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Influence of Langmuirian Adsorption of Reactant and Product upon Charge-Transfer Processes in Polarography

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On the basis of the diffusion layer concept, the influence of a Langmuirian adsorption of reactant and product upon voltametric curves at dropping and stationary electrodes is considered. The surface concentrations of the electroactive species affect the charge-transfer process for relatively high values of the rate constant, k_s , at the standard potential. A progressive decrease in k_s causes (i) the polarographic normal wave following the adsorption prewave to become irreversible and to shift toward increasing overvoltages in the case of predominant adsorption of the product, and (ii) the polarographic normal wave to merge with the following adsorption postwave in the case of predominant adsorption of the reactant. If the adsorption coefficients of the reactant O and of the product R are of different orders of magnitude, an appreciable difference is observed between the slopes of the normal waves given, respectively, by solutions of O and R of equal concentrations. Thus the electroactive substance preferentially adsorbed gives waves with higher slopes. If the adsorption coefficients of reactant and product are of the same order of magnitude, no pre- or postwaves are to be expected and an increase in the concentration of the reactant causes a decrease in the slope of the normal wave until the minimum slope corresponding to total irreversibility is reached. Simultaneously, the wave shifts toward increasing overvoltages.

Introduction

Since the pioneering work of Brdička¹ on the nature of adsorption waves, a great deal of work has been devoted to the study of adsorption effects upon polarographic currents. In interpreting adsorption waves, Brdička¹ claims that the adsorbed molecules of reactant or of product are not reduced or oxidized in the normal wave but rather in the adsorption postwave or prewave. This amounts to stating that a substance, which is in the condition of being specifically adsorbed and therefore of occupying the inner Helmholtz plane, can be electroreduced or -oxidized at the outer Helmholtz plane without passing through the adsorbed state. This assumption is in contrast with several experimental findings. Thus the presence of maxima in the polarographic waves of several organic substances has been interpreted^{2,3} as due to a slow charge transfer involving the specifically adsorbed reactant. The anomalous behavior of these waves is attributable to a change in the adsorption coefficient of the reactant with applied potential.

The aim of the present note is to show the effect of the electrode coverage by reactant and product upon the rate of the charge-transfer process in the case of a Langmuirian adsorption. It will be shown that the equations for the polarographic current derived by Brdička¹ hold even when the electroactive substances exchange charges with the electrode exclusively in the adsorbed state.

Formulation of the Problem

Consider a simple redox system O-R where neither O nor R is involved in reactions other than the charge-transfer process



Under these assumptions the volume concentrations C_O and C_R of O and R satisfy Fick's second law, which must be corrected for the convective motion due to the expansion of the drop in the case of diffusion toward a dropping electrode. Assume that the charge-transfer process is slow and involves only those molecules of O and R which are specifically adsorbed. Under these circumstances the two following boundary conditions can be written

$$D(\partial C_O / \partial x)_{x=0} = 1/A \, d(A\Gamma_O)/dt + k_f \Gamma_O - k_b \Gamma_R \quad (2)$$

$$D(\partial C_R / \partial x)_{x=0} = 1/A \, d(A\Gamma_R)/dt - k_f \Gamma_O + k_b \Gamma_R \quad (3)$$

Here A is the area of the electrode surface, Γ_O and Γ_R are the surface concentrations of O and R, respectively, D is the diffusion coefficient, which for simplicity has been considered equal for the two species, and k_f , k_b are the rate constants for the forward and backward electrode processes. Equation 2 expresses the fact that the amount of O reaching the electrode in the unit time equals the amount of O accumulating plus that reacting at the electrode surface in the same unit time. Analogous considerations can be made for eq 3 when the species R is considered. The boundary conditions (2) and (3) hold both at a stationary electrode and at a dropping

(1) R. Brdička, *Z. Elektrochem.*, **48**, 278 (1942).

(2) J. Koryta, *ibid.*, **64**, 23 (1960).

(3) A. B. Ershler, G. A. Tedoradze, and S. G. Mairanovskii, *Dokl. Akad. Nauk SSSR*, **145**, 1324 (1962).

electrode. In the former case, A is constant while in the latter the dependence of A on the electrolysis time t is expressed by the relation

$$A = A_0 t^{2/3} \quad (4)$$

where A_0 is the area of the electrode at $t = 1$ sec. The faradaic current due to the electrode process 1 is given by

$$\begin{aligned} i/(nF) &= AD(\partial C_O/\partial x)_{x=0} - d(A\Gamma_O)/dt = \\ &= -AD(\partial C_R/\partial x)_{x=0} + d(A\Gamma_R)/dt = \\ &= A(k_f\Gamma_O - k_b\Gamma_R) \end{aligned} \quad (5)$$

It should be noted that according to the concept of charge separation and recombination introduced by Delahay,⁴ the current flowing along the external circuit does not necessarily coincide with the Faradaic current. Assuming that only the oxidized species is present in the bulk of the solution, we write

$$\left. \begin{array}{l} C_O = C_O^* \\ C_R = 0 \end{array} \right\} \text{ for } \left\{ \begin{array}{l} x \geq 0, t = 0 \\ x \rightarrow \infty, t > 0 \end{array} \right. \quad (6)$$

The asterisk denotes bulk concentrations.

