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Conductometric Determination of Ion-pair Formation Constants of Tris(ethylenediamine)cobalt(III) Ion with Maleate and Fumarate Ions in Aqueous Solutions

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The conductance behavior of mixtures was investigated for the systems tris(ethylenediamine)cobalt(III)-chloride-sodium maleate and tris(ethylenediamine)cobalt(III)chloride-sodium fumarate in aqueous solutions of various ionic strengths at 25°C. Appreciable deviation of the measured conductivity from additivity was attributed to the ion-pair formation of tris(ethylenediamine)cobalt(III) ion with maleate Ma^{2-} and fumarate Fu^{2-} ions. The concentration formation constants K_c at various ionic strengths were determined by means of computer analysis of the deviation. The thermodynamic ion-pair formation constants K at 25°C were as follows: $\log K=3.60$ for $[Co(en)_3]^{3+}\cdot Ma^{2-}$ and $\log K=2.95$ for $[Co(en)_3]^{3+}\cdot Fu^{2-}$.

In a previous paper,[1] the continuous variation method was applied to the determination of the ion-pair formation constants of $[Co(NH_3)_6]^{3+}\cdot SO_4{}^{2-}$ and $[Co(en)_3]^{3+}\cdot SO_4{}^{2-}$ from the conductance measurement of $[Co(NH_3)_6]Cl_3$—Na_2SO_4 and $[Co(en)_3]Cl_3$—Na_2SO_4 mixtures. The good agreement of the results obtained with those of Jenkins and Monk[2] suggests that the conductance measurement of mixtures is a useful method for determining formation constants, particularly when applied to the systems of relatively high ionic strengths where the theoretical equations of conductance behavior lose their validity. The method is also applicable to the study of ion-pair formation in systems where a pure sample is difficult to obtain.

This paper deals with the application of the continuous variation method to the conductometric determination of ion-pair formation constants of tris(ethylenediamine)cobalt(III) ion with maleate and fumarate ions at 25°C in aqueous solutions of varying ionic strengths. The results will provide some information on the *cis-trans* isomeric effect in the ion-pair formation.

Experimental

Materials. Tris(ethylenediamine)cobalt(III)chloride was prepared according to the procedure in literature[3]; the sample was purified by two recrystallizations from its aqueous solution containing a few drops of acetic acid. Sodium maleate, Na_2Ma, of analytical reagent grade was washed by ethanol and ethyl ether, then dried at 80°C until it became constant in weight. Sodium fumarate, Na_2Fu, of analytical reagent grade was purified by recrystallization from its aqueous solution. The purity of the samples was examined by conventional chemical analysis of the components and by conductivity measurements in aqueous solutions. Chemical analysis and conductivity measurements gave the results shown in Tables 1 and 2, respectively. The limiting ionic equivalent conductivity λ^0 of $[Co(en)_3]^{3+}$ was in agreement with that reported by Jenkins and Monk,[2] and the λ^0-values

TABLE 1. RESULTS OF CHEMICAL ANALYSIS
(calculated values are shown in parenthesis)

Material	Component (%)					
	C	H	N	Co	Na	Cl
$[Co(en)_3]Cl_3$	20.11 (20.85)	7.02 (7.00)	23.90 (24.32)	16.82 (17.05)	—	30.16 (30.78)
$Na_2Ma\cdot H_2O$	26.96 (26.98)	2.69 (2.26)	—	—	26.13 (25.82)	—
Na_2Fu	30.07 (30.02)	1.62 (1.26)	—	—	29.06 (28.73)	—

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[1] S. Katayama and R. Tamamushi, This Bulletin, **43**, 2354 (1970).

[2] I. L. Jenkins and C. B. Monk, *J. Chem. Soc.*, **1951**, 68.

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

Table 2. Equivalent conductivities, Λ, of $[Co(en)_3]Cl_3$, Na_2Ma and Na_2Fu in aqueous solutions of various concentrations at 25°C

10^4C (equiv./l)	Λ		
	$[Co(en)_3]Cl_3$	Na_2Ma	Na_2Fu
0.00	151.0_5 (74.7)	111.0 (60.9)	111.0 (60.9)
5.00	143.3	—	—
6.67	—	107.2	106.8
15.00	137.0	—	—
20.00	—	104.8	104.0
50.00	125.7	—	—
66.67	—	99.8	99.2
150.00	111.8	—	—
200.00	—	92.5	92.4
500.00	94.8	—	—
666.67	—	83.0	83.7

