

SOME BASIC VIEWS ON THE INFLUENCE OF REACTANT ADSORPTION ON WAVE SHAPES IN D.C., A.C. AND LINEAR SWEEP VOLTAMMETRY*

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(Received 21st June 1975)

ABSTRACT

A comprehensive discussion is presented of the basic views and quantitative expressions which are needed to understand the influence of adsorption of electroactive species on the shapes of the waves in d.c. polarography, a.c. polarography and linear sweep voltammetry. It is shown that it is either the non-stationary nature of the techniques or the non-stationary nature of the electrode surface area (or both) which shows up the influence of adsorption.

INTRODUCTION

Though electrochemical analysis methods as d.c. polarography, a.c. polarography and linear sweep voltammetry were originally developed on the basis of simple models of electrode reactions, i.e. solely controlled by diffusion and single electron transfer processes, frequently complications arise, necessitating extension of the theory. One cause of complications is the phenomenon of reactant adsorption, which was invoked for the first time by Brdička [1] to explain the experimental finding of the so-called "prewaves" in d.c. polarograms. Later also "postwaves" have been observed [2] and it was originally thought [3] that only the occurrence of such separate waves provides evidence of the influence of reactant adsorption in d.c. polarography, the main wave being unaffected. However, detailed experiments performed by Bond and Hefter [4,5], have shown that the phenomenon may also manifest itself by a distortion of the d.c. or a.c. polarogram or just an anomalous value of the half-wave potential of a seemingly "normal" polarogram. Similarly, Wopschall and Shain [6,7] have shown that linear sweep voltammograms may exhibit either two peaks or a single (sometimes enhanced) peak at a shifted peak potential. In a.c. polarography, the effect is shown up mainly by enhancement of the peak and anomalous values of the phase angle, due to the special behaviour of the equivalent circuit, as described by Sluyters and coworkers [8,9].

Reactant adsorption is likely to occur in the study of organic electrode

* In honour of Academician A.N. Frumkin's 80th birthday.

reactions, but also of metal complexes, if the ligand is specifically adsorbed ("anion-induced adsorption" [10]). In both categories quite a number of systems have been investigated experimentally.

There is, however, some confusion in the literature as regards the theoretical understanding, most probably because the combination of electrode reactions and adsorption processes leads to a number of divergent possible starting points e.g. reaction via the adsorbed or the free particles, limited or infinite rates of ad- and desorption, limited or infinite rates of charge transfer. We came to this view after having been involved in a discussion with Bond and Hefter [4,5] about the thermodynamic and kinetic backgrounds of the topic, which in the end, due to a suggestion by Barker [12], led to a rather simple description of the effect of reactant adsorption in d.c. polarography at the dropping mercury electrode [13].

The purpose of this paper is to compare a number of recent publications, including our own, in order to obtain a clear view of the most simple model for electrode processes involving reactant adsorption.

(1) THE MODEL

Generally the processes occurring at the electrode surface can be represented by a scheme, which is nearly identical to that given by Feldberg [14]:



So, both O and R are involved in an adsorption—desorption reaction, which has to be described by means of an isotherm. We will adopt the Langmuir isotherm, bearing in mind that most of the following considerations will also hold for other isotherms [14]. For adsorption of two species we have

$$\Gamma_{\text{O}} = K_{\text{O}} c_{\text{O}} \Gamma_{\text{S}} / (1 + K_{\text{O}} c_{\text{O}} + K_{\text{R}} c_{\text{R}}) \quad (1)$$

$$\Gamma_{\text{R}} = K_{\text{R}} c_{\text{R}} \Gamma_{\text{S}} / (1 + K_{\text{O}} c_{\text{O}} + K_{\text{R}} c_{\text{R}}) \quad (2)$$

where Γ_{O} and Γ_{R} are the surface excesses, c_{O} and c_{R} the surface concentrations, Γ_{S} the maximum surface excess and $K_{\text{O}} = k_{aO}/k_{dO}$, $K_{\text{R}} = k_{aR}/k_{dR}$.

