[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MICHIGAN]

The Time-dependence of the Diffusion-controlled Polarographic Current

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The experimental polarographic current *vs.* time relationship cannot be explained by the simple hypothesis, common to all previous theoretical developments, of constant initial concentration at the time when each drop begins to form, even when the degree of rigor of the mathematical development of the hypothesis is very high, and when account is taken of the inaccuracy of many of the other physical assumptions entering the formulation of the mathematical theory. The postulatory basis of the theory was therefore revised to contain the alternate hypothesis that at the beginning of drop formation the region of solution around the electrode tip is depleted of electroactive material because of its removal by electrolysis at the preceding drop. Mathematical development of the revised diffusion problem for the dropping mercury electrode leads to a prediction for the current–time relationship which is substantially in agreement with the experimental data even during the early stages of drop growth. It can be inferred that the existence of a depleted region is an essential part of the physical situation. The mathematical development is capable of an indefinite amount of improvement through the fitting of certain parameters to the experimental data. Full account has been taken of all inexact procedures and assumptions in evaluating the reliability of the results; none of the former are considered to affect seriously the validity of the conclusions stated here.

The theory of the diffusion-controlled current at the dropping mercury electrode (DME) has passed through a series of developments each more sophisticated than the last[1] culminating in the work of Matsuda[1f] who has carried the mathematical part of the theory to a point of great rigor, and whose method is capable of extension (at the cost of computational labor) to any degree of accuracy. While the prevailing evidence indicates that the equations so developed can account satisfactorily for most of the factors that influence the magnitude of the diffusion current,[2] there exist discrepancies between theory and experiment in what is perhaps the most critical phenomenon of the process: the time-dependence of the current.

The discrepancies have been of two sorts: in many cases the experimentally observed average currents are lower than those predicted by theory and careful studies of the growth of current as a function of time have shown that the $^1/_6$ power–time relation predicted by theory is not obeyed at all during the first portion of drop-life and only obeyed approximately thereafter.[3,4] A recent study[5] has shown that these discrepancies cannot be explained by mathematical shortcomings in the existing theory and that the time-dependence of the rate of flow of mercury from the capillary, suggested[3b] as the cause of the discrepancies, can only partially account for them. It seems necessary, therefore, to make a postulatory revision in the theory.

The Boundary Value Problem for Diffusion in a Depleted Region

Airey and Smales[3a] have suggested that the freshly forming drop at the DME begins its growth in a region of the solution partially depleted by the electrolysis at the preceding drop. The purpose of the analysis which follows is to determine whether the experimental current–time relationship can be accounted for on the basis of this hypothesis. Three complicated and interdependent phenomena then would be occurring simultaneously: (1) the growth of the drop and consequent movement of the solution; (2) diffusion of material from the undepleted region of the solution into the depleted region; and (3) diffusion within the depleted region to the electrode surface.

To obtain the concentration or the flux for this situation, a boundary value problem consisting of the differential equation

$$\frac{\partial C}{\partial t} = D\left(\frac{\partial^2 C}{\partial r^2} + \frac{2}{r}\frac{\partial C}{\partial r}\right) - \frac{\gamma}{3r^2}\frac{\partial C}{\partial r} \quad (t > 0,\ r_0 < r < \infty) \qquad (1)$$

and boundary conditions

$$C(r,0) = C_0F(\mathrm{r}) \qquad (0 < r < \infty) \qquad (2)$$

$$C(r_0,t) = 0 \qquad (t > 0) \qquad (3)$$

$$\lim_{r\to\infty} C(r,t) = C_0 \qquad (t > 0) \qquad (4)$$

would have to be solved. In order to incorporate the new postulate into the theory, it is necessary to discard the usual boundary condition of constant initial concentration and to replace it by a new one, equation 2, where $F(r)$ is an arbitrary initial distribution function having values between 0 and 1, chosen so as to best represent the physical situation. C represents concentration; C_0, the bulk solution concentration; $C(r,t)$, the time-dependent concentration distribution; t, time; D, the diffusion coefficient; r, the radial distance; r_0, the time-dependent drop radius; and γ denotes the constant quantity $3m/4\pi d$ (*cf.* subsequent equation 5).

