November, 1992] © *1992 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, ***65***, *2901—2909 (1992)* 2901

Conductometric Study of Ion Association between Tris(ethylenediamine)cobalt(III) Ion and Monovalent Anions at Temperatures from 0 to 50 °C

Haruhiko Yokoyama,* Tomoko Ohta, and Masayasu Iida[†]
Department of Chemistry, Yokohama City University,
Seto, Kanazawa-ku, Yokohama 236
[†] Department of Chemistry, Faculty of Science, Nara Women's University,
Kita-uoya-nishi-machi, Nara 630

(Received June 8, 1992)

The conductivities for aqueous solutions of the chloride, bromide, iodide, nitrate, and perchlorate of the tris(ethylendiamine)cobalt(III) complex, $[Co(en_3)]^{3+}$, were measured with varying temperatures from 0 to 50 °C. The ion-association constants (K_A) of the complex ion with the anions had minimum values at temperatures (t_{min}) characteristic of the salts. The values of t_{min} increased in the order $Cl^- < Br^- < I^- < NO_3^- < ClO_4^-$. The order in magnitude of K_A at 25 °C was $ClO_4^- < NO_3^- < I^- < Cl^- < Br^-$, but was somewhat dependent on the temperature. Both the K_A and t_{min} values for the halides of $[Co(en)_3]^{3+}$ were larger than those of the hexaamminecobalt(III) complex, $[Co(NH_3)_6]^{3+}$; the difference in K_A was greatest for the iodide. The entropy and enthalpy changes in the ion association of $[Co(en)_3]^{3+}$ with the halide ions were smaller than those of $[Co(NH_3)_6]^{3+}$. These results suggested that the hydration of $[Co(en)_3]^{3+}$ was relatively weak and its hydration water molecules in the vicinity of the methylene groups could be more easily substituted by the structure-breaker anions, compared with the water molecules around the amino groups. The K_A and t_{min} values for the nitrate and perchlorate of $[Co(en)_3]^{3+}$ were smaller than those of $[Co(NH_3)_6]^{3+}$, and both the entropy and enthalpy changes of ion association for the former salts were more positive. This was attributed to the decrease in the fraction of the contact ion pairs formed by the hydrogen bonding between the polar hydrogen atoms of the complexes and the oxygen atoms of the anions.

Conductivity measurements over a wide temperature range for electrolyte solutions can provide detailed information concerning ion–ion and ion–solvent interactions, especially from the thermodynamic viewpoint.[1–5] From a conductometric study at temperatures between 0 and 50 °C for aqueous solutions of $[Co(NH_3)_6]X_3$ (X=Cl, Br, I, NO_3, ClO_4)[5] we found that the ion-association constants (K_A) between the complex ion and the monovalent anions had minimum values at t_{min}; the values of t_{min} increased in the order $Cl^- < Br^- < I^- < NO_3^- < ClO_4^-$ and were correlated with standard entropy and enthalpy changes for the ion associations at a given temperatures. The presence of t_{min} for the halides could be explained as being due to the weak hydrations of the anions. The remarkable increases in the K_A values with decreasing temperatures for the nitrate and perchlorate, as well as the relatively small entropy and enthalpy changes compared with those of the halides, were ascribed to specific short-range interactions, such as hydrogen bonding, between the ammine hydrogen atoms of the complex and the oxygen atoms of the anions in the contact ion pairs.

To confirm the validity of the above interpretations and to investigate the dependence of the ion-association behavior on the properties of the complex ions, we studied the ion association of the tris(ethylenediamine)cobalt(III) complex ion with monovalent anions by measuring the conductivities of aqueous solutions of $[Co(en)_3]X_3$ (X=Cl, Br, I, NO_3, ClO_4). Although many studies concerning the outer-sphere interactions between the $[Co(en)_3]^{3+}$ complex and various anions have been carried out using various methods,[6–12] there is no detailed information concerning their thermodynamics. The $[Co(en)_3]^{3+}$ complex has two kinds of groups with different characteristics: One is the hydrophilic amino groups; the other is the hydrophobic methylene group. The amino group is presumed to contribute to the contact ion-pair formation, in analogy with the ammine ligand of the $[Co(NH_3)_6]^{3+}$ complex; the methylene group behaves differently. Exact conductivity measurements over a wide temperature range for the $[Co(en)_3]X_3$ systems are expected to provide useful information concerning the ion–ion and ion–solvent interactions which take place in the outer sphere of the complex ion, especially from a thermodynamic point of view.

Experimental

Materials. Tris(ethylenediamine)cobalt(III) chloride was prepared as described in the literature[13] and recrystallized twice from water. The nitrate of the complex was prepared in a similar manner from cobalt(II) nitrate hexahydrate. The bromide, iodide, and perchlorate were obtained by adding aqueous solutions of hydrobromic acid, potassium iodide, and perchloric acid, respectively, into solutions of the chloride; they were then reprecipitated. All of the salts were recrystallized one or two times from water. An analysis of the anions in the complex salts was made using ion-chromatography with a Shimadzu HIC-6A; the absence of the chloride ion in perchlorate was also ascertained by adding silver nitrate. All of the reagents used were of reagent grade (Wako · Pure Chemical Industries). Preparation of the bromide and the iodide was made in a dark room. The obtained complex salts were air-dried and the number of water of crystallization ($n(H_2O)$) was determined by both the Karl-Fischer method (with an AQ-5 Aquacounter of Hiranuma Sangyo Co.) and the use of an Abderhalden dryer; $n(H_2O)$ were 3.31, 3.30, 1.00, 0.00_9, 0.00_2 for the chloride, bromide, iodide, nitrate, and perchlorate, respectively. The densities of the crystals at 25.0 °C were determined in the manner described previously[5] as being 1.51, 1.90, 2.35, 1.72, and 1.87 g cm^{-3} for the chloride, bromide, iodide, nitrate, and perchlorate, respectively. The average value of the molar extinction coefficients of the complex salts at λ_{max}=466 nm observed using a Hitachi 340 spectrophotometer were 88.2±0.3 mol^{-1} dm^3 cm^{-1}. The molar conductivity of the complex ion derived from each salt (as described later) was in agreement with each other within ±0.1%.

Solutions. All solutions were made by weight just before carrying out conductivity measurements. Corrections for the buoyancy by air were made with weighed values for salts and water. The conductivity of water[2] used for the solutions was always lower than 1×10^{-7} S cm^{-1} at 25 °C after dissolved carbon dioxide was removed.[5] The molar solution concentrations were calculated by using their estimated densities while assuming at each temperature the same increment with concentration as those observed at 25 °C (as described previously[5]). Density measurements of solutions at 25 °C were carried out using a vibrating-tube SS-D-200 twin-type densimeter of Shibayama Scientific Co.[14] The density of water at each temperature was obtained from an experimental equation given by Kell.[15] The molalities (m) and molar concentrations (c) of the solutions are given in Tables 1 and 2, respectively.

