1304 © *1984 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, *57*, *1304—1311 (1984)* [Vol. 57, No. 5

Conductivity and Ion Association of Some Diastereoisomeric Salts in Water. I. Δ-[Co(NO$_2$)$_2$(en)$_2$]Δ-[Co(edta)] and Λ-[Co(NO$_2$)$_2$(en)$_2$]Δ-[Co(edta)] at 15, 25, and 35 °C

Haruhiko Yokoyama

Department of Chemistry, Yokohama City University, 22-2 Seto, Kanazawa-ku, Yokohama 236

(Received October 4, 1983)

Electric conductivities of the diastereoisomeric salts, $\Delta(-)_{589}$-[Co(NO$_2$)$_2$(en)$_2$]$\Delta(+)_{546}$-[Co(edta)] and Λ-$(+)_{589}$-[Co(NO$_2$)$_2$(en)$_2$]$\Delta(+)_{546}$-[Co(edta)], were measured in water at 15, 25, and 35 °C. Results were analyzed in terms of the conductivity equations of Fuoss-Hsia and Pitts. The obtained values of the ion-association constant are large and decrease with increasing temperature. The results can not be entirely explained by the electrostatic theories of ion association and suggest the formation of contact ion pairs, attributable to the existence of interactions other than simple electrostatic ones between the complex ions. No appreciable difference is found in the obtained thermodynamic parameters of ion association between the two salts. Ion-solvent interactions and effective sizes of the dissolved complex ions are also discussed in connection with the estimation of the closest distance of approach of the ions.

In recent years, many studies have been made on the stereoselectivity in ion association between optically active ions.[1—8] In particular, the association of L-tartrate ion with Δ- and Λ-[Co(en)$_3$]$^{3+}$ was widely investigated. Appearance of the stereoselectivity is attributed to the differences in structure and stability of ion pairs, and suggests the existence of ion–ion interactions other than simple electrostatic ones such as the Bjerrum-type ion association.[9,10] The hydrogen-bonding has often been presumed to be the most probable extra interaction for the association of [Co(en)$_3$]$^{3+}$ with dicarboxylate ions or other anions.[4—8,11,12] Such extra interactions are of importance for studies of ion–ion and ion-solvent interactions in the vicinity of dissolved complex ions. However, they are not necessarily investigated well.

Optically active *cis*-bis(ethylenediammine)dinitrocobalt(III) ion and (ethylenediaminetetraacetato)cobaltate(III) ion are frequently used as agents for resolution of optical isomers of complex ions.[13] The absolute configurations for $(-)_{589}$-enantiomer of *cis*-[Co(NO$_2$)$_2$(en)$_2$]$^+$ and $(+)_{546}$-enantiomer of [Co(edta)]$^-$ have been determined to be Δ-form by X-ray diffraction studies.[14,15] With respect to the solubilities of the diastereoisomeric salts, Δ-[Co(NO$_2$)$_2$(en)$_2$]Δ-[Co(edta)] and Λ-[Co(NO$_2$)$_2$(en)$_2$]Δ-[Co(edta)], the former is less soluble than the latter in water. The stereoselectivity has been observed on the rate of amino-hydrogen exchange of Δ- and Λ-[Co(NO$_2$)$_2$(en)$_2$]$^+$ in aqueous mixed electrolyte solutions containing Λ-[Co(edta)]$^-$.[16] However, no detailed information has been provided about the nature of the interactions between the complex ions. In the present study, conductivities of the above diastereoisomeric salts in water were observed at 15, 25, and 35 °C. From the analysis of conductivity data, we examined whether extra interactions are present between the complex ions or not, and whether these interactions, if present, are stereoselective or not.

The reason why such 1:1-type salts were chosen is given below. Strong 1:1 electrolytes such as sodium chloride have been usually thought to dissociate almost completely into ions in aqueous solutions.[17a] This is consistent with the prediction from the electrostatic theories of ion association.[9,10] Both ions, *cis*-[Co(NO$_2$)$_2$(en)$_2$]$^+$ and [Co(edta)]$^-$, are monovalent ones of large size. Simple electrostatic interactions may therefore be considered to be almost absent. This makes it easy to discuss the experimental results. The conductivity measurements were made with solutions of single salts alone. Consequently, the analysis of experimental data is very simple compared to the case for mixed electrolyte solutions with which most of the above studies on stereoselectivity have been carried out. The coexistence of other ions complicates not only the analysis but the explanation of results, owing to competitions or cooperative phenomena on ion association.[18]

The conductivity method is very effective to investigate ion association of 1:1 electrolytes, because it is very sensitive to a lowering of the conductivity due to the formation of noncharged ion pairs. Moreover, conductivity data obtained for 1:1 electrolytes can be precisely analyzed by using the excellent theoretical conductivity equations of Fuoss-Hsia and Pitts for a symmetrical electrolyte.[19,20] Pethybridge and Spiers have measured conductivities of the following 1:1 salts in water at 25 °C: *trans*-[Co(NO$_2$)$_2$(en)$_2$]X- (X$^-$=Cl$^-$, Br$^-$, I$^-$, NO$_3^-$, ClO$_4^-$, and [Co(edta)]$^-$), *cis*-[Co(NO$_2$)$_2$(en)$_2$]X (X$^-$=I$^-$ and NO$_3^-$), and M[Co(edta)] (M$^+$=Li$^+$, Na$^+$, K$^+$, and Et$_4$N$^+$).[21,22] They analyzed their experimental data by use of the equations of Fuoss-Hsia and Pitts and found out that each electrolyte is slightly associated in water. The results obtained in the present study will be compared to theirs.

The measurements of conductivity were made by employing the linear-bridge conductometer developed by Katayama *et al.*[23] This apparatus is very favorable to examine a temperature dependence of conductivity since the temperature of the solution can be detected simultaneously with the observation of conductivity. The enthalpy and entropy of ion association will be estimated from the temperature dependence of the ion-association constant and will be used to discuss the nature of interactions between the complex ions.

Experimental

Materials. *Δ- and Λ-[Co(NO$_2$)$_2$(en)$_2$]X (X$^-$=Br$^-$ and*

I^-): The optically active bromide salts were prepared following the method of Dwyer and Garvan[24] from the nitrite of the racemic complex,[25] and were recrystallized from warm water (*ca.* 60 °C) by cooling in ice immediately after filtration. The recrystallization was repeated until a constant rotation result was obtained. The iodide salts were obtained by adding potassium iodide to aqueous solutions of the purified bromide salts, and recrystallized in the same manner as the bromide salts. Each salt was air-dried at room temperature. The $[\alpha]_{589}$ values of Δ- and Λ-$[Co(NO_2)_2(en)_2]Br$ were $-44°\pm1°$ and $+44°\pm1°$, respectively. Those of the iodides of Δ- and Λ-complexes were $-39°\pm1°$ and $+39°\pm1°$, respectively.

