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Conductometric Study of Ion Association between Tris(oxalato)chromate(III) and Alkali Metal Ions at Temperatures from 0 to 50 °C

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(Received April 11, 1994)

Conductivities for aqueous solutions of alkali metal salts of tris(oxalato)chromate(III) ($[Cr(ox)_3]^{3-}$) were measured at various temperatures from 0 to 50 °C. Ion-association constants (K_A) between the complex ion and alkali metal ions increased in the order $Li^+ \ll Na^+ < K^+ < Rb^+ < Cs^+$ and had minimum values ($K_{A(min)}$) at characteristic temperatures (t_{min}) in the observed temperature range except for the lithium ion. The appearance of minima of K_A suggested the formation of contact ion pairs besides that of solvent-separated ones. The contact ion-pair formation was considered to be assisted by weak hydration of alkali metal ions and enhanced with decreasing their hydration strength. The lithium ion was presumed to form only solvent-separated ion pairs on the basis of extremely small ion-association constants. Temperature dependence of $\log K_A$ for each ion association could be represented by the equation: $\log K_A = p(t-t_{min})^2 + \log K_{A(min)}$. A common relationship between p and t_{min} was found out for the ion-association systems of $[Cr(ox)_3]^{3-}$, $[Co(NH_3)_6]^{3+}$, and $[Co(en)_3]^{3+}$ (en=ethylenediamine), and p was expressed by an empirical quadratic equation in t_{min}. The standard enthalpy changes of ion association (ΔH°_{as}) at any temperature for these complex systems could be reproduced within ± 0.2 kJ mol^{-1} by use of these equations with the experimental t_{min}. Hydration behavior of $[Cr(ox)_3]^{3-}$ was also discussed based on limiting molar conductivities and their temperature dependence.

Wide temperature-range conductivity measurements of electrolyte solutions can provide valuable information concerning ion–ion and ion–solvent interactions.[1—5] From the conductometric studies at temperatures between 0 and 50 °C for aqueous solutions of $[Co(NH_3)_6]X_3$ and $[Co(en)_3]X_3$ (X=Cl, Br, I, NO_3, ClO_4),[4,5] we found that the ion-association constants (K_A) between the complex ions and the monovalent anions had mostly a minimum at particular temperatures (t_{min}) which depended on combination of complex ions and the counteranion. The appearance of t_{min} was closely related to hydration strength of the ions and also to formation of contact ion pairs where hydrogen bonding was sometimes significant. Similar phenomena were observed also for potassium nitrate, potassium perchlorate, and potassium sulfate which have no interionic hydrogen bonding, and were attributed to contact ion-pair formations assisted by weak hydration of the ions.[2,3]

Conductivity measurements in aqueous solutions have been made to estimate the ion-association constants for anionic complex systems including $[Fe(CN)_6]^{3-}$,[6—8] $[Co(CN)_6]^{3-}$,[9] $[Co(ox)_3]^{3-}$,[10] $[W(CN)_8]^{3-}$,[8] $[Co(edta)]^-$ (edta=ethylenediaminetetraacetate ion),[11,12] $[Co(gly)(ox)_2]^{2-}$ (gly=glycinate ion),[13] and $[Co(mal)_2(en)]^-$ (mal=malonate ion).[14] However, no detailed information of temperature dependence of the ion associations has been given, although it is of interest in connection with the cationic complex systems described above.[1—5] In the present study, through conductivity measurements of aqueous solutions of $M_3[Cr(ox)_3]$ (M=Li, Na, K, Rb, Cs) at various temperatures between 0 and 50 °C, the ion association between $[Cr(ox)_3]^{3-}$ and alkali metal ions was investigated in order to elucidate the nature of ion association and the relation with hydration of ions in the anionic complex systems.

Experimental

Materials. Potassium tris(oxalato)chromate(III) was prepared according to the method described by Bailar and Jones[15] from potassium oxalate, oxalic acid, and potassium dichromate(2−). Lithium and sodium salts of the complex were prepared in the same manner by use of corresponding alkali metal salts instead of potassium salts. Rubidium or cesium salt of the complex was synthesized in a similar manner with rubidium or cesium carbonate, chromium(VI) oxide, and oxalic acid as starting materials which were mixed in water with a molar ratio of 3 : 1 : 4.5 for Rb^+ (or Cs^+) : Cr(VI) : $H_2C_2O_4$. All reagents used were of reagent grade; rubidium and cesium carbonates were purchased from Soekawa Chemical Co. and the other reagents from Wako Pure Chemical Industries. Each complex salt prepared was recrystallized twice from hot water and air-dried at room temperature. Numbers of water of crystallization, $n(H_2O)$, were determined by the Karl–Fischer method with an AQ-5 Aquacounter of Hiranuma Sangyo Co. through measuring the quantity of water expelled from salts by heating at 150 °C. The values of $n(H_2O)$ were 5.91, 4.93, 2.79, 2.72, and 1.88 for lithium, sodium, potassium, rubidium, and cesium salts of the complex, respectively. The densities of crystals at 25.0 °C were determined as 1.83, 1.93, 2.12, 2.57, and 2.95 g cm^{-3}, respectively, in the same manner described previously.[4] Absorption spectra of the complex salts were measured by a Hitachi 340 spectrophotometer and average values of molar extinction coefficients at two major absorption maxima in the visible region were 75.9±0.2 mol^{-1} dm^3 cm^{-1} (λ=570 nm) and 96.5±0.3 mol^{-1} dm^3 cm^{-1} (λ=420 nm).

Solutions. Preparation of conductivity solutions and determination of molar concentrations were carried out in the same manner as described previously.[4,5,14] Density measurements of solutions were made at 25 °C by using a vibrating-tube SS-D-200 densimeter of the Shibayama Scientific

Co.[16)] Ten solutions of concentration from 0.0002 to 0.0010 $mol\,dm^{-3}$ were examined.