Conductivity Measurements. The conductivity measuremets were made at 1 kHz with a Fuso 360 linear-bridge conductometer in the manner described previously[1,5] at 11 temperatures between 0 and 50 °C. Throughout the measurements the solutions of the bromide and the iodide were protected from light. The cell constant used was 0.13720 cm^{-1} at 25 °C; its change with temperature was corrected by using −0.0014% for an elevation of 1 °C. The resistance values were calibrated using a precision decade resistance box (Dekabox DB62, Elecro Scientific Industries; accuracy ±0.02%). The precision of the temperature measurements was ±0.003 °C and the accuracy of the temperature was ±0.01 °C.

Results

Table 3 lists the observed molar conductivities of the complex salts ($\Lambda(\mathrm{MX_3}/3)$, where M^{3+} is the complex ion and X^- is the anion). The analysis was carried out in the same manner as described previously,[5] assuming the following ion-pair formation:

$$[\mathrm{Co(en)_3}]^{3+} + \mathrm{X}^- \rightleftharpoons [\mathrm{Co(en)_3}]^{3+}\mathrm{X}^-, \qquad (1)$$

where triple-ion formation was regarded as being negligible in the dilute solutions investigated. The equilibrium constant (K_{A}, the ion-association constant) for Eq. 1 is given by

Table 1. Molalities of $[\mathrm{Co(en)_3}]\mathrm{X_3}$ Solutions Used for Conductivity Measurements

Solution No.	$m/10^{-4}$ mol kg^{-1}				
	X=Cl	X=Br	X=I	X=NO$_3$	X=ClO$_4$
1	1.9681	1.9513	1.9663	1.9630	1.9651
2	2.5608	2.5571	2.5595	2.5501	2.5633
3	3.2448	3.2402	3.2452	3.2453	3.2470
4	4.0096	4.0006	4.0070	4.0098	4.0110
5	4.8461	4.8328	4.8497	4.8521	4.8469
6	5.7723	5.7575	5.7538	5.7766	5.7636
7	6.7718	6.7562	6.7623	6.7652	6.7694
8	7.8470	7.8292	7.8630	7.8214	7.8770
9	9.0043	8.9951	9.0043	9.0097	9.0147
10	10.0551	10.1709	10.2742	10.5309	10.2451

Table 2. Molar Concentrations of the $[\mathrm{Co(en)_3}]\mathrm{X_3}$ Solutions Used for Conductivity Measurements[a)]

Solution No.	c (25.0 °C)/10^{-4} mol dm^{-3}				
	X=Cl	X=Br	X=I	X=NO$_3$	X=ClO$_4$
1	1.9622	1.9455	1.9604	1.9571	1.9592
2	2.5531	2.5494	2.5518	2.5424	2.5556
3	3.2350	3.2304	3.2354	3.2355	3.2371
4	3.9975	3.9885	3.9948	3.9976	3.9987
5	4.8314	4.8181	4.8348	4.8373	4.8320
6	5.7546	5.7398	5.7360	5.7588	5.7457
7	6.7510	6.7353	6.7412	6.7442	6.7482
8	7.8227	7.8048	7.8383	7.7970	7.8521
9	8.9762	8.9669	8.9758	8.9813	8.9859
10	10.0235	10.1387	10.2413	10.4974	10.2121

a) Molar concentrations at 25.0 °C, c (25.0 °C), are shown; those at the other temperatures (t/°C) are given by $c(t)=c(25.0\,°\mathrm{C})f(t)$, where $f(t)$=1.00280(0.0 °C), 1.00293(5.0 °C), 1.00266(10.0 °C), 1.00206(15.0 °C), 1.00116(20.0 °C), 0.99860(30.0 °C), 0.99698(35.0 °C), 0.99516(40.0 °C), 0.99315(45.0 °C), and 0.99096(50.0 °C).

Table 3A. Molar Conductivities of [Co(en)$_3$]Cl$_3$ in Aqueous Solutions

Solution No.	Λ (MX$_3$/3)/S cm^2 mol^{-1} at temperature/°C										
	0.0	5.0	10.0	15.0	20.0	25.0	30.0	35.0	40.0	45.0	50.0
1	74.21	86.53	99.55	113.24	127.51	142.35	157.76	173.66	190.05	206.91	224.16
2	73.55	85.77	98.65	112.20	126.35	141.05	156.30	172.04	188.23	204.91	221.97
3	72.96	85.08	97.86	111.28	125.30	139.87	154.97	170.56	186.62	203.14	220.01
4	72.29	84.28	96.94	110.22	124.09	138.50	153.46	168.88	184.76	201.09	217.81
5	71.65	83.55	96.07	109.24	122.98	137.25	152.06	167.33	183.04	199.22	215.78
6	71.05	82.82	95.25	108.29	121.91	136.06	150.72	165.84	181.40	197.38	213.72
7	70.47	82.16	94.48	107.41	120.91	134.93	149.46	164.44	179.85	195.68	211.87
8	69.83	81.40	93.60	106.41	119.78	133.65	148.04	162.85	178.10	193.75	209.76
9	69.25	80.72	92.82	105.51	118.76	132.51	146.76	161.44	176.54	192.05	207.89
10	68.75	80.14	92.15	104.75	117.90	131.54	145.67	160.24	175.20	190.56	206.25

Table 3B. Molar Conductivities of [Co(en)$_3$]Br$_3$ in Aqueous Solutions

Solution No.	Λ (MX$_3$/3)/S cm^2 mol^{-1} at temperature/°C										
	0.0	5.0	10.0	15.0	20.0	25.0	30.0	35.0	40.0	45.0	50.0
1	75.73	88.13	101.18	114.88	129.17	144.02	159.42	175.30	191.64	208.45	225.65
2	75.22	87.53	100.50	114.10	128.30	143.04	158.31	174.06	190.25	206.90	223.94
3	74.30	86.46	99.27	112.69	126.71	141.25	156.30	171.83	187.82	204.26	221.06
4	73.73	85.82	98.52	111.84	125.73	140.15	155.10	170.51	186.35	202.65	219.31
5	73.25	85.23	97.83	111.06	124.86	139.17	154.00	169.29	185.01	201.16	217.69
6	72.59	84.44	96.93	110.03	123.70	137.87	152.55	167.69	183.24	199.22	215.57
7	71.81	83.55	95.91	108.86	122.39	136.41	150.93	165.88	181.27	197.06	213.19
8	71.35	83.01	95.29	108.16	121.58	135.50	149.92	164.76	180.03	195.69	211.72
9	70.56	82.08	94.21	106.95	120.21	133.97	148.21	162.87	177.96	193.44	209.25
10	69.88	81.30	93.33	105.93	119.07	132.69	146.78	161.31	176.23	191.54	207.19

