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Solution Chemistry of the Actinides

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Abstract

The redox and complexation behavior of the actinide ions in aqueous solution is reviewed. An equation is offered to calculate the ionic radii of actinide cations in different oxidation states and coordination numbers. The models for hydration are reviewed with emphasis on those involving long range ordering of a solvent sheath. Some selected values for hydration constants reflect the problems of studying actinide ions in near-neutral or basic solutions. A simple modified BORN equation is shown to provide values of the complexation constants in very good agreement with experimental values. Interpretation of the entropy and enthalpy changes for complexation is discussed in terms of a model of desolvation plus cation-anion combination. Some general observations on redox and complexation kinetics are offered to indicate possible directions for further studies.

I. Introduction

Since the earliest days of the Manhattan Project, much of the interest in the solution chemistry of the actinide elements has been directly associated with the separation science of these elements. Whether dealing with a few kilograms of plutonium or a few atoms of mendeleium, the primary motive in most studies of actinide solutions was the isolation and purification of these elements rather than expansion of our knowledge about their fundamental chemical behavior. International interest in nuclear fuel reprocessing methods, which typically involves acid solutions, is a continuing motivation for actinide research. Lately, studies of actinide behavior in neutral and basic solutions have attempted to provide answers on the fate of these elements in potential nuclear waste disposal sites and in the environment. Even beyond these applied concerns, the actinides have a richly diverse chemistry in solution which provides sufficient justification to the solution chemist for their continuing study. In this review, the focus is on the fundamental aspects of actinide solution chemistry; if well understood, these can serve as the basis for direction of the studies of a more applied nature.

II. Oxidation states in solution

The actinide ions exhibit an unusually broad range of oxidation states in aqueous solution - from II to VII. Following the normal pattern for polyvalent cations, lower oxidation states are stabilized by more acidic conditions while high oxidation states are more stable in basic solutions. Of course, this generalization can be negated by other factors, such as complexing, and these trends in the relative stability of different oxidation states can be reversed. For example, the greater strength of complexing of M(IV) cations relative to that of M(III) can significantly increase the apparent redox stability of the M(VI) species compared to M(III). Pu(III) is stable to air and water in acid solutions but in the presence of acetate or EDTA (pH 3.5), it partially oxidizes to Pu(IV) [1]. Similarly, the greater tendency to hydrolysis of Pu(IV) causes Pu(III) in aqueous solution to be oxidized to Pu(IV) in neutral media $E^0(\text{III}$ → (IV) = $-0.98 \text{V}$ in 1 M HClO$_4$ vs. +0.63 V at pH 7) [2]. Methods of preparation of the different oxidation states have been discussed recently by AHRLAND et al. [3] and MYASOEDOV [4]. Disproportionation reactions, leading to several oxidation states simultaneously in solution is a significant aspect of actinide chemistry, particularly for some IV and V species. Such reactions have been discussed also in ref. [3, 4, and 5]. In the following section, the various oxidation states found in aqueous solution for the different actinides are briefly reviewed.

M(I)

The existence of M(I) has been reported by MIKHEEV and coworkers [6] but studies by other groups [7] have failed to provide confirmation.

M(II)

Both Md(II) and No(II) form readily in aqueous solution and No(II) is the most stable species of that element. Cf(II), Es(II) and Pm(II) have been shown to have much lower stability than the III state [4]. Am(II), Cm(II) and Cf(II) were produced in acid solution for periods of 10-100 msec by pulse radiolysis [8, 9].

M(III)

This is the most stable oxidation state in aqueous solutions for the actinides Am-Md and Lw. However, as noted previously, other states can be made predominant in basic or in strongly complexing solutions. Pu(III) and Np(III) are rather easily obtained although U(III) is such a strong reducing agent that it is difficult to maintain in solution.

M(IV)

Th(IV) is the common and stable state for that element. Pa(IV), U(IV) and Np(IV) do not react with water but are oxidized by O$_2$. Pu(IV) is stable only in concentrated acids and at low concentrations of Pu(IV). The IV state of Am, Cm, Bk and Cf can be produced in alkaline solutions by persulfate oxidation. The presence of potassium phosphotungstate, K$_{10}$P$_4$W$_{17}$O$_{61}$, stabilizes these species by complexation [4]. Am(IV) and Bk(IV) are relatively stable and can be produced by a variety of oxidation techniques. Am(IV), Cm(IV) and Cf(IV) have also been produced in aqueous solution by pulse radiolysis.
M(V)
The MO\textsubscript{2}\textsuperscript{4} ion can be formed in solution by the actinides Pa through Am. This is the most stable state for Pa although it is uncertain whether the better formulation of the aqueous species is PaO\textsubscript{2}\textsuperscript{2+} or PaO(OH)\textsuperscript{2+} [10]. NpO\textsubscript{2}\textsuperscript{4} is stable except at high acidities and high concentrations under which conditions it disproportionates. UO\textsubscript{2}\textsuperscript{4} and PuO\textsubscript{2}\textsuperscript{4} increase in stability as the pH is increased but have a strong tendency to disproportionate. AmO\textsubscript{2}\textsuperscript{4} is a strong oxidant; it also disproportionates in highly acid solutions. There is evidence that PuO\textsubscript{2}\textsuperscript{4} may be the predominant plutonium species in solution in natural waters [11].

M(VI)
U, Np, Pu and Am form MO\textsubscript{2}\textsuperscript{6+} ions in solution with the stability decreasing in the order U > Pu > Np > Am. UO\textsubscript{2}\textsuperscript{6+} is the most stable uranium species while AmO\textsubscript{2}\textsuperscript{6+} is a strong oxidizing agent although it can be formed quantitatively in basic solutions of phosphotungstic acids.

M(VII)
In acid solutions, Np(VII) and Pu(VII) are reduced rapidly by water but the reduction is considerably slower in basic solution. Am(VII) is reported to form but is so unstable even in alkaline solution that it oxidizes Np(VI) and Pu(VI) to their VII state in 1-2 M NaOH [12]. However, research at Argonne and Los Alamos has failed to produce Am(VII) under the conditions reported earlier [12]. The M(VII) species seems to be trigenerative, corresponding most simply to MO\textsubscript{2}\textsuperscript{3+} but the more likely correct formulation is MO\textsubscript{2}(OH)\textsubscript{3} [14].

