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Carbonate Complexation of Dioxoneptunium(VI) at 25 °C: Its Effect on the Np(V)/Np(VI) Potential[1a]

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The carbonate complexation constants for dioxoneptunium(VI) were derived from potentiometric titrations of neptunium(VI) under different carbon dioxide partial pressures in the range between pH 5.0 and 8.0. The values obtained are similar to those of the dioxouranium(VI). The carbonate-containing species that attain a significant concentration in this pH range are $(NpO_2)_2CO_3(OH)_3^-$, $NpO_2(CO_3)_2^{2-}$, and $NpO_2(CO_3)_3^{4-}$. The constants of Np(VI) and those previously obtained for Np(V) were used to calculate potentials of the couple under conditions similar to those found in nature. It was found that Np(VI) can be stable in a natural environment between pH 7 and 10. However, this requires rather oxidizing conditions. Direct equilibrium potential measurements of the Np(V)/Np(VI) couple were made at the micromolar concentration range. These were used to assess the reliability of the complexation schemes of both oxidation states, and no gross departures were found.

Introduction

Interest in the chemistry of the actinides in aqueous solutions of compositions similar to that of natural waters stems from a need to develop a predictive ability regarding the transport characteristics of these elements in nature. This knowledge is of importance, as one element among other considerations, to assess the safety of storage and/or disposal of spent nuclear fuel in natural formations. The actinide elements of most concern, because of their relative concentration in spent fuel, decay periods, and toxicity are uranium, neptunium, plutonium, and americium. Neptunium is of particular concern since predictions based on thermodynamic considerations[1b] show that Np(V) would be the anticipated oxidation state of this element in a natural environment. It is assumed that neptunium in this oxidation state would be more mobile because of the relatively low charge and polarizing power of the NpO_2^+ ion, which in turn leads to weaker chemical interactions with available ligands. On the other hand, in carbonate media, the formal potential of the Np(V)/Np(VI) couple is displaced with respect to that in a noncomplexing medium by about −0.7 V.[2] This suggests the possible existence of Np(VI) in a natural environment in spite of the strong oxidizing character of the uncomplexed NpO_2^{2+} ion. The 0.7-V displacement is an extreme condition requiring the highest degree of complexation of both Np(V) and Np(VI), which corresponds with the formation of tricarbonato species, and occurs at carbonate concentrations that are not typical of natural waters. The question then remains as to what is the potential of the couple under conditions found in nature that would probably involve the formation of complexes with less than three carbonate ligands. To answer this, the hydrolytic and carbonate complexation constants for each oxidation state are required. Available in the literature are data concerning Np(V)[3] while the data for Np(VI) are limited to a study of its hydrolytic behavior.[4] The present work was undertaken to obtain the carbonate complexation constants for Np(VI) that were missing. The experimental approach chosen to derive this information was based on potentiometric titrations with perchloric acid of freshly prepared neptunium(VI) carbonate solutions maintained under known CO_2 partial pressures. Additionally, confirmatory evidence was sought for the complexation schemes of both Np(V) and -(VI) on the basis of equilibrium potential measurements of the Np(V)/Np(VI) couple.

Experimental Section

A 0.0656 M neptunium(V) stock solution was used as the neptunium source for all the experiments. Its preparation has been previously described.[3] Other chemicals were of AR quality. Deionized water, doubly distilled, was used to prepare all the solutions.

Electrochemical preparations and measurements were performed with a Model 173 potentiostat and Model 179 digital coulometer from Princeton Applied Research in a H-shaped cell. The cell contained a fine-glass frit in the connecting tube. A coil made of gold wire, 0.7 mm in diameter, with an area of about 17.0 cm^2 was used as working electrode. Platinum wire was used as a counterelectrode and a calomel electrode with saturated sodium chloride inner electrolyte as reference.

