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Conductometric Study of First and Second Ion Associations of Hexaamminecobalt(III) and Tris(ethylenediamine)cobalt(III) Ions with Sulfate Ions at Temperatures from 0 to 50 °C

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Conductivity measurements for aqueous solutions of sulfates of hexaamminecobalt(III) ($[Co(NH_3)_6]^{3+}$) and tris(ethylenediamine)cobalt(III) ($[Co(en)_3]^{3+}$) complexes have been made at various temperatures from 0 to 50 °C. The conductivity data were analyzed to obtain the first ion-association constants, but could not be completely explained if the second ion association (triple-ion formation between ion pair and sulfate ion) was not taken into consideration. The ion-association constants had minimum values at particular temperatures and were significantly larger than those predicted by electrostatic ion-association theories. Excess thermodynamic functions for the first ion association over the theoretical prediction were estimated and explained by assuming the ion–ion and ion–water hydrogen bonding. The excess entropy and enthalpy changes were significantly increased with increasing temperature, while the Gibbs free energy change was little dependent on temperature; these results were attributed to the destruction of bulk water structure with temperature. A similar contribution of hydrogen bonding was present in the second ion association besides the electrostatic interaction between the anion and the ion pair having a large dipole moment. The difference between $[Co(NH_3)_6]^{3+}$ and $[Co(en)_3]^{3+}$ in hydrogen bonding is also discussed.

Wide temperature-range conductivity measurements of complex salt solutions can provide valuable information on the outer-sphere interactions of complex ions with counter ions and water molecules. From the measurements for aqueous solutions of $[Co(NH_3)_6]X_3$ and $[Co(en)_3]X_3$ (X=Cl, Br, I, NO_3, ClO_4; en=ethylenediamine) at temperatures between 0 and 50 °C, we found that the first ion-association constants ($K_{A(1)}$) each had a minimum at a particular temperature.[1,2] For nitrate and perchlorate of $[Co(NH_3)_6]^{3+}$, the values of $K_{A(1)}$ remarkably increased with decreasing temperature, suggesting the presence of specific short-range interactions such as hydrogen bonding between hydrogen atoms of ammine ligands and oxygen atoms of the anions.[1] Relatively weak ion associations between $[Co(en)_3]^{3+}$ and these oxoanions were explained as mainly due to steric hindrance of the methylene groups of ethylenediamine ligands on the hydrogen bonding.[2]

A sulfate ion has a structure similar to that of a perchlorate ion, but is more strongly hydrated in aqueous solution because sulfate ions have a high affinity for hydrogen atoms of polar groups of the complex ions. The ion-association constants ($K_{A(1)}$) between $[Co(NH_3)_6]^{3+}$ or $[Cr(en)_3]^{3+}$ and SO_4^{2-} were larger than those expected from ion-association theories.[3,4] This deviation was attributed to hydrogen bonding between the ions.[5] It is of interest to determine what temperature dependence is found out in such strong hydrogen bonding systems. Osugi and co-workers[6] reported that the value of $K_{A(1)}$ for the $[Co(NH_3)_6]^{3+}$–SO_4^{2-} system had a maximum at a certain temperature. However, the conclusion should be reexamined, since this observation is contrary to that for the monovalent anions.[1]

In the present study, conductivities of aqueous solutions of $[Co(NH_3)_6]_2(SO_4)_3$ and $[Co(en)_3]_2(SO_4)_3$ were measured at temperatures from 0 to 50 °C in order to determine the exact temperature dependence of the ion-association constants and elucidate the excess thermodynamic functions related to hydrogen bonding. The analyses were made by considering the second ion association between the complex ions and sulfate ion.

Experimental

Materials. Chlorides of hexaamminecobalt(III) and tris(ethylenediamine)cobalt(III) complexes were prepared as described previously.[1,2] Hexaamminecobalt(III) sulfate was prepared by adding concentrated sulfuric acid to an aqueous solution of the chloride and then cooling the solution in an ice bath. The precipitate was washed many times with an ethanol–water mixture. The aqueous solution in which the product was dissolved was somewhat acidic, but no chloride ion was detected as silver chloride. The recrystallization was made three times from hot water by cooling with ice. The acidity of the last solution became pH=6. The crystal obtained effloresced in the air. The number of water of crystallization ($n(H_2O)$) was 2.97. The density of the crystal was 1.782 $g\,cm^{-3}$ at 25.0 °C. Molar extinction coefficients of the complex ion at absorption maxima, $\lambda_{max}=339$ and 475 nm, were 46.0 and 56.8 $mol^{-1}\,dm^3\,cm^{-1}$, respectively, which were in close agreement with those for the chloride (46.0 and 56.9 $mol^{-1}\,dm^3\,cm^{-1}$, respectively).

Tris(ethylenediamine)cobalt(III) sulfate was prepared by double decomposition between chloride of the complex and silver sulfate in water. After silver chloride was removed the filtrate was concentrated and cooled to room temperature. The highly viscous oily substance which precipitated was treated with ethanol for the crystallization. The product was ascertained to contain no silver or chloride ion and was recrystallized from water with ethanol through the oily state in the same manner. After air-drying the number of $n(H_2O)$ of the sulfate was determined as 5.99 and its density was 1.620 $g\,cm^{-3}$ at 25 °C. Molar extinction coefficients of the complex ion at absorption maxima, $\lambda_{\max}=338$ and 466 nm, were 79.1 and 87.9 $\mathrm{mol^{-1}\,dm^3\,cm^{-1}}$, respectively; these were close to those for the chloride (79.3 and 87.9 $\mathrm{mol^{-1}\,dm^3\,cm^{-1}}$, respectively). All of the reagents used were of reagent grade (Wako Pure Chemical Industries).

