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Ion-pair Formation of Some Substitution-inert Complexes and Sulfate Ions. Determination of Association Constants Using Polarographic Diffusion Current

By Nobuyuki TANAKA, Kazuko OGINO (née EBATA) and Gen SATÔ*

Department of Chemistry, Faculty of Science, Tohoku University, Katahira-cho, Sendai

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The polarographic diffusion current of some tervalent substitution-inert complex cations decreases by the addition of sulfate. From the change in diffusion current the association constants of substitution-inert complex and sulfate ions are obtained at ionic strength 0.1 ($NaClO_4$) and 25°C. The values are 69 ± 8, 58 ± 8 and 4×10 for $[Co(NH_3)_6]^{3+}$–SO_4^{2-}, $[Cr(NH_3)_6]^{3+}$–SO_4^{2-} and $[Cr(H_2O)_6]^{3+}$–SO_4^{2-} respectively. The formation of $[Co(NH_3)_6]^{3+}$–HSO_4^- is negligibly small compared with that of $[Co(NH_3)_6]^{3+}$–SO_4^{2-}.

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* Present address: Department of Chemistry, Sophia University, Chiyoda-ku, Tokyo.

It has been reported that the polarographic reduction waves of tervalent complex cations such as $[Co(NH_3)_6]^{3+}$ and $[Cr(NH_3)_6]^{3+}$ are affected by the presence of sulfate[1-5]; the half-wave potential shifts to more negative potentials and the diffusion current decreases upon the addition of sulfate. These were attributed mainly to the effect of ion-pair formation of the tervalent complex cations and sulfate ions. The shift in the half-wave potential was used for the determination of the association constants both in the case of a reversible electrode process[2,5] and in that of an irreversible electrode process[4]. However, the change of the structure of the electrical double layer caused by the addition of sulfate ions affects the rate of the electrochemical step, and hence the half-wave potential when the electrode process is irreversible. In such cases, it seems not appropriate to determine the association constant from the change of the half-wave potential.

In this paper, a method for the determination of the association constant using the polarographic diffusion current is presented and is applied to the ion-pairs $[Co(NH_3)_6]^{3+}$–SO_4^{2-}, $[Cr(NH_3)_6]^{3+}$–SO_4^{2-} and $[Cr(H_2O)_6]^{3+}$–SO_4^{2-}.

Experimental

Hexamminecobalt(III) perchlorate and hexamminechromium(III) perchlorate were obtained by the precipitation from aqueous solutions of the corresponding chlorides by the addition of perchloric acid, the chlorides of the ammine complexes being prepared with procedures given in literatures.[6,7] The solution of hexaquochromium(III) in perchloric acid was obtained by the reduction of sodium dichromate with hydrogen peroxide.[8]

Measurements were carried out at 25°C in solutions of ionic strength 0.1 ($NaClO_4$) containing 0.005% gelatin and an appropriate amount of perchloric acid. The diffusion current was recorded with a Yanagimoto PB-4 pen-recording polarograph.

Treatment of the Data

Consider the electrode reaction

$$M^{m+} + X^{x-} \rightleftarrows MX^{(m-x)+} \tag{1}$$

$$M^{m+} \text{ or } MX^{(m-x)+} + ne \rightarrow \text{Reduction product} \tag{2}$$

where M^{m+} corresponds to a complex cation, X^{x-} a counter ion and $MX^{(m-x)+}$ an ion-pair. The magnitude of the polarographic diffusion current for this system depends on the ion-pair formation: When reaction 1 is in equilibrium, the apparent diffusion coefficient, D, is given by[9,10]

$$D = \frac{D_M + KD_{MX}C_X}{1 + KC_X} \tag{3}$$

where C_X is the concentration of X^{x-}, D_M and D_{MX}, the diffusion coefficients of M^{m+} and $MX^{(m-x)+}$ respectively and K the association constant of M^{m+} and X^{x-}:

