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Neptunium(IV) Hydrous Oxide Solubility under Reducing and Carbonate Conditions

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Solubility of Np(IV) hydrous oxide was approached from the oversaturation direction in the presence of reducing agents ($Na_2S_2O_4$, metallic Fe, metallic Zn) with and without 0.01 M total carbonate and in the range pH 6–14.2. In all of the above solutions in this range contacting Np(IV) hydrous oxide, Np concentrations were at or below the detection limit for Np ($\sim 10^{-8.3}$ M). No evidence was found for any amphoteric behavior of Np(IV). Although it was not possible to determine absolute hydrolysis constant or carbonate complexation constant values for Np(IV) from these experiments, the results do set an upper limit of $\log \beta_5^* < -24.7$ for $Np^{4+} + 5H_2O \rightleftharpoons Np(OH)_5^- + 5H^+$ and of $\log \beta_n$ ($Np^{4+} + nCO_3^{2-} \rightleftharpoons Np(CO_3)_n^{4-2n}$) <22.5, <27.9, <33.2, <38.5, and <41.6 for β_1–β_5, respectively. The results provide no evidence for such reactions, but if they are assumed to occur, these upper limits are many orders of magnitude lower than previously reported.

Introduction

Under reducing conditions such as those that might be present at some of the proposed radioactive waste disposal sites, actinides, especially uranium and neptunium, will be present in the tetravalent state. Therefore, solubility data for tetravalent actinide compounds are needed to determine the potential hazards of disposing of actinide-containing wastes in geologic repositories. Predictions about the solubility of different actinide compounds have recently been reported by several authors.[1-7] These predictions, for the most part, are based on thermodynamic data that are selected from unreliable and questionable experimental values and/or are in most cases estimated on the basis of techniques of uncertain validity. For example, the second, third, and fourth U(IV) hydrolysis constants have been estimated by assuming linear arithmetic progression among the logarithms of the equilibrium constants[8] from questionable experimental data[9] for the fifth hydrolysis constant. These data in turn have been applied to other actinides as well. However, Ryan and Rai[10] conducted careful experiments but found no evidence for the existence of the fifth U(IV) hydrolysis species, thereby casting serious doubt on the accuracy of values of the second, third, and fourth hydrolysis constants as well.

Moskvin and Gelman[11] studied Pu(IV) carbonate complexes in concentrated (0.36–3.6 M) carbonate solution, concluded that only the $PuCO_3^{2+}$ complex was present, and reported its formation constant value as $\beta_1 = K_1 = 9.1 \times 10^{46}$ on the basis of the solubility of Pu(IV) hydrous oxide as a function of carbonate concentration at pH 11.5. As was pointed out several years ago by one of the present authors to another[12] who was reviewing the entire field of plutonium chemistry, this value is much too high to be believable. Despite this and apparently because the Moskvin and Gelman[11] value was the only available experimental value until recently, several authors[2,13,14] who reviewed actinide thermodynamic data in the past have chosen to include this value (or a somewhat revised value based on the Moskvin and Gelman[11] data) in their calculations without critical comment as to its validity. This value for the Pu(IV) carbonate complex has been assumed to apply to other tetravalent actinides as well. Recently, Kim et al.[15] reported values for all of the formation constants of the Pu(IV) carbonate complexes $PuCO_3^{2+}$ through $Pu(CO_3)_5^{6-}$. Their value of $\beta_1 = 1.3 \times 10^{47}$ is slightly higher than even the Moskvin and Gelman[11] value. There are a variety of reasons for completely rejecting such carbonate formation constant values; four are discussed briefly. First, the formation constant for complexes between hard-acid metals and hard-base ligands having a constant ligand atom (in this case oxygen) can be semiquantitatively related to ligand basicity (as measured by acid association constant) and metal ion charge density. On this basis and by comparison of

