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Kinetics of actinide complexation reactions

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Abstract

We report herein a summary of what is known about actinide complexation kinetics. The systems include actinide ions in the four principal oxidation states (III, IV, V, and VI) and complex formation and dissociation rates with both simple and complex ligands. Complex formation reactions tend to be rapid, accessible only to rapid-scan and equilibrium perturbation techniques. Complex dissociation reactions exhibit a wider range of rates and are generally more accessible using standard analytical methods. Literature results are described and correlated with the known properties of the individual ions. © 1998 Elsevier Science S.A.

Keywords: Actinide; Kinetics; Complexation; Activation parameters; Mechanism; Ligand

1. Introduction

The kinetics of oxidation-reduction reactions of actinide ions in solution have been investigated in significant detail [1,2]. Correlations between kinetic and thermodynamic parameters, for example the Marcus theory [3] that relates ΔG^{o} with ΔG^{*} for outer-sphere electron transfer reactions, have been demonstrated for certain actinide redox reactions [1]. Fifty years of study of the chemistry of the 5f elements has produced a surprisingly small number of investigations of the kinetics of their complex formation and dissociation reactions [1]. Perhaps this is because such reactions are seldom rate limiting in actinide processing. As a result, the kinetics of electron transfer reactions of actinide ions and their complexes are better understood than ligand exchange reactions for the same metal ions.

One might predict that the kinetics of actinide complexation reactions should be straightforward as compared with complex formation and dissociation reactions of the d-transition series metals. The best available data indicate that solvent exchange rates for actinide ions are rapid, covalent interactions with ligands represent a minor contribution to overall bond strength, and directed valence effects are absent. However, the variety of oxidation states, high coordination/solvation numbers in aqueous solution, and the geometric restrictions imposed by the linear dioxo cations of An(V, VI) provide interesting variations that make studies of actinide complexation kinetics a challenging field for research.

Our objective in studies of actinide complexation kinetics is to provide new insights into the nature of the interaction between the actinide aquo ions, important chelating agents, and solvent water to guide development of new reagents for actinide processing and environment restoration. In the present report, we will review literature reports on actinide complexation kinetics, with particular emphasis on our recent work on actinide complexes with phosphonic acid ligands.

2. Experimental

Reports from the literature describe the results of actinide complexation chemistry using a variety of experimental techniques including stopped-flow spectrophotometry, pulse radiolysis, temperature-jump, NMR, solvent extraction separation methods, and conventional spectrophotometry. The reader is referred to the original reports for details of the experimental techniques.

The bulk of the work done in our laboratories on actinide phosphonate complexes has been done by stopped flow spectrophotometry. The experimental set-up and data analysis procedures have been described in several recent publications [4–8]. Because the actinide aquo ions are not strongly colored, application of spectrophotometric techniques like stopped-flow must rely on the use of strongly colored chelating agents, either as the subject ligands or as indicators of the free metal ion in the reaction of interest.

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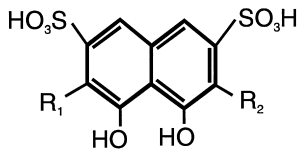

Fig. 1. Generic structure of chromotropic acid derivatives.

Derivatives of chromotropic acid (Fig. 1) have proven to be most useful in our investigations. We have investigated in particular the rates of complex formation of a variety of actinide cations with Arsenazo III and with Chlorophosphonazo III. We have in turn used these reagents as indicators of the free metal ion concentration to study the kinetics of complexes of actinide ions with ligands that do not form colored complexes with actinide ions.

3. Results and discussion

Metal ion complex formation reactions in aqueous solution typically conform to the Eigen mechanism [9], in which the hydrated metal ion first forms a solvent-separated ion pair with the ligand,

$$M(H_2O)_n^{3+} + L(H_2O)_m^{-} = (H_2O)_{n-1}M(H_2O)L(H_2O)_m^{2+} \quad (1)$$

This reaction is considered to be a rapid pre-equilibrium and is seldom rate limiting. The solvent-separated ion pair loses a water molecule to form a contact ion pair or precursor complex,

$$(H_2O)_{n-1}M(H_2O)L(H_2O)_m^{2+} = (H_2O)_{n-1}M \cdot L(H_2O)_m^{2+} + H_2O, \quad (2)$$

which then rearranges to form the activated complex, $[(H_2O)_{n-1}ML(H_2O)_m^{2+}]^*$

$$(H_2O)_{n-1}M \cdot L(H_2O)_m^{2+} = [ML(H_2O)_{n+m-1-x}^{2+}]^* + xH_2O. \quad (3)$$

This process may involve changes in the hydration of the precursor complex and potentially release of waters of hydration to the bulk. The activated complex then relaxes into the thermodynamically favorable conformation of the final complex. For polydentate ligands, the rate controlling step often involves an intramolecular rearrangement of the bound ligand followed by bond formation to form the chelated complex.

