Inorganic Chemistry

ANL/CHM/PP--87026

ACTINIDE COMPLEXATION KINETICS: RATE AND MECHANISM OF DIOXONEPTUNIUM (V) REACTION WITH CHLOROPHOSPHONAZO III*

Glenn Fugate, Janine F. Feil-Jenkins, James C. Sullivan, and Kenneth L. Nash

Chemistry Division
Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439-4831

RECEIVED
DEC 09 1996
OSTI

Abstract

The rates of complex formation and dissociation in the system NpO_2^+ - Chlorophosphonazo III (2, 7-bis(4-chlorophosphonobenzeneazo)-1, 8-dihydroxynapthalene-3, 6-disulfonic acid-CLIII) has been investigated by stopped-flow spectrophotometry. In addition, limited studies have been made of the rates of reaction of La^{3+}, Eu^{3+}, Dy^{3+}, and Fe^{3+} with CLIII. The rate determining step in each system is an intramolecular process, the NpO_2^+-CLIII reaction proceeding by a first order approach to equilibrium in the acid range from 0.1 to 1.0 M. Complex formation occurs in a process independent of acidity, while both acid dependent and independent dissociation pathways are observed. The activation parameters for the complex formation reaction are $\Delta H^* = 46.2(\pm 0.3)$ kJ/m and $\Delta S^* = 7(\pm 1)$ J/mK (I = 1.0 M). The corresponding parameters for the acid dependent and independent dissociation pathways are $\Delta H^* = 38.8(\pm 0.6)$ kJ/m, $\Delta S^* = -96(\pm 18)$ J/mK, $\Delta H^* = 70.0(\pm 0.1)$ kJ/m and $\Delta S^* = 17(\pm 1)$ J/mK, respectively. An isokinetic relationship is observed between the activation parameters for CLIII complex formation with NpO_2^+, UO_2^{2+}, Th^{4+}, and Zr^{4+}. The rates of CLIII complex formation reactions for Fe^{3+}, Zr^{4+}, NpO_2^+, UO_2^{2+}, Th^{4+}, La^{3+}, Eu^{3+}, and Dy^{3+} correlate with the cation radius rather than the charge/radius ratio.

MASTER

---

*Work performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, U. S. Department of Energy, under contract number W-31-109-ENG-38.

Introduction

The rates of complex formation reactions of f elements with complex ligand species have been most extensively investigated for trivalent lanthanide cations.[1] By comparison complexation kinetics of actinide cations has received relatively little attention, particularly for the transuranium elements.[2] However, since the light 5f elements demonstrate coordination properties intermediate between the 4f and d-transition elements, investigation of their complexation kinetics could provide an important linkage between these classes of metal ions. In particular, the effects of the multiple oxidation states of actinides and the sterically hindered dioxo cations on complex formation and dissociation rates are of interest.

The ligand, Chlorophosphonazo III (CLIII), (2,7-bis(4-chloro-2-phosphonobenzeneazo)-1, 8-dihydoxynapthalene-3, 6-disulfonic acid) is an excellent probe for studies that delineate the influence of the properties of 4f and 5f metal ions (ionic radius, formal charge, electronic structure) upon the rates of complexation reactions. Phosphonic acid complexants are somewhat unusual in their ability to form strong complexes with polyvalent metal ions in media of moderate acidity. We have recently developed significant new information on the thermodynamics and kinetics of lanthanide and actinide complexation by phosphonates.[3-9] A previous study[3] has demonstrated an unexpected inverse correlation between cation radii and rates for CLIII complex formation with the tetravalent cations of Zr(IV) and Th(IV). A subsequent investigation of the kinetics of uranyl complexation by CLIII[4] indicated a distinct difference between the mechanism at low acidity and in molar acid, and established the relative rate for complexation by CLIII of $Th^{4+} > UO_2^{2+} > Zr^{4+}$. The present study explores the effect of variation in the formal charge in a restricted cation geometry by comparison of the results previously obtained for dioxouranium(VI) with dioxoneptunium(V) as the cation. A limited number of experiments have treated lanthanide and Fe(III) complex formation rates with CLIII to examine trivalent cation behavior in this system.

Experimental

Reagents. The perchloric acid and sodium perchlorate stock solutions were prepared and standardized by conventional techniques. The CLIII was purchased from Fluka and stock solutions were prepared by weight. To insure oxidation state purity of the Np(V), an aliquot of an existing stock solution was first oxidized (to Np(VI)) with sodium bromate, then reduced to Np(V) with sodium nitrite. NaOH was added to precipitate $NpO_2(OH)$, and the precipitate washed with distilled water until the supernatant was pH neutral. The washed hydroxide readily dissolved in 1 M $HClO_4$. The Np stock solution was assayed spectrophotometrically at 617 nm using the molar absorptivity of 23.7 $\underline{M}^{-1}$ cm^{-1}.[10] $La(ClO_4)_3$, $Eu(ClO_4)_3$, and $Dy(ClO_4)_3$ solutions were prepared from previously characterized lab stocks. Iron solutions were prepared from $Fe(ClO_4)_3$ solid and standardized spectrophotometrically with KSCN.

Procedures. Most of the kinetic studies used a Hi-Tech stopped flow instrument with a rapid-scan diode array detection system. A 486DX2 computer used the Hi-Tech data acquisition and kinetic analysis program. This system permits observations of both free ligand disappearance and complex formation in a single experiment and enables kinetic analysis at multiple wavelengths. Several replicate determinations were made for each set of experimental conditions. For the lanthanides and Fe(III) studies, the photomultiplier detector was used instead of the diode array.

CLIII was the limiting reagent in most experiments, held constant at 4×10^{-5} $\underline{M}$. Neptunium concentrations were varied between 2×10^{-5} $\underline{M}$ and 1×10^{-4} $\underline{M}$. Ionic strength was constant at 1.0 $\underline{M}$ except for selected experiments which examined the effect of ionic strength on the rate. The effect of [H^+] and temperature on the rate was also determined. For the lanthanides, it was possible to measure only a single rate at equimolar concentrations ([Ln] = [CLIII] = $4x10^{-5}$ M) and one acidity (2 M). Reaction rates were too fast for the stopped-flow technique at higher [Ln] or lower acid. One set of experiments was run in the Fe(III)-CLIII system at 0.1 M ionic strength, T = 25.0 °C, and [H^+] = 0.02 M to measure the complex formation rate for this system.

