Conductance of Some High Valence Type Electrolytes in Mixed Solvents. II. Conductance of Pentaamminenitrocobalt(III) and Tris(1,10-phenanthroline)iron(II) Sulfates in Water-Ethylene Glycol Mixtures at 25 °C*

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Conductance data are reported for dilute solutions of pentaamminenitrocobalt(III) sulfate, $[Co(NO_2)(NH_3)_5]SO_4$, and tris(1,10-phenanthroline)iron(II) sulfate, $[Fe(phen)_3]SO_4$ in water–ethylene glycol mixed solvents at 25 °C. The conductance data were analyzed in terms of the 1957 Fuoss-Onsager and Fuoss-Hsia equations. While the application of the 1957 Fuoss-Onsager equation to $[Fe(phen)_3]SO_4$ data suggested a complete dissociation of the salt over the entire range of solvent compositions, the Fuoss-Hsia equation fitted the data better and yielded K_A values which are in accord with the ion association theories. $[Co(NO_2)(NH_3)_5]SO_4$ had a higher association constant in the range of solvent composition studied (0 to 40% ethylene glycol) than the predictions of the ion association theories.

In a previous paper[1] we reported the conductance data of $[Fe(phen)_3]SO_4$ in a water–methanol mixed solvent at 25 °C. The association constant of the salt was estimated to be 40 in water by the analysis of the data with the Fuoss-Hsia equation[2] in the form developed by Fernandez-Prini.[3]

Masterton and Biery[4] reported that $[Co(NO_2)(NH_3)_5]SO_4$ is much more ion-paired than has been calculated from the ion association theory, the association constants being 400 in water at 25 °C. Since the values of the association constants of bivalent metal sulfates are 150—250 in water and those of the *m*-benzenedisufonates of bivalent metals are much lower than the constants of the corresponding sulfate, the complex salt seems to be the most highly associated 2:2-type sulfate in water.[5]

It seemed interesting to study the association equilibiria of the complex salts in water–organic solvent systems. Thus, the conductance of $[Co(NO_2)(NH_3)_5]SO_4$ and $[Fe(phen)_3]SO_4$ in water–ethylene glycol mixtures was measured at 25 °C, and the association constants thus derived were compared with the predictions of the ion association theories.

Experimental

Materials. The $[Co(NO_2)(NH_3)_5]SO_4$ was synthesized as has been described in the literature.[6] The $[Co(NO_2)(NH_3)_5]Cl_2$ was prepared by reaction between $[CoCl(NH_3)_5]Cl_2$ and sodium nitrate; it was then converted to $[Co(NO_2)(NH_3)_5]SO_4$. The raw crystals were recrystallized repeatedly from a hot aqueous solution by adding ethanol and then dried at 105 °C. The procedure was carried out in the dark as far as possible to avoid nitrito-form contamination. The purity of the sample was checked by means of its UV and IR spectra, by elementary analysis (Found: N, 29.25; H, 5.32%. Calcd: N, 29.37; H, 5.28%), and by a total-cation determination untilizing cation-exchange resin.

The $[Fe(phen)_3]SO_4$ was prepared and purified as has been described in the previous paper.[1]

The ethylene glycol was dried with anhydrous sodium sulfate and fractionally distilled at 5 Torr. The specific conductivity was less than 7×10^{-8} ohm^{-1} cm^{-1}.

Apparatus and Measurement. The conductance measurement was performed by a transformer bridge (with a reproducibility of 0.005%) and a 3—10 kHz audio oscillator. Two flask-type cells with constants of 0.11631 and 0.09695 cm^{-1} were used. The temperature of the liquid paraffin bath was controlled at 25.000±0.005 °C.

The dilution method of a stock solution was not suitable for the preparation of $[Co(NO_2)(NH_3)_5]SO_4$ solutions because of the low solubility of the salt. The samples (10—20 mg) were weighed in small polyethylene dishes 10 mm in diameter, and the dishes were thrown into the cell. The conductivity was measured after each dissolution of samples.