Conductivity Measurements. Conductivity measurements were made at 1 kHz with a Fuso 360 linear-bridge conductometer under the same temperature conditions as observed in precious works,[1,2] where detailed descriptions of the measurements and the procedures were given.[1,2] The minor conductivity changes due to the very slow decomposition[1] of hexaamminecobalt(III) complex within 0.02% at 0 °C and 0.08% at 50 °C for molar conductivities were corrected. Fifteen or fourteen solutions of concentrations from 0.5 to 4.4×10^{-4} $\mathrm{mol\,dm^{-3}}$ were examined.

Results

Observed molar conductivities per 1/6 $\mathrm{mol\,dm^{-3}}$ salt, Λ ($\mathrm{M_2X_3/6}$), corresponding to equivalent conductivities, where $\mathrm{M^{3+}}$ is complex ion and $\mathrm{X^{2-}}$ is sulfate ion, have been deposited[7] together with molalities (m) and molar concentrations (c) of solutions.

The analyses were made by assuming the following ion-association equilibria, for the reaction described later:

$$\mathrm{M^{3+}+X^{2-}\rightleftharpoons M^{3+}X^{2-}}, \tag{1}$$

$$\mathrm{M^{3+}X^{2-}+X^{2-}\rightleftharpoons M^{3+}X^{2-}X^{2-}}. \tag{2}$$

The first and the second ion-association constants, $K_{\mathrm{A(1)}}$ and $K_{\mathrm{A(2)}}$, for Eqs. 1 and 2, respectively, are given by

$$K_{\mathrm{A(1)}}=(1-\alpha-\beta)y_{\mathrm{MX}}/[c\alpha(1+2\alpha-2\beta)y_{\mathrm{M}}y_{\mathrm{X}}], \tag{3}$$

$$K_{\mathrm{A(2)}}=\beta y_{\mathrm{MXX}}/[c(1-\alpha-\beta)(1+2\alpha-2\beta)y_{\mathrm{MX}}y_{\mathrm{X}}], \tag{4}$$

where c is the molar concentration of the complex salt; α and β are the fractions of free complex ion and triple ion, respectively ($[\mathrm{M^{3+}}]=2c\alpha$, $[\mathrm{M^{3+}X^{2-}X^{2-}}]=2c\beta$, $[\mathrm{M^{3+}X^{2-}}]=2c(1-\alpha-\beta)$, $0\leqq\alpha\leqq1$, $0\leqq\beta\leqq3/4$, $\alpha+\beta\leqq1$). Activity coefficients of $\mathrm{M^{3+}}$, $\mathrm{X^{2-}}$, $\mathrm{M^{3+}X^{2-}}$, and $\mathrm{M^{3+}X^{2-}X^{2-}}$ (y_{M}, y_{X}, y_{MX}, and y_{MXX}, respectively) were represented by the Debye–Hückel equation:

$$\log y_i=-Az_i^2I^{1/2}/(1+Ba_iI^{1/2}), \tag{5}$$

where A and B have their usual meanings, z_i is the ionic charge number of i-ionic species, a_i is the so-called closest distance of approach of ions for i-ionic species, and I is ionic strength given by

$$\begin{aligned}I&=15c-6[\mathrm{M^{3+}X^{2-}}]-8[\mathrm{M^{3+}X^{2-}X^{2-}}]\\&=(3+12\alpha-4\beta)c.\end{aligned} \tag{6}$$

According to the additivity rule for ionic conductivities represented by

$$\begin{aligned}6c\Lambda(\mathrm{M_2X_3/6})=&3[\mathrm{M^{3+}}]\lambda(\mathrm{M^{3+}/3})+2[\mathrm{X^{2-}}]\lambda(\mathrm{X^{2-}/2})\\&+[\mathrm{M^{3+}X^{2-}}]\lambda(\mathrm{M^{3+}X^{2-}})+[\mathrm{M^{3+}X^{2-}X^{2-}}]\lambda(\mathrm{M^{3+}X^{2-}X^{2-}}),\end{aligned} \tag{7}$$

we can express molar conductivities of the salt as follows:

$$\begin{aligned}\Lambda(\mathrm{M_2X_3/6})&=(\alpha-\beta/3)\{\lambda(\mathrm{M^{3+}/3})+\lambda(\mathrm{X^{2-}/2})\}\\&\quad+(1-\alpha-\beta)/3\times\{\lambda(\mathrm{M^{3+}X^{2-}})+\lambda(\mathrm{X^{2-}/2})\}\\&\quad+(\beta/3)\{\lambda(\mathrm{M^{3+}/3})+\lambda(\mathrm{M^{3+}X^{2-}X^{2-}})\}\\&=(\alpha-\beta/3)\Lambda_{\mathrm{F}}(\mathrm{M_2X_3/6})+\{(1-\alpha-\beta)/3\}\Lambda_{\mathrm{F}}\{\mathrm{(MX)_2X/2}\}\\&\quad+(\beta/3)\Lambda_{\mathrm{F}}\{\mathrm{M(MXX)_3/3}\},\end{aligned} \tag{8}$$

where λ denotes ionic molar conductivity and $\Lambda_{\mathrm{F}}(\mathrm{M_2X_3/6})$, $\Lambda_{\mathrm{F}}\{\mathrm{(MX)_2X/2}\}$, and $\Lambda_{\mathrm{F}}\{\mathrm{M(MXX)_3/3}\}$ correspond to molar conductivities of hypothetical unassociated 3 : 2, 1 : 2, and 3 : 1 electrolytes, respectively, which were expressed by the following Robinson–Stokes equations:[1,2,8,9]

$$\Lambda_{\mathrm{F}}(\mathrm{M_2X_3/6})=\{\lambda^\infty(\mathrm{M^{3+}/3})+\lambda^\infty(\mathrm{X^{2-}/2})\}-S_{32}I^{1/2}/(1+Ba_{32}), \tag{9}$$

$$\begin{aligned}\Lambda_{\mathrm{F}}\{\mathrm{(MX)_2X/2}\}=&\{\lambda^\infty(\mathrm{M^{3+}X^{2-}})+\lambda^\infty(\mathrm{X^{2-}/2})\}\\&-S_{12}I^{1/2}/(1+Ba_{12}),\end{aligned} \tag{10}$$

