

THE INVESTIGATION OF THE ADSORPTIVE BEHAVIOUR OF ELECTROACTIVE SPECIES BY MEANS OF ADMITTANCE ANALYSIS

PART I. THEORY OF THE CASE OF REVERSIBLE CHARGE TRANSFER

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ABSTRACT

A comprehensive treatment is given of the relationships concerning the interfacial admittance of an electrode at which a reversible electrode reaction with reactant adsorption proceeds. It is shown that these relationships permit the determination of the parameters of a postulated isotherm, as well as the potential dependence of the free energy of adsorption, the latter irrespective of the isotherm chosen. Procedures to analyse the admittance spectra are developed and the attainable accuracy and reliability of such analyses are critically discussed. It is shown that the information to be obtained is highly detailed, provided that internal checks are carefully applied.

(I) INTRODUCTION

Many faradaic oxidation–reduction reactions are accompanied by specific adsorption of the reactants and/or products at the electrode–solution interface. The fundamental theory in such a case is very complex if it is desired to account in general for finite rates of charge transfer, adsorption/desorption and diffusional mass transfer. Therefore, in practical situations an attempt is usually made to interpret experimental data with simplified theories, i.e. based on the assumption that simplifying conditions are fulfilled.

The most frequently adopted model is that of the “reversible interfacial processes”, i.e. both charge transfer and adsorption/desorption are non-rate determining, so that the only source of relaxation is the diffusion of the reacting and adsorbing/desorbing species. The well-known chronocoulometry technique is based on this principle almost by definition, because it is performed by stepping the electrode potential from the pre-faradaic region (after assessment of adsorption equilibrium) to the limiting current region, where the time dependence of the charge passing the interface is governed solely by diffusion. The result is that the originally adsorbed amount can be determined fairly directly as a function of the initial potential [1,2]. The method is, however, limited to initial potentials *outside* the faradaic region,

where the oxidation or reduction current is zero.

The information obtained with chronocoulometry, essentially a large-amplitude dc technique, can be fruitfully complemented by application of the complex admittance method which is essentially a small-amplitude ac technique. It has been shown [3,4] that especially *within* the faradaic region the interfacial admittance is extremely sensitive to the effects of reactant adsorption, as regards both its frequency dependence and its dc potential dependence. This sensitivity is due to the derivational character of the admittance parameters, exhibiting large values in the faradaic region where surface concentrations and surface excesses change strongly with the potential.

Although this makes the theoretical background of the ac method more complex, it can be expected that the information obtained will be more detailed. The admittance method comprises both "ac and dc aspects", and if in both aspects the assumption of reversible charge transfer and reversible adsorption/desorption is justified, the information obtained concerns solely the thermodynamics of the adsorption behaviour.

In our opinion, this view on the potentialities of the ac technique has not been fully recognized until now. The adsorption phenomenon was considered rather as a complication than as a bonus. In recent studies of some practical examples in this laboratory the ideas stated above could be successfully applied.

The theory required for a complete analysis of admittance experiments has been gradually developed during the period 1967-77. As a result the relevant publications [4-10] are rather randomly distributed and not very well known. For this reason we thought it worth while to collect the final conclusions in a more surveyable way in order to reconsider thoroughly what really can be achieved in an admittance analysis, assuming that the interfacial processes are reversible. In this paper we wish to communicate the details of this study, which resulted in some new conclusions as well as a general outline of the potentialities of the admittance method.

(II) THEORY

(II.1) Recapitulation of the basic principles

Our treatment is confined to a *reversible electrode reaction* $O + ne \rightleftharpoons R$ (standard potential E^0) with possible adsorption of O and R. Also, the adsorption processes are supposed to be reversible, i.e. their rates are not determined by an activation process. If other complications such as slow homogeneous reactions involving O or R are absent, then the total of events at the interface is described by Fick's second law of diffusion with the appropriate boundary conditions [5] which we have summarized in Table I.

For the discussions in this paper the following remarks are useful to recall:

(1) The *fundamental* boundary conditions (I) are the *flux equations* accounting for simultaneous occurrence of electron transfer and ad- or desorption.

(2) The *additional* boundary conditions (II) are for our case *thermodynamic*

TABLE I

Summary of boundary conditions to the diffusion equation in case of reversible charge transfer and reversible adsorption of O and R

(I) *Fundamental conditions*

$$c_O(\infty, t) = c_O^*, \quad c_R(\infty, t) = c_R^* \quad (1)$$

$$D_O(\partial c_O / \partial x)_{x=0} = -j_F / nF + (1/A) d(A\Gamma_O) / dt \quad (2)$$

$$D_R(\partial c_R / \partial x)_{x=0} = j_F / nF + (1/A) d(A\Gamma_R) / dt \quad (3)$$

j_F = faradaic current density; A = electrode surface area; c_O^*, c_R^* = initial concentrations; Γ_O, Γ_R = surface excesses.

(II) *Additional conditions*

$$c_O(0, t) / c_R(0, t) = \exp[(nF/RT)(E - E^0)] \quad (4)$$

$$\Gamma_O = f[E, c_O(0, t)] \quad (5)$$

$$\Gamma_R = f[E, c_R(0, t)] \quad (6)$$

(III) *Conditions for double-layer charging*

$$j_C = (1/A) d(Aq) / dt \quad (7)$$

$$q = f(E, \Gamma_O, \Gamma_R) \quad (8)$$

j_C = charging current density; q = charge density on the metal.

relationships, because we have assumed that both the faradaic and the adsorptive processes are reversible, i.e. they virtually obey equilibrium relationships applied to the surface excesses and the concentrations $c_O(0, t)$ and $c_R(0, t)$ at the interface. One of these, the Nernst equation, does not need further explanation. Equations (5) and (6) generally express that the surface excesses are related to the interfacial concentrations through some adsorption isotherm, which has to be specified at some stage of any investigation in terms of a function of *two variables*, E and $c_O(0, t)$, or E and $c_R(0, t)$, or $c_O(0, t)$ and $c_R(0, t)$, or of two different combinations of these variables. The reason for this statement is that eqn. (4) restricts the degree of freedom to the choice of only two independent variables. It has been pointed out that it is indeed profitable to choose the two parameters E and ψ , the latter defined by [4]

$$\psi = D_O^{1/2} c_O(0, t) + D_R^{1/2} c_R(0, t) \quad (9)$$

This will be discussed in sections (II.2) and (II.3).

(3) The faradaic current density j_F cannot be measured separately from the charging current density j_C . If there were no adsorption it would be permissible to make the charge density q equal to that of the interface electrode/supporting electrolyte, but in the presence of (specific) reactant adsorption it must be recognized that q is dependent on both the electrode potential and the surface excesses, as is the case in eqn. (8). In view of eqns. (5–7), this must also mean that q is fully determined by a function of two of the three variables, E , c_O , c_R , or of E and ψ [4].

The best way to complete the theory of the current-potential characteristic is first to solve the diffusion problem, preferably by means of the method of Laplace transforms [8], and next to make the results explicit by inserting an appropriate isotherm. In fact, such a procedure is advocated in the work of Reinmuth and Balasubramanian [10], which demonstrates that far-reaching general conclusions can be drawn from studies employing controlled-potential perturbation(s). The only restriction made in their work is that, if both O and R are possibly adsorbed, the isotherms are of the form:

$$\beta_O(E)c_O(0,t) = (\Gamma_O/\Gamma_m) f[(\Gamma_O + \Gamma_R)/\Gamma_m] \quad (10a)$$

$$\beta_R(E)c_R(0,t) = (\Gamma_R/\Gamma_m) f[(\Gamma_O + \Gamma_R)/\Gamma_m] \quad (10b)$$

where Γ_m is the maximum surface excess and β_O and β_R the adsorption coefficients; $-RT \ln \beta_i$ equals the free energy of adsorption ΔG_{ads} . (But in fact, the activity coefficients of O and R are incorporated in the β 's.)