$$K = C_{MX}/(C_M C_X) \tag{4}$$

where C_M and C_{MX} denote concentrations of M^{m+} and $MX^{(m-x)+}$ respectively. When values of D_M and D at various C_X are available, several methods,[11] i. e., elimination methods, linear plots methods and curve fitting methods, can be used for the calculation of the association constant. Among them, one of the linear plots methods is most appropriate in the present case. Eq. 3 is transformed to

$$\frac{C_X}{D_M - D} = \frac{1 + KC_X}{K(D_M - D_{MX})} \tag{5}$$

where the left-hand side can be obtained experimentally. Equation 5 shows that when its left-hand side is plotted against C_X, a straight line is obtained and from the ratio of its slope and intercept, the association constant is obtained.

The advantage of this method is that it can be applied both to reversible and to irreversible electrode processes, irrespective of the relative electroactivity of M^{m+} and $MX^{(m-x)+}$.

Results

Since a part of sulfate ion combines with hydrogen ion to form hydrogensulfate ion in solutions of $pH < 3$, the effect of hydrogensulfate ion on the equilibrium of the ion association was examined with hexamminecobalt(III) which shows a well-difined one-electron reduction wave both in neutral and in acid media. A series of measurements was carried out in solutions with 0.08 M hydrogen ion and in neutral solutions. The changes in current at −0.7 V. vs. SCE (saturated calomel electrode) with the increase of sodium sulfate concentration are shown in Figs. 1 and 2. In Fig. 1, where the abscissa is the total concentration of sulfate (the sum of sulfate ion and hydrogensulfate ion), the change of the current in acid media is less pronounced than that in neutral media. The sulfate ion concentration, which was calculated

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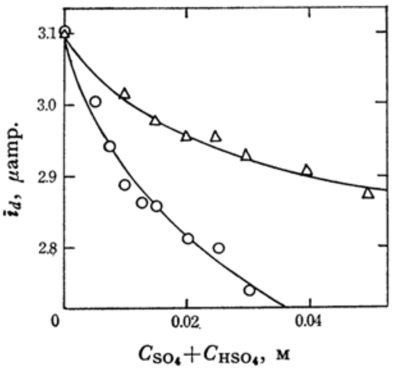

Fig. 1. Variation of the mean diffusion current ($\bar{i}_d$) of the reduction wave of $[Co(NH_3)_6]^{3+}$ with the change of the total sulfate concentration in neutral solutions (○) and in solutions containing 0.08 M hydrogen ion (△).

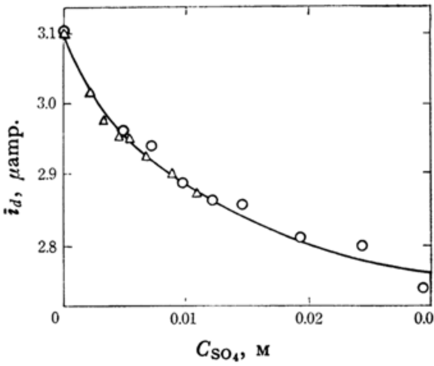

Fig. 2. Variation of the mean diffusion current ($\bar{i}_d$) of the reduction wave of $[Co(NH_3)_6]^{3+}$ with the change of the concentration of sulfate ion in neutral solutions (○) and in solutions containing 0.08 M hydrogen ion (△).

from the total sulfate and the hydrogen ion concentrations and the second dissociation constant of sulfuric acid,* is taken as the abscissa in Fig. 2, where the two sets of plots lie almost on a single curve. It may be concluded from these plots that the association of hydrogensulfate ion is negligible compared with that of sulfate ion.

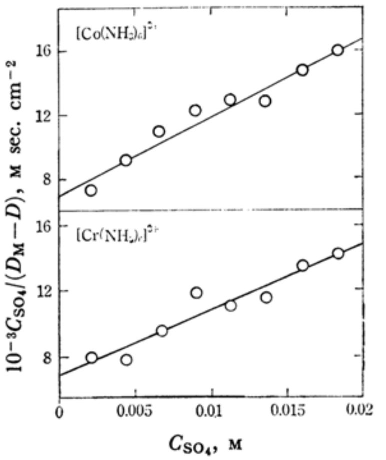

Fig. 3. Relation between the value of the left-hand side of Eq. 5 and sulfate concentration.

