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Conductometric Study of Ion Association of Hexaamminecobalt(III) Complexes in Ethanol + Water

Suheyla Pura* and Gulten Atun[†]

University of Istanbul, Engineering Faculty, Department of Chemistry, 34850 Avcilar, Istanbul, Turkey

The conductivities of the chloride, bromide, iodide, nitrate, and perchlorate of the hexaamminecobalt(III) complex were measured in (10−70) mass % ethanol + water at temperatures between (10 and 50) °C. The ion association constants (K_A) were determined by analyzing the conductivity data in terms of the Robinson−Stokes equations. Ion association constants calculated for all complex salts in ethanol + water increased, dependent on the amount of ethanol. This was equivalent to the ion association constants increasing with a decrease in the relative permittivity of the mixed solvents. While K_A values increased with increasing temperature for the chloride and bromide, the iodide of $[Co(NH_3)_6]^{3+}$ indicated some disorder. It was observed that these values decreased dependent on the temperature for oxoacid ions. The ion association constants of the complex ion with the anions had minimum values (K_{min}) 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 standard entropy and enthalpy changes of ion association in ethanol + water were calculated from an equation by using K_{min} and t_{min} values. The entropy and enthalpy changes were investigated dependent on temperature and amount of ethanol. The limiting molar conductivities of complex ion and monovalent anions in the mixed solvents were estimated from our experimental data using the Kohlraush equation.

Introduction

In the previous studies the ion association of hexaamminecobalt(III) ion, $[Co(NH_3)_6]^{3+}$, with various anions had been investigated extensively, in aqueous solutions by conductometric methods.[1−3] But the temperature dependence was not investigated, although this complex is one of the simplest available.

Yokoyama and Kon measured the electrical conductivities of aqueous solutions of various monovalent anions of hexaamminecobalt(III) ion at temperatures between (10 and 50) °C, and the ion association constants and the thermodynamic parameters were calculated. The association constants (K_A) were determined using the Robinson−Stokes equations to provide a better fit to the conductivity data. The order in the magnitude of K_A among the salts was dependent on temperature. K_A values in aqueous solutions increased in the order $I^- \approx ClO_4^- < Br^- < NO_3^- \approx Cl^-$. The conductivity measurements over a wide temperature range were expected to provide useful information concerning some specific short-range interactions.[4]

It seemed interesting to study the association equilibrium of the unsymmetrical complex salts in water + organic mixtures. Thus, conductance measurements of some complex salts in water + ethanol mixtures were carried out to see the change in association equilibrium with the variation of the composition of the solvent mixture. The aim in the present study was to investigate the interaction of solvent and temperature on the interaction with monovalent anions of a cobalt(III) complex.

In the present study, electrical conductivities of (10−70) mass % ethanol + water mixtures of the chloride, bromide, iodide, nitrate, and perchlorate of hexaamminecobalt(III) were measured at nine temperatures between (10 and 50) °C. From these conductivity data, the temperature dependence of the limiting molar conductivities of the complex ion and monovalent anions in various ethanol + water mixtures was determined in this study. The standard entropy and enthalpy changes calculated from these constants were investigated according to amount of ethanol and temperature.

Experimental Section

Materials. Hexaamminecobalt(III) chloride was synthesized as described in the literature[5] and recrystallized twice from water. The bromide, iodide, nitrate, and perchlorate of the complex were obtained by adding aqueous solutions of hydrobromic acid, potassium iodide, nitric acid, 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. The absence of the chloride ion in the nitrate and in the perchlorate was ascertained by adding silver acetate to their aqueous solutions. The preparation of iodide and bromide was made in a dark room.[5] All reagents used were pro analysis from Merck. The complex salts obtained were air-dried and ascertained to be anhydrous. The identification of the complex compounds was checked by means of their UV spectra, as described in the literature.[6,7]

Solutions. All solutions were made by mass just before carrying out conductivity measurements. The water used for the solutions was redistilled. Its conductivity was 2.5×10^{-6} S·cm^{-1} at 25 °C after dissolved carbon dioxide was removed as described below. The conductivity of ethanol was 4.1×10^{-8} S·cm^{-1} at 25 °C.

Viscosity and Density Measurements. Density measurements of (10−70) mass % ethanol + water mixtures were performed by using a Wertheim pycnometer of 10 cm^3

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* E-mail: spura@istanbul.edu.tr. Fax: +902125911997.
[†] E-mail: gultena@istanbul.edu.tr.

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Table 1. Molar Conductivities of $[Co(NH_3)_6]Cl_3$ in Ethanol (1) + Water (2)