Feldberg distinguishes two electrode reactions, viz. between the non-adsorbed species (R1) and between the adsorbed species (R2). In principle, however, one could think of two other reactions viz. between adsorbed O and non-adsorbed R (R3) and between non-adsorbed O and adsorbed R (R4). Where relevant, we will mention these reactions.

If desired, one can assign different standard potentials to the different reactions. E.g. E_1^0 , pertaining to (R1) can be defined as the potential of an electrode in equilibrium with equal concentrations of unadsorbed O and R; E_2^0 , pertaining to (R2), can be defined as the potential of an electrode in equilibrium with equal concentrations (or surface excesses) of adsorbed O and R. Heyrovský and Heyrovská [5] distinguish these two potentials by the somewhat misleading expressions "standard *volume* redox potential" (E_1^0) and "standard *surface* redox potential" (E_2^0). They state erroneously that the latter would be meaningful only in methods where an electrode is polarized and, therefore, not in potentiometry. In our opinion this is not correct, because according to the definitions both standard potentials are thermodynamic quantities and should, therefore, also apply to equilibrium situations. Moreover, there is a relation between E_1^0 and E_2^0 since at equilibrium both exchange reactions will proceed and two Nernst equations may be written:

$$E_{\text{eq}} = E_1^0 + (RT/nF) \ln(c_{\text{O}}^*/c_{\text{R}}^*) \quad (3)$$

$$E_{\text{eq}} = E_2^0 + (RT/nF) \ln(c_{\text{Oads}}^*/c_{\text{Rads}}^*) = E_2^0 + (RT/nF) \ln(\Gamma_{\text{O}}^*/\Gamma_{\text{R}}^*) \quad (4)$$

With eqns. (1) and (2) this leads to

$$E_2^0 = E_1^0 - (RT/nF) \ln(K_{\text{O}}/K_{\text{R}}) \quad (5)$$

or

$$E_2^0 = E_1^0 - (\Delta G_{\text{O}}^0 - \Delta G_{\text{R}}^0)/nF \quad (6)$$

where ΔG_{O}^0 and ΔG_{R}^0 are the standard free energies of adsorption of O and R.

If an attempt is made to apply a similar reasoning to (R3) or (R4), a difficulty arises, because e.g. for (R3) c_{Oads} must be related explicitly to Γ_{O} . Quite primitively, one can say that $c_{\text{Oads}} = \Gamma_{\text{O}}/l$, if l is the thickness of the adsorption layer. Writing the Nernst equation as

$$E_{\text{eq}} = E_3^0 + (RT/nF) \ln(c_{\text{Oads}}^*/c_{\text{R}}^*) \quad (7)$$

one obtains

$$E_3^0 = E_1^0 - (RT/nF) \ln\{(K_{\text{O}}\Gamma_{\text{S}}/l)/(1 + K_{\text{O}}c_{\text{O}}^* + K_{\text{R}}c_{\text{R}}^*)\} \quad (8)$$

Evidently, E_3^0 is concentration-dependent. It is doubtful, however, if an approach like this is useful or even meaningful (see also next sections).

In order to discuss the implications of the model described for the electrochemical behaviour of a system it is essential to distinguish two extreme cases, viz. the case where the rates of adsorption and desorption are virtually zero ("frozen" desad-equilibria) and the opposite case where k_{a} and k_{d} are sufficiently large to achieve instantaneous equilibrium between adsorbed species and surface concentrations.

(2) "FROZEN" ADSORPTION-DESORPTION EQUILIBRIA

If the rate constants of the adsorption processes are so small that within the characteristic electrolysis time no appreciable transformation of "free" species into adsorbed species or vice versa occurs, the four reactions (R1) to (R4) may proceed independently, each in its own potential region. If the electrode reactions are reversible, the "half-wave potentials" in d.c. polarography or "peak-potentials" in other methods will be related to the standard free energies of adsorption and consequently the waves will be situated in a certain order. This is most easily seen for (R1) and (R2) from eqns. (5) and (6). Qualitatively for the reduction of O and O_{ads} it can be said that

- (a) if $K_O > K_R$, reaction (R2) produces a postwave
- (b) if $K_O < K_R$, reaction (R2) produces a prewave
- (c) if $K_O = K_R$, one has $E_2^0 = E_1^0$ and both (R1) and (R2) occur at the same potential.

