[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Characteristics of Irreversible Waves and Kinetic Currents at the Rotated Dropping Mercury Electrode[1]

BY Y. OKINAKA AND I. M. KOLTHOFF

RECEIVED JULY 22, 1959

Comparison is made of characteristics of irreversible waves and kinetic currents at the conventional (d.m.e.) and the rotated dropping mercury electrode (r.d.m.e.). The half-wave potential of totally irreversible waves is considerably more negative at the r.d.m.e. than at the d.m.e. On the basis of the diffusion layer concept an expression is derived to account for the difference. An approximate expression is derived to evaluate kinetic parameters of a totally irreversible electrode reaction from the current–potential curve obtained at the r.d.m.e. The derived expressions are verified for the reduction of nickel ions in a sodium perchlorate solution containing polyacrylamide and for the reduction of copper ions in a perchloric acid solution containing Triton X-100. Because of the greater rate of mass transfer at the r.d.m.e. a species yielding a wave at the d.m.e. which has the characteristics of a reversible reaction, may give an irreversible wave at the r.d.m.e. This is illustrated by results obtained with a mixture of vanadic and vanadous ions in dilute sulfuric acid and with cupric ions in a sodium perchlorate solution. The expression for the kinetic current at the r.d.m.e. derived on the basis of the reaction layer concept is the same as that at the d.m.e. Experimental results obtained with glucose and pyruvic acid show that the thickness of the reaction layer is the same at the two electrodes and independent of the speed of rotation of the electrode.

In previous communications characteristics of the mass transfer controlled limiting current at the r.d.m.e. were discussed extensively in comparison with those at the conventional d.m.e.[2–5] This paper deals with totally irreversible waves, criterion of reversibility of the wave form and kinetic currents at the r.d.m.e. Characteristics of reversible waves were discussed already in the previous papers[2,4] in which a semi-empirical interpretation was given to account for observed differences in half-wave potentials of reversible waves at the d.m.e. and at the r.d.m.e. Equations for reversible waves have now been derived in more explicit form but will not be presented here because they are of little practical interest.

All considerations and experimental examples in this paper are restricted to situations where no maxima in current occur or where such maxima are completely suppressed by the addition of a suitable surface-active compound.

Experimental

Materials.—Conductivity water and high purity Linde nitrogen were used throughout. All inorganic chemicals were C.P. grade and used without further purification. Nickel perchlorate was prepared by adding an excess perchloric acid to the nitrate and evaporating to dryness. The nickel content of the perchlorate solution was determined gravimetrically by weighing as nickel dimethylglyoxime. A solution of cupric ions was obtained by dissolving an approximately weighed amount of copper perchlorate in water and determining the copper content iodometrically. A solution containing both vanadic and vanadous ions was prepared by electrolysis of a vanadyl sulfate solution which was prepared by reducing a solution of approximately known concentration of ammonium vanadate in 0.5 M sulfuric acid by passing sulfur dioxide gas. The electrolysis was carried out using a platinum anode and a mercury pool cathode in a cell with compartments separated by a sintered glass disk. Nitrogen was kept passing during electrolysis. The electrolysis was continued until a polarogram showed a clear composite wave. Concentrations of vanadic and vanadous ions were not determined separately. Pyruvic acid was purified by vacuum distillation and its solution was prepared by dissolving an accurately weighed amount in water. This solution was stored in a refrigerator. A 0.5% stock solution of polyacrylamide (PAM 75, American Cyanamid Co., New York) was prepared by dissolving the polymer in warm water. Triton X-100 ($C_8H_{17}(C_6H_4)(OCH_2CH_2)_{9-10}$-OH) was obtained from Rohm and Haas Co., Philadelphia, Pa., and its solution was prepared by dissolution in water.

Electrodes.—The r.d.m.e. used in all experiments had an attachment to vary the height of the mercury column, as was described in a previous paper.[3] The distance between the orifice and the center of rotation was 7.31 mm. and the diameter of the orifice 0.7 mm. The reference electrode was a saturated calomel electrode unless otherwise noted.

Current Measurements.—Average currents were measured with a Leeds and Northrup Electrochemograph Type E or a Sargent Polarograph Model XXI. Maximum currents were measured with the Leeds and Northrup instrument without damping. Accurate measurements for wave analysis and of kinetic currents were made by operating the instruments manually. Currents have been corrected for the residual current. All experiments were carried out in a thermostat maintained at 25 ± 0.1°.

