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Np(V) complexation with carbonate in aqueous solutions studied by spectrophotometric titration at various temperatures

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The complexation of neptunium (V) with carbonate has been studied at temperatures from 10 to 70°C in 0.1 M $LiClO_4$ by spectrophotometry. Three NpO_2^+-CO_3^{2-} complex species, $NpO_2(CO_3)_n^{(2n-1)-}$ (n = 1, 2, 3), are identified and the stability constants are calculated by using the absorption spectra in Near-IR region collected from titrations at varying temperatures. The enthalpies and entropies are calculated with van't Hoff equations in the temperature range of 10 to 70°C, indicating the formation of all NpO_2^+-CO_3^{2-} complexes are mainly entropy driven. The structures of the NpO_2^+-CO_3^{2-} complex species in aqueous solutions are also reviewed. Based on the molar absorptivity of Np(V) in Near-IR region the structure of $NpO_2(CO_3)_2^{3-}$ is re-constructed as $NpO_2(CO_3)_2(H_2O)^{3-}$of low symmetry but not as $NpO_2(CO_3)_2(H_2O)_2^{3-}$of high symmetry suggested in a previous study.

Introduction

The migration and geochemical behaviour of actinide ions in aquatic systems is mainly determined by the physicochemical properties of complexes formed with naturally occurring ligands including dissolved small ligands and fixed bonding sites on the surface of soil and minerals. As the most stable pentavalent ion in the actinide series, Np(V) existing as NpO_2^+ in aqueous solutions, is of particular interest. Because of its low tendency toward hydrolysis and its weak sorption on natural minerals, Np(V) might migrate to the far-field in the event of accidental release during the spent fuel reprocessing and transient storage of high level waste, and in the surrounding environments of nuclear waste repository.[1,2] Indeed, in aqueous solutions equilibrated with atmosphere, unlike actinide ions other than pentavalent trans-dioxo cations, the speciation and chemical behaviour of Np(V) is mainly governed by the carbonate complexation but not hydrolysis, the predominant solution species have been found to be $NpO_2(CO_3)_n^{(2n-1)-}$ (n = 1, 2, 3) which correlate nicely with the known solid phase salts $MNpO_2(CO_3)$, $M_3NpO_2(CO_3)_2$, and $M_5NpO_2(CO_3)_5$ (M = monovalent cation).[3-10] The formation stability constants for these species in solutions of varying ionic strength have been determined by a number of researchers using a variety of methods.[4,5,8,9] The values of the stability constants for the first two complex anions are reasonably well understood, while those for $NpO_2(CO_3)_3^{5-}$ are more scattered. These measured stability constants have been evaluated and some have been used by the U.S. Nuclear Regulatory Commission (NRC) Surface Complexation Models (SCMs) to simulate the migration of neptunium (V).[11]

However, to predict the migration of radionuclides at temperatures other than around 25°C requires the thermodynamic parameters under corresponding conditions. For instance, the post-closure chemical environment in the proposed underground Yucca Mountain geological repository is expected to be at near neutral pH, slightly oxidizing, and at elevated temperatures.[12] In previous studies,[4-10] the stability constants of Np(V)-cabonate complexes are reported most at or near 25 °C. In contrast, data on the complexation of Np(V) with carbonate at elevated temperatures are scarce, and there is no study where the temperature effect on the complexation has been evaluated to be reliable. The lack of stability constants at elevated temperatures and enthalpy data makes it difficult to predict the migration behavior of Np(V) in the environment of the repository at elevated temperatures.

In addition, in previous studies the stability constants of Np(V)-carbonate complexes were mostly determined by solubility measurement, due to the limited solubility (10^{-4}-10^{-7} M) of these $M_{2n-1}NpO_2(CO_3)_n$ (n = 1, 2, or 3) solid phases. There are few studies in which other methods, such as solvent-solvent extraction[9] and CE-ICP-SFMS, were used.[13] The reported stability constants in these studies for $NpO_2(CO_3)^-$ and $NpO_2(CO_3)_2^{3-}$ are in good agreement, while the values for $NpO_2(CO_3)_3^{5-}$ are very scattered even though the different ionic strength is taken into account.

