Conclusions

The proton-transfer reactions

$$CuH_{-2}L^- + H_3O^+ \longrightarrow CuH_{-1}L + H_2O$$
$$CuH_{-1}L + OH^- \longrightarrow CuH_{-2}L^- + H_2O$$

are many orders of magnitude slower than the usual diffusion-controlled rate constants for reactions with H_3O^+ and OH^-. The reactions of different acids and bases with copper(II) triglycine fit the theoretical kinetic behavior outlined by Eigen[16] which relates the rate constants to ΔpK values. The limiting rate step in these reactions does not result from diffusion but rather from the necessity to break and rearrange coordinate bonds to copper.

Two reaction paths are proposed for the proton transfer, one which ought to be encountered for most acids and bases (I $\rightleftarrows$ II $\rightleftarrows$ III $\rightleftarrows$ IV) and another (I $\rightleftarrows$ V $\rightleftarrows$ IV) which is limited to the reaction of very strong bases (near the base strength of OH^-) with $CuH_{-1}L$ or to the reaction of very weak acids (near the acid strength of H_2O) with $CuH_{-2}L^-$.

The copper-imide bond in $CuH_{-2}L^-$ is not easily broken, and the preferred dissociation occurs after the addition of a proton to the peptide nitrogen. Thus, EDTA does not react as a nucleophilic group with $CuH_{-2}L^-$ but rather as the acid H_2EDTA^{2-}, just furnishing a proton to give more labile coordination which permits rearrangement to a copper–triglycine complex more sterically favorable for EDTA coordination. Other ligands, less sterically hindered, can react as nucleophiles with $CuH_{-2}L^-$.[23]

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[23] (a) G. K. Pagenkopf and D. W. Margerum, *J. Am. Chem. Soc.*, 90, 502 (1968); (b) submitted for publication.

Ligand Penetration Rates into Metal Ion Coordination Spheres. Aluminum(III), Gallium(III), and Indium(III) Sulfates

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Abstract: Kinetics of the sulfate ion complexing with Al(III), Ga(III), and In(III) have been measured by the pressure-jump and temperature-jump techniques. The measurements were carried out in acid solutions (pH 1–3) in order to minimize hydrolysis and polymerization. For each system a single relaxation time was observed; moreover, for each system the inverse relaxation time could be interpreted only as the sum of two parallel pathways, one with sulfate reacting with the solvated metal ion and the other with sulfate reacting with the monohydroxy metal ion. The zero ionic strength forward rate constants for Al(III), Ga(III), and In(III) are 1.2×10^3, 2.1×10^4, and $2.6 \times 10^5\ M^{-1}\ sec^{-1}$ for the direct reaction and 8.5×10^5, 1.0×10^5, and $2.5 \times 10^7\ M^{-1}\ sec^{-1}$ for the monohydroxy route, respectively. These results were consistent with the Eigen–Tamm mechanism for the stepwise formation of metal complexes. The first-order ligand penetration rate constants were estimated to be 1, 20, and 300 sec^{-1} for the three ions. That for Al(III) is in excellent agreement with the water lifetime as recently measured by nmr. The value for Ga(III) is substantially less than the water exchange rate. As a result, it is concluded that sulfate penetration into the primary coordination sphere of the metal ion proceeds *via* a largely SN1 mechanism for Al and primarily by an SN2 mechanism for Ga; In also appears to be SN2.

The development of relaxation techniques[2] has permitted the investigation of very rapid chemical processes whose half-lives are between several seconds and 10^{-10} sec. A particularly large amount of data is now available for elementary steps in metal complexing reactions.[3,4] To date, experimental studies have been largely confined to the alkali, alkaline earth, and the divalent first-row transition metal ions. Relatively few experimental studies of rapidly reacting trivalent metal ion systems have been undertaken, presumably because such ions are subject to complications due to hydrolysis and polymerization. It is the purpose of this investigation to kinetically characterize three such systems: aqueous Al(III), Ga(III), and In(III).

Eigen[5] lists the characteristic rate constants for water displacement in the inner coordination sphere as 10^0–10^1 and $10^{1.5}$–$10^{2.5}$ sec^{-1} for gallium and indium, respectively. These were obtained apparently from the extrapolation of rate data for other charge types. Geier[6] conducted a kinetic study of the complexing of several trivalent metal ions, including In^{3+}, with murexide.

Experimental Section

Materials. All metals were obtained as the sulfates (99.9%) from Rare and Fine Chemicals Inc. A small amount of each salt

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[2] *E.g.*, M. Eigen and L. de Maeyer, "Technique of Organic Chemistry," Vol. VIII, A. Weissberger, Ed., Interscience Publishers, New York, N. Y., 1963, Chapter XVIII and references contained therein.

[3] M. Eigen, *Z. Elektrochem.*, 60, 115 (1960).

[4] M. Eigen and R. G. Wilkins, "Mechanisms of Inorganic Reactions," Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965.

[5] M. Eigen, *Pure Appl. Chem.*, 6, 97 (1963).

[6] G. Geier, *Z. Elektrochem.*, 69, 617 (1965).

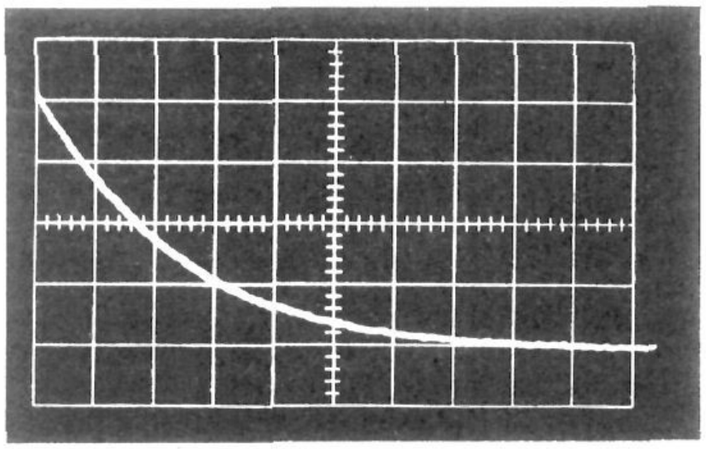

Figure 1. Pressure-jump relaxation trace in 3.8×10^{-3} M $Ga_2(SO_4)_3$ at pH 2.64: vertical scale, 0.02% resistance change; horizontal scale, 5-msec/division.