Finally, it is mentioned here that for the combined application of dc and ac potential control (the method applied in this work) it is convenient to separate the variables involved, c_i , Γ_i , j , E , into a "dc part" and an "ac part", indicated systematically by notations as $c_i(0,t) = \bar{c}_i + \Delta c_i$, etc. As for the dc parts, it is useful to summarize the abbreviations of some frequently occurring functions. This is done in Table 2.

TABLE 2

Some relations and notations concerning the dc variables

(i)	$\bar{c}_O/\bar{c}_R = \exp(\varphi) \quad \varphi = (nF/RT)(\bar{E} - E^0)$
(ii)	$D_O^{1/2}\bar{c}_O/D_R^{1/2}\bar{c}_R = \exp(\zeta) \quad \zeta = (nF/RT)(\bar{E} - E_{1/2}')$
(iii)	$\bar{\psi} = D_O^{1/2}\bar{c}_O + D_R^{1/2}\bar{c}_R$ $= D_O^{1/2}\bar{c}_O [1 + \exp(-\zeta)]$ $= D_R^{1/2}\bar{c}_R [\exp(\zeta) + 1]$
(iv)	$\sigma_O = (RT/n^2F^2\sqrt{2})(D_O^{1/2}\bar{c}_O)^{-1}$ $\sigma_R = (RT/n^2F^2\sqrt{2})(D_R^{1/2}\bar{c}_R)^{-1} \quad \sigma_O + \sigma_R = \sigma \text{ (Warburg coefficient)}$
(v)	$\sigma_O/\sigma = [\exp(\zeta) + 1]^{-1}$ $\sigma_R/\sigma = [1 + \exp(-\zeta)]^{-1}$

(II.2) The interfacial admittance

The frequency dependence of the complex interfacial admittance $Y = Y' + iY''$ is described by the equations of Timmer et al. [4]:

$$Y' = \frac{\omega^{1/2}}{2\sigma} + \omega(C_{LF} - C_{HF}) \frac{u}{(u+1)^2 + 1} \quad (11a)$$

$$Y'' = \frac{\omega^{1/2}}{2\sigma} + \omega(C_{LF} - C_{HF}) \frac{u+2}{(u+1)^2 + 1} + \omega C_{HF} \quad (11b)$$

where

$$\sigma = \sigma_O + \sigma_R \quad (\text{see Table 2}) \quad (12)$$

$$u/\omega^{1/2} = u' = \sqrt{2} \times [\partial(\Gamma_O + \Gamma_R)/\partial\psi]_E \quad (13)$$

$$C_{LF} = (\partial q/\partial E)_\psi + nF\{(\sigma_O/\sigma)(\partial\Gamma_O/\partial E)_\psi - (\sigma_R/\sigma)(\partial\Gamma_R/\partial E)_\psi\} \quad (14)$$

$$C_{HF} = (\partial q/\partial E)_{\Gamma_O + \Gamma_R} + nF(\partial\Gamma_O/\partial E)_{\Gamma_O + \Gamma_R} \quad (15)$$

According to eqns. (11) the interfacial admittance is additively composed of three parallel branches: (1) the classical Warburg admittance $(\omega^{1/2}/2\sigma)(1+i)$; (2) the "adsorption admittance" which has a form identical to the admittance derived for diffusion-controlled adsorption of non-electroactive species [11]; (3) the capacity C_{HF} which replaces the double-layer capacity C_d of the supporting electrolyte alone (see Fig. 1). At low frequencies ($u \ll 1$) the adsorption admittance becomes equal to $i\omega(C_{LF} - C_{HF})$ so that the total capacity parallel to the Warburg impedance is C_{LF} (the "low-frequency capacity"). The limit of the adsorption admittance at high frequencies is given by $[\omega^{1/2}(C_{LF} - C_{HF})/u'](1+i)$, a "Warburg-like impedance", so that then the parallel capacity is C_{HF} (the "high-frequency capacity"); see also Fig. 1.

The variable ψ (see eqn. 9) was introduced for two reasons. Firstly, it helps to obtain the admittance equations in a most surveyable form in terms of the four parameters of eqns. (12)–(15). Secondly, the dc part of it, $\bar{\psi} = D_O^{1/2}\bar{C}_O + D_R^{1/2}\bar{C}_R$ is, under normal polarographic conditions, equal to $D_O^{1/2}C_O^* + D_R^{1/2}C_R^*$, and thus invariant at variation of the dc potential \bar{E} . Therefore, integration of, for example, the C_{LF} parameter has a physical and even a thermodynamic meaning.

The latter point, however, is no longer valid if reactant adsorption affects the dc behaviour, which happens in the case of stronger adsorption. Therefore, it was proposed by Wijnhorst et al. [9] to define the "concentration variable" in a different way:

$$\psi' = D_O^{1/2}c_O(0, t) + D_R^{1/2}c_R(0, t) + f(t_m)[\Gamma_O + \Gamma_R] \quad (16)$$

where $f(t_m)$ must be derived from the theory describing the dc part (reversible charge transfer plus adsorption) such that $\bar{\psi}'$ becomes equal to $D_O^{1/2}c_O^* + D_R^{1/2}c_R^*$ and thus invariant (see also section II.4). With this concept new admittance expressions

were derived which appear to be only slightly different from Timmer's expressions.

In the course of the present work we found it more cumbersome to calculate the potential dependence of Wijnhorst's parameters compared to those of Timmer. Therefore, we decided to work with eqns. (11)–(15) and to handle the problem of non-invariant $\bar{\psi}$ in a better way. The principle is that the partial derivatives involved can be easily transformed into each other; e.g. for Γ_O it can be derived that

$$(\partial\Gamma_O/\partial E)_\psi = [1 + f(t_m)(\partial\Gamma_O/\partial\psi)_E](\partial\Gamma_O/\partial E)_\psi \quad (17)$$

The derivation of this relation is given in Appendix I.

(II.3) Relations between the partial derivatives for adsorption of O

Independently of the further specification of the isotherms (eqn. 10), it is possible to derive relationships between the partial derivatives of q and Γ occurring in eqns. (12)–(15), which are useful in the interpretation of experimental results. For the general case of O and R adsorption this is done in Appendix II. Here we discuss the more surveyable case that only O is adsorbed, i.e. Γ_R is set equal to zero.

In the earlier studies [4,5] it was considered as a complication that the two partial derivatives $(\partial q/\partial E)_\psi$ and $(\partial\Gamma_O/\partial E)_\psi$ contained in one parameter, C_{LF} , could not be determined separately. Later it was shown [9] that $(\partial q/\partial E)$ can be eliminated from C_{LF} with the aid of the thermodynamic relationship:

$$q - q^0(E) = RT\Gamma_O(d \ln \beta_O/dE) \quad (18)$$

where $q^0(E)$ is the charge density in the absence of adsorption; so, $dq^0/dE = C_d$ equals the double-layer capacity of the supporting electrolyte.

