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Hydrodynamic Voltammetry with the Convection Electrode. IV. The Measurements of the Kinetic Parameters of the Electrode Reaction. Part II

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The convection electrode system was applied to the determination of the kinetic parameters of the electrode reaction. By analyzing the observed current-voltage curve, the parameters of α and k° were calculated; for the ferric-ferrous system in 0.1M perchloric acid, α and k° were found to be 0.63 and 7.6×10^{-3} cm/sec respectively, while for the hexammine cobaltic-cobaltous system in 1M ammonia-ammonium chloride, they were 0.65 and 4.5×10^{-6} cm/sec respectively.

In the preceding paper[1] the convection electrode system with the rotating disk as a stirrer was applied to the measurement of the rate constant of the electrode reaction. The results were in good agreement with the published data.[2]

In investigating the kinetics of the electrode reaction using the voltammetry, the rate of mass transfer should be faster than that of electron transfer. At the present convection electrode the rate of mass transfer can be increased by increasing the tangential velocity of the rotating disk. That is, any reversible current-voltage curve can apparently be made irreversible due to such an increased mass transfer. Therefore, it is considered that the use of the convection electrode is very suitable for the determination of a moderately fast electron-transfer rate by voltammetry.

In the present investigation, the kinetic parameters for the Fe(III)-Fe(II) system in a 0.1M perchloric acid solution, and for the Co(III)-Co(II) system in an ammonia-ammonium chloride solution, will be measured, and good results will be obtained.

Experimental

Materials. All the chemicals used were of a chemically pure grade.

Electrodes and Apparatus. The electrode system and the apparatus were the same as had been described in a previous paper.[3] In the present investigation, the pretreatment of the platinum electrode was carried out as follows: the platinum electrode was oxidized anodically for 1 min at +1.5 V *vs.* SCE in 0.1M perchloric acid, and then 0 V *vs.* SCE was applied to it for 3 min in nitrogen-bubbled 0.1M perchloric acid.

Measurements. A Yanagimoto Polarograph, Model PA 102, was used for recording the current-voltage curve. A saturated calomel electrode was used as a reference electrode. An electrolytic solution was kept at 25±0.1°C.

Results and Discussion

The Upper Limit of the Tangential Velocity of the Rotating Disk. It would be possible to determine the rate parameters of a moderately rapid electron-transfer process by increasing the

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[1] J. Suzuki, This Bulletin, **42**, 3487 (1969).

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

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

mass transfer sufficiently, that is, by increasing the tangential velocity of the rotating disk. When the tangential velocity exceeds a certain value, however, the flow passing through the electrode changes from a laminar to a turbulent one. Since the relations derived in the previous paper[1] for the determination of the rate parameters can be applied only to the laminar flow, the tangential velocity of the rotating disk must be limited to the value below which the flow is kept laminar.

On the other hand, one can anticipate, from the value of dimentionless parameter, the Reynolds number (*Re*), whether or not the conditions of the flow passing over the electrode surface will be laminar. However, the critical *Re* value for the present convection electrode, the value at which the flow passing through the electrode changes from a laminar to a turbulent one, is not clear. Nevertheless, assuming that the condition of the flow passing over the convection electrode surface is similar to that of the flow passing through the rotating disk electrode,[4] the critical *Re* value at the convection electrode can be estimated to be of the order of 10^4.

Assuming a diameter of the convection electrode surface (working part plus shield) of 0.50 cm and the kinematic viscosity of an electrolytic solution of 10^{-2} cm^2/sec, the highest velocity for the laminar flow is found to be about 200 cm/sec; this corresponds to a tangential velocity of the rotating disk of about 500 cm/sec.

Upper Limit of the Rate Constant which can be determined. Under the initial condition of $C_R=0$, Eq. (12), which was derived in the preceding paper,[1] is transformed into this form:

$$i=\frac{i_l{}^c}{1+e^{\zeta}}\cdot\frac{\Lambda e^{-\alpha\zeta}(1+e^{\zeta})}{0.61+\Lambda e^{-\alpha\zeta}(1+e^{\zeta})} \tag{1}$$

where:

$$\zeta=\frac{nF}{RT}(E-E^r_{1/2}) \tag{2}$$

and:

$$\Lambda=k^\circ\left(\frac{f_O}{D_O{}^{2/3}}\right)^{1-\alpha}\left(\frac{f_R}{D_R{}^{2/3}}\right)^{\alpha}\left(\frac{v}{d}\right)^{-1/2}\nu^{1/6} \tag{3}$$

