An Alternative Display of Potentiostatic Measurements. II. Electrochemical Determination of Outer-sphere Association Constants of Several Substitution-inert Complexes with Sulfate Ions

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A modified technique for the potentiostatic method has been applied to the study on the outer-sphere association of some substitution-inert complex cations with sulfate ions. The association constants were determined from the change in limiting time as function of the concentration of sulfate ions at ionic strength 0.2 and 25 °C: 29±3 for $[Co(NH_3)_6]^{3+}$–SO_4^{2-}, 23±2 for $[Co(en)_3]^{3+}$–SO_4^{2-}, 34±3 for $[Co(H_2O)(NH_3)_5]^{3+}$–SO_4^{2-}, 18±2 for $[Cr(NH_3)_6]^{3+}$–SO_4^{2-}, 21±2 for $[Cr(en)_3]^{3+}$–SO_4^{2-}, 19±2 for $[Cr(H_2O)(NH_3)_5]^{3+}$–SO_4^{2-}, 13±2 for $[Cr(urea)_6]^{3+}$–SO_4^{2-}. The ratios of the diffusion coefficient of the univalent ion pairs to that of tervalent substitution-inert complex cations were also obtained. From these ratios, the diffusion coefficients of the univalent ion pairs were calculated; these were found to be close to those of univalent complex ions with similar structures.

The potentiostatic method has been recognized as the principal tool for the investigation of electrode kinetics. Previous studies[1,2] have demonstrated an alternative mode of potentiostatic measurement, which analyzes the relationship between the potential and the time required to reach a constant sampling current in the potentiostatic measurement.[1] The instrumental design of an automatic recording of potential-time curves of this mode was described in the first paper of this series.[3] The chief advantage of this mode is that the limiting time at diffusion-controlled potential is directly proportional to the diffusion coefficient,[1] whereas, in the normal potentiostatic method, the limiting current is proportional to the square root of diffusion coefficients. Thus, the modified potentiostatic method is convenient for detection of the diffusion coefficient in a series of measurements.

It has been reported that the polarographic diffusion current and the chronopotentiometric transition time for some tervalent cations, such as $[Cr(NH_3)_6]^{3+}$,[4] $[Cr(en)_3]^{3+}$,[5] $[Cu(urea)_6]^{3+}$,[6] $[Co(NH_3)_6]^{3+}$,[7] and $[Co(en)_3]^{3+}$,[8] decrease upon the addition of sulfate ions. This decrease is attributed mainly to the effect of outer-sphere association of the tervalent cations and the sulfate ions; the diffusion coefficient of the sulfate ion decreases upon the formation of ion pairs. The decrease in the polarographic diffusion current[9,10] and in the chronopotentiometric transition time[11] was used for the determination of the association constant.

In this paper, a method for the determination of association constants with the aid of the modified potentiostatic method is presented and applied to the ion pairs: $[Cr(urea)_6]^{3+}$–SO_4^{2-}, $[Cr(H_2O)(NH_3)_5]^{3+}$–SO_4^{2-}, $[Cr(NH_3)_6]^{3+}$–SO_4^{2-}, $[Cr(en)_3]^{3+}$–SO_4^{2-}, $[Co(NH_3)_6]^{3+}$–SO_4^{2-}, $[Co(en)_3]^{3+}$–SO_4^{2-}, and $[Co(H_2O)(NH_3)_5]^{3+}$–SO_4^{2-}.

Experimental

The complexes, $[Cr(urea)_6](ClO_4)_3$,[12] $[Cr(NH_3)_6](ClO_4)_3$,[13] $[Cr(H_2O)(NH_3)_5](ClO_4)_3$,[13] $[Cr(en)_3](ClO_4)_3$,[14] $[Co(NH_3)_6](ClO_4)_3$,[15] and $[Co(en)_3](ClO_4)_3$[16] were prepared according to the literature and converted to perchlorate salt. All other chemicals used were of guranteed reagent-grade. Redistilled water was used to prepared the solutions of desired concentrations. Polyethylene glycol dodecyl ether (LEO: mean molecular weight, 862) was used as the maximum suppressor.