The rates of the disproportionation reactions as well as the rates of many of the redox reactions of the actinides can be markedly influenced by the chemical nature of the reactants and the products. For example, the reduction of M(VI) to M(V) requires extensive rearrangement of the primary coordination sphere of MO\textsubscript{2} (i.e. change of the linear dioxo structure) prior to electron transfer. This results in an activation barrier such that a disproportionation reaction such as

\[3 \text{Pu}^{4+} + 2 \text{H}_2\text{O} = 2 \text{Pu}^{3+} + \text{PuO}_2\textsuperscript{2+} + 4 \text{H}^+\]

requires about 200 hours in 0.5 M HCl to attain equilibrium. By contrast, the reaction:

\[\text{Np}^{3+} + \text{NP}_2\textsuperscript{2+} = \text{Np}^{4+} + \text{NP}_2\textsuperscript{4+}\]

is very fast, presumably because it occurs via rapid electron exchange in two half reactions: Np\textsuperscript{3+} \rightarrow Np\textsuperscript{4+} and NpO\textsubscript{2}\textsuperscript{4+} \rightarrow NpO\textsubscript{2}\textsuperscript{2+}.

Photochemically induced redox reactions of U, Np and Pu were reviewed recently by TOTH et al. [15]. For U(VI) and Pu(VI) the general reaction:

\[\text{MO}_2\textsuperscript{2+} + \text{R} + \text{hv} \rightarrow \text{MO}_2\textsuperscript{4+} + \text{R}^+\]

has been found to take place when R is an alcohol, an aldehyde, hydrazine or hydroxylamine. The MO\textsubscript{2} species disproportionates to M\textsuperscript{4+} and MO\textsubscript{2}\textsuperscript{2+} with a rate which is dependent on acidity and MO\textsubscript{2}\textsuperscript{2+} concentration. The quantum efficiency in 1 M acid with C\textsubscript{2}H\textsubscript{5}OH present is 50 times greater for UO\textsubscript{2}\textsuperscript{2+} (250-600 nm) than for PuO\textsubscript{2}\textsuperscript{2+} (<350 nm). Direct photochemical reduction occurs in this same system:

\[\text{Pu}^{4+} + \text{R} + \text{hv} \rightarrow \text{Pu}^{3+} + \text{R}^+\]

Neptunium in the III, IV and V states is oxidized in sequential one electron transfer reactions to Np(VI) by absorption of 390 nm radiation in perchloric acid solutions. However, photochemical reduction can occur also in acid solutions when ethanol is present whereby Np(VI) is reduced in steps to Np(III). In HNO\textsubscript{3} solutions, these photochemical reactions are complicated by the photolytic reduction of NO\textsubscript{2}. As a result, Np(VI) and Np(IV) solutions can be converted completely to Np(V).

The redox photochemistry of the actinides would seem to be a promising research field for both basic and applied interest.

Fig. 1 gives the oxidation potentials for U, Np and Pu at pH 0 [3] and, as estimated by ALLARD et al. [16], at pH 8 and 14.

\[
\begin{array}{cccc}
\text{U(III)} & \text{U(V)} & \text{U(VI)} \\
-0.631 & 0.615 & +0.065 \\
-1.95 \pm 0.17 & 0.08 \pm 0.12 & -0.32 \pm 0.09 \\
-2.78 \pm 0.36 & -0.03 \pm 0.24 & -0.49 \pm 0.24 \\
\end{array}
\]

\[
\begin{array}{cccc}
\text{Np(III)} & \text{Np(VI)} \\
+0.155 & +1.136 \\
-1.13 \pm 0.14 & +0.38 \pm 0.24 \\
-1.48 \pm 0.12 & +0.38 \pm 0.24 \\
\end{array}
\]

\[
\begin{array}{cccc}
\text{Pu(III)} & \text{Pu(VI)} \\
+0.982 & +0.916 \\
-1.170 & +0.60 \pm 0.04 \\
-1.04 \pm 0.24 & +0.16 \pm 0.24 \\
\end{array}
\]

Fig. 1. Redox potential diagram for U, Np and Pu. The reduction potentials as listed are for the pH values: pH = 0; pH = 8; pH = 14.

III. Coordination number and radii

The actinide cations are "hard acids" — that is, their bonding in complexes is rather well described by an electrostatic model and they show strong preference for oxygen donor atoms. There is evidence for some greater degree of covalency in actinide-ligand bonds than in analogous lanthanide-ligand bonds, but, for both groups of metals, the ionic character of the bonding is predominant. This is true for the metal-oxygen and metal-nitrogen donor bonds prevalent in complexes in aqueous solution [17] as well as for the metal-carbon bonds in organometallic compounds [18].

As a result of the ionic nature of the bonding, actinide cations do not display the restricted stereochemistry typical of the d transition elements. The coordination number and
the geometry of the coordination sphere in the d elements are strongly influenced by the overlap of the metal and ligand orbitals. By contrast, in the ionic interactions of actinide complexes, the number and arrangement of the ligands are determined primarily by steric and electrostatic factors. This leads to a range of coordination numbers from 6 to 12 observed for complexes with simple actinide cations while for the oxygenated cations, such as UO$_2^+$, coordination numbers of 2 to 8 are reported.

Little direct evidence can be found on the coordination number of actinides in aqueous solutions. However, coordination numbers of 8 and 9 are the most likely for trivalent lanthanide systems [17], and it is reasonable that this is also true for trivalent actinides. Even in polydentate complexes such as AmEDTA$^{3-}$, the coordination sphere of the actinide cation probably includes 3 or 4 water molecules. For tetravalent species, the smaller cation size may result in smaller values — 7 and 8.

