

**Figure 9.** Computer fits of the calculated to the observed cesium-133 chemical shifts in (a) DMA and (b) DMF with added DC21C7. Calculations were based on the formation of only 1:1 complexes and on the formation of both 1:1 and 2:1 (DC21C7:Cs<sup>+</sup>) complexes. Note the different ordinate scales for parts a and b.

**Table IV.** Logarithms of the Formation Constants and the Limiting Chemical Shifts (ppm) of Cs<sup>+</sup> Complexes with DC21C7 and DC24C8 at 25 °C

solvent	log $K_1$	log $K_2$	$\delta$ (1:1)	$\delta$ (2:1)
Cs <sup>+</sup> -DC21C7				
FA	2.4 ± 0.3	1.51 ± 0.03	11.5 ± 0.8	24.2 ± 0.2
NMF	>4	2.8 ± 0.3	13 ± 1	20.4 ± 0.3
DMF	>4	3.1 ± 0.5	18 ± 1	21.9 ± 0.1
DMA	>4	2.2 ± 0.2	24.08 ± 0.03	24.88 ± 0.03
Cs <sup>+</sup> -DC24C8				
FA	2.0 ± 0.2	1.23 ± 0.02	5.4 ± 0.5	10.8 ± 0.1
NMF	2.6 ± 0.5	1.67 ± 0.06	4.5 ± 0.5	8.63 ± 0.08
DMF	3.2 ± 0.2	1.37 ± 0.05	5.4 ± 0.1	8.86 ± 0.06
DMA	3.0 ± 0.4	1.9 ± 0.3	12.6 ± 0.6	11.4 ± 0.1

mental data clearly better fit the two-step reaction. This is illustrated in Figure 9 for the DC21C7-Cs<sup>+</sup> system in (a) DMA and (b) DMF.

As seen in Table IV, the limiting chemical shifts of the 2:1 complexes do not differ significantly among the solvents utilized, thus providing further indication of the sandwich structure of these species. Their numerical values differ, reflecting the different chemical environments of the Cs<sup>+</sup> in the two L<sub>2</sub>Cs<sup>+</sup> complexes; however, the ~10 ppm difference is small relative to the broad span of cesium-133 chemical shifts. Formation constants of the complexes, also given in Table IV, show that both 1:1 and 2:1

complexes are reasonably stable.

These results are very much at variance with previous results from our and other laboratories.<sup>7</sup> With the sole exception of (DB21C7)<sub>2</sub>Cs<sup>+</sup> reported by Frensdorff in methanol solutions,<sup>6</sup> sandwich complexes have not been observed in solutions when the size of the cation is equal to or smaller than that of the crown ether cavity. (The diameter of Cs<sup>+</sup> is 3.38 Å; cavity sizes of DC21C7 and DC24C8 are 3.4-4.3 and >4 Å respectively.<sup>5</sup>)

Dicyclohexano crown ethers are much more flexible than their dibenzo analogs. The rather stable 1:1 complexes of Cs<sup>+</sup> with DC21C7 and DC24C8 likely form with rather open conformations of the macrocyclic ring. In both cases, molecular models clearly demonstrate that more puckered conformations (with smaller ring cavities) can be taken by the various cis isomers in which four proximal oxygen atoms point above the ring, with the remainder below. Such conformations would readily permit formation of sandwich complexes with Cs<sup>+</sup>, the cation being coordinated with four oxygen atoms on each macrocycle and the rings skewed in relation to one another to form a snug cavity, which would maximize the ion-ligand interaction. Attempts to isolate single crystals of these 2:1 complexes unfortunately have proven unsuccessful.

### Conclusions

The hitherto unsuspected formation of 2:1 sandwich complexes in cases where  $r_{\text{cation}} < r_{\text{ligand}}$  necessitates review of literature values of many formation constants of crown ether-alkali-metal cation complexes that were determined under the assumption that the above condition precluded the second complexation step.

Our results confirm previous observations that while the consonance between the sizes of the ligand cavity and that of the cation has an important influence on the stability of a cation-ligand complex, it is only one of several important factors that determine the extent of the reaction. Certainly ligand-solvent interaction is also an important factor. Since the formation of crown ether complexes results from an ion-dipole interaction,<sup>24</sup> it is not surprising that the dielectric constant of the medium also affects the extent of the complexation reaction. In fact our results show that in solvents with high dielectric constant, formamide and *N*-methylformamide, the complexes are generally less stable than in the other two solvents. On the other hand, all four solvents have very similar dipole moments and similar donicities, and these factors should similarly affect complexation constants.

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## Kinetics of Dissociation of Thorium(IV) Bound to PMA and PMVEMA

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The kinetics of dissociation of Th(IV) from its complexes with polymaleic acid (PMA) and poly(methyl vinyl ether)maleic acid (PMVEMA) were found to follow rate expressions that reflected seven separate terms ranging in lifetimes between 0.1 s and almost 1 h. The fraction of thorium dissociating by any one of the seven paths depended on the length of time during the first 2 days that the thorium had been bound to the polyelectrolyte prior to dissociation. After 48 h of binding, no further change was observed in the dissociation kinetics. These observations are interpreted in terms of the present models of metal-polyelectrolyte interaction.