Results and Discussion

Totally Irreversible Waves.—No attempt was made to derive a rigorous equation for totally irreversible waves, which would encounter insurmountable mathematical difficulties. The approach given is based on the concept of diffusion layer and hence is approximate.[6] The wave equation for a totally irreversible reduction process in general is given by[6]

$$E = E_{1/2} - \frac{RT}{\alpha n_a F}\ln\frac{i}{i_l - i} \qquad (1)$$

with

$$E_{1/2} = E^0 + \frac{RT}{\alpha n_a F}\ln\frac{k_{s,h}\delta}{D} \qquad (2)$$

in which α is the transfer coefficient, n_a is the number of electrons involved in the rate-determining step, i is the current on the wave, i_l is the limiting current, E^0 is the standard potential of the given couple (activity coefficients are neglected), $k_{s,h}$ is the formal heterogeneous rate constant at E^0, δ is the thickness of the diffusion layer, D is the diffusion coefficient of the reducible species, $E_{1/2}$ is the half-wave potential, and E, R, T and F have their usual significance. We consider only average currents during the drop life and accordingly δ is the average thickness of the diffusion layer. Furthermore, we assume that

---

[1] This investigation was supported by a research grant from the National Science Foundation.

[2] W. Stricks and I. M. Kolthoff, THIS JOURNAL, **78**, 2085 (1956).

[3] Y. Okinaka and I. M. Kolthoff, *ibid.*, **79**, 3326 (1957).

[4] I. M. Kolthoff and Y. Okinaka, *Anal. Chim. Acta*, **18**, 83 (1958).

[5] I. M. Kolthoff, Y. Okinaka and T. Fujinaga, *ibid.*, **18**, 295 (1958).

[6] See, for example, P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience Publishers, Inc., New York, N. Y., 1954, Chapter 9.

the value of δ at potentials on the wave is the same as the diffusion layer thickness in the limiting current region or for the mass transfer controlled process. Then we can write

$$\delta = nFADC/i_l \qquad (3)$$

in which A is the average surface area of the mercury drop and C is the concentration of the reducible species in the bulk of the solution. Denoting the rate of mercury flow, the drop time and the density of mercury by m, t and d, respectively, A becomes

$$A = (12\,\pi/5)(3mt/4\pi d)^{2/3} \qquad (4)$$

On the other hand, neglecting the contribution of minor terms, i_l at the r.d.m.e. is given by[3]

$$i_l = 0.434nFCD^{2/3}U^{1/2}\nu^{-1/6}(mt)^{1/3} \qquad (5)$$

where i_l is expressed in amp., C in moles/cc., D in cm.^{2}/sec., m in g./sec., t in sec., U is the speed of rotation of the electrode in cm./sec. and ν is the kinematic viscosity of the solution in cm.^{2}/sec. Substituting expressions 4 and 5 for A and i_l in 3, we obtain

$$\delta_{\text{r.d.m.e.}} = 1.18D^{1/3}U^{-1/2}\nu^{1/6}(mt)^{1/6} \qquad (6)$$

where $\delta_{\text{r.d.m.e.}}$ is expressed in cm. From eq. 2 and 6 we obtain

$$(E_{1/2})_{\text{r.d.m.e.}} = E^0 + \frac{RT}{\alpha n_a F}\ln\frac{1.18k_{s,h}\,\nu^{1/6}}{D^{2/3}} + \frac{RT}{\alpha n_a F}\ln\frac{(mt)^{1/6}}{U^{1/2}} \qquad (7)$$

This equation implies that the half-wave potential at the r.d.m.e. as compared to that at the d.m.e. is shifted to more negative potentials with increasing speed of rotation, but is independent of the height of the mercury column, for the drop weight mt is constant for a given electrode at a constant speed of rotation.

At the conventional d.m.e., on the other hand, the ratio of the average current on a totally irreversible wave to the average diffusion current is given by[7]

$$\frac{i}{i_d} = \frac{0.87k_{f,h}t^{1/2}/D^{1/2}}{1 + 0.87k_{f,h}t^{1/2}/D^{1/2}} \qquad (8)$$

where $k_{f,h}$ is the rate constant at a given potential on the wave, and is related to $k_{s,h}$ and E by

$$k_{f,h} = k_{s,h}\exp\left[-\frac{\alpha n_a F}{RT}(E - E^0)\right] \qquad (9)$$

Substituting eq. 9 for $k_{f,h}$ in eq. 8 and using $i/i_d = 0.5$ at $E = E_{1/2}$ yields

$$(E_{1/2})_{\text{d.m.e.}} = E^0 + \frac{RT}{\alpha n_a F}\ln\frac{0.87k_{s,h}}{D^{1/2}} + \frac{RT}{\alpha n_a F}\ln t^{1/2} \qquad (10)$$

As has been confirmed experimentally,[8,9] the half-wave potential at the d.m.e. varies with drop time and hence with the height of the mercury column. This is in contrast to the relation at the r.d.m.e. predicted by eq. 7.

