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Effects of the Double Layer Structure and the Ion Association on Electrode Processes of Some Substitution-inert Complex Ions

Kazuko OGINO (née EBATA) and Nobuyuki TANAKA

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

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The current-potential curves of some substitution-inert complex ions are affected by the change in the composition of the supporting electrolyte. The change in the one-electron reduction wave of hexaquochromium(III) ions with the increase in the concentration of sodium perchlorate and sodium iodide is analyzed in terms of the effect of the structure of the electrical double layer. The addition of sodium sulfate at a constant ionic strength of 0.1 shifts the half-wave potentials of hexaquochromium(III), hexamminechromium(III) and hexamminecobalt(III) ions to more negative potentials. In the case of hexamminecobalt(III), the shift is much greater than in the cases of the former two complex ions. These phenomena are interpreted to be due to the effects of the double layer structure and of the ion association.

In a previous paper,1) the effect of sulfate ions on the polarographic diffusion current of hexamminecobalt(III), hexamminechromium(III) and hexaquochromium(III) ions was reported. The addition of sulfate ions also cause a negative shift of the half-wave potential.2,3) The shift in the half-wave potential of some cobalt(III) complex ions was considered to be due to the ion association.2) The rate of the electrochemical step is influenced also by the change in the structure of the electrical double layer accompanying the change in the composition of solution.

In this paper, the current-potential relationship of the totally irreversible electrode process under the influence of the structure of the double layer is derived in consideration of the effect of mass tranfer, and then, the influence of the composition of the supporting electrolyte on the reduction wave of some substitution-inert complex cations is analyzed in terms of the effects of the double layer structure and of the ion association.

Derivation of the Current-Potential Relationship

Matsuda and Delahay4) gave a general solution in the form of Laplace transform for the boundary value problem of the electrode process

$$\mathrm{A}^{z+} + ne \rightarrow \text{Product} \tag{1}$$

at a stationary plane electrode under the influence of the double layer structure. The concentration of A^{z+} at the closest approach (pre-electrode layer), which is denoted by C, is given by the following equation according to Matsuda and Delahay:

$$\mathrm{L}C = \exp(-z\boldsymbol{F}\phi_0/\boldsymbol{RT})\left[\frac{C^\circ}{s} - \frac{\{\mathrm{L}(i/n\boldsymbol{F}q)\}}{\sqrt{Ds}}G\right] \tag{2}$$

where ϕ_0 is the potential at the pre-electrode layer relative to the bulk of the solution, z, the charge of the reacting particle, C°, the concentration of A^{z+} in the bulk of the solution, s, the parameter of the transformation, i, the current and q, the electrode area. The symbol L denotes the Laplace transformation. The function G is involved,[*1] but can be expanded as

$$G = 1 + a\sqrt{s}/(\kappa\sqrt{D}) + \cdots \tag{3}$$

with

$$a = \frac{\exp\{\boldsymbol{F}(\pm|z| - |z_e|/2)|\phi_0|/\boldsymbol{RT}\} - 1}{\pm|z/z_e| - 1/2} - \frac{\exp\{\boldsymbol{F}(\mp|z| - |z_e|/2)|\phi_0|/\boldsymbol{RT}\} - 1}{\mp|z/z_e| - 1/2} \tag{4}$$

where κ is the Debye-Hückel reciprocal length, z_e, the charge of the symmetrical indifferent electrolyte. The upper and the lower signs in front of $|z/z_e|$ correspond to the cases $z\phi_0>0$ and $z\phi_0<0$, respectively.

We introduced into Eq. (2) another boundary condition which was considered to be valid for a totally irreversible reduction process:

$$i/n\boldsymbol{F}q = kC \tag{5}$$

where k is the rate constant of Reaction 1 and is related to k_0, the true rate constant for $\phi_0=0$, by

$$k = k_0 \exp(n\alpha\boldsymbol{F}\phi_0/\boldsymbol{RT}) \tag{6}$$

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1) N. Tanaka, K. Ogino and G. Satô, This Bulletin, **39**, 366 (1966).

2) A. A. Vlček, "Progress in Inorganic Chemistry," ed. by F. A. Cotton, Interscience Publishers, New York (1963), p. 211.

3) N. Tanaka, K. Ebata and G. Satô, This Bulletin, **36**, 912 (1963).

