Registry No. (nmpH)$_2$CuCl$_4$ (green), 51751-77-0; (nmpH)$_2$CuCl$_4$ (yellow), 51751-78-1.

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Dependence of Rates of Complex Formation on Ionic Strength and Chelation. Samarium Sulfate and Malonate

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An attempt has been made to correlate overall rate constants for metal complex formation reactions obtained by transient relaxation methods with the rate constants for the rate-determining step obtained by the ultrasound absorption technique. Sound absorption measurements on aqueous samarium sulfate solutions have been made as a function of the ionic strength of the medium. The supporting electrolyte was NaClO$_4$. No significant dependence of the rate constant for the rate-controlling step on ionic strength was observed. In the sound absorption spectra of aqueous samarium malonate solutions a new relaxation was observed at frequencies lower than that for samarium sulfate. This new relaxation has been attributed to a rate-determining ring-closure step. On a complete steady-state kinetic analysis of the multistep complex formation mechanism there was fair agreement between the calculated overall forward-rate constant and the value obtained experimentally by transient methods.

Introduction

The complexation of a metal ion by a ligand in solution can, in general terms, be described by the equation

$$M + L \rightleftarrows ML \tag{1}$$

If the process is fast it is possible to study it by transient and by steady-state relaxation techniques. The former approach usually gives overall forward (k_f) and backward (k_b) rate constants while the latter yields stepwise rate constants (k_{ij}). The correlation between rate constants from the various methods can lead to a fuller interpretation of the overall stepwise mechanism which involves an uncertain number of steps. It is the purpose of this article to attempt such a correlation.

Excluding competing reactions such as hydrolysis etc., the generalized observed rate law for the formation of ML according to (1) is given by[3]

$$d[ML]/dt = k_f[M][L] - k_b[L] \tag{2}$$

The reaction involves a number of successive steps only one of which is rate controlling.[4] Three types of mechanisms have been described which are equally compatible with the rate law:[5] (1) dissociative, D; (2) associative, A; and (3) interchange, I. The mechanistic labels are descriptive of the fundamental differences in the structures of the activated complex. In terms of a multistep mechanism for complex formation the Diebler–Eigen (DE) concept[4] or some modification of it is still in favor. Two-step mechanisms are as prevalent as the original three-step (DE) mechanism in the current literature.

Much effort has been directed at the means for distinguishing a particular mechanism and in the majority of cases the evidence appears to favor a dissociative mechanism in which the rate-controlling step is cleavage of the metal–water bond to produce a metal ion of reduced coordination number in the transition state.[3] Working on this premise the overall effective forward rate constant can be related to k_{34}, the constant for the rate-controlling step in the (DE) description, by the equation[3] $k_f = K_o k_{34}$, where K_o is the outer ion-pair formation constant usually calculated from theory.[6,7] If the mechanism is truly dissociative, then k_{34} is equal to k_{ex}, the rate constant for solvent exchange. According to the steady-state kinetic analysis of the multistep process this elementary correlation between rate constants is only valid when the rate constants for the previous faster steps are much greater than the rate constants for the rate-determining step.[8] In cases where the rate of water exchange is rapid there is poor correlation between k_f measured and k_f calculated using $k_f = K_o k_{34}$. Some improvement is obtained if a steady-state kinetic analysis is done, replacing K_o by a function which consists only of rate constants for the faster steps.[8,9] The function which gives the best correspondence between observed rate constants is indicative of the number of steps in the mechanism.

An example of a system in which water exchange on the cation is rapid and for which a number of kinetic studies

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have been made by transient and steady-state relaxation techniques is the series of trivalent rare earth ions.[9] Two attempts have been made to correlate the observed rate constants using the steady-state kinetic approach.[8,9] The correlations suffered from the fact that, apart from acetate which is complicated by the formation of a bis(acetato) complex,[10,11] at no time has it been possible to use the same ligand for both the transient and acoustic studies. Experimental limitations and solute solubilities have restricted the concentration ranges available to study. However if the mechanism is truly dissociative, rates should be ligand independent. No agreement was found between the measured and calculated rate constants k_f which led both authors[8,9] to conclude that chelation was occurring and was the rate-determining step with the organic ligands murexide,[12] anthranilate,[13,14] and oxalate[15] (transient methods) but not with acetate[10,11] and the inorganic ligands sulfate[16-23] and nitrate.[8,24,25]

The original intent of this work was to use murexide or anthranilate in complexation with samarium in an acoustic study. Both ligands had been previously used in temperature-jump work.[12-14] If a chelation step is indeed present, this should contribute an additional feature to the familiar sound absorption spectrum of samarium sulfate.[16-23] To obtain a measurable absorption distinguishable from that of the solvent, solution concentrations had to be on the order of 0.1 M. This was not possible because of the low solubility of the compounds.

