Electrostatic and Hydrophobic Interactions in the Ion Associations between Tripositive Complex Ions and Sulfonate Anions

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The ion associations of $[Co(NH_3)_6]^{3+}$, $[Cr(en)_3]^{3+}$(en=ethylenediamine), *lel*$_3$-$[Cr(R\text{-chxn})_3]^{3+}$ (*lel*$_3$=*lel, lel,lel-*, and chxn=*trans*-1,2-cyclohexanediamine), $[Co(bpy)_3]^{3+}$ (bpy=2,2′-bipyridine), $[Co(phen)_3]^{3+}$(phen=1,10-phenanthroline), and $[Cr(phen)_3]^{3+}$ with Cl^-, SO_4^{2-}, $CH_3SO_3^-$, $C_6H_5SO_3^-$, $(CH_2SO_3)_2^{2-}$, and *m*-$C_6H_4(SO_3)_2^{2-}$ were investigated at 25 °C by means of conductivity measurements of aqueous mixed electrolyte solutions with a stoichiometrically constant ionic strength of 0.01 $mol\,dm^{-3}$. The ion-association constants thus obtained were compared with each other and also with those estimated by the use of electrostatic theories of ion association. Some specific interactions besides such usual electrostatic ones were found to play important roles in the ion associations of SO_4^{2-} with $[Co(NH_3)_6]^{3+}$ and $[Cr(en)_3]^{3+}$, in those of $C_6H_5SO_3^-$ and *m*-$C_6H_4(SO_3)_2^{2-}$ with $[Co(phen)_3]^{3+}$, $[Cr(phen)_3]^{3+}$, and $[Co(bpy)_3]^{3+}$, and in those of SO_4^{2-}, $C_6H_5SO_3^-$, and *m*-$C_6H_4(SO_3)_2^{2-}$ with *lel*$_3$-$[Cr(R\text{-chxn})_3]^{3+}$. The specific interactions existing in the first group were presumed to be short-range electrostatic ones, such as hydrogen-bonding, and in the second group, the so-called hydrophobic ones. The complex ion, *lel*$_3$-$[Cr(R\text{-chxn})_3]^{3+}$, seemed to have both interactions, depending on the counter anions.

The kinetics of the aquations of cobalt(III) or iron(II)-complex cations having hydrophobic ligands are, unusually, affected by the presence of sulfonate anions.[1-3] These unusual effects have been ascribed to hydrophobic interactions between the complex cations and the sulfonate anions. In these cases, the hydrophobic interaction affects the reactions with an electrostatic one. In the present study, the ion-association constants between several tripositive metal complex ions with hydrophobic or hydrophilic ligands and various anions with hydrophobic or hydrophilic groups were obtained by the conductivity method in order to establish what kinds of cations and anions form ion pairs more easily than would be expected from pure electrostatic interaction. Conductivity measurements were made at a stoichiometrically constant ionic strength (I_{st}=0.01) according to the continuous-variation method, the usefulness of which has previously been demonstrated for the mixed systems of $[Co(NH_3)_6]Cl_3$-Na_2SO_4 and $[Co(en)_3]Cl_3$-Na_2SO_4.[4] This method was confirmed to be useful and convenient for the investigation of ion association by means of changing counterions, although the absolute values of the ion-association constants still include some uncertainties, dependending on the assumptions made on the analysis. As the present purpose is to examine systematically the specific interactions by comparing the various ion-association constants obtained, this method is expected to be applicable. Various kinds of complex cations and anions (listed in the synopsis) were used to examine whether or not specific interactions such as the hydrophobic one between the ions are present. The magnitudes of specific interactions contributing to the ion association were estimated by comparing the experimental ion-association constants with those calculated from electrostatic theories of ion association.[5-7]