4) H. Matsuda and P. Delahay, *J. Phys. Chem.*, **64**, 332 (1960).

[*1] For the complete form of the function G, see Ref. 4.

where α is the transfer coefficient. Strictly, the rate constant k_0 itself is not necessarily constant by the change of the composition of solution because it is a function of the activity coefficient of the reactant, f_A, and that of the activated complex, $f^{\neq}$, as

$$k_0 = (k_0)_{f=1} f_A / f^{\neq} \qquad (7)$$

In the treatment below, the effect of the change of the ratio $f_A/f^{\neq}$ by the change of the composition of solution and of the potential is not taken into consideration as it is supposed to be small compared to the effects of the double layer structure and of the ion association.

Equation (5) is transformed as

$$\mathrm{L}(i/n\boldsymbol{F}q) = k\mathrm{L}C \qquad (8)$$

By retaining only two terms in Eq. (3) and by substituting Eq. (8) into Eq. (2), one obtains

$$\mathrm{L}C = C^{\circ}/[b\sqrt{s}\{\sqrt{s} + k/(b\sqrt{D})\}] \qquad (9)$$

with

$$b = ak/(\kappa D) + \exp(z\boldsymbol{F}\phi_0/\boldsymbol{RT}) \qquad (10)$$

where D is the diffusion coefficient of the reacting particle. From the inverse transform of Eq. (9) and Eq. (5), Eq. (11) is obtained:

$$i = n\boldsymbol{F}qC^{\circ}\sqrt{D/t}\,\lambda \exp(\lambda^2) \operatorname{erfc} \lambda \qquad (11)$$

where

$$\lambda = k\sqrt{t}/(b\sqrt{D}) \qquad (12)$$

For sufficiently large value of λ, Eq. (11) becomes

$$i = n\boldsymbol{F}qC^{\circ}\sqrt{D/(\pi t)} = i_d \qquad (13)$$

where i_d is the same with the diffusion current observed in the absence of ϕ_0 effect. It is clear from Eq. (11) that the current does not exceed the value of i_d, when there is an attraction of the reacting particle.

The apparent rate constant of an irreversible process is of the order of $\sqrt{D/(\pi t)}$ in the potential region near the half-wave potential. For $z\phi_0 < 0$, the apparent rate constant is larger than k (*cf.* Eqs. (6) and (16)). Therefore, the first term in Eq. (10) can be neglected in view of the large value of κ compared to that of $1/\sqrt{Dt}$, as

$$b = \exp(z\boldsymbol{F}\phi_0/\boldsymbol{RT}) \qquad (14)$$

In the absence of the effect of the double layer structure, the current in a totally irreversible reaction is given also by Eq. (11) with

$$\lambda = k_0\sqrt{t/D} \qquad (15)$$

A comparison of Eq. (12) with Eq. (15) shows the apparent rate constant k_{app} of Reaction (1) under the influence of the double layer structure is given by

$$k_{app} = k_0 \exp\{(n\alpha - z)\boldsymbol{F}\phi_0/\boldsymbol{RT}\} \qquad (16)$$

Equation (11) can be approximated as

$$\frac{i}{i_d} = \frac{2.2\lambda}{1 + 2.2\lambda} \qquad (17)$$

By considering the relation

$$k_0 = (k_0)_{E^{\circ}_{1/2}} \exp\{-\alpha n\boldsymbol{F}(E - E^{\circ}_{1/2})/\boldsymbol{RT}\} \qquad (18)$$

the following equation is derived from Eqs. (16) and (17):

$$E = E^{\circ}_{1/2} - \frac{2.3\boldsymbol{RT}}{n\alpha\boldsymbol{F}} \log\frac{i}{i_d - i} - \frac{z - n\alpha}{n\alpha}\,\phi_0 \qquad (19)$$

where $E^{\circ}_{1/2}$ is the true half-wave potential for $\phi_0 = 0$. This relation is similar to that valid in the Tafel region[5] where the effect of mass transfer can be neglected. Equation (19) shows that the ordinary log-plot does not necessarily give a straight line with a slope of $2.3\boldsymbol{RT}/(n\alpha\boldsymbol{F})$, while the corrected log-plot according to

$$E - \phi_0 = E^{\circ}_{1/2} - \frac{2.3\boldsymbol{RT}}{n\alpha F}\left(\log\frac{i}{i_d - i} + \frac{zF}{2.3\boldsymbol{RT}}\phi_0\right) \qquad (20)$$

should give a straight line with a slope of $2.3\boldsymbol{RT}/(\alpha n\boldsymbol{F})$, from which the transfer coefficient can be calculated.

