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Kinetics of Outer-Sphere Ion-Pair Formation of Aqueous $[Co(NH_3)_6]_2(SO_4)_3$ and $[Co(en)_3]_2(SO_4)_3$ at 25°[1]

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Ultrasonic absorption results of aqueous $[Co(NH_3)_6]_2(SO_4)_3$ and $[Co(en)_3]_2(SO_4)_3$ at 25° in the frequency range 10–250 MHz are reported. The relaxations observed are interpreted as due to a process of ionic association between $Co(NH_3)_6^{3+}$ or $Co(en)_3^{3+}$ and SO_4^{2-}.

Introduction

Substitution reactions in the first coordination sphere of Co(III) ions are characteristically slow reactions. They have served as models to study octahedrally coordinated stereochemical reactions, so that a body of literature exists nowadays on this subject.[2] Outer-sphere complexation or ion-pair formation of Co(III) salts was known to happen very fast. For instance, Posey and Taube[3] studied the reaction of $Co(NH_3)_5H_2O^{3+}$ with SO_4^{2-} spectrophotometrically. They noticed a sudden change in the uv spectrum of the cation upon addition of SO_4^{2-} ions followed by a slow reaction of substitution of the inner coordinated H_2O by the anion. They also attributed the rapid initial change of the spectrum to outer-sphere interaction or ion-pair formation. Completely shielded ions like $Co(NH_3)_6^{3+}$ and $Co(en)_3^{3+}$ have been known since the time of Werner and Jørgensen. More recently, it has been established by various tools (Table I) that they are associated with SO_4^{2-} as well as other ions. In fact, the average association constant gives for $[Co(NH_3)_6]_2(SO_4)_3$ $\bar{K}_a = 2300\ M^{-1}$ and for $[Co(en)_3]_2(SO_4)_3$ $\bar{K}_a = 1400\ M^{-1}$ (Table I). No information, however, exists on the rates of ion-pair formation. It would have been conceivable that a diffusion or close to diffusion rate should have been observed in view of the presumably weak coordination of water in the second coordination sphere. In an nmr study of the association of $[Cr(en)_3]^{3+}$ with PF_6^-, Stengle and Langford[4] concluded that water had to be coordinated around the cation and that association had to imply the removal of one of these coordinated waters. It was of interest, therefore, to engage in a kinetic study of the association rates and mechanisms of $Co(NH_3)_6^{3+}$ and $[Co(en)_3]^{3+}$ with SO_4^{2-}. Ultrasonic pulse techniques have been found suitable for such a study.

Experimental Section

TABLE I

ASSOCIATION CONSTANTS FOR $[Co(NH_3)_6]_2(SO_4)_3$ AND $[Co(en)_3]_2(SO_4)_3$ AT INFINITE DILUTION IN WATER AT 25°

Log K_a	Method	Ref
	$[Co(NH_3)_6]_2(SO_4)_3$	
3.56	Conductance	*a*
3.46	Polarography	*b*
3.21	Polarography	*c*
3.30	Chronopotentiometry	*d*
3.32	Spectrophotometry	*e*
2.95	Spectrophotometry	*f*
2.89	Spectrophotometry	*g*
3.26	Spectrophotometry	*h*
3.52	Solubility	*i*
3.60	Solubility	*j*
	$[Co(en)_3]_2(SO_4)_3$	
3.45	Conductance	*a*
2.72	Polarography	*k*
3.22	Chronopotentiometry	*d*
2.93	Spectrophotometry	*l*
3.10	Spectrophotometry	*h*