Conductivity Measurements. Conductivity measurements were made at 1 kHz with a Fuso 360 linear-bridge conductometer in the manner described previously[4,5,12)] at temperatures of 5 °C interval between 0 and 50 °C. Cell Constant of the conductivity cell used was 0.1371 cm^{-1} at 25 °C and its change with temperature was regarded as −0.0014% for elevation of 1 °C.[2)] The resistance values were calibrated by use of a precision decade resistance box (Dekabox DB62, Electro Scientific Industries; accuracy ±0.02%). Precision of the temperature measurements was ±0.003 °C and accuracy of the temperature was ±0.01 °C.

Results

Observed molar conductivities, $\Lambda(M_3A/3)$, where M^+ is the alkali metal ion and A^{3-} is the complex ion, were deposited as Tables S-1, S-2, and S-3[17)] together with molalities (m) and molar concentrations (c) of solutions. The conductivity data were analyzed in a similar manner to that described previously,[3—5)] assuming the following ion-pair formation:

$$M^+ + [Cr(ox)_3]^{3-} \rightleftharpoons M^+[Cr(ox)_3]^{3-}, \qquad (1)$$

where the triple-ion formation was regarded to be negligible in dilute solutions investigated. The equilibrium constant (K_A, the ion-association constant) for Eq. 1 is given by

$$K_A = (1-\alpha)y_{MA}/[(2+\alpha)c\alpha y_M y_A], \qquad (2)$$

where c is molar concentration of the salt; α is fraction of free complex ion, and y_M, y_A, and y_{MA} are activity coefficients of M^+, A^{3-}, and M^+A^{3-}, respectively, which were represented by the Debye–Hückel equation. Molar conductivity of the salt can be expressed by

$$\Lambda(M_3A/3) = \alpha\Lambda_F(M_3A/3) + 2(1-\alpha)\Lambda_F\{M_2(MA)/2\}/3, \qquad (3)$$

where $\Lambda_F(M_3A/3)$ and $\Lambda_F\{M_2(MA)/2]$ correspond to molar conductivities of hypothetical unassociated 1:3 and 1:2 electrolytes, respectively, and were expressed by the Robinson–Stokes equation.[3,4,18)] Limiting molar conductivities of alkali metal ions, $\lambda^\infty(M^+)$, at a given temperature (t in °C) were estimated from

$$\lambda^\infty(M^+) = \lambda^\infty(25°C) + a(t-25) + b(t-25)^2 + c(t-25)^3, \quad (4)$$

where $\lambda^\infty(25\ °C)$, a, b, and c are constants, dependent on the ions, of which values are given in Table 1. The limiting molar conductivity of the ion pair, $\lambda^\infty(M^+A^{3-}/2)$, was assumed to be equal to 2/3 of that of the complex ion, $\lambda^\infty(A^{3-}/3)$, according to previous studies.[4,5)] For the effect of this assumption on the results, the previous paper[4)] should be referred to. Values of $\lambda^\infty(A^{3-}/3)$ can be experimentally determined by the analyses of the conductivity data.

The closest distance of approach of ions (a) in the theoretical equations of Robinson–Stokes and Debye–Hückel is difficult to be experimentally determined. In the present study, assuming that cations and anions could approach into contact to each other, the values of a were regarded as 4.4, 4.7, 5.1, 5.2, and 5.4 Å for lithium, sodium, potassium, rubidium, and cesium salts of the complex, respectively, equal to the sums of the ionic radii estimated from Shannon–Prewitt's radii[20)] and the effective ionic radius of $[Cr(ox)_3]^{3-}$ (3.7_1 Å) derived by use of Glueckauf's equation[16,21)] from the partial molar volume (V_i^∞) of the complex ion by regarding the complex ion as a spherical one. Shannon–Prewitt's radii[20)] of Na^+, K^+, Rb^+, and Cs^+ were taken as 1.02, 1.38, 1.49, and 1.70 Å, respectively, by regarding their coordination numbers as six and that of Li^+ was taken as 0.67 Å by considering its four or six coordination number.

For a given value of a, a calculation was performed in order to determine the values of K_A and $\lambda^\infty(A^{3-}/3)$ by a least-squares procedure minimizing $\sigma(=[\sum\{\Lambda(\text{obsd})-\Lambda(\text{calcd})\}^2/(n-2)]^{1/2})$. The values of dielectric constant and viscosity (η_0) of water used were taken from the same literature described previously.[4,5)] The ion-association constants (K_A) obtained for each salt are summarized in Table 2 together with prediction for K_A based on the electrostatic theories of ion association.[22—24)] Average values of $\lambda^\infty(A^{3-}/3)$ derived are listed in Table 3.

The $\log K_A$ values obtained are plotted against temperature (t) in Fig. 1 where the minimum is found in each salt except lithium salt. The temperature dependence of $\log K_A$ was represented by the following quadratic equation in t:

$$\log K_A = p(t - t_{\min})^2 + \log K_{A(\min)}, \qquad (5)$$

where $\log K_{A(\min)}$ is the minimum value of $\log K_A$, $t_{\min}$ is the temperature giving $\log K_{A(\min)}$, and p corresponds to the curvature of a parabola; their values are summarized in Table 4. As shown with solid lines in Fig. 1, $\log K_A$ values can be well reproduced by Eq. 5 with these parameter values. The following equations for the standard entropy and enthalpy changes of ion association, ΔS°_{as} and ΔH°_{as}, can be derived from Eq. 5.

