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Electric Conductivity and Viscosity Studies of Aqueous Solutions of Nitroamminecobalt(III) Complexes

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The ionic equivalent conductivities at infinite dilution, viscosity B-coefficients, partial molal volumes, and ionic radii of nitroamminecobalt(III) complex ions have been determined in aqueous solutions at 25°C. From the conductivity data, the thermodynamic association constants of the polyvalent complex cations with chloride ions have been calculated. The log K values at 25°C are 1.5 for $[Co(NH_3)_6]^{3+}$-Cl^- and 1.3 for $[Co(NO_2)(NH_3)_5]^{2+}$-Cl^- respectively. Some factors, which will determine the B-coefficients of complex ions, have been briefly discussed.

Electric conductivities and viscosities of electrolyte solutions give some important information on the ion-ion and ion-solvent interactions. This paper will deal with the conductivity and viscosity studies of aqueous solutions of nitroamminecobalt(III) complexes at various dilutions.*1 The ionic equivalent conductivities at infinite dilution and the formation constants of possible ion-pairs will be determined. The viscosity B-coefficients of the Jones and Dole equation will be briefly discussed in terms of the size and shape, orienting, and distorting effects of the ions.

Experimental

Materials. $[Co(NH_3)_6]Cl_3$,1) $[Co(NO_2)(NH_3)_5]Cl_2$,2) *cis*- and *trans*-$[Co(NO_2)_2(NH_3)_4]Cl$,2) and $NH_4[Co(NO_2)_4(NH_3)_2]$2) were prepared according to the procedures described in the literature. These samples were carefully purified by two recrystallizations; their purity was examined by means of paper chromatography3) and by the chemical analysis of the components. The cobalt content was determined by the EDTA titration;4) the NH_3 (or NH_4^+) content, by the conventional Kjeldahl method; and the chloride content, by the ion-exchange or the Mohr method. In the determination of the NO_2 group, it was first oxidized with a known amount of potassium permanganate, and the excess of potassium permanganate was titrated with oxalic acid. The analysis gave the results as shown in Table 1.

The conductivity water of low specific conductance ($<2\times10^{-7}\Omega^{-1}cm^{-1}$) was prepared according to the following procedure. De-ionized water was first distilled by an all-glass apparatus, and the dissolved carbon dioxide was removed by bubbling pure nitrogen gas through the water for more than 10 hr. This water was passed through a column of ion-exchange resins just before use.

Conductivity Measurements. The electric conductivity was measured at 1000 c/s by a Universal Impedance Bridge Model 291B of the Electro Scientific

TABLE 1. RESULTS OF THE CHEMICAL ANALYSIS OF NITROAMMINECOBALT(III) COMPLEXES
(The calculated values are shown in parentheses)

Complex	Co, %	NH_3, %	NO_2, %	Cl^-, %	NH_4^+, %
$[Co(NH_3)_6]Cl_3$	22.0 (22.0)	38.0 (38.1)	—	39.5 (39.7)	—
$[Co(NO_2)(NH_3)_5]Cl_2$	22.4 (22.5)	32.2 (32.6)	17.7 (17.6)	26.8 (27.1)	—
cis-$[Co(NO_2)_2(NH_3)_4]Cl$	23.2 (23.1)	26.7 (26.7)	36.3 (36.1)	13.9 (13.9)	—
trans-$[Co(NO_2)_2(NH_3)_4]Cl$	23.1 (23.1)	26.5 (26.7)	36.2 (36.1)	13.9 (13.9)	—
$NH_4[Co(NO_2)_4(NH_3)_2]$	20.2 (19.9)	12.0 (11.5)	62.0 (62.3)	—	5.7 (6.1)

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*1 The conductivity measurements were carried out by S. K., and the viscosity and density measurements by T. I. The full data will be reported in the Reports of the Institute of Physical and Chemical Research.

1) W. Conard Fernelius (Ed.), "Inorganic Syntheses," Vol. II, McGraw-Hill Book Company, Inc., New York (1946), p. 216.

2) S. M. Jörgensen, *Z. anorg. Chem.*, **17**, 455 (1898).

3) Y. Yamamoto, A. Nakahara and R. Tsuchida, *Nippon Kagaku Zassi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **75**, 232 (1954).

4) S. Takamoto, *ibid.*, **81**, 457 (1960).