### Introduction

The binding of metal ions to polyelectrolytes has been described by a two-state model. In the "site-bound" state the cations are in direct contact with one or more charged groups of the poly-

electrolyte. This binding is analogous to inner-sphere complexation in coordination chemistry. The second type of interaction has been called "atmospheric", "territorial", "condensed", and "delocalized" binding. In this state, the cations are associated generally with

the polyelectrolyte but retain freedom to move about the surface of the polyelectrolyte.

Manning<sup>1</sup> emphasizes the territorially bound ions in his condensation model, which adequately describes the binding of monovalent ions. Many workers<sup>2-4</sup> have expanded on the condensation model in order to explain the binding properties of polyelectrolytes but with only moderate success. Wennerstrom et al.<sup>3</sup> showed that such theories are in significant disagreement with experimental results for binding of divalent cations and concluded that statistical mechanical treatments based solely on territorial binding are inadequate for polyvalent cation-polyelectrolyte systems. Presumably, this inadequacy reflects the presence of site binding in the system.

Previously, the binding of  $\text{Am}^{3+}$ ,  $\text{UO}_2^{2+}$ , and  $\text{Th}^{4+}$  at tracer concentrations to the synthetic polyelectrolytes polymaleic acid (PMA), polyethylenemaleic acid (PEMA), and poly(methyl vinyl ether) maleic acid (PMVEMA) was measured by a radiotracer technique.<sup>5</sup> These polyelectrolytes were chosen because they have only carboxylate groups that would bind the actinides and, thus, represent relatively simple polyelectrolyte anions. At least two constants were required to fit the binding data, but no further insight into the nature of the metal-polyelectrolyte interaction was obtained. In this study, the kinetics of formation and dissociation of Th(IV) complexes of polymaleic acid and poly(methyl vinyl ether) maleic acid were studied between pH 4.2 and 5.9 to elucidate the nature of the thorium-polyelectrolyte interaction and the relative roles of site and territorial binding.

### Experimental Section

**Reagents.** The reagent arsenazo III (3,6-bis[(2-arsenophenyl)azo]-4,5-dihydroxy-2,7-naphthalenedisulfonic acid) (99.9%) was obtained from Aldrich Chemical Co. and used with no purification. A stock solution of Th(IV) was prepared by dissolving  $\text{Th}(\text{ClO}_4)_4 \cdot 3\text{H}_2\text{O}$  in 0.0010 M  $\text{HClO}_4$ . The concentrations of thorium in the stock solutions were measured by passing aliquots through a column of Dowex 50W-X8 cation-exchange resin (20–50 mesh) and titrating the acid liberated in the eluant with 0.1000 M NaOH.

The synthetic polyelectrolytes were from Polysciences, Inc., and were used with no purification. The polyelectrolytes were a mixture of molecular weights of about 5000–40 000 u. A measurement by vapor-phase osmometry indicated an average molecular weight of ca. 13 000 u. Stock solutions of PMA and PMVEMA were prepared by dissolving the solid polyelectrolyte in a sufficient amount of 0.0500 M NaOH to completely neutralize the polyelectrolyte. The concentration of the polyelectrolyte solution measured as hydrogen ion equivalents per liter (i.e., carboxylic acid concentration) was determined by titrating the excess base in the polyelectrolyte solution with 0.1000 M  $\text{HClO}_4$ .

Stock solutions of acetate and MES (4-morpholineethanesulfonic acid) buffers were made from Aldrich chemicals. The ionic strengths were adjusted with sodium perchlorate to an ionic strength of 0.10 M.

**Ligand-Exchange Technique.** The dissociation of thorium from PMA and PMVEMA was studied by using a ligand-exchange technique. After a preset time, the thorium-polyelectrolyte complex was dissociated by introduction of arsenazo III, which forms a more stable complex with thorium than the polyelectrolyte molecule. Arsenazo III has a large shift in the maximum wavelength of absorbance upon complexation with thorium. From stoichiometric relations and the spectroscopic data, the amount of thorium bound to the polyelectrolyte at any given time was calculated. In each experiment, the total concentrations were as follows:  $\text{Th}^{4+}$ ,  $1 \times 10^{-5}$  M; PMA or PMVEMA,  $2 \times 10^{-4}$  M; arsenazo III,  $2.5 \times 10^{-5}$  M.

All experiments that involved absorbance measurements requiring longer than approximately 1 min after the initiation of the exchange reaction were done by using a Tracor Northern Model TN 6050 spectrometer. The absorbance at 670.2 nm (the absorption maximum of the thorium-arsenazo III complex) was measured. Experiments at other than ambient temperature were performed in a 1.00-cm quartz-jacketed flow cell connected to a constant-temperature water bath.

Experiments that required visible absorption measurements on the time scale of 0.030–60 s were performed at Argonne National Laboratory

with a Durrum D-110 stopped-flow spectrometer interfaced to an SL-I-1123 computer.