Microscopic reversibility requires that complex dissociation reactions follow this pathway in reverse. Complex dissociation is typically investigated by addition of a competing metal ion or chelating agent that is more strongly bound by the components of the subject complex to displace the system from its thermodynamically stable condition. Complex dissociation reactions are often catalyzed by H^+, particularly in acidic solutions.

According to the above outlined mechanism for complex formation, the rate of solvent water exchange represents an upper limit to the rate of complex formation. Such rates have not been reported for the trivalent actinides but have been discussed for the heavy lanthanides, which are chemically analogous. Merbach et al. [10] have reported that second order rate constants for water exchange are directly proportional to the cation radius of trivalent lanthanides and are experimentally accessible by NMR spectroscopy only for Dy–Lu. We can estimate that the water exchange rates for Am(III)–Cf(III) range between 1×10^9 and 1×10^8 M^{-1} s^{-1} assuming a linear correlation with the lanthanides based on cation radius. Water exchange rates for tetravalent (Keiner et al. [11] report that U(IV) rates are complex) and pentavalent actinide cations have not been reported and cannot be reliably estimated by comparison with the trivalent ions. Tomiyasu and Fukutomi [12] have reported NMR data that allow estimate of the first order rate constant for water exchange by UO_2^{2+} in d6-acetone (1.1×10^6 s^{-1} at 25°C), that is independent of $[H_2O]$. Given the differences in the properties of acetone and water, this value probably represents a lower limit for the water exchange rate of UO_2^{2+} in water.

3.1. Trivalent actinide complexes

The rate of the complex formation reaction of Am^{3+} with trans-1,2-diaminocyclohexano-*N*,*N*,*N*′,*N*′-tetraacetic acid (CDTA) in acetate buffer solutions was studied by stopped-flow spectrophotometry [13]. The rate determining step for complex formation is an acid-dependent intramolecular process that appears to be limited by the rate of formation of an Am bond to the amine nitrogen. The activation parameters for the reaction are $E_a = +59.0$ kJ/mol and $\Delta S^* = -19$ J/mol-K. The dissociation rate of $AmCDTA^-$ was observed to be more similar to that of the isoelectronic $EuCDTA^-$ than to the dissociation rate of $NdCDTA^-$, whose cationic radius (and hence electrostatic attraction for the ligand) is closest to that of Am^{3+}. This result suggests a possible minor covalent contribution in the binding of Am to the amine.

The rate of dissociation of trivalent trans-americium actinides with a variety of aminopolycarboxylate complexants has been investigated by Choppin and coworkers [14–18]. Most of these studies were conducted using radiotracer concentrations of the target metal ions and solvent extraction/ion exchange separation techniques. Metal complex dissociation reactions are catalyzed by both H^+ and acetate ion in most systems.

3.2. Tetravalent actinide complexes

Nikitina et al. [19] have studied the dissociation kinetics of tetravalent actinide complexes with aminopolycarbox-

ylate ligands CDTA and DTPA (diethylenetriamine-*N,N,N′,N″,N″*-pentaacetic acid) using Arsenazo III as a colorimetric indicator for actinides. The rate of acid catalyzed dissociation of the Th^{4+} and U^{4+} CDTA complexes are nearly identical ($k_{Th}=0.25\ M^{-1}\ s^{-1}$, $k_U=0.27\ M^{-1}\ s^{-1}$) while the rates for dissociation of the corresponding Np^{4+} ($k_{Np}=0.048\ M^{-1}\ s^{-1}$) and Pu^{4+} ($k_{Pu}=0.010\ M^{-1}\ s^{-1}$) are successively lower. The activation entropies are increasingly negative across the series ($\Delta S^{*}_{Th}=-67$ J/mol-K, $\Delta S^{*}_{U}=-86$ J/mol-K, $\Delta S^{*}_{Np}=-109$ J/mol-K, $\Delta S^{*}_{Pu}=-152$ J/mol-K) indicating a strongly associative reaction mechanism. The increasingly unfavorable activation entropies are compensated by reduced activation enthalpy barriers across the series ($\Delta H^{*}_{Th}=+56.4$ kJ/mol, $\Delta H^{*}_{U}=+50.6$ kJ/mol, $\Delta H^{*}_{Np}=+47.8$ kJ/mol, $\Delta H^{*}_{Pu}=+38.7$ kJ/mol).