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formation constants of a variety of oxygen donor complexes such as carboxylates etc. of tetravalent actinides and other metal ions of similar charge density, a reasonable value for the formation constant of $PuCO_3^{2+}$ of about 10^{12} with an upper limit of about 10^{15} is reached. Second, the formation constant, β_1, of the Pu(IV) ethylenediaminetetracetic acid (EDTA)[13] complex is about 10^{26}. EDTA has virtually the same basicity as carbonate, the first and second acid association constants are nearly identical for EDTA and carbonate,[16] and EDTA is hexadentate whereas CO_3^{2-} is at most a "short-bite" bidentate. On the basis of the well-known chelate effect,[17] it can be expected that at least β_2, and most likely β_3 ($\beta_3 = K_1K_2K_3$) and possibly β_4 for carbonate, should be smaller than β_1 for EDTA. (The only reason that β_1 for EDTA could conceivably be smaller than β_3 for carbonate would be because two of the EDTA donor atoms are nitrogen instead of oxygen.) On the basis of a reasonable decreasing progression in K_1, K_2, K_3, etc., this would also indicate a likely value of no more than about 10^{12} for β_1 for Pu(IV) carbonate. Third, formation of $PuCO_3^{2+}$ at high pH can be expressed as

$$PuO_2 \cdot xH_2O + CO_2 + 2H^+ \rightleftharpoons PuCO_3^{2+} + (x + 1)H_2O \quad (1)$$

It can be seen from the pH dependence of this reaction, if the $PuCO_3^{2+}$ species had a sufficiently large formation constant to allow an even measurable concentration of such an ion in the solutions studied by Moskvin and Gelman,[11] namely pH 11.5 and 0.36–3.6 M CO_3^{2-} solutions having equilibrium CO_2 pressures less than that of air, it would be the principal species present in strong acid solutions (such as >1 M $HClO_4$) in equilibrium with the CO_2 content of air. Because such carbonate complexes are not observed, the conclusions of Moskvin and Gelman[11] and Kim et al.[15] are most certainly incorrect. Equations similar to eq 1 can be extended to higher carbonate complexes (and to other metals with highly insoluble hydroxides or hydrous oxides) to show that only anionic complexes can contribute to any appreciable extent to solubility in carbonate or bicarbonate solutions. Since, in the case of tetravalent actinides, anionic complexes involve at least three carbonates, solubilities can be expected to drop rapidly with decrease in carbonate concentration below those known to occur in >1 M carbonate–bicarbonate solutions. Fourth, the measured Pu(IV) concentration[18] in equilibrium with Pu(IV) hydrous oxide at pH 8 in equilibrium with air is definitely $<10^{-10}$ M, whereas the value predicted from the results of Kim et al.[15] or Moskvin and Gelman,[11] using the hydrous oxide solubility product of Rai,[19] is approximately 4×10^8 M.

The Np(IV)–ammonium carbonate system has been studied[20] by a solubility method at pH values of 8.6–8.8 and up to 2.2 M $(NH_4)_2CO_3$. It was concluded that the single species $Np(OH)_4CO_3^{2-}$ was formed with a formation constant from the Np^{4+} ion of 1.20×10^{53}. Unfortunately, the method used to calculate this constant was completely erroneous. Errors included subtraction of a large constant value from all the measured solubilities in order to make this fit a first-power carbonate dependence, assumption that total carbonate plus bicarbonate is entirely carbonate at pH values where bicarbonate predominates and the carbonate to bicarbonate ratio is pH dependent, and provision of no evidence that the assumed "$Np(OH)_4 \cdot xH_2O$" was the equilibrium solid phase in these Np(IV)-saturated concentrated ammonium carbonate solutions, whereas three different ammonium tetravalent actinide (An) carbonate salts, $(NH_4)_2An(CO_3)_3 \cdot xH_2O$, $(NH_4)_4An(CO_3)_4 \cdot xH_2O$, and $(NH_4)_6An(CO_3)_5 \cdot xH_2O$, have been reported[21] to have been isolated from ammonium carbonate solutions. Correction of the first two of these errors indicates that the reported solubilities actually show somewhat less than a half-power dependence on carbonate. In addition, the single absorption spectrum presented[20] would appear to indicate an appreciable fraction of Np(VI), or an impurity with a similar absorption spectrum. If, as assumed,[20] Np(IV) hydrous oxide is the solid phase and $Np(OH)_4CO_3^{2-}$ is the solution species, the Np(IV) solubility in these strong carbonate solutions would be pH independent above about 11.5 where carbonate dominates but would decrease markedly below this pH as carbonate converts to bicarbonate. This is the opposite of what was found for Pu(IV) by the same author,[11] and also his Pu(IV) solubilities[11] were much less at pH 11.5 than were the Np(IV) solubilities[20] at pH 8.6–8.8 for the same range of total carbonate levels. We have also observed a greater solubility of U(IV) in bicarbonate than in carbonate solutions. On these bases, the conclusions of ref 20 appear to be without merit.