If only the oxidized form is adsorbed, reaction (R2) will not proceed, but besides the main reaction R1, a postwave due to (R3) may occur, because the reduction of adsorbed O requires more free energy than that of non-adsorbed O. Conversely, if only the reduced form is adsorbed, (R4) may lead to a prewave. There are no quantitative treatments of these cases in literature, but — again qualitatively — it can be said that the separation between the half-wave potentials of pre- or post-wave and main wave is related to the standard free energy of adsorption.

It must be noted that there may be practical reasons which can prohibit observations of a prewave or postwave under the described conditions. E.g. for reduction at the DME the initial surface excess of O will be zero, so that reactions (R2) and (R3) can not occur. Also, currents due to (R2), (R3) or (R4) can only be observed as transients, since once an adsorbed amount is exhausted, or saturation coverage is reached, the current will approximate zero, in contrast with the current due to (R1), which also in the stationary state is maintained by diffusion. Moreover slow adsorption-desorption processes are rather rare. One should be cautious, therefore, in ascribing the occurrence of pre- or post-waves to the proceeding of separate electrode reactions via adsorbed species.

(3) INSTANTANEOUSLY ACHIEVED ADSORPTION-DESORPTION EQUILIBRIA

In this case all four reactions (R1)–(R4) are coupled by the existence of the adsorption equilibrium. If, for example, O is reduced via (R1), the depletion of O at the electrode surface will evoke not only a subsequent delivery by diffusion, but also a partial desorption of O_{ads} . The increased surface concentration of R will lead to an additional adsorption of R. So, the net result is transfer of O_{ads} into R_{ads} , but via reaction (R1) instead of (R2). If, on the other hand, charge transfer proceeds via the adsorbed species, O will be transferred into R via reaction (R2) and the two adsorption reactions.

It is not possible to see a priori which pathway represents the mechanism

of the electrode reaction. Feldberg [14] assumes that reactions (R1) and (R2), with different rate constants, may proceed in principle simultaneously. Then the current i is given by

$$i/nF = a_s[k_{b1}c_R - k_{f1}c_O] + [k_{b2}\Gamma_R - k_{f2}\Gamma_O] \quad (9)$$

where c_O and c_R are concentrations at the electrode surface, Γ_R and Γ_O are surface excesses. The term a_s represents the fraction of the surface available for electron transfer by nonadsorbed species [14]. The idea underlying this is that the adsorbed species partially block the "normal" electrode reaction. This is questionable, since it is also not unusual that "normal" electron transfer is even facilitated by adsorbed species (e.g. bridging effects). However, it is imaginable that at a site where a charged or uncharged particle of O is adsorbed, the "free" O-particle is repelled.

Eqn. (9) can also be written as

$$i/nF = a_s k_{f1} [c_R \exp(\phi_1) - c_O] + k_{f2} [\Gamma_R \exp(\phi_2) - \Gamma_O] \quad (10)$$

$$\text{with } \phi_1 = (nF/RT) (E - E_1^0) \quad (11a)$$

$$\phi_2 = (nF/RT) (E - E_2^0) \quad (11b)$$

With eqns. (1), (2) and (5) this leads to

$$i/nF = \{a_s k_{f1} + K_O k_{f2} \Gamma_s / (1 + K_O c_O + K_R c_R)\} [c_R \exp(\phi_1) - c_O] \quad (12)$$