Table I. Equilibrium Constants[a] at 25°

Reaction	Log K		
	$I = 0$	$I = 0.1^b$	$I = 0.6$
$Al^{3+} + SO_4^{2-} = AlSO_4^+$	3.20	1.87	1.30
$AlSO_4^+ + SO_4^{2-} = Al(SO_4)_2^-$	1.90	1.19	1.00
$Al^{3+} + H_2O = AlOH^{2+} + H^+$	−5.19	−5.74	−5.97
$Ga^{3+} + SO_4^{2-} = GaSO_4^+$	2.99		
$Ga^{3+} + H_2O = GaOH^{2+} + H^+$	−2.80		
$GaOH^{2+} + H_2O = Ga(OH)_2^+ + H^+$	−3.50		
$In^{3+} + SO_4^{2-} = InSO_4^+$	3.74		
$In^{3+} + H_2O = InOH^{2+} + H^+$	−3.42[c]		
$H^+ + SO_4^{2-} = HSO_4^-$	2.00	1.56	1.36

[a] L. Sillen and A. Martell, Ed., "Stability Constants," Special Publication No. 17, The Chemical Society, London, 1964, except when noted. [b] Reference 19a. [c] Corrected to $I = 0$ by the Davies equation from a measurement in 6.32×10^{-3} M $In_2(SO_4)_3$: E. Hattox and T. DeVries, *J. Am. Chem. Soc.*, **58,** 2128 (1936).

was dissolved in triply distilled degassed water. Solutions were analyzed by evaporating aliquots to dryness and firing to the oxide. The stock solutions were quantitatively diluted to provide a range of concentrations. The pH was varied by the dropwise addition of KOH or HNO_3 in conjunction with a pH meter (Beckman Expandomatic).

Instrumentation. Kinetic measurements were carried out by two techniques: pressure-jump and temperature-jump spectrometry. The former technique was found to be more useful for most of the measurements since the electrical conductivity detection is very sensitive to metal complexing processes involving charge neutralization. In this method,[7] pressure is uniformly applied to a dual conductivity cell. One side contains the electrolyte under investigation. The other contains a solution of KCl which has approximately the same conductivity as the experimental solution but exhibits no relaxation phenomena of its own. The pressure is transferred to the dual cells by means of flexible rubber membranes. At about 30 atm a brass disk ruptures, releasing the pressure within about 10 μsec. Relaxation times longer than this time can be obtained directly by monitoring the difference in conductivity between the two solutions as a function of time. The relaxation spectrum of each solution was displayed on the screen of a storage oscilloscope (Tektronix 549), photographed, and enlarged. The relaxation times were evaluated from at least three photographs. In almost all instances the relaxation effects were large and virtually noise free (Figure 1); as a result, the relaxation times could be determined to about ±5%.

Since the changes in conductance due to the pressure dependence of mobilities, density, and ionic atmosphere follow the pressure step virtually instantaneously, the total conductance change due to concentration changes is given[8] by

$$\frac{\delta l}{l} = \frac{\sum|z_\mathrm{r}|u_\mathrm{r}\nu_\mathrm{r} - \sum|z_\mathrm{p}|u_\mathrm{p}\nu_\mathrm{p}}{\sum|z_n|u_nC_n}\frac{\mathrm{d}C_\mathrm{r}}{\mathrm{d}\ln K}\left[\left(\frac{\partial \ln K}{\partial P}\right)_\mathrm{T} + \left(\frac{\partial \ln K}{\partial T}\right)_\mathrm{P}\left(\frac{\partial T}{\partial P}\right)_\mathrm{S}\right](\delta P) \quad (1)$$

where l is the specific conductance, z is the charge, u is the mobility, C is the concentration (M), and n refers to all ionic species.[9] The term $\mathrm{d}C_\mathrm{r}/\mathrm{d}\ln K$ is a function of concentration, degree of dissociation, and activity coefficients and may be obtained in a straightforward manner[2,10] for each system under investigation. To a fair approximation the second term in brackets may be neglected, such that one has just $(\partial \ln K/\partial P)_\mathrm{T} = -\Delta V°/RT$. Thus, the relaxation time is obtained from the time course of the effect; the amplitude of the effect (given by eq 1) may, under certain conditions, yield the volume change $\Delta V°$ for the process under study.

For the measurements by the temperature-jump technique,[2] an electrical discharge instrument purchased from Messanlagen Studiengesellschaft[11] was used in conjunction with the indicator xylenol blue. No electrolyte was added to hold the ionic strength constant. As a result, the data from both techniques were strictly comparable. In all instances where comparisons were made, identical solutions gave the same relaxation time by either method (Table II). Blanks, consisting of the identical conditions except that the nitrate was used instead of the sulfate, showed no relaxation effects in the time range studied.