The rare earth malonate complexes had been studied in detail by Gelles and Nancollas[26] and proved to be of simple 1:1 stoichiometry, to be stable, and to be metal chelates. A solubility study showed us that a narrow but fairly high concentration range, very dependent upon the pH of the solution, was accessible. A knowledge of the ionic strength dependence of the stepwise rate constants becomes important at these relatively high concentration levels and it was considered profitable to get this information before embarking on a detailed study of the malonate complex. This work describes the study of the kinetics of formation of the samarium sulfate complex as a function of the ionic strength.

It has been suggested that the lack of correspondence in rate data among the various methods might in part be due to medium effects.[14] Since this work was done we have completed a study of the dependence of k_f for samarium murexide on temperature and ionic strength using the dissociation field effect or E-jump relaxation technique.[27] The discussion is centered around the correlation of observed rate constants for malonate and sulfate with the most recent data at 25° for murexide[27] assuming, of course, a dissociative or ligand-independent mechanism.

Experimental Section

Measurement of the absorption of ultrasonic energy was made at selected frequencies between 5 and 65 MHz using the pulse technique. Frequencies were measured using an Eldorado Inc. frequency counter, Model 1615, and were reproducible to ±0.01 MHz over a long period of time in excess of that required to complete the scan of frequencies in a single experiment. Chemical absorption in excess of the medium absorption expressed as $\alpha_{chem}\lambda$ (db), the absorption per wavelength, was obtained by taking the difference between solution and medium absorptions ($\alpha_T\lambda - \alpha_M\lambda$). This required the measurement of sound velocity in the various supporting electrolytes which was done by counting beats between successive pulses in the propagated sound beam as a function of distance. A temperature of 25 ± 0.05° was maintained for all measurements.

Solutions. Samarium sulfate and samarium perchlorate of 99.9% purity were obtained from the American Potash and Chemical Corp. Sodium perchlorate, used for preparing high ionic strength media, was Baker "Analyzed" reagent grade. All the salts were dried under vacuum at 25° for several days and stored over silica gel in a vacuum desiccator. Equivalent weight determinations were made by cation exchange and titration with standard potassium hydroxide (Baker "Analyzed"). Sodium perchlorate solutions of 0.5 and 0.75 M were prepared using deionized water, and solid samarium sulfate was added to reach the required concentrations. The study could not be extended to higher concentrations of sodium perchlorate because of the insolubility of samarium sulfate.

For the malonate study a stock solution of samarium perchlorate (~1 M) was prepared using deionized water. Malonic acid of 99.0% purity (Baker "Analyzed" reagent) was used without further purification. The analysis of data from potentiometric titrations of 0.01 M acid with standard potassium hydroxide for ionization constants gave excellent agreement with the literature values.[28] Solutions of samarium malonate were prepared by adding a known aliquot of stock samarium perchlorate to 25 ml of stock malonic acid such that the ratio of the molar analytical concentrations of metal to acid was approximately 1:1. A delicate balance between the insolubility of samarium malonate and a measurable sound absorption had to be maintained which accounts for the narrow concentration range studied. The proportion of complex in the solution was varied by titrating with standard potassium hydroxide to 0.25, 0.40, and 0.50 neutralization and the pH of each final solution recorded. Increasing the metal to acid ratio above 1:1 and extending the degree of neutralization beyond 0.50 resulted in the immediate precipitation of samarium malonate. At lower total analytical concentrations and at metal to acid ratios less than 1:1 the total sound absorption of the solution was only slightly in excess of that of the solvent. A very rapid onset of precipitation always occurred at pH ~3.0. Below pH 3.0 hydrolysis of Sm^{3+} is unimportant and does not complicate the interpretation.