Results and Discussion

The decrease in absorptivity of CLIII at 550 nm and the increase in absorptivity at 614 and 664 nm due to the formation of a Np(V)-CLIII complex at 25 °C and reactant concentrations of [Np(V)] = [CLIII] = $4.0x10^{-5}$ M ([H^+] ≈ 0.1 M) are shown in Figure 1a. The spectral characteristics at 0.1 M acid are consistent with literature reports on the Np(V)-CLIII complex, though the λ_{max} values are 6-8 nm lower than in the literature report.[11] The essential double maximum for the metal complexes is observed in each of the systems previously reported. For Np(V) experiments at 1.0 M acid (Figure 1b), the metal complex absorption band at 614 nm is not observed.

Ferguson, et al.[12] have reported spectra of CLIII as a function of pH. Their results combined with the protonation constants reported by Men'kov and Nepomnyashchaya[13] can be used to suggest a correlation between the spectral bands for the free CLIII ligand and specific ligand protonated species. The broad band at 550 nm correlates with the free ligand species H_8L, H_7L^-, H_6L^{2-}, H_5L^{3-}, which represent species generated by consecutive ionization of the two sulfonates and first ionization of each phosphonate group. The 660 nm band is correlated with ionization of the second proton from each phosphonate while the 614 nm band corresponds to the ligand species created by ionization of the phenols. These spectral features in CLIII are stimulated at lower pH by metal-ion coordination.

In strong acid media (0.7-1.0 M) and at low [Np(V)], it appears that the metal ion is coordinated only to the phosphonate groups of CLIII (Figure 2a), as evidenced by activation of the 664 nm chromophore only. In more dilute acid and higher [Np(V)], the equilibrium apparently shifts to a different species in which the metal ion bound to phosphonate displaces the protons from the phenols to activate the 614 nm chromophore forming a tetradentate complex (Figure 2b). This tetradentate structure has been previously suggested by Budesinsky.[14] It is important to note that the kinetic results were apparently not effected by this distribution of species implying that there is a common mechanism for the dissociation of both the bidentate and tetradentate species.

The tetradentate complex involves the formation of one six-member ring between the metal ion and the two phenol groups and two 10-member rings involving the metal-phosphonate-phenol groups. Ordinarily, the latter would not be expected to contribute substantially to complex stability. However, molecular mechanics calculations indicate[4] that the CLIII ligand is quite "stiff". As a result, no significant vibrational or rotational degrees of freedom are lost by the ligand upon formation of the tetradentate complex. The stiffness of CLIII imparts a preorganization of the ligand ionic atoms akin to that observed in crown ethers.

The values calculated for the first order rate parameter k, (s^{-1}), at $4x10^{-5}$ M Np(V) and CLIII, $[H^+] = 0.1$, T = 25.0 °C are 23 (±2) at 550 nm, 27 (±1) at 614 nm and 26.1 (±0.8) at 664 nm (where the uncertainties are at the $\pm 2\sigma$ level). The fact that the kinetic data are fit by a first order rate law under the second order conditions indicates that the rate determining step is an intramolecular process.[15] Under the same conditions as above except [CLIII] = $8x10^{-5}$ M, the value calculated for k = 30 (±4) s^{-1}. This result implies the absence of 1:2 (Np(V):CLIII) complexes under these conditions. The rate is linearly dependent upon the Np(V) concentration as is illustrated in Figure 3. Similar linear plots with finite positive intercept are observed over the ranges of temperature and [H^+] that were studied.

Table 1 summarizes the values calculated for the slopes (k_1) and intercept (k_{int}) of the k_{obs} vs $[Np]_t$ plots as a function of [H^+] and T. The slopes are independent of [H^+] while the intercept values increase with increasing [H^+]. The linear relationship between k_{int} and [H^+] is maintained throughout the temperature range investigation. The empirical form of the rate law is:

$$k_{obs} = k_1[NpV] + k_2 + k_3\,[H^+] \qquad (1)$$

where k_1 corresponds to the complex formation reaction and k_2, k_3 are respectively acid independent and acid dependent dissociation rate constants. The rate constants as a function of temperature are shown in Table 2. From these rate constants we can calculate the % dissociation by both acid independent and acid dependent pathways. They range from a low of ~1% acid dependent at [H^+] = 0.1, T = 25.0 °C to 47% at [H^+] = 1.0, T = 5.0 °C.

We were able to measure the rate of complex formation for the La^{3+}-CLIII, Eu^{3+}-CLIII, and Dy^{3+}-CLIII systems under only one set of conditions. At 2 M acid, the second order rate constants are $k_{La} = 4.24\ (\pm 0.46)\times 10^7\ \underline{M}^{-1}s^{-1}$, $k_{Eu} = 4.79\ (\pm 0.96)\times 10^7\ \underline{M}^{-1}s^{-1}$, $k_{Dy} = 2.54\ (\pm 0.57)\times 10^7\ \underline{M}^{-1}s^{-1}$. These reaction rates are computed based on a small absorptivity change, implying that the degree of Ln-CLIII complex formation under these conditions is slight. The rates for this reaction are approximately an order of magnitude slower than the reported rates of water exchange for lanthanide aquo ions,[16] implying that water exchange on the free Ln^{3+} cation is not rate limiting. Micskei et al. (17) have reported that the rate of exchange of inner-sphere wafer molecules in Gd^{3+} complexes with aminopolycarboxylate ligands (determined by ^{17}O NMR spectrometry) are about an order of magnitude slower than that of the aquo ion ($Gd(H_2O)_8^{3+}$). The similarity between their results and ours suggests that solvent exchange in the metal complex may be important in the Ln^{3+}-CLIII system as well.

In the Fe(III)-CLIII system, no appreciable reaction was observed at 1-2 M acid media. The rate of Fe(III)-CLIII complex formation was measurable at 0.02 M $HClO_4$, I = 0.1 M monitoring the rate of disappearance of the CLIII band at 550 nm. The data were resolved into two parallel first order processes. Both rate constants (k and k') were a linear function of [Fe^{3+}]. The intercepts of the plots were not distinguishable from zero. Second order rate constants for the two processes were 1.54 (±0.04)x10^4 M^{-1} s^{-1} and 1.70(±0.02)x10^3 M^{-1} s^{-1}. A two component rate was previously reported in the Zr^{4+}-CLIII system, and interpreted in terms of parallel pathways describing the eaction of CLIII with Zr^{4+} and $Zr(OH)^{3+}$. It is likely that a similar argument would explain the Fe^{3+}-CLIII results.

