Conductance of Some High Valence Type Electrolytes in Mixed Solvents. I. Conductance of Tris(1,10-phenanthroline)iron(II) Sulfate and Chloride in Water–Methanol Mixtures at 25 °C*

Eiji Kubota and Masatoki Yokoi

Department of Chemistry, Faculty of Science, Shinshu University, Asahi, Matsumoto 390

(Received February 2, 1976)

The conductance of tris(1,10-phenanthroline)iron(II) sulfate, $Fe(phen)_3SO_4$, and chloride, $Fe(phen)_3Cl_2$, has been measured in water–methanol mixed solvent at 25 °C. The data of the sulfate could be explained by means of the Fuoss-Onsager equation (1957) and the Fuoss-Onsager-Skinner equation (1965) on the assumption that the salt is completely dissociated in the entire composition range of the solvent system. Application of the Fuoss-Hsia equation which contains a $c^{3/2}$ term gave association constants increasing from a value of $K_A=40$ in water to $K_A=3900$ in methanol. The $\log K_A$ *vs.* $1/D$ plot is in good agreement with ion association theoreies. The limiting equivalent conductance of $Fe(phen)_3^{2+}$ ion was estimated to be 34.3 in water and 62.3 in methanol.

The behavior of 1 : 1 electrolyte in various solvents has been investigated extensively by conductance measurements.¹⁾ The extended Fuoss-Onsager theory²⁾ was applied satisfactorily to the analysis of the data, ion association being studied in low dielectric constant media. On the other hand, the investigation of the high valence type electrolyte solutions was often restricted to aqueous solutions because of the limited solubility of the electrolytes in organic solvents. *m*-Benzenedisulfonates of bivalent metals were studied in methanol³⁾ and some aqueous organic mixture solvents.⁴⁾ Tris(1,10-phenanthroline)iron(II) ion is a large bivalent cation, the salts having sufficient solubility in methanol. Thus conductance measurements of the salts in water–methanol mixtures were undertaken for the purpose of studying the change in ion association equilibrium with the variation of the composition of the solvent mixture.

Experimental

Materials. $Fe(phen)_3SO_4$ was prepared by adding a little excess amount of GR 1,10-phenanthroline to the aqueous iron(II) sulfate solution.⁵⁾ The solution was concentrated at below 60 °C and the sulfate was precipitated by addition of acetone. The precipitate was dissolved again in water, the procedure being repeated several times. The precipitate was finally crystallized from water and dried at room temperature.

$Fe(phen)_3Cl_2$ was prepared by adding sodium chloride to the aqueous solution of the sulfate and recrystallized from water.⁵⁾

The water content of the sulfate and chloride dried in a dessicator containing silica gel or calcium chloride was not stoichiometric. The number of the water of crystallization was usually less than five. The total cation concentration of each stock solution ($\approx 10^{-2}$ M) was analyzed with Dowex 50-X2 ion exchange resin. The purity of the samples was further checked by spectrophotometry.

Solvents. Methanol was purified by distillation over the activated magnesium and aluminum amalgam.⁶⁾ It was then redistilled, the middle fraction being collected. The specific conductivity was less than 8×10^{-8} ohm⁻¹ cm⁻¹. Conductivity water was obtained by passing distilled water through a mixed bed ion exchange resin. The specific conductivity was less than 3×10^{-7} ohm⁻¹ cm⁻¹.

Apparatus and Measurement. A Jones-type bridge was used for the conductance measurement, alternative current of 3—10 kHz being applied to the bridge. The standard resistors had a precision of ±0.02% and the bridge showed a reproducibility of ±0.005%. Two flask type cells of cell constants of 0.14520 and 0.23322 cm⁻¹ were used. The solutions were prepared by adding a certain quantity of the stock solution from a weighing burette to the solvent placed in the cell. Resistance values were obtained by extrapolation to infinite frequency. The temperature of the liquid paraffin bath was controlled to 25.000±0.005 °C. The viscosity *B* coefficients of $Fe(phen)_3SO_4$ in water and 100% methanol were measured with calibrated Cannon-Fenske type viscometers.