It has been found that spectrophotometric titration is a powerful technique for thermodynamically and structurally investigating the complexation of Np(V) with a variety of ligands. For the complexation of Np(V) with carbonate, to overcome the problems caused by the limited solubility of the complexes, synthesis employing different counterion was used to separately provide 10^{-3} M solutions of $NpO_2(CO_3)^-$ and

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$NpO_2(CO_3)_2^{3-}$ in tetrabutylammonium (TBA) carbonate electrolyte solutions, and $NpO_2(CO_3)_3^{5-}$ in sodium carbonate/perchlorate solutions. These solutions of relatively high concentration provided great opportunity to investigate the molecular structures of these environmentally important complex species with EXAFS spectroscopy and to precisely measure the UV-Vis-near IR absorption spectra of $NpO_2(CO_3)^-$, $NpO_2(CO_3)_2^{3-}$, and $NpO_2(CO_3)_3^{5-}$ in aqueous solutions.[14]

To provide reliable thermodynamic data and structural information on the complexation of Np(V) with carbonate at elevated temperatures, we have studied the complexation of Np(V) with carbonate at varying temperatures by spectrophotometry. We find that solution employing lithium cation provides up to 2×10^{-4} M solutions of all three Np(V)-carbonate complexes. The relatively high concentrations are unprecedented and afford the opportunity to determine the stability constants by spectrophotometric titration, and to get insight the structure of the complexes by interpreting the change in absorption originating from the f-f transitions of Np(V) during the titrations. Stability constants of Np(V)-carbonate complexes at 10 to, 40, 55, and 70 °C are determined by spectrophotometry, and the average enthalpies of complexation are calculated by vant Hoff's equation. More important, the structures of the Np(V)-carbonate complexes are reviewed based on the relationship between the geometry of the Np(V) complex and the optical absorption in UV/Vis/NIR region originated from the f-f transition of Np(V).

Experimental

Chemicals and Preparation of Np(V) Samples

All chemicals were reagent grade or higher. Deionized and boiled water was used in the preparations of all the solutions. The ionic strength of all the solutions used in the experiments was adjusted to 0.1 mol/L at 25 °C by adding appropriate amounts of lithium perchlorate, the error caused by adding Li_2CO_3 during the titrations were ignored.

The stock solution of Np(V) in perchloric acid was prepared as following. Solid neptunium dioxide (NpO_2) was dissolved in concentrated $HClO_4$ with a few drops of concentrated HCl under low heating. After dissolution, the excess $HClO_4$ and the small amount of HCl were driven away by fuming the solution, and the neptunium in the solution was oxidized to Np(VI) during fuming, resulting in a pink solution. Into the pink solution of Np(VI), a small amount of $NaNO_2$ was added to reduce Np(VI) to Np(V), giving a green solution. The Np(V) was then precipitated as hydroxide with 1 M NaOH. The precipitates were washed three times with d deionized/istilled water to ensure the removal of excess NaOH, and dissolved with appropriate amount of 1 M $HClO_4$, then the pH value was adjusted to about pH 3 with 1.00 mmol/L LiOH. Absorption spectra were collected to confirm that Np(V) was the only oxidation state in the stock solution. The concentration of Np(V) was determined by the absorbance at 980.2 nm with molar absorptivity (ε) of 395 $cm^{-1}M^{-1}$. The free acid in the Np(V) stock solution was determined with Gran titration.

Absorption Spectra

The absorption spectra of Np(V) in solutions titrated with CO_3^{2-} solution at different temperatures were collected on a Cary6000i spectrometer in the wavelength region between 900 to 1150 nm with 0.05 nm interval and 0.2 nm spectral band width (SBW). Quartz cells of 10 mm path length were used. The temperature of the sample was controlled within ± 0.2 °C with a temperature controller. The stability constant of the Np(V)-carbonate complexes (on the molarity scale) was calculated by nonlinear least-squares regression using the HypSpec program.

