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Notes

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Hydrolysis and Carbonate Complexation of Dioxoneptunium(V) in 1.0 M $NaClO_4$ at 25 °C

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Knowledge about the behavior of the actinides in aqueous media of compositions similar to those of groundwaters is required in order to model the transport characteristics of these elements in the geosphere. Neptunium is an element of particular concern because of its relatively long decay period and relative abundance in nuclear waste. The most probable oxidation state for this element in a natural environment is V,[1] which in this case takes the form of the singly charged neptunyl ion, NpO_2^+. The relatively low charge and polarizing power of this ion lead to the prediction that it would form weak complexes. This prediction is borne out by examining the limited data base of stability constants of complexes of the species with a variety of ligands.[2] Particularly lacking in the literature is reliable information on the complexation of NpO_2^+ by hydroxyl or carbonate ions. An estimate of $-\log Q_H = 8.85$ for the first hydrolysis constant of NpO_2^+ was obtained by Kraus and Nelson[3] from potentiometric titrations in 0.1 M Cl^- media. Evidence of carbonate complexation of NpO_2^+ was observed in studies[4,5] of the solubility behavior of neptunyl carbonate solids in carbonate media. However, the ionic strength was not controlled and no reliable data are obtained.

The present work was aimed at obtaining data on the hydrolysis and carbonate complexation of NpO_2^+ which in turn could be used to establish speciation schemes of this ion under conditions similar to those found in nature.

The experimental approach chosen was based on the determination of neptunium solubility of a well-defined solid phase as a function of carbonate concentration in a medium of constant ionic strength.

Experimental Section

Stock Solutions. A Np(V) stock solution, 0.0655 M, was prepared from high-purity NpO_2 supplied by the Isotopes Sales Division of the Oak Ridge National Laboratory. The solid NpO_2 was dissolved by prolonged treatment with hot concentrated HNO_3 and evaporation to dryness. This procedure was repeated twice, and the residue was dissolved in concentrated $HClO_4$. The solution was evaporated to dryness and the residue dissolved in water and then treated with a 0.1 M $NaNO_2$ solution. This last treatment converts pink Np(VI) into emerald green Np(V). The Np(V) solution was treated with 1.0 M NaOH to produce a greenish gray precipitate of NpO_2OH. The solid was washed a few times with water and treated with the stoichiometric amount of 0.1 M $HClO_4$. The Np concentration of this solution was determined by radiometric means and this concentration then confirmed by coulometric means. The latter procedure also showed the absence of Np(VI) in the solution.

A sodium carbonate solution, 0.0970 M, was prepared from reagent grade Na_2CO_3. The ionic strength of this solution was adjusted to 1.0 M by addition of the appropriate amount of $NaClO_4$.

Solid-Phase $NaNpO_2CO_3 \cdot 3.5H_2O$. This crystalline compound was prepared in situ in a series of centrifuge tubes by addition of Na_2CO_3 in a 1:1 mole ratio to a NpO_2^+ solution. The gelatinous precipitate initially formed was aged at 25 °C for 8 days with slow stirring in the presence of excess Na_2CO_3 (0.025 M). This treatment produced a crystalline solid that settled by gravity within a few minutes. The settling time was comparable, under the same conditions, to that of a suspension of well-characterized $UO_3 \cdot 2H_2O$ having a particle size of ≥ 2 μm. This rough test suggests that the particle size of the neptunium compound might be in the same size range.