$K\Delta$-[Co(edta)]·$2H_2O$: The optically active potassium salt was prepared following the method of Dwyer and Garvan.[26] The obtained salt was purified by fractional crystallization and air-dried at room temperature. The value of $[\alpha]_{546}$ was $+1010°\pm5°$.

Δ-[Co(NO_2)$_2$(en)$_2$]Δ-[Co(edta)]·$3H_2O$: This less soluble diastereoisomeric salt was prepared by adding $K\Delta$-[Co(edta)]·$2H_2O$ to an aqueous solution of Δ-$[Co(NO_2)_2(en)_2]Cl$, which was prepared by the double decomposition of the iodide of the complex and silver chloride in warm water (*ca.* 60°C). The obtained salt was recrystallized from warm water (*ca.* 45 °C) by the addition of ethanol. The absence of potassium and chloride ions was ascertained by adding sodium tetraphenylborate and silver nitrate, respectively, to an aqueous solution of the salt. After air-drying at room temperature, the number of molecules of the crystal water was confirmed to be three by the dehydration under vaccum by the use of a Cahn electrobalance.[27] The value of $[\alpha]_{546}$ was $+574°\pm5°$. The density of the crystal was 1.7_4 g cm^{-3} at 25 °C.

Λ-[Co(NO_2)$_2$(en)$_2$]Δ-[Co(edta)]·H_2O: This more soluble diastereoisomeric salt was prepared by adding ethanol to a warm aqueous solution (*ca.* 60 °C) containing equimolar proportions of the salts: Λ-$[Co(NO_2)_2(en)_2]I$ and $K\Delta$-[Co(edta)]·$2H_2O$. The obtained salt was recrystallized twice from warm water (*ca.* 40 °C) by adding ethanol and was air-dried at room temperature. The check for potassium and iodide ions and the confirmation of the number of molecules of the crystal water were performed in the manner described above. The value of $[\alpha]_{546}$ was $+735°\pm5°$. The density of the crystal was 1.7_9 g cm^{-3} at 25 °C.

ORD and Electronic Absorption Spectra of the Diastereoisomeric Salts in Dilute Aqueous Solutions. The measurements of ORD and absorption spectra were carried out with a JASCO ORD/UV-5 spectropolarimeter and a Hitachi 139 spectrophotometer. The molar rotation of Δ-$[Co(NO_2)_2(en)_2]\Delta$-[Co(edta)] in water was identical with the sum of those of Δ-$[Co(NO_2)_2(en)_2]Br$ and $K\Delta$-[Co(edta)] at any wave length from about 340 to 700 nm within the experimental error. A similar additivity was observed for Λ-$[Co(NO_2)_2(en)_2]\Delta$-[Co(edta)]. The absorption spectra of both diastereoisomeric salts in the wave length region of about 280 to 700 nm agreed with each other and with the prediction from those of *cis*-$[Co(NO_2)_2(en)_2]Br$ and K[Co(edta)] within the experimental error.

Conductivity Measurements. All solutions were made up by weight just before conductivity measurements. The conductivity of water used for the preparation was lower than 2.0×10^{-7} S cm^{-1} at 25 °C. The concentration of solutions on the molar scale at each temperature was determined by density measurements.

The conductivity measurements were made at 1000 Hz with a Fuso 360 linear-bridge conductometer according to the procedure described by Katayama *et al.*[23] The conductivity cell used was a four-necked flask with a 250 cm^3 capacity which was equipped with a thermistor, a nitrogen inlet, a magnetic stirrer, and two platinized platinum electrodes. The cell constant was 0.13702 cm^{-1}.

The conductivities of solutions were measured at 15.0, 25.0, and 35.0 °C in an atmosphere of purified nitrogen gas. Before the beginning of the measurements, dissolved carbon dioxide was removed by bubbling moistened nitrogen gas through the solution in the cell for about 50 min. During the bubbling, the solution was cooled to a temperature a little below 15 °C. The measurement was started from this temperature. The solution was warmed slowly at a speed of 0.02—0.03 °C/min to a temperature a little above 15 °C, while the change of resistance of the solution was recorded together with that of resistance of the thermistor inserted in the cell. Immediately after the recording, the solution was warmed at a high speed of 0.5—0.8 °C/min to a temperature a little below 25 °C. Subsequent procedures were made in a similar manner. A set of runs was accomplished in every case within about 2.5 h after the preparation of the solution. Throughout the measurements, the solution was protected from light.

The resistance readings of the linear bridge were calibrated by the substitution method with a precision decade resistance box (Dekabox DB62, Electro Scientific Industries; accuracy ±0.02%). The observed conductivity data were corrected for the conductivity of the solvent and for the minor conductivity change considered to be due to the aquation of *cis*-$[Co(NO_2)_2(en)_2]^+$.[28] The reproducibility of the conductivity measurements was about ±0.1%. The precision of the temperature measurements was ±0.003 °C.

Density Measurements. The density measurements were performed at (25.00±0.02) °C with all solutions used for the conductivity measurements, employing an Ostwald-type pycnometer of 10 cm^3 capacity. An approximately linear relationship was found between concentrations and densities for solutions of each diastereoisomeric salt. The density of the most concentrated solution was also measured at 15.0 and 35.0 °C to determine its molar concentration; these values were used to estimate that of the other solutions where a similar linear relationship was assumed to hold at these temperatures. The density measurements for solutions of *cis*-$[Co(NO_2)_2(en)_2]Br$ and K[Co(edta)] were carried out at 25.0 °C by using an Ostwald-type pycnometer of 50 cm^3 capacity, in order to estimate the partial molar volumes of the complex ions.

Results

Hereafter, the diastereoisomeric salts, $\Delta(-)_{589}$-$[Co(NO_2)_2(en)_2]\Delta(+)_{546}$-[Co(edta)] and $\Lambda(+)_{589}$-$[Co(NO_2)_2(en)_2]\Delta(+)_{546}$-[Co(edta)], will be often expressed by the abbreviations, Δ-Δ and Λ-Δ salts, respectively.

The observed values of molar conductivity, Λ (obsd), are summarized in Tables 1 and 2, where c is the molar concentration of a salt. In Fig. 1, the values of Λ (obsd) for each salt are plotted against those of $\sqrt{c}$. No appreciable difference in the plot is present between the Δ-Δ and Λ-Δ salts at any temperature.