All experiments were performed at 25 ± 0.1 °C in 1.0 M $NaClO_4$ as supporting electrolyte. Hydrogen ion concentrations were determined, with 0.001 M H^+ in 1.0 M $NaClO_4$ as reference, with a combination-glass electrode in which the inner electrolyte had been replaced with AgCl-saturated 1.0 M $NaClO_4$.

Neptunium(VI) carbonate solutions, approximately 10^{-3} M Np, containing a known amount of alkalinity, about 10^{-2} M Na^+, were prepared for each run by the addition of an aliquot of the Np(V) stock, which had a neutral pH, to a solution containing sodium carbonate held in the electrochemical cell. The resulting slurry of $NaNpO_2CO_3$ was electrochemically oxidized for about 16 h at +0.5 V vs. the NaCl saturated calomel electrode (SSCE). Coulometric measurements were used to derive the concentrations of the solutions. These were also analyzed by radiometric means, yielding good agreement. The resulting solutions were transferred to a titration cell held in a controlled-temperature bath and then saturated in different runs with analyzed gas mixtures containing CO_2 at 300 ppm, 0.3, 1.0, and 3.0%. The gas mixtures used were presaturated with water vapor. The values of carbon dioxide partial pressures in equilibrium with the solutions were calculated correcting for the incorporation of water vapor and the daily variations in barometric pressure. Titrant, 0.1 M $HClO_4$–0.9 M $NaClO_4$, was introduced stepwise by means of a microsyringe. Typically a 9.0 cm^{-3} of Np solution was titrated with 1.0 cm^{-3} of acid.

Results and Discussion

Duplicate or triplicate runs for each CO_2 partial pressure were conducted. An exception was that with 300 ppm of CO_2, which proved to be very slow in reaching equilibrium after each acid addition and produced precipitates near the neutralization point. Therefore, only the initial stages of the titration at the low CO_2 partial pressure were included in the data analysis. Standard deviations were about 0.01 pH unit for the initial and final stages of the titrations and larger deviations, up to 0.1 pH unit, for the steepest sections of the titration curves. A solution was back-titrated with Na_2CO_3 around the neutralization point finding no hysteresis. Typical results of ti-

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Table I. Typical Titration Data of Neptunyl Carbonate-Sodium Carbonate Solutions with 0.1 M $HClO_4$[a]

run	−log $[H^+]$	$[HClO_4]$, mL	run	−log $[H^+]$	$[HClO_4]$, mL
1	8.585	0	3	7.333	0
	9.237	0.20		7.129	0.20
	8.124	0.40		6.924	0.40
	7.983	0.50		6.636	0.60
	7.805	0.60		6.010	0.70
	7.601	0.65		5.376	0.75
2	7.751	0		5.117	0.80
	7.496	0.20	4	6.902	0
	8.332	0.40		6.716	0.20
	7.036	0.60		6.469	0.40
	6.783	0.65		6.030	0.60
	5.325	0.75		5.283	0.70
	4.826	0.85		5.000	0.75
				4.802	0.80

[a] $-\log P_{CO_2}$, initial [Np] (mM), initial [Na^+ (alkalinity)], mM: run 1 3.497, 1.22, 8.79; run 2 −2.550, 1.21, 8.78; run 3 −2.030, 1.12, 8.98; run 4 1.552, 1.24, 8.75.

trations are given in Table I.

Data Analysis

The data analysis is essentially the same as that used for the uranyl system previously described.[5] In this case the data base consisted of 69 observations. Briefly, the conditional stability constants refer to the genralized equation

$$aNpO_2{}^{2+} + bCO_2 + cH_2O \rightleftarrows (NpO_2)_a(CO_3)_b(OH)_{c-b}{}^{2a-b-c} + (b + c)H^+ \quad (1)$$

For simplicity $c - b = x$, $b + c = y$, and $2a - b - c = z$. Then

$$^*\beta_{\mathrm{abc}} = \frac{[\mathrm{abx}^z][H^+]^y}{[NpO_2{}^{2+}]^a[p^bCO_2]}$$

where a stands for neptunyl, b for carbonate, and x for hydroxide. Then, [abx^z] represents a given complex with a charge z. Species are designated by a set of three numbers, for example 1,3,0 is $NpO_2(CO_3)_3{}^{4-}$ and 3,0,5 is $(NpO_2)_3(OH)_5{}^+$.