Equation (18) has been derived from the electrocapillary equation for the ideally reversible electrode [12], together with the implication of the general definition of the adsorption isotherm, eqn. (10), that the surface excess of Γ_i is a function of the product $\beta_i c_i$. Therefore we have:

$$(\partial\Gamma_i/\partial c_i)_{\beta_i} = [d\Gamma_i/d(\beta_i c_i)]\beta_i$$

$$(\partial\Gamma_i/\partial\beta_i)_{c_i} = [d\Gamma_i/d(\beta_i c_i)]c_i$$

or

$$c_i(\partial\Gamma_i/\partial c_i)_{\beta_i} = \beta_i(\partial\Gamma_i/\partial\beta_i)_{c_i} \quad (19)$$

Until now it was not noticed that this property of the isotherm also delivers a relationship between the two partial derivatives of Γ_O itself, occurring in the parameters u' , eqn. (13) and C_{LF} , eqn. (14). In view of eqns. (4) and (9) we can write:

$$\beta_O c_O(0, t) = \frac{\beta_O D_O^{-1/2}}{1 + (D_R/D_O)^{1/2} \exp[-(nF/RT)(E - E^0)]} \psi \quad (20a)$$

$$= \epsilon_O \psi \quad [\epsilon_O = f(E)] \quad (20b)$$

Thus, $\Gamma_O = f(\epsilon_O \psi)$ and

$$\psi(\partial \Gamma_O / \partial \psi)_{\epsilon_O} = \epsilon_O (\partial \Gamma_O / \partial \epsilon_O)_{\psi} \quad (21)$$

and finally,

$$\begin{aligned} (\partial \Gamma_O / \partial E)_{\psi} &= (\psi / \epsilon_O) (d \epsilon_O / d E) (\partial \Gamma_O / \partial \psi)_E \\ &= \left\{ \frac{nF/RT}{\exp(\zeta) + 1} + \frac{d \ln \beta_O}{d E} \right\} \bar{\psi} \left(\frac{\partial \Gamma_O}{\partial \psi} \right)_E \end{aligned} \quad (22)$$

where ζ is defined in Table 2.

(II.4) The meaning of the admittance parameters

With eqns. (18) and (22) it is possible to reconsider the definition of the three adsorption parameters, eqns. (13)–(15), simplified with $\Gamma_R = 0$. With $\sigma_O/\sigma = [\exp(\zeta) + 1]^{-1}$, cf. Table 2, inserted, we obtain:

$$(C_{HF} - C_d) = RT \Gamma_O (d^2 \ln \beta_O / d E^2) \quad (23)$$

$$(C_{LF} - C_{HF}) = \left\{ \frac{1}{\exp(\zeta) + 1} + \frac{RT}{nF} \frac{d \ln \beta_O}{d E} \right\} nF \left(\frac{\partial \Gamma_O}{\partial E} \right)_{\psi} \quad (24)$$

$$u' = (\partial \Gamma_O / \partial \psi)_E \sqrt{2} \quad (25)$$

$$\frac{(C_{LF} - C_{HF})}{u'} = \left\{ \frac{1}{\exp(\zeta) + 1} + \frac{RT}{nF} \frac{d \ln \beta_O}{d E} \right\}^2 \frac{n^2 F^2}{RT} \frac{\bar{\psi}}{\sqrt{2}} \quad (26)$$

Clearly, the thermodynamic relationships discussed in section (II.3) prompt us to combine the four original parameters C_d , C_{HF} , C_{LF} and u' to four "new" parameters with a logical and useful meaning as defined in eqns. (23)–(26). Especially, it may be noted that the one defined in eqn. (26) is in fact the "Warburg parameter" of the

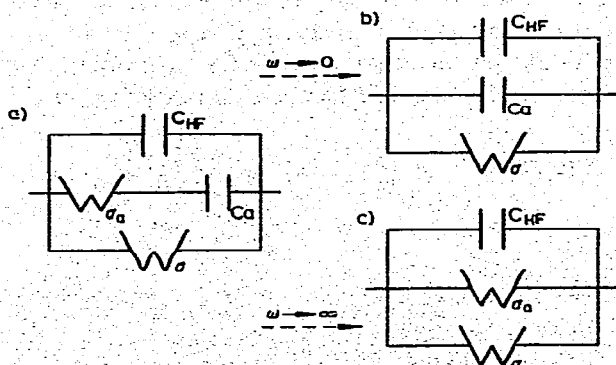


Fig. 1. Equivalent circuit for a reversible electrode reaction with reactant adsorption: (a) general; (b) low-frequency limit; (c) high-frequency limit. $(2\sigma_a)^{-1} = (C_{LF} - C_{HF})/u'$ and $C_a = C_{LF} - C_{HF}$.

adsorption admittance in Fig. 1: $(C_{LF} - C_{HF})/u' \equiv 1/2\sigma_a$. Its definition has some analogy with that of the classical "faradaic" Warburg coefficient:

$$\frac{1}{2\sigma} = \frac{\exp(\zeta)}{[\exp(\zeta) + 1]^2} \frac{n^2 F^2}{RT} \frac{\bar{\psi}}{\sqrt{2}} \quad (27)$$

Finally, it is mentioned here that eqns. (24) and (26) can be combined to eliminate the term between brackets:

$$2\sigma_a(C_{LF} - C_{HF})^2 = u'(C_{LF} - C_{HF}) = \frac{RT\sqrt{2}}{\bar{\psi}} \left\{ \left(\frac{\partial \Gamma_O}{\partial E} \right)_{\psi} \right\}^2 \quad (28)$$

As far as we can see, this function does not have a physical meaning in the sense of the equivalent circuit, but it may be useful to determine Γ_O straightforwardly via integration.

(II.5) Potential dependence of the admittance parameters for adsorption of O only

From the foregoing it follows that it is only necessary to specify $\bar{\psi}$ and $(\partial \Gamma_O / \partial \psi)_E$ in order to obtain explicit expressions for the parameters defined by eqns. (24)–(28) as a function of the dc potential. The first- and second-order derivative of $\ln \beta_O$ (the free adsorption energy) with respect to E are then considered as (adjustable) parameters. First we will consider the question of specifying

$$\bar{\psi} = D_O^{1/2} \bar{c}_O + D_R^{1/2} \bar{c}_R = D_O^{1/2} \bar{c}_O [1 + \exp(-\zeta)]:$$

(1) The simplest approximation is

$$\bar{\psi} = D_O^{1/2} c_O^* + D_R c_R^* \quad (29)$$

which would hold, according to the Cottrell equation or the Ilkovič equation, for linear diffusion to a stationary and an expanding plane respectively, in the absence of effects of reactant adsorption on the dc parts of $c_O(0, t)$ and $c_R(0, t)$.

(2) However, it has been pointed out [11,13] that in case of spherical electrodes [stationary sphere or expanding sphere (DME) with a radius r_0], eqn. (29) is not sufficiently accurate to describe the potential dependence of, for example, the Warburg coefficient. For a stationary sphere it is possible to derive a rather rigorous alternative from the relation [14]:

$$D_O^{1/2} [c_O^* - \bar{c}_O] [1 + (\pi t_m D_O)^{1/2} r_0^{-1}] + D_R^{1/2} [c_R^* - \bar{c}_R] [1 \pm (\pi t_m D_R)^{1/2} r_0^{-1}] = 0$$

giving, with $D_O^{1/2} \bar{c}_O = D_R^{1/2} \bar{c}_R \exp \zeta$:

$$\bar{\psi} = \frac{\exp(\zeta) + 1}{\xi_O \exp(\zeta) + \xi_R} [D_O^{1/2} c_O^* \xi_O + D_R^{1/2} c_R^* \xi_R] \quad (29a)$$

with

$$\xi_i = 1 \pm (\pi t_m D_i)^{1/2} r_0^{-1} \quad (\text{stationary sphere}) \quad (30a)$$

The plus sign pertains to a solution soluble species, the minus sign to a species dissolving in the electrode phase (metal amalgam). As for the expanding sphere, there is less certainty about the best approximation, but it may be reasonable to adopt eqn. (29a) with the following expression for ξ_O and ξ_R [15]:

$$\xi_i = 1 \pm 1.03(t_m D_i)^{1/2} r_0^{-1} \quad (\text{expanding sphere}) \quad (30b)$$

Both eqns. (30a) and (30b) correspond to the so-called diffusion-layer approximation [11]. A detailed analysis of the correctness of this approximation has been made by Guidelli [14].