The data of the density, d, obtained for aqueous solutions of the diastereoisomeric salts can be reproduced as a function of c:

$$d(\Delta\text{-}\Delta\text{ salt, }25\,°\text{C})/\text{g cm}^{-3} = (0.99704\pm0.00002) + (0.301\pm0.003)c$$

and

$$d(\Lambda\text{-}\Delta\text{ salt, }25\,°\text{C})/\text{g cm}^{-3} = (0.99705\pm0.00002) + (0.299\pm0.003)c.$$

TABLE 1. MOLAR CONDUCTIVITIES OF Δ-[Co(NO$_2$)$_2$(en)$_2$]Δ-[Co(edta)] IN AQUEOUS SOLUTIONS AT 15, 25, AND 35 °C

Temp=15 °C		Temp=25 °C		Temp=35 °C	
$\frac{c}{10^{-3}\ \mathrm{mol\ dm^{-3}}}$	$\frac{\Lambda(\mathrm{obsd})}{\mathrm{S\ cm^2\ mol^{-1}}}$	$\frac{c}{10^{-3}\ \mathrm{mol\ dm^{-3}}}$	$\frac{\Lambda(\mathrm{obsd})}{\mathrm{S\ cm^2\ mol^{-1}}}$	$\frac{c}{10^{-3}\ \mathrm{mol\ dm^{-3}}}$	$\frac{\Lambda(\mathrm{obsd})}{\mathrm{S\ cm^2\ mol^{-1}}}$
1.0064	39.57	1.0043	50.31	1.0013	61.87
1.4646	39.04	1.4616	49.64	1.4572	61.01
1.9495	38.59	1.9454	49.08	1.9396	60.36
2.4314	38.15	2.4263	48.52	2.4190	59.62
3.0350	37.64	3.0287	47.91	3.0195	58.94
3.8935	37.10	3.8854	47.24	3.8737	58.13
5.0228	36.42	5.0125	46.38	4.9973	57.10
6.4907	35.71	6.4773	45.57	6.4577	56.00
8.3986	34.69	8.3813	44.29	8.3560	54.59
10.478	33.84	10.456	43.25	10.425	53.47

TABLE 2. MOLAR CONDUCTIVITIES OF Λ-[Co(NO$_2$)$_2$(en)$_2$]Δ-[Co(edta)] IN AQUEOUS SOLUTIONS AT 15, 25, AND 35 °C

Temp=15 °C		Temp=25 °C		Temp=35 °C	
$\frac{c}{10^{-3}\ \mathrm{mol\ dm^{-3}}}$	$\frac{\Lambda(\mathrm{obsd})}{\mathrm{S\ cm^2\ mol^{-1}}}$	$\frac{c}{10^{-3}\ \mathrm{mol\ dm^{-3}}}$	$\frac{\Lambda(\mathrm{obsd})}{\mathrm{S\ cm^2\ mol^{-1}}}$	$\frac{c}{10^{-3}\ \mathrm{mol\ dm^{-3}}}$	$\frac{\Lambda(\mathrm{obsd})}{\mathrm{S\ cm^2\ mol^{-1}}}$
1.0417	39.61	1.0396	50.31	1.0364	61.80
1.5322	38.97	1.5291	49.55	1.5244	60.92
2.0226	38.58	2.0184	49.06	2.0123	60.34
2.5025	38.12	2.4974	48.50	2.4899	59.62
2.9623	37.79	2.9562	48.12	2.9472	59.22
4.0161	37.06	4.0078	47.21	3.9957	58.11
5.1694	36.34	5.1586	46.31	5.1430	57.02
6.5361	35.66	6.5224	45.50	6.5027	55.90
8.1154	34.85	8.0984	44.48	8.0739	54.80
10.505	33.84	10.483	43.25	10.451	53.35

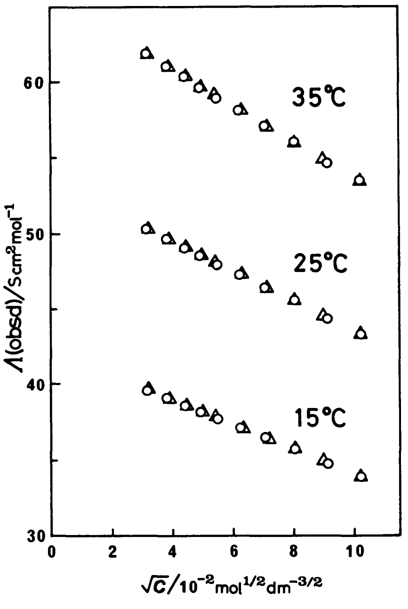

Fig. 1. Plot of Λ(obsd) against $\sqrt{c}$.
○, Λ(obsd) values for the Δ-Δ salt; △, Λ(obsd) values for the Λ-Δ salt.

From these data, the values of the partial molar volume of a salt at infinite dilution, V^{∞}(salt), were evaluated to be 318±4 cm^3 mol^{-1} for the Δ-Δ salt and 320±4 cm^3 mol^{-1} for the Λ-Δ salt according to the conventional manner.[29]

The values of V^{∞}(salt) for *cis*-[Co(NO$_2$)$_2$(en)$_2$]Br and K[Co(edta)] were estimated to be 175±2 and 181±2 cm^3 mol^{-1}, respectively, from the density data of their solutions: d(*cis*-[Co(NO$_2$)$_2$(en)$_2$]Br, 0.009972 mol dm^{-3}, 25 °C)=0.99880 g cm^{-3} and d(K[Co(edta)], 0.009161 mol dm^{-3}, 25 °C)=0.99893 g cm^{-3}. From these results, the values of the partial molar volume of an ion, V^{∞}(ion), can be estimated to be 145±2 and 177±2 cm^3 mol^{-1} for *cis*-[Co(NO$_2$)$_2$(en)$_2$]$^+$ and [Co(edta)]$^-$, respectively, using V^{∞}(Br$^-$, 25 °C)=30.1 cm^3 mol^{-1} and V^{∞}(K$^+$, 25 °C)=3.6 cm^3 mol^{-1}.[29,30] The sum of the partial molar volumes of the complex ions, 322±3 cm^3 mol^{-1}, agreeds closely with the above values of V^{∞}(salt) obtained for the diastereoisomeric salts.