Results

Samarium Sulfate in High Ionic Strength Media. Excess sound absorption spectra at approximately constant analytical solute concentration and as a function of ionic strength are shown in Figure 1 (the solid lines are calculated single relaxation curves). The curve for zero sodium perchlorate is taken from a previous publication.[23] A complete listing of chemical absorption data ($\alpha_{chem}\lambda$, db), averaged from a number of independent experiments, as a function of frequency is given in Table I. The position of maximum absorption has moved down in frequency by approximately 10 MHz while the total amplitude has been decreased by 10-15%.

There is general agreement[17-25] that the observed relaxa-

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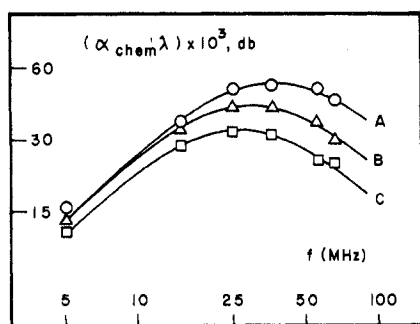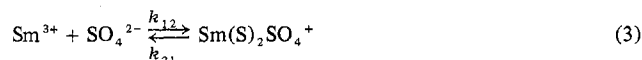(28) E. Gelles and G. H. Nancollas, *J. Chem. Soc.*, 4847 (1956).

Figure 1. Excess sound absorption spectra, $(\alpha_{chem}\lambda) \times 10^3$, db, vs. frequency in MHz for samarium sulfate solutions: (A) 18.51×10^{-3} F, in water; (B) 18.53×10^{-3} F, in 0.5 M NaClO$_4$; (C) 15.09×10^{-3} F, in 0.75 M NaClO$_4$.

Table I. Chemical Absorption $(\alpha_{chem}\lambda \times 10^3)$, db, as a Function of Frequency

				f, MHz			
		5.1	15.30	25.40	35.61	56.02	66.10
Samarium Sulfate ($I = 0.5\,M$)							
	9.31	9.30	17.93	22.32	20.23	15.70	15.20
$10^3 C_0$, F	18.53	15.68	32.34	40.83	40.08	35.03	29.60
	22.05	18.26	43.57	48.31	52.54	43.97	40.94
Samarium Sulfate ($I = 0.75\,M$)							
	10.00	12.19	13.78	17.10	17.27	12.88	11.67
$10^3 C_0$, F	12.52	12.72	21.81	24.93	23.74	19.05	17.17
	15.09	12.30	28.02	32.18	31.40	24.20	23.47
Samarium Malonate							
	25	13.70	11.44	7.82	7.80	4.53	3.93
% neutralizn	40	14.11	13.58	9.79	8.80	7.28	6.63
	50	14.82	13.63	11.31	9.86	8.16	7.80

tion can be attributed to the third step in the (DE) three-step mechanism for complex formation, eq 5, *i.e.*, the rate-

$$\text{Sm}^{3+} + \text{SO}_4^{2-} \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} \text{Sm}(S)_2\text{SO}_4^+ \tag{3}$$

$$\text{Sm}(S)_2\text{SO}_4^+ \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} \text{Sm}(S)\text{SO}_4^+ \tag{4}$$

$$\text{Sm}(S)\text{SO}_4^+ \underset{k_{43}}{\overset{k_{34}}{\rightleftharpoons}} \text{SmSO}_4^+ \tag{5}$$

controlling step. If a two-step mechanism is preferred, eq 3 and 4 are combined into one diffusion-controlled step.[22] Although steps are discrete with discrete rate constants, relaxations may be coupled, *viz.*, if $2\tau_{i+1} \simeq \tau_1$, where τ is a relaxation time. To obtain rate constants for two closely coupled relaxations, it is required that the roots to the secular determinant, which correlates τ with the rate constants and the solute concentration variable θ, be found.[29] The two roots are

$$\tau^{-1}{}_{I,II} = {}^1/{}_2 \, [S \pm \sqrt{S^2 - 4P}] \tag{6}$$

where $S = k_{12}\theta + k_{21} + k_{23} + k_{32}$ and $P = k_{12}\theta(k_{23} + k_{32}) + k_{21}k_{32}$. If $k_{12}, k_{21} \gg k_{23}, k_{32}$, then eq 6 simplifies to

$$\tau^{-1}{}_I \simeq S \simeq k_{12}\theta + k_{21} \tag{7}$$

and

$$\tau^{-1}{}_{II} \simeq k_{32} + \frac{k_{12}\theta}{k_{12}\theta + k_{21}} = k_{32} + \Phi k_{23} \tag{8}$$

