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Polarographic Behaviors and Potentiostatic Determination of Kinetic Parameters for the Electrode Reaction of *trans*-1,2-Cyclohexanediaminetetraacetatochromate(III) Complexes

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The polarogographic behaviors of *trans*-1,2-cyclohexanediaminetetraacetatochromate(III) complex have been studied. The complex is reduced reversibly at the dropping mercury electrode in the solution which contains 0.4 M sodium chloride, 0.1 M acetate buffer and 2×10^{-6} M polyoxyethylene lauryl ether. The kinetic parameters of this oxidation-reduction process have been determined from the potentiostatic measurements at 25°C. The measured parameters are: the standard potential ($E_0)_{ms}=-1.198$ V *vs.* SCE, the standard rate constant $(k_s)_{ms}=2.9\times10^{-2}$ cm sec^{-1}, the transfer coefficient for cathodic process $(\alpha_c)_{ms}=0.33$ and that for anodic one $(\alpha_a)_{ms}=0.67$. The Frumkin correction for the electrical double layer has been applied to these parameters and the corrected values thus obtained are: $(E_0)_{corr}=-1.198$ V *vs.* SCE, $(k_s)_{corr}=0.93$ cm sec^{-1}, $(\alpha_c)_{corr}=0.40$ and $(\alpha_a)_{corr}=0.57$.

The theoretical treatment of the potentiostatic method for the study of fast electrode reactions and its application to the oxidation-reduction processes of Cr(II)-EDTA/Cr(III)-EDTA and Co(II)-EDTA/Co(III)-EDTA systems have been reported,[1-3] where EDTA means ethylenediaminetetraacetic acid. A ligand, *trans*-1,2-cyclohexanediaminetetraacetic acid (CyDTA), which is very similar to EDTA, also forms a stable chelate with chromium(III) ion[4] in difference of a more bulky ion.

In this report, the polarographic behaviors of Cr(III)-CyDTA have been studied and the kinetic parameters of the electrode reaction have been measured by the potentiostatic method. The Frumkin correction has been applied for the effect of electrical double layer at the electrode solution interface.

Experimental

Reagents. The stock solution of *trans*-1,2-cyclohexanediaminetetraacetatochromate(III) complex was prepared by adding the solution of hexaaquochromium(III) perchlorate (0.1 M) to the solution of disodium *trans*-1,2-cyclohexanediaminetetraacetate (0.1 M), and by heating on the water-bath for half an hour. Then, the solution was passed through a cation exchanger Dowex 50W-X8 to remove unreacted chromium ions. The concentration of the complex was determined polarographically after oxidizing chromium(III) to chromate with hydrogen peroxide.[5] All other chemicals used were of guaranteed reagent-grade.

Apparatus. Polarographic measurements were carried out with a Yokogawa Polarocorder POL-11. The potentiostat used was constructed in this laboratory and its characteristics were described previously.[3] The dropping mercury electrode used for polarographic measurements had an *m*-value of 2.02 mg sec^{-1} and a drop time t_d of 4.05 sec in 0.5 M sodium chloride solution at -0.5 V *vs.* SCE and at 63 cm mercury height. The visible absorption spectra of the solution was measured with a Hitachi EPU-2 spectrophotometer. Electrolysis at constant potential was carried out with a Yanagimoto Controlled Potential Electrolyser.

Results and Discussion

Polarographic Studies. The complex ion has two absorption maxima in the visible region at 18.3×10^3 cm^{-1} (ν_1, $\log\varepsilon_1=2.05$) and 25.4×10^3 cm^{-1} (ν_2, $\log\varepsilon_2=2.39$), respectively. No apparent change in visible spectra was found in the pH range from 4.2 to 7.7, and this may suggest that the predominant complex species have the ligand coordinated to the chromium(III) ion as a pentadentate or hexadentate in the same way in Cr(III)-EDTA complex.

Polarograms were obtained in a solution containing 1.0 mM Cr(III)-CyDTA, 0.4 M NaCl, 0.1 M acetate or phosphate buffer (pH 4.2 to 7.7) and 2×10^{-6} M polyoxyethylene lauryl ether (LEO) at 25°C. Examples are given in Fig. 1. As seen in Table 1, the half-wave potentials were at -1.200

1) N. Tanaka and A. Yamada, *Electrochim. Acta*, **14**, 491 (1969).

2) A. Yamada and N. Tanaka, This Bulletin, **42**, 1600 (1969).

3) A. Yamada and N. Tanaka, *Sci. Repts. Tohoku Univ. Series I*, **52**, 73 (1969).

