POLARIZABILITY AND NONPOLARIZABILITY OF OIL–WATER INTERFACES WITH RELEVANCE TO A.C. IMPEDANCE MEASUREMENTS

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Dedicated to the memory of Prof. J. Heyrovský on the occasion of his centenary.

We have estimated the degree of polarizability of a polarized oil–water interface used as a working interface and that of the nonpolarizability of a nonpolarized interface used as a reference oil–water interface from the numerical calculation of dc and ac current vs potential behavior at both interfaces. Theoretical equations of dc and ac currents for simultaneous cation and anion transfer of supporting electrolytes have been derived for the planar stationary interface for reversible and quasi-reversible cases. In the derivation, the migration effect and the coupling of the cation and anion transfers have been incorporated. The transfer of ions constituting a supporting electrolyte contributes to the total admittance of the interface even in the region where the interface may be considered as polarized in dc sense, as pointed out first by Samec et al. (*J. Electroanal. Chem. 126*, 121 (1981)). Moreover, the reference oil–water interface is not ideally reversible, so that the contribution from this interface to the measured admittance cannot be negligible, unless the area of the reference oil–water interface is much larger than that of the working oil–water interface. The effect of non–ideality of the reference oil–water interface on the determination of double layer capacitances and kinetic parameters of charge transfer at the working oil–water interface has been estimated.

The quality of the oil–water interfaces, i.e., the degree of the polarizability, is of decisive importance in assessing the electrochemical data, in particular, the data obtained from ac impedance measurements. There have been a number of studies of oil–water interfaces using ac techniques[1–13] for obtaining the double layer capacitance and the kinetic parameters of ion transfer. A typical example of the cell used in such electrochemical measurements is the system (A)

I	II	III	IV	V	VI	VII
Ag	AgCl	0·1 M TBACl (water)	0·1 M TBATPB (oil)	0·1 M LiCl (water)	AgCl	Ag	(A)
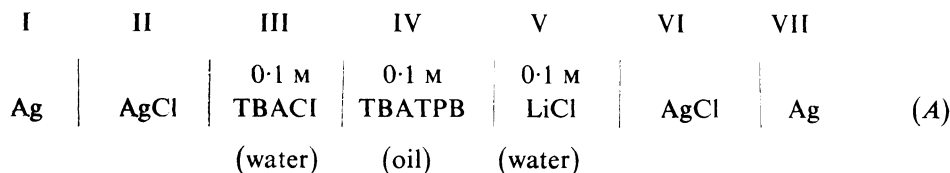
where TBACl and TBATPB stand for tetrabutylammonium chloride and tetrabutyl-ammonium tetraphenylborate. The interface between phases IV and V is the polarized oil–water interface serving as a working interface. Although the thermodynamic definition of an ideally polarized interface is unequivocal[14,15], the polarizability of actual interfaces is relativistic; the polarized range of an interface varies depending on what is to be measured at the interface. If we are concerned with the dc properties of charge–transfer processes, e.g., cyclic voltammetric determination of an ion concentration in sub–mmol order, the width of the polarization range of the interface can be as wide as 300 mV (ref.[16]). However, in ac impedance measurements, the impedance due to the ion transfer of supporting electrolyte ions can contribute to the measured impedance even within this potential window, as was first suggested by Samec et al.[1]. The equivalent circuit of this interface may then be represented as a parallel combination of the double layer capacitance, C_{dl}, with the ion-transfer impedance for supporting electrolytes, Z_b (cirvuit a in Fig. 1). When estimating the double layer capacitance, Samec et al.[1,3–5] took account of the contribution of Z_b to the measured impedance assuming that the charge transfer of supporting electrolyte ions was reversible. In actual cases, the ion transfer of supporting electrolyte ions may not be completely reversible. In Cell (A), the base currents at the positive and negative ends of the potential window are due primarily to the TPB^- and TBA^+ ion transfer from the oil to the aqueous phase, respectively. Since the rate of the transfer of these ions having larger ionic radii is not completely reversible[17–19], it seems necessary to extend the study of the effect of base currents on impedance measurements to a quasi-reversible case.
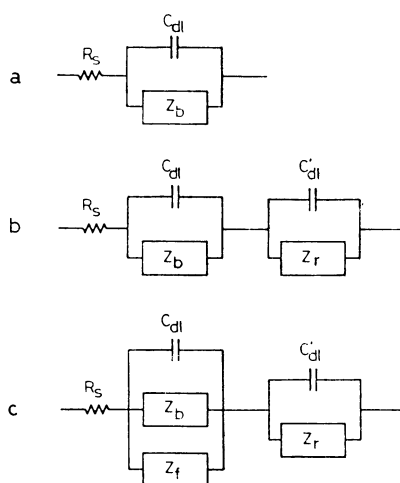