The rates of complex formation for Th^{4+}, U^{4+}, and Np^{4+} with Arsenazo III [20] and that for Th^{4+} and Zr^{4+} with the structurally related ligand Chlorophosphonazo III [5] have been reported. These ligands, derivatives of chromotropic acid, coordinate to the actinides through arsenate or phosphonate and phenolic groups. The relative freedom of movement of the coordinating groups is somewhat hindered by the structure of the chromotropic acid backbone, hence the ligand can be considered as predisposed for complex formation. In all systems, the rate determining step of the reaction appears to be intramolecular rearrangement of bonds in the precursor complex. The rate of formation of Th(CLIII) is about fourfold faster than that of Th(AAIII) (in 2.0 M acid). The activation parameters indicate that the mechanisms of complex formation for the two systems are substantially different, despite the structural similarity of the ligands. For Th(AAIII), $\Delta S^{*}=-15$ J/mol-K, $\Delta H^{*}=+32.3$ kJ/mol while the corresponding parameters for Th(CLIII) are $\Delta S^{*}=+88$ J/mol-K, $\Delta H^{*}=+60$ kJ/mol. The former parameters are consistent with a mildly associative process while the latter indicate a dissociative reaction pathway. The contrast is curious as reactants and conditions are so similar. In the AAIII system, k_{Np} is smaller than k_{Th} and the slower rate correlates with a more negative (unfavorable) ΔS^{*} for Np. The rate of formation of Zr(CLIII) is 30 times slower than that of Th(CLIII), largely due to a sharply higher ΔH^{*} for Zr^{4+}.

3.3. Pentavalent actinide complexes

We have recently reported results of the first two studies of the complexation kinetics of NpO_2^+ [7,8]. The rate of complex formation and dissociation of NpO_2^+ by CLIII in acidic perchlorate solutions appears to be governed by the rate of association of NpO_2^+ with the phosphonate (R-PO_3H_2) groups of CLIII. In 1 M $HClO_4$, spectral characteristics indicate that NpO_2^+ is coordinated only to the phosphonate groups while in 0.1 M $HClO_4$/0.9 M $NaClO_4$ both the phosphonates and phenols are bound. Molecular modeling calculations indicate that the four donor atoms of CLIII can readily accommodate the planar coordination requirements of NpO_2^+. Activation parameters for both complex formation and the acid-independent dissociation reactions indicate that the rate determining step is an entropy neutral process ($\Delta S^{*}_{f}=7$ J/mol-K, $\Delta S^{*}_{d}=+17$ J/mol-K). This suggests that the precursor complex is structurally very similar to the activated complex. The acid catalyzed dissociation reaction is associative.

In addition, we have studied the rate of NpO_2^+ complex formation by AAIII in pH 4–5 acetate buffer solutions and used AAIII to study the complexation of NpO_2^+ by methanediphosphonic acid (MDPA) and 1-hydroxyethane-1,1-diphosphonic aid (HEDPA) [8]. First order kinetics govern the NpO_2^+-AAIII reaction under all conditions indicating an intramolecular rate-determining step. The activation parameters are consistent with a dissociative reaction mechanism ($\Delta S^{*}=+31$ J/mol-K, $\Delta H^{*}=+48.4$ kJ/mol). The 1:1 NpO_2^+-MDPA and NpO_2^+-HEDPA complexes are formed in a rate process that is essentially entropy neutral ($\Delta S^{*}_{MDPA}=-12$ J/mol-K, $\Delta S^{*}_{HEDPA}=-12$ J/mol-K) but the dissociation of these complexes is associative ($\Delta S^{*}_{MDPA}=-29$ J/mol-K, $\Delta S^{*}_{HEDPA}=-46$ J/mol-K).