Contributions of the reactions (R3) and (R4) can be introduced in a similar way. A general version of eqn. (9) reads

$$\begin{aligned} i/nF &= a_s [k_{b1} c_R - k_{f1} c_O] + [k_{b2} \Gamma_R - k_{f2} \Gamma_O] \\ &+ [k_{b3} c_R - k_{f3} \Gamma_O] + k_{b4} [\Gamma_R - k_{f4} c_O] \\ &= (a_s k_{b1} + k'_{b2} + k_{b3} + k'_{b4}) c_R - (a_s k_{f1} + k'_{f2} + k'_{f3} + k_{f4}) c_O \end{aligned} \quad (13)$$

with appropriate expressions for the primed rate constants, which are easily derived from the Langmuir relations (1) and (2). At equilibrium $i = 0$ and $c_R = c_R^*$, $c_O = c_O^*$, so

$$\begin{aligned} (a_s k_{b1} + k'_{b2} + k_{b3} + k'_{b4}) &= (a_s k_{f1} + k'_{f2} + k'_{f3} + k_{f4}) \exp(\phi_1) \\ &= k_f^a \exp(\phi_1) \end{aligned} \quad (14)$$

and again

$$i/nF = k_f^a [c_R \exp(\phi_1) - c_O] \quad (15)$$

So, the eventual rate equation is of the conventional type, in terms of E_1^0 , the surface concentrations and an apparent forward rate constant. It is conceivable that a peculiar wave shape may occur as a consequence of the possible

complex potential dependence of k_f^a . However, if k_f^a is sufficiently large, the reaction is reversible and then the wave-shape is not influenced by any rate constant. In that case there is no possibility to distinguish which pathway is followed in the electrode process.

In other words, for example, the "normal" reaction (R1) may be completely blocked ($a_s = 0$), whereas reaction (R2) or (R3) may be fast. In that case the same current-voltage curve is observed as in the reversed case.

Therefore confusion may arise from the statement in Brdička's original treatment [1], where it is said that the shift of the reduction to a more positive potential (prewave) is caused by a lowering of the free energy by the adsorption of product. Similar statements can be found in other papers, e.g. of Wopschall and Shain [6]: "As the free energy of adsorption increases, the adsorbed reactant is more difficult to reduce and the reduction occurs at a more cathodic potential; if the free energy is further increased, the adsorbed material is sufficiently difficult to reduce so that a separated peak (in linear sweep voltammetry) is observed for the reduction process." Also Bond and Hefter [5] consider the anomalies in their polarographic experiments as an indication that "the reduction occurs in the adsorbed state" and, since "a lowering of free energy would be associated with specific adsorption", a "negative shift in $E_{1/2}$ would be observed".

Considerations like these suggest a purely thermodynamic explanation of shifts in half-wave or peak potentials and the occurrence of pre- and postwaves. In Heyrovský's and Heyrovská's paper [15] it is said explicitly that the so-called surface redox potential (cf. eqn. 4) corresponds to the adsorption wave in polarography. This was also said more implicitly in Bond's and Hefter's first paper [4], which prompted us to show that in polarography anomalies due to adsorption cannot be explained on a thermodynamic basis.

In fact, it is the description of mass balance, to be added to the description of charge transfer, which is responsible for deviations from "normal behaviour" in the case of adsorption.

(4) THE MASS BALANCE EQUATIONS

If in an electrode reaction O is converted into R or vice versa, gradients of the concentrations arise at the electrode surface. Normally mass balance is accounted for by the flux equations

$$i/nF = -AD_O(\delta c_O/\delta x)_{x=0} = AD_R(\delta c_R/\delta x)_{x=0} \quad (16)$$

If there is the possibility of adsorption, the electrode reaction can also cause the adsorbed amounts to increase or decrease. Delahay [16] has shown that this can be accounted for by the modified flux equations

$$\begin{aligned} i/nF &= -AD_O(\delta c_O/\delta x)_{x=0} + d(A\Gamma_O)/dt \\ &= AD_R(\delta c_R/\delta x)_{x=0} - d(A\Gamma_R)/dt \end{aligned} \quad (17)$$

in which A is the surface area and i is the faradaic current. In fact Delahay has argued that it is not correct to treat the faradaic current separately, because it cannot be separated a priori from the charging current. Usually, the charging current is separated nevertheless, by assuming that it is equal to that in the absence of electroactive species and thus can be determined separately [9].

