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Conductometric Studies on the Ion-pair Formations of $[Cr(NH_3)_6]^{3+}$, $[Co(NH_3)_6]^{3+}$, $[Cr(en)_3]^{3+}$, and $[Co(en)_3]^{3+}$ with Several Anions in Aqueous Solutions

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The thermodynamic ion-association constants (K) of $[Cr(NH_3)_6]^{3+}$, $[Co(NH_3)_6]^{3+}$, $[Cr(en)_3]^{3+}$, and $[Co(en)_3]^{3+}$ with several anions in aqueous solutions were determined using the conductometric method. The log K values obtained at 25.0 °C are 1.1_7 for $[Cr(NH_3)_6]^{3+}$–SCN^-, 1.3_4 for $[Cr(en)_3]^{3+}$–SCN^-, 1.3_0 for $[Co(NH_3)_6]^{3+}$–SCN^-, 1.3_4 for $[Co(en)_3]^{3+}$–SCN^-, 1.6_8 for $[Co(en)_3]^{3+}$–Br^-, 1.4_6 for $[Co(en)_3]^{3+}$–I^-, 1.3_7 for $[Co(en)_3]^{3+}$–ClO_4^-, 3.2_0 for $[Cr(NH_3)_6]^{3+}$–$C_2O_4^{2-}$, and 2.9_7 for $[Cr(en)_3]^{3+}$–$C_2O_4^{2-}$. The results indicate that the SCN^- ion has less of a tendency to associate with the complex cations than do other univalent anions, the K values of SCN^- being of the same order of magnitude as those of ClO_4^-, and that the K values of chromium(III) complex cations with several anions are slightly smaller than those of the corresponding cobalt(III) complex cations.

In order to clarify the factors that influence the extent to which ions associate in aqueous solutions, the ion-association constants of ion-pairs have been determined by various researchers[1–10] using various methods. In previous papers,[11,12] Takahashi *et al.* have reported that the ion-association constants determined using the conductometric and spectrophotometric methods were not very different from each other, and that the electrostatic interaction between ions is the dominant influence.

Also, it was found that the internal conjugate base (ICB) effect[13] should be considered in ion-pair formation.

In the present paper, conductometric studies of the ion-pairs, $[Co(en)_3]^{3+}$–X^- (X=SCN, Br, I, ClO_4), $[Cr(NH_3)_6]^{3+}$–SCN^-, $[Cr(en)_3]^{3+}$–SCN^-, $[Co(NH_3)_6]^{3+}$–SCN^-, $[Cr(NH_3)_6]^{3+}$–$C_2O_4^{2-}$, and $[Cr(en)_3]^{3+}$–$C_2O_4^{2-}$ are presented. Some factors are briefly discussed from the viewpoint given in previous papers.[11,12]

Experimental

The compounds used in this study were prepared according to procedures described in the literature. Each compound was carefully purified by triple recrystallization from redistilled water. The purity was examined using conventional chemical analysis of the components; the results are in very good agreement with the theoretical values. Solutions of different concentrations were carefully prepared using conductivity water having an electrolytic conductivity lower than 4×10^{-7} S cm^{-1}. The electrolytic conductivities were measured with the same apparatus and using the same procedures previously described.[11,12]

Results and Discussion

The relations between the molar conductivities, Λ, of the complexes and the ionic strength (I) are shown in Figs. 1—3; the broken lines indicate the theoretical Onsager lines for the fully ionized electrolyte. The molar conductivities of the oxalates shown in Fig. 3 have large deviations, indicating that there is strong ion-association between $[Cr(NH_3)_6]^{3+}$ or $[Cr(en)_3]^{3+}$ and $C_2O_4^{2-}$.

Table 1 presents the limiting molar conductivity, $\Lambda°$, of each complex determined by the Onsager extrapolation method,[14] and also the limiting molar conductivity, $\lambda°$, of each complex cation calculated from the $\Lambda°$ value. However, the $\Lambda°$ ($1/6\,M_2(C_2O_4)_3$) was assumed to be equal to the sum of the $\lambda°$ ($1/3\,M^{3+}$) value for the corresponding complex cation obtained in this study and in previous studies[11,12] and the value (74.2 S cm^2 mol^{-1}) for $\lambda°$ ($1/2\,C_2O_4^{2-}$), because the Onsager method was not considered to be appropriate for higher-valent electrolytes; the $\Lambda°$ ($1/6\,[Cr(NH_3)_6]_2(C_2O_4)_3\cdot5H_2O$) and $\Lambda°([Cr(en)_3]_2(C_2O_4)_3)$ values thus estimated are 172.6 and 147.8 S cm^2 mol^{-1}, respectively.* The so-called Stokes radii, r_s, of these complex cations