From eq. 7 and 10 the difference in half-wave potential at the d.m.e. and at the r.d.m.e. at 25° is given by

$$(E_{1/2})_{\text{d.m.e.}} - (E_{1/2})_{\text{r.d.m.e.}} = \frac{0.0591}{\alpha n_a}\log\left[0.74D^{1/6}U^{1/2}\nu^{-1/6}t_{\text{d.m.e.}}{}^{1/2}\,(mt)_{\text{r.d.m.e.}}{}^{-1/6}\right] \qquad (11)$$

As a typical example, current-potential curves obtained with solutions of nickel perchlorate in 0.1 M sodium perchlorate containing 0.01% polyacrylamide are shown in Fig. 1. The current scale is normalized in this figure to make the comparison clear. The wave at the d.m.e. (m = 0.001122 g./sec. at h = 44 cm.) was obtained with 9.44 × 10^{-4} M nickel, and the half-wave potential was found equal to −1.003 volt, where t was 6.12 sec. The wave at the r.d.m.e. (210 r.p.m., U = 16.1 cm./sec., m = 0.01258 g./sec. at h = 62. cm.) was obtained with 1.89 × 10^{-4} M nickel and had a half-wave potential of −1.050 volt, where t was equal to 2.95 sec. Thus the half-wave potential at the r.d.m.e. was 0.047 volt more negative than that at the d.m.e. Putting the above values of m, t and U and D = 0.60 × 10^{-5} cm.^{2}/sec.,[10] ν = 0.897 × 10^{-2} cm.^{2}/sec. (measured with an Ubbelohde viscometer) and αn_a = 0.62 (*vide infra*) into eq. 11, the calculated difference in half-wave potential becomes 0.052 volt, which is in good agreement with the observed difference of 0.047 volt.

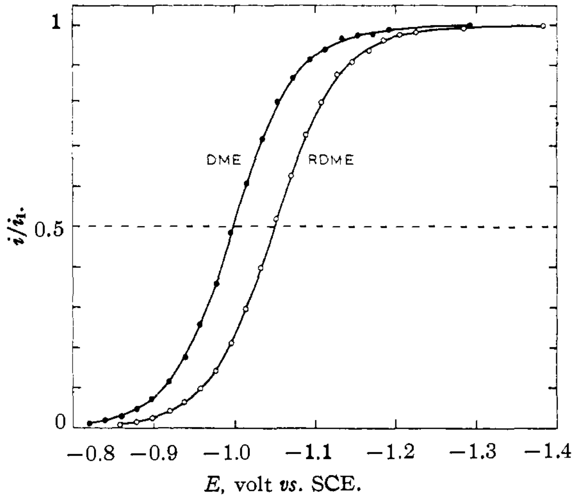

Fig. 1.—Nickel waves in 0.1 M sodium perchlorate in the presence of 0.01% polyacrylamide; r.d.m.e., 210 r.p.m.

Values of αn_a and the rate constant can be determined in the following manner from the current–potential curve obtained with the r.d.m.e. From eq. 1 and 2 we have

$$\frac{i}{i_l} = \frac{1}{1 + \dfrac{D}{k_{s,h}\delta}\exp\left[\dfrac{\alpha n_a F}{RT}(E - E^0)\right]} \qquad (12)$$

Using relations 6 and 9, the above equation becomes

$$\frac{i}{i_l} = \frac{1.18k_{f,h}\nu^{1/6}U^{-1/2}D^{-2/3}(mt)^{1/6}}{1 + 1.18k_{f,h}\nu^{1/6}U^{-1/2}D^{-2/3}(mt)^{1/6}} \qquad (13)$$

or

$$k_{f,h} = \frac{i/i_l}{1.18\nu^{1/6}U^{-1/2}D^{-2/3}(mt)^{1/6}(1 - i/i_l)} \qquad (14)$$

This expression allows the calculation of $k_{f,h}$ from the measurement of the ratio i/i_l at various po-

---

(7) J. Koutecky, *Collection Czechoslov. Chem. Communs.*, **18**, 597 (1953).

(8) P. Delahay, THIS JOURNAL, **75**, 1430 (1953).

(9) P. Kivalo, K. B. Oldham and H. A. Laitinen, *ibid.*, **75**, 4148 (1953).

(10) R. H. Sanborn and E. F. Orlemann, *ibid.*, **77**, 3726 (1955).

tentials on the wave. In view of the relation

$$\log k_{f,h} = \log k_{f,h}^0 - \frac{\alpha n_a}{0.0591} E \text{ at } 25° \qquad (15)$$

where $k_{f,h}^0$ is the rate constant at $E = 0$, a plot of $\log k_{f,h}$ calculated by using eq. 14 *vs.* E is expected to yield a straight line. Thus values of αn_a and $k_{s,h}$ are expected to be determinable from the slope of this line and by its extrapolation to E^0.

The nickel wave at the r.d.m.e. shown in Fig. 1 was analyzed by this method. As shown in Fig. 2 (line 1), the plot of $\log k_{f,h}$ *vs.* E yielded a perfectly straight line, from which the value of αn_a was found to be equal to 0.62. From an extrapolation of this line, the rate constant $k_{s,h}$ at the standard potential of nickel(II)–nickel metal couple[11] was found equal to 4.2×10^{-9} cm./sec. Line 2 in Fig. 2 was obtained from the wave at the d.m.e. shown in Fig. 1 by applying Koutecky's method using average currents (*cf.* eq. 8). It is seen that the agreement between the two lines is quite satisfactory. Values of αn_a and $k_{s,h}$ found from line 2 are 0.65 and 3.3×10^{-9} cm./sec., respectively.

