

ON THE IMPEDANCE OF GALVANIC CELLS

XVIII. THE POTENTIAL DEPENDENCE OF THE FARADAIC IMPEDANCE IN THE CASE OF AN IRREVERSIBLE ELECTRODE REACTION, AND ITS APPLICATION TO A.C. POLAROGRAPHY

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(Received March 5th, 1966; in revised form May 27th, 1966)

INTRODUCTION

The study of the faradaic impedance has proved to be useful in fundamental investigations of electrode reactions, especially for the determination of the kinetic parameters of comparatively fast reactions *i.e.*, reactions, that are reversible with respect to d.c. current. Until now few practical applications are known of the analysis of irreversible reactions by means of the faradaic impedance, probably because the importance of such a study is not sufficiently recognized. In particular, cell impedance measurements as a function of potential may be useful, not only as a check of the d.c. analysis, but also for the evaluation of double-layer parameters and possibly for obtaining more information about the reaction mechanism itself. Examples of irreversible electrode reactions, that have been studied in this way, are the H^+/H_2 reaction¹ at a dropping mercury electrode (D.M.E.) and the $Zn^{2+}/Zn(Hg)$ reaction^{2,3} at a streaming mercury electrode (S.M.E.). For the latter system, unexpectedly, two peaks in the impedance plot were observed; these were misinterpreted for lack of a good theory for the faradaic impedance, as will be shown.

It is worthwhile, therefore, to have theoretical expressions of the faradaic impedance as a function of potential in the case of an irreversible reaction, particularly if both the oxidized (O) and reduced (R) form of the reactant are present. Such expressions might be derived from the work of MATSUDA⁴, who gives a rigorous theory of the faradaic alternating current as a function of potential, or from the less rigorous, but more accessible treatment of AYLWARD *et al.*⁵ on the same subject. In both treatments, however, it is supposed that only O is present and that the D.M.E. is used. Moreover, little attention has been paid to general conclusions which can be drawn in relation to a.c. polarography. In this paper an analogous treatment will be given for the case in which both O and R of the reactant are present and for different kinds of electrodes (such as the S.M.E.). The relevant consequences of the resulting equations will be discussed as an introduction to experimental studies to be described in the near future.

THEORY

In order to obtain expressions for the faradaic impedance, it will be assumed that the mass transfer due to the a.c. current and due to the d.c. current do not in-

fluence each other and that it is permissible to treat these two processes separately, as is done by most authors^{5-7,10}. The current-voltage relationship for an electrode reaction is

$$i = nFk_{sh} \left[C_R \exp \left\{ \frac{\alpha nF}{RT} (E - E_0) \right\} - C_O \exp \left\{ \frac{-\beta nF}{RT} (E - E_0) \right\} \right] \quad (1)$$

where C_O and C_R , the concentrations at the electrode surface, are functions of the potential, E , and the bulk concentrations, C_O^* and C_R^* ; $\beta = 1 - \alpha$, and the other symbols have their usual meaning. For impedance measurements a small alternating voltage, V_{ac} , is superposed on the d.c. voltage, E_{dc} , so that $E - E_0 = V_{ac} + E_{dc} - E_0$. The surface concentrations in that case are $C_O = \bar{C}_O + \Delta C_O(t)$ and $C_R = \bar{C}_R - \Delta C_R(t)$, in which \bar{C} is the surface concentration due to the direct current, i_{dc} , and $\Delta C(t)$ is caused by the alternating current, $i_m \sin \omega t$. Equation (1) becomes

$$i_{dc} + i_m \sin \omega t = nFk_{sh} \left[(\bar{C}_R - \Delta C_R(t)) \exp \left\{ \alpha \varphi + \frac{\alpha nF}{RT} V_{ac} \right\} - (\bar{C}_O + \Delta C_O(t)) \exp \left\{ -\left(\beta \varphi + \frac{\beta nF}{RT} V_{ac} \right) \right\} \right] \quad (2)$$

in which $\varphi = (nF/RT)(E - E_0)$. If the terms $\exp((\alpha nF/RT)V_{ac})$ and $\exp(-(\beta nF/RT)V_{ac})$ in eqn. (2) are expanded as a Fourier series and terms containing products of V_{ac} and ΔC or powers of V_{ac} higher than unity are neglected (because $V_{ac} \ll RT/nF$) eqn. (2) reduces to

$$i_{dc} + i_m \sin \omega t = nFk_{sh} \left[\left(1 + \frac{\alpha nF}{RT} V_{ac} \right) \bar{C}_R \exp(\alpha \varphi) - \left(1 - \frac{\beta nF}{RT} V_{ac} \right) \bar{C}_O \exp(-\beta \varphi) - \Delta C_R(t) \exp(\alpha \varphi) - \Delta C_O(t) \exp(-\beta \varphi) \right] \quad (3)$$

The direct current density is given by

$$i_{dc} = nFk_{sh} [\bar{C}_R \exp(\alpha \varphi) - \bar{C}_O \exp(-\beta \varphi)] \quad (4)$$