Although our recent experimental results (unpublished results of Rai, Swanson, and Ryan; estimates from Strickert and Rai[22]) put the logarithm of the solubility product of Np(IV) hydrous oxide at about −53.5, the data for (1) Np(IV) hydrolysis constants, (2) redox boundary between Np(IV) and Np(V), and (3) Np(IV) carbonate complexes are not available. These data are needed to determine Np concentrations in equilibrium with Np(IV) compounds under waste disposal site pH, E_h, and carbonate concentrations. Therefore, this study was undertaken to determine the solubility of Np(IV) hydrous oxide under reducing conditions, a range in pH values, and carbonate concentration as high as might be expected under waste site conditions.

Experimental Section

Reagents. Neptunium-237 was purified by anion exchange in nitric acid,[23] was essentially free (<34 ppm ^{239}Pu and ~2 ppm ^{240}Pu) of other α-emitting elements or isotopes, and contained <100 ppm other metallic impurities. The anion-exchange product was thermally evaporated to incipient denitration, with conversion to Np(VI). The residue was diluted about 10-fold with 12 M HCl and was again taken to incipient solidification, and this step was repeated five or six more times to thoroughly remove nitrates. The final solution was taken up in 6 M HCl. H_2O_2 (30%) was added to the solution to the point of precipitation of large amounts of Np(IV) peroxide, but thermal decomposition of the H_2O_2 produced about 15% reoxidation to Np(V) with the remainder Np(IV). The solution was then reduced to a mixture of Np(IV) and Np(III) in the cathode compartment of a partitioned electrolytic cell using a Pt-gauze cathode and graphite anode. The Np(III) reverted rapidly to Np(IV) in the presence of air. Np(IV) remained stable in the 1.35 M Np–6 M HCl stock solution.

Deionized water was deaerated by boiling and thorough sparging at room temperature with an inert gas (>99.99% N_2 or Ar with only a few parts per million oxygen). Two different NaOH stock solutions (10.5 and 1.93 M) were prepared in an inert atmosphere from a new bottle of reagent grade pellets of NaOH. The 10.5 M NaOH solution was found to contain 0.0152 M carbonate[10] and was treated with a 7.5% excess of $BaCl_2$ to reduce carbonate through $BaCO_3$ precipitation. This solution was kept in a closed container in an inert atmosphere for several weeks before use. The 1.93 M NaOH solution, freshly prepared at the time of the experiments, was used only in experiments involving the effects of carbonate on the solubility of Np(IV) hydrous oxide.

Because the precise E_h boundary, as a function of pH, between Np(IV) and Np(V) is not known and because appropriate redox agents to study this boundary have also not been tested, several redox agents were tested for their efficiency in maintaining Np in the reduced state. These redox agents included $Na_2S_2O_4$, Fe, Ni, Pb, and Zn. $Na_2S_2O_4$ was obtained from Sigma Chemical, and an alkaline 1 M stock solution was prepared under N_2 immediately before use. Iron (powder, 325 mesh), Ni (powder, grade 1), and Pb (powder, 200 mesh) were from Alfa Products, and Zn (dust) was from the Scientific Supply Co.

General Procedures. All experiments were conducted in a glovebox with a prepurified N_2 (99.99% with a few ppm oxygen) atmosphere. Basic solutions of 0.05 M $Na_2S_2O_4$ in glass centrifuge tubes were spiked with 0.03 mL of Np(IV) stock solution containing approximately 10 mg of Np, taking care that the solutions never became acidic. Solution

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Table I. Equilibrium Constants and Standard Reduction Potentials for Different Redox Agents[26]

reaction	log *K*	E°, V
$2SO_3^{2-} + 2H_2O + 2e^- \rightleftharpoons S_2O_4^{2-} + 4OH^-$	−37.86	−1.12
$Fe^{2+} + 2e^- \rightleftharpoons Fe$	−13.82	−0.409
$Zn^{2+} + 2e^- \rightleftharpoons Zn$	−25.79	−0.763
$Pb^{2+} + 2e^- \rightleftharpoons Pb$	−4.25	−0.126
$Ni^{2+} + 2e^- \rightleftharpoons Ni$	−7.77	−0.23

volumes were adjusted to 40 mL, and pH values were adjusted to cover a range of pH 8–12.5 with perchloric acid or the carbonate-free NaOH stock solution. A 40-mL portion of 0.105, 0.42, 0.63, 0.84, 1.05, 1.55, and 2.10 M NaOH (carbonate free) containing 0.05 M $Na_2S_2O_4$ was also each spiked with 0.03 mL of Np(IV) stock solution. The precipitation of Np(IV) hydrous oxide and neutralization of excess acid consumed only 0.004 M, which is about 4% of the lowest hydroxide concentration used. Samples were sealed immediately after preparation and shaken until analyzed.

