BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 3487—3490 (1969)

Hydrodynamic Voltammetry with the Convection Electrode. III. The Measurements of the Kinetic Parameters of the Electrode Reaction. Part I

Junsuke SUZUKI

Faculty of Education, Shizuoka University, Oiwa, Shizuoka

(Received June 11, 1969)

We have proposed the determination of the kinetic parameters of the electrode reaction by means of convective voltammetry. At the pushed-out mercury-drop convection electrode (PM-DCE), the ratio of the current on a totally-irreversible wave to the limiting current was derived as follows:

$$\frac{i}{i_l}=\frac{1.64\,k_{\mathrm{R}}D_{\mathrm{O}}{}^{-2/3}v^{-1/2}\nu^{1/6}d^{1/2}}{1+1.64\,k_{\mathrm{R}}D_{\mathrm{O}}{}^{-2/3}v^{-1/2}\nu^{1/6}d^{1/2}}$$

This equation was applied to the determination of the kinetic parameters for the electro-reduction of cupric ions in a 0.1 M perchloric acid solution containing 0.05% Triton X-100. It was found that the values of αn and k° the kinetic parameters are 0.59 and 4.2×10^{-9} cm/sec respectively.

In our previous papers,[1,2] the convection electrode system developed by the present authors was applied to the microdetermination of electroactive substances. The results showed that it had a high sensitivity and a good reproducibility. At the convection electrode in the laminar flow, the limiting current, i_l, was found to be given by:[3,4]

$$i_l=0.61n\boldsymbol{F}ACD^{2/3}v^{1/2}\nu^{-1/6}d^{-1/2}$$

where n is the number of electrons involved in the electrode reaction; $\boldsymbol{F}$, the Faraday constant; A, the area of the electrode surface; C, the bulk concentration of electroactive substances; D, the diffusion coefficient of an electroactive substance; v, the tangential velocity of the rotating disk; ν, the kinematic viscosity of the solution, and d, the diameter of the convection electrode (the working part plus the non-working shield). The rate of mass transfer at the convection electrode can be controlled by changing the tangential velocity of the rotating disk.

In the present paper, the use of the convection electrode for the study of the kinetics of the electrode reactions will be investigated and the rate constant

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[1] J. Suzuki and T. Ozaki, This Bulletin, **37**, 230, 789 (1964).

[2] T. Ozaki, J. Suzuki, and F. Mori, *Bunseki Kagaku (Japan Analyst)*, **13**, 889 (1964).

[3] J. Suzuki, *Rev. Polarography*, **15**, 21 (1968).

[4] J. Suzuki, *ibid.*, **16**, 69 (1969).

for the electro-reduction of cupric ions in 0.1 M perchloric acid containing 0.05% Triton X-100 will be determined by analyzing the current-voltage curve.

Theoretical

In the quantitative treatment of the electrode reaction, it is necessary to consider the rates of both the mass and the electron transfer. For the reduction of an oxidized species, *Ox*, to a reduced species, *Red*, when both of the species are soluble, the simplest electrode reaction can be presented in the form of:

$$Ox + n\,e = Red \tag{1}$$

where n is the number of the electron.

The net electron transfer may be given by the difference between the rates of a forward (reduction) process and a backward(oxidation) one. The corresponding rates are expressed as follows, in accordance with the treatment of Kimball:[5]

$$\text{forward process:} \quad R_R = k_R \cdot a_O{}^\circ \tag{2}$$

$$\text{backward process:} \quad R_O = k_O \cdot a_R{}^\circ \tag{3}$$

where k_R and k_O denote the rate constants of the first order. Therefore, the net electron transfer is given as follows:

$$\begin{aligned} R = R_R - R_O &= k_R a_O{}^\circ - k_R a_R{}^\circ \\ &= k_R f_O C_O{}^\circ - k_O f_R C_R{}^\circ \end{aligned} \tag{4}$$

where a° and C° denote the activities and concentrations at the electrode surface respectively; f, the activity coefficient, and the subscripts, O and R, the oxidized and reduced forms of the electroactive species.