FIG. 1

Equivalent circuits of oil–water interfaces. a A polarized oil–water interface, b a polarized oil–water interface in series with a non-polarized oil–water interface, c a polarized oil–water interface in presence of ion transfer of a depolarizer ion. R_s is a solution resistance, Z_b, Z_r, and Z_f are the ion-transfer impedances for supporting electrolyte ions, a potential determining ion, and a depolarizer ion, respectively

Moreover, the impedance of the oil-water interface between phases III and IV may not be negligible, unless the area of this interface is sufficiently larger than that of the working interface. This impedance directly contributes to the measured total impedance in ac measurements with two-electrode system (Fig. 1b)[6,9,10]. In four-electrode mode, another oil–water interface is frequently used as a current carrying auxiliary interface[20,21], which gives rise to the same problem. An auxiliary platinum electrode dipped in the oil phase has also been used. In this case, the impedance at the platinum–organic solvent interface seems unpredictable nor controllable. Although there have been several studies of the equilibrium[22,23] and stationary[24] properties of nonpolarized oil–water interfaces, little attention has been paid to its ac response. The purpose of this study was to derive the theoretical expressions for ac as well as dc responses of both polarized and nonpolarized interfaces and to numerically evaluate the contributions of the non-idealities of both interfaces to the measured double layer capacitance and kinetic parameters of charge transfer reactions.

THEORETICAL

In the following, the oil phase and water phase are designated as O and W. The inner potential of the aqueous phase with respect to that in the oil phase is denoted as $\Delta_O^W \varphi$ and the current, I, is taken to be positive, when positive charge is transferred from the aqueous phase to the oil phase. We will confine our treatment to a stationary planar interface in potentiostatic conditions. Both phases are supposed to be infinitely large in depth, so that the semi-infinite linear condition is satisfied for describing the mass transfer. The coordinate x is assumed to be normal to the interface, at which $x = 0$, and oriented towards the bulk of the aqueous phase. Since we are concerned with the transfer of supporting electrolyte ions, migration effect should be taken into account. To date, the migration-diffusion problem at oil–water interface has been treated only for dc polarography[16] and chronopotentiometry[25-27]. Although our primary concern is the ac response, we shall also derive the equations for dc responses, which are the basis for deriving ac responses. The dc current vs potential expressions will also be useful, e.g., in estimating the standard ion-transfer potential of supporting electrolyte ions from current vs potential curves[28-30].

POLARIZED OIL–WATER INTERFACE

We consider the system:

$$
\begin{array}{c|c}
\text{K, A} & \text{K}', \text{A}' \\
\text{(oil)} & \text{(water)}
\end{array}
$$
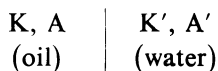
where K and K′ are cations and A and A′ are anions. We assume that KA and K′A′ are completely dissociated and only the cationic and anionic components constituting

the supporting electrolyte in O, i.e., K and A, can be transferable across the interface, as is the case of TBA$^+$ and TPB$^-$ ions in Cell (A). The Nernst–Planck equation describing the transport of K of A in O is

$$f_i^O = -D_i^O \frac{\partial c_i^O}{\partial x} - D_i^O c_i^O \frac{z_i \mathbf{F}}{\mathbf{R}T} \frac{\partial \varphi^0}{\partial x} , \tag{1}$$