**Calculations.** Each data set for experiments in which the exchange reaction was followed for greater than 1 min consisted of 50–75 data points. Data sets for the 0.03–60-s reaction times (studied by stopped-flow) consisted of 250 data points. In all experiments, the rate parameters were determined by a nonweighted simplex nonlinear regression analysis of the absorbance vs time data with an average residual difference between observed and calculated absorbance of less than 0.005. The number of first-order terms in each analysis was independently determined by a kinetic spectrum technique developed<sup>6</sup> for multiple first-order decay systems.

A minimum of two, but usually more, kinetic experiments were performed for each set of experimental conditions. All uncertainties on kinetic parameters were determined by curvature matrix evaluation during the nonlinear regression analysis of the data and were found to be comparable to the deviation found from analysis of replicate kinetic experiments. The reported standard errors correspond to  $2\sigma$ .

**Ion-Exchange Procedure.** An ion-exchange technique<sup>7</sup> was used to measure changes in thorium-polyelectrolyte binding as a function of time after addition of Th(IV) to the solution of polyelectrolyte. Columns (1.2-cm i.d. and 5.7-cm length) of the cation-exchange resin Dowex-50, 100–200 mesh in the sodium form, were equilibrated with acetate buffer of the desired pH prior to the experiment.

An aliquot of thorium stock solution, spiked with  $^{230}\text{Th}$ , was added to a buffered polyelectrolyte solution. At various time intervals, 1.000-mL samples of the solution were withdrawn and passed through the resin bed in about 10 s. Three additional 1.000-mL rinses were required for complete rinsing of the bed. Thorium that was weakly bound or unbound to the polyelectrolyte remained in the ion-exchange resin, while more strongly bound thorium passed through the column with the polyelectrolyte solution. The eluant was counted for  $\alpha$  decay of  $^{230}\text{Th}$  by using liquid scintillation counting.<sup>5</sup>

### Results

The polyelectrolytes were determined to have carboxylate capacities of 17.2 mequiv/g for PMA and 11.5 mequiv/g for PMVEMA. In the kinetic experiments, the ratio of millimoles of Th(IV) to milliequivalents of carboxylate groups was 1:20.

The ion-exchange experiment revealed that, under the conditions of these studies, the amount of thorium more strongly (relative to binding to the resin) bound to the polyelectrolyte remained a constant 70% over the time period of 10 min to 48 h after initial mixing of the Th(IV) and the polyelectrolyte. We conclude that the rate of the initial association was fast and the initial association reaction complete within 10 min.

With thorium, arsenazo III forms a very stable complex with an absorption peak at 670.2 nm. Below pH 6 uncomplexed arsenazo III has very slight absorption at this wavelength. In the stopped-flow experiments at Argonne, complexation of Th(IV) and arsenazo III was found to take place in less than 10 ms at pH 4.20. A spectrophotometric titration showed that thorium, at pH 4.20, formed a complex with two arsenazo III molecules, i.e.,  $\text{Th}(\text{arsenazo III})_2$ . Superimposed absorption spectra taken during the course of the exchange reaction showed an isobestic point at 587.9 nm between the peak at 670.2 nm due to  $\text{Th}(\text{arsenazo III})_2$  and that at 550 nm due to the uncomplexed arsenazo III peak. This provided further evidence that only one complex was formed by thorium and arsenazo III. Experiments were performed with arsenazo III concentrations from 2.5 to 10 times greater than that of thorium with no change in the dissociation rate of thorium from the polyelectrolytes. Thus, it was concluded that arsenazo III does not interfere with the dissociation of thorium from the polyelectrolytes.

The kinetic spectrum analysis method<sup>6,8</sup> was used to ascertain the number of components in these reactions. This information, in turn, was used with a simplex nonlinear regression analysis<sup>9</sup> to obtain the first-order decay terms. The kinetic spectra provided graphic representations of the overall dissociation reaction at a

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**Table I.** Rate Data for Th-PMA Dissociation: Shorter Lived Terms ( $k$ ,  $s^{-1}$ )

(a) pH Variation				
pH	$k_1$	$k_2$	$k_3$	$k_4$
4.20	$6.58 \pm 0.54$	$2.81 \pm 0.20$	$0.375 \pm 0.023$	$0.177 \pm 0.012$
5.09	$6.04 \pm 0.56$	$2.79 \pm 0.17$	$0.374 \pm 0.027$	$0.170 \pm 0.015$
5.94	$6.84 \pm 0.57$	$2.82 \pm 0.22$	$0.374 \pm 0.024$	$0.170 \pm 0.015$
pH	$\%(k_1)$	$\%(k_2)$	$\%(k_3)$	$\%(k_4)$
4.20	$3.69 \pm 1.21$	$18.1 \pm 3.7$	$2.38 \pm 0.26$	$44.7 \pm 5.9$
5.09	$5.44 \pm 2.42$	$11.0 \pm 2.9$	$1.03 \pm 0.18$	$61.3 \pm 7.1$
5.94	$7.32 \pm 1.56$	$10.6 \pm 2.9$	$7.13 \pm 1.55$	$47.3 \pm 6.5$
pH	$\sum\%(k_1 + k_2 + k_3 + k_4)$	pH	$\sum\%(k_1 + k_2 + k_3 + k_4)$	
4.20	$68.8 \pm 7.1$	5.94	$72.4 \pm 7.5$	
5.09	$78.7 \pm 8.0$			

