub><sup>-</sup> with solvent cations. In other words, the apparent masses of two O atoms become different resulting the YXZ-(C<sub>∞v</sub>) type molecule of Np<sup>V</sup>O<sub>2</sub><sup>-</sup> in the concentrated systems. This indicates that the v<sub>3</sub> 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 v<sub>3</sub> band of Np<sup>V</sup>O<sub>2</sub><sup>-</sup> is hence attributable to the complexation of Np(V) with A<sup>+</sup> and AE<sup>2+</sup> (A: Li or Cs, AE: Ca or Ba) via the oxo moiety of Np<sup>V</sup>O<sub>2</sub><sup>-</sup>.

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, v<sub>3</sub>/v<sub>1</sub>, for Np<sup>V</sup>O<sub>2</sub><sup>-</sup> 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<sup>2</sup>, where Z and r are valence and ionic radius, respectively. The high v<sub>3</sub>/v<sub>1</sub> ratio of the concentrated LiCl system demonstrated that the CCI between Np<sup>V</sup>O<sub>2</sub><sup>-</sup> and Li<sup>+</sup> occurs.

### 3.2. v<sub>1</sub> shift of Np<sup>V</sup>O<sub>2</sub><sup>-</sup> and Np<sup>IV</sup>O<sub>2</sub><sup>2+</sup>

The v<sub>1</sub> shift of uranyl is known as a probe to understand the substitution reaction of ligands in the equatorial plane. In concentrated chloride systems, the v<sub>1</sub> frequency decreases with the increase of Cl concentration [9]. This suggests that the bond strength of U-O<sub>ax</sub> decreases via the substitution of water molecules in the equatorial plane by Cl<sup>-</sup> ions. The same trend was found for Np<sup>IV</sup>O<sub>2</sub><sup>2+</sup> [9]. It is of interest that the correlation could find in Np<sup>V</sup>O<sub>2</sub><sup>-</sup>.

The v<sub>1</sub> frequencies of Np<sup>V</sup>O<sub>2</sub><sup>-</sup> are shown as functions of molal concentration of Cl in solvent alkali chlorides and alkaline earth chlorides. The data of concentrated CaCl<sub>2</sub> systems in our previous study [9] are shown together.

The v<sub>1</sub> frequencies of Np<sup>V</sup>O<sub>2</sub><sup>-</sup> are shown as functions of molal concentration of Cl in solvent ACI and AECl<sub>2</sub> (Figure 3). The v<sub>1</sub> frequency of hydrated Np<sup>V</sup>O<sub>2</sub><sup>-</sup>, Np<sup>V</sup>O<sub>2</sub>(H<sub>2</sub>O)<sub>5</sub>, has been reported to be 766-767 cm<sup>-1</sup> [9 and references therein]. All the v<sub>1</sub> frequencies of Np<sup>V</sup>O<sub>2</sub><sup>-</sup> shown in Figure 3 showed similar values with a variety of ~10 cm<sup>-1</sup>. Though the formation constant of Np<sup>V</sup>O<sub>2</sub>Cl is smaller than that of Np<sup>IV</sup>O<sub>2</sub>Cl<sup>-</sup> [10], in a recent study [11], the association of Np<sup>V</sup>O<sub>2</sub><sup>-</sup> with Cl<sup>-</sup> was found in a
concentrated NaCl-CaCl₂ system. In the same manner as our previous study [9], the v₁ frequency change of Np⁶⁺O₄⁺ via the ligand exchange of H₂O by Cl⁻ was tested by using ab initio method. The association of Np⁵⁺O₅⁻ with Cl⁻ depressed the v₁ frequency of ~10 cm⁻¹. This magnitude of change was not distinguished in Fig. 3.

In Figure 4, the v₁ frequencies of Np⁶⁺O₅⁺²⁺ 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 v₁ frequency of Np⁵⁺O₅⁺²⁺ varies widely about 30 cm⁻¹ and is proportional to that of UO₂²⁺. As well as the U(VI) case, the v₁ shift of Np(VI) neptunyl is concluded to be a probe to understand the substitution reaction of ligands in the equatorial plane.

### 4. Conclusion

High Raman intensity of the v₃ mode of Np⁶⁺O₄⁺ was found for a concentrated LiCl system. This resulted from the CCI between Np⁶⁺O₄⁺ and Li⁺ via the oxo moiety of Np⁵⁺O₅⁻. The solvent alkali and alkaline earth cations having larger polarizing power induced the larger CCI. The v₁ frequency of Np⁵⁺O₅⁺²⁺ decreased with the increase of Cl concentration of solvent, and was proportional to that of UO₂²⁺.

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