Formulation of a Soluble Problem.—The introduction of condition (2) into the rigorous boundary value problem for the dropping mercury electrode[1] converted an already difficult problem into one which proved completely intractable. Since no

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(1) (a) D. Ilkovic, *Collection Czechoslov. Chem. Communs.*, **6**, 498 (1934); (b) D. Ilkovic, *J. chim. phys.*, **35**, 129 (1938); (c) T. Kambara and I. Tachi, "Proceedings of the First International Polarographic Congress," Prague, 1951, Part I, p. 126; (d) J. J. Lingane and B. A. Loveridge, THIS JOURNAL, **72**, 438 (1950); (e) D. MacGillavry and E. K. Rideal, *Rec. trav. chim.*, **56**, 1013 (1937); (f) H. Matsuda, *Bull. Chem. Soc. Japan*, **26**, 342 (1953); (g) M. v. Stackelberg, *Z. Elektrochem.*, **45**, 466 (1939); (h) H. Strehlow and M. v. Stackelberg, *ibid.*, **54**, 51 (1950).

(2) I. M. Kolthoff and J. J. Lingane, "Polarography," 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1952.

(3) (a) L. Airey and A. A. Smales, *Analyst*, **75**, 287 (1950); (b) J. J. Lingane, THIS JOURNAL, **75**, 788 (1953); (c) H. A. McKenzie, *ibid.*, **70**, 3147 (1948); (d) J. H. Schulman, H. B. Battey and D. G. Jelatis, *Rev. Sci. Instr.*, **18**, 226 (1947); (e) G. S. Smith, *Nature*, **163**, 290 (1949); (f) F. L. Steghart, *Chem. and Ind. (London)*, 157 (1948).

(4) J. K. Taylor, R. E. Smith and I. L. Cooter, *J. Research Natl. Bur. Standards*, **42**, 387 (1949).

(5) (a) J. M. Markowitz, Ph.D. Thesis, University of Michigan, 1958; (b) J. M. Markowitz and P. J. Elving, *Chem. Revs.*, **58**, 1047 (1959).

rigorous solution to the problem stated in equations 1 to 4 could be achieved, it was necessary to revert to a simpler model, retaining the one essentially new feature, the existence of a depleted region. Faced with a choice of models, none of which seemed preferable to any other on grounds of rigor,[5] it seemed most suitable to choose the simplest. The model chosen was that of Lingane and Loveridge,[1d] who, to account for the factor of drop growth, introduced the factor ${}^3/_7$ into rigorous solutions for stationary plane and spherical electrodes. The following procedure was adopted: solutions were sought to the relatively simple problems of diffusion to a plane electrode with inhomogeneous initial concentration distribution (referred to hereafter as the plane approximation) and the corresponding problem for a spherical electrode (the spherical approximation). The surface concentration gradients derived from these solutions contain the quantity Dt; wherever this combination occurred, the Lingane and Loveridge factor, ${}^3/_7$, was associated with it to account for the effect of drop growth. The surface area terms in the expression for the flux were replaced by the time-dependent area of the growing drop, for which the radius is defined by

$$r_0^3 = \frac{3mt}{4\pi d} = \gamma t \tag{5}$$

where d is the density of mercury (13.6 g. cm.$^{-3}$), m the rate of flow of mercury and t is the time. In detail, the following boundary value problems were solved.

The plane approximation

$$\frac{\partial C}{\partial t} = D\,\frac{\partial^2 C}{\partial x^2} \qquad (0 < x < \infty,\ t > 0) \tag{6}$$

$$C(x,0) = C_0 F(x) \qquad (0 < x < \infty) \tag{7}$$

$$C(0,t) = 0 \qquad (t > 0) \tag{8}$$

$$\lim_{x \to \infty} C(x,t) = C_0 \qquad (t > 0) \tag{9}$$

The spherical approximation

$$\frac{\partial C}{\partial t} = D\left(\frac{\partial^2 C}{\partial r^2} + \frac{2}{r}\,\frac{\partial C}{\partial r}\right) \qquad (r_0 < r < \infty,\ t > 0) \tag{10}$$

$$C(r,0) = C_0 F(r) \qquad (r_0 < r < \infty) \tag{11}$$

$$C(0,t) = 0 \qquad (t > 0) \tag{12}$$

$$\lim_{r \to \infty} C(r,t) = C_0 \qquad (t > 0) \tag{13}$$

The foremost criterion for the success of the approach outlined above is that the solutions of the problems of diffusion to stationary plane and spherical electrodes with inhomogeneous initial concentration distributions, as modified by the Lingane and Loveridge factor, ${}^3/_7$, should converge to, respectively, the Ilkovic equation and the Lingane–Loveridge equation when the depleted region thickness, μ, is allowed to vanish. (μ will necessarily be a function of the time, since the drop is expanding. As μ goes to zero, the situation becomes identical with that in the classical Ilkovic problem.) It will be found that this criterion is satisfied in all cases.