Directly tied to the question of coordination number is that of the proper radius to assign the actinide cations. Solid state structural determinations have been concerned, for the most part, with CN = 6 compounds, although other systems such as Th(IV) of CN = 6—12 and U(VI) of CN = 2, 4, 6—8 have been studied. SHANNON [19] has published the most comprehensive list of such data and used them to calculate the “effective ionic radii” which include consideration of coordination number, electronic spin, covalency, repulsive forces and polyhedral distortion. These radii are assumed to be independent of the coordination sphere and are directly additive (to the donor atom radius) for ionic bonds. The values of the effective radii of SHANNON for CN = 6 are listed in Table 1.

Comparison of the radii derived by SHANNON with those calculated by these equations show that $r_4$, $r_7$, and $r_8$ agree to ± 0.01 Å while $r_5$, $r_{10}$ and $r_{12}$ to ± 0.02 Å.

### IV. Hydration and hydrolysis

Several authors have proposed hydration numbers for trivalent actinides. LEBEDEV [20] estimated values of $S^0_{aq}$ for the An(III) ions, obtaining values in reasonable agreement with those reported by FUGER and OETTING from a critical evaluation of the literature values [21]. The values were used to obtain an estimate of the hydration number of 7.0 ± 0.1. GOLDMAN and MORSS [22] reported a value of 5.1 from a semiempirical calculation based on an electrostatic hydration model. Experimental measurements of the ionic migration velocities in an electric potential gradient were used with STOKES' Law equation [23] to calculate values from 13.6 (Am) to 16.9 (Fm). These values agree with the net hydration numbers (first + second sphere) of trivalent lanthanide cations obtained by various techniques [24]. These numbers are related to a first sphere hydration of 8 to 10 [25, 26] for the trivalent cations.

The values of the hydration numbers in the preceding paragraph are based on calculations which assume that the experimental data are related to a cation species with a definite, small number of waters attached in one (or, at most, two) layers. An alternate model of hydration is based on the orienting effect of the cation on a larger volume of water molecules. The structuring imposed by this cationic orientation competes with that of the normal 3-dimensional hydrogen-bonded order of water [27] to produce a net hydration effect.

Support for a model of this longer range cationic ordering effect has been offered for trivalent lanthanides based on the crystal field splitting of Gd(III)$_{aq}$ [28]. These splittings are attributed to second order crystal field operators whose coefficients converge slowly with distance. The conclusion is that the hydration effect on the water structure extends over a volume as large as 50 Å around each cation. Moreover, the symmetry at the rare earth cation site is very low and C$_{2v}$ at maximum.

Further support for a model of a long range, more general structuring effect in hydration of cations is found in Fig. 2. The correlation of $S^0_{aq}$ with the ionic charge density is consistent with a regularly increasing hydrational structuring as the cationic orienting effect, proportional to $Z^2/r$, increases. Such a model is not inconsistent with data such as the cationic electromigration velocities but is not consistent with interpretation of such data in terms of definite “hydration numbers”.

If the model of large hydrate “icebergs” is accepted, the correlation in Fig. 2 suggests that the tetravalent actinides have even larger solvated structures — perhaps twice as large as the trivalent cations. Also, for MO$_2^+$ species, Fig. 2 suggests that the hydration structure is smaller than for the M(III) species and the low charge

<table>
<thead>
<tr>
<th>Actinide</th>
<th>Oxidation state</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>III</td>
</tr>
<tr>
<td>Th</td>
<td>1.04</td>
</tr>
<tr>
<td>Pa</td>
<td>1.025</td>
</tr>
<tr>
<td>U</td>
<td>1.01</td>
</tr>
<tr>
<td>Np</td>
<td>1.00</td>
</tr>
<tr>
<td>Pu</td>
<td>0.975</td>
</tr>
<tr>
<td>Am</td>
<td>0.97</td>
</tr>
<tr>
<td>Cm</td>
<td>0.96</td>
</tr>
<tr>
<td>Bk</td>
<td>0.95</td>
</tr>
</tbody>
</table>

These CN = 6 radii, $r_6$, can be converted to radii for other coordination numbers, $r_n$, by using the following relationships:

$$
\begin{align*}
    r_4 &= r_6 - 0.21 \\
    r_7 &= r_6 + 0.06 \\
    r_8 &= r_6 + 0.12 \\
    r_9 &= r_6 + 0.17 \\
    r_{10} &= r_6 + 0.22 \\
    r_{12} &= r_6 + 0.27
\end{align*}
$$
density of $\text{MO}_2^{+}$ cations has relatively little structuring effect on the solvent.

The importance of the extensive hydration of the III, IV and VI species is seen in the values of the thermodynamic parameters of complexion reactions. For many complexion reactions, the entropy and enthalpy changes are both positive, but since $|\Delta S| > |\Delta H|$ in most cases, the result is a favorable (negative) free energy change. The positive values for $\Delta S$ and $\Delta H$ are interpreted to be a result of the dehydration which accompanies complexion. Thus, the thermodynamic driving force for many actinide complexion reactions is the increased entropy resulting from the disruption of the hydrate structure associated with the metal cation when it interacts with a ligand [17, 29]. These thermodynamic parameters are discussed more extensively in a later section.

A significant aspect of actinide hydration is the importance, as the pH increases, of hydrolysis reactions such as:

$$M^{n+} + m H_2O = M(OH)_{m}^{+(n-m)} + m H^+$$

The strength of hydrolysis follows the pattern:

$$M^{4+} > MO_2^{+2} > Pu^{+3} > MO_2^{+}$$

which differs from that in Fig. 2 for the hydration entropies, i.e.,

$$Pu^{+4} > Pu^{+3} > PuO_2^{+2} > PuO_2^{+}$$

The hydrate entropies are related simply to the net positive charge on the cationic species. However, the hydrolysis reaction is the result of interaction of a water molecule with the metal atom itself — i.e., $Pu$ in $PuO_2^{+2}$. The hydrolysis order indicates that the charge on $Pu$ in $PuO_2^{+2}$ is actually between $+3$ and $+4$ and probably about $+3.3$.