where i is K or A, f_i^O is the flux of i in O, z_i the ionic charge including its sign, c_i^O the concentration of i in O, φ^0 the inner potential in O, $\mathbf{F}$ the Faraday constant, $\mathbf{R}$ the gas constant, T the absolute temperature. For simplicity, we assume that $z_K = |z_A|$. The current, I, is given by

$$\frac{I}{\mathbf{F}A} = -(z_K f_K^O + z_A f_A^O) = I_K + I_A , \tag{2}$$

where I_K and I_A are the partial currents carried by K and A in O and A is the area of the interface. Because the electroneutrality condition,

$$c_K^O = c_A^O = c_S^O , \tag{3}$$

holds everywhere in O, the diffusion of K and A in O obeys a single diffusion equation:

$$\frac{\partial c_S^O}{\partial t} = D_S^O \frac{\partial^2 c_S^O}{\partial x^2} , \tag{4}$$

where

$$D_S^O = \frac{2 D_K^O D_A^O}{D_K^O + D_A^O} \tag{5}$$

and c_K^O, c_A^O and c_S^O are the concentrations of K, A, and the salt KA in O. We assume that a sufficient amount of supporting electrolyte. K′A′, is present in W, so that the migration effect in this phase is negligible. Then, for the diffusion of K and A in W, we have

$$\frac{\partial c_K^W}{\partial t} = D_K^W \frac{\partial^2 c_K^W}{\partial x^2} \tag{6}$$

and

$$\frac{\partial c_A^W}{\partial t} = D_A^W \frac{\partial^2 c_A^W}{\partial x^2} , \tag{7}$$

where c_i^W and D_i^W (i is K or A) are the concentration and the diffusion coefficient of ion i in W.

The initial conditions are:

$$t = 0 \,, \quad x \leqq 0 : c_S^O = {}^b c_S^O \,. \tag{8}$$

$$t = 0 \,, \quad x \geqq 0 : c_K^W = 0 \,, \quad c_A^W = 0 \,, \tag{9}$$

where ${}^b c_S^O$ is the initial concentration of KA in O. The boundary conditions are:

$$t > 0 \,, \quad x \to -\infty : c_S^O = {}^b c_S^O \tag{10}$$

$$t > 0 \,, \quad x \to \quad \infty : c_K^W = 0 \,, \quad c_A^W = 0 \,. \tag{11}$$

The condition for the continuity of the flux at the interface gives

$$f_K^O \big|_{x=0} = f_K^W \big|_{x=0} \tag{12}$$

and

$$f_A^O \big|_{x=0} = f_A^W \big|_{x=0} \,. \tag{13}$$

These two conditions are equivalent and reduce to:

$$D_S^O \frac{\partial c_K^O}{\partial x}\bigg|_{x=0} = \left(1 - t_K^O\right) D_K^W \frac{\partial c_K^W}{\partial x}\bigg|_{x=0} + t_K^O D_A^W \frac{\partial c_A^W}{\partial x}\bigg|_{x=0} \,, \tag{14}$$

where t_K^O is the transference number of K in O:

$$t_K^O = \frac{D_K^O}{D_K^O + D_A^O} \tag{15}$$

and

$$t_A^O = 1 - t_K^O \,. \tag{16}$$

By using the Laplace transform, surface concentrations of K and A in O and W, $c_S^O(0, s)$, $c_K^W(0, s)$ and $c_A^W(0, s)$ may be represented as

$$c_S^O(0, s) = \frac{{}^b c_S^O}{s} + \frac{1}{FA(D_S^O s)^{1/2}} \left[\frac{t_A^O}{z_K} I_K + \frac{t_K^O}{z_A} I_A \right] \tag{17}$$

$$c_i^W(0, s) = -\frac{I_i}{z_i FA(D_i^W s)^{1/2}} \,, \tag{18}$$

where i stands for K or A and s is the transformed variable. Equation (17) shows that the currents I_K and I_A are coupling with each other. This is a unique feature of the simultaneous ion transfer of cation and anion without supporting electrolyte.

