BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 1600—1603 (1969)

Determination of Kinetic Parameters of the Electrode Reaction of Ethylenediaminetetraacetatoaquochromate(III) Ions by the Potentiostatic Method

Akifumi YAMADA and Nobuyuki TANAKA

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

(Received November 22, 1968)

Kinetic parameters of the electrode reaction of ethylenediaminetetraacetatoaquochromate(III)/ethylenediaminetetraacetatoaquochromate(II) at the dropping mercury electrode have been determined by the potentiostatic method in sodium chloride solutions of ionic strength 0.5 containing 0.1 M acetate buffer. The measured standard rate constant $(k_s)_{ms}$ is 2.1×10^{-1} cm sec^{-1} and the measured transfer coefficients $(\alpha_c)_{ms}$ and $(\alpha_a)_{ms}$ are 0.58 for the cathodic and 0.39 for the anodic process. The correction for the effect of the electrical double layer has been made on these parameters. The values obtained are: $(k_s)^c_{corr}=1._7\times 10$ cm sec^{-1}, $(\alpha_c)_{corr}=0.54$ and $(\alpha_a)_{corr}=0.43$. The standard potential -1.220 V *vs.* SCE determined by the potentiostatic method is compared with -1.218 V *vs.* SCE obtained by the measurement of the equilibrium potential. These values are in good agreement within the experimental error.

The reduction of ethylenediaminetetraacetatoaquochromate(III) (Cr(III)-EDTA) ions at the dropping mercury electrode was studied by Pecsok and co-workers[1] over a wide range of pH. These authors showed that the electrode reaction of Cr(III)-EDTA proceeds reversibly at the dropping mercury electrode and they reported the values of the polarographic half-wave potential at various pH's. Kinetic parameters of the electrode reaction, however, have not been reported yet for either Cr(III)-EDTA or Cr(II)-EDTA complexes.

In this study, the theoretical treatment of the potentiostatic method for the study of fast electrode reactions, which was reported previously,[2] has been applied to the electrode reaction of Cr(III)-EDTA ions on the dropping mercury electrode and the kinetic parameters have been determined.

Experimental

Hydrogen ethylenediaminetetraacetatoaquochromate(III) was prepared according to the method of Hamm.[3] Cr(II)-EDTA was prepared with Cr(III)-EDTA by electrolytic reduction. Redistilled water was used to prepare the solution of a desired concentration. The potentiostat was constructed in this laboratory[4] with an operational amplifier. The rise time and the input impedance are 3 μsec and 100 MΩ, respectively. A dropping mercury electrode of a long drop time (about 60 sec) was used for a cathode. The resistance of this capillary was 2.00 Ω at room temperature. The potential of the working electrode was measured against a saturated calomel electrode (SCE) with a Luggin

---

[1] R. L. Pecsok, L. D. Shields and W. P. Schaefer, *Inorg. Chem.*, **3**, 114 (1964).

[2] N. Tanaka and A. Yamada, *Electrochim. Acta*, in press.

[3] R. E. Hamm, *J. Am. Chem. Soc.*, **75**, 5670 (1953).

[4] unpublished.

capillary. A platinum wire electrode served as an auxiliary electrode. Electrolytic solutions were deaerated by bubbling purified nitrogen gas through the solution. Measurements were made at 25°C in solutions of ionic strength 0.5 (NaCl) containing 0.1 M acetate buffer. The pH of the solution was kept at 5.0 in order to avoid the formation of acid complexes.[1,5] Correction was made for the charging current, although the charging current decreased to zero within 30 to 40 μsec in most cases.

Results

Some preliminary measurements of current-potential behavior following the application of potential step were made with Cr(III)-EDTA ions at the slowly dropping mercury electrode. Figure 1 shows a typical example of a cathodic current-potential curve of Cr(III)-EDTA ions which was obtained in an acetate buffer solution of pH 5.0. The current was measured at 0.5 msec after the beginning of the electrolysis. Figure 2 shows plots of the logarithmic function of the current against the electrode potential. Plots of $\log\{I/(I_d-I)\}$ *vs.* E, where I is the current density, I_d, the limiting diffusion current density, and E, the electrode potential, yielded a straight line with a reciprocal slope of 60 mV and a half-wave potential of -1.222 V *vs.* SCE.