The variation of the concentration of free (non-hydrolyzed) cation with pH is shown for plutonium in Fig. 3. These curves are based on estimated values of the hydrolysis constants [16] but are of sufficient accuracy to indicate the pH values at which hydrolysis becomes significant (e.g., $\sim 6-8$ for $Pu^{+3}$, $\sim 7-8$ for $Pu^{+4}$, $9-10$ for $PuO_2^{+}$ and $4-5$ for $PuO_2^{+2}$).

![Fig. 2. The correlation between $-\Delta S$ and $Z^2/r$ for the radius, $r$, the C.N. = 6 values are used for Na(I), Ca(II) and PuO$^{+2}$, that of C.N. = 8 for Pu(IV), that of C.N. = 9 for Pu(III) and that of C.N. = 4 for PuO$^{+2}$.

![Fig. 3. The effect of hydrolysis, as a function of pH, on the concentration of hydrated Pu cationic species. The initial ($log [Pu]$ at pH = 0) concentrations are those at pH = 8 which correspond to the $K_{sp}$ values of the hydroxide precipitate of each species.

Hydrolysis constants of the actinides reported by different authors are rarely in agreement. Some values which seem to be the most reliable are listed in Table 2. SULLIVAN and coworkers [30] used a technique involving pulse radiolysis + transient conductivity to obtain their data in Table 2 while the $M(III)$ values were measured by a solvent extraction technique which minimizes the experimental problems encountered in hydrolysis studies [31]. Other estimated and experimental values can be found in ref. [3, 16, 32 and 33].

<table>
<thead>
<tr>
<th>$An$</th>
<th>$pK_i$</th>
<th>Concentration of $An$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$UO_2^{+2}$</td>
<td>5.2</td>
<td>$2 - 5 \times 10^{-4}$ M ($I = 0$)</td>
<td>30</td>
</tr>
<tr>
<td>$NaO_2^{+2}$</td>
<td>5.4</td>
<td>$2 - 5 \times 10^{-4}$ M ($I = 0$)</td>
<td>30</td>
</tr>
<tr>
<td>$PuO_2^{+2}$</td>
<td>6.3</td>
<td>$2 - 5 \times 10^{-4}$ M ($I = 0$)</td>
<td>30</td>
</tr>
<tr>
<td>$NpO_2^{+}$</td>
<td>8.75</td>
<td>$5 \times 10^{-4}$ M ($I = 0$)</td>
<td>30</td>
</tr>
<tr>
<td>$Np^{+4}$</td>
<td>2.3</td>
<td>$2 \times 10^{-3}$ M ($I = 2.0$ M)</td>
<td>32</td>
</tr>
<tr>
<td>$NpO^{+3}$</td>
<td>4.5</td>
<td>$2 - 5 \times 10^{-4}$ M ($I = 0$)</td>
<td>30</td>
</tr>
<tr>
<td>$Am^{+3}$</td>
<td>7.84</td>
<td>$0.05$ Trace ($I = 0.7$ M)</td>
<td>31</td>
</tr>
</tbody>
</table>

The hydrolysis of $M^{+4}$ and $MO_2^{+2}$ species follows a stepwise pattern

$$M \rightarrow M(OH) \rightarrow M(OH)_2 \rightarrow etc.$$
between monomer and oligomer is dependent on the actinide concentration. For example, using the hydrolysis values of ref. [16], at pH 5 and \((\text{UO}_2^2\text{)}_{\text{Total}} \sim 0.05 \text{M}\), the ratio of U in \((\text{UO}_2\text{)}_2\text{(OH)}_2\text{)}^2\) to that in \(\text{UO}_2\text{(OH)}_4\text{)}^+\) is ca. 4 while at pH 5 and \((\text{UO}_2^2\text{)}_{\text{Total}} \sim 10^{-4} \text{M}\), the ratio is ca. 0.004.

The hydrolysis of Pu\(^{4+}\) can result in the formation of polymers which are rather intractable to reversal to simpler species. As a result of this irreversible polymerization, the validity of \(K_p\) values for Pu(OH)\(_4\) should be questioned. For \([\text{Pu(IV)}]_T > 10^{-6} \text{M}\), hydrolytic polymers of a wide range of molecular weights can be formed even in moderately acid solutions. Initially, such polymers can be readily decomposed to simple in solution by acidification or by oxidation to Pu(VI). However, as the polymers age, the decomposition process requires increasingly rigorous treatment. The rate of such irreversible aging varies with temperature, Pu(IV) concentration, the nature of the anions present in solution, etc. A reasonable model would involve initial formation of aggregates with hydroxy bridging (Fig. 4a) which age to structures with oxygen bridging (4b). The relative percentage of oxygen bridges presumably determines the relative inertness of the polymer. These polymers are sorbed on vessel walls, ion exchange resins, etc. Their depolymerization depends on the conditions of formation as well as on their age and is best accomplished for aged solutions by treatment first with a strong oxidant [to form Pu(VI)] followed by a strong reductant [to form Pu(III)].

![Fig. 4. Possible model for the 'irreversible' aging of hydrolyzed polymers wherein hydroxy bridges (a) are replaced by oxo bridges (b).](image)

V. Complexation

The limitations on this review present any attempt to survey in depth the rather extensive literature on complexation reactions of the actinides. Instead, the general principles involved in the formation of actinide complexes are discussed with consideration of a few ligand systems as examples.

Perhaps the most basic aspect of actinide cations is their "hard acid" property. This means that their bonding to ligands is well described as electrostatic interaction with covalency playing a quite minor role. As hard acids, these cations interact preferentially with hard bases such as oxygen or fluoride atoms rather than softer bases such as nitrogen, sulfur or phosphorous donors. The actinides do interact with these soft bases in organic solvents of low solvating power but, except for nitrogen, do not do so in aqueous solution where the soft base would have to replace water, which is a hard base. Interaction of actinide cations with nitrogen donors in aqueous systems usually occurs when one or more oxygen donor sites are also present, as in the aminocarboxylates. In these systems, it is likely that the oxygen donors have produced sufficient desolvation that the nitrogen donor can interact without further displacement of \(\text{H}_2\text{O}\).