The stability constants were derived by a computer fit[6] of the data that involved the solution of two functions: one defining charge balance and the other the neptunium material balance

$$F(1) = [H^+] + 2[NpO_2{}^{2+}] + [Na^+] - [HCO_3{}^-] - 2[CO_3{}^{2-}] - [OH^-] - [ClO_4{}^-] + \textstyle\sum z{}^*\beta_{\mathrm{abc}}[NpO_2{}^{2+}]^a[p^bCO_2][H^+]^{y-}$$

$$F(2) = [Np]_t - [NpO_2{}^{2+}] - \textstyle\sum a{}^*\beta_{\mathrm{abx}}[NpO_2{}^{2+}]^a[p^bCO_2][H^+]^{y-}$$

where $[Np]_t$ is the total neptunium concentration.

The least-squares procedure[6] minimizes the differences between the observed pH values and those calculated with a set of variable parameters. No weighting factors were used for the data.

The formation of hydrolytic species cannot be excluded in the pH range covered in this study; thus, consideration was given to their contribution to the speciation scheme. In addition to the carbonate and mixed hydroxo–carbonato 1,2,0, 1,3,0, and 2,1,3 species, the initial scheme incorporated, as fixed parameters, the stability constants of the hydrolytic species described by Cassol et al.,[4] namely 1,0,1, 2,0,2, and 3,0,5.

No bicarbonate-containing species were included in the fit in spite of the fact that this ligand is present at relatively large concentrations in the system. Bicarbonate is a poor ligand, giving complexes in very few instances. A thorough search in the uranyl(VI) and neptunyl(V) systems[3,5] failed to show any bicarbonato complexes.

The existence of the mixed hydroxo–carbonato species 2,1,3 has been demonstrated in the uranyl system.[5] This stoichiometry has also been observed in solids isolated from the neutralization of uranyl sulfate solutions.[7] Its inclusion in the scheme for the neptunyl(VI) system was considered justified, and it proved to be a requirement for obtaining good fits.

There is little doubt about the existence of the 1,2,0 and 1,3,0 species in the uranyl system. Their corresponding stability constants have been repeatedly determined as described in Langmuir's critical review[8] of complexation and solubility data.

A number of species were tested as alternates or in addition to those mentioned above. The results of these attempts are summarized in Table II. Fit 2 shows the effect of removing the contribution of the hydrolytic species. The species 3,0,7 was tested because it existence has been adduced[9,10] in the uranyl hydrolytic scheme. The stability constant derived in the present study for this species is $-\log {}^*\beta = 28.13 \pm 0.75$. The contribution of this species in relation to the total neptunium concentration is rather small, and therefore it was not included in the final speciation scheme. The 3,0,7 species was also tested as an alternate of 2,1,3 because of the relative similarity in charge, but the fit degraded considerably. Similarly tested was the species 3,6,0, which has been observed[11] to form in the uranyl system as a product in the first acidification of the $UO_2(CO_3)_3{}^{4-}$ ion. In this case, inclusion of the 3,6,0 species gave a $-\log {}^*\beta$ value for this species of 50.13 ± 3.7. Here again, the contribution of such species to the scheme is very small. Substitution of 1,2,0 by 3,6,0 degraded considerably the fit, thus leading to the rejection of the 3,6,0 species. Finally a 3,1,3 species was tested. This mixed hydroxo–carbonato species has been detected in the uranyl system by Ciavatta et al.[12] Use of the reported value of its stability constant as a fixed parameter in addition to the initial scheme showed insignificant concentrations for 3,1,3. On the other hand, if the stability constant was allowed to vary, a $-\log {}^*\beta$ value of 14.79 ± 0.36 was found that increased considerably the contribution of this species. However, this resulted in a relatively large covariance between the β values of 3,1,3 and 2,1,3. Substitution of 2,1,3 by 3,1,3 led to a poor fit. The species 3,1,3 may be present in the system, but its inclusion was not considered justified because its contribution takes place at around pH 5.0 coincidently with a large number of other species (1,0,0; 1,0,1; 2,0,2; 3,0,5; 2,1,3). A much larger data base would be required to sort the speciation scheme at that pH value.