$$\begin{aligned}\Lambda_{\mathrm{F}}(\mathrm{M(MXX)_3/3})=&\{\lambda^\infty(\mathrm{M^{3+}/3})+\lambda^\infty(\mathrm{M^{3+}X^{2-}X^{2-}})\}\\&-S_{31}I^{1/2}/(1+Ba_{31}),\end{aligned} \tag{11}$$

where λ^∞ denotes limiting ionic molar conductivity and S has its usual meaning including λ^∞ and z_i. Theoretical expression for S_{32}, S_{12}, and S_{31} were taken as those for hypothetical states including only $\mathrm{M_2X_3}$ (α=1), $\mathrm{(MX)_2X}$ (α=β=0), $\mathrm{M(MXX)_3}$ (α=1/4, β=3/4), respectively.

The values of closest distance of approach of ions (a_i, a_{32}, a_{12}, a_{31}) in theoretical equations were assumed to be equal to the distance between complex ion and sulfate ion (a) which was taken as the sum of effective ionic radii (r_{ef}) derived from partial molar volumes of the ions: a=5.43 Å for the $\mathrm{[Co(NH_3)_6]^{3+}}$–$\mathrm{SO_4^{2-}}$ system and a=5.90 Å for the $\mathrm{[Co(en)_3]^{3+}}$–$\mathrm{SO_4^{2-}}$ system from r_{ef}=3.10 Å ($\mathrm{[Co(NH_3)_6]^{3+}}$),[1] 3.57 Å ($\mathrm{[Co(en)_3]^{3+}}$),[2] and 2.33 Å ($\mathrm{SO_4^{2-}}$).[8]

Limiting molar conductivities of ions, $\lambda^\infty(\mathrm{M^{3+}/3})$ and $\lambda^\infty(\mathrm{X^{2-}/2})$, at a given temperature (t in °C) were estimated from

$$\lambda^\infty=\lambda^\infty(25\ {}^\circ\mathrm{C})+a(t-25)+b(t-25)^2+c(t-25)^3, \tag{12}$$

where $\lambda^\infty(25\ {}^\circ\mathrm{C})$, a, b, and c are constants; their values are given in Table 1. Limiting molar conductivities of ion pairs, $\lambda^\infty(\mathrm{M^{3+}X^{2-}})$, were assumed to be equal to $\lambda^\infty(\mathrm{M^{3+}/3})/3$, according to the procedure described previously.[11] The same assumption was made for $\lambda^\infty(\mathrm{M^{3+}X^{2-}X^{2-}})$.

The calculation was carried out in the following way. The values of $K_{\mathrm{A(1)}}$ at observed concentrations were calculated for an assumed value of $K_{\mathrm{A(2)}}$ and averaged to estimate the standard deviation σ ($=[\Sigma\{\Lambda(\mathrm{obsd})-\Lambda(\mathrm{calcd})\}^2/(n-2)]^{1/2}$). The values of

Table 1. Parameter Values in Eq. 12 for Limiting Molar Conductivities of Ions, $\lambda^\infty(\mathrm{M}^{3+}/3)$ and $\lambda^\infty(\mathrm{X}^{2-}/2)$

Ion	λ^∞ (25 °C) S cm^2 mol^{-1}	a S cm^2 mol^{-1}K^{-1}	$b\times10^3$ S cm^2 mol^{-1}K^{-2}	$c\times10^5$ S cm^2 mol^{-1}K^{-3}	Ref.
$[\mathrm{Co(NH_3)_6}]^{3+}$	99.56	2.0729	7.212	−3.30	1
$[\mathrm{Co(en)_3}]^{3+}$	74.11	1.6728	7.166	−2.75	10
$\mathrm{SO_4^{2-}}$	79.83	1.7027	6.698	−0.54	8

$K_{\mathrm{A(1)}}$ (averaged) and $K_{\mathrm{A(2)}}$ minimizing σ were regarded as the best ones; these are summarized in Tables 2 and 3,[12] together with the theoretical ones estimated by electrostatic theories of ion association.[3,4,13]

Figures 1 and 2 show plots of $\log K_{\mathrm{A(1)}}$ and $\log K_{\mathrm{A(2)}}$ against temperature (t), respectively, where minima for $K_{\mathrm{A(1)}}$ and $K_{\mathrm{A(2)}}$ are found in each salt. Their temperature dependence was expressed by the following empirical equation:

$$\log K_{\mathrm{A}(i)} = p(t-t_{\mathrm{min}})^2 + \log K_{\mathrm{A}(i)\mathrm{min}}, \qquad (13)$$

where $\log K_{\mathrm{A}(i)\mathrm{min}}$ is the minimum value of $\log K_{\mathrm{A(1)}}$ or $\log K_{\mathrm{A(2)}}$, t_{min} is the temperature giving $\log K_{\mathrm{A}(i)\mathrm{min}}$, and p corresponds to the curvature of a parabola. As shown with solid lines in Figs. 1 and 2, experimental values of $\log K_{\mathrm{A(1)}}$ and $\log K_{\mathrm{A(2)}}$ could be well reproduced by use of Eq. 13 with parameter values given in Table 4. The standard entropy and enthalpy changes of ion association, $\Delta S^\circ_{\mathrm{as}(i)}$ and $\Delta H^\circ_{\mathrm{as}(i)}$, respectively, were obtained in a similar manner to that described previously[1,2] and are shown in Tables 5 and 6, together with the theoretical values for the first ion association.[13,14]

Table 2. First and Second Ion-Association Constants ($K_{\mathrm{A(1)}}$/dm^3 mol^{-1} and $K_{\mathrm{A(2)}}$/dm^3 mol^{-1}) between $[\mathrm{Co(NH_3)_6}]^{3+}$ and $\mathrm{SO_4}^{2-}$