The Diffusion Layer Treatment

The diffusional problem 2, 3, and 6 will not be solved rigorously, but rather by following the approximate procedure based on the diffusion layer concept. In this connection, the mean current \bar{i} will be derived by assuming that during electrolysis at constant potential the volume concentrations \bar{C}_O and \bar{C}_R of the species O and R at the electrode surface remain constant. It follows that Γ_O and Γ_R do not change with time at constant potential, provided adsorption equilibrium is achieved. Under these simplifying assumptions, integration of eq 5 over the period of electrolysis t_1 yields

$$\frac{\bar{i}}{nF} = \frac{1}{nFt_1} \int_0^{t_1} i \, dt = \frac{D}{t_1} \int_0^{t_1} A \left(\frac{\partial C_O}{\partial x} \right)_{x=0} dt - \frac{\Gamma_O}{t_1} \int_0^{t_1} \frac{dA}{dt} dt \quad (7)$$

$$\frac{\bar{i}}{nF} = -\frac{D}{t_1} \int_0^{t_1} A \left(\frac{\partial C_R}{\partial x} \right)_{x=0} dt + \frac{\Gamma_R}{t_1} \int_0^{t_1} \frac{dA}{dt} dt \quad (8)$$

$$\frac{\bar{i}}{nF} = \frac{1}{t_1} \int_0^{t_1} A \, dt \cdot (k_f\Gamma_O - k_b\Gamma_R) \quad (9)$$

If electrolysis is carried out at an electrode of constant area, eq 7, 8, and 9 assume the following simplified forms

$$\frac{\bar{i}}{nF} = \frac{DA}{t_1} \int_0^{t_1} \left(\frac{\partial C_O}{\partial x} \right)_{x=0} dt \quad (10)$$

$$\frac{\bar{i}}{nF} = -\frac{DA}{t_1} \int_0^{t_1} \left(\frac{\partial C_R}{\partial x} \right)_{x=0} dt \quad (11)$$

$$\frac{\bar{i}}{nF} = A(k_f\Gamma_O - k_b\Gamma_R) \quad (12)$$

On the basis of the diffusion layer concept, let us place

$$\begin{aligned} \frac{D}{t_1} \int_0^{t_1} A \left(\frac{\partial C_O}{\partial x} \right)_{x=0} dt &= l(C_O^* - \bar{C}_O); \\ \frac{D}{t_1} \int_0^{t_1} A \left(\frac{\partial C_R}{\partial x} \right)_{x=0} dt &= -l\bar{C}_R \end{aligned} \quad (13)$$

where the expression for l depends on the particular type of diffusion under study. Thus for linear diffusion

$$l = 2AD^{1/2}/(\pi^{1/2}t_1^{1/2}) \quad (14)$$

while for diffusion toward a dropping mercury electrode

$$l = [12D/(7\pi)]^{1/2} A_0 t_1^{1/6} \quad (15)$$

A mathematical justification for the approximate relations 13–15 can be given by recalling that, in view of Duhamel's theorem, the flux $D(\partial C/\partial x)$ at $x = 0$ of a species obeying the diffusion equation uncomplicated by kinetic terms is related to the concentration $C(O,t)$ of this species at the electrode surface through the equation

$$D \int_0^{t_1} \left(\frac{\partial C}{\partial x} \right)_{x=0} dt = \left(\frac{D}{\pi} \right)^{1/2} \int_0^{t_1} \frac{C^* - C(O,t)}{(t_1 - t)^{1/2}} dt \quad (16)$$

for a plane electrode, and through the equation

$$\begin{aligned} \left(\frac{7\pi D}{3} \right)^{1/2} \int_0^{t_1} \left(\frac{\partial C(x,t)}{\partial x} \right)_{x=0} t^{2/3} dt = \\ \int_0^{t_1^{1/3}} \frac{C^* - C(O,t)}{\lambda^{1/2}} d\lambda \end{aligned} \quad (17)$$

where $\lambda = t_1^{1/3} - t^{1/3}$, for a dropping electrode. Assume that the rate of change of $C(O,t)$ with time is much less than those of the ratio $1/(t_1 - t)^{1/2}$ in eq 16 and of the ratio $t^{2/3}/(t_1^{1/3} - t^{1/3})^{1/2}$ in eq 17. Under these conditions, which are approximately satisfied in the majority of cases, $C^* - C(O,t)$ can be brought out of the integral sign in eq 16 and 17 with sufficient confidence. By doing so we immediately obtain eq 13–15. The substantial validity of the approximate approach based on the diffusion layer concept is demonstrated by the satisfactory agreement existing between the results obtained by this approach and those obtained by rigorous numerical procedures.⁵ In particular it must be noted that the approximate procedure followed by Levich, *et al.*,⁶ in the treatment of diffusion-controlled adsorption at plane and dropping electrodes for different types of isotherms is perfectly equivalent to the diffusion layer approach. The boundary value problem con-

(4) P. Delahay, *J. Phys. Chem.*, **70**, 2373 (1966).

(5) J. Heyrovsky and J. Kůta, "Principles of Polarography," Academic Press, New York, N. Y., 1966, pp 339–400.

(6) V. G. Levich, B. I. Khaikin, and E. D. Belokolos, *Elektrokhimiya*, **1**, 1273 (1965).

sidered in the present note reduces to that examined by the above authors when we let k_f and k_b tend to zero, *i.e.*, when no Faradaic current flows through the electrode. The approximate equation obtained by Levich and coworkers⁶ for the case of Langmuirian adsorption gives results in fairly good agreement with those derived by a rigorous numerical procedure. In fact, the accuracy of the approximate analytical solution is better than 8%.