Here, $i_l{}^c$ is the cathodic limiting current; the other symbols have been identified in the preceding paper.[1]

Equation (1) is completely analogous to the general equation of the current-voltage curve, which was derived theoretically by Matsuda, for the reduction or oxidation process in polarography[5] and in voltammetry.[6]

According to the magnitude of k°, the characteristics of the current-voltage curve can be classified into three kinds:[1] (a) reversible, (b) quasi-reversible,[7] and (c) irreversible. The magnitude of k° corresponding to each of these cases can then be estimated, as is shown in Table 1.

TABLE 1. CHARACTERS OF THE CURRENT-VOLTAGE CURVE

Character	Magnitude of k°
Reversible	$>1.5\times10^{-2}(v/d)^{1/2}$
Quasi-reversible	$1.5\times10^{-2}(v/d)^{1/2}>k^\circ>1.3\times10^{-6}(v/d)^{1/2}$
Totally irreversible	$<1.3\times10^{-6}(v/d)^{1/2}$

Assuming $f_O=f_R=1$, $D_O=D_R=10^{-5}$ cm^2/sec, $\alpha=0.5$, and $\nu=10^{-2}$ cm^2/sec.

In order to determine the rate constant by analyzing the current-voltage curve, it is necessary in practice that the curve have a quasi-reversible or an irreversible character. Therefore, the upper limit of the rate constant, k°, which could be determined by the present hydrodynamic voltammetry is considered to be about 1.5×10^{-2} $(v/d)^{1/2}$ (*cf.* Table 1). On the other hand, the highest tangential velocity of the rotating disk, *v*, for the laminar flow is 500 cm/sec, as has been mentioned above. Consequently, the upper limit of the rate constant so determined can be estimated to be 0.47 cm/sec, when *d* is 0.50 cm.

Fe(III)-Fe(II) System in Perchloric Acid Media. It is well-known that the redox reaction of a ferric-ferrous system in a perchloric acid solution is a moderately fast one-electron transfer

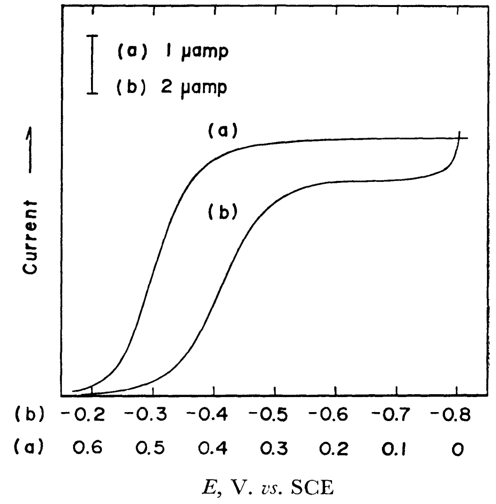

Fig. 1. The typical current-votage curves obtained by using the convection electrode.
(a) 3.72×10^{-4}M Fe^{3+} in 0.1M $HClO_4$
(b) 1×10^{-4}M $Co(NH_3)_6{}^{3+}$ in 1M NH_3+1M NH_4Cl

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[4] V. G. Levich, "Physicochemical Hydrodynamics," Prentice-Hall, Inc., Englewood Cliffs, N. J. (1962), p. 71.

[5] H. Matsuda and Y. Ayabe, This Bulletin, **28**, 422 (1955).

[6] H. Matsuda, *J. Electroanal. Chem.*, **15**, 109 (1967).

[7] P. Delahay, *J. Amer. Chem. Soc.*, **75**, 1430 (1953).

process.

The current-voltage curves for the reduction of a ferric ion in absence of a ferrous ion were recorded at the tangential velocities of the rotating disk ranging from 62.8 to 188.4 cm/sec. A typical current-voltage curve thus obtained is shown in Fig. 1.

The rate constant of electron transfer can be evaluated only when the observed current-voltage curve shows a sufficient deviation from a reversible character. Such deviation can be most easily checked by means of the following equation:8)

$$E_{3/4} - E_{1/4} = \frac{0.059}{n}\ \mathrm{V} \qquad (4)$$

where $E_{3/4}$ and $E_{1/4}$ are the potentials at the three-quarter and at the one-quarter limiting currents respectively. That is, if the current is controlled only by mass transfer, the difference between the potentials at $E_{3/4}$ and $E_{1/4}$ on the observed current-voltage curve equals $(0.059/n)$ V. In the present case, this difference was evaluated as 81 mV from Fig. 1 at the tangential velocity of the rotating disk of 188.4 cm/sec.