For experiments using metal reductants, 0.03-mL portions of Np(IV) stock solution were added to glass centrifuge tubes containing 40 mL of deaerated deionized water and 0.1 g of Fe, Ni, Pb, or Zn powders. The pH values of these suspensions were adjusted to cover a range of 2.5–8.5, and they were equilibrated as discussed above.

For the carbonate studies, samples containing 0.05 M $Na_2S_2O_4$ or 2.5 mg of Fe/mL and 0.01 M $NaHCO_3$ were adjusted to a range in pH values with HCl or freshly prepared NaOH stock solution (1.93 M) and were equilibrated as discussed above.

Measurements. Redox potentials were measured with a platinum electrode calibrated against quinhydrone buffers. The pH was measured to within 0.025 unit with a combination-glass electrode calibrated against pH buffers covering the range of pH values in the experiments.

Because of the inadequacy of centrifugation alone,[18] Amicon type F-25 Centriflo membrane cones (Amicon Corp., Lexington, MA) with effective 25 000 molecular weight cutoffs and approximately 18-Å pore sizes were used to effectively separate solids from solutions. Pretreatment steps, as suggested by Rai,[19] consisted of (1) washing and equilibrating the filters with deionized waters adjusted to the pH values of the given samples to avoid precipitation or dissolution of the solid phase due to change in the pH during filtration, and (2) passing a small aliquot of the sample through the filters (this filtrate was discarded) to saturate any possible adsorption sites on the filters and filtration containers.

Oxidation state analyses of the Np stock solution were by spectrophotometry and of dilute Np solutions were by solvent extraction techniques. Neptunium(IV) concentrations were determined from 0.5 M TTA in xylene extractions from nearly equal volumes of filtered solutions containing ~1 M HCl from which only monomeric Np(IV) extracts.[24] The total and solvent-extracted Np concentrations were determined by liquid scintillation α counting using Packard Insta-Gel and a Beckman (Model LS-9800) counter. The minimum detectable counts and thus the detection limits were determined by eq 2 from Curie,[25] where T is the counting time in minutes and R_B is the background rate (background divided by counting time in minutes).

$$\text{minimum detectable count rate} = 2.71/T + 4.65(R_B/T)^{1/2} \quad (2)$$

Results and Discussion

The thermodynamic equilibrium constants and standard equilibrium potentials of redox agents ($Na_2S_2O_4$, Zn, Fe, Ni, and Pb in order of increasing potential) used in this study are shown in Table I. Because these redox agents (1) are not redox buffers, (2) have not been previously tested as to whether they are kinetically active and appropriate for the Np system, and (3) have not been previously tested for their pH range of applicability, the measured redox values may not have any meaning in the thermodynamic sense. The intention in this study was to maintain low redox potential, not necessarily a fixed potential, where higher oxidation states of Np are not the dominant species in solution or at least are below our measurement detection limit. Under oxidizing conditions comparable to air, Np(V) is the dominant solution oxidation state and the solubility will decrease by a factor of 10 with each unit decrease in pe (negative logarithm of the electron activity) as noted in eq 3. The solubility in terms of

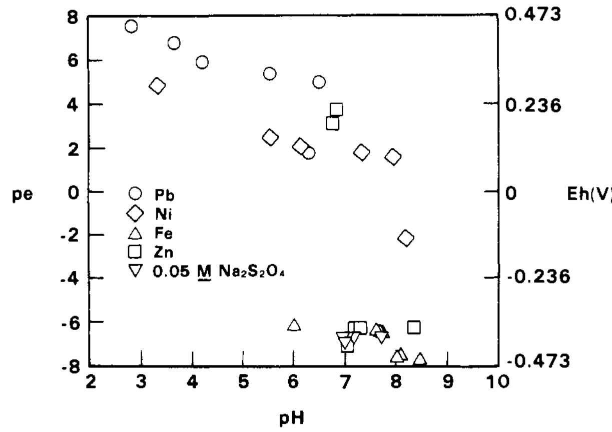

Figure 1. Redox potentials, measured with a platinum electrode, of Np(IV) hydrous oxide suspensions containing different redox agents after about 8 days of equilibration.