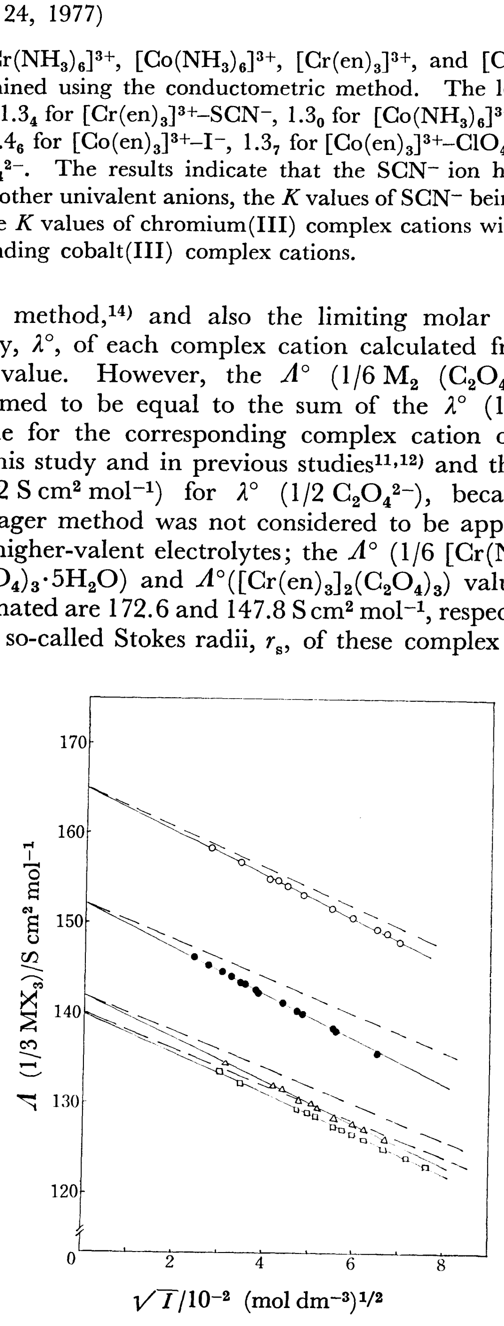

Fig. 1. The Onsager plots of hexaamminechromium(III) thiocyanate (-○-), tris(ethylenediamine)cobalt(III) iodide (-●-), tris(ethylenediamine)cobalt(III) perchlorate (-△-), and tris(ethylenediamine)-chromium(III) thiocyanate (-□-) in aqueous solutions at 25.0 °C.

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* When Onsager's method for determining the $\Lambda°$ values is applied to the conductivities of the oxalates, the approximate $\Lambda°(1/6[Cr(NH_3)_6]_2(C_2O_4)_3\cdot5H_2O)$ and $\Lambda°(1/6[Cr(en)_3]_2(C_2O_4)_3$ values are 173 and 148 S cm^2 mol^{-1}, respectively.

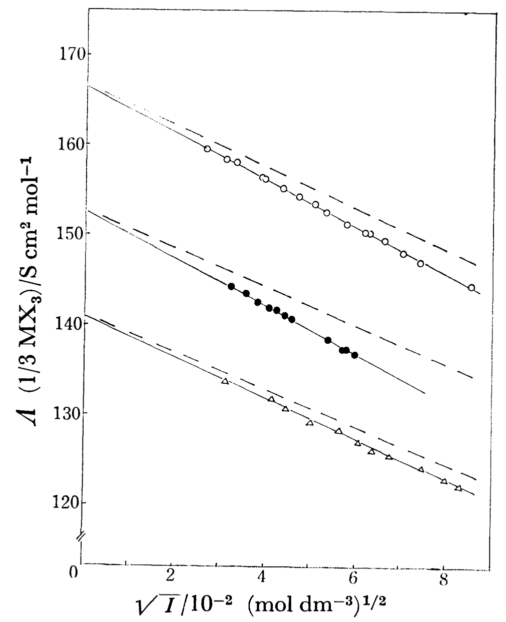

Fig. 2. The Onsager plots of hexaamminecobalt(III) thiocyanate (-○-), tris(ethylenediamine)cobalt(III) bromide (-●-), and tris(ethylenediamine)cobalt(III) thiocyanate (-△-) in aqueous solutions at 25.0 °C.