$$\Delta S_{as}{}^\circ = 2.303R\{\log K_{A(\min)} + p(3t - t_{\min} + 546.3)(t - t_{\min})\}, \qquad (6)$$

$$\Delta H_{as}{}^\circ = 4.605pR(t + 273.15)^2(t - t_{\min}). \qquad (7)$$

The values of ΔS°_{as} and ΔH°_{as} at several temperatures obtained by use of Eqs. 6 and 7 are given in Tables 5 and 6 together with their uncertainties and with the theoretical values.[25)]

Discussion

Ion Association of $[Cr(ox)_3]^{3-}$ with Alkali Metal Ions. The ion-association constants shown in Table 2 or in Fig. 1 seem to increase in the order $Li^+ \ll Na^+ < K^+ < Rb^+ < Cs^+$ at a given temperature,

Table 1. Parameter Values in Eq. 4 for Limiting Molar Conductivities of Ions, $\lambda^{\infty}(\mathrm{M}^+)$ and $\lambda^{\infty}(\mathrm{A}^{3-}/3)$[a)]

Ion	λ^{∞}(25°C)	a	$b\times10^3$	$c\times10^5$	Ref.
	$\mathrm{S\,cm^2\,mol^{-1}}$	$\mathrm{S\,cm^2\,mol^{-1}\,K^{-1}}$	$\mathrm{S\,cm^2\,mol^{-1}\,K^{-2}}$	$\mathrm{S\,cm^2\,mol^{-1}\,K^{-3}}$	
$\mathrm{Li^+}$	38.64	0.8899	4.408	−2.04	19
$\mathrm{Na^+}$	50.15	1.0916	4.715	−1.15	19
$\mathrm{K^+}$	73.50	1.4326	4.056	−3.18	19
$\mathrm{Rb^+}$	77.81	1.4795	3.840	−4.53	19
$\mathrm{Cs^+}$	77.26	1.4479	3.825	−2.05	19
$[\mathrm{Cr(ox)_3}]^{3-}$	80.98	1.7636	6.951	−1.28	This work

a) Equation 4 was used also to express the temperature dependence of $\lambda^{\infty}(\mathrm{A}^{3-}/3)$.

Table 2. Ion-Association Constants (K_A) between $[\mathrm{Cr(ox)_3}]^{3-}$ and Alkali Metal Ions[a)]

t	$K_\mathrm{A}/\mathrm{dm^3\,mol^{-1}}$					Theoretical K_A[c)]	
°C	M=Li[b)]	M=Na	M=K	M=Rb	M=Cs	E-Y-Y[d)]	Bjerrum[e)]
0.0	7.2±3.0(16.5±2.9)	35.4±2.7	40.3±4.1	43.1±4.5	46.8±1.5	36.3—26.8	49.4—36.2
5.0	7.2±3.0(16.6±2.9)	34.7±2.8	39.0±4.1	41.5±4.4	45.1±1.4	37.1—27.3	50.5—37.0
10.0	7.4±2.9(17.0±2.8)	33.7±2.6	38.1±4.0	40.7±4.4	44.0±1.4	38.0—27.9	51.6—37.8
15.0	7.6±2.9(17.3±2.8)	33.6±2.7	37.7±4.0	39.9±4.5	43.0±1.4	38.9—28.6	52.9—38.7
20.0	7.9±2.9(17.7±2.9)	32.9±2.7	37.5±4.0	39.2±4.5	42.4±1.4	39.9—29.3	54.2—39.7
25.0	8.3±2.9(18.2±2.9)	32.6±2.7	37.2±4.0	38.8±4.5	41.9±1.4	41.0—30.0	55.7—40.8
30.0	8.5±2.8(18.7±2.8)	32.6±2.7	37.2±4.0	38.7±4.5	41.6±1.5	42.2—30.8	57.2—42.0
35.0	9.1±2.8(19.4±2.8)	32.6±2.7	37.6±4.0	38.6±4.4	41.4±1.4	43.5—31.7	58.9—43.2
40.0	9.6±2.7(20.1±2.6)	32.9±2.8	37.7±4.0	38.6±4.4	41.5±1.4	44.9—32.7	60.7—44.5
45.0	10.2±2.6(20.9±2.5)	33.2±2.8	38.1±4.0	38.9±4.5	41.8±1.5	46.3—33.7	62.6—45.9
50.0	10.8±2.5(21.7±2.4)	33.6±2.8	38.5±4.0	39.2±4.6	42.2±1.6	47.9—34.7	64.6—47.4

a) The values of a were assumed to be 4.4, 4.7, 5.1, 5.2, and 5.4 Å for lithium, sodium, potassium, rubidium, and cesium salts, respectively. b) The values in parentheses were obtained by assuming a=7.2 Å. c) Calculated by assuming a=4.4—5.4 Å. d) Theories of Ebeling[22)] and Yokohama and Yamatera.[23)] e) Ref. 24.

Table 3. Average Values of Limiting Molar Conductivities of $[\mathrm{Cr(ox)_3}]^{3-}$, $\lambda^{\infty}(\mathrm{A}^{3-}/3)$[a)]

t	$\lambda^{\infty}(\mathrm{A}^{3-}/3)$
°C	$\mathrm{S\,cm^2\,mol^{-1}}$
0.0	41.44±0.36
5.0	48.59±0.34
10.0	56.12±0.35
15.0	64.05±0.38
20.0	72.35±0.44
25.0	80.98±0.50
30.0	89.98±0.57
35.0	99.30±0.62
40.0	108.94±0.67
45.0	118.93±0.69
50.0	129.22±0.68

a) The values of $\lambda^{\infty}(\mathrm{A}^{3-}/3)$ obtained for each system were deposited as Tables S-4.[17)]

Table 4. Values of Parameters in Eq. 5 Representing the Temperature Dependence of Ion-Association Constants between $[\mathrm{Cr(ox)_3}]^{3-}$ and Alkali Metal Ions

