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Studies of the Complexes of Np(V) with Inorganic Ligands by Solvent Extraction with Thenoyltrifluoroacetone and 1,10-Phenanthroline. I. Carbonato Complexes

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The complex formation of Np(V) in a carbonate medium has been studied in 1 mol dm^{-3} NaClO$_4$ at pH 6.5—8.3 and 25 °C using the solvent-extraction method with thenoyltrifluoroacetone (TTA) and 1,10-phenanthroline. The formation constants of the complexes of Np(V) with CO$_3^{2-}$ were $\log(\beta_1/\text{mol}^{-1}\,\text{dm}^3)=4.14\pm0.01$ and $\log(\beta_2/\text{mol}^{-2}\text{dm}^6)=6.78\pm0.01$, with no indication of the formation of HCO$_3^-$ complexes. Based on these constants, the distribution of chemical species of neptunium are discussed under various conditions encountered in natural water.

The solution chemistry of neptunium has received much attention in recent years since the ^{237}Np in radioactive wastes will have a long-term radiological toxicity in the human environment. Since this element most probably exists as a quinquevalent state in neutral solutions, the study of the complex formations of Np(V) in aqueous solutions is very important for the understanding of the behavior of this element in natural water.

In spite of this importance, quinquevalent neptunium has not been extensively studied due to its reduced reactivity with various ligands as a result of its low ionic potential. However, recent studies[1,2] by means of solvent extraction with thenoyltrifluoroacetone (TTA) and 1,10-phenanthroline (phen) revealed that Np(V) still forms considerably stable complexes with many organic ligands such as hydroxy carboxylic acids, dicarboxylic acids, amino carboxylic acids and some other widely used chelating reagents.

This induced us to study the complex formation of Np(V) with some inorganic anions using the same solvent extraction technique. Among inorganic anions, the carbonate ion deserves special attention because of its pronounced tendency to interact with cations and because of its wide distribution in the environment. Since the formation of carbonato complexes is expected to affect the movement of neptunium in natural water, reliable stability constants are required for estimating the behavior of the element in the environment.

The present paper deals with the determination of the formation constants of Np(V)–carbonato complexes by means of solvent extraction with TTA and phen, and the distribution of chemical species of neptunium in solutions under various conditions are discussed based on the obtained results.

Experimental

Reagents. The ^{239}Np tracer was prepared by milking from ^{243}Am (obtained from the Commissariat a l'Energie Atomique) by the method of Sill,[4] and adjusted to the quinquevalent state by evaporation to dryness and dissolution in water.[5] Thenoyltrifluoroacetone and 2-morpholinoethanesulfonic acid monohydrate (MES) were obtained from Dojindo Laboratories (Kumamoto, Japan) and used without further purification. The solutions of these chemicals were freshly prepared just prior to use.

Procedures. To avoid the possible contamination by any complex-forming substances or by neptunium with a valence state other than quinquevalent (which might be introduced during milking), the following back-extraction procedure was adopted. The ^{239}Np tracer was first extracted into an organic (3-methyl-1-butanol or dichloromethane) solution containing the desired concentrations of TTA and phen. A 4-cm^3 portion of this organic solution containing ^{239}Np was then mechanically shaken for 15 min (140 times/min) at 25±1 °C in a glass tube with the same volume of aqueous solution containig 1 mol dm^{-3} sodium perchlorate, buffer reagents (a proper mixture of 0.1 mol dm^{-3} of MES and 0.1 mol dm^{-3} of tris(hydroxymethyl)aminomethane (THAM)) and a variable concentration of sodium hydrogencarbonate. After phase separation, a 1-cm^3 portion of each phase was pipetted into a counting tube and the γ-activity of each phase was measured with a well-type NaI(Tl) scintillation counter. The remaining part of the aqueous phase was used for the pH measurement.

Calculation of Stability Constants. The distribution ratio D of Np(V) in the presence of the complexing agent (X) can be expressed by:

$$D = D_0/(1+\sum\beta_n[\text{X}]^n), \tag{1}$$

where D_0 is the distribution ratio of Np(V) in the absence of the complexing agent, and β_n is the overall formation constant of the Np(V) complex with the ligand X (charges of ions are omitted for simplicity). Equation 1 is equivalent to linear function:

$$y = f(x), \tag{2}$$

where

$$y = 1/D,$$

$$f(x) = 1/D_0 + \sum(\beta_n/D_0)x^n,$$

and

$$x = [\text{X}].$$

A set of data (x_i, y_i) was analyzed by the least-squares method to determine the β_n values. Since the counting-time of the γ-activity was set to make the relative statistical errors of the total counts approximately constant, residuals of observed ratios, y, were expected to be proportional to the value of $1/D$ from error propagation rules. Although the observed value of $1/D$ is not error free, this value gives a good basis for an estimate of the weight of the observation. Therefore, the least-squares fitting was carried out to minimize the following sum of the weighted squares of the residuals:

$$S = \sum\{y_i - f(x_i)\}^2/y_i^2. \quad (3)$$

This procedure is nearly equivalent to obtain a best fit of the plots of log D against log [X] to Eq. 1.