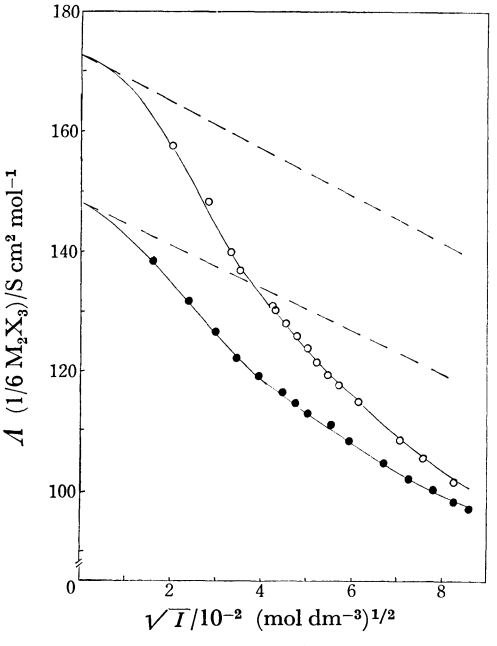

Fig. 3. The Onsager plots of hexaamminechromium(III) oxalate (-○-) and tris(ethylenediamine)chromium(III) oxalate (-●-) in aqueous solutions at 25.0 °C.

Table 1. The limiting molar conductivity of chromium(III) and cobalt(III) complexes (MX_3), and the complex cations (M^{3+}) in aqueous solutions at 25.0 °C

Complex	Molar conductivity (S cm^2 mol^{-1})	
	Λ° (1/3MX$_3$)	λ°(1/3M^{3+})
$[Cr(NH_3)_6](SCN)_3$	164.6	98.1
$[Cr(en)_3](SCN)_3$	139.7	73.2
$[Co(NH_3)_6](SCN)_3$	165.7	99.2
$[Co(en)_3](SCN)_3$	140.7	74.2
$[Co(en)_3]Br_3$	152.1	74.0
$[Co(en)_3]I_3\cdot H_2O$	151.4	74.6
$[Co(en)_3](ClO_4)_3$	141.4	74.0

Table 2. The limiting molar conductivity and the Stokes radius, r_S, of complex cations aqueous solutions at 25.0 °C

Complex cations	λ°(1/3M^{3+}) (S cm^2 mol^{-1})	r_S (Å)
$[Cr(NH_3)_6]^{3+}$	98.1	2.81
	98.5[11]	2.80[11]
	98.5[12]	2.80[12]
$[Cr(en)_3]^{3+}$	73.2	3.76
	73.4[11]	3.75[11]
	74.1[12]	3.72[12]
$[Co(NH_3)_6]^{3+}$	99.2	2.78
	99.2[1]	2.78[1]
	99.0—99.7[4,7]	2.78—2.76[4,7]
$[Co(en)_3]^{3+}$	74.2	3.71
	74.7[1]	3.69[1]

determined from the conductivity data of this study are summarized in Table 2, in which the results reported previously are also presented. The degrees of dissociation of the possible ion-pairs were determined according to the successive approximation method described by Jenkins and Monk[1] and, then, the thermodynamic ion-association constants, K, were calculated from both the degree of dissociation obtained and the activity coefficients of the ions as estimated from the Debye-Hückel limiting equation. In the present calculation, the limiting conductivities of the ion-pairs was estimated from the relations,

$$\frac{\lambda^\circ(1/2M^{3+}X^-)}{\lambda^\circ(1/3M^{3+})}=\frac{2}{3}$$

and

$$\frac{\lambda^\circ(M^{3+}C_2O_4^{2-})}{\lambda^\circ(1/3M^{3+})}=\frac{1}{3}.$$

The results are given in Table 3, together with those which have been determined by various researchers using various methods.

If the closest approach of the two ions of the ion-pair is assumed to be equal to the sum of their Stokes radii, the K value can be estimated from the Bjerrum theory.[15] Table 4 shows the log K values calculated theoretically.

On the basis of the results given in Table 3, it appears reasonable to conclude that the K values of chromium(III) complex cations with several anions are a little smaller than those of the corresponding cobalt(III) complex cations. A similar conclusion has been drawn in previous studies.[11,12] Although the detailed comparison of the K values obtained using the same method on a given ion-pair was limited, it was also likely that the K values for $[M(NH_3)_6]^{3+}$ (M=Cr, Co) with such ions as ClO_4^-, NO_3^-, $C_2O_4^{2-}$, and SO_4^{2-} are a little larger than those for $[M(en)_3]^{3+}$ with the respective anions. Since the Stokes radii of $[M(en)_3]^{3+}$ are larger