Results and Discussion

The observed conductance values are given in Tables 1 and 2 for the sulfate and the chloride, respectively.

The conductance data of the sulfate were analyzed first by the Fuoss-Onsager (1957)²⁾ and Fuoss-Onsager-Skinner (1965)⁷⁾ equations for symmetrical electrolytes. The form of the former equation for unassociated electrolytes⁸⁾ is

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

where Λ_0 is the equivalent conductance at infinite dilution, c is the molar concentration, S is the Onsager slope. Coefficients S, E and J are dependent on temperature, dielectric constant D, viscosity η of the solvent, and Λ_0. J is also a function of ion size parameter $\mathring{a}$.

The conductance equation for associated electrolytes is

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

where K_A is the association constant, $f_\pm$ is the mean activity coefficient, and γ is the degree of dissociation. The $f_\pm$'s were calculated by the extended Debye-Hückel theory⁹⁾ with the same ion size parameter $\mathring{a}$ as that in J.

In the case of electrolytes containing large ions, the Jc term is replaced by $(J-B\Lambda_0)c$, where B is the viscosity B coefficient of the electrolyte in the solution.

---

* Presented in part at the 21th Conference on Coordination Chemistry of Chemical Society of Japan, Nagoya, October, 1971; also at the 27th Anual Meeting of the Chemical Society of Japan, Nagoya, October, 1972.

Table 1. Equivalent conductances and concentrations of $Fe(phen)_3SO_4$ in water-methanol at 25 °C[a,b)]

10^4c	Λ	10^4c	Λ	10^4c	Λ
0% Methanol $D=78.30$ $10^3\eta=8.903$		20% Methanol $D=69.95$ $10^3\eta=14.00$		40% Methanol $D=60.93$ $10^3\eta=15.93$	
1.7449	108.28	3.3222	69.113	3.3426	55.332
2.1891	107.64	3.9045	68.631	4.2818	54.618
2.1982	107.26	4.4100	68.288	4.8797	54.198
2.3916	107.13	5.2756	67.700	5.6334	53.773
3.0204	106.32	6.1300	67.198	7.3160	52.850
3.1801	106.05	7.1049	66.720	8.6318	52.230
4.7348	104.51	9.2170	65.751	9.7974	51.822
4.8243	104.50	10.890	65.061	11.795	51.140
6.7251	102.98	12.911	64.420	13.935	50.501
8.1661	102.04	15.104	63.725	15.929	49.984
8.7436	101.66	19.911	62.656		
11.171	100.45				
11.634	100.15				
12.946	99.606				
13.912	99.149				
16.024	98.300				
16.620	98.087				
60% Methanol $D=51.61$ $10^3\eta=14.03$		80% Methanol $D=42.58$ $10^3\eta=10.06$		100% Methanol $D=32.70$ $10^3\eta=5.445$	
3.0998	54.141	2.0453	61.211	2.0213	71.307
3.7259	53.418	3.0450	58.903	2.3577	69.390
4.4924	52.696	4.7475	55.848	3.3124	65.096
5.1893	52.105	5.3592	55.001	3.9301	62.855
6.1165	51.437	5.6976	54.561	5.3710	58.883
7.3333	50.600	7.0787	52.980	6.8495	55.832
8.9194	49.698	7.9637	52.102	8.5750	53.106
10.746	48.843	8.9017	51.302	9.0710	52.365
12.215	48.201	11.377	49.601	10.335	50.845
13.603	47.735			11.601	49.418

a) c, in M dm^{-3}; Λ, in ohm^{-1} cm^2 equiv.$^{-1}$. b) D, dielectric constant; η, viscosity(poise), Ref. 29.

The form of the equation (1965) for unassociated electrolytes is

$$\Lambda = \Lambda_0 - Sc^{1/2} + E'c\log(6E_1'c) + Lc \tag{3}$$

and for associated electrolytes

$$\Lambda = \Lambda_0 - Sc^{1/2}\gamma^{1/2} + E'c\gamma\log(6E_1'c\gamma) + Lc\gamma - K_A c\gamma\Lambda f_\pm^2 \tag{4}$$

where L is a parameter depending on $\mathring{a}$.