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Table II. Relaxation Frequencies and Concentration Data for Samarium Sulfate

$10^3 C_0$, F	$10^3\theta$, F	$2\pi f_3$, MHz	Rms
$I \to 0$			
18.51	6.91	236 ± 5	0.14
9.76	5.10	228 ± 5	0.04
4.88	3.38	214 ± 7	0.03
$I = 0.5\,M$			
22.05	4.65	193 ± 6	1.39
18.53	4.12	188 ± 4	0.60
9.31	2.54	167 ± 4	0.48
$I = 0.75\,M$			
15.09	4.30	169 ± 3	0.30
12.52	3.75	160 ± 4	0.53
10.00	3.18	157 ± 6	1.00

respectively. Little coupling is anticipated in the samarium sulfate sound spectra since recent high-frequency measurements on divalent metal sulfates[30] have placed the next higher relaxation, which is much lower in amplitude, at frequencies in the range 400–600 MHz, more than an order of magnitude higher than those observed here. Since the maximum observed falls within the narrow frequency range used, we have sufficient confidence in fitting the data to a single relaxation curve.

In the calculation of rate constants we are forced into a dilemma. Making the assumption that k_{34} and k_{43} are much smaller in magnitude than the preceding rate constants, eq 3 and 4, so that the approximation holds that

$$2\pi f_3 = k_{43} + \Phi k_{34} \tag{9}$$

k_{34} is found to be similar in magnitude to k_{21} calculated. The approximation therefore is not strictly valid. However to treat the data according to eq 6 would require accurate high-frequency data not yet available. Under these circumstances we have been forced to accept an inexact approximation. However, the same assumption has been made for the analysis of rate data in water[23] so perhaps the comparison of rate constants as a function of ionic strength will be internally consistent if not absolutely exact.

The method used to obtain the relaxation frequencies has been described in detail elsewhere.[23] It basically consists of fitting the experimental data to the theoretical equation for a single relaxation

$$(\alpha_{chem}\lambda)_{calcd} = \frac{2(\alpha_{chem}\lambda)_{max}(f/f_3)}{1 + (f/f_3)^2} \tag{10}$$

using a weighted nonlinear least-squares deviation routine in a converging grid search. The goodness of fit is given as the root-mean-square (rms) deviation, Table II.

The expanded form of the concentration variable Φ in eq 9 is given by

$$\Phi = \theta / \{K_{12}^{-1}K_{23}^{-1} + (1 + K_{23}^{-1})\theta\} \tag{11}$$

where K_{12} and K_{23} are the equilibrium constants for eq 3 and 4, respectively. θ is calculated from the overall thermodynamic formation constant K and is defined by the equation

$$\theta = \Pi_f\{[\bar{M}] + [\bar{L}] + [\bar{L}](\partial \ln \Pi_f / \partial \ln \beta)_{C_0}\} \tag{12}$$

where Π_f is the activity coefficient, the bars represent equilibrium concentrations, β is the degree of association, and C_0 is the analytical salt concentration. In excess inert electrolyte for samarium sulfate using the conditional formation

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constant K_c to calculate β, the expression for θ simplifies to $\theta = (5 - 2\beta)C_0$. Values of K_c of 76 and 40 at ionic strengths 0.5 and 0.75 M, respectively, were obtained by interpolation from literature data.[31]

The graphical solution of eq 9 presents a number of difficulties and a mathematical solution has been adopted.[9] By combining eq 9 and 11 with the equation for the overall formation constant in terms of the stepwise association constants, *viz.*

$$K_c = K_{12}(1 + K_{23} + K_{23}K_{34})$$ (13)

a three-parameter equation is obtained

$$2\pi f_3 = \left\{ \frac{1 + K_c\theta}{1 + K_{12}(K_{23} + 1)\theta} \right\} k_{43}$$ (14)

which can be solved by simultaneous solution if measurements are made on a sufficient number of solute concentrations. Three procedures were used to solve eq 14, all of which produced essentially identical results for k_{34} and k_{43} under the specific ionic strength conditions: (1) K_{12}, calculated from the theoretical Bjerrum equation,[7] was corrected to the high ionic strength conditions and two equations were solved simultaneously for K_{23} and k_{43}; (2) three experimental f_3 values and three θ values were used in the simultaneous solution for K_{12}, K_{23}, and k_{43}; (3) the data were treated in terms of a two-step mechanism using two experimental points and substituting K_{13} for $K_{12}(K_{23} + 1)$ in eq 14. Results of the calculations are collected in Table III. The resultant K_{13} value is in excellent agreement with that calculated from the Bjerrum[7] equation (930) using a distance of closest approach $\overset{\circ}{a}$ equal to 6 Å which is the sum of ionic radii plus one water molecule diameter.