Solution of the Equations.—Both problems are more or less elementary. A solution to the first is available[6] but the solution found here by the operational method using the Laplace transform calculus is more useful and was derived independently. Likewise, the solution of the second problem given here is independent; no similar problem was found in the literature. Details of the solutions are given elsewhere (pp. 242–250 of reference 5a).

The concentration function for the plane approximation is

$$C(x,t) = \frac{C_0}{\sqrt{\pi}}\left[\int_{-x/2\sqrt{Dt}}^{\infty} F(x + 2\sqrt{Dt}\,\lambda)e^{-\lambda^2}\,d\lambda - \int_{x/2\sqrt{Dt}}^{\infty} F(-x + 2\sqrt{Dt}\,\lambda)e^{-\lambda^2}\,d\lambda\right] \tag{14}$$

Use of the operational method permitted the derivation of a general equation for the flux at the origin, independent of equation 14

$$\phi_0 = -D\left(\frac{\partial C}{\partial x}\right)_{x\,=\,0} = -2C_0\sqrt{\frac{D}{\pi t}}\int_0^{\infty} \lambda F(2\sqrt{Dt}\,\lambda)e^{-\lambda^2}\,d\lambda \tag{15}$$

The corresponding solutions for the spherical approximation are

$$C(r,t) = \frac{C_0}{r\sqrt{\pi}}\left[\int_{(r_0\,-\,r)/2\sqrt{Dt}}^{\infty} (r + 2\sqrt{Dt}\,\lambda)\,F(r + 2\sqrt{Dt}\,\lambda)e^{-\lambda^2}\,d\lambda - \int_{(r\,-\,r_0)/2\sqrt{Dt}}^{\infty} (-r + 2r_0 + 2\sqrt{Dt}\,\lambda)F(r_0 + 2\sqrt{Dt}\,\lambda)e^{-\lambda^2}\,d\lambda\right] \tag{16}$$

$$\phi_0 = -\frac{2C_0}{r_0}\sqrt{\frac{D}{\pi t}}\int_0^{\infty} \lambda(r_0 + 2\sqrt{Dt}\,\lambda)\,F(r_0 + 2\sqrt{Dt}\,\lambda)e^{-\lambda^2}\,d\lambda \tag{17}$$

In these equations λ is a variable of integration, and the functional notation, $F(\ )$, represents a transformation of coördinates from those of $F(x)$ or $F(r)$ to those enclosed in the parentheses.

To make use of equations 15 or 17, a concentration distribution function of some specific form must be introduced for F. Introduction of the function $F = 1$, *i.e.*, $\mu = 0$, leads, as has been suggested earlier, to expressions for the flux at stationary electrode

$$\phi_0 = -\frac{C_0}{\sqrt{\pi Dt}} \tag{18}$$

for the plane case, and to

$$\phi_0 = C_0\left(\frac{1}{r_0} + \frac{1}{\sqrt{\pi Dt}}\right) \tag{19}$$

for the spherical case.[2]

The nature of the functions $F(x)$ or $F(r)$ to be used in order to reproduce the experimental data is a matter of trial. Some functions which were obviously unsuitable because of the physical situation were tried because of the simplicity of the integrations required; others, more suitable, such as the error function and the sine integral function,[7] were not tried for the opposite reason.[5a] The most successful has been one of parabolic

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(6) (a) R. V. Churchill, "Modern Operational Mathematics in Engineering," McGraw–Hill Book Co., New York, N. Y., 1944; (b) R. Courant, "Differential and Integral Calculus," 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1937.

