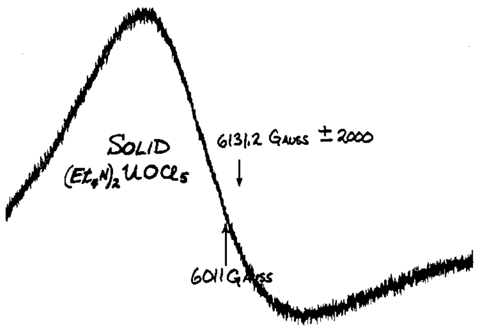

Figure 4.—The esr spectrum of pure solid $[(C_2H_5)_4N]_2UOCl_5$ at ambient temperature.

to electronic spectra of the $UOCl_5{}^{2-}$ species, with all evidence that the organic molecules are indeed coordinated. The spectra, to be more fully explored in a future paper which will deal with other U(V) complexes now in preparation and study, support all of the deductions made in this paper regarding the $UOCl_5{}^{2-}$ spectrum. The esr spectra of the new compounds are more complicated and correspondingly more interesting and these also will be discussed at a later time.

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CONTRIBUTION FROM THE LABORATORIO DI CHIMICA E TECNOLOGIA DEI RADIOELEMENTI DEL CONSIGLIO NAZIONALE DELLE RICERCHE, PADUA, ITALY, AND ISTITUTO DI CHIMICA GENERALE, UNIVERSITÀ DI CATANIA, CATANIA, ITALY

Soluble Intermediates in the Hydrolysis of Neptunium(VI) and Comparison with Other Actinides(VI)

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The soluble hydroxo complexes of the neptunyl(VI) ion have been studied in aqueous solution with 1 *M* (Na)ClO_4 at 25° by emf measurements of $[H^+]$. Trial values of the equilibrium constants were estimated by graphical procedures and refined by a least-squares program. The main species produced and their refined hydrolysis constants are as follows: NpO_2OH^+, $\log {}^*\beta_{11} = -5.17 \pm 0.03$; $(NpO_2)_2(OH)_2{}^{2+}$, $\log {}^*\beta_{22} = -6.68 \pm 0.02$; $(NpO_2)_3(OH)_5{}^+$, $\log {}^*\beta_{53} = -18.25 \pm 0.02$. Comparison of these results with some available data on the hydrolysis of uranyl(VI) and plutonyl(VI) indicates a close analogy in hydrolysis schemes for the three ions. The trend in acidity with increasing atomic number is briefly discussed.

Introduction

The four actinide elements uranium, neptunium, plutonium, and americium in their 6+ oxidation states exist in acid solution as hydrated species of the type $MO_2{}^{2+}$ [1] and these species constitute a series of ions which are interesting for comparative studies.

As far as the hydrolytic behavior in aqueous solutions of these oxy cations is concerned the most detailed studies available relate to the uranyl(VI) ion.[2,3] From these studies it is now well known that by increasing the pH of an acidic U^{VI} solution soluble hydroxo species are formed, which are predominantly polynuclear in nature, and finally, on addition of sufficient base, highly insoluble products are obtained. In particular, by means of accurate experimental methods and adequate treatments of the data, it has been possible more recently to determine the stoichiometry and the formation constants of the soluble hydroxo complexes present in important amounts in U^{VI} solutions with various ionic media.[4-11]

Data regarding the hydrolytic reactions of Pu^{VI} are rather scant in the literature. Until 1955 there were some studies of Kraus and his collaborators carried out by acid–base titrations and high-speed centrifugations (see references in ref 3). From those works it was possible to acquire some fundamental information on the hydrolytic behavior of plutonyl(VI), but the polynuclear species were not identified and their equilibrium constants were not obtained. Some data on this subject were subsequently published by Russian workers,[12,13] but they differ considerably from those reported by Kraus. More recently, in our laboratory the hydrolytic reactions of Pu^{VI} were reexamined experimentally in 1 *M* perchlorate medium at 25° and the soluble hydroxo complexes present in important amounts in the range $0 \leqslant \bar{n} \leqslant 1$ ($\bar{n}$ is the average number of OH^- bound per $PuO_2{}^{2+}$) were determined together with their equilibrium constants.[14]

There is essentially no published information regarding the hydrolytic reactions of Am^{VI}.