Samarium Malonate. The excess sound absorption spectra of the malonate solutions (Figure 2) show the existence of an additional relaxation at lower frequencies over the samarium sulfate spectra. There was poor correspondence of the data with the equation for a single relaxation, eq 10, using the procedure outlined above. Accordingly the spectra were analyzed in terms of two relaxations. One of these relaxations could involve only the ligand and indeed a relaxation with $f_{max} \simeq 13$ MHz has been reported and attributed to the second ionization equilibrium of malonic acid.[32] However the possibility that this is observed is dismissed because the excess absorption, $\alpha_{chem}\lambda$, for a 0.5 M malonic acid solution at pH 2.64 is ~2 × 10^{-4} db compared to a total absorption of ~15 × 10^{-3} db for solutions of the metal complex in which the free [HMal$^-$] is on the order of 3 × 10^{-2} M maximum. The approximate position of the upper relaxation almost coincides with that of the sulfate absorption and by analogy it was assigned to the corresponding step in the formation of the malonate complex of samarium. Since under the conditions of the experiment there is no thermodynamic evidence for the existence of complexes involving more than one ligand per metal ion,[26] the lower frequency relaxation was assigned to a ring-closure step

$$M \overset{L}{\underset{S}{\diagdown}} \overset{k_{45}}{\underset{k_{54}}{\rightleftarrows}} M \supset L + S$$ (15)

Contributions to the total absorption spectrum from

Table III. Rate and Stepwise Association Constants for Samarium Sulfate

Constant	$I \to 0$			$I = 0.5\,M$			$I = 0.75\,M$		
	1[a]	2	3	1	2	3	1	2	3
K_c	4400	4400	4400	76	76	76	40	40	40
K_{12}	436	1.01		7.5	1.03		4.0	0.9	
K_{23}	1.5	916.0		2.6	28.5		2.6	15.1	
K_{13}			960			30.4			15.3
$10^{-8}k_{34}$, sec^{-1}	3.3	2.1	2.1	2.4	1.6	1.6	2.5	1.7	1.7
$10^{-7}k_{43}$, sec^{-1}	6.3	5.6	5.7	9.6	10.0	10.3	9.9	10.0	10.2
K_{34}	5.3	3.8	3.6	2.6	1.6	1.5	2.6	1.6	1.6

[a] Key: (1) K_{12} calculated from Bjerrum equation; (2) simultaneous solution of eq 10 for K_{12}, K_{23}, and k_{43}; (3) two-step analysis; simultaneous solution of eq 10 for K_{13} and k_{43}.
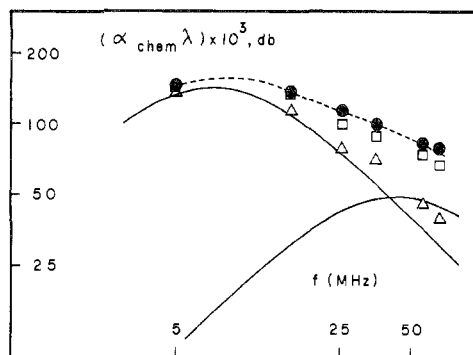

Figure 2. Excess sound absorption spectra, $(\alpha_{chem}\lambda) \times 10^3$, db, *vs.* frequency in MHz for samarium malonate solutions: ●, 50% neutralized; □, 40% neutralized; △, 25% neutralized.

multiple relaxations are usually considered to be additive

$$(\alpha_{chem}\lambda)_{calcd} = \frac{2(\alpha_{chem}\lambda)_{max,3}(f/f_3)}{1 + (f/f_3)^2} +$$
$$\frac{2(\alpha_{chem}\lambda)_{max,4}(f/f_4)}{1 + (f/f_4)^2}$$ (16)

The four parameters were calculated as before except that the analysis had to be modified to include a reiterative procedure. From a previous acoustic study of the rare earth acetates,[10] an analogous low-frequency relaxation ($f_4 \simeq 6$ MHz) was observed and was found to be essentially independent of the cation and the solute concentration. This fact enabled us to restrict the search for the lower maximum frequency to a very narrow range (6.0–8.0 MHz) and to fit the three remaining parameters to the criterion of a minimum rms deviation, Table IV. Using the parameters for the 0.5 neutralized solution the solid lines in Figure 2 were constructed.