(b) Temperature Variation (pH = 4.20)

$T$ , °C	$k_1$	$k_2$	$k_3$	$k_4$
2.0	$6.71 \pm 0.52$	$3.02 \pm 0.20$	$0.410 \pm 0.035$	$0.203 \pm 0.019$
25.0	$6.58 \pm 0.54$	$2.81 \pm 0.20$	$0.375 \pm 0.023$	$0.177 \pm 0.012$
40.0	$6.33 \pm 0.54$	$2.79 \pm 0.20$	$0.390 \pm 0.017$	$0.191 \pm 0.011$
	$k_1$	$k_2$	$k_3$	$k_4$
$E_a^a$	$-3.6 \pm 2.3$	$-3.5 \pm 1.7$	$-4.0 \pm 3.0$	$-3.9 \pm 3.0$
$\Delta S^*a$	$-273 \pm 33$	$-280 \pm 29$	$-258 \pm 33$	$-280 \pm 33$

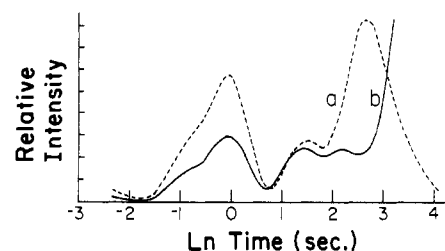
<sup>a</sup>Units for activation energies are kJ/mol. Units for activation entropies are J/(mol·K).

**Table II.** Rate Constants for Th-PMA Dissociation: Longer Lived Terms ( $k$ ,  $min^{-1}$ )

(a) pH Variation			
pH	$k_5$	$k_6$	$k_7$
4.20	$0.944 \pm 0.069$	$0.409 \pm 0.028$	$0.0967 \pm 0.010$
4.62	$1.04 \pm 0.05$	$0.219 \pm 0.017$	$0.072 \pm 0.007$
5.09	$1.00 \pm 0.07$	$0.454 \pm 0.042$	$0.109 \pm 0.012$
5.50	$0.475 \pm 0.04$	$0.082 \pm 0.072$	$0.038 \pm 0.003$
5.94	$0.477 \pm 0.04$	$0.097 \pm 0.010$	$0.025 \pm 0.002$
pH	$\%(k_5)$	$\%(k_6)$	$\%(k_7)$
4.20	$9.6 \pm 2.5$	$16.7 \pm 3.5$	$5.2 \pm 1.3$
4.62	$4.2 \pm 1.3$	$11.5 \pm 2.7$	$5.6 \pm 1.6$
5.09	$5.1 \pm 1.5$	$3.1 \pm 0.7$	$13.1 \pm 3.5$
5.50	$2.4 \pm 0.5$	$18.6 \pm 2.7$	$11.7 \pm 2.4$
5.94	$1.6 \pm 0.6$	$9.5 \pm 1.6$	$16.5 \pm 3.7$
pH	$\sum\%(k_5 + k_6 + k_7)$	pH	$\sum\%(k_5 + k_6 + k_7)$
4.20	$31.5 \pm 4.5$	5.50	$32.7 \pm 3.6$
4.62	$21.3 \pm 3.4$	5.94	$27.6 \pm 4.1$
5.09	$21.3 \pm 3.9$		
(b) Temperature Variation (pH = 4.20)			
$T$ , °C	$k_5$	$k_6$	$k_7$
2.0	$0.453 \pm 0.035$	$0.153 \pm 0.011$	$0.041 \pm 0.004$
25.0	$0.994 \pm 0.069$	$0.409 \pm 0.028$	$0.097 \pm 0.010$
40.0	$1.74 \pm 0.11$	$0.739 \pm 0.006$	$0.161 \pm 0.012$
	$k_5$	$k_6$	$k_7$
$E_s^a$	$25.2 \pm 2.1$	$27.6 \pm 2.4$	$23.5 \pm 1.7$
$\Delta S^*a$	$-202 \pm 17$	$-202 \pm 13$	$-227 \pm 17$

<sup>a</sup>Units for activation energies are kJ/mol. Units for activation entropies are J/(mol·K).

particular set of conditions. These were used to obtain initial guesses of parameters in the nonlinear regression program, thereby reducing the number of iterations required for convergence. The simplex analysis gave the values for the rate constants and the fraction of thorium dissociating by each pathway, which are reported in the tables. Kinetic spectra were obtained for samples in which the dissociation reaction was initiated after 2, 6, 12, 24, 48, and 72 h of contact time of the thorium and the polyelectrolytes. The kinetic spectra varied as the contact time increased to 48 h but were invariant for contact times greater than 48 h. Sample sets of the data are available in ref 10.