[a] I. L. Jenkins and C. B. Monk, *J. Chem. Soc.*, 68 (1951). [b] A. A. Vlcek, Proceedings of the 6th International Conference on Coordination Chemistry, 1961, p 590. [c] N. Tanaka, K. Ogino, and G. Sato, *Bull. Chem. Soc. Japan*, **39**, 366 (1966). [d] N. Tanaka and A. Yamada, *Z. Anal. Chem.*, **224**, 117 (1967). [e] See ref 3. [f] W. D. Bale, C. W. Davies, and C. B. Monk, *Trans. Faraday Soc.*, **52**, 816 (1956). [g] C. W. Davies and C. B. Monk, *J. Am. Chem. Soc.*, **80**, 5032 (1958). [h] N. Tanaka, Y. Kobayashi, and M. Kamada, *Bull. Chem. Soc. Japan*, **40**, 12 (1967). [i] C. W. Davies, *J. Chem. Soc.*, 2421 (1930). [j] S. H. Laurie and C. B. Monk, *ibid.*, 3343 (1963). [k] H. A. Laitinen and M. W. Grieb, *J. Am. Chem. Soc.*, **77**, 5201 (1955). [l] K. Ogino and U. Saito, *Bull. Chem. Soc. Japan*, **40**, 826 (1967).

Materials.—$[Co(NH_3)_6]_2(SO_4)_3$ and $[Co(en)_3]_2(SO_4)_3$ were obtained from Alpha Chemicals. These products were checked by standard cobalt analysis and SO_4^{2-} analysis by cation exchange and titration of SO_4^{2-} by Tham. Solutions were prepared by volume and subsequent analysis. The ultrasonic technique and procedure of measurements has been described elsewhere.[5]

Results and Calculations

In Table II the results for the absorption coefficients α (nepers cm^{-1}) at the frequencies f (MHz) investigated are reported. (Solubility limited the range of concentration that could be studied for $[Co(NH_3)_6]_2(SO_4)_3$.) In Figures 1 and 2 the data expressed as excess absorption per wavelength $\alpha_{exc}\lambda$ are reported *vs.* the frequency f. $\alpha_{exc}\lambda = (\alpha - \alpha_0)(u/f)$ where α_0 is the

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[1] This work is part of the thesis of A. Elder in partial fulfillment for the requirements of the degree of Master in Sciences from the Polytechnic Institute of Brooklyn.

[2] (a) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1967; (b) C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, Inc., New York, N. Y., 1965.

[3] F. Posey and H. Taube, *J. Am. Chem. Soc.*, **78**, 15 (1956).

[4] T. R. Stengle and C. H. Langford, *J. Phys. Chem.*, **69**, 3299 (1965).

[5] S. Petrucci, *ibid.*, **71**, 1174 (1967); S. Petrucci and M. Battistini, *ibid.*, **71**, 1181 (1967).

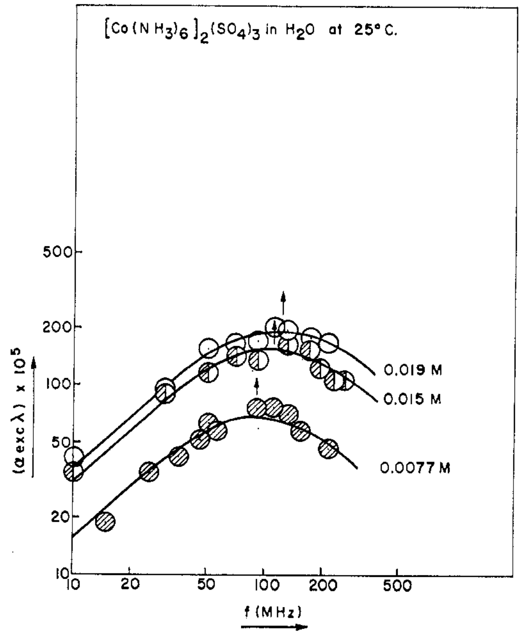

Figure 1.—Plot of $\alpha_{exc}\lambda$ *vs.* f for $[Co(NH_3)_6]_2(SO_4)_3$.

