

THE FARADAIC ADMITTANCE OF ELECTROCHEMICAL PROCESSES

III. THE FREQUENCY DEPENDENCE

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INTRODUCTION

Recent experimental studies of the faradaic admittance for the Cd(II)-Cd(Hg) system, which were designed to test the validity of proposed equations^{1,2} for the phase angle, φ , between the faradaic alternating current and the alternating potential for simple redox processes,

$$\cot \varphi = 1 + \frac{1}{k} \left(\frac{\omega D}{2} \right)^{\frac{1}{2}} \quad (1)$$

$$\cot \varphi = 1 - \frac{1}{k} \left(\frac{\omega D}{2} \right)^{\frac{1}{2}} \quad (2)$$

indicated that neither equation satisfactorily described the results obtained³. $\cot \varphi$ was not, in general, a linear function of $\omega^{\frac{1}{2}}$; the observed relation was linear in some cases at low frequencies and in other cases at high frequencies, but in all cases was non-linear over a considerable part of the frequency range investigated. The observed relationship between $\cot \varphi$ and ω also changed with the total depolarizer concentration and with the ratio of the concentrations of the oxidized and reduced species present in the bulk phases at a particular value of the polarizing potential. Moreover, $\cot \varphi$ was less than 1 in nitrate- and chloride-base electrolytes, but greater than 1 in sulphate solutions. The inadequacy of equations (1) and (2) is also indicated by a survey of the literature³ and by unpublished work on the Tl(I)-Tl(Hg) system⁴.

It is evident that equations (1) and (2) do not satisfactorily describe the faradaic admittance for systems which are generally regarded as simple, polarographically-reversible ones. Attempts to derive a more satisfactory equation are complicated by the questions as to which of these equations is a mathematically valid outcome of the theoretical treatment and as to why each seems operative in certain cases only for a restricted frequency range.

The present discussion, which is based on an examination of the basis on which the equations have been derived, reveals a reason for the inadequacy of the treatment at other than low frequencies and indicates why various types of relationships between $\cot \varphi$ and ω are experimentally obtained.

SYMBOLS USED

E	polarizing potential
E_c^0	formal standard potential (defined by $C_o = C_R = C$ at $i = 0$)
v	sinusoidal alternating potential
V	amplitude of sinusoidal alternating potential; $v = V \cos \omega t$
ω	angular frequency (radians/sec)
Δi	the amplitude of the alternating current
φ	phase angle between the faradaic alternating current and the alternating potential
θ	phase angle between the alternating potential and the periodic concentration changes
n	number of electrons transferred per molecule
k	heterogeneous rate constant of the electrochemical reaction
α	transfer coefficient of the electrochemical reaction
C_o	interface concentration of the oxidized species
C_R	interface concentration of the reduced species
ΔC_R	amplitude of the concentration changes of the reduced species at the electrode surface
D	geometric mean of the diffusion coefficients of the oxidized and reduced species
D_R	diffusion coefficient of the reduced species
t	time
A	area of the electrode
F	Faraday
R	gas constant
T	absolute temperature

ANALYSIS OF THE THEORETICAL TREATMENTS

Derivations resulting in equations (1) and (2) have been performed in two apparently different ways^{1,5}, in which the faradaic alternating current is expressed, (a) as the result of the flux at the electrode surface due to the periodic diffusion processes involving the depolarizer, and (b) in terms of the rate of the periodic redox reaction occurring in the interface. Closer examination of the actual mathematical expressions involved shows that the assumptions used, and thus the treatments themselves, are essentially the same.

In the one case, solving FICK's diffusion law with the appropriate boundary conditions gives the alternating current, δi , as¹

$$\delta i = \Delta i \cos(\omega t + \varphi) \quad (3)$$

$$\delta i = n F A D_R \Delta C_R (\omega/2D_R)^{1/2} [\cos(\omega t + \theta) - \sin(\omega t - \theta)] \quad (4)$$

By comparing equations (3) and (4), φ can be related to θ , the phase angle between the alternating potential and the periodic concentration changes:

$$\varphi = \theta + \pi/4 \quad (5)$$

The current is also expressed as the result of the electrochemical reaction in the

interface by the familiar equation,

$$i = nFAk \{C_o \exp [-\alpha nF(E - E_e^0)/RT] - C_R \exp [(1 - \alpha)nF(E - E_e^0)/RT]\} \quad (6)$$