**Figure 1.** Kinetic spectra of thorium dissociation from PMA. Conditions for the reaction were  $[PMA] = 2.017 \times 10^{-4}$  mequiv carboxylate/mL,  $[Th^{4+}] = 1.005 \times 10^{-5}$  M,  $[arsenazo\ III] = 2.508 \times 10^{-5}$  M, pH = 4.20, and  $T = 25$  °C. The contact times were (a) 1 min and (b) 48 h.**Table III.** Rate Constants for Th-PMVEMA Dissociation: Shorter Lived Terms ( $k$ ,  $s^{-1}$ )

(a) pH Variation			
pH	$k_1$	$k_2$	$k_3$
4.20	$1.76 \pm 0.14$	$0.254 \pm 0.021$	$0.179 \pm 0.012$
5.09	$1.76 \pm 0.15$	$0.248 \pm 0.019$	$0.0796 \pm 0.0053$
5.94	$1.80 \pm 0.17$	$0.291 \pm 0.028$	$0.0190 \pm 0.0014$
pH	$\%(k_1)$	$\%(k_2)$	$\%(k_3)$
4.20	$0.21 \pm 0.07$	$0.14 \pm 0.07$	$74.6 \pm 3.9$
5.09	$0.25 \pm 0.07$	$0.16 \pm 0.07$	$79.5 \pm 4.1$
5.94	$0.20 \pm 0.07$	$0.13 \pm 0.07$	$74.5 \pm 4.0$
pH	$\sum\%(k_1 + k_2 + k_3)$	pH	$\sum\%(k_1 + k_2 + k_3)$
4.20	$74.9 \pm 3.9$	5.94	$74.8 \pm 4.0$
5.09	$79.9 \pm 4.1$		
(b) Temperature Variation (pH = 4.20)			
$T$ , °C	$k_1$	$k_2$	$k_3$
2.0	$1.72 \pm 0.12$	$0.254 \pm 0.21$	$0.082 \pm 0.005$
25.0	$1.76 \pm 0.14$	$0.256 \pm 0.20$	$0.179 \pm 0.012$
40.0	$1.76 \pm 0.14$	$0.258 \pm 0.20$	$0.258 \pm 0.021$
	$k_1$	$k_2$	$k_3$
$E_a^a$	$-2.0 \pm 1.9$	$-3.6 \pm 2.8$	$18 \pm 1.6$
$\Delta S^*a$	$-255 \pm 30$	$-276 \pm 33$	$-207 \pm 17$

<sup>a</sup>Units for activation energies are kJ/mol. Units for activation entropies are J/(mol·K).

The analysis of the Th-PMA dissociation gave seven first-order terms; there were four "fast" paths in the lifetime range of 0.1 to about 10 s and three "slow" paths with lifetimes from 1 to 40 min. Tables I and II provide data on the rate constants as a function of pH and temperature. These data are for dissociation after the thorium had been bound to the PMA for over 48 h. Generally, the rates of the faster paths were relatively insensitive to pH changes, while that of the longer lived dissociations apparently decreased with increasing pH. Similarly, the longer lived processes were more sensitive to temperature changes.

To avoid misunderstandings about our data analysis, we emphasize that the short-lived and the long-lived parameters were obtained from separate sets of experiments. Each individual data set for a set of conditions and a particular time frame was found to require either three or four first-order components. The number of first-order components and their approximate values were determined by the kinetic spectrum analysis technique.<sup>6</sup> The original data set was then reanalyzed with this number of first-order components by a regression analysis of the 50–250 data points. The number and values of the rate constants for either the fast or the slow experiments were thus obtained by two independent analytical techniques from the original data. The combination of the fast and the slow experiments resulted in a total of seven first-order rate constants for both the PMA and PMVEMA systems.

The effect of predissociation contact time on the fast paths is shown in Figure 1. Increasing this predissociation contact time