Table 3. Logarithmic association constants for infinite dilution at 25.0 °C

Ion-pair	$\log (K/\mathrm{mol^{-1}\,dm^3})$	Method$^{\mathrm{a)}}$	Investigators	Ref.
$[\mathrm{Cr(NH_3)_6}]^{3+}\text{-}\mathrm{ClO_4^-}$	1.1_8	cond	Takahashi, Koiso, and Tanaka (1974)	11
	$1.0_0^{\mathrm{c)}}$	sp	Takahashi, Koiso, and Tanaka (1974)	11
$[\mathrm{Co(NH_3)_6}]^{3+}\text{-}\mathrm{ClO_4^-}$	1.4_0	cond	Katayama and Tamamushi (1968)	7
$[\mathrm{Cr(en)_3}]^{3+}\text{-}\mathrm{ClO_4^-}$	1.0_2	cond	Takahashi, Koiso, and Tanaka (1974)	11
$[\mathrm{Cr(en)_3}]^{3+}\text{-}\mathrm{ClO_4^-}$	$1.2_0^{\mathrm{c)}}$	sp	Takahashi, Koiso, and Tanaka (1974)	11
	$0.9_0^{\mathrm{c)}}$	sp	Takahashi and Koiso (1976)	12
$[\mathrm{Co(en)_3}]^{3+}\text{-}\mathrm{ClO_4^-}$	1.3_7	cond	Present study	
$[\mathrm{Cr(NH_3)_6}]^{3+}\text{-}\mathrm{SCN^-}$	1.1_7	cond	Present study	
$[\mathrm{Co(NH_3)_6}]^{3+}\text{-}\mathrm{SCN^-}$	1.3_0	cond	Present study	
$[\mathrm{Cr(en)_3}]^{3+}\text{-}\mathrm{SCN^-}$	1.3_4	cond	Present study	
$[\mathrm{Co(en)_3}]^{3+}\text{-}\mathrm{SCN^-}$	1.3_4	cond	Present study	
$[\mathrm{Cr(NH_3)_6}]^{3+}\text{-}\mathrm{I^-}$	1.2_9	cond	Takahashi, Koiso, and Tanaka (1974)	11
	1.3_4	sp	Takahashi, Koiso, and Tanaka (1974)	11
$[\mathrm{Co(NH_3)_6}]^{3+}\text{-}\mathrm{I^-}$	1.3_8	cond	Katayama and Tamamushi (1968)	7
$[\mathrm{Cr(en)_3}]^{3+}\text{-}\mathrm{I^-}$	1.4_2	cond	Takahashi, Koiso, and Tanaka (1974)	11
	1.3_3	sp	Takahashi, Koiso, and Tanaka (1974)	11
$[\mathrm{Co(en)_3}]^{8+}\text{-}\mathrm{I^-}$	1.4_6	cond	Present study	
$[\mathrm{Cr(NH_3)_6}]^{3+}\text{-}\mathrm{Cl^-}$	1.3_7	cond	Takahashi and Koiso (1976)	12
$[\mathrm{Co(NH_3)_6}]^{3+}\text{-}\mathrm{Cl^-}$	1.4_9	cond	Jenkins and Monk (1951)	1
	1.5	cond	Tamamushi, Isono, and Katayama (1967)	4
$[\mathrm{Cr(en)_3}]^{3+}\text{-}\mathrm{Cl^-}$	1.5_8	cond	Takahashi and Koiso (1976)	12
	1.6_5	sp	Takahashi and Koiso (1976)	12
$[\mathrm{Co(en)_3}]^{3+}\text{-}\mathrm{Cl^-}$	1.7_2	cond	Jenkins and Monk (1951)	1
$[\mathrm{Cr(NH_3)_6}]^{3+}\text{-}\mathrm{Br^-}$	1.5_7	cond	Takahashi and Koiso (1976)	12
$[\mathrm{Co(NH_3)_6}]^{3+}\text{-}\mathrm{Br^-}$	1.6_5	cond	Katayama and Tamamushi (1968)	7
$[\mathrm{Cr(en)_3}]^{3+}\text{-}\mathrm{Br^-}$	1.5_0	cond	Takahashi and Koiso (1976)	12
	1.4_6	sp	Takahashi and Koiso (1976)	12
$[\mathrm{Co(en)_3}]^{3+}\text{-}\mathrm{Br^-}$	1.6_8	cond	Present study	
$[\mathrm{Cr(NH_3)_6}]^{3+}\text{-}\mathrm{NO_3^-}$	1.5_3	cond	Takahashi and Koiso (1976)	12
$[\mathrm{Co(NH_3)_6}]^{3+}\text{-}\mathrm{NO_3^-}$	1.6_3	cond	Katayama and Tamamushi (1968)	7
$[\mathrm{Cr(en)_3}]^{3+}\text{-}\mathrm{NO_3^-}$	1.4_9	cond	Takahashi and Koiso (1976)	12
$[\mathrm{Cr(NH_3)_6}]^{3+}\text{-}\mathrm{SO_4^{2-}}$	$3.1_4^{\mathrm{b*)}}$	pol	Tanaka, Ogino, and Satô (1966)	3
	$3.1_5^{\mathrm{b*)}}$	chron	Tanaka and Yamada (1967)	6
$[\mathrm{Co(NH_3)_6}]^{3+}\text{-}\mathrm{SO_4^{2-}}$	$3.2_1^{\mathrm{b*)}}$	pol	Tanaka, Ogino, and Satô (1966)	3
	3.5_6	cond	Jenkins and Monk (1951)	1
	$3.3_0^{\mathrm{b*)}}$	chron	Tanaka and Yamada (1967)	6
	$3.2_6^{\mathrm{b**)}}$	sp	Tanaka, Kobayashi, and Kamada (1967)	5
$[\mathrm{Cr(en)_3}]^{3+}\text{-}\mathrm{SO_4^{2-}}$	$2.9_9^{\mathrm{b*)}}$	chron	Tanaka and Yamada (1967)	6
$[\mathrm{Co(en)_3}]^{3+}\text{-}\mathrm{SO_4^{2-}}$	3.4_5	cond	Jenkins and Monk (1951)	1
	$3.1_0^{\mathrm{b**)}}$	sp	Tanaka, Kobayashi, and Kameda (1967)	5
	$3.2_2^{\mathrm{b*)}}$	chron	Tanaka and Yamada (1967)	6
$[\mathrm{Cr(NH_3)_6}]^{3+}\text{-}\mathrm{C_2O_4^{2-}}$	3.2_0	cond	Present study	
$[\mathrm{Co(NH_3)_6}]^{3+}\text{-}\mathrm{C_2O_4^{2-}}$	3.2_5	cond	Katayama and Tamamushi (1968)	7
$[\mathrm{Cr(en)_3}]^{3+}\text{-}\mathrm{C_2O_4^{2-}}$	2.9_7	cond	Present study	