(7) E. Jahnke and F. Emde, "Funtiontafeln mit Formeln und Kurven," Dover Publications, New York, N. Y., 1945.

form

$$F(x) = \begin{cases} \frac{x^2}{\mu^2}(2\mu - x) & \text{when } 0 < x < \mu \\ 1 & \text{when } x > \mu \end{cases} \quad (20)$$

or, its spherical counterpart

$$F(r) = \begin{cases} \frac{r - r_0}{\mu^2}[2\mu - (r - r_0)] & \text{when } 0 < (r - r_0) < \mu \\ 1 & \text{when } (r - r_0) > \mu \end{cases} \quad (21)$$

These equations describe quadrants of parabolas symmetrical about the line x (or r) $= \mu$ and opening downward. μ is therefore the limit of the region of concentration inhomogeneity; it is the depleted region thickness. These functions satisfy continuity requirements at $x = \mu$, and are therefore *a priori* physically reasonable.

Expression of Depleted Region Thickness.—Having selected a trial initial concentration distribution, it is then necessary to choose a value for μ, the depleted region thickness. This must be a function of time and must be related to the amount of electrolysis at the preceding drop. The number of moles of material electrolyzed at a given drop could not be very different from what would be predicted by the Ilkovic equation

$$N_\tau = \int_0^\tau \phi_0 A \, \mathrm{d}t = C_0 \int_0^\tau 4\pi r_0^2 \sqrt{\frac{7D}{3\pi t}} \, \mathrm{d}t \quad (22)$$

$$N_\tau = \frac{6}{7}\sqrt{\frac{7}{3}}\, \gamma^{2/3} C_0 D^{1/2} \tau^{7/6} \quad (23)$$

where N_τ represents the number of moles electrolyzed during the drop life-time, τ, and ϕ_0 is the flux calculated in the classical Ilkovic derivation.[1]

The approximations involved in the use of equation 23 involve not only the use of the Ilkovic equation, but also the lack of precise knowledge of how much of the depleted solution is dragged from the region of the capillary tip by the fall of the previous drop. These questions will be discussed again. To account for the latter factor, a multiplicative constant, q, which varies from zero to 1, will be introduced on the right of equation 23.

The solution volume required to contain N_τ moles will depend partly on the kind of distribution function, $F(x)$ or $F(r)$, used. Usually, it will be necessary to integrate over the distribution function from 0 to μ and divide by μ in order to find the average concentration. Then the volume will be given by N_τ/pC_0, where p is a fraction between zero and 1 representing the average value of F, the initial concentration distribution function.

The time-dependence of μ can be introduced by the use of the obvious fact that N_τ/pC_0 is conserved in time, *i.e.*, because of the incompressibility of liquids, the original depleted volume must be conserved regardless of its distortion by the drop growth. It must be true, therefore, that, assuming a spherical disposition of the depleted solution

$$\frac{4}{3}\pi(r_0 + \mu)^3 = \frac{N_\tau}{pC_0} + \frac{4}{3}\pi r_0^3 \quad (24)$$

from which

$$\mu = \left(\frac{3}{4\pi}\frac{N_\tau}{pC_0} + r_0^3\right)^{1/3} - r_0 \quad (25)$$

Actually, it is unlikely that the disposition of the depleted region is exactly spherical. It will be expedient, however, to assume that it is spherical and to take account of the possible lack of sphericity in considering the result.

If the value of N_τ from equation 23 is introduced into equation 25, and evaluated in terms of m and t, and the constants are lumped

$$\mu = \left(0.015 m^{2/3} D^{1/2} \tau^{7/6} \frac{q}{p} + 0.176 mt\right)^{1/3} - 0.259 m^{1/3} t^{1/3} \quad (26)$$

The Time–Current Relation.—The flux for the plane approximation and the concentration distribution of equation 20 can be shown[5a] to be

$$\phi_0 = -C_0\sqrt{\frac{D}{\pi t}}\left[\frac{2\sqrt{\pi Dt}}{\mu}\,\mathrm{erf}\,\frac{\mu}{2\sqrt{Dt}} + \frac{4Dt}{\mu^2}\left(e^{-\mu^2/4Dt} - 1\right)\right] \quad (27)$$