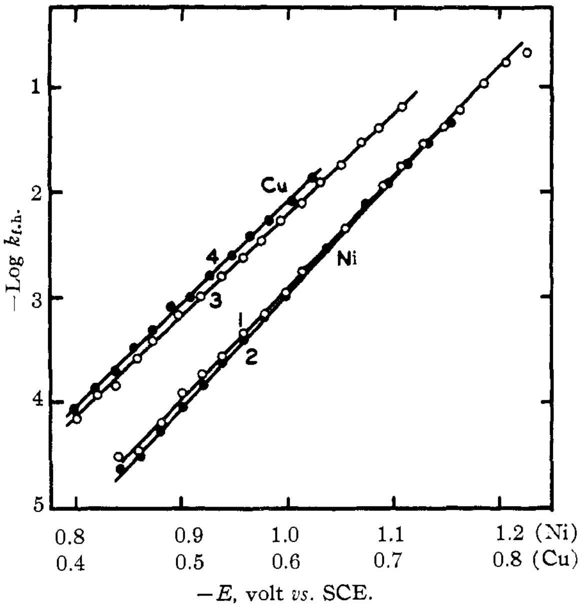

Fig. 2.—Variation of $\log k_{f,h}$ with potential for the reduction of nickel ion in 0.1 *M* sodium perchlorate in the presence of 0.01% polyacrylamide (1, 2) and for the reduction of copper ion in 0.1 *M* perchloric acid in the presence of 0.05% Triton X-100 (3, 4); 1, 3, r.d.m.e. (210 r.p.m.); 2, 4, d.m.e.

As another example, current–potential curves obtained with solutions of cupric ions (2.27×10^{-3} *M* for d.m.e., 2.08×10^{-4} *M* for r.d.m.e.) in 0.1 *M* perchloric acid containing 0.05% Triton X-100 were analyzed to evaluate kinetic parameters. We reported recently[12] that the reduction wave of cupric ion in acid media at the d.m.e., which is only slightly irreversible in the absence of surface-active substances, becomes completely irreversible when a large amount of Triton X-100 is added. The wave is shifted about 0.5 volt in the negative direction. Results of the analysis of the irreversible waves are shown in Fig. 2 (lines 3 and 4). The electrodes were the same as the ones used for the nickel experiment. Line 3 was obtained from the wave at the r.d.m.e., and gives the values $\alpha n_a = 0.57$ and $k_{s,h} = 6.4 \times 10^{-9}$ cm./sec. (referred to the standard potential of copper(II)–copper amalgam, +0.033 volt *vs.* S.C.E.).[13] The analysis of the wave at the d.m.e. made by applying Koutecky's rigorous method using maximum currents at the end of the drop life yielded a straight line which is given by line 4 in Fig. 2,[12] from which αn_a and $k_{s,h}$ were found to be equal to 0.59 and 4.4×10^{-9} cm./sec., respectively. Values of D and ν used in the calculation of $k_{f,h}$ were 8.52×10^{-6} cm.²/sec. (determined with the d.m.e. using the Ilkovic equation) and 0.892×10^{-2} cm.²/sec., respectively. The difference between the rate constants determined by the two methods is somewhat greater in this case, which must be attributed to the approximate nature of the theoretical treatment at the r.d.m.e.

Reversibility of a Wave.—It is generally recognized that the degree of reversibility of an electrode reaction as indicated by the shape of a polarographic wave is entirely dependent on the relative magnitude of two competing rate processes, *i.e.*, of mass transfer and electron transfer processes. Irreversible waves are obtained when the mass transfer rate is comparable or greater than the electron transfer rate, while reversible waves are obtained when the rate of electron transfer is much greater than the rate of mass transfer. The rate of mass transfer at the r.d.m.e. is significantly greater than that at the d.m.e. because of the effect of convective transfer, whereas the rate of electron transfer should be independent of the rotation of the electrode. Accordingly, the criterion of reversibility at the r.d.m.e. should be different from that at the d.m.e.

A general discussion of criterion of reversibility of a wave with convective mass transfer has been given by Jordan.[14] For an electrode reaction represented by

$$\text{O} + n\text{e} = \text{R} \qquad (16)$$

in which O and R are both soluble in the solution, and the activity coefficients of O and R are assumed to be equal to unity and the mass transport coefficients λ of the two species are assumed to be the same, he obtained expression (17) at the standard potential of the given couple

$$\frac{i}{i_l} = \frac{1}{\lambda/k_{s,h} + 2} \qquad (17)$$

This equation was derived under the condition that the solution does not contain R initially, and indicates that when $\lambda/k_{s,h} << 2$, $i/i_l = 1/2$ at the standard potential; *i.e.*, under this condition the half-wave potential is equal to the standard potential and the wave shape corresponds to a

---

[11] Since the standard nickel amalgam potential is unknown, the standard potential of nickel ion–nickel metal, −0.250 volt *vs.* N.H.E., was chosen as a convenient reference point. W. M. Latimer, "Oxidation Potentials," 2nd ed., Prentice–Hall Inc., Englewood Cliffs, N. J., 1952, p. 200.