The measurements for the determination of association constants were carried out in 0.003 N perchloric acid solutions because it was reported that the reduction wave of hexamminechromium(III) is not well-defined in neutral media, but well-defined in acid solutions,[3,12] and that hexaquochromium(III) ions polymerize and hydrolyze in pH ranges higher than 3 and lower than 0.[8] In plotting the left-hand side of Eq. 5, the sulfate concentration, C_{SO_4}, was obtained by subtracting the concentrations of the ion-pair and the hydrogensulfate from the total sulfate concentration. The diffusion coefficient was calculated by the Ilkovič equation from the mean diffusion currents at −0.8 V. in the case of hexamminecobalt(III) and those at −1.1 V. in the cases of hexamminechromium(III) and hexaquochromium(III). The values of D_M were obtained from the diffusion current observed in the absence of sodium sulfate. The plots of of Eq. 5 are shown in Fig. 3. The slopes and the intercepts of the straight lines were calculated by the method of least square, and the association constants were obtained as given in Table I.

TABLE I. ASSOCIATION CONSTANTS OF ION-PAIRS
$\mu=0.1$, 25°C

Ion-pair	K
$[Co(NH_3)_6]^{3+}-SO_4^{2-}$	69±8
$[Cr(NH_3)_6]^{3+}-SO_4^{2-}$	58±8
$[Cr(H_2O)_6]^{3+}-SO_4^{2-}$	4×10

Discussion

The association constant of hexamminecobalt(III) with sulfate ion has been reported by several researchers[13]; the logarithmic constant at infinite dilution ranges between 2.89 and 3.60. Corrected for the effect of activity coefficient,[14] the logarithmic association constant at infinite dilution obtained from our result becomes 3.21, which is in agreement with the values in the literature, and with that expected from Bjerrum's theory[15] of ion as-

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* The pK_a of the second dissociation step of sulfuric acid at ionic strength 0.1 was taken as 1.6, which was obtained from the value at infinite dilution (L. G. Sillén and A. E. Martell, "Stability Constants of Metal-Ion Complexes," Chemical Society, London (1964), p. 232.) by correcting for the effect of activity coefficient.

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sociation due to coulombic interaction between tervalent and bivalent ions of opposite charge at the distance of closest approach 5 Å.

The association constant of $[Cr(NH_3)]_6{}^{3+}-SO_4{}^{2-}$ has not been reported. Though detailed comparison of the constant with that of $[Co(NH_3)_6]^{3+}-SO_4{}^{2-}$ is limited because of the rather large error, it may be said that $[Cr(NH_3)_6]^{3+}-SO_4{}^{2-}$ is slightly less stable than $[Co(NH_3)_6]^{3+}-SO_4{}^{2-}$.

In the case of hexaquochromium(III), only a rough estimate of the association constant is obtained because of the rather small change in diffusion eoefficient accompanying association. But it may be concluded that the value of K for $[Cr(H_2O)_6]^{3+}-SO_4{}^{2-}$ is about the same with or less than those for [hexammine complexes]$^{3+}-SO_4{}^{2-}$, contrary to the result by Tsuchiya and Umayahara[16] who reported that the association constant of $[Cr(H_2O)_6]^{3+}-SO_4{}^{2-}$ was about twenty times larger than that of $[Co(NH_3)_6]^{3+}-SO_4{}^{2-}$.

In deriving Eq. 5, only the association of one cation and one anion was taken into consideration. With the precision of the present experiment it is difficult to determine the extent of the ion association involving more than one sulfate ion. The formation of such species is negligibly small compared with the formation of the species such as $[Co(NH_3)_6]^{3+}-SO_4{}^{2-}$, as far as the association is assumed to depend mainly on the coulombic interaction between ions.

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