As for the hydrolysis of Np^{VI}, the only data available at the present time are those reported by Kraus and Nelson.[3,15] They refer to acid–base titrations which

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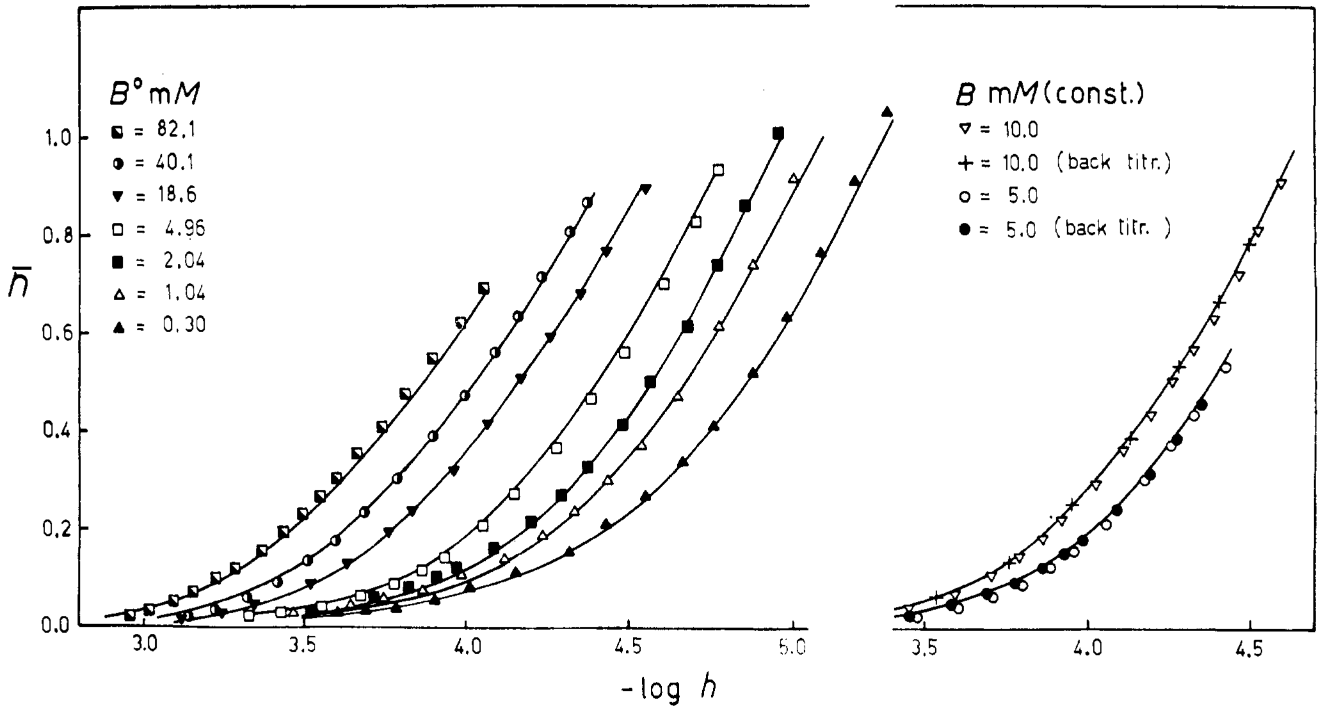

Figure 1.—Average number of OH^- ions bound per NpO_2^{2+}, $\bar{n}$, as a function of $-\log h$. Curves have been drawn through points computed with the constants obtained by a least-squares fit (Table I).

were carried out in order to establish the relative acidities of the MO_2^{2+} ions (M = U, Np, Pu). From the titration curves it was concluded that the acidity of the NpO_2^{2+} ion is intermediate between those of the UO_2^{2+} and PuO_2^{2+} ions. Further, it was ascertained that there are differences in the precipitation behavior of the three ions and that during the titration of all three elements soluble polymeric hydrolysis products are formed. However, quantitative data on the mechanism of hydrolysis of Np^{VI} were not obtained.