Alkaline metal ion	$\mathrm{p}\times10^5$	t_min	$\log K_{\mathrm{A(min)}}$
	$\mathrm{K^{-2}}$	°C	
$\mathrm{Li^+}$	4.99±0.46	−12.5±3.5	0.843±0.006
	(2.59±0.20	−22.4±3.7	1.202±0.004)[a)]
$\mathrm{Na^+}$	3.76±0.23	31.1±0.4	1.513±0.001
$\mathrm{K^+}$	3.82±0.30	28.8±0.3	1.570±0.001
$\mathrm{Rb^+}$	3.88±0.18	34.9±0.5	1.586±0.001
$\mathrm{Cs^+}$	4.11±0.12	35.5±0.3	1.617±0.001

a) Obtained by assuming a=7.2 Å.

although the orders between the adjacent metal ions except $\mathrm{Li^+}$ are not necessarily obvious since their K_A values are close to each other within the experimental error. This order is opposite to the prediction by ion-association theories[22—24)] that K_A decreases with increasing a, but in agreement with the order of increase of the standard Gibbs free energy of hydration ($\Delta G^\circ_\mathrm{hy}$) for alkali metal ions: −481, −375, −304, −281, and −258 kJ mol^{-1} at 25 °C for $\mathrm{Li^+}$, $\mathrm{Na^+}$, $\mathrm{K^+}$, $\mathrm{Rb^+}$, and $\mathrm{Cs^+}$, respectively.[26)] This means that the ion association is enhanced with weakening hydration strength of alkali metal ions.

The extremely weak ion association between $\mathrm{Li^+}$ and $[\mathrm{Cr(ox)_3}]^{3-}$ as revealed in Fig. 1 is attributable to strong hydration of $\mathrm{Li^+}$. Significantly small values of K_A compared with the theoretical ones[22—24)] suggest that contact ion pair are not formed between these ions. Then the value of a taken as 4.4 Å for $\mathrm{Li^+}$–$[\mathrm{Cr(ox)_3}]^{3-}$ may not be appropriate since this distance was estimated

Table 5. Standard Entropies of the Ion Association in Aqueous Solution, ΔS°_{as}, at Several Temperatures

t	$\Delta S_{as}{}^{\circ}/\mathrm{J\,K^{-1}\,mol^{-1}}$					Theoretical values[b)]	
°C	M=Li[a)]	M=Na	M=K	M=Rb	M=Cs	E-Y-Y[c)]	Bjerrum[d)]
5.0	25.7±3.7(30.9±1.6)	19.0±1.8	20.8±2.4	18.7±1.4	18.4±1.0	40.3—37.3	42.6—40.2
15.0	32.0±1.9(34.4±0.9)	22.5±1.0	24.4±1.2	22.2±0.8	22.0±0.5	42.5—39.2	44.7—42.2
25.0	38.8±1.3(38.1±0.6)	26.4±0.7	28.4±0.9	26.1±0.5	26.1±0.4	44.6—41.3	46.8—44.3
35.0	46.2±2.1(42.1±0.9)	30.7±1.0	32.9±1.3	30.4±0.8	30.7±0.6	46.9—43.4	48.9—46.4
45.0	54.2±4.2(46.5±1.8)	35.5±2.1	37.8±2.7	35.2±1.6	35.8±1.1	49.2—45.5	51.1—48.5

a) Values in parentheses were derived from the K_A values obtained by assuming $a=7.2$ Å. b) Calculated by assuming $a=4.4$—5.4 Å. c) Theories of Ebeling[22)] and Yokohama and Yamatera.[23)] d) Ref. 24.

Table 6. Standard Enthalpies of the Ion Association in Aqueous Solution, ΔH°_{as}, at Several Temperatures

t	$\Delta H_{as}{}^{\circ}/\mathrm{kJ\,mol^{-1}}$					Theoretical values[b)]	
°C	M=Li[a)]	M=Na	M=K	M=Rb	M=Cs	E-Y-Y[c)]	Bjerrum[d)]
5.0	2.6±1.0(2.1±0.5)	−2.9±0.5	−2.7±0.6	−3.4±0.4	−3.7±0.3	2.86—2.72	2.79—2.83
15.0	4.4±0.6(3.1±0.2)	−1.9±0.3	−1.7±0.4	−2.4±0.2	−2.7±0.2	3.46—3.28	3.37—3.40
25.0	6.4±0.4(4.2±0.2)	−0.8±0.2	−0.5±0.3	−1.3±0.2	−1.5±0.1	4.10—3.88	3.98—4.00
35.0	8.6±0.6(5.4±0.3)	0.5±0.3	0.9±0.4	0.0±0.2	−0.1±0.2	4.77—4.51	4.62—4.64
45.0	11.1±1.3(6.7±0.6)	2.0±0.7	2.4±0.8	1.5±0.5	1.5±0.4	5.50—5.18	5.31—5.30

a) Values in parentheses were derived from the K_A values obtained by assuming $a=7.2$ Å. b) Calculated by assuming $a=4.4$—5.4 Å. c) Theories of Ebeling[22)] and Yokohama and Yamatera.[23)] d) Ref. 24.