Discussion

Analysis of Conductivity Data. The plot of Λ (obsd) against $\sqrt{c}$ gives a straight line in each case, but

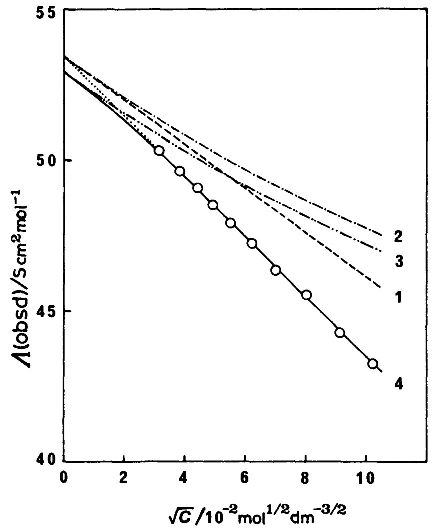

Fig. 2. Λ(obsd) values and theoretical curves for the Δ–Δ salt at 25 °C.
○, Λ(obsd) values.
Curve 1 (----) is the Onsager limiting slope drawn with a value of 53.45 S cm^2 mol^{-1} for the limiting molar conductivity, Λ^∞, obtained by extrapolation of Λ(obsd) to $\sqrt{c}=0$. Curves 2 (—·—) and 3 (—··—) are Fuoss-Hsia's theoretical curves for a completely dissociated electrolyte with $\Lambda^\infty=53.45$ and 52.93 S cm^2 mol^{-1}, respectively, on the assumption of a value of 7.0 Å for the closest distance of approach of ions. Curve 4 (——) is the theoretical curve of Fuoss-Hsia or Pitts with a set of a, K, and Λ^∞ values given in Table 3 (each set ranging $a=1$—9 Å gives almost the same curve).

does not obey the Onsager limiting law,[17b)] as illustrated in Fig. 2. Further, the Λ (obsd) values lie considerably below the theoretical curves predicted for a completely dissociated electrolyte by the conductivity equation of Fuoss-Hsia.[19)] Such negative deviations from the theoretical curves are considered to be due to the ion association. In this study, the conductivity data were analyzed by assuming the following ion association between the complex ions:

$$M^+ + A^- \rightleftharpoons M^+A^-, \qquad (1)$$

where the symbol M^+ refers to the complex cation, Δ-[Co(NO$_2$)$_2$(en)$_2$]$^+$ or Λ-[Co(NO$_2$)$_2$(en)$_2$]$^+$, and the symbol A^- to the complex anion, Δ-[Co(edta)]$^-$. The analysis was made by using the Fuoss-Hsia equation[19)] and the Pitts equation[20)] for a symmetrical electrolyte.

The Fuoss-Hsia equation can be written symbolically as

$$\Lambda=\alpha(\Lambda^\infty-\Delta\Lambda_e)[1+(\Delta X/X)]/(1+1.5\phi), \qquad (2)$$

where α is the degree of dissociation, Λ^∞ is the limiting molar conductivity, $\Delta\Lambda_e$ is the electrophoretic term, $\Delta X/X$ is the relaxation term, and 1.5ϕ corresponds to the term related to the obstruction effect.[17c)] The symbol ϕ denotes the volume fraction occupied by the obstructions, approximated by $(4\pi N_A c/3000)(a/2)^3$ where N_A is the Avogadro number and a is the closest distance of approach of ions. The expressions for the electrophoretic and relaxation terms have been given by Fuoss and Hsia. The electrophoretic term is a function of αc, a, T, z, η_0, and, ε, where T is the absolute temperature, z is the absolute value of charge number of ions, and η_0 and ε are the viscosity and the dielectric constant of the solvent, respectively. The relaxation term is a function of these parameters and Λ^∞.

The Pitts equation for an incompletely dissociated electrolyte can be written symbolically as

$$\Lambda^\infty-(\Lambda/\alpha) = \Lambda^\infty P_1 + P_2 - P_3, \qquad (3)$$

where P_1 is a function of αc, a, T, z, and ε, and where P_2 and P_3 are functions of these parameters as well as η_0. In practice, however, the following modified equation was used for the analysis instead of Eq. 3:

$$\Lambda = \alpha[\Lambda^\infty(1-P_1)-P_2+P_3]/(1+1.5\phi), \qquad (4)$$

This obtained by rearranging Eq. 3 and introducing an obstruction term identical with that involved in Eq. 2.

The ion-association constant, K, was estimated for a given value of a in the following way. With an assumed value of Λ^∞, the degree of dissociation, α, was calculated by usig Eq. 2 or 4 through a successive approximation. The result was inserted in the following equation to obtain the value of K:

$$K = \frac{1-\alpha}{\alpha^2 c y_M y_A}, \qquad (5)$$

where y_M and y_A are the activity coefficients of the free ions, expressed by the Debye-Hückel equation:

$$\log y_M = \log y_A = -A_{DH}\sqrt{\alpha c}/(1+B_{DH}a\sqrt{\alpha c}), \qquad (6)$$

where A_{DH} and B_{DH} represent the theoretical coefficients.[17d)] In these calculations, the values of η_0 and ε of water were taken from the monograph of Robinson and Stokes.[17e)] The best-fit values of Λ^∞ and K for a given a value were determined by the least-squares method with the molar conductivity, Λ.

In Table 3, the results obtained on the assumption of several values for a are summarized, together with the values of the standard deviation, σ.[31)] The obtained values of Λ^∞ are not much dependent on a, whereas those of K are somewhat changed by the choice of the value of a. The best values of Λ^∞ and K as well as of a are usually determined by the minimization of σ. However, this is not necessarily a good criterion for the determination of the best parameter values, because, as can be seen from Table 3, the variation of σ with a is only slight over a rather wide range of a and the value of a giving the minimum value of σ depends on the conductivity equation used for the analysis. The former reason is substantiated by the fact that the Λ(obsd) values can be theoretically reproduced well with any set of the values of Λ^∞ and K for $a=1$—9 Å as illustrated in Fig. 2. Further details have been described in the earlier papers.[31)] We shall discuss what value of a should be taken as the best value after considering the effective sizes of the dissolved complex ions.

Ionic Radii of the Complex Ions and Ion-Solvent Interactions. From the results of the conductivity measurements, we can obtain the information concerning

TABLE 3. Λ^∞ AND K VALUES AT 25 °C FOR THE Δ-Δ AND Λ-Δ SALTS OBTAINED WITH THE FUOSS-HSIA EQUATION (Eq. 2) AND THE PITTS EQUATION (Eq. 4) BY ASSUMING SEVERAL VALUES FOR a

