

## ADSORPTION, AUTOINHIBITION AND AUTOCATALYSIS IN POLAROGRAPHY AND IN LINEAR POTENTIAL SWEEP VOLTAMMETRY

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In polarography, or in linear potential sweep voltammetry, if one puts aside the case of surface kinetic waves studied by Mairanovskii<sup>1</sup>, two principal effects can result from the adsorption of the depolarizer and/or of the product of the electrochemical reaction:

(i) The adsorption of the molecule results in a change in its energy, which can make the electrochemical reaction easier or more difficult.

The first interpretation of this kind of effect was given by Brdička<sup>2,3</sup> as early as 1942 in several fundamental papers: when the electrochemical reaction is reversible, the adsorption of O or R results in the formation of a prewave or a postwave on the polarogram. In classical polarography, no rigorous theoretical analysis of the experimental data (see ref. 4a) had been published before our first paper<sup>5</sup>. Another study<sup>5,2</sup> appeared later. In linear potential sweep voltammetry, our first publication<sup>6</sup> and another simultaneous study<sup>7</sup> were preceded only by an isolated attempt<sup>8</sup> to calculate the equation of the  $i$ - $E$  curves. Solutions for the adsorption of intermediates have been derived<sup>7,0-7,2</sup>; the equations are often similar to those which we have obtained.

On the other hand, practically no study had been made of the case when the electrochemical reaction is irreversible.

The results of our investigations are given in the first part of the present paper.

(ii) The electrochemical process can be modified by a film of adsorbed molecules.

A large number of studies<sup>4,9</sup> have been devoted to the investigation of electrode processes influenced by a film due to the adsorption of an *electroinactive foreign substance*. The film can cause either an *inhibition*<sup>4</sup>, or an *acceleration*<sup>4,10,11</sup> of the electrochemical reaction.

Essentially the same type of phenomena can occur in the absence of any foreign substance, when the depolarizer alone is present in the solution. The film is then due to the adsorption of the depolarizer itself or of a form which appears in the course of the electrochemical reaction. These phenomena can thus be called *autoinhibition*<sup>12</sup> and *autocatalysis*<sup>13</sup> (autoacceleration) phenomena. They are frequent, especially in organic polarography; before the beginning of our investigations, however, no systematic study of these effects had been made, although a few isolated cases had been mentioned<sup>9,14-16</sup>.

These phenomena are discussed in the second part of this paper.

Throughout this article, we shall assume that the adsorption process is so rapid that it does not control the kinetics of adsorption; in other words, the adsorption process is the most rapid of all the factors which limit the rate of adsorption. This assumption is justified, since the rate of adsorption of organic molecules is in general very large<sup>17a</sup>.

We shall also assume, unless otherwise stated, that the maximum values of the surface concentrations ( $\Gamma_m$  values) can be regarded as constant in the region of potential considered. This assumption is not unreasonable, since we generally shall have to deal with potential ranges of a few tenths of a volt. Even if the  $\Gamma_m$  values vary slightly, the general conclusions will remain valid. Likewise, we shall also assume that the adsorption coefficients are independent of  $E$ .

The mathematical treatments presented here generally deal with the case of a *strong adsorption*; i.e. it is assumed that as long as the surface of the electrode is not saturated, practically all the molecules are adsorbed as soon as they approach the surface: the concentration in the solution near the surface remains very small. The solutions thus derived and the analysis of the problems under these conditions may however be useful for the understanding of cases when adsorption is weaker.

We shall in general consider reduction processes and give the modifications which are necessary to obtain the expressions for an oxidation process.

The symbols and units used, which are listed in the table at the end of the paper, are essentially those of Delahay<sup>18</sup>, with a few modifications and additions.

## PART I. EFFECT OF ADSORPTION ON THE ELECTROCHEMICAL REACTION

### (1) Reversible surface electrochemical reaction

Let us consider a reaction of the type  $O + ne \rightleftharpoons R$ , where O and R are both adsorbed on the surface of the electrode.

In order to obtain an expression for the current  $i$ , the differential equations for diffusion must be solved; the initial conditions (reduction process) are:  $c_O(x, 0) = c$  and  $c_R(x, 0) = 0$ .

The boundary conditions can be obtained as follows:

A first condition is written by expressing that the total amount of substance adsorbed at time  $t$  (after the beginning of the electrolysis) is equal to the amount of O initially adsorbed plus the total amount brought to, or removed from, the electrode by diffusion between time zero and time  $t$ :

$$A\Gamma_O + A\Gamma_R = A\Gamma_O(0) + D_O \int_0^t A \left( \frac{\partial c_O}{\partial x} \right)_{x=0} dt + D_R \int_0^t A \left( \frac{\partial c_R}{\partial x} \right)_{x=0} dt \quad (1)$$

$A$  is the electrode area,  $\Gamma_O$  and  $\Gamma_R$  the surface concentrations of O and R.  $\Gamma_O(0)$  the value of  $\Gamma_O$  at time  $t=0$ .

$\Gamma_O$  and  $\Gamma_R$  are related to the volume concentrations at the electrode surface by the adsorption isotherm.

If it is assumed, for example, that the adsorption obeys a Langmuir isotherm:

$$\Gamma_{\text{O}} = \Gamma_{\text{O},m} \frac{b_{\text{O}}c_{\text{O}}(0, t)}{1 + b_{\text{O}}c_{\text{O}}(0, t) + b_{\text{R}}c_{\text{R}}(0, t)} \quad (2)$$

$$\Gamma_{\text{R}} = \Gamma_{\text{R},m} \frac{b_{\text{R}}c_{\text{R}}(0, t)}{1 + b_{\text{O}}c_{\text{O}}(0, t) + b_{\text{R}}c_{\text{R}}(0, t)} \quad (3)$$

Hence

$$\Gamma_{\text{O}}/\Gamma_{\text{R}} = \frac{b_{\text{O}}\Gamma_{\text{O},m}c_{\text{O}}(0, t)}{b_{\text{R}}\Gamma_{\text{R},m}c_{\text{R}}(0, t)} \quad (4)$$

The Nernst equation applied to the volume concentrations can be written:

$$\frac{c_{\text{O}}(0, t)}{c_{\text{R}}(0, t)} = \exp \frac{nF}{RT} (E - E^0) = \theta \quad (5)$$

By combining eqns. (4) and (5), one obtains:

$$\frac{\Gamma_{\text{O}}}{\Gamma_{\text{R}}} = \frac{b_{\text{O}}\Gamma_{\text{O},m}}{b_{\text{R}}\Gamma_{\text{R},m}} \theta = \eta \quad (6)$$

By replacing the value of  $\theta$  from (5) in eqn. (6), one derives the following relationship:

$$\eta = \exp \left\{ \frac{nF}{RT} \left[ E - \left( E^0 - \frac{2.3RT}{nF} \log_{10} \frac{b_{\text{O}}\Gamma_{\text{O},m}}{b_{\text{R}}\Gamma_{\text{R},m}} \right) \right] \right\} \quad (7)$$

The second boundary condition is thus given by eqn. (6). Furthermore, one has  $c_{\text{O}}(x, t) \rightarrow c$  and  $c_{\text{R}}(x, t) \rightarrow 0$  when  $x \rightarrow \infty$ .

The solution of the diffusion equations in the general case would, under these conditions, involve considerable mathematical difficulties. However, if one assumes that O and R are both very adsorbable ( $b_{\text{O}}$  and  $b_{\text{R}}$  very large), the boundary conditions can be simplified, and the expression of the current can be easily obtained, in classical polarography<sup>5</sup> as well as in linear potential sweep voltammetry<sup>6</sup>. Although it is difficult to determine theoretically the limiting values of the adsorptivity which are necessary for this assumption to hold, an experimental verification, based on the use of the equation of Koryta, can easily be made (*cf.* paragraphs (1B) and (2B) and eqn. (25))

(A) Classical polarography

(a) Equation of the  $i=f(t)$  curves<sup>5,25</sup>. At the beginning of the electrolysis ( $t=0$ ), the area of the drop is equal to zero, and no substance is adsorbed. One has thus  $\Gamma_{\text{O}}(0)=0$ .

O and R being very adsorbable, one has  $c_{\text{O}}(0, t) \ll c$  and  $c_{\text{R}}(0, t) \ll c$  so long as there is no compact film on the surface of the electrode (after the time  $t_m$  at which the film becomes compact, the solution rehomogenizes and  $c_{\text{O}}(0, t)$  and  $c_{\text{R}}(0, t)$  increase).

As  $c_{\text{O}}(0, t) \ll c$ , the flux of O has its maximum value (the conditions are identical with those corresponding to the derivation of the Ilkovic equation):

$$t < t_m \quad D_{\text{O}}A \left( \frac{\partial c_{\text{O}}}{\partial x} \right)_{x=0} = 0.85 \pi^{-\frac{1}{2}} (7/3)^{\frac{1}{2}} m^{\frac{2}{3}} D_{\text{O}}^{\frac{1}{3}} ct^{\frac{2}{3}} \quad (8)$$

(It is assumed that the presence of adsorbed molecules on the surface of the electrode has no effect on the diffusion, which is the case if the distribution of the molecules is homogeneous; see beginning of Part II of this paper and refs. 55 and 56.)

On the other hand, as  $c_R(0, t) \ll c$ , the third term on the right in eqn. (1) may be neglected with respect to the other terms, *i.e.* one can neglect the amount of molecules of R which leave the electrode by diffusion, when compared to the amount of those which remain adsorbed. Equation (1) thus reduces to:

$$\Gamma_O + \Gamma_R = \frac{D_O}{A} \int_0^t A \left( \frac{\partial c_O}{\partial x} \right)_{x=0} dt = 0.74 D_O^{\frac{1}{2}} c t^{\frac{1}{2}} \quad (9)$$

Equation (9) is analogous to the equation of Koryta<sup>19,20</sup>, derived for the case of an electroinactive adsorbate.

The current is given by:

$$i = nF \frac{d(A\Gamma_R)}{dt} - nFD_R A \left( \frac{\partial c_R}{\partial x} \right)_{x=0}$$

*i.e.*, as the current corresponding to the molecules which diffuse away from the electrode can be neglected with respect to the current corresponding to the molecules which remain adsorbed:

$$i = nF \frac{d(A\Gamma_R)}{dt} \quad (10)$$

From eqns. (6), (9) and (10) we obtain:

$$t < t_m \quad i = \frac{7.08 \times 10^4 nm^{\frac{3}{2}} D_O^{\frac{1}{2}} c t^{\frac{1}{2}}}{1 + \eta} = \frac{i_d}{1 + \eta} \quad (11)$$

This equation holds for a prewave as well as for a postwave.

For  $t > t_m$ , the situation is more complicated. Equation (6) is still valid; we shall assume first that  $\Gamma_{O,m} = \Gamma_{R,m} = \Gamma_m$ . Equation (9) then becomes:

$$\Gamma_O + \Gamma_R = \Gamma_m \quad (12)$$

In the derivation of the current, the case of a prewave must be distinguished from the case of a postwave.

In the case of a *prewave* a fraction only of the molecules of O reaching the electrode by diffusion can adsorb (on the free surface appearing as a function of time owing to the growth of the drop). A rehomogenization process takes place and  $c_O(0, t)$  increases. According to eqn. (5)  $c_R(0, t)$  must also increase. However, for values of the potential corresponding to the prewave,  $\theta \gg 1$  and if  $t$  is not too large with respect to  $t_m$ , the absolute value of  $c_R(0, t)$  will remain small. Under these conditions, the diffusion of R will still be negligible and the current will still be given by eqn. (10).

From (6), (10) and (12), we obtain:

$$t > t_m ; \Gamma_{O,m} = \Gamma_{R,m} = \Gamma_m \quad i = \frac{5.47 \times 10^4 nm^{\frac{3}{2}} \Gamma_m t^{-\frac{1}{2}}}{1 + \eta} = \frac{i_a}{1 + \eta} \quad (13)$$

For a *postwave*, after time  $t_m$  and for values of the potential corresponding to the rise or to the plateau of the postwave, the flux of O retains its maximum

value: all the molecules of O which reach the electrode either adsorb or are reduced; a first part is adsorbed without being reduced, a second part is adsorbed and then reduced (adsorption current), the third part is reduced *through the film* (diffusion current).

The current is thus equal to the diffusion current (given by the Ilkovic equation) less the hypothetical current  $nF d(A\Gamma_O)/dt$  which would correspond to the molecules which are adsorbed without being reduced:

$$t > t_m ; \Gamma_{O,m} = \Gamma_{R,m} = \Gamma_m \quad i = i_d - nF \frac{d(A\Gamma_O)}{dt}$$

Whence, in view of eqns. (6) and (12):

$$t > t_m ; \Gamma_{O,m} = \Gamma_{R,m} = \Gamma_m \quad i = 7.08 \times 10^4 nm^3 D_O^{\frac{1}{2}} ct^{\frac{1}{2}} - 5.47 \times 10^4 nm^3 \Gamma_m t^{-\frac{1}{2}} \eta / (1 + \eta) \tag{14}$$

The value of  $t_m$  can be deduced from eqn. (9), in which  $\Gamma_O + \Gamma_R = \Gamma_m$ :

$$t_m = 1.82 \Gamma_m^2 / D_O c^2 \tag{15}$$

By substituting in eqns. (11) and (14) the value of  $D_O$  given by eqn. (15), and by slightly transforming eqn. (13) and the second term on the right in eqn. (14), one obtains:

$t < t_m$  (prewave and postwave)

$$i = \mathcal{I} \frac{1.75(t/t_m)^{\frac{1}{2}}}{1 + \eta} \tag{16}$$

$t > t_m$  ;  $\Gamma_{O,m} = \Gamma_{R,m}$  (prewave)

$$i = \mathcal{I} \frac{(t/t_m)^{-\frac{1}{2}}}{1 + \eta} \tag{17}$$

$t > t_m$  ;  $\Gamma_{O,m} = \Gamma_{R,m}$  (postwave)

$$i = \mathcal{I} \left\{ 1.75(t/t_m)^{\frac{1}{2}} - \frac{\eta}{1 + \eta} (t/t_m)^{-\frac{1}{2}} \right\} \tag{18}$$

with  $\mathcal{I} = 5.47 \times 10^4 nm^3 \Gamma_m t_m^{-\frac{1}{2}}$ .

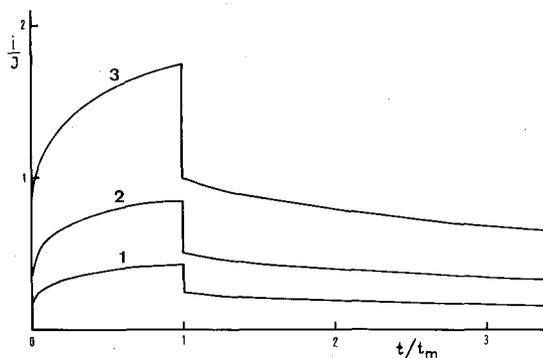


Fig. 1. Theoretical variation of current for a prewave (eqn. 16 for  $t < t_m$  and eqn. 17 for  $t > t_m$ ). (1)  $\eta = 3$ ; (2)  $\eta = 1$  (half-wave potential  $E_{\frac{1}{2},a}$ ); (3)  $\eta = 0$  (plateau of the prewave).