Analysis was carried out according to the method of Fuoss[8)] and Kay[10)] applying both 1957 and 1965 theories to the observed $c-\Lambda$ data.

The conductance data of the chloride, 2 : 1 type unsymmetrical electrolyte, were analyzed using the Fuoss-Edelson technique,[11)] based on the Onsager limiting theory. The second association to form the nonconducting species as $MA^+ + A^- \rightleftarrows MA_2$ was assumed to be negligible, only the equilibrium $M^{2+} + A^- \rightleftarrows MA^+$ being considered. It was also assumed that $\lambda_{MA^+} = 1/2\lambda_{M^{2+}}$. The Debye-Hückel limiting theory[12)] was used for the calculation of the activity coefficient f_{2+}. Λ_0 and K_A are the adjustable parameters. They were determined finally by extrapolation.

Table 2. Equivalent conductances and concentrations of $Fe(phen)_3Cl_2$ in water-methanol at 25 °C[a)]

10^4c	Λ	10^4c	Λ	10^4c	Λ
0% Methanol $D=78.30$ $10^3\eta=8.903$		20% Methanol $D=69.95$ $10^3\eta=14.00$		40% Methanol $D=60.93$ $10^3\eta=15.93$	
1.5694	108.21	1.5820	71.010	2.2729	56.786
2.0332	107.96	2.3041	70.612	3.1029	56.365
2.2691	107.54	2.9353	70.249	4.0519	55.967
3.5838	106.81	5.2676	69.318	5.6200	55.480
5.4804	105.76	8.4920	68.399	7.6521	54.977
8.0381	104.98	11.152	67.816	10.651	54.311
9.1204	104.43	14.083	67.262	14.526	53.599
12.451	103.40			20.635	52.739
60% Methanol $D=51.61$ $10^3\eta=14.03$		80% Methanol $D=42.58$ $10^3\eta=10.06$		100% Methanol $D=32.70$ $10^3\eta=5.445$	
2.4275	56.100	1.6605	67.381	1.4743	108.23
2.8863	55.768	3.3682	65.500	2.5915	107.26
3.3092	55.539	5.5051	63.863	3.7608	106.50
4.3059	55.108	6.1547	63.522	5.1994	105.71
4.8409	54.846	6.9758	63.078	6.9131	104.90
7.9237	53.773	9.4788	61.820	9.7950	103.74
11.493	52.867	12.216	60.810	12.386	102.83
16.637	51.708				

a) Table 1, a) and b).

All the calculations were performed on FACOM 230-60, HITAC 8800/8700, and HITAC 10-II remote batch system computers[13)] using the program in FORTRAN IV.[14)]

The data of $Fe(phen)_3SO_4$ were fitted with both Eqs. 1 and 3 of complete dissociation over the entire range of the solvent composition. However, application of Eq. 2 or 4 for an associated electrolyte gave negative K_A values. The values of Λ_0 and $\mathring{a}$ ($\mathring{a}_J$ from Eq. 1 and $\mathring{a}_L$ from Eq. 3) obtained are summarized in Table 3, which also includes the values of $\sigma\Lambda$, the standard deviation, calculated by means of the expression

$$\sigma\Lambda = \left[\frac{\Sigma(\Lambda_{\text{exp.}} - \Lambda_{\text{calcd}})^2}{(N-3)}\right]^{1/2} \tag{5}$$

where N is the number of experimental points.

The $\mathring{a}_J$'s and $\mathring{a}_L$'s are about 7.0 Å. There seems to be no systematic change of the value with solvent composition. The viscosity correction was examined for the data of water and 100% methanol. The calculated parameters are also given in Table 3. The correction gave no noticeable change in the parameter values.

The ionic conductance data of $Fe(phen)_3Cl_2$ were analyzed by the Fuoss-Edelson technique and the Λ_0 and K_A values obtained are given in Table 4.