Activation parameters for the formation and dissociation of the Np(V)-CLIII complex are given in Table 3. Standard deviations in the activation parameters reflect the experimental uncertainties in the resolved rate parameters. Activation parameters were also calculated for the Np-CLIII results in 0.1 M $HClO_4$ (for complex formation only). The most notable feature of this table is the near zero ΔS^* for complex formation and acid independent dissociation at I = 1.0 M.

Calculations based on literature values for CLIII protonation constants[13] indicate that both phosphonate groups of CLIII are fully-protonated at [H^+] >0.1 M.[4] The dominant ligand species is $H_6(CLIII)$,$^{2-}$ assuming both sulfonate groups are ionized. We have assumed $NpO_2(H_2O)_4^+$ is the dominant species in discussion of a mechanism. The hydration number of NpO_2^+ does not effect the mechanism.

The absence of any significant acid dependence in the complex formation rate requires either no H^+ loss in the overall reaction, or that deprotonation occurs in steps subsequent to the rate-determining-step. Earlier investigations of the thermodynamics of Th(IV) complexes with methane diphosphonic acid indicated the formation of complexes without H^+ displacement from PO_3H_2, the Th^{4+} ion interacting through the phosphoryl oxygen (P=O). We have drawn the complexed species with NpO_2^+ bound to the phosphoryl oxygen (P=O), but we have no a priori evidence that the phosphonates are not ionized upon binding NpO_2^+. Certain mechanistic considerations for acid catalyzed dissociation favor the latter picture (i.e., NpO_2-O-P=O).

To accommodate the experimental observations and these structural features, the following sequence of reactions is postulated to describe Np(V)-CLIII complex formation):

$$NpO_2(H_2O)_4^+ + H_6(CLIII)^{2-} \rightleftharpoons NpO_2(H_2O)_4^+ \bullet H_6(CLIII)^{2-} \quad (3)$$

$$NpO_2(H_2O)_4^+ \bullet H_6(CLIII)^{2-} \rightleftharpoons (NpO_2(H_2O)_3\, H_6(CLIII))^- + H_2O \quad (4)$$

$$(NpO_2(H_2O)_3\, H_6(CLIII))^- \rightleftharpoons [NpO_2(H_2O)_2\, H_6(CLIII)^-]^\ddagger + H_2O \quad (5)$$

Reaction 3 is the formation of the outer sphere "ion pair" or solvent-separated complex (in accordance with the Eigen mechanism). In 4, a water molecule is displaced from the inner coordination sphere by one of the unionized phosphonate groups ($-PO_3H_2$) to form the precursor complex. The net cratic entropy for 3+4 should be about zero. The transformation of the precursor complex to the activated complex is given as reaction 5. The small ΔS^* implies that the precursor and activated complex are structurally similar.

Through this step, the reaction sequence is independent of [H^+]. The spectral features shown in Figure 1 imply that the activated complex has two relaxation pathways available leading to the formation of the bidentate or tetradentate complex (Figure 2).

At 0.1 M ionic strength, the second order rate constant for complex formation (T = 25.0 °C, [H^+] = 0.1 M) is 2.4 times faster than at I = 1.0 M ionic strength ($3.08\text{x}10^5$ $M^{-1}s^{-1}$ vs. $1.28\text{x}10^5$ $M^{-1}s^{-1}$). The activation parameters are $\Delta H^* = 60.5$ (±0.1) kJ/m, $\Delta S^* = 62$ (±1) J/mK, both of which are more positive than at I = 1.0 M. By comparison with the activation parameters at I = 1.0 M, calculations indicate that the increased energy barrier (ΔH^*) opposes the rate of complexation (by ~300) while the decreased order in the system (ΔS^*) leads to a net increase in the rate (by ~750) of complex formation. One possible explanation for the higher ΔS^* is the loss of a second inner-sphere water molecule upon transformation from the precusor to activated complex. Such a process would be facilitated in a less dense medium.

Considering now the rate of complex dissociation, spectral evidence indicated that the species we have designed as the bidentate chelate is dominant for [CLIII] > [NpO_2^+] and at [H^+] ≥ 0.7 M. The tetradentate species is indicated in more dilute acid. There is substantial overlap between these species. Because the data are well-correlated independent of the species distribution, we conclude that a common mechanism accounts for the dissociation of both the bidentate and tetradentate complexes. The rate of NpO_2^+ - O=P$(OH)_2$-R bond breaking must therefore be rate limiting.

The parallel dissociation pathways correspond to the spontaneous breaking of the NpO_2 - O=P bond, and the H^+ catalyzed dissociation of the Np-O=P bond. The small positive ΔS^* for the H^+ independent pathway is consistent with minimal structural difference between the stable complex and the activated complex. The relatively large ΔH^*

implies that this is a moderately strong bond. The acid catalyzed dissociation reaction is characterized by a large negative ΔS^* (-96 J/m-K), consistent with an associative reaction. The enthalpy barrier to dissociation is considerably reduced for this reaction (ΔH^* = 38.8 kJ/m).

Correlation of CLIII Rate Data. Though isokinetic plots must be approached with caution (as discussed by Linert (18)), the correlation of ΔH^* and ΔS^* for a series of related reactions can provide insight into the nature of the common reaction. We have prepared such a plot for the rate of complex formation between Np(V), U(VI),[4] Th(IV)[3] and Zr(IV)[3] with CLIII. These metal ions represent formal charges from +1 to +4 and present the geometric restriction of the dioxo cations for Np(V) and U(VI). The isokinetic plot for this system is shown in Figure 4. The activation parameters (ΔH^* and ΔS^*) are roughly proportional to the charge density of the cations ($Zr^{4+} > Th^{4+} > UO_2^{2+} = NpO_2^+$). The lower activation entropies and the apparent leveling of the relationship between ΔH^*, ΔS^* and z/r of the dioxo cations may reflect the tendency of the "yl" oxygens to participate in hydrogen bonding interactions with the protonated phosphonate groups[7] of CLIII. The planar arrangement of donor groups imposed by the dioxo cations does not disrupt the isokinetic relationship. The isokinetic relationship suggests that the ligand donor atoms adopt a similar planar configuration in its complexes with the nominally spherical ions Th(IV) and Zr(IV). It also confirms that the relatively slow rate of the Zr(IV)-CLIII complex formation reaction is not the result of a changed reaction mechanism.

Superficially, the relative rate of complex formation of Np(V), U(VI) and Th(IV) complexes with CLIII in 1-2 M acid is in the expected order for a reaction controlled by electrostatic factors. However, earlier results on Zr(IV) and additional information developed in this study on the trivalent ions La, Eu, Dy, and Fe(III) violate this relationship. The lanthanides react faster than Th(IV) while both Fe(III) and Zr(IV) react more slowly. Clearly, the electrostatic argument does not correlate this extended series.