	Experimental		Theoretical[a)]	
t/°C	$K_{\mathrm{A(1)}}$	$K_{\mathrm{A(2)}}$	$K_{\mathrm{A(1)}}$	$K_{\mathrm{A(2)}}$
−0.01	3586±13	147±11	843	4.7
5.04	3547±13	141±11	867	4.8
10.06	3529±14	138±11	894	4.9
15.05	3534±14	138±12	923	5.0
20.01	3562±15	138±12	955	5.2
24.95	3614±15	140±15	990	5.3
29.85	3692±15	139±13	1028	5.4
34.72	3788±16	140±14	1069	5.6
39.55	3907±16	142±15	1112	5.7
44.36	4048±16	144±15	1160	5.9
49.13	4209±17	148±16	1211	6.0

a) Theoretical values estimated with a=5.43 Å by use of ion-association theories of Ebeling[3] and Yokoyama–Yamatera;[4] the free ions and the ion pair were regarded as spherical ions having no dipole moment.

Table 3. First and Second Ion-Association Constants ($K_{\mathrm{A(1)}}$/dm^3 mol^{-1} and $K_{\mathrm{A(2)}}$/dm^3 mol^{-1}) between $[\mathrm{Co(en)_3}]^{3+}$ and $\mathrm{SO_4}^{2-}$

	Experimental		Theoretical[a)]	
t/°C	$K_{\mathrm{A(1)}}$	$K_{\mathrm{A(2)}}$	$K_{\mathrm{A(1)}}$	$K_{\mathrm{A(2)}}$
0.0	3152±19	122±17	663	4.3
5.0	3131±17	117±14	681	4.4
10.0	3120±16	119±14	700	4.5
15.0	3137±16	116±14	722	4.6
20.0	3168±16	117±14	745	4.7
25.0	3218±17	118±15	771	4.8
30.0	3286±18	121±15	799	4.9
35.0	3380±21	122±18	829	5.1
40.0	3488±20	126±15	861	5.2
45.0	3623±21	128±15	897	5.3
50.0	3781±21	130±14	935	5.5

a) See the note of Table 2; a=5.90 Å.

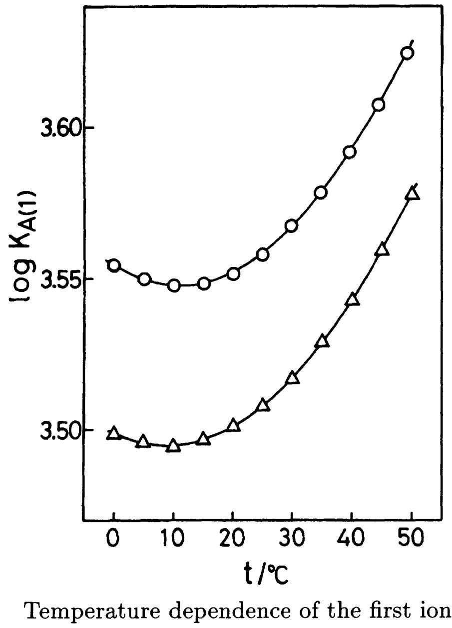

Fig. 1. Temperature dependence of the first ion-association constants for the systems of $[\mathrm{Co(NH_3)_6}]^{3+}$–$\mathrm{SO_4}^{2-}$ (○) and $[\mathrm{Co(en)_3}]^{3+}$–$\mathrm{SO_4}^{2-}$ (△).

Discussion

Necessity for Considering the Second Ion Association. Conductivity data for sulfates of $[\mathrm{Co(NH_3)_6}]^{3+}$ and $[\mathrm{Co(en)_3}]^{3+}$ have usually been analyzed by considering only the first ion association.[5,6,11] Such analyses can be made by use of Eqs. 3, 5, 6, 8, 9, and 10, assuming β=0. However, the ion-association constants ($K_{\mathrm{A(1)}}$) obtained increased with increasing concentration, as displayed in Fig. 3, suggesting the presence of higher order interactions. The assumption of the second

Table 4. Values of Parameters in Eq. 13 Representing Temperature Dependence of First and Second Ion-Association Constants ($K_{A(1)}$ and $K_{A(2)}$) between Complex Ions and Sulfate Ion

Complex ion		$\frac{p\times10^5}{K^{-2}}$	$\frac{t_{min}}{°C}$	$\log K_{A(i)min}$
$[Co(NH_3)_6]^{3+}$	$K_{A(1)}$:	5.29±0.09	10.9±0.3	3.548±0.001
	$K_{A(2)}$:	4.30±0.50	22.3±0.3	2.139±0.001
$[Co(en)_3]^{3+}$	$K_{A(1)}$:	4.88±0.05	8.7±0.2	3.495±0.001
	$K_{A(2)}$:	4.11±0.77	15.5±1.8	2.070±0.001

Table 5. Standard Entropies, $\Delta S^\circ_{as(1)}$, and Standard Enthalpies, $\Delta H^\circ_{as(1)}$, of First Ion Association of the Complex Ions with Sulfate Ion at Several Temperatures

t/°C	$\Delta S^\circ_{as(1)}$/J K^{-1} mol^{-1}				$\Delta H^\circ_{as(1)}$/kJ mol^{-1}			
	$[Co(NH_3)_6]^{3+}$	$[Co(en)_3]^{3+}$	Theoretical[a]		$[Co(NH_3)_6]^{3+}$	$[Co(en)_3]^{3+}$	Theoretical[a]	
5.0	64.6±0.7	65.0±0.3	69.9[b]	66.9[c]	−0.9±0.2	−0.5±0.1	3.8[b]	3.5[c]
15.0	70.3±0.4	70.3±0.2	72.8	69.6	0.7±0.1	1.0±0.1	4.6	4.3
25.0	76.6±0.3	76.2±0.1	75.8	72.4	2.5±0.1	2.7±0.1	5.5	5.1
35.0	83.5±0.4	82.7±0.2	78.9	75.3	4.6±0.1	4.7±0.1	6.4	6.0
45.0	91.0±0.8	89.7±0.4	82.2	78.3	7.0±0.2	6.9±0.2	7.5	6.9

a) Theories of Ebeling[3] and Yokoyama–Yamatera[4] were used. b) Theoretical values estimated with a=5.43 Å assumed for the $[Co(NH_3)_6]^{3+}$–$SO_4{}^{2-}$ system. c) Theoretical values estimated with a=5.90 Å assumed for the $[Co(en)_3]^{3+}$–$SO_4{}^{2-}$ system.