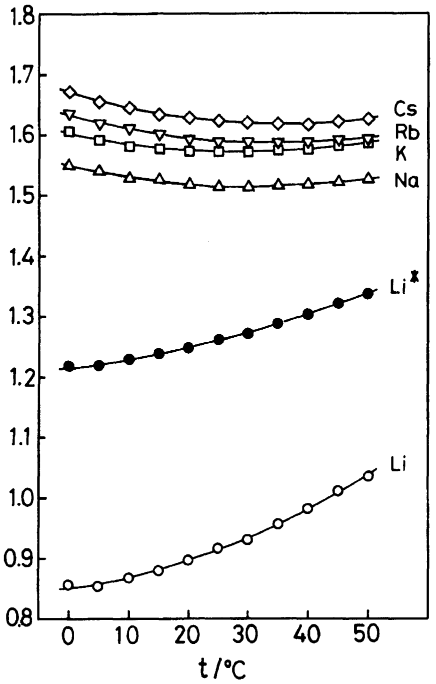

Fig. 1. Temperature dependence of the ion-association constants for the M^+–$[Cr(ox)_3]^{3-}$ system; M=Li(○), Na(△), K(□), Rb(▽), and Cs(◇); Li*(●) denotes the values obtained with $a=7.2$ Å. The solid lines were obtained by Eq. 5 with the parameter values given in Table 4.

by assuming that the ions could approach into contact to each other. For this reason, we reanalyzed the conductivity data with an assumption of $a=7.2$ Å which was obtained by adding the diameter of water molecule (2.8 Å) to 4.4 Å, supposing that only solvent-separated ion pairs interposing one or more water molecules between Li^+ and $[Cr(ox)_3]^{3-}$ were formed in solution. The results are shown with parentheses in Table 2 and in Fig. 1. The K_A values obtained are close to the theoretical ones: 18.5 (0 °C), 20.6 (25 °C), and 23.7 (50 °C) $dm^3\,mol^{-1}$ for $a=7.2$ Å.[22,23)] This agreement implies that the above assumption is reasonable and no specific interaction is included in their ion association. The other parameter values derived on this assumption are shown with parentheses in Tables 4, 5, and 6.

The temperature dependence having minima of K_A except for Li^+ can not be explained by the simple ion-association theories,[22—24)] although the K_A values are roughly similar to the theoretical ones shown in Table 2. Such a temperature dependence has been previously found in aqueous solutions of KNO_3,[2)] $KClO_4$,[2)] K_2SO_4,[3)] $[Co(NH_3)_6]X_3$,[4)] and $[Co(en)_3]X_3$[5)] where X represents monovalent ions. The appearance of a minimum of K_A was usually explained by contact ion-pair formation assisted by weak hydration or structure-breaking effect of the ions. The minima of K_A observed for M^+–$[Cr(ox)_3]^{3-}$ systems may also concern with such properties of alkali metal ions. Potassium, rubidium, and cesium ions are regarded as structure breakers of which efficiency may increase with decreasing temperature because water has higher structure at lower temperature. Then, the structure-breaking effect is presumed to enhance the ion association with decreasing temperature.

The feature of temperature dependence of K_A and the values of K_A for M^+–$[Cr(ox)_3]^{3-}$ (M=K, Rb, Cs) are similar to those observed for $[Co(NH_3)_6]^{3+}$–I^-: K_A

(25 °C)=38 $\mathrm{dm^3\,mol^{-1}}$ and t_{min}=25.9°C (a=5.3 Å).[4,5] This similarity may be due to the fact that the values of a and $\Delta G^\circ_{\mathrm{hy}}$ of counterions of the complex ions are similar between both systems, where $\Delta G^\circ_{\mathrm{hy}}$ (25 °C) of $\mathrm{I^-}$ is equal to −283 $\mathrm{kJ\,mol^{-1}}$ close to that of $\mathrm{Rb^+}$,[26] suggesting the presence of contact ion pairs between $\mathrm{M^+}$ and $\mathrm{[Cr(ox)_3]^{3-}}$ because $\mathrm{[Co(NH_3)_6]^{3+}}$ and $\mathrm{I^-}$ has been confirmed to form contact ion pairs besides solvent-separated ones through spectrophotometric measurements for visible-ultraviolet spectra.[27] Contact ion-pair formation sometimes causes new absorption band or shift of charge transfer band of the complex. However, the ion association between alkali metal ions and $\mathrm{[Cr(ox)_3]^{3-}}$ gives no absorption spectrum change. This situation is similar to that for visible-ultraviolet spectra of $\mathrm{[Co(NH_3)_6]\,(ClO_4)_3}$ in aqueous solution[28] although the ion-association constants between $\mathrm{[Co(NH_3)_6]^{3+}}$ and $\mathrm{ClO_4^-}$ obtained by conductivity measurements can not be sufficiently explained without assuming contact ion-pairs formation.[4] From these consideration and the extreme difference of the ion-association behavior of $\mathrm{K^+}$, $\mathrm{Rb^+}$, and $\mathrm{Cs^+}$ from that of $\mathrm{Li^+}$, these alkali metal ions are supposed to form contact ion pairs with $\mathrm{[Cr(ox)_3]^{3-}}$ besides solvent-separated ones.

The sodium ion is more strongly hydrated than $\mathrm{K^+}$, $\mathrm{Rb^+}$, and $\mathrm{Cs^+}$ and is a borderline ion between structure maker and breaker in aqueous solution. Its ion-association behavior against $\mathrm{[Cr(ox)_3]^{3-}}$ is similar to that of $\mathrm{K^+}$ rather than $\mathrm{Li^+}$, although the experimental values of K_A are somewhat smaller than those predicted by the ion-association theories[22,23] on the assumption of the contact distance for a (4.7 Å). If a=7.5 Å including the diameter of water molecule is assumed for $\mathrm{Na^+}$–$\mathrm{[Cr(ox)_3]^{3-}}$, experimental K_A values are increased by about 9 $\mathrm{dm^3\,mol^{-1}}$, while the theoretical values[22,23] decrease to $K_\mathrm{A}/\mathrm{dm^3\,mol^{-1}}$=17.6 (0 °C), 19.7 (25 °C), and 22.6 (50 °C) which are about half the experimental ones. The minimum of K_A was still appeared at 26.2 °C although shifted to slightly lower temperature. These results imply that the ion-association behavior of $\mathrm{Na^+}$ can not be explained by the ion-association theories similarly to that of $\mathrm{K^+}$, $\mathrm{Rb^+}$, and $\mathrm{Cs^+}$ and suggest that contact ion pairs are also formed, opposing relatively strong hydration of $\mathrm{Na^+}$.