(Limiting ionic equivalent conductivities, λ°, of $[Co(en)_3]^{3+}$, Ma^{2-} and Fu^{2-} are shown in parenthesis)

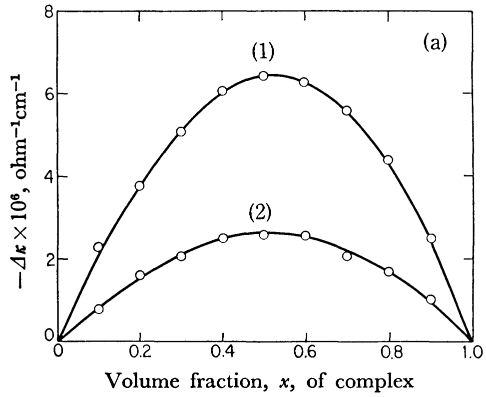
of Ma^{2-} and Fu^{2-} were in fairly good agreement with the results of Topp and Davies.[4]

Preparation of Solutions. Each solution of different ionic strengths was carefully prepared by using the conductivity water of low specific conductivity ($<2\times10^{-7}$ ohm^{-1} cm^{-1}) in an atmosphere of purified nitrogen gas, and the pH-values of these solutions were adjusted to 9 with sodium hydroxide. In aqueous solutions of pH 9 the concentrations of HMa^- and HFu^- ions can be ignored.

Conductivity Measurement. The electric conductivities of mixtures were measured by mixing the solutions of same ionic strength at various volume fractions. The apparatus and the reproducibility of measurements were the same as those described previously.[1] All measurements were carried out in a water-thermostat of 25.000±0.005°C which was electrically grounded.

Results and Discussion

In tris(ethylenediamine)cobalt(III)chloride—sodium maleate and tris(ethylenediamine)cobalt(III)chloride–sodium fumarate mixtures (systems I and II, respectively), a large deviation of the measured conductivity from additivity was observed at each ionic strength. The deviation, $\Delta\kappa$, of the mixture, consisting of a C_1 molar solution of tris(ethylenediamine)cobalt(III)chloride (abbreviated as MCl_3) and a C_2 molar solution of



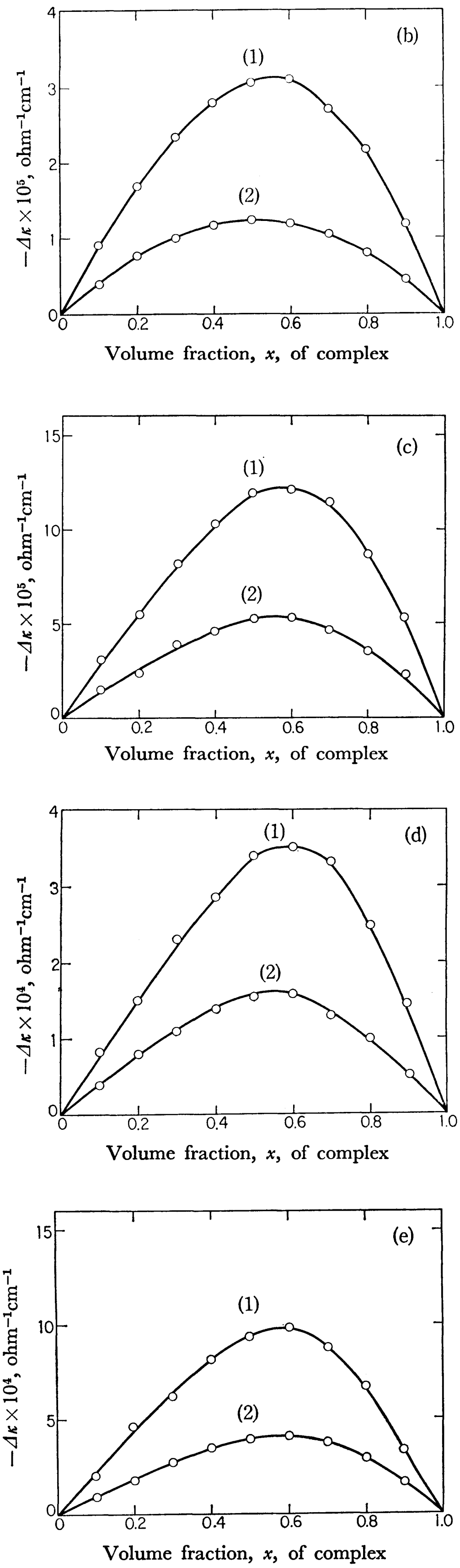


Fig. 1. Deviation of the observed conductivity from additivity, $\Delta\kappa$, as a function of the volume fraction, x, of complex (1000 Hz, 25°C).
(1) $[Co(en)_3]Cl_3$-Na_2Ma, (2) $[Co(en)_3]Cl_3$-Na_2Fu.
Ionic strength: (a) 0.001, (b) 0.003, (c) 0.01, (d) 0.03, (e) 0.1.