A final scheme that included three carbonate-containing species was obtained. The calculated constants with their corresponding uncertainties are given in Table III. The corresponding uranyl species are also given for comparison purposes. The results show stronger complexation for neptunyl than for uranyl although the differences are relatively small.

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Table II. Least-Squares Fit of Titration Data[a]

fit	2,1,3	1,2,0	1,3,0	X[b]	S[c]	D[d]
1	18.60 ± 0.07	17.71 ± 0.07	30.18 ± 0.12		0.379	0.076
2	18.60	17.71	30.18		0.516	0.086
3	18.59 ± 0.08	17.69 ± 0.07	30.16 ± 0.12	28.13 ± 0.75	0.373	0.076
4	...	17.55 ± 0.08	30.10 ± 0.18	27.35 ± 0.16	1.230	0.137
5	18.60 ± 0.08	17.64 ± 0.08	30.20 ± 0.12	50.13 ± 3.70	0.387	0.077
6	18.58 ± 0.10	...	30.10 ± 0.13	47.64 ± 0.40	0.747	0.106
7	18.64	17.74	30.19	16.2	0.383	0.075
8	18.39 ± 0.12	17.60 ± 0.09	30.07 ± 0.12	14.79 ± 0.36	0.335	0.072
9	18.64	17.74	30.19	15.70 ± 0.42	0.384	0.075
10	...	17.21 ± 0.29	30.05 ± 0.64	14.11 ± 0.84	8.363	0.356

[a] Cassol et al. β values for 1,0,1, 2,0,2, and 3,0,5 were used as fixed parameters in all fits except 2 (for which no hydrolytic species were considered). Values with uncertainties attached (corresponding to 1σ) were varied and fixed if given without uncertainties. [b] X stands for an additional species: 3,0,7 for fits 3 and 4; 3,6,0 for fits 5 and 6; 3,1,3 for fits 7-10. [c] $S = \Sigma(\text{obsd} - \text{calcd})^2$. [d] $D = (S/\text{data points} - \text{parameters varied})^{1/2}$.

Table III. Stability Constants for the Carbonate Complexation of Dioxoneptunium(VI) in the pH Range 5-8 at 25 °C and 1.0 M Ionic Strength

	this work		uranium species[13]	
species	$-\log {}^*\beta$	$\log {}^{**}\beta$[a]	$-\log {}^*\beta$	$\log {}^{**}\beta$
2,1,3	18.60 ± 0.07		18.63[b]	
1,2,0	17.71 ± 0.07	16.51	...	14.91
1,3,0	30.18 ± 0.12	21.15	...	20.23

[a] Expressed as formation constants after inclusion of the carbonic acid equilibria; thus, $\log {}^{**}\beta_{130} = \log \beta_{130} - 3 \log ({}^*Q_1 Q_2)$, where $\log {}^*Q_1 = -7.56$ includes Henry's constant and $\log Q_2 = -9.55$. [b] This value is from ref 5, and it was obtained at $I = 0.1$ M. All other constants are for a medium with $I = 1.0$ M.

In the case of the mixed hydroxo–carbonato species there is a close similarity between uranyl and neptunyl ions.