There is strong evidence that the entropy of complexation of actinide cations primarily reflects the desolvation of the cation [34]. Fig. 5 shows the relationship between the measured entropy for Am(III) chelation and the number of carboxylate groups in the ligand. Although the data for Am(III) is limited, the fact that the trend for Am(III) parallels that of the more extensive data for Sm(III) supports the same interpretation for both, i.e., the same degree of dehydration of the cation by each of the carboxylate ligands of the ligands. The nitrogen in the aminocarboxylate ligands seems to play no role in the \(\Delta S\) value [35]. However, the enthalpy values show no such correlation for the aminocarboxylate complexation and are more exothermic than expected from carboxylate complexation alone, indicating the effect of actinide-nitrogen interaction. Further evidence for Ln−N bonding in aminocarboxylate complexes is provided by NMR spectra [36] which, by implication, also argues for An−N bonding in actinide complexes.

![Fig. 5. The correlation of \(\Delta S\), the entropy of complexation [35], and \(n\), the number of carboxylate groups in the ligand: \(0 = \text{Sm(III)}\); \(x = \text{Am(III)}\); 1 = acetate; 2 = \(\alpha\)-picolinate; 3 = malonate; 4 = dipicolinate; 5 = NTA; 6 = HEDTA; 7 = EDTA.](image)
The radioactive nature of the transuranium elements places limitations on the techniques which can be used to study complexation in solution since the radioisolation accompanying macroscopic concentrations of the cations can perturb seriously the measurements. Consequently, many complexation studies have used tracer concentrations with a two-phase distribution technique such as ion-exchange or solvent extraction.

In studies where different oxidation states of an actinide have been complexed by the same ligand, the sequence of complexing strength most commonly observed is that discussed for the hydrolysis reactions; i.e.:

$$M^{4+} > MO_2^{2+} > M^{3+} > MO^{2+}$$

The sequence $M^{4+} > M^{3+}$ is expected from the ionic nature of the $\text{M}^{m+} - X^{m-}$ interaction which should increase with $n$ for constant $m$. The observation that the complexing strength of the $MO_2^{2+}$ cations is greater than the $M^{3+}$ cations can be understood by assuming that the central metal atom, $M$, in the linear $[O-M-O]^+$ cation has an effective charge that is greater than +3. It is this effective charge that determines the strength of complexing since the ligand binds in the equatorial positions about the linear $MO_2^{2+}$. WADT [40] recently analyzed $\text{UO}_2^{2+}$ by the relativistic core potential method and obtained a value of +2.4 for the atomic charge on the uranium. However, the effective charge in the equatorial plane would be expected to exceed this value and an estimate of an effective charge of +3.3 (±0.1) was obtained from analysis of complexation by $\text{F}^-$ anions [41]. Similar evaluation of the stability constants for $\text{NpO}_2^-$ and $\text{NpO}_2\text{SO}_4$ lead to an estimated effective charge on the Np atom in the linear $\text{NpO}_2$ species of 2.3 ± 0.2.

The free energy

The ionic nature of actinide complexes is supported by the correlation between the experimental free energy of complexation and that calculated by an equation which is based on electrostatic interaction between cation and anion. MUNZIE [42] proposed the use of a modified BORN equation which included a temperature dependent dielectric constant. In our laboratory we use this equation but with an empirical dielectric constant which is dependent only on the cationic charge. For the complexation reaction:

$$M^{+Z_1}_\text{(aq)} + X^{-Z_2}_\text{(aq)} = M^{+Z_1}_\text{(aq)}X^{-Z_2}_\text{(aq)}$$

the equation has the form ($\Delta G$ in kJ·m⁻¹):

$$\Delta G = -\frac{(1.387 \times 10^3)Z_1Z_2}{D_e d_{12}} - RT\nu \ln 55.5 + RT\Sigma \ln f$$

(1)

where

- $D_e$ = effective dielectric constant
- $Z_1$, $Z_2$ = ionic charges of cation and anion
- $\nu = -1$

The second term ($RT\nu \ln 55.5$) accounts for the effect of two species reducing to one ("static effect") and the final term corrects for the ionic strength of the solution. The correlation of experimental values with the calculation of $-\Delta G_1$ by equation 1 for fluoride complexation ($Z_2 = 1.0$) is shown in Fig. 6 [41] where $D_e = 80$ for $M^{4+}$ cations, 57 for $M^{3+}$ and 41 for $M^{4+}$.

![Fig. 6. The correlation of experimental values of $-\Delta G$ for formation of MF complexes with the values calculated by equation (1). The solid lines show the calculated values as a function of $1/d_{12}$ (ref. [41]).](image)

Equation 1 has been found to be useful also for calculation of the free energy of complexation by organic ligands. In these systems, the value of $Z_2$ is set proportional to the acidic constant of the donor sites (or to $\Sigma K_{a_i}$ for polydentate ligands). Fig. 7 is the relation between $Z_2$ and $\Sigma K_{a_i}$, which we obtained by using equation (1) with experimental free energies of protonation, holding all values constant except $Z_2$. These values of $Z_2$, in turn, were used with equation (1) to estimate the $\Delta G_1$ of complexation of Am(III) and Np(IV) by aminoacarboxylic ligands, of Am(III) and Th(IV) by acetate and of Th(IV) by malonate. The comparison of experimental and cal-
of complexation of trivalent actinide cations are similar to the analogous data for the trivalent lanthanide complexation. Since the models developed from the lanthanide data are based on ionic interaction, it is not surprising to find that they also explain actinide data rather satisfactorily. In general, the enthalpy and entropy changes on complexation of the actinide cations are associated largely with changes in the hydration of these cations and of the anionic ligands. Complexation results in a decrease in the hydration of the ions which provides a positive entropy contribution as a result of the increase in the randomness of the system. This dehydration makes an endothermic (positive) enthalpy contribution as a result of the breakage of the ion-water and water-water bonding in the hydrated species. Generally, the joining of cation and ligand in the complex results in an enthalpy and an entropy contribution that is negative in both instances since such complexation forms cation-anion bonds ($\Delta H = -$) and decreases the randomness of the system ($\Delta S = -$). The observed net changes, positive or negative, reflect the relative extent of the opposed contributions of dehydration and cation-ligand combination.