In Figure 5 are presented the rates of formation for Np(V), U(VI), Th(IV), Zr(IV), La(III), Eu(III), Dy(III), and Fe(III) complexes with CLIII as a function of the cation radii. The radii are from Shannon[19] and correspond to CN=6 for U(VI), Np(V), Zr(IV), and Fe(III) (low spin) and CN=8 for Th(IV) and the lanthanides. The linear correlation is 0.986 for this series indicating that the size of the cation governs the rate of complexation of the metals. This relationship is supported qualitatively by Ferguson et al.[12] who report that CLIII reacts with the large Ca^{2+} cation at pH 2, but not with Mg^{2+} at pH <7. Molecular mechanics calculations provide no particular insight to the relative rates of the larger cations. These calculations do indicate some fractional structural stress in CLIII when coordinated to the small Fe(III) and Zr(IV) in the tetradentate coordination mode. A rather large "cavity" is formed by the four oxygen donor atoms in the free CLIII ligand. Calculations suggest a hemispherical "hole" in CLIII with a diameter of ~4.6-4.7 Å. This hole is quite close to the estimated diameter of the hydrated lanthanide cations.[20] The nominal good fit of such species in CLIII should promote hydrogen bonding between the ligand donor groups and the hydrated cation in the solvent-separated species. As the metal ion and its primary coordination sphere shrink, the metal ion is less strongly held by these hydrogen bonding interactions, and the smaller metal ion can more easily escape from the nacent complex. Electrostatic effects describing attraction of metal by ligand must be of secondary importance partly due to the shielding of charge by the hydration sphere of the cation in the precursor complex.

Conclusion

We can draw several conclusions relevant to metal ion coordination by this ligand system, and to the comparison of metal complexation rates of d and f transition elements in coordination compounds from this investigation. Characterization of metal complex spectra suggest that the stable complexes are tetradentate with the metal ions coordinated to both phosphonates and both phenols in CLIII in dilute acid. At > 0.7 M acid and low concentrations of NpO_2^+, the metal ion is bound only to the phosphonates. Np results suggest that initial coordination occurs between the metal ion and phosphonate groups. However, this association appears to occur without ionization of the phosphonate, at $[H^+] \geq 0.1$ M. The rate of dissociation of NpO_2^+ from the phosphonate groups is rate limiting whether the phenols are bound or not.

An isokinetic relationship exists for the formation of CLIII complexes with NpO_2^+, UO_2^{2+}, Zr^{4+}, and Th^{4+} suggesting the commonality of the mechanisms. Activation parameters are superficially correlated with the charge density (z/r) of the metal ions, but are only slightly effected by the presence of the "yl" oxygens in NpO_2^+ and UO_2^{2+}. In contrast, reaction rates are correlated with cation size irrespective of the charge. This suggest that the inner sphere waters of the metal ion in the precursor complex partially shield the ligand from the cation charge. It also suggests that hydrogen bonding between waters of the inner hydration sphere and ligand donor atoms is important in determining the rate of reaction. The observation of a kinetics based size-selectivity effect in a ligand only partially preorganized further suggests that it may be possible to design size-selective ligands without large-scale, rigid organization of ligand donor atoms (as in crown ethers).

REFERENCES

(1) Nash, K. L.; Sullivan, J. C. "Kinetics of complexation and redox reactions of the lanthanides in aqueous solution" in Handbook of the Physics and Chemistry of Rare Earths, Vol. 15, (K. A. Gschneidner, Jr. and L. Eyring, eds.) Elsevier Science Publishers, B.V., pp. 347-391, 1991.

(2) Nash K. L.; Sullivan J. C. "Kinetics and mechanisms of actinide redox and complexation reactions" in Advances in Inorganic and Bioinorganic Reaction Mechanisms, (A. G. Sykes, ed.), Academic Press, London, pp. 205-213, 1986.

(3) Feil-Jenkins, J. F.; Nash, K.; Sullivan, J. C. "Kinetics of the complexation reactions between Th(IV), Zr(IV) and Chlorophosphonazo III" *Radiochim. Acta,* in press.

(4) Feil-Jenkins, J. F.; Sullivan, J. C.; Nash, K. L. "Kinetics of the Complexation of dioxouranium(VI) with Chlorophosphonazo III" *Radiochim. Acta,* in press.

(5) Hines, M. A.; Sullivan, J. C.; Nash, K. L. *Inorg. Chem.* **1993,** *32*, 1820.

(6) Nash, K. L.; Horwitz, E. P. *Inorg. Chim. Acta* **1990**, *169*, 245.

(7) Nash, K. L. *Radiochim. Acta* **1993,** *61,* 147.

(8) Nash, K. L. *Radiochim. Acta* **1991,** *54,* 171.

(9) Nash, K. L.; Rao, L. F.; Choppin, G. R. "A calorimetric and laser induced fluorescence investigation of the complexation geometry of selected europium-(gem)diphosphonate complexes in acidic solutions" *Inorganic Chemistry*, in press.

(10) Sjoblom, R.; Hindman, J. C. *J. Am. Chem. Soc.* **1951**, , 1744.

(11) Chudinov, E. G.; Yakovlev, G. N. *Soviet Radiochemistry* **1962**, *4(5),* 526. Translated from *Radiokhimiya* **1962**, *4(5),* 601.

(12) Ferguson, J. W.; Richard, J. J.; O'Laughlin, J. W.; Banks, G. V. *Anal. Chem.* **1964,** *36*, 796.

(13) Men'kov, A. A.; Nepomnyashchaya, N. A. *Russian Journal of Inorganic Chemistry* **1977**, *22(8),* 1155. Translated from *Zhurnal Neorganicheskii Khimiya* **1977**, *22,* 2135.

(14) Budesinsky, B. "Monoarylazo and bis(arylazo) derivatives of chromotropic acid as photometric reagents" in *Chelates in Analytical Chemistry, Vol. 2* (H. A. Flaschka and A. J. Barnard, Jr. eds.) Marcel Dekker, New York, pp. 1-91, 1969.

(15) Nyssen, G. A.; Margerum, D. W. *Inorg. Chem.* **1970**, *9*, 1814.

(16) Cossy, C.; Helm, L.; Merbach, A. E. *Inorg. Chem.* **1989**, *28*, 2699.