Returning to the problem under study, it should be noted that so far we have not made any assumptions as to the nature of the adsorption isotherm relating the surface concentrations Γ_O and Γ_R to the corresponding volume concentrations \bar{C}_O and \bar{C}_R at the electrode surface. Consequently, any isotherm could be introduced into the equations previously derived. Since, however, we intend to consider the simultaneous adsorption of both the species O and R, it is more convenient to use the Langmuir isotherm which, unlike other commonly used isotherms (*e.g.*, the Temkin or Frumkin isotherms) is based on the assumption that the adsorption energy of all sites is unaffected by adsorption on neighboring sites. On assuming that the propositions on which the Langmuir isotherm is based are encountered, one has

$$K_O \bar{C}_O (1 - \theta) = \Gamma_O / \Gamma_m; K_R \bar{C}_R (1 - \theta) = \Gamma_R / \Gamma_m \quad (18)$$

where K_O and K_R are the adsorption coefficients of O and R, respectively, θ is the degree of coverage of the electrode and Γ_m is the maximum number of moles adsorbed per unit area of the electrode. For simplicity we shall assume that both O and R have the same value of Γ_m . Since O and R are the only species adsorbed at the electrode, the degree of coverage θ is given by

$$\theta = (\Gamma_O + \Gamma_R) / \Gamma_m \quad (19)$$

Upon combining eq 18 and 19 the surface concentrations Γ_O and Γ_R are readily obtained

$$\Gamma_O = \Gamma_m K_O \bar{C}_O / (1 + K_O \bar{C}_O + K_R \bar{C}_R);$$

$$\Gamma_R = \Gamma_m K_R \bar{C}_R / (1 + K_O \bar{C}_O + K_R \bar{C}_R) \quad (20)$$

In view of eq 9 and 20, the mean current is expressed by the equation

$$\frac{\bar{i}}{nF} = \frac{\frac{1}{t_1} \int_0^{t_1} A dt}{1 + K_O \bar{C}_O + K_R \bar{C}_R} \Gamma_m (k_f K_O \bar{C}_O - k_b K_R \bar{C}_R) \quad (21)$$

Taking into account the well known relations between the rate constants k_f and k_b and the applied potential

$$k_f = k_f^\circ \exp \left[-\frac{\alpha nF}{RT} (E - E_0) \right];$$

$$k_b = k_b^\circ \exp \left[(1 - \alpha) \frac{nF}{RT} (E - E_0) \right]$$

where α is the transfer coefficient, and choosing the reference potential E_0 so as to satisfy the equality $\Gamma_m k_f^\circ K_O = \Gamma_m k_b^\circ K_R \equiv k_s$, eq 21 becomes

$$\frac{\bar{i}}{nF} = \frac{1}{t_1} \int_0^{t_1} A dt \frac{k_s}{1 + K_O \bar{C}_O + K_R \bar{C}_R} \times$$

$$\left\{ \bar{C}_O \exp \left[-\frac{\alpha nF}{RT} (E - E_0) \right] - \bar{C}_R \exp \left[(1 - \alpha) \frac{nF}{RT} (E - E_0) \right] \right\} \quad (22)$$

In eq 22 $1/t_1 \int_0^{t_1} A dt$ equals A for a stationary electrode and $3/5 A_0 t_1^{1/2}$ for a dropping electrode. The reference potential E_0 , previously chosen, coincides with the standard potential of the redox couple O-R as appears from eq 22 upon setting $\bar{i} = 0$ and equating \bar{C}_O , \bar{C}_R to the corresponding bulk concentrations. Replacement of eq 4, 13, 15, and 20 into eq 7 and 8 and rearrangement yields the following expressions for the mean current at a dropping mercury electrode

$$\frac{\bar{i}}{nF} = \left(\frac{12D}{7\pi} \right)^{1/2} A_0 t_1^{1/2} (C_O^* - \bar{C}_O) -$$

$$A_0 t_1^{-1/2} \frac{\Gamma_m K_O \bar{C}_O}{1 + K_O \bar{C}_O + K_R \bar{C}_R} \quad (23)$$

$$\frac{\bar{i}}{nF} = \left(\frac{12D}{7\pi} \right)^{1/2} A_0 t_1^{1/2} \bar{C}_R +$$

$$A_0 t_1^{-1/2} \Gamma_m \frac{K_R \bar{C}_R}{1 + K_O \bar{C}_O + K_R \bar{C}_R} \quad (24)$$

Upon combining the right-hand sides of eq 23 and 24, \bar{C}_R is readily obtained as a function of \bar{C}_O

$$\bar{C}_R = (-b + [b^2 - 4K_R(12Dt_1/7\pi)^{1/2}c]^{1/2}) / [2K_R \times (12Dt_1/7\pi)^{1/2}] \quad (25)$$

where

$$b = \Gamma_m K_R + (12Dt_1/7\pi)^{1/2} (1 + K_O \bar{C}_O + K_R \bar{C}_O - K_R C_O^*)$$

and

$$c = \Gamma_m K_O \bar{C}_O + (12Dt_1/7\pi)^{1/2} (\bar{C}_O - C_O^*) (1 + K_O \bar{C}_O)$$

Equations 22-25 express the polarographic current-potential characteristic in an implicit form. Thus if \bar{C}_O is given a series of values ranging from 0 to C_O^* , the corresponding values of \bar{C}_R are readily obtained from eq 25. The introduction of these couples of values of \bar{C}_O and \bar{C}_R into eq 23 (or alternatively 24) and 22 leads to the couples of values of \bar{i} and $(E - E_0)$ corresponding to the same value of \bar{C}_O and consequently to the theoretical wave form.