Table 6. Standard Entropies ($\Delta S^\circ_{as(2)}$) and Enthalpies ($\Delta H^\circ_{as(2)}$) of Second Ion Association of the Complex Ions with Sulfate Ion at Several Temperatures

t/°C	$\Delta S^\circ_{as(2)}$/J K^{-1} mol^{-1}		$\Delta H^\circ_{as(2)}$/kJ mol^{-1}	
	$[Co(NH_3)_6]^{3+}$	$[Co(en)_3]^{3+}$	$[Co(NH_3)_6]^{3+}$	$[Co(en)_3]^{3+}$
5.0	33±4	35±6	−2.2±1.0	−1.3±1.7
15.0	38±3	39±4	−1.0±0.6	−0.1±0.9
25.0	42±2	44±2	0.4±0.4	1.3±0.7
35.0	48±3	49±4	2.0±0.7	2.9±1.0
45.0	53±5	55±7	3.8±1.4	4.7±2.2

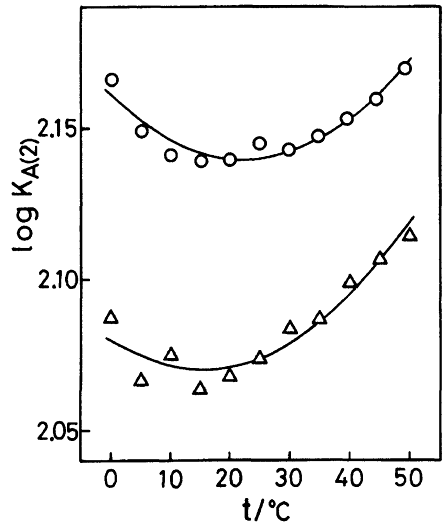

Fig. 2. Temperature dependence of the second ion-association constants for the systems of $[Co(NH_3)_6]^{3+}$–$SO_4{}^{2-}$ (○) and $[Co(en)_3]^{3+}$–$SO_4{}^{2-}$ (△).

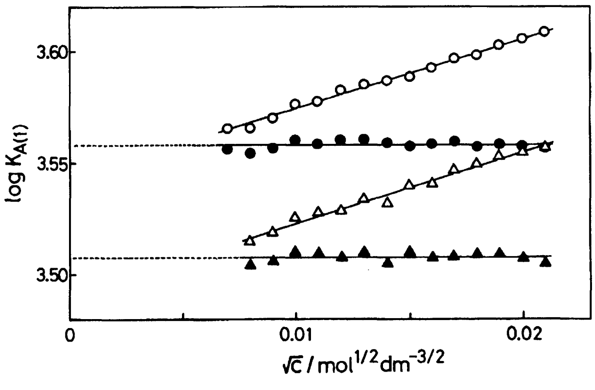

Fig. 3. The first ion-association constants at 25 °C obtained by ignoring the second ion associations (open symbols) and those obtained by assuming the second ion-association constants given in Tables 2 and 3 (solid symbols) for the systems of $[Co(NH_3)_6]^{3+}$–$SO_4{}^{2-}$ (○ and ●) and $[Co(en)_3]^{3+}$–$SO_4{}^{2-}$ (△ and ▲). The solid lines are straight lines obtained by the least-squares method.

ion association (triple-ion formation) with an appropriate value of $K_{A(2)}$ could give almost constant values of $K_{A(1)}$ independent of concentration, as shown in Fig. 3. If one wants to obtain such constant values of $K_{A(1)}$, ignoring the second ion association, unreasonably small values of $\lambda^{\infty}(M^{3+}X^{2-})$ such as $\lambda^{\infty}(M^{3+}/3)/14$ for the $[Co(NH_3)_6]^{3+}SO_4{}^{2-}$ ion pair and $\lambda^{\infty}(M^{3+}/3)/30$ for the $[Co(en)_3]^{3+}SO_4{}^{2-}$ ion pair at 25 °C must be supposed. This means that the second ion association is worth taking into consideration.

Stepwise ion associations including the second and higher order ones have been observed for the $[Co(NH_3)_6]^{3+}$–$SO_4{}^{2-}$ and $[Co(en)_3]^{3+}$–$SO_4{}^{2-}$ systems by potentiometric measurements in mixed electrolyte solutions of ionic strength 0.1—0.5 by Mironov and coworkers.[15,16] Stepwise ion associations were also observed by optical rotation measurements on the $[Co(en)_3]^{3+}$–$S_2O_3{}^{2-}$ system[17] and circular dichroism measurements on the $[Co(en)_3]^{3+}$–SeO_3^{2-} system.[18] The present observation for the second ion association is qualitatively consistent with these works.