Treatment of Data. The equilibrium constants for the various complexing and hydrolysis processes are summarized in Table I. Some of the hydrolysis equilibrium constants require some comment. There has been considerable controversy in the literature concerning not only the log K values, but also the nature of the species present. While several investigators were able to interpret their data on the basis of simple monomers, the Scandanavian school in particular has postulated that highly charged polymeric species predominate for indium[12] and aluminum.[13] This apparent discrepancy is explained in part by the fact that the polymers were found in "aged" solutions, which required relatively long times for equilibration (typically hours or days) and in part by the high ionic strength often used (3 M). A high ionic strength would tend to render highly charged polymers more stable. In a recent study of hydrolysis in dilute aluminum solutions, Frink and Peech[14] found only the species $AlOH^{2+}$ and no evidence for dimers or polymers. Eyring's[15] very recent kinetic study of proton transfer supported the species $AlOH^{2+}$, but was totally inconsistent with a dimerization. All the measurements reported in the present study were carried out in freshly prepared solutions in order to avoid significant amounts of polymeric species.

Since the ionic strength was not held constant during the experiments, it was necessary to estimate the activity coefficients for the various charged species. The Davies equation, which has been shown[16] to be quite reliable for estimates of activity coefficients up to $I = 0.1$, was used for this purpose.[17] The highest ionic strength used in the Ga system was well below this value. In fact, the numerical results in the In system, where the ionic strength was as high as 0.19, were largely insenitive to small changes in the parameters involved in the Davies equation. In the Al^{3+} system, the ionic strength was too high (0.6) to be so handled. Since, however, stability constants were reported both for $I = 0$ (K^0) and for $I = 0.6$ (K_c), the activity coefficient function $\gamma_{Al}\gamma_{SO_4}/\gamma_{AlSO_4}$ could be obtained from their ratio. The individual activity coefficients were separated by assuming that log γ_i was proportional, at constant ionic strength, to z_i^2 for each species.

Results

A computer program was written to solve the coupled equilibria simultaneously for equilibrium con-

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(7) (a) H. Hoffman, J. Stuehr, and E. Yeager, "Chemical Physics of Ionic Solutions," B. E. Conway and R. G. Barradas, Ed., John Wiley and Sons, Inc., New York, N. Y., 1966, Chapter 14; (b) H. Strehlow and M. Becker, *Z. Elektrochem.*, **63,** 457 (1959).

(8) Ref 7a, p 258.

(9) Products (subscript p), reactants (r), and nonreacting ions.

(10) J. E. Stuehr and E. Yeager, "Physical Acoustics," Vol. 2, Part A, W. Mason, Ed., Academic Press, New York, N. Y., 1965, p 383 ff.

(11) Göttingen, West Germany.

(12) G. Biedermann, *Arkiv Kemi*, **9,** 277 (1956).

(13) (a) C. Brosset, G. Biedermann, and L. Sillen, *Acta. Chem. Scand.*, **8,** 1917 (1954); (b) J. Aveston, *J. Chem. Soc.*, 4438 (1965).

(14) C. R. Frink and M. Peech, *Inorg. Chem.*, **2,** 473 (1963).

(15) L. D. Holmes, D. L. Cole, and E. M. Eyring, *J. Phys. Chem.*, **72,** 301 (1968).

(16) C. W. Davies, "Ion Association," Butterworth Inc., Washington, D. C., 1962, p 41 ff.

(17) If one held the ionic strength constant (by adding, *e.g.*, 0.1 M KNO_3 to each solution), the rate constants for a 3–2 charge type valid at this ionic strength would be more difficult to convert to the zero ionic strength values desired.

Table II. Equilibrium[a] and Kinetic Results

C^0, M[b]	$\bar{C}_{H}$, M	$\bar{C}_{Me}$, M	$\bar{C}_{MeOH}$, M	$\bar{C}_{MeSO_4}$, M	$\bar{C}_{SO_4}$, M	$\bar{C}_{Me(SO_4)_2}$, M	τ^{-1}, sec^{-1} [e]
				a. $Al_2(SO_4)_3$			
2.00[f]	4.8[g]	1.02[f]	0.0228[h]	0.165	0.0807	0.133	5.41[c] P
2.00	1.6	0.846	0.0567	0.161	0.0955	0.154	5.71[c] P
2.00	0.44	0.773	0.188	0.159	0.103	0.164	6.76[c] P
2.00	0.29	0.763	0.282	0.159	0.104	0.165	8.47[c] P
2.00	0.15	0.753	0.538	0.158	0.105	0.166	12.5[c] P
2.00	0.09	0.749	0.891	0.158	0.106	0.167	13.3[c] P
2.00	0.09	0.749	0.891	0.158	0.106	0.167	16.9[d] P
2.00	1.0	0.806	0.0863	0.160	0.0995	0.159	5.75[d] P
2.00	0.37	0.768	0.223	0.159	0.104	0.164	7.00[d] P
2.00	0.058	0.746	1.38	0.159	0.106	0.167	20.9[d] P
0.20	0.118	0.0814	0.467	0.00956	0.0153	0.00226	12.1[c] P
0.10	0.118	0.116	0.670	0.0208	0.0232	0.00748	12.0[c] P
				b. $Ga_2(SO_4)_3$			
3.80[i]	2.72[i]	3.40[i]	9.97[h]	3.12[i]	7.27[i]		152 P, T
2.85	2.67	2.58	8.29	2.21	5.58		152 P
1.90	2.62	1.78	6.32	1.33	3.79		152 P
0.45	2.54	0.941	3.88	0.532	2.03		152 P
3.80	4.51	3.75	6.65	3.17	6.72		113 P
3.80	1.75	3.04	13.9	2.99	7.72		210 P
2.85	2.17	2.43	9.71	2.19	5.73		150 P
2.85	1.98	2.38	10.4	2.16	5.81		173 P
1.90	1.77	1.57	8.40	1.27	4.01		185 P
1.90	1.54	1.51	9.17	1.23	4.10		204 P
2.85	3.00	2.66	7.57	2.23	5.47		129 P
				c. $In_2(SO_4)_3$			
4.86[g]	2.21[g]	1.30[g]	0.716[h]	8.43[g]	3.63[g]		1020 P, T
4.86	1.67	1.20	0.871	8.53	3.96		1230 T
4.86	1.11	1.09	1.20	8.64	4.41		1430 T
4.86	0.765	1.02	1.62	8.70	4.74		1670 T
4.86	0.554	0.978	2.14	8.74	4.98		2010 T
4.86	0.451	0.956	2.58	8.76	5.11		2310 P, T
2.43	1.14	0.668	0.834	4.19	2.18		1140 T
2.43	0.884	0.631	1.02	4.23	2.31		1200 T
2.43	0.532	0.580	1.56	4.26	2.52		1670 T
2.43	0.413	0.562	1.95	4.29	2.61		2040 T

