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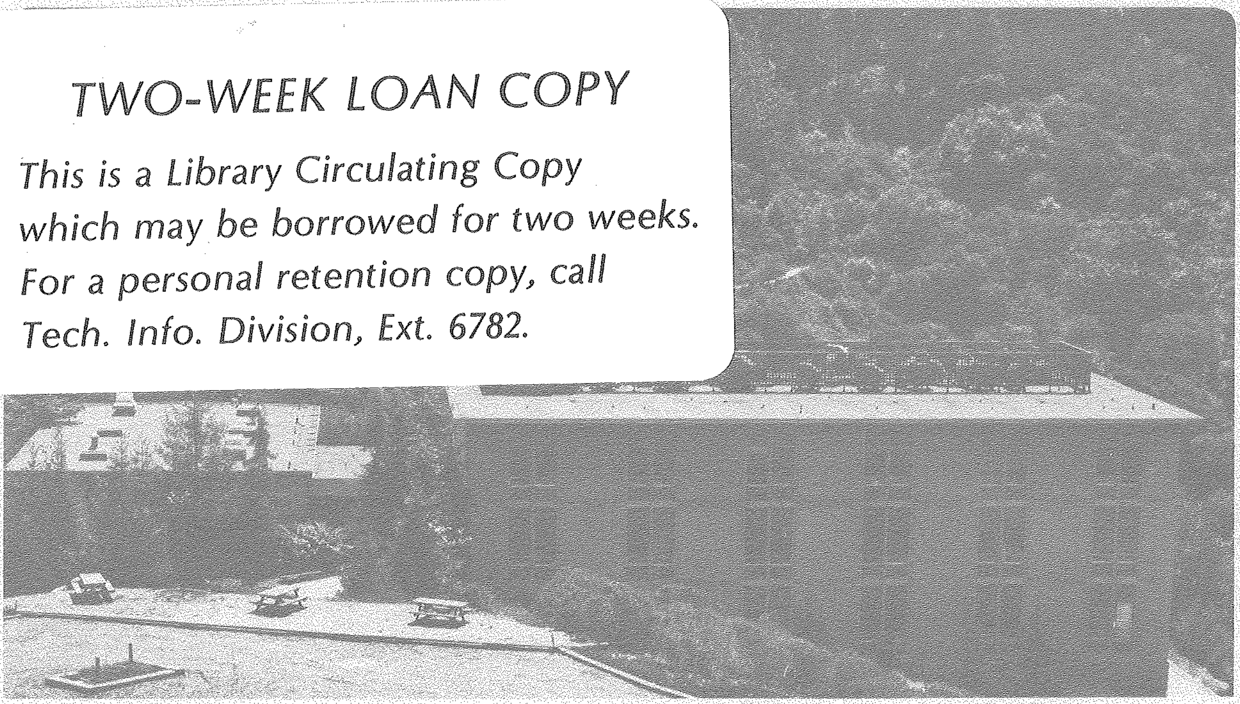

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Characteristics of the Dropping-Mercury Electrode Below the Limiting Current

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Abstract

A model has been developed to describe the combined effect of electrochemical kinetics, ohmic potential drop, and mass transfer for a metal-deposition reaction at a dropping-mercury electrode. Current, potential, and surface concentration are expressed in terms of two parameters which characterize the results. For certain parameters, even in the presence of an excess of supporting electrolyte, the current density from a metal-deposition reaction can exceed the mass-transfer limit calculated by Ilkovič.

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Introduction

Polarographic analysis with a dropping-mercury electrode is usually carried out in the presence of a large excess of indifferent, nonreacting electrolyte. This serves to reduce the ohmic potential drop in the solution and to reduce the effect of the electric field on the movement of reacting ionic species. For a sufficiently large applied potential, the current to the drop is limited by the rate of diffusion and convection and corresponds to a zero concentration of reactant at the surface. In this situation, the cathodic current density is given by the Ilkovič equation[1-3], provided that the volumetric flow rate of mercury through the capillary is constant.

Theoretical equations for polarographic limiting currents have also been developed for a number of systems involving specific combinations of chemical and electrochemical reactions[4-9]. These studies have focused attention on the interactions between homogeneous and heterogeneous processes and, generally, the importance of ohmic potential drop in the solution and surface overpotentials for the electrochemical reactions has not been evaluated. However, early qualitative studies indicated that, if there is insufficient supporting electrolyte, the current due to one discharging species could produce an electric field that enhances the limiting current for other reactants[1,10].

The influence of ohmic potential drop on the distribution of current has been analyzed for disk, ring, and ring-disk electrodes[11-13], as well as for planar[14], tubular[15], and spherical electrodes[16]. With smaller electrolyte conductivity, the distributions of current and concentration become more nonuniform and, under some circumstances, local current densities can exceed the local limiting current. A review of current and potential distributions for various geometries is given by Newman[17].

The instantaneous current and the average current to a dropping mercury electrode in a binary salt solution have been calculated[18]. This analysis showed that ohmic potential drop can prevent the attainment of a limiting current during the initial stage of growth of the drop, particularly if the applied voltage is small.

In this paper, a general model is presented for the dropping mercury electrode below the limiting current. The analysis includes the effects of mass transfer, ohmic potential drop in the solution, and electrode kinetics. Factors that govern the relative importance of these effects are identified for the example of a metal deposition reaction.

It is pointed out that the general approach presented here can be used to evaluate experimental situations different from traditional polarography. For example, the potential may not be constant throughout the life of the drop; the drop may not grow with the cube root of time.

