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Application of the Continuous Variation Method to the Conductometric Determination of Formation Constants—Hexamminecobalt(III) Chloride - Sodium Sulfate and Tris(ethylenediamine)cobalt(III) Chloride - Sodium Sulfate Systems

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The conductance behavior of mixtures was investigated with the following systems in aqueous solutions of various ionic strengths at 25°C; NaCl - KCl, NaCl - $NaClO_4$, NaCl - Na_2SO_4, $[CO(NH_3)_6]\ Cl_3$ - Na_2SO_4 and $[CO(en)_3]Cl_3$ - Na_2SO_4. Appreciable deviations of the measured conductivities from additivity were observed in the last two systems involving the cobalt(III) complexes. The deviation was attributed to the ion-pair formation of the complex cations with sulfate ions; the ion-pair formation constants at various ionic strengths were determined by means of computer analysis of the deviation without relying on the Onsager conductance equation. The thermodynamic ion-pair formation constants at 25°C were as follows: $\log K = 3.5_3$ for $[CO(NH_3)_6]^{3+}\cdot SO_4^{2-}$ and $\log K = 3.6_0$ for $[CO(en)_3]^{3+}\cdot SO_4^{2-}$. The analysis of conductance behavior of mixtures was proved to be a useful method of studying ion-pair formation particularly at relatively high ionic strengths.

The method of continuous variations is a useful technique for determining both stoichiometric compositions and equilibrium constants of complexes in solutions. The application of this method to the conductometric determination of formation constants appears to have the advantage that the measured quantities can be analysed, in principle, without relying on the quantitative validity of the Onsager conductance equation; this advantage is particularly important when the method is applied to the systems of relatively high ionic strengths.[1] This approach, however, when applied rather loosely, often gives results which are inconsistent with those obtained by other methods, and the utility of the method has been subjected to critical discussions.[2,3] The complication involved in the application of continuous variation method to the study of the conductance behavior of mixtures lies in the fact that the deviation of the observed conductance from additivity may be caused not only by specific ionic interactions but also by the effect of the added ions on the mobility of the ions.[3,4]

This paper deals with the application of continuous variation method to the conductometric determination of ion-pair formation constants of hexamminecobalt(III) and tris(ethylenediamine)-coblt(III) ions with sulfate ions at some varying ionic strengths. The additivity rule was also examined with some mixtures of simple electrolytes, in which no specific individual effects is expected.

Experimental

Procedure and Apparatus. The electric conductivities of mixtures were measured by mixing the solutions of the same ionic strength at various volume fractions. A precision a.c. bridge (HBS-5M, Ando Electric Co., Ltd.), operated at 1000 Hz, was used for conductivity measurements; the balance of the bridge was detected by a tuned null-detector of high sensitivity. The resistance readings of the bridge were calibrated by the substitution method with a precision decade resistance box (Dekastat RS-624, Electro Scientific Industries; accuracy, ±0.005%). The resolution of the apparatus was about one part per million, and the reproducibility of conductivity measurements was better than 0.1%. Two dipping-type cells similar to that described in previous papers[5,6] were used; the cell constants were 0.1945 and 0.7704 cm^{-1}, respectively, as determined with standard potassium chloride solutions. All measurements were carried out in a water-thermostat of 25.000±0.005°C.

Hexamminecobalt(III) chloride and tris(ethylenediamine)cobalt(III) chloride were prepared according to the procedure described in literature;[7] these samples were purified by three recrystallizations from their aqueous solutions containing a few drops of acetic acid. The conventional chemical analysis and conductivity measurement showed that the samples obtained were of very high purity. Sodium sulfate of analytical reagent grade was dried at 120°C until it reached constant weight. All other chemicals were of analytical reagent grade. Each solution was carefully prepared by using the conductivity water of low specific conductance ($<2\times10^{-7}$ ohm^{-1} cm^{-1}) in an atmosphere of purified nitrogen gas.

Results

Mixtures of Simple Electrolytes. The conductance behavior of sodium chloride - potassium chloride and sodium chloride - sodium perchlorate mixtures showed no appreciable deviation from additivity at ionic strength, I, of 0.01 as shown in Fig. 1 (curves (1) and (2)). Sodium chloride - sodium sulfate mixtures of $I=0.01$ and 0.1, however, gave slightly smaller conductivities than those expected from additivity; the deviation reached the maximum value of about 0.5% at the volume fraction, x, of 0.5—0.6 (Fig. 1, curve (3)).