In an independent test the NpO_2^+/CO_3^{2-} mole ratio in the solid was established by following the neptunium concentration remaining in solution as substoichiometric amounts of carbonate were introduced in a stepwise manner. A plot of [Np] vs. $[CO_3^{2-}]$ produced a straight line with a slope of −1.026, and the least-squares regression showed a coefficient of 0.999. The NpO_2^+/CO_3^{2-} mole ratio in the aged solid was found to be also 1. This was established by a potentiometric titration with 0.1 M $HClO_4$ of a suspension of $NaNpO_2CO_3$. Dissolution of the solid with the assumed composition requires 2 mol of acid/mol of neptunium, and this was indeed the result found. Finally, the solid was identified as $NaNpO_2CO_3 \cdot 3.5H_2O$ by comparison of its X-ray diffraction pattern with that of this compound previously characterized by Volkov et al.[6]

Although a bis(carbonato) salt might be formed in the system, this phase is not present unless the medium contains ≥ 0.3 M Na_2CO_3,[6] which is beyond the concentration range covered in this study. Thus, the solubility determinations involved only the mono(carbonato) salt as ascertained by the previous tests.

Equilibrations. The tubes containing $NaNpO_2CO_3 \cdot 3.5H_2O$ were centrifuged, and the supernatant was replaced with 1.0 M $NaClO_4$. The solids were suspended and centrifuged again. This procedure was repeated two more times. Finally, aliquots of the carbonate stock solution were introduced to cover a range of concentrations up to 0.1 M. The mixtures were equilibrated for 7 days at 25.0 ± 0.1 °C, sampled after centrifugation, and reequilibrated for an additional 4-day period. The additional equilibration did not produce significant changes in the neptunium concentration of the solutions. A number of the mixtures were then saturated with a gas mixture containing 1.0% CO_2 in nitrogen in order to determine whether bicarbonate complexation could contribute to the solubility. The tubes were sealed and equilibrated for 10 days. After this period the mixtures were centrifuged and sampled. The mixtures were saturated once more with the CO_2 gas mixture and reequilibrated for an additional 7-day period. As in the previous case there were no significant changes in the neptunium concentration of the solutions.

Solution Analyses. Neptunium was determined by radiometric means. Hydrogen ion concentration was determined by using a combination glass electrode with a solution 0.001 M H^+ in 1.0 M $NaClO_4$ as a reference. The electrolyte in the electrode was replaced with AgCl-saturated 1.0 M $NaClO_4$ to minimize junction potentials. Carbonate concentrations were derived from the hydrogen ion concentration, the known total carbon content, and the dissociation constants of carbonic acid. These were determined in the same medium and found to be $-\log Q_1 = 6.03 \pm 0.004$ and $-\log Q_2 = 9.55 \pm 0.02$.

Results and Discussion

Results of the solubility measurements are given in Table I and are shown in Figure 1. Equilibration of some of the samples with 1% CO_2 was done in order to determine whether HCO_3^- complexation takes place. Saturation with CO_2 has the effect of lowering the pH and considerably increasing the

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Table I. Neptunium Solubility of $NaNpO_2CO_3 \cdot 3.5H_2O$ in 1.0 M $NaClO_4$ Containing Varying Amounts of CO_3^{2-}

sample[a]	−log [Np]	−log [Np] (calcd)	−log $[H^+]$	−log $[CO_3^{2-}]$	−log $[HCO_3^-]$
1	4.32	4.28	8.08	5.80	4.33
2	4.36	4.35	8.21	5.71	4.38
3	5.22	5.24	8.99	4.44	3.89
4	5.40	5.38	9.31	3.98	3.74
5	5.48	5.44	9.62	3.54	3.61
6	5.52	5.42	9.94	3.05	3.46
7	5.38	5.33	10.15	2.71	3.32
8	5.13	5.17	10.37	2.39	3.21
9	4.89	4.93	10.55	2.09	3.09
10	4.55	4.43	10.72	1.64	2.81
11	3.50	3.51	10.99	1.03	2.47
6′	4.87	4.84	6.96	5.22	2.61
7′	5.21	5.26	7.21	4.63	2.32
8′	5.41	5.49	7.51	4.06	2.03
9′	5.52	5.55	7.79	3.52	1.76
10′	5.42	5.47	8.08	2.95	1.48

[a] Primed samples were in equilibrium with a CO_2 partial pressure of $10^{-2.027}$ atm. The other samples were in a closed system with a small head space and under their own equilibrium CO_2 partial pressures.