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

[13] I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. 1, Interscience Publishers, Inc., New York, N. Y., 1952, p. 227.

[14] J. Jordan, *Anal. Chem.*, **27**, 1708 (1955).

reversible electrode reaction. Evidently deviation from reversibility becomes increasingly greater with increasing value of $\lambda/k_{s,h}$. For a given system, the value of $\lambda/k_{s,h}$ is about three times greater at the r.d.m.e. than at the d.m.e., as can be seen by putting actual numerical values in expressions

$$\lambda_{\text{r.d.m.e.}} = i_l/nFAC = 0.85D^{2/3}U^{1/2}\nu^{-1/6}(mt)^{-1/6} \quad (18)$$

$$\lambda_{\text{d.m.e.}} = i_d/nFAC = 1.23D^{1/2}t^{-1/2} \quad (19)$$

in which λ's are taken to mean average values of mass transport coefficients during the life time of a mercury drop, and i_l, i_d and A are given by eq. 5, the Ilkovic equation and eq. 4, respectively. For example, for $D = 10^{-5}$ cm.²/sec., $t = 3$ sec., $U = 15$ cm./sec., $\nu = 0.9 \times 10^{-2}$ cm.²/sec. and m (r.d.m.e.) = 0.01 g./sec., we obtain $\lambda_{\text{r.d.m.e.}} = 6 \times 10^{-3}$ cm./sec. and $\lambda_{\text{d.m.e.}} = 2 \times 10^{-3}$ cm./sec. Thus the degree of irreversibility of the wave form is expected to be greater at the r.d.m.e. than at the d.m.e., when $k_{s,h}$ of the given system is not sufficiently large.

This situation was found to occur with the vanadium(III)–vanadium(II) system, as is illustrated in Fig. 3 by composite waves obtained with a mixture of vanadic and vanadous ions in 0.5 M sulfuric acid solution. Both in the absence and presence of starch, a single well-defined composite wave was obtained at the d.m.e.; the wave in the absence of starch (Fig. 3, I) is practically reversible in agreement with Lingane,[15] while the deviation from reversibility becomes slightly greater in the presence of starch (Fig. 3, II). At the r.d.m.e. (210 r.p.m.) the cathodic wave is clearly separated from the anodic wave, which is a typical irreversible behavior. The cathodic and anodic currents at the r.d.m.e. were much greater in the absence than in the presence of starch because of the stirring effect[2,3] (maxima of the second kind) in the absence of a surface-active substance.

Neither gelatin nor polyacrylamide (PAA) was suitable as maximum suppressor; the former is reported to make the vanadium wave more irreversible at the d.m.e.,[15,16] while irregular current oscillations were observed by us in the presence of PAA. Starch was found to be a more suitable suppressor for this particular system but the wave was made more irreversible as its concentration was increased. Anionic surface-active substances would be expected to make the vanadium wave more reversible because of an electrostatic effect between the negatively charged adsorbed substance at the electrode surface and positively charged vanadium ions. Actually, however, sodium dodecyl sulfate was found to distort the vanadium wave. No further effort has been made to study effects of various surface-active substances, because the example shown in Fig. 3 suffices to demonstrate the difference in degree of reversibility at the d.m.e. and at the r.d.m.e.

After the present work was finished, Randles[17] reported a value of 1.39×10^{-3} cm./sec. for $k_{s,h}$ of the vanadium system in 1 M sulfuric acid at 15.3°, which was derived from an analysis of the composite wave at the d.m.e. and from a.c. impedance measurements. Assuming that at 25° the rate constant becomes equal to about 3×10^{-3} cm./sec., and using eq. 17 and the λ values given above as an example, the values of i/i_l at the standard potential become 0.4 at the d.m.e. and 0.25 at the r.d.m.e. instead of 0.50 for reversible behavior. These values predict that the vanadium wave should be much more irreversible at the r.d.m.e. than at the d.m.e.