From the observed current-voltage curve at the tangential velocity of 188.4 cm/sec, a series of values of the rate constants, k_R, at the applied potential, E, were calculated by using Eq. (5), which was itself obtained by rearranging the Eq. (13) derived in the preceding paper.1) Then the plots of log k_R *vs.* $(E-E^\circ)$ were made for each current-voltage curve.

$$k_R = k^\circ \exp\left[\alpha(E^\circ - E)n\boldsymbol{F}/\boldsymbol{RT}\right]$$
$$= \frac{1}{\dfrac{i_l^c - i}{i}\cdot\dfrac{f_O}{m_O} - \dfrac{f_R}{m_R}\exp\left[(E-E^\circ)n\boldsymbol{F}/\boldsymbol{RT}\right]} \qquad (5)$$

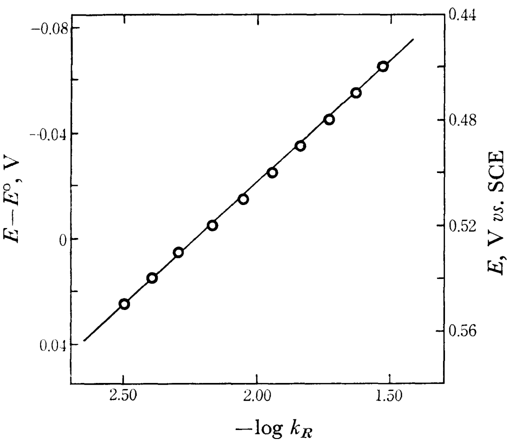

Fig. 2. The plots of log k_R *vs.* E.
Concentration of Fe^{3+}: 3.72×10^{-4}M in 0.1M $HClO_4$
Tangential velocity of rotating disk: 188.4 cm/sec

where m is the mass transfer coefficient.3,9,10) A typical plot is shown in Fig. 2.

As was predicted by Eq. (5), a linear relation between log k_R and $(E-E^\circ)$ was obtained. Therefore, the slope of this line equals 2.303 $\boldsymbol{RT}/\alpha n$ and the intercept at $E=E^\circ$ equals (2.303 $\boldsymbol{RT}/\alpha n$) log k°. The rate parameters obtained are given in Table 2.

Table 2. Kinetic parameters for Fe(III)-Fe(II) system in 0.1M perchloric acid

k°, cm/sec	α	Ref.
$(7.6\pm1.5)\times10^{-3}$	0.63 ± 0.02	this work
$(1.1\pm0.2)\times10^{-2}$	0.78 ± 0.04	10)
5.3×10^{-3}	—	11)*

* In 1.0M perchloric acid.

The value of k° obtained is considered to be reliable on the basis of a comparison with the results of Jordan and Javick,10) and of Randles and Somerton.11)

Co(III)-Co(II) System in Ammonium Buffer Media. It is well-known that ammine complexes of cobalt(III) are inert, and those of cobalt(II), labile. The heterogeneous electroreduction of hexammine cobaltic salts has already been investigated in detail by several workers.12–15) The results showed that the character of the electrode reaction of cobaltic to cobaltous species is a totally irreversible process, followed by a chemical reaction. This mechanism may be shown as follows:

$$Co(NH_3)_6^{3+} + e \xrightarrow{\text{irrev.}} Co(NH_3)_6^{2+} \qquad (6)$$

$$Co(NH_3)_6^{2+} \overset{\text{fast}}{\rightleftharpoons} \sum_{n=0}^{6} Co(NH_3)_{6-n}^{2+} \qquad (7)$$

The proportions of the complexes with various n values in Reaction (7) depend upon the concentration of free ammonia in the supporting electrolyte solution.

Because the electron transfer step of Reaction (6) is totally irreversible,14,16,17) the succeeding

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8) Z. Galus and R. N. Adams, *J. Phys. Chem.*, **67**, 866 (1963).

9) J. Jordan, *Anal. Chem.*, **27**, 1708 (1955).

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

11) J. E. B. Randles and K. W. Somerton, *Trans. Faraday Soc.*, **48**, 937 (1952).