Experimental

Materials. The complex salts, $[Co(NH_3)_6]Cl_3$ (Complex **1**),[8] $[Cr(en)_3]Cl_3\cdot 3H_2O$ (Complex **2**),[9] *lel,lel,lel*-$[Cr(chxn)_3]Cl_3\cdot 3H_2O$ (Complex **3**),[10] $[Co(bpy)_3]Cl_3\cdot 4H_2O$ (Complex **4**),[11] and $[Co(phen)_3]Cl_3\cdot 5H_2O$ (Complex **5**),[11] were prepared and recrystallized according to the methods in the literature. The $[Cr(phen)_3]Cl_3\cdot 6H_2O$ complex (Complex **6**) was obtained from the perchlorate;[12] an aqueous solution of the perchlorate was passed through chloride ion-exchange resin, and then the chloride was crystallized from the solution in a rotating evaporator. The recrystallization was performed from a water-ethanol solution with the addition of benzene. The purities of the crystals were confirmed by elemental analyses of the hydrogen, carbon, and nitrogen and by comparing the maxima of the absorption spectra with the literature values. The results of the elemental analysis were as follows. **Complex 2** Found: C, 18.1; H, 7.9; N, 21.6%. Calcd for $[Cr(en)_3]Cl_3\cdot 3H_2O$: C, 18.4; H, 7.7; N, 21.4%. **Complex 3** Found: C, 43.0; H, 8.2; N, 16.5%. Calcd for $[Cr(chxn)_3]Cl_3$: C, 43.2; H, 8.5; N, 16.8%. **Complex 4** Found: C, 50.6; H, 4.5; N, 12.0%. Calcd for $[Co(bpy)_3]Cl_3\cdot 4H_2O$: C, 51.0; H, 4.6; N, 11.9%. **Complex 5** Found: C, 53.7; H, 4.0; N, 10.6%. Calcd for $[Co(phen)_3]Cl_3\cdot 5H_2O$: C, 54.3; H, 4.3; N, 10.6%. **Complex 6** Found: C, 54.0; H, 4.2; N, 10.1%. Calcd for $[Cr(phen)_3]Cl_3\cdot 6H_2O$: C, 53.6; H, 4.5; N, 10.4%. The number (n_h) of the water of crystallization in the metal-complex crystals were determined by both Karl-Fischer titrations and elemental analyses. The n_h values of both the 1,10-phenanthroline complexes given above were less than those in the literature.[11,12]

The sodium halides and the sodium sulfate used were guaranteed reagents of Wako Pure Chemical Industries, Ltd. The sodium methanesulfonate was obtained by neutralization of methanesulfonic acid with aqueous sodium hydroxide and was recrystallized from a water-methanol solution. The sodium benzenesulfonate, of a practical grade from the same company, was recrystallized from a water-ethanol solution and dried at 80 °C in vacuo. The sodium ethanedisulfonate and *m*-benzenedisulfonate were also purchased from the Wako Co. in practical grades. They included significant amounts of sodium sulfate as an impurity; these impurities were removed as follows. The aqueous solutions of the reagents were passed over the cation resin of Dowex-50W-X8 (H-type), and the eluate was neutralized with a $Ba(OH)_2$ aqueous solution. Through this procedure, the sulfate ion was removed as a $BaSO_4$ precipitate. The remaining solution containing the barium disulfonate was passed again over the cation resin of Dowex-50W-X8(Na type) and was then condensed to crystallize out the sodium salt in a rotating evaporator. The crystals thus obtained were dried in a vacuum at 120 °C. The purity of the crystal was confirmed by elemental analyses of the carbon and hydrogen. Found: C, 10.4; H, 1.8%. Calcd for $Na_2(CH_2SO_3)_2$: C, 10.3; H, 1.8%. Found: C, 25.2; H, 1.6%. Calcd for $Na_2C_6H_4(SO_3)_2$: C, 25.5; H, 1.4%.

Conductivity Measurements. The conductivity measurements were performed with an admittance linear bridge (Fuso 362A) operated at 1 kHz. The conductivity cell with platinized platinum electrodes (cell constants: 0.4315 cm^{-1} or 0.1519 cm^{-1}) was fixed in a double layer bath controlled to 25.000±0.005 °C. The conductivity of water used for the preparation of solutions was usually about 6×10^{-7} S cm^{-1}. Aqueous mixed electrolyte solutions with a stoichiometrically constant ionic strength ($I_{st}=0.01$) were prepared by mixing xv dm^3 of a 0.001667 mol dm^{-3} MCl_3 solution (M is a complex ion) and $(1-x)v$ dm^3 of a 0.01 mol dm^{-3} NaA (A is a monovalent anion) solution or of a 0.003333 mol dm^{-3} Na_2A (A is a divalent anion) solution, where x and $1-x$ are the volume fractions of the respective solutions involved in the volume v of a mixed solution. Conductivities were measured for eleven solutions, from $x=0$ to 1 at 0.1 intervals, for each mixed electrolyte system.