Subtraction of (4) from (3) yields

$$i_m \sin \omega t = nFk_{sh} \left[\frac{nF}{RT} V_{ac} \{ \alpha \bar{C}_R \exp(\alpha \varphi) + \beta \bar{C}_O \exp(-\beta \varphi) \} - \{ \Delta C_R(t) \exp(\alpha \varphi) + \Delta C_O(t) \exp(-\beta \varphi) \} \right] \quad (5)$$

Equations for $\Delta C_O(t)$ and $\Delta C_R(t)$ have been given by WARBURG⁸

$$\Delta C(t) = \frac{i_m}{nF} \left(\frac{1}{2\omega D} \right)^{\frac{1}{2}} (\sin \omega t - \cos \omega t) \quad (6)$$

Substitution of (6) into (5) and rearrangement leads to

$$V_{ac} = \frac{RT i_m \sin \omega t}{n^2 F^2 k_{sh} \{ \alpha \bar{C}_R \exp(\alpha \varphi) + \beta \bar{C}_O \exp(-\beta \varphi) \}} + \frac{RT}{n^2 F^2 \sqrt{2\omega}} \cdot \frac{D_R^{-\frac{1}{2}} \exp(\alpha \varphi) + D_O^{-\frac{1}{2}} \exp(-\beta \varphi)}{\alpha \bar{C}_R \exp(\alpha \varphi) + \beta \bar{C}_O \exp(-\beta \varphi)} \cdot i_m (\sin \omega t - \cos \omega t) \quad (7)$$

Equation (7) can be presented in the form of the faradaic impedance, Z_f , with

$$Z_f = \theta + \sigma \omega^{-1/2} (1 - j) \quad (8)$$

$$\theta = \frac{RT}{n^2 F^2 k_{sh} \{ \alpha \bar{C}_R \exp(\alpha \varphi) + \beta \bar{C}_O \exp(-\beta \varphi) \}} \quad (9)$$

$$\sigma = \frac{RT}{n^2 F^2 \sqrt{2}} \cdot \frac{D_R^{-1/2} \exp(\alpha \varphi) + D_O^{-1/2} \exp(-\beta \varphi)}{\alpha \bar{C}_R \exp(\alpha \varphi) + \beta \bar{C}_O \exp(-\beta \varphi)} \quad (10)$$

In the reversible case, $\exp \varphi = \bar{C}_O / \bar{C}_R$ may be introduced, reducing (9) and (10) to the well-known expressions of Randles¹¹. The same holds for the equilibrium potential, φ_{eq} .

The next step is to obtain expressions for \bar{C}_O and \bar{C}_R as a function of φ . These expressions may be derived from the theory of semi-infinite linear diffusion or from the steady-state theory^{9,10}; in this paper the latter will be followed, since its mathematics are less involved. Moreover, the steady-state concept may be used as a model for different types of electrodes, as only a suitable estimation has to be made for the thickness of the diffusion layer, δ . According to the steady-state theory, the surface concentrations are^{3,6}:

$$\bar{C}_O = \frac{C_O^* \left[a_O + \frac{a_O}{a_R} \exp(\alpha \varphi) \right] + C_R^* \exp(\alpha \varphi)}{a_O + \frac{a_O}{a_R} \exp(\alpha \varphi) + \exp(-\beta \varphi)} \quad (11a)$$

$$\bar{C}_R = \frac{C_O^* \exp(-\beta \varphi) + C_R^* \left[a_R + \frac{a_R}{a_O} \exp(-\beta \varphi) \right]}{a_R + \exp(\alpha \varphi) + \frac{a_R}{a_O} \exp(-\beta \varphi)} \quad (11b)$$

in which the terms $a_O = D_O / \delta_O k_{sh}$ and $a_R = D_R / \delta_R k_{sh}$ reflect the influence of the irreversibility of the electrode reaction. Substitution of (11) into (9) and (10) leads to the desired equations for θ and σ .

$$\theta = \frac{RT}{n^2 F^2 k_{sh}} \cdot \frac{a_O + \frac{a_O}{a_R} \exp(\alpha \varphi) + \exp(-\beta \varphi)}{a_O \exp(-\beta \varphi) \left[\beta + \frac{1}{a_R} \exp(\alpha \varphi) \right] C_O^* + \exp(\alpha \varphi) [\alpha a_O + \exp(-\beta \varphi)] C_R^*} \quad (12a)$$

$$\sigma = \frac{RT}{n^2 F^2 \sqrt{2}} \{ D_R^{-1/2} \exp(\alpha \varphi) + D_O^{-1/2} \exp(-\beta \varphi) \} \\ \times \frac{a_O + \frac{a_O}{a_R} \exp(\alpha \varphi) + \exp(-\beta \varphi)}{a_O \exp(-\beta \varphi) \left[\beta + \frac{1}{a_R} \exp(\alpha \varphi) \right] C_O^* + \exp(\alpha \varphi) [\alpha a_O + \exp(-\beta \varphi)] C_R^*} \quad (12b)$$

In the derivation of these equations no special assumptions have been made; they are valid for reversible as well as irreversible reactions.