Salt	$\frac{a}{\text{Å}}$	With Eq. 2 (Fuoss-Hsia)			With Eq. 4 (Pitts)		
		$\frac{\Lambda^\infty}{\text{S cm}^2\text{ mol}^{-1}}$	$\frac{K}{\text{dm}^3\text{ mol}^{-1}}$	$\frac{\sigma}{\text{S cm}^2\text{ mol}^{-1}}$	$\frac{\Lambda^\infty}{\text{S cm}^2\text{ mol}^{-1}}$	$\frac{K}{\text{dm}^3\text{ mol}^{-1}}$	$\frac{\sigma}{\text{S cm}^2\text{ mol}^{-1}}$
Δ-Δ	1.0	52.90±0.07	7.9±0.7	0.0691	52.91±0.07	8.5±0.6	0.0682
	3.0	52.92±0.07	9.5±0.6	0.0673	52.93±0.07	10.0±0.6	0.0671
	5.0	52.93±0.07	10.9±0.6	0.0668	52.93±0.07	11.0±0.6	0.0670
	7.0	52.93±0.07	11.8±0.6	0.0671	52.92±0.07	11.9±0.6	0.0673
	9.0	52.90±0.07	12.2±0.7	0.0681	52.91±0.07	12.4±0.7	0.0684
	11.0	52.86±0.08	12.1±0.8	0.0730	52.88±0.07	12.7±0.7	0.0705
Λ-Δ	1.0	52.96±0.04	8.1±0.6	0.0422	52.98±0.04	8.7±0.6	0.0415
	3.0	52.99±0.04	9.7±0.5	0.0411	52.99±0.04	10.1±0.5	0.0410
	5.0	53.00±0.04	11.0±0.5	0.0410	53.00±0.04	11.2±0.5	0.0410
	7.0	52.99±0.04	12.0±0.5	0.0410	52.99±0.04	12.0±0.5	0.0411
	9.0	52.97±0.04	12.4±0.6	0.0418	52.97±0.04	12.6±0.6	0.0416
	11.0	52.93±0.05	12.3±0.6	0.0459	52.95±0.05	12.8±0.6	0.0433

the ionic radii of the complex ions in the following way. From the values of Λ^∞(25 °C) for a=1—9 Å, the sum of the limiting molar conductivities of *cis*-[Co(NO$_2$)$_2$(en)$_2$]$^+$ and [Co(edta)]$^-$ is considered to be 52.9 to 53.0 S cm^2 mol^{-1}. For Λ^∞([Co(edta)]$^-$, 25 °C), a value of 26.17±0.10 S cm^2 mol^{-1} has been reported by Pethybridge and Spiers.[22] The use of this value leads to Λ^∞(*cis*-[Co(NO$_2$)$_2$(en)$_2$]$^+$, 25 °C)=26.8±0.1 S cm^2 mol^{-1}.[32] By employing these Λ^∞(ion) values, the Stokes radii, r_s,[33] are evaluated to be 3.4$_4$ Å for *cis*-[Co(NO$_2$)$_2$(en)$_2$]$^+$ and 3.5$_2$ Å for [Co(edta)]$^-$.

The ionic radii of the complex ions can also be estimated from their partial molar volumes, V^∞(ion). According to Glueckauf's study,[34] V^∞(ion) of a univalent ion of large size is expressed by

$$V^\infty(\text{ion}) = 2.52(r+0.55)^3 - 33/(r+1.38), \qquad (7)$$

where r corresponds to the crystallographic radius of the ion. The first term refers to the intrinsic volume of the ion and the second term to the electrostriction volume loss. Equation 7 was employed for the estimation of the ionic radii of the complex ions by regarding these ions as spherical. Substituting V^∞(ion)= 145±2 cm^3 mol^{-1} for *cis*-[Co(NO$_2$)$_2$(en)$_2$]$^+$ and V^∞(ion)=177±2 cm^3 mol^{-1} for [Co(edta)]$^-$ in Eq. 7, we obtain r=3.3$_7$ Å and 3.6$_3$ Å, respectively. The r value is in fair agreement with the r_s value for each complex ion. This suggests that both complex ions are not appreciably hydrated.

Information relating to the ion-solvent interaction can be provided from the temperature dependence of the Walden products: Λ^∞(salt)η_0/10^{-4} S N s mol^{-1}= 0.474 (15 °C), 0.471 (25 °C), and 0.468 (35 °C) which are calculated from the averaged values of Λ^∞(salt) obtained for the Δ-Δ and Λ-Δ salts. These Λ^∞(salt)η_0 values decrease slightly as the temperature increases. The temperature coefficient, d ln {Λ^∞(salt)η_0}/dT, is evaluated to be -6×10^{-4} K^{-1} close to that of Me$_4$N$^+$.[35] This implies that at least one of *cis*-[Co(NO$_2$)$_2$(en)$_2$]$^+$ and [Co(edta)]$^-$ is a structure-breaker. The latter ion may be classified as a structure-breaker from the fact that the viscosity B{[Co(edta)]$^-$} coefficient in the Jones-Dole equation increases with increasing temperature.[36] For *cis*-[Co(NO$_2$)$_2$(en)$_2$]$^+$, there is no available information about the temperature dependence of the B coefficient. However, it is interesting that the values of V^∞(ion) and Λ^∞(ion) for *cis*-[Co(NO$_2$)$_2$(en)$_2$]$^+$ are very closely similar to those for tetrakis(2-hydroxyethyl)ammonium ion, (HOCH$_2$CH$_2$)$_4$N$^+$: V^∞(ion)=146.8 cm^3 mol^{-1} [37] and Λ^∞(ion)=27.0 S cm^2 mol^{-1} at 25 °C.[38] Both the Walden product Λ^∞(ion)η_0 and the B(ion) coefficient for (HOCH$_2$CH$_2$)$_4$N$^+$ are known to be nearly independent of temperature.[35,38]

From the above consideration, the complex ions, *cis*-[Co(NO$_2$)$_2$(en)$_2$]$^+$ and [Co(edta)]$^-$, are presumed to have no hydration shell and to be able to come into contact to each other. Therefore, it seems reasonable that the value of a is taken to be equal to the sum of the values of r or r_s obtained for the complex ions: a=7.0$_0$ Å from the r values or a=6.9$_6$ Å from the r_s values. These values of a are considered to be moderate values because the prediction from the distance between the central cobalt(III) atoms of the two complex ions ranges from about 5 to 9 Å dependent on the direction of approach of the ions. Such a range arises from the unsymmetrical shape of the complex ions and the complexity of their surface. For these reasons, the best value of a was assumed to be equal to 7.0 Å for the diastereoisomeric salts in water.