TABLE II

RESULTS FOR ABSORPTION COEFFICIENTS α AND EXCESS SOUND ABSORPTION COEFFICIENTS PER WAVELENGTH $\alpha_{exc}\lambda$ AT THE FREQUENCIES INVESTIGATED FOR THE SYSTEMS STUDIED

f, MHz	α, cm^{-1}	10^5 $\alpha_{exc}\lambda$	f, MHz	α, cm^{-1}	10^5 $\alpha_{exc}\lambda$	f, MHz	α, cm^{-1}	10^5 $\alpha_{exc}\lambda$
			$[Co(NH_3)_6]_2(SO_4)_3$					
c = 0.0077 M			c = 0.015 M			c = 0.019 M		
10	0.0362	21.3	10	0.0449	34.5	10	0.0487	40.1
15	0.0682	18.7	30	0.374	88	30	0.382	91.5
25	0.195	34.5	50	0.944	118	50	1.08	159
35	0.365	40.8	70	1.73	139	70	1.84	163
45	0.599	51.0	90	2.59	135	90	2.77	168
50	0.753	60.9	130	5.18	169	110	4.09	194
55	0.875	57.1	170	8.06	150	130	5.36	190
90	2.22	76.7	190	9.50	123	170	8.38	178
110	3.23	77.9	230	13.30	108	210	12.01	165
130	4.34	71.6	250	15.54	108			
150	5.52	57.0						
210	10.35	46.0						
			$[Co(en)_3]_2(SO_4)_3$					
			c = 0.025 M					
c = 0.01 M			First run			Second run		
15	0.0806	31.1	30	0.514	150			
25	0.138	53.2	50	1.33	234	15	0.129	79
35	0.445	75.2	70	2.54	315	25	0.368	139
45	0.714	89.4	90	4.67	485	35	0.713	190
65	1.42	113	110	5.54	393	45	1.08	211
75	1.82	117	130	7.02	381	55	1.61	258
85	2.37	137	150	9.06	411	65	2.06	261
95	2.83	134	190	12.68	374	75	2.84	321
105	3.34	130				85	3.58	351
125	4.47	124				95	4.51	399
135	5.07	117						
145	5.88	130						
175	8.20	125						
c = 0.05 M								
First run			Second run			c = 0.09 M		
10	0.119	191	10	0.121	148	10	0.194	258
30	0.816	309	50	2.07	456	30	1.43	617
50	2.07	455	70	4.13	653	50	3.46	873
70	3.69	560	90	5.80	669	70	5.93	1041
90	5.80	673	110	8.41	784	90	9.60	1225
110	7.83	705	130	10.54	787	110	11.87	1256
130	10.43	774	150	12.00	705	130	15.54	1363
150	12.48	753	170	15.39	797	150	18.81	1386
			190	16.55	679	190	27.35	1532
			210	19.47	697	230	35.0	1532
			250	24.07	619	250	37.2	1400

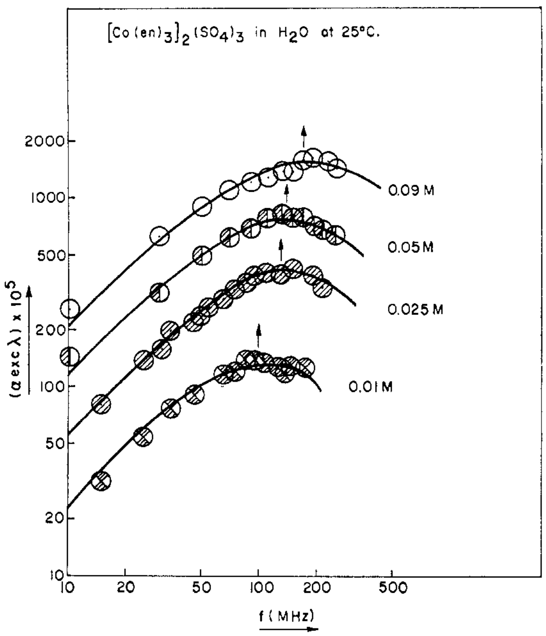

Figure 2.—Plot of $\alpha_{exc}\lambda$ *vs.* f for $[Co(en)_3]_2(SO_4)_3$.

solvent absorption, u the solvent velocity, and λ the wavelength. The values $\alpha_0/f^2 = 22 \times 10^{-17}$ cm^{-1} sec^2 and $u = 1500$ m/sec have been retained. The solid lines are the theoretical functions for a single relaxation.[6]

$$\alpha_{exc}\lambda = 2\mu_{max}\left[\frac{f/f_r}{1 + (f/f_r)^2}\right] \tag{1}$$

The results for μ_{max} and f_r are reported in Table III. (Blank experiments with a 0.07 M solution of $Co(en)_3(ClO_4)_3$ showed absence of relaxation processes in the same frequency range investigated for the sulfates.)