The conductance data of the sulfate could be inter-

Table 3A. Conductance parameters for Fe(phen)$_3$SO$_4$ in water-methanol at 25 °C, calculated from Fuoss-Onsager equation[a)]

Solvents (wt%)	Λ_0	$\mathring{a}_J$	$\sigma\Lambda$	N
0	114.58±0.06	7.06±0.08	0.14	17
0[b)]	114.55±0.06	7.30±0.08	0.14	17
20	75.74±0.07	6.81±0.08	0.11	11
40	61.99±0.06	6.95±0.08	0.08	10
60	62.65±0.08	6.91±0.07	0.10	10
80	72.64±0.06	6.66±0.03	0.08	9
100	96.05±0.35	6.78±0.07	0.50	10
100[b)]	96.05±0.35	6.84±0.07	0.50	10

Table 3B. Conductance parameters for Fe(phen)$_3$SO$_4$ in water-methanol at 25 °C, calculated from Fuoss-Onsager, Skinner equation[a)]

Solvents (wt%)	Λ_0	$\mathring{a}_L$	$\sigma\Lambda$	N
0	114.58±0.07	7.06±0.08	0.14	17
20	75.73±0.07	6.81±0.09	0.11	11
40	61.98±0.07	6.95±0.08	0.09	10
60	62.65±0.09	6.90±0.07	0.11	10
80	72.63±0.07	6.66±0.04	0.08	9
100	96.00±0.42	6.79±0.07	0.50	10

a) Λ_0, limiting conductance (ohm^{-1} cm^2 equiv.$^{-1}$); $\mathring{a}_J$, $\mathring{a}_L$, ion size parameter (Å); $\sigma\Lambda$, standard deviation of N, experimental points. b) With viscosity corrections; $B=1.9_3$ (0%); $B=3.7_8$ (100% Methanol).

Table 4. Conductance parameters for Fe(phen)$_3$Cl$_2$ in water-methanol at 25 °C, calculated from Fuoss-Edelson technique[a)]

Solvents (wt%)	Λ_0	λ_0^-	λ_0^+	K_A	$\sigma\Lambda$	N
0	110.61	76.35[b)]	34.26	6	0.07	8
20	72.73			6	0.02	7
40	58.70			3	0.02	8
60	58.70			5	0.01	8
80	70.82			19	0.09	7
100	114.63	52.38[c)]	62.25	—	0.43	8

a) K_A, ion association constant (M^{-1} dm^3); $\lambda_0\pm$, limiting ionic conductance (ohm^{-1} cm^2 equiv.$^{-1}$). b) Ref. 27. c) Ref. 28.

preted by means of the conductance equation of complete dissociation in a solvent of a high methanol content. The association constants of *m*-benzenedisulfonates of vibalent metals were reported to be of the order of 10^4 in methanol at 25°C.[3,4)] The ion association theories of Bjerrum,[15)] Fuoss[16)] and Yokoyama-Yamatera[17)] predict fairly large values of association constant for 2 : 2 electrolyte in methanol. It seems to be difficult to explain why Fe(phen)$_3$SO$_4$ is completely dissociated in a low dielectric constant solvent such as aqueous methanol even though it contains a large ion.

The Fuoss-Onsager equation has been frequently used to represent the conductance of a hypothetical completely dissociated electrolyte. Within the last few years use of a more complete conductance equation according to Fuoss and Hsia[18)] in the form of Fernandez-Prini,[19)]

$$\Lambda = \Lambda_0 - Sc^{1/2} + Ec\log c + J_1c - J_2c^{3/2} \tag{6}$$

has been discussed in a number of publications.[20)] Coefficient J_2 is also a function of $\mathring{a}$. The combination of equations,

$$K_A = (1-\gamma)/(c\gamma^2 f_\pm{}^2)$$

and

$$\Lambda = \gamma(\Lambda_0 - Sc^{1/2}\gamma^{1/2} + Ec\gamma\log c\gamma + J_1c\gamma - J_2c^{3/2}\gamma^{3/2}) \tag{7}$$