Analysis

At currents below, but at an appreciable fraction of, the limiting current, it is necessary to consider the surface overpotential associated with the electrode reaction, the ohmic potential drop in the bulk of the solution, and concentration variations near the drop surface. The analysis presented here is restricted to a single electrode reaction with stoichiometry represented by:

$$\sum_i s_i M_i^{z_i} \rightarrow ne^- . \tag{1}$$

A polarization equation of the form

$$i = i_o \left[e^{\alpha_a F\eta_s/RT} - e^{-\alpha_c F\eta_s/RT} \right] \tag{2}$$

can be used to express the dependence of the reaction rate on the surface overpotential, $\eta_s = V - \Phi_o - U_o$. The exchange current density can be written as

$$i_o = i_{o,ref} \prod_i \left(\frac{c_{i,o}}{c_{i,ref}} \right)^{\gamma_i} \prod_k a_k^{\gamma_k} , \tag{3}$$

and the theoretical open circuit cell potential is given by[19]

$$U_o = U^\theta - U^\theta_{ref} - \frac{RT}{nF} \sum_i s_i \, \ell n \, \frac{c_{i,o}}{\rho_o} + \frac{RT}{n_{ref}F} \sum_i s_{i,ref} \, \ell n \, \frac{c_{i,ref}}{\rho_o} , \tag{4}$$

provided that activity-coefficient corrections can be neglected. Furthermore, exponents γ_i for ionic species in Eq. (3) are given the values

$$\gamma_i = q_i + \frac{\alpha_c s_i}{n} \tag{5}$$

where $q_i = -s_i$ for a cathodic reactant and is zero otherwise[20]. For a metal deposition reaction, and with a reference electrode of the same kind, Eq. (4) reduces to

$$U_o = \frac{-s_i RT}{nF} \, \ell n \left(\frac{\theta_i}{\theta_m} \right) , \tag{6}$$

where $\theta_i = c_{i,o}/c_{i,ref}$ and $\theta_m = c_{m,o}/c_{m,ref}$. Here and for the remainder of the paper the subscript i refers to the metal ion. The activity coefficients of metallic species are assumed to be unity. Consequently, substitution of Eqs. (3), (5), and (6) into Eq. (2) gives, on rearrangement:

$$i = i_{o,ref}\left[\theta_m e^{\alpha_a F(V-\Phi_o)/RT} - \theta_i e^{-\alpha_c F(V-\Phi_o)/RT}\right] . \tag{7}$$

Furthermore, the bulk solution potential Φ_o can be evaluated at the drop surface from the resistance relationship for a spherical drop in a solution of uniform conductivity.

$$\Phi_o = \frac{ir_o}{\kappa} \tag{8}$$

For radial growth of a mercury drop without tangential surface motion, the reactant concentration obeys the equation of convective diffusion in the form

$$\frac{\partial c_i}{\partial t} + v_r \frac{\partial c_i}{\partial r} = \frac{D_i}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial c_i}{\partial r}\right) , \tag{9}$$

where the velocity v_r is determined by the growth rate of the drop:

$$v_r = \left(\frac{r_o}{r}\right)^2 \frac{dr_o}{dt} . \tag{10}$$

Equation (9) can be expressed in terms of the normal distance y from the surface of the drop, provided that the diffusion layer is thin compared to the drop radius throughout the lifetime of the drop:

$$\frac{\partial c_i}{\partial t} - \frac{2y}{r_o}\frac{dr_o}{dt}\frac{\partial c_i}{\partial y} = D_i \frac{\partial^2 c_i}{\partial y^2} . \tag{11}$$

A similar equation applies inside the sphere, but with the diffusion coefficient D_s of the discharged reactant in mercury.

The diffusion equation can be solved subject to the conditions

$$\begin{aligned} c_i &= c_{i,\infty} \quad \text{for} \quad t \leq 0 \\ c_i &\to c_{i,\infty} \quad \text{as} \quad r \to \infty \quad \text{for} \quad t > 0 \\ c_i &= c_{i,o}(t) \quad \text{at} \quad r = r_o \quad \text{for} \quad t > 0 \end{aligned} \tag{12}$$

By superposition, the results can be used to express the concentration derivative at the surface in terms of an integral over the variation of surface concentration during the drop lifetime[21]:

$$\left.\frac{\partial c_i}{\partial y}\right|_{y=o} = -\frac{2r_o^2}{\pi^{1/2}} \int_o^t \left.\frac{dc_{i,o}}{dt}\right|_{t=t_o} \frac{dt_o}{\left[4D_i \int_{t_o}^{t} r_o^4 dt\right]^{1/2}} \tag{13}$$

The surface fluxes, both inside and outside the drop, can be related to the instantaneous current density by an expression of the form:

$$\frac{s_i i}{nF} = D_i \left.\frac{\partial c_i}{\partial y}\right|_{y=o} \tag{14}$$

This equation is restricted not only to the large excess of supporting electrolyte, where the effects of migration can be neglected, but also to the absence of appreciable charging of the double layer, a process which does not follow Faraday's law. Concentration changes within the drop can be related to external changes by equating the superposition integrals for the two regions through Eq. (14). This gives

$$\theta_m = \theta_m(0) + \left(\frac{D_i}{D_s}\right)^{1/2} \frac{1-\theta_i}{\theta_s} , \tag{15}$$

where $\theta_s = c_{m,ref}/c_{i,ref}$.

The model presented here is more general than the approach taken by Ilkovič since two basic constraints made in his development can be removed. Namely, the potential can vary throughout the life of the drop and can be expressed, for example, as

$$V = V_{int} + \beta t$$

where β is the scan rate of the applied potential. Also it is not necessary to maintain a constant flow rate of mercury through the capillary. Removal of the last constraint is particularly important in evaluating the characteristics of modern polarographic equipment. Although results presented here do not evaluate the importance of scan rate and constant flowrate, it is appropriate to indicate the general utility of this model.

When the volumetric flowrate of mercury is constant, the growth rate is given as

$$r_o = \gamma t^{1/3} . \tag{16}$$

With this growth rate, the governing equations (7) and (13) for the dropping-mercury electrode below the limiting current can be expressed in dimensionless form as

$$\phi_o = -N \int_0^{N^{-6}} \left. \frac{d\theta_i}{d(N^{-6})} \right|_{N=N_1} \frac{d(N_1^{-6})}{\left\{1- \left[(N_1^{-6})/(N^{-6})\right]^{7/3}\right\}^{1/2}} \tag{17}$$

$$\phi_o N^2 = K\left[\theta_m e^{-\alpha_a(E+\phi_o)/\alpha_c} - \theta_i e^{E+\phi_o}\right] , \tag{18}$$

where $\phi_o = \alpha_c F r_o i/\kappa RT$, $E = -\alpha_c FV/RT$, and N^{-6} is a dimensionless time given by

$$N^{-6} = \left[\left(\frac{\kappa RT s_i}{\alpha_c n F^2 c_{i,\infty} \gamma}\right)^2 \frac{3\pi}{7D_i}\right]^3 t . \tag{19}$$

The dimensionless parameter K represents a combination of quantities associated with kinetic, ohmic, and mass-transfer effects:

$$K = \frac{7i_{o,ref}}{3\pi}\left(\frac{\alpha_c F\gamma}{\kappa RT}\right)^3 \left(\frac{Fn}{s_i} c_{i,\infty}\right)^2 D_i \ . \qquad (20)$$

In Eqs. (17) and (18), ϕ_o and θ_i are dependent variables and N^{-6} is the independent variable. The parameters E and K are expected to have a significant impact on the system behavior, whereas α_a/α_c , D_i/D_s, and $\theta_s\theta_m(0)$ are of relatively minor importance and should not influence the results markedly.