Conductivity measurements of aqueous single-salt solutions at low concentrations (10^{-4}—10^{-3} mol dm^{-3}) were also carried out in order to obtain the limiting molar conductivities of the following ions: $[Cr(en)_3]^{3+}$, *lel*$_3$-$[Cr(chxn)_3]^{3+}$, $[Co(bpy)_3]^{3+}$, $[Co(phen)_3]^{3+}$, $[Cr(phen)_3]^{3+}$, $CH_3SO_3^-$, $C_6H_5SO_3^-$, $(CH_2SO_3)_2^{2-}$, and *m*-$C_6H_4(SO_3)_2^{2-}$. Chlorides of the complex cations and sodium salts of the above anions were used for the measurements.

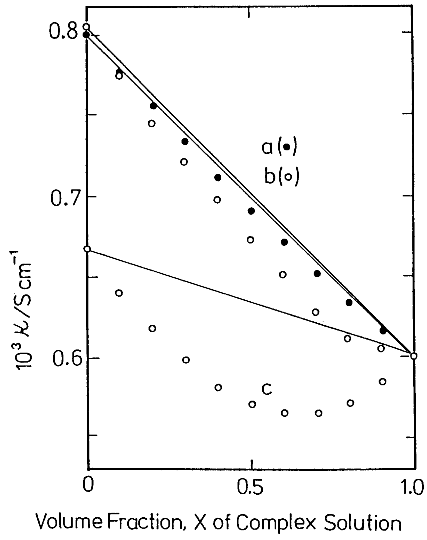

Fig. 1. Observed conductivities (κ_{mix}) of mixed electrolyte solutions as a function of the volume fraction, x, of the complex salt solution.
($I_{st}=0.01$, 25 °C)
a) $[Co(phen)_3]Cl_3$-$C_6H_5SO_3Na$ system. b) $[Co(phen)_3]Cl_3$-Na_2SO_4 system. c) $[Co(phen)_3]Cl_3$-*m*-$C_6H_4(SO_3Na)_2$ system. Solid lines are κ_{add}.

Results

Figure 1 shows some typical conductivities (κ_{mix}) of aqueous mixtures of electrolytes including c_1x mol dm^{-3} of MCl_3 and $c_2(1-x)$ mol dm^{-3} of Na_nA ($n=1$ or 2) as functions of the volume fraction (x) of the complex salt solution at a stoichiometrically constant ionic strength of 0.01.

The observed κ_{mix} values deviated negatively from the hypothetical additivity(κ_{add}) given by solid lines in Fig. 1; the deviations of κ_{mix} from κ_{add} given by:

$$\Delta\kappa = \kappa_{mix} - \kappa_{add} = \kappa_{mix} - (x\kappa_1 + (1-x)\kappa_2), \tag{1}$$

were assumed to be due to the ion association between M^{3+} and A^- (or A^{2-}), similar to the assumption made by Katayama and Tamamushi.[4] The conductivity data obtained for the MCl_3-Na_nA mixtures ($n=1$ or 2) were analyzed by considering the following ion-association equilibria:

$$M^{3+} + Cl^- = M^{3+}Cl^- \tag{2}$$

and:

$$M^{3+} + A^{n-} = M^{3+}A^{n-}, \tag{3}$$

The other equilibria, such as the formations of Na^+A^{n-} and triple ions, were disregarded. The ion-association constants at $I_{st}=0.01$ are given by:

$$K_C(MA) = \frac{[MA]}{[M][A]} = \frac{[MA]}{(c_1x - [MA] - [MCl])\{c_2(1-x) - [MA]\}} \tag{4}$$

$$K_C(MCl) = \frac{[MCl]}{[M][Cl]} = \frac{[MCl]}{(c_1x - [MA] - [MCl])(3c_1x - [MCl])}. \tag{5}$$

On such assumptions, we can express κ_{mix} and κ_{add} as follows:

$$\begin{aligned} 10^3\kappa_{mix} &= \lambda_M(c_1x - [MA] - [MCl]) + \lambda_A\{c_2(1-x) - [MA]\} \\ &\quad + \lambda_{MA}[MA] + \lambda_{MCl}[MCl] + n\lambda_{Na}c_2(1-x) \\ &\quad + \lambda_{Cl}(3c_1x - [MCl]) \\ &= (\lambda_M + 3\lambda_{Cl})c_1x + (n\lambda_{Na} + \lambda_A)c_2(1-x) \\ &\quad + (\lambda_{MA} - \lambda_M - \lambda_A)[MA] + (\lambda_{MCl} - \lambda_M - \lambda_{Cl})[MCl] \end{aligned} \tag{6}$$