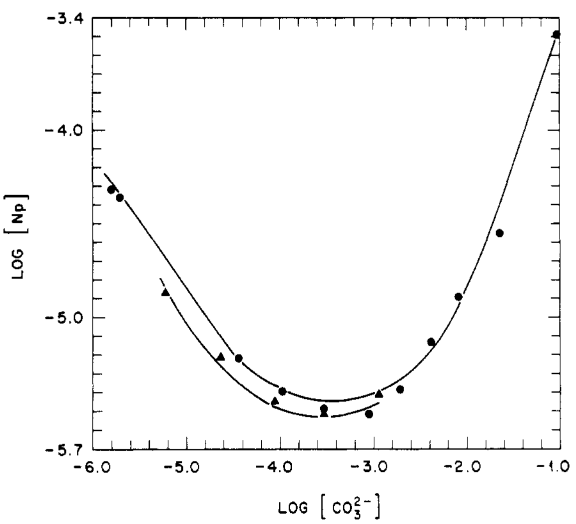

Figure 1. Solubility of $NaNpO_2CO_3 \cdot 3.5H_2O$ as a function of carbonate concentration. ● and ▲ are experimental values respectively under their own CO_2 partial pressure and at $-\log(P_{CO_2}\text{ (atm)}) = 2.027$. Lines are drawn through calculated values.

$[HCO_3^-]/[CO_3^{2-}]$ ratio. The shift in pH suppresses hydrolysis, giving slightly lower solubility values because the contribution of the soluble $NpO_2OH(aq)$ species is virtually eliminated.

The data were analyzed by using the nonlinear least-squares program ORGLS.[7] The program considered the following equilibria, with the water activity and hydration of the solid being ignored:

$$NaNpO_2CO_3(s) \rightleftarrows Na^+ + NpO_2^+ + CO_3^{2-} \quad (1)$$

for which the solubility product expression

$$K_{sp} = [Na^+][NpO_2^+][CO_3^{2-}]\gamma_{Na^+}\gamma_{NpO_2^+}\gamma_{CO_3^{2-}} \quad (2)$$

Since the determinations were carried out at constant $[Na^+]$ expression 2 is transformed into

$$Q_{sp} = \frac{K_{sp}}{[Na^+]\gamma_{Na^+}\gamma_{NpO_2^+}\gamma_{CO_3^{2-}}} = [NpO_2^+][CO_3^{2-}] \quad (3)$$

Table II. Hydrolytic and Carbonate Complexation Constants of NpO_2^+

$-\log Q_{sp} = 10.14 \pm 0.04$	$\log \beta_{12} = 7.11 \pm 0.07$
$-\log Q_H = 9.12 \pm 0.15$	$\log \beta_{13} = 8.53 \pm 0.09$
$\log \beta_{11} = 4.49 \pm 0.06$	

Hydrolysis of the NpO_2^+ produces the species NpO_2OH as described by

$$NpO_2^+ + H_2O \rightleftarrows NpO_2OH + H^+$$

for which

$$Q_H = \frac{[NpO_2OH][H^+]}{[NpO_2^+]} \quad (4)$$

Substitution of $[NpO_2^+]$ from expression 3 gives

$$Q_H = \frac{[NpO_2OH][H^+][CO_3^{2-}]}{Q_{sp}} \quad (5)$$

Similar substitutions in the expressions for the stepwise complexation of NpO_2^+ by CO_3^{2-} lead to

$$\beta_{11} = \frac{[NpO_2CO_3^-]}{Q_{sp}} \quad (6)$$

$$\beta_{12} = \frac{[NpO_2(CO_3)_2^{3-}]}{Q_{sp}[CO_3^{2-}]} \quad (7)$$

$$\beta_{13} = \frac{[NpO_2(CO_3)_3^{5-}]}{Q_{sp}[CO_3^{2-}]^2} \quad (8)$$

The values for the parameters Q_{sp}, Q_H, β_{11}, β_{12}, and β_{13} are derived from a neptunium material balance

$$\sum Np = [NpO_2^+] + [NpO_2OH] + [NpO_2CO_3^-] + [NpO_2(CO_3)_2^{3-}] + [NpO_2(CO_3)_3^{5-}]$$

after substitution of expressions 3, 5, 6, 7, and 8 in the above equation.