3.4. Hexavalent actinide complexes

The kinetics of complexation for hexavalent actinide ions have been studied for a wider variety of ligand types and over a wider range of acidity than any other actinide species. In addition, there have been a number of studies of solvent exchange reactions of uranyl in non-aqueous solvents, which have been reviewed by Tomiyasu and Fukutomi [12] and Lincoln [21]. The reader is referred to these excellent reviews for details of the non-aqueous chemistry of UO_2^{2+}.

Two temperature-jump studies investigated the rate of formation and dissociation of UO_2^{2+} complexes with SO_4^{2-}, chloroacetate, acetate, SCN^- [22] and that for formation of $[(UO_2)_2(OH)_2]^{2+}$ [23]. The relative order of complex formation rates was acetate$>SCN^->SO_4^{2-}>$ chloroacetate. Formation of the 1:2 complex was observed to occur more rapidly than the 1:1 species. The authors suggest that waters of solvation in uranyl complexes are held less strongly than in the corresponding aquo ions. The dimerization of $UO_2(OH)^+$ occurred in a process with a similar rate constant ($k_2=116\ M^{-1}\ s^{-1}$).

Hydrogen peroxide is known to form complexes with a number of metal ions including a technologically important insoluble complex with Pu^{4+} [24]. We have reported the rates of complex formation for 1:1 AnO_2^{2+}-H_2O_2 complexes (UO_2^{2+} at pH 5 [25], in $NaHCO_3$, and in Na_2CO_3 [26], NpO_2^{2+} in Na_2CO_3 [26], and PuO_2^{2+} in $NaHCO_3$, [27]). The complexes with NpO_2^{2+} and PuO_2^{2+} were identified as intermediates in the reduction of the triscarbonato com-

plexes of these metal ions to the respective pentavalent oxidation states. For the UO_2^{2+} system, the rates are fastest at pH 5 ($k_2 = 1.31 \times 10^4$ M^{-1} s^{-1}) and slowest in $NaHCO_3$ ($k_2(NaHCO_3) = 254$ M^{-1} s^{-1}, $k_2(Na_2CO_3) = 565$ M^{-1} s^{-1}). The activation parameters did not clearly define the mode of coordination of H_2O_2 to the metal ion/carbonate complex among the possibilities: (1) displacement of CO_3^{2-} by H_2O_2, (2) expansion of the coordination sphere without loss of CO_3^{2-}, or (3) coordination through the 'yl' oxygen.

Among the more interesting systems studied are the complexes formed with polydentate chelating agents. Ekstrom and Johnson [28] reported the rate of formation of the 1:1 complex between UO_2^{2+} and 4-(2-pyridylazo)resorcinol (PAR) in the pH 1–4 range. Though these authors ultimately conclude that the system is too complex for reliable mechanistic interpretation, they do report a second order rate constant for complex formation of $k_2 = 3.26 \times 10^4$ M^{-1} s^{-1} and activation parameters consistent with an associative reaction mechanism ($\Delta H^* = +34.2$ kJ/mol, $\Delta S^* = -44$ J/mol-K).

The rate of reaction of UO_2^{2+} with Arsenazo III has been reported [29,30]. Pippin and Sullivan [29] reported the rate and activation parameters for both complex formation and dissociation. Both complex formation and the acid independent dissociation of the complex occurs by an associative process ($\Delta S_f^* = -42$ J/mol-K, $\Delta S_d^* = -65$ J/mol-K). The results of Ishii et al. [30], conducted at a lower ionic strength, are in substantial agreement. The rate of complex formation for UO_2^{2+}-Arsenazo III (in 1–2 M acid) is about 10 times faster than that for UO_2^{2+}-PAR. This probably results from the more-favorable preorientation of ligand donor atoms in AAIII.

We have reported results on the rates of complexation of UO_2^{2+} with CLIII and with selected diphosphonic acid chelating agents, including HEDPA and MDPA [4,6,8]. These chelating agents share the common characteristic of coordinating to UO_2^{2+} by singly ionized phosphonic acid groups ($R\text{-}PO_3H^-$). Results of the UO_2^{2+}-CLIII experiments indicate a complex dependence of the rate of reaction on the ionic strength. The reaction is independent of I at $[H^+] > 1.0$ M and strongly inversely dependent at $[H^+] < 0.1$ M. The activation enthalpy for complex formation is lowest in 2.0 M $HClO_4$ (36.1 kJ/mol), highest in 0.05 M $HClO_4$/1.95 M $NaClO_4$ (56.1 kJ/mol). In 0.05 M $HClO_4$/0.05 M $NaClO_4$, the activation enthalpy barrier is intermediate between these extremes (45.2 kJ/mol). The rate determining step under all conditions is an intramolecular process.