It seemed to us worthwhile to provide quantitative information about the nature and the formation constants of the hydroxo complexes formed in Np^{VI} solutions. These data are expected to be helpful for a better characterization of the properties of Np^{VI} in solution and also for making more profitable a comparison with the behavior of the other actinide(VI) ions under the same experimental conditions.

This paper presents acidity measurements of solutions containing neptunyl(VI) at various concentrations in the range 0.3–80 m*M*. The measurements were made at a temperature of 25° and in a medium 1 *M* in $(Na)ClO_4$.

Experimental Section

Preparation of Solution.—Neptunium (isotope ^{237}Np) was purified before use by absorption on Dowex 1X4 anion-exchange resin from 8 *M* nitric acid as neptunium(IV) and eluted in 0.3 *M* nitric acid.[16] The eluate was concentrated to about 1 *M* nitric acid, obtaining in this way a neptunium(V) solution. The neptunium(V) hydroxide was then precipitated with sodium hydroxide, washed carefully with water, and dissolved in 1 *M* perchloric acid to give a solution of neptunium(V).

The neptunium(VI) solutions were prepared by electrolytic oxidation of a neptunium(V) solution (electrodes of platinum wire, cathode and anode compartments separated by fine sintered-glass disks, magnetic agitator in the anode compartment).

The oxidation state of neptunium was checked spectrophotometrically. The observed absorption spectra of neptunium(VI) in perchloric acid solution were very similar to those already reported by other authors.[17] The absence of appreciable amounts of neptunium(V) and -(IV) was checked by absence of absorption at their respective absorption bands.[17]

The concentration of neptunium was determined by potentiometric titration of a separated aliquot of the NpO_2^{2+} solution with standard iron(II) solution.[18]

The concentration of the free perchloric acid in the Np^{VI} solution was determined by way of ionic-exchange analysis on a cationic resin in the hydrogen ion form (Dowex 50W-X4). If a total concentration of acid $[H^+]_t$ is found, then the original $[H^+] = [H^+]_t - 2[NpO_2^{2+}]$.

Using standard solutions of NaOH and $NaClO_4$, the solutions containing $NpO_2(ClO_4)_2$, $HClO_4$, and $NaClO_4$ were eventually adjusted to the concentration required for the measurements.

Spectrophotometric measurements at various times indicate that in these solutions neptunium(VI) is stable enough for our purposes. No appreciable reduction is observable during the first 24 hr; only after 2 days roughly 0.5% of neptunium(V) is detectable. The measurements were performed on fresh solutions.

Reagent grade sodium perchlorate was recrystallized three times from water and the stock solutions were standardized by ionic-exchange analysis on a cationic resin in the hydrogen ion form.

Perchloric acid solution was standardized against $KHCO_3$ and checked against standard NaOH solution.

Sodium hydroxide solutions were prepared by dilution with deaerated water of a saturated NaOH p.a. solution, which was left standing in a polyethylene bottle for several days. Standardizations were carried out with potassium acid phthalate and by titration with HCl.

Apparatus and Procedure.—The experiments were carried out as potentiometric titrations using the cell: Ag|AgCl|50 m*M* NaCl, 950 m*M* $NaClO_4$ (saturated with AgCl)||*B* m*M* $NpO_2(ClO_4)_2$, *H* m*M* $HClO_4$, (1000 − 2*B* − *H*) m*M* $NaClO_4$|glass electrode. Reference half-cell, salt bridge, and J-shaped liquid junction were of the "Wilhelm" type.[19] A Beckman Type E-2/40495 glass electrode was used. The silver–silver chloride

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electrode was of the thermal–electrolytic type.[20] Cell potentials were read using a Leeds and Northrup K-5 potentiometer with a Cary 31-V electrometer as null point indicator. The cell was immersed in an oil thermostat at 25 ± 0.1°.