The analysis of the data for stepwise rate constants has become exceedingly complex. We have already outlined the coupling difficulty in the sulfate interpretation. Since samarium malonate is also a 3:2 electrolyte, K_{12} and k_{21} will have the same theoretical values and the coupling will recur. In addition to this difficulty, there is close coupling between the two observed relaxations for samarium malonate which also invalidates the assumption that $k_{34}, k_{43} \gg k_{45}, k_{54}$. With no data at higher frequencies we chose to use the K_{12} and K_{23} values obtained for sulfate in spite of the false assumption. This is not too unrealistic since both are 3:2 electrolytes. The remaining rate constants will have no more than comparative significance. Equation 6 was solved for k_{34}, k_{43}, k_{45}, and k_{54} with the modification that $S = k_{34}\Phi + k_{43} + k_{45} + k_{54}$ and $P = k_{34}\Phi(k_{45} + k_{54}) + k_{43}k_{54}$. The quantity Φ is given by eq 11.

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Table IV. Relaxation Parameters for Samarium Malonate

% neutralizn	$2\pi f_3$, MHz	$10^3(\alpha_{chem}\lambda)_{max,3}$, db	$2\pi f_4$, MHz	$10^3(\alpha_{chem}\lambda)_{max,4}$, db	Rms
25	307 ± 10	12.5	45.8 ± 3	3.3	0.50
40	294 ± 10	14.1	44.8 ± 2	3.6	0.29
50	283 ± 8	14.0	44.0 ± 2	4.9	0.09

Table V. Experimental Conditions and Equilibrium Parameters for Samarium Malonate

% neutralizn	$10^2 m$, F	$10^2 a$, F	$10^2[\text{Sm}^{3+}]$, F	$10^5[\text{Mal}^{2-}]$, F	$10^3[\text{Sm-Mal}^+]$, F	$10^2\Pi_f$	$10^3\Theta$, F	Φ
25	8.06	8.16	7.89	1.68	1.72	2.46	1.94	0.314
40	7.22	7.32	6.77	5.15	4.47	2.37	1.60	0.291
50	6.75	6.82	5.94	9.92	8.13	2.34	1.39	0.274

Equilibrium ion concentrations required for the calculation of θ in eq 12 were determined in a standard iterative calculation around the mass balance equations for total acid a and total metal m

$$a = [\text{H}_2\text{Mal}] + [\text{HMal}^-] + [\text{Mal}^{2-}] + [\text{SmMal}^+] \quad (17)$$

$$m = [\text{Sm}^{3+}] + [\text{SmMal}^+] \quad (18)$$

and the formation constant equation

$$K = \frac{[\text{SmMal}^+]}{[\text{Sm}^{3+}][\text{Mal}^{2-}]\gamma_1^{12}} \quad (19)$$

in which γ_1 is the activity coefficient of a univalent ion. It follows that $\Pi_f = \gamma_1^{12}$. Literature values[28] were used for the acid ionization constants, $K_1 = 1.41 \times 10^{-3}$ and $K_2 = 2.14 \times 10^{-6}$, and a value for $K = 5.4 \times 10^4$ was obtained by interpolation in a plot of formation constant *vs.* atomic number for the malonate complexes of the rare earth series.[26] γ_1 was calculated using the Davies equation[33]

$$-\log \gamma_1 = 0.509\{(\mu^{1/2}/1 + B\overset{\circ}{a}\mu^{1/2}) - 0.3\mu\} \quad (20)$$

with $\overset{\circ}{a}$ taken equal to 8.86 Å to be consistent with earlier calculations,[23] and the ionic strength μ is given by the equation

$$\mu = {}^1/_2\{[\text{K}^+] + [\text{H}^+] + 9[\text{Sm}^{3+}] + [\text{SmA}^+] + [\text{HMal}^-] + 4[\text{Mal}^{2-}] + [\text{ClO}_4^-]\} \quad (21)$$

Iteration was terminated when successive γ_1 values agreed to within 0.001. Ionic strengths were calculated to be on the order of 0.4 M, in excess of the limit where use of the Davies equation is recommended.[33] This weakness in the mathematical treatment should be remembered when considering the ultimate conclusions of the study. The experimental conditions and the results of the calculations are given in Table V.