$i=f(t)$  curves calculated from eqns. (16) to (18) for a prewave and a postwave are shown in Figs. 1 and 2.

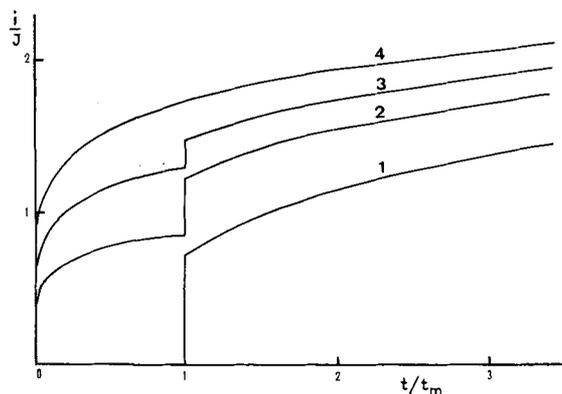


Fig. 2. Theoretical variation of current for a postwave (eqn. 16 for  $t < t_m$  and eqn. 18 for  $t > t_m$ ). (1)  $\eta \rightarrow \infty$  (plateau of the main wave, before the postwave); (2)  $\eta = 1$  (half-wave potential of the postwave); (3)  $\eta = \frac{1}{3}$ ; (4)  $\eta = 0$  (plateau of the postwave).

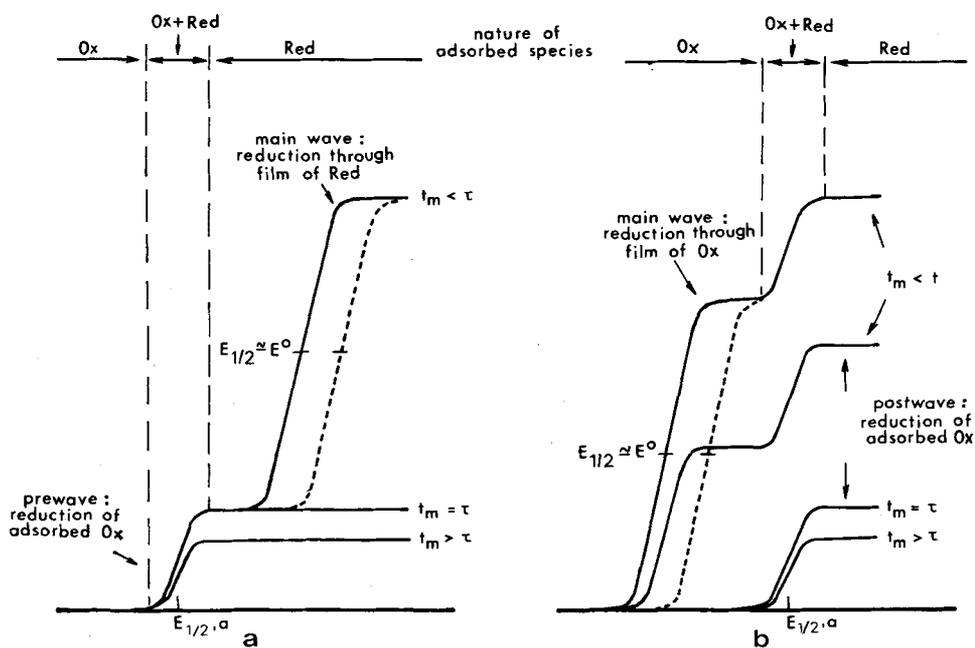


Fig. 3. Theoretical polarograms. (a) Prewave; (b) postwave. (-----) In (a) inhibition of reduction by film of Red; in (b) inhibition of reduction by film of Ox.

The derivation of the current along the "main" wave, which corresponds to the reduction of O either *through a film* of R (prewave) or *through a film* of O (postwave) is a priori difficult. If  $t_m < \tau$  a rehomogenization process will occur after time

$t_m$  and  $c_O(0, t)$  and  $c_R(0, t)$  will increase. For a certain value of the potential the molecules of O in the solution near the surface will begin to be reduced, giving rise to the "main" wave. This shows that the prewave or the postwave appears alone when  $t_m \geq \tau$ , the main wave appearing only when  $t_m < \tau$  (Fig. 3). Under these conditions, the evaluation of  $c_O(0, t)$  and  $c_R(0, t)$  is not easy. However, if the concentration  $c$  in the bulk of the solution is sufficiently large,  $t_m$  is much smaller than the drop time  $\tau$ , and the solution is rehomogenized well before  $\tau$ , nearly from the beginning of the life of the drop. If the film does not disturb the electrochemical reaction, *i.e.* if it does not inhibit or accelerate the reaction (see discussion at the end of the paper), the conditions are virtually the same as in the case of a normal diffusion wave. The main wave is then identical to a reversible wave, with  $E_{\frac{1}{2}} \simeq E^0$ .

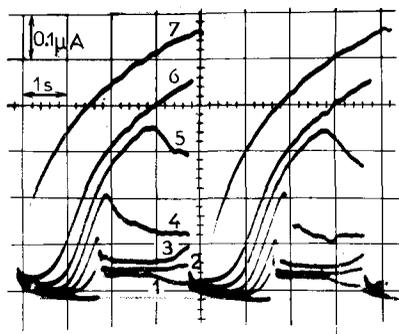


Fig. 4.  $i-t$  curves for reduction of tetramethylthiuram disulfide. pH 6; water-ethanol 1/1;  $c = 1.4 \times 10^{-4}$  mol  $l^{-1}$ ;  $m = 2.10$  mg  $s^{-1}$ . Potential from 1 to 7:  $-0.360, -0.405, -0.425, -0.450, -0.465, -0.515, -0.565$ .

Examples of prewaves are numerous (see *e.g.* ref. 21). As was shown in the case of methylene blue<sup>5</sup>, the  $i-t$  curves vary as predicted by eqns. (16) and (17) and Fig. 1. The decrease of the current at time  $t_m$  is however less sudden than predicted by the theory, which is due to the fact that the hypothesis on the influence of the film on diffusion is no longer valid when the coverage approaches 1 (*cf.* Part II, and refs. 4 and 59). On the other hand, postwaves are less common, and the  $i-t$  curves have hardly been studied experimentally (see, however, ref. 22). Figure 4 shows an example of such curves, which present the expected shape, with a sharp rise in current at time  $t_m$ ; the value of  $t_m$  agrees well with the calculated value<sup>25</sup>.

(b) *Equation of the adsorption wave.* Let us first distinguish in the case of a postwave (eqn. 18) the adsorption current from the "diffusion" current.

The "adsorption" current, for  $t > t_m$ , is given by the molecules of O which can adsorb owing to the growth of the drop, and which are then reduced:

$$t > t_m; \Gamma_{O,m} = \Gamma_{R,m} \quad i = nFA d(A\Gamma_R)/dt$$

As eqns. (6) and (12) are still valid, one readily derives for the adsorption current eqns. (13) or (17).

The "adsorption" current has thus in the case of a postwave the same expression as in the case of a prewave. Consequently, in both cases the mean

adsorption current  $\bar{i}$  is given by the following expressions:

$$t_m < \tau ; \Gamma_{O,m} = \Gamma_{R,m} \quad \bar{i} = \frac{1}{\tau} \int_0^{t_m} i' dt + \frac{1}{\tau} \int_{t_m}^{\tau} i'' dt \quad (18')$$

$$t_m > \tau \quad \bar{i} = \frac{1}{\tau} \int_0^{\tau} i' dt$$

$i'$  and  $i''$  being the currents given by eqns. (16) and (17) respectively.

One obtains:

$$t_m < \tau ; \Gamma_{O,m} = \Gamma_{R,m} = \Gamma_m \quad \bar{i} = \frac{8.20 \times 10^4 nm^3 \Gamma_m \tau^{-\frac{1}{2}}}{1 + \eta} = \frac{\bar{i}_a}{1 + \eta} \quad (19)$$

$$t_m \geq \tau \quad \bar{i} = \frac{6.07 \times 10^4 nm^3 D_O^{\frac{1}{2}} c \tau^{\frac{1}{2}}}{1 + \eta} = \frac{\bar{i}_d}{1 + \eta} \quad (20)$$

The equation of the adsorption wave (eqns. 19 and 20) is thus always identical to the equation of a reversible diffusion wave. In view of eqn. (7) it can be written in the form ( $\Gamma_{O,m} = \Gamma_{R,m}$ ):

$$E = E^0 - (2.3RT/nF) \log(b_O/b_R) + (2.3RT/nF) \log[(\bar{i}_1 - \bar{i})/\bar{i}] \quad (21)$$

$\bar{i}_1$  is the limiting current on the plateau of the adsorption wave ( $\bar{i}_1 = \bar{i}_a$  for  $t_m < \tau$ , and  $\bar{i}_1 = \bar{i}_d$  for  $t_m \geq \tau$ ) (Fig. 3).

The value of  $b_O/b_R$  can be calculated from the value of the half-wave potential  $E_{\frac{1}{2},a} = E^0 - (2.3RT/nF) \log(b_O/b_R)$ . (See however ref. 74.)

If  $b_O = b_R$ ,  $E_{\frac{1}{2},a} = E^0$ ; the adsorption wave appears at the same potential as the normal wave. It still exists, but cannot be seen: the polarogram has a normal shape. Likewise the  $i=f(t)$  curve has always a normal shape although a part of the current still corresponds to the reduction of the adsorbed molecules, the other part corresponding to the reduction through the film.

These results remain valid if  $b_O$  is not too different from  $b_R$ . If  $b_O/b_R = 10^{\pm 1}$  for instance,  $E_{\frac{1}{2},a} - E^0$  is equal to 59 mV for  $n=1$ , and the waves are not separated.

When  $b_O \approx b_R$ , the use of linear potential sweep voltammetry is advantageous, as will be shown later.

According to eqn. (20), the current on the plateau of the prewave  $\bar{i}_1$  (obtained for  $\eta \rightarrow 0$ ), is proportional to  $m^{\frac{3}{2}} \tau^{\frac{1}{2}}$  (or to  $h^{\frac{1}{2}}$ ,  $h$  being the height of the mercury reservoir) when  $t_m \geq \tau$ , i.e. when the bulk concentration is small enough for the adsorption wave to appear alone. Equation (19) shows that  $\bar{i}_1$  is proportional to  $m^{\frac{3}{2}} \tau^{-\frac{1}{2}}$  (or  $h$ ) when  $t_m < \tau$ , i.e. as soon as the bulk concentration is large enough for both the normal and the adsorption waves to appear (Fig. 3).

If  $\Gamma_{O,m} \neq \Gamma_{R,m}$  the preceding equations are modified. It can easily be shown that

$$t_m = \frac{1.82}{D_O c^2} \left( \frac{\Gamma_{R,m} + \eta \Gamma_{O,m}}{1 + \eta} \right)^2 \quad (22)$$

$t_m$  depends on the potential and varies between  $1.82 \Gamma_{O,m}^2 / D_O c$  for  $\eta \rightarrow \infty$  ( $E \rightarrow \infty$ , foot of the adsorption wave) and  $1.82 \Gamma_{R,m}^2 / D_O c$  for  $\eta \rightarrow 0$  ( $E \rightarrow \infty$ , plateau of the adsorption wave). (We assume that O and R adsorb independently, i.e. the

adsorption of one of them does not modify the adsorption of the other.)

For  $t < t_m$ , the adsorption current is still given by eqn. (11). For  $t > t_m$ , one has:

$$i = 5.47 \times 10^4 nm^3 t^{-\frac{3}{2}} (\Gamma_{R.m} + \eta \Gamma_{O.m}) / (1 + \eta)^2 \tag{23}$$

From eqns. (11) and (23), the mean adsorption current for  $t_m < \tau$  can easily be shown to be:

$$\bar{i} = 8.20 \times 10^4 nm^3 \tau^{-\frac{3}{2}} (\Gamma_{R.m} + \eta \Gamma_{O.m}) / (1 + \eta)^2 \tag{24}$$

while eqn. (20) still holds for  $t_m \geq \tau$ .

When  $t_m \geq \tau$ , the equation of the adsorption wave is still identical to the equation of a reversible diffusion wave; as shown by eqn. (24), this is no longer true when  $t_m < \tau$ , i.e. when both waves are observed.

If, moreover,  $\Gamma_{O.m}$  and  $\Gamma_{R.m}$  are functions of the potential, eqns. (20) and (22) still hold. The equation of the wave always differs from the equation of a reversible wave even for  $t_m > \tau$ , since  $\eta$  is not a simple exponential function of  $E$  (cf. eqn. 7). A similar result is obtained if  $b_O$  and  $b_R$  are functions of the potential.

The solution for the general case, when either O, or R, or both O and R are weakly or strongly adsorbed, has been derived rigorously only for semi-infinite linear diffusion using a linear adsorption isotherm<sup>23</sup>. The solutions obtained have been transposed to the case of the dropping mercury electrode, and lead to a semi-quantitative evaluation of the current: in the case of a prewave, for example, when R alone is strongly adsorbed, the  $i-t$  curves along the prewave are different from those given above. On the plateau, however, the curves are identical to those obtained when O and R are both strongly adsorbed, since the same conditions are fulfilled in both cases: the film is made only of the strongly adsorbed molecules of R.

(B) Linear potential sweep voltammetry

Let us consider the case of a reduction, O and R being strongly adsorbable. From the beginning of the life of the drop until time  $t_1$ , corresponding to the starting of the potential sweep, the potential of the electrode is kept at a constant value  $E_i$  (initial potential). If  $E_i$  is adjusted at a value for which O can be adsorbed, a certain amount of O will have diffused towards the surface of the electrode and be adsorbed at time  $t_1$ . Taking  $t_1$  as the origin of times for the electrolysis ( $t=0$ ) one has then in eqn. (1)  $\Gamma_O(0) = \Gamma_O(t_1)$ .

O being strongly adsorbed,  $\Gamma_O(t_1)$  is given by the equation of Koryta<sup>19, 20</sup> (cf. eqn. 9, in which  $\Gamma_R = 0$  and  $t = t_1$ ):

$$\Gamma_O(t_1) = 0.74 D_O^{\frac{1}{2}} c t_1^{\frac{1}{2}} \tag{25}$$

The film of O becomes compact at time  $t_1$  for a concentration  $c_m$  defined by:

$$\Gamma_{O.m} = 0.74 D_O^{\frac{1}{2}} c_m t_1^{\frac{1}{2}}$$

If  $c < c_m$ , the film is not compact ( $\Gamma_O(t_1) < \Gamma_{O.m}$ ).  $c_O(0, t)$ , and consequently  $c_R(0, t)$ , remain practically equal to zero up to time  $t_1$ . If the potential sweep rate is large enough (in practice for  $v$  larger than a few tenths of a  $V s^{-1}$  under the usual conditions, e.g. for  $t_1 \approx 10$  s) one can neglect the amount of O or R

brought to, or removed from the surface of the electrode by diffusion during the sweep (last two terms on the right in eqn. (1)), when compared to the amount which remains adsorbed. Equation (1) reduces to:

$$\Gamma_{\text{O}} + \Gamma_{\text{R}} = \Gamma_{\text{O}}(t_1) \quad (26)$$

Under these conditions only one peak will be observed, which we shall designate as "adsorption" peak (reduction of adsorbed molecules).