$$NpO_2{\cdot}H_2O \rightleftharpoons NpO_2^+ + xH_2O + e^- \quad (3)$$

Np(IV) is independent of pe as shown in eq 4. As pe decreases

$$NpO_2{\cdot}xH_2O \rightleftharpoons Np^{4+} + 4OH^- + (x-2)H_2O \quad (4)$$

(more reducing) further, the dominant solution oxidation state will become Np(III) whose concentration increases by a factor of 10 per unit decrease in PE as shown in eq 5. From the

$$NpO_2{\cdot}xH_2O + e^- \rightleftharpoons Np^{3+} + 4OH^- + (x-2)H_2O \quad (5)$$

logarithm of the solubility product of $NpO_2{\cdot}xH_2O$ of −53.5 (unpublished data of Rai, Swanson, and Ryan) and accepted Np(III)–Np(IV) and Np(IV)–Np(V) redox potentials, it is easily shown that above pH 3 in the absence of hydrolysis Np(IV) would never be the dominant solution oxidation state at any value of pe. At all pH values, the minimum solubilities of $NpO_2{\cdot}xH_2O$ as a function of pe will occur when the concentration of Np(IV) species is at a maximum relative to Np(III) and Np(V) species. Where this occurs will depend on all the hydrolysis constants for the three oxidation states. In any case, regardless of pe, the measured solubility will be an upper limit for Np(IV) because its concentration is pe independent. The measured redox potentials of many of the equilibration solutions containing various reducing agents are shown in Figure 1. The values show that $Na_2S_2O_4$, Fe, and Zn in general maintained redox potentials close to the boundary at which water is reduced to produce H_2. Lead and nickel did not maintain such low potentials, and measured solubilities in these solutions were well above the detection limig ($10^{-4.4}$–$10^{-7.5}$ M). Oxidation state analyses of these solutions by TTA extraction indicated that essentially all the Np was in oxidized form, either Np(V) or Np(VI), in all samples. No further attempt was made to interpret these results.

The Np concentrations in the presence of $Na_2S_2O_4$ are reported in Table II. The results indicate that Np concentrations at pH values >7.7 are below are near the detection limit of Np ($10^{-8.3}$ M). Although the original samples were adjusted to obtain a large range (pH 8–14.2) and separation in pH among samples, the pH values of those initially at or below pH 11.0 dropped and were found to be between pH 6.99 and 7.11. Since oxidation of $S_2O_4^{2-}$ consumes hydroxide (Table I), it is felt that this pH decrease in the initially low hydroxide samples is due to oxidation by residual O_2 present in the solutions or from the glovebox atmosphere. The further disproportionation of $S_2O_4^{2-}$ under acidic conditions producing a variety of products such as sulfur and thiosulfate is known to be rapid,[17] and this also lowers pH. Thus, the reducing power of $S_2O_4^{2-}$ would be affected. The samples with pH values of <7.2 on an average contained Np 1.5 orders of magnitude higher than the detection limit ($10^{-8.3}$ M). Despite our low measured potentials, we believe this is a result of ineffectiveness of $S_2O_4^{2-}$ at the lower pH values either because of the complexing ability of its disproportionation products or because of the effect

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Table II. Measured Np(IV) Hydrous Oxide Solubilities at a 9- to 12-Day Contact Time in 0.05 M $Na_2S_2O_4$ Solutions Adjusted to Different pH Values with NaOH

no.	pH[a]	PE[b]	log [Np, M]
600	6.99	−6.69	−6.46
601	7.05	−6.63	−6.98
602	7.12	−6.63	−6.67
603	6.95	−6.57	−6.47
604	7.11	−6.66	−6.81
605	7.10	−6.69	−6.89
606	7.71	−6.71	−8.02
607	11.24	−6.84	<−8.29
608	12.36	−6.79	<−8.29
609	12.46	−6.66	<−8.29
610	12.91	−6.59	<−8.29
611	13.19	ND	<−8.29
612	13.46	ND	<−8.29
613	13.63	ND	<−8.29
614	13.75	ND	<−8.29
615	13.85	ND	−8.26
616	14.03	ND	−8.06
617	14.18	−8.16	−7.92

[a] The starting pH values of sample no. 600–607 were adjusted to 8.0, 8.5, 9.0, 9.5, 10.0, 10.5, 11.0, and 11.5, respectively. Samples no. 610–617 contained 0.015, 0.21, 0.42, 0.63, 0.84, 1.05, 1.55, and 2.10 M NaOH, respectively. The pH values of these samples were calculated from the NaOH concentrations and mean ionic activities reported by Hamer and Wu.[27] [b] ND = not determined.