and

$$\begin{aligned} 10^3\kappa_{add} &= \lambda_M x(c_1 - [MCl]_{x=1}) + \lambda_A c_2(1-x) + \lambda_{MCl}x[MCl]_{x=1} \\ &\quad + n\lambda_{Na}c_2(1-x) + \lambda_{Cl}x(3c_1 - [MCl]_{x=1}) \\ &= (\lambda_M + 3\lambda_{Cl})c_1x + (n\lambda_{Na} + \lambda_A)c_2(1-x) \\ &\quad + x(\lambda_{MCl} - \lambda_M - \lambda_{Cl})[MCl]_{x=1} \end{aligned} \tag{7}$$

where [MCl] and [MA] are the concentrations of $M^{3+}Cl^-$ and $M^{3+}A^{n-}$ respectively in the mixtures; where $[MCl]_{x=1}$ is that of $M^{3+}Cl^-$ in the simple salt solution of $MCl_3(x=1)$, and where λ_M, λ_A, λ_{Na}, λ_{Cl}, λ_{MCl}, and λ_{MA} are the molar conductivities of the corresponding ionic species (the ionic charges are abbreviated). The first and the second terms of the final equation in Eq. 6 correspond to the conductivities of complex salts (MCl_3) and sodium salts (Na_nA) respectively if they are assumed to be completely dissociated in the single-salt systems. Assuming that these terms are approximately equal to those in Eq. 7, we can derive the following equations from Eqs. 1, 6, and 7:

$$10^3\Delta\kappa = [MA]\Delta\lambda_{MA} + \delta, \tag{8}$$

where

$$\Delta\lambda_{MA} = \lambda_{MA} - \lambda_M - \lambda_A, \tag{9}$$

and

$$\delta = ([MCl] - x[MCl]_{x=1})\Delta\lambda_{MCl}, \tag{10}$$

where

$$\Delta\lambda_{MCl} = \lambda_{MCl} - \lambda_M - \lambda_{Cl}. \tag{11}$$

Katayama and Tamamushi[4] assumed that the [MCl]/[MA] ratio was small enough to neglect the [MCl] in the mixed systems of $[Co(NH_3)_6]Cl_3$-Na_2SO_4 or $[Co(en)_3]Cl_3$-Na_2SO_4. By putting $\delta=0$ in Eq. 8 and $[MCl]=0$ in Eq. 4, they reduced the number of unknown parameters to two ($K_c(MA)$ and $\Delta\lambda_{MA}$); they then analyzed their conductivity data in two manners: (1) by treating $\Delta\lambda_{MA}$ as an unknown adjustable parameter and (2) by giving $\Delta\lambda_{MA}$ values independently estimated. Although the analysis by the first method is simpler than that by the second one, the former gives $K_c(MA)$ values with systematic errors much larger than those given by the latter method. This is because $K_c(MA)$ and $\Delta\lambda_{MA}$ compensate for each other, as may be presumed from Eqs. 4 and 8. We, therefore, used the second method in the present analysis; we took into account the formation of $M^{3+}Cl^-$, since the condition of $[MCl]/[MA] \ll 1$ did not hold for the systems with $\log K_c(MA) <$ c.a. 2.6—2.7.

Table 1. Limiting Molar Conductivities of Ions, $\lambda_{ion}^{\infty}/S\,cm^2\,mol^{-1}$

Ion	λ_{ion}^{∞}	Ion	λ_{ion}^{∞}
Na^+	50.1[a]	Cl^-	76.4[a]
$[Co(NH_3)_6]^{3+}$	306[a]	SO_4^{2-}	160[b]
$[Cr(en)_3]^{3+}$	227	$CH_3SO_3^-$	49.8(48.8)[c]
*lel*3-$[Cr(chxn)_3]^{3+}$	135	$C_6H_5SO_3^-$	34.9
$[Co(bpy)_3]^{3+}$	167	$(CH_2SO_3)_2^{2-}$	138
$[Co(phen)_3]^{3+}$	156	*m*-$C_6H_4(SO_3)_2^{2-}$	119(119.2)[d]
$[Cr(phen)_3]^{3+}$	160		

a) Data from Ref. 20. b) Data from Ref. 21. c) Data(in parentheses) from Ref. 22. d) Data(in parentheses) from Ref. 23.