The quantity $^3/_7$ is now associated with the product Dt wherever the latter occurs in conformity with the procedure of Lingane and Loveridge.[1d] The equivalent spherical area, $4\pi r_0^2$, is introduced, and, if the usual Ilkovic equation terms are lumped into a constant k, the result is

$$i = kt^{1/6}\left[\frac{2\sqrt{3\pi Dt/7}}{\mu}\,\mathrm{erf}\,\frac{\mu}{2\sqrt{3Dt/7}} + \frac{12Dt}{7\mu^2}\left(e^{-7\mu^2/12Dt} - 1\right)\right] \quad (28)$$

By appropriate series expansion of the error function and the exponential, it can be shown that the bracketed factor, which might be called the *depletion factor*, reduces to 1 when μ approaches zero, corresponding to the classical derivations of the Ilkovic equation with constant initial concentration. Thus, in the limit of vanishing depleted region, equation 28 approaches the Ilkovic equation.

The depletion factor for the spherical case, corresponding to equation 17, in which the spherical approximation is used from the beginning is

$$\left[\frac{2\sqrt{3\pi Dt/7}}{\mu}\,\mathrm{erf}\,\frac{\mu}{2\sqrt{3Dt/7}} + \frac{12Dt}{7\mu^2}\left(e^{-7\mu^2/12Dt} - 1\right) + \frac{\sqrt{3\pi\, Dt/7}}{r_0} - \left(\frac{\mu^2 + 18/7\, Dt}{\mu^2 r_0}\right)\sqrt{3\pi Dt/7}\,\mathrm{erf}\,\frac{\mu}{2\sqrt{3Dt/7}} - \frac{6Dt}{7\,\mu r_0}\left(e^{-7\mu^2/12Dt} - 4\right)\right] \quad (29)$$

Comparing expression 29 with equation 28, it can be seen that the depletion factor of the former is much more complicated, containing three additional terms.

Comparison with Experimental Behavior

Of the data available on the current–time relationship, those of Taylor, Smith and Cooter[4] are the most detailed, particularly at small values of the time. Consequently, the current–time behavior predicted by equation 28 was compared with these data. For this purpose, the reported experimental constants[4] were introduced into equation 28: concentration, C_0, 3.018 mM; diffusion coefficient of Cd(II), D, 7.2×10^{-6} cm.^{2}/sec.; mass rate of mercury flow, m, 2.305 mg./sec.; drop life-time, τ, 3.392 sec.

For the distribution described by equation 20, the average value of the concentration is easily shown to be $2C_0/3$. Consequently, the value of p to be assigned in equation 26 is $^2/_3$. When all these constants are introduced and adjustment made so that the ordinary experimental quantities give current in microamperes, the behavior of the current as a function with time is given by

$$i/t^{1/6} = 21.1 \left[\frac{\sqrt{\pi t}}{9.80\nu} \operatorname{erf} \frac{9.80\nu}{\sqrt{t}} + \frac{t}{96.0\nu^2} \left(e^{-96.0\nu^2/t} - 1\right)\right] \quad (30)$$

where

$$\nu = (1.07q + t)^{1/3} - t^{1/3} \quad (31)$$

The constant, q, representing the fraction of the depleted volume not carried away by the preceding drop, must be assigned by trial.

Figure 1 presents a comparison of the experimental data of Taylor, *et al.*, with the current–time relation calculated by the present method using both the plane and the spherical approximation. In both calculations the value 0.2 was assigned to q. The calculated results show excellent agreement with the experimental curve, the agreement being somewhat better in the case of the spherical approximation. Note that at large t the plane approximation approaches the horizontal Ilkovic equation line while the spherical approximation approaches the sloped line characteristic of two-term solutions, such as that of Lingane and Loveridge.