**Table IV.** Rate Constants for Th-PMVEMA Dissociation: Longer Lived Terms ( $k$ ,  $\text{min}^{-1}$ )

(a) pH Variation				
pH	$k_4$	$k_5$	$k_6$	$k_7$
4.20	$1.23 \pm 0.11$	$0.665 \pm 0.051$	$0.300 \pm 0.023$	$0.157 \pm 0.011$
4.62	$1.25 \pm 0.12$	$0.435 \pm 0.037$	$0.282 \pm 0.022$	$0.130 \pm 0.011$
5.09	$1.18 \pm 0.13$	$0.475 \pm 0.042$	$0.282 \pm 0.022$	$0.121 \pm 0.010$
5.50		$0.703 \pm 0.064$	$0.270 \pm 0.021$	$0.104 \pm 0.007$
5.94		$0.664 \pm 0.058$	$0.084 \pm 0.007$	$0.037 \pm 0.003$
pH	$\%(k_4)$	$\%(k_5)$	$\%(k_6)$	$\%(k_7)$
4.20	$4.84 \pm 1.49$	$6.07 \pm 1.51$	$10.3 \pm 2.4$	$3.84 \pm 0.73$
4.62	$4.05 \pm 1.32$	$5.30 \pm 1.65$	$4.64 \pm 1.33$	$5.05 \pm 1.56$
5.09	$3.50 \pm 0.92$	$3.46 \pm 0.96$	$3.51 \pm 0.92$	$9.62 \pm 2.41$
5.50		$5.94 \pm 1.29$	$9.01 \pm 1.48$	$15.1 \pm 0.8$
5.94		$3.58 \pm 0.97$	$17.7 \pm 3.4$	$3.94 \pm 0.82$
pH	$\sum\%(k_4 + k_5 + k_6 + k_7)$	pH	$\sum\%(k_4 + k_5 + k_6 + k_7)$	
4.20	$25.1 \pm 3.3$	5.50	$30.1 \pm 4.2$	
4.62	$19.0 \pm 2.9$	5.94	$25.2 \pm 3.6$	
5.09	$20.1 \pm 2.1$			

(b) Temperature Variation (pH = 4.20)

$T$ , °C	$k_4$	$k_5$	$k_6$	$k_7$
2.0	$1.29 \pm 0.03$	$0.302 \pm 0.025$	$0.100 \pm 0.010$	$0.0319 \pm 0.00$
25.0	$1.23 \pm 0.11$	$0.665 \pm 0.051$	$0.300 \pm 0.023$	$0.157 \pm 0.01$
40.0	$1.24 \pm 0.02$	$1.07 \pm 0.07$	$0.584 \pm 0.044$	$0.336 \pm 0.02$
	$k_4$	$k_5$	$k_6$	$k_7$
$E_a^a$	$-3.3 \pm 3.0$	$21.8 \pm 2.9$	$31.7 \pm 2.6$	$38.5 \pm 2.9$
$\Delta S^*^a$	$-296 \pm 34$	$-217$	$-191 \pm 16$	$-174 \pm 15$

<sup>a</sup> Units are activation energies are kJ/mol. Units for activation entropies are J/(mol·K).

from 1 min to 48 h generally caused an increase in the percentage dissociation by slower paths. For 1-min contact time, all the dissociation occurred by the four fast paths, whereas for 48-h contact time, only ca. 75% was accounted for by these paths.

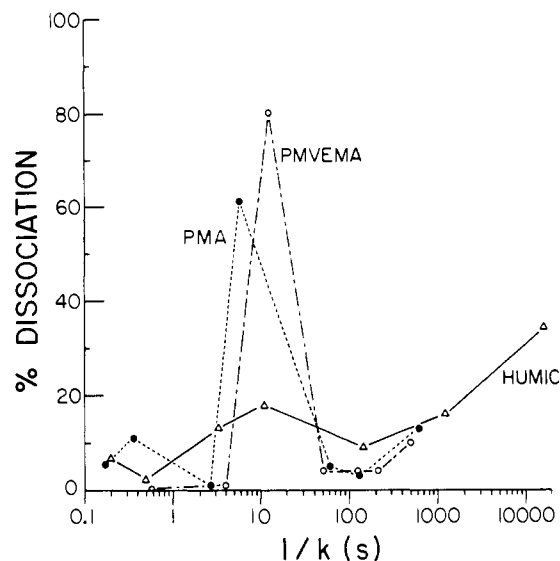
Dissociation of thorium from PMVEMA was studied under the same conditions. As for the Th-PMA system, the cation-exchange-resin studies showed no change in thorium binding within the time frame of the experiments, i.e., from 10 min to 72 h after initial mixing of the Th(IV) and PMVEMA solutions. For the Th-PMVEMA system, the kinetic spectrum analysis indicated a dissociation process that is described by a rate equation with seven first-order (in Th-PMVEMA) terms. Three terms had "half-lives" in the range of seconds, and four paths involved times of minutes. The rate constants for different pH and temperature values are listed in Tables III and IV. These data are for systems in which the thorium was bound to the PMVEMA over 48 h prior to dissociation.

The Th-PMVEMA data reflected the effect of pH on the terms associated with the rate constants  $k_3$ ,  $k_6$ , and  $k_7$ . These were also the terms of greater temperature sensitivity. As in the Th-PMA system, about 75% of the dissociation occurred via the short-lived paths and the dissociation was sensitive to predissociative contact time, requiring 48-h contact time for constant dissociation kinetics.

## Discussion

The effect of predissociation contact time on the dissociation kinetics was observed also for the thorium-humic acid system. The rapid initial uptake of the thorium must be associated with interaction of cations with the surface of the polyelectrolyte molecules, via site and territorial binding. The effect of the cations in neutralizing a part of the net anionic charge of the polyelectrolyte would induce conformational changes in the polyelectrolyte. This is accompanied by relocation of some of the thorium cations to interior, less labile binding sites. Apparently, this process of conformational change and thorium relocation proceeds over a 2-day period. Such a model is consistent with the increase of the population of longer lived paths (presumably, interior binding sites) as the predissociation contact time increases.