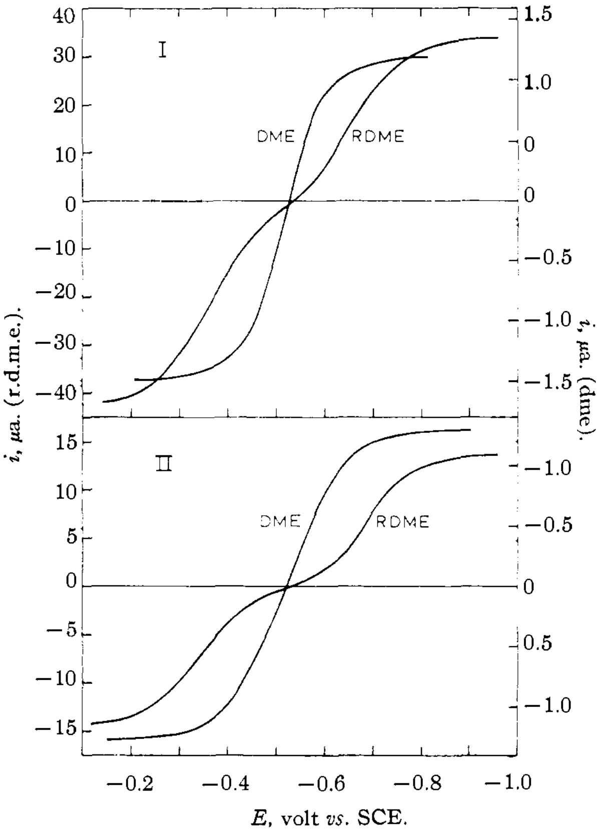

Fig. 3.—Composite waves of a mixture of vanadic and vanadous ions in 0.5 M sulfuric acid at the d.m.e. and at the r.d.m.e. (210 r.p.m.): I, no surface-active substance; II, 0.01% starch. Total vanadium concentration was 9×10^{-4} M.

As another example to illustrate the difference in reversibility at the two electrodes, current–potential curves and their analyses obtained with copper ions (2×10^{-4} M for d.m.e., 1×10^{-4} M for r.d.m.e.) in 0.1 M sodium perchlorate containing 0.01% polyacrylamide are shown in Fig. 4. It is clear that the wave form at the d.m.e. corresponds to a practically reversible reaction, while that obtained at the r.d.m.e. (210 r.p.m.) deviates considerably from reversibility. It was ascertained that the observed difference is not due to the effect of polyacrylamide. The wave obtained at the d.m.e. in the absence of polyacrylamide did not exhibit maxima at this low concentration of copper and was exactly the same as that obtained in the presence of 0.01% or 0.1% polyacrylamide (*cf.* Fig. 1 in ref. 12). The wave at the r.d.m.e. was also unaffected by increasing the concentration of polyacrylamide from 0.01 to 0.1%.

---

[15] J. J. Lingane, THIS JOURNAL, **67**, 182 (1945).
[16] J. J. Lingane and L. Meites, *ibid.*, **69**, 1021 (1947).
[17] J. E. B. Randles, *Can. J. Chem.*, **37**, 238 (1959).

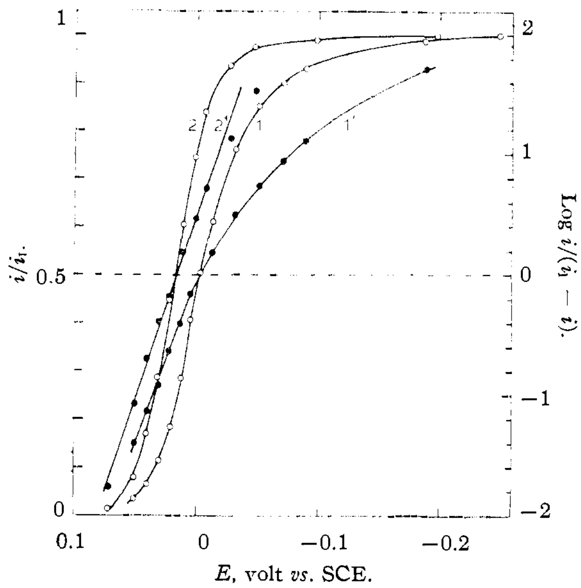

Fig. 4.—Reduction waves of copper ions (1, 2) and their analyses (1′, 2′) in 0.1 M sodium perchlorate in the presence of 0.01% polyacrylamide: 1, 1′, r.d.m.e. (210 r.p.m.); 2, 2′, d.m.e.

Kinetic Currents.—The kinetic current at the ordinary d.m.e. has been interpreted successfully on the assumption that the chemical reaction controlling the kinetic current occurs in a layer of certain thickness at the electrode surface.[18–21] It is shown in this section that the concept of the reaction layer can be applied also to interpret characteristics of kinetic currents at the r.d.m.e.