In the above treatment, the effect of the growth of the mercury electrode is not taken into consideration. In the current-potential relationship given by Eq. (19), this effect is not considered to be serious similarly as in the current-potential relationship in the absence of the effect of the double layer structure.

Experimental

The complex compounds used were prepared by the procedures described previously.[1] The current-time curves during the life of a mercury drop were recorded using a Rikadenki ERJ1 recorder with an RLDC-201 preamplifier. In the following sections, the word "current", denoted by i, means the maximum current observed just before the detachment of the mercury drop, unless otherwise stated. The dropping mercury electrode used had an m-value of 2.11 mg/sec and a drop-time t_d of 4.22 sec in a deaerated 0.2 M potassium nitrate solution at −0.5 V *vs.* SCE and at 59 cm of mercury height. A saturated calomel electrode (SCE) with a large surface area served as an anode. All measurements were carried out at 25°C.

Results

The current-potential curve of the one-electron reduction wave of hexaquochromium(III) ions in a sodium perchlorate solution was affected by the concentration of perchlorate ions as shown in Fig. 1. The half-wave potential was shifted to more negative potentials and the reciprocal slope of the log-plot became larger by the increase in the perchlorate concentration. Results given in Fig. 1 were analyzed according to Eqs. (19) and (20).

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[5] K. Asada, P. Delahay and A. K. Sundaram, *J. Am. Chem. Soc.*, **83**, 3396 (1961).

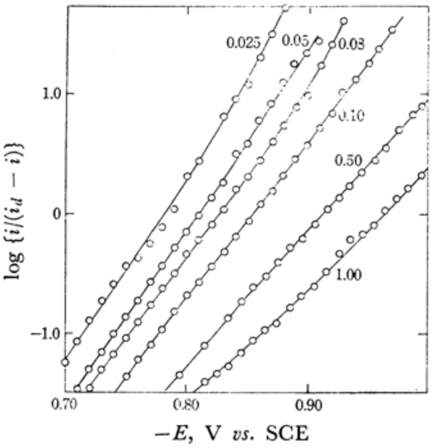

Fig. 1. Log-plots of 1.11$_5$ mM hexaquochromium(III) perchlorate in solutions containing various concentrations of sodium perchlorate, 0.0115 N perchloric acid and 0.005% gelatin. The figure on each line indicates the total concentration of perchlorate in the solution. In the solutions with less than 0.1 M perchlorate, the concentrations of the complex and perchloric acid were lowered appropriately.

In the analyses below, it was assumed that Reaction (1) takes place at the outer Helmholtz plane. The values of ϕ_0, the potential at the outer Helmholtz plane were computed from the Gouy-Chapman theory by Eq. (21),6),*2 because in the potential region in question, the specific adsorption of perchlorate ions was not significant.

$$(E - E_z) - \phi_0 = \pm\left[\frac{\boldsymbol{RT}\varepsilon}{2\pi K_i^2}\sum_j C_j\left\{\exp\left(-\frac{z_j\boldsymbol{F}\phi_0}{\boldsymbol{RT}}\right) - 1\right\}\right]^{1/2} \quad (21)$$

In Eq. (21), K_i is the integral capacity of the Helmholtz double layer, E_z, the electrode potential at zero charge, ε, the dielectric constant, and C_j is the bulk concentration of ion j of valence z_j in mol/cm^3. The values of ϕ_0 thus obtained were in agreement with those obtained experimentally by Grahame and Parsons7) in potassium chloride solutions in the negative potentail region, where the specific adsorption of anions was absent. In such a potential region, the ϕ_0 potential is identical in all electrolytes with univalent cations.8)

The half-wave potentials in Fig. 1 were found to be linear with the ϕ_0 potential as is expected from Eq. (19). When values of n and z were taken to be 1 and 3 respectively, α was obtained to be 0.65 from the slope of the plots of $E_{1/2}$ vs. ϕ_0.