(3) For linear diffusion *including the effect of reactant adsorption* a simple modification of eqn. (29) has been derived [9]:

$$\bar{\psi} = D_O^{1/2} c_O^* + D_R^{1/2} c_R^* - f(t_m) \bar{\Gamma}_O \quad (29b)$$

[Note that we maintain here the original definition of $\psi = D_O^{1/2} c_O(0, t) + D_R^{1/2} c_R(0, t)$, whereas in ref. 9 it was proposed to define a new function called ψ , which is the same as ψ' in our eqn. (16); see section (II.2).] The basis for eqn. (29b) was laid by Levich et al. [16] as early as 1965, by deriving its analogue for adsorption of a non-electroactive species. The connection with reactant adsorption was made in the general treatment of Reinmuth and Balasubramanian [10]. Discussions about its application in the calculation of theoretical dc polarograms have been published by us [17] and by Guidelli and Pezzatini [18]. The latter treatment most clearly shows that the expression is approximate in the same way as the diffusion-layer approach in, for example, the Ilkovič equation. The functions to be inserted for $f(t_m)$ are [9, 17]

$$f(t_m) = (\pi/4t_m)^{1/2} \quad (\text{stationary plane}) \quad (31a)$$

$$f(t_m) = (7\pi/12t_m)^{1/2} \quad (\text{expanding plane}) \quad (31b)$$

The accuracy of these approximations is estimated at better than 8% for the stationary plane [16], and better than 3% for the expanding plane [17].

(4) In view of what is said under (2), it may be necessary also to account for some kind of a spherical correction. For the stationary sphere it could be inferred from Guidelli's treatment [18] that $\bar{\psi}$ can be expressed by

$$\bar{\psi} = \frac{\exp(\xi) + 1}{\xi_O \exp(\xi) + \xi_R} [D_O^{1/2} c_O^* \xi_O + D_R^{1/2} c_R^* \xi_R - f(t_m) \bar{\Gamma}_O] \quad (29c)$$

with

$$\xi_i = 1 \pm (\pi t_m D_i)^{1/2} (2r_0)^{-1} \quad (30c)$$

However, probably because of the approximate nature of the diffusion-layer approaches, the combination of eqns. (29c) and (30c) does not reduce to the combination of eqn. (29a) and (30a) for $t_m \rightarrow \infty$ or $\Gamma_O \rightarrow 0$. Therefore, it may be better to maintain the definition in eqn. (30a) to be inserted into eqn. (29c). The same applies to the approximation of the expanding sphere. Fortunately, the contribution of the adsorption term is usually not very large so that the inconsistency will not have serious consequences.

The expression obtained for $\bar{\psi}$ is still implicit, since, of course, $\bar{\Gamma}_O$ as a function of \bar{E} is not known *a priori*. In most practical situations an iteration procedure can be applied, i.e. first neglecting the term $f(t_m)\bar{\Gamma}_O$ and next introducing it as a correction calculated from the primary results. The alternative is to make eqn. (29c) explicit by postulating *a priori* an adsorption isotherm.

Postulation of an isotherm is required in any case if the whole set of parameters of eqns. (23)–(27), determined as a function of potential, has to be interpreted. Thus far only a Langmuir isotherm has been considered for this purpose [9,19]:

$$\bar{\Gamma}_O = \frac{\beta_O \bar{c}_O}{1 + \beta_O \bar{c}_O} \Gamma_m = \frac{\beta_O D_O^{-1/2} \bar{\psi}}{1 + \exp(-\zeta) + \beta_O D_O^{-1/2} \bar{\psi}} \Gamma_m \quad (32)$$

(in view of eqn. 20). Evidently also this expression is implicit. After insertion of eqn. (29c) $\bar{\psi}$ can be solved. The result is

$$\bar{\psi} = \frac{1}{2} \left\{ \psi^* - \frac{\exp(\zeta) + 1}{\xi_O \exp(\zeta) + \xi_R} \Gamma_m f(t_m) - \frac{\exp(-\zeta) + 1}{\beta_O D_O^{1/2}} \right. \\ \left. + \sqrt{\left[\psi^* - \frac{\exp(\zeta) + 1}{\xi_O \exp(\zeta) + \xi_R} \Gamma_m f(t_m) - \frac{\exp(-\zeta) + 1}{\beta_O D_O^{1/2}} \right]^2 + 4\psi^* \frac{\exp(-\zeta) + 1}{\beta_O D_O^{1/2}}} \right\} \quad (33)$$

with

$$\psi^* = \left[D_O^{1/2} \xi_O c_O^* + D_R^{1/2} \xi_R c_R^* \right] \frac{\exp(\zeta) + 1}{\xi_O \exp(\zeta) + \xi_R}$$

Further implications of eqns. (32) and (33) for the interpretation of admittance data will be discussed in section (III.3).

(III) ASPECTS OF DATA ANALYSIS

(III.1) General remarks

The controlled variables in impedance measurements are the frequency ω of the ac perturbation, the dc potential \bar{E} and the bulk concentration(s) c_i^* of the reacting species. A general rule is that one has to choose optimal combinations of these in order to achieve the optimum of information, both qualitative and quantitative. This holds in particular for c_i^* and \bar{E} : at potentials far from the half-wave potential the concentration must be high for the interfacial admittance to differ substantially from the normal double-layer admittance.

However, in the case of reactant or product adsorption, the choice of concentration is more delicate, because it also determines which range of the isotherm is covered (the linear part, the horizontal part or the intermediate part).

On the other hand, practical and more trivial circumstances usually limit the

ranges of ω , and c_i^* to be applied. Based on practical experience we will assume, therefore, that these ranges are confined as follows:

$$70 \text{ Hz} < \omega/2\pi < 5000 \text{ Hz} \quad \text{or} \quad 20 < \omega^{1/2} < 180 \text{ s}^{-1/2}$$

$$0.03 \times 10^{-6} < c_O^* < 3 \times 10^{-6} \text{ mol cm}^{-3}$$

Further, it will be assumed that $c_R^* = 0$, $n = 2$ and $D_O^{1/2} = 3 \times 10^{-3} \text{ cm s}^{-1/2}$ (leading to $10^{-10} < c_O^* D_O^{1/2} < 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1/2}$).

For the isotherm parameters the following will be considered as realistic:

$$10^4 < \beta_O < 10^8 \text{ mol}^{-1} \text{ cm}^3 \quad \text{and} \quad 10^{-10} < \Gamma_m < 10^{-9} \text{ mol cm}^{-3}$$

Some theoretical predictions with similar starting-points have been made by Mooring and the present authors [19], in a study focused on the shape of ac polarograms. In the paper presented here our attention is merely focused on the question of obtaining information about the adsorption behaviour.

(III.2) Frequency spectra; limiting cases

We will consider the following three functions:

$$Y' \omega^{-1/2} = \frac{1}{2\sigma} + \frac{C_{LF} - C_{HF}}{u'} \frac{u^2}{u^2 + 2u + 2} \quad (34)$$

$$Y'' \omega^{-1/2} = \frac{1}{2\sigma} + \frac{C_{LF} - C_{HF}}{u'} \frac{u^2 + 2u}{u^2 + 2u + 2} + \frac{C_{HF}}{u'} u \quad (35)$$

$$[Y'' - Y'] \omega^{-1} = [C_{LF} - C_{HF}] \frac{2}{u^2 + 2u + 2} + C_{HF} \quad (36)$$