The governing equations (17) and (18) are solved by a stepwise numerical procedure that involves discretization of the integral equation and a Newton-Raphson technique to obtain values for ϕ_o and θ_i at each time step[22,23]. Since the variables may vary very rapidly at short times, it is necessary to vary the step size to ensure accurate results. In addition, the initial singularity in equation (17) is avoided by using a short-time series expansion for the concentration derivative over the first time interval.

Results and Discussion

The time dependence of the dimensionless potential ϕ_o is presented in figure 1 for several values of the parameters E and K . This diagram also depicts changes in the instantaneous current density through the relationship, $\phi_o = \alpha_c F r_o i/\kappa RT$.

Lines of slope 1/3, 0, and -1/6 represent the kinetic, ohmic, and mass-transfer limits, respectively. Figure 1 illustrates that it is not

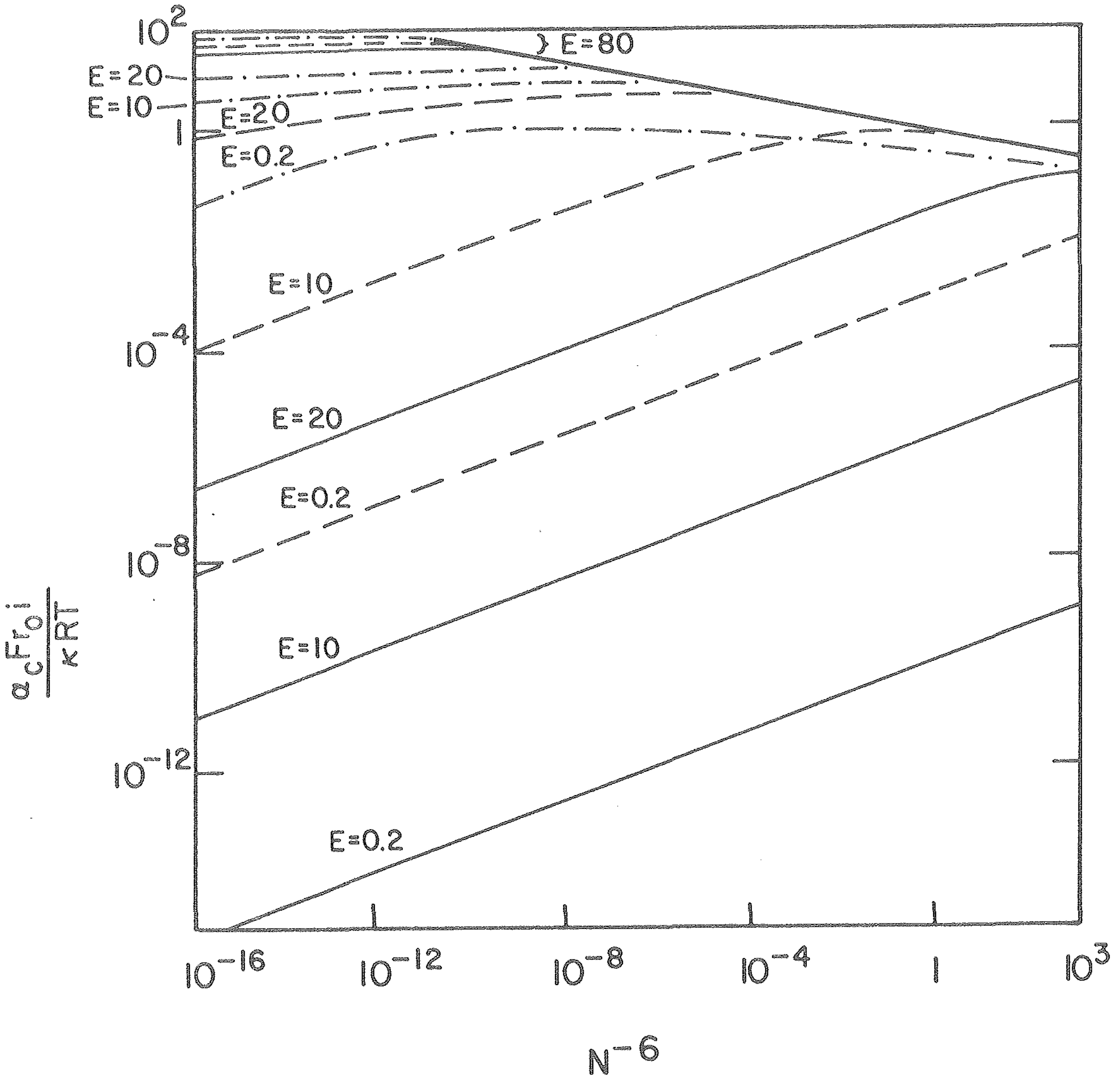

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Fig. 1. Time dependence of dimensionless, instantaneous current density, $\phi_o = \alpha_c Fr_o i/\kappa RT$, for a metal deposition reaction at a growing mercury drop. Parameter values: $D_i/D_s = 1.0$; $\alpha_a/\alpha_c = 1.0$; $\theta_s = 1.0$; $\theta_m(0) = 0.0$; $c_{i,ref} = c_{i,\infty}$

———————— $K = 10^{-10}$

– – – – – – – $K = 10^{-3}$

– . – . – . – $K = 10^{4}$

possible to generalize the results for large and small values of E and K. Clearly, both parameters are influential in determining ϕ_o. For large times and moderate to large values of E, ϕ_o is independent of K and E in accordance with the Ilkovic equation. However, at short times, kinetic factors and, subsequently, ohmic factors can prevent attainment of the mass-transfer limit. These effects are particularly important for small values of K or E. A reduction in K corresponds to a smaller exchange current density, bulk reactant concentration, diffusion coefficient, or drop growth rate, or a larger electrolyte conductivity. A larger electrolyte conductivity will also reduce the ohmic potential drop in the solution, and consequently ohmic limitations are less prevalent with small values of K, for a specified magnitude of E. Furthermore, the effect of K is more pronounced at small values of E.