Results

The distribution ratio of Np(V) in the presence of a complexing agent can be expressed by Eq. 1. In the presence of a polybasic acid as a complexing agent, however, there is a possibility of the formation of different types of complexes; that is, the ligands in different stages of dissociation can react with Np(V). When ligands HL and L (charges omitted) can react with Np(V) in solution, the ratio D_0/D, the reciprocal of which is equivalent to the fraction of neptunium in the form of free ion (NpO_2^+), is given by:

$$D_0/D = 1 + \sum\beta'_n[\mathrm{HL}]^n + \sum\beta_n[\mathrm{L}]^n, \quad (4)$$

where β'_n and β_n are the overall formation constants of the respective complexes:

$$\beta'_n = [\mathrm{M(HL)}_n]/[\mathrm{M}][\mathrm{HL}]^n, \quad (5)$$

$$\beta_n = [\mathrm{ML}_n]/[\mathrm{M}][\mathrm{L}]^n, \quad (6)$$

where $M=NpO_2^+$. The concentration of HL and L can be related in terms of the acid dissociation constant:

$$K_a = [\mathrm{H}][\mathrm{L}]/[\mathrm{HL}]. \quad (7)$$

Thus, Eq. 4 becomes:

$$\begin{aligned} D_0/D &= 1 + \sum B'_n[\mathrm{HL}]^n \\ &= 1 + \sum B_n[\mathrm{L}]^n, \end{aligned} \quad (8)$$

where

$$B'_n = \beta'_n + \beta_n K_a^{\,n}/[\mathrm{H}]^n, \quad (9)$$

and

$$B_n = \beta'_n[\mathrm{H}]^n/K_a^{\,n} + \beta_n. \quad (10)$$

Measurement of D as a function of [HL] or [L] leads to the apparently constant values of B'_n or B_n, provided that the extraction is carried out in a medium buffered at constant pH. Since B'_n or B_n is the function of pH, as expressed by Eq. 9 or 10, a set of B'_n or B_n obtained at various pH discloses the contribution of each series of complex formation to give the constant values, β'_n and β_n.

Six series of experiments were carried out on solutions ranging from pH 6.5 to 8.3 to obtain a distribution ratio at various added concentrations of sodium hydrogencarbonate. In each series of experiments, the distribution ratio was obtained in a medium buffered at constant pH. The pH of the aqueous phase drifted during extraction; the pH after shaking differed from the initial pH by less than 0.4 unit in each series of experiments and the experimental values of D were corrected to those at a constant pH by using experimental extraction curves which were obtained previously.[3] The concentration of a particular species of carbonate, [HCO_3^-] or [CO_3^{2-}], at an equilibrium pH was calculated according to the following relationship:

$$\begin{aligned} C_\mathrm{L} &= [\mathrm{H_2CO_3}] + [\mathrm{HCO_3^-}] + [\mathrm{CO_3^{2-}}] \\ &= [\mathrm{H_2CO_3}](1+K_1/[\mathrm{H^+}] + K_1K_2/[\mathrm{H^+}]^2), \end{aligned} \quad (11)$$

where

$$K_1 = [\mathrm{H^+}][\mathrm{HCO_3^-}]/[\mathrm{H_2CO_3}] = 10^{-6.02}\ \mathrm{mol\ dm^{-3}}, \quad (12)$$

$$K_2 = [\mathrm{H^+}][\mathrm{CO_3^{2-}}]/[\mathrm{HCO_3^-}] = 10^{-9.57}\ \mathrm{mol\ dm^{-3}}, \quad (13)$$

at 25 °C, μ=1.0.[6] In the calculation, the concentration of the undissociated acid in the organic phase was assumed to be negligibly small. To ascertain the validity of this assumption, two kinds of solvents, 3-methyl-1-butanol and dichloromethane, were used as an organic diluent. Plots of log(D/D_0) *vs.* log([HCO_3^-]/mol dm^{-3}) and log([CO_3^{2-}]/mol dm^{-3}) are given in Figs. 1 and 2, respectively. The plots in Figs. 1 and 2 give the values of B'_n and B_n in Eq. 8, respectively, if HL and L denote HCO_3^- and CO_3^{2-}, respectively. Since the the plots in Fig. 2 indicate that the B_n values in Eq. 10 are independent of pH, it can be safely concluded that the complex formation of Np(V)