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[4] N. E. Topp and C. W. Davies, *J. Chem. Soc.*, **1940**, 87.

Na_2B ($B^{2-}=Ma^{2-}$ or Fu^{2-}) at the volume fractions x and $(1-x)$, respectively, is given by the equation

$$10^3\Delta\kappa = 10^3\kappa - C_1 x \Lambda_m(MCl_3) - C_2(1-x)\Lambda_m(Na_2B) \quad (1)$$

where κ is the specific conductivity of the mixture, and Λ_m the molar conductivity of the species specified in parenthesis at the ionic strength of the mixture. Figures 1(a—e) show the deviation as a function of volume fraction x of the complex. The $\Delta\kappa$-values of system I were always larger than those of system II, and the deviation reached a maximum at x=0.5—0.6 in each case.

The following ion-pair formations are expected to occur in systems I and II.

$$M^{3+} + B^{2-} \rightleftarrows M^{3+}\cdot B^{2-}$$
$$M^{3+} + Cl^{-} \rightleftarrows M^{3+}\cdot Cl^{-}$$
$$Na^{+} + B^{2-} \rightleftarrows Na^{+}\cdot B^{2-}$$

where M^{3+} represents tris(ethylenediamine)cobalt(III) cation. In the present discussion, however, the contribution of ion-pair formation of $M^{3+}\cdot Cl^-$ and $Na^+\cdot B^{2-}$ is neglected, and the deviation of the observed conductivities from additivity is assumed to be entirely due to the formation of $M^{3+}\cdot B^{2-}$. This assumption seems to be reasonable, because the formation constants of $M^{3+}\cdot Cl^-$ and $Na^+\cdot B^{2-}$ should be much smaller than those of $M^{3+}\cdot B^{2-}$.

The deviation $\Delta\kappa$ is then related to the molar concentration of ion-pair $M^{3+}\cdot B^{2-}$ by the equation

$$[M^{3+}\cdot B^{2-}] = \frac{10^3\Delta\kappa}{\alpha} \quad (2)$$

$$\begin{aligned} \alpha &= |z(M^{3+}\cdot B^{2-})|\lambda(M^{3+}\cdot B^{2-}) - |z(M^{3+})|\lambda(M^{3+}) \\ &\quad - |z(B^{2-})|\lambda(B^{2-}) \\ &= \lambda(M^{3+}\cdot B^{2-}) - 3\lambda(M^{3+}) - 2\lambda(B^{2-}) \end{aligned} \quad (3)$$

where z is the charge number of ionic species, and λ the ionic equivalent conductivity at the ionic strength of the mixture.

The concentration formation constants K_c of $M^{3+}\cdot B^{2-}$ were determined by analysing the $\Delta\kappa$-values according to the same methods given previously.[1] In method (i) the K_c-values were obtained by estimating the values of parameter α at each ionic strength, while in method (ii) a set of K_c and α for the best fit between the observed and calculated $\Delta\kappa$-values was obtained by computer calculation. Table 3 summarizes the concentration formation constants thus determined for $[Co(en)_3]^{3+}\cdot Ma^{2-}$ and $[Co(en)_3]^{3+}\cdot Fu^{2-}$ at various ionic strengths, I.

The thermodynamic formation constants K were then determined by the extrapolation of the log K_c *vs.* $\sqrt{I}$ plots as shown in Fig. 2, and are given in the first line of Table 3. The values of log K obtained by the two methods of calculation are in relatively good agreement. The computer calculation, however, is expected to give more reliable K_c-values particularly at higher ionic strengths, because the analysis can be made without introducing arbitrariness into the estimation of parameter α.