If the standard rate constant k_s is very high (in practice > 10 cm/sec), since \bar{i} cannot exceed the value for

the diffusion limiting current, the term within the braces in eq 19 becomes negligible. Upon equating this term to zero one immediately obtains the Nernst equation, as applied to the volume concentrations of O and R at the electrode surface

$$\bar{C}_O/\bar{C}_R = \exp[nF/RT(E - E_0)] = \theta \quad (26)$$

If K_O tends to zero, eq 23, 24, and 26 express the well known theoretical characteristic derived by Brdička¹ and relative to a reversible process $O + ne \rightleftharpoons R$ with Langmuirian adsorption of the electrode product. This characteristic exhibits a prewave. Analogously, if we let K_R tend to zero, eq 23, 24, and 26 yield the theoretical wave form relative to a reversible process with Langmuirian adsorption of the reactant, derived by Brdička and characterized by the presence of a post-wave. From the way in which eq 26 has been derived it is evident that we need not postulate the occurrence of the electrode process in the adsorbed state along the pre- or postwave and at the outer Helmholtz plane along the normal wave.

Discussion and Conclusions

The solid curves in Figure 1 represent a series of polarographic waves obtained from eq 22, 23, 24, and 25 for $n = 1$, $\alpha = 0.5$, $C_O^* = 10^{-6}$ mol/cm³, $D = 10^{-5}$ cm²/sec, $t_1 = 3$ sec, $\Gamma_m = 5 \times 10^{-10}$ mol/cm², $K_O = 10^4$ cm³/mol, $K_R = 10^9$ cm³/mol and for different values of k_s . These curves, which illustrate the case of a predominant adsorption of the product R with respect to the reactant O are characterized by the presence of a prewave. When k_s decreases, the length of the plateau separating the prewave from the remaining part of the total wave (*i.e.*, the so-called "normal" wave) increases while the slope of this latter part progressively diminishes reaching a limiting value for $k_s \leq 10^{-1}$ cm/sec. A further decrease in k_s leaves the slope of the normal wave unchanged but causes the wave to shift toward more negative potentials. In this connection it should be noted that in the absence of adsorption phenomena a polarographic wave reaches its minimum slope, corresponding to the total irreversibility of the electrode process, for $k_s \leq 5 \times 10^{-4}$ cm/sec while it is practically reversible for $k_s \geq 10^{-1}$ cm/sec. The presence of prewaves in the solid curves of Figure 1 must be ascribed to the amount of R which, after its formation from O, remains adsorbed at the surface of the dropping electrode. The contribution to the polarographic current due to this amount of R is expressed by the second term on the right-hand side of eq 24. The drawn-out shape of the curves of Figure 1 for such high values of the standard rate constant k_s as 1 cm/sec is due to the influence exerted by the surface concentration of O, and especially of R, upon the term $k_s/(1 + K_O\bar{C}_O + K_R\bar{C}_R)$ in eq 22. Since this term reduces to k_s in the absence of adsorption, we can call it "apparent standard rate constant." When

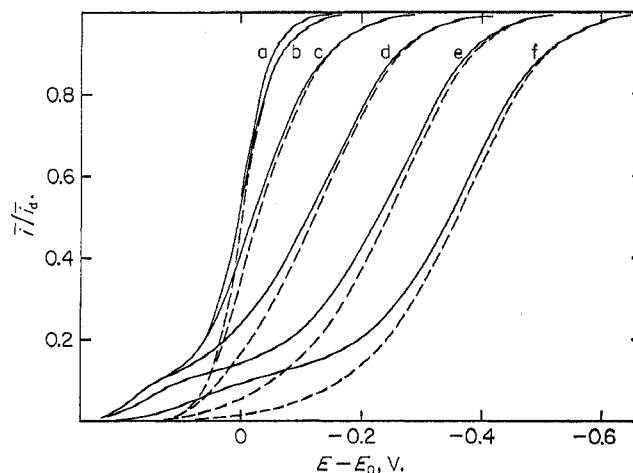


Figure 1. Ratio \bar{i}/\bar{i}_d of the mean current \bar{i} , at a given potential E , to the mean diffusion limiting current, $\bar{i}_d = nFIC_O^*$, as a function of $E - E_0$. The solid curves a, b, c, d, e, and f have been derived from eq 22, 23, 24, and 25 for $C_O^* = 10^{-6}$ mol/cm³, $D = 10^{-5}$ cm²/sec, $t_1 = 3$ sec, $\Gamma_m = 5 \times 10^{-10}$ mol/cm², $K_O = 10^4$ cm³/mol, $K_R = 10^9$ cm³/mol, $n = 1$, $\alpha = 0.5$, and for k_s values equal to ∞ , 10, 1, 10^{-1} , 10^{-2} , and 10^{-3} cm/sec, respectively. The dashed curves have been derived from eq 28 for the same values of C_O^* , K_O , K_R , k_s , n , α , and $l/(i/t_1 \int_0^t A dt)$ employed in the calculation of the solid curves partially superimposed to them.

$K_O\bar{C}_O + K_R\bar{C}_R$ is appreciably greater than 1, the value for the apparent standard rate constant, which strongly affects the dependence of the current upon potential (see eq 22), becomes sensibly lower than the value for the true standard rate constant, k_s .