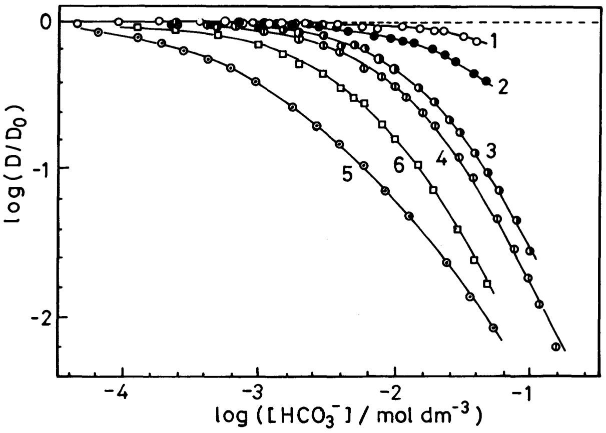

Fig. 1. Plots of log(D/D_0) *vs.* log([HCO_3^-]/mol dm^{-3}). pH: (1) 6.50, (2) 7.00, (3) 7.50, (4) 7.80, (5) 8.30, (6) 8.11. (1)—(5): $C_{TTA}=10^{-4}$ mol dm^{-3}, $C_{phen}=10^{-2}$ mol dm^{-3} in 3-methyl-1-butanol.
(6): $C_{TTA}=10^{-3}$ mol dm^{-3}, $C_{phen}=10^{-2}$ mol dm^{-3}, in dichloromethane.

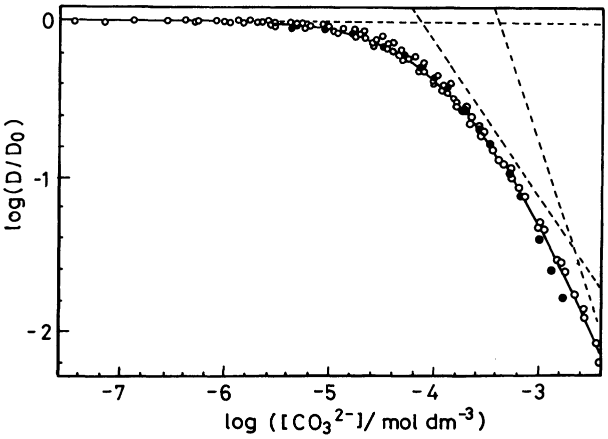

Fig. 2. Plots of log(D/D_0) *vs.* log([CO_3^{2-}]/mol dm^{-3}).
○: pH 6.50—8.30, $C_{TTA}=10^{-4}$ mol dm^{-3}, $C_{phen}=10^{-2}$ mol dm^{-3}, in 3-methyl-1-butanol.
●: pH 8.11, $C_{TTA}=10^{-3}$ mol dm^{-3}, $C_{phen}=10^{-2}$ mol dm^{-3} in dichloromethane.

with HCO_3^- is negligibly small in the pH region investigated, that is, only the carbonate ion CO_3^{2-} participates in the complex formation. We cannot distinguish between MCO_3^- and $M(OH)(HCO_3)^-$; the behavior of these species in the solvent extraction system is identical since the latter merely differs from the former in having an additional H_2O. However, it is quite unreasonable to imagine the formation of $M(OH)(HCO_3)^-$ since even a positively charged NpO_2^+ ion does not form any complexes with an HCO_3^- ion. The formation of mixed hydroxo-carbonato complexes such as $M(OH)(CO_3)^{2-}$, $M(OH)_2(CO_3)^{3-}$, $M(OH)(CO_3)_2^{4-}$, *etc.* can also be eliminated since the formation of these kinds of complexes would give a pH dependence to a family of plots of $\log(D/D_0)$ *vs.* $\log([CO_3^{2-}]/\text{mol dm}^{-3})$. This can be easily understood when we regard $CO_3 \cdot nH_2O^{2-}$ as HL and $OH \cdot CO_3 \cdot (n-1)H_2O^{3-}$ as L in Eqs. 8—10. Therefore, we can conclude that only carbonate complexes are present in the solution within the pH range studied. A least-squares study of these six series of experiments (113 points) resulted in:

$$\log(\beta_1/\text{mol}^{-1}\text{dm}^3) = 4.14 \pm 0.01,$$

$$\log(\beta_2/\text{mol}^{-2}\text{dm}^6) = 6.78 \pm 0.01.$$

Although higher complexes such as $M(CO_3)_3^{5-}$ cannot be excluded, it was difficult to detect them because the concentration of CO_3^{2-} and pHs greater than those adopted in the present experiment would result in the oxidation of Np(V) to Np(VI), as discussed below.