The behavior of the cell was checked in the range $1.5 \leqslant \mathrm{pH} \leqslant 3.5$ with standard perchloric acid solutions (1 *M* with $NaClO_4$) usually both before and after a series of measurements. The emf was described by the equation

$$E = E^\circ + 59.16 \log [\mathrm{H}^+] - 0.07[\mathrm{H}^+] \qquad (1)$$

The neptunyl(VI) solutions in the titration vessel were prepared by adding, with a microburet, known volumes of a standard NaOH solution (1 *M* in $NaClO_4$) to a known volume (20 ml) of a starting solution of the composition: B° m*M* $NpO_2(ClO_4)_2$, H° m*M* $HClO_4$, $(1000 - 2B^\circ - H^\circ)$ m*M* $NaClO_4$.

Two titrations were carried out in both directions. In these cases the total NpO_2^{2+} concentration was held constant, $B = B^\circ$, by adding equal volumes of an acid neptunyl(VI) solution of concentration $2B^\circ$ and a NaOH solution to the starting solution. The back-titrations were carried out by adding equal volumes of the same neptunyl(VI) solution and a $HClO_4$ solution to the partly hydrolyzed solution.

The solution in the titration vessel was stirred both by bubbling through at a slow rate N_2 gas purified and presaturated with 1 *M* $NaClO_4$ solution and by using a magnetic agitator.

In all the titrations equilibrium was obtained within 5 min and after that the potentials measured were constant to ±0.1 mV.

With all the concentrations of neptunyl(VI) examined a point was reached during the titration when precipitation began. This was shown by drift of potentials in a direction that corresponded to a continually increasing acidity of the solution. The measurements herein considered relate to solutions in which precipitation had certainly not yet begun.

The actual oxidation state of the neptunium was checked after each titration by absorption spectroscopy and no appreciable reduction of Np^{VI} was detected.

All the operations with neptunium were performed in special glove boxes.

Results and Discussion

Potentiometric measurements were carried out with nine neptunyl(VI) solutions having different concentrations. The free hydrogen ion concentration, *h*, for each point was calculated from eq 1. From *h* and the analytical data *B* and *H*, the average number of ligands OH^- bound to one NpO_2^{2+}, $\bar{n} = (h - H)B^{-1}$, was obtained for each point along a series of measurements.

The data in the form of $\bar{n}$ as a function of $-\log h$ are illustrated in Figure 1. Since from this diagram $\bar{n}$ appears to be dependent on the total NpO_2^{2+} concentration, it is evident that polynuclear hydroxo complexes are formed.[19]

As can be seen on the right side of Figure 1, for two series of measurements with *B* held constant there is a good agreement between the data obtained from titration of an acid NpO_2^{2+} solution and from back-titration of the partly hydrolyzed solution. This demonstrates that, at least for $\bar{n}$ values from 0 up to about 1, the hydrolytic reactions are reversible and that the experimental measurements refer to a system in actual equilibrium.

According to the nomenclature of the Chemical Society Tables,[2] for the hydrolytic reactions

$$q\mathrm{NpO_2}^{2+} + p\mathrm{H_2O} \rightleftharpoons (\mathrm{NpO_2})_q(\mathrm{OH})_p{}^{(2q-p)+} + p\mathrm{H}^+ \qquad (2)$$

the equilibrium constants, $^*\beta_{pq}$, are defined as

$$^*\beta_{pq} = \frac{[(\mathrm{NpO_2})_q(\mathrm{OH})_p{}^{(2q-p)+}][\mathrm{H}^+]^p}{[\mathrm{NpO_2}^{2+}]} \qquad (3)$$

As preliminary steps in the analysis of the data, calculations were made of the average number of hydroxo group, $\bar{p}$, and of neptunyl(VI) ions, $\bar{q}$, in the hydrolyzed species, as suggested by Sillén.[21] From the results of this treatment the dimer $(NpO_2)_2(OH)_2^{2+}$ was assumed to be the most important species in the range $0.1 < \bar{n} < 0.5$ and a rough value of its formation constant, $^*\beta_{22}$, was calculated. With only this constant it was impossible to reproduce the experimental data at lower and higher $\bar{n}$ values.