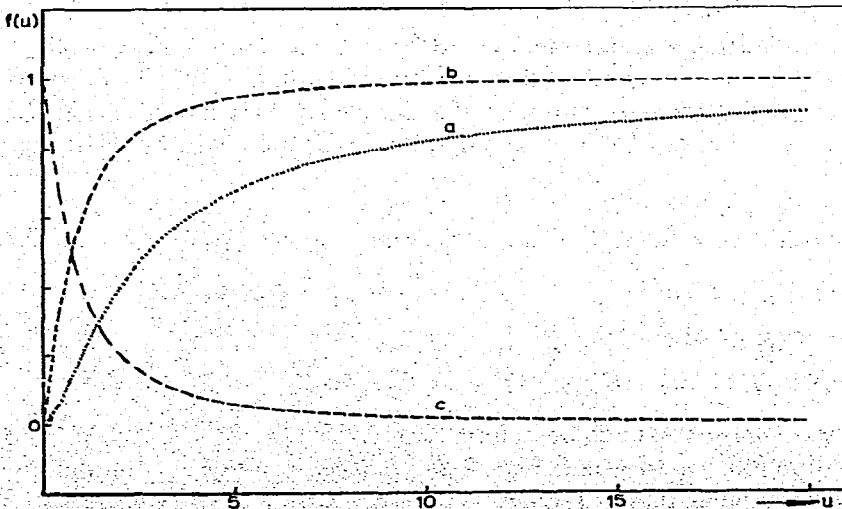


Fig. 2. Frequency dependence of the adsorption admittance, represented by the following functions of u : (a) $u^2/(u^2 + 2u + 2)$, eqn. (34); (b) $(u^2 + 2u)/(u^2 + 2u + 2)$, eqn. (35); (c) $2/(u^2 + 2u + 2)$, eqn. (36).

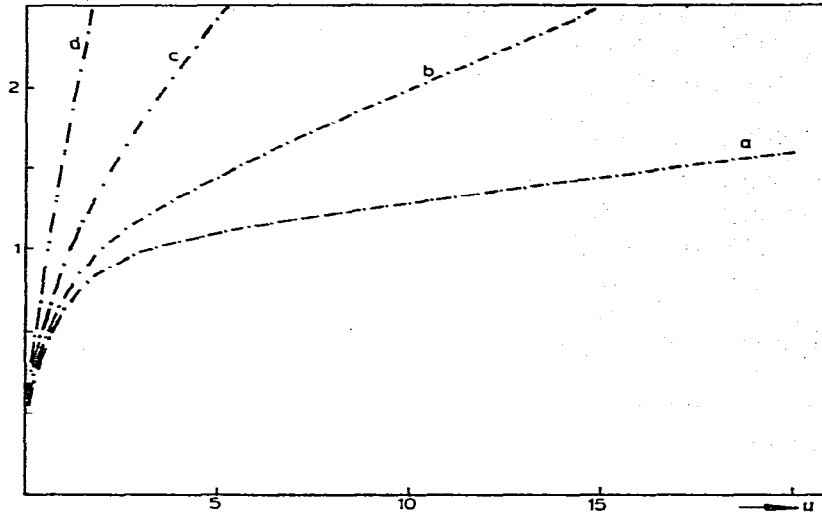


Fig. 3. Frequency dependence of $Y''\omega^{-1/2}$, represented by curve (b) of Fig. 2, added respectively to: (a) $0.03u$; (b) $0.1u$; (c) $0.3u$; (d) u . The specified numbers represent different ratios of $C_{HF}/(C_{LF} - C_{HF})$.

The advantage of eqns. (34) and (36) is that they contain only three parameters. The advantage of the notation employed is that the frequency dependence of the left-hand parts (experimental data) is expressed by the dimensionless quantity $u = u'\omega^{1/2}$. In Figs. 2 and 3 the terms containing u are plotted against u . Note that only for eqn. (35) has an assumption to be made about the relative magnitude of $C_{LF} - C_{HF}$ vs. C_{HF} .

Naturally, all the admittance parameters could be determined unambiguously if an infinite frequency range were covered. Since this is not the case it must be examined in what way different sections of the curves in Figs. 2 and 3 can be analysed. The low-frequency and high-frequency limits especially will be discussed.

(III.2.1) Low-frequency limits

If u approaches zero, the u -dependent terms become respectively:

$$\text{eqn. (34): } [(C_{LF} - C_{HF})/u']u^2/2 = [\tfrac{1}{2}(C_{LF} - C_{HF})u']\omega^2$$

$$\text{eqn. (35): } [(C_{LF} - C_{HF})/u']u + [C_{HF}/u']u = C_{LF}\omega^{1/2}$$

$$\text{eqn. (36): } (C_{LF} - C_{HF})(1 - u) + C_{HF} = C_{LF} - (C_{LF} - C_{HF})u'\omega^{1/2}$$

Evidently in total *three parameters* can be determined, viz. $1/2\sigma$, $(C_{LF} - C_{HF})u'$ and C_{LF} , from straight-line plots as shown in Figs. 4 and 5. Concerning u' , it can only be stated that it must be smaller than a certain value required for the straight lines to appear. However, such a condition involves the risk that the linearity is apparent within the experimental accuracy, but with an erroneous slope. From the pictures

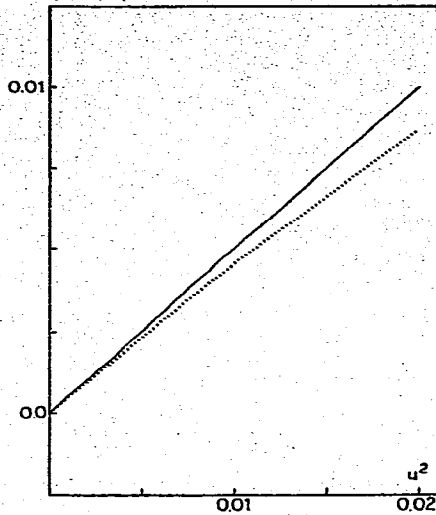


Fig. 4. Low-frequency limiting behaviour of eqn. (34): (-----) $u^2/(u^2 + 2u + 2)$ vs. u^2 ; (—) limiting slope at $u^2 = 0$ (equal to $\frac{1}{2}$).

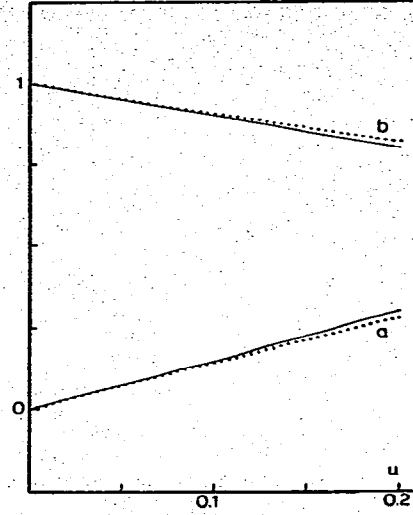


Fig. 5. Low-frequency limiting behaviour of: (a) eqn. (35); (b) eqn. (36). (-----) (a) $(u^2 + 2u)/(u^2 + 2u + 2) + 0.3u$ vs. u ; (b) $2/(u^2 + 2u + 2)$ vs. u . (—) limiting slope at $u = 0$ (equal to 1.3 and -1 respectively).

shown we deduced that apparent linearity will be achieved for the following:

eqn. (34): $u < 0.1$, error in slope: ca. 10%

$u < 0.14$, error in slope: ca. 14%

eqn. (35): $u < 0.1$, error in slope: ca. 3%

$u < 0.2$, error in slope: ca. 7%

eqn. (36): $u < 0.1$, error in slope: ca. 3%

$u < 0.2$, error in slope: ca. 7%

In all cases the intercepts at $u = 0$ are almost not in error, which means that $1/2\sigma$ and C_{LF} are in any case obtained very precisely. The random accuracy in the third parameter $(C_{LF} - C_{HF})u'$ cannot be predicted generally because this strongly depends on its magnitude compared to $1/2\sigma$ or C_{LF} ; in other words, $(C_{LF} - C_{HF})u'$ might be so small that it could not be detectable (see also section III.3).