Discussion

Figure 3 shows the fraction of Np(V) in the form of a particular carbonato complex as a function of carbonate ion concentration at equilibrium, evaluated using the stability constants obtained in the present experiment. NpO_2^+ predominates when the equilibrium carbonate concentration is lower than $10^{-4.5}$ mol dm^{-3}. The equilibrium concentration of various species in distilled water exposed to air can be estimated with the use of Eq. 11 and Henry's law:

$$K_H = [H_2CO_3]/P_{CO_2}, \tag{14}$$

where P_{CO_2} is a partial pressure of carbon dioxide. By substituting $K_H = 10^{-1.48}$ mol dm^{-3} atm^{-1},[7] $P_{CO_2} = 10^{-3.5}$ atm, pK_1=6.02, pK_2=9.57, and

$$[H^+] \simeq [HCO_3^-], \tag{15}$$

we obtain:

$$[H_2CO_3] = 10^{-5.0}\ \text{mol dm}^{-3},$$

$$[H^+] = [HCO_3^-] = 10^{-5.5}\ \text{mol dm}^{-3},$$

$$[CO_3^{2-}] = 10^{-9.6}\ \text{mol dm}^{-3},$$

and

$$C_L = 10^{-4.8}\ \text{mol dm}^{-3}.$$

When experiments are carried out which exclude the dissolution of more carbon dioxide than the equilibrium concentration in distilled water exposed to air, Np(V) does not form substantial amount of carbonato complexes since the concentration of the carbonate ion never exceeds $C_L = 10^{-4.8}$ mol dm^{-3}. In some natural systems like sea water and inland water, however, the pH is controlled by other coexisting components than dissolved carbon dioxide. Hence, the concentration of carbon dioxide depends on the equilibrium pH controlled by the solutes. At equilibrium, the concentration of the carbonate ion can be expressed as:

$$[CO_3^{2-}] = P_{CO_2}K_HK_1K_2/[H^+]^2. \tag{16}$$

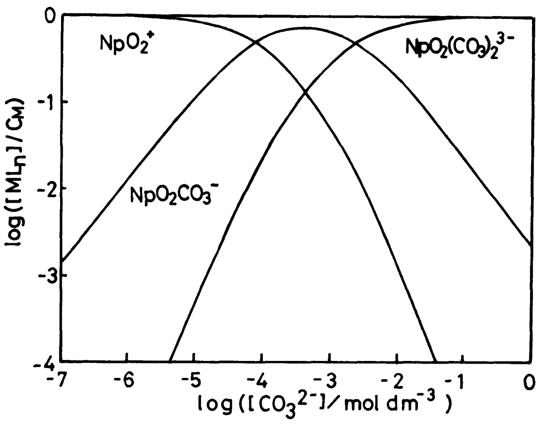

Fig. 3. Logarithmic diagram of the Np(V)-carbonate system.

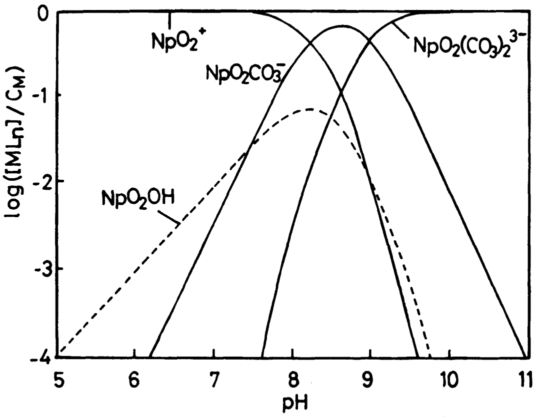

Fig. 4. Logarithmic diagram of the Np(V)-carbonate-hydroxide system at $P_{CO_2} = 10^{-3.5}$ atm.

Figure 4 shows the fractional distribution of the chemical species of Np(V) in a solution in equilibrium with an atmosphere of $P_{CO_2} = 10^{-3.5}$ atm as a function of pH. In the calculation, hydrolysis constants of Np(V) are taken from the table compiled by Allard *et al.*[8]

$$[MOH]/[M^+][OH^-] = 10^{5.0}\ \text{mol}^{-1}\ \text{dm}^3,$$

$$[M(OH)_2^-]/[M^+][OH^-]^2 = 10^{10}\ \text{mol}^{-2}\ \text{dm}^6.$$

As compared with the diagram in the absence of carbon dioxide,[9] chemical species of Np(V) predominating in a slightly alkaline solution drastically change from hydroxo to carbonato complexes. The precipitation of hydroxides should be markedly suppressed in the presence of an equilibrium amount of carbonate ions.