According to a treatment previously reported,[4] the values of λ_{ion} at $I_{st}=0.01$ were estimated by the use of the Onsager limiting equation[13] from their limiting molar conductivities (λ_{ion}^{∞}) (given in Table 1, where the values for λ_M^{∞} and λ_A^{∞} were estimated from the molar conductivities of single salts extrapolated to an infinite dilution by means of the Onsager plot). The values of λ_{MA}^{∞} and λ_{MCl}^{∞} were approximated to be $\{(3-n)^2/9\}\lambda_M^{\infty}$ in a manner similar to be previously described.[4,14] This approximation is based on the Stokes law, where it is assumed that the Stokes radius of $M^{3+}A^{n-}$ or $M^{3+}Cl^-$ is close to that of M^{3+} and that the hydrodynamics of the ion pairs is controlled by that of the complex cations. This approximation is rather rough, but the contribution of λ_{MA} values to the $\Delta\lambda_{MA}$ values estimated for $M^{3+}A^{2-}$ is only about 10%. The uncertainty of $\Delta\lambda_{MA}$ values, therefore, may have a negligible effect on the $K_c(MA)$ values for $M^{3+}A^{2-}$, but it may still have a significant effect on those for $M^{3+}A^-$.[15] Even in the latter case, a relative comparison for a given cation must be useful with changing kinds of counter anions.

Table 2. Ion-Pair Formation Constants, $\log(K_c/dm^3\,mol^{-1})$, between the Tripositive Metal Complex Cations and the Monovalent Anions and the Differences, $\Delta\log(K_c/dm^3\,mol^{-1})$, between the Experimental Values and the Theoretical Values. (25 °C, $I_{st}=0.01$).

		Experimental $\log K_c$	Theoretical $\log K_c$		$\Delta\log K_c$ (=$\log K_c$ (exp)$-$ $\log K_c$ (theor))	
			Fuoss	E-Y-Y	Fuoss	E-Y-Y
$[Co(NH_3)_6]^{3+}$	: Cl^-	1.40±0.06	1.11	1.27	0.29	0.13
	$CH_3SO_3^-$	1.30±0.04	1.05	1.19	0.25	0.11
	$C_6H_5SO_3^-$	1.27±0.03	1.03	1.14	0.24	0.13
$[Cr(en)_3]^{3+}$	: Cl^-	1.40±0.03	1.06	1.21	0.34	0.19
	$CH_3SO_3^-$	1.26±0.05	1.03	1.14	0.23	0.12
	$C_6H_5SO_3^-$	1.34±0.05	1.02	1.10	0.32	0.24
*lel*3-$[Cr(chxn)_3]^{3+}$	: Cl^-	1.56±0.04	1.03	1.14	0.53	0.42
	$CH_3SO_3^-$	1.26±0.05	1.02	1.08	0.24	0.18
	$C_6H_5SO_3^-$	1.42±0.06	1.03	1.05	0.39	0.37
$[Co(bpy)_3]^{3+}$	: Cl^-	1.26±0.04	1.02	1.11	0.24	0.15
	$CH_3SO_3^-$	1.00±0.04	1.02	1.06	−0.02	−0.06
	$C_6H_5SO_3^-$	1.60±0.05	1.03	1.02	0.57	0.58
$[Co(phen)_3]^{3+}$	: Cl^-	1.26±0.06	1.02	1.09	0.24	0.17
	$CH_3SO_3^-$	a)	1.03	1.04	a)	a)
	$C_6H_5SO_3^-$	1.70±0.03	1.04	1.01	0.66	0.69

a) The deviation, $\Delta\kappa$, was too small for us to obtain the exact associaton constant.

Table 3. Ion-Pair Formation Constants, $\log(K_c/\mathrm{dm^3\,mol^{-1}})$, between the Tripositive Metal Complex Cations and the Divalent Anions and the Differences, $\Delta\log(K_c/\mathrm{dm^3\,mol^{-1}})$, between the Experimental Values and the Theoretical Values. (25 °C, $I_{st}=0.01$).