		$\Lambda(MX_3/3)/S\cdot cm^2\cdot mol^{-1}$								
mass % w_1	10^4c/M	10.0 °C	15.0 °C	20.0 °C	25.0 °C	30.0 °C	35.0 °C	40.0 °C	45.0 °C	50.0 °C
10	2.0	100.80	105.75	111.47	115.60	124.08	132.06	140.58	149.46	158.60
	2.6	100.15	104.66	109.78	114.43	122.56	129.98	138.72	147.51	156.19
	3.2	99.31	103.55	108.72	113.25	121.61	128.69	137.12	145.99	153.78
	4.0	98.35	102.22	107.21	112.10	119.85	127.09	135.25	143.77	151.92
	4.9	97.43	100.71	105.78	110.78	118.27	125.48	133.60	141.58	149.63
	5.8	96.31	99.92	104.79	109.40	116.69	124.13	131.96	139.78	147.33
	6.7	95.28	99.12	103.64	108.37	115.75	122.71	130.55	138.26	145.00
	7.8	94.59	98.16	102.68	107.01	114.25	121.06	128.89	136.48	143.53
	9.0	93.80	97.13	101.29	106.07	112.96	119.67	127.01	134.58	141.47
	9.9	92.77	96.28	100.40	105.25	110.24	118.62	125.93	132.45	139.29
30	2.0	73.50	78.56	83.78	90.95	98.70	107.21	115.73	124.78	135.36
	2.6	72.15	77.55	82.47	89.46	97.07	105.41	113.60	123.10	132.86
	3.2	71.31	76.23	81.65	87.69	96.05	103.84	111.82	120.73	130.87
	4.0	70.35	74.73	80.58	86.35	94.12	101.88	110.05	118.79	128.31
	4.9	69.14	73.66	79.40	85.47	92.37	99.98	108.09	116.83	126.04
	5.8	67.83	72.44	78.10	84.12	90.68	98.18	106.25	114.74	123.98
	6.7	67.07	71.34	76.93	82.91	89.02	96.43	104.69	113.30	122.06
	7.8	66.05	70.14	75.73	81.53	87.69	94.30	103.04	111.35	119.85
	9.0	65.18	68.93	74.47	80.06	86.01	92.77	101.29	109.82	117.81
	9.9	64.63	68.08	73.15	79.18	84.74	91.80	99.83	107.96	116.08
50	2.0	51.10	59.92	68.87	78.95	90.24	101.53	112.90	124.78	137.45
	2.6	50.08	58.57	67.72	77.54	88.40	98.85	110.31	122.00	133.96
	3.2	49.44	57.28	66.12	76.22	86.36	96.75	107.37	119.41	130.44
	4.0	48.30	56.40	64.96	74.37	84.60	94.42	104.72	115.97	126.55
	4.9	47.43	55.25	63.59	72.51	82.59	92.16	102.00	112.51	123.45
	5.8	46.34	53.97	62.43	70.98	80.22	90.10	99.64	109.40	120.09
	6.7	45.76	53.03	61.25	69.45	78.92	87.95	97.07	106.07	116.16
	7.8	45.05	51.70	60.07	68.51	77.01	85.92	94.67	103.04	112.08
	9.0	44.18	50.60	58.54	66.90	75.04	83.78	91.99	100.27	109.04
	9.9	43.41	49.42	57.09	66.08	73.63	81.90	89.93	97.56	106.09
70	2.0	38.50	47.25	58.20	69.10	80.37	91.60	102.25	111.40	121.95
	2.6	37.69	46.08	56.81	67.23	78.08	89.04	98.85	106.85	116.58
	3.2	36.31	45.37	55.47	65.22	76.22	86.53	95.41	103.53	112.34
	4.0	35.70	44.42	53.95	64.15	74.02	83.42	91.95	99.05	107.50
	4.9	34.86	43.16	52.45	62.16	71.94	81.14	88.67	94.95	102.45
	5.8	34.28	42.29	51.17	61.01	70.01	78.59	85.21	91.41	98.21
	6.7	33.43	41.46	50.01	58.51	68.39	76.09	81.01	87.55	93.87
	7.8	33.03	40.49	48.79	57.31	66.17	73.73	79.92	83.15	88.58
	9.0	32.04	39.48	47.64	55.78	64.08	71.00	77.16	80.37	84.13
	9.9	30.97	38.31	46.33	54.98	62.67	68.41	73.29	76.19	80.46

Table 2. Densities of Ethanol (1) + Water (2)

	$\rho/g\cdot cm^{-3}$			
t/°C	10 mass % w_1	30 mass % w_1	50 mass % w_1	70 mass % w_1
10.0	0.984 ± 0.002	0.959 ± 0.003	0.922 ± 0.002	0.877 ± 0.003
15.0	0.983 ± 0.003	0.956 ± 0.002	0.917 ± 0.001	0.873 ± 0.002
20.0	0.982 ± 0.002	0.954 ± 0.002	0.914 ± 0.003	0.858 ± 0.001
25.0	0.980 ± 0.002	0.952 ± 0.003	0.910 ± 0.002	0.863 ± 0.002
30.0	0.979 ± 0.003	0.950 ± 0.002	0.906 ± 0.003	0.860 ± 0.002
35.0	0.977 ± 0.001	0.947 ± 0.001	0.903 ± 0.002	0.857 ± 0.003
40.0	0.976 ± 0.002	0.945 ± 0.003	0.900 ± 0.002	0.854 ± 0.001
45.0	0.974 ± 0.002	0.943 ± 0.001	0.897 ± 0.003	0.852 ± 0.002
50.0	0.973 ± 0.001	0.941 ± 0.002	0.894 ± 0.001	0.850 ± 0.002

Table 3. Viscosities of Ethanol (1) + Water (2)

	η/mPa·s			
t/°C	10 mass % w_1	30 mass % w_1	50 mass % w_1	70 mass % w_1
10.0	1.921 ± 0.003	3.323 ± 0.004	3.043 ± 0.004	2.965 ± 0.004
15.0	1.712 ± 0.003	3.004 ± 0.003	2.785 ± 0.003	2.573 ± 0.004
20.0	1.514 ± 0.004	2.885 ± 0.004	2.592 ± 0.004	2.148 ± 0.003
25.0	1.328 ± 0.004	2.666 ± 0.003	2.262 ± 0.003	1.854 ± 0.004
30.0	1.160 ± 0.003	2.412 ± 0.004	1.842 ± 0.004	1.642 ± 0.003
35.0	1.024 ± 0.004	2.228 ± 0.003	1.525 ± 0.003	1.395 ± 0.004
40.0	0.890 ± 0.003	2.013 ± 0.004	1.325 ± 0.004	1.192 ± 0.004
45.0	0.761 ± 0.004	1.800 ± 0.004	1.185 ± 0.004	1.065 ± 0.003
50.0	0.638 ± 0.004	1.695 ± 0.004	0.982 ± 0.003	0.945 ± 0.004

capacity coupled with a thermometer. The change of temperature during the density measurements was ±0.01 °C. The estimated uncertainty of the measured density is $\pm 0.002\ g\cdot cm^{-3}$.