The parameter E is a dimensionless applied potential which includes the cathodic transfer coefficient for the deposition reaction. As E is increased, ohmic factors have progressively more impact upon the short-time behavior. The ohmic limit is given by

$$\phi_o = E \; . \tag{21}$$

For $E = 80$ the three curves in figure 1 are almost horizontal and superimposed upon each other. However, even under these conditions, the curves are not precisely horizontal due to the finite rate of the electrochemical reaction. The mass-transfer limit is represented by

$$\frac{\phi_o}{N} = 1 - \exp\left(\frac{nE}{s_i\alpha_c}\right) \tag{22}$$

where

$$\frac{\phi_o}{N} = \frac{i}{i_{lim}} = 1 - \frac{c_{i,o}}{c_\infty} \tag{23}$$

At large applied potentials, the intersection of the ohmic and mass-transfer limits can be identified from eq. (21) and eq. (22) as $\phi_o = N = E$.

Figure 2 shows the time dependence of the average current density defined by

$$i_{avg} = \frac{1}{T_d} \int_o^{T_d} i \, d \, t \tag{24}$$

for fixed values of E and K . This average current is made dimensionless in the same manner as figure 1. Total currents can be obtained directly from the relation $I = 4\pi r_o^2 i$. Figures 1 and 2 are analogous, except that the magnitude of the current densities in figure 2 have been altered in accordance with eq. (24).

The time dependence of the surface concentration is presented in figure 3. Rapid reductions in composition are observed for large values of E and K , in keeping with the early onset of mass-transfer limitations predicted in figure 1, for similar conditions. With small applied potentials, and particularly for small values of K , kinetic factors can control the deposition rate, and the corresponding variations in concentration are less marked.

Figure 4 shows the variations in instantaneous current density normalized with the mass-transfer limiting current density defined by eq. (23). Values in excess of the mass-transfer limit of Ilkovič are obtained. This is similar to results obtained with disk[11], ring[12], and plane[14] electrodes. In transient stagnant-diffusion-cell experiments,

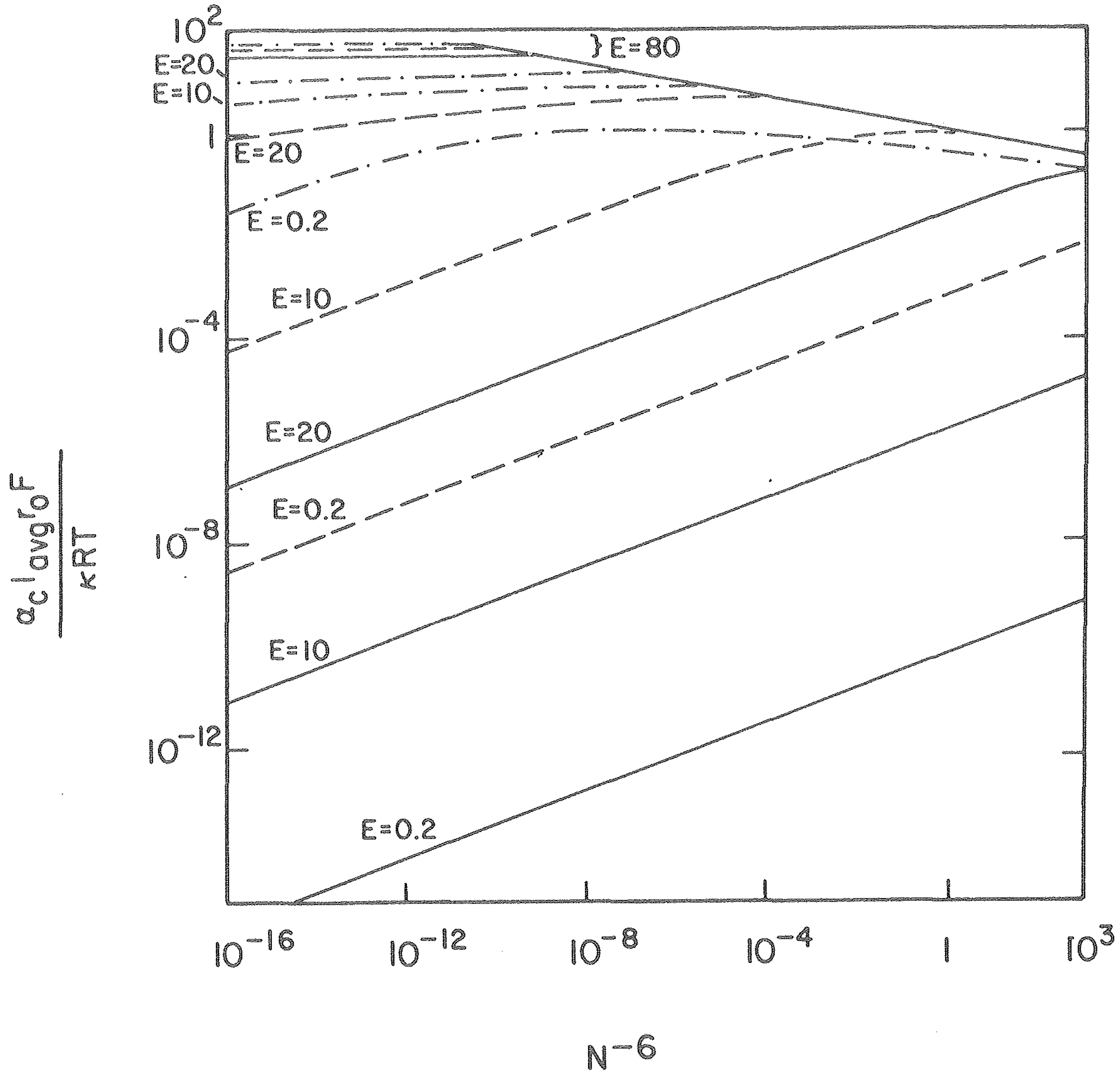

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Fig. 2. Time dependence of dimensionless average current density, $\alpha_c Fr_o i_{avg}/\kappa RT$, for a metal deposition reaction at a growing mercury drop. Parameters as in Fig. 1.