Our study shows that the ion-pair formation constant of $[Co(en)_3]^{3+}\cdot Ma^{2-}$ is about 3 times larger than that of $[Co(en)_3]^{3+}\cdot Fu^{2-}$. A similar tendency of maleate and fumarate ions towards ion-pair formation has been reported by Topp and Davies[4] for $Ba^{2+}\cdot Ma^{2-}$, $Ba^{2+}\cdot Fu^{2-}$, $Ca^{2+}\cdot Ma^{2-}$, and $Ca^{2+}\cdot Fu^{2-}$ in aqueous solutions at 25°C, where the K-value of $Ba^{2+}\cdot Ma^{2-}$ was found to be about 5 times as large as that of $Ba^{2+}\cdot Fu^{2-}$, and the K-value of $Ca^{2+}\cdot Ma^{2-}$ to be about 3 times as large as that of $Ca^{2+}\cdot Fu^{2-}$.

TABLE 3. LOGARITHM OF CONCENTRATION FORMATION CONSTANTS, log K_c, OF ION-PAIRS $[Co(en)_3]^{3+}\cdot Ma^{2-}$ AND $[Co(en)_3]^{3+}\cdot Fu^{2-}$ AT 25°C AND AT VARIOUS IONIC STRENGTHS, I

(The values of log K, K being thermodynamic formation constant, are also included)

I	log K_c			
	$[Co(en)_3]^{3+}\cdot Ma^{2-}$		$[Co(en)_3]^{3+}\cdot Fu^{2-}$	
	Method (i)	Method (ii)	Method (i)	Method (ii)
0[a]	3.56	3.60	3.15	2.95
0.001	3.37	3.31	2.86	2.83
0.003	3.26	3.46	2.64	2.51
0.01	2.93	3.32	2.28	2.61
0.03	2.52	3.06	1.89	2.20
0.1	1.94	2.43	1.28	2.21

a) values in this line correspond to log K.

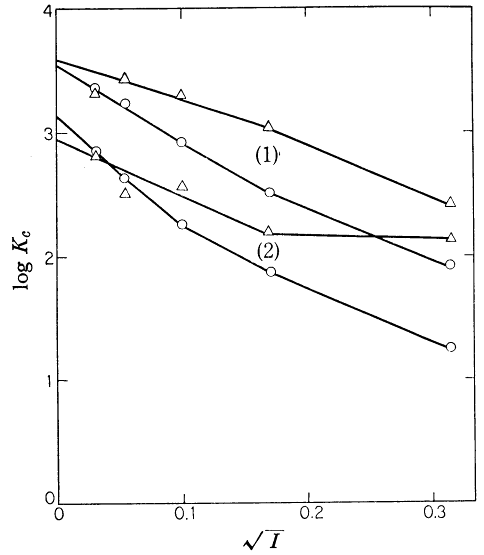

Fig. 2. Concentration formation constants of (1) ion-pair $[Co(en)_3]^{3+}\cdot Ma^{2-}$ and (2) ion-pair $[Co(en)_3]^{3+}\cdot Fu^{2-}$ as a function of ionic strength (25°C).

-○-: determined by estimating α (method (i))

-△-: determined by computer calculation (method (ii))

According to Bjerrum's theory of electrostatic interactions,[5] the ion-pair formation constant between ions i and j of opposite charge in aqueous solutions at 25°C is given by the equation

$$\begin{aligned} \log K &= 0.4386 + 3\log|z_i z_j| + \log Q(b) \\ \log b &= \log|z_i z_j| - 7.1468 - \log a \end{aligned} \quad (4)$$

where $Q(b)$ is a function of b, and a the distance of closest approach of the ions. Introducing the values of log K given in Table 3 into Eq. (4), we obtain a=4 Å for $[Co(en)_3]^{3+}\cdot Ma^{2-}$ and a=6 Å for $[Co(en)_3]^{3+}\cdot Fu^{2-}$

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[5] C. B. Monk, "Electrolytic Dissociation," Academic Press, London (1961), pp. 272—275.

respectively. On the other hand, the Stokes radii of $[Co(en)_3]^{3+}$, Ma^{2-}, and Fu^{2-}, calculated from their limiting ionic equivalent conductivities, are: $r_s([Co(en)_3]^{3+})=3.7$ Å and $r_s(Ma^{2-}, Fu^{2-})=3.0$ Å. It is interesting to note that the a-value for $[Co(en)_3]^{3+}\cdot Ma^{2-}$ is significantly smaller than the sum of the Stokes radii of the ions. The result suggests that the charge distribution in ions and/or some interactions other than electrostatic attraction should be considered in the ion-pair formation between $[Co(en)_3]^{3+}$ and Ma^{2-} or Fu^{2-}.

The present work provides further evidence for the *cis-trans* isomeric effect in the ion-pair formation. However, much more information will be needed for a discussion on the isomeric effect.

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