Attempts were made to obtain supporting physicochemical evidence for the presence of the species included in the fit. Spectroscopic and electrochemical observations made at different stages in the titration were useful in the case of the uranyl system in detecting the different species;[5,14] however, those techniques were not useful for studying neptunium. Electronic spectra were not distinct enough with neptunium to make unambiguous assignments. Similarly, reduction waves observed by voltammetry or differential-pulse polarography could not be assigned. The difficulty in the case of neptunium stems from the potential range involved that is too oxidizing for the use of a dropping mercury electrode. Use of solid electrodes such as platinum, gold, or glassy carbon did not give unambiguous signals due to interferences caused by sorption phenomena and surface oxides.

The results of the fit are illustrated in Figure 1, which gives a set of calculated titration curves for each CO_2 partial pressure along with the experimental points.

The set of constants derived from the fit was used in deriving speciation schemes for different carbon dioxide partial pressures. These are presented in a condensed manner in Figure 2 which shows the average charge of the species as a function of pH and pCO_2. The average charge for the species is derived from the expression

$$\bar{z}(\text{Np}) = \sum z[\text{abx}^z]/[\text{Np}]_t$$

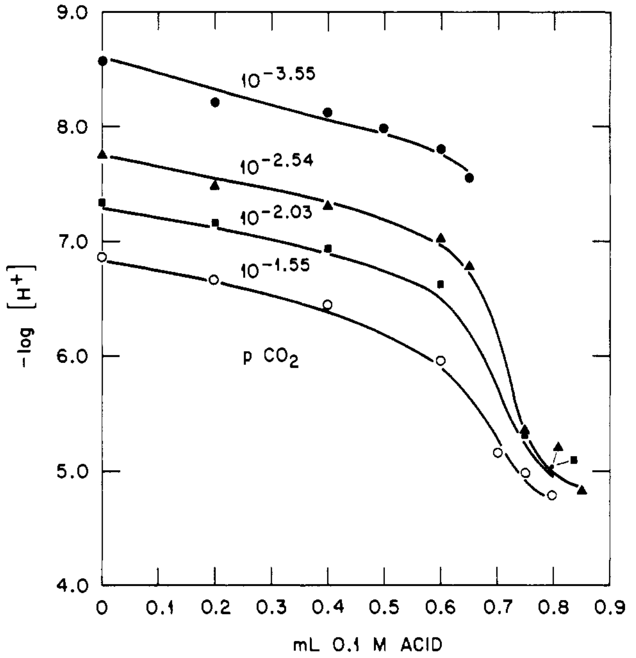

Figure 1. Typical titration curves of Np(VI) solutions (8.9 cm^{-3} $\sim 10^{-3}$ M) with 0.1 M $HClO_4$. Solid curves show calculated values using the complexation constants given in Table III.

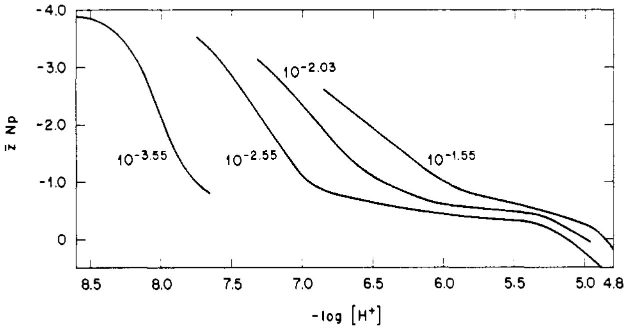

Figure 2. Average charge of neptunium(VI) species as a function of pH and pCO_2.

It is seen that at relatively high pH values and consequently higher carbonate concentrations the dominant species is $NpO_2(CO_3)_3^{4-}$. Under these conditions the system shows an average charge close to −4.0. As the pH is decreased, the contribution of the dicarbonate becomes important, but it is limited to a relatively narrow pH range as reflected by the relatively steep transition into a flatter portion with a value of $\bar{z}(\text{Np}) = -0.5$. The latter represents the region of stability for the hydroxo–carbonato species. Finally, cationic species such as the hydrolysis products and uncomplexed neptunyl ion would take the curve to the limiting value of +2.0 at relatively high acidity. Also observed is the fact that as the partial pressure of carbon dioxide increases, the ratio of dicarbonate to hydroxo carbonate also increases.