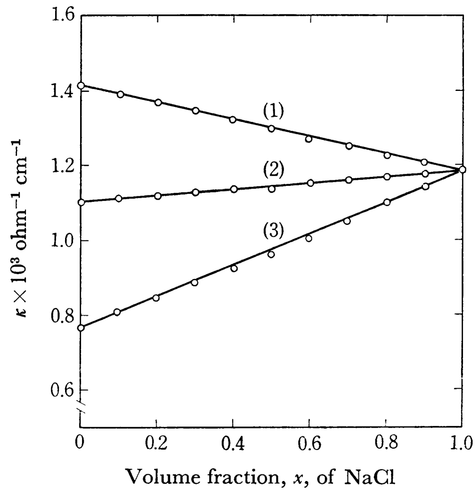

Fig. 1. Conductance behavior of mixtures (ionic strength, 0.01) of simple electrolytes measured at 1000 Hz and at 25°C.

(1) NaCl - KCl, (2) NaCl - $NaClO_4$, (3) NaCl-Na_2SO_4.

○, experimental; —, calculated by assuming additivity.

$[Co(NH_3)_6]Cl_3$ - Na_2SO_4 and $[Co(en)_3]Cl_3$ - Na_2SO_4 Mixtures. In hexamminecobalt(III) chloride-sodium sulfate and tris(ethylenediamine) cobalt(III) chloride - sodium sulfate mixtures a large departure of the measured conductance from additivity was observed at each ionic strength: the deviation, $\Delta\kappa$, between the measured and calculated conductivities is shown in Figs. 2 (a—e) as a function of the volume fraction, x, of the complex. The conductivities of the mixtures were always smaller

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[1] C. W. Davies, "The Structure of Electrolytic Solutions," ed. by W. J. Hamer, John Wiley and Sons, Inc., New York (1959), p. 24.

[2] G. H. Nancollas, "Interactions in Electrolyte Solutions," Elsevier Publishing Co., Amsterdam (1966), pp. 30—31, and literature cited there.

[3] C. W. Davies, "Ion Association," Butterworths, London (1962), pp. 27—31.

[4] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York (1967), pp. 200—203.

[5] S. Katayama, *Rept. I. P. C. R.*, **42**, 243 (1966).

[6] R. Tamamushi, T. Isono and S. Katayama, This Bulletin, **40**, 334 (1967).

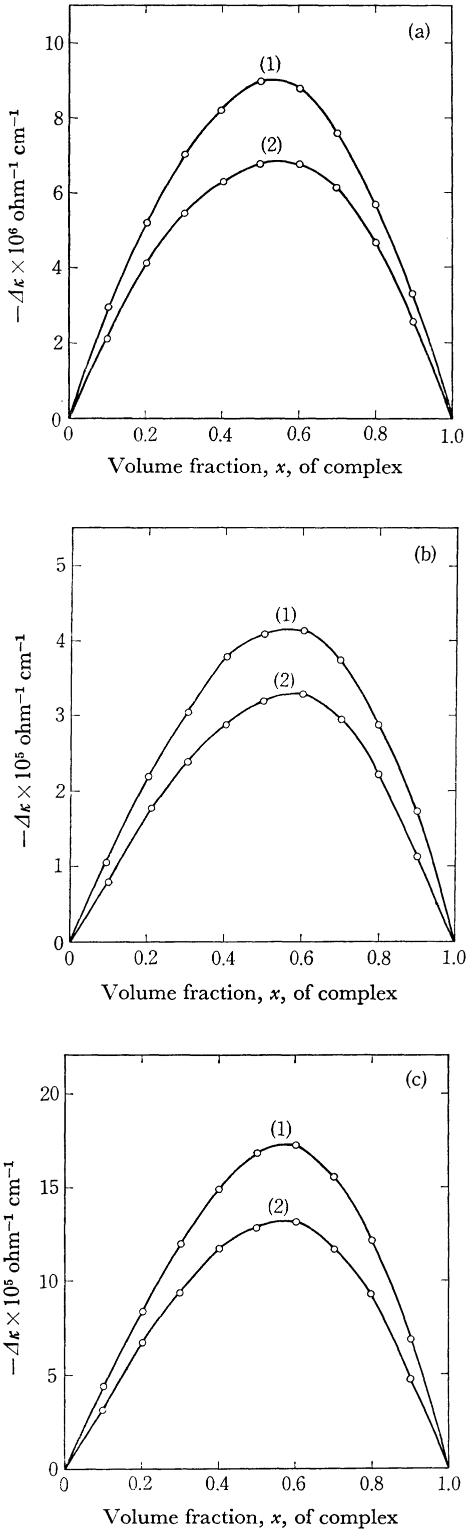
[7] W. C. Fernelius (ed.), "Inorganic Syntheses," II, McGraw-Hill, New York (1946), pp. 217, 221.