In order to gain some information on the other complexes present in important amounts the method of curve fitting was used. A normalized projection map[19,22] was first computed for only the two complexes NpO_2OH^+ and $(NpO_2)_2(OH)_2^{2+}$. A comparison of this map with the experimental data plotted in the form $\log B$ *vs.* $(-\log h)_{\bar{n}}$ gave a fairly good fit in the range $0 < \bar{n} < 0.5$. Thus, there was an indication of appreciable concentrations of the simple mononuclear monohydroxo complex in the solutions and a trial value of the formation constant $^*\beta_{11}$ was estimated.

Normalized maps with three parameters were subsequently calculated in order to try the best fit with all the experimental data available. Maps were obtained by combining the species having $(\bar{p},\bar{q})$ values (1,1) and (2,2) with each of the larger complexes (3,2), (4,3), and (5,3).

The best fit was obtained with the map calculated for the set (1,1)–(2,2)–(5,3). The defining equations for this map are

$$\mathrm{B} = v + uv + 2u^2v^2 + 3\mathrm{R}u^5v^3$$

$$\mathrm{B}\bar{n} = uv + 2u^2v^2 + 5\mathrm{R}u^5v^3$$

where $\mathrm{B} = B^*\beta_{22}/^*\beta_{11}{}^2$, $v = {}^*\beta_{22}b/^*\beta_{11}{}^2$ ($b = [\mathrm{NpO_2}^{2+}]$), $u = {}^*\beta_{11}/h$, and $\mathrm{R} = {}^*\beta_{53}/^*\beta_{22}{}^2\,{}^*\beta_{11}$.

From the best fit shown in Figure 2, the values log

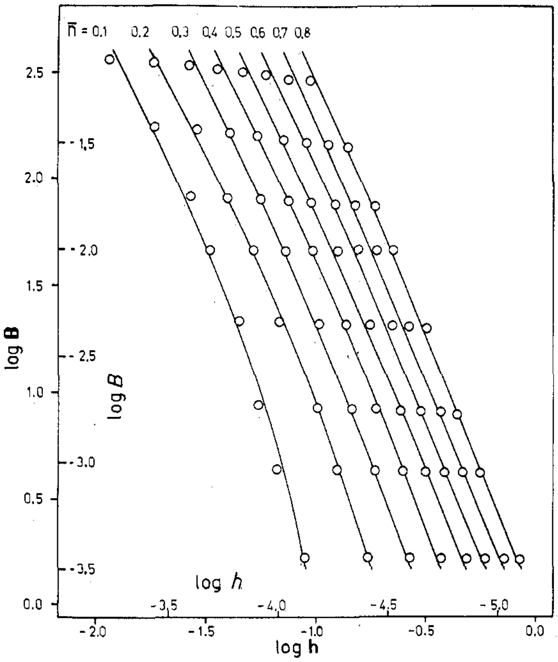

Figure 2.—Log *B* *vs.* $(\log h)_{\bar{n}}$ for the hydrolysis of NpO_2^{2+} superimposed on the normalized map log B *vs.* $(\log \mathrm{h})_{\bar{n},\mathrm{R}}$ calculated for the set of hydroxo complexes (1,1)–(2,2)–(5,3) (for this map R = 2).

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$^*\beta_{11} = -5.1$, log $^*\beta_{22} = -6.7$, and log $^*\beta_{53} = -18.2$ were obtained.

A least-squares refinement of these three parameters was carried out with all the experimental data using a Fortran program[23] for the IBM 7094 computer.