Viscosity mesurements were made with a viscometer of Ostwald type. The flow time for the viscometer, ranging between 400 and 800 s, was measured with a precision stop watch. The experimental viscosity data were accurate to 0.004. Redistilled water was employed to calibrate the viscometer. The temperature was controlled with a thermostated water bath with a precision of ±0.01 °C.

Conductivity Measurements. The conductivity measurements were performed with a Metrohm Herisau E 365 model conductometer at nine temperatures between 10 and 50 °C. The conductivity cell used was a three-necked flask with a water jacket which was equipped with a nitrogen inlet and two platinized platinum electrodes. The cell constant was $1.41\ cm^{-1}$ at 25 °C, and its change with temperature was about ±0.01 in steps of 5 °C.

Before the beginning of the measurements, dissolved carbon dioxide was removed by bubbling moistened nitrogen gas through the solution in the cell for about 0.5 h. In any given solution the measurements were carried out by starting at 10 °C and elevating the temperature in steps of 5 °C. Throughout the measurements an atmosphere of nitrogen was maintained over the solution. All conductivity measurements of solutions of the bromide and the iodide were carried out while protecting the solutions from light.

The conductance measurements in (10−70) mass % ethanol + water mixtures of five complex salts were carried out for 10 different concentrations. The reproducibility of the measurements was examined by repeating each ex-

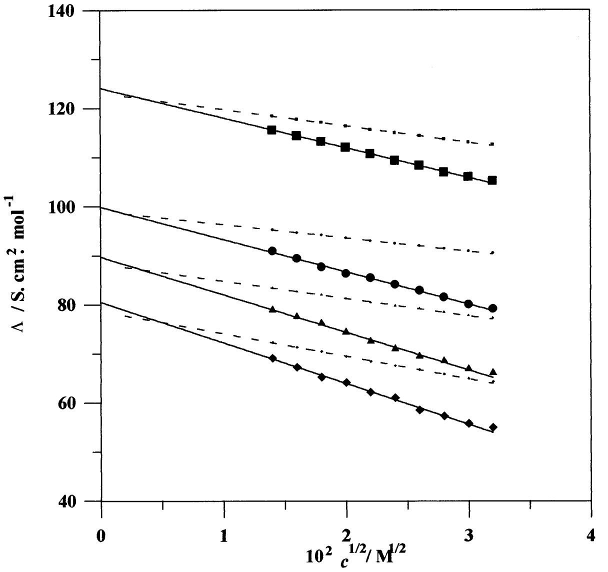

Figure 1. Effect of solvent on $[Co(NH_3)_6]Cl_3$ at 25 °C: ■, 10 mass % ethanol; ●, 30 mass % ethanol; ▲, 50 mass % ethanol; ◆, 70 mass % ethanol.

perimental run several times. The reproducibility of the conductivity measurements was within 0.05%. The accuracy of the temperature was ±0.01 °C.

Results and Discussion

Analysis of Conductivity Data. From conductivity measurements in (10−70) mass % ethanol + water mixtures, the observed molar conductivities of the complex salts ($\Lambda(MX_3/3)$, where M^{3+} is the complex ion and X^- is the anion) have been found, in general, to increase in the order $Cl^- < Br^- < NO_3^- < I^- < ClO_4^-$. This order may be dependent on increasing of the limiting molar conductivities calculated by using the Kohlraush equation at nine temperatures for the bromide, iodide, nitrate, and perchlorate ions in the mixed solvents. This situtation looks like the behavior of the $Fe(Phen)_3^{2+}$ complex in methanol + water mixtures.[8] The molar conductivities of solutions for 10 different concentrations in these mixtures decreased with increasing concentration, as expected from conductivity equations. The observed molar conductivities of $[Co(NH_3)_6]Cl_3$ are given in Table 1 as an example.

The analysis was carried out by assuming the following ion-pair formation in a similar manner to that employed by Jenkins and Monk,[1] although different theoretical equations for conductivities and activity coffecients were used in the present analysis.

$$[Co(NH_3)_6]^{3+} + X^- \leftrightarrow [Co(NH_3)_6]^{3+}X^- \qquad (1)$$

where triple-ion formation was regarded as being negligible in the mixtures investigated. The association equilibrium was assumed, and the symbols M^+ and X^- refer to the complex cation and the complex anion, respectively.

From the additivity rule for ionic conductivities, the molar conductivity of the salt can be expressed as

$$\begin{aligned}\Lambda(MX_3) &= \alpha[\lambda(M^{3+}/3) + \lambda(X^-)] + \\ &\qquad 2(1-\alpha)[\lambda(M^{3+}X^-/2) + \lambda(X^-)]/3 \\ &= \alpha\Lambda_F(MX_3/3) + 2(1-\alpha)\Lambda_F(MXX_2/2)/3 \qquad (2)\end{aligned}$$

where the λ values are the ionic molar conductivities and $\Lambda_F(MX_3/3)$ and $\Lambda_F(MXX_2/2)$ correspond to the molar conductivities of hypothetical unsymmetrical 3:1 and 2:1 electrolytes, respectively. While the Onsager limiting equation had been used in the previous studies,[1,3] the Robinson−Stokes equation was used here to provide a better fit to the data.[9]