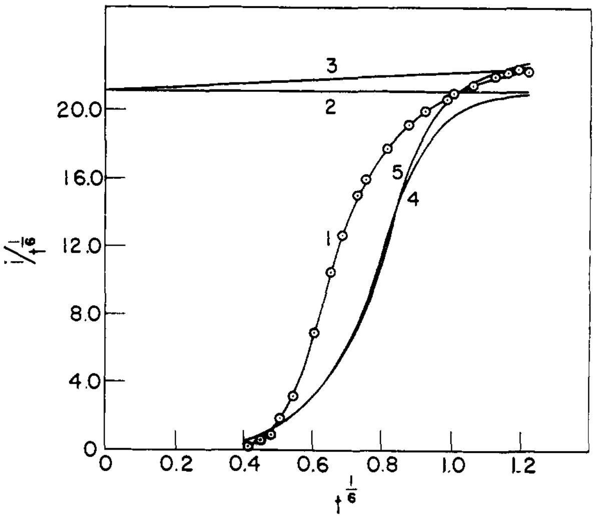

Fig. 1.—Theoretical and experimental current–time dependence at the dropping mercury electrode: (1) experimental data of Taylor, Smith and Cooter[4]; (2) theoretical curve based on simple Ilkovic equation; (3) theoretical curve based on Matsuda equation[1f] (very little difference exists in the slopes of the curves obtained from any of the two-constant solutions, *e.g.*, Lingane and Loveridge,[1d] Strehlow and von Stackelberg,[1h] etc.); (4) theoretical curve based on the proposed solution: plane approximation, parabolic initial gradient; (5) theoretical curve based on the proposed solution: spherical approximation, parabolic initial gradient.

Evaluation of the Proposed Solution

In the present study the consequences of the hypothesis that at a dropping mercury electrode the drop grows in a region of solution initially partially depleted in electroactive molecules by electrolysis at the preceding drop have been quantitatively developed. The behavior predicted in terms of the current–time relationship is substantially that encountered experimentally even during the initial stages of drop growth. However, before any conclusions about the success of the hypothesis can be drawn, it is necessary to evaluate a number of assumptions, which were made in the course of the analysis principally because of the lack of detailed experimental information about certain areas of physical behavior, and to attempt to estimate their effect on the result.

Convection Effect.—Most of the assumptions made are substantive in the sense that they are estimates of the magnitude or behavior of physical quantities. However, the mathematical procedure used includes an assumption of a different kind; for reasons that have been made clear, the Lingane and Loveridge method[1d] was used to account for the effect of convection due to drop growth on the magnitude of the current. The effect of this assumption, unlike that of the substantive ones, is difficult to assess. If one compares the Lingane and Loveridge approach with that of Matsuda[1f] in which this assumption was not required, one finds little difference in the formulas for the current derived by the respective methods. By analogy, it seems probable that the effect of the Lingane and Loveridge assumption on the present result is of the same small order.

Constancy of Mercury Flow.—It was assumed in the analysis that m, the mass rate of flow of mercury from the capillary, is constant throughout the drop life-time. This assumption is certainly incorrect.[2,3b,5b] However, very little is known, either theoretically or experimentally, about the nature of the time-dependence of m. Poiseuille's law frequently is combined with expressions relating to the back-pressure generated by the surface tension of a pendant mercury drop to obtain an expression for the flow rate of mercury as a function of time.[2] The difficulty with this procedure is that Poiseuille's law is valid only for conditions of *steady flow* and for liquids which wet the capillary, while expressions for the back-pressure are derived from a consideration of surface tension *equilibrium*, *i.e.*, for a *static* pendant drop. Thus the validity of the resulting equations, which express m as a function of the time, is open to question.

Lingane[3b] used such equations in discussing his data on the time-dependence of the current; from his discussion and by independent calculation, it appears that the instantaneous value of m is from 20 to 40% smaller at the beginning of drop formation than at the end. Granting the approximate validity of the equations, this variation is not nearly enough to explain the time-dependence of the current, unless, as Lingane points out, the introduction of a time-dependent m into the boundary value problem at the outset should considerably alter the form of the solution.

On the other hand, the physical drop, however small, is larger than the "mathematical" drop at the outset of drop life, since the former is always finite while the latter vanishes at time zero. Therefore, regardless of variations in the actual rate of flow of mercury, the current at the physical drop should exceed that at a mathematical drop immediately after the inception of drop formation because of the difference in their areas, *if the concentration is initially uniform.* Since the reverse is true when the mathematical drop is that considered in the "classical" derivations of the current–time relationship, it can be concluded that no argument based on the time-variation of m can explain completely the disparity between "classical" theory and experiment. It follows also that in the present derivation, in which the concentration is not initially uniform, the difference cited between mathematical and physical drop becomes unimportant.

Complete rigor in the inclusion of the time-dependence of m appears to be impossible at present because of mathematical difficulties. The results of the present analysis clearly indicate, however, that such inclusion should complement rather than replace the hypothesis introduced here. Very likely, the theoretical curves of Fig. 1 would be displaced upwards by a few per cent. at larger values of t and downwards by a somewhat larger percentage at low values of t, if a complete description of the variation of m were incorporated.