(17) Micskei, M.; Heum, L.; Brücher, E.; Merbach, A. E. *Inorg. Chem.* **1993**, *32,* 3844.

(18) Linert, W. *Chem. Soc. Rev.* **1994**, *23*, 429.

(19) Shannon, R. D. *Acta Cryst. A* **1976**, *32*, 751.

(20) Rizkalla, E. N.; Choppin, G. R. "Lanthanides and actinides hydration and hydrolysis" in *Handbook of the Physics and Chemistry of the Rare Earths, Vol. 18* (K. A. Gschneidner, Jr. and L. Eyring, eds.) Elsevier Science Publishers, Amsterdam, 1994, pp. 529-558.

DISCLAIMER

Figure Captions

Figure 1. Diode array traces of the reaction between 4.0×10^{-5} M NpO_2^+ and 4.0×10^{-5} M Chlorophosphonazo III as a function of acidity at I = 1.0 M, T = 25.0 °C.

a) $[HClO_4] = 1.0$ M

b) $[HClO_4] = 0.1$ M

Figure 2. Hypothetical structure of tetradentate complexes of NpO_2^+ with Chlorophosphonazo III.

a) bidentate species

b) tetradentate species

Figure 3. First order rate constants for NpO_2^+ + CLIII at 4.0×10^{-5} M CLIII, 0.1 M $HClO_4$, T = 25.0 °C, I = 1.0 M as a function of $[NpO_2^+]$.

Figure 4. Isokinetic plot for the reactions of NpO_2^+, UO_2^{2+}, Th^{4+}, and Zr^{4+} with CLIII.

Figure 5. Correlation of second order complex formation rates of Fe^{3+}, Zr^{4+}, La^{3+}, Eu^{3+}, Dy^{3+}, Th^{4+}, UO_2^{2+}, NpO_2^+ with CLIII as a function of cation radius.

Table 1. Resolved rate constants (k_{sl}, k_{int}) for the reaction of NpO_2^+ + CLIII as a function of temperature and $[H^+]$ at I = 1.0 M, [CLIII] = 4.0×10^{-5} M, $[NpO_2^+]$ from 1×10^{-5} to 1×10^{-4} M.

$[HClO_4]$ (M)	k_{slope} $(/10^4)(M^{-1}\ sec^{-1})$	k_{int} (sec^{-1})	T (±0.1) (C)
0.1	2.22(±0.14)	3.101(±0.078)	5.1
0.3	1.99(±0.08)	4.344(±0.045)	5.1
0.5	2.88(±0.13)	5.133(±0.072)	5.1
0.7	2.41(±0.12)	5.846(±0.064)	5.0
1.0	3.21(±0.11)	6.443(±0.062)	5.0
0.1	3.86(±0.36)	4.606(±0.209)	9.9
0.3	4.87(±0.08)	5.014(±0.042)	9.9
0.5	4.85(±0.06)	6.360(±0.033)	9.9
0.7	4.98(±0.14)	7.573(±0.079)	9.9
1.0	5.92(±0.81)	8.298(±0.421)	9.9
0.1	6.24(±0.12)	5.467(±0.044)	14.9
0.3	6.80(±0.14)	7.979(±0.051)	14.9
0.5	7.14(±0.21)	9.985(±0.078)	14.9
0.7	7.07(±0.32)	11.91(±0.02)	14.9
1.0	7.57(±0.19)	13.59(±0.07)	14.9
0.1	8.14(±0.43)	8.610(±0.162)	20.0
0.3	5.82(±0.14)	12.92(±0.05)	20.0
0.5	7.95(±0.26)	15.83(±0.10)	20.0
0.1	11.56(±1.13)	12.43(±0.95)	25.0
0.3	11.35(±0.63)	17.31(±0.52)	25.0
0.5	14.03(±1.53)	24.53(±0.75)	25.0
0.7	14.12(±0.24)	27.38(±0.24)	25.0
1.0	12.91(±3.89)	28.80(±2.49)	25.0

[a] $1\times10^{-5}\leq[Np(V)]\leq8\times10^{-5}$ M, CLIII = 4×10^{-5} M, I = 1.0 M maintained with $NaClO_4$.

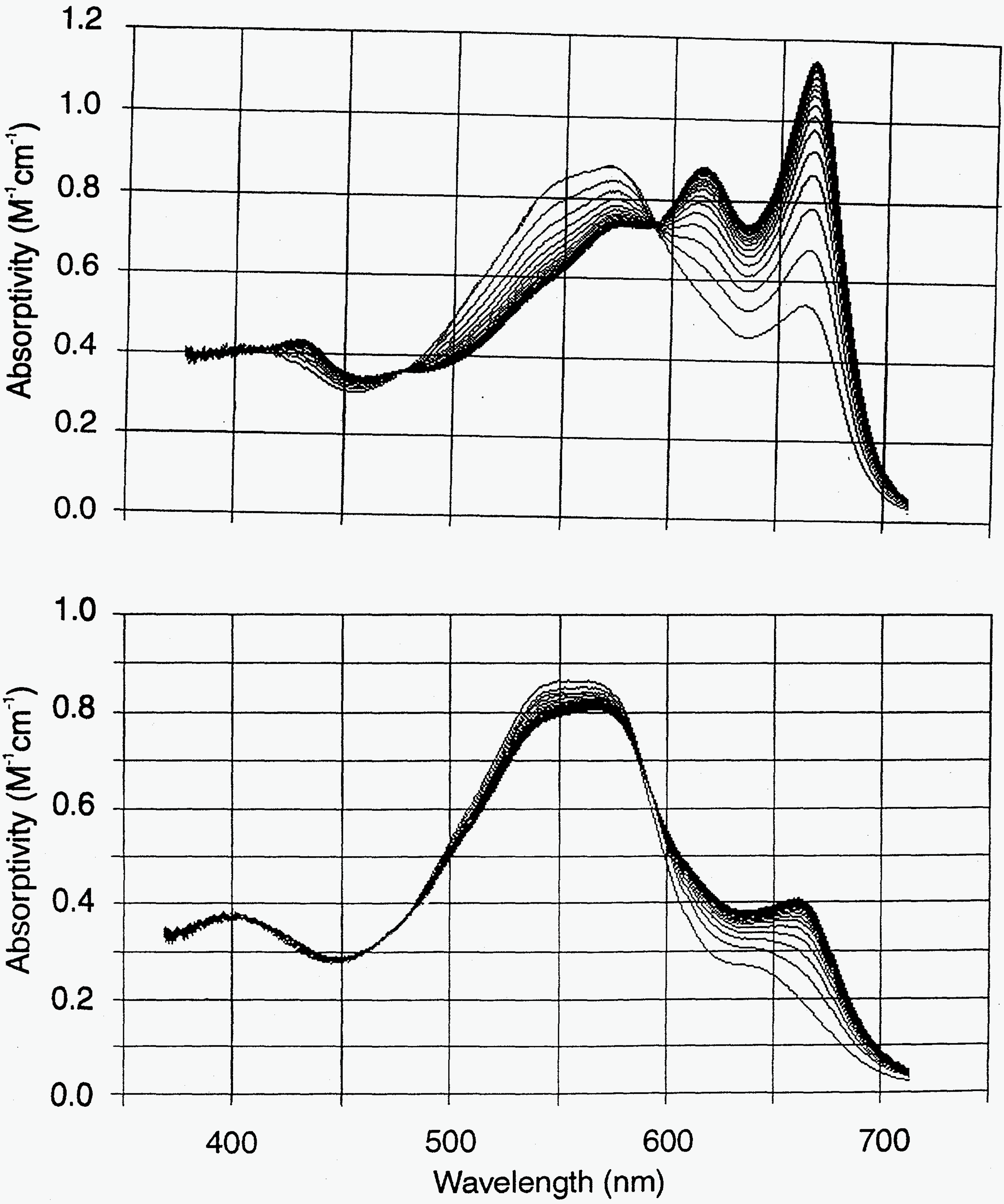
Table 2. Derived rate constants for complex formation (k_1) and dissociation (k_2-acid independent, k_3-acid dependent) for NpO_2^+ + CLIII at 1.0 M ionic strength.[a]