The situation under consideration involves the superposed application of a small sinusoidal alternating potential, v , of amplitude V at E_e^0 ; thus

$$E - E_e^0 = v = V \cos \omega t \quad (7)$$

$$C_o = C + \delta C_o = C + \Delta C_o \cos (\omega t + \theta) \quad (8)$$

$$C_R = C + \delta C_R = C + \Delta C_R \cos (\omega t + \theta) \quad (9)$$

and

$$\Delta C_o = -\Delta C_R \quad (10)$$

Substituting equations (7) to (9) into equation (6) gives

$$i = nFAk \{(C + \delta C_o) \exp [-\alpha nFv/RT] - (C + \delta C_R) \exp [(1 - \alpha)nFv/RT]\} \quad (11)$$

By equating equations (4) and (11), and setting coefficients of $\sin \omega t$ equal in the resulting expression, an explicit equation for $\cot \varphi$ can be obtained. However, both equations (1) and (2) have been reported^{1,2} to result from this procedure; the discrepancy arises in assigning plus or minus signs to the quantities δi and δC_R in equations (4) and (11) (*cf.* ATEN⁶).

FREQUENCY LIMITATION ON PROPOSED EQUATIONS

The first problem to be resolved can be stated in the form: Is it equally legitimate to write equation (11) in the form

$$\delta i = nFAk \{(C - \delta C_o) \exp [-\alpha nFv/RT] - (C - \delta C_R) \exp [(1 - \alpha)nFv/RT]\} \quad (12)$$

or does the sign convention used in equation (4) imply only one of equations (11) and (12) is permissible? If both equations are correct, then equations (1) and (2) can both result from the treatment; if only one is valid, then either equation (1) or (2) is incorrect. The following discussion shows that an unequivocal assignment of plus and minus signs to the periodic quantities δi , v , δC_o and δC_R can be made only in the limiting case of low frequencies ($k \gg \sqrt{\omega D}$), where equations (1) and (2) both become

$$\cot \varphi = 1 \quad (13)$$

Setting equations (4) and (11) equal, and dividing throughout by the term $(nFAk)$, results in

$$\frac{\Delta C_R}{k} \left(\frac{\omega D}{2}\right)^{\frac{1}{2}} [\cos (\omega t + \theta) - \sin (\omega t + \theta)] = (C + \delta C_o) \exp [-\alpha nFv/RT] - (C + \delta C_R) \exp [(1 - \alpha)nFv/RT] \quad (14)$$

In the limiting case where $k \gg \sqrt{\omega D}$, equation (14) yields

$$\frac{C + \delta C_o}{C + \delta C_R} = \exp (nFv/RT) \quad (15)$$

which is the reversible electrode equation written for the case of a small sinusoidal alternating potential applied to E_e^0 . When equation (15) holds, the concentrations of the electroactive species are, *at every instant*, in equilibrium with the electrode potential *i.e.*, the periodic concentration and potential changes proceed reversibly without polarization effects. Furthermore, equation (13) applies and the variation with time of δi , v and δC can be described graphically as in Fig. 1A.