Table 3C. Molar Conductivities of [Co(en)$_3$]I$_3$ in Aqueous Solutions

Solution No.	Λ (MX$_3$/3)/S cm^2 mol^{-1} at temperature/°C										
	0.0	5.0	10.0	15.0	20.0	25.0	30.0	35.0	40.0	45.0	50.0
1	75.37	87.66	100.63	114.23	128.42	143.16	158.46	174.22	190.45	207.12	224.23
2	74.69	86.88	99.71	113.19	127.25	141.85	156.98	172.85	188.61	205.10	221.99
3	74.11	86.21	98.94	112.31	126.27	140.74	155.73	171.21	187.14	203.49	220.23
4	73.48	85.47	98.09	111.34	125.15	139.49	154.35	169.66	185.41	201.57	218.12
5	72.86	84.75	97.24	110.38	124.07	138.28	153.00	168.18	183.79	199.81	216.20
6	72.24	84.00	96.41	109.42	123.00	137.08	151.67	166.71	182.17	198.04	214.27
7	71.61	83.29	95.59	108.48	121.94	135.90	150.35	165.23	180.56	196.26	212.34
8	71.00	82.58	94.77	107.56	120.90	134.73	149.07	163.83	179.01	194.57	210.49
9	70.40	81.88	93.98	106.66	119.88	133.60	147.80	162.43	177.47	192.90	208.66
10	69.75	81.12	93.11	105.67	118.78	132.36	146.44	160.93	175.83	191.11	206.73

Table 3D. Molar Conductivities of [Co(en)$_3$](NO$_3$)$_3$ in Aqueous Solutions

Solution No.	Λ (MX$_3$/3)/S cm^2 mol^{-1} at temperature/°C										
	0.0	5.0	10.0	15.0	20.0	25.0	30.0	35.0	40.0	45.0	50.0
1	73.13	84.91	97.33	110.34	123.92	138.01	152.62	167.68	183.18	199.12	215.45
2	72.52	84.20	96.50	109.41	122.87	136.84	151.32	166.24	181.57	197.35	213.49
3	71.91	83.50	95.70	108.49	121.83	135.67	149.99	164.78	179.99	195.61	211.60
4	71.26	82.74	94.83	107.51	120.71	134.41	148.61	163.24	178.30	193.77	209.59
5	70.67	82.05	94.04	106.59	119.69	133.27	147.35	161.85	176.76	192.07	207.74
6	70.06	81.34	93.23	105.67	118.66	132.12	146.07	160.44	175.21	190.37	205.88
7	69.45	80.64	92.42	104.77	117.64	130.98	144.81	159.04	173.68	188.70	204.05
8	68.85	79.95	91.63	103.86	116.62	129.85	143.54	157.65	172.14	187.02	202.22
9	68.24	79.24	90.81	102.94	115.58	128.68	142.25	156.22	170.57	185.31	200.37
10	67.53	78.42	89.88	101.88	114.39	127.35	140.77	154.59	168.79	183.35	198.22

Table 3E. Molar Conductivities of $[Co(en)_3](ClO_4)_3$ in Aqueous Solutions

Solution No.	Λ $(MX_3/3)$/S cm^2 mol^{-1} at temperature/°C										
	0.0	5.0	10.0	15.0	20.0	25.0	30.0	35.0	40.0	45.0	50.0
1	70.22	81.73	93.87	106.64	119.96	133.80	148.16	162.98	178.24	193.93	210.01
2	69.67	81.09	93.14	105.80	119.02	132.75	146.99	161.69	176.82	192.34	208.26
3	69.07	80.40	92.35	104.90	118.00	131.61	145.71	160.27	175.25	190.64	206.40
4	68.53	79.77	91.63	104.07	117.07	130.55	144.54	158.97	173.83	189.08	204.71
5	67.96	79.11	90.86	103.19	116.08	129.45	143.33	157.63	172.35	187.46	202.94
6	67.41	78.46	90.11	102.35	115.13	128.39	142.15	156.33	170.93	185.92	201.26
7	66.83	77.78	89.34	101.47	114.13	127.28	140.91	154.96	169.42	184.26	199.43
8	66.29	77.16	88.63	100.63	113.22	126.26	139.77	153.71	168.03	182.75	197.85
9	65.73	76.52	87.89	99.82	112.28	125.21	138.61	152.41	166.62	181.21	196.11
10	65.16	75.85	87.13	98.97	111.31	124.13	137.42	151.12	165.20	179.63	194.41

Table 4. Ion-Association Constants (K_A) between $[Co(en)_3]^{3+}$ and Anions and Limiting Molar Conductivities of $[Co(en)_3]^{3+}$, λ^∞ $(M^{3+}/3)$

t	λ^∞ $(M^{3+}/3)$[a]	K_A/dm^3 mol^{-1}					Theoretical K_A values[b]	
°C	S cm^2 mol^{-1}	X=Cl	X=Br	X=I	X=NO$_3$	X=ClO$_4$	E-Y-Y[c]	Bjerrum[d]
0.0	37.21±0.05	53.2±1.2	60.4±4.3	53.9±1.0	52.7±0.6	42.6±0.7	26.9—23.9	36.4—31.6
5.0	43.74±0.03	53.0±1.1	59.7±4.2	52.6±1.0	51.1±0.5	41.0±0.7	27.5—24.4	37.2—32.3
10.0	50.71±0.05	53.0±1.2	59.0±4.2	51.6±1.1	49.7±0.5	39.8±0.7	28.1—24.9	38.1—33.0
15.0	58.13±0.06	53.4±1.3	58.6±4.2	50.7±1.1	48.6±0.5	39.1±0.6	28.7—25.5	39.0—33.8
20.0	65.94±0.07	53.5±1.3	58.2±4.3	50.2±1.1	47.9±0.5	38.0±0.6	29.4—26.1	40.0—34.7
25.0	74.12±0.07	54.0±1.3	58.2±4.3	49.8±1.1	47.3±0.5	37.4±0.6	30.2—26.8	41.0—35.7
30.0	82.66±0.08	54.7±1.3	58.4±4.4	49.7±1.2	47.0±0.5	36.9±0.6	31.0—27.5	42.2—36.7
35.0	91.53±0.09	55.5±1.3	58.8±4.4	49.8±1.2	46.9±0.5	36.6±0.6	31.9—28.3	43.4—37.8
40.0	100.71±0.09	56.5±1.4	59.3±4.3	49.9±1.4	47.0±0.6	36.6±0.6	32.8—29.1	44.7—39.0
45.0	110.21±0.09	58.0±1.3	60.1±4.3	50.3±1.5	47.4±0.6	36.6±0.6	33.8—30.0	46.2—40.2
50.0	119.99±0.13	59.3±1.3	60.9±4.3	51.2±1.7	47.9±0.6	36.8±0.7	34.9—30.9	47.7—41.6

a) Average values of λ^∞ $(M^{3+}/3)$ obtained from each system. b) Calculated by assuming a=5.38—5.87 Å. c) Theories of Ebeling[21] and Yokoyama and Yamatera.[22] d) Ref. 23.