Results and discussion

Stability Constants at Varying Temperatures

Figure 1 shows representative sets of absorption spectra for the titrations of Np(V) with carbonate at 10 and 70 °C. For the first several additions of carbonate solution into NpO_2^+ solution, the intensity of the absorption band at 980.2 nm that belongs to the free NpO_2^+ cation decreased and a new band appeared at 991 nm, which corresponds to the formation of $NpO_2(CO_3)^-$. As the concentration of carbonate was further increased, the intensities at 991 nm decreased and another new absorption peak appeared at 998 nm as a shoulder at longer wavelength side which is ascribed to the formation of the second complex species, $NpO_2(CO_3)_2^{3-}$. With more additions of carbonate solution, the new peak at 998 nm for $NpO_2(CO_3)_2^{3-}$ reached the highest intensity and then decreased, but no new peak appeared at longer wavelength which could be attributed to the formation of $NpO_2(CO_3)_3^{5-}$. Apparently, the patterns of the changes in the spectra for the successive formation of the three complexes are different. For the first two complexes, the formation is indicated by the decrease of the absorbance of the preceding species accompanied by the appearance of new absorption band of successive complexes at longer wavelengths. In contrast, for the third complex $NpO_2(CO_3)_3^{5-}$, its formation is indicated just by the decrease of the absorbance of $NpO_2(CO_3)_2^{3-}$ but not accompanied by the appearance of an new absorption band.

These observation about the change in the spectra during the titration is consistent with the results in previous work in which the spectra of the three Np(V)/carbonate complexes were separately collected from different media.[14]

NpO_2^+ has linear structure as well as other actinyls, and all of its low-lying electron states have same parity. The dominated absorption band of NpO_2^+ at 980 nm and other bands in UV/Vis/NIR region in aqueous solution originate from $5f\rightarrow5f$ transitions, which are allowed because there are 5 H_2O molecules equatorially coordinated to NpO_2^+ breaking the inversion symmetry of isolated NpO_2^+. In theory, rebuilding the inversion symmetry in complexes of NpO_2^+ will forbid the $5f\rightarrow5f$ transitions, hence the absorption bands cannot be observed.

Due to the high symmetry of $NpO_2(CO_3)_3^{5-}$, in the first coordination sphere Np(V) sits at the invention center surrounded by eight oxygen atoms, two from neptunyl itself

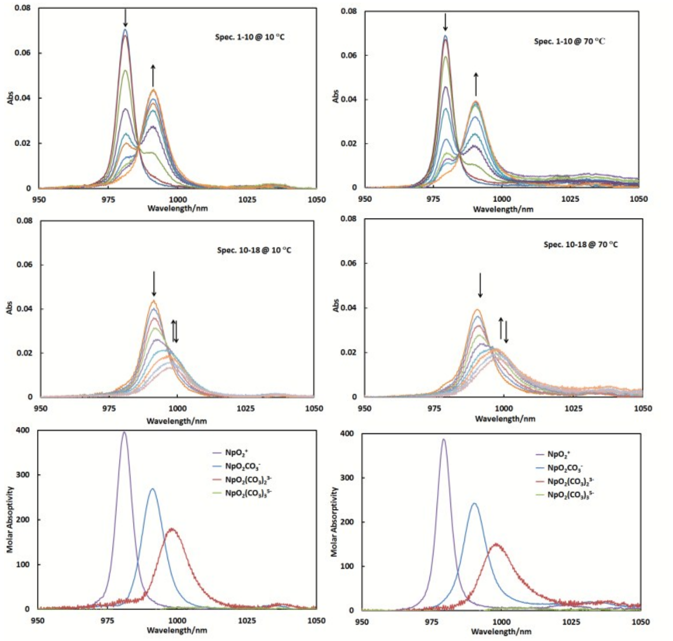

Figure 1 Representative spectrophotometric titration of Np(V)-CO_3^{2-} complexation. Upper: spectra collected during a titration (normalized) at 10 °C and 70 °C; Lower: molar absorption spectra from deconvolution. Starting solution: 0.1 M $LiClO_4$ at pH 3, V = 1.000 mL, $C_{Np(V)}$ = 0.178 mM; titrant solution: 0.100 M Li_2CO_3.