[a] $\bar{C}_{Me(OH)_2}$ and $\bar{C}_{HSO_4}$ can be calculated from the Me and SO_4 mass balances, respectively. [b] In terms of $Al_2(SO_4)_3$, $Ga_2(SO_4)_3$, and $In_2(SO_4)_3 \cdot 5H_2O$. [c] Data from ref 19a. [d] Data from ref 7a. [e] Method: P = pressure jump, T = temperature jump. [f] Values in columns ×10. [g] Values in column ×10². [h] Values in column ×10⁴. [i] Values in column ×10³.

$$\begin{array}{ccc} \text{I} & & \text{III} \\ Me^{3+} + SO_4^{2-} & \underset{k_{31}}{\overset{k_{13}}{\rightleftharpoons}} & MeSO_4^{+} \\ \| & & \| \\ MeOH^{2+} + SO_4^{2-} & \underset{k_{64}}{\overset{k_{46}}{\rightleftharpoons}} & HOMeSO_4 \\ + & & + \\ H^+ & & H^+ \\ \text{IV} & & \text{VI} \end{array} \qquad \text{(A)}$$

centrations and activity coefficients. For the latter, the ionic strength was calculated without activity corrections, and then the concentrations were recalculated with the equilibrium constants corrected to the proper ionic strength value. This reiterative procedure was repeated until convergence (generally fewer than five repetitions). These results, with the experimentally measured relaxation times, are given in Table II.

Of the several reaction schemes considered,[18] the only one found to fit the data quantitatively was scheme A[19] where Me^{3+} represents the free (hydrated) metal ion, $MeOH^{2+}$ is the monohydroxy species, and $HOMeSO_4$ is the sulfato complex formed therefrom. The proton-transfer reactions (represented by = signs), including metal ion hydrolysis, were taken to be rapid[20] compared to the complexing steps represented by arrows. In addition, the sulfate ion is coupled *via* a rapid proton transfer to the HSO_4^- ion. The correction factor [1 + α, where $\alpha = \bar{C}_I/(K_I + \bar{C}_H)$] resulting, where applicable, from the indicator preequilibrium, was sufficiently close to unity in all instances to be omitted from the relaxation time expression.

$$\frac{d(\delta C_{MeSO_4} + \delta C_{HOMeSO_4})}{dt} = k_{13}\frac{\gamma_{Me}\gamma_{SO_4}}{\gamma_1^{\ddagger}}\left[\bar{C}_{Me}\left(1 + \frac{d\ln\gamma_{Me}}{d\ln\bar{C}_{SO_4}} + \frac{d\ln\gamma_{SO_4}}{d\ln\bar{C}_{SO_4}} - \frac{d\ln\gamma_1^{\ddagger}}{d\ln\bar{C}_{SO_4}}\right)\delta C_{SO_4} + \bar{C}_{SO_4}\delta C_{Me}\right] - k_{31}\frac{\gamma_{Me}\gamma_{SO_4}}{\gamma_1^{\ddagger}}\left[1 + \frac{d\ln\gamma_{MeSO_4}}{d\ln\bar{C}_{MeSO_4}} - \frac{d\ln\gamma_1^{\ddagger}}{d\ln\bar{C}_{MeSO_4}}\right]\delta C_{MeSO_4} + k_{46}\frac{\gamma_{MeOH}\gamma_{SO_4}}{\gamma_0^{\ddagger}}\left[\bar{C}_{MeOH}\left(1 + \frac{d\ln\gamma_{MeOH}}{d\ln\bar{C}_{SO_4}} + \frac{d\ln\gamma_{SO_4}}{d\ln\bar{C}_{SO_4}} - \frac{d\ln\gamma_0^{\ddagger}}{d\ln\bar{C}_{SO_4}}\right)\delta C_{SO_4} + \bar{C}_{SO_4}\delta C_{MeOH}\right] - k_{64}\frac{\gamma_{HOMeSO_4}}{\gamma_0^{\ddagger}}\left[1 + \frac{d\ln\gamma_{HOMeSO_4}}{d\ln\bar{C}_{HOMeSO_4}} - \frac{d\ln\gamma_0^{\ddagger}}{d\ln\bar{C}_{HOMeSO_4}}\right]\delta C_{HOMeSO_4} \quad (2)$$

For a small perturbation from equilibrium, the rate

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(18) These included the steps I–III and IV–VI individually and coupled to hydrolysis, as well as $MeOH + HSO_4 \rightleftharpoons MeSO_4 + H_2O$, individually or coupled to the pathway I–III.

(19) *Cf.* (a) B. Behr and H. Wendt, *Z. Elektrochem.*, **66**, 223 (1962); (b) F. Cavasino, *J. Phys. Chem.*, **72**, 1378 (1968).