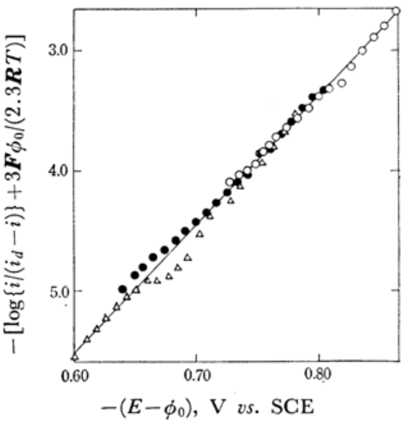

Fig. 2. Corrected log-plots of hexaquochromium(III) in 0.025 M (△), 0.05 M (●) and in 0.10 M (○) perchlorate solutions (for details of the composition of solution, see Fig. 1).

Corrected log-plots were prepared according to Eq. (20) as given in Fig. 2. All the plots in Fig. 2 lie near a single straight line, which can be expressed by Eq. (22).

$$E - \phi_0 = -1.11 - \frac{2.3\boldsymbol{RT}}{0.65\times 3\boldsymbol{F}}\left(\log\frac{i}{i_d - i} + \frac{3\boldsymbol{F}}{2.3\boldsymbol{RT}}\phi_0\right) \quad (22)$$

The value of α in Eq. (22) agrees with that obtained above by the use of Eq. (19). The value of $E^\circ_{1/2}$ obtained in Eq. (22) is far more negative than the observed half-wave potential.

Log-plots of hexaquochromium(III) in sodium iodide solutions were not the same as those in sodium perchlorate solutions of the same concentration as can be seen from Fig. 3. The plots in iodide solutions lie at considerably less negative potentials with smaller slopes than those in perchlorate solutions. Iodide ions are adsorbed specifically at the mercury-solution interface even in the negative potentials where hexaquochromium(III) is reduced, and make the ϕ_0 potential more negative than in perchlorate solutions. Corrected log-plots according to Eq. (20) were prepared using ϕ_0 potentials reported by Grahame for potassium iodide solutions9) and reproduced in Fig. 4. The large difference in the plots in Fig. 3 was much reduced in Fig. 4.

The addition of sodium sulfate for keeping the total ionic strength constant to be 0.1($NaClO_4$) affected the one-electron reduction waves of hexamminecobalt(III), hexamminechromium(III) and hexaquochromium(III) ions. See Fig. 5. In the case of the latter two complex ions, only small parallel shifts to more negative potentials were observed. The calculation of ϕ_0 potentials by the use of Eq. (21) shows that they change

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*2 In the computation, the integral capacity of the Helmholtz double layer was taken to be 20 μF/cm^2.

6) M. Breiter, M. Kleinerman and P. Delahay, *J. Am. Chem. Soc.*, **80**, 5111 (1958).

7) D. C. Grahame and R. Parsons, *ibid.*, **83**, 1291 (1961).

8) D. C. Grahame and B. A. Soderberg, *J. Chem. Phys.*, **22**, 449 (1954).

9) D. C. Grahame, *J. Am. Chem. Soc.*, **80**, 4201 (1958).

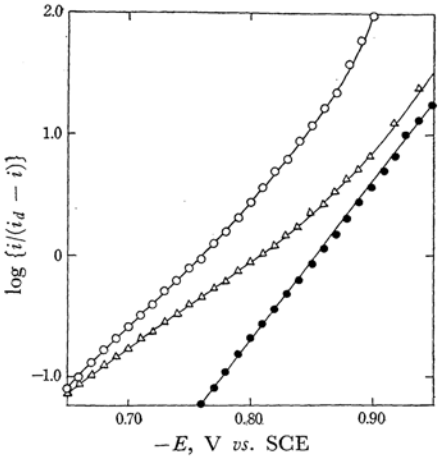

Fig. 3. Log-plots of hexaquochromium(III) perchlorate in 0.025 M (○), 0.10 M (△) sodium iodide and in 0.10 M sodium perchlorate (●) solutions. All the solutions contained perchloric acid by 1/10 of the concentrations of the sodium salts. The concentrations of hexaquochromium(III) were 0.28 mM in the first solution and 1.11_5 mM in the latter two solutions.