and six in the equatorial plane from three carbonate anions, so that the f-f transitions of Np(V) are almost completely forbidden and no absorption band is observed corresponding to the band of NpO_2^+ ion at 980 nm region.

With the assumption of three complex species formed during the titrations, the formation constants are determined from the spectra using HypSpec program. The calculation is performed with the set-up of the 1:3 species having the absorption band related to the band of NpO_2^+ at 980.2 nm, even though the factor analysis by the HypSpec program indicated that there are only three Np(V) species of strong absorption.[18] The spectra are best-fit with the formation of NpO_2^+-CO_3^{2-} complexes as described by equation (1), and there is no clear evidence of forming complexes containing OH^- and HCO_3^-.

$$NpO_2^+ + n\,CO_3^{2-} = NpO_2(CO_3)_n^{(2n-1)-} \qquad (n = 1, 2, 3) \qquad (1)$$

The calculated molar absorbance of the species is depicted in Figure 1. The calculation produces a very weak molar absorbance for the 1:3 species $NpO_2(CO_3)_3^{5-}$, which could be ignored in comparison with the relatively strong absorption of the other two complexes and the free NpO_2^+ ion. These results suggested that the 1:3 species has no or very weak absorption relative to that of NpO_2^+ at 980.2 nm.

The stability constants of Np(V)-CO_3^{2-} complexes at 10, 25, 40, 55, and 70°C are calculated and listed in Table 1. Literature values at different ionic strengths at around 25°C are provided for comparison in Table S1. The variation of the spectra in Figure 1 and the calculated stability constants in Table 1 indicate that the complexation of Np(V) with carbonate is fairly strong, and it is minimally affected by temperature from 10 to 70°C. Compared with the stability constants in previous studies, the value we measured for the 1:1 complex is in fair agreement, while the values for the 1:2 and 1:3 complexes are much smaller. The significant difference between our results and those in previous studies might come from the limitation of the solubility measurement methods. The solubility of the solid complexes used in previous studies might change with the surface morphology of the solids, and it might take very long time to reach the equilibria.[5,8,10,16,17] These factors might be the reason that the values for the stability constants of the 1:2 and 1:3 complexes in literature are scattered.

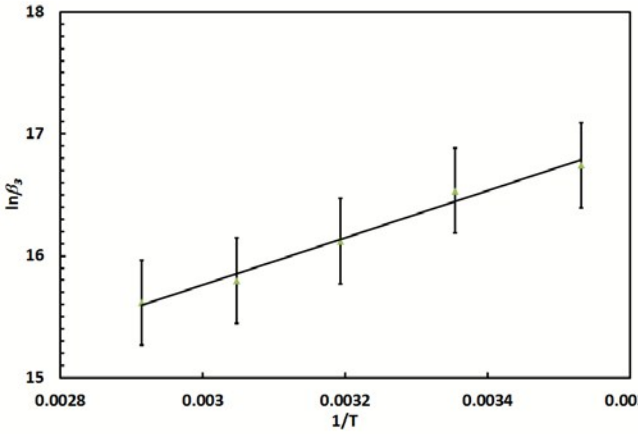

Figure 2 Plots of lnβ_3 vs. 1/T for Np(V)-carbonate complexation in 0.1 M $LiClO_4$.