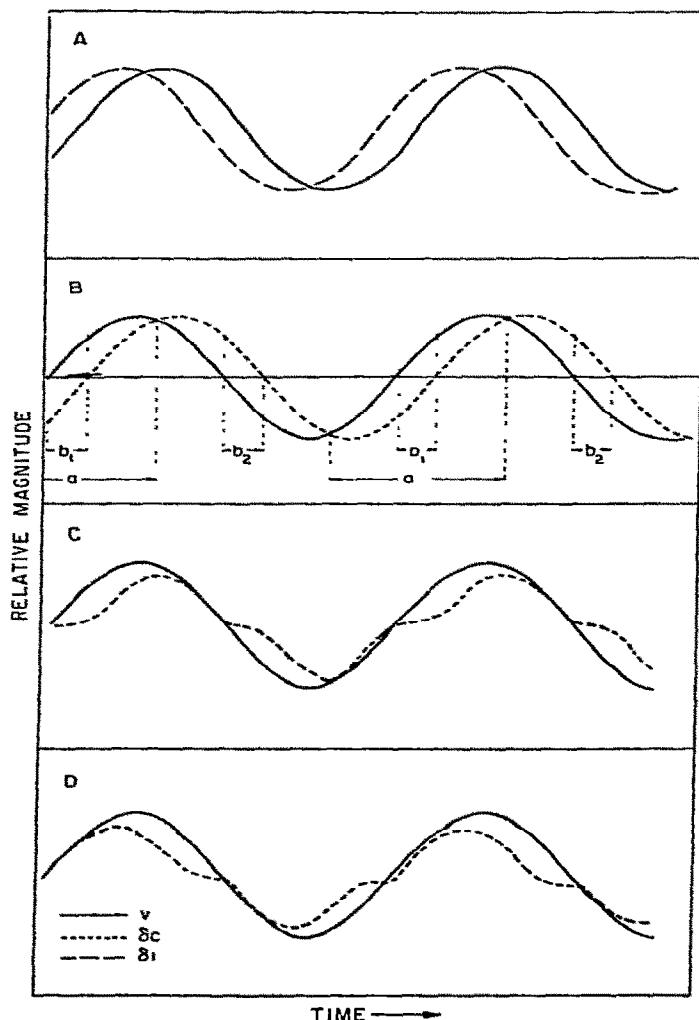


Fig. 1. Variation with time of the periodic quantities v (solid line), δC (dotted line) and δi (dashed line). A: the changes in concentration of the electroactive species are in equilibrium with the electrode potential (the curves for v and δc coincide). B: the concentration changes are *not* in equilibrium with the electrode potential (case at higher frequencies). C and D: same situation as in B, but with account taken of possible rectifying effects.

Since the left-hand side of equation (14) is not zero at higher frequencies, equation (15) becomes an inequality and the relative concentrations of oxidized and reduced forms at any instant differ from the ratio given by this equation. The difference may manifest itself in one of two ways: a preferential accumulation of the oxidized form or

of the reduced form, as compared to conditions of reversibility; which occurs, will depend on the nature of the system under investigation.

The effect of higher frequencies can be described in terms of the earlier equations by the statement that the phase angle θ between the concentration changes and the potential is zero at sufficiently low frequencies (*cf.* Fig. 1A), but has a finite value at higher frequencies. Obviously, this statement describes the same situation as that outlined in the previous paragraph: the concentration changes of the electroactive species are not in equilibrium with the electrode potential. Since there is no *a priori* way of knowing whether the oxidation or the reduction process is more hindered, *i.e.*, whether the reduced or oxidized form is present in excess at any instant, there is also no way of deciding whether θ will be positive or negative; which possibility occurs depends on the particular system involved.

Furthermore, at higher frequencies the effect of polarization, when formulated as the phase shift θ , changes continuously in magnitude and sign with time during the cycle of the sinusoidal variations (Fig. 1B). During the time intervals "a", the concentration changes are more "negative" than under equilibrium conditions (corresponding to accumulation of oxidized or reduced form, according to the sign convention used in writing the NERNST equation); at other times during the cycle, the concentration changes are more "positive". If during the time intervals "b₁", there is an accumulation of, *e.g.*, oxidized form making the potential, *e.g.*, more positive than its equilibrium value, and correspondingly during intervals "b₂" an accumulation of reduced form making the potential more negative, then at other times during the cycle, accumulation of the oxidized form makes the potential more negative and of excess reduced form more positive.

It is, therefore, clearly not possible to make any logically consistent assignment of plus and minus signs to the periodic quantities δi , v , δC_O and δC_R under conditions where the frequency is not limitingly small. This conclusion enables us to understand the significance of the discrepancy between equations (1) and (2), and the fact that experimental results³ qualitatively support both equations (in the sense that $\cot \varphi$ is sometimes greater than 1 and sometimes less than 1), but neither equation quantitatively (since the observed relation between $\cot \varphi$ and ω^\dagger is not linear at all frequencies, and changes with concentrations of electroactive species although these do not appear in the equations).

Consequently, there would seem to be no justification for preferring one of equations (11) and (12) rather than the other, since we cannot unequivocally assign plus or minus signs to the periodic quantities; thus, the mathematical treatment can lead equally to equation (1) or (2). Whether $\cot \varphi$ for a particular system is greater or less than 1 at higher frequencies, depends on whether the oxidation or the reduction process is preferentially hindered or favoured.

Such a conclusion does not, however, resolve the problem illustrated in Fig. 1B, whereby it becomes necessary to use different sign conventions, during successive parts of the periodic changes, to describe the relation between concentrations and potential. To overcome this anomaly, it is sufficient to realize that under the influence of the alternating potential, rectification effects are produced; in particular, the alternating current contains harmonics of the fundamental frequency. Consequently, neither the current nor the concentration changes can validly be regarded as having a sinusoidal form; the relation between concentration changes and potential might

therefore be expected to resemble that of Figs. 1C and 1D rather than of Fig. 1B, and the two possible situations of oxidation or reduction being more hindered would differ from one another somewhat in the way in which Figs. 1C and 1D differ.