If  $c > c_m$ ,  $\Gamma_{\text{O}}$  reaches its maximum value  $\Gamma_{\text{O},m}$  for a time  $t_m < t_1$ . Time  $t_m$  can be readily deduced from eqn. (9) in which  $\Gamma_{\text{R}} = 0$ ,  $\Gamma_{\text{O}} = \Gamma_{\text{O},m}$  and  $t = t_m$ :

$$t_m = 1.82 \Gamma_{\text{O},m}^2 / c^2 D_{\text{O}}$$

Between times  $t_m$  and  $t_1$ , a rehomogenization of the solution takes place, and  $c_{\text{O}}(0, t)$  increases. A new peak will appear, which is due to the reduction of the molecules which are not adsorbed at time  $t_1$ , and which reach the surface of the electrode by diffusion during the potential sweep<sup>24</sup>. We shall call this peak "diffusion" peak. Theoretically this peak should not be identical to a normal diffusion peak<sup>18a</sup>, for the concentration distribution in the solution for  $t=0$  is different. However, when the concentration is large enough,  $t_m$  becomes very short, the solution rehomogenizes rapidly, and is again practically homogeneous for  $t=0$ ; the conditions are thus virtually the same as for a normal diffusion peak.

The diffusion peak can either be preceded by the adsorption peak ( $b_{\text{O}} < b_{\text{R}}$  for a reduction, cf. classical polarography), or be followed by it ( $b_{\text{O}} > b_{\text{R}}$ ), or appear at the same potential ( $b_{\text{O}} \approx b_{\text{R}}$ ).

(a) *Simple reversible reaction*<sup>6, 24, 25</sup>  $\text{O} + n\text{e} \rightleftharpoons \text{R}$ . Let us first assume that  $c < c_m$ , i.e. that the film on the surface of the drop is not compact. Equation (6) still holds,  $E$  being given by the relationship (for a reduction):  $E = E_i - vt$ , where  $v$  is the rate of potential change. The area of the drop  $A$  can be regarded as constant if the sweep rate is large enough, and eqn. (10) becomes:

$$i = nFA d\Gamma_{\text{R}}/dt \quad (27)$$

From eqns. (6), (26) and (27), one obtains for  $i$ :

$$i = [(nF)^2/RT] Av\Gamma_{\text{O}}(t_1)\eta/(1+\eta)^2 \quad (28)$$

or, at 25°C:

$$i = 3.76 \times 10^6 An^2 v\Gamma_{\text{O}}(t_1)\eta/(1+\eta)^2 \quad (29)$$

The function  $G = \eta/(1+\eta)^2$  exhibits for  $\eta=1$  a maximum whose value is 0.25. From (7), one deduces for the peak potential

$$E_p = E^0 - (2.3RT/nF) \log(b_{\text{O}}\Gamma_{\text{O},m}/b_{\text{R}}\Gamma_{\text{R},m})$$

The corresponding peak current is:

$$i_p = 9.40 \times 10^5 An^2 v\Gamma_{\text{O}}(t_1) \quad (30)$$

If  $c < c_m$ ,  $\Gamma_{\text{O}}(t_1) < \Gamma_{\text{O},m}$ ;  $\Gamma_{\text{O}}(t_1)$  is given by eqn. (25). By replacing in eqn. (30), one obtains:

$$c < c_m \quad i_p = 6.96 \times 10^5 An^2 vcD_{\text{O}}^{1/2} t_1^{1/2} \quad (31)$$

which shows that  $i_p$  is proportional to  $c$ .

Let us consider now the case when  $c > c_m$  (the film of O is compact for  $t=0$ ).

If  $\Gamma_{O,m} = \Gamma_{R,m}$ , one has:

$$c > c_m \quad i_p = 9.40 \times 10^5 A n^2 v \Gamma_m \tag{32}$$

If  $\Gamma_{O,m}$  is different from  $\Gamma_{R,m}$  the problem is more complex. If  $\Gamma_{O,m} > \Gamma_{R,m}$  for example, a certain amount of molecules of O can be desorbed by molecules of R during the potential sweep; the current would then be smaller than predicted by eqn. (29) in which  $\Gamma_O(t_1) = \Gamma_{O,m}$ . Moreover the peak will be deformed. Likewise, if  $\Gamma_{O,m} < \Gamma_{R,m}$  a further adsorption of molecules during the sweep will be possible, which will result in a higher current and a deformation of the peak. If a variation of  $\Gamma_{O,m}$  or  $\Gamma_{R,m}$  occurs suddenly at a certain potential value, a new current can appear under the form of a secondary peak. Such a peak has been observed for example in the case of methylene blue (see ref. 6, Fig. 2, peak A<sub>2</sub>), and is possibly due to that kind of effect.

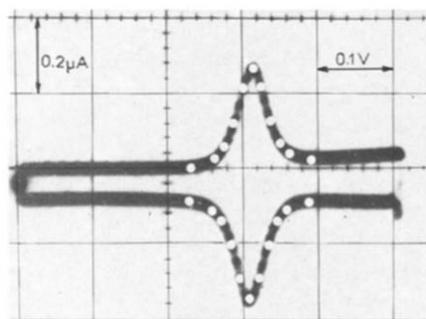
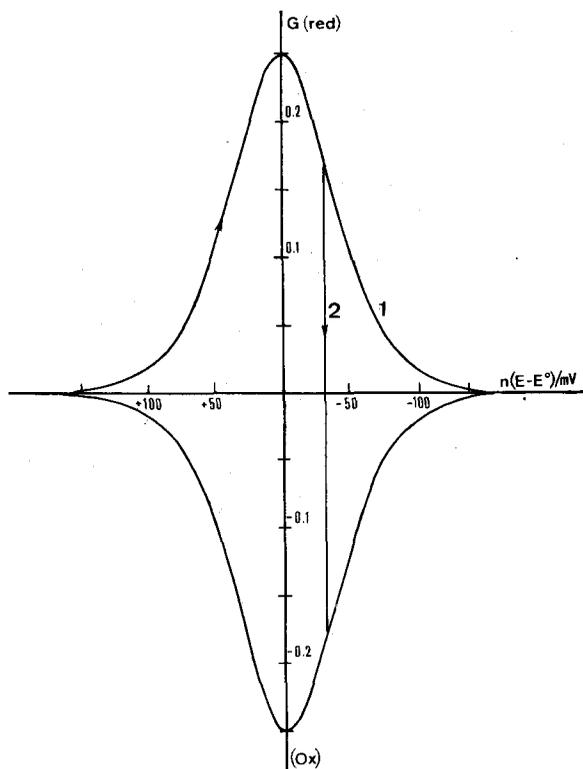


Fig. 5. Theoretical adsorption peaks (function  $G = \pm \eta/(1 + \eta)^2$ ). (1) The potential is reversed after the current has practically dropped to zero; (2) the potential is reversed along the peak.

Fig. 6. Adsorption peaks for benzo(c)cinnoline. pH 11; water-ethanol 9:1;  $c = 4.5 \times 10^{-6} \text{ mol l}^{-1}$ ;  $v = 0.25 \text{ V s}^{-1}$ ;  $t_1 = 8 \text{ s}$ ;  $m = 0.219 \text{ mg s}^{-1}$ . The theoretical values (points) have been calculated (eqn. 29) with:  $A = 1.36 \times 10^{-2} \text{ cm}^2$ ;  $n = 2$ ;  $v = 0.25 \text{ V s}^{-1}$ ;  $\Gamma_O(t_1) = 2.0 \times 10^{-11} \text{ mol cm}^{-2}$  (this value was obtained by graphical integration of the peak).

These results lead to the following conclusions:

For  $c < c_m$  i.e. when the film is not compact, a change in  $b_O$ ,  $b_R$ ,  $\Gamma_{O,m}$  or  $\Gamma_{R,m}$  results only (cf. expression of  $E_p$ ) in a shift of the peak along the potential axis. The adsorption peak has thus always the same shape; in particular, the width of the peak at mid-height  $\delta$  is equal to  $90.6/n$  mV. The peak is symmetrical with respect to the ordinate axis (Fig. 5). These results still hold for  $c > c_m$  if  $\Gamma_{O,m} = \Gamma_{R,m}$ . Figure 6 shows a comparison between an experimental curve and the values calculated by means of eqn. (29); the agreement is quite good.

In other cases<sup>24</sup>, the width of the peak is different from the theoretical value  $90.6/n$ ; this may be due to the fact that the adsorption does not obey a Langmuir isotherm<sup>74</sup>. For methylene blue, the width depends on the concentration<sup>6</sup>.

It can readily be seen that in the case of an oxidation, the current is still given by eqn. (29), in which  $\Gamma_O(t_1)$  has been replaced by  $\Gamma_R(t_1)$ , with a minus sign on the right instead of a plus sign. The value of the peak potential must thus be the same for the oxidation peak and for the reduction peak, in contrast with the difference of  $56/n$  mV which is observed in the case of diffusion peaks<sup>18b</sup>. This is confirmed experimentally although a difference of a few mV is often observed between the peak potentials (Fig. 6 and refs. 24 and 25).

The calculations presented in this paragraph have been made under the assumption that O and R are very adsorbable ( $b_O$  and  $b_R$  very large). That this condition is fulfilled can be verified experimentally: the value of  $\Gamma_O(t_1)$  can be determined by graphical integration of the area of the adsorption peak; the value obtained for different values of  $t_1$  must obey the law of Koryta (eqn. 25), which means that practically all the molecules which diffuse towards the electrode remain adsorbed; when there is no kinetic complication (see next paragraph) the integration of the oxidation peak must give the same result.

If  $b_O \simeq b_R$  the adsorption peaks are obtained alone for  $\Gamma_O(t_1) < \Gamma_{O,m}$

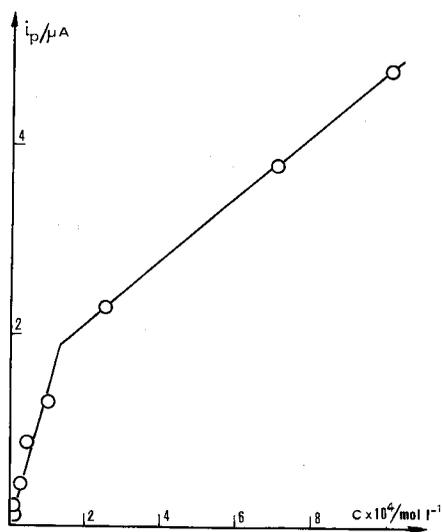


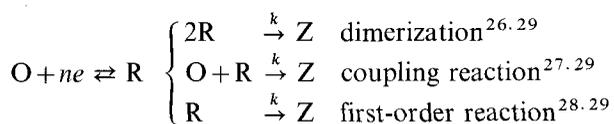
Fig. 7.  $i_p$ - $c$  graph for the reduction peak of phenazine.  $\text{HClO}_4$  0.1 M; water-ethanol 4:1;  $v=0.6$  V  $\text{s}^{-1}$ ;  $t_1=8$  s.

( $c < c_m$ ) even though in classical polarography neither a prewave nor a postwave appears (Fig. 6). The method is thus advantageous in that case for the study of adsorption. When  $c > c_m$  the height of the adsorption peak becomes independent of  $c$ , and the diffusion peak appears, superimposed with the adsorption peak. The slope of the graph  $i_p = f(c)$  changes abruptly when  $c = c_m$  (Fig. 7) for the slope of the straight line is different for the adsorption peak (eqn. 31) and for the diffusion peak (ref. 18, eqn. 6-17); it is generally larger for the adsorption peak. (For further details, and other examples, see ref. 24.)

The theory also accounts for one of the most peculiar characteristics of adsorption peaks, which had been mentioned long ago: the proportional dependence of the peak current on the sweep rate  $v$ .

Another consequence of the theory is that the shape of the oxidation peak remains the same whatever the potential at which the scan is reversed (Fig. 5) (this was verified experimentally<sup>23</sup>). This can be advantageous in certain cases, since a study will be possible even if the separation from other peaks is not complete.

(b) *Reversible reaction followed by an irreversible chemical reaction*<sup>26-31</sup>. A theoretical study has been made of the three cases:



with the same hypotheses as in the simple case: strong adsorption of O and R, Langmuir adsorption. Owing to the chemical reaction, the oxidation peak is smaller than the reduction peak. The peak potential  $E_p$  of the reduction peak varies proportionally to  $\log v/kc$  for second-order reactions, or  $\log v/k$  for the first-order reaction, when  $v$  is small.

The main criteria permitting a distinction to be made between the different types of reaction are: the slope of the variation of  $E_p$  with  $\log v$ , the dependence of the height of the oxidation peak on the switching potential, and the study of the variation of the width  $\delta$  at mid-height with  $v$  or  $c$ . The rate constant of the chemical reaction can be calculated from a comparison of the height of the oxidation peak with that of the reduction peak, or from the graph  $E_p = f(\log v)$ .

The theory has been applied to the determination of the dimerization rate constant of mercurio-organic radicals<sup>31</sup> and to the study of the benzidine rearrangement on the surface of a mercury electrode<sup>30</sup>. The results obtained for the benzidine rearrangement are of special interest: the surface rate constant is about 150 times smaller than the volume rate constant. Two explanations can be given; the hydrazobenzene molecule can adopt a configuration in which the two benzene rings lie virtually in same plane. The potential at which the experiments are carried out being much more positive than the potential of zero charge, the two benzene rings must lie flat on the surface, owing to the interaction of the  $\pi$  electrons with the metal<sup>46-48</sup> (this interaction is not hindered by the fact that the molecule is diprotonated<sup>49</sup> before the rearrangement takes place). A first explanation for the decrease of the rate of the surface reaction was given previously<sup>30</sup>: during the rearrangement, the formation of the polar transition complex must necessarily be preceded by the desorption of one of the rings, which causes a decrease in the

rate because of the supplementary activation energy which has to be supplied. An alternative explanation is as follows: the metal surface acts as an electron withdrawing substituent, because it draws off the  $\pi$  electrons from the molecule. This can explain the decrease, for it is well known that the rate of the benzidine rearrangement is reduced by electron withdrawing substituents<sup>49</sup>.

(2) *Totally irreversible surface reaction*

The adsorption of the product of the electrochemical reaction, if the occurrence of autoinhibition phenomena is excluded, cannot exert any influence on the electrochemical reaction. Only the adsorption of the depolarizer can modify the reaction.

(A) *Classical polarography*

The adsorption of the depolarizer can result in two types of waves:

(i) If the reduction (or oxidation) of the depolarizer is rendered *more difficult* by its adsorption, one can theoretically observe a postwave. No experimental example of such a postwave has been hitherto reported. In all the cases where a greater difficulty of reduction has been shown to result from the adsorption of the depolarizer (see *e.g.* ref. 32, Figs. 8, 10 and 3), autoinhibition phenomena due to a film of the depolarizer itself are simultaneously observed; these phenomena which lead to typical polarograms (*cf.* Part II), preclude the observation of a prewave.

(ii) The hypothesis has been made, on the contrary, that the adsorption facilitates the reduction<sup>33,34</sup> (or the oxidation), although no unambiguous corresponding experimental example has been reported.