To quantitatively evaluate the effect of temperature on the complexation of Np(V) with carbonate, the logβ vs. 1/T are plotted in Figure 2 and Figure 1S (van’t Hoff plot). The excellent linearity of the van’t Hoff plots indicates the enthalpy of the complexation is nearly constant in the temperature range (10-70°C). From the linear fit of the plots, the enthalpies for the reaction described in equation (1) in 0.1 M $LiClO_4$ in the temperature rand of 10 - 70 °C are calculated to be -10.2 ± 1.5, 0.4 ± 1.7, -16.1 ± 2.0 kJ/mol, respectively for the three complexes. The temperature effect and the enthalpies for the complexation Np(V) with carbonate illustrate that the complexation is mainly entropy-driven.

To convert the stability constants measured at 0.1 M ionic strength to the values at the standard state preferred by common compilations of thermodynamic data, the specific ion interaction (SIT) approach has been used to calculate the formation constants at zero ionic strength. The detailed approaches and procedures are described elsewhere and the formation constants in molarity (logβ) are adopted in molality (logβ_m) without further correction.[19] Because there are no values available for the ion interaction coefficients ε(Li^+, $NpO_2(CO_3)^{(2n-1)-}$, n= 1, 2, 3)($kg{\cdot}mol^{-1}$) for the three NpO_2^+-CO_3^{2-} complex anions with Li^+, the values for the complexes with Na^+ are used instead.

Re-visiting the structures of Np(V)-CO_3^{2-} complexes

The spectrophotometric titrations of NpO_2^+ with ligands not only provide information for determining thermodynamic data, but also can reveal structural character details of the complexes, especially while complexes with an inversion center are involved during the titration.

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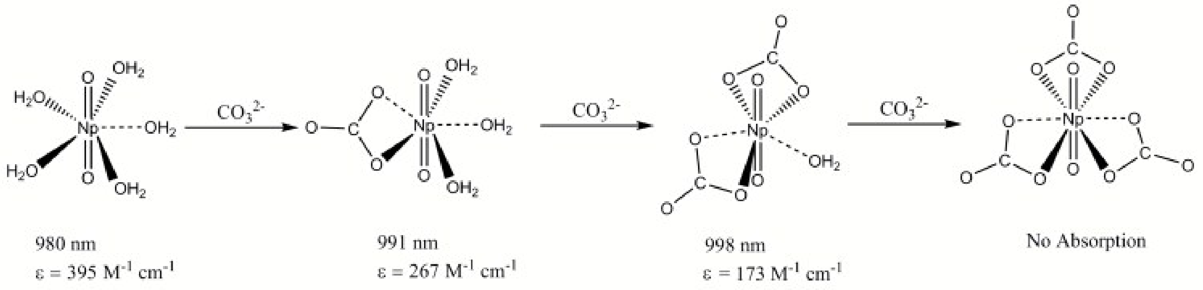

Scheme 1. Successive complexation of $[NpO_2(H_2O)_5]^+$ with carbonate and the corresponding changes in symmetry and absorption band.

In their pioneering work, D. Clark and the co-authors proposed the structures for those three Np(V)-CO_3^{2-} complexes based on the information from EXAFS study.[14] The well-defined Np-C distances 2.93-2.98 Å in those three complexes indicate the bidentate carbonate ligation. With two O per bidentate carbonate ligand, the remainder of O atoms in the equatorial plane of NpO_2^+ are ascribed to H_2O molecules, yielding their proposed molecular structures. The change in coordination number of five in the equatorial plane in the 1:1 complex to six in the 1:2 and 1:3 complexes seems to be reasonable, and has been accepted in late studies as model, especially in computation studies.[20, 21]

However, our results of spectrophotometric titrations depict the clear absorption band at 998nm for the 1:2 complex $NpO_2(CO_3)^{3-}$. This raises question about the structure of the complex. If the structure of the complex was as the proposed one, Np(V) should be sitting at an inversion center, then there should be no absorption, due to the forbidden f-f transitions. The clear absorption band of $NpO_2(CO_3)_2^{3-}$ suggests that there might not be two but only one water molecule in the equatorial plane of $NpO_2^+$with two bidentate carbonate anions and the absorption and the structures of the complexes can be illustrated as in Scheme 1. Indeed, the proposed structure for the 1:3 complex is confirmed by our results. All the three carbonate anions coordinating to the central NpO_2^+ as bidentate provide six O in the first coordination shell in the equatorial plane, giving a centroinversional geometry in which the f-f transitions are forbidden and no corresponding absorption are observed.