Generally, the standard entropy and enthalpy of ion association ($\Delta S^\circ_{\mathrm{as}}$ and $\Delta H^\circ_{\mathrm{as}}$) as predicted by the ion-association theories[22—24] are expected to be increased with decreasing standard hydration entropy and enthalpy of ions ($\Delta S^\circ_{\mathrm{hy}}$ and $\Delta H^\circ_{\mathrm{hy}}$). However, the values of $\Delta S^\circ_{\mathrm{as}}$ or $\Delta H^\circ_{\mathrm{as}}$ are similar to one another between $\mathrm{Na^+}$, $\mathrm{K^+}$, $\mathrm{Rb^+}$, and $\mathrm{Cs^+}$. Especially the values of $\Delta S^\circ_{\mathrm{as}}$ and $\Delta H^\circ_{\mathrm{as}}$ for $\mathrm{Na^+}$ are thought to be significantly small if we consider $\Delta S^\circ_{\mathrm{hy}}/\mathrm{J\,K^{-1}\,mol^{-1}}$= −107.3 ($\mathrm{Na^+}$), −67.1 ($\mathrm{K^+}$), −60.4 ($\mathrm{Rb^+}$), −53.7 ($\mathrm{Cs^+}$), and $\Delta H^\circ_{\mathrm{hy}}/\mathrm{kJ\,mol^{-1}}$=−407 ($\mathrm{Na^+}$), −324 ($\mathrm{K^+}$), −299 ($\mathrm{Rb^+}$), −274 ($\mathrm{Cs^+}$) at 25 °C.[26] This suggests the position of $\mathrm{Na^+}$ within the contact ion pairs to be considerably restricted. The values of $\Delta S^\circ_{\mathrm{as}}$ and $\Delta H^\circ_{\mathrm{as}}$ at 25 °C for $\mathrm{M^+}$–$\mathrm{[Cr(ox)_3]^{3-}}$ (M=K, Rb, Cs) are somewhat smaller than those for $\mathrm{[Co(NH_3)_6]^{3+}}$–$\mathrm{I^-}$ ($\Delta S^\circ_{\mathrm{as}}$= 29.9±0.4 $\mathrm{J\,K^{-1}\,mol^{-1}}$ and $\Delta H^\circ_{\mathrm{as}}$=−0.1±0.1 $\mathrm{kJ\,mol^{-1}}$), although iodide ion has $\Delta S^\circ_{\mathrm{hy}}$=−57.0 $\mathrm{J\,K^{-1}\,mol^{-1}}$ and $\Delta H^\circ_{\mathrm{hy}}$=−300 $\mathrm{kJ\,mol^{-1}}$ comparable to those of $\mathrm{Rb^+}$ or $\mathrm{Cs^+}$,[26] Therefore, the contact ion pairs of $\mathrm{K^+}$, $\mathrm{Rb^+}$, and $\mathrm{Cs^+}$ with $\mathrm{[Cr(ox)_3]^{3-}}$ may be more sterically restricted than that of $\mathrm{[Co(NH_3)_6]^{3+}}$–$\mathrm{I^-}$.

From X-ray diffraction measurements of 0.57 $\mathrm{mol\,dm^{-3}}$ solutions of $\mathrm{Cs_3[Rh(ox)_3]}$ and $\mathrm{Cs_3[Cr(ox)_3]}$ with isomorphous substitution between Rh(III) and Cr(III), two kinds of cesium ions were found to exist at positions of 4.0 and 6.5 Å from central metal atoms with the number of about 0.2 and 1.0, respectively.[29] These cesium ions were presumed to be in contact with coordinated oxygen atoms and non-coordinated ones of the oxalato ligands, respectively, where especially the latter contact ion pair had a bridge structure with interposing an oxalato ligand.[29] The X-ray diffraction study[29] supports the above explanations of the thermodynamic parameters obtained by present conductivity measurements.

The ion-association constant for $\mathrm{NH_4^+}$–$\mathrm{[Co(ox)_3]^{3-}}$ has been obtained through conductivity measurements by Tanaka and Koseki as log K_A=1.5$_3$ at 25 °C,[10] comparable to those for the present $\mathrm{[Cr(ox)_3]^{3-}}$ systems. This similarity may be attributed to the fact that $\mathrm{NH_4^+}$ has $\Delta G^\circ_{\mathrm{hy}}$ (25 °C)=−292 $\mathrm{kJ\,mol^{-1}}$ close to those of $\mathrm{K^+}$ and $\mathrm{Rb^+}$.[26] By polarographic measurements at 25 °C, Tanaka and Koseki also obtained log K_A=1.9$_4$ for $\mathrm{Na^+}$–$\mathrm{[Co(ox)_3]^{3-}}$,[10] somewhat larger than that for $\mathrm{Na^+}$–$\mathrm{[Cr(ox)_3]^{3-}}$. It is not obvious which the difference is due to that in the experimental methods.