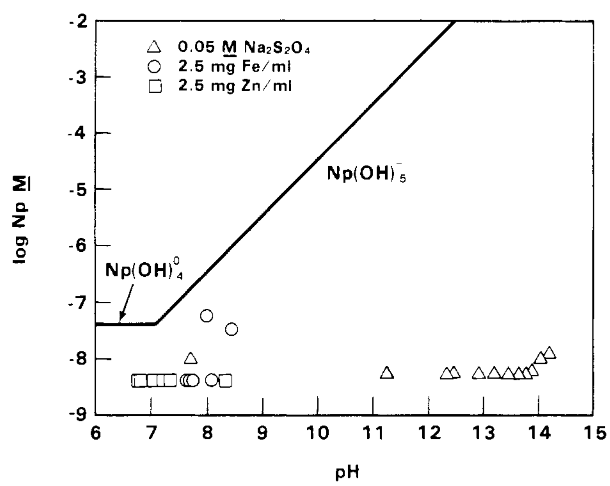

Figure 2. Measured apparent solubilities of Np(IV) hydrous oxide in different redox agents (detection limit for Np $\sim 10^{-8.3}$–$10^{-8.4}$ M). Solid lines represent predicted solubilities from currently available thermodynamic data with log $K_{sp} = -53.5$ from unpublished data of Rai, Swanson, and Ryan and the values of hydrolysis constants ($Np^{4+} + nH_2O \rightleftharpoons Np(OH)_n^{4-n} + nH^+$) of $Np(OH)_4^0$ (log $\beta_4^* = 9.9$) and of $Np(OH)_5^-$ (log $\beta_5^* = -17$) from Allard et al.[1]

on its reducing ability. This conclusion is supported by the solubility results using iron or zinc as reductants, where in the range pH 6–7.5 all samples were found to be below the detection limit of $10^{-8.3}$ M Np. Because of the pH dependence of the dithionite–sulfite couple (Table I), both iron and zinc should be stronger reducing agents than dithionite in this pH region and the oxidation products, Fe(II) and Zn(II), should be adequately soluble to not add a complication in their use.

The solubilities, using $Na_2S_2O_4$ in the higher pH region and Fe and Zn in the lower pH region, plotted in Figure 2 show that under reducing condition and pH values >6 the Np concentrations in solutions contacting Np(IV) hydrous oxide (approached from oversaturation direction) are near or below the detection limit for Np of $10^{-8.3}$ M. The experimental results are compared in Figure 2 with values based on thermodynamic predictions using the logarithm of the solubility product value of −53.5 (unpublished data of Rai, Swanson, and Ryan) for eq 4 and the estimated hydrolysis constant data reported by Allard et al.[1] The experimental results show no evidence for amphoteric behavior of Np(IV) and thus the existence of $Np(OH)_5^-$, consistent with our earlier results on U(IV),[10] which is in sharp contrast to predictions based on estimated thermodynamic data. If it is assumed that the $Np(OH)_5^-$ species exists at all, the log β_5^* value of the fifth hydrolysis constant (eq 6) must be <−24.7 as compared with −17

$$Np^{4+} + 5H_2O \rightleftharpoons Np(OH)_5^- + 5H^+ \quad (6)$$

estimated by Allard et al.[1] Because the reported values of the second, third, and fourth hydrolysis constants were estimated by interpolation between the first and fifth constants, they must also be considered incorrect even if the interpolation method[8] is considered valid.