TABLE 2. IONIC EQUIVALENT CONDUCTIVITIES AT INFINITE DILUTION, λ°, B-COEFFICIENTS, PARTIAL MOLAL VOLUMES, $\overline{V}^\circ$, AND IONIC RADII, r_S AND r_V, OF NITROAMMINECOBALT(III) IONS IN AQUEOUS SOLUTIONS AT 25°C

Complex ion	λ°	B, l mole^{-1}	$\overline{V}^\circ$, l mole^{-1}	r_S, Å	r_V, Å
$[Co(NH_3)_6]^{3+}$	99.5	0.14_0	0.05_5	2.76	2.3_3
$[Co(NO_2)(NH_3)_5]^{2+}$	65.8	0.19_1	0.07_2	2.79	2.5_4
cis-$[Co(NO_2)_2(NH_3)_4]^+$	34.5	0.19_3	0.09_5	2.66	2.7_9
trans-$[Co(NO_2)_2(NH_3)_4]^+$	34.0	0.26_0	0.09_6	2.69	2.8_1
$[Co(NO_2)_4(NH_3)_2]^-$	33.1	0.15_2	0.13_4	2.77	3.1_3

Industries. A modified dipping-type conductivity cell with platinized platinum electrodes was used; the outside of the cell was covered with amber glass in order to minimize the photo-chemical decomposition of the complexes. After the air in the cell had been expelled by passing pure nitrogen through the bottom inlet, the solution was poured into the cell and the electrodes were settled. Pure nitrogen was gently streamed over the surface of the solution during the conductivity measurement. The cell constant was determined with 0.1 and 0.01 N solutions of purified potassium chloride.

All solutions were carefully prepared in the atmosphere of carbon dioxide-free nitrogen, and a newly prepared solution was used in each measurement. The measurements were carried out in a water-thermostat of 25±0.01°C. The reproducibility of rosistance readings was usually better than 0.1%.

Viscosity and Density Measurements. Viscosity measurements were made with a viscometer of the Ostwald type. The flow time for the viscometer, ranging between 100 and 200 sec, was measured to within 0.05 sec with a precision stop watch. Densities of the solutions were determined by using a Weld pycnometer of 10 m*l* capacity. All measurements were carried out in a water thermostat of 25±0.01°C.

Solutions of the complexes were made up with redistilled conductivity water. Most of these complexes decompose slowly in aqueous solutions, and, therefore, each measurement was carried out within five hours after the preparation of the solution.

The reproducibility of the measurements was examined by repeating each experimental run several times. The relative viscosity and density data were accurate to 0.0005 and 0.0001, respectively.

Results

Electric Conductivities. The conductivities of aqueous solutions of nitroamminecobalt(III) complexes generally increased with the lapse of time after the preparation of the solution; this is probably due to the slow decomposition of the complexes in aqueous solutions.[5] Therefore, the equivalent conductivities at the time zero, which were determined by the extrapolation of the conductivities against time, were used in the following analysis.

The limiting equivalent conductivities, Λ°, of nitroamminecobalt(III) complexes were determined according to Onsager's method of extrapolation,[6] and the ionic equivalent conductivities of the complex ions at infinite dilution, λ°, were obtained from the Λ° values by subtracting the λ° of chloride ion (76.3_5) or that of ammonium ion (73.5_5).[7] The results are shown in Table 2.

Viscosities and Partial Molal Volumes. The viscosity data were analysed by means of the Jones and Dole equation,[8]

$$\left(\frac{\eta}{\eta^\circ}-1\right) = A\sqrt{C} + BC \qquad (1)$$

where η is the viscosity of the solution, η°, that of the pure solvent, C, the concentration of the solution, and A and B are constants. The B-coefficients of the complexes were determined by applying the least-square method to the linear portion of the relation between $\{(\eta/\eta^0)-1\}/\sqrt{C}$ and $\sqrt{C}$. The partial molal volumes, $\overline{V}^\circ$, of the complexes were calculated from the density data.

The third and the fourth columns of Table 2 show the B-coefficients and the partial molal volumes of the complex ions, which were obtained from the corresponding values of the complexes by subtracting the B[9] and $\overline{V}^\circ$[10] values of chloride and ammonium ions ($B_{Cl^-}=-0.00_7$, $B_{NH_4^+}=-0.00_7$, $\overline{V}^\circ_{Cl^-}=25.3$ cm^3 mole^{-1}, $\overline{V}^\circ_{NH_4^+}=10.6$ cm^3 mole^{-1}).