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

where c is the molar concentration of the salt; α is the fraction of the free complex ion; and y_M, y_X, and y_{MX} are the activity coefficients of M^{3+}, X^-, and $M^{3+}X^-$, respectively, represented by the Debye–Hückel equation. The molar conductivity of the salt can be expressed by

$$\Lambda(MX_3/3) = \alpha\Lambda_F(MX_3/3) + 2(1-\alpha)\Lambda_F\{(MX)X_2/2\}/3, \qquad (3)$$

where $\Lambda_F(MX_3/3)$ and $\Lambda_F\{(MX)X_2/2\}$ correspond to the molar conductivities of hypothetical unassociated 3 : 1 and 2 : 1 electrolytes, respectively, and were expressed by the Robinson–Stokes equation.[16] The limiting molar conductivity of the anions, λ^∞ (X^-), at a given temperature (t in °C) was estimated from

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

where λ^∞ (25 °C), a, b, and c are constants which depend on the ions and were taken from the literature.[2,5,17] The limiting molar conductivity of the ion pairs, λ^∞ $(M^{3+}X^-/2)$, was assumed to be equal to 2/3 of that of the complex ion, λ^∞ $(M^{3+}/3)$, according to previous studies.[5-8] The values of λ^∞ $(M^{3+}/3)$ can be experimentally determined by analyzing the conductivity data.

The values of the closest distance of approach of ions (a) in the theoretical equations of Robinson–Stokes and Debye–Hückel were assumed to be equal to the sums of the radii of the complex ion and the anions: 5.38, 5.52, 5.73, 5.62, and 5.87 Å for chloride, bromide, iodide, nitrate, and perchlorate, respectively. These values were calculated using Pauling's radii of Cl^- (1.81 Å), Br^- (1.95 Å), and I^- (2.16 Å) and the effective radii of NO_3^- (2.05 Å),[2] ClO_4^- (2.30 Å),[2] and $[Co(en)_3]^{3+}$ (3.57 Å) derived from their partial molar volumes using Glueckauf's equation;[14,18] the average value of the partial molar volume of the complex ion at infinite dilution was estimated to be 116.0±0.4 cm^3 mol^{-1} at 25 °C through density measurements of the conductivity solutions.

For a given value of a, a calculation was made in order to determine the values of K_A and λ^∞ $(M^{3+}/3)$ by a least-squares method in which σ $(=\{\sum[\Lambda(\text{obsd})-\Lambda(\text{calcd})]^2/(n-2)\}^{1/2})$ is minimized, as described previously.[1] The values of dielectric constant and viscosity (η_0) of water used for the calculation were taken from the literature.[19,20] The ion-association constants (K_A) observed for each salt are summarized in Table 4 together with predictions based on the electrostatic theories of ion association[21–23] and the average values of λ^{∞} ($M^{3+}/3$).

The following ion-association constants at 25 °C have been given in the literature[6–8] and are smaller than those shown in Table 4: K_A (25 °C)/dm^3 mol^{-1}=53[6] or 28[8] (X=Cl), 48[7] or 28[8] (X=Br), 29 (X=I),[7] 19 (X=NO_3),[8] and 23[7] or 14[8] (X=ClO_4). The differences are mainly attributed to the use of the Onsager limiting equation in these studies. If the limiting equation is used to analyze the present conductivity data, we also obtain smaller K_A values: K_A(25 °C)/dm^3 mol^{-1}=34±2 (X=Cl), 38±5 (X=Br), 28±2 (X=I), 25±2 (X=NO_3), and 14±1 (X=ClO_4). The Onsager limiting equation does not include the ion-size parameter (a) and gives relatively small molar conductivities compared to those determined using extended conductivity equations. Although the Robinson–Stokes equation is not necessarily the best extended equation for unsymmetrical electrolytes, it could well reproduce the experimental conductivities of 1 : 1 electrolytes, giving reasonable a values similar to those obtained using the Fuoss–Onsager equation for symmetrical electrolytes.[16] Since our previous studies[4,5] concerning unsymmetrical electrolytes such as K_2SO_4 or $[Co(NH_3)_6]X_3$ were also carried out using the Robinson–Stokes equation, the present results can be directly compared with their results.

The log K_A values obtained in the present study are plotted vs. temperature (t) in Fig. 1, where the minimum is found in each salt. Their temperature dependence can be expressed 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 5. As shown by the solid lines in Fig. 1, the log K_A values can be well reproduced by Eq. 5 using these parameter values. Equation 5 was also used to derive the standard entropy and enthalpy changes for ion

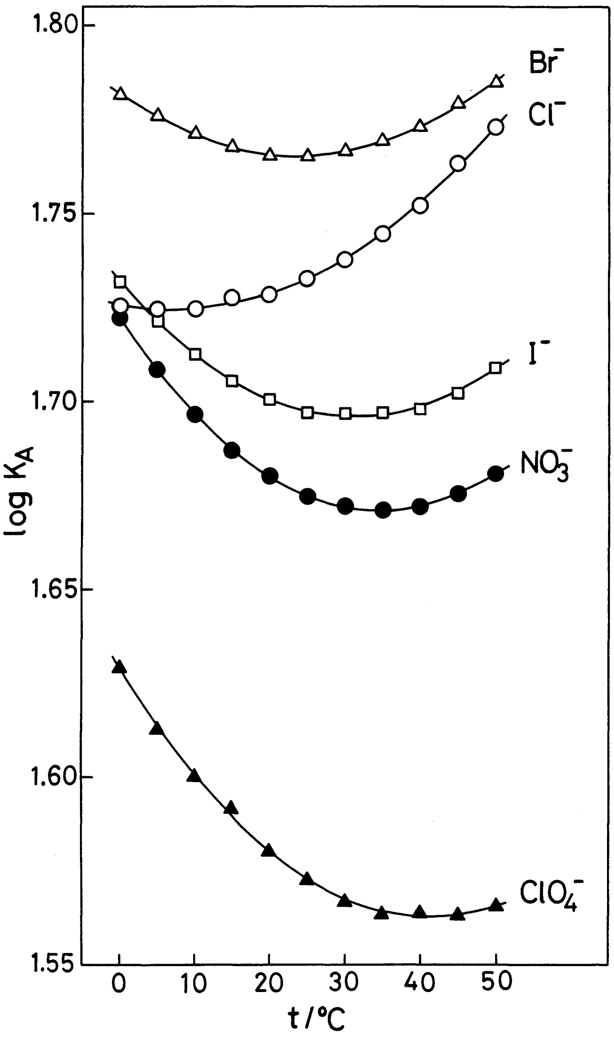

Fig. 1. Temperature dependence of the ion-association constants between $[Co(en)_3]^{3+}$ and the monovalent anions; the chloride (○), bromide (△), iodide (□), nitrate (●), and perchlorate (▲).