	Experimental $\log K_c$	Theoretical $\log K_c$		$\Delta\log K_c$ (=$\log K_c$ (exp)− $\log K_c$ (theor))	
		Fuoss	E-Y-Y	Fuoss	E-Y-Y
$[\mathrm{Co(NH_3)_6}]^{3+}:\mathrm{SO_4}^{2-}$	3.02±0.01 (2.98)[a]	2.52	2.48	0.50	0.54
$(\mathrm{CH_2SO_3})_2{}^{2-}$	2.35±0.01	2.27	2.31	0.08	0.04
m-$\mathrm{C_6H_4(SO_3)_2}^{2-}$	2.32±0.01	2.20	2.27	0.12	0.05
$[\mathrm{Cr(en)_3}]^{3+}:\ \mathrm{SO_4}^{2-}$	2.79±0.02	2.34	2.36	0.45	0.43
$(\mathrm{CH_2SO_3})_2{}^{2-}$	2.35±0.02	2.14	2.23	0.21	0.12
m-$\mathrm{C_6H_4(SO_3)_2}^{2-}$	2.38±0.02	2.09	2.20	0.29	0.18
lel_3-$[\mathrm{Cr(chxn)_3}]^{3+}:\mathrm{SO_4}^{2-}$	2.89±0.01	2.14	2.23	0.75	0.66
$(\mathrm{CH_2SO_3})_2{}^{2-}$	2.43±0.01	2.01	2.14	0.42	0.29
m-$\mathrm{C_6H_4(SO_3)_2}^{2-}$	2.64±0.01	1.97	2.14	0.67	0.50
$[\mathrm{Co(bpy)_3}]^{3+}:\mathrm{SO_4}^{2-}$	2.09±0.02	2.08	2.19	0.01	−0.10
$(\mathrm{CH_2SO_3})_2{}^{2-}$	2.23±0.01	1.96	2.11	0.27	0.12
m-$\mathrm{C_6H_4(SO_3)_2}^{2-}$	2.45±0.01	1.93	2.08	0.52	0.37
$[\mathrm{Co(phen)_3}]^{3+}:\mathrm{SO_4}^{2-}$	1.98±0.02	2.05	2.17	−0.07	−0.19
$(\mathrm{CH_2SO_3})_2{}^{2-}$	2.21±0.02	1.94	2.09	0.27	0.12
m-$\mathrm{C_6H_4(SO_3)_2}^{2-}$	2.65±0.01	1.91	2.07	0.74	0.58
$[\mathrm{Cr(phen)_3}]^{3+}:\mathrm{SO_4}^{2-}$	1.95±0.01	2.05	2.17	−0.10	−0.22
$(\mathrm{CH_2SO_3})_2{}^{2-}$	2.13±0.01	1.94	2.09	0.19	0.04
m-$\mathrm{C_6H_4(SO_3)_2}^{2-}$	2.62±0.02	1.91	2.07	0.71	0.55

Calculations to obtain $K_c(\mathrm{MA})$ values were, therefore, made with Eqs 4, 5, and 8—11 by taking into account the effect of the ion association of $\mathrm{Cl^-}$, coexisting in solutions as a counter ion of the complex, on the ion-association constants. In order to estimate the $K_c(\mathrm{MCl})$ values, we also measured the conductivities of $\mathrm{MCl_3}$-NaCl mixtures at $I_{st}=0.01$, and analyzed them by the use of these equations:

$$[\mathrm{MCl}] = 10^3\Delta\kappa/\Delta\lambda_{\mathrm{MCl}} + x[\mathrm{MCl}]_{x=1}, \tag{12}$$

and

$$K_c(\mathrm{MCl}) = \frac{[\mathrm{MCl}]}{(c_1x-[\mathrm{MCl}])\{c_2(1-x)+3c_1x-[\mathrm{MCl}]\}}. \tag{13}$$

Equation 12 was derived by putting [MA]=0 into Eqs. 8—11. The values of $K_c(\mathrm{MCl})$ were obtained by successive approximations with Eqs. 12 and 13 for each composition of the solutions. Table 2 lists the $\log K_c(\mathrm{MCl})$ values thus obtained, which were then used to obtain $\log K_c(\mathrm{MA})$.

The $\log K_c(\mathrm{MA})$ values are summarized in Tables 2 and 3. In obtaining the values, all analyses were performed by ignoring the changes in the ionic strength due to the ion association. In the solution of $x=0.5$ of the $[\mathrm{Co(NH_3)_6}]^{3+}$-$\mathrm{SO_4}^{2-}$ system, the ionic strength decreased by about 25%. If we consider this effect, we must use Eq. 7 including the λ_{ion} values at a depressed ionic strength (I_{dep}) in order to estimate κ_{add}, the expression of which may be given approximately by:

$$10^3\kappa_{\mathrm{add}} = \Lambda(\mathrm{MCl_3}, I=I_{\mathrm{dep}})c_1x + \Lambda(\mathrm{Na}_n\mathrm{A}, I=I_{\mathrm{dep}})c_2(1-x), \tag{14}$$