Discussion

Ionic Equivalent Conductivities. Only a few conductivity data of nitroamminecobalt(III) complexes have been reported in literature.[11-13] The ionic equivalent conductivity of $[Co(NH_3)_6]^{3+}$ ion at infinite dilution given in Table 2 is in good agreement with that (99.2) reported by Jenkins

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[5] Y. Tsunoda and A. Ouchi, *ibid.*, **82**, 447 (1961).

[6] L. Onsager, *Physikal. Z.*, **28**, 277 (1927).

[7] R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworths, London (1959).

[8] Gr. Jones and M. Dole, *J. Am. Chem. Soc.*, **51**, 2950 (1929).

[9] R. W. Gurney, "Ionic Processes in Solution," McGraw-Hill Book Company, Inc., New York (1953), Chap. 9.

[10] R. H. Stokes and R. A. Robinson, *Trans. Faraday Soc.*, **53**, 301 (1957).

[11] J. C. Bailar, Jr. (Ed.), "The Chemistry of Coordination Compounds," Reinhold Publishing Corporation, New York (1956), pp. 113—118.

[12] G. S. Hartley, *Trans. Faraday Soc.*, **33**, 457 (1937).

[13] I. L. Jenkins and C. B. Monk, *J. Chem. Soc.*, **1951**, 68.

and Monk,[13] while Hartley reported a slightly higher value (101.9).[12] The λ° values of nitroamminecobalt(III) ions are approximately proportional to their valencies; this suggests that the size of these complex ions is nearly the same in aqueous solutions. From the conductivity data the so-called Stokes radii, r_s, of the complex ions were determined by the equation,

$$r_s = 91.6|z|/\lambda^\circ \quad (r_s \text{ in Å}) \qquad (2)$$

where z is the ionic charge. In the fifth and the sixth columns of Table 2, the Stokes radii are compared with the ionic radii, r_v, estimated from the partial molal volumes, $\overline{V}^\circ$, of the ions according to Stokes-Robinson's equation,[10]

$$\overline{V}^\circ = 4.35 \times 10^{24} \cdot r_v{}^3$$
$$(r_v \text{ in cm and } \overline{V}^\circ \text{ in m}l\cdot\text{mole}^{-1}) \qquad (3)$$

The Stokes radii of nitroamminecobalt(III) ions are comparable with the r_v values and are of reasonable order.

Ion-pair Formation. The equivalent conductivities of the 1 : 1 valence-type complex salts, *i. e. cis-* and *trans-*$[Co(NO_2)_2(NH_3)_4]Cl$ and $NH_4[Co(NO_2)_4(NH_3)_2]$, obeyed the Onsager limiting equation at relatively low concentrations (<2 mM); the differences between the observed and the calculated conductivities were less than 0.4% for *cis-*$[Co(NO_2)_2(NH_3)_4]Cl$, 0.3% for *trans-*$[Co(NO_2)_2(NH_{34})]Cl$, and 0.1% for $NH_4[Co(NO_2)_4(NH_3)_2]$, respectively. Therefore, no appreciable contribution of the ion-pair formation is expected in these systems.

The Λ *vs.* $\sqrt{C}$ plot of $[Co(NH_3)_6]Cl_3$, however, showed a significant deviation from the theoretical Onsager line, which is in agreement with the results of Jenkins and Monk.[13] A similar but smaller deviation was also observed with $[Co(NO_2)(NH_3)_5]Cl_2$. These deviations will be presumably due to ion-pair formation between the complex cations and chloride ions.

From the conductivity data, the degrees of dissociation, α, of the possible ion-pairs, $[Co(NH_3)_6]^{3+}$–Cl^- and $[Co(NO_2)(NH_3)_5]^{2+}$–Cl^-, were determined according to the successive approximation method described by Jenkins and Monk,[13] and, then, the thermodynamic association constants, K, were calculated by assuming the activity coefficients of the ions estimated from the Debye-Hückel limiting equation. The results are shown in Table 3. In the present calculation, the λ° values of $[Co(NH_3)_6]^{3+}$–Cl^- and $[Co(NO_2)(NH_3)_5]^{2+}$–Cl^- were assumed to be equal to two-thirds of λ° of $[Co(NH_3)_6]^{3+}$ and to one-half of λ° of $[Co(NO_2)(NH_3)_5]^{2+}$, respectively. This rather arbitrary assumption does not seem to introduce a significant error in the results.