(III.2.2) High-frequency limits

For u approaching infinity, the following reduced expressions for the u -dependent terms are valid:

$$\text{eqn. (34): } [(C_{LF} - C_{HF})/u'] [1 - 2/u]$$

$$\text{eqn. (35): } [(C_{LF} - C_{HF})/u'] [1 - 4/u^2] + [C_{HF}/u'] u$$

$$\text{eqn. (36): } [(C_{LF} - C_{HF})] 2/u^2 [1 - 2/u] + C_{HF}$$

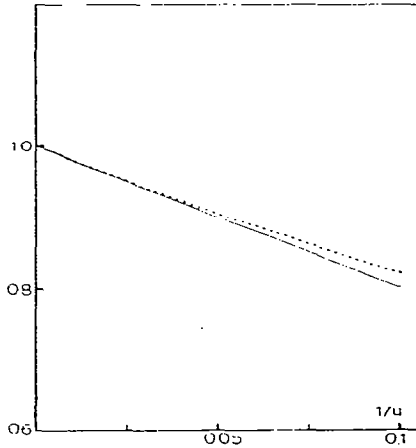


Fig. 6. High-frequency limiting behaviour of eqn. (34). (-----) $u^2/(u^2 + 2u + 2)$ vs. $1/u$; (—) limiting slope at $1/u=0$ (equal to -2).

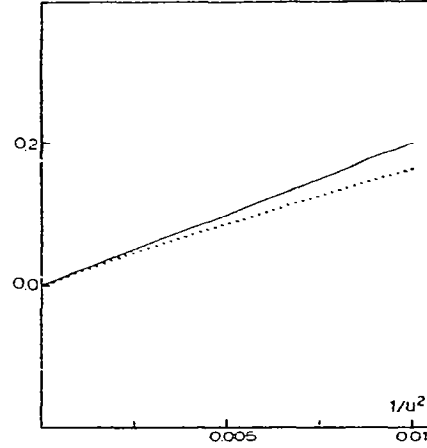


Fig. 7. High-frequency limiting behaviour of eqn. (36). (-----) $2/(u^2 + 2u + 2)$ vs. $1/u^2$; (—) limiting slope at $1/u^2=0$ (equal to 2).

These approximations become realistic for $u > 10$, as is shown in Figs. 6 and 7. Again only three quantities can be determined, namely:

$$(1/2\sigma) + (C_{LF} - C_{HF})/u' = (1/2\sigma) + (1/2\sigma_a) \quad \text{from } Y'\omega^{-1/2} \text{ or } Y''\omega^{-1/2}$$

$$2(C_{LF} - C_{HF})/(u')^2 = 1/\sigma_a u' \quad \text{from } Y'\omega^{-1/2} \text{ or } (Y'' - Y')\omega^{-1}$$

and

$$C_{HF} \quad \text{from } Y''\omega^{-1/2} \text{ or } (Y'' - Y')\omega^{-1}$$

A problem is, of course, the separation of $1/2\sigma$ and $1/2\sigma_a$. The solution could be as follows: determine C_{HF} either from the slope of $Y''\omega^{-1/2}$ vs. $\omega^{1/2}$ or from the intercept of $(Y'' - Y')\omega^{-1}$ vs. ω^{-1} . Then plot $Y'\omega^{-1/2}$ vs. $Y'' - Y' - \omega C_{HF}$, which should give a straight line, according to the relation:

$$Y'\omega^{-1/2} = (1/2\sigma) + (2/u')[Y'' - Y' - \omega C_{HF}] \quad (37)$$

which is easily derived from eqns. (34) and (36). The information obtained is $1/2\sigma$ and $2/u'$ separately, and thus also $C_{LF} - C_{HF}$, etc. In practice the accuracy of these exercises will be rather bad if $Y'' - Y'$ is only slightly larger than ωC_{HF} .

(III.2.3) Fitting in the intermediate frequency region

From the foregoing it follows that the *four* admittance parameters can be determined separately only if (part of) the frequency range $0.2/u' < \omega^{1/2} < 10/u'$ is available, i.e. the range where the plots in Figs. 2 and 3 show significant curvature.

Still, the fitting should be performed with great care because of the tendency of the adsorption admittance to conjugate with the capacitive branch at low ω and with the Warburg branch at high ω (see Fig. 1).

In practical situations we found it most useful to apply a fitting procedure, in which only the value of u' is scanned to find the best one for plots of $Y'\omega^{-1/2}$ vs. $u^2/(u^2 + 2u + 2)$ and of $(Y'' - Y')\omega^{-1}$ vs. $2/(u^2 + 2u + 2)$, which should be straight lines with intercepts $1/2\sigma$, or C_{HF} , and slopes $(C_{LF} - C_{HF})/u'$ or $C_{LF} - C_{HF}$ respectively. Examples of this procedure will be discussed in a succeeding paper [20].

(III.3) Potential dependence, orders of magnitude and possibility of internal checks

Now the question must be discussed how the parameters obtained from the frequency spectrum analysis can be interpreted further to draw conclusions about the adsorption behaviour. To this end, the expected potential dependence and magnitudes of the various parameters should be considered.

(1) $(C_{LF} - C_{HF})$ and u' . The theoretical potential dependence of these parameters in the case of Langmuirian adsorption has been discussed in ref. 19. Therefore, we only summarize the relevant features, as follows:

(a) A $(C_{LF} - C_{HF})$ vs. \bar{E} plot is peak-shaped; the peak potential E_p depends strongly on $\beta_O c_O^*$ unless $\beta_O c_O^* \ll 1$.

(b) A u' vs. \bar{E} plot is either S-shaped, for $\beta_O c_O^* \leq 1$, or peak-shaped, for $\beta_O c_O^* > 1$.

(c) If $\beta_O c_O^* \ll 1$ then $(C_{LF} - C_{HF})$ is proportional to $\beta c_O^* \Gamma_m$, and u' is proportional to $\beta_O \Gamma_m / D_O^{1/2}$ (independent of c_O^*). If $\beta_O c_O^* \gg 1$ then $C_{LF} - C_{HF}$ is proportional to only Γ_m , but u' is proportional to $\Gamma_m / (c_O^* D_O^{1/2})$.

(d) Both the potential dependence of $(C_{LF} - C_{HF})$ and u' are weakly, but significantly, influenced by the value(s) attained by $d \ln \beta_O / dE$.

It can be concluded that the adsorption isotherm can be characterized quite precisely after analysis of the two parameters. Probably this also holds for more involved isotherms, although it will be more difficult to distinguish between several effects, e.g. potential dependence of β_O vs. the mutual interaction effect in Frumkin-type adsorption.

Orders of magnitude can be greatly diverse; an indication is given by the following ranges:

	$(C_{LF} - C_{HF})_{\text{peak}}$	u'_{max}
$\beta_O c_O^* \ll 1$:	$0.7\text{--}70 \mu\text{F cm}^{-2}$	$0.15 \times 10^{-3}\text{--}0.15 \text{ s}^{1/2}$
$\beta_O c_O^* \gg 1$:	$400\text{--}4000 \mu\text{F cm}^{-2}$	$0.02\text{--}2 \text{ s}^{1/2}$

These values are deduced from the conditions assumed in section (III.1).