where $\Lambda(\mathrm{MCl_3}, I=I_{\mathrm{dep}})$ and $\Lambda(\mathrm{Na}_n\mathrm{A}, I=I_{\mathrm{dep}})$ are the molar conductivities of the single salts at $I=I_{\mathrm{dep}}$ and can roughly be estimated by assuming a linear relationship between $\Lambda(\mathrm{MCl_3})$ or $\Lambda(\mathrm{Na}_n\mathrm{A})$ and $\sqrt{I}$. The change in $\Delta\lambda_{\mathrm{MA}}$ or $\Delta\lambda_{\mathrm{MCl}}$ with the decrease in the ionic strength can be easily estimated in the same way as has been described in the text, but this change is relatively slight compared with that in $\Delta\kappa(=\kappa_{\mathrm{mix}}-\kappa_{\mathrm{add}})$. These corrections lead to larger K_c values (0.02—0.03 in $\log K_c$). However, the extrapolation of $\log K_c$ values from $I=I_{\mathrm{dep}}$ to $I=0.01$ decreases them again. The resulting change in $\log K_c$ at $x=0.5$ after all the corrections were −0.03—−0.05, dependent on the mixed systems. These values should decrease with the approach of x to 0 or 1. As is shown in Table 3, the standard deviations for the $\log K_c$ values were less than 0.02 over a wide x range for each system; this finding indicates that the effect of the decrease in the ionic strength will not be so large as has been estimated above.

Discussion

Tables 2 and 3 show that the ion-association constants obtained are largely dependent on the kind of ion besides the ionic charge. In order to estimate the contribution of the usual long-range electrostatic interactions to the ion-association constants obtained, we calculated the ion-association constants from the electrostatic theories of Fuoss[5] and of Ebeling[6]-Yokoyama-Yamatera[7] (abbreviated to E-Y-Y) by assuming the ions to be spherical. The values of a (the closest distance of the approach of the ions) were assumed to be equal to the sums of the effective ionic radii (r_{ef}), as estimated from the van der Waals volumes of the ions. These volumes were calculated

Table 4. Ionic Radii Used for the Theoretical Calculation of the Ion-Association Constants

	$10\ r_{ef}/\mathrm{nm}$	
$[Co(NH_3)_6]^{3+}$	3.10	a)
$[Cr(en)_3]^{3+}$	3.62	a)
lel$_3$-$[Cr(chxn)_3]^{3+}$	4.45	b)
$[Co(bpy)_3]^{3+}$	4.80	c)
$[Co(phen)_3]^{3+}$	4.98	c)
$[Cr(phen)_3]^{3+}$	4.98	c)
Cl^-	1.82	a)
$CH_3SO_3^-$	2.57	d)
$C_6H_5SO_3^-$	3.09	d)
SO_4^{2-}	2.33	e)
$(CH_2SO_3)_2^{2-}$	3.15	d)
m-$C_6H_4(SO_3)_2^{2-}$	3.39	a)

a) See Ref. 17. b) See Ref. 24. c) Estimated from their ionic partial molar volumes (see Ref. 26). d) Estimated on the basis of the method in Refs. 16 and 17. e) See Ref. 21.