The rate constants of k_R and k_O can be defined as:

$$k_R = k^\circ \exp\left[-\alpha(E-E^\circ)n\boldsymbol{F}/\boldsymbol{R}T\right] \tag{5}$$

$$k_O = k^\circ \exp\left[(1-\alpha)(E-E^\circ)n\boldsymbol{F}/\boldsymbol{R}T\right] \tag{6}$$

Here, k° is the specific rate constant at the standard potential, E°, where k_R, k_O, and k° equal each other; α, the transfer coefficient, and $\boldsymbol{F}$, $\boldsymbol{R}$, and T, the usual thermodynamic signature.

By combining Eqs. (4), (5), and (6), the net current at the potential, E, is given as follows:

$$\begin{aligned} \frac{i}{n\boldsymbol{F}A} &= k^\circ \exp\left[\alpha(E^\circ-E)n\boldsymbol{F}/\boldsymbol{R}T\right] f_O \cdot C_O{}^\circ \\ &\quad - k^\circ \exp\left[(1-\alpha)(E-E^\circ)n\boldsymbol{F}/\boldsymbol{R}T\right] f_R \cdot C_R{}^\circ \end{aligned} \tag{7}$$

where i is the net current at the electrode surface of A cm^2.

On the other hand, the rate of mass transfer, that is, the flux at the electrode surface, depends upon the mechanism of mass transfer, diffusion, forced convection, *etc.*

The rate of mass transfer is in proportion to the difference between the bulk concentration of electroactive substances and their concentration at the electrode surface. Therefore, the rate of mass transfer is given by:

$$\text{for oxidized species:} \quad j_O = m_O(C_O - C_O{}^\circ) \tag{8}$$

$$\text{for reduced species:} \quad -j_R = m_R(C_R{}^\circ - C_R) \tag{9}$$

Here, m denotes the mass transfer coefficient, which was in a previous work[3] determined at the convection electrode as follows:

$$m = 0.61\, D^{2/3} v^{1/2} \nu^{-1/6} d^{-1/2} \tag{10}$$

Assuming a steady state, one has:

$$\frac{i}{n\boldsymbol{F}A} = j_O = -j_R = m_O(C_O - C_O{}^\circ) = m_R(C_R{}^\circ - C_R) \tag{11}$$

From Eqs. (7) and (11), the following equation is obtained:

$$\frac{i}{n\boldsymbol{F}A} = \frac{\left(\begin{array}{c} m_O(f_O C_O \exp\left[\alpha(E^\circ-E)n\boldsymbol{F}/\boldsymbol{R}T\right] \\ -f_R C_R \exp\left[(1-\alpha)(E-E^\circ)n\boldsymbol{F}/\boldsymbol{R}T\right]) \end{array}\right)}{\left(\begin{array}{c} (m_O/k^\circ) + f_O \exp\left[\alpha(E^\circ-E)n\boldsymbol{F}/\boldsymbol{R}T\right] \\ +(m_O/m_R) f_R \exp\left[(1-\alpha)(E-E^\circ)n\boldsymbol{F}/\boldsymbol{R}T\right]) \end{array}\right)} \tag{12}$$

Under the initial condition of $C_R=0$, Eq. (12) becomes:

$$\begin{aligned} \frac{i_l - i}{i} &= \frac{m_O}{k^\circ f_O} \exp\left[\alpha(E-E^\circ)n\boldsymbol{F}/\boldsymbol{R}T\right] \\ &\quad + \frac{m_O f_R}{m_R f_O} \exp\left[(E-E^\circ)n\boldsymbol{F}/\boldsymbol{R}T\right] \end{aligned} \tag{13}$$

where i_l is the limiting current, which is equal to $n\boldsymbol{F}AC_O m_O$.

Equation (13) represents a current-voltage curve-equation for a stationary electrode-moving solution system.