In part III and VI of this series^{6,7} also, expressions for Z_f were derived as a function of potential assuming, however, that the reaction behaves reversibly with

respect to d.c. current. The *reversible* equations for θ and σ are, in the present notation

$$\theta = \frac{RT}{n^2 F^2 k_{sh}} \cdot \frac{\exp(\beta\varphi) + \frac{a_R}{a_O} \exp(-\alpha\varphi)}{C_O^* + \frac{a_R}{a_O} C_R^*} \quad (13a)$$

$$\sigma = \frac{RT}{n^2 F^2 \sqrt{2D_R}} \cdot \frac{\left[\exp(\frac{1}{2}\varphi) + \frac{a_R}{a_O} \exp(-\frac{1}{2}\varphi) \right]^2}{C_O^* + \frac{a_R}{a_O} C_R^*} \quad (13b)$$

These equations will now be discussed.

ANALYSIS OF CELL IMPEDANCES IN THE CASE OF IRREVERSIBLE ELECTRODE REACTIONS

Measurements of the cell impedance at the equilibrium potential as a function of frequency are useful for the determination^{11,12} of k_{sh} from the value of θ . For low k_{sh} -values, however, θ becomes large with respect to the double-layer impedance; consequently the ohmic resistance, R_Ω , and the double-layer capacitance, C_d , dominate the cell impedance which for this reason contains little information about the electrode reaction. In part VI of this series⁷ it was derived that, under the usual conditions, for a 10% accuracy θ should not exceed 1000 Ωcm^2 ; this means (*cf.* the Randles equation¹¹) that for measurements at the equilibrium potential, $n^2 k_{sh} (C_O^*)^\alpha (C_R^*)^\beta > 10^{-10}$ should hold. With concentrations in the usual order of 10^{-5} mole/cm³, it follows that $k_{sh} > 10^{-5}/n^2$ cm sec⁻¹; therefore k_{sh} -values lower than 10^{-5} cm sec⁻¹ cannot be determined in this way. Higher concentrations could be used, because migration besides diffusion has no influence on the cell impedance for these irreversible reactions, decreasing this limit to perhaps 10^{-7} cm sec⁻¹. From (12a) it follows that θ may be smaller at potentials away from the equilibrium potential (*cf.* θ -curves in Figs. 1 and 2.) and it could therefore be possible to extend the attainable k_{sh} -range by measurements at non-equilibrium potentials. In the following, this will be examined more closely.

In Figs. 1 and 2, values of θ and $\sigma\omega^{-\frac{1}{2}}$ are represented as a function of potential; these values have been calculated numerically, using the data: $n=2$, $\alpha=0.7$, $D_O = \frac{1}{2}D_R = 8 \cdot 10^{-6}$ cm² sec⁻¹, $\delta_O = \delta_R/\sqrt{2} = 5 \cdot 10^{-3}$ cm, $\nu/\omega = 80$ sec⁻¹ and several k_{sh} -values, for $C_O^* = 10^{-6}$ mole/cm³ and $C_O^* = C_R^* = 10^{-6}$ mole/cm³, respectively. These data correspond to the values normally found for the $Zn^{2+}/Zn(Hg)$ reaction at a D.M.E. For a D.M.E. the best expression for δ is

$$\delta = \sqrt{\frac{3}{7} \pi D t} \quad (14)$$

For a S.M.E. the results will be qualitatively the same, the difference with a D.M.E. is caused only by the different value of δ . Obviously $\sigma\omega^{-\frac{1}{2}}$ is not negligibly small at any potential, even for very small k_{sh} -values. In addition, therefore, the quantity q has to be considered, which in practice is obtained easily from the impedance measurements⁷ with $\bar{Z} = Z' - jZ''$

$$\frac{(Z - R_\Omega)^2 + (Z'')^2}{Z' - R_\Omega} = q = \theta + \sigma\omega^{-\frac{1}{2}} + \frac{\sigma^2\omega^{-1}}{\theta + \sigma\omega^{-\frac{1}{2}}} \quad (15)$$

In Figs. 1 and 2, values of $1/q$, corresponding with θ and $\sigma\omega^{-1/2}$, are plotted against potential. If q is determined at different frequencies, θ and σ can be evaluated (frequency variation method). The accuracy of the results will depend on the accuracy of q and on the ratio $p = \theta/\sigma\omega^{-1/2}$: if p is large, the error in σ is large; if p is small, θ contains a large error. At a fixed potential this ratio is independent of concentration