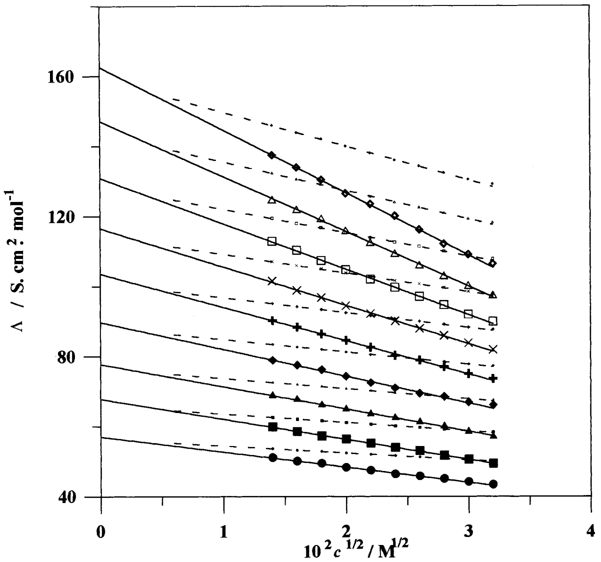

Figure 2. Temperature effect on $[Co(NH_3)_6]Cl_3$ in a 50 mass % ethanol + water mixture: ●, 10 °C; ■, 15 °C; ▲, 20 °C; ◆, 25 °C; +, 30 °C; ×, 35 °C; □, 40 °C; △, 45 °C; ◇, 50 °C.

For a 3:1 electrolyte (MX_3)

$$\Lambda_F(MX_3/3) = [\lambda^\infty(M^{3+}/3) + \lambda^\infty(X^-)] - s_{31}I^{1/2}/(1 + Ba_{31}I^{1/2}) \qquad (3)$$

$$s_{31} = B_1'\Lambda^\infty(MX_3/3) + B_2'$$

and for a 2:1 electrolyte $(MX{\cdot}X_2)$

$$\Lambda_F(MX{\cdot}X_2/2) = [\lambda^\infty(M^{3+}X^-/2) + \lambda^\infty(X^-)] - s_{21}I^{1/2}/(1 + Ba_{21}I^{1/2}) \qquad (4)$$

$$s_{21} = B_1'\Lambda^\infty(MX{\cdot}X_2/2) + B_2'$$

where the λ^∞ values are the limiting molar conductivities, B_1' and B_2' are expressed according to the Onsager's limiting equation, a is the closest distance of approach of ions, s and B have their usual meannings, and I is the ionic strength. The values of a_{31} in eq 3 for the chloride, bromide, iodide, nitrate, and perchlorate were taken to be 4.91, 5.05, 5.26, 5.15, and 5.40 Å, respectively, and the effective ionic radius of $[Co(NH_3)]^{3+}$ (3.10 Å) was derived from their partial molar volumes by use of Glueckauf's equation.[4] The values taken for a_{31} in eq 2 were assumed to be the same also for a_{21} in eq 3.[4]

The parameter B_1' is function of ϵ (relative permittivity values of (10−70) mass % ethanol + water mixtures),[10,11] and B_2' is a function of ϵ and η (viscosity values of ethanol + water mixtures). Therefore, the values of ϵ and η for solvent and the value of $\lambda^\infty(X^-)$ in the mixtures are needed for the analysis of conductivity data.

The experimental density and viscosity values measured for (10−70) mass % ethanol + water mixtures are given in Tables 2 and 3, respectively using these data.

$\Lambda - c^{1/2}$ curves plotted according to amount of solvent indicated a deviation from theoretical values calculated by the Robinson−Stokes equation ($\Lambda - c^{1/2}$ curves plotted for

Table 4. Parameter Values in Eq 5 for Limiting Molar Conductivities of Ions

mass % ethanol	ion	λ^∞(25 °C)	a	10^3b	10^5c
		$S\cdot cm^2\cdot mol^{-1}$	$S\cdot cm^2\cdot mol^{-1}\cdot K^{-1}$	$S\cdot cm^2\cdot mol^{-1}\cdot K^{-2}$	$S\cdot cm^2\cdot mol^{-1}\cdot K^{-3}$
10	Cl^-	53.46	0.6315	9.869	−3.850
	Br^-	60.05	0.7498	9.936	−4.780
	I^-	65.80	0.6084	8.988	−4.251
	NO_3^-	62.22	0.6432	8.825	−3.920
	ClO_4^-	66.61	0.5458	8.568	−4.124
	$[Co(NH_3)_6]^{3+}$	71.55	0.7827	9.999	−3.870
30	Cl^-	35.18	0.6310	9.761	−5.000
	Br^-	39.99	0.6161	7.634	−4.850
	I^-	48.98	0.5579	9.051	−4.504
	NO_3^-	46.43	0.4379	8.635	−3.425
	ClO_4^-	54.73	0.7139	8.590	−4.022
	$[Co(NH_3)_6]^{3+}$	64.52	0.9661	9.064	−4.500
50	Cl^-	53.46	0.6316	9.859	−5.200
	Br^-	32.76	0.8120	9.352	−4.912
	I^-	42.69	0.6831	9.454	−4.721
	NO_3^-	40.79	0.6312	8.006	−3.155
	ClO_4^-	51.19	1.0898	9.562	−3.749
	$[Co(NH_3)_6]^{3+}$	63.13	1.8413	9.973	−4.900
70	Cl^-	23.15	0.6337	9.888	−5.354
	Br^-	27.40	0.8072	9.672	−5.090
	I^-	38.88	0.7178	9.585	−4.751
	NO_3^-	33.74	0.8038	8.332	−3.031
	ClO_4^-	49.72	1.0965	9.717	−3.590
	$[Co(NH_3)_6]^{3+}$	56.85	2.0826	9.258	−5.213

$Co[(NH_3)_6]Cl_3$ are given in Figure 1 as an example. The curves (dashed lines) plotted using calculated molar conductivity values were compared with the curves (solid lines) plotted according to observed molar conductivity values. The observed conductivity curves lie slightly below the calculated conductivity curves. This deviation from observed values may be attributed to ion-pair formation between the complex cation and monovalent anions. The deviation will be high according to the magnitude of the association constant of the ion pair.