Let us consider the case of a reduction: a shift of the wave towards more positive potentials will be observed.

If the reduced form is not adsorbed, the whole wave will be shifted and deformed and no prewave will appear. When the current is not too small compared to the diffusion current, nothing limits the adsorption, since O is destroyed by reduction on the surface of the electrode.

If the reduced form is strongly adsorbed and prevents O from being adsorbed, a prewave will appear, since the surface of the electrode will be blocked as soon as a compact film of the reduced form is built.

It will thus be difficult to distinguish the present case from two others, which give similar results and which are caused by the adsorption of the reduction product (see Part II):

— The autocatalysis by the reduction product, which results also in a shift of the wave towards more positive potentials;

— An autoinhibition by the reduction product, which gives rise to a wave presenting the appearance and the characteristics of a prewave.

A study of the adsorption of the depolarizer and of the reduced form will help to make a distinction between the two types.

Another criterion will be given by the study of the  $i=f(t)$  curves. Let us assume (O is very adsorbable) that the reaction scheme is as follows: diffusion of O towards the electrode—adsorption—reduction in the adsorbed state. The expression of the current  $i$  at any potential along the wave can be calculated as follows:

$$i = nF A k_f \Gamma_O = nF A \Gamma_O k_f^0 \exp(-\alpha n_x F E / RT) \quad (33)$$

On the other hand, O being very adsorbable, the total amount of molecules which have reached the electrode at time  $t$  is given by the equation of Koryta<sup>19,20</sup>. The superficial concentration  $\Gamma_O$  at time  $t$  will then be equal to that amount less the amount which has disappeared in the reduction on a unit surface:

$$\Gamma_O = 0.74 c D_O^{1/2} t^{1/2} - \frac{1}{nFA} \int_0^t i dt \quad (34)$$

By solving the system of eqns. (33) and (34), (with  $A = 0.85 \text{ m}^2 \text{ t}^{2/3}$ ) one obtains<sup>23</sup> at 25°C:

$$i = 7.08 \times 10^4 \text{ nm}^3 c D_O^{1/2} t^{1/2} s^{-1/2} e^{-s} \int_0^s x^{1/2} e^x dx \quad (35)$$

with  $s = k_f t$ .

At the foot of the wave (positive values of  $E$ ,  $k_f$  small), or at the beginning of the  $i=f(t)$  curve ( $t$  small),  $s$  is small, and eqn. (35) can be written:

$$i = 6.07 \times 10^4 \text{ nm}^3 c D_O^{1/2} k_f t^{7/6} \quad (36)$$

The  $i-t$  curves at the foot of the wave must thus have a typical shape and vary proportionally to  $t^{7/6}$ , as in the case of an acceleration of the reaction by a foreign substance<sup>10,11</sup>. This result must hold, whether the product of the reduction is adsorbed or not: at the foot of the wave the concentration of R is not large enough to disturb eventually the reduction. At the foot of the wave for an autocatalysis by the product of the reaction  $i$  varies exponentially with time<sup>35</sup>; for an inhibition by the product of the reaction  $i$  is proportional to  $t^{2/3}$  at the foot of the wave<sup>36-39</sup> (see Part II).

(B) *Linear potential sweep voltammetry*<sup>24, 25, 40</sup>

As in the reversible case, the adsorption peak will appear alone if  $c < c_m$  ( $\Gamma_O(t_1) < \Gamma_m$ ); if  $c > c_m$ , the diffusion peak will also be obtained.

In order to calculate the expression of  $i$ , we shall still assume that the potential sweep rate is so large that the amount of molecules brought to the electrode by diffusion during the potential sweep is negligible when compared to the amount adsorbed, and that  $A$  can be regarded as constant. Let us consider the case of a reduction;  $i$  is still given by eqn. (33) in which  $E = E_i - vt$ .

Another equation is obtained by expressing that  $\Gamma_O$  is equal to the initial superficial concentrations  $\Gamma_O(t_1)$  less the amount which has disappeared in the reduction:

$$\Gamma_O = \Gamma_O(t_1) - \frac{1}{nFA} \int_0^t i dt \quad (37)$$

From (33) and (37), with the condition that  $\Gamma_O = \Gamma_O(t_1)$ , for  $t=0$ , one obtains:

$$i = (F^2/RT) n \alpha n_x v \Gamma_O(t_1) \exp[\exp(-aE_i + g)] \exp[-aE + g] \cdot \exp[-\exp(-aE + g)] \quad (38)$$

with  $a = \alpha n_x F / RT$  and  $g = \ln(k_f^0 / av)$ .

The value of the peak potential  $E_p$  is obtained from the derivative  $di/dE$

$$E_p = g/a = (2.3 RT/\alpha n_x F) \log_{10}(RTk_f^0/\alpha n_x Fv)$$

The peak current is obtained by substituting  $E$  by  $E_p = g/a$  in eqn. (38).

If the starting potential is positive enough compared to the peak potential  $\exp[\exp(-aE_i + g)] = \exp[\exp - a(E_i - E_p)] \approx 1$  (1.02 for example for  $\alpha n_x = 0.5$  and  $E_i - E_p = 0.2$  V); eqn. (38) simplifies to:

$$i = (F^2/RT)n\alpha n_x v \Gamma_O(t_1) \exp\{-a(E - E_p)\} \exp\{-\exp[-a(E - E_p)]\} \quad (39)$$

and, for the peak current:

$$i_p = e^{-1}(F^2/RT)n(\alpha n_x)Av\Gamma_O(t_1) \quad (40)$$

$$F^2/RT = 3.76 \times 10^6 \text{ at } 25^\circ\text{C}$$

In the case of an oxidation,  $\alpha$  must be replaced by  $1 - \alpha$  and the minus sign preceding  $\alpha n_x F(E - E_p)/RT$  must be replaced by a plus sign, and  $i$  is negative. An equation similar to (39) has been obtained independently by Voloshin<sup>41</sup>.

The variation of the function  $G = i/3.76 \times 10^6 n \alpha n_x Av \Gamma_O(t_1)$  is shown in Fig. 8. The peak is asymmetrical; it always has the same shape, which is not affected by a change in the sweep rate  $v$ , or in  $k_f^0$ . A change in the values of  $v$  or  $k_f^0$  causes only a shift of the peak along the potential axis. The width of the peak depends on  $\alpha n_x$ . At mid-height, the width  $\delta$  is equal to  $62.5 \alpha n_x$  mV for a reduction (for an oxidation,  $\delta = 62.5 (1 - \alpha)n_x$ ). As shown by eqn. (40)  $i_p$  varies linearly with  $v$ , as in the case of a reversible reaction.

As in the reversible case, the calculations are valid only if the adsorption of O is large enough. This condition is verified if the values of  $\Gamma_O(t_1)$ , obtained by

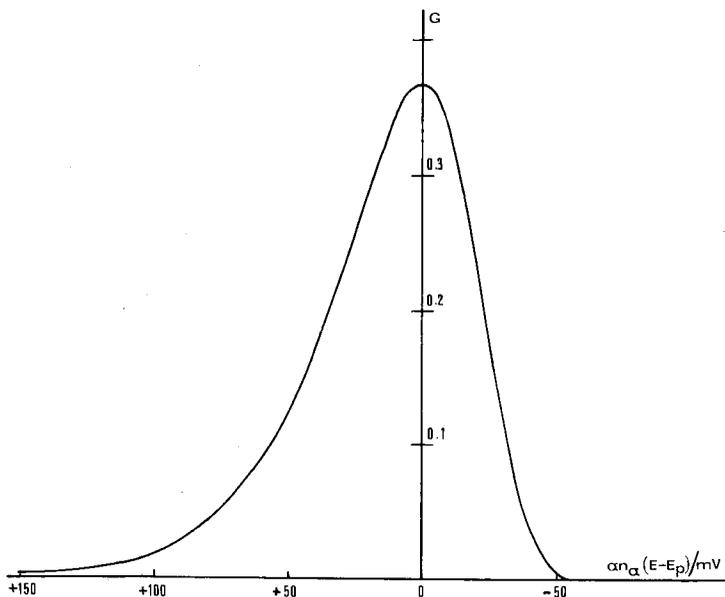


Fig. 8. Variations of function  $G$  (irreversible peak, eqn. 39) with  $\alpha n_x (E - E_p)$ .

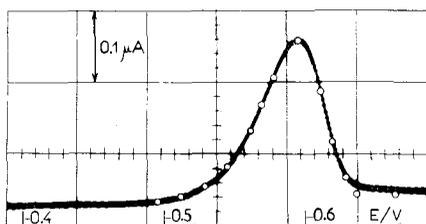


Fig. 9. Adsorption peak of *trans*-4',4''-dipyridyl-1,2-ethylene.  $H_2SO_4$  0.05 M; water;  $c=0.5 \times 10^{-5}$  mol  $l^{-1}$ ;  $v=0.1$  V  $s^{-1}$ ;  $E_i=-0.3$  V;  $t_1=8$  s. The theoretical values (points) have been calculated (eqn. 39) with  $\Gamma_0(t_1)=0.39 \times 10^{-10}$  mol  $cm^{-2}$  (value obtained by graphical integration of the peak);  $A=1.7 \times 10^{-2}$   $cm^2$ ;  $\alpha n_2=1.20$ ;  $n=2$ .

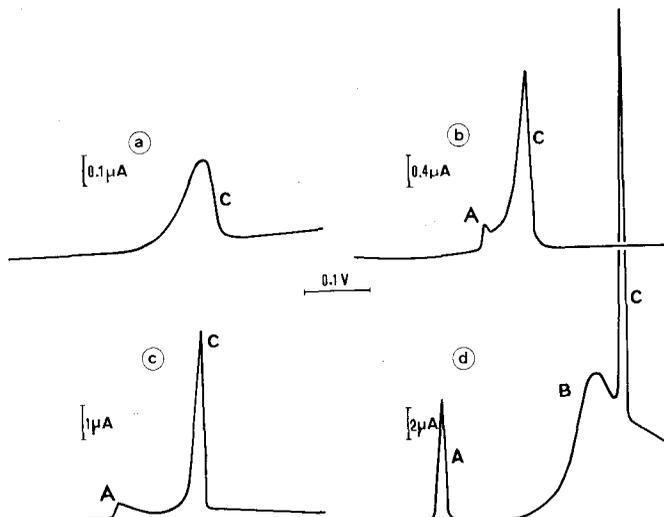


Fig. 10. Peaks of *trans*-4',4''-pyridyl-1,2-ethylene. pH 6.6 (Britton-Robinson); water;  $E_i=-0.55$  V;  $t_1=8$  s;  $v=0.1$  V  $s^{-1}$ ;  $m=0.257$  mg  $s^{-1}$ .  $c=(a) 0.5 \times 10^{-5}$ , (b)  $3 \times 10^{-5}$ , (c)  $8 \times 10^{-5}$ , (d)  $4 \times 10^{-4}$  mol  $l^{-1}$ .

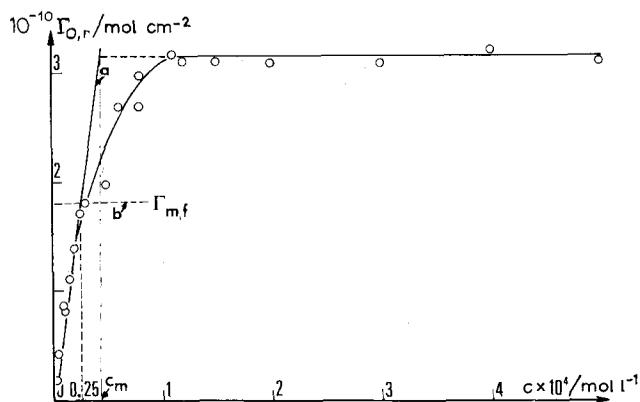


Fig. 11. Variations of  $\Gamma_{O,r}$  with  $c$ . Same conditions as for Fig. 10. (a) Theoretical variation calculated from the equation of Koryta with  $D=8.1 \times 10^{-6}$   $cm^2$   $s^{-1}$ ; (b) calculated maximum superficial concentration for a flat orientation.

graphical integration of the peak, follow the law of Koryta (eqn. 25) for different values of  $t_1$  (cf. ref. 40, Fig. 3).

As long as the film of depolarizer is not compact, the equations agree quite well with the experimental findings (see e.g. Fig. 9 for the shape of the curves, and ref. 40 for the variation of  $i_p$  and  $E_p$  with  $v$ ).

When the film is *compact* before the beginning of the electrolysis ( $\Gamma_O(t_1) = \Gamma_m$ ), the peak generally takes an abnormal shape<sup>24, 25, 32, 42</sup> which cannot be explained by the preceding theory. It becomes very narrow (a few mV) and very sharp.

A particularly typical example is given by *trans*-4',4''-dipyridyl-1,2-ethylene: the adsorption peak C (reduction of the film) (Fig. 10) is always well defined and separated from the diffusion peak B which corresponds to the reduction through the film of depolarizer<sup>32</sup>. Peak A corresponds to a modification of the structure of the film (see Part II of this paper).

By graphical integration of the area of peak C, the value  $\Gamma_{O,r}$  of  $\Gamma_O$  at the potential of the reduction can be calculated. The values obtained in that way are given in Fig. 11. Under the conditions used for the experiment ( $t_1 = 10.5$  s,  $D = 8.1 \times 10^{-6}$  cm<sup>2</sup> s<sup>-1</sup>), one can distinguish three zones of concentration<sup>24, 25</sup>.

*Zone III* ( $c > 10^{-4}$  mol l<sup>-1</sup>). In this zone,  $\Gamma_{O,r}$  reaches a constant maximum value,  $\Gamma_m = 3.16 \times 10^{-10}$  mol cm<sup>-2</sup>, which corresponds to 52 Å<sup>2</sup> for the area occupied by one molecule. This value is twice as large as for pyridine and its methyl derivatives<sup>43</sup>, which are adsorbed perpendicularly to the electrode<sup>43-45</sup>. In view of the fact that the molecule can lie in a plane, this result shows that the orientation is also perpendicular in the case of dipyriddyethylene, the molecule being in a lengthwise position rather than standing up (Fig. 15): for a standing up position the area would be the same as for pyridine, instead of twice as large; moreover, one of the nitrogen atoms would have to be in contact with the mercury surface, which is not likely<sup>44, 45</sup>. It also shows that the film is compact, as in the case of pyridine.

*Zone I* ( $c < 2.5 \times 10^{-5}$  mol l<sup>-1</sup>). The experimental value of  $\Gamma_{O,r}$  in this zone is equal to the value calculated from the equation of Koryta,  $\Gamma_{O,r} = 0.74 D_O^{\frac{1}{2}} c t_1^{\frac{1}{2}}$ . This shows that all the molecules are adsorbed as soon as they reach the surface and that diffusion alone is the limiting factor. As shown in the next paragraph, the molecule lies flat on the surface of the electrode. The maximum superficial concentration calculated for an area of 90 Å<sup>2</sup> corresponding to a flat orientation is  $\Gamma_{m,f} = 1.8 \times 10^{-10}$  mol cm<sup>-2</sup>; according to the equation of Koryta ( $D_O = 8.1 \times 10^{-6}$  cm<sup>2</sup> s<sup>-1</sup>) this value  $\Gamma_{m,f}$  is reached when  $c = 2.5 \times 10^{-4}$  mol l<sup>-1</sup>. Thus, in zone I,  $\Gamma_{O,r}$  is always smaller than  $\Gamma_{m,f}$ ; the film is not compact.