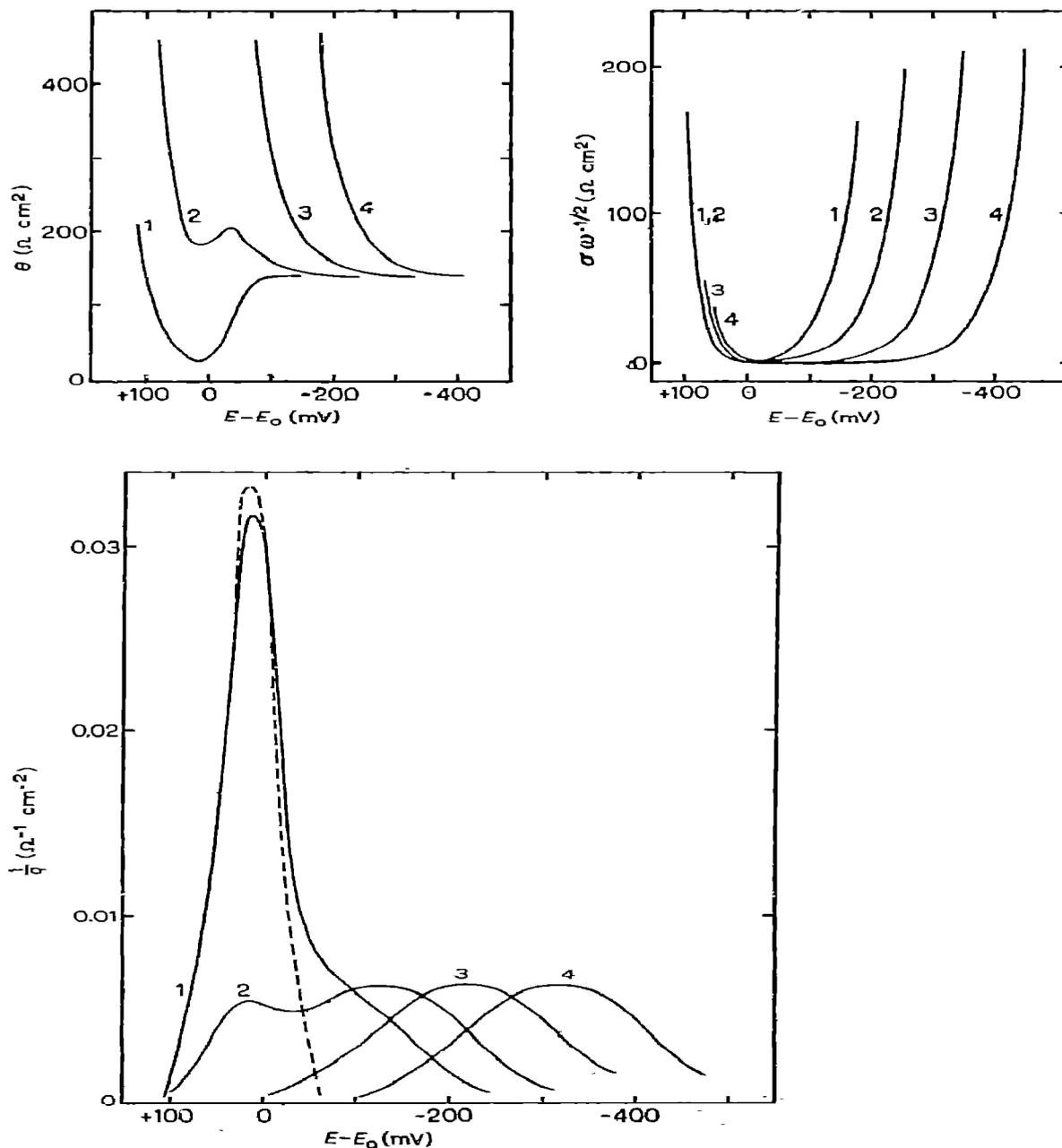


Fig. 1. Plots of θ , $\sigma\omega^{-1/2}$ and $1/q$ against d.c. potential for $C_R^* = 0$, according to eqns. (12) and (15). Value of k_{sh} in cm/sec: (1), $5 \cdot 10^{-3}$; (2) 10^{-3} ; (3) 10^{-4} ; (4) 10^{-5} ; For other data see text. (---); Plot of $1/q$ against d.c. potential for $C_R^* = 0$, according to the reversible eqn (13) for $k_{sh} = 5 \cdot 10^{-3}$ cm/sec.