Consider an electrode process preceded by a first-order chemical reaction represented by

$$\mathrm{Y} \underset{k_b}{\overset{k_f}{\rightleftarrows}} \mathrm{O} \xrightarrow{+\,ne} \mathrm{R} \qquad (20)$$

in which substance Y is not reduced at the potential where substance O is reduced, and k_f and k_b are the rate constants for the forward and backward chemical reactions. It is assumed that the chemical equilibrium is greatly in favor of Y and the concentration of substance O in the bulk of the solution can be neglected. It is further assumed that a sufficiently negative potential is applied so that all molecules of O produced in the reaction layer are reduced instantaneously and hence the concentration of substance O in the reaction layer is negligibly small. Under these conditions, the number of moles of O produced in the reaction layer per unit time per unit area is given by $\mu \cdot k_f C_t^0$, where μ is the thickness of the reaction layer and C_t^0 is the concentration of substance Y in the reaction layer at time t. The instantaneous current is then proportional to this quantity and given by

$$i_t = nFA_t\mu k_f C_t^0 \qquad (21)$$

When the rate of the transformation from Y to O is sufficiently small as compared to the rate of transport of substance Y from the bulk of the solution to the electrode, the current becomes entirely kinetically controlled and the concentration C_t^0 in the reaction layer at the electrode surface can be regarded as being equal to the bulk concentration C. The average kinetic current both at the d.m.e. and r.d.m.e. is then given by

$$i_k = nFA\mu k_f C = 0.51 nF\mu k_f C(mt)^{2/3} \qquad (22)$$

in which i_k is expressed in amp., μ is cm., k_f in sec.$^{-1}$, C in moles/cc., and m and t in g./sec. and sec.

The assumptions made above to derive this equation are ideally fulfilled in the reduction of glucose. The kinetic current of glucose at the d.m.e. is postulated to be controlled by the rate of transformation of the non-reducible ring form to the reducible aldehyde form.[19,22] The equilibrium concentration of the reducible form and the rate of the transformation are both so small that the current is entirely kinetically controlled. In order to test eq. 22, experiments were carried out with 0.05 M glucose in 0.01 M lithium hydroxide at various speeds of rotation of the electrode. Results are given in Table I. The observed kinetic current was found to decrease with increasing speed of rotation, even though the mass-transfer controlled limiting current at the r.d.m.e. greatly increases with increasing speed of rotation between 0 and 300 r.p.m.[2,3] The constancy of $i_k/(mt)^{2/3}$ shown in the last column of Table I indicates that the decrease in current is simply related to the decrease in drop time with increasing speed of rotation, and also that the thickness of the reaction layer μ is constant at various speeds of rotation. The two results at 210 r.p.m. show that the kinetic current at the r.d.m.e. like that at the d.m.e. is independent of the height of the mercury reservoir. Since the mass-transfer controlled limiting current at the r.d.m.e. is also practically independent of the mercury pressure,[3] the dependence of current on the mercury pressure cannot be used to detect kinetic nature of the current at the r.d.m.e. However, kinetic currents can be identified at the r.d.m.e. by determining the effect of rate of stirring upon the value of the limiting current. This effect is quite different on kinetic current than on a limiting current controlled by mass transfer.

Table I

Kinetic Currents of 0.05 M Glucose in 0.01 M Lithium Hydroxide

R.p.m.	h	m g./sec.	t, sec.	i_k[a] × 10^6, amp.	$i_k/(mt)^{2/3}$ × 10^4, amp./g.$^{2/3}$
0	52	0.01035	3.61	26.0	2.33
75	52	.01035	3.22	23.6	2.28
210	52	.01035	2.07	18.7	2.42
210	34	.00687	3.14	18.3	2.36

[a] Measured at −2 volts vs. mercury pool anode.

The average value of μk_f calculated from the values of $i_k/(mt)^{2/3}$ in Table I by using eq. 22 was found equal to 4.8 × 10^{-5} cm./sec. No surface-active substances were added in these experiments, because such substances were found to

---

(18) K. Wiesner, *Z. Elektrochem.*, **49**, 164 (1943).

(19) K. Wiesner, *Collection Czechoslov. Chem. Communs.*, **12**, 64 (1947).

(20) R. Brdicka and K. Wiesner, *ibid.*, **12**, 138 (1947).

(21) R. Brdicka, *ibid.*, **12**, 212 (1947).

(22) P. Delahay and J. E. Strassner, This Journal, **74**, 893 (1952).

cause a distortion of the wave. Not only was the kinetic current decreased considerably but also the wave was displaced to more negative potentials. As long as the current is entirely kinetically controlled, no "maxima" effects are involved and therefore it is unnecessary to add surface-active substances.

TABLE II

KINETIC CURRENTS OF 4 × 10^{-4} *M* PYRUVIC ACID IN 0.05 *M* PHOSPHATE BUFFER OF *p*H 6.80

Elect.	R.p.m.	*h*, cm.	*m*, g./sec.	*t*, sec.	$i_k{}^a$ × 10^6, amp.	$i_k/(mt)^{2/3}$ × 10^5, amp./g.$^{2/3}$
D.M.E.	..	82	0.002124	2.92	0.370	1.10
	..	52	.001307	4.73	0.350	1.04
R.D.M.E.	75	82	.01654	3.08	1.50	1.09
	150	82	.01654	2.51	1.32	1.10
	210	82	.01654	2.04	1.14	1.09
	210	42	.00847	3.92	1.14	1.10

[a] Measured at −1.4 volts *vs.* S.C.E.