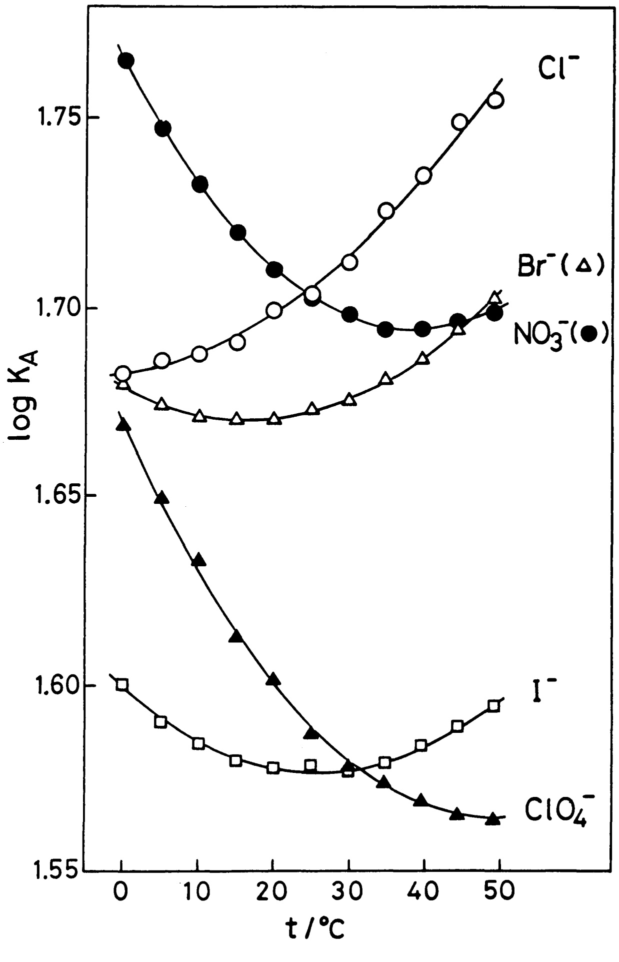

Fig. 2. Temperature dependence of the ion-association constants between $[Co(NH_3)_6]^{3+}$ and the monovalent anions; the chloride (○), bromide (△), iodide (□), nitrate (●), and perchlorate (▲); quoted from Ref. 5.

Table 5. Values of Parameters in Eq. 5 Representing the Temperature Dependence of Ion-Association Constants between $[Co(en)_3]^{3+}$ and Anions

Anion	$p\times10^5$	t_{min}	$\log K_{A(min)}$
	K^{-2}	°C	
Cl^-	2.66±0.11	7.3±0.8	1.724±0.001
Br^-	2.89±0.08	23.7±0.1	1.765±0.001
I^-	3.64±0.07	31.4±0.2	1.696±0.001
NO_3^-	4.24±0.04	34.7±0.1	1.671±0.001
ClO_4^-	3.86±0.14	41.4±0.6	1.563±0.001

association in an aqueous solution, ΔS_{as}° (aq) and ΔH_{as}° (aq):

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

and

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

The values of ΔS_{as}° (aq) and ΔH_{as}° (aq) at several temperatures are given in Tables 6 and 7 with uncertainties, and are compared with their theoretical values.[24]

Discussion

Ion Association of $[Co(en)_3]^{3+}$ with the Halide Ions. The ion-association constants between $[Co(NH_3)_6]^{3+}$ and the monovalent anions previously reported[5] are given as a plot of $\log K_A$ vs. t in Fig. 2. The $\log K_A$ values at any temperature for the halides of $[Co(en)_3]^{3+}$ (Fig. 1) are larger than those of $[Co(NH_3)_6]^{3+}$, in spite of $[Co(en)_3]^{3+}$ having a relatively large effective ionic radius, r_{ef}=3.57 Å, compared with r_{ef}=3.10 Å of $[Co(NH_3)_6]^{3+}$. The differences in $\log K_A$ become remarkable in the order chloride<bromide<iodide and are increased as the temperature is decreased. These phenomena are related to the increase in t_{min} and to the following orders in magnitude of $\log K_A$ for the $[Co(en)_3]^{3+}$ system: $Br^- > I^- \approx Cl^-$ at 0 °C, $Br^- > Cl^- > I^-$ at 25 °C; $Cl^- \approx Br^- > I^-$ at 50 °C, which are different from those for the $[Co(NH_3)_6]^{3+}$ system. However, by considering the parameter values given in Table 5, the order at temperatures higher than 70 °C is presumed to be $Cl^- > Br^- > I^-$, which is consistent with that in the $[Co(NH_3)_6]^{3+}$ system and with a prediction based on the ionic sizes of the anions through the electrostatic theories of ion association.[21-23]

The order in magnitude of ΔS_{as}° (aq) and ΔH_{as}° (aq) is iodide<bromide<chloride at any temperature. Both values of ΔS_{as}° (aq) and ΔH_{as}° (aq) are smaller than their theoretical values and the differences are increased with decreasing temperature. The negative values of ΔH_{as}° (aq) at temperatures lower than t_{min} cannot be interpreted by the ion-association theories.[21-24] The appearance of such ΔH_{as}° (aq) for the bromide and iodide of $[Co(NH_3)_6]^{3+}$ has been attributed to the structure-breaking effect of the anions.[5] For the $[Co(en)_3]^{3+}$ system this explanation is also effective, but not sufficient, because the differences in $\log K_A$ between these two complexes depend on the anions.

In order to interpret the thermodynamics of ion

Table 6. Standard Entropies of the Ion Association in Aqueous Solutions, ΔS_{as}°(aq), at Several Temperatures

t	ΔS_{as}°(aq)/J K^{-1} mol^{-1}					Theoretical values[a)]	
°C	X=Cl	X=Br	X=I	X=NO_3	X=ClO_4	E-Y-Y[b)]	Bjerrum[c)]
5.0	32.4±0.9	28.2±0.6	22.7±0.6	19.3±0.3	15.9±1.1	37.3—36.2	40.2—39.3
15.0	35.3±0.5	31.1±0.4	26.1±0.4	23.1±0.2	19.2±0.6	39.3—38.1	42.3—41.4
25.0	38.5±0.4	34.2±0.3	29.9±0.3	27.4±0.2	22.9±0.4	41.3—40.1	44.3—43.5
35.0	42.1±0.5	37.7±0.4	34.0±0.4	32.1±0.2	27.1±0.7	43.4—42.2	46.4—45.6
45.0	46.0±1.0	41.5±0.7	38.7±0.7	37.4±0.4	31.6±1.3	45.6—44.3	48.5—47.7

a) Calculated by assuming a=5.38—5.87 Å. b) Theories of Ebeling[21] and Yokoyama and Yamatera.[22] c) Ref. 23.