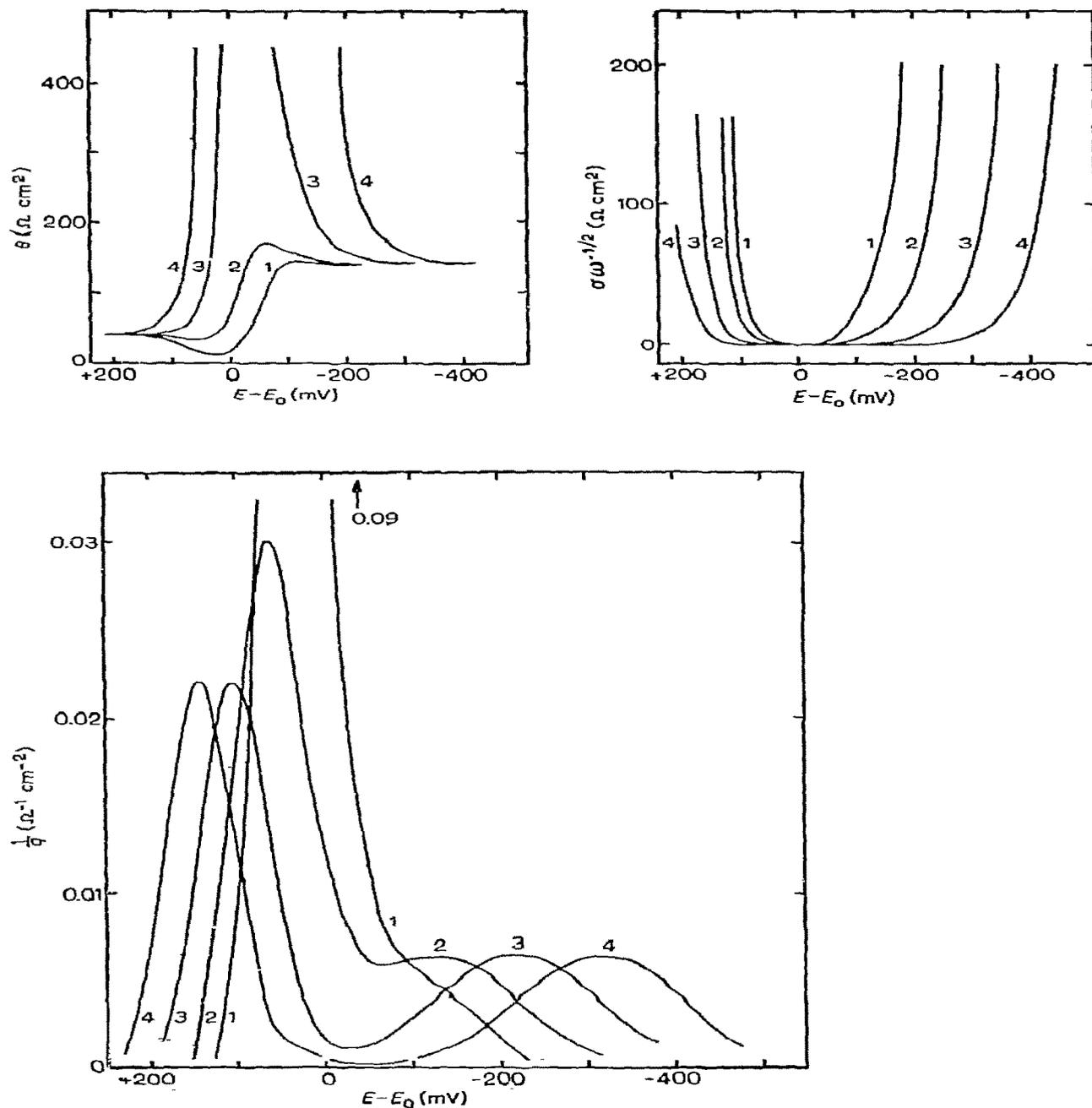


Fig. 2. Plots of θ , $\sigma\omega^{-1/2}$ and $1/q$ against d.c. potential for $C_{O^*} = C_{R^*} = 10^{-6}$ mole/cm³ according to eqns. (12) and (15):
 Value of k_{sh} in cm/sec: (1) $5 \cdot 10^{-3}$; (2) 10^{-3} ; (3) 10^{-4} ; (4) 10^{-5} . For other data see text.

$$\dot{p} = \frac{\sqrt{2\omega}}{k_{sh}} \cdot \frac{I}{D_R^{-1/2} \exp(\alpha\varphi) + D_G^{-1/2} \exp(-\beta\varphi)} \quad (16)$$

If the double-layer capacitance is independent of the concentration of the reactant, the value of \dot{p} itself can be determined (as was pointed out in part VI⁷) from impedance

measurements for varying concentration, at fixed potential and frequency (concentration variation method). This is done most easily from a plot of $Z''/[(Z'')^2 + (Z' - R_\Omega)^2]$ against $(Z' - R_\Omega)/[(Z'')^2 + (Z' - R_\Omega)^2]$, which should be a straight line with slope, $1/p + 1$, and intercept, ωC_d . In this case, θ and σ can be evaluated from q at a single frequency.

From Figs. 1 and 2 it can be concluded that, in fact, q may be relatively small at certain potentials, so that θ may be accessible for small k_{sh} -values. If, however, the interpretation of the results has to be based on the general equation (12a), only a numerical calculation, probably by trial and error, of k_{sh} (and α) seems to be possible. In special cases, however, simplified versions of (12) can be applied.

Possible simplifications

(i) a_O and a_R can be neglected. If $\alpha a_O \ll \exp(-\beta\varphi)$, and $\beta a_R \ll \exp(\alpha\varphi)$, eqn. (12) reduces to the reversible eqns. (13). It is common use to suppose that this is the case for $k_{sh} > 10^{-2}$ cm sec⁻¹ (system reversible to d.c. current¹⁰). It follows, however, from Table 1 that this is not true for the whole potential region of the $1/q$ wave. For $k_{sh} = 10^{-2}$ cm sec⁻¹, the approximation is sufficiently close only at potentials near to E_0 (compare also the broken curve in Fig. 1).