*Zone II* ( $2.5 \times 10^{-5} < c < 10^{-4}$  mol l<sup>-1</sup>). In that zone, if the orientation was perpendicular the surface concentration would be smaller than  $\Gamma_m$ . All the molecules reaching the surface would be adsorbed, i.e. the value of  $\Gamma_{O,r}$  would still be given by the equation of Koryta (Fig. 11a) up to concentration  $c_m$ . The value of  $\Gamma_{O,r}$  being smaller than the value predicted by the equation of Koryta, the molecules necessarily have an oblique orientation. The setting up of the molecules vertically is thus opposed by a certain resistance and can be obtained only by an increase in the concentration, which leads to the conclusion that the molecules lie flat on the surface for  $c < 2.5 \times 10^{-5}$  mol l<sup>-1</sup>. As shown by several workers, such an orientation is due to the interaction between the  $\pi$ -electrons and the mercury

surface<sup>46-48, 17b</sup>.

In zone I, peak C has the normal shape predicted by the theory (*cf.* Figs. 8, 9 and 10).

In zone II, the peak potential does not change, but the peak is deformed, which can be caused either by the new orientation of the molecules, or by the crowding of the surface, or by the existence of interactions between the molecules (see below).

In zone III, the peak takes a very particular shape: it becomes very sharp and narrow (Fig. 10d), and the peak potential  $E_p$  becomes abruptly 130 mV more negative<sup>24</sup> when  $c$  is larger than  $10^{-4}$  mol  $l^{-1}$  (*cf.* Fig. 10a, b, c and d). This shift shows that the reduction becomes more difficult when the film is compact. This result cannot be attributed to an orientation effect: for  $c = 8 \times 10^{-4}$  mol  $l^{-1}$ , the molecules already approach the vertical orientation, but the value of  $E_p$  is still normal. The phenomenon is due to the compactness of the film and can be explained as follows: attraction forces<sup>17b, 50</sup> arise between the closely packed molecules, with the result that the energy barrier which has to be overcome in the reduction is increased. The fact that  $E_p$  becomes suddenly more negative only when the molecules approach the vertical position confirms that the attraction forces come into play for this position, but do not arise when the molecules have a flat or an oblique orientation<sup>48</sup>. The peculiar shape of the peak is due to a "deblocking" effect<sup>24, 25</sup>: the compactness of the film renders its reduction more difficult, but as soon as a small fraction of the molecules have been reduced, the film is no longer compact. The conditions which prevail for the reduction of the rest of the molecules are similar to those existing when  $\Gamma_{O,r} < \Gamma_m$ . At the potential of the peak, the reaction rate is then very large, and practically all the molecules are reduced together (the reduced form is actually adsorbed itself, and forms a mixed film with the depolarizer<sup>32</sup>, but in this film the attraction forces no longer exist).

The behaviour described above with dipyriddyethylene as an example ought to be observed generally for substances irreversibly reduced or oxidized in compact films. Other examples are given by 2',2''-dipyridyl-1,2-ethylene<sup>32</sup> and 2',2''-dipyridyl-acetylene<sup>32</sup>; an interesting case is that of  $\alpha$ -nitrocamphor<sup>32, 42</sup>. Our results can also explain anomalous peaks which have been reported in the literature<sup>51-69</sup>. The superposition of the diffusion and of the adsorption peaks, for  $c > c_m$  leads, as in the reversible case, to non-linear  $i_p = f(c)$  graphs<sup>24</sup> (*cf.* Fig. 7).

## PART II. AUTOINHIBITION AND AUTOCATALYSIS

Our early results led us to propose a first classification of *autoinhibition* processes<sup>12</sup>. We have subsequently slightly modified this classification on the basis of new data<sup>36, 38</sup>.

Three main simple types can be distinguished:

- (I) The inhibiting film is constituted of the molecules of the depolarizer itself.
- (II) The molecules of the film result from a chemical reaction which occurs parallel with the inhibited electrochemical reaction.
- (III) The film is made of the final product of the inhibited electrochemical reaction.

These simple types can be used as a basis for the discussion of more complex cases.

*Autocatalysis* processes are much less common, and only a few examples of catalysis by the product of the electrochemical reaction have so far been reported; in all of them, the reduction of a nitro group is involved: the first case was mentioned by Person for the reduction of substituted nitropyrroles<sup>13</sup>; as we have shown<sup>53</sup>, 4-(or 5-)nitroimidazole behaves similarly and offers a very favourable example for a quantitative study<sup>55</sup>; as far as we know, the only other case (reduction of certain derivatives of 1-phenyl 2-nitro 1-ethanol) has been reported more recently by Leibzon *et al.*<sup>54</sup>.

The derivation of the expressions of the polarographic current is based on different assumptions, according to whether the reaction is irreversible or reversible.

When the electrochemical reaction is *irreversible*, the inhibition or the catalysis takes place from the very beginning of the formation of the film (*cf.* ref. 4) and one can assume as a first approximation that the rate constant  ${}_a k_{f,h}$  of the electrode process is a linear function of the coverage<sup>4b</sup>:

$${}_a k_{f,h} = k_{f,h}(1 - \Theta) + {}_1 k_{f,h} \Theta \quad (41)$$

with

$$k_{f,h} = k_{f,h}^0 \exp(-\alpha n_\alpha FE/RT) \quad (42)$$

$${}_1 k_{f,h} = {}_1 k_{f,h}^0 \exp(-\alpha' n_\alpha' FE/RT) \quad (43)$$

If  $k_{f,h}^0 \gg {}_1 k_{f,h}^0$  an autoinhibition is observed; in the reverse case an autocatalysis occurs. In the case of an autoinhibition, we shall assume in the derivation of the current, that  ${}_1 k_{f,h}^0$  is negligible when compared to  $k_{f,h}^0$ ; the current decreases gradually.

Let us consider now a *reversible* reaction on any part of the wave, or an irreversible reaction on the plateau of the wave, when the reaction rate becomes very large (the current in the absence of inhibition is limited only by diffusion). It has been shown<sup>55,56</sup> that, if the dimensions of the inhibiting centres are much less than the thickness of the diffusion layer, there is no effect on the mass transport until the film becomes compact. This will in particular be the case if the distribution of the molecules of the film is uniform. Let  $t_m$  be the time when the film becomes compact; the current will be normal as long as  $t < t_m$ , and decrease suddenly when  $t = t_m$ . Actually, however, as was shown experimentally by Kůta<sup>4,57,58</sup> in the case of the inhibition by an electroinactive substance, the decrease is less sudden than required by the theory, because the condition given above for the structure of the film is no longer obeyed: when the coverage approaches 1, the dimensions of the inhibiting centres are no longer negligible when compared to the thickness of the diffusion layer; the problem has been treated mathematically by Matsuda<sup>59</sup>.

The situation should be different if the distribution of the film is not uniform, *e.g.* if the film is composed of islets on which the electrode reaction does not occur (this case could correspond for instance to a crystallization around centres of inhomogeneousness on the surface). If the dimensions of the islets are large when compared to the mean diffusion path, and if one neglects the influence of the boundary between the islets and the free surface, diffusion will bring molecules only to the free surface. The inhibition will thus result in a decrease of the effective surface of the electrode. The current will be given by  $i = i_n(1 - \Theta)$ ,  $i_n$  being the current when there is no inhibition.

We shall consider in what follows only the case of a strong adsorption.

The surface concentration  $\Gamma$  of the inhibiting or accelerating form will then be given by an expression of the following type:

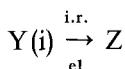
$$\Gamma = (1/nFA\nu) \int_0^t i dt \tag{44}$$

in which  $\nu$  is the number of molecules of the depolarizer which are necessary to form one molecule of the film.

(1) Autoinhibition phenomena

(A) Type I. Inhibition by the depolarizer itself<sup>12,32,36,38,42</sup>

The reaction takes place according to the scheme



$i$  designates the inhibiting form, and i.r. the inhibited electrochemical reaction.

The inhibiting process is as follows (case of a reduction): the molecules of the depolarizer  $Y$  adsorb at the surface of the electrode and form a film which inhibits the electrochemical reaction; for sufficiently high concentrations, the film covers the whole surface and becomes compact in a few hundredths of a second (cf. equation of Koryta<sup>19,20</sup>). On the other hand, owing to their adsorption, the molecules of the film are less easily reduced (their reduction takes place at a more negative potential). When the inhibition is strong, no current will flow up to the potential  $E_d$  for which the film is destroyed by reduction (the destruction could also eventually occur because of a natural desorption of the molecules). If the reduction of the film takes place within a few millivolts, as e.g. in the case of *trans*-4',4''-dipyridyl-1,2-ethylene (cf. Part I), the rapid destruction of the film results in a sudden increase of the current from zero to the diffusion plateau (Fig. 12a).

If the reduction takes place through the film before the potential  $E_d$  is reached, the polarogram will have the shape shown in Fig. 12b. The same phenomenon can be observed on a 2nd or 3rd wave<sup>53,36</sup>.

We have reported in 1961 the first examples<sup>12</sup> of this type of autoinhibition (reduction of dipyridylethylenes). Since then, we have been able to find numerous other compounds showing the same behaviour, e.g. 2',2''-dipyridylacetylene<sup>23</sup>,

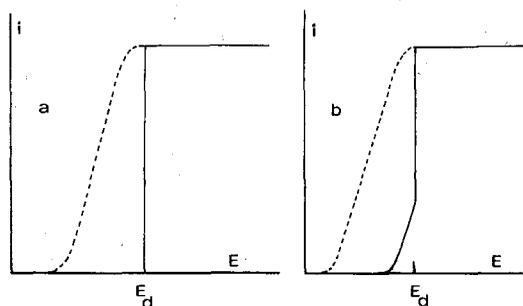


Fig. 12. Theoretical polarograms for autoinhibition by the depolarizer. (-----) Polarogram which would be observed in absence of inhibition.

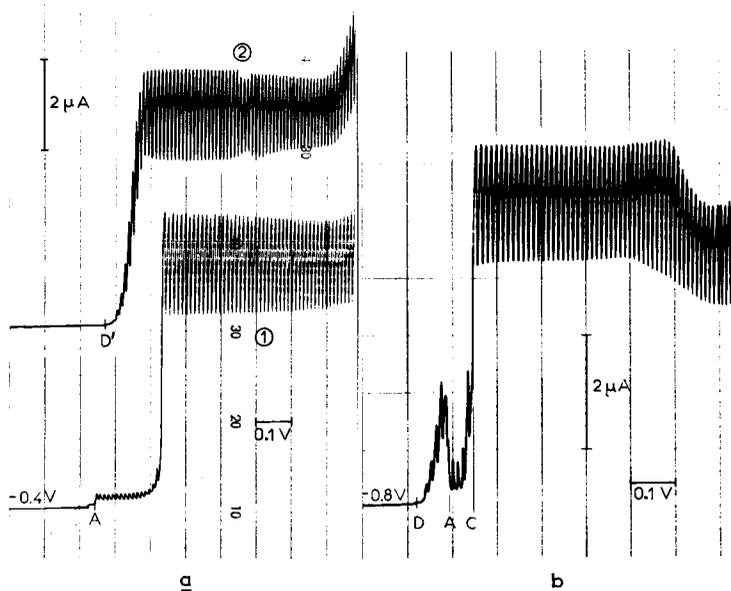


Fig. 13. Polarograms of *trans*-4',4''-dipyridyl-1,2-ethylene. (a) pH 6.4. (1)  $c = 8 \times 10^{-4} \text{ mol l}^{-1}$ ; (2) same concentration, in the presence of 4',4''-dipyridyl-1,2-ethane saturated in solution. (b) pH 9.9.  $c = 8 \times 10^{-4} \text{ mol l}^{-1}$ .

3-benzoylpyridine N-oxide oxime<sup>23</sup>, 4-phenylpyridine<sup>23</sup>,  $\alpha$ -nitrocamphor<sup>42</sup>, etc. Other examples have been reported recently<sup>67-69</sup>.

We shall examine in greater detail the case of *trans*-4',4''-dipyridyl-1,2-ethylene<sup>12,32</sup> (for a complete discussion, see ref. 32). Between pH values of about 2 and 11, the polarogram shows a vertical increase of current (Fig. 13a (1)). In acid ( $2 < \text{pH} < 4$ ), and alkaline ( $8 < \text{pH} < 11$ ) medium, moreover, another anomaly appears: the wave begins normally, and the inhibition only takes place suddenly at a certain potential A (Fig. 13b). This can be explained as follows: the depolarizer film possesses two main different structures—structure I (or II) for potential values more positive than A; under this structure the film does not inhibit the reduction, which takes place through it, giving rise to the first part of the wave. Similarly, the reduction of metallic cation such as  $\text{Pb}^{2+}$  or  $\text{Cd}^{2+}$  takes place normally through the film<sup>32</sup>. Structure III is for potential values more negative than A; under this structure, the film possesses strongly inhibiting properties: not only does it inhibit the reduction of the depolarizer, but also the reduction of  $\text{Pb}^{2+}$  or  $\text{Cd}^{2+}$  ions. The reduction current of  $\text{Pb}^{2+}$ , *e.g.*, which is normal in the presence of film I, drops to zero in the presence of film III. When the pH is changed, potential A is shifted relatively to potential  $E_d$ , which explains the shape of the polarograms for different pH values (Fig. 14).

If the inhibiting film of dipyridylethylene is displaced by a non-inhibiting film of a foreign substance, such as gelatin, or dipyridylethane, the polarogram reverts to its normal shape (Fig. 13a (2)).

The value of the maximum superficial concentration  $\Gamma_m$  for the two different structures of the film has been determined:

For structure I, one obtains<sup>36</sup>, from the study of the variation of the interfacial tension by the drop-time method  $\Gamma_m = 3.6 \times 10^{-10} \text{ mol cm}^{-2}$  *i.e.*  $46 \text{ \AA}^2$  per molecule. For structure III, the graphical integration<sup>24,25</sup> of the area of the adsorption peak C, (amount of electricity consumed in the reduction of the film, see Part I of this paper) gives  $\Gamma_m = 3.2 \times 10^{-10} \text{ mol cm}^{-2}$ . The value of  $\Gamma_m$ , allowing for the experimental errors, is thus virtually the same in both cases, *i.e.* as we have already shown, the film is compact, with the plane of the molecules perpendicular to the surface. The difference in the inhibiting properties of the film cannot therefore be found in a different orientation or compactness.

The transition from one structure to the other is marked, in cyclic voltammetry, by a system of sharp reversible peaks (Fig. 10, reduction peak A) (for a whole system, with oxidation peak A', see ref. 32, Fig. 13). When passing from I to III, moreover, a sudden decrease of the capacity is observed. The peak potential of A and A' depends on pH; the peaks cannot however be ascribed to a reaction between a proton and the molecule, for the diquaternized compound shows similar peaks, whose potential is independent of pH<sup>23</sup>. These results have led us to assume<sup>24</sup> that peak A is due to the expulsion of molecules of water or ions from film I to give to film III.