4) A. R. Selmer-Olsen, *Anal. Chim. Acta*, **26**, 482 (1962).

5) I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. 2, Interscience, New York (1952), p. 455.

Table 1. Effect of pH and surface-active substance on the polarogram of 1.0 mM Cr(III)-CyDTA in solutions containing 0.4 M NaCl and 0.1 M buffer (acetate or phosphate*) at 25°C

Surface-active substance	pH	$\bar{i}_d$ μA	$E_{1/2}$ V *vs.* SCE	Slope of log plot mV
2×10^{-6} M LEO	4.20	−3.00	−1.201	62
2×10^{-6} M LEO	4.46	−2.98	−1.202	61
2×10^{-6} M LEO	4.67	−3.00	−1.200	61
2×10^{-6} M LEO	5.02	−3.00	−1.200	61
2×10^{-6} M LEO	5.47	−2.99	−1.202	62
2×10^{-6} M LEO	*6.85	−2.97	−1.202	62
2×10^{-6} M LEO	*7.72	−2.85	−1.202	62
free		maximum wave		
1×10^{-6} M LEO	4.67	−3.00	−1.200	61
2×10^{-6} M LEO	4.67	−3.00	−1.200	61
5×10^{-6} M LEO	4.67	−2.95	−1.202	64
10×10^{-6} M LEO	4.67	−2.92	−1.204	67
5×10^{-4}% gelatin	4.67	−3.01	−1.201	61
5×10^{-3}% gelatin	4.67	−2.96	−1.202	62

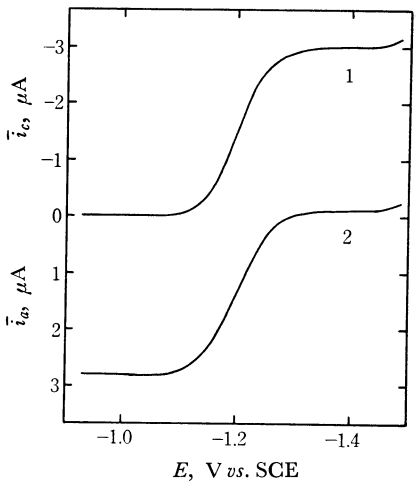

Fig. 1. Polarograms of 1.0 mM Cr-CyDTA complex in solutions of pH 4.7 containing 0.4 M NaCl, 0.1 M acetate buffer and 2×10^{-6} M LEO at 25°C: (1) Cathodic wave of Cr(III)-CyDTA; (2) anodic wave of Cr(II)-CyDTA produced by electrolytic reduction with a mercury pool electrode.

V *vs.* SCE in both cathodic and anodic processes and the limiting current, which was diffusion controlled, was of a one-electron reduction. These and the slope of log-plot indicated that the electrode processes of Cr(II, III)-CyDTA complexes are reversible. Little changes in cathodic current and $E_{1/2}$ were observed in this pH region; this may indicate that the complex species present in the solution and at the electrode surface is only one species, $[Cr(III)\text{-}CyDTA]^-$ for oxidant and $[Cr(II)\text{-}CyDTA]^{2-}$ for reductant ions.

The effect of surface-active substance on the polarographic wave was relatively small unless the concentration of the substance was too high; in the case of LEO, for example, unless its concentration exceeded about 10^{-5} M, as shown in Table 1.

Electrolysis was carried out in a deaerated solution containing 1.0 mM Cr(III)-CyDTA, 0.4 M NaCl, 0.1 M acetate buffer (pH 4.7) and 2×10^{-6} M LEO with the mercury pool electrode, the potential of which was set at −1.40 V *vs.* SCE at 25°C. A polarogram of the solution after electrolysis was given in Fig. 1, which showed a limiting diffusion current used for the determination of Cr(II)-CyDTA complex. Diffusion coefficients of Cr(III)-CyDTA and Cr(II)-CyDTA were 5.5×10^{-6} cm^2 sec^{-1} and 5.4×10^{-6} cm^2 sec^{-1}, respectively. These values are smaller than those of Cr-EDTA complexes, and seem to be reasonable because the sizes of Cr-CyDTA ions are larger than those of Cr-EDTA ions.

From these results mentioned above, the electrode process is considered as,

$$[Cr(III)\text{-}CyDTA]^- + e \rightleftarrows [Cr(II)\text{-}CyDTA]^{2-} \quad (1)$$

in which any chemical reaction, *e.g.* protonation reaction, is not involved appreciably in the range of pH 4.2 to 7.7.