Potential of the Np(V)/Np(VI) Couple in the Presence of Carbonate Ions

A series of calculations were made in order to define the effect of carbonate concentration on the potential of the Np-

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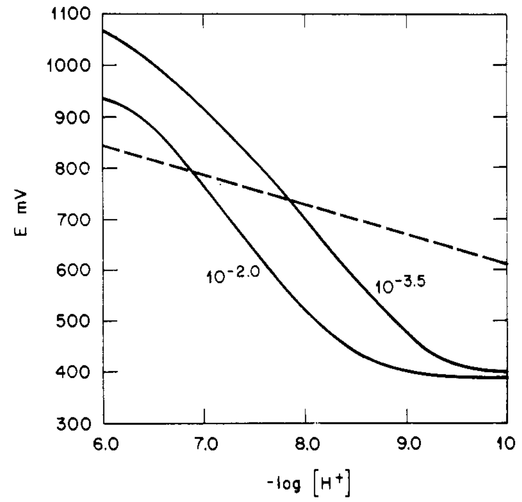

Figure 3. Calculated potentials vs. NHE of the Np(V)/Np(VI) couple as a function of pCO_2. Values of the formation constants are those in Table III and in ref 3. Dashed line represents the thermodynamic limit for water decomposition.

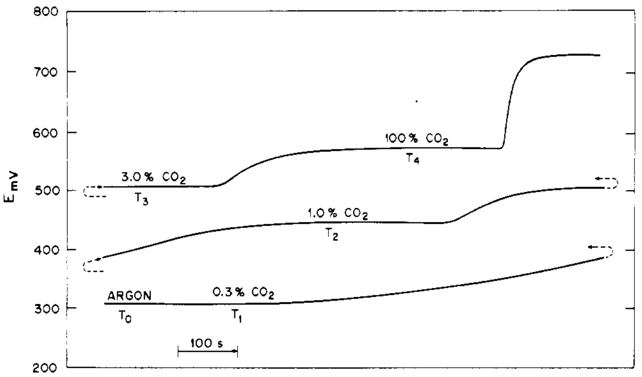

Figure 4. Folded recorder trace showing the effect of variations of the CO_2 partial pressure on the potential vs. SSCE of the Np(V)/Np(VI) couple. T_0 marks the initial point of the experiment; subsequent *T*'s mark switching points of the cover gas. Corresponding pH values were 10.01, 7.83, 7.33, 6.81, and 5.33.

(V)/Np(VI) couple. These considered the complexation scheme for each oxidation state and their corresponding material balances. Thus, the concentration ratio of uncomplexed NpO_2^{2+} and NpO_2^+ as a function of carbonate concentration could be derived. Potentials were calculated by using the Nernst equation, taking the literature value of +1.137 V[15] as the reference potential for the couple in a noncomplexing medium, in this case 1.0 M $HClO_4$. The results of these calculations are presented in Figure 3 which shows values of potentials vs. pH at two different carbon dioxide pressures for equimolar mixtures of Np(V) and -(VI) at a neptunium concentration of 10^{-6} M. It can be seen that the potentials of the couple become lower than the thermodynamic limit of water oxidation (given by dashed line), thus suggesting the possible existence of neptunium(VI) under conditions observed in ground waters.[16] However, this would require a rather oxidizing environment.

The *E* vs. pH plots in Figure 3 approach asymptotically a limiting value of 400 mV vs. NHE, which would correspond to full complexation of both the Np(V) and -(VI) oxidation states. This calculated value is more negative, by about 60 mV, than the value reported by Wester and Sullivan,[2] which was based on voltammetric measurements, while Simakin et al.[17] found a value of 430 ± 10 mV vs. NHE for the potential of the couple based on coulometric determinations. These differences are relatively small considering the fact that the effect of total complexation causes a displacement of 700 mV.