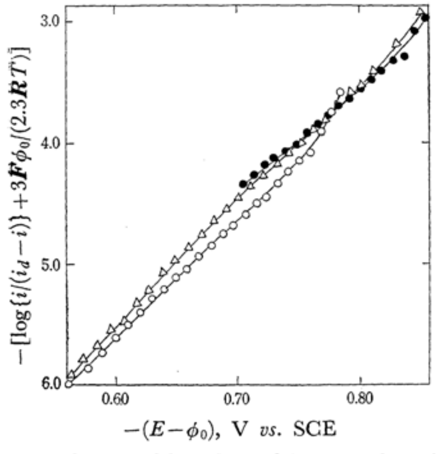

Fig. 4. Corrected log-plots of hexaquochromium(III) in 0.025 M (○), 0.10 M (△) sodium iodide and in 0.10 M sodium perchlorate (●) solutions (for details of the composition of solution, see Fig. 3).

with the increase in the concentration of sodium sulfate when the ionic strength is kept constant with sodium perchlorate. Corrected log-plots according to Eq. (20) are given in Fig. 6 for hexamminechromium(III) ions. Although these plots gave straight lines, there was a parallel shift of about 45 mV for the plots at $C_{Na_2SO_4}=0.03$ M as compared to those at $C_{Na_2SO_4}=0$. A shift of 70 mV was observed in the case of hexaquochromium(III) ions.

If it is assumed that the complex ion associating with the anion X^{x-} is less electroactive than the free complex ion and that the ion association

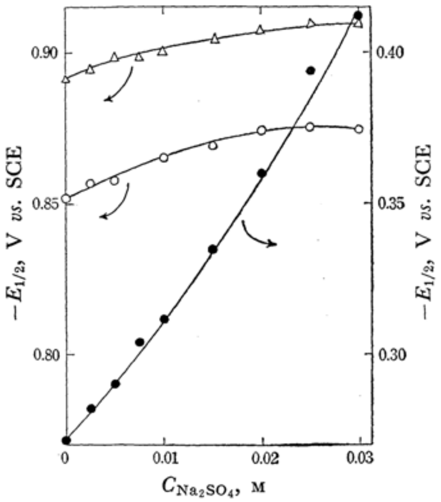

Fig. 5. The change of the half-wave potential of hexamminecobalt(III) (●), hexamminechromium(III) (△) and hexaquochromium(III) (○) by the addition of sodium sulfate. The composition of solution is 1.0 mM complex salt +0.01 N perchloric acid +0.005% gelatin (in the case of the cobalt(III) complex, 0.002% gelatin); ionic strength, 0.1(NaClO₄).

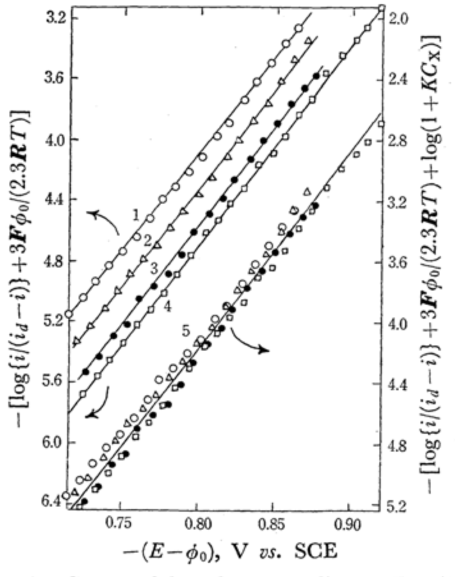

Fig. 6. Corrected log-plots according to Eq. (20) (1 to 4) and Eq. (23) (5) of 1.00 mM hexamminechromium(III) obtained in solutions in the absence (○) and presence of 0.01 M (△), 0.02 M (●) and 0.03 M (□) sodium sulfate (for details of the composition of solution, see Fig. 5).

process is in equilibrium, the equation,

$$E-\phi_0=E^{\circ}_{1/2}-\frac{2.3\boldsymbol{RT}}{\alpha n\boldsymbol{F}}\left\{\log\frac{i}{i_d-i}+\log(1+KC_{\rm X})+\frac{z\boldsymbol{F}}{2.3\boldsymbol{RT}}\phi_0\right\} \qquad (23)$$

is obtained instead of Eq. (20), where C_X is the bulk concentration of X^{x-} ions which exist in a large excess over the complex ions and K, the association constant. Using the association constants of $[Cr(NH_3)_6]^{3+}$-SO_4^{2-} and $[Cr(H_2O)_6]^{3+}$-SO_4^{2-}, which were determined to be 58 and 4×10 respectively by the measurement of the polarographic diffusion current,1) the corrected log-plots of hexamminechromium(III) and hexaquochromium(III) in sulfate solutions were prepared according to Eq. (23). The plots of hexamminechromium(III) are shown in Fig. 6. The deviation the in plots obtained according to Eq. (23) was found to be within ±5 mV. It was found to be within ±15 mV in the case of hexaquochromium(III) ions.