TABLE 1

Difference between the $1/q$ -values, for different d.c. potentials, calcd. from (13) and the general eqns. (12) for $k_{sh} = 10^{-2}$ cm sec⁻¹, $C_O^* = C_R^* = 1$ mM, other data as in Fig. 1.

φ	$(1/q)_{rev.}$	$(1/q)_{gen.}$	Difference (%)
+6	0.017	0.025	32
+4	0.073	0.087	16
+2	0.150	0.165	9
0	0.143	0.143	0
-2	0.055	0.057	4
-4	0.014	0.020	30
-6	0.003	0.009	66

TABLE 2

Error in k_{sh} , if k_{sh} is calcd. from experiments at the peak-potential, by application of (13a) instead of the general expression (12a).

k_{sh} (cm sec ⁻¹)	Difference at peak (%)
10^{-2}	4
$6 \cdot 10^{-3}$	7
$4 \cdot 10^{-3}$	9
$2 \cdot 10^{-3}$	15
10^{-3}	20

In part VI of this series⁷ it was proposed to determine k_{sh} -values from the peak value ($1/q_m$) of $(1/q)$. If the reversible eqn. (13a) for θ is used, the result will be correct only for $k_{sh} \gg 2 \cdot 10^{-3}$ cm sec⁻¹, as can be calculated from the inequalities given before, inserting normal values for a D.M.E. and⁷ $\varphi_{peak} = \ln(\alpha a_R / \beta a_O)$. The error in the k_{sh} -value, calculated from (13a) instead of from the general eqn. (12a), increases with the irreversibility of the reaction (Table 2) and at the peak-potential only for $k_{sh} > 10^{-2}$ cm sec⁻¹ is (13a) a good approximation for (12a).

(ii) a_O is large compared to $\exp(-\beta\varphi)$ for $\varphi \ll 0$. Only this case will be treated here, as for $\varphi \gg 0$ a similar reasoning holds. If $\exp(\alpha\varphi)$ is negligibly small compared to $\exp(-\beta\varphi)$, βa_O and $\beta a_O C_O^* / C_R^*$, which is fulfilled for $\varphi < -10$ if $k_{sh} < 10^{-2}$ cm sec⁻¹ and $C_O^* / C_R^* > 0.1$ with α not too extreme, (12a) reduces to

$$\theta = \frac{RT}{n^2 F^2 k_{sh}} \cdot \frac{a_O + \exp(-\beta\varphi)}{a_O \beta C_O^* \exp(-\beta\varphi)} \quad (17)$$

For $a_0 \gg \exp(-\beta\varphi)$ this reduces further to

$$\theta = \frac{RT}{n^2 F^2 k_{sh}} \frac{\exp(+\beta\varphi)}{\beta C_0^*} \quad (18)$$

Simultaneously $\sigma = RT/n^2 F^2 \beta C_0^* \sqrt{2D_0} = \text{constant}$. The total faradaic impedance, however, is almost equal to θ ($p = \theta/\sigma\omega^{-1} = (\sqrt{2\omega D_0}/k_{sh}) \exp(\beta\varphi) \approx a_0 \exp(\beta\varphi) \gg 1$).

The descending branches of θ in Figs. 1 and 2 for $\varphi \ll 0$ can be described by (18). Plotting $\log \theta$ against φ under these conditions gives a straight line, the slope yielding the value of β , and the intercept at $\varphi = 0$ the value of k_{sh} . In part X of this series¹, eqn. (18) was applied intuitively to the hydrogen reduction on mercury, without proof of its validity. This procedure is correct, if $\varphi < -10$, $a_0 > 10 \exp(-\beta\varphi)$ and $\theta < 10^3 \Omega \text{cm}^2$ (higher values of θ cannot be measured accurately⁷). The latter two conditions yield

$$\frac{5 \cdot 10^{-10}}{n^2 C_0^*} < k_{sh} \exp(-\beta\varphi) < 2 \cdot 10^{-4} \quad (19)$$

The extrapolation of the $\log \theta$ vs φ plot, for obtaining a correct k_{sh} -value, requires that the curve is a straight line for a sufficiently large potential region e.g., 100 mV.

If $n^2 C_0^*$ is chosen $= 5 \cdot 10^{-5} \text{ mole cm}^{-3}$, (19) reduces to

$$10^{-5} < k_{sh} \exp(-\beta\varphi) < 2 \cdot 10^{-4}$$

For $k_{sh} = 10^{-5} \text{ cm sec}^{-1}$ this inequality is fulfilled for $-4 < \varphi < 0$, which is, as a rule, a too limited potential region. Moreover $\varphi < -10$ is not fulfilled. For $k_{sh} \leq 10^{-10} \text{ cm sec}^{-1}$ the proposed procedure can be used (for $k_{sh} = 10^{-10} \text{ cm sec}^{-1}$ $-24 < \varphi < -15$ holds). If C_0^* is chosen larger than $10^{-5} \text{ mole/cm}^3$, even larger k_{sh} -values can be measured. It can be concluded that very low k_{sh} -values can be measured with this a.c. technique and that it is therefore possible to make a comparison between the results of a.c. and d.c. methods.