Comparisons with Other Conductivity Studies. Although usual conductivity studies of the ion association between complex ions and sulfate ion have ignored the second ion association, the resultant values of $K_{A(1)}$ were not so extremely different from the present results, because the second ion association was fairly weak compared with the first one. This is exemplified by $\log K_{A(1)}=3.54$, estimated from the logarithmic value of 3.02 at $I=0.01$ (25 °C) for the $[Co(NH_3)_6]^{3+}$–$SO_4{}^{2-}$ system obtained by the continuous variation method.[5]

Jenkins and Monk[11] obtained $K_{A(1)}=3610\ dm^3\ mol^{-1}$ for the $[Co(NH_3)_6]^{3+}$–$SO_4{}^{2-}$ system at 25 °C by use of the limiting equations of Debye–Hückel and Onsager,[9] corresponding to Eqs. 5, 9, 10, and 11, in which the terms involving a were neglected. This $K_{A(1)}$ value was also comparable to ours; the use of limiting equations for the analysis of the present conductivity data gave $K_{A(1)}=3575\ dm^3\ mol^{-1}$ and $K_{A(2)}=206\ dm^3\ mol^{-1}$ for the $[Co(NH_3)_6]^{3+}$–$SO_4{}^{2-}$ system. For the $[Co(en)_3]^{3+}$–$SO_4{}^{2-}$ system the same workers[11] presented $K_{A(1)}=2820\ dm^3\ mol^{-1}$ at 25 °C; this value is considerably smaller than ours: $K_{A(1)}=3178\ dm^3\ mol^{-1}$ ($K_{A(2)}=174\ dm^3\ mol^{-1}$) estimated with the limiting equations. The disagreement is probably due to the presence of impurities in their working solutions.[11] From reanalyses of Jenkins–Monk's conductivity data,[11] we could find a concentration dependence of $K_{A(1)}$ similar to the one observed in the present study, although it was somewhat obscured because of scattering in $K_{A(1)}$, due to some poor data being included.

The use of the limiting equations for the estimation of $K_{A(2)}$ is not recommended, because it leads to large values, beyond the range of experimental errors as well as the uncertainties, described later, which are caused by the arbitrariness in the assumptions for $\lambda^{\infty}(M^{3+}A^{2-})$ and a.

Osugi and co-workers[6] obtained $K_{A(1)}$ (25 °C)$=5.13\times10^3\ dm^3\ mol^{-1}$ for the $[Co(NH_3)_6]^{3+}$–$SO_4{}^{2-}$ system according to Jenkins–Monk's procedure,[11] but using the value of $\Lambda^{\infty}(M_2X_3/6)$ estimated from the extrapolation on the plots of Λ(obsd) vs. $c^{1/2}$. This was 187.0 $S\ cm^2\ mol^{-1}$ at 25 °C, larger than 179.39 $S\ cm^2\ mol^{-1}$ calculated by use of Eq. 12 with the parameter values in Table 1. The above $K_{A(1)}$ value, considerably larger than ours and Jenkins–Monk's, was mainly attributable to the use of such as apparent value of $\Lambda^{\infty}(M_2X_3/6)$.

The temperature dependence of $K_{A(1)}$ was reported by Osugi and co-workers[6] to have a maximum, contrary to the present observation. This could be corrected by excluding some poor data at 30 °C; the corrected values of $K_{A(1)}$ increased with increasing temperature from 25 to 40 °C without maximum.

First Ion Association and Its Temperature Dependence. The values of $K_{A(1)}$ obtained were only slightly dependent on the assumptions for $\lambda^{\infty}(M^{3+}X^{2-})$ and a: The $K_{A(1)}$ values increased by 0.8—1.0% for a 10%-increase from $\lambda^{\infty}(M^{3+}X^{2-})=\lambda^{\infty}(M^{3+}/3)/3$ and by 0.1—0.2% for a 1 Å-increase from $a=5.43$ or 5.90 Å. As demonstrated by these examples, the following discussion is hardly affected by the uncertainties which arise from some arbitrary assumptions in the analysis.

The first ion-association constants between the complex ions and sulfate ion are significantly larger than those predicted by the ion-association theories,[3,4,13] suggesting the presence of specific short-range interactions such as hydrogen bonding. The phenomenon that the ion-association constant has a minimum at t_{min} is similar to those observed for the ion-association systems of $[Co(NH_3)_6]X_3$,[1] $[Co(en)_3]X_3$ ($X^-=Cl^-$, Br^-, I^-, $NO_3{}^-$, $ClO_4{}^-$),[2] and $M_3[Cr(ox)_3]$ ($M^+=Li^+$, Na^+, K^+, Rb^+, Cs^+; ox=oxalate ion).[19]

The appearance of t_{min} is attributed to the increase of $\Delta H^{\circ}_{as(1)}$ with increasing temperature giving $\Delta H^{\circ}_{as(1)}=0$ at t_{min}. The increasing $\Delta H^{\circ}_{as(1)}$ means that the standard heat capacity change of ion association, $\Delta C^{\circ}_{p,as(1)}$, has a positive sign: $\Delta C^{\circ}_{p,as(1)}/kJ\ K^{-1}\ mol^{-1}=0.20$ for $[Co(NH_3)_6]^{3+}$–$SO_4{}^{2-}$ and 0.19 for $[Co(en)_3]^{3+}$–$SO_4{}^{2-}$ at 25 °C. Such ion-association behavior is partly in agreement with the theoretical prediction[3,4] that $\Delta C^{\circ}_{p,as(1)}$ and p in Eq. 13 are positive in aqueous solutions at $t\geqq0°C$, but not inconsistent with the prediction $\Delta H^{\circ}_{as(1)}>0$ at $t\geqq0°C$ corresponding to $t_{min}<0°C$. The positive theoretical values of $\Delta C^{\circ}_{p,as(1)}$ and p are due to a decrease of solvent dielectric constant with increasing temperature. The negative values of $\Delta H^{\circ}_{as(1)}$ at lower temperatures suggest the presence of some exothermic interactions in addition to the endothermic one due to the long-range electrostatic force. The most probable exothermic interactions between the complex ions and sulfate ion is hydrogen bonding, because these ions have suitable groups and atoms.