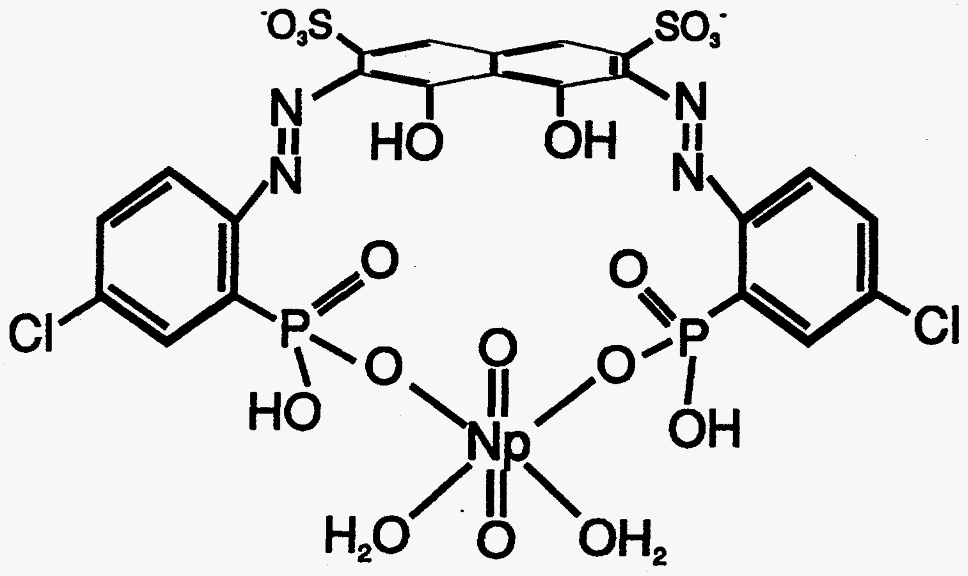
k_1 (M^{-1} sec^{-1})($x10^4$)	k_2 sec^{-1})	k_3 (M^{-1} sec^{-1})	T (±0.1) (C)
2.541(±0.117)	3.56(±0.09)	3.14(0.49)	5.1
4.894(±0.288)	5.30(±0.14)	3.64(0.59)	9.9
6.966(±0.192)	9.14(±0.16)	4.94(0.79)	14.9
7.306(±0.276)	17.59(±0.38)	7.34(0.79)	20.0
12.79(±1.48)	22.53(±2.67)	11.22(4.56)	25.0

[a] $k_{obs} = k_1[Np(V)] + k_2 + k_3 [H^+]$.

Table 3. Activation parameters for the complex formation and dissociation reactions of Np(V) - CLIII.

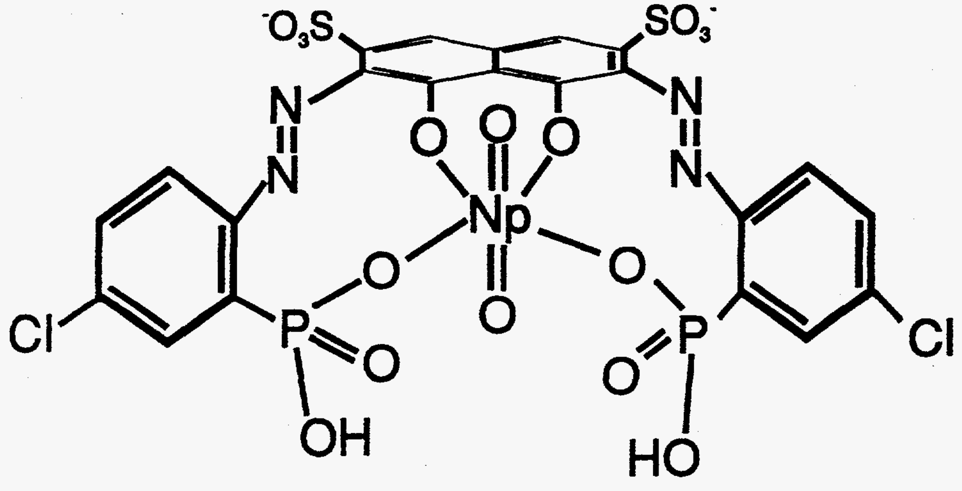
Rate Parameter	1(M)	ΔH^* (kJ/mole)	ΔS^* (J/mole K)
k_f	1.0	46.2(0.3)	7(±1)
k_{rd}	1.0	38.8(0.6)	-96(±18)
k_{ri}	1.0	70.0(0.1)	17(1)
k_f	0.1	60.5(3.4)	62(1)


1.2
1.0
0.8
0.6
0.4
0.2
0.0
Absorptivity ($M^{-1}cm^{-1}$)
1.0
0.8
0.6
0.4
0.2
0.0
Absorptivity ($M^{-1}cm^{-1}$)
400
500
600
700
Wavelength (nm)