In many treatments [1,3,6], eqn. (17) is considered as if i is split up into two parts, a "diffusion current" and an "adsorption current". To do this a priori is artificial, because from the foregoing section it has become clear that there is no reason to suppose that $d(A\Gamma_O)/dt = -d(A\Gamma_R)/dt$. Instead, eqn. (17), together with the equations for the isotherms, have to be used as boundary conditions for solving Fick's second law

$$\delta c_i / \delta t = D \delta^2 c_i / \delta x^2 \quad (18)$$

The third boundary condition is either the rate equation (15) for the general case or the Nernst equation

$$c_O / c_R = \exp(\phi_1) \quad (19)$$

for the reversible case. The latter gives more simple relationships.

The adsorption terms in eqn. (17), containing both the surface area and the surface excess, require special attention. They can be written as

$$d(A\Gamma_i)/dt = A d\Gamma_i/dt + \Gamma_i dA/dt \quad (20)$$

The first term on the right-hand side is important in any nonstationary method, the second term is only different from zero at electrodes with time-dependent surface area.

(5) IMPLICATIONS FOR VARIOUS TECHNIQUES

(i) A.c. techniques

For reversible systems the electrode impedance of a system with reactant adsorption has been derived by Timmer [9] and Delahay [17], by expressing $d\Gamma_i/dt$ either as [9]

$$d\Gamma_i/dt = (\delta\Gamma_i/\delta E)_\psi dE/dt + (\delta\Gamma_i/\delta\psi) d\psi/dt \quad (21)$$

or as [17]

$$d\Gamma_i/dt = (\delta\Gamma_i/\delta E)_{c_i} dE/dt + (\delta\Gamma_i/\delta c_i) dc_i/dt \quad (22)$$

In eqn. (21) one has $\psi = c_O D_O^{1/2} + c_R D_R^{1/2}$. Eqns. (21) and (22) are equivalent since c_O , c_R and E are related by the Nernst equation.

The equivalent circuit (Fig. 1) is represented by three parallel branches, viz. a pure capacitance, a Warburg impedance and an "adsorption impedance". Although the capacitance has principally a different meaning, there are reasons

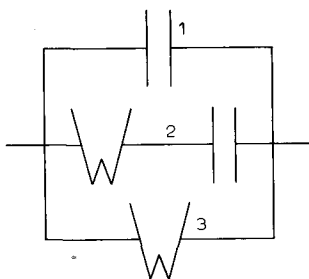


Fig. 1. Equivalent circuit of the electrode impedance. (1) High-frequency capacity; (2) adsorption impedance; (3) Warburg impedance.

to assume that it is approximately equal to the double layer capacitance in the absence of the electroactive species [9]. The Warburg impedance is identical to that in the absence of reactant adsorption. So, the current is essentially divided into three parts, viz. a “charging current”, a “diffusion current” and an “adsorption current”. The latter, however, contains contributions from the diffusion process and it would therefore be erroneous to say that it is directly correlated to the adsorption terms in eqn. (17).

The equivalent circuit holds, irrespective of the adsorption isotherms. Its implications, e.g. for a.c. polarography, should be examined on the basis of a particular isotherm. We intend to communicate on this subject in the near future.

Impedance expressions for the non-reversible case have also been derived [18,19]. They are very complex and it is hard to describe the implications generally.

(ii) *Linear sweep voltammetry*

Many treatments on the role of adsorption in this technique have been published. The most authoritative ones appear to be that of Wopschall and Shain [6] and of Feldberg [14]. The former authors present a conversion of the mass transfer problem into two complex integral equations, which are solved numerically to predict linear sweep voltammograms at a stationary electrode. It is shown that weak adsorption of reactant leads to enhancement and a cathodic shift of the peak, whereas strong reactant adsorption gives rise to a postpeak. Weak adsorption of product appears to have little influence on the cathodic scan peak (only a positive shift in peak potential), but strong adsorption of product causes a prepeak. As said before, the occurrence of post- and prepeaks is incorrectly formalized as due to an increase resp. a decrease in the energy required for the reduction.