(20) Holmes, Cole, and Eyring[15] in fact measured the hydrolysis rate constant k_{11} for Al^{3+} and found it to be 4.4 × 10⁹ M^{-1} sec^{-1}.

of restoration is given by (charges omitted) eq 2, where δC_i represents the perturbed concentrations, γ_i's are the indicated activity coefficients, and $\gamma_1{}^{\ddagger}$ and $\gamma_0{}^{\ddagger}$ are the activity coefficients of the singly charged and uncharged transition states, respectively. Substitution of the appropriate mass balance and preequilibrium relationships[21] into eq 2 yields an equation of the form $\mathrm{d}\delta C_i/\mathrm{d}t = -(1/\tau)\delta C_i$, which gives the expression for the (slow) relaxation time (eq 3), where F_1, F_2, F_3, and

$$\tau^{-1} = k_{13}F_1 + k_{31}F_2 + k_{46}F_3 + \frac{K^0{}_{36}F_2[1 + (\mathrm{d}\ln\gamma_{\mathrm{MeSO_4}}/\mathrm{d}\ln\bar{C}_{\mathrm{MeSO_4}})]}{\bar{C}_{\mathrm{H}}}\,k_{64} \tag{3}$$

the primed symbols therein are defined as

$$F_1 = \frac{\gamma_{\mathrm{Me}}\gamma_{\mathrm{SO_4}}}{\gamma_1{}^{\ddagger}}\left[\bar{C}_{\mathrm{Me}}\left(1 + \frac{\mathrm{d}\ln\gamma_{\mathrm{Me}}}{\mathrm{d}\ln\bar{C}_{\mathrm{SO_4}}} + \frac{\mathrm{d}\ln\gamma_{\mathrm{SO_4}}}{\mathrm{d}\ln\bar{C}_{\mathrm{SO_4}}} - \frac{\mathrm{d}\ln\gamma_1{}^{\ddagger}}{\mathrm{d}\ln\bar{C}_{\mathrm{SO_4}}}\right) + \right.$$
$$\left. \bar{C}_{\mathrm{SO_4}}\frac{\bar{C}'_{\mathrm{H}}\left[\bar{C}'_{\mathrm{SO_4}} + C_{\mathrm{H}}\left(1 + \frac{\mathrm{d}\ln\gamma_{\mathrm{SO_4}}}{\mathrm{d}\ln\bar{C}_{\mathrm{SO_4}}}\right)\right] + K'_{\mathrm{a}}(\bar{C}'_{\mathrm{MeOH}} + \bar{C}'_{\mathrm{H}})}{K'_{\mathrm{a}}(K'_{14} + \bar{C}'_{\mathrm{MeOH}}) + \bar{C}'_{\mathrm{H}}(K'_{\mathrm{a}} + \bar{C}'_{\mathrm{SO_4}})}\right]$$

$$F_2 = \frac{\bar{C}'_{\mathrm{SO_4}}[K'_{14} + \bar{C}'_{\mathrm{H}}] + \left[K'_{\mathrm{a}} + \bar{C}_{\mathrm{H}}\left(1 + \frac{\mathrm{d}\ln\gamma_{\mathrm{SO_4}}}{\mathrm{d}\ln\bar{C}_{\mathrm{SO_4}}}\right)\right][K'_{14} + \bar{C}'_{\mathrm{H}} + \bar{C}'_{\mathrm{MeOH}}]}{K'_{\mathrm{a}}(K'_{14} + \bar{C}'_{\mathrm{MeOH}}) + \bar{C}'_{\mathrm{H}}(K'_{\mathrm{a}} + \bar{C}'_{\mathrm{SO_4}})}$$

$$F_3 = \frac{\gamma_{\mathrm{MeOH}}\gamma_{\mathrm{SO_4}}}{\gamma_0{}^{\ddagger}}\left[\bar{C}_{\mathrm{MeOH}}\left(1 + \frac{\mathrm{d}\ln\gamma_{\mathrm{MeOH}}}{\mathrm{d}\ln\bar{C}_{\mathrm{SO_4}}} + \frac{\mathrm{d}\ln\gamma_{\mathrm{SO_4}}}{\mathrm{d}\ln\bar{C}_{\mathrm{SO_4}}} - \frac{\mathrm{d}\ln\gamma_0{}^{\ddagger}}{\mathrm{d}\ln\bar{C}_{\mathrm{SO_4}}}\right) + \right.$$
$$\left. \bar{C}_{\mathrm{SO_4}}\frac{\bar{C}_{\mathrm{H}}\left(1 + \frac{\mathrm{d}\ln\gamma_{\mathrm{SO_4}}}{\mathrm{d}\ln\bar{C}_{\mathrm{SO_4}}}\right)(K'_{14} + \bar{C}'_{\mathrm{MeOH}}) + K'_{14}(K'_{\mathrm{a}} + \bar{C}'_{\mathrm{SO_4}})}{K'_{\mathrm{a}}(K'_{14} + \bar{C}'_{\mathrm{MeOH}}) + \bar{C}'_{\mathrm{H}}(K'_{\mathrm{a}} + \bar{C}'_{\mathrm{SO_4}})}\right]$$

$$\bar{C}'_{\mathrm{H}} = \bar{C}_{\mathrm{H}}\left(1 + \frac{\mathrm{d}\ln\gamma_{\mathrm{MeOH}}}{\mathrm{d}\ln\bar{C}_{\mathrm{MeOH}}}\right);\quad \bar{C}'_{\mathrm{SO_4}} = \bar{C}_{\mathrm{SO_4}}\left(1 + \frac{\mathrm{d}\ln\gamma_{\mathrm{H}}}{\mathrm{d}\ln\bar{C}_{\mathrm{H}}}\right);\quad \bar{C}'_{\mathrm{MeOH}} = \bar{C}_{\mathrm{MeOH}}\left(1 + \frac{\mathrm{d}\ln\gamma_{\mathrm{H}}}{\mathrm{d}\ln\bar{C}_{\mathrm{H}}}\right)$$

$$K'_{\mathrm{a}} = K_{\mathrm{a}}\left(1 + \frac{\mathrm{d}\ln\gamma_{\mathrm{HSO_4}}}{\mathrm{d}\ln\bar{C}_{\mathrm{HSO_4}}}\right);\quad K'_{14} = K_{14}\left(1 + \frac{\mathrm{d}\ln\gamma_{\mathrm{Me}}}{\mathrm{d}\ln\bar{C}_{\mathrm{Me}}}\right)$$

The (reasonable) assumption was made that $K_{36} \ll K_{14}$. The equilibrium constants for scheme A are related by $K^0{}_{13}K^0{}_{36} = K^0{}_{14}K^0{}_{46}$.