The rate of complexation of UO_2^{2+} by HEDPA and MDPA has been investigated in both 0.01–0.1 M acid [4] and in pH 4.6 acetate buffer solutions [8]. In the pH 1–2 range, complex formation and dissociation reactions for MDPA, HEDPA and ethane-1,2-diphosphonic acid (E12DPA) occur at a rate measurable by stopped flow spectrophotometry. Both the complex formation and acid catalyzed dissociation reactions occur by an associative process, as indicated by the moderate negative activation entropies. In acetate buffer solutions, only the complex formation reactions occur at a measurable rate. For both UO_2^{2+}-MDPA and UO_2^{2+}-HEDPA the rate of complex formation is about two times slower at pH 4.6 than in 0.1–0.01 M acid (e.g. for MDPA, $k_{pH4.6} = 3740$ M^{-1} s^{-1}, $k_{pH1-2} = 6813$ M^{-1} s^{-1}). Activation parameters indicate that the complex formation reactions occur by an associative process.

3.5. Correlations and observations

One of the fundamental characteristics of the solution chemistry of trivalent actinides is that these metal ions interact more strongly with soft(er) donor atoms than the corresponding lanthanide cations. As an example, for species of comparable cationic radius (e.g. Am^{3+}/Nd^{3+}), the stability constants of the actinide-aminopolycarboxylate complexes are typically 10–50 times larger for the actinide. Though thermodynamic studies do not provide concrete evidence of enhanced interaction strength of trivalent actinides with the softer amino groups [31], rate constants for H^+ catalyzed dissociation indicate a slightly slower rate of dissociation for the actinide (Fig. 2). As M–N bond breaking and making is considered to be rate limiting for aminopolycarboxylate complexes, this observation can be taken as evidence for enhanced interaction strength. It should be noted that the relative rates of dissociation do not fully account for the differences in thermodynamic stability.

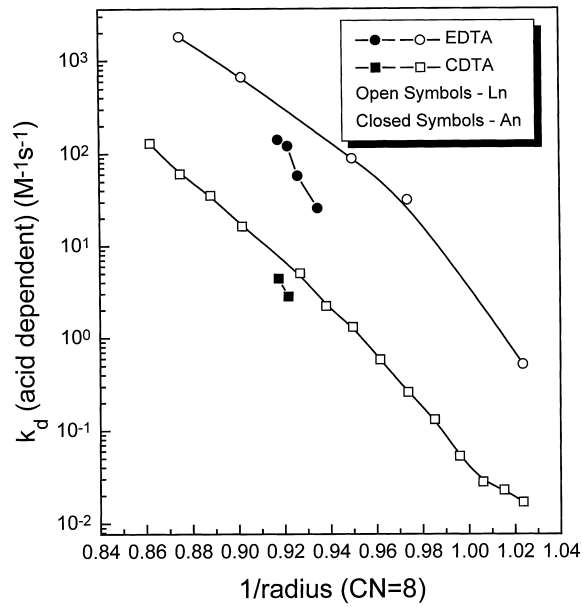

Fig. 2. Acid-dependent dissociation rate constant for trivalent lanthanide and actinide complexes with EDTA and CDTA as a function of the cationic radius.

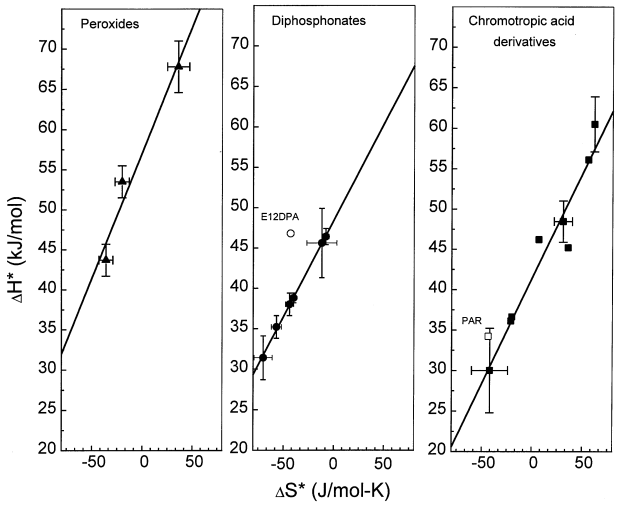

Fig. 3. Isokinetic plots for complex formation reactions of three classes of ligands (hydrogen peroxide, diphosphonic acids, chromotropic acid derivatives) with dioxoactinide cations (UO_2^{2+}, NpO_2^{2+}, NpO_2^{+}).