It is now clear why equations (1) and (2) cannot be quantitatively correct. It is not legitimate to write the alternating current in the sinusoidal form of equation (3) or to use sinusoidal concentration changes as boundary conditions for solving FICK'S law as was done in arriving at equation (4). A rigorous treatment of the problem would first need to consider all polarization effects at one instant of time, and then to generalize for a sinusoidal alternating potential, rather than to assume, *a priori*, a sinusoidal form for the alternating current and periodic concentration changes.

RATIONALIZATION OF EXPERIMENTAL RESULTS

The experimental results previously cited³ can be qualitatively interpreted on the basis of the conclusions that neither equation (1) nor (2) can be correct, and that the difference between them—whether $\cot \varphi$ is greater or smaller than 1 at higher frequencies—probably corresponds to the difference in behaviour of systems where either the oxidation or reduction process is more hindered by the polarization effects which appear at other than limitingly low frequencies. This can be done by using the magnitude of $(\cot \varphi - 1)$ as a measure of the magnitude of the polarization effects and its sign as an indication of whether the oxidation or reduction process lags behind the field at higher frequencies (*cf.* equations (1) and (2)).

At low frequencies, the alternating current is limited by the rate of the periodic diffusion processes (*cf.* the relevant expressions⁷) and hence the polarization effects produced will depend mainly on the relative diffusibilities of the oxidized and reduced species. (The diffusibilities will depend on both the values of the diffusion coefficients D_O and D_R , and on the concentrations of the electroactive species, since the diffusion coefficients may change with concentration and the periodic diffusion processes may not be completely independent of the overall diffusion gradient; *cf.* the discussion of this question by ATEN⁶).

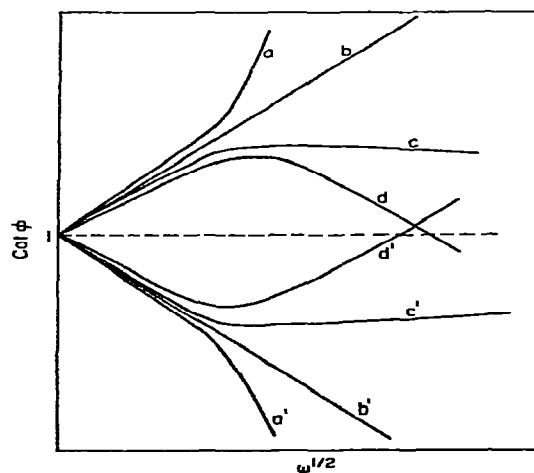


Fig. 2. Variation in observed relationships between $\cot \varphi$ and $\omega^{1/2}$ as affected by the relative magnitudes and signs of polarization effects at high and low frequencies.

At appreciably high frequencies, the rate of the electron-transfer process becomes limiting; the polarization effects will now depend on the relative ease of the electron-transfer step in the forward or backward direction, *i.e.*, presumably on the magnitude of the transfer coefficient.

Consequently, the observed polarization effect could change in magnitude and in sign over a sufficiently wide frequency range. If the polarization effect at low frequencies is denoted by $p(D)$ and that at high frequencies by $p(\alpha)$, it is possible to envisage situations which would produce $\cot \varphi$ vs. $\omega^{1/2}$ curves similar to those shown in Fig. 2: (1) curves a and a' represent cases where $p(\alpha)$ is greater than $p(D)$, but both are of the same sign; (2) curves b and b' show a special case where the effects are equal and of the same sign; (3) in curves c and c' $p(D)$ is greater than $p(\alpha)$, but of the same sign; (4) in curves d and d', the two effects have opposite sign, *e.g.*, a situation where the oxidation process is favoured at lower frequencies but reduction is easier at higher frequencies.

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SUMMARY

Recent experimental studies have demonstrated the inadequacy of proposed equations for the faradaic admittance, particularly in respect to the frequency dependence. Existing treatments of the faradaic admittance can give rise to two contradictory equations for the frequency dependence, these equations being identical only at very low frequencies. The difference between these conflicting equations has a counterpart in the different behavior of two types of systems, which arise from the fact that either oxidation or reduction may be preferentially affected by polarization effects. Previous experimental results on the variation of the faradaic admittance with frequency can be qualitatively interpreted on this basis.

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