From the curves in Figure 1 it is evident that the treatment previously outlined bridges the gap between the Brdička adsorption prewaves, which are encountered in the reduction of reversible systems, and the so-called adsorption "pseudo-prewaves," which are characterized by an irreversible normal wave. According to several authors,^{7,8} the difference between Brdička prewaves and pseudo-prewaves is of a substantial nature, in the sense that the former are caused by a facilitation of the reversible electrode process due to the energy gain resulting from adsorption of products, while the latter are the result of an inhibited electrode reaction, the inhibition being caused by a surface film due to the products. This film should become compact at the plateau between the pseudo-prewave and the second wave so that the prewave should be caused by a nearly uninhibited electrolysis of reactant particles while the second wave should correspond to the discharge of the same particles inhibited by a compact layer of products. Thus Mairanovskii⁷ claims that pseudo-prewaves should not be considered as true prewaves but rather as main (normal) waves. In this sense their half-wave

(7) S. G. Mairanovskii, "Catalytic and Kinetic Waves in Polarography," Plenum Press, New York, N. Y., 1968, pp 109-110.

(8) R. W. Schmid and C. N. Reilly, *J. Amer. Chem. Soc.*, **80**, 2087 (1958).

potential should be close to the standard potential, E_0 , of the redox system and in no case should it be shifted with respect to E_0 in the direction opposite to that of increasing overvoltages. As a matter of fact, from Figure 1 it is apparent that such a drastic distinction between Brdička prewaves and pseudo-prewaves does not exist, since a wholly gradual passage from the former to the latter type of prewaves is observed when the true standard rate constant k_s decreases. The position of the half-wave potentials of the cathodic prewaves in Figure 1 on the positive side of E_0 shows that even if k_s is so low that an irreversible second wave is observed, the prewave must be considered as originated by an electrode process simultaneously facilitated by the energy gain resulting from adsorption of electrode products and inhibited by the gradual decrease in the apparent standard rate constant resulting from such an adsorption. It must be noted that the apparent standard rate constant, unlike k_s , varies along the rising portion of the total wave. In the case illustrated by Figure 1 and corresponding to the preferential adsorption of the electrode product, an increase in \bar{i}/i_d causes the total amount of O and R adsorbed at the electrode surface to grow and consequently the apparent rate constant to decrease. The gradual passage from Brdička prewaves to pseudo-prewaves is confirmed by the experimental finding that in acid solutions ($\text{pH} \leq 1$) the normal wave of riboflavin, which is a typical example of a substance giving a Brdička prewave, is only slightly reversible.⁹

There is, however, a class of pseudo-prewaves which is not adequately accounted for by the present treatment. They are due to the irreversible formation of a film of insoluble reaction products which inhibits the electrode reaction more as the current increases. The plateau of these prewaves is reached when the penetration of the reactant through the insoluble film becomes the rate-determining step. "Penetration currents" of this type have been observed during the anodic polarization of dropping mercury electrodes in the presence of compounds forming insoluble mercury salts.¹⁰⁻¹² Possible diagnostic criteria for the distinction between these prewaves and the prewaves of Figure 1, which correspond to the reversible adsorption of the electrode product R, must aim at verifying the irreversibility of film formation. A technique which can be usefully employed in this respect is chronoamperometry at a hanging mercury drop.¹³

The solid curves in Figure 2 represent some polarographic wave forms obtained from eq 22, 23, 24, and 25 for the same values of α , n , C_O^* , D , t_1 , Γ_m employed in Figure 1, for $K_O = 10^9 \text{ cm}^3/\text{mol}$, $K_R = 10^4 \text{ cm}^3/\text{mol}$, and for different values of k_s . In the present case the adsorption of reactant is predominant and the waves corresponding to k_s values $\leq 10^{-1} \text{ cm/sec}$ exhibit a postwave. A decrease in k_s produces a shift of the normal wave toward more negative potentials with the con-

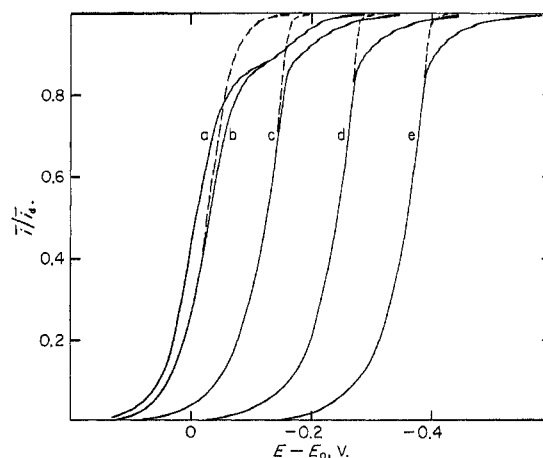


Figure 2. Ratio \bar{i}/i_d of the mean current \bar{i} , at a given potential E , to the mean diffusion limiting current, $i_d = nFIC_O^*$, as a function of $E - E_0$. The solid curves a, b, c, d, and e have been derived from eq 22, 23, 24, and 25 for $C_O^* = 10^{-6} \text{ mol/cm}^3$, $D = 10^{-5} \text{ cm}^2/\text{sec}$, $t_1 = 3 \text{ sec}$, $\Gamma_m = 5 \times 10^{-10} \text{ mol/cm}^2$, $K_O = 10^9 \text{ cm}^3/\text{mol}$, $K_R = 10^4 \text{ cm}^3/\text{mol}$, $n = 1$, $\alpha = 0.5$, and for k_s values equal to ∞ , 1, 10^{-1} , 10^{-2} , and 10^{-3} cm/sec , respectively. The dashed curves have been derived from eq 28 for the same values of C_O^* , K_O , K_R , k_s , n , α , and $l/(1/t_1 \int_0^{t_1} A dt)$ employed in the calculation of the solid curves partially superimposed to them.