TABLE III

RESULTS OF RELAXATION FREQUENCIES f_r AND MAXIMUM EXCESS ABSORPTION PER WAVELENGTH $(\alpha_{exc}\lambda)_{max}$ FOR THE SYSTEMS INVESTIGATED[a]

c, M	f_r, MHz	$10^5\alpha_{exc}\lambda_{max}$	ΔV, mol/cm^3
	$[Co(NH_3)_6]_2(SO_4)_3$		
0.0077	95	70	16.1
0.015	110	155	16.4
0.019	120	200	16.6
	$[Co(en)_3]_2(SO_4)_3$		
0.010	100	130	16.4
0.025	120	380	18.1
0.05	140	750	18.7
0.09	170	1500	22.9

[a] Average error in $f_r \simeq \pm 10\%$. Average error in $(\alpha_{exc})_{max} \simeq \pm 10\%$.

Discussion

These data have been interpreted as due to the ionic association of the cobalt–amine cation and SO_4^{2-}

$$Co(NH_3)_6^{3+} + SO_4^{2-} \underset{k_R}{\overset{k_f}{\rightleftharpoons}} Co(NH_3)_6^{3+},SO_4^{2-} \tag{2a}$$

or

$$Co(en)_3^{3+} + SO_4^{2-} \underset{k_R}{\overset{k_f}{\rightleftharpoons}} Co(en)_3^{3+},SO_4^{2-} \tag{2b}$$

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(6) J. Lamb in "Physical Acoustics," Vol. II, part A, W. P. Mason, Ed., Academic Press, New York, N. Y., 1965.

According to the Eigen[7] theory for a single relaxation, the relaxation time τ $(=(2\pi f_r)^{-1})$ is correlated to the forward and reverse rates k_f and k_R by the relation

$$\tau^{-1} = k_f\theta + k_R \tag{3}$$

For a 3:2 electrolyte θ can be calculated in the following way. Assume the dissociation scheme

$$\underset{c}{[Co(NH_3)_6]_2(SO_4)_3} \rightleftharpoons \underset{2c(1-\sigma)}{2[Co(NH_3)_6](SO_4)^+} + \underset{c}{SO_4^{2-}} \rightleftharpoons \underset{2c\sigma}{2Co(NH_3)_6^{3+}} + \underset{(2\sigma+1)c}{3SO_4^{2-}}$$

where c is the stoichiometric concentration of the electrolyte and σ is the degree of dissociation of the ion pair.

For an electrolyte $(AB)^{n-m}$ dissociating into A^{n+} and B^{n-} Eigen[7] has calculated the function $\theta(c)$ as

$$\theta(c) = \frac{\gamma_A\gamma_B}{\gamma_{AB}}\left\{c_A\left[1 + \frac{\partial \ln (\gamma_A\gamma_B/\gamma_{AB})}{\partial \ln c_B}\right] + c_B\right\} \tag{4}$$

where γ_A, γ_B, and γ_{AB} are the activity coefficients of the three species (omitting charge symbols) and c_A and c_B are the ionic equilibrium concentrations.