Ion-Ion Interactions. The results obtained by assuming 7.0 Å as the best value of a are shown in Table 4. The K values for each salt are considerably larger than those predicted by the electrostatic theories of ion association.[9,10,39] According to the Bjerrum theory,[9] the values of K are expected to be equal to zero since the Bjerrum critical distance q (=3.58 Å at 25 °C for a 1:1 electrolyte)[17g] is smaller than 7.0 Å. From the theoretical equation presented by Yokoyama and Yamatera,[40] the values of K/dm^3 mol^{-1} are estimated to be 0.23 (15 °C), 0.24 (25 °C), and 0.25 (35 °C). The Fuoss theory[39] predicts 2.38 (15 °C), 2.41 (25 °C), and 2.44 (35 °C)

TABLE 4. Λ^{∞} AND K VALUES AT 15, 25, AND 35 °C FOR THE Δ-Δ AND Λ-Δ SALTS OBTAINED BY ASSUMING $a=7.0$ Å WITH THE FUOSS-HSIA EQUATION (Eq. 2) AND THE PITTS EQUATION (Eq. 4)

Salt	Temp / °C	With Eq. 2 (Fuoss-Hsia)		With Eq. 4 (Pitts)	
		Λ^{∞} / S cm^2 mol^{-1}	K / dm^3 mol^{-1}	Λ^{∞} / S cm^2 mol^{-1}	K / dm^3 mol^{-1}
Δ-Δ	15	41.66 ± 0.04	12.9 ± 0.4	41.66 ± 0.04	12.9 ± 0.4
	25	52.93 ± 0.07	11.8 ± 0.6	52.92 ± 0.07	11.9 ± 0.6
	35	65.03 ± 0.08	11.0 ± 0.8	65.02 ± 0.09	11.1 ± 0.8
Λ-Δ	15	41.72 ± 0.04	13.1 ± 0.7	41.72 ± 0.04	13.2 ± 0.7
	25	52.99 ± 0.04	12.0 ± 0.5	52.99 ± 0.04	12.0 ± 0.5
	35	65.12 ± 0.05	11.4 ± 0.5	65.11 ± 0.05	11.4 ± 0.5

TABLE 5. THERMODYNAMIC PARAMETERS OF ION ASSOCIATION, $\Delta G°$, $\Delta H°$, AND $\Delta S°$, AT 25 °C OBTAINED BY ASSUMING $a=7.0$ Å

		$\Delta G°$ / kJ mol^{-1}	$\Delta H°$ / kJ mol^{-1}	$\Delta S°$ / J K^{-1} mol^{-1}
Experimental value				
with Eq. 2(Fuoss-Hsia)	Δ-Δ	-6.12 ± 0.13	-5.8 ± 0.4	1.1 ± 1.6
	Λ-Δ	-6.16 ± 0.11	-5.3 ± 0.7	2.9 ± 2.8
with Eq. 4(Pitts)	Δ-Δ	-6.13 ± 0.13	-5.7 ± 0.3	1.4 ± 1.4
	Λ-Δ	-6.17 ± 0.12	-5.3 ± 0.7	3.0 ± 2.8
Theoretical value				
by Yokoyama-Yamatera[40)]		3.55	3.54	−0.03
by Fuoss[39)]		−2.18	0.93	10.4

for K/dm^3 mol^{-1}.

The K value for each salt decreases as the temperature is raised, contrary to the prediction from the electrostatic theories. This tendency means that the ion association is an exothermic reaction. The standard enthalpy and entropy of ion association, $\Delta H°$ and $\Delta S°$, were estimated from the temperature dependence of the ion-association constant. The $\Delta H°$ value was derived from the slope of a linear plot of $\log K$ against T^{-1}, while the $\Delta S°$ value was calculated from the equation, $\Delta S° = (\Delta H° - \Delta S°)/T$, where $\Delta G°$ is the standard Gibbs free energy of ion association. The obtained values of $\Delta G°$, $\Delta H°$, and $\Delta S°$ are shown in Table 5 and are compared with those predicted by the electrostatic theories of ion association.[39,40)]

Table 5 shows that the relation, $\Delta H° < T\Delta S° \approx 0$, is valid for the observed values of $\Delta H°$ and $\Delta S°$. This relation is distinct from $T\Delta S° > \Delta H° > 0$ obtained for the ion association of 2:2 electrolytes such as $MgSO_4$.[23,41)] The negative $\Delta H°$ values can not be predicted from the ion-association theories.[39,40)] Such values of $\Delta H°$ will be attributed to the existence of short-range forces almost independent of the dielectric constant of the medium. The $\Delta S°$ values nearly equal to zero may suggest that the ion association occurs without the release of the hydration water molecules of the complex ions. This is consistent with the presumption that the complex ions, *cis*-$[Co(NO_2)_2(en)_2]^+$ and $[Co(edta)]^-$, are not appreciably hydrated. Consequently, the comparatively large values of K for each salt are considered to imply the formation of contact ion pairs resulting from interactions other than simple electrostatic ones between the complex ions.

It has been found that tetraalkylammonium halides, R_4NX, are slightly associated in water and the K values of the salts decrease with increasing temperature in a similar manner as observed in the present study.[42)] Pethybridge and Spiers have reported the fact that the K values in water for 1:1 electrolytes including R_4NX increase with increasing the sum of the crystallographic radii, $\sum r$(cryst).[21,22,43)] Such a trend is the reverse of that predicted by the ion-association theories of Bjerrum[9)] and Yokoyama-Yamatera.[10)] The Fuoss theory predicts that the ion-association constant increases with increasing the a value at $a > 2q/3$ ($a > 2.39$ Å at 25 °C).[17h)] However, his theory can not also give the negative $\Delta H°$ value for any ion association in water. Therefore, the phenomenon of ion association of 1 : 1 electrolytes is considered to be due to existence of ion–ion interactions other than the simple electrostatic ones.

Pethybridge and Spiers have expressed graphically the relationship between K and $\sum r$ (cryst).[21,22,43)] If we estimate the value of K for the diastereoisomeric salts from this relationship, a value of 4—5 dm^3 mol^{-1} can be obtained.[44)] However, this value of K is much smaller than the experimental ones given in Table 4. This implies that different kinds of extra interactions exist between the complex ions. The most effective interaction among them may be the hydrogen-bonding between the hydrogen atoms of amino groups of *cis*-$[Co(NO_2)_2(en)_2]^+$ and the oxygen atoms of calboxyl groups of $[Co(edta)]^-$. The ion-association constants of the Δ-Δ and Λ-Δ salts are somewhat larger than that of *trans*-$[Co(NO_2)_2(en)_2][Co(edta)]$: $K \approx 9\ dm^3\ mol^{-1}$.[4,5] This may be mainly attributed to the difference not only in the magnitude of the dipole moment of the complex cations, but in the ease of the formation of the hydrogen bonds. In the case of the *trans*-isomer, the nitro groups are considered to be more unfavorably located for the hydrogen-bonding than in the case of the *cis*-isomer.