Modified potentiostatic measurements were carried out by means of the modified pulse polarograph described in a previous paper.[3] A digital multimeter (Takeda Riken TR-6355) and a universal counter (Takeda Riken TR-5104G) were used; the potential and the time were thus measured precisely. A three-electrode cell equipped with a saturated calomel electrode (Yanagimoto MR-P2-05-1) and a platinum wire electrode were employed. The DME with a flow rate of 1.17 mg s^{-1} and a drop time of 2.0 s in 0.5 M (1 M=1 mol dm^{-3}) of NaCl was used. Electrolytic solutions were deaerated by bubbling purified nitrogen gas through the solution for 20 min. Measurements were made at 25 °C in solutions of ionic strength of 0.2 containing appropriate amounts of maximum suppressors. Ionic strength was adjusted with NaCl (for chromium(III) complexes) or with $NaNO_3$ (for cobalt(III) complexes).

Results and Discussion

From the modified potentiostatic measurements, the association constant can be determined in the following way. Consider the association reaction

$$M^{3+} + Z^{2-} \rightleftharpoons M^{3+}Z^{2-}, \qquad (1)$$

where M^{3+} represents a complex cation, Z^{2-}, a sulfate anion and $M^{3+}Z^{2-}$, an ion pair. Since the dissociation and the association of ion pairs are very rapid, the apparent diffusion coefficient (D) is given by[17,18]

$$D = \frac{D_M + Kc_Z D_{MZ}}{1+Kc_Z}, \qquad (2)$$

where c_Z means the concentration of Z^{2-}, D_M, and D_{MZ} are the diffusion coefficient of M^{3+} and $M^{3+}Z^{2-}$, respectively, and K is the association constant of $M^{3+}Z^{2-}$ given by

$$K = c_{MZ}/c_M c_Z. \qquad (3)$$

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Here c_M and c_{MZ} are the concentration of M^{3+} and $M^{3+}Z^{2-}$, respectively.

The observed limiting time (t) of the modified potentiostatic method in the presence of ion pairs can be expressed as follows:[1,2]

$$\sqrt{t} = nFc^{\circ}\sqrt{D}/\sqrt{\pi}I, \qquad (4)$$

where c° is the bulk concentration of the electroactive species; n, the number of electrons; F, the Faraday constant; and I, the constant sampling current in the modified potentiostatic method. From Eqs. 2 and 4, one can deduce the following relation:

$$\left(\frac{c_M}{c}\right)^2\left(\frac{t}{t_M}\right) = \frac{1+Kc_Z\xi}{1+Kc_Z} \qquad (5)$$

with

$$\sqrt{t_M} = nFc^{\circ}_M\sqrt{D_M}/\sqrt{\pi} \text{ and } \xi = D_{MX}/D_M, \qquad (6)$$

where t_M is the limiting time which is obtained when the bulk concentration of M^{3+} is c°_M and no ion pair is formed. The left-hand side of Eq. 5 is obtained experimentally, and plotted as a function of c_Z; a hyperbola is obtained, from which the association constant can be calculated.

Equation 5 can be transformed to

$$\frac{c_Z}{1-\left(\frac{c^{\circ}_M}{c^{\circ}}\right)^2\left(\frac{t}{t_M}\right)} = \frac{1+Kc_Z}{K(1-\xi)}. \qquad (7)$$

Equation 7 indicates that the plot of $c_Z/[1-(c^{\circ}_M/c^{\circ})^2\times(t/t_M)]$ *versus* c_Z will give a straight line and the association constant K can be determined from the ratio of its slope to its intercept. The ratio (ξ) of the diffusion coefficient of ion pairs $M^{3+}Z^{2-}$ to that of complex cation M^{3+} can then be obtained from the intercept.