For the case in question, calling $A = Co(NH_3)_6^{3+}$ (or $Co(en)_3^{3+}$) and $B = SO_4^{2-}$ and omitting charge symbols in the subscripts, one has

$$\theta(c) = \frac{\gamma_A\gamma_B c}{\gamma_{AB}}\left[4\sigma + 1 + \sigma(2\sigma + 1)\frac{\partial \ln (\gamma_A\gamma_B/\gamma_{AB})}{\partial\sigma}\right] \tag{5}$$

The activity coefficient expression $\gamma_A\gamma_B/\gamma_{AB}$ can be calculated from the electrostatic interactions between free ions

$$[Co(NH_3)_6]_2(SO_4)_3 \rightleftharpoons 2Co(NH_3)_6^{3+} + 3SO_4^{2-}$$

$$\gamma_\pm^5\{[Co(NH_3)_6]_2(SO_4)_3\} = \gamma_A^2\gamma_B^3 = \gamma_{\pm,3:2}^5$$

and

$$[Co(NH_3)_6SO_4^+]_2,SO_4^{2-} = 2Co(NH_3)_6SO_4^+ + SO_4^{2-}$$

$$\gamma_\pm^3\{[Co(NH_3)_6SO_4^+]_2,SO_4^{2-}\} = \gamma_{AB}^2\gamma_B = \gamma_{\pm,1:2}^3$$

The symbols 3:2 and 1:2 refer for convenience to the electrolyte type. The species $[Co(NH_3)_6]_2(SO_4)_3$ and $[Co(NH_3)_6SO_4]_2SO_4$ represent no physical entities in solution but only electrostatic interactions in order to calculate the mean ionic coefficients. Then

$$\frac{\gamma_A\gamma_B}{\gamma_{AB}} = \frac{\gamma_{\pm,3:2}^{5/2}}{\gamma_{\pm,1:2}^{3/2}} \tag{6}$$

and

$$\theta(c) = \frac{\gamma_{\pm,3:2}^{5/2}}{\gamma_{\pm,1:2}^{3/2}}c\left[4\sigma + 1 + \sigma(2\sigma + 1)\frac{\partial \ln (\gamma_{\pm,3:2}^{5/2}/\gamma_{\pm,1:2}^{3/2})}{\partial\sigma}\right] \tag{7}$$

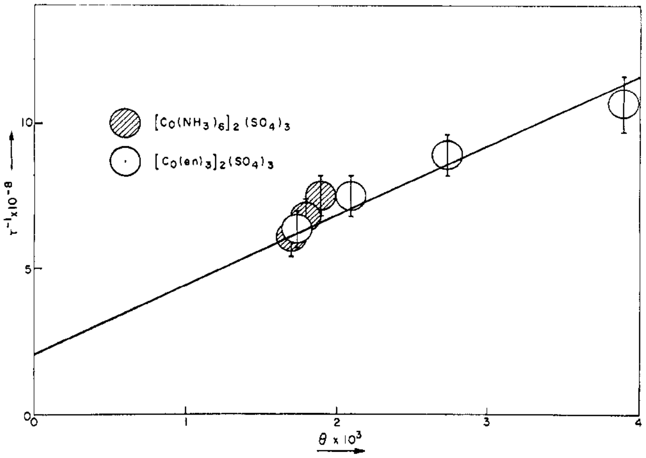

Figure 3.—Plot of τ^{-1} *vs.* θ for the electrolytes investigated.

The calculations of $\gamma_{\pm,3:2}$ and $\gamma_{\pm,1:2}$ have been performed by the aid of the Davies[8] type of extended Debye–Hückel laws

$$\log \gamma_\pm = -0.50|Z_1Z_2|\left[\frac{I^{1/2}}{1 + I^{1/2}} - BI\right] \tag{8}$$

where $0.50|Z_1Z_2|$ is the Debye–Hückel coefficient, and B has been set equal to 0.30.[8] I is the ionic strength given by

$$I = \frac{1}{2}\sum_j c_jZ_j^2 = \left(\frac{1}{2}\right)(6)(1 + 4\sigma)c = 3(1 + 4\sigma)c \tag{9}$$

where c_j and Z_j are the concentration and charge of the species j. Equation 8 has been combined with the expression

$$K_a = \frac{C_{AB}}{C_AC_B}\frac{\gamma_{AB}}{\gamma_A\gamma_B} = \frac{1 - \sigma}{\sigma(2\sigma + 1)c}\frac{\gamma_{\pm,1:2}^{3/2}}{\gamma_{\pm,3:2}^{5/2}} \tag{10}$$