yields the following expression for associated electrolytes:

$$\Lambda = \Lambda_0 - Sc^{1/2}\gamma^{1/2} + Ec\gamma\log c\gamma + J_1c\gamma - J_2c^{3/2}\gamma^{3/2} - K_A c\gamma\Lambda f_\pm{}^2 \tag{8}$$

where $f_\pm$ is calculated by Eq. 9[9)] following the extended Debye-Hückel theory:

$$-\log f_\pm = \frac{Ac^{1/2}\gamma^{1/2}}{(1+B\mathring{a}c^{1/2}\gamma^{1/2})} \tag{9}$$

where A and B depend upon the solvent properties.[21)]

The coefficients J_1 and J_2 in Eqs. 6 and 8 are

$$J_1 = \sigma_1\Lambda_0 + \sigma_2;\quad J_2 = \sigma_3\Lambda_0 + \sigma_4 \tag{10}$$

where

$$\sigma_1 = \frac{(\kappa\mathring{a}b)^2}{24c}\left[1.8147 + 2\ln\frac{\kappa\mathring{a}}{c^{1/2}} + \frac{2(2b^2+2b-1)}{b^3}\right] \tag{10a}$$

$$\sigma_2 = \alpha\beta + \frac{\beta\kappa\mathring{a}}{c^{1/2}} - \frac{\beta\kappa\mathring{a}b}{16c^{1/2}}\left[1.5337 + \frac{4}{3b} + 2\ln\frac{\kappa\mathring{a}}{c^{1/2}}\right] \tag{10b}$$

$$\sigma_3 = \frac{b^2(\kappa\mathring{a})^3}{24c^{3/2}}\left[0.6094 + \frac{4.4748}{b} + \frac{3.8284}{b^2}\right] \tag{10c}$$

$$\sigma_4 = \frac{\beta(\kappa\mathring{a}b)^2}{24c}\left[\frac{2(2b^2+2b-1)}{b^3} - 1.9384\right] + \frac{\alpha\beta\kappa\mathring{a}}{c^{1/2}} + \frac{\beta(\kappa\mathring{a})^2}{c} - \frac{\beta b(k\mathring{a})^2}{16c}\left[1.5405 + \frac{2.2761}{b}\right] - \frac{\beta^2\kappa\mathring{a}b}{16c^{1/2}\Lambda_0}\left[\frac{4}{3b} - 2.2194\right] \tag{10d}$$

In Eqs. 10a—10d, α and β are the relaxation and the electrophoretic coefficients, respectively, and b is Bjerrum's parameter given by $b=Z^2e^2/(\mathring{a}DkT)$.[22)]

Application of Eq. 8 was examined for the data of sulfate for the entire solvent composition range. Yokoyama and Yamatera applied the Fuoss-Hsia equation to our conductance data[24)] of the sulfate in water and reported $K_A=36$.[23)]

Starting with preliminary values for Λ_0 and $\mathring{a}$ obtained from the Fuoss-Onsager equation, the corresponding parameters appearing in Eq. 8 were calculated by numerical computations.[14)] The program,[13)] operating essentially according to the method of Kay,[10)] involved successive approximation of γ until $|\gamma_i - \gamma_{i-1}| \leqq 1\times10^{-6}$ and iterative determinations of Λ_0, K_A, and $\mathring{a}$ by solving equations of the form

$$\Delta\Lambda = \frac{\partial\Lambda}{\partial\Lambda_0}\Delta\Lambda_0 + \frac{\partial\Lambda}{\partial K_A}\Delta K_A + \frac{\partial\Lambda}{\partial\mathring{a}}\Delta\mathring{a} \tag{11}$$

for each experimental point. The calculations were discontinued when $\Delta\mathring{a} \leqq 1\times10^{-13}$ and finally the $\sigma\Lambda$ value was calculated by Eq. 5.