From the relation given by the equation,

$$E_e = (E_0)_{eq} + 0.0591 \times \log\{[\text{Cr(III)-EDTA}]/[\text{Cr(II)-EDTA}]\} \quad \text{at } 25°\text{C} \qquad (1)$$

the standard oxidation-reduction potential $(E_0)_{eq}$ of the reaction

$$\text{Cr(III)-EDTA} + e \rightleftharpoons \text{Cr(II)-EDTA}$$

is obtained by plotting $\log\{[\text{Cr(III)-EDTA}]/[\text{Cr(II)-EDTA}]\}$ against equilibrium potential E_e. The results are shown in Fig. 3. The value of $(E_0)_{eq}$ and the reciprocal slope of the plots were calculated to be -1.218 V *vs.* SCE and 57.8 mV, respectively. The concentration of each complex was determined by the potentiostatic or the polarographic method.

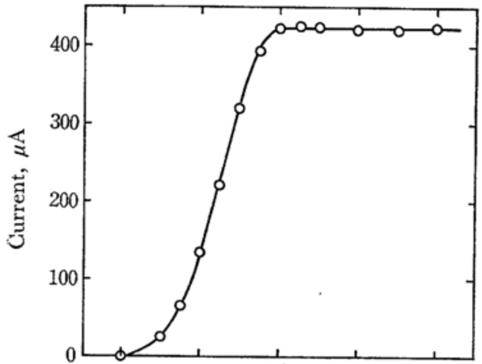

Fig. 1. Current-potential relations for the reduction of 2 mM Cr(III)-EDTA which were obtained by the potentiostatic method in the solutions containing 0.1 M acetate buffer and 0.4 M NaCl (pH 5.0) at 25°C. Surface area of the electrode is 0.0346 cm². The currents were measured at 0.5 msec after the beginning of electrolysis.

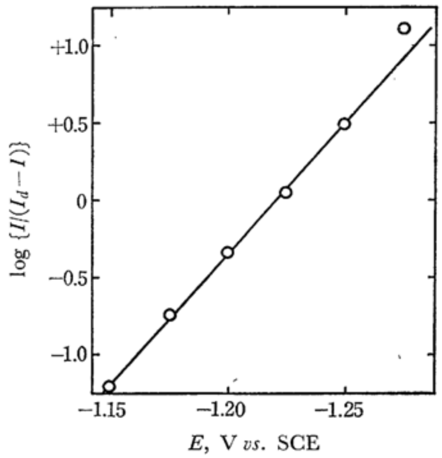

Fig. 2. Log-plots for the reduction of 2 mM Cr(III)-EDTA which were obtained by the potentiostatic method in the solutions containing 0.1 M acetate buffer and 0.4 M NaCl (pH 5.0) at 25°C. The currents were measured at 0.5 msec after the beginning of electrolysis.

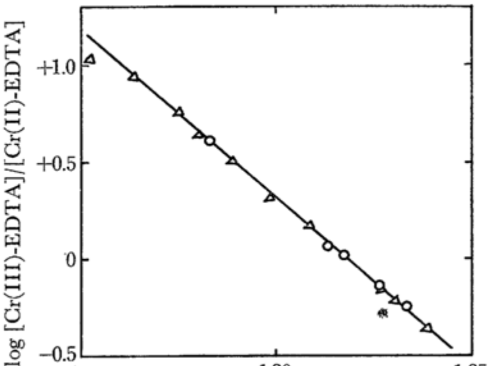

Fig. 3. Reaction of log [Cr(III)-EDTA]/[Cr(II)-EDTA] in Eq. (1) *vs.* equilibrium potential E_e which was obtained in the solutions containing 0.1 M acetate buffer and 0.4 M NaCl (pH 5.0) at 25°C. The concentration of each complex was determined by the potentiostatic method (indicated with ○) or by the polarographic method (indicated with △). In the case of polarographic measurement, the solution contains 2×10^{-6} M LEO as a maximum suppressor.

---

5) G. Schwarzenbach, R. Gut and G. Anderegg, *Helv. Chim. Acta,* **37**, 937 (1954).