Table 7. Standard Enthalpies of the Ion Association in Aqueous Solutions, ΔH_{as}°(aq), at Several Temperatures

t	ΔH_{as}°(aq)/kJ mol^{-1}					Theoretical values[a)]	
°C	X=Cl	X=Br	X=I	X=NO_3	X=ClO_4	E-Y-Y[b)]	Bjerrum[c)]
5.0	−0.2±0.3	−1.6±0.2	−2.8±0.2	−3.7±0.1	−4.2±0.3	2.72—2.67	2.83—2.91
15.0	0.6±0.2	−0.8±0.1	−1.9±0.1	−2.7±0.1	−3.2±0.2	3.28—3.23	3.40—3.49
25.0	1.6±0.1	0.1±0.1	−0.8±0.1	−1.4±0.1	−2.2±0.2	3.88—3.81	4.00—4.10
35.0	2.7±0.2	1.2±0.1	0.5±0.1	−0.0±0.1	−0.9±0.2	4.51—4.43	4.63—4.74
45.0	3.9±0.4	2.4±0.3	1.9±0.2	1.7±0.2	0.5±0.5	5.19—5.09	5.30—5.40

a) Calculated by assuming a=5.38—5.87 Å. b) Theories of Ebeling[21] and Yokoyama and Yamatera.[22] c) Ref. 23.

association it is convenient to divide it into the following hypothetical steps demonstrated previously:[5)]

$$\begin{tikzcd}
M^{3+}\,(gas) + X^-\,(gas) \arrow[r, "\text{Step 2}"] & M^{3+}X^-\,(gas) \arrow[d, "\text{Step 3}"] \\
M^{3+}\,(aq) + X^-\,(aq) \arrow[u, "\text{Step 1}"] \arrow[r] & M^{3+}X^-\,(aq)
\end{tikzcd}$$

The first step is to transfer the free ions from an aqueous solution to the gas phase (dehydration process); the second step involves the ion-association process in the gas phase; the third step is to transfer the ion pair from gas phase into water (hydration process). Therefore, $\Delta G_{as}°$ (aq), $\Delta S_{as}°$ (aq), and $\Delta H_{as}°$ (aq) for ion association in an aqueous solution are generally given by

$$\begin{aligned}\Delta Y_{as}°\ (aq) &= \Delta Y_{hy}°\ (M^{3+}X^-) - \Delta Y_{hy}°\ (M^{3+}) \\ &\quad - \Delta Y_{hy}°\ (X^-) + \Delta Y_{as}°\ (gas),\end{aligned} \tag{8}$$

where $\Delta Y°$ is a generalized expression for $\Delta G°$, $\Delta S°$, and $\Delta H°$; the subscript (hy) refers to the hydration and $\Delta Y_{as}°$ (gas) denotes the parameters for ion association in the gas phase. Both $\Delta Y_{hy}°$ for each ionic species and $\Delta Y_{as}°$ (gas) for the ion association between opposite charge ions are negative quantities.

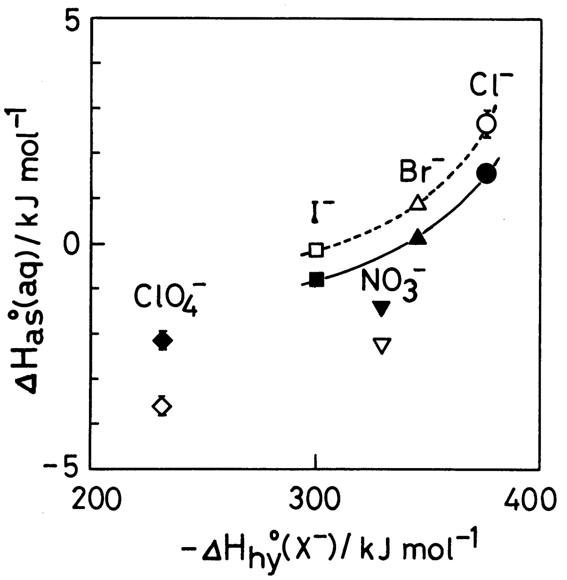

Fig. 4. Relationship between $\Delta H_{as}°$ (aq) and $-\Delta H_{hy}°$ (X^-) at 25 °C for the $[Co(en)_3]^{3+}$ (solid symbols) and $[Co(NH_3)_6]^{3+}$ (open symbols)[5)] systems; the solid line is drawn for the halides of $[Co(en)_3]^{3+}$ and the dashed line for those of $[Co(NH_3)_6]^{3+}$.

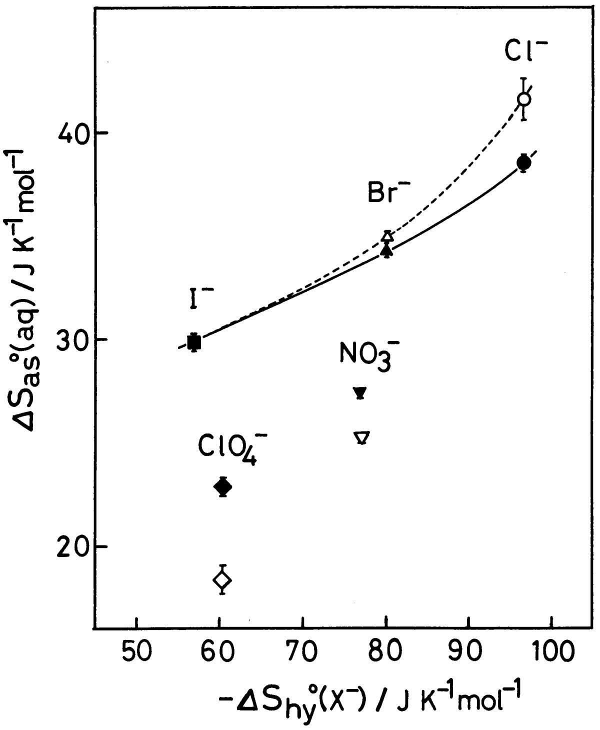

Fig. 3. Relationship between $\Delta S_{as}°$ (aq) and $-\Delta S_{hy}°$ (X^-) at 25 °C for the $[Co(en)_3]^{3+}$ (solid symbols) and $[Co(NH_3)_6]^{3+}$ (open symbols)[5)] systems; the solid line is drawn for the halides of $[Co(en)_3]^{3+}$ and the dashed line for those of $[Co(NH_3)_6]^{3+}$.

In Figs. 3 and 4, $\Delta S_{as}°$ (aq) and $\Delta H_{as}°$ (aq) are plotted against $-\Delta S_{hy}°$ (X^-) and $-\Delta H_{hy}°$ (X^-), respectively, at 25 °C, where the values of $\Delta S_{as}°$ (aq) or $\Delta H_{as}°$ (aq) for the halides increase with increasing $-\Delta S_{hy}°$ (X^-) or $-\Delta H_{hy}°$ (X^-).[25)] This suggests that the reduction in the anion hydrations on ion association is increased by increasing their hydration strength. Analogously, $\Delta S_{as}°$ (aq) and $\Delta H_{as}°$ (aq) of $[Co(en)_3]^{3+}$ smaller than those of $[Co(NH_3)_6]^{3+}$, except $\Delta S_{as}°$ (aq) for the iodide, may suggest that the hydration of $[Co(en)_3]^{3+}$ is relatively weak. The difference in the Gibbs free energy change, $\Delta\Delta G_{as}°$ (aq), is equal to $\Delta G_{as}°$ (aq, $[Co(en)_3]^{3+}$) $-\Delta G_{as}°$ (aq, $[Co(NH_3)_6]^{3+}$), and is shown as a function of the temperature in Fig. 5, where its sign for the halides is negative. This may also indicate a weaker hydration of $[Co(en)_3]^{3+}$.