TABLE 5. CONDUCTANCE PARAMETERS FOR $Fe(phen)_3SO_4$ IN WATER-METHANOL AT 25 °C, CALCULATED FROM FUOSS-HSIA EQUATION IN THE FORM FERNANDEZ-PRINI[a]

Solvents (wt%)	q	Λ_0	$\mathring{a}_{J_2}$	K_A	$\sigma\Lambda$	N
0	14.3	114.33±0.10	12.9±0.5	35± 5	0.09	17
0[b]	14.3	114.33±0.10	12.8±0.5	34± 5	0.09	17
20	16.0	75.44±0.07	13.2±0.3	61± 4	0.04	11
40	18.4	61.78±0.07	14.8±0.2	120± 6	0.02	10
60	21.7	62.22±0.11	17.4±0.2	282±12	0.03	10
80	26.3	74.40±0.28	19.8±0.4	868±39	0.09	9
100	34.3	105.97±0.36	25.4±0.1	3939±63	0.08	10
100[b]	34.3	105.90±0.37	25.4±0.1	3905±64	0.08	10

a) q, Bjerrum's distance (Å). b) With viscosity corrections; $B=1.9_3$ (0%); $B=3.7_8$ (100% Methanol).

Different combinations of the values for Λ_0, K_A, and $\mathring{a}$ may provide almost equally good fits of the conductance equation to the experimental data. In order to investigate the dependence of $\sigma\Lambda$ on $\mathring{a}$ calculations were repeated for a series of ionic separation $\mathring{a}$ between 5 and 30 Å with 0.05 Å increments.

The results are summarized in Table 5. The viscosity correction was examined for the data of water and 100% methanol. The correction made little effect on the parameter values as in the case of analysis by Eq. 1 or 3. The association was observed in the whole range of solvent composition. The $\sigma\Lambda$'s are slightly improved as compared with the values in Table 3. The Λ_0's are very close to those of Table 3 in the solvent of low methanol content, but larger than that obtained from the assumption of complete dissociation in pure methanol. The $\mathring{a}$ values change with the solvent composition, increasing from 12.9 Å in water to 25.5 Å in methanol. The variation of $\mathring{a}$ is parallel to that of the Bjerrum's critical distance q given by $q=Z^2e^2/(2DkT)$,[22] which varies from 14.3 Å to 34.3 Å (Table 5). The results might be regarded to be in close accordance with the results of Justice[25] and other authors,[26] who set $\mathring{a}=q$ in the analysis of 1 : 1 type slightly associated electrolytes.

Log K_A is plotted against reciprocal of dielectric constant in Fig. 1. The ionic crystal radius sum of the complex sulfate is estimated to be about 10 Å. The K_A values are calculated from the ion association theories of Bjerrum, Fuoss and Yokoyama-Yamatera for contact distance of 10 Å and are also plotted in Fig. 1. The observed points start under the line of Yokoyama-Yamatera theory and cross the line, but they are all in the range between the prediction of the Bjerrum and Fuoss theories. The application of Fuoss-Hsia equation[18] to the analysis of the present data seems to be more satisfactory, the results being consistent with the prediction of the ion association theories.

The limiting ionic conductance of the complex ion in water was estimated from the Λ_0 values by substructing $\lambda_{Cl^-}=76.35$[27] for the chloride or $\lambda_{SO_4^{2-}}=80.0$[27] for the sulfate. These values coincide with 34.3. In methanol, the ionic conductance of the complex ion is estimated from the Λ_0 of the chloride as 62.3 ($\lambda_{Cl^-}=52.4$[28]). The ratio of λ^+ of the complex ion in water to that in methanol is close to the ratio for tetraethylammonium ion whose λ^+ is 32.6 in water[27] and 60.5 in methanol.[28] This resemblance would be due to a similar charge to radius ratio of both ions. The limiting ionic conductance of sulfate ion in methanol is about 44 if we use $\lambda^+=62.3$ from the Λ_0 in Table 5. The value should be further checked by the measurements of conductance and transference number for other sulfates in methanol.