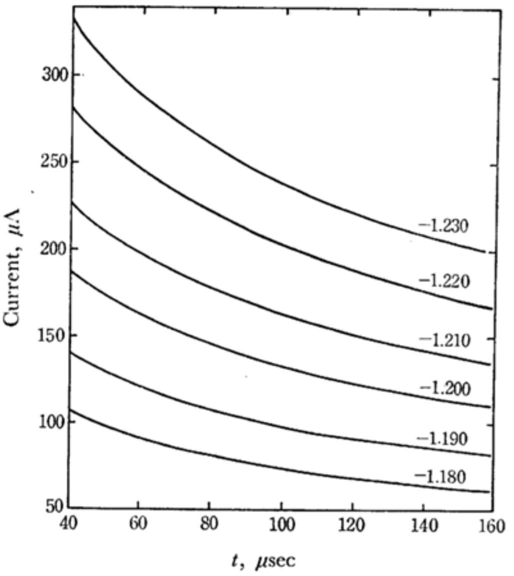

Fig. 4. Current-time relations for the reduction of 1 mM Cr(III)-EDTA which were obtained by the potentiostatic method in the solutions containing 0.1 M acetate buffer and 0.4 M NaCl (pH 5.0) at 25°C. Surface area of the electrode is $0.0346\ \text{cm}^2$. The figure on each curve indicates the controlled electrode potential (V *vs.* SCE).

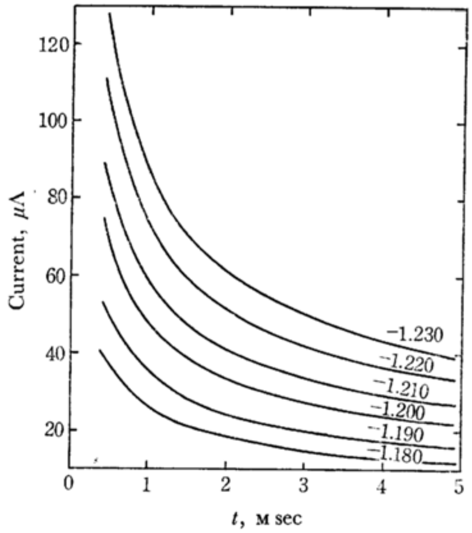

Fig. 5. Current-time relations for the reduction of 1 mM Cr(III)-EDTA which were obtained by the potentiostatic method in the solutions containing 0.1 M acetate buffer and 0.4 M NaCl (pH 5.0) at 25°C. Surface area of the electrode is $0.0346\ \text{cm}^2$. The figure on each curve indicates the controlled electrode potential (V *vs.* SCE).

Examples of current-time curves obtained at various electrode potentials are given in Figs. 4 and 5. Charging currents were immediately decreased to zero within 30 to 40 μsec.

If only the oxidant O is present initially in the solution and the reductant R is generated *in situ*, the relation between current and time on the potentiostatic method can be represented by the equations,[2)]

$$I\sqrt{t}/I_\tau\sqrt{\tau}=\sqrt{\pi}\lambda_{ms}\sqrt{t}\exp(\lambda^2{}_{ms}\sqrt{t})\operatorname{erfc}(\lambda_{ms}\sqrt{t}) \qquad (\tau\gg t) \qquad (2)$$

$$(k_c)_{ms}=I_\tau\sqrt{\pi}\lambda_{ms}\sqrt{\tau}/n\boldsymbol{F}C_0{}^\circ \qquad (3)$$

$$(k_a)_{ms}=\lambda_{ms}\sqrt{D_\mathrm{R}}-\sqrt{D_\mathrm{R}/D_\mathrm{O}}\ (k_c)_{ms} \qquad (4)$$

In Eqs. (2) to (4), I means the current density at time t, τ the sufficiently long time (*e.g.*, $\lambda_{ms}\sqrt{\tau}>5$), I_τ the current density at time τ, D the diffusion coefficient, and $(k_a)_{ms}$ and $(k_c)_{ms}$ are the measured anodic and the measured cathodic rate constant at a given potential.

Since the left-hand side of Eq. (2) and t are measurable, the values of λ_{ms} at various potentials can be determined. With these λ_{ms} values the rate constant $(k_c)_{ms}$ and $(k_a)_{ms}$ are determined provided the diffusion coefficients are known. The current-time relations shown in Figs. 4 and 5 were analyzed by means of these equations for the potentiostatic method with the results given in Table 1. The diffusion coefficients were calculated from the measurements of limiting current density following the application of potential step. They are $6.3\times10^{-6}\ \text{cm}^2\ \text{sec}^{-1}$ for Cr(III)-EDTA and $5.6\times10^{-6}\ \text{cm}^2\ \text{sec}^{-1}$ for Cr(II)-EDTA.