The measurements for the determination of association constants were carried out in the solutions containing 0.01 M acetate buffer, since it was reported that the reduction waves of chromium(III) and cobalt(III) complexes used are not well-defined in neutral solutions, but are well-defined in acidic solutions.[4,5,19,20] An amount of 2—4 μM LEO was added to the solution to prevent the streaming effect.[5,21]

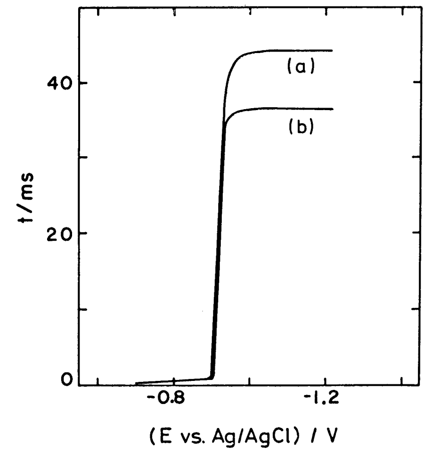

Fig. 1. An example of potential-time curves for the modified potentiostatic method with 0.5 mM $[Cr(NH_3)_6](ClO_4)_3$ obtained in (a) 0.195 M NaCl and (b) 0.065 M Na_2SO_4 containing 5 mM acetate buffer and 2 μM LEO at 25 °C. The measurements were made at 6.0 μA of sampling current.

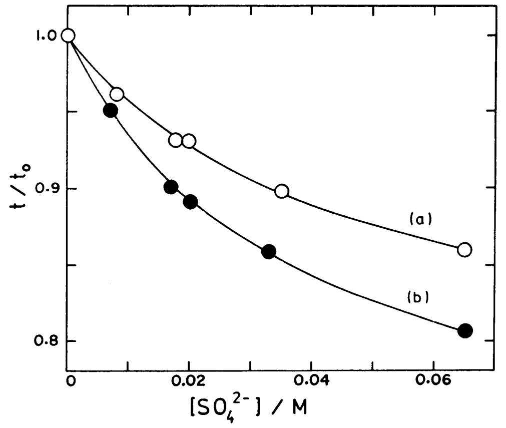

Fig. 2. Variation of the limiting time for the reduction of (a) $[Co(en)_3]^{3+}$ and (b) $[Co(NH_3)_6]^{3+}$ with the change in the concentration of sulfate ions, observed in the solutions containing 5 mM acetate buffer+(a) 4 μM LEO or (b) 2 μM LEO.

—— Indicates the calculated, and ●, ○ the experimental values.

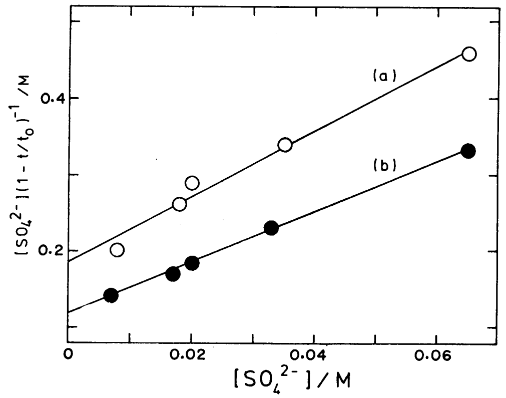

Fig. 3. Relation between the value of the left-hand side of Eq. 7 and sulfate concentration.

(a): $[Co(en)_3]^{3+}$, (b): $[Co(NH_3)_6]^{3+}$.