The $\Lambda - c^{1/2}$ curves depending on temperature showed that the conductivity increased with temperature in ethanol + water mixtures and that molar conductivities of complexes deviated especially from the Robinson−Stokes equation at 45 and 50 °C (Figure 2 is given as an example for a 50% (mass) ethanol + water mixture). Thus, a higher deviation for the curves plotted at high temperatures has been observed.

The limiting molar conductivities $\lambda^\infty(X)$ for the ions at a given temperature (t in °C) were estimated from

$$\lambda^\infty(X) = \lambda^\infty(25\ °C) + a(t - 25) + b(t - 25)^2 + c(t - 25)^3 \tag{5}$$

where λ^∞(25 °C), a, b, and c are constants depending on the ions. Equation 5 was used also to express the temperature dependence of $\lambda^\infty(M^{3+}/3)$. The limiting molar conductivity of $[Co(NH_3)_6]^{3+}$ in ethanol + water mixtures is calculated by the Kohlraush equation. The estimated limiting molar conductivities of the ions and the a, b, and c constants with their unities are shown in Table 4. The limiting molar conductivities for chloride anions in (10−70) mass % ethanol + water mixtures at 25 °C were taken to be 53.46, 35.18, 26.13, 23.15 S. cm^2. mol^{-1}, respectively.[12] The limiting molar conductivities for Br^-, I^-, NO_3^-, and ClO_4^- are also calculated by the Kohlraush equation, using those values of $[Co(NH_3)_6]^{3+}$ calculated in ethanol + water mixtures.

Although the limiting molar conductivity of the complex ion, $\lambda^\infty(M^{3+}/3)$, could be estimated from the analysis of the conductivity data, those of ion pairs, $\lambda^\infty(M^{3+}X^-/2)$, were virtually impossible to estimate experimentally and were assumed to be equal to $^2/_3\lambda^\infty(M^{3+}/3)$, as suggested in previous studies.[1,4]

Ion Association Constants and Their Temperature Dependence. The ion association costants were determined by analyzing the conductivity data with eqs 1−5, fixing values of a_{31}, a_{21}, and $\lambda^\infty(X^-)$, on the basis of the following assumptions.

The equilibrium constant (the association constant), K_A, for eq 1 is written

$$K_A = (1 - \alpha)\gamma_{MX}/[c\alpha(2 + \alpha)\gamma_M\gamma_X] \tag{6}$$

where c is the molar concentration of the salt, α is the fraction of the free complex ion, and γ_M, γ_X, and γ_{MX} are the activity coefficients of M^{3+}, X^-, and $M^{3+}X^-$, respectively, which are represented by the Debye−Hückel equation.[4]

$$\gamma_i = -Az_i^2 I^{1/2}/(1 + Ba_i I^{1/2}) \tag{7}$$

where A (Debye−Hückel equation) and B have their usual meanings, z_i is the ionic charge number, I is the ionic strength, given by $I = 3c(1 + \alpha)$, and a_i is the closest distance of approach of ions.

The ion association constants (K_A) obtained for complexes of chloride, bromide, iodide, nitrate, and perchlorate of hexaammine Co(III) in mixtures are shown in Table 5.

As the amount of ethanol was increased, K_A values indicated an increase. This may be attributed to the association constants increasing with a decrease in the relative permittivity of the solvent. These results are in good agreement with many studies dealing with this subject.[13,14] K_A values with increasing temperature increased in the order $Cl^- > Br^- > I^-$ for halide ions. This order may be connected with increasing radii of anions. Although K_A values indicated some disorder for iodide, they decreased for nitrate and perchlorate. Specific short-range interactions between the oxoacid ions and the complex ion were considered to be strengthened with decreasing temperature. The most probable short-range interaction is the hydrogen bonding between the hydrogen atoms of NH_3 ligands of the $[Co(NH_3)_6]^{3+}$ ion and the oxygen atoms of the oxoacid ions. In this case it may be important that two

Table 5. Ion Association Constants for Complex Salts in Ethanol (1) + Water (2)