We have reported previously [7] the existence of a linear correlation between the rate of formation of CLIII complexes and the cationic radius for Fe^{3+}, La^{3+}, Eu^{3+}, Nd^{3+}, Th^{4+}, Zr^{4+}, UO_2^{2+}, and NpO_2^{+}, independent of the cationic charge. The implication of this result is that the kinetics of interactions between these metal ions and CLIII are independent of the strength of the electrostatic attraction between the metal ions and the chelating agent. It has been suggested that this result might indicate that the rate of solvent exchange in the precursor complex is rate limiting in these systems.

Isokinetic plots (Fig. 3) indicate that dioxoactinide cations (UO_2^{2+}, NpO_2^{2+}, and NpO_2^{+}) react via a common mechanism with structurally similar ligands. However, not all systems conform to the same isokinetic plot, from which we infer that the kinetics are influenced by the solution chemistry of the dioxocations and the ligand geometry.

The relationship between complex stability (i.e. thermodynamics) and the rate of complex formation and dissociation reactions provides additional insight into the nature of the interaction between metal ions and the donor atoms of chelating ligands in solution. Nyssen and Margerum [32] surmised that the rate of complex formation for lanthanide complexes with CDTA did not vary appreciably across the lanthanide series. The steady increase in complex stability that is observed as a function of atomic number was attributed to the steady decline in the rate of complex dissociation with decreasing ionic radius. The H^+ catalyzed dissociation rates for lanthanide complexes with EDTA and CDTA and trivalent actinide complexes with EDTA, CDTA, TMDTA (trimethylenediamine tetraacetic acid), and HEDTA (*N*-(hydroxyethyl)ethylenediamine-*N*,*N*′,*N*′-triacetic acid) are plotted as a function of stability constants for the corresponding complexes in Fig. 4. The log-log plot for the collected equilibrium and rate data are linearly correlated ($r^2 = 0.976$) with a slope of $-0.73(\pm 0.03)$ implying that the differences in complex stability are almost fully attributable to differences in the rate of complex dissociation.

In contrast, the relationship between thermodynamics and kinetics of complexation for dioxoactinyl reactions with several ligands is more strongly related to complex formation rates. In Fig. 5, the rates of complex formation and dissociation of NpO_2^{+} and UO_2^{2+} complexes with phosphonic acid ligands (MDPA, HEDPA, E12DPA, and CLIII), Arsenazo III, and simple monodentate ligands are shown. In both sets of results, the plot of log K_{eq} (k_f/k_d) vs. log k_f has the steeper slope ($\approx +0.85$) indicating that differences in complex stability are more strongly a function of the complex formation than dissociation.

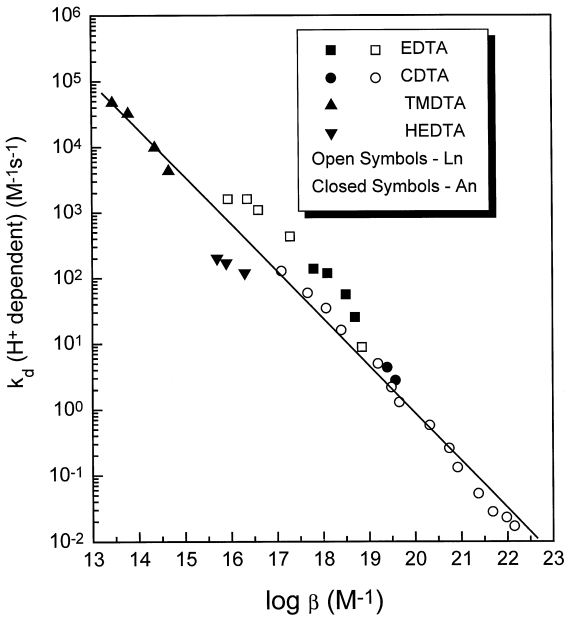

Fig. 4. Relationship between acid-catalyzed dissociation reactions of trivalent actinide complexes with aminopolycarboxylate ligands and thermodynamic stability of the respective complexes.