Figure 1 shows a typical example of a potential-time curve of the modified potentiostatic method for $[Cr(NH_3)_6]^{3+}$ ions which was obtained in solution with and without sulfate ions. The time was measured at a sampling current of 6 μA. It can be seen from Fig. 1 that the limiting time by means of the modified potentiostatic method decreased due to the presence of sodium sulfate. An example of the change in limiting time with the increase in the concentration of sodium sulfate is shown in Fig. 2 for $[Co(NH_3)_6]^{3+}$–SO_4^{2-} and $[Co(en)_3]^{3+}$–SO_4^{2-}. The value of t_0 was obtained with the solution of the bulk concentration $c^{\circ}_M(c^{\circ}_M=c^{\circ})$ containing no sodium sulfate. A linear plot of Eq. 7 for $[Co(NH_3)_6]^{3+}$–SO_4^{2-} and $[Co(en)_3]^{3+}$–SO_4^{2-} is also given in Fig. 3.

The association constant (K) and the ratio of the diffusion coefficient (ξ) were calculated by the method of least squares. The results are given in Table 1. Comparison of the association constants of chromium(III) complexes with those of cobalt(III) ones having the same ligands showed that the association constants of the chromium(III) complexes studied were smaller than those of the corresponding cobalt(III) ones.

The association constants of hexaamminecobalt(III) and tris(ethylenediamine)cobalt(III) with sulfate ion have been reported by several researchers.[22] The logarithmic constants of $[Co(NH_3)_6]^{3+}$–SO_4^{2-} at infinite dilution range between 2.89 and 3.71 and those of $[Co(en)_3]^{3+}$–SO_4^{2-} range between 2.72 and 3.45. Corrected for the effect of activity coefficient,[23] the logarithmic association constant at infinite dilution obtained from the present result becomes 3.19 for $[Co(NH_3)_6]^{3+}$–SO_4^{2-} and 2.88 for $[Co(en)_3]^{3+}$–SO_4^{2-}. The values obtained in this study are in good agreement with those in the literature, and with that expected from Bjerrum's theory[24] of ion association due to coulombic interaction between tervalent and bivalent ions of opposite charge at the distance of closest approach, 5—6 Å. Similarly, the values of $[Cr(NH_3)_6]^{3+}$–SO_4^{2-} obtained in this study also agree well with those obtained by other electrochemical methods.[2]

The association constant and the ratio of diffusion coefficients for ion pairs $[Co(NH_3)_6]^{3+}$–SO_4^{2-}, $[Co(en)_3]^{3+}$–SO_4^{2-}, $[Cr(NH_3)_6]^{3+}$–SO_4^{2-} and $[Cr(en)_3]^{3+}$–SO_4^{2-} are compared with those obtained by chronopotentiometry.[22] They are given in Table 2, though the ionic strength in the measurements is different. The association constants of the present work ($\mu=0.2$) were approximately one third of those at $\mu=0.1$, whereas the ratios of diffusion coefficients were not so different for the two ionic strengths.

Table 1. Association constants at $\mu=0.2$ and the ratio of the diffusion coefficients (25 °C)

Ion pair	K	ξ
$[Co(NH_3)_6]^{3+}$–SO_4^{2-}	29±3	0.7_0
$[Co(en)_3]^{3+}$–SO_4^{2-}	23±2	0.7_7
$[Co(H_2O)(NH_3)_5]^{3+}$–SO_4^{2-}	34±3	0.7_6
$[Cr(NH_3)_6]^{3+}$–SO_4^{2-}	18±2	0.6_6
$[Cr(en)_3]^{3+}$–SO_4^{2-}	21±2	0.8_0
$[Cr(H_2O)(NH_3)_5]^{3+}$–SO_4^{2-}	19±2	0.7_0
$[Cr(urea)_6]^{3+}$–SO_4^{2-}	13±2	0.7_6

Table 2. Association constants and the ratio of the diffusion coefficients ξ at $\mu=0.2$ and $\mu=0.1$ (25 °C)

Ion pair	$\mu=0.2$		$\mu=0.1$[11]	
	K	ξ	K	ξ
$[Co(NH_3)_6]^{3+}$–SO_4^{2-}	29±3	0.7_0	93± 8	0.6_8
$[Co(en)_3]^{3+}$–SO_4^{2-}	23±2	0.7_7	99±15	0.8_2
$[Cr(NH_3)_6]^{3+}$–SO_4^{2-}	18±2	0.6_6	61± 7	0.6_7
$[Cr(en_3)_6]^{3+}$–SO_4^{2-}	21±2	0.8_0	58± 8	0.8_7