Diagrams for a tracer neptunium-carbonate-hydroxide system at $P_{CO_2} = 10^{-3.5}$ atm were constructed in the

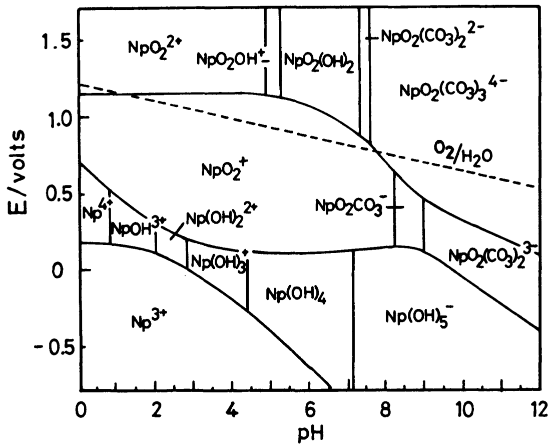

Fig. 5. Potential-pH diagram of tracer neptunium–carbonate–hydroxide system at $P_{CO_2}=10^{-3.5}$ atm.

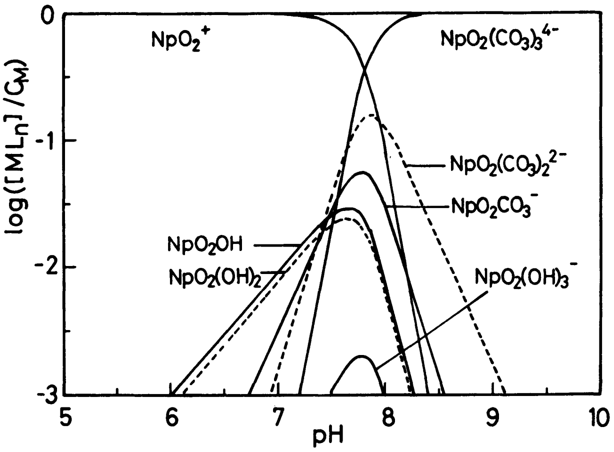

Fig. 6. Logarithmic diagram of tracer neptunium–carbonate–hydroxide system at $P_{CO_2}=10^{-3.5}$ atm and $P_{O_2}=1/5$ atm.

same manner as previously described.[9] They are shown in Figs. 5 and 6 in the form of potential-pH and fraction-pH diagrams. Hydrolysis constants and standard potentials for redox reactions were taken from a table compiled by Allard *et al.*[8] Since reliable data for carbonato complexing of Np(VI) are unavailable,[10] the data for U(VI):[6]

$$\log(\beta_1/\mathrm{mol^{-1}\,dm^3}) = 9.02,$$

$$\log(\beta_2/\mathrm{mol^{-2}\,dm^6}) = 16.22,$$

and

$$\log(\beta_3/\mathrm{mol^{-3}\,dm^9}) = 21.54$$

for

$$\beta_m = [\mathrm{UO_2(CO_3)_m}^{2-2m}]/[\mathrm{UO_2}^{2+}][\mathrm{CO_3}^{2-}]^m,$$

were used as a substitute. Since uranium and neptunium in the same valence state generally have similar formation constants, a small disparity in the constants of U(VI) and Np(VI) will only slightly influence the predictions. The formation of carbonato complexes of Np(III) and Np(IV) are considered negligible as compared with the formation of hydroxo complexes by the analogy of other ter- and quadrivalent actinoids. The fraction-pH diagram was constructed at the potential of the solution in equilibrium with 1/5 atm O_2:

$$E = 1.219 + (RT/F)\ln([\mathrm{H^+}]/\mathrm{mol\,dm^{-3}}). \tag{16}$$

This potential is shown by a dashed line in Fig. 5. Figures 5 and 6 clearly indicate that the sexivalent state is stabilized by carbonato complexing in slightly alkaline solutions at P_{CO_2}=1/5 atm. Even under reducing conditions, neptunium is not expected to form hydroxides which lead to precipitation but to form soluble carbonato complexes of Np(VI) or Np(V). Since it is not unusual for natural water to experience this kind of condition, the concentration of a carbonate ion must be carefully estimated or analyzed in order to predict the geochemical behavior of neptunium.

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