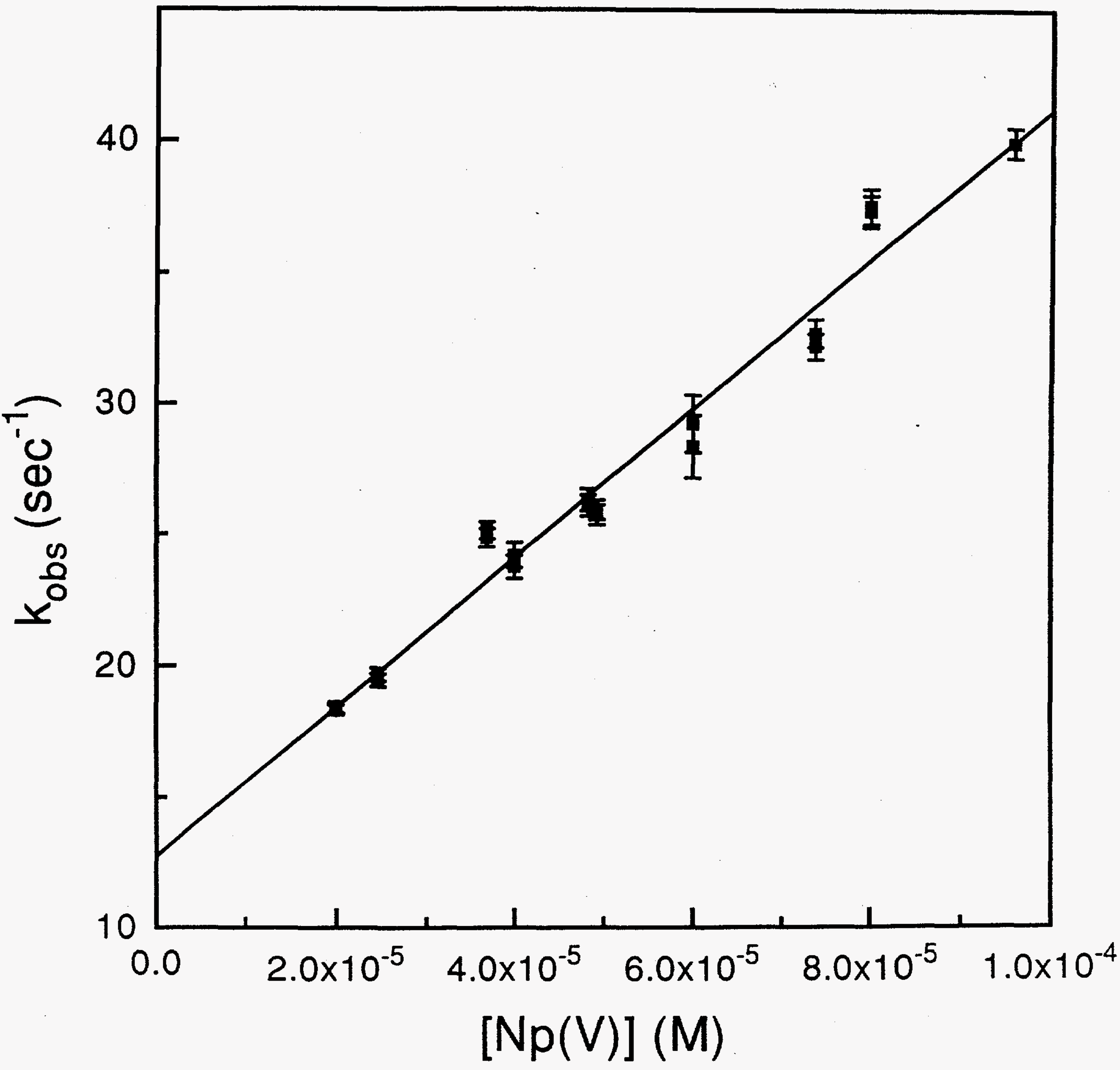
-O3S
SO3-
N
N
HO
OH
N
N
O
O
Cl
P
Cl
P
O
O
O
HO
Np
OH
H2O
O
OH2