(iii) a_0 is small compared to $\exp(-\beta\varphi)$ for $\varphi \ll 0$. Again only $\varphi \ll 0$ will be treated here. Starting from (17) and postulating $a_0 \ll \exp(-\beta\varphi)$, or $\exp(-\beta\varphi) > 2 \cdot 10^{-2}/k_{sh}$, one obtains

$$\theta_- = \frac{RT}{n^2 F^2} \frac{\delta_0}{C_0^* D_0 \beta} \quad (20)$$

$$\sigma = \frac{RT}{n^2 F^2 \sqrt{2D_0}} \frac{\exp(-\beta\varphi)}{a_0 \beta C_0^*}$$

Thus, θ becomes constant, independent of k_{sh} and potential, for $\varphi \ll 0$ (cf. the θ -curves in Figs. 1 and 2 for $\varphi \ll 0$).

Surprisingly, $1/q$ reaches a maximum in this potential region, the value of which is approximately equal to $1/\theta_-$, given by (20). The peak-potential of this wave is given by

$$(\varphi_-)_m = -\frac{1}{\beta} \ln \left[\frac{1}{k_{sh}} \left(\frac{2\omega D_0^3}{\delta_0^2} \right)^{\frac{1}{2}} \right] \quad (21)$$

As $1/q$ is proportional to C_0^* even for very low k_{sh} -values, a straight calibration line will be obtained on plotting $(1/q)_m$ against concentration. For a 10% accuracy,

$C_O^* > 10^{-7}/n^2$ mole cm^{-3} should hold, which can be derived in an analogous way as in ref. 7. It is worthwhile to stress that this limit is independent of k_{sh} .

For $\varphi \gg 0$, another peak appears in the $1/q$ -plot, the height of which is approximately equal to the reciprocal of the limiting value of θ on the anodic side

$$\theta_{-} = \frac{RT}{n^2 F^2} \cdot \frac{\delta_R}{C_R^* D_R \alpha} \quad (22)$$

Thus, this peak height is proportional to C_R^* and this concentration can be evaluated from it, if $C_R^* > 10^{-7}/n^2$ mole/ cm^3 .

THE A.C. POLAROGRAPHY OF IRREVERSIBLE ELECTRODE REACTIONS

From the definition (15) of q it follows that $1/q$ is identical to Y_F' , the real component of the faradaic admittance. Consequently, the $1/q$ - E plot represents the theoretical *in-phase a.c. polarogram*. The absolute value of the faradaic admittance is equal to $Y_F' \sqrt{1 + 1/(p+1)^2}$, which means that the theoretical *normal a.c. polarogram* is approximately identical with the $1/q$ - E plot if $p > 2$.

According to the *reversible* eqns. (13), the maximum value of $1/q$ would decrease for decreasing k_{sh} -values, so that a very irreversible reaction would not exhibit a detectable peak in an a.c. polarogram, as is generally assumed. DELMASTRO AND SMITH¹³, for example, make this supposition, although in our opinion their calculated a.c. polarograms disprove their own assumption. From the general eqns. (12), however, it follows that, in fact, for small k_{sh} the faradaic alternating current is very small at potentials near to E_0 , but increases on cathodic polarization forming a substantial peak (Fig. 1). As pointed out in the preceding section, the peak height is proportional to C_O^* and with increasing irreversibility reaches a limiting value, independent of k_{sh} . The peak width also becomes constant. The peak potential shifts away from E_0 to more negative values for decreasing k_{sh} (*cf.* (21)).

The question then arises, whether the peak current is large enough to be detectable, compared to the capacity current. For normal polarographic conditions (*e.g.*, $C_O^* = 5$ mM, $n = 2$, $\alpha = 0.5$, $C_d = 25$ $\mu\text{F cm}^{-2}$, frequency 100 Hz) $1/q_m = 0.04$ $\Omega^{-1} \text{cm}^{-2}$ and $\omega C_d = 0.01$ $\Omega^{-1} \text{cm}^{-2}$, so that the a.c. wave can be detected easily.

Another striking conclusion is, that with both O and R present, two very distinct peaks occur in the a.c. polarogram, even for moderately irreversible electrode reactions. The occurrence of two peaks could be interpreted as indicating that two different electrode reactions take place (*cf.* ref. 18). Evidently, for irreversible reactions this is not necessarily true. Curve 2 in Fig. 1 also shows two maxima although $C_R^* = 0$, similar to the curve published by MATSUDA⁴ for the same conditions. This splitting up of the a.c. wave is quite accidental because it appears only for $k_{sh} \sim 10^{-3}$ cm sec^{-1} . For other k_{sh} -values only one peak appears for $C_R^* = 0$ and therefore these two maxima are of different nature from the two peaks occurring in an a.c. polarogram for low k_{sh} -values with both O and R present. Therefore, even the occurrence of two peaks with only O present, does not prove unequivocally that two reactions take place.