The percentage of dissociation by each path vs the half life of the path is shown in Figure 2. The data are for pH = 5.09 and



**Figure 2.** Relationship between the % dissociation and the reciprocal of the dissociation rate constants for the paths observed for the Th-PMA and Th-PMVEMA systems (pH 5.09,  $T = 25.0$  °C,  $\geq 48$ -h contact time).

$\geq 48$ -h predissociation contact. The values for Th(IV) dissociation from humic acid<sup>8</sup> are also shown. For all three polyelectrolytes, dissociation by the longest lived of the fast paths ( $t_{1/2}$  ca. 5–13 s) and of the slow paths ( $t_{1/2} \geq 10$  min) are the dominant modes. The dissociation from humic acid is decreased in the 5–13-s domain, which may be related to its larger average molecular weight (ca. 28 000 u) compared to that of the PMA and PMVEMA (ca. 13 000 u) as this would result in a larger fraction of internal binding sites. Assuming that the molecular weight distributions and the molecular shapes are the same, the greater chemical inhomogeneity of humic acid may also be responsible for a higher number of the longer lived sites.

Figure 2 suggests a model in which thorium dissociation from polyelectrolytes occurs via two major modes, each of which has several observable subpaths. A possible scenario involves relatively fast dissociation by cations bound to outer (surface) sites. Such dissociation changes the electrostatic field of the polyelectrolyte molecule, which induces conformational changes that, in turn, result in the more rapid release of the cations that are bound to sites that become more exposed. This model is consistent with the relative insensitivity to pH of the faster (surface) dissociation and the shortening of the lifetimes with increased pH of the longer (interior) dissociation. This pH effect probably reflects the conformational changes whereby increased ionization (higher pH) causes opening of the polymer structure.

In general, the activation energies are smaller (in some cases, even slightly negative) for the short-lived binding. The large, negative entropies of activation plus the small activation enthalpies suggest little change in the hydration between the free and the bound Th(IV) as dehydration would lead to a positive entropy change. This is consistent with the "condensed" cations of Manning's model. The more positive activation energies as well as the somewhat more positive entropies of activation of the longer lived terms are consistent with processes involving Th(IV) bound to specific carboxylate sites.

Obviously, we cannot associate the shorter lived terms directly with condensation. The shorter lived terms account for 70–75% of the Th(IV), while the ion-exchange resin experiments indicate about 30% is "weakly" bound. There is probably some intermediate situation between condensed and site bound that accounts for this difference between the weakly bound and the short-lived thorium. Perhaps, an investigation of the kinetics of the changes during the initial 48 h of contact time may be fruitful in clarifying the nature of the spectrum of binding moves of metals to even simple (monofunctional) polyelectrolytes. The net process must reflect the cooperative effects of electrostatic and conformational

changes as dissociation occurs. A more complete description of the mechanisms of metal ion dissociation from polyelectrolyte molecules must await additional studies on the effects of cationic charge, molecular weight, average functional group density of the polyelectrolyte, etc.

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## Adducts of Zirconium and Hafnium Tetrachlorides with Neutral Lewis Bases. 2. Kinetics and Mechanism: A Variable-Temperature and -Pressure <sup>1</sup>H NMR Study<sup>1,2</sup>