The possibility of obtaining experimental data by direct measurement of the potential of the Np(V)/Np(VI) couple under conditions of partial complexation was considered very small. This would result from the constraints imposed by the relatively low solubility of the Np(V) carbonate salts, which would limit any determination to the micromolar concentration range.[3] It was indeed rewarding to observe in scouting experiments, conducted at the micromolar concentration range, that considerable potential shifts occurred when mixtures of Np(V) and -(VI) were saturated in sequence with gas mixtures containing different CO_2 concentrations. The pH of the solutions was initially adjusted by the addition of Na_2CO_3 to bring the system within a range where partial complexation would take place. The potential shifts suggested that the ratio of uncomplexed NpO_2^{2+}/NpO_2^+ was changing as the concentration of carbonate varied. This in turn was a consequence of variations in the CO_2 partial pressure of the system. These experiments were conducted in the same H-cell used for the electrochemical preparations. Potential readings were made with the built-in electrometer in the Model 173 potentiostat. Immersion of the reference electrode either into the Np-free electrolyte side of the cell or into the neptunium solution produced differences of about 1 mV, thus suggesting that junction potentials were relatively small. The initial experiments involved the preparation of a Np(VI) solution by the electrochemical oxidation of a Np(V) aliquot after the addition of a known amount of Na_2CO_3. Half of the solution was withdrawn when the oxidation was completed and replaced with an equal volume of a Np(V) of the same total Np concentration. This solution was then saturated in sequence with gas mixtures of different CO_2 concentrations while the potential of the cell was monitored. The potential was observed to increase in stages, reaching a plateau for each CO_2 mixture. A typical recorder tracing is given in Figure 4. The potentials observed were relatively close to the values calculated for each condition. A source of uncertainty in these measurements was the possibility that the ratio of the Np(V) and -(VI) was not 1/1 as initially prepared. The possibility existed, given the very low neptunium concentrations (2×10^{-6} M), that small amounts of impurities or sorption phenomena could alter that ratio. A procedure was developed to establish with more certainty the relative proportions of Np(V) and -(VI) in a mixture. This consisted of adding in sequence Np(V) in the form of small volume spikes to a Np(VI) solution. The effect of the spikes on the potential was found to be Nernstian; thus, the first addition would produce a large potential change since no significant amounts of Np(V) were present at that point while the second spike of an equal volume would produce a doubling of the Np(V) concentration. This would translate into a 17.8-mV change, and a third spike would produce an additional drop in potential but in this case of only 10.4 mV. The addition of Np(V) spikes served the double purpose of acting as a probe for the amount of Np(V) present and to adjust the Np(V)/Np(VI) ratio. The potential determinations were complemented with radiometric determinations to confirm the total Np concentration at each stage of a run.

The procedure described above proved to be very useful in detecting sources of error. In a few occasions the second spike produced a response that was larger than 17 mV, thus indicating that the initial spike had been partially oxidized. This problem was found to be caused by a reaction between the

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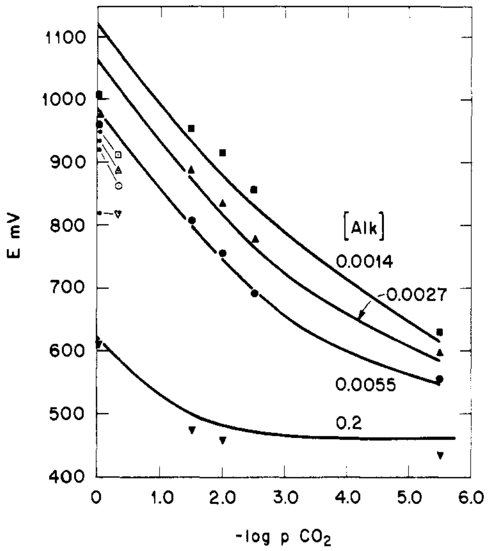