$[Fe(phen)_3]SO_4$ had enough solubility for preparing the stock solution over the complete range of solvent compositions.

Results and Discussion

The conductance data of $[Co(NO_2)(NH_3)_5]SO_4$ and $[Fe(phen)_3]SO_4$ in water–ethylene glycol are given in Tables 1 and 2 respectively.

The data were analyzed by means of the Fuoss-Onsager (1957) equation:[7]

$$\Lambda = \Lambda_0 - Sc^{1/2}\gamma^{1/2} + Ec\gamma\log c\gamma + Jc\gamma - K_A c\gamma\Lambda f_\pm^2, \quad (1)$$

where the symbols have their usual meanings.[1] The f's were calculated from the extended Debye-Hückel theory, including the ion-size parameter, $\mathring{a}$. The coefficient, J, is also a function of $\mathring{a}$; the adjustable parameters are thus Λ_0, K_A, and $\mathring{a}$. The results of the computer analysis of the $[Co(NO_2)(NH_3)_5]SO_4$ data are summarized in Table 3.

The application of Eq. 1 to the $[Fe(phen)_3]SO_4$ data gave negative K_A values, as in the data for the salt in a water–methanol mixture.[1] Thus, the data were fitted by means of Eq. 2 for unassociated electrolytes:[7]

$$\Lambda = \Lambda_0 - Sc^{1/2} + Ec\log c + Jc. \quad (2)$$

Here, the adjustable parameters are Λ_0 and $\mathring{a}$. The results are given in Table 4.

For the $[Fe(phen)_3]SO_4$ data in water–methanol, the Fuoss-Hsia[2] equation was applied in the form of Eq. 3 developed by Fernandez-Prini:[3]

$$\Lambda = \Lambda_0 - Sc^{1/2}\gamma^{1/2} + Ec\gamma\log c\gamma + J_1c\gamma - J_2c^{3/2}\gamma^{3/2} - K_A c\gamma\Lambda f_\pm^2. \quad (3)$$

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TABLE 1. EQUIVALENT CONDUCTANCES AND CONCENTRATIONS OF $[Co(NO_2)(NH_3)_5]SO_4$ IN WATER–ETHYLENE GLYCOL AT 25 °C[a,b]

0% Ethylene glycol $D=78.30$ $10^3\eta=8.903$		10% Ethylene glycol $D=75.93$ $10^3\eta=11.40$		20% Ethylene glycol $D=73.25$ $10^3\eta=14.50$		30% Ethylene glycol $D=70.43$ $10^3\eta=18.30$		40% Ethylene glycol $D=67.30$ $10^4\eta=23.90$	
10^4c	Λ	10^4c	Λ	10^4c	Λ	10^4c	Λ	10^4c	Λ
0.81562	135.06	0.75060	108.60	1.3390	83.099	0.73736	66.446	1.4415	48.393
1.1627	133.15	1.4165	105.50	2.2305	79.931	1.4932	63.524	2.2746	46.024
1.3006	132.60	2.1559	102.61	3.1271	77.296	2.2686	61.087	3.1991	43.946
1.7636	130.34	2.9798	99.815	4.1033	74.948	3.0706	59.083	4.2445	42.053
2.0948	128.92	3.7614	97.718	4.9826	73.116	3.9176	57.304	5.0779	40.761
2.7598	126.54	4.7133	95.305	5.8667	71.558	4.8122	55.566	6.0095	39.496
3.1299	125.20	5.7809	93.017	7.0449	69.621	5.8846	53.972	7.0822	38.257
3.3635	124.59	6.8444	90.973	8.3689	67.753	7.0000	52.488	7.9862	37.351
4.0820	122.43	8.2655	88.610	9.3785	66.490	8.3381	50.860	8.9833	36.430
4.5080	121.28	9.2510	87.129	10.442	65.189	9.7533	49.318	10.063	35.554
5.2253	119.49	10.513	85.366	11.545	64.103	10.831	48.336	11.222	34.693
5.7822	118.10	11.472	84.153	12.692	62.922	11.843	47.469	12.412	33.908
6.3016	116.98	12.438	83.100	13.929	61.853	12.726	46.781	13.609	33.181
7.2328	115.08	14.499	80.944	15.301	60.718				
7.3927	114.78								
8.1406	113.36								
8.3004	113.07								
9.1147	111.68								
10.104	110.13								
10.259	109.91								
11.109	108.61								
11.319	108.26								