4-Phenylpyridine shows exactly the same behaviour<sup>23</sup>, with two different structures of the film; only the second structure inhibits the reduction of metallic cations and that of phenylpyridine itself.

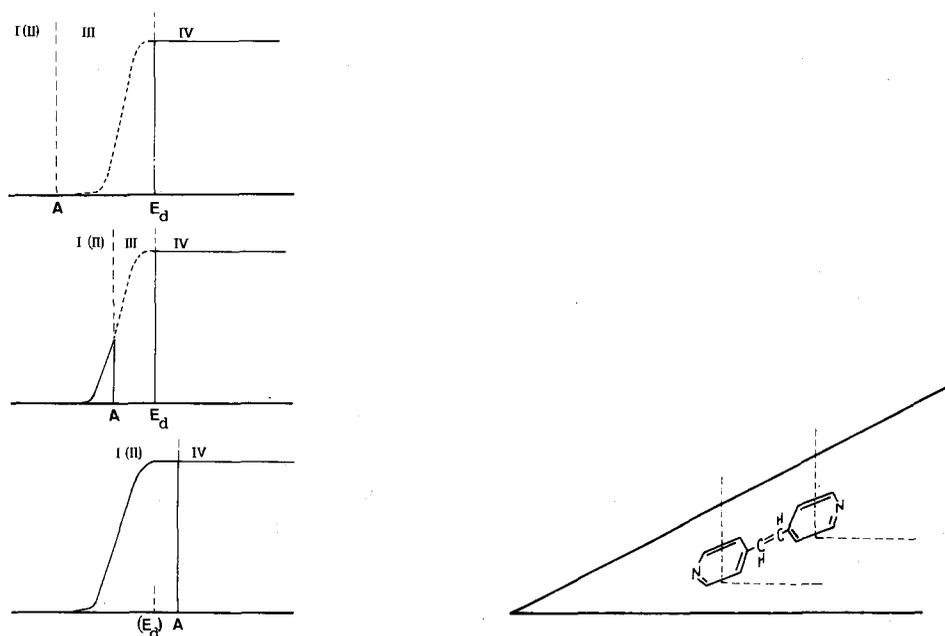


Fig. 14. Theoretical polarograms: (-----) Current that would be obtained if there was no inhibition. (I, II) Non-inhibiting film of dipyridylethylene; (III) inhibiting film of dipyridylethylene; (IV) non-inhibiting film of dipyridylethane.

Fig. 15. Orientation of adsorbed dipyridylethylene molecules in compact film.

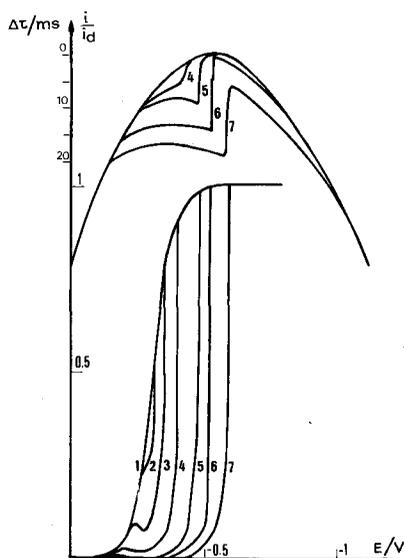
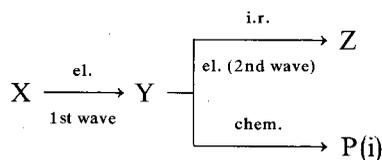


Fig. 16. Polarograms and drop-time curves of  $\alpha$ -nitrocamphor.  $\text{H}_2\text{SO}_4$  0.5 M; water. (1)  $c = 10^{-4}$  and  $2 \times 10^{-4}$  mol  $\text{l}^{-1}$ ; (2)-(7)  $c = 3.75 \times 10^{-4}$ ,  $5 \times 10^{-4}$ ,  $6.15 \times 10^{-4}$ ,  $10^{-3}$ ,  $1.5 \times 10^{-3}$ , and  $2.5 \times 10^{-3}$  mol  $\text{l}^{-1}$ .

In the case of  $\alpha$ -nitrocamphor<sup>42</sup>, the adsorption becomes important only for  $c > 2 \times 10^{-4}$  mol  $\text{l}^{-1}$ , so that the transition from the normal to the inhibited wave can be clearly seen (Fig. 16). Under certain conditions, the sharp adsorption peak C is observed only during the reverse sweep, which, together with the study of  $i-t$  curves, leads to the conclusion that a mixed film of the depolarizer and the reduction product is formed<sup>42</sup>.

(B) Type II. The inhibiting film is formed through a chemical reaction which is parallel to the inhibited electrochemical reaction<sup>36,60</sup>

The reaction takes place according to the scheme:



The electrochemical reaction  $\text{Y} \rightarrow \text{Z}$  is inhibited by a film of P obtained by a chemical transformation of Y. The inhibited reaction can be irreversible or, at least theoretically, reversible.

Although it has been reported only recently for the first time<sup>36</sup>, this type of inhibition is rather frequent. It can be encountered every time the electrochemical reaction proceeds in two separate stages and in particular when Y can dimerize, the dimer being generally strongly adsorbable because of its higher molecular weight. In non-aqueous medium, where most of the reactions proceed through a first  $1e$  stage, this type of inhibition could also be of importance.

The peculiar shape of the  $i-t$  curves is shown in Figs. 17 and 18 in a case when

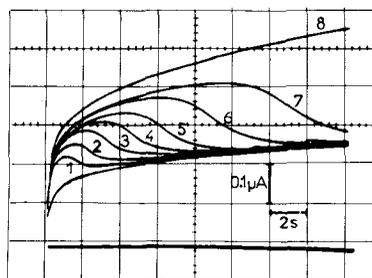
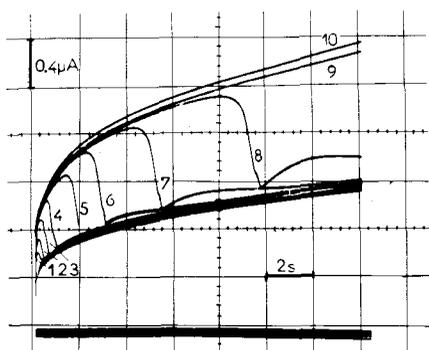


Fig. 17. 3-Pyridylmercuriacetate. NaOH  $M$ ;  $c=1.0 \times 10^{-3} \text{ mol l}^{-1}$ .  $i-t$  curves for the second wave (first drop). Potential from 1 to 10:  $-0.950, -1.030, -1.040, -1.045, -1.050, -1.055, -1.060, -1.065, -1.100, -1.150 \text{ V}$ .

Fig. 18. Same as Fig. 17 with  $c=0.2 \times 10^{-3} \text{ mol l}^{-1}$ . Potential from 1 to 8:  $-0.880, -0.890, -0.900, -0.905, -0.910, -0.915, -0.920, -1.050 \text{ V}$ .

the electrochemical reaction  $X \rightarrow Y$  is not inhibited. They can be explained as follows:

The total instantaneous current  $i$  is composed of two parts: the diffusion current  $i_d$  on the plateau of the first wave,  $i_d = 7.08 \times 10^4 nm^3 D_x ct^{\frac{1}{2}}$ , and the current  $i_2$  corresponding to the reduction along the second wave ( $Y \rightarrow Z$ ).

At the beginning of the electrolysis, practically no product P is formed, and  $i_2$  has its normal value. At time  $t_1$  when the surface is covered with a compact film of P, the inhibition takes place, and  $i_2$  drops to zero; only  $i_d$  is then observed.  $t_1$  is larger, the more negative the potential: the number of molecules of Y obtained for a certain value of the time is always the same whatever the potential. P is formed by the molecules of Y which escape the reduction to Z; when the potential is made more negative, a greater amount of Y is reduced, and the number of molecules available to form P is smaller at a given value of  $t$ ; it takes a longer time for the film to become compact.

As results from the above discussion, the second wave is shifted towards more negative potentials (Fig. 19): for a given value of the potential along the second wave, the mean current is smaller than the normal mean current which would be observed if there was no inhibition. The shift is larger, the higher the concentration, for time  $t_1$  decreases when the concentration increases. The experimental values of the shift are considerable, of the order of 200 mV for a tenfold increase in the concentration<sup>60</sup>; the shift cannot therefore be mistaken for that resulting from the dimerization reaction<sup>61</sup>, which is about ten times smaller. The second wave often shows a sharp rise in current<sup>36,60</sup>, which has been accounted for by a detailed study<sup>60</sup>.

The theoretical  $i=f(t)$  curves can be derived<sup>38</sup> by making the following assumptions:

The rate of the chemical reaction is so large that it does not control the rate of formation of the film.

Even in the absence of inhibition, the equation of the  $i-t$  curve on the second wave is modified by the chemical reaction (see *e.g.* ref. 61 for a dimeriza-

tion). We shall however make the simplifying assumption that  $i_2$  is given by the normal expression which is valid in the absence of chemical reaction.

The surface concentration  $\Gamma$  of P can be expressed as follows: the film is formed by those of the molecules of Y obtained in the first stage which are not reduced in the second stage.

If  $n$  and  $n_2$  are the numbers of electrons involved respectively in the first and the second stage, we can write:

$$\Gamma = (1/FAv) \int_0^t (i_d/n - i_2/n_2) dt \quad (45)$$

(a) *The electrochemical reaction  $Y \rightarrow Z$  is irreversible.* If  $i_2$  is small when compared to the diffusion current (i.e. at the foot of the wave), one can write, by neglecting  ${}_1k_{f,h}$  in eqn. (41)

$$i_2 = n_2 F A k_{f,h} c (1 - \Gamma/\Gamma_m) \quad (46)$$

From (45) and (46), one obtains:

$$i_2 = 5.47 \times 10^4 n_2 m^{\frac{3}{2}} (v\Gamma_m)^{\frac{3}{2}} k_{f,h}^{\frac{1}{2}} c^{\frac{3}{2}} e^s \int_0^s x^{-\frac{1}{2}} e^{-x} dx \\ - 7.08 \times 10^4 n_2 m^{\frac{3}{2}} D_x^{\frac{1}{2}} (v\Gamma_m)^{\frac{1}{2}} k_{f,h}^{-\frac{1}{2}} c^{\frac{3}{2}} e^s \int_0^s x^{\frac{1}{2}} e^{-x} dx \quad (47)$$

$$\text{with } s = k_{f,h} ct/v\Gamma_m. \quad (48)$$

$t_1$  is obtained by equating (47) to zero.

(b) *The electrochemical reaction is reversible.* In the case of a sudden inhibition,  $i_2$  is normal ( $i_2 = i_{d,2}/(1 + \xi\theta)$ ) up to time  $t_1$ , when it falls down to zero.  $t_1$  is readily derived from (45), in which  $t$  is replaced by  $t_1$ , and  $\Gamma$  by  $\Gamma_m$ . One obtains<sup>62</sup>:

$$t_1 = [1.82(v\Gamma_m)^2/Dc^2][(1 + \xi\theta)/\xi\theta]^2 \quad (49)$$

The case of a gradual inhibition (inhomogeneous film) has also been treated<sup>38</sup>.

Aromatic organomercurial compounds with the general formula RHgX are a good example of this type of inhibition. The first stage is reversible, and the second, inhibited stage, irreversible.  $i-t$  curves are shown in Figs. 17 and 18.

For small concentrations (Fig. 18), as shown above, the wave is but little shifted with respect to the normal wave (cf. Fig. 19b). At the foot of the wave the rate constant of the electrochemical reaction, which depends exponentially on  $E$  (cf. eqn. 42) is small (in the absence of inhibition the current would be controlled only by the rate of the electrochemical reaction). Inhibition takes place progressively and the current is given by eqn. (47).

For high concentrations (Fig. 17), the shift is important and the foot of the inhibited wave appears at potentials corresponding to the plateau of the normal wave (Fig. 19c).  $k_{f,h}$  is large even at the foot of the wave, and diffusion becomes the limiting factor; the current  $i_2$  is virtually normal up to time  $t_1$ , when it brutally falls down to zero. The  $i-t$  curves are however only qualitatively similar to those corresponding to a reversible reaction, but a detailed discussion shows that the equations derived for a reversible reaction are not applicable quantitatively<sup>62</sup>.

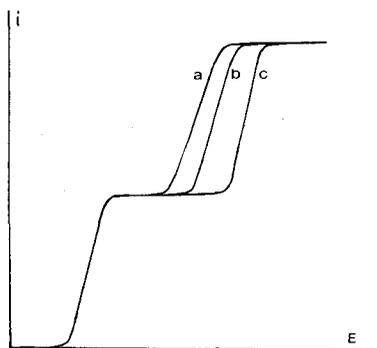


Fig. 19. Theoretical polarograms for case II. (a) Without inhibition ( $c \rightarrow 0$ ); (b) low concentration; (c) high concentration.

The same type of inhibition is found in the case of aromatic aldehydes and ketones, *e.g.* naphthaldehyde<sup>36</sup>, or substituted benzaldehydes at high concentrations<sup>63, 23</sup>.

An inhibition of the first stage of the electrochemical reaction is often simultaneously observed. In the case of organomercurials<sup>60</sup> and aldehydes<sup>36, 63</sup>, it affects only the beginning of the first wave (*cf.* type III). In the reduction of pyridyl pyridinium dichloride, on the other hand, the first stage is inhibited (the current is completely suppressed) for all potential values up to the reduction potential of the second wave<sup>23</sup>.

(C) *Type III. Inhibition by a product of the inhibited electrochemical reaction*<sup>12, 37-39, 66</sup>

Examples of this case are rather numerous; their intuitive interpretation is simple: in the case of a reduction, *e.g.* when the potential is made more negative, the current increases, until the surface of the electrode is covered by the product of the reaction; this causes a limitation of the current until a new increase of current is observed, due *e.g.* to a reduction through the film, or to the desorption of the product of the reaction (Fig. 20).

Although they actually correspond to the beginning of the normal wave, autoinhibition waves of this type are generally similar in shape to Brdicka prewaves, because the current is limited in both cases by the presence on the electrode of a film of the product of the electrochemical reaction; they can thus be called *pseudo-prewaves* (Fig. 20b, c). An exception arises when the film is formed, or acquires inhibiting properties (*cf.* ref. 15), only at a certain value of the potential along the wave or on the plateau of the wave (Fig. 20 d, e). In all cases the limiting inhibited current  $i_1$  exhibits the same characteristics as the limiting current of a Brdicka prewave as regards the variation with the concentration or with the height of the mercury reservoir. A careful study of the mechanism of the electrochemical reaction is thus necessary in order to distinguish the two types of waves.