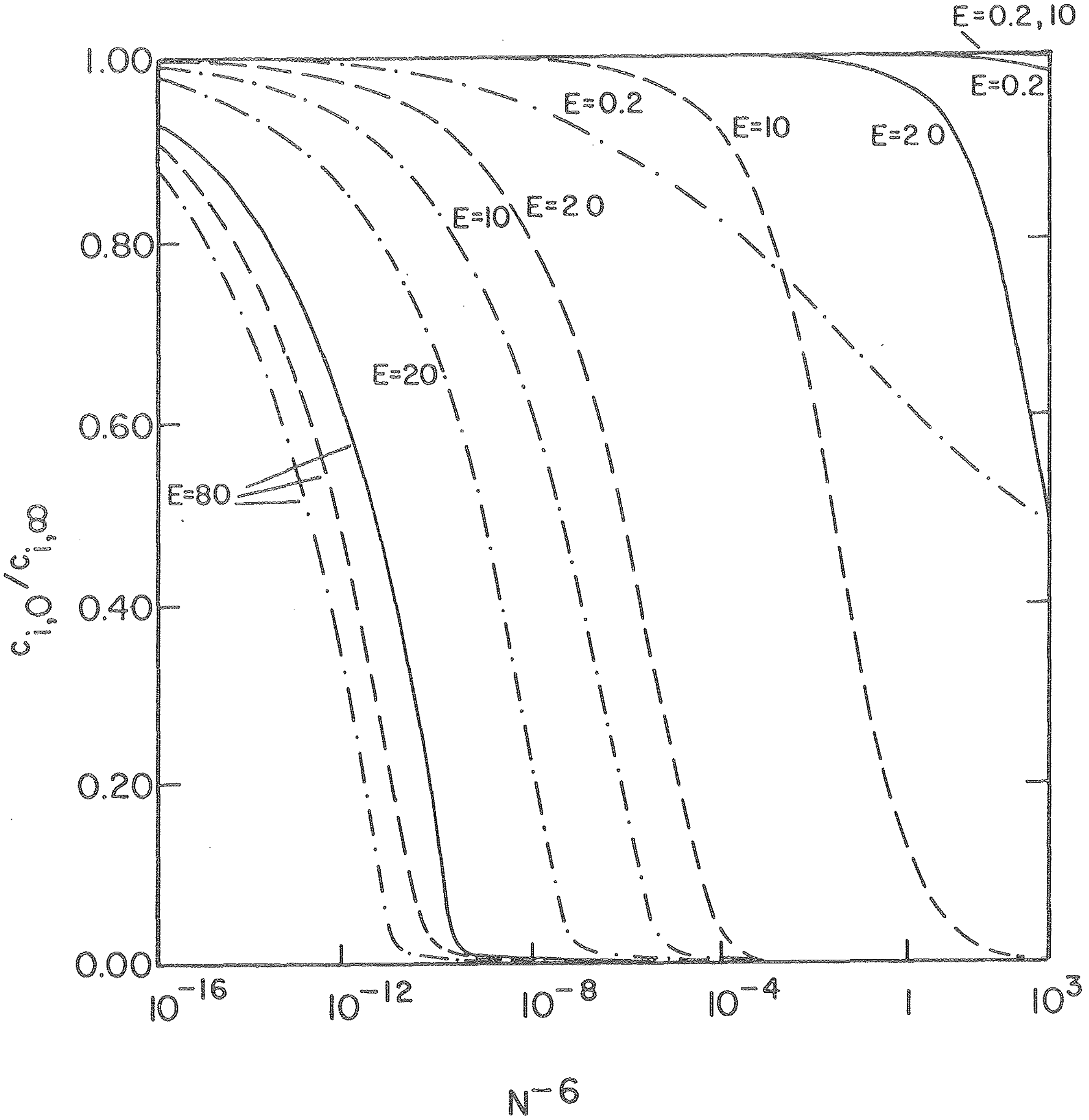

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Fig. 3. Time dependence of dimensionless surface concentration, θ_1. Parameters as in Fig. 1.