a) c, in mol dm^{-3}; Λ, in ohm^{-1} cm^2 $equiv^{-1}$. b) D, dielectric constant; η, viscosity(poise), Ref. 19).

TABLE 2. EQUIVALENT CONDUCTANCES AND CONCENTRATIONS OF $[Fe(phen)_3]SO_4$ IN WATER–ETHYLENE GLYCOL AT 25 °C[a]

20% Ethylene glycol $D=73.25$ $10^3\eta=14.50$		40% Ethylene glycol $D=67.30$ $10^3\eta=23.90$		60% Ethylene glycol $D=60.50$ $10^3\eta=41.30$		80% Ethylene glycol $D=51.80$ $10^3\eta=79.50$		100% Ethylene glycol $D=37.70$ $10^3\eta=169.0$	
10^4c	Λ	10^4c	Λ	10^4c	Λ	10^4c	Λ	10^4c	Λ
1.3565	69.889	2.0101	40.173	2.6545	23.226	2.6402	11.507	2.0997	4.7133
2.0994	69.111	2.3156	40.029	4.0023	22.871	3.4761	11.333	2.4603	4.6467
2.9888	68.402	2.8292	39.749	5.2773	22.522	5.0588	11.110	3.1656	4.5532
4.3533	67.492	3.8810	39.249	6.3007	22.294	6.1119	10.970	3.9743	4.4689
5.3797	66.965	4.8364	38.832	7.4408	22.054	7.8546	10.770	4.7148	4.4076
5.9415	66.698	6.3137	38.307	8.5096	21.852	9.1025	10.637	5.3202	4.3476
6.6305	66.399	8.7512	37.672	9.6793	21.662	9.9287	10.571	6.1617	4.2938
6.9474	66.254	12.326	36.853	12.167	21.281	13.255	10.304	6.9619	4.2440
7.4935	66.064							7.8798	4.1923
8.2785	65.779							9.1063	4.1298
								10.007	4.0910
								10.752	4.0559

a) Table 1, a) and b).

The application improved $\sigma\Lambda$ and gave reasonable K_A values. Therefore, the fitting of the present data to Eq. 3 was examined.

The best-fit values of Λ_0, K_A, and $\mathring{a}$ were calculated by a successive approximation for the series of initial values of the ion-size parameter, $\mathring{a}_i$, between 1—28 Å with 0.05 Å intervals. $\sigma\Lambda$ is defined as:

$$\sigma\Lambda = \left[\frac{\sum(\Lambda_{\text{exptl}}-\Lambda_{\text{calcd}})^2}{N-3}\right]^{1/2}, \quad (4)$$

where N is the number of experimental points.

An example of the results is shown graphically in Fig. 1 for the $[Co(NO_2)(NH_3)_5]SO_4$ data in water. The solid lines of Fig. 1 indicate the variation in Λ_0, K_A, $\sigma\Lambda$,

Table 3. Conductance parameters for $[Co(NO_2)(NH_3)_5]SO_4$ in water–ethylene glycol at 25 °C, calculated from the Fuoss-Onsager equation[a)]

Solvents (wt %)	Λ_0	$\mathring{a}_J$	K_A	$\sigma\Lambda$	N
0	142.64±0.06	7.9±0.3	281±6	0.06	22
10	115.09±0.06	7.7±0.3	363±3	0.05	14
20	91.50±0.08	7.9±0.3	480±9	0.05	14
30	71.54±0.08	7.5±0.5	610±15	0.06	13
40	55.96±0.04	8.2±0.2	923±8	0.02	13

a) Λ_0, limiting conductance (ohm^{-1} cm^2 equiv^{-1}); $\mathring{a}_J$, ion-size parameter(Å); K_A, ion association constant (dm^3 mol^{-1}); $\sigma\Lambda$, standard deviation of N, experimental points.