Table 7. Excess Free Energy, Entropy, and Enthalpy for First Ion Association between the Complex Ions and Sulfate Ion over the Theoretical Prediction[a)]

	$[Co(NH_3)_6]^{3+}$			$[Co(en)_3]^{3+}$		
t	$\Delta G^\circ_{\mathrm{as}(1)}$(ex)	$\Delta S^\circ_{\mathrm{as}(1)}$(ex)	$\Delta H^\circ_{\mathrm{as}(1)}$(ex)	$\Delta G^\circ_{\mathrm{as}(1)}$(ex)	$\Delta S^\circ_{\mathrm{as}(1)}$(ex)	$\Delta H^\circ_{\mathrm{as}(1)}$(ex)
°C	$\mathrm{kJ\,mol^{-1}}$	$\mathrm{J\,K^{-1}\,mol^{-1}}$	$\mathrm{kJ\,mol^{-1}}$	$\mathrm{kJ\,mol^{-1}}$	$\mathrm{J\,K^{-1}\,mol^{-1}}$	$\mathrm{kJ\,mol^{-1}}$
5.0	−3.26	−5.2	−4.7	−3.53	−2.0	−4.0
15.0	−3.22	−2.4	−3.9	−3.52	0.7	−3.3
25.0	−3.21	0.8	−3.0	−3.54	3.8	−2.4
35.0	−3.24	4.6	−1.8	−3.60	7.4	−1.3
45.0	−3.30	8.8	−0.5	−3.69	11.4	−0.1

a) Values predicted by theories of Ebeling[3)] and Yokoyama–Yamatera[4)] were used as a criterion.

Table 8. Roughly Estimated Values of Excess Free Energy, Entropy, and Enthalpy for Second Ion Association between the Complex Ions and Sulfate Ion

	$[Co(NH_3)_6]^{3+}$			$[Co(en)_3]^{3+}$		
t	$\Delta G^\circ_{\mathrm{as}(2)}$(ex)	$\Delta S^\circ_{\mathrm{as}(2)}$(ex)	$\Delta H^\circ_{\mathrm{as}(2)}$(ex)	$\Delta G^\circ_{\mathrm{as}(2)}$(ex)	$\Delta S^\circ_{\mathrm{as}(2)}$(ex)	$\Delta H^\circ_{\mathrm{as}(2)}$(ex)
°C	$\mathrm{kJ\,mol^{-1}}$	$\mathrm{J\,K^{-1}\,mol^{-1}}$	$\mathrm{kJ\,mol^{-1}}$	$\mathrm{kJ\,mol^{-1}}$	$\mathrm{J\,K^{-1}\,mol^{-1}}$	$\mathrm{kJ\,mol^{-1}}$
5.0	-3.8_3	$-3._9$	−4.9	-3.6_7	$-1._0$	−4.0
15.0	-3.8_0	$-1._6$	−4.3	-3.6_8	$1._3$	−3.3
25.0	-3.8_0	$1._1$	−3.5	-3.7_0	$4._1$	−2.5
35.0	-3.8_3	$4._3$	−2.5	-3.7_6	$7._2$	−1.5
45.0	-3.8_9	$7._9$	−1.4	-3.8_5	$10._8$	−0.4

The ion association of $[Co(NH_3)_6]^{3+}$ with nitrate and perchlorate ions exhibited the minimum $K_{A(1)}$ value at a relatively high temperature such as $t_{\mathrm{min}}=38.6$ and 48.5 °C, respectively,[1)] in spite of the values of $K_{A(1)}$ not so much different from the theoretical ones.[3,4)] Although a certain t_{min} over 50 °C for $[Co(NH_3)_6]^{3+}$–SO_4^{2-} was expected by considering extremely large $K_{A(1)}$ values compared with the theoretical ones,[3—5)] the actual t_{min} was unexpectedly small, as shown in Table 4. The reason is explained in the following discussion.

Excess Thermodynamic Functions on the First Ion Association. The excess thermodynamic functions, $\Delta G^\circ_{\mathrm{as}(1)}$(ex), $\Delta S^\circ_{\mathrm{as}(1)}$(ex), and $\Delta H^\circ_{\mathrm{as}(1)}$(ex), shown in Table 7, were estimated by subtracting the theoretical values[3,4)] from the experimental ones and might be closely related to the hydrogen bonding on the ion–ion and ion–water interactions.

The hydrogen bonding between the complex ion and sulfate ion is probably performed by releasing some water molecules hydrogen bonded to the ions. The ion–ion hydrogen bonding reduces both entropy and enthalpy of the ion association, while the ion–water hydrogen bond cleavage increases them. The small negative or positive values of $\Delta S^\circ_{\mathrm{as}(1)}$(ex) and $\Delta H^\circ_{\mathrm{as}(1)}$(ex) for the hydrogen bonding system are due to the cancellation between these opposite effects. The latter effect for $\Delta H^\circ_{\mathrm{as}(1)}$(ex) prevents the appearance of the minimum $K_{A(1)}$ at high temperature and leads to small values of t_{min}, where the following temperature dependence of $\Delta H^\circ_{\mathrm{as}(1)}$(ex) is also concerned.

The $\Delta S^\circ_{\mathrm{as}(1)}$(ex) and $\Delta H^\circ_{\mathrm{as}(1)}$(ex) are found to be increased with increasing temperature, while $\Delta G^\circ_{\mathrm{as}(1)}$(ex) is little dependent on temperature, due to the compensation between $\Delta S^\circ_{\mathrm{as}(1)}$(ex) and $\Delta H^\circ_{\mathrm{as}(1)}$(ex), although $\Delta G^\circ_{\mathrm{as}(1)}$(ex) has a small maximum at a certain temperature. In spite of the usual expectation for the ion–ion hydrogen bonding to be weakened with increasing temperature, the decrease of $\Delta G^\circ_{\mathrm{as}(1)}$(ex) accompanied by the appearance of the maximum means that the release of water molecules hydrogen–bonded is rapidly promoted.