Fig. 8. Comparison of the $\Delta G$ calculated by equation (1) and the $\Delta G$ from experiment: $\blacklozenge$ = Am(III); $\times$ = Th(IV); $\circ$ = Np(IV). The solid line represents $\Delta G$ (calc) = $\Delta G$ (exper.).

culated values is shown in Fig. 8. The value used for $D_e$ was 57 for Am(III) and 50 for Th(IV) and Np(IV); for all the ligands, $r_2 = 1.55 \text{ Å}$ while $r_1$ was obtained from Table 1 (CN = 8). The calculated and experimental values for UO$_2^{2+}$ with acetate and malonate show similar agreement when $Z_1$ (UO$_2^{2+}$) = 3.2 and $D_e = 55$. For NpO$_2$ Mal$^{-1}$ when $Z_1$ (NpO$_2^{2+}$) = 2.3 and $D_e = 65$, the calculated $\Delta G$ agreed with the experimental value.

All of the polydentate ligand systems which showed agreement between experimental and calculated $\Delta G$ values involved 5 or 6 membered chelate rings. By that criterion, poor agreement between the calculated and experimental value [35] for UO$_2$NTA$^{-1}$ indicates that the experimental value is probably incorrect. The experimental values for complexes of chelate rings of 7 or more members were progressively lower than the calculated values as the ring size increased.

Enthalpy and entropy changes

The thermodynamic parameters (i.e., $\Delta G$, $\Delta H$, and $\Delta S$) of the formation of 1:1 actinide-ligand complexes.

Fig. 9 shows the linearity of the relationship between the enthalpy and entropy of complexation for a variety of mononuclear complexes. It has been proposed that such a linear relationship between $\Delta H$ and $\Delta S$ is evidence that the major factor(s) determining the value of these terms has a common base, thereby leading to a systematic variation [43]. In actinide complexation, the common factor is most probably the dehydration step. This correlation of $\Delta H$ and $\Delta S$ has also been described in terms of a compensation effect. For the net complexation reaction, two steps can be written:

1. $\text{M(H}_2\text{O)}^z_\text{n}^+ + \text{X(H}_2\text{O)}^y_\text{p}^– \rightarrow \text{M(H}_2\text{O)}^z_\text{m}^+ + \text{X(H}_2\text{O)}^y_\text{q}^– + (n–m+p–q)\text{H}_2\text{O}$

2. $\text{M(H}_2\text{O)}^z_\text{m}^+ + \text{X(H}_2\text{O)}^y_\text{q}^– \rightarrow \text{MX(H}_2\text{O)}^w_\text{m}^+ + \text{X(H}_2\text{O)}^y_\text{q}^–$
Denoting step (1) as \( d \) (= dehydration) and step (2) as \( c \) (= complexation), we can write:

\[
-\Delta G = -\Delta G^d - \Delta G^c = -\Delta H^d - \Delta H^c + T\Delta S^d + T\Delta S^c
\]

The compensation effect assumes \(-\Delta G^d \approx 0\) (since all the hydrated systems remain in equilibrium with bulk solvent [44]), thus

\[
\Delta H^d \approx T\Delta S^d
\]

Moreover, since \( \Delta H \) and \( \Delta S \) are positive for most complexation reactions,

\[
|\Delta H^d| > |\Delta H^c| \quad \text{and} \quad |\Delta S^d| > |\Delta S^c|.
\]

This leads to the interesting situation in which the entropy and enthalpy changes are reflective primarily of step (1), (the dehydration), while \( \Delta G \) is related almost completely to step (2), (the complexation). This model also explains why eq. (1) is so successful even though it seemingly ignores the dehydration part of the reaction.

**Inner vs. outer sphere formation**

EIGEN [45] has proposed that the formation of complexes proceeds sequentially as:

\[
M_{(aq)} + X_{(aq)} \overset{(1)}{\longrightarrow} [M(H_2O)_nX]_{(aq)} \overset{(2)}{\longrightarrow} [M(H_2O)X]_{(aq)} \overset{(3)}{\longrightarrow} MX_{(aq)}
\]

The first step is diffusion controlled while the second represents the formation of an “outer sphere” complex in which the metal ion and the ligand are separated by at least one molecule of water. In the final step, this outer sphere complex ejects the water and forms an “inner sphere” complex in which the metal and ligand are directly associated. Some ligands cannot displace the water and complexation apparently terminates with the formation of the outer sphere complex. Actinide cations form both inner and outer sphere complexes.

For the labile actinide complexes, it is often quite difficult to distinguish between inner and outer sphere complexes. This situation is complicated further by the fact that formation constants for some of these complexes when determined by optical spectrometry are often lower than those of the same system determined by other means such as potentiometry, solvent extraction, etc. This has led some authors to identify the former as “inner sphere” constants and the latter as “total” constants. However, others have shown that such assignments cannot be correct [46, 47] even if the optical spectra of the solvated cation and the outer sphere complex are indistinguishable while that of the inner sphere complex is different. In all these techniques, the “total” stability constant should be obtained and, as yet, no explanation can be given for the different values by different techniques. Based on the previous discussion of the thermodynamic parameters, \( \Delta H \) and \( \Delta S \) values can be used, with caution, to obtain insight into the outer vs. inner nature of actinide complexes. For inner sphere complexation, the hydration sphere is insufficiently disrupted and the net entropy and enthalpy changes are usually positive. This is particularly true for polydentate chelation. In outer sphere complexes, the dehydration sphere appears to be only partially disrupted, since the net enthalpy is exothermic. The corresponding entropy change is also negative due to the ordering of ionic charges without a compensating disordering which could result from extensive disruption of the hydration sphere.