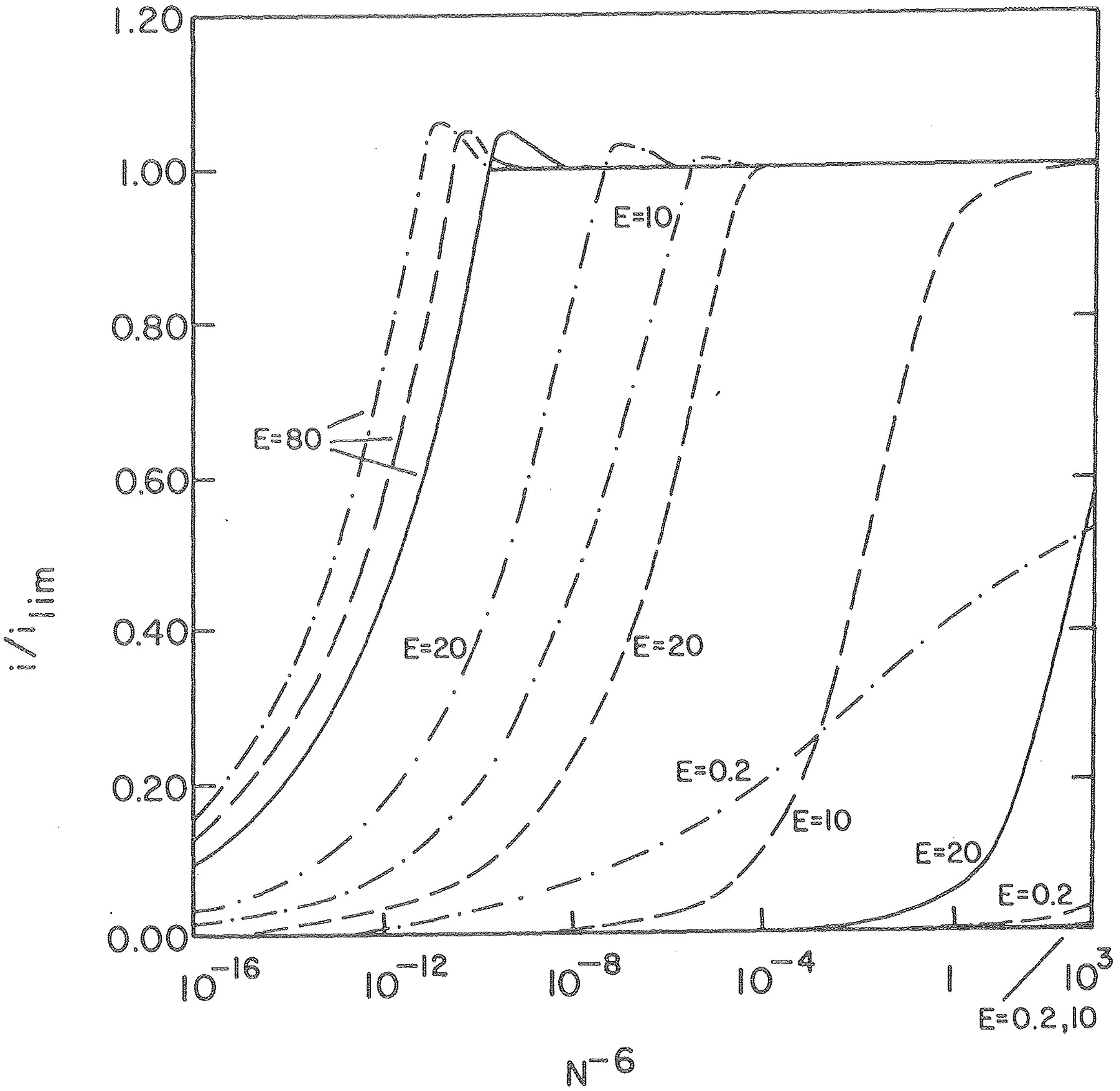

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Fig. 4. Time dependence of the instantaneous current density normalized with the instantaneous current density in the mass-transfer limit. Parameters as in Fig. 1.

current densities measured and calculated by Hsueh and Newman were found to overshoot the mass transfer limit[24]. Material adjacent to the drop surface that does not react at short times can do so, subsequently, when kinetic and ohmic factors no longer limit the reaction rate. In contrast, figure 5 illustrates the average current density obtained from eq. (24) which rises monotonically to the average limiting current density calculated with the Ilkovic equation. The average current density cannot exceed the average limiting current density.

Figures 1-5 pertain to the behavior of an individual drop. An example of polarographic curves for a metal deposition reaction is presented in figure 6. The parameters for the two curves are given in Table 1. The curves result from a number of drops formed sequentially over a range of potentials. The different values of $i_{o,ref}$ illustrate their effect on attainment of the mass-transfer plateau.

The analysis considered above does not account for the capacitive current needed to charge the mercury-solution interface. To assess the effects of the capacitive current the total current can be expressed as

$$I = I_f + I_{nf} \tag{25}$$

where for linear kinetics

$$I_f = 4\pi r_o^2 \, i_{o,ref} \frac{F}{RT} (\alpha_a + \alpha_c)(V - \Phi_o - U_o) \; . \tag{26}$$

The capacitive term is

$$I_{nf} = \frac{d}{dt}\left[4\pi r_o^2 \left\{q_o + C[V - \Phi_o - U_o]\right\}\right] \tag{27}$$