for the calculation of the quantity $\theta(c)$; an iterative calculation has been performed starting from the ratio $\gamma_{\pm,1:2}^{3/2}/\gamma_{\pm,3:2}^{5/2} = 1$ in eq 10, obtaining a zero approximation value of σ, and substituting it into eq 8 specialized for 3:2 and 1:2 electrolytes. A new ratio $\gamma_{\pm,1:2}^{3/2}/\gamma_{\pm,3:2}^{5/2}$ is obtained and then introduced into eq 10 and the cycle is repeated until convergence is obtained. Generally, five iterations are enough to obtain convergence to within a few per cent in σ and the activity coefficient ratios.

In Figure 3 the values of τ^{-1} *vs.* θ for the two electrolytes investigated are reported. It appears that the two electrolytes give comparable results within experimental error.

In Table IV the results for k_f and k_R are also reported. They are compared with the diffusion-controlled rates k_D and k_{-D} calculated through the Von Smoluchowski–Debye[9] and Eigen[10] equations. These equations

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(7) M. Eigen and L. DeMaeyer in "Technique of Organic Chemistry," Vol. VIII, part 2, A. Weissberger, Ed., John Wiley & Sons, Inc., New York, N. Y., 1963.

(8) C. W. Davies, "Ion Association," Butterworth and Co. Ltd., London, 1962.

(9) M. Von Smoluchowski, *Physik. Z.*, **17**, 557 (1916); P. Debye, *Trans. Electrochem. Soc.*, **82**, 265 (1942).

(10) M. Eigen, *Z. Physik. Chem.* (Frankfurt), **1**, 176 (1954).

TABLE IV

CALCULATED VALUES OF THE FORWARD AND REVERSE RATES k_f AND k_R FOR $[Co(NH_3)_6]_2(SO_4)_3$ AND $[Co(en)_3]_2(SO_4)_3$ IN WATER AT 25°. CALCULATED DIFFUSION-CONTROLLED RATES k_D AND k_{-D} ASSUMING $a = 4.5 \times 10^{-8}$ CM. AVERAGE ASSOCIATION CONSTANT CALCULATED FROM ULTRASONIC DATA $\bar{K}$(US)

$10^{-11}k_f$, M^{-1} sec^{-1}	$10^{-7}k_R$, sec^{-1}	$10^{-11}k_D$, M^{-1} sec^{-1}	$10^{-7}k_{-D}$, sec^{-1}	$\bar{K}$(US), M^{-1}
2.4 ± 0.5	20 ± 10	1.0	3.3	1200

modified by the introduction of the Stokes–Einstein equation[5] read

$$k_D = \frac{2NkT}{3000\eta}\left(2 + \frac{r_A}{r_B} + \frac{r_B}{r_A}\right)\left(\frac{-b}{e^{-b} - 1}\right) \quad M^{-1}\ \mathrm{sec}^{-1}$$

$$k_{-D} = \frac{kT}{2\pi\eta}\left(\frac{1}{(r_A + r_B)r_A r_B}\right)\left(\frac{-b}{1 - e^{b}}\right) \quad \mathrm{sec}^{-1} \tag{11}$$

where r_A and r_B are the ionic radii, N is the Avogadro number, k is the Boltzmann constant, η is the solvent viscosity, T is the absolute temperature, and b is the Bjerrum parameter $(=|Z_A Z_B|e^2/aDkT)$. In the last expression Z_A and Z_B are the ionic charges, e is the electron charge, D is the dielectric constant of the solvent, and a is the minimum distance of approach between ions, $a = r_A + r_B$. It has been set equal to 4.5×10^{-8} cm in accord with the estimate of Kielland[11,12] of the ion-size parameter.

The quantities $r_A = 3.5 \times 10^{-8}$ cm and $r_B = 1 \times 10^{-8}$ cm have been retained. The estimates for r_A and r_B are very crude but, fortunately, eq 11 are not very sensitive to the relative size of the quantities r_A and r_B.