Equilibrium potentials of this oxidation-reduction process were measured polarographically, using the Nernst's equation at 25°C. A straight line was obtained with a reciprocal slope of 61 mV by plotting E_e *versus* $\log\{[Cr(III)\text{-}CyDTA]/[Cr(II)\text{-}CyDTA]\}$, as shown in Fig. 2. The standard potential $(E_0)_e$ was found to be −1.199 V *vs.* SCE.

Determination of Kinetic Parameters by Means of Potentiostatic Method. When an electrode reaction is expressed as,

$$O + ne \rightleftarrows R \quad (2)$$

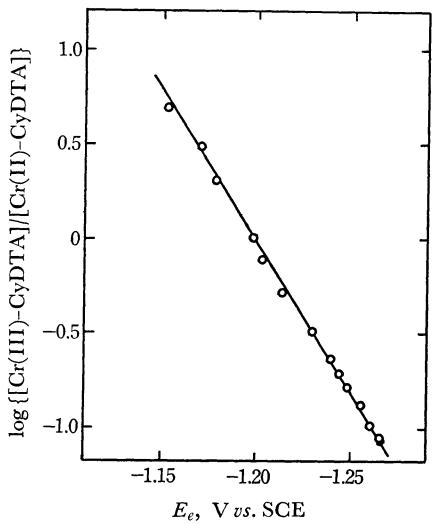

Fig. 2. Relation between equilibrium potential E_e and log{[Cr(III)-CyDTA]/[Cr(II)-CyDTA]} at 25°C. Each concentration was determined polarographically. Cr(II)-CyDTA was prepared by electrolytic reduction with a mercury pool electrode in the solution of pH 4.7 containing Cr(III)-CyDTA, 0.4 M NaCl, 0.1 M acetate buffer and 2×10^{-6} M LEO.

the relation between cathodic current i and t, time after the beginning of the electroreduction at a given potential, can be represented by the equations,[1-2]

$$\left(\frac{i}{i_d}\right)_t \Big/ \left(\frac{i}{i_d}\right)_\tau = \sqrt{\pi}\,\lambda_{ms}\sqrt{t}\exp(\lambda_{ms}^2 t)\operatorname{erfc}(\lambda_{ms}\sqrt{t}) \qquad \sqrt{\tau} \gg \sqrt{t} \tag{3}$$

$$(k_c)_{ms} = \lambda_{ms}\left(\frac{i}{i_d}\right)_\tau \sqrt{D_O} \tag{4}$$

$$(k_a)_{ms} = \lambda_{ms}\left\{1-\left(\frac{i}{i_d}\right)_\tau\right\}\sqrt{D_R} \tag{5}$$

where

$$\lambda_{ms} = \frac{(k_c)_{ms}}{\sqrt{D_O}} + \frac{(k_a)_{ms}}{\sqrt{D_R}} \tag{6}$$

D_O and D_R are the diffusion coefficients of oxidant and reductant, respectively. Since the ratio of $(i/i_d)_t$ to $(i/i_d)_\tau$ and time, t, are measurable, λ_{ms} can be evaluated at various potentials. The measured rate constants of the cathodic and the anodic process, $(k_c)_{ms}$ and $(k_a)_{ms}$, can be obtained with these λ_{ms} values. Kinetic parameters*1 of the electrode reaction are calculated from the relations,

$$(k_c)_{ms} = (k_s)_{ms}\exp\left[-\frac{(\alpha_c)_{ms}n\boldsymbol{F}}{\boldsymbol{RT}}(E-(E_0)_{ms})\right] \tag{7}$$

$$(k_a)_{ms} = (k_s)_{ms}\exp\left[\frac{(\alpha_a)_{ms}n\boldsymbol{F}}{\boldsymbol{RT}}(E-(E_0)_{ms})\right] \tag{8}$$

*1 The notations of parameters used here except $(k_s)_{corr}$, which corresponds practically to $(k_s)^c{}_{corr}$, are identical with those described previously.[2]

Plotting $\log(k_c)_{ms}$ against E and $\log(k_a)_{ms}$ against E (Fig. 3), the measured standard potential $(E_0)_{ms}$ can be obtained from the point of intersection of two straight lines, each slope of which gives the measured transfer coefficients $(\alpha_c)_{ms}$ and $(\alpha_a)_{ms}$ for the cathodic and the anodic process, respectively. The values of $(i/i_d)_t$ and $(i/i_d)_\tau$ which were obtained at various potentials and also those of $(k_c)_{ms}$ and $(k_a)_{ms}$ calculated therefrom are given in Table 2.