4. Conclusion

Though the kinetics of actinide complexation reactions have not been extensively investigated, those reports in the literature provide ample evidence for the value of such studies. We have presented correlations that indicate a fundamental difference between the complexation process for spherically symmetrical cations and the structurally restricted dioxoactinyl cations. It is also apparent to us that the limited information available on the thermodynamics and kinetics of actinide solvation phenomena must be

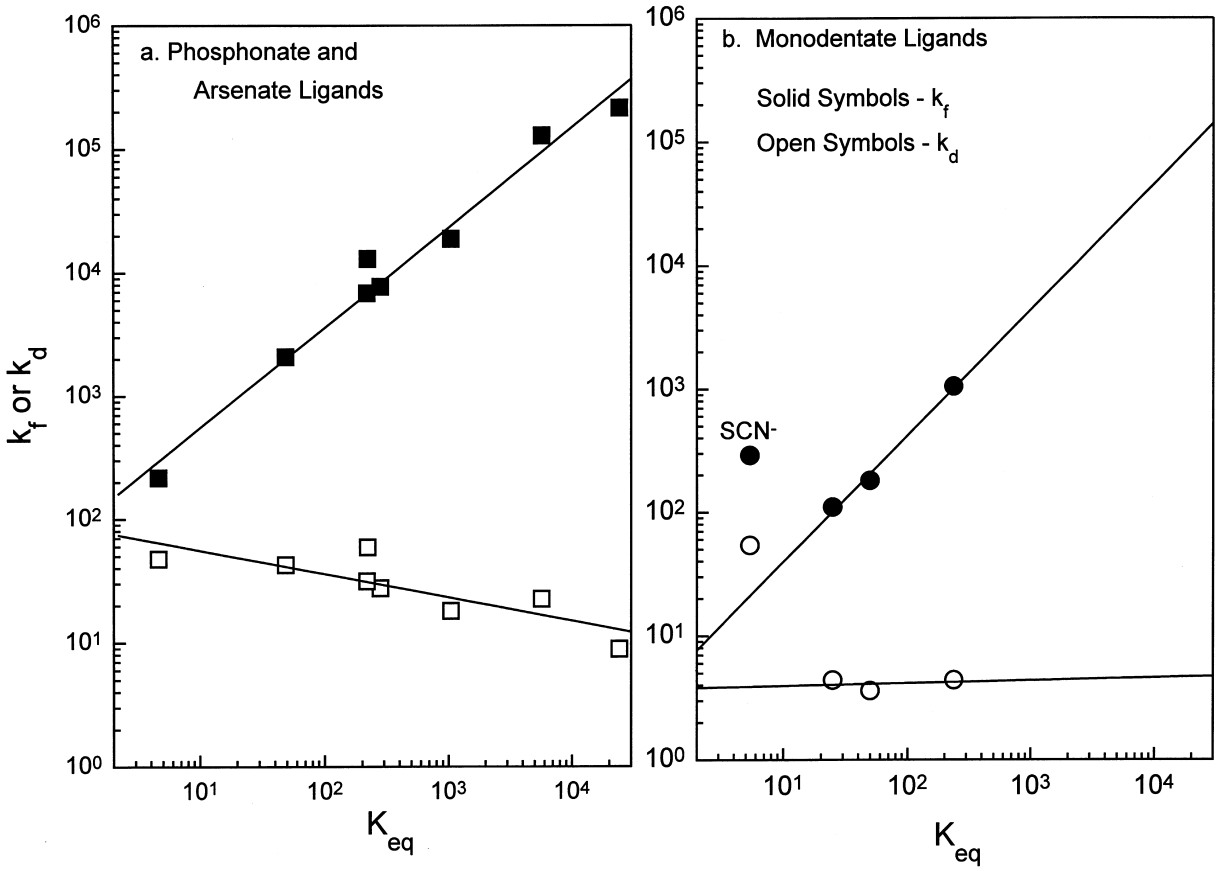

Fig. 5. Relationship between complex formation and dissociation rate constants and thermodynamic stability of the complexes for reactions of dioxoactinide cations with (a) phosphonate and arsenate ligands, (b) monodentate ligands.

expanded to extend our ability to interpret actinide complexation reactions.

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