a) Methods of measurement: cond—conductivity, sp—spectrophotometry, pol—polarography, and chron—chronopotentiometry. b) The values calculated from concentration constants obtained at $I=0.10$(*) ($\mathrm{mol\,dm^{-3}}$) and $I=0.07$(**) ($\mathrm{mol\,dm^{-3}}$). c) These values were determined indirectly.[11,12]

than that of $[\mathrm{M(NH_3)_6}]^{3+}$, this view is to be expected so far as the ion-association is assumed to depend only on Coulombic interaction between the ions. Therefore, it appears appropriate to state that the electrostatic interaction between ions is the dominant influence among various factors in the process of ion-pair formation of the complex cation with oxoacid anions, such as $\mathrm{ClO_4^-}$, $\mathrm{NO_3^-}$, $\mathrm{C_2O_4^{2-}}$, and $\mathrm{SO_4^{2-}}$. Furthermore, Table 2 also indicates that the K values of the complex cations with $\mathrm{SCN^-}$ are smaller than those with other univalent anions, except for $\mathrm{ClO_4^-}$. That is, the extent of association is about the same in the perchlorate and thiocyanate systems. The smaller tendency of the complex cations to associate with $\mathrm{SCN^-}$ is probably due to the fact that the $\mathrm{SCN^-}$ is not only of low charge and large size, but also that it is a linear ion. Thus, the $\mathrm{SCN^-}$ ion may possess rotational entropy which would be lost on ion-association.[16]

TABLE 4. LOGARITHMIC ASSOCIATION CONSTANTS CALCULATED FROM BJERRUM'S THEORY OF THE ION-PAIRS IN AQUEOUS SOLUTIONS AT 25.0 °C

Ion-pair	log (K/mol^{-1} dm^3)
$[Cr(NH_3)_6]^{3+}$-SCN^-	1.7_6
$[Cr(en)_3]^{3+}$-SCN^-	1.6_3
$[Co(NH_3)_6]^{3+}$-SCN^-	1.7_7
$[Co(en)_3]^{3+}$-SCN^-	1.6_4
$[Co(en)_3]^{3+}$-Br^-	1.6_7
$[Co(en)_3]^{3+}$-I^-	1.6_7
$[Co(en)_3]^{3+}$-ClO_4^-	1.6_4
$[Cr(NH_3)_6]^{3+}$-$C_2O_4^{2-}$	3.0_8
$[Cr(en)_3]^{3+}$-$C_2O_4^{2-}$	2.9_0

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