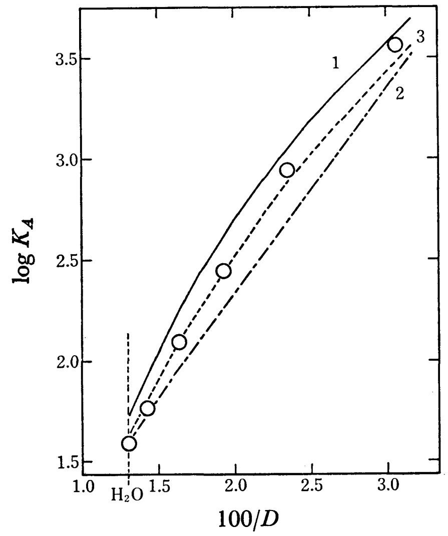

Fig. 1. Plots of log K_A vs. 1/D.
○, Present work at 25 °C. Curves 1, 2, and 3 are theoretical curves due to Bjerrum (——), Fuoss (– – –) and Yokoyama-Yamtera's (----) theories with $\mathring{a}$ = 10 Å.

The authors wish to thank the staff of the Nagoya University Computation Center, Tokyo University Computation Center and Shinshu University Remote Batch Computation Center for the use of computers.

References

1) a) G. J. Janz and R. P. T. Tomkins, "Nonaqueous Electrolytes Handbook," Vol. 1, Academic Press, New York-London (1972), p. 145, 1063; *ibid.*, Vol. 2 (1973), p. 800; b) R. Fernandez-Prini, "Physical Chemistry of Organic Solvent Systems," ed. by A. K. Convington and T. Dickinson, Prenum Press, London-New York (1973), p. 588; c) A. D'Aprano and R. M. Fuoss, *J. Solution Chem.*, **3**, 45 (1974); *ibid.*, **4**, 91 (1975); *ibid.*, **4**, 175 (1975); d) L. Broadwater and R. L. Kay, *ibid.*, **4**, 745 (1975).

2) a) R. M. Fuoss and L. Onsager, *J. Phys. Chem.*, **61**, 668 (1957); b) R. M. Fuoss and Accascina, "Electrolytic Conductance," Interscience Publishers, New York, N. Y. (1959), Chap. VIII—XVII.

3) R. Lovas, G. Macri and S. Petrucci, *J. Am. Chem. Soc.*, **92**, 6502 (1970).

4) a) E. Kubota, M. Yokoi, and S. Shikata, *Nippon Kagaku Zasshi*, **85**, 89 (1964); b) M. Yokoi and E. Kubota, *ibid.*, **86**, 894 (1965); c) H. Tsubota and G. Atkinson, *J. Phys. Chem.*, **71**, 1131 (1967).

5) a) F. Blau, *Monatsh.*, **19**, 669 (1898); b) P. Pfeiffer and Fr. Tappermann, *Z. Anorg. Chem.*, **215**, 273 (1933).

6) a) H. Lund and J. Bjerrum, *Ber.*, **64**, 210 (1931); b) A. A. Maryott, *J. Am. Chem. Soc.*, **63**, 3079 (1941); c) H. Hartley and H. R. Raikes, *J. Chem. Soc.*, **1925**, 524.

7) R. M. Fuoss, L. Onsager, and J. F. Skinner, *J. Phys. Chem.*, **69**, 2581 (1965).

8) a) R. M. Fuoss, *J. Am. Chem. Soc.*, **81**, 2659 (1959); b) Ref. 2b, Chap. XV—XVII.

9) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworths, London (1965), p. 229.

10) R. L. Kay, *J. Am. Chem. Soc.*, **82**, 2099 (1960).

11) R. M. Fuoss and D. Edelson, *J. Am. Chem. Soc.*, **73**, 269 (1951).

12) Ref. 9, p. 230.

13) FACOM 230-60, Nagoya University Computation Center; HITAC 8800/8700, Tokyo University Computation Center; HITAC 10-II remote batch system, connected to Tokyo University Computation Center.

14) Registered to Nagoya University Computation Center's libraries.

15) a) N. Bjerrum, *Kgl. Danske Videnskab. Selskab.*, **7**, No. 9 (1926); b) S. Petrucci, "Ionic Interactions," Vol 1, Academic Press, New York-London, (1971), p. 121.