than those expected from additivity and showed an extreme at $x=0.5$—0.7 in each system.

Discussion

The conductivity of electrolyte mixtures is never strictly additive because of the effect of added ions on the time of relaxation;[4] in our present systems, however, this effect is shown to be negligibly small in comparison with the specific individual effects as seen from Figs. 1 and 2. Therefore, the deviation of the observed conductivities of the cobalt(III) complex - sodium sulfate mixtures from additivity may be attributed entirely to the ion-pair formation of the complex cation with sulfate ions.

Let us consider the conductance of the solution prepared by mixing xV cc of a C_1 molar solution of $\mathrm{M}_{\nu_M}^{z_M}\mathrm{A}_{\nu_A}^{z_A}$ and $(1-x)V$ cc of a C_2 molar solution of



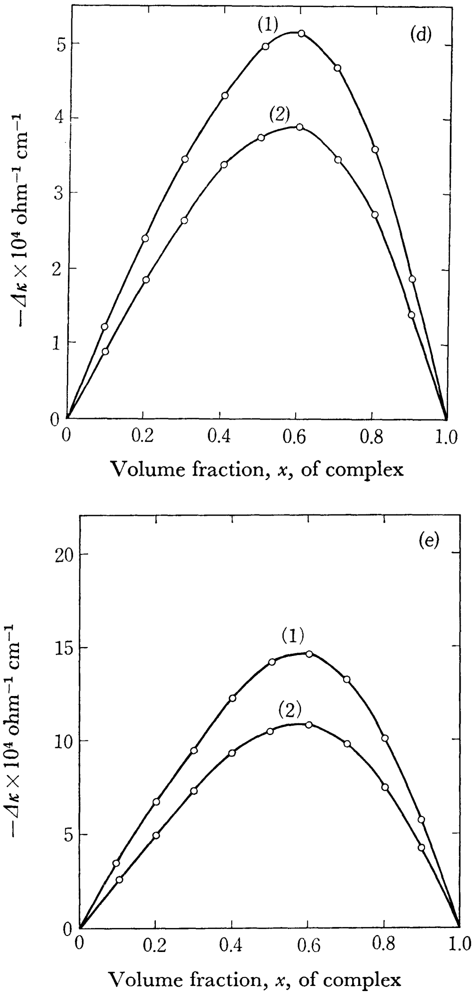


Fig. 2. Deviation of the observed conductivity from additivity, $\Delta\kappa$, as a function of the volume fraction, x, of the complex (1000 Hz, 25°C).

(1) $[\mathrm{Co(NH_3)_6}]\mathrm{Cl_3}$ - $\mathrm{Na_2SO_4}$, (2) $[\mathrm{Co(en)_3}]\mathrm{Cl_3}$ - $\mathrm{Na_2SO_4}$.

Ionic strength: (a) 0.001, (b) 0.003, (c) 0.01, (d) 0.03, (e) 0.1.

$\mathrm{N}^{z_\mathrm{N}}_{\nu_\mathrm{N}}\mathrm{B}^{z_\mathrm{B}}_{\nu_\mathrm{B}}$ to give the solution of total volume V; the concentrations, C_1 and C_2, are adjusted so that the apparent ionic strength of the mixtures is independent of x. In the following presentation of ions and ion-pairs, the ionic charge for each species will be omitted for the sake of simplicity. If the following ion-pair formations are assumed in the mixture,