TABLE 1. KINETIC PARAMETERS OF THE ELECTRODE REACTION OF Cr(III)-EDTA/Cr(II)-EDTA IN 0.1 M ACETATE BUFFER+0.4 M NaCl (pH 5.0) 25°C

E V *vs.* SCE	$(k_c)_{ms}$ cm sec^{-1}	$(k_a)_{ms}$ cm sec^{-1}	$(k_c)_{corr}$* cm sec^{-1}	$(k_a)_{corr}$* cm sec^{-1}
−1.180	0.085_2	0.37_8	0.098_8	0.43_8
−1.190	0.10_5	0.32_1	0.11_9	0.36_4
−1.200	0.13_7	0.27_4	0.15_3	0.30_5
−1.210	0.16_6	0.24_2	0.18_3	0.26_7
−1.220	0.20_8	0.20_5	0.22_6	0.22_3
−1.230	0.23_5	0.16_0	0.25_2	0.17_1

* Calculated with the assumption that no specific adsorption takes place and ϕ_0 is constant over the potential region under investigation.

Kinetic parameters of the electrode reaction are calculated from the relations,[*1,2)]

$$(k_c)_{ms}=(k_s)_{ms}\ \exp\left[-\frac{(\alpha_c)_{ms}n\boldsymbol{F}}{\boldsymbol{R}T}(E-(E_0)_{ms})\right] \qquad (5)$$

$$(k_a)_{ms}=(k_s)_{ms}\ \exp\left[+\frac{(\alpha_a)_{ms}n\boldsymbol{F}}{\boldsymbol{R}T}(E-(E_0)_{ms})\right] \qquad (6)$$

where $(k_s)_{ms}$ is the measured standard rate constant, $(E_0)_{ms}$ the measured standard potential, $(\alpha_c)_{ms}$

[*1] $(\alpha_c)_{ms}$ and $(\alpha_a)_{ms}$ are denoted as α_{ms} and β_{ms}, respectively, in Ref. 2.

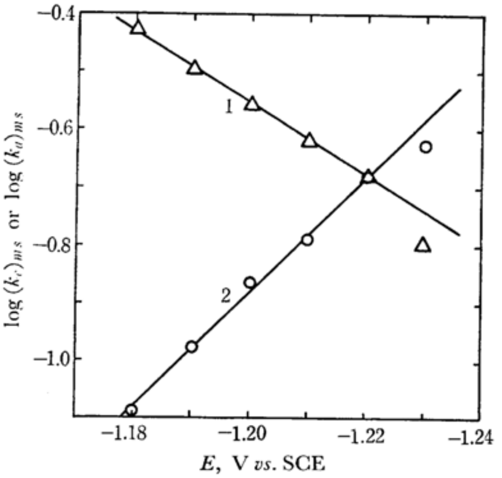

Fig. 6. Relations of (1) $\log (k_a)_{ms}$ *vs.* E and (2) $\log (k_c)_{ms}$ *vs.* E obtained with 1 mM Cr(III)-EDTA in the solutions containing 0.1 M acetate buffer and 0.4 M NaCl (pH 5.0) at 25°C

and $(\alpha_a)_{ms}$ are the measured cathodic and the measured anodic transfer coefficient, respectively, and $\boldsymbol{F}$, $\boldsymbol{R}$ and T have their usual meanings. The relation of $\log(k_a)_{ms}$ *vs.* E and that of $\log(k_c)_{ms}$ *vs.* E are shown in Fig. 6. Using the values given in Table 1 the following kinetic parameters were obtained:

$$(E_0)_{ms} = -1.220 \text{ V } vs. \text{ SCE}$$
$$(k_s)_{ms} = 2.1\times 10^{-1} \text{ cm sec}^{-1}$$
$$(\alpha_c)_{ms} = 0.58, \quad (\alpha_a)_{ms} = 0.39$$