	K_A/dm^3·mol^{-1}			
t/°C	10 mass % w_1	30 mass % w_1	50 mass % w_1	70 mass % w_1
$[Co(NH_3)]_6Cl_3$				
10.0	102.1 ± 1.3	235.3 ± 1.4	340.3 ± 1.3	460.6 ± 1.2
15.0	105.1 ± 1.2	242.9 ± 1.5	355.2 ± 1.2	480.1 ± 1.6
20.0	107.1 ± 1.5	252.6 ± 1.3	369.8 ± 1.6	501.5 ± 1.7
25.0	110.4 ± 1.4	266.7 ± 1.4	387.5 ± 1.5	526.3 ± 1.5
30.0	114.4 ± 1.2	279.4 ± 1.4	405.1 ± 1.4	550.8 ± 1.3
35.0	119.5 ± 1.3	295.3 ± 1.6	425.0 ± 1.6	575.7 ± 1.4
40.0	124.8 ± 1.4	311.0 ± 1.4	446.2 ± 1.5	599.8 ± 1.8
45.0	130.9 ± 1.5	328.5 ± 1.3	469.1 ± 1.7	628.2 ± 1.6
50.0	136.7 ± 1.6	347.9 ± 1.4	492.1 ± 1.5	658.6 ± 1.5
$[Co(NH_3)]_6Br_3$				
10.0	119.6 ± 1.3	273.8 ± 1.3	407.1 ± 1.2	541.9 ± 1.2
15.0	119.3 ± 1.4	272.8 ± 1.5	404.6 ± 1.3	538.4 ± 1.5
20.0	123.2 ± 1.5	283.5 ± 1.4	421.4 ± 1.5	559.4 ± 1.4
25.0	128.2 ± 1.4	295.5 ± 1.4	437.6 ± 1.4	581.7 ± 1.6
30.0	133.3 ± 1.7	309.9 ± 1.6	453.1 ± 1.2	601.2 ± 1.7
35.0	138.4 ± 1.5	322.8 ± 1.7	471.3 ± 1.3	624.3 ± 1.5
40.0	143.6 ± 1.6	336.0 ± 1.5	491.2 ± 1.7	649.5 ± 1.4
45.0	148.8 ± 1.8	347.9 ± 1.4	509.7 ± 1.5	672.5 ± 1.3
50.0	154.2 ± 1.7	361.0 ± 1.5	528.9 ± 1.6	695.8 ± 1.2
$[Co(NH_3)]_6I_3$				
10.0	106.3 ± 1.2	251.5 ± 1.5	366.8 ± 1.3	479.5 ± 1.2
15.0	104.2 ± 1.3	246.9 ± 1.6	360.9 ± 1.4	473.6 ± 1.3
20.0	103.0 ± 1.6	243.9 ± 1.7	357.7 ± 1.6	471.9 ± 1.4
25.0	102.6 ± 1.4	242.8 ± 1.5	356.8 ± 1.4	470.8 ± 1.5
30.0	103.0 ± 1.5	243.3 ± 1.6	357.1 ± 1.3	472.9 ± 1.6
35.0	103.2 ± 1.6	244.8 ± 1.4	361.2 ± 1.5	476.1 ± 1.4
40.0	104.1 ± 1.7	246.9 ± 1.5	365.3 ± 1.6	481.6 ± 1.6
45.0	105.0 ± 1.8	249.1 ± 1.6	370.1 ± 1.4	486.8 ± 1.6
50.0	106.2 ± 1.6	252.9 ± 1.5	375.7 ± 1.6	494.2 ± 1.8
$[Co(NH_3)]_6(NO_3)_3$				
10.0	161.1 ± 1.3	345.0 ± 1.3	518.8 ± 1.2	670.5 ± 1.2
15.0	154.3 ± 1.2	333.7 ± 1.2	496.8 ± 1.3	650.0 ± 1.3
20.0	148.5 ± 1.4	321.6 ± 1.4	477.4 ± 1.4	632.6 ± 1.5
25.0	143.8 ± 1.6	311.2 ± 1.4	463.2 ± 1.5	612.8 ± 1.4
30.0	138.4 ± 1.5	300.9 ± 1.5	445.4 ± 1.4	596.4 ± 1.5
35.0	135.2 ± 1.4	291.0 ± 1.4	429.1 ± 1.4	577.8 ± 1.4
40.0	135.5 ± 1.3	291.2 ± 1.7	429.7 ± 1.5	583.7 ± 1.5
45.0	136.5 ± 1.5	292.7 ± 1.5	431.2 ± 1.6	586.5 ± 1.6
50.0	137.5 ± 1.4	293.9 ± 1.7	432.9 ± 1.8	593.3 ± 1.7
$[Co(NH_3)]_6(ClO_4)_3$				
10.0	141.3 ± 1.4	310.0 ± 1.3	465.0 ± 1.3	604.5 ± 1.2
15.0	134.5 ± 1.3	299.4 ± 1.4	447.4 ± 1.5	586.8 ± 1.3
20.0	128.6 ± 1.4	290.6 ± 1.5	429.0 ± 1.4	570.7 ± 1.5
25.0	122.7 ± 1.5	283.7 ± 1.4	417.3 ± 1.6	552.8 ± 1.6
30.0	118.4 ± 1.6	276.4 ± 1.6	404.0 ± 1.8	540.9 ± 1.4
35.0	114.9 ± 1.5	269.5 ± 1.8	396.4 ± 1.7	527.8 ± 1.5
40.0	112.8 ± 1.5	265.0 ± 1.7	391.2 ± 1.9	521.7 ± 1.8
45.0	111.6 ± 1.4	262.1 ± 1.9	387.3 ± 1.5	516.8 ± 1.7
50.0	110.0 ± 1.6	293.9 ± 1.8	386.5 ± 1.8	512.9 ± 1.9

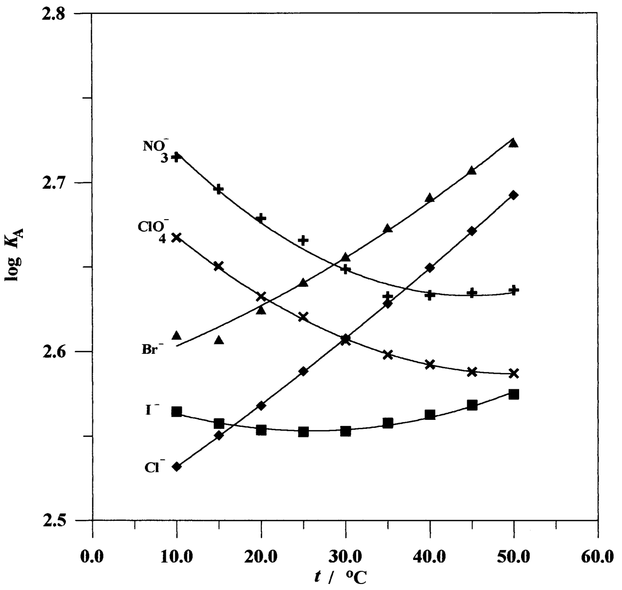

Figure 3. Temperature dependence of the ion association constants of the chloride (◆), bromide (▲), iodide (■), nitrate (+), and perchlorate (×) in a 50 mass % ethanol + water mixture.