Sphericity of Depleted Region.—The depleted region was assumed to be spherical, which is certainly not true; the assumption can only represent an averaging of the asymmetry of the true shape of the depleted region. Some portions of the depleted shell are thin, leading to a steep concentration gradient and a localized high discharge rate of electroactive species at the electrode surface; elsewhere, the shell is thicker and the local current lower. It is not unreasonable to suppose that the total current, over the whole drop surface, might closely correspond to a uniform shell of depletion of a fictitious average thickness. If a less symmetrical shape were chosen for the depleted region, it would be necessary at some point in the mathematical development to perform an integration of the flux over this region; a kind of averaging would thus be necessary in any case. In addition, there is no experimental information available which could lead to a preference for any one possible shape over any other. The assumption of sphericity therefore seems both reasonable and expedient. Once this choice is made, a natural corollary is that the initial distribution of concentration in the depleted region is a function only of the radial distance.

The actual choices of a particular distribution function and of the fraction, q, representing the amount of depleted solution remaining after the fall of the previous drop, are not assumptions, *per se*, because these choices are made by trial only after the general mathematical development is complete. Moreover, the behavior of the current as a function of time is quite sensitive to such choice; the function selected controls the general appearance of the current–time function, and q its lateral position. Thus, the present solution, somewhat like that of Matsuda,[1f] is capable of indefinite improvement by a process akin to curve fitting.

Stirring Effect.—Heretofore it has been tacitly assumed that the fall of each successive drop causes no stirring of the solution left behind. Intuitively, this assumption seems improbable; in fact, many experimental oddities of polarography have been ascribed to anomalous "stirring" effects, without, however, careful definition of what was meant by "stirring" or precise experimental verification. However, two particularly appropriate studies[8] of the motion of spherical particles undergoing acceleration reveal that laminar flow about the particle prevails for an unexpectedly long period as the velocity increases. Smooth laminae of flow-streams continue to exist about the particle up to relatively high velocities, and the onset of the usual separation at the trailing end of the drop, as well as the general appearance of turbulence, seem to be considerably delayed by the mere fact of acceleration. It is reasonable to suppose, then, that in the first few millimeters of free fall, laminar flow of solution would persist about the just-separated mercury drop. Under these circumstances, a stirring motion of the solution, consisting of the intertangling of the flow laminae, would be extremely doubtful.[9]

A phenomenon which very well might occur, however, and which would superficially resemble stirring, is a circulation of the solution caused by the pumping action of the falling drops.[8] This circulation would extend throughout the whole solution and would consist of a downward motion of solution with the drop and resulting upward motion at the boundaries of the containing vessel. The downward circulation would lag the fall of the drop slightly and would be directed along the capillary axis with consequent distortion of the shape of the depleted region left by a given drop into a more or less cylindrical shape. If the diameter to length ratio of such a cylindrical region became small enough, no mathematical "averaging" procedure, by which an equivalent spherical volume replaced the cylindrical volume, could be adequate. The experimental result of such a phenomenon would be a very steep concentration gradient at the sides of the growing drop with a consequent high current. This current would be at its highest when the circulation velocity caused by the preceding drop was at its maximum in the neighborhood of the capillary tip.

For a slowly forming drop any disturbance resulting from such a circulation phenomenon would occur early in the drop life, at which time any exaltation of the current would be hard to distinguish from the normal growth of current (see Fig. 1). However, because of the pumping time lag mentioned, the same exaltation could occur for very rapidly growing drops, whose life-time is very short, when the drop is nearly full grown, and the increase would appear as a maximum on the current–time plot. Such a maximum is, in fact, displayed by one of the curves in Lingane's study[3b] (curve 1) which curve represents the shortest of the variety of drop life-times used, in qualitative support of the argument developed above.

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(8) (a) M. R. Carsten, *Trans. Am. Geophys. Union*, **33**, 713 (1952); (b) R. W. Moorman, Ph.D. Thesis, State University of Iowa, 1955.

(9) I. I. McKeown, personal communication.

None of the other assumptions necessary for the mathematical analysis of the extended Ilkovic problem (sphericity of the drop, isolation of the drop, etc.) are innovations, and none should have any important effect on the results. They have all been discussed previously, *e.g.*, reference 5b.