Discussion

Since the measured rate constants $(k_c)_{ms}$ and $(k_a)_{ms}$, which were determined by the above-mentioned method, involve the influence of the electrical double layer, the correction for the effect of the double layer is necessary. The Levich and the Frumkin correction²⁾ were made on the assumption that no specific adsorption took place and that the value of ϕ_0 was constant in the potential region under investigation:*2

$$(k_c)_{corr} = (k_c)_{ms}\left[1-\frac{\zeta_{\mathrm{O}}}{\kappa D_{\mathrm{O}}}(k_c)_{ms}-\frac{\zeta_{\mathrm{R}}}{\kappa D_{\mathrm{R}}}(k_a)_{ms}\right]^{-1} \quad (7)$$

$$(k_a)_{corr} = (k_a)_{ms}\left[1-\frac{\zeta_{\mathrm{O}}}{\kappa D_{\mathrm{O}}}(k_c)_{ms}-\frac{\zeta_{\mathrm{R}}}{\kappa D_{\mathrm{R}}}(k_a)_{ms}\right]^{-1} \quad (8)$$

with

$$\zeta_j = \frac{\exp\,[(|z_j|-|z|/2)\boldsymbol{F}\phi_0/\boldsymbol{R}T]-1}{+|z_j/z|-1/2} \quad (9)$$

$$1/\kappa = \sqrt{\boldsymbol{R}T\varepsilon/8\pi z^2\boldsymbol{F}^2C_t} \quad (10)$$

where z_j is the ionic charge of the jth species, z the charge of the symmetrical indifferent electrolyte, ϕ_0 the difference of potential across the diffuse double layer from the plane of closest approach to the bulk of solution, ε the dielectric constant, C_t the total concentration of a z-z indifferent electrolyte.

Corrected kinetic parameters are determined by the relation,*3,2)

$$(k_c)_{corr} = (k_s)_{corr}\ \exp\left[-\frac{(\alpha_c)_{corr}n\boldsymbol{F}}{\boldsymbol{R}T}(E-(E_0)_{corr})\right] \quad (11)$$

$$(k_a)_{corr} = (k_s)_{corr}\ \exp\left[+\frac{(\alpha_a)_{corr}n\boldsymbol{F}}{\boldsymbol{R}T}(E-(E_0)_{corr})\right] \quad (12)$$

$$(k_s)_{corr} \fallingdotseq (k_s)^c_{corr}\ \exp[((\alpha_c)_{corr}n-z_{\mathrm{O}})\boldsymbol{F}\phi_0)/\boldsymbol{R}T] \quad (13)$$

where $(k_s)_{corr}$ is the corrected rate constant at $E=(E_0)_{corr}$ and $(k_s)^c_{corr}$ is the corrected standard rate constant expressed in terms of concentration for the cathodic process.

In order to estimate the potential ϕ_0, the differential capacity and the electrocapillary curve of the supporting electrolyte were measured by the conventional method. The equipment for these measurements was previously described.⁶⁾ The value of ϕ_0 was calculated to be −0.073 V at −1.220 V *vs.* SCE by the Gouy-Chapman theory.⁷⁾

The rate constants at various potentials which were determined by this procedure are also given in Table 1. The corrected kinetic parameters were as follows:

$$(E_0)_{corr} = -1.220 \text{ V } vs. \text{ SCE}$$
$$(k_s)_{corr} = 2.2\times 10^{-1} \text{ cm sec}^{-1}$$
$$(\alpha_c)_{corr} = 0.54$$
$$(\alpha_a)_{corr} = 0.43$$
$$(k_s)^c_{corr} = 1._7\times 10 \text{ cm sec}^{-1}$$

The standard potential $(E_0)_{corr}$ was found to be the same, within the experimental error, with $(E_0)_{eq}$ which was obtained by the measurement of the equilibrium potential.

The authors are grateful to Dr. Reita Tamamushi, the Institute of Physical and Chemical Research, for his valuable suggestion on this study. They also thank the Ministry of Education for the financial support granted for this research.

[*2] $(k_c)_{corr}$ and $(k_a)_{corr}$ are denoted as $(k_c)_{app}$ and $(k_a)_{app}$, respectively, in Ref. 2.

[*3] $(k_s)_{corr}$, $(k_s)^c_{corr}$, $(E_0)_{corr}$, $(\alpha_c)_{corr}$ and $(\alpha_a)_{corr}$ are denoted as $(k_s)_{app}$, $(k_s)^c_{app}$, $(E_0)_{app}$, α_{app} and β_{app}, respectively, in Ref. 2.

---

6) R. Tamamushi and N. Tanaka, *Z. physik. Chem., Neue Folge*, **28**, 158 (1961).

7) M. Breiter, M. Kleinerman and P. Delahay, *J. Am. Chem. Soc.*, **80**, 51 (1958).