Table 4. Conductance parameters for $[Fe(phen)_3]SO_4$ in water–ethylene glycol at 25 °C, calculated from the Fuoss-Onsager equation[a)]

Solvents (wt %)	Λ_0	$\mathring{a}_J$	$\sigma\Lambda$	N
0[b)]	114.58 ±0.06	7.06±0.08	0.14	17
20	73.61 ±0.03	8.9 ±0.2	0.04	10
40	43.29 ±0.05	7.6 ±0.2	0.08	8
60	25.70 ±0.07	7.3 ±0.2	0.07	8
80	13.06 ±0.05	7.6 ±0.2	0.06	8
100	5.712±0.026	8.1 ±0.2	0.04	12

a) Table 1, a). b) Ref. 1.

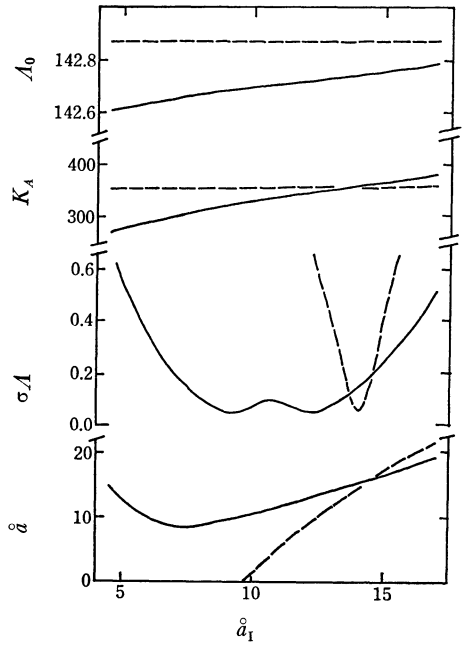

Fig. 1-A. Values of parameters and standard deviations as a function of $\mathring{a}_I$ for $[Co(NO_2)(NH_3)_5]SO_4$ in water. The units of Λ_0 and $\sigma\Lambda$ are ohm^{-1} cm^2 equiv^{-1} and those of K_A are dm^3 mol^{-1}. The broken lines are calculated by fixing $\mathring{a}=q$ in the J_1 and $f_\pm$ terms.

and $\mathring{a}$ with the change in $\mathring{a}_I$. While the K_A and Λ_0 values increase with the $\mathring{a}_I$, $\sigma\Lambda$ has two similar minima corresponding to the $\mathring{a}$ values of 9.0 and 12.0 Å. In Fig. 2, the $\sigma\Lambda$ values are shown as contour lines with the