Figure 5. Potential of the Np(V)/Np(VI) couple vs. NHE as a function of pCO_2 for different initial alkalinities. Solid curves show calculated values. Filled symbols are experimental values while the empty symbols mark the thermodynamic limit for water decomposition. The pH values for each condition may be derived from the [alk] and pCO_2. See ref 18.

initial Np(V) introduced and surface oxides on the electrode that were generated during the preparation stage of the Np(VI). Apparently the potential imposed on the electrode during the oxidation was too high. The problem was solved by conducting the oxidation at a lower potential. The presence of surface oxides on the electrode was detected by means of cyclic voltammetry, in the absence of neptunium.

Finally, a series of experiment was conducted in which Np(V)/Np(VI) mixtures having different levels of initial alkalinity were saturated in sequence with CO_2 mixtures. The potentials observed proved to be consistently higher, by about 60 mV, than the calculated values using the complexation constants for Np(VI) obtained in the first portion of this study and the set of constants for Np(V) previously obtained.[3] A better fit was obtained by adjusting $-\log {}^*\beta_{120}$ and $-\log {}^*\beta_{130}$ respectively, from 17.71 to 18.69 and from 30.18 to 31.29. The results of these experiments and the corresponding calculated curves are shown in Figure 5. It is seen that there is a good agreement for most of the points. Marked departures are observed for the three solutions of lower alkalinity in equilibrium with pure CO_2. Apparently these solutions did not reach the calculated potentials because they were too oxidizing and exceeded the thermodynamic limit for water decomposition. These limits are indicated by the unfilled symbols at the left margin of the figure. The potentials of these solutions reached a maximum and after a few minutes started to drop. Apparently the Np(VI) was being consumed by reaction with the solvent. This led to deposition of a film of Np on the electrode that prevented its use for subsequent experiments unless it was removed by an acid rinse.

The direct potential measurements provided an independent means to judge the reliability of the speciation schemes of both the Np(V) and Np(VI). There is a reasonable agreement between the two experimental approaches. Changing the values of ${}^{**}\beta_{120}$ and ${}^{**}\beta_{130}$ by about 1 log unit gives a boundary to the uncertainties in the experiments. The difference gives an indication that the value of ${}^*\beta_{130}$ for Np(V) may have been underestimated by about 1 log unit or that the values of the formation constants ${}^{**}\beta_{120}$ and ${}^{**}\beta_{130}$ derived by the potentiometric titrations may have been overestimated also by 1 log unit. This would bring the results of neptunium(VI) more closely in line with those of uranium(VI). If the difference is split between the Np(V) and Np(VI) sets of constants, then the uncertainty is about 0.5 log unit for each constant. Conversely, the titration data suggest that the direct potential readings might be biased by about 60 mV. The sources of these discrepancies cannot be assigned. In any event, this difference shows that there are no gross departures for the speciation schemes of either Np(V) or -(VI).

Conclusions

Neptunium(VI) is strongly complexed by carbonate, much more so than neptunium(V). This implies that neptunium(VI), in spite of being a strong oxidant, could be stabilized by carbonate complexation in a natural environment in the pH 7.0–10.0 range. However, this would require a ground water having an equilibrium potential of ≥400 mV vs. NHE.

Direct equilibrium potential measurements of the Np(V)/Np(VI) couple are feasible in the micromolar range. This finding is significant, not only because it allowed a way to assess the reliability of the speciation schemes of Np(V) and -(VI) in carbonate media but because it provides a useful tool that is applicable to a concentration range restricted to few techniques. This may be applied to similar studies such as the determination of complexation schemes for other actinide couples with a number of different ligands or to studies of sorption phenomena.

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