If desired, the product $(C_{LF} - C_{HF})u'$, divided by $RT\sqrt{2}/\bar{\psi}$, can be integrated to obtain $\bar{\Gamma}_O$ as a function of potential. This may serve as a check on the calculated isotherm characteristics. On the other hand, if $u'\omega^{1/2}$ is so small that only the product $(C_{LF} - C_{HF})u'$ can be determined (section III.2.1), the integration procedure is the only possibility. The other quantity known in this case is C_{LF} , which

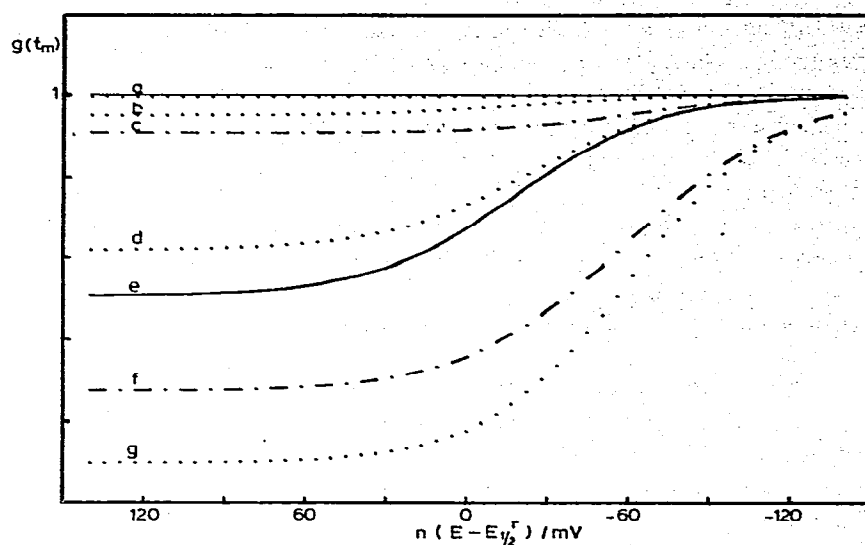


Fig. 8. The correction factor $g(t_m)$ for the influence of adsorption on the dc part of ψ , cf. eqn. (38), as a function of $(E - E_{1/2}^r)$. As a model the Langmuir isotherm is chosen, with parameters as follows: $\Gamma_m / (D_O^{1/2} c_O^0)$: (a) 1; (b) 1; (c) 10; (d) 1; (e) 10^{-1} ; (f) 10; (g) 1; $\beta_{OC} c_O^0$: (a) 10^{-2} ; (b) 10^{-1} ; (c) 10^{-1} ; (d) 1; (e) 10; (f) 1; (g) 10; $f(t_m) = 0.75$.

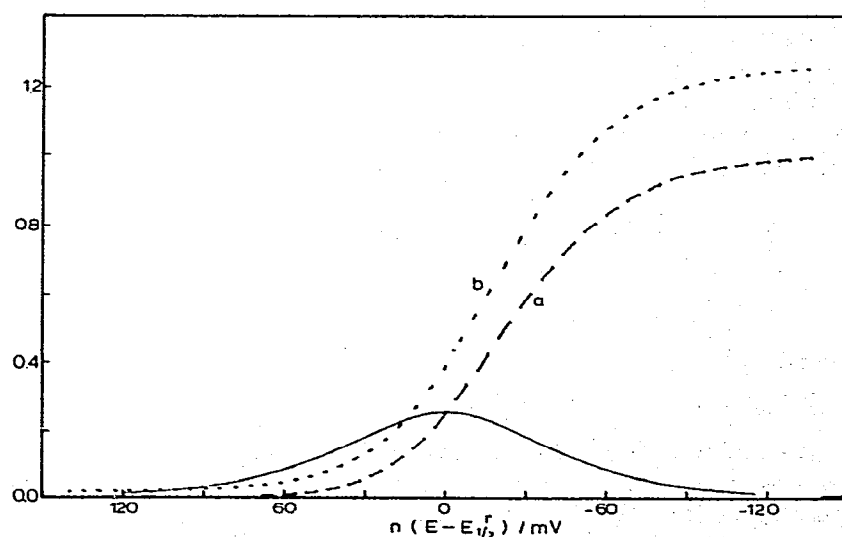


Fig. 9. Potential dependence of the two Warburg parameters, normalized by dividing by $(n^2 F^2 / RT)(\bar{\psi} / \sqrt{2})$. (—) $1/2\sigma$. (- - - -) (a) $1/2\sigma_a$ for $d \ln \beta / dE = 0$; (b) $1/2\sigma_a$ for $d \ln \beta / dE = 0.2 \times (nF/RT)$.

according to eqns. (23) and (24) is more complex to analyse.

(2) $\bar{\psi}$. As mentioned in section (II.4), the numerical analysis of $C_{LF} - C_{HF}$ and u' must also account for the dependence of $\bar{\psi}$ on Γ_O . To demonstrate the magnitude of this effect we calculated it in the form of a correction factor $g(t_m)$ defined as [9]

$$g(t_m) = 1 - \frac{f(t_m)\Gamma_O}{\psi^*} = \frac{\bar{\psi}}{\psi^*} \frac{\xi_O \exp(\zeta) + \xi_R}{\exp(\zeta) + 1} \quad (38)$$

with the aid of eqn. (33). Under the conditions assumed in section (III.1) the effect varies from negligible to drastic, as can be seen in Fig. 8.

(3) $(C_{LF} - C_{HF})/u'$ and $1/2\sigma$. These two quantities are important as they provide an internal check, after being divided by $(n^2F^2/RT)(\bar{\psi}/\sqrt{2})$. The remaining functions have an utmost characteristic potential dependence, *regardless of the type of isotherm*. This is shown in Fig. 9, where the potentiality of determining (or checking) the value of $d \ln \beta_O / dE$ from $(C_{LF} - C_{HF})/u'$ is also indicated.

(4) $C_{HF} - C_d$. The importance of this quantity is even more direct, because when it is found to differ from zero, one knows that $\ln \beta_O$ is (at least) a quadratic function of \bar{E} . Except for weak adsorption, C_{HF} values are most often obtained quite precisely, so that the criterion is pretty sharp and can also be utilized in a quantitative way.

(IV) CONCLUSION

The foregoing discussions clearly show that it will be possible to study the adsorption characteristics of electroactive species by analysing admittance spectra at different potentials in the faradaic region. It is most important to note that such an analysis should be performed with great care in order to avoid erroneous fitting results which, unfortunately, are apt to occur. However, because of the numerous relationships involved, a number of useful checks are applicable, some of them even irrespective of the type of isotherm to be chosen. We intend to verify these statements experimentally in a succeeding paper concerning the adsorption of Cd(II) from bromide and iodide solutions [20].

APPENDIX I

Derivation of eqn. (17)

From eqns. (9) and (16) it follows that, if $\Gamma_R = 0$,

$$\psi = \psi' - f(t_m)\Gamma_O \quad (A1)$$

Since $\Gamma_O = f(E, \psi)$ we can write for the total derivative of Γ_O with respect to E :

$$\frac{d\Gamma_O}{dE} = \left(\frac{\partial \Gamma_O}{\partial E} \right)_{\psi} + \left(\frac{\partial \Gamma_O}{\partial \psi} \right)_E \frac{d\psi}{dE} \quad (A2)$$

or, with eqn. (A1):

$$\frac{d\Gamma_O}{dE} = \left(\frac{\partial \Gamma_O}{\partial E} \right)_{\psi} + \left(\frac{\partial \Gamma_O}{\partial \psi} \right)_E \left[\frac{d\psi'}{dE} - f(t_m) \frac{d\Gamma_O}{dE} \right] \quad (A3)$$

On the other hand, since also $\Gamma_O = f(E, \psi')$ we can write:

$$\frac{d\Gamma_O}{dE} = \left(\frac{\partial \Gamma_O}{\partial E} \right)_{\psi'} + \left(\frac{\partial \Gamma_O}{\partial \psi'} \right)_E \frac{d\psi'}{dE} \quad (A4)$$

If $d\Gamma_O/dE$ is eliminated from eqns. (A3) and (A4), we obtain:

$$\begin{aligned} & \left\{ 1 + f(t_m) \left(\frac{\partial \Gamma_O}{\partial \psi} \right)_E \right\} \left\{ \left(\frac{\partial \Gamma_O}{\partial E} \right)_{\psi'} + \left(\frac{\partial \Gamma_O}{\partial \psi'} \right)_E \frac{d\psi'}{dE} \right\} \\ &= \left(\frac{\partial \Gamma_O}{\partial E} \right)_{\psi} + \left(\frac{\partial \Gamma_O}{\partial \psi} \right)_E \frac{d\psi'}{dE} \end{aligned} \quad (A5)$$