In Eqs. (12) and (13) m_O/k° was defined as the "irreversibility index" (IRI) by Jordan and Javick.[6] The character of the current-voltage curve depends upon the IRI value; that is, the current-voltage curve varies from reversible to irreversible with an increase in the IRI value, as is shown below.

a) $\boldsymbol{m_O/k^\circ \ll 1}$. In Eq. (13), the first term on the right hand side can be neglected; it is clear that the current-voltage curve has a reversible character, that is,

$$E = E^\circ - \frac{\boldsymbol{R}T}{n\boldsymbol{F}} \ln\left(\frac{D_O}{D_R}\right)^{2/3} \cdot \frac{f_R}{f_O} - \frac{\boldsymbol{R}T}{n\boldsymbol{F}} \ln \frac{i}{i_l - i} \tag{14}$$

$$E_{1/2}{}^r = E^\circ - \frac{\boldsymbol{R}T}{n\boldsymbol{F}} \ln\left(\frac{D_O}{D_R}\right)^{2/3} \cdot \frac{f_R}{f_O} \tag{15}$$

where $E_{1/2}{}^r$ is the reversible half-wave potential.

b) $\boldsymbol{m_O/k^\circ \approx 1}$. In this case, the current-voltage curve obeys Eq. (13).

c) $\boldsymbol{m_O/k^\circ \gg 1}$. In Eq. (13), the last term on the right hand side can be neglected; that is, the current-voltage curve has an irreversible character.

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5) G. E. Kimball, *J. Chem. Phys.*, **8**, 199 (1940).

6) J. Jordan and R. A. Javick, *Electrochimica Acta*, **6**, 23 (1962).

$$E = E^\circ + \frac{\boldsymbol{RT}}{\alpha n\boldsymbol{F}} \ln \frac{1.64k^\circ \nu^{1/6}}{D_O{}^{2/3}} + \frac{\boldsymbol{RT}}{\alpha n\boldsymbol{F}} \ln \left(\frac{d}{v}\right)^{1/2} - \frac{\boldsymbol{RT}}{\alpha n\boldsymbol{F}} \ln \frac{i}{i_l - i} \tag{16}$$

Equation (16) is rearranged in the following manner:

$$\frac{i}{i_l} = \frac{1.64k_R D_O{}^{-2/3} v^{-1/2} \nu^{1/6} d^{1/2}}{1 + 1.64k_R D_O{}^{-2/3} v^{-1/2} \nu^{1/6} d^{1/2}} \tag{17}$$

This is analogous to the equations for an irreversible wave derived by Koutecky[7] and by Okinaka and Kolthoff.[8] Equation (17), also, allows us to calculate the values of k_R from the measurement of the i/i_l ratio at various potentials on the current-voltage curve obtained with the convection electrode, and a plot of the calculated log k_R *vs.* the potential may yield a straight line. The values of α and k° can be determined from the slope of this line and from its intercept at the potential of E° respectively.

Experimental

Materials. All the chemicals were of a chemical pure grade and were used without further purification. A solution of cupric ions was prepared by dissolving copper perchlorate in redistilled water, and the copper content was determined by titrating with a standard EDTA solution. A stock solution of Triton X-100 was prepared by dissolution in redistilled water.

Electrodes. The electrode system, a pushed-out mercury-drop convection electrode (PMDCE), used in the present investigation was almost the same as has been described in previous papers[9,10] with the exception of the orientation of the working surface against the liquid flow (Fig. 1). A saturated calomel electrode was used as the reference electrode.

Measurements. A current-voltage curve was recorded by using a Yanagimoto Polarograph, Model PA 102. All the solutions were kept at 25±0.1°C.

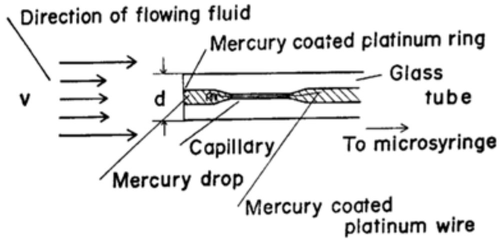

Fig. 1. Pushed-out mercury-drop convection electrode assembly.