The increase of K_A with decreasing hydration strength of metal ions has been also observed on the following ion associations: $\mathrm{M^+}$–$\mathrm{NO_3^-}$ ($\mathrm{Na^+<K^+<Cs^+}$),[2] $\mathrm{M^+}$–$\mathrm{ClO_4^-}$ ($\mathrm{K^+<Rb^+<Cs^+}$),[2] $\mathrm{M^+}$–$\mathrm{[W(CN)_8]^{3-}}$ ($\mathrm{Na^+<K^+<Rb^+<Cs^+}$),[8] $\mathrm{M^{2+}}$–$\mathrm{[Fe(CN)_6]^{3-}}$ and $\mathrm{M^{2+}}$–$\mathrm{[Co(ox)_3]^{3-}}$ ($\mathrm{Mg^{2+}<Ca^{2+}<Sr^{2+}<Ba^{2+}}$).[7,10] The ion association for $\mathrm{M^{2+}}$–$\mathrm{[Co(ox)_3]^{3-}}$ was investigated through polarographic measurements by Tanaka and Koseki;[10] the order at ionic strength 0.1 was not clear. They regarded the ion pairs formed as only solvent-separated ones because of no detectable change in visible, ultraviolet, and infrared absorption spectra; the absorption maximum at 1389 $\mathrm{cm^{-1}}$ for $\mathrm{[Co(ox)_3]^{3-}}$ was not changed by adding the divalent metal ions in aqueous potassium salt solution although the maximum in solid state depended on the counter metal ions[10] Carefulness is required for such a comparison, since oxalato ligands of the complex ion in solid state may be differently distorted dependent on crystal form, metal ion size, and number of water of crystallization; the complex ion is usually surrounded by counterions more than their average number because of sharing between adjacent complex ions. However, in the ion as-

Table 7. Partial Molar Volume (V_i^∞), Effective Ionic Radius (r_{ef}),[a] Temperature Coefficient of Walden Product ($d\ \ln(\lambda^\infty\eta_0)/dT$) at 25 °C, and Stokes Radius (r_s) at 0, 25, 50 °C for the Complex Ions at Infinite Dilution

Complex ion	$V_i^\infty/\mathrm{cm^3\,mol^{-1}}$	r_{ef}/Å	r_s/Å			$d\ \ln(\lambda^\infty\eta_0)/dT/\mathrm{K^{-1}}$	Ref.
			0°C	25°C	50°C		
$[Cr(ox)_3]^{3-}$	135.9±2.6	3.71	3.32	3.41	3.48	-1.01×10^{-3}	This work
$[Co(NH_3)_6]^{3+}$	55.9±0.9	3.10	2.61	2.78	2.89	-1.95×10^{-3}	4
$[Co(en)_3]^{3+}$	116.0±0.4	3.57	3.70	3.73	3.75	-0.20×10^{-3}	5[b]

a) Estimated from V_i^∞ by use of Glueckauf's equation.[21] b) Ref. 30.

sociation of $[Co(ox)_3]^{3-}$ with Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}, ion pairs formed may be mostly solvent-separated ones, considering their strong hydration having large negative hydration free energies ($\Delta G^\circ_{hy}/\mathrm{kJ\,mol^{-1}}$) of −1838 ($Mg^{2+}$) to −1258 ($Ba^{2+}$)[26] at 25 °C and a large Bjerrum's critical distance of ion association (21.4 Å for 2 : 3 electrolytes in water at 25 °C).[24]

Empirical Rules between ΔH°_{as} and t_{min} and between p and t_{min}. Temperature dependence of $\log K_A$ for M^+–$[Cr(ox)_3]^{3-}$ could be expressed by using Eq. 5 with positive p values of the order of 10^{-5} K^{-2} similarly to observed previously.[2—5] The values of ΔH°_{as} (25 °C) for the $[Co(NH_3)_6]^{3+}$ and $[Co(en)_3]^{3+}$ systems could be reproduced by a quadratic equation in t_{min}, suggesting the presence of correlation between t_{min} and p in Eq. 5.[5] Then, the p values obtained in the present study were plotted against t_{min}, compared with the cationic complex systems in Fig. 2, where for Li^+–$[Cr(ox)_3]^{3-}$ the result of a=7.2 Å was used since that of a=4.4 Å gave a large deviation. A relationship seems to exist between p and t_{min}, regardless of different complex systems. The solid line in Fig. 2 represents p values calculated with the following equation derived by a least squares calculation:

$$p = 2.63\times10^{-5} + 1.75\times10^{-7}t_{min} + 5.52\times10^{-9}t_{min}^{\ 2}. \quad (8)$$

Although the reproduction for p by Eq. 8 was not necessarily sufficient, most of experimental ΔH°_{as} values obtained for the above complex systems could be reproduced within ±0.2 $\mathrm{kJ\,mol^{-1}}$ from Eqs. 7 and 8 with experimental t_{min} values. Figure 3 demonstrates an agreement between the experimental values of ΔH°_{as} (25 °C) and the calculated ones represented as a solid line. Equations 7 and 8 also could give good approximations for ΔH°_{as} of ion association of K^+–NO_3^-,[2] K^+–ClO_4^-,[2] and K^+–SO_4^{2-}:[3] t_{min}/°C=29.9±1.0, 35.6±0.4, 6.4±3.7, and ΔH°_{as} (25 °C)/$\mathrm{kJ\,mol^{-1}}$ = −0.5±0.5, −1.8±0.2,

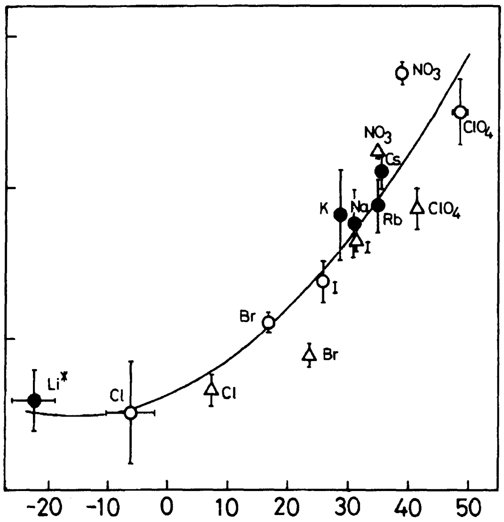

Fig. 2. Correlation of p with t_{min} for the ion-association systems: M^+–$[Cr(ox)_3]^{3-}$ (●; M=Li, Na, K, Rb, and Cs), $[Co(NH_3)_6]^{3+}$–X^- (○; X=Cl, Br, I, NO_3, and ClO_4),[4] and $[Co(en)_3]^{3+}$–X^- (△; X=Cl, Br, I, NO_3, and ClO_4);[5] Li*(●) denotes the value obtained with a=7.2 Å. The solid line was drawn by use of Eq. 8.