a

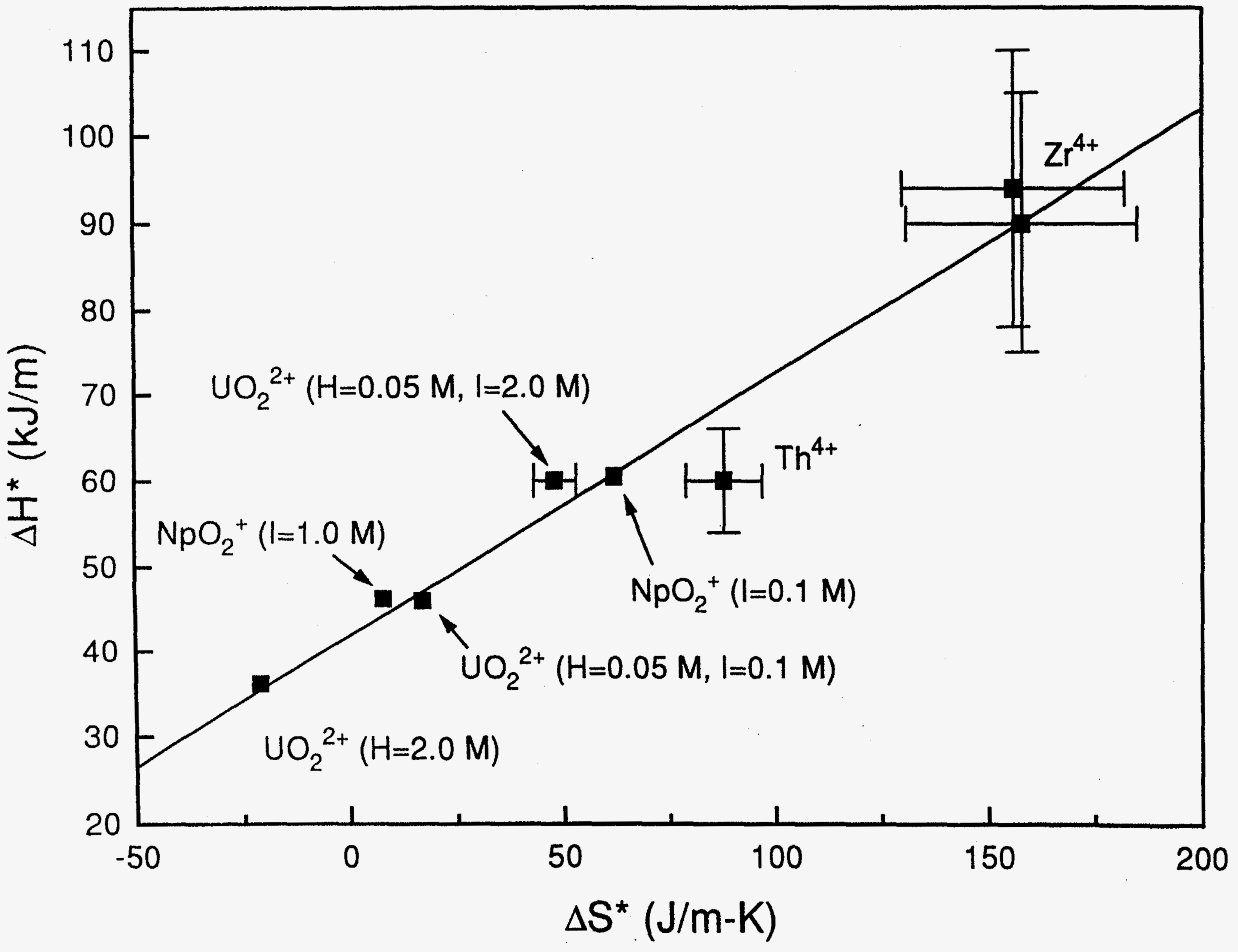


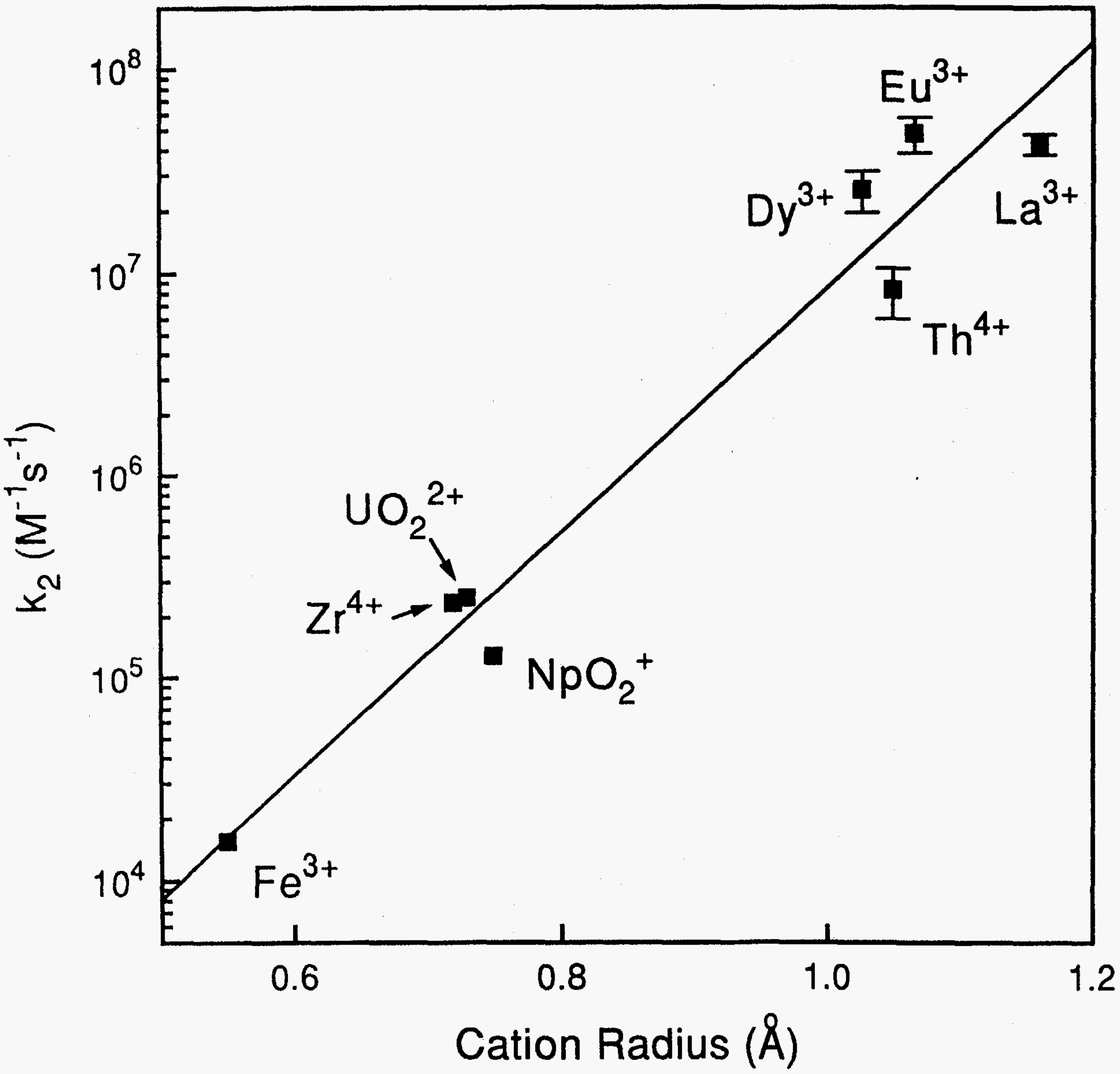
-O3S
SO3-
N
N
O
O
O
N
N
Np
O
O
Cl
P
O
O
P
Cl
O
OH
HO

b



k_{obs} (sec^{-1})
10
20
30
40
0.0
2.0x10^{-5}
4.0x10^{-5}
6.0x10^{-5}
8.0x10^{-5}
1.0x10^{-4}
[Np(V)] (M)


Zr^{4+}
Th^{4+}
UO$_2^{2+}$ (H=0.05 M, I=2.0 M)
NpO$_2^+$ (I=1.0 M)
NpO$_2^+$ (I=0.1 M)
UO$_2^{2+}$ (H=0.05 M, I=0.1 M)
UO$_2^{2+}$ (H=2.0 M)
ΔH* (kJ/m)
110
100
90
80
70
60
50
40
30
20
-50
0
50
100
150
200
ΔS* (J/m-K)


10^8
10^7
10^6
10^5
10^4
k_2 ($M^{-1}s^{-1}$)
0.6
0.8
1.0
1.2
Cation Radius (Å)
Eu^{3+}
Dy^{3+}
La^{3+}
Th^{4+}
UO_2^{2+}
Zr^{4+}
NpO_2^+
Fe^{3+}