16) a) R. M. Fuoss, *J. Am. Chem. Soc.*, **80**, 5059 (1958); b) Ref. 15b, p. 132.

17) a) H. Yokoyama and Yamatera, *Chem. Lett.*, **1973**, 337; b) H. Yokoyama and Yamatera, *Bull. Chem. Soc. Jpn.*, **48**, 1770 (1975).

18) a) R. M. Fuoss and K. L. Hsia, *Proc. Natl. Acad. Sci. U.S.*, **57**, 1550 (1966); *ibid,*. **58**, 1818 (1967); b) K. L. Hsia and R. M. Fuoss, *J. Am. Chem. Soc.*, **90**, 3055 (1968).

19) R. Fernandez-Prini, *Trans.Faraday Soc.*, **65**, 3311 (1969).

20) a) D. F. Evans and D. Gardam, *J. Phys. Chem.*, **72**, 3281 (1968); b) A. D'Aprano and R. M. Fuoss, *ibid.*, **72**, 4723 (1968); c) Y. C. Chiu and R. M. Fuoss, *ibid.*, **72**, 4123 (1968); d) R. Fernandez-Prini, *Trans. Faraday Soc.*, **64**, 2146 (1968); e) E. Baumgartner, M. Busch, and R. Fernandez-Prini, *J. Phys. Chem.*, **74**, 1821 (1970); f) A. D'Aprano, *ibid.*, **75**, 3290 (1971); g) E. M. Hanna, A. D. Pethybrige, and E. J. Prue, *Electrochim. Acta*, **16**, 677 (1971); *J. Phys. Chem.*, **75**, 291 (1971); *J. Solution Chem.*, **3**, 563 (1974); h) M. L. Jansen and H. L. Yeager, *J. Phys. Chem.*, **77**, 3089 (1973); *ibid.*, **78**, 1380 (1974); i) P. Beronius, *Acta Chem. Scand.*, **A28**, 77 (1974); *ibid.*, **A29** (1975); j) C. F. Mattina and R. M. Fuoss, *J. Phys. Chem.*, **79**, 1604 (1975); k) Ref. 1b, p. 525; l) Ref. 26b, 26c, 26d).

21) Ref. 9, p. 230.

22) Ref. 15.

23) H. Yokoyama and H. Yamatera, *Bull. Chem. Soc. Jpn.*, **48**, 2708 (1975).

24) Presented in part at the 21th Conference on Coordination Chemical Society of Japan, Nagoya, October. 1971.

25) a) J. C. Justice. *J. Chim. Phys. Physicochim. Biol.*, **65**, 353 (1968); J. C. Justice, R. Bury, and C. Treiner, *ibid.*, **65**, 1780, (1968); J. C. Justice. *ibid.*, **66**, 1193 (1969); C. Treiner and J. C. Justice, *ibid.*, **68**, 56 (1971); b) J. C. Justice, *Electrochem. Acta*, **16**, 701 (1971).

26) a) M. A. Matesich, J. A. Nadas, and D. F. Evans, *J. Phys. Chem.*, **74**, 4568 (1970); D. F. Evans, J. A. Nadas, and M. A. Matesich, *ibid.*, **75**, 1708 (1971); M. A. Matesich, J. Knoefel, H. Feldman, and D. F. Evans, *ibid.*, **77**, 363 (1973); b) C. DeRossi, B. Sesta, M. Battistini, and S. Petrucci, *J. Am. Chem. Soc.*, **94**, 2961 (1972); c) J. Barthel, J. C. Justice, and R. Wachter, *Z. Phys. Chem.*, **84**, 100 (1973); d) E. Reard and J. C. Justice, *J. Solution Chem.*, **3**, 633 (1974).

27) Ref. 9, pp. 463, 465.

28) M. Spiro, Ref. 1b, p. 673.

29) R. G. Bates and R. A. Robinson, "Chemical Physics of Ionic Solutions," ed. by B. E. Conway and R. G. Barradas, Wiley, N. Y. (1966), p. 211.