Returning now to the expression for θ, eq 12, $[\text{Mal}^{2-}] \ll [\text{Sm}^{3+}]$ and the derivative term is itself much less than 1. Using the approximation that $\theta \simeq \Pi_f[\text{Sm}^{3+}]$, the values for Φ were calculated as described.

The resultant rate constants are collected in Table VI (column *a*). Included for comparison are those rate constants calculated using the same K_{12} and K_{23} values but assuming that $k_{34}, k_{43} \gg k_{45}, k_{54}$; *i.e.*, the relaxations are distinct and limiting equations of the form of eq 7 and 8 are applicable. A significant difference is observed in all constants except k_{34}. In other interpretations where Φ was calculated using different values for K_{12} and K_{23} and the whole mechanism was treated as a three step, in which K_{13} replaced $K_{12}(1 + K_{23})$, no change in the variation of Φ with concentration and, therefore, no change in the rate constants were observed.

Table VI. Rate and Stepwise Association Constants for Samarium Malonate

Constant	a	b
$10^{-4}K_c$	5.4	5.4
K_{12}	436	436
K_{23}	1.5	1.0
$10^{-8}k_{34}$, sec^{-1}	7.1	6.6
$10^{-7}k_{43}$, sec^{-1}	7.1	1.1
K_{34}	10.0	6.0
$10^{-7}k_{45}$, sec^{-1}	5.3	7.3
$10^{-6}k_{54}$, sec^{-1}	8.1	3.7
K_{45}	6.5	19.6

a Results of complete determinant solution, eq 13. *b* Results of analysis in terms of discrete steps.

Discussion

The thermodynamic formation constant for SmSO_4^+ complexation is related to conditional formation constants K_c by $K = K_c/\gamma_1^{12}$. Since the activity coefficient appears to the twelfth power, K_c decreases rapidly with increasing ionic strength. In a recent E-jump study of the kinetics of samarium murexide complexation[27] a significant decrease in the overall forward rate constant, k_f, with increasing ionic strength was observed. This decrease is to be expected from the Bronsted-LaMer theory[34] for a reaction involving ions of opposite charge. From the present results for samarium sulfate little dependence of k_{34} on a change in ionic strength is observed. This too is not unexpected since in the rate-controlling step, characterized by k_{34}, the ions are already in contact. Consequently, the decrease in the formation constant K with increasing ionic strength is primarily taken up by the decrease in the constants for the more rapid outer ion-pair formation steps. Overall and stepwise rate constants under all medium conditions can be correlated by the equation $k_f = K_0\Pi_f k_{34}$, where K_0 is the formation constant for all prior steps at $\mu \to 0$. In attempting such a correlation one usually finds that the experimental conditions used to measure k_f differ from those used in the determination of k_{34}. We can proceed now with the assurance that the effect of ionic strength on a stepwise rate constant is insignificant.

A substantial amount of rate data is available for rare earth complexation reactions from studies in which a variety of relaxation techniques have been used.[8-25,27] At no time however has the same ligand been used for both transient (T-jump, P-jump, E-jump) and steady-state (acoustics) methods. The correlation therefore depends upon the not generally accepted fact that the mechanism is dissociative and therefore ligand independent. For a typical k_f we have chosen to use the E-jump value of $8.2 \times 10^8 M^{-1}$ sec^{-1} for samarium murexide[27] at 25° and $\mu \to 0$. This was previously shown to be consistent with the value of $0.96 \times 10^8 M^{-1}$

(33) C. W. Davies, "Ion Association," Butterworths, London, 1962.

(34) A. D. Pethybridge and J. E. Prue, *Progr. Inorg. Chem.*, 17, 327 (1972).

$\sec^{-1}$ for the same system measured by T jump at 12° and 0.1 M and with the value of 0.64 × 10⁸ M^{-1} $\sec^{-1}$ for samarium anthranilate also from T jump at 12.5° and $\mu = 0.2$ M. For stepwise constants we will use the k_{34} and k_{45} values obtained here for samarium sulfate and samarium malonate, respectively.