Case a. Reversible Ion Transfer

When the ion transfers of both K and A are reversible, we can use the Nernst eqution for the surface concentration of K and A:

$$\frac{c_i^O(0, t)}{c_i^W(0, t)} = \exp\left[\frac{z_i F}{RT}(\Delta_O^W \varphi - \Delta_O^W \varphi_i^O)\right],\qquad(19)$$

where i is K or A and $\Delta_O^W \varphi_i^O$ is the standard ion-transfer potential.

Dc *current is potential curve*: By solving Eqs (4), (6) and (7), we obtain:

$$\frac{I}{FA} = -\frac{c_S^O \sqrt{D_S^O}}{(\pi t)^{1/2}}\left[\frac{z_K q + z_A p}{pq + (1 - t_K^O) q + t_K^O p}\right],\qquad(20)$$

where

$$p = \left(\frac{D_S^O}{D_K^W}\right)^{1/2} \exp\left[\frac{z_K F}{RT}(\Delta_O^W \varphi - \Delta_O^W \varphi_K^O)\right]\qquad(21a)$$

and

$$q = \left(\frac{D_S^O}{D_A^W}\right)^{1/2} \exp\left[\frac{z_A F}{RT}(\Delta_O^W \varphi - \Delta_O^W \varphi_A^O)\right].\qquad(21b)$$

Equation (20) has been derived in case of $z_K = |z_A| = 1$ (ref.[16]).

When $p \to \infty$, Eq. (20) reduces to

$$\frac{I}{FA} = -\frac{c_S^O \sqrt{D_S^O}}{(\pi t)^{1/2}}\frac{z_A}{q + t_K^O}\qquad(22)$$

and when $q \to \infty$,

$$\frac{I}{FA} = -\frac{c_S^O \sqrt{D_S^O}}{(\pi t)^{1/2}}\frac{z_K}{p + t_A^O}.\qquad(23)$$

Equations (22) and (23) are similar to the expression for the conventional migration currents[31]. Sum of Eqs (22) and (23) does not reproduce Eq. (20), because a simple arithmetic sum of Eqs (22) and (23) does not take account of the coupling of the flows of K and A in O, which was originally implied in Eq. (20). Hence, strictly speaking, the half wave potentials for anodic and cathodic currents in Eq. (20)

do not agree with those derived from Eqs (22) and (23), i.e.,

$$E_{1/2,i} = \Delta_O^W \varphi_i^0 + \frac{RT}{z_i F} \ln \left(\frac{D_S^O}{D_A^W} \right)^{1/2} + \frac{RT}{z_i F} \ln t_i^O .\qquad (24)$$

The degree of the coupling becomes greater with narrowing the potential window, $\Delta\Delta_O^W\varphi^0 = \Delta_O^W\varphi_A^0 - \Delta_O^W\varphi_K^0$, and is greatest in the middle of the window at a given value of $\Delta\Delta_O^W\varphi^0$. However, even when $\Delta\Delta_O^W\varphi^0 = 0\cdot100$ V, the error in the current calculated using Eqs (22) and (23) does not exceed 1%.

The potential at $I = 0$ is a kind of a mixed-potential and is given by

$$E = \frac{1}{z_K + |z_A|} \frac{RT}{F} \ln \left[\frac{z_K}{|z_A|} \left(\frac{D_K^W}{D_A^W} \right)^{1/2} \right] + \frac{1}{z_K + |z_A|} (z_K \Delta_O^W \varphi_K^0 + |z_A| \Delta_O^W \varphi_A^0) .$$
$$(25)$$

This expression is valid irrespective of the presence of coupling. In addition, the diffusion potential generally develops in O in this system[24]. Here, we will not treat this problem.