Although the negative $\Delta\Delta G_{as}°$ (aq) for the halides in Fig. 5 is apparently based upon the decrease in $\Delta H_{as}°$ (aq), the difference in $\Delta\Delta G_{as}°$ (aq) between the halides is controlled by that in $\Delta S_{as}°$ (aq) and the relatively largest $-\Delta\Delta G_{as}°$ (aq) for the iodide is due to no appreciable change in $\Delta S_{as}°$ (aq), as shown in Figs. 3 and 4. These results are presumed to be caused by the following double-faced properties of $[Co(en)_3]^{3+}$: One is the hydrophilic property of the amino groups; the other is the hydrophobic property of the methylene groups. The hydration water molecules in the vicinity of the amino groups are partially bound by hydrogen bonding, and are more stabilized than those surrounding the methylene groups. The former water molecules can be substituted by the anion when some gain in the free energy is possible. This situation may be similar to that in the ammine ligands of $[Co(NH_3)_6]^{3+}$. The ion-association constants of $[Co(NH_3)_6]^{3+}$ with the halide ions suggested that

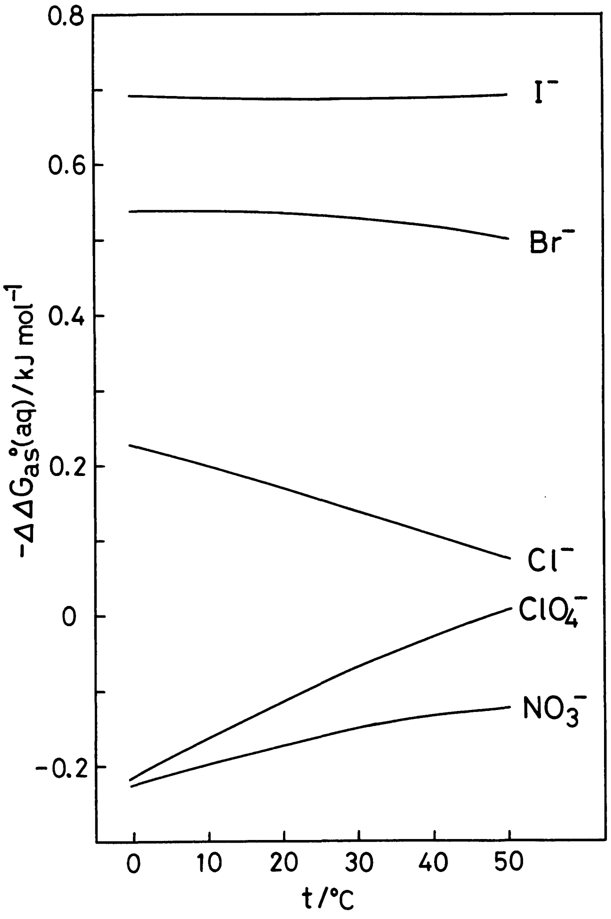

Fig. 5. Temperature dependence of $\Delta\Delta G_{as}°$ (aq), equal to $\Delta G_{as}°$ (aq, $[Co(en)_3]^{3+}$)$-\Delta G_{as}°$ (aq, $[Co(NH_3)_6]^{3+}$), calculated by use of Eq. 5.

replacement of the hydration water molecules surrounding the complex ion by the anions becomes easier in the order $Cl^- > Br^- > I^-$; this should be consistent with the order in the interaction strength between the ligand and the anion in the gas phase, considering the relatively strong hydration of the chloride ion.

Introduction of the methylene groups makes the hydration of the complex ion unstable, and the hydration water molecules in the neighborhood of these groups may be more easily substituted by the anions. The order in the easiness of such substitution is presumed to be $I^- > Br^- > Cl^-$ from their hydration strength if we assume no appreciable specific interaction between the methylene group and the anions. The relatively large $-\Delta\Delta G_{as}°$ (aq) for the iodide indicates that this anion prefers the methylene groups to the amino groups. No difference in $\Delta S_{as}°$ (aq) between the iodides of $[Co(en)_3]^{3+}$ and $[Co(NH_3)_6]^{3+}$ suggests that the structure-breaking effect of the iodide ion for the hydration around the methylene groups is largest among the halide ions.

The values of $-\Delta\Delta G_{as}°$ (aq) for the chloride gradually decrease with increasing temperature. This is attributed to the fact that the contribution of directional interactions around the amino groups to ion association is larger than that of other halide ions. The directional interactions of $[Co(en)_3]^{3+}$ with Cl^- are more disturbed than $[Co(NH_3)_6]^{3+}$ by its rotational motion strengthened with increasing temperature, since the major polar hydrogen atoms are distributed around the C_3-axis of $[Co(en)_3]^{3+}$.

Ion Associations of $[Co(en)_3]^{3+}$ with the Nitrate and Perchlorate Ions. The ion associations between $[Co(en)_3]^{3+}$ and the oxoanions (NO_3^- and ClO_4^-) are seen to be weaker than those for $[Co(NH_3)_6]^{3+}$ from Figs. 1, 2, and 5. This is opposite to the expectation from the results concerning the halides, since the oxoanions have strong structure-breaking properties.5) The remarkable increases in log K_A for the $[Co(NH_3)_6]^{3+}$ system with dereasing temperature (Fig. 2) and relatively small $\Delta S_{as}°$ (aq) values, compared with those for the halides (Fig. 3), suggest the presence of specific short-range interactions, such as hydrogen bonding between the ammine ligands of the complex and the oxoanions of which two or three oxygen atoms concern the interactions at the same time; such directional interactions lead to the reduction of $\Delta S_{as}°$ (aq) due to the loss of the rotational entropy of the anions.5) Since in the case of $[Co(en)_3]^{3+}$ hydrogen bonding is possible only in the vicinity of the amino groups and is somewhat hindered by the methylene groups, the contact ion pairs formed by hydrogen bonding are presumed to be reduced. If this reduction effect overcomes the promotion effect of ion association caused by the relatively weak hydration around the methylene groups, the resulting values of log K_A or $-\Delta G_{as}°$ (aq) would decrease. The values of $\Delta S_{as}°$ (aq) for the nitrate and perchlorate of $[Co(en)_3]^{3+}$ are larger than those of $[Co(NH_3)_6]^{3+}$, shown in Fig. 3; this is attributed to the decrease in the rotational entropy loss. The larger values of $\Delta H_{as}°$ (aq) in Fig. 4 are mainly due to the decrease in the inter-ionic interaction energy in addition to that in the rotational enthalpy loss.