q_o is the charge on the interface when $V - \Phi_o = U_o$. Substitution

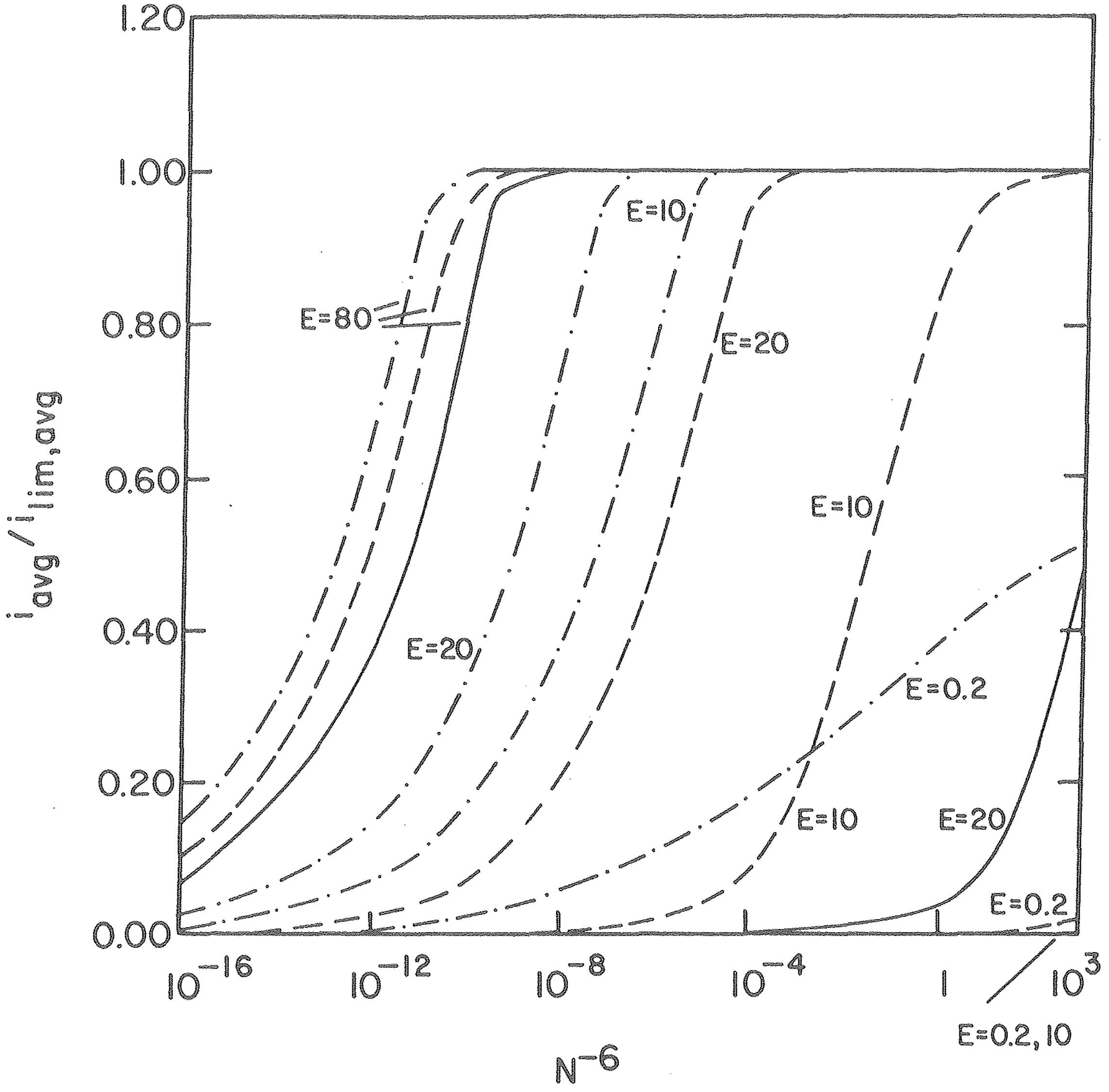

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Fig. 5. Time dependence of the average current density normalized with the average current density predicted with the Ilkovič equation. Parameters as in Fig. 1.

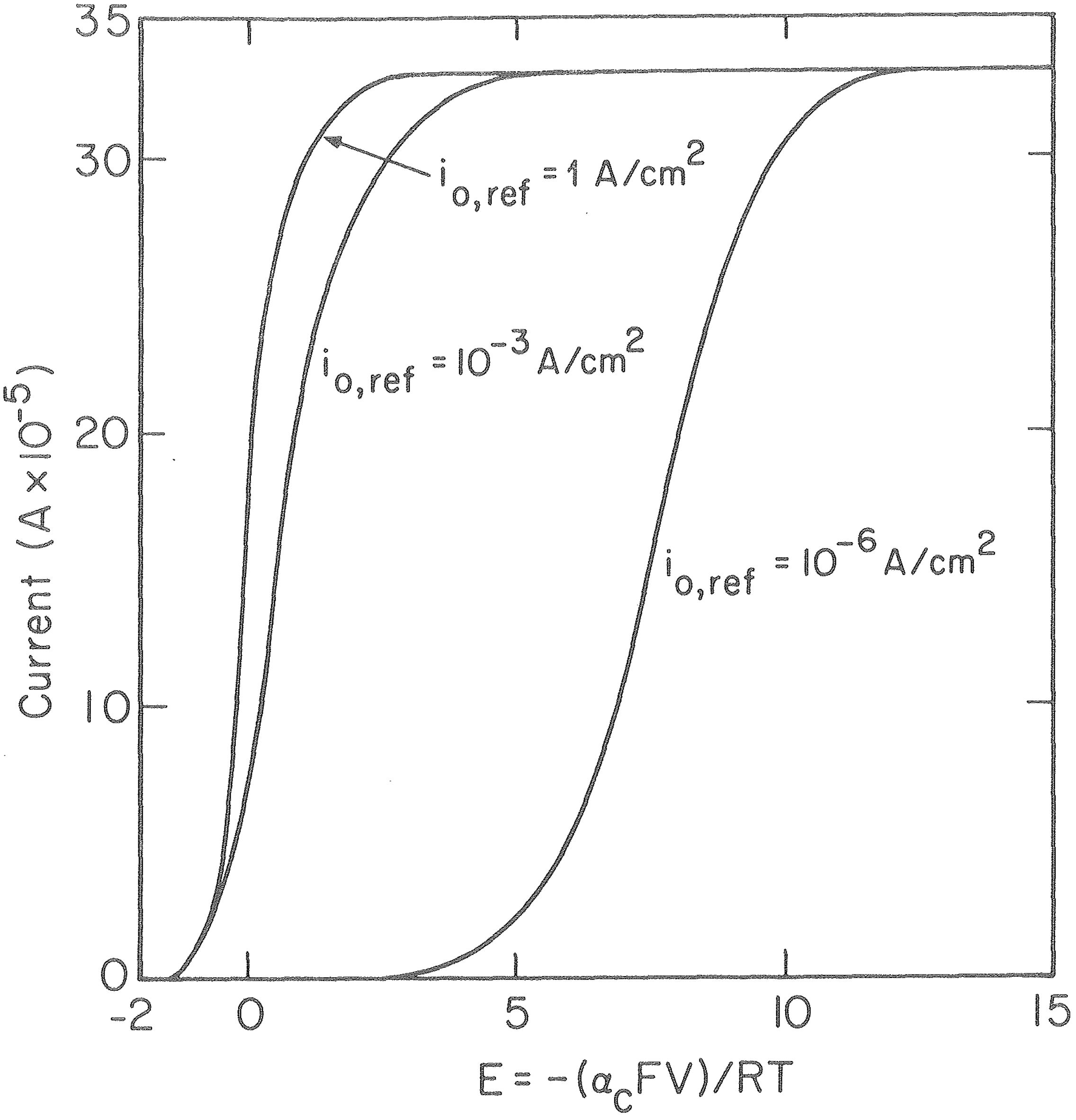

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Fig. 6. The effect of $i_{o,ref}$ on attainment of the mass-transfer plateau. Curves are for a number of drops at constant potential formed sequentially.