Stereoselectivity. The ion pairs, Δ-$[Co(NO_2)_2(en)_2]^+\Delta$-$[Co(edta)]^-$ and Λ-$[Co(NO_2)_2(en)_2]^+\Delta$-$[Co(edta)]^-$, can not be stereochemically the same. However, as shown in Table 5, no appreciable difference between the two ion pairs is found in the thermodynamic properties of ion-pair formation. Although the $\Delta H°$ value of the Δ-Δ salt seems to be slightly smaller than that of the Λ-Δ salt, it is indefinite because of the experimental error. The difference in solubilities of the Δ-Δ and Λ-Δ salts would have to be interpreted from that in their crystal structures.

Yamatera and Fujita have observed the rate of amino-hydrogen exchange of Δ- and Λ-$[Co(NO_2)_2(en)_2]^+$ ($0.039\ mol\ dm^{-3}$) under the presence of Λ-$[Co(edta)]^-$ ($0.035\ mol\ dm^{-3}$) in D_2O and found out that the rate constant for the Λ-complex cation is 0.86 times that for the Δ-complex cation.[16] The hydrogen-deutrium exchange rate is thought to be slowed down by means of the ion association. If the hydrogen-deutrium exchange rate of the associated complex cations were negligibly small compared with that of the free ion, the degree of dissociation for the Λ-complex cation should be 0.86 times that for the Δ-complex cation. However, such a large difference in the degree of dissociation can not be derived from the present results. Therefore, in order to explain the difference in the observed rate constant, the associated complex cations should be supposed to contribute to the hydrogen-deutrium exchange rate. In addition, the extent of the contribution of the associated Δ-complex cation should be greater than that of the associated Λ-complex cation. The hydrogen-deutrium exchange of $[Co(en)_3]^{3+}$ has been considered to be assisted by the OD^- ion.[5] If a similar mechanism is assumed also in the case of Δ- and Λ-$[Co(NO_2)_2(en)_2]^+$, the difference in the extent of the contribution to the exchange rate between the two associated complex cations may be attributed to the difference in the ease of N–H bond breaking caused by the association with Λ-$[Co(edta)]^-$ as well as the difference in the affinity of the associated complex cations with the OD^- ion.

The author is gratefully indebted to Professor Nobuyoshi Shinohara of Yokohama City University for his helpful discussion, Dr. Masataka Ozaki for the use of a Cahn electrobalance, and Dr. Shunzo Katayama of the Institute of Physical and Chemical Research for his helpful advice and suggestions on the conductivity measurements. I would also like to thank Mr. Michio Nishimura for his asistance. The present work was partially supported by a Grant-in-Aid for Scientific Research No. 354227 from the Ministry of Education, Science and Culture.

References

1) K. Ogino and U. Saito, *Bull. Chem. Soc. Jpn.*, **40**, 826 (1967).

2) H. Yamatera and M. Fujita, *Bull. Chem. Soc. Jpn.*, **42**, 3043 (1969).

3) H. Yoneda, K. Miyoshi, S. Suzuki, and T. Taura, *Bull. Chem. Soc. Jpn.*, **47**, 1661 (1974).

4) M. Fujita and H. Yamatera, *Bull. Chem. Soc. Jpn.*, **49**, 1301 (1976).

5) M. Fujita and H. Yamatera, *Bull. Chem. Soc. Jpn.*, **50**, 2672 (1977).

6) H. Yokoyama, The Proceedings of the 27th Conference on Coordination Chemistry of the Chemical Society of Japan, Matsumoto, September 1977, p. 87.

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

8) A. Tatehata, M. Iiyoshi, and K. Kotsuji, *J. Am. Chem. Soc.*, **103**, 7391 (1981).

9) N. Bjerrum, *Kgl. Danske Videnskab. Selskab.*, **7**, No. 9 (1926).

10) H. Yokoyama and H. Yamatera, *Bull. Chem. Soc. Jpn.*, **48**, 1770, 3002 (1975).

11) K. Miyoshi, C. E. Oh, and H. Yoneda, *Bull. Chem. Soc. Jpn.*, **53**, 2815 (1980).

12) S. F. Mason and B. J. Norman, *J. Chem. Soc., A*, **1966**, 307.

13) W. T. Jordan and B. J. Brennan, L. R. Froebe, and B. E. Douglas, *Inorg. Chem.*, **12**, 1827 (1973).

14) K. Matsumoto and H. Kuroya, *Bull. Chem. Soc. Jpn.*, **45**, 1755 (1972).

15) K. Okamoto, T. Tsukihara, J. Hidaka, and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **51**, 3534 (1978).

16) Ref. 2. The footnote in Ref. 2 is related to $[Co(en)_3]^{3+}$, $[Co(NO_2)_2(en)_2]^+$, and tartrate ion, and in the case of *l*-$[Co(edta)]^-$ the notation *l* denotes $(-)_{546}$(private communication, 1981).

17) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," 2nd ed, Butterworths, London (1959). a) Chaps. 7, 9, and 14; b) Chap. 7, p. 142; c) Chap. 11, pp. 310—313; d) Chap. 9, p. 229; e) Appendix 1.1, p. 457; g) Chap. 14; h) Appendix 14.3, p. 551.

18) Represented by the ion association of complex cations with perchlorate ion added to solutions in order to hold a constant ionic strength. See, for example, Ref. 3; H. Yokoyama and H. Yamatera, The Proceedings of the 20th Conference on Coordination Chemistry of the Chemical Society of Japan, Tokyo, November 1970, p. 57; L. Johansson, *Coord. Chem. Rev.*, **12**, 241 (1974).

19) R. M. Fuoss and K. -L. Hsia, *Proc. Natl. Acad. Sci. U. S. A.*, **57**, 1550 (1967); **58**, 1818 (1968).

20) E. Pitts, *Proc. R. Soc. London, Ser. A*, **217**, 43 (1953); E. Pitts, B. E. Tabor, and J. Daly, *Trans. Faraday Soc.*, **65**, 849 (1969).

21) A. D. Pethybridge and D. J. Spiers, *J. Chem. Soc., Faraday Trans. 1*, **9**, 64 (1976).

22) A. D. Pethybridge and D. J. Spiers, *J. Chem. Soc., Faraday Trans. 1*, **9**, 73 (1976).

23) S. Katayama, *Bull. Chem. Soc. Jpn.*, **46**, 106 (1973); *J. Solution Chem.*, **5**, 241 (1976); *Rep. I. P. C. R.*, **53**, 212 (1977); K. Takahashi, S. Katayama, and R. Tamamushi, *ibid.*, **49**, 13 (1973).

24) F. P. Dwyer and F. L. Garvan, *Inorg. Synth.*, **6**, 195 (1960).

25) J. Springbørg and C. E. Chäffer, *Inorg. Synth.*, **14**, 63

(1973).

26) F. P. Dwyer and F. L. Garvan, *Inorg. Synth.*, **6**, 192 (1960).