12) J. B. Willis, J. A. Friend and D. P. Mellor, *J. Amer. Chem. Soc.*, **67**, 1680 (1945).

13) H. A. Laitinen, J. C. Bailar, H. F. Holtzclan and J. V. Quagliano, *ibid.*, **70**, 2999 (1948).

14) H. A. Laitinen and P. Kivalo, *ibid.*, **75**, 2198 (1953).

15) N. Maki, Y. Shimura and R. Tsuchida, This Bulletin, **32**, 23 (1959).

16) A. A. Vlcek, "Proceedings of the Sixth International Conference on Coordination Chemistry," Macmillan, New York (1961), pp. 509—603.

17) L. N. Klatt and W. J. Blaedel, *Anal. Chem.*, **39**, 1065 (1967).

chemical reaction of Reaction (7) has no effect upon the reduction step of hexammine coblat(III) ions. Therefore, the rate constant for the heterogeneous electrode reaction of hexammine cobalt(III) can be evaluated using the same equation as that used for an ordinary totally irreversible process.[1]

The kinetics of the electrode reaction of the hexammine cobalt(III) ion in 1 M ammonia-ammonium chloride was investigated by using a convection electrode. A typical current-voltage curve for the reduction of hexammine cobalt(III) is shown in Fig. 1.

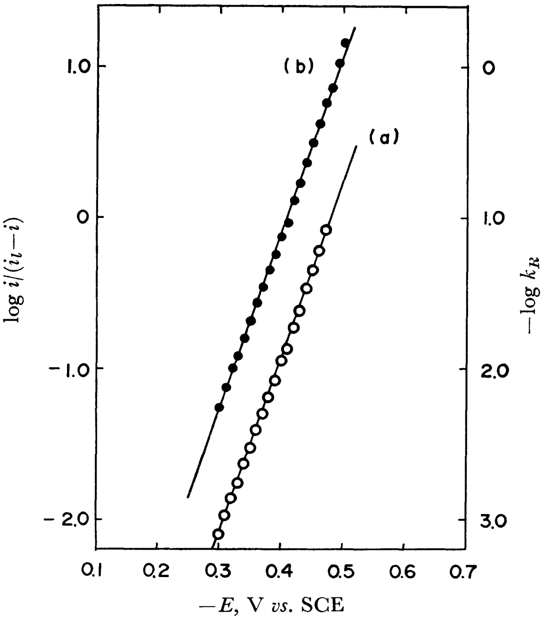

Fig. 3. The polts of $\log k_R$ *vs.* E and of $\log i/(i_l-i)$ *vs.* E.
(a) Plots of $\log k_R$ *vs.* E, (b) Plots of $\log i/(i_l-i)$ *vs.* E. Concentration of $Co(NH_3)_6^{3+}$: 1×10^{-4} M in 1 M NH_3+1 M NH_4Cl. Tangential velocity of the rotating disk: 188.4 cm/sec

The values of the rate constant, k_R, can be calculated from the i/i_l ratio at various potentials on the current-voltage curve. Figure 3 shows the plots of $\log k_R$ *vs.* E and of $\log i/(i_l-i)$ *vs.* E; both plots give straight lines. The kinetic parameters, α and k°, can be estimated from Fig. 3.

The former was calculated from the slope of line (a) or line (b), and the latter, from the intercept at the standard potential, E°, to line (b). The standard potentials of the hexammine cobaltic-cobaltous couple were calculated from Latimer's data[18] as −0.100 V *vs.* SCE. They are summarized in Table 3.

Table 3. Kinetic parameters for $Co(NH_3)_6Cl_3$ system in 1 M NH_3+1 M NH_4Cl

Tangential velocity v, cm/sec	α	k° $\times10^{-6}$ cm/sec
94.2	0.67±0.01	5.0±0.4
125.6	0.65±0.02	5.5±0.8
157.0	0.64±0.02	3.5±0.5
188.4	0.65±0.02	4.1±0.2
Average	0.65	4.5

The values of the kinetic parameters obtained at the convection electrode are in good agreement with those in a previously-published paper,[17] in which the parameters of α and k° are 0.61 and 6×10^{-6} cm/sec respectively in 1 F ammonia-ammonium chloride; these values were obtained by using the tubular platinum electrode.

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[18] W. M. Latimer, "Oxidation Potential" 2nd Ed., Prentice-Hall, New York (1952), p. 214.