The $\mathrm{d}\ln\gamma_i/\mathrm{d}\ln\bar{C}_i$ terms arise because the ionic strength of the solutions was not held constant. They can be obtained from a suitable analytical expression, *e.g.*, differentiation of the Davies equation (eq 4).[22] The various $\mathrm{d}I/\mathrm{d}\bar{C}_i$ terms themselves will contain terms of the form $\mathrm{d}\ln\gamma_j/\mathrm{d}\ln\bar{C}_j$, derived from the preequilibrium and mass-balance equations. Here too a computer reiterative technique was used to obtain the $\mathrm{d}\ln\gamma_i/\mathrm{d}\ln\bar{C}_i$ terms. Convergence was reached within three repetitions. It is important to note that these terms make only minor contributions to the relaxation times, even at the highest ionic strengths used in this study. As a result, the reliability of the Davies equation in predicting the $\mathrm{d}\ln\gamma_i/\mathrm{d}\ln\bar{C}_i$ terms is not a major

$$\frac{\mathrm{d}\ln\gamma_i}{\mathrm{d}\ln\bar{C}_i} = -1.15z_i{}^2\bar{C}_i \times \left[\frac{1}{2(1 + I^{1/2})I^{1/2}} - \frac{1}{2(1 + I^{1/2})^2} - 0.3\right]\frac{\mathrm{d}I}{\mathrm{d}\bar{C}_i} \tag{4}$$

issue. In fact, ignoring them completely results in rate constants which differ from those reported here by only 10% for Ga(III) and 20% for In(III). Inclusion of the terms brought about a systematic improvement in the fit of the data that was most pronounced for In.

For purposes of evaluation, $\tau^{-1}/[F_1 + (F_2/K^0{}_{13})]$ was graphed *vs.* $[F_3 + (K^0{}_{14}F_2/K^0{}_{13}\bar{C}_{\mathrm{H}})\,(1 + \mathrm{d}\ln\gamma_{\mathrm{MeSO_4}}/\mathrm{d}\ln\bar{C}_{\mathrm{MeSO_4}})]/[F_1 + (F_2/K^0{}_{13})]$ (Figure 2). The slope of this graph is k_{46} and the intercept k_{13}. In addition a graph of $\tau^{-1}/(K^0{}_{13}F_1 + F_2)$ *vs.* $[(K^0{}_{13}/K^0{}_{14})F_3 + (F_2/\bar{C}_{\mathrm{H}})](1 + \mathrm{d}\ln\gamma_{\mathrm{MeSO_4}}/\mathrm{d}\ln\bar{C}_{\mathrm{MeSO_4}})/(K^0{}_{13}F_1 + F_2)$ yielded k_{31} and the product $k_{64}K^0{}_{36}$ as the intercept and slope,

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[21] *I.e.*

$$\delta C_{\mathrm{Me}} + \delta C_{\mathrm{MeSO_4}} + \delta C_{\mathrm{HOMeSO_4}} + \delta C_{\mathrm{MeOH}} = 0$$
$$\delta C_{\mathrm{HSO_4}} + \delta C_{\mathrm{MeSO_4}} + \delta C_{\mathrm{HOMeSO_4}} = 0$$
$$\delta C_{\mathrm{HSO_4}} + \delta C_{\mathrm{Me}} + \delta C_{\mathrm{H}} + \delta C_{\mathrm{MeSO_4}} = 0$$
$$K_{14}\left(1 + \frac{\mathrm{d}\ln\gamma_{\mathrm{Me}}}{\mathrm{d}\ln\bar{C}_{\mathrm{Me}}}\right)\delta C_{\mathrm{Me}} = \bar{C}_{\mathrm{MeOH}}\left(1 + \frac{\mathrm{d}\ln\gamma_{\mathrm{H}}}{\mathrm{d}\ln\bar{C}_{\mathrm{H}}}\right)\delta C_{\mathrm{H}} + \bar{C}_{\mathrm{H}}\left(1 + \frac{\mathrm{d}\ln\gamma_{\mathrm{MeOH}}}{\mathrm{d}\ln\bar{C}_{\mathrm{MeOH}}}\right)\delta C_{\mathrm{MeOH}}$$
$$K_{36}\left(1 + \frac{\mathrm{d}\ln\gamma_{\mathrm{MeSO_4}}}{\mathrm{d}\ln\bar{C}_{\mathrm{MeSO_4}}}\right)\delta C_{\mathrm{MeSO_4}} = \bar{C}_{\mathrm{HOMeSO_4}}\left(1 + \frac{\mathrm{d}\ln\gamma_{\mathrm{H}}}{\mathrm{d}\ln\bar{C}_{\mathrm{H}}}\right)\delta C_{\mathrm{H}} + \bar{C}_{\mathrm{H}}\left(1 + \frac{\mathrm{d}\ln\gamma_{\mathrm{HOMeSO_4}}}{\mathrm{d}\ln\bar{C}_{\mathrm{HOMeSO_4}}}\right)\delta C_{\mathrm{MeSO_4}}$$
$$K_{\mathrm{a}}\left(1 + \frac{\mathrm{d}\ln\gamma_{\mathrm{HSO_4}}}{\mathrm{d}\ln\bar{C}_{\mathrm{HSO_4}}}\right)\delta C_{\mathrm{HSO_4}} = \bar{C}_{\mathrm{SO_4}}\left(1 + \frac{\mathrm{d}\ln\gamma_{\mathrm{H}}}{\mathrm{d}\ln\bar{C}_{\mathrm{H}}}\right)\delta C_{\mathrm{H}} + \bar{C}_{\mathrm{H}}\left(1 + \frac{\mathrm{d}\ln\gamma_{\mathrm{SO_4}}}{\mathrm{d}\ln\bar{C}_{\mathrm{SO_4}}}\right)\delta C_{\mathrm{SO_4}}$$

where K_i's are the finite ionic strength equilibrium constants.