Indeed, by imposing $r_A = r_B = a/2$ eq 11 become

$$k_D = \frac{8NkT}{3000\eta}\left(\frac{-b}{e^{-b} - 1}\right)$$

$$k_{-D} = \frac{2kT}{\pi\eta a^3}\left(\frac{-b}{1 - e^{b}}\right) \tag{12}$$

and the calculated k_D and k_{-D} change from the reported 1.0×10^{11} M^{-1} sec^{-1} and 3.3×10^7 sec^{-1} to 0.70×10^{11} M^{-1} sec^{-1} and 2.3×10^7 sec^{-1}, respectively.

From Table IV it may be seen that k_D is a factor of 2.4 smaller than the observed k_f while k_{-D} is a factor of 6 smaller than the observed k_R. The discrepancies between k_f, k_R and k_D, k_{-D} are within reasonable expectancy due to the approximations involved in the calculations of θ, k_D, and k_{-D}. These approximations may be summarized as follows: (1) use of the Davies equations for the activity coefficients at the present concentrations; (2) use of "static" activity coefficients in the dynamical situation in question when the rates involved are comparable to the rates of rearrangement of the ionic atmosphere; (3) use of the electrostatic factors $-b/(e^{-b} - 1)$ and $-b/(1 - e^{b})$ to calculate the quantities k_D and k_{-D} (these factors are derived from the Debye Hückel potential valid at very dilute solutions); (4) use of the Stokes–Einstein relation equating diffusional and viscous flow.

Calculations of the volume change[7] ΔV corresponding to the association process are possible from the measured $\mu_{max} = (\alpha_{exc}\lambda)_{max}$ at $f = f_r$. Eigen[7] has calculated

$$\Delta V = \left\{\frac{2\mu_{max}RT\beta}{\pi}\left[\sum_i \frac{\nu_i^2}{c_i} + \sum_j \frac{\nu_j^2}{c_j} + \sum_i \nu_i^2 \frac{d \ln f_i}{dc_i} + \sum_j \nu_j^2 \frac{d \ln f_j}{dc_j}\right]\right\}^{1/2} \tag{13}$$

where μ_{max} is the maximum excess absorption per wavelength, β is the solvent compressibility, the symbols i and j refer to the reagents and products of reaction, and the quantity in brackets for a 3:2 electrolyte is equal to

$$\left[\frac{1}{2(1 - \sigma)c} + \frac{1}{(2\sigma + 1)c} + \frac{1}{2\sigma c} + \frac{1}{2c}\frac{d \ln (\gamma_{\pm,3:2}{}^{5/2}/\gamma_{\pm,1:2}{}^{3/2})}{d\sigma}\right] \tag{14}$$

In Table III the results for the calculated ΔV are reported. It may be seen that the ΔV are of the order of 20 cm^3/mol, what one could expect for the change in volume associated with the elimination of a molecule of water during the process. Spiro, *et al.*,[13] by dilatometry, have found for the system $[Co(NH_3)_6](ClO_4)_3 + Na_2SO_4$ at ionic strength 0.1 values of ΔV very similar to the ones reported in this work. The definite trend with concentration of the ΔV could be due to a breakdown of the theory (for the used activity coefficients with concentration), or to the possible overlapping of two steps in the association process. Unfortunately, the second possibility, if existing, is beyond the resolving power of the method used, for the present case.

Conclusions

It seems from the above that the process of association and *vice versa* occurs with rates comparable to diffusion-controlled rates. However, the size of the volume change corresponds to the elimination of a molecule of water. This water might be loosely coordinated around the cations in accord with the observations of Stengle and Langford[4] for similar systems.

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(11) J. Kielland, *J. Am. Chem. Soc.*, **59**, 1675 (1937).

(12) N. Tanaka, Y. Kobayashi, and M. Kamada, *Bull. Chem. Soc. Japan*, **40**, 12 (1967).

(13) T. G. Spiro, A. Revesz, and J. Lee, *J. Am. Chem. Soc.*, **90**, 4000 (1968).