An attempt was made to introduce an additional NpO_2HCO_3 species in the fit, but this was rejected after very low values with very large uncertainties were obtained for its formation constant. Inspection of Table I also confirms the absence of HCO_3^- complexation; as an example, samples 3 and 7′ have similar carbonate concentrations but the HCO_3^- concentration in the latter is larger by a factor of 40 and in spite of this no enhancement in the neptunium concentration is observed.

The values of the parameters with their associated uncertainties are listed in Table II. The lines in Figure 1 were drawn through the calculated values of neptunium solubilities with this set of constants. An assessment of their reliability is considered below.

Calculations were made of the stability constants on the basis of statistical considerations[8] with the assumptions that (a) the carbonate ligands are bidentate, (b) there are six coordination sites available, and (c) the value of $\log \beta_{11}$ is 4.49. These considerations lead to the prediction that $\log \beta_{12}$ and $\log \beta_{13}$ should be respectively 8.29 and 11.13 instead of 7.11 and 8.53 as found. This discrepancy indicates that in this case purely statistical considerations are not sufficient to reliably predict the values of the stability constants and that additional factors have to be taken into account. Thus, consideration of electrostatic effects would lower the value of the predicted stability constants since the formation of the tricarbonate complex requires that the doubly charged CO_3^{2-} must bind

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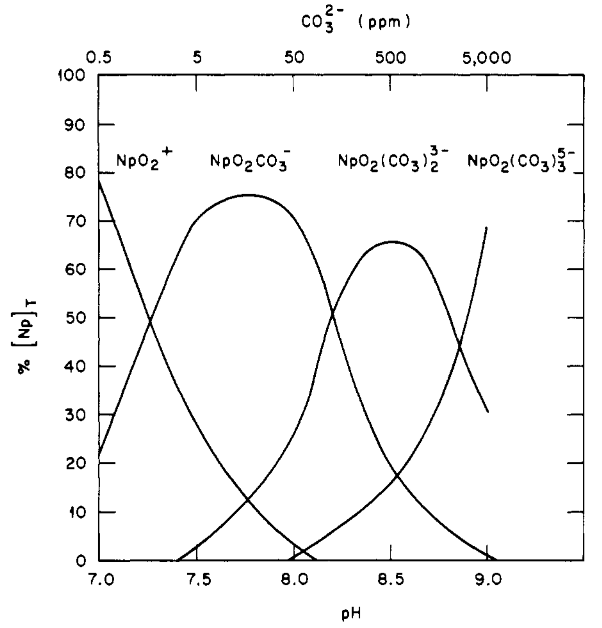

Figure 2. Neptunium(V) speciation scheme under a carbon dioxide partial pressure of $10^{-2.0}$ atm.