Table 1 Stability constants of Np(V) complexation with carbonate at different temperatures.

Reaction	T/°C	Ionic medium	log β	log β_m^0	ΔH kJ·mol-1	ΔS J·K-1·mol-1
$NpO_2^+ + CO_3^{2-} = NpO_2(CO_3)^-$	10	0.1 M $LiClO_4$	4.28 ± 0.12	4.67 ± 0.26	-8.6 ± 1.5	58.6 ± 5.0
	25	0.1 M $LiClO_4$	4.17 ± 0.12	4.57 ± 0.26		
	40	0.1 M $LiClO_4$	4.06 ± 0.15	4.48 ± 0.27		
	55	0.1 M $LiClO_4$	4.01 ± 0.15	4.44 ± 0.28		
	70	0.1 M $LiClO_4$	3.95 ± 0.18	4.40 ± 0.30		
$NpO_2^+ + 2CO_3^{2-} = NpO_2(CO_3)_2^{3-}$	10	0.1 M $LiClO_4$	6.09 ± 0.15	6.04 ± 0.28	0.3 ± 1.7	117 ± 7.0
	25	0.1 M $LiClO_4$	6.12 ± 0.18	6.06 ± 0.30		
	40	0.1 M $LiClO_4$	6.10 ± 0.18	6.05 ± 0.31		
	55	0.1 M $LiClO_4$	6.11 ± 0.18	6.05 ± 0.31		
	70	0.1 M $LiClO_4$	6.11 ± 0.15	6.06 ± 0.31		
$NpO_2^+ + 3CO_3^{2-} = NpO_2(CO_3)_5^{5-}$	10	0.1 M $LiClO_4$	7.27 ± 0.21	5.92 ± 0.31	-21.0 ± 2.0	40.6 ± 9.7
	25	0.1 M $LiClO_4$	7.18 ± 0.24	5.80 ± 0.35		
	40	0.1 M $LiClO_4$	7.01 ± 0.27	5.58 ± 0.36		
	55	0.1 M $LiClO_4$	6.86 ± 0.27	5.40 ± 0.35		
	70	0.1 M $LiClO_4$	6.78 ± 0.33	5.27 ± 0.41		

Ionic strength: 0.1 M $LiClO_4$

Conclusions

The complexation of NpO_2^+ with carbonate has been investigated in aqueous systems for several decades, and this work presents the first study at varying temperatures to evaluate the temperature effect. The negative values and the very small positive value of the enthalpies for the formation of the Np(V)-carbonate complexes indicate the complexation is mainly entropy-driven. The thermodynamic information reported here may enable more accurate modeling of neptunyl(V) carbonate reactivity on the surface of minerals and the migration of Np(V) in the environment. The additional structural information provides structural models with which to evaluate the application of the emerging computation method to actinide chemistry research.

These findings suggest that the spectrophotometric titration method may be very useful in the study of Np(V) complexes of low solubility.

Acknowledgements

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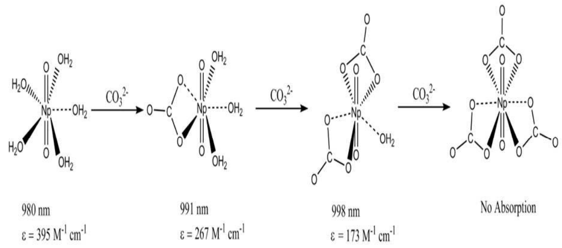

NpO_2^+ can form carbonate complexes, the first two complexes absorb in UV/Vis/NIR region but the third is ‘silent’ due to its high symmetry.