[22] Equation 4 was derived from the general expression $\mathrm{d}\ln\gamma_i/\mathrm{d}\ln\bar{C}_i = C_i[\Sigma_j(\partial\ln\gamma_j/\partial\bar{C}_j)(\delta C_j/\delta C_i)]$, where i represents the particular species in question, j encompasses all species, and $\delta C_j/\delta C_i$ are the mass balance relationships.[21]

Table III. Kinetic Results for Metal Complexing in Al(III), Ga(III), and In(III) at 25°

	Al		Ga	In
	I = 0.6	I = 0	I = 0	I = 0
k_{13}, M^{-1} sec^{-1}	1.5×10^1	1.2×10^3	2.1×10^4	2.6×10^5
k_{31}, sec^{-1}	7.4×10^{-1}	7.5×10^{-1}	2.2×10^1	4.9×10^1
k_{46}, M^{-1} sec^{-1}	5.1×10^4	8.5×10^5	1.0×10^5	2.5×10^7
$k_{64}K^0_{36}$, M sec^{-1}	3.0×10^{-3}	3.8×10^{-3}	1.7×10^{-1}	1.5
k_{23}, sec^{-1}		~1	~2×10^1	~3×10^2
k_{H_2O}, sec^{-1} [a]		0.80	1.1×10^4	. . .
r_+, Å		0.50	0.62	0.81

[a] Reference 29.

respectively. All graphs were subjected to least-squares fit.

It is interesting to note that at constant pH the results for the Al and Ga systems seemingly imply that the relaxation times are concentration independent within the limits of experimental error. For this to be exactly true, eq 3 would reduce to the form

$$\tau^{-1} = k_{31} + \frac{K^0_{36}}{\bar{C}_H} k_{64} \tag{5}$$

in which τ^{-1} varies inversely as the hydrogen ion concentration. The experimental observation of such a dependence in fact led Behr and Wendt[19a] to assume that eq 5 was the correct form. Equation 5 is obtained by eliminating the concentration-dependent terms early in the derivation. As shown below, this is not justified. To do so therefore results in an internally inconsistent treatment. The explanation for the apparent $1/\bar{C}_H$ dependence is as follows. The function F_1 is virtually constant in all Al and Ga solutions measured ($K^0_{13}F_1$ for Ga varies from 0.71 to 0.88 over the entire range of experimental conditions). In addition the function F_3 varies approximately as $1/\bar{C}_H$; as a result it would appear that τ^{-1} varies inversely with $\bar{C}_H$. Thus the concentration dependence inherent in F_1 and F_3 is largely masked. The In system alone displayed a clearly detectable concentration dependence.

The data for Al^{3+} warrant some comment. The values in Table II include the earlier measurements of Behr and Wendt[19a] (BW) as well as measurements from our own laboratory.[7a] The two sets of data are in complete accord. As pointed out above, BW attributed the apparent concentration independence of τ to the limiting form of eq 3 given by eq 5. This is easily shown to be invalid; the apparent fit is due to the fortuitous constancy of $K^0_{13}F_1$, as noted above for Ga^{3+}: this quantity varies from 4.8 to 6.0 for Al^{3+} over the entire pH range. As a result, although the data could be fitted to eq 5, the rate constant k_{31} so obtained by BW was in error by approximately a factor of 6 at I = 0.6. We have obtained internally consistent values for the slow rate constants in scheme A both at I = 0.6 and I = 0. Data from both laboratories, at several pH's and concentrations, were consistent with the I = 0 analysis (Figure 2a) to ±20%.

The values of the rate constants for each system are given in Table III. The rate constants k_{46} for the pathway involving the hydrolyzed metal ion ($MeOH^{2+}$) vary as follows: In > Al > Ga. This irregular order is exactly the same as that shown by the hydrolysis equilibrium constants for the three ions.

Discussion

According to Eigen and coworkers,[23] a great deal of evidence has been accumulated which supports a mechanism for ion association and complex formation in solution. This mechanism, based largely upon the interpretation of ultrasonic absorption in 2:2 electrolytes, may be schematically shown in scheme B, where

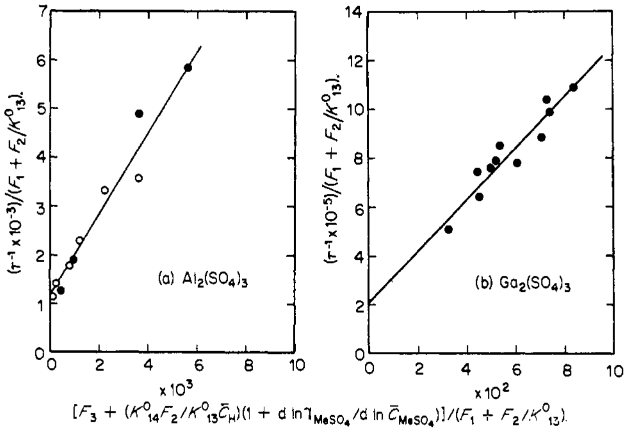

Figure 2. Concentration and pH dependence of the relaxation times for (a) aluminum(III) and (b) gallium(III) sulfates at 25°; ○, data from ref 15.

$$\begin{array}{ccccc} \text{I} & & \text{II} & & \text{III} \\ Me_{aq}^{z+} + L^{z-} & \overset{K_{12}}{=\!=} & Me^{z+}\cdot OH_2\cdot L^{z-} & \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} & (MeL)_{aq}^{(z_+ + z_-)} + H_2O \end{array} \tag{B}$$

step I–II represents the diffusion-controlled formation of the outer-sphere complex with metal ion and ligand still separated by one water molecule.[24] The stability constant for this step is represented by K_{12}. The last, and rate-determining, step (II–III) is the formation of the contact (inner-sphere) complex.