A number of authors^{5,14-17} have reported theoretical and experimental studies concerning the drop-time dependence of a.c. polarographic currents. If in addition to diffusion, some process influences kinetically the d.c. current, the surface concentra-

tions and hence the a.c. current are time-dependent. For irreversible reactions the slow electron transfer is such a process.

From (14) and (20) it follows that for very irreversible electrode reactions $(I/q_-)_m$ is proportional to $t^{-1/2}$. This is verified by the data of AYLWARD AND HAYES¹⁴ for the quasi-reversible reduction of the cadmium-EDTA complex. If the peak heights from their Table 1 are plotted against $t^{-1/2}$, a straight line is obtained, Fig. 3 (note that there exists also a pre-wave in the reduction of the cadmium-EDTA complex which is an electrode reaction preceded by a chemical reaction and shows also a time-dependency, their Table 3). AYLWARD AND HAYES¹⁴ assume that the time-dependence of the peak height for the oxidation of an amalgam is caused by streaming at the mercury surface. Streaming will certainly influence the time-dependence of an a.c. current, but

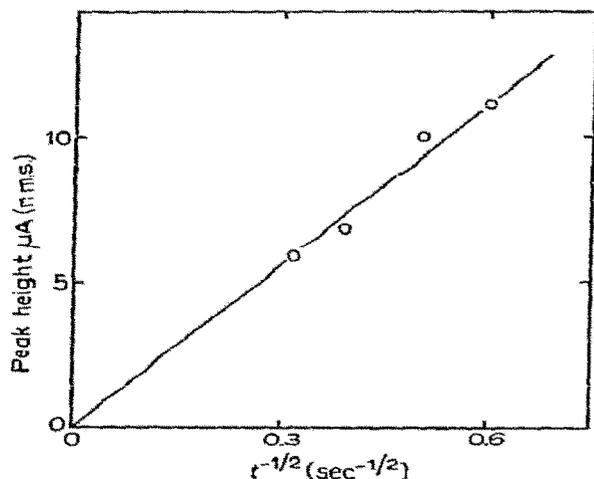


Fig. 3. The a.c. peak height for the reduction of the cadmium-EDTA complex as a function of $t^{-1/2}$ from data published by AYLWARD AND HAYES¹⁴.

even if there is no streaming, the currents will be time-dependent for irreversible reactions (*cf.* (22) together with (14)).

DISCUSSION

As was mentioned in the introduction, general theories on a.c. polarography (valid for reversible and irreversible systems) are given by MATSUDA⁴ and AYLWARD *et al.*⁵, but only for $C_R^* = 0$, so that a comparison with our results can be made only for this case. AYLWARD *et al.* made the same approximations as in this paper and showed that the resulting a.c. current compares favourably with the more rigorous, but still not exact expressions for a D.M.E. of MATSUDA. According to DELMASTRO AND SMITH¹³, the latter lie closest to their more correct expressions for a D.M.E., so that it can be concluded that our expressions, which are more accessible, are a good approximation for a D.M.E.

The numerically calculated polarograms of MATSUDA⁴ and AYLWARD *et al.*⁵ are similar to the curves in Fig. 1. It can be calculated that for their curves the peaks are proportional to β for low k_{sh} -values, as predicted by (20). The curves given by MATSUDA also show that the peak reaches a limiting value for decreasing k_{sh} -values,

although he did not state both facts explicitly, perhaps because of the complexity of his equations.

To our knowledge, it has not been stated before in the literature that (i) even very irreversible systems still exhibit peaks in an a.c. polarogram, the peak height being independent of k_{sh} and proportional to α or β (eqns. (20) and (22)) and (ii) that two distinct peaks occur in an a.c. polarogram for irreversible systems with both O and R of the reactant present.

In a recent publication³ we reported the occurrence of at least two peaks in the a.c. polarograms of the $Zn^{2+}/Zn(Hg)$ reaction in 1 M KCl in the presence of a surface-active substance; $\text{per}_{\text{ct}}^{\text{+}}$ was thought to give further evidence for the hypothesis, that the reaction proceeds *via* univalent zinc. The present results suggest that this hypothesis is untenable.

We shall communicate on the mechanism of the zinc reaction more extensively in a further paper and describe experimental results supporting the theory presented here.

ACKNOWLEDGEMENT

This investigation was supported in part by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organisation for the Advancement of Pure Research (ZWO).

SUMMARY

A theoretical treatment for the potential dependence of the faradaic impedance, in the case that the electrode reaction behaves irreversibly with respect to the direct current, using the steady-state concept, is presented. An analysis of the expressions obtained in the complex impedance plane is given and a method is described to measure even a very small rate constant, k_{sh} . The consequences for a.c. polarography are discussed. It has been found that even very irreversible electrode reactions exhibit substantial peaks in an a.c. polarogram. If only the oxidized form of the reactant is present, one peak appears even for very small k_{sh} -values. For decreasing k_{sh} , the peak height decreases to a limiting value, independent of k_{sh} and sufficiently large to be detectable in an a.c. polarogram. If both the oxidized and reduced form are present, two peaks occur for irreversible systems, the peak heights again being independent of the k_{sh} -value.

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