The kinetic current of pyruvic acid was studied as another example. This acid is known to produce double waves at the d.m.e. in the *p*H range between 4 and 8 because of the fact that the undissociated form of the acid is reduced at a more positive potential than the pyruvate ion. The height of the first wave is partially or completely controlled by the rate of recombination of hydrogen and pyruvate ions.[21,23,24] As is to be expected, similar double waves are observed at the r.d.m.e. The recombination process is a second-order reaction, but if the hydrogen ion concentration is kept constant by using a proper buffer solution, the treatment becomes essentially the same as for a first-order reaction. At a sufficiently small hydrogen ion concentration, the concentration of the undissociated acid is so small that the current on the first wave is entirely controlled by the rate of recombination. The kinetic current observed under such conditions is given by equation 22 in which μk_f is replaced by $\mu k_f[H^+]$.

Experimental results obtained with a solution of 4 × 10^{-4} *M* pyruvic acid in a 0.05 *M* phosphate buffer at *p*H 6.80 are shown in Table II. Again, constant values of $i_k/(mt)^{2/3}$ were found both at the d.m.e. and at the r.d.m.e. at different heights of the mercury reservoir and at the r.d.m.e. at different speeds of rotation. The average value of μk_f calculated from these data was found equal to 1.7 × 10^6 cm.^{4} sec.$^{-1}$ mole.$^{-1}$. No surface-active substances were used in these experiments for the same reason as has been given in the description of the glucose experiment.

The nature of catalytic currents is essentially the same as that of kinetic currents, which was confirmed experimentally by measuring the catalytic current produced by hydrogen peroxide in the reduction of ferric ions. Since no further interesting feature was found, detailed results are not presented.

MINNEAPOLIS, MINN.

---

[23] J. Koutecky and R. Brdicka, *Collection Czechoslov. Chem. Communs.*, **12**, 337 (1947).

[24] P. Delahay and T. J. Adams, THIS JOURNAL, **74**, 1437 (1952).

[CONTRIBUTION FROM THE COATES CHEMICAL LABORATORY, LOUISIANA STATE UNIVERSITY]

Application of the Potentiostatic Method to Electrode Processes with Fast Coupled Chemical Reaction—Kinetics of Dissociation of Monochloroacetic Acid

BY PAUL DELAHAY AND SYOTARO OKA[1] (WITH AN APPENDIX BY HIROAKI MATSUDA)[2]

RECEIVED JULY 10, 1959

It is shown that the kinetics of the chemical reaction preceding charge transfer in so-called "kinetic processes" can be studied by the potentiostatic method even for reactions which are too fast for polarographic study. Current–time curves are recorded with an electronic potentiostat and oscilloscope at a potential corresponding to the limiting current (i_l) range, and rate constants are calculated from a plot of $i_l t^{1/2}$ against $t^{1/2}$. Application is made to the kinetics of dissociation of monochloroacetic acid in 50–50 water–ethanol mixture (by volume) at an ionic strength of 1. Rate constants at 25°: (1.8 ± 0.5) × 10^6 sec.$^{-1}$ for dissociation, and (1.3 ± 0.3) × 10^{10} l. mole^{-1} sec.$^{-1}$ for recombination. Sources of error on these data are discussed. Experimental methods are outlined.

Electrode processes with a preceding coupled chemical reaction (so-called "kinetic processes") have been studied extensively in polarography since the classical work of Brdicka and co-workers and occasionally by the galvanostatic method (chronopotentiometry). The potentiostatic method,[3] since the development of electronic potentiostats with fast response, has not been applied to kinetic processes to our knowlege. Yet, this method and the galvanostatic method can be applied to chemical reactions which are too fast for kinetic study by polarography. The argument is as follows.

The limiting current for a kinetic process is controlled by the kinetics of the chemical reaction and diffusion of the reactants; and the influence of the latter process increases with the duration of electrolysis. Current–time curves in the potentiostatic method can be recorded in 10^{-3} sec. or even a shorter time, *i.e.*, in a time which compares very favorably with the drop time in polarographic electrolysis. Limiting currents which are practically diffusion-controlled in polarography still may exhibit a kinetic character in the potentiostatic method.

Quantitatively, according to Koutecky and Brdicka[4] the limiting current i_l for the first-order process $Z \rightleftarrows O + ne = R$, in which Z is not reduci-

---

[1] On leave from Shimadzu Seisakusho Ltd., Instruments Division, Kyoto.

[2] Research Associate, 1958–1959; on leave from the Government Chemical Industrial Research Institute, Tokyo.

[3] H. Gerischer and W. Vielstich, *Z. physik. Chem.* (*Frankfurt*), **3**, 16 (1955); **4**, 10 (1955).

[4] J. Koutecky and R. Brdicka, *Collection Czechoslov. Chem. Communs.*, **12**, 337 (1947).