TABLE 3. DEGREES OF DISSOCIATION, α, AND THERMODYNAMIC ASSOCIATION CONSTANTS, K, OF $[Co(NH_3)_6]^{3+}$–Cl^- AND $[Co(NO_2)(NH_3)_5]^{2+}$–Cl^- AT 25°C

(a) $[Co(NH_3)_6]^{3+}$–Cl^-

Molar concn., mM	α	log K
0.05	0.994_4	1.6_3
0.0625	0.996_3	1.3_6
0.10	0.991_8	1.5_2
0.125	0.989_1	1.5_5
0.167	0.985_8	1.5_6
0.25	0.987_3	1.3_5
0.50	0.957_1	1.6_5
1.00	0.957_1	1.4_1

(b) $[Co(NO_2)(NH_3)_5]^{2+}$–Cl^-

Molar concn., mM	α	log K
0.10	0.996_4	1.2_9
0.125	0.995_6	1.2_9
0.167	0.993_9	1.3_1
0.25	0.987_0	1.4_8
0.50	(0.993_9)	(0.8_7)
1.00	0.980_0	1.1_2

The association constant of $[Co(NH_3)_6]^{3+}$–Cl^- given in Table 3 is in good agreement with that (log K=1.49) reported by Jenkins and Monk.[13] However, these values obtained from the conductivity data are significantly lower than that (log K= 2.59) determined by Evans and Nancollas from the spectroscopic data.[14] No association constants of $[Co(NO_2)(NH_3)_5]^{2+}$–Cl^- has been reported in literature to compare with the present result.

The association constant of ion-pairs due to purely electrostatic or electrovalent interactions between ions can be estimated according to Bjerrum's theory.[15] If the distance of closest approach of the two ions of an ion-pair is assumed to be equal to the sum of their Stokes radii, the values of log K of $[Co(NH_3)_6]^{3+}$–Cl^- and $[Co(NO_2)(NH_3)_5]^{2+}$–Cl^- are expected to be 1.8 and 1.0, respectively. These values, however, must be considered to be approximate ones because of the assumptions involved in Bjerrum's treatment.

Although the agreement between the theoretically calculated association constants and those determined from the conductivity data is not very good, the present values of log K for $[Co(NH_3)_6]^{3+}$–Cl^- and $[Co(NO_2)(NH_3)_5]^{2+}$–Cl^- may be concluded to be of the right order.

In the present discussion, only the association of one cation and one chloride ion was considered. The limited accuracy of our conductivity measurements makes it difficult to detect the possible but small contribution due to the ion-pairs involving more than one chloride ions.

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14) M. G. Evans and G. H. Nancollas, *Trans. Faraday Soc.*, **49**, 363 (1953); G. H. Nancollas, *J. Chem. Soc.*, **1955**, 1458.

15) C. B. Monk, "Electrolytic Dissociation," Academic Press, London (1961), pp. 272—275.

Viscosity B-Coefficients of the Complex Ions. The B-coefficients of nitroamminecobalt(III) complex ions in aqueous solutions are positive at room temperatures (Table 2), and, therefore, they are all structure-forming ions.⁹⁾ According to Stokes and Mills, the B-coefficient can be represented by the relation,

$$\eta^{E} + \eta^{A} + \eta^{D} = \eta^{\circ}BC \qquad (4)$$

where η^{E} is the viscosity increment due to the size and shape of an ion, η^{A}, that due to the orientation of polar molecules by the ionic field, and η^{D}, the viscosity change associated with distortion of the solvent structure.¹⁶⁾ The viscosity changes η^{E} and η^{A} are positive, while η^{D} will be negative. Equation 4 suggests that the sign of the B-coefficient is determined by a competition between $(\eta^{E}+\eta^{A})$ and η^{D}.

In large molecular ions such as tetra-alkylammonium ions, the size and shape effect would be expected to be large and predominant, while the orienting and distorting effects would be reasonably small and assumed to be similar in a series of these ions. In the B-coefficients of nitroamminecobalt(III) ions, however, besides the size and shape effect the orienting and distorting effects would be supposed to play an important role, because the ions have different charges and NH_3 to NO_2 ratios. A similar consideration will be made in the case of some chloroammineplatinum(IV) complex ions.¹⁷⁾

The partial molal volume of an ion is considered to be determined not only by the size and shape of the ion but also by its interaction with solvent molecules. Therefore, the B-coefficient is expected to have a close relation with $\overline{V}^{\circ}$. In order to examine this relation, however, much more accurate data of viscosities and densities will be required.

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16) R. H. Stokes and R. Mills, "Viscosity of Electrolytes and Related Properties," Pergamon Press, Oxford (1965), Chap. 4.

17) E. R. Nightingale, Jr., and J. F. Kuecker, *J. Phys. Chem.*, **69**, 2197 (1965).