Using trial values estimated for the equilibrium constants of other hydroxo species, the following schemes were also tried with the least-squares program: (2,2)-(5,3), (1,1)-(2,2)-(3,2), (2,2)-(3,2), (1,1)-(2,2)-(4,3), (2,2)-(4,3), (1,1)-(2,2)-(3,2)-(5,3), (1,1)-(2,2)-(4,3)-(5,3), (1,1)-(2,1)-(5,3), (1,1)-(2,1)-(2,2)-(5,3).

The most significant results of these calculations are illustrated in Figure 3 as plots of the least-squares residual ($\bar{n}_{\text{obsd}} - \bar{n}_{\text{calcd}}$) obtained with four sets of complexes for five titrations. The results for the other four titrations show an analogous trend, but the values of least-squares residual comparatively smaller would make their graphic illustration not clear. The relevant constants, their standard error, σ, and the standard deviations to the fit, $\sigma_{\bar{n}}$, are also reported.

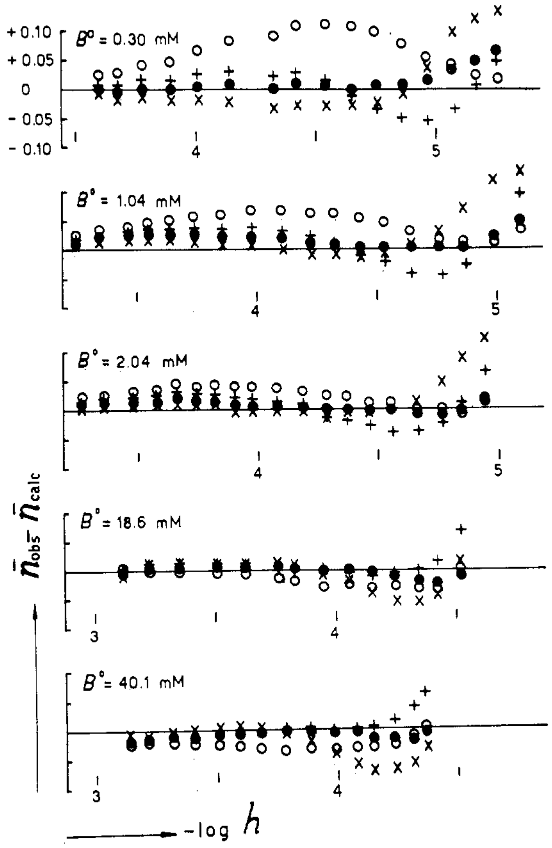

Figure 3.—Least-squares residuals, $\bar{n}_{\text{obsd}} - \bar{n}_{\text{calc}}$, obtained with four hydrolysis schemes for five titrations at different NpO_2^{2+} concentrations. Symbols represent four different schemes: ●: $^*\beta_{11} = 6.81 \times 10^{-6}$, $^*\beta_{22} = 2.09 \times 10^{-7}$, $^*\beta_{53} = 5.59 \times 10^{-19}$, $\sigma_{\bar{n}} = 0.017$. ○: $^*\beta_{22} = 2.83 \times 10^{-7}$, $^*\beta_{53} = 5.53 \times 10^{-19}$, $\sigma_{\bar{n}} = 0.034$. +: $^*\beta_{11} = 4.44 \times 10^{-6}$, $^*\beta_{22} = 1.93 \times 10^{-7}$, $^*\beta_{32} = 2.63 \times 10^{-12}$, $\sigma_{\bar{n}} = 0.026$. ×: $^*\beta_{11} = 1.03 \times 10^{-5}$, $^*\beta_{22} = 1.29 \times 10^{-7}$, $^*\beta_{43} = 3.47 \times 10^{-14}$, $\sigma_{\bar{n}} = 0.045$.

As can be seen the best reproduction of the experimental data is obtained with the set of complexes (1,1)-(2,2)-(5,3), which agrees with the result obtained by the curve-fitting method.

Exclusion of the (1,1) species from the schemes examined makes the agreement with the data worse, as, for instance, a comparison between the points ● and ○ shows in Figure 3. Therefore, the mononuclear complex NpO_2OH^+ seems to be of some importance.