Frumkin Correction. All measured parameters involve the influence of the electrical double layer. On the assumption that neither reactant nor supporting electrolyte is specifically adsorbed, we can consider the effect of the double layer ac-

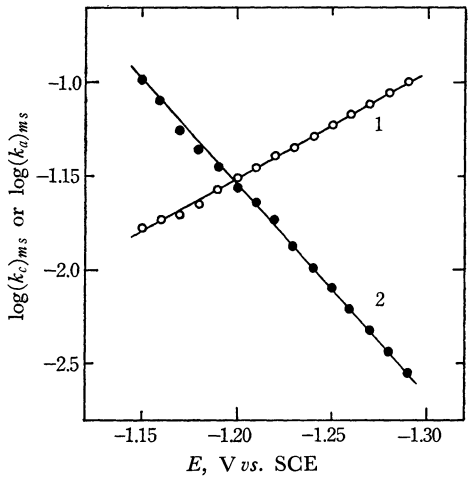

Fig. 3. Relations of (1) $\log(k_c)_{ms}$ *vs.* E and (2) $\log(k_a)_m$ & *vs.* E obtained with 1 mM Cr(III)-CyDTA in the solution of 4.7 containing 0.4 M NaCl, 0.1 M acetate buffer and 2×10^{-6} M LEO at 25°C.

TABLE 2. MEASURED KINETIC DATA OF THE ELECTRODE REACTION OF Cr(III)-CyDTA IN 0.1 M ACETATE BUFFER + 0.4 M NaCl + 2×10^{-6} M LEO (pH 4.7) 25°C

E V *vs.* SCE	$(i/i_d)_t$*	$(i/i_d)_\tau$**	$(k_c)_{ms}$ cm sec^{-1}	$(k_a)_{ms}$ cm sec^{-1}
−1.170	0.16_7	0.25_2	0.019_5	0.055_4
−1.180	0.21_5	0.33_1	0.022_7	0.043_8
−1.190	0.25_2	0.42_0	0.026_6	0.035_2
−1.200	0.29_7	0.51_6	0.030_3	0.027_2
−1.210	0.34_6	0.60_0	0.035_4	0.022_5
−1.220	0.39_7	0.68_6	0.040_6	0.017_7
−1.230	0.44_6	0.77_1	0.045_5	0.012_9
−1.240	0.49_6	0.83_2	0.052_0	0.010_0
−1.250	0.54_4	0.87_9	0.059_1	0.0078_0
−1.260	0.59_1	0.91_4	0.066_6	0.0060_0

* Time after beginning of electrolysis: $t=0.51_4$ msec

** Time after beginning of electrolysis: $\tau=0.11_0$ sec

cording to the Frumkin correction.

The values of ϕ_2 potential at the outer Helmholtz plane of double layer were determined by the measurements of the differential capacity and the electrocapillary curve of the supporting electrolyte solution. The ϕ_2 potentials thus obtained were shown in Fig. 4.

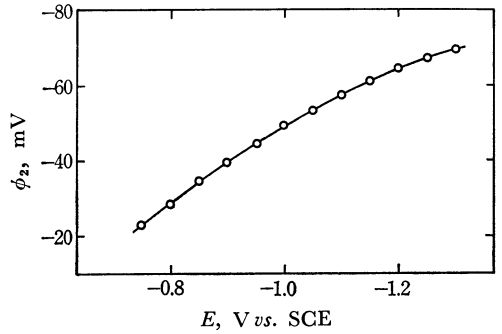

Fig. 4. Values of ϕ_2 potential at outer Helmholtz plane as a function of the electrode potential E. ϕ_2 was measured in the solution of pH 4.7 containing 0.4 M NaCl, 0.1 M acetate buffer and 2×10^{-6} M LEO at 25°C, under the assumption that no specific adsorption took place.