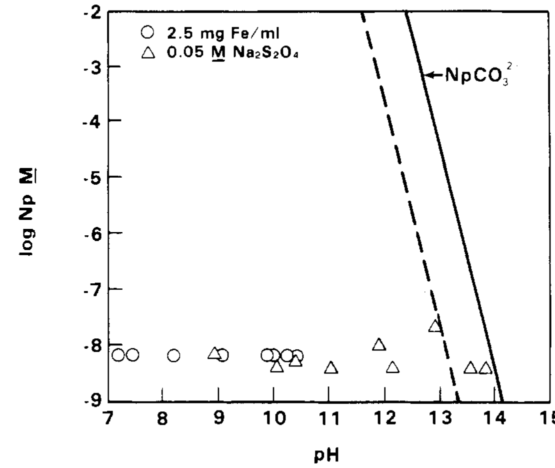

Figure 3. Measured solubility of Np(IV) hydrous oxide in the presence of 0.01 M total carbonate and Fe and $Na_2S_2O_4$ as reductants (detection limit for Np $\sim 10^{-8.2}$–$10^{-8.4}$ M). Using log $K_{sp} = -53.5$ for Np(IV) hydrous oxide from unpublished data of Rai, Swanson, and Ryan and (1) assuming values of log β_1 for Pu(IV) carbonate complex[15] apply to Np, the calculated activity of $NpCO_3^{2+}$ is represented by the solid lind and (2) assuming log β_1 of Np(IV) carbonate to be lower than log β_1 of Pu(IV) carbonate by the same ratio that the logarithm of the association constant, log $(1/K_{sp})$, of Np(IV) hydrous oxide is lower than that of Pu(IV) hydrous oxide, the calculated activity of $NpCO_3^{2+}$ is given by the dashed line. The activities of higher carbonate complexes, and thus the total Np(IV) hydrous oxide solubility, would be several orders of magnitude higher than that of $NpCO_3^{2+}$ on the basis of the published[15] values of β_2–β_5.

The effect of 0.01 M total carbonate on the Np(IV) hydrous oxide solubility in the appropriate pH range and in the presence of $Na_2S_2O_4$ and Fe as reductants was studied (Figure 3). The results show that the Np concentrations are near or below the detection limit, as is the case in the absence of carbonate, indicating no measureable effect of 0.01 M total carbonate on the solubility of Np(IV) hydrous oxide. The thermodynamic data for Pu(IV) carbonate complexes reported by Kim et al.[15] if assumed to apply to the adjacent actinide Np, indicates that Np(IV) hydrous oxide should have been very soluble. Although we cannot calculate from our data the value for the Np carbonate complexes, our experimental results show that the values for the carbonate complexes reported by Kim et al.[15] are very much in error. On the basis of our data, the values for log β_1 through log β_5 (eq 7) must be <22.5,

$$Np^{4+} + nCO_3^{2-} \rightleftharpoons Np(CO_3)_n^{4-2n} \quad (7)$$

<27.9, <33.2, <38.5, and <41.6, respectively; whereas, the corresponding log β_1 through log β_5 for Pu(IV) carbonate complexes reported by Kim et al.[15] are 47.1, 55.0, 57.9, 59.6, and 62.4, respectively. These calculations show that the log β_n values reported in the literature are >18 orders of magnitude too high. The actual values for the carbonate complexes are expected to be several orders of magnitude lower than the limits calculated from our data.

Although it is not possible to determine either absolute hydrolysis constant or carbonate complexation constant values for Np(IV) from these results, several significant conclusions can be drawn: (1) Solubility of Np(IV) hydrous oxide under reducing conditions can be used to set upper limits on solubility-controlled concentrations of Np, and these concentrations are below the maximum permissible concentrations in uncontrolled discharge.[28] (2) Most carbonate ground waters (<0.01 M total carbonate) will not significantly increase the Np(IV) hydrous oxide solubility above the maximum permissible concentrations. (3) Contrary to predictions based on thermodynamic data reported in the literature, no evidence was found for amphoteric behavior of Np(IV). (4) The values of tetravalent actinide carbonate complexes reported in the literature are grossly in error.

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Stabilization of the Monovalent Nickel Complex with 1,4,8,11-Tetraazacyclotetradecane in Aqueous Solutions by N- and C-Methylation. An Electrochemical and Pulse Radiolysis Study

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The divalent nickel complexes with 1,4,8,11-tetraazacyclotetradecane (L_1), 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (L_2), *meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (L_3), and 1,4,5,7,7,8,11,12,14,14-decamethyl-1,4,8,11-tetraazacyclotetradecane (L_4) were reduced by reactions with e_{aq}^- and $CO_2^-\cdot$ and by electrochemical reactions in aqueous solutions. The redox potentials of the NiL_i^{2+}/NiL_i^+ couples are −1.58, −1.15, −1.42, and −0.98 V vs. SCE for i = 1, 2, 3, and 4, respectively. The UV absorption bands of NiL_i^+ are attributed to CTTS transitions. The kinetics of reduction of $Co(NH_3)_6^{3+}$, $Ru(NH_3)_6^{3+}$, O_2, and N_2O by NiL_i^+ are reported and discussed. The self-exchange rates of reaction between NiL_i^+ and NiL_i^{2+} were calculated by using the Marcus cross relation. The EPR spectra of NiL_2^+ and NiL_4^+ are reported. The complexation of NiL_i^{2+} by OH^- was studied. The results are discussed in detail. NiL_2^+ and NiL_4^+ are suggested as new, powerful, easily attainable single-electron-reducing agents that can be used over a wide pH range in aqueous solutions.