Ac *current vs potential curve*: In the following, we assume that the scan rate of the dc potential, v, is so slow that the condition:

$$\omega \Delta E \gg v \qquad (26)$$

is satisfied, where ω is angular frequency and ΔE is the amplitude of applied ac voltage. This condition ensures that the dc response of the system is separable from the ac component[32]. Then, ac impedance due to the transfer of K and A, Z_b, is given by

$$Z_b = \frac{RT}{F^2 A \, ^b c_S^O (D_S^O \omega)^{1/2}} \frac{(pq + t_A^O q + t_K^O p)^2}{pq(p + q + z_K^2 t_K^O + z_A^2 t_A^O - z_K z_A)} . \qquad (27)$$

Case b. Quasi-Reversible Ion Transfer

Dc *current* vs *potential curve*: The boundary condition in this case is, instead of the Nernst equation

$$\frac{I_i}{z_i F A k_i^0} = c_i^W(0, t) \left(\frac{D_i^W}{D_S^O} \right)^{\alpha_i/2} e^{\alpha_i j_i} - c_i^O(0, t) \left(\frac{D_i^W}{D_S^O} \right)^{-\beta_i/2} e^{-\beta_i j_i}, \qquad (28)$$

where i is K or A, k_i^0 is the standard rate constant of ion transfer, $j_K = \ln p$, $j_A = \ln q$, α_i is the transfer coefficient, and $\beta_i = 1 - \alpha_i$. In Eq. (28) the Butler–Volmer relation between the rate constant of ion transfer and $\Delta_O^W\varphi$ has been assumed. An

analytical solution of Eqs (3), (6), and (7) with the condition given by Eqs $(8)-(11)$, (14), and (28) is considerably complicated, though solvable, due to the coupling of the flows of K and A. Since the degree of the coupling is very small for usual cases, we hereafter neglect this effect and assume that the total dc and ac currents are given by the sum of two corresponding currents for K and A without coupling. Then, for dc current

$$\Psi_{i,0}(t) = -\frac{k_i^0}{\mathscr{D}_i} e^{-\beta_i j_i} e^{\lambda_i^2 t} \mathrm{erfc}(\lambda_i t^{1/2}) , \tag{29}$$

where $\Psi_{i,0}(t)$ is the reduced current defined by

$$\Psi_{i,0}(t) = \frac{I_{dc,i}}{z_i F A \, {}^b c_S^0 (D_S^0)^{1/2}} . \tag{30}$$

In Eq. (29), $\mathscr{D}_i$ and λ_i are given by

$$\mathscr{D}_i = (D_S^0)^{\alpha_i/2} (D_i^W)^{\beta_i/2} \tag{31}$$

and

$$\lambda_i = \frac{k_i^0}{\mathscr{D}_i} \left[e^{\alpha_i j_i} + (1 - t_i^0) e^{-\beta_i k_i} \right] . \tag{32}$$

Ac *current* vs *potential curve*: The ac response due to the transfer of ion i(i is K or A) can be expressed in terms of an impdeance, $Z_{b,i}$, and the phase angle, Θ_i,

$$Z_{b,i} = \frac{Z_{rev,i}}{F_i(t)} \left[\frac{1 + (1 + (2\omega)^{1/2}/\lambda_i)^2}{2} \right]^{1/2} , \tag{33}$$

$$\cot \Theta_i = 1 + (2\omega)^{1/2}/\lambda_i , \tag{34}$$

where

$$Z_{rev,i} = \left[\frac{F^2 A \, {}^b c_S^0 (D_S^0 \omega)^{1/2}}{RT} \frac{e^{j_i}}{(e^{j_i} + (1 - t_i^0)^2} \right]^{-1} \tag{35}$$

and

$$F_i(t) = 1 + e^{-\alpha_i j_i} [\alpha_i e^{j_i} - (1 - t_i^0)\beta_i] \frac{\mathscr{D}_i}{k_i^0} \Psi_{i,0}(t) . \tag{36}$$

Thus, the ion-transfer impedance depends on t through Eq. (36), when the ion transfer is not reversible. Since the standard rate constant of ion transfer would not be smaller than 10^{-4} cm s^{-1} for usual supporting electrolyte ions, the time dependence of the impedance is negligible in practical time scale of ac voltammetry, e.g.,

scan rate of ca 1 mV s^{-1}. Equations $(29)-(36)$ are similar to the equations derived in the absence of migration[33], but the difference is that the transference number appears in Eqs (32), (35), and (36). Neglecting the coupling of K and A, we obtain for the total impedance of simultaneous transfer of K and A,

$$Z_b = \frac{Z_{b,K} Z_{b,A}}{Z_{b,K} + Z_{b,A}} . \tag{37}$$

NONPOLARIZED OIL–WATER INTERFACE

We consider the system:

$$\begin{array}{c|c} \text{K, A}'' & \text{K, A}' \\ \text{(oil)} & \text{(water)} \end{array}$$
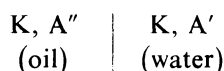
where K is the potential determining ion. In this case both O and W contain a certain amount of potential determining ion. The condition that the transfer of counter ions, A′ and A″, across the interface is negligible has been examined[21,22] and, here, the two phases are assumed to be in contact equilibrium, i.e., only K is transferable across the interface. For dc response in a quasi-reversible case, instead of Eq. (29),

$$\Psi_{i,0}(t) = \frac{k_i^0}{\mathscr{D}_i} \left[\frac{{}^b c_S^W}{{}^b c_S^O} \xi e^{\alpha_i j_1} - e^{-\beta_i j_1} \right] e^{\lambda_i^2 t} \mathrm{erfc}(\lambda_i t^{1/2}) \tag{38}$$

where

$$\lambda_i = \frac{k_i^0}{\mathscr{D}_i} \left[(1 - t_i^W) e^{\alpha_i j_1} + (1 - t_i^O) e^{-\beta_i k_1} \right] \tag{39}$$

and

$$\xi = (D_S^W / D_S^O)^{1/2} \tag{40}$$

$$\mathscr{D}_i = (D_S^W)^{\beta_i/2} (D_S^O)^{\alpha_i/2} . \tag{41}$$

$\Psi_{i,0}(t)$ in this case is also defined by Eq. (30). In Eqs $(38)-(41)$, i denotes the potential determining ion (K) and ${}^b c_S^W$ and ${}^b c_S^O$ are the bulk concentrations of KA′ in W and KA″ in O. The impedance and the phase angle are expressed as Eqs (33) and (34), respectively. In this case, $F_i(t)$ is given by

$$F_i(t) = \frac{(1 - t_i^O)/(1 - t_i^W) + e^{j_1}}{1 + ({}^b c_S^W / {}^b c_S^O) [(1 - t_i^O)/(1 - t_i^W)] \xi} \left\{ \xi \alpha_i \frac{{}^b c_S^W}{{}^b c_S^O} + \beta_i e^{-j_1} \right.$$

$$+ \frac{\beta_i (1 - t_i^O) e^{-j_1} - \alpha_i (1 - t_i^W)}{\lambda_i} \left[\frac{k_i^0}{\mathscr{D}_i} (\xi e^{\alpha_i j_1} ({}^b c_S^W / {}^b c_S^O) - e^{-\beta_i j_1}) - \Psi_{i,0}(t) \right] \right\} \tag{42}$$

and $Z_{rev,i}$ is given by

$$Z_{rev,i} = \frac{RT}{F^2 A \, ^bc_S^O (D_S^O)^{1/2}} \frac{(1 - t_K^O)\left[(1 - t_K^O)/(1 - t_K^W) + e^{j_1}\right]}{(\omega)^{1/2} e^{j_1}}$$

$$\cdot \left[1 + \frac{^bc_S^W(1 - t_K^O)}{^bc_S^O(1 - t_K^W)} \zeta\right]^{-1}. \tag{43}$$