Different schemes are possible:

*Type III-1.* In the simplest case, the inhibiting form is the product of the electrochemical reaction, according to the scheme:

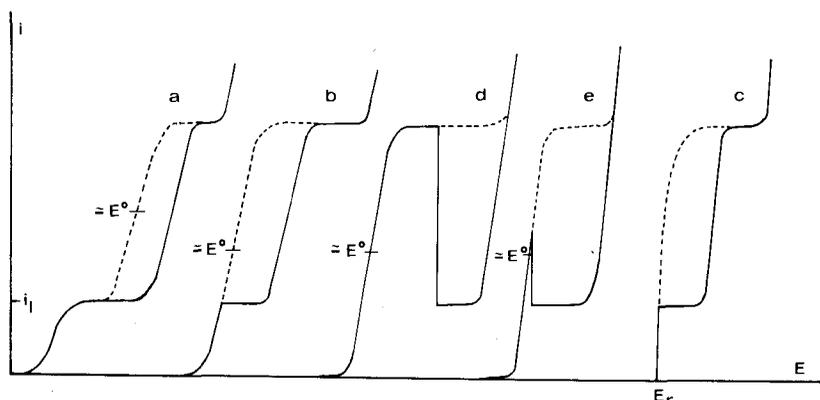
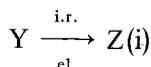
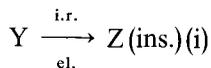


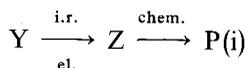
Fig. 20. Prewaves and pseudo-prewaves (inhibition by the product of the electrochemical reaction). (a) Adsorption (Brdicka) prewave, with autoinhibition by film of Red. (b, c) Autoinhibition pseudo-prewaves. (-----) Polarogram which would be obtained if there was no inhibition. The approximate value of  $E^0$  is indicated, when the reaction is reversible.



*Type III-2.* The film is formed by the deposition of an insoluble substance (insoluble compound with mercury):



*Type III-3.* The inhibiting form is produced through a chemical reaction:



$Z \rightarrow P$  can be a first-order or a second-order reaction. As in the case of type II, we shall assume that the rate of formation of the film is not controlled by the rate of the chemical reaction and that the current, even in the absence of inhibition would be given by the normal expression; *i.e.*, we shall neglect, if  $Y \rightarrow Z$  is reversible, the modification of the current due to the chemical reaction<sup>64, 65</sup>.

The electrochemical reaction  $Y \rightarrow Z$  can be reversible or irreversible. If it is irreversible, the current at the foot of the wave is given by the same expression in all three cases, since the rate of formation of the film is limited only by the rate of the electrochemical reaction.

The case of a reversible reaction is more complex. If  $Y$  is not adsorbed, or less strongly adsorbed than  $Z$ , a Brdicka prewave will appear in cases III-1 and III-3 simultaneously with the autoinhibition phenomena.

(a) *Totally irreversible reaction.* At the foot of the wave, when  $i$  is small when compared to  $i_d$ , the rate of the electrode process is not limited by diffusion. Assuming that  ${}_1k_{f,h}$  in eqn. (41) is negligible, the current is expressed by:

$$i = nFAck_{f,h}(1 - \Gamma/\Gamma_m) \quad (50)$$

By introducing into (50) the value of  $\Gamma$  given by (44), and solving the resulting differential equation, one obtains:

$$i = 5.47 \times 10^4 nm^{\frac{2}{3}} (v\Gamma_m)^{\frac{2}{3}} k_{f,h}^{\frac{1}{3}} c^{\frac{1}{3}} e^{-s} \int_0^s x^{-\frac{1}{3}} e^x dx \tag{51}$$

with

$$s = ct k_{f,h} / v\Gamma_m \tag{52}$$

The variation of the function of  $s$ ,  $F(s)$ , in eqn. (51) is shown in Fig. 21.  $i$  being proportional to  $F(s)$ , and  $t$  to  $s$ , the curve gives the shape of the  $i-t$  curve. When  $s \rightarrow \infty$  ( $t \rightarrow \infty$ ),  $F(s) \rightarrow s^{-\frac{1}{3}}$ , and  $i \rightarrow i_a = 5.47 \times 10^4 nm^{\frac{2}{3}} v\Gamma_m t^{-\frac{1}{3}}$ : the coverage tends towards 1, and the current becomes proportional to the rate of increase in the area of the drop, as is the case for a Brdicka prewave.

The function  $F(s)$  exhibits a maximum equal to 0.89 for  $s=1.4$ ; the corresponding values  $i_m$  and  $t_m$  of  $i$  and  $t$  can be deduced from (51) and (52):

$$i_m = 4.86 \times 10^4 nk_{f,h} m^{\frac{2}{3}} (v\Gamma_m)^{\frac{2}{3}} c^{\frac{1}{3}} \tag{53}$$

$$\log t_m = \log(1.4 v\Gamma_m / ck_{f,h}^0) + 0.43 \alpha n_\alpha FE/RT \tag{54}$$

On the plateau of the pseudo-prewave ( $E \rightarrow -\infty$ ), the  $i-t$  curves are identical

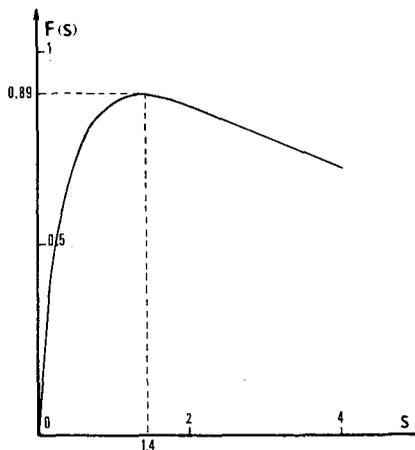


Fig. 21. Theoretical  $i-t$  curves for a pseudo-prewave (irreversible reaction).

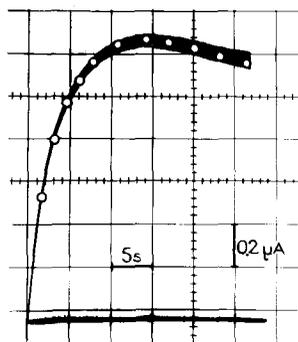


Fig. 22.  $i-t$  curves for reduction of As(III). HCl 0.82 M-NaCl 0.1 M.  $E = -0.340$  V;  $c = 2.48 \times 10^{-3}$  mol  $l^{-1}$ . The circles are the calculated values (eqn. 51).

with those obtained for a Brdicka prewave, since the molecules are reduced as soon as they reach the surface: the film becomes compact for  $t = t_m$ . The variation of the limiting current with the height of the mercury reservoir or with the concentration is thus the same as for a Brdicka prewave.

A good experimental example of this case is given<sup>39</sup> by the reduction of As(III). The  $i-t$  curves are in excellent agreement with the values predicted by eqn. (51) (Fig. 22), and eqns. (53) and (54) are verified.

(b) *Reversible reactions.* In the case of a sudden inhibition (homogeneous film), the expression of the current is readily obtained<sup>66</sup>.

Before the time  $t_m$  for which the film becomes compact, the current  $i$  is equal to the normal current  $i_n$  which would flow in the absence of inhibition for the same value of the potential. By expressing (a strong adsorption is assumed) that the amount of molecules which are adsorbed on the surface at time  $t_m$  is equal to the amount brought by diffusion up to  $t_m$ , one obtains:

$$v\Gamma_m = (1/nFA) \int_0^{t_m} i_n dt \quad (55)$$

After time  $t_m$ , the electrode is covered with a compact inhibiting film. The electrochemical reaction can however proceed on the free surface which appears as a function of time owing to the growth of the drop. The current  $i_a$  is thus equal to  $nFv\Gamma_m dA/dt$ :

$$i_a = 5.47 \times 10^4 nm^{\frac{2}{3}} v\Gamma_m t^{-\frac{1}{3}} \quad (56)$$

Cases III-1 and III-3. For a reduction:

$$i_n = 7.08 \times 10^4 nm^{\frac{2}{3}} D_y^{\frac{1}{2}} ct^{\frac{1}{2}} / (1 + \xi\theta)$$

From (55):

$$t_m = 1.82(v\Gamma_m)^2(1 + \xi\theta)^2/c^2D_y \quad (57)$$

In view of this equation,  $i_n$  takes the form:

$$i_n = 5.47 \times 10^4 nm^{\frac{2}{3}} v\Gamma_m t_m^{-\frac{1}{3}} \times 1.75(t/t_m)^{\frac{1}{2}} \quad (58)$$

On the other hand,  $i_a$  can be written in the form:

$$i_a = 5.47 \times 10^4 nm^{\frac{2}{3}} v\Gamma_m t_m^{-\frac{1}{3}} \times (t/t_m)^{-\frac{1}{3}} \quad (59)$$

$i_n$  and  $i_a$  can be expressed in another more convenient form. When  $\theta \rightarrow 0$  (plateau of the adsorption wave)  $t_m$  approaches the value  $t_k$  given by the equation of Koryta,

$$t_k = 1.82(v\Gamma_m)^2/c^2D_y \quad (60)$$

hence

$$t_m = t_k(1 + \xi\theta)^2 \quad (61)$$

By substituting this value in eqns. (58) and (59), one obtains:

$$t < t_m \quad i_n = 5.47 \times 10^4 nm^{\frac{2}{3}} v\Gamma_m t_k^{-\frac{1}{3}} [1.75/(1 + \xi\theta)](t/t_k)^{\frac{1}{2}} \quad (62)$$

$$t > t_m \quad i_a = 5.47 \times 10^4 nm^{\frac{2}{3}} v\Gamma_m t_k^{-\frac{1}{3}} (t/t_k)^{-\frac{1}{3}} \quad (63)$$

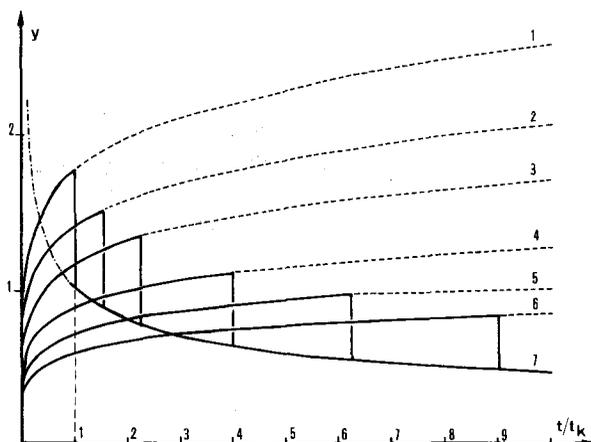


Fig. 23. Theoretical  $i-t$  curves for a pseudo-pretwave (reversible reaction). (a) Cases III-1 and III-3 (reduction). (1-6)  $y=1.75(1+\xi\theta)^{-1}(t/t_k)^{\frac{1}{2}}$  with  $\xi\theta$  and  $n(E-E^0)=0$  ( $-\infty$ ); 0.25 ( $-35.5$  mV); 0.50 ( $-17.8$  mV); 1 (0 mV); 1.5 (10.4 mV); 2 (17.8 mV). (7)  $y=(t/t_k)^{-\frac{1}{2}}$ . (b) Case III-2 (oxidation) (1-6)  $y=1.75(1-\zeta)(t/t_k)^{\frac{1}{2}}$  with  $\zeta$  and  $n(E-E_r)=0$  ( $+\infty$ );  $\frac{1}{2}$  (41.3 mV);  $\frac{1}{3}$  (28.2 mV);  $\frac{1}{4}$  (17.7 mV);  $\frac{2}{5}$  (13.0 mV);  $\frac{2}{3}$  (10.4 mV). (7)  $y=(t/t_k)^{-\frac{1}{2}}$ .

Figure 23 gives the curves for different values of the potential. A comparison of these equations with eqns. (16) and (17) shows that the  $i=f(t)$  curves have the same shape as the curves obtained for a Brdicka pretwave. Only the evolution with potential is different: in the case of a Brdicka pretwave, when both the oxidized and the reduced forms are strongly adsorbed,  $t_m$  is independent of the potential, or varies between narrow limits (*cf.* eqn. 22). For the pseudo-pretwave,  $t_m$  depends on the potential (*cf.* eqn. 61), and varies from infinity at the foot of the wave ( $\theta \rightarrow \infty, E \rightarrow \infty$ ) to  $t_k$  on the plateau of the pseudo-pretwave ( $\theta \rightarrow 0, E \rightarrow -\infty$ ). On the plateau of the pseudo-pretwave, the  $i-t$  curves are identical with the  $i-t$  curves obtained in the case of a Brdicka pretwave (eqns. (62) and (63) are identical with (16) and (17) when  $\theta \rightarrow 0$ ). This explains the fact that we have mentioned above, that the characteristics of the variation of the limiting current with the concentration, or with the height of the mercury reservoir is the same as for a Brdicka pretwave (see Part I of this paper).

The equation of the pseudo-pretwave can be determined in the same way as for a pretwave. The mean current is calculated from eqns. (58) and (59) using eqn. (18').

$$t_m < \tau \quad \bar{i} = 8.20 \times 10^4 nm^{\frac{3}{2}} v \Gamma_m \tau^{-\frac{1}{2}} \tag{64}$$

$$t_m \geq \tau \quad \bar{i} = 6.07 \times 10^4 nm^{\frac{3}{2}} D_y^{\frac{1}{2}} c \tau^{\frac{1}{2}} / (1 + \xi\theta) \tag{65}$$

These equations show that the current remains identical with the current for the uninhibited process (eqn. 65), up to the potential for which  $t_m = \tau$ , when it suddenly reaches its limiting value (eqn. 64) (Fig. 20b). The shape of the pseudo-pretwave is thus theoretically different from that of a pretwave.

Case III-2. We shall consider the case of an oxidation:

One has:

$$i_n = -7.08 \times 10^4 nm^{\frac{3}{2}} D_y^{\frac{1}{2}} (c - 10^{-3}/\theta) t^{\frac{1}{2}} \tag{66}$$

From (55), one deduces:

$$t_m = 1.82(v\Gamma_m)^2/D_y(c - 10^{-3}/\theta)^2 \quad (67)$$

In view of eqn. (67), the current  $i_n$  takes the form given by eqn. (58).  $i_a$  is still given by eqn. (59), preceded by a minus sign. These equations can be written in another more convenient form:

When  $\theta \rightarrow \infty$  (plateau of the adsorption wave)  $t_m \rightarrow t_k$  (eqn. 60). One has thus:

$$t_m = t_k/(1 - \zeta)^2 \quad (68)$$

with

$$\zeta = 10^{-3}/\theta c$$

It can readily be shown<sup>66</sup> that:

$$\zeta = \exp(nF(E_r - E)/RT) \quad (69)$$

$E_r$  being the potential at the beginning of the wave (Fig. 20c).

The current takes the following form:

$$t < t_m \quad i_n = -5.47 \times 10^4 nm^3 v \Gamma_m t_k^{-3/2} \times 1.75(1 - \zeta)(t/t_k)^{3/2} \quad (70)$$

$$t > t_m \quad i_a = -5.47 \times 10^4 nm^3 v \Gamma_m t_k^{-3/2} (t/t_k)^{-3/2} \quad (71)$$

For a reduction, these equations are still valid if  $1/\theta$  is replaced by  $\theta$ , and  $\zeta$  by  $1/\zeta$ , and if the minus sign before the current is changed to a plus sign.

The  $i-t$  curves are shown in Fig. 23. Here again, as in case III-3 they have the same shape as for a Brdicka prewave, as can be ascertained by a comparison of eqns. (70) and (71) with (16) and (17). The pseudo-prewave shows the same angular shape as in the preceding case,  $\bar{t}$  being given by eqn. (64) for  $t_m < \tau$  and by eqn. (66) for  $t_m > \tau$  (with a minus sign) (Fig. 20c).