**Fig. 10. Relationships between log \( \beta_{\text{total}} \) (experimental), log \( \beta_{\text{inner}} \) (calculated) and log \( \beta_{\text{outer}} \) (calculated) and the pK\(_a\) for the ligands Cl\(_n\)CH\(_3\)\(_{n-1}\)CO\(_2^+\) (\( n = 0 - 3 \)).**

These considerations lead, for trivalent actinides, to assignment of a predominant outer sphere character to the halide, nitrate, sulfonate and trichloroacetate complexes and an inner sphere character to the fluoride, iodate, sulfate and acetate complexes. The complexes of Cl\(_n\)CH\(_3\)\(_{n-1}\)CO\(_2^+\) ligands were studied by \(^{139}\)La(III) nmr spectroscopy [48] and the estimated fraction of inner sphere complexation agreed well with that calculated using a value of \( \beta(\text{inner}) \) obtained with equation (1). For Am(III), the log \( \beta \), \( (i = \text{inner}) \) calculated by eq. (1) allowed estimation of log \( \beta_0 \) (\( o = \text{outer} \)) from: \( \beta_0 \) (experimental) = \( \beta_1 + \beta_0 \). The curves in Fig. 10 are based on the \( \beta_1 \) and \( \beta_0 \) so calculated and indicate that for monobasic ligands with pK\(_a\) \( \leq 2 \), outer sphere complexation is dominant for trivalent actinides while for pK\(_a\) \( \geq 2 \), an inner sphere nature is expected. A similar study of complexation by these same ligands of other actinide cations [49] indicates that the change from predominantly inner sphere to predominantly outer sphere complexation is associated with ligand pK\(_a\) as follows:

<table>
<thead>
<tr>
<th>outer sphere</th>
<th>inner sphere</th>
</tr>
</thead>
<tbody>
<tr>
<td>M(IV):</td>
<td>( &lt; \sim 1.0 &gt; )</td>
</tr>
<tr>
<td>MO(_2^+):</td>
<td>( &lt; \sim 1.7 &gt; )</td>
</tr>
<tr>
<td>M(III):</td>
<td>( &lt; \sim 2 &gt; )</td>
</tr>
</tbody>
</table>
Since the $|\Delta H|$ and $|\Delta S|$ values for inner sphere complexation are larger than for outer sphere formation, the experimental values would be likely to be endothermic for systems in which both types of complexes are present unless the inner sphere complex is present to less than 10–30% of the total complexation.

**Cation-cation complexes**

A rather unique aspect of actinide solution chemistry is the formation of "cation-cation" complexes. Sullivan et al. [50] first reported the existence of complexes between pentavalent actinides, $\text{MO}^{+1}$, and multiply charged cations such as $\text{Cu}^{II}$, $\text{Fe}^{III}$, $\text{Th}^{IV}$, as well as oxygenated species like $\text{UO}_2^{2-}$. A recent study using Raman spectroscopy [51] confirmed the existence of these complexes as well as demonstrating the presence of $\text{NP}_2^{2+}$ dimers in acidic solutions. These dimers are not sensitive to pH and, obviously, are not hydrolytic polymers of the type formed in $\text{Mo}^{4+2}$ solutions.

Two models for these cation-cation complexes have been proposed:

$$\text{I} \quad O = \text{M}(V) = O - \text{M}(VI)$$

$$\text{II} \quad O = \text{L}$$

Model I has been supported by Sullivan [52] and Vadavato [53]. The second structure is that proposed in solution and in the solid for the hydrolytic dimers of $\text{MO}_2^{2+}$ species where $\text{L} = \text{OH}^-$ or $\text{H}_2\text{O}$. However, the experimental data, including recent studies by wide angle X-ray scattering [54], do not provide a firm basis to choose either model.

**VI. Kinetics**

**Redox**

Generally, redox reactions of actinide species have, for discussion of kinetic effects, been divided into two groups – those which involve electron transfer only (e.g., $\text{Pu}^{+3} \rightarrow \text{Pu}^{+4}$) and those which also require formation and/or rupture of metal-oxygen bonds (e.g., $\text{Pu}^{+4} \rightarrow \text{PuO}_2^{2+}$). In most systems studied, the first group of reactions of simple electron exchange are fast. By contrast, these redox reactions which also involve metal-oxygen bond changes tend to be slower. These are, indeed, generalizations and reactions observed in the first group (e.g., $\text{Pu}^{+3} + \text{PuO}_2^{2-} \rightarrow \text{Pu}^{+4} + \text{PuO}_2^{1+}$) can be slower than some in the second group (e.g., $\text{U}^{+4} + \text{NP}_2^{2+} = \text{UO}_2^{4+} + \text{NP}_2^{+}$). The wide variation in rates within the second group can be illustrated by the disproportion reaction $2\text{MO}_2^{4+} \rightarrow \text{M}^{+4} + \text{MO}_2^{2+}$ in 1.0 M acid: $\text{UO}_2^{4+}, k = 4 \times 10^2$; $\text{NP}_2^{2+}, k = 9 \times 10^{-9}$; $\text{PuO}_2^{4+}, k = 3.6 \times 10^{-3}$ [55, 56, 57].

The simple electron exchange reactions would be expected to show no rate dependency on hydrogen ion concentration. However, in some reactions studied, it seems probable that the activated complex involves a bridged hydrolyzed species, e.g., $\text{M}^{+3}(\text{OH})_n\text{Fe}^{+3}$ – which could have some dependency on the pH of the medium. For the second type of redox reactions, if formation of a metal-oxygen bond occurs, a negative dependency on ($H^+$) is expected. Such a reaction would be:

$$\text{Np}^{+4} + \text{Fe}^{+3} + 2\text{F}_2\text{O} = \text{NP}_2^{2+} + \text{Fe}^{+2} + 4\text{H}^+$$

for which the rate expression is found to have a ($H^+$)$^{-3}$ term [58]. By contrast, reactions in which $\text{M-O}$ bonds are broken are found to have rate expressions in which a term for hydrogen ion concentration occurs with a positive exponent as, e.g.,

$$\text{NP}_2^{2+} + \text{Fe}^{+2} + 4\text{H}^+ = \text{Np}^{+4} + \text{Fe}^{+3} + 2\text{H}_2\text{O}$$

whose rate expression has a ($H^+$)$^{+1}$ term [58].