From the steady-state analysis of a three-step mechanism in which it is assumed that step 1 is fast compared to subsequent steps it can be shown that

$$K_o = K_{12}k_{23}/(k_{32} + k_{34}) \qquad (22)$$

Since the rare earth ions exchange water rapidly, a further approximation, that $k_{32} = k_{34}$, can be made in which case $k_f = \frac{1}{2}K_{12}K_{23}\Pi_f k_{34}$. Using this expression, with $\Pi_f \simeq 0.2$ and $k_{34} = 3.3 \times 10^8$ $\sec^{-1}$, k_f is calculated to be 2 × 10¹⁰ M^{-1} $\sec^{-1}$, which because of the assumptions made might not have been expected to give a good correlation. Making neither of the preceding assumptions the general three-step derivation gives

$$K_o = \frac{k_{12}k_{23}}{k_{21}(k_{32} + k_{34}) + k_{23}k_{34}} \qquad (23)$$

A value of $k_f = 2.7 \times 10^9$ M^{-1} $\sec^{-1}$ was obtained using the following rate constants: $k_{12} = 3.2 \times 10^{10}$ M^{-1} $\sec^{-1}$ calculated from the Debye-Smoluchowski equation[35] with $a = 8.86$ Å; $k_{21} = 7.3 \times 10^7$ $\sec^{-1}$ calculated from k_{12}/K_{12} where $K_{12} = 436$; an arbitrary value for $k_{23} = 1 \times 10^9$ $\sec^{-1}$; $k_{32} = 6.7 \times 10^8$ $\sec^{-1}$ equal to k_{23}/K_{23}. Neither of these calculated k_f values agrees with the experimental value for samarium murexide. Since k_{34} cannot be in error by more than a factor of 2 in spite of the interpretative assumptions, the lack of correspondence may be interpreted to mean that the mechanisms differ between the sulfate and murexide complexation reactions.

Turning our attention then to samarium malonate where a chelation step is proposed, the correlation equation becomes $k_f = K_o \Pi_f k_{45}$. Expressing K_o in terms of rate constants from a steady-state analysis of a four-step mechanism, in which no assumptions are made with regard to the relative magnitudes of the stepwise rate constants, the equation is

$$K_o = \frac{k_{12}k_{23}k_{34}}{k_{21}k_{32}(k_{43} + k_{45}) + k_{34}k_{45}(k_{21} + k_{23})} \qquad (24)$$

Assuming the sulfate values for k_{12}, k_{21}, k_{23}, and k_{32}, which is not too unreasonable since both are 3:2 electrolytes, and using the values for k_{34}, k_{43}, k_{45}, and k_{54} in Table VI (column a), k_f is calculated to be 6 × 10⁸ M^{-1} $\sec^{-1}$, in fair agreement with the value of 8.2 × 10⁸ M^{-1} $\sec^{-1}$ for samarium murexide. For comparison, $k_f = 4.2 \times 10^9$ M^{-1} $\sec^{-1}$ when the approximations are introduced to make $k_f = \frac{1}{2}K_{12}K_{23}K_{34}$· $\Pi_f k_{45}$.

In view of the theoretical limitations introduced by assuming that k_{12}, k_{21}, k_{23}, $k_{32} \gg k_{34}$, k_{43} and the inadequacy of the Davies equation at relatively high ionic strengths, and in the limitation of assuming a dissociative mechanism, the outcome of the correlation is good. It is possible that some parts of these limitations are self-compensating. The gist of the argument is that on retention of the quasiequality $k_{34} \simeq k_{ex}$ for all ligands, the differences in k_f among the sulfate and the other ligands may be rationalized in terms of a steric controlled mechanism;[35] *i.e.*, for malonate, murexide, anthranilate, and oxalate the ring-closure step assumes control. The discrepancy with the sulfate data pointed out many times before[8,9] is apparently resolved. Therefore, k_{34} for sulfate, which is in good agreement with k_{ex}, the rate constant for solvent exchange,[36] is representative of the characteristic unassisted rate of substitution into the rare earth coordination sphere. This comparison has often been made and used as the basis for presuming a dissociative mechanism.

(35) J. C. Williams and S. Petrucci, *J. Amer. Chem. Soc.*, **95**, 7619 (1973).
(36) R. Marianelli, Ph.D. Dissertation, University of California, Berkeley, Calif., 1966.