Feldberg [14] has calculated theoretical voltammograms, using the digital simulation method to solve the mass transfer problem for several cases of reactant adsorption. His circumstances are chosen such, that always two

peaks occur. It is interesting to conclude from his figures that in the potential region of the first peak the surface coverage is maximal, whereas the second peak coincides with a steep decrease of Γ_{O} from Γ_{S} to zero. So, the first peak will be due to the diffusion term in eqn. (17) ($d\Gamma_{\text{O}}/dt = 0$) and the second peak to the adsorption term ($d\Gamma_{\text{O}}/dt$ is maximal). This stresses again that it is the mass balance equation which is responsible for the shape of the voltammogram and not the amount of energy required for the reduction, although, of course, the fact that a second peak occurs is due to adsorption and thus is related to the strength of adsorption.

(iii) D.c. polarography

The most general treatment for electrolysis under potentiostatic conditions has been given by Reinmuth and Balasubramanian [20,21]. They focus their attention to the charge involved in the electrolysis but they indicate that consequences for the instantaneous current are easily derived as the time-derivative of the charge. The general solutions are very complex and can only be evaluated numerically. However, an important conclusion is that in eqns. (17) and (20) the $d\Gamma_{\text{i}}/dt$ term is important at short times, but approaches zero at long times. This means that in the long-time limiting behaviour *at a stationary electrode* the *instantaneous* current becomes equal to the normal diffusion current observed in the absence of adsorption. The *average* current in d.c. polarography still contains an influence of adsorption (though it may be negligible), due to averaging over the whole electrolysis time [20]. At a *non-stationary* electrode, however, (expanding plane or expanding sphere), even the *instantaneous* current is influenced by adsorption, since the term $\Gamma_{\text{i}}(dA/dt)$ remains significant. In fact the less rigorous steady-state approaches given by Brdička [1], Guidelli [22] and more recently by us [13] are equivalent to the long-time limiting case in Reinmuth's treatment.

Although Guidelli's treatment [22] is somewhat complicated by the assumed non-reversible behaviour, it is found that merely the term containing the time-derivative of the surface area may cause the occurrence of a prewave or a post-wave. Recently Laviron [23] has described the occurrence of pre- and post-waves for reversible behaviour, but this treatment is less general, because it is assumed that both the oxidized and the reduced form are strongly adsorbed. We intend to present a detailed communication on the shape of d.c. polarograms for reversible behaviour, without this assumption, in a succeeding paper [24]. An important feature of the results is that, whether pre- or postwaves occur or not, also the main-wave is affected by adsorption, indicating that it is not possible to separate the contributions from diffusion and adsorption completely.

(iv) A.c. polarography

In section (i) attention is paid only to the equivalent circuit, i.e. only to the a.c. aspects. In a.c. polarography it is also necessary to consider the d.c.

aspects connected to the d.c. potential dependency. Thus far the influence of adsorption in the d.c. aspects was not accounted for. From the foregoing section it follows that such an assumption corresponds to the situation of long-time limiting behaviour at a stationary electrode. Even in this case complex a.c. polarograms can be predicted [25], with double waves and non-linear calibration lines. It is impossible to connect this behaviour to the change in free energy of reduction in a simple way. For non-stationary electrodes the situation is even more complex since then the adsorption effect in the d.c. part shows up also.

(6) CONCLUSION

It can be concluded that it is not satisfactory to describe the influence of reactant or product adsorption on wave shapes in various techniques qualitatively in terms of an increase or a decrease in free energy caused by the adsorption. In fact this may lead to misleading ideas and speculations about the mechanism of the electrode reaction and to wrong interpretations of experiments. Of course any change in wave shape must have some relation to the free energy of adsorption, but this should be quantitatively accounted for in terms of the rate equation for charge transfer, the mass balance equation and the proper isotherm.

ACKNOWLEDGEMENT

Many views presented in this paper originate from an intensive exchange of letters between the authors and Dr. A.M. Bond, who also brought a part of the cited literature to our attention.

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