Table 6. Values of Parameters in Eq 8 Representing the Temperature Dependence of Ion Association Constants between $[Co(NH_3)_6]^{3+}$ and Anions

anion	10^5p/K^{-2}	t_{min}/°C	log $K_{A(min)}$
	10 mass % ethanol		
Cl^-	10.67 ± 0.12	10.0 ± 0.3	2.009 ± 0.001
Br^-	10.95 ± 0.11	15.0 ± 0.4	2.076 ± 0.002
I^-	2.63 ± 0.16	25.0 ± 0.2	2.011 ± 0.001
NO_3^-	12.17 ± 0.20	35.0 ± 0.1	2.131 ± 0.002
ClO_4^-	7.61 ± 0.22	50.0 ± 0.2	2.041 ± 0.003
	30 mass % ethanol		
Cl^-	11.26 ± 0.15	10.0 ± 0.2	2.371 ± 0.003
Br−	12.14 ± 0.13	15.0 ± 0.3	2.435 ± 0.002
I^-	3.11 ± 0.15	25.0 ± 0.4	2.385 ± 0.003
NO_3^-	13.20 ± 0.14	35.0 ± 0.3	2.464 ± 0.004
ClO_4^-	6.13 ± 0.20	45.0 ± 0.1	2.419 ± 0.002
	50 mass % ethanol		
Cl^-	12.50 ± 0.16	10.0 ± 0.4	2.531 ± 0.005
Br^-	12.31 ± 0.17	15.0 ± 0.3	2.607 ± 0.006
I^-	5.55 ± 0.19	25.0 ± 0.2	2.552 ± 0.004
NO_3^-	14.45 ± 0.16	35.0 ± 0.5	2.633 ± 0.007
ClO_4^-	5.21 ± 0.22	50.0 ± 0.3	2.587 ± 0.005
	70 mass % ethanol		
Cl^-	12.77 ± 0.20	10.0 ± 0.5	2.663 ± 0.003
Br^-	12.88 ± 0.19	15.0 ± 0.4	2.731 ± 0.002
I^-	4.75 ± 0.15	25.0 ± 0.2	2.672 ± 0.005
NO_3^-	14.50 ± 0.21	35.0 ± 0.2	2.762 ± 0.008
ClO_4^-	4.61 ± 0.17	50.0 ± 0.4	2.710 ± 0.004

or three oxygen atoms of the anions may be part of the hydrogen bonding at the same time. This will lead to considerably large ion association constants at lower temperatures.

The log K_A values obtained in the present study are plotted against temperature (t) in Figure 3 as an example for a merely 50% (mass) ethanol + water mixture. These plots give smooth curves. Each curve has a minimum at a different temperature, t_{min}, characteristic of the salt.

The log K_A temperature dependence can be expressed by the following quadratic equation in t:

$$\log K_A = p(t - t_{min})^2 + \log K_{A(min)} \tag{8}$$

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 6. As shown by the solid lines in Figure 3, the log K_A values can be well reproduced by eq 8 using these parameter values. The values of t_{min} increased in the order $Cl^- < Br^- < I^- < NO_3^- < ClO_4^-$. Equation 8 was also used to derive the standard entropy and enthalpy changes for ion association in an ethanol + water mixture:[15] $\Delta S°$ and $\Delta H°$.

$$\Delta S° = 2.303R\{\log K_{A(min)} + p(3t - t_{min} + 546.3)(t - t_{min})\} \tag{9}$$

and

$$\Delta H° = 4.605pR(t + 273.5)^2(t - t_{min}) \tag{10}$$

The values of $\Delta S°$ and $\Delta H°$ at several temperatures are given in Tables 7 and 8. As shown in these tables, standard

Table 7. Standard Entropies of the Ion Association in Ethanol (1) + Water (2) at Several Temperatures