to the triply charged $NpO_2(CO_3)_2^{3-}$ ion. The reliability of the log β_{13} value found in this work can be further assessed from the following discussion. The $E_{1/2}$ value of the Np(VI/V) couple in carbonate media was found to be constant in the range 0.1–3.0 M Na_2CO_3.[9] This was also observed by Wester and Sullivan[10] in bicarbonate–carbonate solutions in the pH range 8.3–11.2. This behavior indicates an unchanging number of carbonate ligands for Np(V) and Np(VI), which is three according to observations made by Simakin[9] based on the solubility behavior of $Na_3NpO_2(CO_3)_2$ in carbonate media. The stability constant found in this work would also predict that $NpO_2(CO_3)_3^{5-}$ is the dominant species of Np(V) at $[CO_3^{2-}] \geq 0.1$ M. The $E_{1/2}$ value of the Np(VI/V) couple in carbonate media is 0.7 V more negative than that of this couple in a noncomplexing medium.[11] This indicates that the log β_{13} value of the VI species is larger by 11.84 than that of the V species. Using this value and that of log β_{13} for the Np(V) species found in this work gives an estimate of 20.37 for log β_{13} of Np(VI). This estimate is quite reasonable when it is considered that the corresponding log β_{13} value for U(VI) is 21.81.[12] Comparable differences are observed between U(VI) and Np(VI) hydrolytic constants; the value of $-\log \beta_{35}$ is 15.6 for U(VI) and 17.5 for Np(VI).[13] Finally, an additional measure of confidence is derived from the fact that Q_H, as found in this work, is very close to that estimated by Kraus and Nelson.[3]

Raman spectra of the solid used in this study were obtained to further characterize this material. The main features in the spectra of $NaNpO_2CO_3 \cdot 3.5H_2O$ are the bands due to ν_1 vibrations of the NpO_2 moiety at 775 cm^{-1} and those of CO_3, ν_1 at 1100 cm^{-1} and ν_3 at 1404 and 1569 cm^{-1}. The 775-cm^{-1} frequency of the neptunyl symmetric stretch in this compound is similar to that for $Na_3NpO_2(CO_3)_2$, which is 772 cm^{-1}.[14] That such a similarity can occur between these two compounds, in spite of the different stoichiometry, is apparently a consequence of the very similar environments of the NpO_2 moiety in the respective crystal structures as described by Volkov et al.[15] The CO_3 ν_1 band (1100 cm^{-1}) has a higher frequency than that commonly observed for complexed CO_3^{2-}, which is about 1070 cm^{-1}.[16] The $\nu_1(CO_3)$ band in $NaNpO_2CO_3 \cdot 3.5H_2O$ is closer to those of magnesite or dolomite, found respectively at 1096 and 1099 cm^{-1}.[16] This perhaps reflects the ionic character of the lattice, with independent NpO_2 and CO_3 units. On the other hand, the presence of a split ν_3 vibration for CO_3 indicates some degree of coordination between the neptunyl and carbonate moieties. The splitting is less pronounced than that observed in $Na_4UO_2(CO_3)_3$, 1358 and 1630 cm^{-1}.[17] This uranium salt contains distinct $UO_2(CO_3)_3$ moieties as shown by the crystal structure of the related ammonium salt.[18] It appears, then, that the bonding in the neptunium compound is intermediate between a completely ionic structure and one containing definite dioxoneptunium carbonato anions.

The carbonate complexation constants and the hydrolytic constants found in this work were used to calculate a species distribution scheme for Np(V) in the pH range 7.0–9.0 under a partial CO_2 pressure of $10^{-2.0}$ atm. The results are shown in Figure 2. It was found that under the most likely conditions to be found in nature the dominant species would be $NpO_2CO_3^-$ and/or $NpO_2(CO_3)_2^{3-}$. Formation of $NpO_2(CO_3)_3^{5-}$ would require relatively high CO_3^{2-} concentrations, which in turn would require an unusually high degree of oversaturation by the common carbonate minerals. Formation of $NpO_2OH(aq)$ is not favored unless the source of alkalinity in a groundwater is not associated with carbonate ions.

Conclusions

Neptunium(V), in spiite of its general tendency to form weak complexes, forms relatively stable carbonato complexes. This leads to the prediction that this element, under most conditions found in groundwaters, would be present in a complexed form. This finding is of importance in predicting the transport characteristics of this element.

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New Five- and Six-Membered Saturated Heterocycles Containing Sulfur-Nitrogen Bonds

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Following the pioneering work of Becke-Goehring et al.,[3] there has been a steadily growing interest in sulfur–nitrogen

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