The authors wish to thank Dr. H. Strehlow, who called to their attention while the present paper was in proof the fact that W. Hans and W. Henne (*Naturwiss.*, **40**, 524 (1953)) had demonstrated experimentally the effect of depletion on the rate of growth of the polarographic current.

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ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE AVERY LABORATORY OF THE UNIVERSITY OF NEBRASKA]

Polarographic Reduction of Copper Chelates of 1,3-Diketones. III. Solvent Effects

BY E. R. NIGHTINGALE, JR., AND HENRY F. HOLTZCLAW, JR.

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The influence of the solvent upon the polarographic reduction of the copper chelates of some 1,3-diketones has been investigated. The half-wave potential is demonstrated to vary linearly with the reciprocal of the dielectric constant of the solvent, and this is attributed to the difference in the free energy necessary to charge the ionic products of the electrode reaction in the dielectric medium of the various solvents. The diffusion current constants of some chelates are observed to obey a Stokes–Einstein relation when corrected for the differences in the viscosities of the solutions. For certain of the substituted diketones, the Stokes–Einstein relationship is less satisfactory. These deviations are interpreted in terms of the size and structure of the substituted chelate molecule.

Previous articles from these laboratories[1,2] have discussed the polarographic reduction of the copper chelates of several 1,3-diketones in various solvents. In particular, the second paper in this series has considered the relation between the polarographic half-wave potentials observed in the various solvents and the structure and electrophilic character of the chelate ligand. Considerable variation in the diffusion current constants for the reduction of the various copper chelates was reported. No over-all trend in diffusion current constants was apparent, although trends of some significance could be noted by comparing small groups of chelates possessing similar ligands. The present paper investigates the influence of the solvent upon the reduction of the copper chelates and demonstrates that the dielectric constant and viscosity of the solution play important roles in determining the ease of reduction and the magnitude of the reduction current for the electrode reaction in the various solvents.

Experimental

The polarographic procedures and experimental details have been described in the previous papers.[1,2]

The viscosities of the ethanol, 2-methoxyethanol and dioxane solutions were measured at 25.00 ± 0.01° with an Ostwald viscometer. The viscometer was calibrated at 20, 25 and 30° with water and at 25° with 20 and 30% sucrose solutions. Details have been described elsewhere.[3] The viscosities of the three solutions, each 0.1 *M* in potassium nitrate, are 75 vol. % ethanol in water, 0.0214 poise; 75 vol. % methoxyethanol in water, 0.0388 poise; and 75 vol. % dioxane in water, 0.0190 poise. The absolute viscosity of water was taken as 0.008903 poise at 25°.[4] The dielectric constants for the ethanol, methoxyethanol and dioxane solutions have been taken as those of the pure solvents, 37.9,[5] 27.7[6] and 13.6,[5] respectively.

Results and Discussion

When copper(II) is complexed with the various 1,3-diketones, stable chelates with the empirical formulas CuX_2 are formed[7,8] where X is the monobasic chelate ligand. The primary electrode reaction for the reduction of these compounds at the dropping mercury electrode (DME) is given by equation 1

$$CuX_2 + yHg + 2e^- = Cu(Hg)_y + 2X^- \quad (1)$$

However, the chelate ions are the conjugate bases of very weak acids[9] and hydrolyze rapidly in water. Hence, the over-all reaction, for which the electrode potential is a measure of the free energy, is given by

$$CuX_2 + yHg + 2H_2O + 2e^- = Cu(Hg)_y + 2OH^- + 2HX \quad (2)$$

This investigation has considered the effect of the solvent upon (a) the change in the polarographic half-wave potential for the reduction of the copper chelate according to equation 2, and (b) the magnitude of the diffusion current constant for a given copper chelate in the various solvents.

Variation of $E_{1/2}$ with Solvent.—The half-wave potential, $E_{1/2}$, for a rapid (reversible) polarographic reaction is a measure of the standard free energy of the reaction. For slow (irreversible) reactions, the half-wave potential is a function of both the heterogeneous rate constant at a standard potential and the transfer coefficient and is not necessarily related in a simple manner to the free energy for the reaction. An excellent discussion of irreversible polarographic processes has been presented recently by Randles.[10]

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