sequence that this wave finishes by merging with the postwave for $k_s > 10^{-1} \text{ cm/sec}$. The average slope of the normal wave does not change appreciably with decreasing k_s and only a progressive drawing out of the lower portion of the wave ($0 \leq \bar{i}/i_d \leq 0.2$) is observed in passing from $k_s = \infty$ to $k_s = 10^{-1} \text{ cm/sec}$. The slope reached by the waves of Figure 2 at low k_s values is sensibly higher than that exhibited by the waves of Figure 1 corresponding to the same k_s values. This fact can be easily explained by considering that in the case of Figure 2 the total amount of the substances O and R adsorbed at the electrode decreases with increasing current. Hence, contrary to the case of Figure 1, the apparent standard rate constant grows while proceeding along the polarographic wave. The steepness of the curves of Figure 2 corresponding to values of $k_s \leq 10^{-1} \text{ cm/sec}$ increases with \bar{i}/i_d up to $\bar{i}/i_d = 0.85$. The disappearance of the postwave when the electrode process with predominant adsorption of reactant becomes sufficiently slow ($k_s < 10^{-1} \text{ cm/sec}$) can probably explain why postwaves preceded by an irreversible normal wave have never been observed.

Several cases are known where polarographic waves due to an electrode process inhibited by adsorption of

(9) B. Breyer and T. Biegler, *Collect. Czech. Chem. Commun.*, **25**, 3348 (1960).

(10) I. M. Kolthoff and C. Barnum, *J. Amer. Chem. Soc.*, **62**, 3061 (1940).

(11) I. M. Kolthoff and C. S. Miller, *ibid.*, **63**, 1405 (1941).

(12) I. M. Kolthoff, W. Stricks, and N. Tanaka, *ibid.*, **77**, 5211 (1955).

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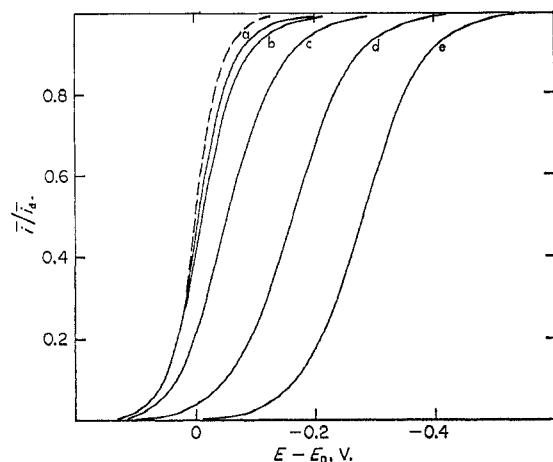


Figure 3. Ratio i/i_a as a function of $E - E_0$. The solid curves a, b, c, d, and e have been derived from eq 22, 23, 24, and 25 for $C_O^* = 10^{-6}$ mol/cm³, $D = 10^{-5}$ cm²/sec, $t_1 = 3$ sec, $\Gamma_m = 5 \times 10^{-10}$ mol/cm², $k_s = 10^{-2}$ cm/sec, $n = 1$, $\alpha = 0.5$ and for values of $K_O = K_R$ equal to 10^5 , 10^6 , 10^7 , 10^8 , and 10^9 cm³/mol, respectively. The dashed curve represents a reversible polarographic wave in the absence of adsorption. The curves a, b, c, d, and e are practically identical with those derivable from eq 29 for the same values of k_s , n , α , $l/(1/t_1 \int_0^t A dt)$ and for K_O^* values equal to 10^{-1} , 1, 10, 10^2 , and 10^3 , respectively.

reactant have a form similar to that of the theoretical curves of Figure 2 with $k_s \leq 10^{-2}$ cm/sec.^{13,14} Thus in buffer solutions in the pH range from 4 to 10 di-(2', 2'') and di-(4', 4'')dipyridyl-1,2-ethylene give cathodic waves which, after an apparently regular start, show a sharp increase in the current.¹³ The slopes of these experimental curves are higher than those of the theoretical curves of Figure 2 but we must recall that these latter curves have been calculated for a constant value of K_O . If we assumed that the adsorption coefficient of the reactant decreases with a shift of the applied potential toward negative values according to a given law, the theoretical curves derived from eq 22, 23, 24, and 25 would exhibit a higher slope.

If O and R have equal adsorption coefficients, the total amount of these two substances which is adsorbed at the electrode does not change appreciably with applied potential, but only the ratio Γ_O/Γ_R between their surface concentrations varies. In the present case neither prewaves nor postwaves are to be expected. Figure 3 shows a series of polarographic current-potential characteristics calculated from eq 22, 23, 24, and 25 for $C_O^* = 10^{-6}$ mol/cm³, $D = 10^{-5}$ cm²/sec, $n = 1$, $\alpha = 0.5$, $t_1 = 3$ sec, $\Gamma_m = 5 \cdot 10^{-10}$ mol/cm², $k_s = 10^{-2}$ cm/sec and for progressively increasing values of $K_O = K_R \equiv K$. If K is $\leq 10^5$ cm³/mol the apparent standard rate constant practically coincides with the true one, k_s , and the polarographic wave (a) which is obtained is identical with that derivable in the absence of adsorption. It must be noted that this wave is very close to the totally reversible wave ($k_s \rightarrow \infty$) repre-

sented by the dashed curve in Figure 3. An increase in K causes a gradual decrease in the slope of the polarographic wave until, for K values in the range from 10^7 to 10^8 cm³/mol, the minimum slope corresponding to total irreversibility is reached. At this point the wave becomes centro-symmetric. A further increase in K leads only to a progressive shift of the half-wave potential, $E_{1/2}$, toward more negative values.