Results and Discussion

Reduction of the Copper(II) Ion in Perchloric Acid Containing Triton X-100. The logarithmic plot of an irreversible wave yields either a straight line or a curve. When the rate of the electrode reaction was not slow enough to increase the over-voltage more than about 0.12/*n* V[11] (*n*, the number of electrons involved in the rate-determining step), the logarithmic plot shows a curve because the backward reaction can not be neglected. Such a wave is "quasi-reversible" and it is to be distinguished from a "totally irreversible wave," which has an over-voltage greater than 0.12/*n* V. In this case, the logarithmic plot yields a straight line. In a recent investigation,[12] the reduction wave of copper(II) ion in 0.1M perchloric acid was found to be quasi-reversible, because the logarithmic plot showed a curve.

The reduction of the cupric ion in a perchloric acid solution gives a one-step wave, but in a solution containing Triton X-100, a non-ionic surface-active substance, it shows two step-waves. The first step-wave has a kinetic character and is very small in comparison with the second step-wave. Kolthoff *et al.*[12] have shown that the kinetic current of this case is caused by the penetration of the copper(II) ion through the adsorbed film of Triton X-100. However, in a perchloric acid solution containing 0.05% Triton X-100 the penetration is negligibly small. This can be attributed to the extremely slow penetration of the cupric ion through the adsorbed film, because the film exhibits a very compact nature. Consequently, the reduction wave of the cupric ion in perchloric acid is slightly irreversible, *i.e.*, quasi-reversible, in the absence of Triton X-100, but in the presence of 0.05% Triton X-100 it becomes completely irreversible. That is, the second step-wave is "totally irreversible," and its half-wave potential at the ordinary DME is shifted about 0.5 V in the negative direction compared with the case of the absence of Triton X-100.[11]

The Determination of the Kinetic Parameters for the Second Step-wave. The observed waves were analyzed by applying Eq. (17); the results are shown in Fig. 2. It can be seen from the figure that the plot of log k_R *vs.* E yields a perfectly straight line. From the intercept of this line and its slope, the values of the rate constant, k°, at the standard potential of the copper(II)-copper amalgam and of αn were determined at four different tangential velocities of the rotating disk; the results are summarized in Table 1. As is shown in the table, the values of k° and αn are almost constant. They agree with the results obtained at the ordinary DME[12] by applying Koutecky's

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[7] J. Kouteckey, *Coll. Czech. Chem. Commun.*, **18**, 597 (1953).

[8] Y. Okinaka and I. M. Kolthoff, *J. Am. Chem. Soc.*, **82**, 324 (1960).

[9] J. Suzuki, This Bulletin, **39**, 1898 (1966).

[10] J. Suzuki, *ibid.*, **40**, 101(1967).

[11] P. Delahay, *J. Am. Chem. Soc.*, **75**, 1430 (1953).

[12] I. M. Kolthoff and Y. Okinaka, *ibid.*, **81**, 2296 (1959).

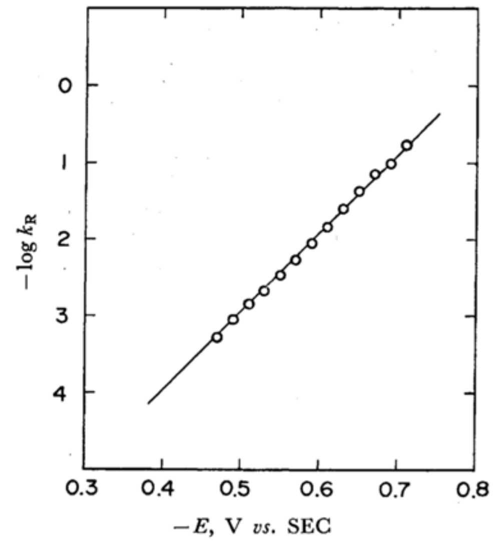

Fig. 2. The plots of $\log k_R$ vs. applied potential for the reduction of cupric ion in 0.1 M perchloric acid containing 0.05% Triton X-100; the tangential velocity of the rotating disk, 157.0 cm/sec.