Arranged forms of Frumkin's equations are expressed as follows:[1]

$$(k_c)'_{ms} \equiv (k_c)_{ms}\exp\left[\frac{z_O F}{RT}\phi_2\right] = (k_s)_{corr}\exp\left[-\frac{(\alpha_c)_{corr}nF}{RT}(E-\phi_2)\right]\times\exp\left[\frac{(\alpha_c)_{corr}nF}{RT}(E_0)_{corr}\right] \quad (9)$$

$$(k_a)'_{ms} \equiv (k_a)_{ms}\exp\left[\frac{z_R F}{RT}\phi_2\right] = (k_s)_{corr}\exp\left[\frac{(\alpha_a)_{corr}nF}{RT}(E-\phi_2)\right]\times\exp\left[\frac{(\alpha_a)_{corr}nF}{RT}(E_0)_{corr}\right] \quad (10)$$

The plots of $\log(k_c)'_{ms}$ *vs.* $(E-\phi_2)$ and those of $\log(k_a)'_{ms}$ *vs.* $(E-\phi_2)$ were found to give straight lines, of which the intersection gave the corrected standard potential $(E_0)_{corr}$ and the corrected standard rate constant $(k_s)_{corr}$ and the slopes did the transfer coefficients $(\alpha_c)_{corr}$ and $(\alpha_a)_{corr}$, respectively (Fig. 5).

Kinetic parameters thus obtained are given in Table 3. The standard rate constants $(k_s)_{ms}$ and $(k_s)_{corr}$ are smaller than those of Cr–EDTA system. This may be supported by the observations that the polarographic reduction wave of Cr(III)–CyDTA complexes was more suppressed by the addition of the same amount of surface-active substances than that of Cr(III)–EDTA complexes. In this connection, it may also be interesting that on electrolysis at a constant potential, the reduced form,

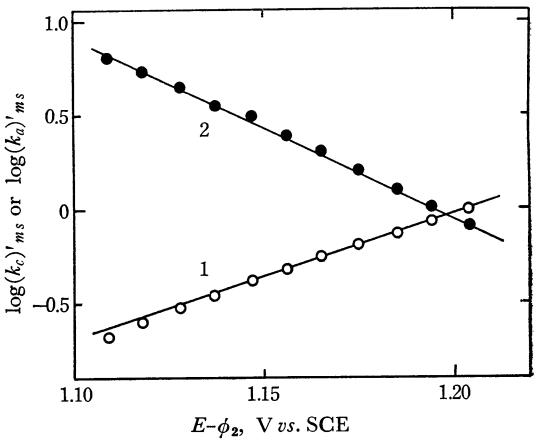

Fig. 5. (1) $\log(k_c)'_{ms}$ *vs.* $(E-\phi_2)$ and (2) $\log(k_a)'_{ms}$ *vs.* $(E-\phi_2)$ obtained with 1.0 mM Cr(III)-CyDTA in the solution of pH 4.7 containing 0.4 M NaCl, 0.1 M acetate buffer and 2×10^{-6} M LEO at 25°C. $(k_c)'_{ms}$ and $(k_a)'_{ms}$ are defined by Eqs. (9) and (10), respectively.

Table 3. Kinetic parameters of the electrode reactions of Cr(II, III)-EDTA[2] and Cr(II, III)-CyDTA systems

	Cr(II)-EDTA/ Cr(III)-EDTA	Cr(II)-CyDTA/ Cr(III)-CyDTA
$(E_0)_{ms'}$ V *vs.* SCE	−1.220	−1.198
$(k_s)_{ms'}$ cm sec^{-1}	0.21	0.029
$(\alpha_c)_{ms}$	0.58	0.33
$(\alpha_a)_{ms}$	0.39	0.67
$(E_0)_{corr'}$ V *vs.* SCE	−1.220	−1.198
$(k_s)_{corr'}$ cm sec^{-1}	17*	0.93
$(\alpha_c)_{corr}$	0.54	0.40
$(\alpha_a)_{corr}$	0.43	0.57

* This value is given for $(k_s)^c_{corr}$ in Ref. 2, which practically corresponds to $(k_s)_{corr}$ in this report.

Cr(II)–CyDTA ion, was more stable than Cr(II)–EDTA ion in the deaerated solution.

The sum of transfer coefficients, $(\alpha_c)_{ms}+(\alpha_a)_{ms}$ or $(\alpha_c)_{corr}+(\alpha_a)_{corr}$, was nearly equal to unity, and this caused $(E_0)_{ms}$ and $(E_0)_{corr}$ to be of the same value with each other.[1] Furthermore, each transfer coefficient, $(\alpha_c)_{corr}$ or $(\alpha_a)_{corr}$, seems to have a tendency to approach to 0.5 by the correction of the effect of the electrical double layer.

The polarographic half-wave potential $(E_{1/2})$, the standard potential obtained by the measurements of the equilibrium potentials, $(E_0)_e$, and those obtained by the potentiostatic method, $(E_0)_{ms}$ and $(E_0)_{corr}$, were in good agreement with each other within the experimental error.

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