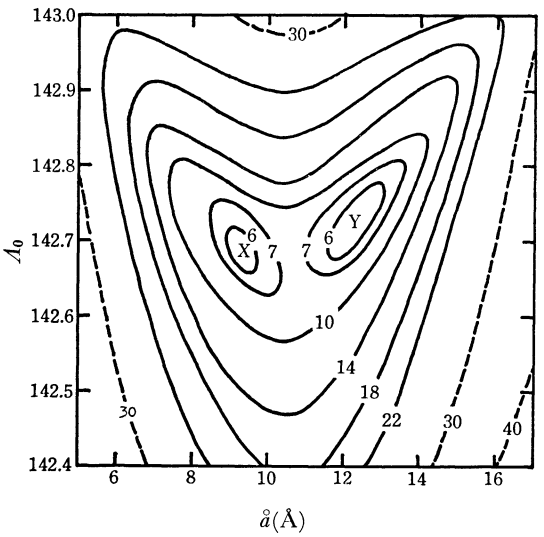

Fig. 1-B. Contour diagram for the $[Co(NO_2)(NH_3)_5]SO_4$ in water. The contour lines illustrate how $\sigma\Lambda$ depends on different conbinations of the Λ_0 and $\mathring{a}$. The figures on the contours represent the values of $10^2\sigma\Lambda$. The minimum at point X, $\sigma\Lambda=0.06$, corresponds to the parameters, $\Lambda_0=142.68$, $K_A=316$, $\mathring{a}=9.2$Å, while the minimum at point Y, $\sigma\Lambda=0.06$, corresponds to $\Lambda_0=142.72$, $K_A=343$, $\mathring{a}=12.4$Å.

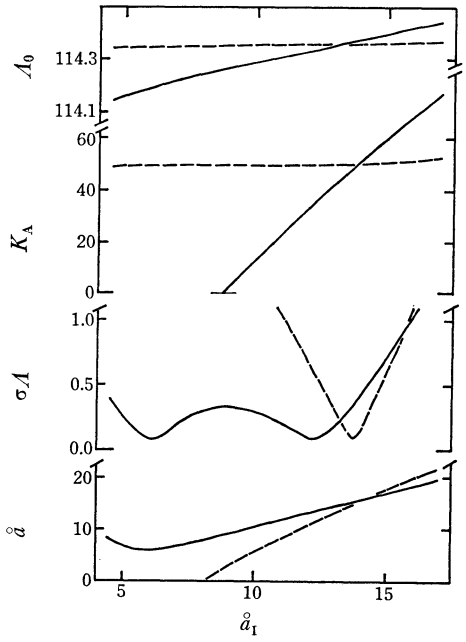

Fig. 2. Values of parameters and $\sigma\Lambda$ as a function of $\mathring{a}_I$ for $[Fe(phen)_3]SO_4$ in water. The broken lines are calculated by fixing $\mathring{a}=q$ in the J_1 and $f_\pm$ terms.

variation in the $\mathring{a}_I$ and Λ_0 values. It is apparent that two sets of parameter values were obtained by the above computation method. For the $[Co(NO_2)(NH_3)_5]SO_4$ data in other water–ethylene glycol solvent systems, two sets of parameter values of the minimum $\sigma\Lambda$ with different $\mathring{a}$ values are obtained. The appearance of the two minima in fitting the conductance data to the Fuoss-Hsia equation were observed for some 1:1-type electrolytes.[8)] It is rather difficult to decide which

TABLE 5-A. CONDUCTANCE PARAMETERS FOR $[Co(NO_2)(NH_3)_5]SO_4$ IN WATER–ETHYLENE GLYCOL AT 25 °C, CALCULATED FROM THE FUOSS-HSIA EQUATION IN THE FERNANDEZ-PRINI FORM[a)]

Solvents (wt %)	q	Λ_0	$\mathring{a}_{J_2}$	K_A	$\sigma\Lambda$	N
0	14.3	142.68±0.05	9.2±0.6	316±3	0.06	22
		142.72±0.05	12.4±0.5	343±3	0.06	
10	14.8	115.15±0.06	8.8±0.7	400±4	0.06	14
		115.20±0.07	12.7±0.5	437±5	0.07	
20	15.3	91.57±0.07	9.5±0.6	527±5	0.05	14
		91.62±0.07	12.5±0.5	560±5	0.05	
30	15.9	71.56±0.08	7.5±1.5	705±10	0.06	13
		71.64±0.10	15.7±0.9	736±12	0.08	
40	16.6	56.03±0.04	9.1±0.5	976±6	0.02	13
		56.10±0.05	14.2±0.4	1047±7	0.02	

TABLE 5-B. CONDUCTANCE PARAMETERS FOR $[Co(NO_2)(NH_3)_5]SO_4$ IN WATER–ETHYLENE GLYCOL CALCULATED FROM THE FUOSS-HSIA EQUATION IN THE FERNANDEZ-PRINI FORM, FIXING $\mathring{a}_1=q$ IN THE J_1 AND $f_\pm$ TERMS[a)]