Since the (2,2) species is necessary to reproduce the experimental data both by graphical and least-squares treatment, the binuclear hydroxo complex $(NpO_2)_2(OH)_2^{2+}$ appears to be the first important polynuclear product formed in hydrolyzed neptunyl(VI) solution.

As for the larger hydroxo complexes, which are certainly formed before precipitation occurs, taking into account the lower $\sigma_{\bar{n}}$ value obtained, it appears reasonable to select the ternuclear complex $(NpO_2)_3(OH)_5^+$ as the most probable soluble species present in important amount, at least under our experimental conditions. It should also be noticed that addition of a fourth species, as for example in the case (1,1)-(2,2)-(4,3)-(5,3) (not shown in Figure 3), did not improve the fit.

Our conclusions about the main soluble hydrolysis products of neptunyl(VI) and their equilibrium constants in 1 *M* perchlorate solution are given in Table I.

TABLE I[a]
HYDROLYSIS CONSTANTS OF MO_2^{2+} IONS (M = U, Np, AND Pu) IN 1 *M* PERCHLORATE SOLUTION AT 25°

Ion	Log $^*\beta_{11}$	Log $^*\beta_{22}$	Log $^*\beta_{53}$	Ref
UO_2^{2+}	−4.77	−6.10	−16.75	5
	. . .	−5.94	−16.41	8
NpO_2^{2+}	−5.17 ± 0.03	−6.68 ± 0.02	−18.25 ± 0.02	This work
PuO_2^{2+}	−5.97 ± 0.05	−8.51 ± 0.05	−22.16 ± 0.03	14

[a] Data from ref 5 are at 20°. $^*\beta_{11}(U)/^*\beta_{11}(Np) = 2.5$,[5] $^*\beta_{22}(U)/^*\beta_{22}(Np) = 5.5$,[8] $^*\beta_{53}(U)/^*\beta_{53}(Np) = 70.1$,[8] $^*\beta_{11}(Np)/^*\beta_{11}(Pu) = 6.5$, $^*\beta_{22}(Np)/^*\beta_{22}(Pu) = 67.7$, and $^*\beta_{53}(Np)/^*\beta_{53}(Pu) = 8.08 \times 10^3$.

Figure 4 illustrates the distribution of hydrolysis products for 10 m*M* total concentration of NpO_2^{2+} as a function of −log *h*.

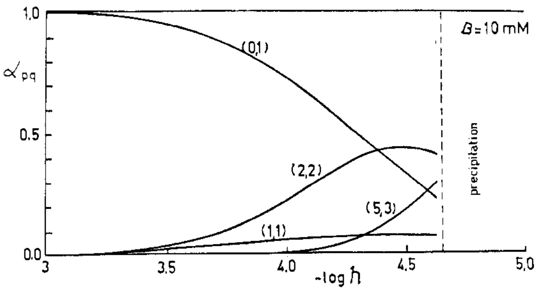

Figure 4.—Distributions of Np^{VI} among the different hydrolysis products as a function of −log *h* in 1 *M* perchlorate for a solution with 10 m*M* Np^{VI}.

In order to make possible a comparison, some available data on the hydrolysis of plutonyl(VI) and uranyl(VI) are included in Table I. The data for plutonyl(VI) were obtained by us under the same experimental conditions as those herein considered for neptunyl(VI). As for uranyl(VI), among numerous data reported in the literature, referring to various ionic media, ionic strength, and temperature, we have selected those that were obtained from measurements made in 1 *M* perchlorate solution. From an experimental work of

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[23] We are indebted to Dr. Richard M. Rush of the Oak Ridge National Laboratory for having very kindly sent us the Fortran program used in his studies on the hydrolysis of uranium(VI) (see ref 5).