$$\mathrm{M} + \mathrm{B} \rightleftharpoons \mathrm{MB},$$

$$\mathrm{M} + \mathrm{A} \rightleftharpoons \mathrm{MA},$$

$$\mathrm{N} + \mathrm{B} \rightleftharpoons \mathrm{NB},$$

the specific conductivity, κ, of the mixture is given by

$$1000\kappa = C_1 x \Lambda_m (\mathrm{M}^{z_\mathrm{M}}_{\nu_\mathrm{M}}\mathrm{A}^{z_\mathrm{A}}_{\nu_\mathrm{A}}) + C_2(1-x)\Lambda_m(\mathrm{N}^{z_\mathrm{N}}_{\nu_\mathrm{N}}\mathrm{B}^{z_\mathrm{B}}_{\nu_\mathrm{B}}) + \alpha[\mathrm{MB}] + \delta \qquad (1)$$

$$\alpha = z_\mathrm{MB}\lambda_\mathrm{MB} - z_\mathrm{M}\lambda_\mathrm{M} - z_\mathrm{B}\lambda_\mathrm{B}$$

where z_i and λ_i are the ionic valence and the ionic equivalent conductance of species i, respectively, Λ_m is the molar conductance, and δ represents the contribution of ion-pairs MA and NB to the specific conductivity.

The deviation of the observed conductivity from additivity is then given by

$$\begin{aligned}\Delta\kappa' \equiv 1000\Delta\kappa &= 1000\kappa - C_1 x \Lambda_m(\mathrm{M}^{z_\mathrm{M}}_{\nu_\mathrm{M}}\mathrm{A}^{z_\mathrm{A}}_{\nu_\mathrm{A}}) \\ &\quad - C_2(1-x)\Lambda_m(\mathrm{N}^{z_\mathrm{N}}_{\nu_\mathrm{N}}\mathrm{B}^{z_\mathrm{B}}_{\nu_\mathrm{B}}) \qquad (2) \\ &= \alpha[\mathrm{MB}] + \delta\end{aligned}$$

Calculating [MB] by Eq. (2) and estimating the concentrations of MA and NB from their formation constants, we can determine the concentration formation constant, K_c, of MB according to the following relation.

$$K_c = \frac{[\mathrm{MB}]}{[\mathrm{M}][\mathrm{B}]} = \frac{\dfrac{\Delta\kappa'-\delta}{\alpha}}{\left(\nu_\mathrm{M}C_1x - [\mathrm{MA}] - \dfrac{\Delta\kappa'-\delta}{\alpha}\right)\left(\nu_\mathrm{B}C_2(1-x) - [\mathrm{NB}] - \dfrac{\Delta\kappa'-\delta}{\alpha}\right)} \qquad (3)$$

In the cobalt(III) complex ($z_\mathrm{M}=3$) - sodium sulfate mixtures, the contribution of [MA], [NB] and δ in Eq. (3) can be neglected without introducing serious errors in the determination of K_c, because the formation constants of MA and NB should be very much smaller than that of MB. Equation (3) is then simplified as

$$K_c = \frac{\dfrac{\Delta\kappa'}{\alpha}}{\left(\nu_\mathrm{M}C_1x - \dfrac{\Delta\kappa'}{\alpha}\right)\left(\nu_\mathrm{B}C_2(1-x) - \dfrac{\Delta\kappa'}{\alpha}\right)} \qquad (4)$$

Small amounts of higher order ion-pairs other than the one-to-one type may be formed between the complex cations and sulfate ions; a preliminary calculation, however, showed that the contribution of such higher order ion-pairs, if any, could be ignored in the present systems.

The determination of K_c according to Eq. (4) requires the knowledge of parameter α; the estimation of α at a given ionic strength involves some arbitrariness. In the present study, we estimated the values of α according to the following procedure: $\lambda([\mathrm{Co(NH_3)_6}]^{3+})$ and $\lambda(\mathrm{SO_4}^{2-})$ were obtained from the equivalent conductivities[8,9] $\Lambda([\mathrm{Co(NH_3)_6}]\mathrm{Cl_3})$, $\Lambda(\mathrm{Na_2SO_4})$ and the corresponding transport numbers[8,10] $t([\mathrm{Co(NH_3)_6}]^{3+})$ and $t(\mathrm{SO_4}^{2-})$; $\lambda(\mathrm{Cl^-})$ from $\Lambda([\mathrm{Co(NH_3)_6Cl_3}])$ and $t([\mathrm{Co(NH_3)_6}]^{3+})$; $\lambda([\mathrm{Co(en)_3}]^{3+})$ from $\Lambda([\mathrm{Co(en)_3}]\mathrm{Cl_3})$ and $\lambda(\mathrm{Cl^-})$; and the λ-values of ion-pair MB were assumed to be equal to $\lambda(\mathrm{M})/3$. A slight change in the actual ionic strength is expected with varying ratio of mixing at a given nominal ionic strength; its effects, however, was ignored in the present calculation. The concentration formation constants thus determined at each nominal ionic strength are given in Tables 1 and 2.