Solvents (wt %)	q	Λ_0	$\mathring{a}_{J_2}$	K_A	$\sigma\Lambda$	N
0	14.3	142.74±0.05	14.0±0.4	358±3	0.06	22
10	14.8	115.22±0.08	14.4±0.6	455±5	0.07	14
20	15.3	91.68±0.07	14.6±0.4	589±5	0.04	14
30	15.9	71.62±0.08	16.1±0.8	734±11	0.06	13
40	16.6	56.14±0.05	16.1±0.4	1077±7	0.03	13

a) q, Bjerrum's distance (Å); $\mathring{a}_{J_2}$, ion-size parameter (Å); Table 1, a).

minimum is preferable. Thus, both sets of parameters are given in Table 5-A, which summarizes the results for $[Co(NO_2)(NH_3)_5]SO_4$.

For the $[Fe(phen)_3]SO_4$ data also, two minima with the lowest $\sigma\Lambda$ value are obtained, but the one corresponding to the lower $\mathring{a}$ has a negative K_A value. The results obtained for the data in water are shown as solid lines in Fig. 3. Similar results were obtained for the data in water–ethylene glycol solvents and for the data[1)] of the $[Fe(phen)_3]SO_4$ in water–methanol. In this case, the minimum $\sigma\Lambda$ values with a negative K_A are disregarded; the results are summarized in Table 6-A.

As another method of fitting the data to Eq. 4, the ion-size parameters appearing in the J_1 and $f_\pm$ terms were fixed as equal to the Bjerrum q values,[9)] and the best-fit $\mathring{a}$ values for the J_2 term were calculated. The results of the calculation are shown as broken lines in Figs. 1 and 3. In this case, a single minimum of $\sigma\Lambda$ was obtained; the corresponding $\mathring{a}_{J_2}$ was close to the q values. Tables 5-B and 6-B summarize the results for $[Co(NO_2)(NH_3)_5]SO_4$ and $[Fe(phen)_3]SO_4$ respectively.

Tables 5-A and 5-B show that, in comparison with the parameters listed in Table 3, the Fuoss-Hsia equation gives the same values of Λ_0 within the limits of error, but the values of K_A and $\mathring{a}$ are a little larger than those obtained by means of the Fuoss-Onsager equation. On the other hand, Tables 6-A and 6-B show that the application of the Fuoss-Hsia equation to the

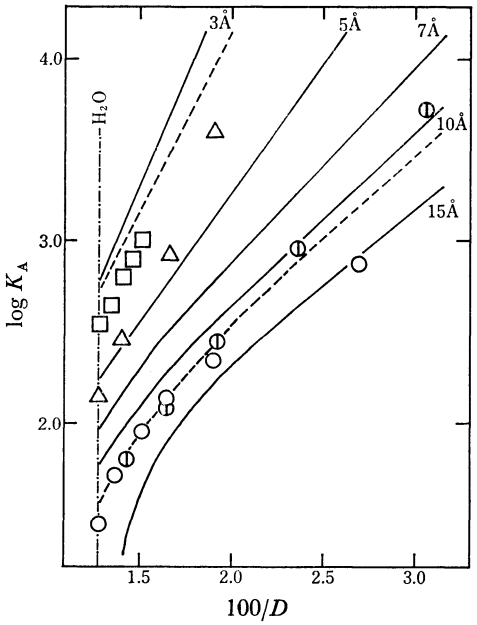

Fig. 3. Plot of log K_A *vs.* $1/D$.
□, $[Co(NO_2)(NH_3)_5]SO_4$ and ○, $[Fe(phen)_3]SO_4$, the present work at 25 °C. △, $MnSO_4$ in water–ethylene glycol and ⊕, $[Fe(phen)_3]SO_4$ in water–methanol at 25 °C. Curves are theoretical curves due to Bjerrum's (——) and Yokoyama-Yamatera's (----) theories[9,16)] with each ion sizes.