RESULTS AND DISCUSSION

Reversible dc Response at the Polarized Interface

. Figure 2 shows the reduced current vs potential curves calculated from Eq. (20), when $z_K = |z_A| = 1$, $\Delta_O^W \varphi_K^O = -0.2$ V, $\Delta_O^W \varphi_A^O = 0.2$ V, $D_K^W/D_A^O = D_K^W/D_A^O = 2$, and at several different values of D_K^O/D_A^O, i.e, different values of t_K^O. In the middle of the potential window, the difference between the currents with and without taking account of the migration is negligible. However, at both ends of the potential window, the current without the migration is significantly lower than that with the migration. In other words, the neglect of the migration may lead to an erroneous estimation of $\Delta_O^W \varphi_i^O$ when one estimates a half-wave potential from the extrapolation of the foot of a base current. It is also seen in Fig. 2 that the change in the transference number appreciably alters the shape of the current vs potential curves.
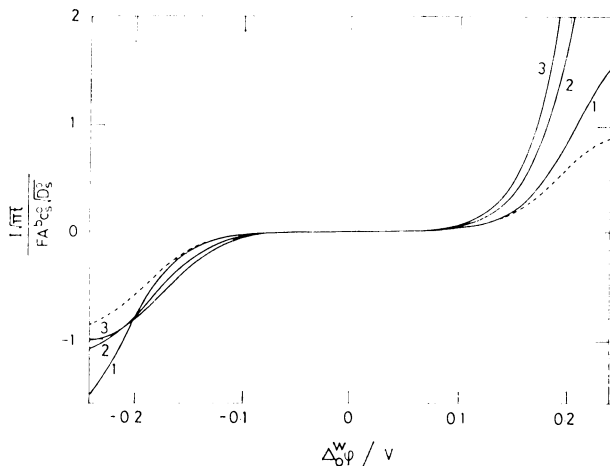

FIG. 2

Reversible dc current vs potential curves in the absence ($- - -$) and presence ($- \cdot -$) of migration in oil phase calculated using Eq. (20) for $t_K^O = 0.500(1)$, $0.167(2)$, and $0.091(3)$. See text for the values of other parameters

Reversible ac *Response at the Polarized Interface*

Figure 3 shows reduced ac current vs potential curves calculated using Eq. (26). The parameters are the same as in Fig. 2. These curves again show that the neglect of the migration will underestimate the admittance due to the transfer of supporting electrolyte ions. Since the ion transfer is reversible, Samec's method[1] is still valid for estimating a double-layer capacitance. When a solution resistance is ideally com-
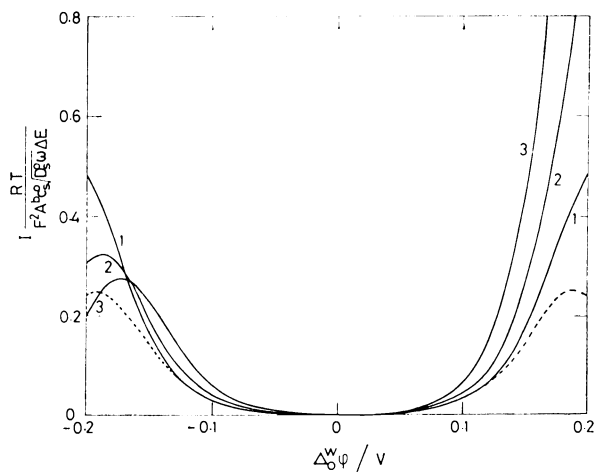

FIG. 3

Reversible ac current vs potential curves in the absence (— — —) and presence (————) of migration in oil phase calculated using Eq. (27) for $t_K^0 = 0.500(1)$, $0.231(2)$, and $0.091(3)$
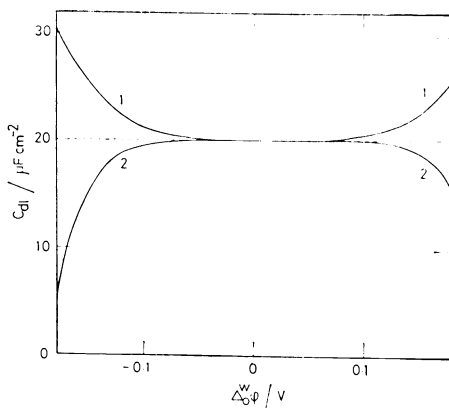

FIG. 4

Potential dependence of apparent C_{dl} values calculated from Eqs (44) (2) and (45) (1) at 50 Hz, when the transfer of supporting electrolyte ions are quasi-reversible ($k_i^0 = 0.001$ cm s^1) and the true C_d value is 20 μF cm^{-2} (···)

pensated for, the double-layer capacitance can also be calculated easily from

$$\omega C_{dl} = Y'' - Y', \tag{44}$$

where Y' and Y'' are the real and imaginary components of a measured total admittance. Obviously, a simplified assumption:

$$\omega C_{dl} = Y'' \tag{45}$$

will not give a correct C_{dl} value at both ends of the potential window.