The arbitrariness arising from the difficulty in the estimation of parameter α can be removed, when the least square method of curve fitting with the aid of a computer is applied to the analysis of the

TABLE 1. LOGARITHM OF CONCENTRATION FORMATION CONSTANTS, $\log K_c$, AT 25°C OF ION-PAIR $[\mathrm{Co(NH_3)_6}]^{3+}\cdot\mathrm{SO_4}^{2-}$ AT VARYING VOLUME FRACTIONS, x, OF THE COMPLEX IN $[\mathrm{Co(NH_3)_6}]\mathrm{Cl_3}$–$\mathrm{Na_2SO_4}$ MIXTURES OF VARIOUS IONIC STRENGTHS, I

x	I				
	0.001	0.003	0.01	0.03	0.1
0.1	3.40	3.10	2.97	2.54	1.90
0.2	3.39	3.25	2.95	2.55	1.94
0.3	3.38	3.23	2.97	2.58	1.96
0.4	3.38	3.28	3.00	2.57	2.03
0.5	3.40	3.25	3.01	2.62	2.08
0.6	3.40	3.28	3.01	2.64	2.10
0.7	3.36	3.26	3.00	2.61	2.06
0.8	3.35	3.25	3.00	2.61	2.03
0.9	3.36	3.30	2.98	2.51	2.05
Average	3.38	3.24	2.99	2.58	2.02
Computer calculation	3.18	3.26	3.03	2.75	2.23

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8) G. S. Hartley and G. W. Donaldson, *Trans. Faraday Soc.*, **33**, 457 (1937).

9) Unpublished measurements of T. Shedlovsky and L. G. Longsworth, quoted by D. A. MacInnes in "Principles of Electrochemistry," Reinhold Publishing Corp., New York (1939), p. 339.

10) L. G. Longsworth, *J. Amer. Chem. Soc.*, **54**, 2741 (1932).

TABLE 2. LOGARITHM OF CONCENTRATION FORMATION CONSTANTS, $\log K_c$, AT 25°C OF ION-PAIR $[\mathrm{Co(en)_3}]^{3+}\cdot\mathrm{SO_4}^{2-}$ AT VARYING VOLUME FRACTIONS, x, OF THE COMPLEX IN $[\mathrm{Co(en)_3}]\mathrm{Cl_3}$-$\mathrm{Na_2SO_4}$ MIXTURES OF VARIOUS IONIC STRENGTHS, I

x	I				
	0.001	0.003	0.01	0.03	0.1
0.1	3.30	3.14	2.71	2.22	1.84
0.2	3.35	3.20	2.89	2.45	1.84
0.3	3.36	3.15	2.86	2.47	1.92
0.4	3.33	3.19	2.92	2.52	1.96
0.5	3.32	3.18	2.90	2.52	1.99
0.6	3.34	3.22	2.92	2.56	2.00
0.7	3.36	3.22	2.89	2.51	2.00
0.8	3.35	3.19	2.91	2.51	1.96
0.9	3.32	3.23	2.81	2.40	1.96
Average	3.34	3.19	2.87	2.47	1.94
Computer calculation	3.42	3.43	2.87	2.56	2.09

following equation representing the deviation, $\Delta\kappa'$, in terms of unknown quantities K_c and α:

$$\Delta\kappa' = \frac{a+b+k_c^{-1}-\sqrt{(a+b+k_c^{-1})^2-4ab}}{2}\cdot\alpha \qquad (5)$$

where

$$a = C_1x, \quad b = C_2(1-x)$$

By this method of computer calculation, a set of K_c and α for the best fit between the observed and calculated $\Delta\kappa'$ values can be definitely determined at each ionic strength; the K_c values obtained are given in the bottom lines of Tables 1 and 2.