Table 1

$c_{i,\infty} = 5.81\mathrm{x}10^{-6}\ \mathrm{mol/cm}^3$

$\alpha_a = 1.5\ ,\quad \alpha_c = 0.5$

$D_i = 7.5\times10^{-6}\ \mathrm{cm}^2/\mathrm{s}$

$\kappa = 0.54373\ (\mathrm{ohm\text{-}cm})^{-1}$

$\gamma = 0.10\ \mathrm{cm/s}^{1/3}$

$t_{\mathrm{drop}} = 1.0\ \mathrm{s}$

Parameters used by R. White and J. Newman, reference 25.

of eq. (26) and eq. (27) into eq. (25) with use of eq. (8) yields

$$4\pi\kappa\gamma t^{1/3}\Phi_o = 4\pi\gamma^2 t^{2/3}\, i_{o,ref}\frac{F}{RT}(\alpha_a + \alpha_c)(V - \Phi_o - U_o)$$
$$+ \frac{8\pi\gamma^2}{3t^{1/3}}\left[q_o + C(V - \Phi_o - U_o)\right]$$
$$- 4\pi\gamma^2\, t^{2/3} C\frac{d\Phi_o}{dt} \qquad (28)$$

This equation can be rearranged to show the importance of the faradaic and nonfaradic contribution to the total current.

$$tC\frac{d}{dt}\left(1 - \frac{\Phi_o}{V-U_o}\right) + \frac{2}{3}C\left(1 - \frac{\Phi_o}{V-U_o}\right) + \frac{i_{o,ref}(\alpha_a+\alpha_c)Ft}{RT}\left(1 - \frac{\Phi_o}{V-U_o}\right)$$
$$= -\frac{2}{3}\frac{q_o}{(V - U_o)} + \frac{\kappa\,\Phi_o\, t^{2/3}}{\gamma(V-U_o)} \qquad (29)$$

The last term on the left side of eq. (29) is the result of the faradaic process; the last term on the right represents the total current; whereas, the remaining terms account for the nonfaradaic process.

The charging current, represented by the second term in eq. (29), should be considered for

$$t < \frac{2}{3}\frac{CRT}{i_{o,ref}(\alpha_a+\alpha_c)F} \quad . \qquad (30)$$

For typical values of the parameters $C = 30\ \mu f/cm^2$, $i_{o,ref} = 10^{-4}\ A/cm^2$, $(\alpha_a + \alpha_c) = 1$, the nonfaradaic current is equivalent to the faradaic current at about 5 ms.

The above criterion expressed in eq. (30) actually applies only for

$$\frac{i_{o,ref}(\alpha_a+\alpha_c)}{2\kappa}\;\frac{F\gamma}{RT}\left(\frac{C\gamma}{3\kappa}\right)^{1/2} < 1 \tag{31}$$

(the usual case). In the contrary case, the charging current (represented by the first term in eq. (29)) would need to be considered for

$$t < (C\gamma/3\kappa)^{3/2} \tag{32}$$

One should be reminded that eq. (29) has not considered mass-transfer effects.

Summary and Conclusions

A model is presented for the current and potential distributions of a dropping-mercury electrode below the limiting current. Results are dependent upon a potential parameter E and an additional parameter K which reflects the relative importance of the kinetic, ohmic, and mass-transfer resistances. For relatively large values of these parameters, the instantaneous current density of a metal deposition reaction in the presence of an excess of supporting electrolyte can exceed the mass-transfer limiting value given by Ilkovič.

Acknowledgment

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Nomenclature

a_k	relative activity of species k
C	capacity of the double layer; c/V-cm^2
c_i	concentration of species i , mol/cm^3
$c_{i,o}$	surface concentration of species i , mol/cm^3
$c_{i,ref}$	reference concentration of species i , mol/cm^3
$c_{i,\infty}$	bulk concentration of species i , mol/cm^3
$c_{m,o}$	surface concentration of discharged metal, mol/cm^3
$c_{m,ref}$	reference concentration of discharged metal, mol/cm^3
D_i	diffusion coefficient of species i in the electrolyte, cm^2/s
D_s	diffusion coefficient of discharged metal in mercury, cm^2/s
E	dimensionless applied voltage, $E = -\alpha_c FV/RT$
F	Faraday's constant (96487 C/mol)
i	instantaneous current density, A/cm^2
i_{avg}	average current density defined by eq. (24)
i_{lim}	current density in mass-transfer limit, as predicted with the Ilkovič equation, A/cm^2
$i_{lim,avg}$	average current density in mass transfer limit, A/cm^2
i_o	exchange current density, A/cm^2
$i_{o,ref}$	exchange current density at reference concentrations of reactants and products, A/cm^2
I	total current, A

K	dimensionless parameter defined by eq. (20)
M_i	symbol for the chemical formula of species i
n	number of electrons transferred in electrode reaction
n_{ref}	number of electrons transferred in reference electrode reaction
N	dimensionless parameter defined by eq. (19)
q_i	reaction order for cathodic reactants
q_o	charge on the mercury-solution interface at open circuit, C/cm^2
r	radial coordinate, cm
r_o	drop radius, cm
R	universal gas constant (8.3143 J/mol·K)
s_i	stoichiometric coefficient of species i in electrode reaction
$s_{i,ref}$	stoichiometric coefficient of species i in reference electrode reaction
t	time, s
T	absolute temperature, K
T_d	drop lifetime, s
U_o	theoretical open-circuit potential for electrode reaction at the composition prevailing locally at the drop surface, relative to a reference electrode of a given kind, V
U_j^θ	standard electrode potential for reaction j, V
V	applied voltage, V
v_r	radial velocity, cm/s

y	distance from drop surface, $y = r - r_o$, cm

Greek Letters

α_a	transfer coefficient in anodic direction
α_c	transfer coefficient in cathodic direction
γ	constant defined by eq. (16)
γ_i	exponent in eq. (3) and defined by eq. (6)
γ_k	exponent in eq. (3)
η_s	surface overpotential, V
θ_i	dimensionless reactant concentration, $c_{i,o}/c_{i,ref}$
θ_m	dimensionless product concentration, $c_{m,o}/c_{m,ref}$
$\theta_m(0)$	initial dimensionless product concentration
θ_s	ratio of reference concentrations, $c_{m,ref}/c_{i,ref}$
κ	solution conductivity, mho/cm
ρ_o	density of pure solvent, g/cm^3
Φ_o	electric potential in the solution, immediately adjacent to the drop surface, V
ϕ_o	dimensionless electric potential, $\phi_o = \alpha_c F r_o i/\kappa RT$

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