	$\Delta S°/J \cdot K^{-1} \cdot mol^{-1}$				
t/°C	$[Co(NH_3)_6]Cl_3$	$[Co(NH_3)_6]Br_3$	$[Co(NH_3)_6]I_3$	$[Co(NH_3)_6](NO_3)_3$	$[Co(NH_3)_6](ClO_4)_3$
10 mass % w_1					
15.0	44.4 ± 2.9	39.8 ± 0.8	35.6 ± 1.7	12.5 ± 0.9	10.8 ± 1.9
25.0	57.2 ± 1.8	51.7 ± 0.5	38.4 ± 0.8	24.8 ± 0.5	17.6 ± 0.8
35.0	71.2 ± 1.6	65.4 ± 0.8	38.8 ± 0.6	38.5 ± 0.8	25.3 ± 1.5
45.0	86.5 ± 2.1	80.4 ± 1.2	39.1 ± 1.5	53.5 ± 1.7	33.8 ± 1.1
30 mass % w_1					
15.0	51.6 ± 2.6	46.6 ± 1.1	42.3 ± 1.6	22.0 ± 0.7	27.1 ± 2.1
25.0	65.2 ± 1.5	60.7 ± 0.9	45.6 ± 0.4	33.9 ± 0.2	32.3 ± 0.6
35.0	79.9 ± 1.2	76.2 ± 0.6	49.4 ± 1.0	47.2 ± 1.5	39.2 ± 1.7
45.0	96.0 ± 1.8	93.1 ± 1.5	53.4 ± 1.9	61.8 ± 1.8	53.9 ± 1.3
50 mass % w_1					
15.0	55.4 ± 2.4	49.9 ± 1.3	42.8 ± 1.5	19.6 ± 0.9	30.6 ± 2.3
25.0	70.4 ± 1.7	64.2 ± 0.7	48.9 ± 0.5	34.2 ± 0.5	35.3 ± 0.8
35.0	86.8 ± 1.8	79.9 ± 0.9	55.5 ± 0.8	50.4 ± 0.8	40.5 ± 1.6
45.0	104.6 ± 2.6	97.0 ± 1.4	62.8 ± 1.5	68.3 ± 1.7	46.4 ± 1.4
70 mass % w_1					
15.0	58.1 ± 2.7	52.3 ± 1.5	46.0 ± 1.6	22.0 ± 1.6	35.2 ± 1.8
25.0	73.4 ± 1.4	67.2 ± 0.3	51.2 ± 0.8	36.6 ± 0.8	39.3 ± 1.5
35.0	90.2 ± 1.6	83.7 ± 1.2	56.8 ± 0.4	52.9 ± 1.4	43.9 ± 1.7
45.0	108.4 ± 2.7	101.6 ± 1.7	63.1 ± 1.9	70.8 ± 1.5	49.1 ± 1.6

Table 8. Standard Enthalpies of the Ion Association in Ethanol (1) + Water (2) at Several Temperatures

	$\Delta H°/kJ \cdot mol^{-1}$				
t/°C	$[Co(NH_3)_6]Cl_3$	$[Co(NH_3)_6]Br_3$	$[Co(NH_3)_6]I_3$	$[Co(NH_3)_6](NO_3)_3$	$[Co(NH_3)_6](ClO_4)_3$
10 mass % w_1					
15.0	1.7 ± 0.3	0.0	−0.8 ± 0.4	−7.7 ± 0.3	−8.5 ± 0.7
25.0	5.4 ± 0.5	3.7 ± 0.4	0.0	−4.1 ± 0.5	−6.5 ± 0.5
35.0	9.7 ± 0.4	7.9 ± 0.5	0.9 ± 0.7	0.0	−4.1 ± 0.6
45.0	14.5 ± 0.6	12.7 ± 0.4	2.0 ± 0.5	4.7 ± 0.4	−1.5 ± 0.4
30 mass % w_1					
15.0	1.8 ± 0.6	0.0	−1.0 ± 0.2	−8.4 ± 0.4	−5.8 ± 0.5
25.0	5.8 ± 0.4	4.1 ± 0.3	0.0	4.5 ± 0.6	−4.1 ± 0.6
35.0	10.2 ± 0.3	8.8 ± 0.2	1.1 ± 0.4	0.0	−4.2 ± 0.7
45.0	15.3 ± 0.5	14.1 ± 0.3	2.4 ± 0.4	5.1 ± 0.3	0.0
50 mass % w_1					
15.0	2.0 ± 0.4	0.0	1.7 ± 0.7	−9.2 ± 0.8	−5.8 ± 0.3
25.0	6.4 ± 0.5	4.2 ± 0.6	0.0	−4.9 ± 0.5	−4.4 ± 0.4
35.0	11.4 ± 0.6	8.9 ± 0.7	2.0 ± 0.6	0.0	−2.8 ± 0.7
45.0	16.9 ± 0.3	14.3 ± 0.5	4.3 ± 0.4	5.6 ± 0.4	2.0 ± 0.5
70 mass % w_1					
15.0	2.0 ± 0.5	0.0	−1.5 ± 0.9	−9.2 ± 0.4	−5.1 ± 0.5
25.0	6.5 ± 0.7	4.5 ± 0.7	0.0	−4.9 ± 0.2	−3.9 ± 0.8
35.0	11.6 ± 1.2	9.3 ± 0.5	1.7 ± 0.9	0.0	−2.5 ± 0.6
45.0	17.3 ± 0.7	14.9 ± 1.0	3.6 ± 1.0	5.6 ± 0.8	1.8 ± 0.4

entropy and enthalpy changes for ion association increased with increasing temperatures and amount of ethanol for halide ions. The experimental values of $\Delta S°$ were in the order $Cl^- > Br^- > I^-$ at given temperatures. For oxoacid ions, standard entropy and enthalpy changes for ion association indicated some disorder with increasing temperature. The values of $\Delta S°$ for all complex salts were large and positive. This was attributed to the increase in the fraction of the contact ion pairs formed by the hydrogen bonding between the polar hydrogen atoms of the complexes and the anions in mixtures. $\Delta H°$ values were positive for chloride and bromide. The values of $\Delta H°$ for perclorate were found to be more negative than those of other ions. The negative $\Delta H°$ values could not be predicted from the ion association theories.[16,17] Such values of $\Delta H°$ were attributed to the existence of short-range forces almost independent of the relative permittivity of the medium. The most effective short-range interaction of ions was probably hydrogen bonding. The amino groups of a complex could contribute to the hydrogen bonding with molecules of mixtures. The hydrogen bonding between the complex ion and monovalent anions was probably performed by releasing some mixed solvent molecules hydrogen bonding to the ions. The ion−ion hydrogen bonding reduced the enthalpy of the ion association, while hydrogen bond cleavage of ion-mixed solvents increased it.

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Note Added after ASAP Posting

This article was released ASAP on 7/27/2002 before all author changes were made. The correct version (with changes made in eq 2 and the subsequent phrase) was posted on 7/30/2002.

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