Next the terms containing $d\psi'/dE$ are eliminated by noting that, cf. eqn. (A1):

$$\left(\frac{\partial \Gamma_O}{\partial \psi} \right)_E = \left(\frac{\partial \Gamma_O}{\partial \psi'} \right)_E \left(\frac{\partial \psi'}{\partial \psi} \right)_E = \frac{\partial \Gamma_O}{\partial \psi'} \left\{ 1 + f(t_m) \left(\frac{\partial \Gamma_O}{\partial \psi} \right)_E \right\} \quad (A6)$$

If eqn. (A6) is substituted in the right-hand side of eqn. (A5), the result is

$$\left\{ 1 + f(t_m) \left(\frac{\partial \Gamma_O}{\partial \psi} \right)_E \right\} \left(\frac{\partial \Gamma_O}{\partial E} \right)_{\psi'} = \left(\frac{\partial \Gamma_O}{\partial E} \right)_{\psi} \quad (A7)$$

APPENDIX II

Relations between the partial derivatives in the case of adsorption of both O and R

An easier route will be followed than in ref. 9, starting at once with a relation for $\Gamma_O + \Gamma_R$, which follows from eqns. (10):

$$\beta_O c_O + \beta_R c_R = (\Gamma^*/\Gamma_m) f(\Gamma^*/\Gamma_m) \quad (A8)$$

with

$$\Gamma^* = \Gamma_O + \Gamma_R \quad (A9)$$

for simplicity, c_O and c_R are written instead of $c_O(0, t)$ and $c_R(0, t)$.

From the definition of ψ in eqn. (9), it follows that (see also Table 2)

$$\beta_O c_O + \beta_R c_R = \frac{\beta_O D_O^{-1/2} \exp(\xi) + \beta_R D_R^{-1/2}}{1 + \exp(\xi)} \psi = \epsilon \psi \quad [\epsilon = f(E)] \quad (A10)$$

Hence, Γ^* is a function of the product $\epsilon \psi$ and, analogous to eqn. (21),

$$\psi (\partial \Gamma^* / \partial \psi)_{\epsilon} = \epsilon (\partial \Gamma^* / \partial \epsilon)_{\psi} \quad (A11)$$

Equation (A11) will be used, together with the fundamental thermodynamic

relationship [9]:

$$(\partial q^*/\partial \mu_R)_E = (\partial \Gamma^*/\partial E)_{\mu_R} \quad (\text{A12})$$

where

$$q^* = q + nF\Gamma_O \quad (\text{A13})$$

and μ_R is the electrochemical thermodynamic potential of R.

The *left-hand side* partial derivative in eqn. (A12) can be transformed into

$$RT(\partial q^*/\partial \mu_R)_E = \bar{c}_R(\partial q^*/\partial c_R)_E = \bar{c}_R(\partial \psi/\partial c_R)_E(\partial q^*/\partial \psi)_E = \psi(\partial q^*/\partial \psi)_E \quad (\text{A14})$$

cf. Table 2.

The *right-hand side* partial derivative in eqn. (A12) can be transformed into

$$(\partial \Gamma^*/\partial E)_{\mu_R} = (\partial \Gamma^*/\partial \epsilon)_\psi (\partial \epsilon/\partial E)_{c_R} + (\partial \Gamma^*/\partial \psi)_\epsilon (\partial \psi/\partial E)_{c_R} \quad (\text{A15})$$

Since ϵ is only a function of E , we obtain from eqn. (A15) with eqn. (A11) and the definition of ψ , cf. eqn. (9) and Table 2:

$$(\partial \Gamma^*/\partial E)_{\mu_R} = \left[\frac{\psi}{\epsilon} \frac{d\epsilon}{dE} + D_R^{1/2} \bar{c}_R \frac{nF}{RT} \exp(\zeta) \right] \left(\frac{\partial \Gamma^*}{\partial \psi} \right)_E \quad (\text{A16})$$

Finally, from eqns. (A12), (A14) and (A16) it follows that

$$\left(\frac{\partial q^*}{\partial \psi} \right)_E = RT \left[\frac{1}{\epsilon} \frac{d\epsilon}{dE} + \frac{nF}{RT} \frac{\exp(\zeta)}{\exp(\zeta) + 1} \right] \left(\frac{\partial \Gamma^*}{\partial \psi} \right)_E \quad (\text{A17})$$

which can be integrated (at constant E) to

$$q^* = q^0(E) + RT\Gamma^* \left[\frac{1}{\epsilon} \frac{d\epsilon}{dE} + \frac{nF}{RT} \frac{\exp(\zeta)}{\exp(\zeta) + 1} \right] \quad (\text{A18})$$

or

$$q - q^0(E) = -nF\Gamma_O + RT\Gamma^* \left[\frac{1}{\epsilon} \frac{d\epsilon}{dE} + \frac{nF}{RT} \frac{\exp(\zeta)}{\exp(\zeta) + 1} \right] \quad (\text{A19})$$

With the definition of ϵ in eqn. (A10) this is made explicit as follows:

$$q^* - q^0(E) = nF\Gamma^* \frac{\beta_O \exp(\varphi)(\alpha_O + 1) + \beta_R \alpha_R}{\beta_O \exp(\varphi) + \beta_R} \quad (\text{A20})$$

where

$$\varphi = (nF/RT)[\bar{E} - E^0]$$

and

$$\alpha_i = (RT/nF) d \ln \beta_i / dE$$

Using eqn. (A20), the partial derivatives of q with respect to E can be eliminated from the expressions for C_{HF} and C_{LF} , eqns. (15) and (14). Next, using eqn. (A11), a

relation between $C_{LF} - C_{HF}$ and u' , cf. eqn. (13), can be found. The results are as follows:

$$C_{HF} - C_d = \frac{\beta_R \beta_O \exp(\varphi)}{[\beta_O \exp(\varphi) + \beta_R]^2} [\alpha_O + 1 - \alpha_R]^2 \frac{nF}{RT} + \frac{\beta_O \exp(\varphi) \alpha'_O + \beta_R \alpha'_R}{\beta_O \exp(\varphi) + \beta_R} \quad (A21)$$

with

$$\alpha'_i = (RT/nF) d^2 \ln \beta_i / dE^2$$

$$C_{LF} - C_{HF} = \left[\frac{\beta_O \exp(\varphi) \alpha_O + \beta_R (\alpha_R - 1)}{\beta_O \exp(\varphi) + \beta_R} + \frac{1}{\exp(\zeta) + 1} \right] nF \left(\frac{\partial \Gamma^*}{\partial E} \right)_{\psi} \quad (A22)$$

$$\frac{C_{LF} - C_{HF}}{u'} = \left[\frac{\beta_O \exp(\varphi) \alpha_O + \beta_R (\alpha_R - 1)}{\beta_O \exp(\varphi) + \beta_R} + \frac{1}{\exp(\zeta) + 1} \right]^2 \frac{n^2 F^2}{RT} \frac{\bar{\psi}}{\sqrt{2}} \quad (A23)$$

and consequently,

$$(C_{LF} - C_{HF}) u' = \frac{RT\sqrt{2}}{\bar{\psi}} \left\{ \left(\frac{\partial \Gamma^*}{\partial E} \right)_{\psi} \right\}^2 \quad (A24)$$

Equations (A21) and (A22) were also obtained in ref. 9, but eqns. (A23) and (A24) are novel results. Because of their general applicability, these expressions will be useful in the analysis of the more complex case of both O and R adsorption.

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