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In CH<sub>2</sub>Cl<sub>2</sub> and CHCl<sub>3</sub> solution, ZrCl<sub>4</sub>·2L and HfCl<sub>4</sub>·2L adducts (L = Lewis base, given in order of increasing adduct stability: Me<sub>2</sub>O, Cl<sub>2</sub>(Me<sub>2</sub>N)PO, Cl(MeO)<sub>2</sub>PO, (MeO)<sub>3</sub>PO, Cl(Me<sub>2</sub>N)<sub>2</sub>PO) can exist as cis and/or trans isomers. Three reactions can be envisaged in the presence of excess L: (1) *cis*-MX<sub>4</sub>·2L ⇌ *trans*-MX<sub>4</sub>·2L; (2) *cis*-MX<sub>4</sub>·2L + \*L ⇌ *cis*-MX<sub>4</sub>·L\*L + L; (3) *trans*-MX<sub>4</sub>·2L + \*L ⇌ *trans*-MX<sub>4</sub>·L\*L + L. Cis-trans isomerization (eq 1) was found to be the fastest reaction and is characterized by a first-order rate law, activation entropies, ΔS<sup>‡</sup>, between -49 and +14 J K<sup>-1</sup> mol<sup>-1</sup>, activation enthalpies, ΔH<sup>‡</sup>, between 48.0 and 67.8 kJ mol<sup>-1</sup>, and for ZrCl<sub>4</sub>·2(MeO)<sub>3</sub>PO an activation volume, ΔV<sup>‡</sup>, of -1.6 cm<sup>3</sup> mol<sup>-1</sup>. Intramolecular isomerization, with a slightly contracted six-coordinate transition state, was concluded. The second, slower, process observed is intermolecular free ligand exchange on the *trans*- and/or *cis*-MCl<sub>4</sub>·2L adducts. When both intermolecular exchanges occur, the exchange on the *trans* isomer is the faster. The intermolecular exchange reactions were found to obey second-order rate laws, except for MCl<sub>4</sub>·2Cl<sub>2</sub>(Me<sub>2</sub>N)PO (M = Zr, Hf), for which mixed first/second-order rate laws are observed. The second-order intermolecular exchange pathways show very negative ΔS<sup>‡</sup><sub>12</sub> and ΔS<sup>‡</sup><sub>22</sub> values (-131 to -67 J K<sup>-1</sup> mol<sup>-1</sup>), ΔH<sup>‡</sup><sub>12</sub> and ΔH<sup>‡</sup><sub>22</sub> values between 20.1 and 43.1 kJ mol<sup>-1</sup>, and for ZrCl<sub>4</sub>·2(MeO)<sub>3</sub>PO a ΔV<sup>‡</sup><sub>12</sub> value of -11.1 cm<sup>3</sup> mol<sup>-1</sup>. An I<sub>a</sub> mechanism is suggested, without ruling out a limiting A mechanism. The activation parameters for the first-order cis exchange pathway are interpreted in terms of a limiting D mechanism, which is justified in terms of the stability sequence of the adducts. These results for the ZrCl<sub>4</sub>·2L and HfCl<sub>4</sub>·2L adducts contrast with those obtained previously for the TiCl<sub>4</sub>·2L and SnCl<sub>4</sub>·2L adducts. For these latter adducts, first, the intermolecular exchange on the cis isomer is much faster than the isomerization and occurs by a D mechanism and, second, the isomerization process itself is characterized by an expanded transition state. This exemplifies the striking differences in reaction mechanism from Ti(IV) and Sn(IV) to Zr(IV) and Hf(IV) metal chloride adducts. MCl<sub>4</sub>·2L, due to the increase in ionic radius, which favors the changeover from a bond-breaking to a bond-making mechanism.

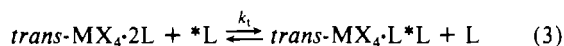
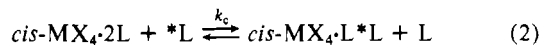
### Introduction

In the previous paper,<sup>3</sup> we showed that ZrCl<sub>4</sub>·2L and HfCl<sub>4</sub>·2L adducts with neutral Lewis bases, L, can exist in CH<sub>2</sub>Cl<sub>2</sub> and CHCl<sub>3</sub> in the cis form, the trans form, or as an equilibrium of both cis and trans isomers. This was in contrast to the situation for TiCl<sub>4</sub>·2L adducts,<sup>4</sup> where the cis adduct strongly predominated, except for those adducts with tetrahydrofuran and the strong donors (MeO)<sub>3</sub>PO, Cl(Me<sub>2</sub>N)<sub>2</sub>PO, and (Me<sub>2</sub>N)<sub>3</sub>PO. However, it is akin to the situation for SnCl<sub>4</sub>·2L,<sup>5,6</sup> where the cis-trans isomerization equilibrium is observed in most cases.

Three reactions can be envisaged in the presence of both *cis*- and *trans*-MCl<sub>4</sub>·2L isomers (M = Sn, Ti, Zr, Hf) and an excess of L. The first reaction is the cis-trans isomerization process:



The second and third reactions involve the exchange of free ligand on the cis and trans isomers:



In the previous studies on the 3d<sup>0</sup> TiCl<sub>4</sub>·2L<sup>7</sup> and the 4d<sup>10</sup>

SnCl<sub>4</sub>·2L<sup>8-10</sup> adducts only the two first reactions (eqs 1 and 2) were observed. The faster reaction was intermolecular exchange on the cis adduct. Both reactions had first-order rate laws and positive activation entropies and volumes. D mechanisms, with five-coordinate intermediates, were concluded for the intermolecular cis substitution. Intramolecular processes, with expanded six-coordinate transition states, were assigned to the isomerization reactions on the basis of smaller, but still positive, activation volumes. This implies that there is little or no direct intermolecular ligand exchange on the trans isomer (eq 3); rather trans substitution is accomplished through three elementary processes: isomerization to the cis isomer, very fast intermolecular ligand exchange on that isomer, and finally isomerization again to the trans isomer.

Zr<sup>4+</sup> (ionic radius *r* = 80 pm<sup>11</sup>) and Hf<sup>4+</sup> (81 pm) are much larger ions than Ti<sup>4+</sup> (68 pm) and Sn<sup>4+</sup> (71 pm), and thus, one may expect large differences in the isomerization and substitution behavior of their MCl<sub>4</sub>·2L adducts. The connection between metal ion size and a dissociative-associative changeover in substitution mechanism is well-known for di- and trivalent metal centers.<sup>12,13</sup> Therefore, in order to provide complete mechanistic assignments, variable-concentration, variable-temperature, and variable-pressure kinetic measurements were undertaken for a series of ZrCl<sub>4</sub>·2L and HfCl<sub>4</sub>·2L adducts.

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