27) Two water molecules of Δ-$[Co(NO_2)_2(en)_2]\Delta$-$[Co(edta)]\cdot 3H_2O$ and the water molecule of Λ-$[Co(NO_2)_2(en)_2]\Delta$-$[Co(edta)]\cdot H_2O$ were dehydrated at room temperature *in vacuo*, while the third water molecule of the former salt was dehydrated by heating above *ca.* 90 °C *in vacuo*.

28) Pethybridge and Spiers have observed the increase with time in the conductivity for *trans*-$[Co(NO_2)_2(en)_2]X$ (X^-= Cl^-, Br^-, I^-, NO_3^-, ClO_4^-, and $[Co(edta)]^-$) and *cis*-$[Co(NO_2)_2(en)_2]X$ ($X^-=I^-$ and NO_3^-): about 0.01% per hour except for *trans*-$[Co(NO_2)_2(en)_2][Co(edta)]$.[21] In the present study, the rate of increase in the conductivity for the diastereoisomeric salts was about 0.02% per hour at 25 °C. This value is consistent with the above value, since the increase per the molar conductivity of the complex cation can be estimated to be equal to about 0.04% per hour in both cases. For *trans*-$[Co(NO_2)_2(en)_2][Co(edta)]$, the rate of increase in the conductivity has been reported to be about 0.1% per hour at 25 °C, much greater than that obtained for the other salts.[21] This abnormal value was explained by suggesting that the aquation of the complex cation is catalyzed by the hydrogen ion liberated as a result of hydrolysis of $[Co(edta)]^-$. If such a phenomenon occurred actually, the rate of increase in the conductivity would have to be accelerated with increase of concentration of the salt. However, no dependence of the rate on the concentration has been found in their study.[21]

29) F. J. Millero, *Chem. Rev.*, **71**, 147 (1971); "The Partial Molal Volumes of Electrolytes in Aqueous Solutions," in "Water and Aqueous Solutions," ed by R. A. Horne, Wiley-Intersciene, New York (1972), Chap. 13.

30) R. Zana and E. Yeager, *J. Phys. Chem.*, **71**, 521 (1967).

31) H. Yokoyama and H. Yamatera, *Bull. Chem. Soc. Jpn.*, **48**, 2708, 2719 (1975).

32) This value is slightly smaller than the value of $27.4\pm0.3\ \mathrm{S\,cm^2\,mol^{-1}}$ reported by Pethybridge and Spiers.[21] A value of $27.7\pm0.4\ \mathrm{S\,cm^2\,mol^{-1}}$ for Λ^∞(*trans*-$[Co(NO_2)_2(en)_2]^+$) has been also given by them.[21] The sum of the values of Λ^∞(*trans*-$[Co(NO_2)_2(en)_2]^+$) and $\Lambda^\infty([Co(edta)]^-)$ becomes $53.87\ \mathrm{S\,cm^2\,mol^{-1}}$, much smaller than the value of $62.26\ \mathrm{S\,cm^2\,mol^{-1}}$ obtained from the experimental data for *trans*-$[Co(NO_2)_2(en)_2][Co(edta)]$.[21] Such discrepancy is not found for the Λ^∞ values of the diastereoisomeric salts in the present study.

33) Expressed by $r_s/\text{Å}=0.820/\Lambda^\infty/(\eta_0/\mathrm{poise})$ where 1 poise$=10^{-1}\ \mathrm{kg\,m^{-1}\,s^{-1}}$. See, for example, Ref. 17, Chap. 2, p. 44.

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

35) R. L. Kay, "Ionic Transport in Water and Mixed Aqueous Solvents," in "Water," ed by F. Franks, Plenum Press, New York (1973), Vol. 3, Chap. 4.

36) M. Yasuda, *Bull. Chem. Soc. Jpn.*, **41**, 139 (1968); K. Mizutani and M. Yasuda, The Proceedings of the 24th Conference on Coordination Chemistry of the Chemical Society of Japan, Kanazawa, October 1974, p. 373.

37) W.-Y. Wen and S. Saito, *J. Phys. Chem.*, **69**, 3569 (1965): estimated from $V^\infty\ \{(HOCH_2CH_2)_4NBr\}=176.9\ \mathrm{cm^3\,mol^{-1}}$ by assuming $V^\infty(Br^-)=30.1\ \mathrm{cm^3\,mol^{-1}}$.[29,30]

38) D. F. Evans, G. P. Cunningham, and R. L. Kay, *J. Phys. Chem.*, **70**, 2974 (1966); G. P. Cunningham, D. F. Evans, and R. L. Kay, *ibid.*, **70**, 3998 (1966).

39) R. M. Fuoss, *J. Am. Chem. Soc.*, **80**, 5059 (1958).

40) Ref. 10. The ion-association constant is given by

$$K=\frac{8\pi N_A a^3}{1000}\sum_{n=1}^{\infty}\frac{b^{2n+2}}{(2n+2)!(2n-1)},$$

where b is the Bjerrum parameter given by $b=z^2e^2/\varepsilon kTa$.

41) H. Yokoyama and H. Yamatera, *Bull. Chem. Soc. Jpn.*, **54**, 2286 (1981).

42) R. Fernandez-Prini, *Trans. Faraday Soc.*, **64**, 2146 (1968).

43) A. D. Pethybridge and D. J. Spiers, *J. Chem. Soc., Chem. Commun.*, **1974**, 423.

44) From the K-$\sum r$ (cryst) graph given in Refs. 21, 22, and 43, a value of 2—3 $\mathrm{dm^3\,mol^{-1}}$ for K can be read at $\sum r$ (cryst)=7.0 Å. However, this value can not be directly used for comparison with that obtained in the present study for the following reason. All the K values shown in the K-$\sum r$ (cryst) graph correspond to those obtained by the analysis with the assumption of a value of 3.58 Å for a. Further, the $\sum r$ (cryst) values for several electrolytes in this graph seem to be somewhat overestimated, as exemplified by the ionic radius of *trans*- or *cis*-$[Co(NO_2)_2(en)_2]^+$ which is assumed to be 4.3 Å, larger than 3.4 Å assumed in the present study. Considering these differences in the treatment, the value of K read at $\sum r$ (cryst)=7.0 Å is thought to have to be raised by about 2 $\mathrm{dm^3\,mol^{-1}}$.

45) In Ref. 21, $K=8\ \mathrm{dm^3\,mol^{-1}}$ is given for this salt. However, this value corresponds to that obtained by the analysis with the assumption of a=3.58 Å. If a=7.0 Å is assumed, a value of about 9 $\mathrm{dm^3\,mol^{-1}}$ is obtained for K.