In the case of hexamminecobalt(III) ions, not only the log-plots were shifted markedly to more negative potentials, but also the slope and the curvature of the plots were changed as shown in Fig. 7.

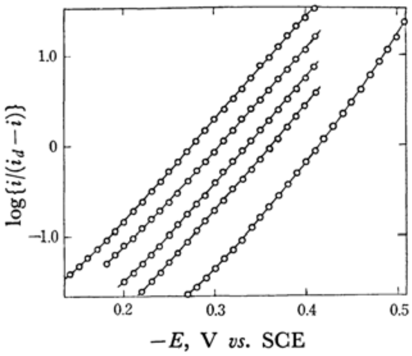

Fig. 7. Log-plots of 1.00 mM hexamminecobalt(III) perchlorate in solutions containing 0.01 N perchloric acid, 0.002% gelatin at ionic strength 0.1 ($NaClO_4$). Sodium sulfate concentrations are from left to right 0, 0.0075, 0.015, 0.020, and 0.030 M respectively.

Discussion

In the electrode process of substitution-labile complex ions, the structure of the reacting particle in the neighborhood of the electrode may differ from that in the bulk of the solution. If the electrode process is preceded by chemical reactions, the system is complicated, since the rate of the chemical reactions is affected by the structure of the electrical double layer. In the electrode process of substitution-inert complex ions, on the other hand, no chemical reactions except such rapid processes as protonation or ion association occur prior to the electrochemical step, and the structure of the reacting particle at the pre-electrode layer is definite. Hence, it is convenient to apply the theory of the double layer effect to electrode kinetics of substitution-inert complex ions.

The current-potential curves of hexaquochromium(III) ions in perchlorate and iodide media could be interpreted by considering the effect of the double layer structure. Thus, the great positive shift in iodide solutions can be concluded to be due to the large negative ϕ_0 potential in iodide solutions even at negative potentials in question.

The apparent transfer coefficients obtained from the slope of the conventional log-plots of hexaquochromium(III) and hexamminechromium(III) may be significantly larger than the true transfer coefficient. Hexamminechromium(III) gave log-plots with slopes of 60 to 65 mV at 25°C3) which would be expected for a reversible electrode process, whereas the corrected log-plots in Fig. 6 gave a slope of 76 mV.

The change of the current-potential curves of hexamminechromium(III) and hexaquochromium(III) ions in sulfate solutions were interpreted as to be due to the effects of both the double layer structure and the ion association. The deviation in the log-plots according to Eq. (23) may partly be due to the difference of ϕ_0 potential used in the calculation and the actual ϕ_0 potential in the solution used.

No analyses were made for log-plots of hexamminecobalt(III) in sulfate solutions, since ϕ_0 potentials are not known for solutions employed in the experiment. Sulfate and perchlorate ions are adsorbed specifically at the mercury-solution interface in potentials of the reduction of hexamminecobalt(III), and ϕ_0 potentials deviate markedly from those calculated using Eq. (21) by a procedure mentioned above. The great shift in the half-wave potential of hexamminecobalt(III) compared to that of the chromium(III) complexes as shown in Fig. 5 may be considered as follows: The ϕ_0 potential at potentials more negative than the electrocapillary maximum becomes more negative as the sulfate concentration increases, but the ϕ_0 potential at potentials less negative than the electrocapillary maximum becomes less negative as the sulfate concentration increases. The rate of the reduction of hexamminecobalt(III) is decelerated by the addition of sulfate ions, because it has a charge of +3 and is reduced at less negative potentials than the electrocapillary maximum. Thus, the effects of both the change in the double layer structure and the ion association make the half-wave potential of hexamminecobalt(III) shift to more negative potentials. The change in the curvature of log-plots as shown in Fig. 7 may be considered to be related to the shape*3 of the ϕ_0 *vs.* E curve near the electrocapillary maximum.

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*3 For example, see Ref. 8, for the shape of the ϕ_0 *vs.* E curve.