In the case of diffusion toward a dropping electrode, the rate of change with electrolysis time of the amounts of O and R adsorbed on the growing drop at constant potential is expressed by the second term on the right-hand side of eq 23 and 24, respectively. These terms obviously cancel out in the case of diffusion toward a stationary electrode. Since it is the contribution of these terms to the current that determines the appearance of pre- and postwaves in the polarographic wave forms, voltametric curves at a stationary electrode do not exhibit pre- or postwaves. The expression for the current at a stationary electrode is obtained by combining eq 10-13 and 20

$$i/(nF) = l(C_O^* - \bar{C}_O) = l\bar{C}_R = \frac{Ak_s}{1 + K_O\bar{C}_O + K_R\bar{C}_R} \{ \bar{C}_O\theta^{-\alpha} - \bar{C}_R\theta^{1-\alpha} \} \quad (27)$$

where θ is defined by eq 26. From eq 27 the theoretical characteristic is readily derived in an explicit form

$$\frac{i}{nF} = \frac{-b + [b^2 + 4AlC_O^*(K_R - K_O)k_s\theta^{-\alpha}]^{1/2}}{2(K_R - K_O)} \quad (28)$$

Here $b = l(1 + K_OC_O^*) + Ak_s(\theta^{-\alpha} + \theta^{1-\alpha})$.

The dashed curves in Figures 1 and 2 express voltametric curves at a stationary electrode. They have been derived from eq 28 for the same values of C_O^* , k_s , K_O , K_R , α , and n employed in the calculation of the solid polarographic curves which are partially superimposed to them. Furthermore, the value of the ratio l/A used for the dashed curves is identical with the value of the analogous ratio $l/(1/t_1 \int_0^t A dt) = 5/3 \cdot \sqrt{12D/(7\pi t_1)}$ used in the calculation of the corresponding solid curves. From the figure it is evident that the effect of the adsorption of O and R on the charge-transfer process is analogous both at a stationary and at a dropping electrode. In the voltametric curves of Figure 1 corresponding to k_s values $\leq 10^{-1}$ cm/sec the polarographic prewave is replaced by an initial portion characterized by a very slow increase in the current. Within this portion the major part of the complete coverage of the electrode by the electrode product, R, is accomplished. In view of eq 27, if we set $K_O = K_R = K$, the current-potential characteristic at a stationary electrode takes the simplified form

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$$\frac{\bar{i}}{\bar{i}_d} = \frac{Ak_s\theta^{-\alpha}}{l(1 + KC_0^*) + Ak_s(\theta^{-\alpha} + \theta^{1-\alpha})} \quad (29)$$

where $\bar{i}_d = nF l C_0^*$ is the mean diffusion limiting current; eq 29 shows that the influence of adsorption of O and R upon the behavior of the theoretical voltametric curves is determined by the value for the product KC_0^* . The curves of Figure 3, calculated for the case of diffusion toward a dropping mercury electrode, are practically identical with those derivable from eq 29 for the same value of $k_s = 10^{-2}$ cm/sec and for KC_0^* values, respectively, equal to 10^{-1} , 1, 10, 10^2 , and 10^3 . For $KC_0^* \geq 10$ the slope of the voltametric curves remains constant while $E_{1/2}$ continues to decrease with increasing KC_0^* . This is clearly expressed by eq 29, if we note that for sufficiently high shifts of $E_{1/2}$ from E_0 , the term $\theta^{1-\alpha}$ can be neglected with respect to $\theta^{-\alpha}$. Under these conditions eq 29 can be written in the form

$$E = E_0 - \frac{RT}{2.3\alpha nF} \log \frac{\bar{i}}{\bar{i}_d - \bar{i}} + \frac{RT}{2.3\alpha nF} \log \frac{Ak_s}{lKC_0^*} \quad (30)$$

This shows that a tenfold increase in C_0^* produces a shift of the half-wave potential by $60/\alpha n$ mV toward more negative values, provided the voltametric curve has reached the minimum slope corresponding to total irreversibility. If the values of K_O and K_R differ even by a single order of magnitude, the voltametric curves which are obtained upon exchanging the values of K_O and K_R , all other parameters remaining unaltered, are characterized by appreciably different slopes, as shown in Figure 4. Owing to the symmetry of the electrode process, such an exchange amounts to substituting R for O in the bulk of the solution.

Many experimental facts, in addition to those previously mentioned, can be adequately interpreted on the basis of the previous treatment, which can be easily extended to other adsorption isotherms as well as to the case of potential dependent adsorption coefficients. Thus many organic compounds give polarographic curves characterized by decreasing slopes and by half-wave potentials shifting toward increasing overvoltages when the concentration of the reactant increases. Such a behavior is typical of several azo compounds. The azobenzene-hydrazobenzene system in a buffer solution at pH 7.25 behaves reversibly on a dropping mercury electrode for overall concentrations of the two species $\leq 10^{-5}$ mol/l.¹⁵ With an increase in the bulk concentration of any of the two species, the system becomes irreversible and the half-wave potentials of the waves given, respectively, by azobenzene and hydrazobenzene shift in opposite directions. Furthermore, the $E_{1/2}$ value for the wave of one of the two species is influenced by the bulk concentration of the other in accord with the