$[Fe(phen)_3]SO_4$ data gives apparently better data, just fitting the results on the data of the salts in water–methanol. The association constant is estimated to increase with a decrease in the solvent dielectric constant. A conductance equation which contains higher terms than c seems to be required as the reference function in the analysis of the conductance data of slightly associated 2:2 electrolytes.

Fuoss has revised his conductance equation recently;[7)] also, an extended conductance equation[10)] including the $c^{3/2}$ term has been proposed by Pitts.[11,12)] These equations will have to be examined for the conductance data of a slightly associated 2:2 electrolyte. At present, the discussion is based on the results obtained by means of the Fuoss-Hsia equation.

Λ_0 value of $[Co(NO_2)(NH_3)_5]SO_4$ obtained here in water, 144.9, is about 2 units lower than that reported by Masterton and Bierly; the association constant obtained is also a little lower than their value. The ionic conductances of $[Co(NO_2)(NH_3)_5]^{2+}$ and $[Fe(phen)_3]^{2+}$ ions in water are obtained as 63.1 and 34.6 by subtracting the $\lambda_0^-=80.0$[13)] of the SO_4^{2-} ion from the Λ_0 values. The latter values are in accord with values, 34.8—34.9, reported by Yamamoto *et al.* in their conductance measurements of the chloride and the bromide in water.[14)] The ionic conductance of the aquo Co^{2+} ion has been reported as 52.8,[15)] while those of the $[Ni(en)_3]^{2+}$ and aquo Ni^{2+} ions were estimated as 58.9 and 49.4[16)] respectively. The substitution of the first hydration-sphere by a ligand gives the ion higher mobility. A large ligand like phenanthroline, which may cover more than the second hydration sphere, will decrease the mobility of the ion.

Table 6-A. Conductance parameters for $[Fe(phen)_3]SO_4$ in water–ethylene glycol at 25 °C, calculated from the Fuoss-Hsia equation in the Fernandez-Prini form

Solvents (wt %)	q	Λ_0	$\mathring{a}_{J_2}$	K_A	$\sigma\Lambda$	N
0[b]	14.3	114.18 ±0.10	6.0±1.0	−28± 5	0.09	17
		114.33 ±0.10	12.9±0.5	35± 5	0.09	
20	15.3	73.20 ±0.05	4.6±2.0	−87± 6	0.02	10
		73.45 ±0.03	15.4±0.4	40± 3	0.01	
40	16.6	42.96 ±0.05	5.1±1.3	−85± 8	0.03	8
		43.09 ±0.06	17.5±0.6	82±10	0.03	
60	18.5	25.15 ±0.05	4.1±1.4	−178±15	0.02	8
		25.39 ±0.08	20.8±0.7	128±20	0.03	
80	21.6	12.65 ±0.02	5.2±0.5	−272±11	0.001	8
		12.86 ±0.04	20.8±0.4	207±19	0.01	
100	29.7	5.354±0.022	6.8±0.4	−696±42	0.007	12
		5.616±0.014	23.0±0.2	759±27	0.05	

Table 6-B. Conductance parameters for $[Fe(phen)_3]SO_4$ in water–ethylene glycol at 25 °C, calculated from the Fuoss-Hsia equation in the Fernandez-Prini form, fixing $\mathring{a}_1=q$ in the J_1 and $f_\pm$ terms[a]

Solvents (wt %)	q	Λ_0	$\mathring{a}_{J_2}$	K_A	$\sigma\Lambda$	N
0[b]	14.3	114.37 ±0.10	13.8±0.5	51± 5	0.09	17
20	15.3	73.45 ±0.03	15.3±0.4	39± 3	0.01	10
40	16.6	43.09 ±0.06	17.1±0.6	72± 9	0.03	8
60	18.5	25.37 ±0.08	19.8±0.7	95±18	0.03	8
80	21.6	12.86 ±0.04	21.1±0.4	228±19	0.01	8
100	29.7	5.650±0.017	25.5±0.2	1131±34	0.005	12

a) q, Bjerrum's distance (Å); $\mathring{a}_{J_2}$, ion-size parameter (Å); Table 1, a). b) Ref. 1.