For the majority of metal ions investigated to date, the rate of ligand penetration, k_{23}, is very nearly the same as the water exchange rate constant, k_{H_2O}, determined by magnetic resonance.[25] This has led to the conclusion that the mechanism of complex formation in such cases was primarily SN1. The only exception among common divalent metal ions appears to be Be^{2+}, for which

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[23] (a) H. Diebler and M. Eigen, *Z. Physik. Chem.* (Frankfurt), **20**, 299 (1959); (b) M. Eigen, *Z. Elektrochem.*, **64**, 115 (1960); (c) M. Eigen and K. Tamm, *ibid.*, **66**, 93, 107 (1962).

[24] If the ligand is strongly solvated, the encounter complex (state II) may have the ligand and metal ion still separated by two hydration layers. In that case an additional (very rapid) step is observed in the relaxation spectrum; see ref 23b,c.

[25] T. J. Swift and R. E. Connick, *J. Chem. Phys.*, **37**, 307 (1962).

k_{H_2O} is some two orders of magnitude faster [26] than the sulfate penetration rate constant.

The situation is not so well defined for rapidly exchanging trivalent metal ions. The rare earth metal ions appear to have ligand penetration rate constants of the same order of magnitude as the water exchange constants, although the series as a whole is not without its unusual features.[6]

The relationship between the observed second-order rate constant k_{13} of scheme A and the first-order rate constant k_{23} of scheme B is $k_{13} = K_{12}k_{23}$. The primarily electrostatic stability constant K_{12} may be estimated from the equation[27] $K_{12} = (4\pi Na^3/3000)\exp(-Z)$, where N is Avogadro's number, a is the encounter complex separation, and Z is the coulombic energy divided by kT. For a 3–2 charge interaction, the calculated value of K_{12} is quite sensitive to the choice of the numerical value of a: for $a = 7.5$ Å (two hydration layers), $K_{12} = 300$; for $a = 5.0$ Å (one layer), $K_{12} = 1000$. The latter was taken as the more reliable estimate.[28] Application of these considerations yields rate consants k_{23} for ligand penetration of approximately 1, 20, and 300 sec^{-1} for Al(III), Ga(III), and In(III), respectively. The calculated values of k_{23} for the latter two systems are within the ranges quoted by Eigen.[5]

Since the completion of the present experimental work, Fiat and Connick[29] have reported a kinetic study of the lifetimes of water molecules in the coordination spheres of Al^{3+} and Ga^{3+} by 0–17 nmr. They found the lifetimes to be 7.5 and 5.5×10^{-4} sec, respectively, at 25°. These correspond to k_{H_2O} values of 0.8 and 1×10^4 sec^{-1} for the two ions. In addition, from the temperature dependence of the exchange process, the activation enthalpy and entropy were found to be 27 kcal/mole and +28 eu for Al^{3+}, and 6.3 kcal/mole and −22 eu for Ga^{3+}. The large numerical differences in the activation parameters for the two ions were attributed to different exchange mechanisms. The high value of $\Delta H^{\ddagger}$ and the positive $\Delta S^{\ddagger}$ for Al^{3+} are consistent with a mechanism in which the coordination decreases in the transition state (from 6 to 5), *i.e.*, an SN1 mechanism. Conversely the relatively small $\Delta H^{\ddagger}$ and large negative $\Delta S^{\ddagger}$ for Ga^{3+} suggest an increase in coordination number in the transition state, *i.e.*, SN2. Our results certainly are in complete agreement with these conclusions. At 25° the sulfate penetration rate is virtually the same as k_{H_2O} for Al^{3+}, as would be true for an SN1 mechanism. The sulfate penetration rate constant for Ga^{3+}, on the other hand, is some three orders of magnitude smaller than the value of k_{H_2O}, indicating a strong ligand dependence. This is characteristic of an SN2 displacement mechanism.

The situation with regard to In^{3+} is somewhat less certain. Nmr water exchange data have not yet appeared. In his study of the trivalent rare earth ions complexing with murexide, Geier[6] also measured the complexation rate constant of In^{3+}. He reported the value $k_{13} = 2 \times 10^6$ M^{-1} sec^{-1} at $I = 0.1$. Since the ligand is singly negatively charged, K_{12} would be about 20 (somewhat less if activity coefficients are considered). As a result, k_{23} is about 10^5 for this ligand, a value considerably larger than the sulfate penetration rate reported here. The implication seems to be that substitution of the solvent molecules surrounding In^{3+} also proceeds by an SN2 mechanism.

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(26) D. Fiat and R. E. Connick, *J. Am. Chem. Soc.*, **88**, 4754 (1966); *cf.* ref 7a and 23a.

(27) M. Eigen, *Z. Physik. Chem.* (Frankfurt), **1**, 176 (1954); *cf.* R. Fuoss, *J. Am. Chem. Soc.*, **80**, 5059 (1958).

(28) The measured over-all stability constant (K_{Σ}) is related to the stability constants in scheme B by $K_{\Sigma} = K_{12} + K_{12}K_{23}$. If $K_{12} = 10^3$, then this means that the ion pairs formed are predominantly outer, rather than inner, sphere. *Cf.* the divalent sulfates (ref 23).

(29) D. Fiat and R. E. Connick, *J. Am. Chem. Soc.*, **90**, 608 (1968).