Relationship between $\Delta H_{as}°$ (aq) and t_{min} and Prediction of Thermodynamic Parameters. A relationship is found between $\Delta H_{as}°$ (aq) and t_{min}, as shown in Fig. 6 where the $\Delta H_{as}°$ (aq) values at 25 °C are used. Plots for the $[Co(en)_3]^{3+}$ system are almost in agreement with those for the $[Co(NH_3)_6]^{3+}$ system previously demonstrated.5) The $\Delta H_{as}°$ (aq) values for both systems can be well reproduced by the following equation:

$$\Delta H_{as}° \text{ (aq, 25 °C)} = 2.29 - 0.0657 t_{min} - 0.00114 t_{min}^2. \qquad (9)$$

The presence of such a relationship can be expected from Eq. 7 if parameter p is an approximate linear function of t_{min}. In practice, p increases roughly with increasing t_{min}, as is shown in Table 5, in a similar manner as that found for the $[Co(NH_3)_6]^{3+}$ system.5)

If Eq. 9 is also valid for the other monovalent anions and information concerning $\Delta H_{as}°$ (aq) and log K_A at 25 °C is available, we can estimate in turn the values of

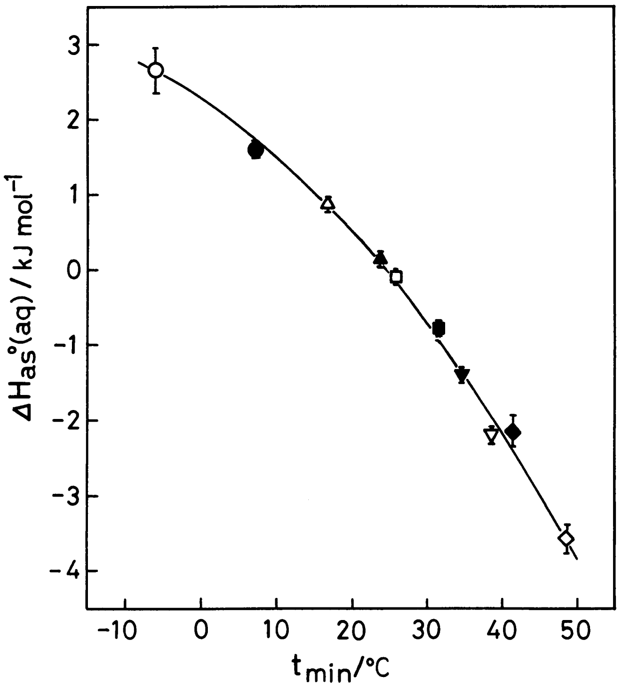

Fig. 6. Correlations of $\Delta H_{as}°$ (aq) at 25 °C with t_{min} for the $[Co(en)_3]^{3+}$ (solid symbols) and $[Co(NH_3)_6]^{3+}$ (open symbols)[5] systems; the chloride (●,○), bromide (▲, △), iodide (■,□), nitrate (▼,▽), and perchlorate (◆,◇). The solid line is drawn by use of Eq. 9.

t_{min}, p, and log $K_{A(min)}$ from Eqs. 9, 7, 5, respectively, to predict those of log K_A, $\Delta H_{as}°$ (aq), and $\Delta S_{as}°$ (aq) at a given temperature by using Eqs. 5—7.

Absolute Values of the Thermodynamic Parameters of Ion Association. The values of the thermodynamic parameters obtained in the present study are not necessarily absolute, since many assumptions are involved in the theoretical conductivity equation, in the treatment with the ion-association system, in the closest distance of approach of ions, and in the limiting molar ionic conductivity of the ion pairs. If different assumptions are made, the values of the obtained thermodynamic parameters may be somewhat changed. However, the relative relatioships between the anions or the complexes and their temperature dependence are presumed 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. A detailed consideration of uncertainties due to the assumptions has been given in the previous work.[5]

References

1) H. Yokoyama, *Bull. Chem. Soc. Jpn.*, **57**, 1304 (1984).

2) H. Yokoyama and T. Ohta, *Bull. Chem. Soc. Jpn.*, **61**, 3073 (1988).

3) H. Yokoyama, Y. Koyama, and Y. Masuda, *Chem. Lett.*, **1988**, 1453.

4) H. Yokoyama and T. Ohta, *Bull. Chem. Soc. Jpn.*, **62**, 345 (1989).

5) H. Yokoyama and H. Kon, *J. Phys. Chem.*, **95**, 8956 (1991).

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

7) T. Takahashi and T. Koiso, *Bull. Chem. Soc. Jpn.*, **51**, 1307 (1978).

8) H. Kaneko and N. Wada, *J. Solution Chem.*, **7**, 19 (1978).

9) M. T. Beck, *Coord. Chem. Rev.*, **3**, 91 (1968).

10) A. Elder and S. Petrucci, *Inorg. Chem.*, **9**, 19 (1970).

11) T. Taura, *J. Am. Chem. Soc.*, **101**, 4221 (1979).

12) Y. Masuda and H. Yamatera, *J. Phys. Chem.*, **87**, 5339 (1983).

13) J. B. Work, "Inorganic Syntheses," ed by W. C. Fernelius, Krieger, New York (1978), Vol. 2, p. 221.

14) H. Yokoyama, M. Mochida, and Y. Koyama, *Bull. Chem. Soc. Jpn.*, **61**, 3445 (1988).

15) G. S. Kell, *J. Chem. Eng. Data*, **12**, 66 (1967).

16) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," 2nd ed, Butterworths, London (1959), Chap. 7.

17) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd ed, Reinhold, New York (1958), p. 233.

18) E. Glueckauf, *Trans. Faraday Soc.*, **61**, 914 (1965).

19) C. G. Malmberg and A. A. Maryott, *J. Res. Natl. Bur. Stand.*, **56**, 1 (1956).

20) Ref. 16, p. 457.

21) W. Ebeling, *Z. Phys. Chem.* (*Leipzig*), **238**, 400 (1968).

22) H. Yokoyama and H. Yamatera, *Bull. Chem. Soc. Jpn.*, **48**, 1770, 3992 (1975).

23) N. Bjerrum, *K. Dan. Vidensk. Selsk.*, **7**, No. 9 (1926).

24) The manners of estimation of the uncertainties for the experimental values and of derivation of the theoretical values from the theoretical equations of K_A[21-23] have been described in Ref. 5.

25) The values of $\Delta S_{hy}°$ (X^-) and $\Delta H_{hy}°$ (X^-) in Figs. 3 and 4 were cited from Y. Marcus, "Ion Solvation," Wiley, New York (1985), Chap. 5. The values of $\Delta S_{hy}°$ (X^-) for Cl^-, Br^-, I^-, NO_3^-, and ClO_4^- were calculated by use of the $\Delta G_{hy}°$ (X^-) and $\Delta H_{hy}°$ (X^-) values given in a table at p. 108 and for the halide ions are by 10 J K^{-1} mol^{-1} larger than those listed at p. 126 which were used in our previous paper (Ref. 5).