Ahrland in 1 *M* perchlorate at 20°,[24] three sets of equilibrium constants were obtained: the first was proposed by Ahrland himself, the second was calculated by Ahrland, Hietanen, and Sillén using the core–link hypothesis,[4] and the third was the result of a reinterpretation of the data carried out by Rush, Johnson, and Kraus using a least-squares program.[5] There is a remarkable discrepancy among the three hydrolysis schemes proposed, the reason for which lies in the different methods of treatment used. It should be remembered that in the last 20 years there has been a continuous improvement in the methods of treatment of data referring to polynuclear systems, and thus the observed discrepancy should not be surprising. Nowadays, with the more refined methods available, it is much easier to draw concordant conclusions using different approaches, as, for instance, in the present work. On the ground of these considerations, of the three different results obtained from the Ahrland measurements, we assume the last one[5] to be the most reliable and therefore only that is reported in Table I. On the other hand, it seems in better accordance with subsequent studies on UO_2^{2+} hydrolysis in 1 *M* perchlorate[5,6,8] and also in 3 *M* perchlorate solution.[9,11]

A first examination of the data in Table I indicates that the three oxy cations in 1 *M* perchlorate solution undergo hydrolysis following substantially the same scheme of reactions. In fact, in all three cases there is no question about the existence of the dimer $(MO_2)_2(OH)_2^{2+}$, and the contribution of the trimer $(MO_2)_3(OH)_5^+$ is also ascertained with reasonable certainty. There is some doubt, however, about the importance of the simple mononuclear MO_2OH^+, the existence of which seems to be supported from our data for plutonyl(VI) and neptunyl(VI) but not from data for uranyl(VI),[5,6,8] except, perhaps, for very low concentration or at higher temperature.[7]

At the present time, this close analogy among the hydrolysis schemes for the three ions must be limited to the range of $\bar{n}$ values from 0 to about 1. At higher $\bar{n}$ values, before precipitation occurs, it is very likely that other polynuclear complexes are formed and they may have different structures. This caution appears to be justified also by taking into account the large differences in the precipitation characteristics of the three actinides(VI), as pointed out by Kraus.[3] In this respect, our experimental data indicate that, on addition of base, neptunyl(VI) and uranyl(VI) are rather similar in their precipitation behavior, whereas plutonyl(VI) differs greatly, having less tendency to form insoluble products.

As for the values of formation constants in Table I, their comparison clearly shows that the three ions exhibit a decrease in acidity with increasing atomic number. This trend was well known from a comparison of the observed pH values at definite $\bar{n}$ as a function of metal concentration.[3] Now that the mechanism of hydrolysis has been demonstrated to be the same, at least in the range $0 \leqslant \bar{n} \leqslant 1$, it is reasonable to assume that the trend in acidity observed is mainly due to a difference in free energy of similar hydrolytic reactions and not to differences in the structures of the hydroxo complexes.

Such a stability drift with atomic number was also pointed out by Ahrland and Brandt for the fluoride complexes of UO_2^{2+} and NpO_2^{2+} [25] and by us for some monocarboxylate complexes of the three actinide(VI) ions.[26]

It was remarked that, on account of the actinide contraction, this drift in properties is the reverse of what would have been expected,[3,25] and therefore some explanations were suggested. To explain the relative tendency toward hydrolysis of UO_2^{2+} and PuO_2^{2+} the idea was proposed that, in consequence of the contraction along the O–M–O axis, PuO_2^{2+} behaves as a larger ion than UO_2^{2+} toward oxygen about the equator.[27] Other suggestions, perhaps more likely, took into consideration the possibility that d-electron orbitals or f-electron orbitals might become less available for bonding with increasing atomic number.

The ratios of the corresponding hydrolysis constants are shown in Table I. It may be of interest to notice that their values indicate a deviation from a regular progression of hydrolytic properties as a function of atomic number. That is, the relative tendency toward hydrolysis makes neptunyl(VI) more different from plutonyl(VI) than from uranyl(VI). It should be mentioned that an analogous conclusion can be drawn from a comparison of the stability constants of some monocarboxylate complexes[26] and, further, that the precipitation characteristics mentioned above may also be significant in this respect.

This particular feature of the variation of properties with atomic number should be considered in any discussion of the factors determining the relative chemical behavior of actinide(VI) ions.

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