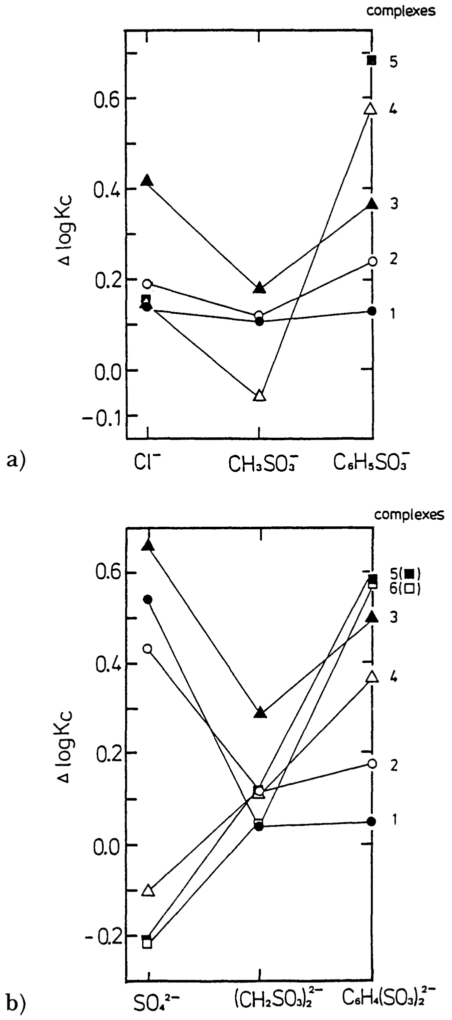

Fig. 2. The $\Delta\log K_c$ values for the formation of ion pairs between M^{3+} and A^{n-} (n=1, 2) where $\Delta\log K_c = \log K_c(\mathrm{exp}) - \log K_c$ (E-Y-Y theor).
M^{3+}=(1) $[Co(NH_3)_6]^{3+}$, (2) $[Cr(en)_3]^{3+}$, (3) *lel*$_3$-$[Cr(chxn)_3]^{3+}$, (4) $[Co(bpy)_3]^{3+}$, (5) $[Co(phen)_3]^{3+}$, (6) $[Cr(phen)_3]^{3+}$
a) For monovalent anion (n=1). b) For divalent anion (n=2).

from the ionic partial molar volumes by the use of Glueckauf's equation[16,17] or from the van der Waals increments of atoms tabulated by Edward.[17,18] The effective ionic radii thus obtained are given in Table 4. As the theoretical values calculated are given for the solutions at an infinite dilution (I=0), they were extrapolated to I=0.01 by the use of the Debye-Hückel equation for activity coefficients.[19] In Tables 2 and 3 the theoretical association constants thus obtained for I=0.01 are listed. The theoretical K_c values are not greatly dependent on the theories used. In several cases, the experimental $\log K_c$ values are significantly larger than the theoretical values. This difference can be attributed to the presence of specific interactions besides the simple electrostatic one. We shall express the contribution of these specific interactions by the differences in $\log K_c$ values: $\Delta\log K_c$ (=$\log K_c$ (exp)$-\log K_c$ (theor)), the values of which are shown in Tables 2 and 3 and also in Fig. 2 (a and b). These results reveal that if both the cation and the anion have hydrophobic groups, the value of $\Delta\log K_c$ is significantly large, while if only either the cation or the anion has them, it is approximately zero. It is also clear that the affinity to the benzenesulfonate ion increases in the order of the cyclohexanediamine (chxn) < the bipyridine(bpy) < the 1,10-phenanthroline (phen) complex. This order corresponds to that of the number of carbon atoms in the ligands, suggesting the presence of hydrophobic interactions. The hydrophobicities of $[Co(phen)_3]^{3+}$ and $[Cr(phen)_3]^{3+}$ are considered to be similar to each other because their $\Delta\log K_c$ values for the *m*-benzenedisulfonate ions are close. A similar $\Delta\log K_c$ value(0.56 from the E-Y-Y theory) was estimated for the ion association between $[Fe(phen)_3]^{2+}$ and *m*-$C_6H_4(SO_3)_2^{2-}$.[25] This result shows that such excess values in the ion-association constants are due to hydrophobic interactions between the ions and that they are not affected by the ionic charges of the complex ions.

For both the disulfonate ions, the chxn complex has a specific affinity and the magnitude is larger than that of the bpy complex in spite of the smaller number of the carbon atoms. This can be ascribed to the property of the chxn complex, which has not only the hydrophobicity, but also the amino protons along the threefold axis (C_3) of symmetry of the complex. The amino protons form hydrogen bonding with the oxygen atoms of the oxoanions to stabilize the ion pairs. This role of the amino protons is supported by the relatively large $\Delta\log K_c$ values for the ion-pairs: $[Cr(chxn)_3]^{3+}\cdot SO_4^{2-}$, $[Co(NH_3)_6]^{3+}\cdot SO_4^{2-}$, and $[Cr(en)_3]^{3+}\cdot SO_4^{2-}$. No specific effects were found in the ion pairs of *m*-$C_6H_4(SO_3)_2^{2-}$ with $[Co(NH_3)_6]^{3+}$ or $[Cr(en)_3]^{3+}$ and of $C_2H_4(SO_3)_2^{2-}$ except for the $[Cr(chxn)_3]^{3+}$ complex, which has slight specific effects. The finding of no such specific interactions is consistent with the fact that the hydrophobic interaction occurs between hydrophobic solutes.

All the specific interactions detected in this study can, therefore, be attributed to the hydrophobic interaction or the hydrogen-bonding.

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