TABLE 1. THE VALUES OF THE KINETIC PARAMETERS FOR THE ELECTRO-REDUCTION OF CUPRIC IONS IN 0.1 M PERCHLORIC ACID CONTAINING 0.05% TRITON X-100 (at 25°C)

v, cm/sec	αn	k°, 10^{-9} cm/sec
94.2	0.59	4.0
125.6	0.59	3.8
157.0	0.59	4.7
188.4	0.59	4.2
Average	0.59	4.2
Standard deviation (%)	—	6.6

equation[7] and at the other electrode.[8]

The Difference in the Half-wave Potential at the DME and at the PMDCE. From Eq. (16), the half-wave potential, $(E_{1/2})_p$, at the PMDCE is given by:

$$(E_{1/2})_p = E^\circ + \frac{\boldsymbol{RT}}{\alpha n \boldsymbol{F}} \ln \frac{1.64 k^\circ \nu^{1/6}}{D_O{}^{1/2}} + \frac{\boldsymbol{RT}}{\alpha n \boldsymbol{F}} \ln \left(\frac{d}{v}\right)^{1/2} \tag{18}$$

Equation (18) shows that the half-wave potential shifts gradually in the negative direction with an increase in the tangential velocity of the rotating disk. That is, the plots of the half-wave potential vs. the logarithmic value of the tangential velocity yield a straight line; the slope of this line is given as:

$$-\frac{\Delta(E_{1/2})_p}{\Delta \log v} = \frac{29.5}{\alpha n}\ (\text{mV}) \tag{19}$$

On the other hand, the half-wave potential at the DME is given as follows:[7,11,13]

$$(E_{1/2})_\text{D} = E^\circ + \frac{\boldsymbol{RT}}{\alpha n \boldsymbol{F}} \ln \frac{0.87 k^\circ}{D_O{}^{1/2}} + \frac{\boldsymbol{RT}}{\alpha n \boldsymbol{F}} \ln t^{1/2} \tag{20}$$

The half-wave potential at the DME varies with the drop time, t.

From Eqs. (18) and (20), the difference between the half-wave potentials at the DME and at the PMDCE is given by:

$$\begin{aligned}\Delta E_{1/2} &= (E_{1/2})_\text{D} - (E_{1/2})_p \\ &= \frac{\boldsymbol{RT}}{\alpha n \boldsymbol{F}} \ln 0.53 \left(\frac{D_O}{\nu}\right)^{1/6} \cdot \left(\frac{v \cdot t}{d}\right)^{1/2}\end{aligned} \tag{21}$$

Table 2 shows the slope of the plots of the half-wave potential vs. the logarithmic value of the tangential velocity in the range from 94.2 to 188.4 cm/sec, and also the difference between the half-wave potential at the DME and at the PMDCE.

TABLE 2. DIFFERENCE IN THE HALF-WAVE POTENTIAL AT DME AND AT PMDCE, AND THE SLOPE OF THE PLOTS OF THE HALF-WAVE POTENTIAL vs. THE TANGENTIAL VELOCITY OF THE ROTATING DISK

v, cm/sec	Difference $\Delta E_{1/2}$, mV		Slope $-\frac{\Delta(E_{1/2})_p}{\Delta \log v}$, mV	
	Obsd	Calcd	Obsd	Calcd
94.2	61	69	>57	>57
188.4	86	84		

Drop time of DME: 3.0 sec at −0.80 V vs. SCE in 0.1 M $HClO_4$+0.05% Triton X-100.

It can be seen from the table that the experimental values of the slope and of the difference in the half-wave potential are in good agreement with the values calculated from Eqs. (19) and (21) respectively.

The author wishes to express his thanks to Professors Nobuyuki Tanaka of Tohoku University and Tokuro Ozaki of Shizuoka University for their helpful discussion, and to Miss Yoko Komiya for her earnest assistance.

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[13] P. Kivalo, K. B. Oldham and H. A. Laitinen, *J. Am. Chem. Soc.* **75**, 4148 (1953).