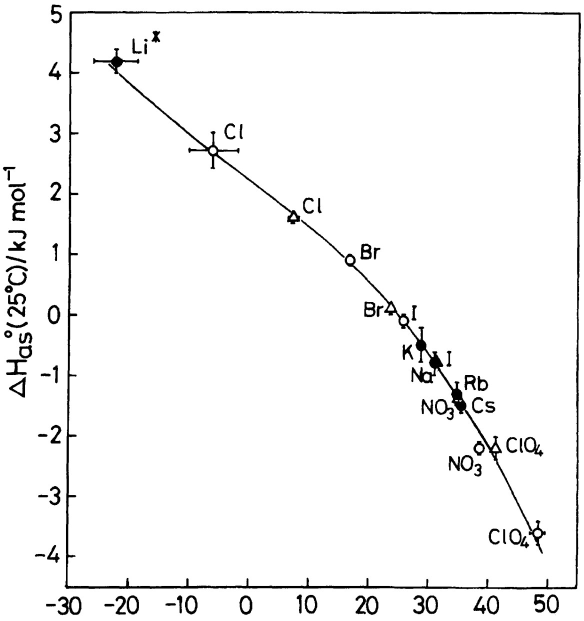

Fig. 3. Correlation of ΔH°_{as} (25 °C) with t_{min} for the ion-association systems: M^+–$[Cr(ox)_3]^{3-}$ (●; M=Li, Na, K, Rb, and Cs), $[Co(NH_3)_6]^{3+}$–X^- (○; X=Cl, Br, I, NO_3, and ClO_4),[4] and $[Co(en)_3]^{3+}$–X^- (△; X=Cl, Br, I, NO_3, and ClO_4);[5] Li*(●) denotes the value obtained with a = 7.2 Å. The solid line was drawn by using Eqs. 7 and 8 as a function of t_{min}.

2.4±0.7, respectively.

As described previously,[5] if we know the values of $\Delta H^\circ_{\mathrm{as}}$ and K_A at 25 °C for similar ion association, we can estimate the values of $t_{\min}$ by Fig. 3, p by Eq. 8, $\log K_{\mathrm{A(min)}}$ and $\log K_\mathrm{A}$ at other temperatures by Eq. 5, and $\Delta H^\circ_{\mathrm{as}}$ and $\Delta S^\circ_{\mathrm{as}}$ at any temperature by Eqs. 6 and 7, successively.

Limiting Molar Conductivities of the Complex Ion and Their Temperature Dependence. Average values of limiting molar conductivities of the complex ion, $\lambda^\infty(\mathrm{A}^{3-}/3)$, given in Table 2 could be expressed with a reproducibility within ±0.02 $\mathrm{S\,cm^2\,mol^{-1}}$ by the same quadratic equation as Eq. 4 in which parameter values were summarized in Table 1. In Table 7, the Stokes radius (r_s) and the temperature coefficient of the Walden product ($\mathrm{d}\ln(\lambda^\infty\eta_0)/\mathrm{d}T$) derived from the values of $\lambda^\infty(\mathrm{A}^{3-}/3)$ are shown together with the partial molar volume (V_i^∞) and the effective ionic radius (r_ef) for $[\mathrm{Cr(ox)_3}]^{3-}$, compared with those for $[\mathrm{Co(NH_3)_6}]^{3+}$ and $[\mathrm{Co(en)_3}]^{3+}$.

The $[\mathrm{Cr(ox)_3}]^{3-}$ ion has smaller r_s than r_ef and negative $\mathrm{d}\ln(\lambda^\infty\eta_0)/\mathrm{d}T$. This implies that this complex ion is a weak structure breaker or a borderline ion because the value of $\mathrm{d}\ln(\lambda^\infty\eta_0)/\mathrm{d}T$ is almost equal to that of sodium ion ($-1.01\times10^{-3}\ \mathrm{K^{-1}}$).[31] From these comparisons the hydration behavior of $[\mathrm{Cr(ox)_3}]^{3-}$ is rather similar to that of $[\mathrm{Co(NH_3)_6}]^{3+}$ than $[\mathrm{Co(en)_3}]^{3+}$. The different hydration behavior of $[\mathrm{Co(en)_3}]^{3+}$ is presumed to be mainly due to the presence of hydrophobic methylene groups having no direct interaction with water molecules.

Absolute Values of the Thermodynamic Parameters of Ion Association. The thermodynamic parameters obtained in the present study are not necessarily absolute since many assumptions are included in the conductivity equation and the values of a and Λ^∞ ($\mathrm{M^+A^{3-}}/2$). If different assumptions are made, the values of the thermodynamic parameters may be somewhat changed. However, the relative relationships between the ions about the ion-association constants and their temperature dependence are considered to be not much affected. The discussion in the present study would therefore not be essentially changed since it has been made based mainly on relative comparisons of the results. More detailed discussion related to these problems has been made in a previous paper.[4]

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31) Derived from Eq. 4 by use of the parameter values given in Table 1.