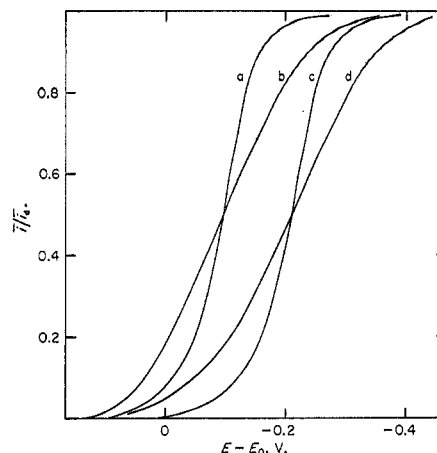


Figure 4. Ratio \bar{i}/\bar{i}_d as a function of $E - E_0$. The curves have been derived from eq 28 for the same values of C_0^* , n , α , and $l/(1/t \int_0^t A dt)$ employed in Figures 1, 2, and 3, for $k_s = 10^{-2}$ cm/sec and for values of K_O and K_R , in cm³/mol, respectively, equal to 10^7 , 10^5 (curve a), 10^5 , 10^7 (curve b), 10^8 , 10^7 (curve c), and 10^7 , 10^8 (curve d).

fact that the apparent standard rate constant is affected by the surface concentrations of both the forms of the redox system. Analogously the unprotonated form of actinomycin- C_1 and chloroactinomycin- C_1 give reversible cathodic waves on mercury only at concentrations $\leq 5 \times 10^{-4}$ mol/l.^{16,17} At higher concentrations of these substances inhibition effects due to adsorption cause the polarographic waves to become irreversible. Analogous phenomena are encountered at stationary electrodes. Thus, the system Tl^{III}/Tl^I in 1 M perchloric acid behaves reversibly at a platinum electrode, platinized for 1 sec at a current density of 1.2 A/cm² for overall concentrations of thallium lower than 5×10^{-5} mol/l.¹⁸ Here too an increase in the concentration of thallium produces a separation of the anodic curve of Tl^I from the cathodic curve of Tl^{III} . The half-wave potentials of these voltametric curves shift toward increasing overvoltages with an increase in the bulk concentration of reactant. Owing to the great tendency of thallium to be adsorbed on platinum,¹⁹ these phenomena can be ascribed to the influence of the surface concentrations of Tl^{III} and Tl^I upon the apparent standard rate constant of the charge-transfer process $Tl^I \rightleftharpoons Tl^{III} + 2e$.

In concluding, the consideration of the influence exerted by the adsorption of the reactant O and of the product R upon the rate of the charge-transfer process leads to the following results. (1) If the adsorption co-

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efficients of O and R are of the same order of magnitude, an increase in the concentration of the reactant O causes a decrease in the slope of the wave until the minimum slope corresponding to total irreversibility is reached. Simultaneously the wave shifts along the potential axis toward more negative values. (2) If the adsorption coefficients of O and R are of different orders of magnitude, besides the above mentioned shift of $E_{1/2}$, an ap-

preciable difference is observed between the slopes of the curves given, respectively, by solutions of O and R of equal concentrations. In this connection the species preferentially adsorbed gives waves with higher slopes.

Further experimental investigations are in progress in this institute in order to point out the influence of adsorption of reactant and electrode products upon polarographic and voltametric curves.

The Adsorption of Dinonylnaphthalenesulfonates

on Metal Oxide Powders¹

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The adsorption of oleophilic rust inhibitors, sodium and barium dinonylnaphthalenesulfonate, from cyclohexane solution on nickel(III) oxide and iron(III) oxide was investigated. Rate data for adsorption of sodium dinonylnaphthalenesulfonate on nickel oxide indicate a complex mechanism of adsorption. An empirical equation was found that accurately describes the data. The log of the uncovered surface plotted against log time was linear. The extrapolated time for 50% coverage was 0.36 min. Experimentally the adsorption process was irreversible. The effect of temperature in the range of 10 to 60° on the adsorption isotherm was negligible. Adsorption isotherm data for sodium dinonylnaphthalenesulfonate were of a Langmuir type. The values of a indicated a more close-packed monolayer on nickel oxide than on iron oxide. The ratio of the molecules per square centimeter for the former and the latter was 1.49. The b values indicated a rather strong interaction at the metal oxide surfaces. Monolayer concentrations were found to be essentially the same irrespective of the salt used.

Introduction

High molecular weight petroleum sulfonates and synthetic sulfonates are receiving increasing military use as corrosion inhibiting additives for lubricants and hydraulic fluids. Dinonylnaphthalenesulfonates, in addition to being excellent corrosion inhibitors, approximate the petroleum sulfonates in structure and rust inhibiting properties and it is reasonable to assume that the adsorption characteristics of the petroleum sulfonates would be similar to the synthetic sulfonates.

Although the mechanism by which alkyl aryl sulfonates function as corrosion inhibitors is still unclear, several investigators have contributed to a better understanding of the corrosion inhibition mechanism by studying parameters affecting adsorption of sulfonate. For example, the presence of water was found to promote adsorption of calcium dinonylnaphthalenesulfonate on steel.² Shropshire recently observed that the degree of adsorption of petroleum sulfonates on calcium carbonate powder was determined by the history or method of preparation of the substrate.³

Smith, Gordon, and Nelson, in a study of the adsorption of calcium dinonylnaphthalenesulfonate at the gold-white oil interface, have reported that the adsorption is completely reversible and that the adsorbed monolayer is subject to displacement by a polyalcohol and poly(dodecyl methacrylate).⁴ Because of the multiplicity of additives in lubricating fluids, the study of competitive reactions are particularly appropriate. We have found that the rust-inhibitive activity of petroleum sulfonates is affected by the choice of solvent; this indicates that the solvent is a parameter of considerable importance.

The purpose of this study was to investigate the adsorption characteristics of sodium and barium di-

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