The association constants of $[Co(H_2O)(NH_3)_5]^{3+}$–SO_4^{2-}, $[Cr(H_2O)(NH_3)_5]^{3+}$–SO_4^{2-} and $[Cr(urea)_6]^{3+}$–SO_4^{2-} have not been reported, but the constant obtained in this study seems appropriate compared with the values for the ion pairs $[Co(NH_3)_6]^{3+}$–SO_4^{2-}, $[Co(en)_3]^{3+}$–SO_4^{2-}, $[Cr(NH_3)_6]^{3+}$–SO_4^{2-} and $[Cr(en)_3]^{3+}$–SO_4^{2-}. Though detailed comparison of the constant with that of $[Cr(NH_3)_6]^{3+}$–SO_4^{2-} is limited, it may be said that $[Cr(urea)_6]^{3+}$–SO_4^{2-} is slightly less stable than $[Cr(NH_3)_6]^{3+}$–SO_4^{2-}.

The diffusion coefficients of ion pairs were calculated by using the diffusion coefficient of tervalent cation and the ratio of the diffusion coefficients, ξ, obtained in this study. They are compared with the diffusion coefficients of ion pairs given in the literature and with those of other univalent complex ions, which are given in Table 3.

Although such a comparison is limited because of insufficient accuracy in the measurement, it may be concluded that the diffusion coefficients of univalent ion pairs differ little from those of univalent complex ions.

In the derivation of Eq. 7, 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 ion-pair formation involving more than one sulfate ion. The formation of such species is negligibly small compared with the ion pairs such as $[Co(NH_3)_6]^{3+}$–SO_4^{2-}, $[Cr(NH_3)_6]^{3+}$–SO_4^{2-}, *etc.*, if the association is assumed to depend mainly on the coulombic interaction between ions.

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Table 3. Diffusion coefficients of ion pairs calculated from ξ and those of other substitution-inert complex ions (25 °C)[a]

Complex ion	$\frac{D}{10^{-6}\,cm^2\,s^{-1}}$	Ion pair	ξ	$\frac{D}{10^{-6}\,cm^2\,s^{-1}}$	
$[Co(NH_3)_6]^{3+}$	8.4[25]	$[Co(NH_3)_6]^{3+}$–SO_4^{2-}	0.7_0	$5._9$	$5._7$[11]
$[Co(en)_3]^{3+}$	6.4[8]	$[Co(en)_3]^{3+}$–SO_4^{2-}	0.7_7	$4._9$	$5._3$[11]
$[Co(H_2O)(NH_3)_5]^{3+}$	7.8[26]	$[Co(H_2O)(NH_3)_5]^{3+}$–SO_4^{2-}	0.7_6	$5._9$	
$[Cr(NH_3)_6]^{3+}$	8.5[4]	$[Cr(NH_3)_6]^{3+}$–SO_4^{2-}	0.6_6	$5._6$	$5._7$[11]
$[Cr(en)_3]^{3+}$	5.9[5]	$[Cr(en)_3]^{3+}$–SO_4^{2-}	0.8_0	$4._7$	$5._1$[11]
$[Cr(H_2O)(NH_3)_5]^{3+}$	8.0[27]	$[Cr(H_2O)(NH_3)_5]^{3+}$–SO_4^{2-}	0.7_0	$5._6$	
$[Cr(urea)_6]^{3+}$	5.0[6]	$[Cr(urea)_6]^{3+}$–SO_4^{2-}	0.7_6	$3._8$	
$[Co(CO_3)(tn)_2]^{+}$	4.8[26]				
$[Cr(NCS)_4(NH_3)_2]^{-}$	6.1[28]				

a) Some of these are calculated from the polarographic diffusion current constant, and consequently are less accurate.

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