The case of a gradual inhibition (inhomogeneous film) has also been treated<sup>36-38</sup> for the three cases. The  $i-t$  curves have a rounded shape similar to the curve in Fig. 21; the current  $i_m$  and the time  $t_m$  corresponding to the maximum of the curve vary with the potential according to the same laws as for a brutal inhibition, the only difference being the numerical coefficients<sup>66</sup>. The only criterion left to distinguish between a gradual or a brutal inhibition is thus the shape of the curve.

A distinction between the two cases is then rendered difficult by the fact that the *experimental* curves do not fall as brutally as they ought to do, as we have mentioned at the beginning of Part II (*cf.* case of methylene blue, and refs. 4 and 59). An experimental study of the anodic wave of  $\text{Cl}^-$  shows however that the variation of  $i$  seems to be too slow to be accounted for only by this last effect<sup>36,66</sup>. The inhibition appears to become progressive at an early stage of the life of the drop, which could be due to the formation of inhomogeneous centres on the surface.

## (2) Autocatalysis<sup>35</sup>

In the case of a catalysis by the product of the electrochemical reaction, the expression of the current at the foot of the wave can be obtained as follows. The current is equal to (case of a reduction):

$$i = nFA_a k_{f,h} c \quad (72)$$

${}_a k_{f,h}$  being given by eqn. (41).

On the other hand  $\Gamma$  is given by eqn. (44), in which we shall assume  $\nu = 1$ . From (44) and (72) one obtains, at 25°C:

$$i = 8.2 \times 10^4 \text{ nm}^{\frac{2}{3}} c k_{f,h} z^{-\frac{2}{3}} (2/3) e^s \int_0^s x^{-\frac{1}{3}} e^{-x} dx \tag{73}$$

with  $z = c({}_1 k_{f,h} - k_{f,h})/\Gamma_m$  and  $s = zt$ . The variation of

$$I = (2/3) e^s \int_0^s x^{-\frac{1}{3}} e^{-x} dx$$

is given in Fig. 24.

For small values of  $s$ , the function  $I$  is equivalent to  $s^{\frac{2}{3}}$ , and (73) becomes:

$$i = 8.2 \times 10^4 \text{ nm}^{\frac{2}{3}} t^{\frac{2}{3}} c k_{f,h}$$

*i.e.* one obtains the normal value of  $i$  in the absence of catalysis. This result expresses the fact that at the beginning of the electrolysis the surface concentration of the product of the electrochemical reaction is so small that it has practically no influence. It shows also that the current will tend to assume its normal value, even for large values of  $t$ , when  $c$  or  ${}_1 k_{f,h} - k_{f,h}$  approaches zero.

For large values of  $s$ , the function  $I$  tends towards the asymptotical value

$$y = \Gamma(\frac{5}{3}) e^s = 0.90 e^s$$

$\Gamma(x)$  being the eulerian function.

Thus, for large values of  $t$ , the current varies exponentially. The variation will be exponential even for small values of  $t$ , when the values of  ${}_1 k_{f,h} - k_{f,h}$  or  $c$  are large.

Figure 24 shows that for a given value of the potential the current is always higher than the current which corresponds to the normal (non-catalysed) reaction. The wave is thus shifted towards more positive potentials.

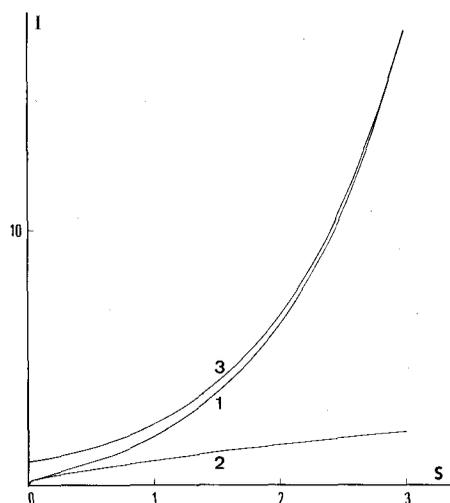


Fig. 24. Variations of function  $I$ . (1) Function  $I$ , (2)  $y = s^{\frac{2}{3}}$ , (3)  $y = 0.90 e^s$ .

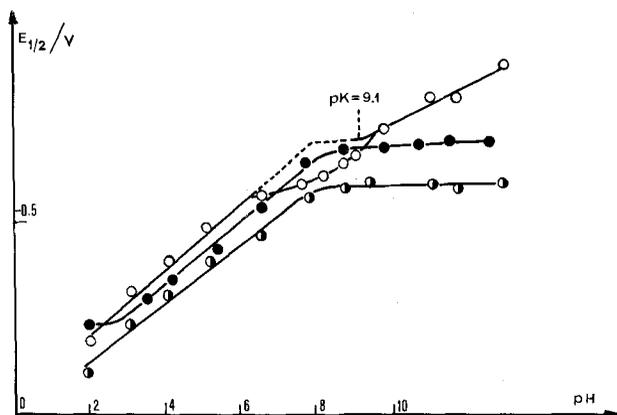


Fig. 25. Curves  $E_{1/2} = f(\text{pH})$ . (○) 4- (or 5-) Nitroimidazole; (●) 1-methyl-4-nitroimidazole; (●) 1-methyl-5-nitroimidazole.  $c = 2 \times 10^{-4} \text{ mol l}^{-1}$ . (-----) Variation which would be observed if there was no autocatalysis.

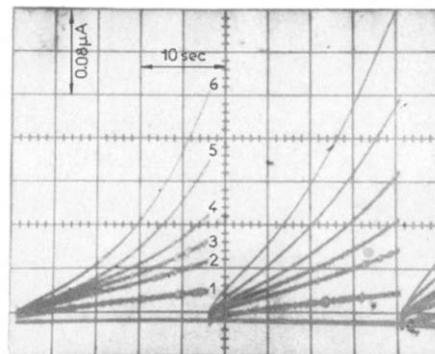


Fig. 26. Experimental  $i-t$  curves for 4- (or 5-) nitroimidazole. First and second drop; pH 7.6; water.  $c = 2.5 \times 10^{-4} \text{ mol l}^{-1}$ ;  $m = 0.236 \text{ mg s}^{-1}$ . Potential (1-6)  $-0.470$ ,  $-0.485$ ,  $-0.490$ ,  $-0.495$ ,  $-0.500$ ,  $-0.505 \text{ V}$ .

As mentioned earlier in this article, a good experimental example of autocatalysis is given by the reduction of 4- (or 5-) nitroimidazole<sup>53,35</sup>. Between pH values of 6 and 10, the wave is shifted towards more positive potentials (Fig. 25). An example of  $i-t$  curves is shown in Fig. 26; their variation is exponential, as predicted by the theory. For the same value of the potential, the current is always higher on the second drop, owing to a transfer of the reduction product, which catalyses the reaction, from the first to the second drop.

## CONCLUSION

The modifications of the polarographic currents caused by adsorption, auto-inhibition or autocatalysis phenomena when a strong adsorption is involved are often important, and can result in characteristic deformations of the shape of the polarograms. The effects of even a strong adsorption are however not always so conspicuous, and can sometimes be inferred only from their consequences on the value of such parameters as  $E_{1/2}$ , or by using more refined methods. Such is the case, for example, for adsorption currents in the sense of Brdicka, when both the oxidized and the reduced form are equally adsorbed: neither a prewave nor a postwave will appear, but characteristic peaks will be obtained in linear potential sweep voltammetry (cf. benzo(c)cinnoline, Fig. 6). Anomalous variations of  $E_{1/2}$  either with concentration or drop time<sup>60</sup>, or with pH<sup>35</sup> can be another consequence; a careful mathematical analysis of the  $i-t$  curves, or of the polarograms is then indispensable.

A certain care must be exercised in judging from the shape of the waves what type of phenomenon is involved, and in distinguishing between autoinhibition processes themselves. A discontinuous increase of current, which is observed at the beginning of the wave for nitrate, bromate and iodate ions is due to other kinds

of effects<sup>4d</sup>. A discontinuous increase can be observed on the other hand either with autoinhibition by the depolarizer itself (type I), or with autoinhibition of type II<sup>60</sup>. A dip in the polarogram can often be caused by a repulsion phenomenon<sup>4e</sup>; it can appear in the 1st or in the 3rd type of autoinhibition (Figs. 13, 14 and 20). Prewaves and pseudo-prewaves appear at first sight as more characteristic, but waves similar in shape can also be observed in other cases (see Fig. 16). It is thus necessary to proceed to a thorough study, including in particular the examination of the adsorbability of the different forms, and of the  $i-t$  curves. As can be inferred from the results presented in this paper, potential sweep voltammetry is particularly suited to this kind of study, because of the possibility it offers to follow the evolution of the phenomena on the same drop, the reversibility etc.

A distinction between Brdicka prewaves and pseudo-prewaves is not always easy, since they possess the same general characteristics (height of the wave independent of concentration and proportional to the height of the mercury reservoir). When the electrode reaction is totally irreversible, the only possibility is a pseudo-prewave. When the reaction is reversible, both kinds of effect can appear simultaneously. If both Ox and Red are strongly adsorbed, the evolution of the  $i-t$  curves with the potential will be that of a Brdicka prewave, since the sudden drop of the current will take place as soon as the film of Ox and Red is compact, and the only effect will be a shift of the main wave (Figs. 3 and 20a). If R only is adsorbed, only an approximate theory has been derived in the case of a Brdicka prewave<sup>23</sup>, and although there is a variation of  $t_m$  with  $E$ , it cannot be used as a criterion. In all cases a determination of the standard potential  $E^0$  of the reaction is indispensable, in order to compare it with the half-wave potentials of the prewave and of the main wave.

Finally, we would like to emphasize the analogy between "surface" and *thin layer* linear potential sweep voltammetry. In surface voltammetry, if the reaction is reversible, the isotherm must be such that a law having the form of the Nernst relationship can be applied to the surface concentrations, which is for example the case with the Langmuir isotherm. The mathematical formulation is the same, since in both cases the sum of the concentrations or of the superficial concentrations is constant, and the Nernst relationship is valid. The surface concentrations and the area of the electrode in surface voltammetry are equivalent respectively to the concentrations and to the volume of the cell in thin layer voltammetry. Mathematical theories valid in both cases can thus be derived<sup>73</sup>.

#### SUMMARY

The effects of a strong adsorption of the depolarizer and/or of the product of the electrochemical reaction on the currents obtained in polarography and in linear potential sweep voltammetry (l.p.s.v.) are considered.

(a) A study of the surface electrochemical reaction (reaction of molecules in the adsorbed state) is presented. Mathematical expressions are derived for the current when the reaction is reversible (Brdicka prewaves or postwaves) for polarography and l.p.s.v. The case where the product of the reaction undergoes an irreversible chemical reaction of the first or second order in l.p.s.v. has been treated. Experimental examples are given: the theory accounts for the characteristics

of the Brdicka prewaves and postwaves and of the adsorption peaks obtained in l.p.s.v.

The equations of the  $i-t$  curves (polarography) and  $i-E$  curves (l.p.s.v.) have also been calculated when the electrochemical reaction is irreversible. These equations are obeyed for small coverages. When the film of the depolarizer is compact anomalies appear, which are due to interactions between the molecules.

(b) The electrochemical process is modified by a film of adsorbed molecules (autoinhibition or autocatalysis).

Three types of autoinhibition are considered: (I) The inhibiting film is constituted of the molecules of the depolarizer itself. (II) The molecules of the film result from a chemical reaction which occurs parallel with the inhibited electrochemical reaction. (III) The film is made of the final product of the inhibited electrochemical reaction. Mathematical expressions for the  $i-t$  curves and for the polarograms have been derived and experimental examples are given. In case III, autoinhibition waves similar in shape to Brdicka prewaves are often observed (pseudo-prewaves); criteria permitting a distinction to be made between prewaves and pseudo-waves are discussed.

The case of an autocatalysis by the product of the reaction has been treated; an experimental example is given.

#### SYMBOLS AND UNITS

##### *Concentrations (mol cm<sup>-3</sup>)*

$c_O(0, t), c_R(0, t)$ : concentrations near the surface of the electrode

$c$ : bulk concentration

$c_m$ : value of  $c$  for which a compact film is formed at time  $t_1$

##### *Superficial concentrations (mol cm<sup>-2</sup>)*

$\Gamma_O, \Gamma_R$  instantaneous concentrations

$\Gamma(0)$  concentration for  $t=0$  (beginning of the electrolysis)

$\Gamma_O(t_1)$  value of  $\Gamma_O$  for  $t=0$  (beginning of the electrolysis, *i.e.* start of potential scan) in linear potential sweep voltammetry

$\Gamma_{O,r}$  value of  $\Gamma_O$  at the potential of the reduction of O

$\Gamma_{O,m}, \Gamma_{R,m}, \Gamma_m$ : maximum value of  $\Gamma_O$  and  $\Gamma_R$

$\Gamma_{m,f}$  maximum value of  $\Gamma_O$  for a flat orientation

##### *Potential (V)*

$E$  electrode potential (measured with an arbitrary origin for irreversible reactions;  $E^0$  is the origin for reversible reactions)

$E^0$  standard potential

$E_i$  initial potential

$E_p$  peak potential

$E_{\frac{1}{2},a}$  half-wave potential of the adsorption prewave or postwave

##### *Time (s)*

$t$  time measured from the beginning of the electrolysis (beginning of drop formation in polarography, beginning of the scan in potential sweep voltammetry)

$t_m, t_i$	time for which the film becomes compact
$\tau$	drop time
$t_k$	time given by the equation of Koryta
$t_1$	delay time (potential sweep voltammetry)

*Rate constants of electrochemical reactions*

$k_f$	rate constant of the surface reaction ( $s^{-1}$ ); $k_f^0$ , its value for $E=0$ ; ${}_a k_{f,h}$ , $k_{f,h}$ , ${}_1 k_{f,h}$ heterogeneous rate constants ( $cm\ sec^{-1}$ ); ${}_1 k_{f,h}^0$ , $k_{f,h}^0$ their value for $E=0$
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*Currents (A) (i instantaneous values,  $\bar{i}$  mean values)*

$i, \bar{i}$	current
$i_d, \bar{i}_d$	diffusion current (Ilkovic eqn.)
$i_a, \bar{i}_a$	adsorption current
$\bar{i}_l$	limiting mean current on the plateau of a prewave, a postwave or a pseudo-prewave
$i_p$	peak current
$i_n$	current in the absence of inhibition

*Other symbols*

$A$	area of the electrode ( $cm^2$ )
$b_o, b_R$	adsorption coefficients ( $cm^3\ mol^{-1}$ )
$m$	rate of flow of capillary ( $g\ s^{-1}$ )
$v$	rate of scan ( $V\ s^{-1}$ )
$\alpha, \alpha'$	transfer coefficients
$\delta$	peak width (mV)
$\eta$	$(b_o, \Gamma_{o,m}/b_R \Gamma_{R,m})\theta$
$\Theta$	coverage
$\theta$	$\exp(nF(E - E^0)/RT)$
$\nu$	number of molecules of the depolarizer necessary to form one molecule of the inhibiting film
$\xi$	$(D_o/D_R)^{\frac{1}{2}}$

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