In Fig. 3 the log K_A's of $[Co(NO_2)(NH_3)_5]SO_4$ and $[Fe(phen)_3]SO_4$ in water–ethylene glycol are plotted against the reciprocal of the dielectric constants of the solvents. The predictions of the ion association theories of Bjerrum[9] and Yokoyama-Yamatera[17] are shown as solid and dotted lines respectively for the specific contact distances. The data of $[Co(NO_2)(NH_3)_5]SO_4$ are on a straight line, which is located on Bjerrum's prediction corresponding to about 3.7 Å.

The size of the $[Co(NO_2)(NH_3)_5]^{2+}$ ion could be estimated from the X-ray crystal analysis data of $[CoCl(NH_3)_5]Cl_2$.[18] The minimum distance of the approach of the cobalt atom and chloride in the crystal is 4.2 Å. The crystal analysis data[19] of anhydrous sulfates of alkaline earth and first-transition metals gave effective radii of the sulfate ions ranging 2.3 to 2.5 Å. If the effective radius of $[Co(NO_2)(NH_3)_5]^{2+}$ is close to that of $[CoCl(NH_3)_5]^{2+}$, the closest distance of approach in the sulfate would be about 4.8 Å. This is larger than the distance found from the location of the log K_A-1/D plot in Fig. 3. The plot of the $MnSO_4$ data in the same solvent system[20] corresponds to a contact distance of 4.6 Å, judging from a comparison with Bjerrum's theory. The minimum distance of Mn^{2+} and SO_4^{2-} separation in the anhydrous $MnSO_4$ crystal is 3.3 Å.[19]

The above results suggest that the main species of association in the $MnSO_4$ solution might be a solvent-separated ion pair. The Mn–SO_4 distance separated by one water molecule would be about 4.8 Å, which is found as the closest distance between metal and sulfur in the $[Ni(OH_2)_6]SO_4$ crystal. On the other hand, in the $[Co(NO_2)(NH_3)_5]SO_4$ solution, the main species of association would be a contact-ion pair, as was suggested by Osugi *et al.* in their interpretation of the pressure dependence of the ion association constant.[12] Interaction between opposite-charged ions other than the coulombic attraction of opposite charges stabilizes the contact-ion pair. Masterton *et al.* suggested that the extra stability of the associated species comes from a dispersion interaction. D'Aproano and Fuoss[22] interpreted the high association constant of TlCl in water–dioxane mixture by calculating the energies due to the interaction between the charges and the induced dipoles. In a 1:1 cobalt complex salt solution, an extra stability of associated species sometimes promotes the K_A value to an order higher.[4] In a 2:2 electrolyte, however, the effect of extrastabilization is not so remarkable as in the 1:1 salt solution, since the charge-charge interaction energy is larger; yet it is clear that the effect is maintained independently of the macroscopic dielectric constant of the solvent.

The data of the log K_A of $[Fe(phen)_3]SO_4$ in water–methanol are plotted in Fig. 3 for purposes of comparison. The plots for the two solvent systems coincide with each other in the water-rich solvent range, but deviate in a high organic solvent content medium. This suggests that solvent-separated association species may contribute by some extent. The overall data points are located close the Yokoyama-Yamatera theory of 10 Å.

In this case, the cation is large enough and is not easily polarizable, and the specific interaction with the sulfate ion contributes little to the extra stability of the contact-ion pair.

All the calculations were performed on HITAC 10-II remote-batch system, FACOM 230-60, and HITAC 8800/8700 computers using the program of FORTRAN IV. The authors wish to thank the staffs of the Shinshu University Remote Batch Computation Center, Nagoya University Computation Center, and Tokyo University Computation Center for the use of the computers.

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