Introduction

We have recently observed that the reduction of the planar isomer of (*C-meso*-1,4,5,7,7,8,11,12,14,14-decamethyl-1,4,8,11-tetraazacyclotetradecane)nickel(II), NiL_4^{2+}, yields the corresponding monovalent complex, which is surprisingly stable in aqueous solutions.[2] The kinetic stability of NiL_4^+ in comparison to that of NiL_3^+, L_3 ≡ *C-meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, was attributed to two main factors; (a) The ligand loss reaction

$$NiL^+ + 2H_3O^+_{aq} \rightarrow Ni^+_{aq} + LH_2^{2+} \quad (1)$$

is hindered or at least considerably slowed down by N-methylation. (b) The two-electron reduction of water

$$NiL^+ + 2H^+ \rightarrow NiL^{3+} + H_2 \quad (2)$$

is endothermic for L = L_4 whereas it is exothermic for L = L_3.[3] The differences in the redox potentials of NiL_4^{2+} and NiL_3^{2+} were attributed to the more hydrophobic nature of NiL_4^{2+} in comparison with that of NiL_3^{2+} and/or to the fact that the nickel–nitrogen bond length is larger in NiL_4^{2+}.[2]

Due to the interest in the effect of macrocyclic ligands on the redox properties of transition-metal complexes in general and nickel complexes specifically,[4-9] we decided to extend these studies. In this report we analyze the effect of nitrogen and carbon methylation of (1,4,8,11-tetraazacyclotetradecane)nickel(II), NiL_1^{2+}, on the redox couple NiL^{2+}/NiL^+ by comparing the chemical properties of NiL_1^+, NiL_2^+, NiL_3^+, and NiL_4^+ (L_2 = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane). In addition to the electrochemical properties and specific rates of redox reactions studied by pulse radiolysis also the visible spectra of NiL^{2+} and pK values for the reaction

$$NiL^{2+} + OH^- \rightleftarrows NiL(OH)^+ \quad (3)$$

are reported. The last two properties are used as indicators for the ligand field strength and for steric hindrance along the z axis in the four complexes studied.

Experimental Section

Materials. The complexes $NiL_1(ClO_4)_2$ and $NiL_3(ClO_4)_2$ were prepared from the free ligands and $Ni(CH_3CO_2)_2$ as earlier described.[9] $NiL_2(ClO_4)_2$ and $NiL_4(ClO_4)_2$ were prepared by N-methylation of $NiL_1(ClO_4)_2$ and $NiL_3(ClO_4)_2$, respectively, with use of the method described by Barefield et al.,[10] i.e. deprotonation by solid KOH and methylation by CH_3I in Me_2SO. The IR spectra of $NiL_2(ClO_4)_2$ and $NiL_4(ClO_4)_2$ in KBr pellets showed no bands due to N–H stretching, and the proton NMR spectra of these complexes were identical with those reported in the literature.[10]

All other materials were of AR grade and were used without further treatment. All solutions were prepared with use of heat-distilled water that was then passed through a Millipore setup, the final resistance being >10 MΩ.

Electrochemical Measurements. A three-electrode cell was used. Working electrodes were a dropping mercury electrode (DME) for polarograms, the Metrohm E 410 hanging-mercury-drop electrode

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(3) $E°$ for the couple $NiL_3(H_2O)_2^{3+}/NiL_3^{2+}$ was estimated as $E°$ = 0.93 V vs. SCE.[4] As $NiL_3(H_2O)_2^{3+}$ has a pK_a at 3.7,[5] $E°$ is even lower in neutral solutions. We were unable to oxidize NiL_4^{2+} even by $Br_2^-\cdot$.[2] Furthermore, the data in this work suggest that $E°_{NiL_4^{3+}/NiL_4^{2+}} > E°_{NiL_3^{3+}/NiL_3^{2+}}$.

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