In the presence of complexing anions an acceleration of the reaction rate is observed. The degree of acceleration is found to follow that of the tendency to form complexes, i.e.,

$$\text{ClO}_4^- < \text{Cl}^- < \text{SO}_4^{2-} < \text{C}_2\text{O}_4^{2-}$$

The complexation of reactants would facilitate the formation of binuclear bridged activated complexes (e.g., $\text{M}^{+3} \cdot \cdot \cdot \text{Cl} \cdot \cdot \cdot \text{MO}_2^{2+}$) by reducing the cation-cation electrostatic repulsion, thereby lowering $\Delta G^\dagger$ and increasing the forward rate. In weakly complexing systems such as perchlorate, hydroxyl bridging accomplishes this. Complexation of the products also would increase the net rate of the forward reaction by decreasing the reverse reaction.

It has been shown that a correlation exists between $\Delta G^0$ (standard reaction free energy) and $\Delta G^\dagger$ (activation free energy) when formation or rupture of $\text{M-O}$ bonds are involved in the redox reaction [59]. However, no such correlation exists for simple electron exchange reactions. However, for both groups of reactions, there is a strong "compensation" effect between $\Delta H^\dagger$ and $\Delta S^\dagger$. As a result, $\Delta G^\dagger$ does not vary greatly for the majority of the actinide redox systems studied. This relative constancy of $\Delta G^\dagger$ is important as it means that various competing reaction mechanisms are likely to have similar values of $\Delta G^\dagger$ (and, hence, similar rates). A set of similar values of $\Delta S^\dagger$ explains the fractional exponents often observed for various terms in actinide redox rate equations as any particular system may have several paths, each contributing significantly to the total rate. Also, reactions which are apparently similar may quite dissimilar rates if the possible paths are influenced differently by relatively "minor" effects (the rate for $\text{NP}_2^{2+} + \text{NP}_2^{2+}$ is almost 10 times greater than that for $\text{Pu}^{+3} + \text{NP}_2^{2+}$). This possibility of
several competing paths and of significant variation in the contribution of each in apparently similar systems makes the study and interpretation of actinide redox reactions complicated indeed.

The formation of the cation-cation complexes discussed earlier no doubt plays a role in the redox reactions of such systems but this role remains to be explored and defined.

Complexation

The rate determining step in the EIGEN mechanism for the formation of complexes is assumed to be a transition from outer sphere to inner sphere. Although problems of radioactivity, etc., make it very difficult to verify the validity of this mechanism for formation of actinide complexes of simple ligands, it is reasonable to assume such validity since the lanthanides seem to follow this mechanism [60, 61].

The kinetics of slower systems have been studied in a few cases. A tracer method was used to study the reaction [62]:

$$\text{An}^{3+} + \text{EuEDTA}^{-1} \rightarrow \text{AnEDTA}^{-1} + \text{Eu}^{3+}$$

where An = Am, Cm, Bk and Cf.

The exchange of An(III) with EuEDTA is a first-order reversible reaction and the forward and reverse rate constants each contain an acid-dependent and an acid-independent term:

$$k_F = k_A \frac{[\text{EuEDTA}^-][\text{An}^{3+}][\text{H}^+]}{[\text{Eu}^{3+}]} + k_B \frac{[\text{EuEDTA}^-][\text{An}^{3+}]}{[\text{Eu}^{3+}][\text{H}^+] + k_D [\text{Eu}^{3+}][\text{AnEDTA}^-]}$$

may be represented schematically as follows (where EDTA is represented by Y):

$$\text{EuY} + \text{An} \leftrightharpoons \text{Eu} \equiv \text{Y} - \text{An} \equiv \text{Eu} = \text{Y} = \text{An}$$

$$\text{Eu} + \text{AnY} \leftrightharpoons \text{Eu} - \text{Y} = \text{An}$$

The lines between Y and the cations indicate the number of carboxylate groups which are bonded to each metal ion (ionic charges have been omitted). For the acid-catalyzed mechanism it was proposed that the first step is a rapid equilibrium in which one of the carboxylate groups of the EDTA complex is protonated. The slow step is either (1) the dissociation of a second carboxylate group from the metal ion or (2) the transfer of a proton from the carboxylate oxygen to the nitrogen. The ligand is then able to dissociate rapidly from the metal ion. In either case the free europium and actinide ions compete for the free, protonated EDTA. Schematically this mechanism is given by:

$$\text{EuY} + \text{H} \rightleftharpoons \text{HEuY} \rightleftharpoons \text{Eu} + \text{H}_2 \text{Y} + \text{An}$$

$$\text{AnY} + \text{H} \rightleftharpoons \text{HAnY} \rightleftharpoons \text{An} + \text{H}_2 \text{Y}$$

Macroscopic level concentrations of Am(III) were used to study the rates of formation and dissociation of AmDCTA (DCTA = trans, 1,2-diaminocyclohexanetetraacetate), respectively, by stopped-flow and conventional spectrophotometric methods [63]. A mechanism was proposed which involves coordination of Am(III) to three acetate groups of H$_2$(DCTA)$_{n-4}$ to form the relatively long-lived intermediate *AmHDCTA which subsequently loses a proton. The slow step of the formation reaction was postulated to be associated with the formation of an americium-donor nitrogen bond.

VII. Conclusions

This review has attempted to provide some understanding of the diversity and complexity of actinide solution chemistry. It is obvious that significant progress has been made in all areas of this field but it is equally obvious that much remains to be done. The problems of working with radioactivity unfortunately has limited the number of laboratories which study these elements. Nevertheless, continuing and vigorous research programs in actinide solution chemistry are needed to further our fundamental knowledge and to answer the questions in applied areas.

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