Such specific temperature dependences of $\Delta G^\circ_{\mathrm{as}(1)}$(ex), $\Delta S^\circ_{\mathrm{as}(1)}$(ex), and $\Delta H^\circ_{\mathrm{as}(1)}$(ex) can probably be attributed to the destruction of bulk water structure with increasing temperature. The water molecules released by the ion–ion hydrogen bonding are transferred into bulk water to decrease the values of $\Delta S^\circ_{\mathrm{as}(1)}$(ex) and $\Delta H^\circ_{\mathrm{as}(1)}$(ex) because of water–water interactions. This effect is reduced by the reduction of the number of water–water hydrogen bonds and the disordering of bulk water structure. The decrease of the Gibbs free energy of water to more negative with increasing temperature[20)] makes easier the transfer of the released water molecules into bulk water and leads to a smaller $\Delta G^\circ_{\mathrm{as}(1)}$(ex).

The values of $K_{A(1)}$ for $[Co(NH_3)_6]^{3+}$–SO_4^{2-} are larger than those for $[Co(en)_3]^{3+}$–SO_4^{2-}. This situation is similar to the ion association for nitrate and perchlorate ions with the complex ions.[2)] The values of $\Delta G^\circ_{\mathrm{as}(1)}$(ex) for the $[Co(en)_3]^{3+}$–SO_4^{2-} system are more negative than those for the $[Co(NH_3)_6]^{3+}$–SO_4^{2-} system. However, this relation does not necessarily mean that the hydrogen bonding is more effective in the former ion association since $\Delta G^\circ_{\mathrm{as}(1)}$(ex) includes also some free energy gain due to the relatively weak hydration of $[Co(en)_3]^{3+}$, which has the poor hydrophilic methylene group.

The free energy gain (ca. -0.7 kJ mol^{-1}) for the iodide of $[Co(en)_3]^{3+}$ was largest among those for the halides observed in the previous study.[2] This value is regarded as approximately equivalent to the excess free energy gain for the $[Co(en)_3]^{3+}$–$SO_4{}^{2-}$ system, since the free energy difference due to the direct interactions between the iodide ion and the complex ion is probably negligible. If the value of -0.7 kJ mol^{-1} is subtracted from $\Delta G^{\circ}_{as(1)}$(ex) for the $[Co(en)_3]^{3+}$–$SO_4{}^{2-}$ system, the remaining values of $\Delta G^{\circ}_{as(1)}$(ex) become less negative than those for the $[Co(NH_3)_6]^{3+}$–$SO_4{}^{2-}$ system, suggesting that the hydrogen bonding between $[Co(NH_3)_6]^{3+}$ and $SO_4{}^{2-}$ is more effective. The free energy gain for the iodide is mainly attributable to the enthalpy gain,[1,2] so the subtraction of it increases $\Delta H^{\circ}_{as(1)}$(ex) for the $[Co(en)_3]^{3+}$–$SO_4{}^{2-}$ system. Considering this point in Table 7, we can say that the stronger hydrogen bonding $[Co(NH_3)_6]^{3+}$–$SO_4{}^{2-}$ system makes $\Delta S^{\circ}_{as(1)}$(ex) and $\Delta H^{\circ}_{as(1)}$(ex) more reduced.

Excess Thermodynamic Functions on the Second Ion Association. The second ion-association constants ($K_{A(2)}$) obtained were somewhat dependent on the assumptions for $\lambda^{\infty}(M^{3+}X^{2-})$ and a: the $K_{A(2)}$ values increased by 15—17% for the $[Co(NH_3)_6]^{3+}$–$SO_4{}^{2-}$ system and by 11—14% for the $[Co(en)_3]^{3+}$–$SO_4{}^{2-}$ system for a 10%-increase from $\lambda^{\infty}(M^{3+}X^{2-})=\lambda^{\infty}(M^{3+}/3)/3$ with holding $\lambda^{\infty}(M^{3+}X^{2-}X^{2-})=\lambda^{\infty}(M^{3+}X^{2-})$; they decreased by 6—8% for a 1 Å-increase from a=5.43 or 5.90 Å. We discuss the second ion association, keeping in mind these uncertainties.

The values of $K_{A(2)}$ obtained are larger than those of ion-association constants for 1 : 2 electrolytes predicted by ion-association theories.[3,4,13] They are rather close to the theoretical values for 2 : 2 electrolytes. The $\Delta S^{\circ}_{as(2)}$ values are also larger and similar to the theoretical ones for 3 : 1 electrolytes.[3,4,13] Although these properties are mainly attributable to the ion pairs, which have large dipole moments besides their net charge, the second ion association may include also some short-range interactions because $K_{A(2)}$ has a minimum at a particular temperature, similarly to observed on the first ion association.

The theoretical equation for ion association between an ion and an ion pair having net charge and large dipole moment is not yet available. However, it may be expressed similarly to the theoretical equation of ion association,[3,4] as a function of the Bjerrum parameter (b)[4,9] given by $b=|z_+z_-|e^2/(4\pi\varepsilon kTa)$ where z_+ and z_- are charge numbers of cation and anion, respectively, and ε is dielectric constant of solvent, from the analogy to the Fuoss–Kraus[21] equation for the triple-ion formation between ion and non-charged ion pair. In order to explore the properties of the short-range interactions on the second ion association, we estimated the electrostatic contribution to the thermodynamic parameters of the second ion association by using the theoretical equation of ion association with a value of b_{12} ($z_+=1$, $z_-=-2$) multiplied by a modification factor g. We assumed g=1.5 by considering the magnitude of the experimental values of $K_{A(2)}$ and $\Delta S^{\circ}_{as(2)}$. The excess thermodynamic parameters thus obtained for the second ion association are shown as $\Delta G^{\circ}_{as(2)}$(ex), $\Delta S^{\circ}_{as(2)}$(ex), and $\Delta H^{\circ}_{as(2)}$(ex) in Table 8.

The values of $\Delta S^{\circ}_{as(2)}$(ex) and $\Delta H^{\circ}_{as(2)}$(ex) and their temperature dependence are very similar to those obtained for the first ion association, and $\Delta G^{\circ}_{as(2)}$(ex) seems to be almost independent of temperature. This similarity suggests that the dominant short-range interaction is the same as assumed for the first ion association, probably hydrogen bonding. For further discussion, the exact theoretical expression of such second ion association needs to be derived.

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