These two methods of calculation resulted in the K_c-values which are in relatively good agreement. The computer method, however, is expected to give more reliable results particularly at higher ionic strengths, because the analysis can be made without assuming a quantitative expression for the

TABLE 3. LOGARITHM OF THERMODYNAMIC FORMATION CONSTANTS, $\log K$, AT 25°C OF ION-PAIRS $[\mathrm{Co(NH_3)_6}]^{3+}\cdot\mathrm{SO_4}^{2-}$ AND $[\mathrm{Co(en)_3}]^{3+}\cdot\mathrm{SO_4}^{2-}$ DETERMINED BY VARIOUS METHODS

Method	$[\mathrm{Co(NH_3)_6}^{3+}\cdot\mathrm{SO_4}^{2-}$	$[\mathrm{Co(en)_3}^{3+}\cdot\mathrm{SO_4}^{2-}$
Conductivity (present method)	3.5_3 a) 3.5_8 b)	3.6_0 a) 3.5_4 b)
Conductivity	3.56[11]	3.45[11]
Spectrophotometry	2.89[12] 3.26[13]	3.10[13] 2.93[14]
Solubility	3.52[15] 3.60[16]	
Polarography	3.46[17] 3.21[18]	2.72[19]
Chronopotentiometry	3.30[20]	3.22[20]

a) determined by means of computer calculation
b) determined dy estimating parameter α

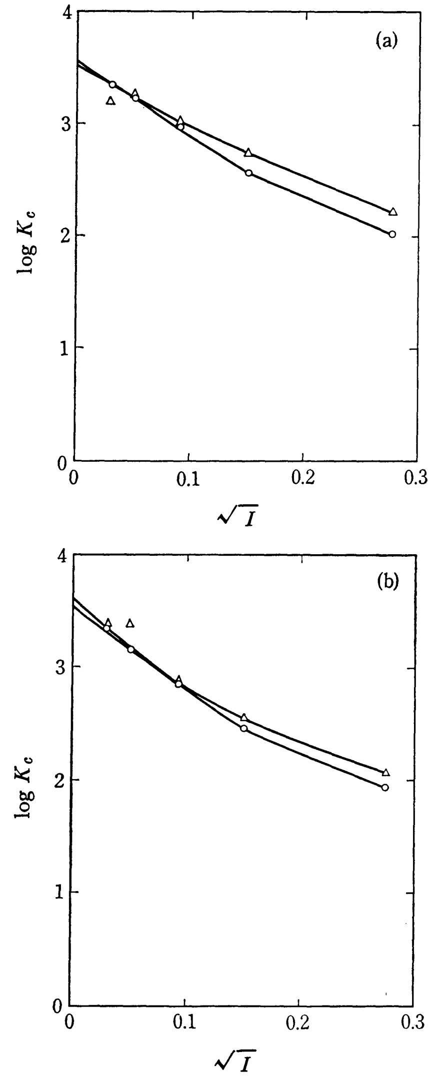

Fig. 3. Concentration formation constants of (a) ion-pair $[\mathrm{Co(NH_3)_6}]^{3+}\cdot\mathrm{SO_4}^{2-}$ and (b) ion-pair $[\mathrm{Co(en)_3}]^{3+}\cdot\mathrm{SO_4}^{2-}$ as a function of ionic strength (25°C).

—○— determined by estimating α
—△— determined by computer calculation

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11) I. L. Jenkins and C. B. Monk, *J. Chem. Soc.*, **1951**, 68.

12) C. W. Davies and C. B. Monk, *J. Amer. Chem. Soc.*, **80**, 5032 (1958).

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14) K. Ogino and U. Saito, *ibid.*, **40**, 826 (1967).

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17) A. A. Vlček, The Proceedings of the 6th ICCC, 590 (1961).

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20) N. Tanaka and A. Yamada, *Z. Anal. Chem.*, **224**, 117 (1967).

conductance behavior of the component ions.

The thermodynamic formation constants were then determined by the extrapolation of the log K_c *vs.* $\sqrt{I}$ plots as shown in Figs. 3(a, b). The results are presented in Table 3, in which the K values determined by other methods are summarized for comparison. The good agreement of our results with those of Jenkins and Monk[11] suggests that the conductance measurement of mixtures is a useful method for determining formation constants if the method is properly applied. A great advantage of the method is expected when it is applied to the systems of relatively high concentrations where the theoretical equations of conductance behavior lose their validity.

We wish to thank Mrs. K. Takahashi for her kind collaboration in programming the computer calculation.