Quasi-Reversible ac *Response at the Polarized Interface*

When the ion transfer of supporting electrolyte ions is not completely reversible, the phase angle is less than $\pi/4$, so that the application of Eq. (44) in quasi-reversible case will result in the underestimation of C_{dl}. We have estimated the errors in C_{dl} value calculated using Eqs (44) and (45), when $k_K^0 = k_A^0 = 10^{-3}$ cm s^{-1} and $\alpha_K = = \alpha_A = 0.5$, assuming that the true C_{dl} has a constant value of 20 μF cm^{-2} and that $\Delta_O^W\varphi_K = -0.343$ and $\Delta_O^W\varphi_A = 0.372$ V, corresponding to the ion-transfer potentials $\Delta_O^W\varphi$ for tetrabutylammonium ion, TPnA$^+$, and TPB$^-$, respectively. The results at $f = 50$ Hz shown in Fig. 4 indicate that, in the middle of the potential window, both Eqs (44) and (45) give good estimates for C_{dl}. At both ends of the potential window, Eqs (44) and (45) under- and overestimate C_{dl}, respectively. The magnitude in errors for the two methods is comparable. However, at lower frequencies, Eq. (45) significantly overestimated C_{dl}, while the error in C_{dl} at $\Delta_O^W\varphi = 0.100$ V remained practically unchanged within 2% when Eq. (44) was used (curves 1 and 2 in Fig. 5).

Effect of Nonpolarized Interface on the Evaluation of C_{dl}

On the determination of the kinetic parameters of ion transfer, the impedance due to the transfer of supporting electrolyte ions can be corrected simply by subtracting the admittance for a base solution from the total admittance for the system containing a depolarizer ion whose kinetic parameters are to be measured. When the


Fig. 5

Frequency dependence of C_{dl} calculated from Eqs (44) (2) and Eq. (45) (1) at $\Delta_O^W\varphi = = 0.100$ V. Other conditions and parameters are the same as in Fig. 4
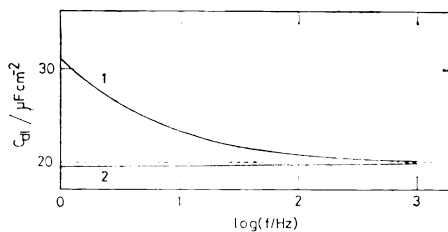
impedance of the nonpolarized oil–water interface is not negligible, the equivalent circuit may be represented by Fig. 1 b, in which the two impedance originating from the two oil–water interfaces are in series. In this case, no simple treatment of data is expected for correcting the influence of the nonpolarized interface. This complicates the evaluation of both C_{dl} and the kinetic parameters of ion transfer.

To minimize the impedance at the nonpolarized interface, *1* a higher rate constant of ion transfer, *2* higher concentrations of the potential determining ion in both phases, and *3* a larger area of the nonpolarized interface in comparison with that of the polarized interface are desired. There are practical restrictions for factors under *1* and *2*, because these contradict the requirement for a wider potential window; preferred in this respect are more hydrophobic ions having larger ionic radii, whose solubility is lower, and the condition for ensuring the contact equilibrium is more stringent[24]. Therefore, the third factor is most easily taken into account experimentally.

By using Eqs (*33*)−(*37*) for the polarized interface and Eqs (*33*), (*34*), (*38*)−(*43*) for the nonpolarized interface, we have estimated the errors in calculated C_{dl} values introduced by the non-ideal behavior of the reference interface. The results shown in Figs 6 and 7 were obtained for the system:

	a M	b M		
	KA$'$	KA$''$	supporting electrolyte	
	(water)	(oil)	(water)	
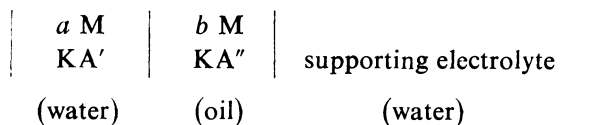
where $k_K^0 = k_{A''}^0 = 10^{-3}$ cm s^{-1}, $\alpha_K = \alpha_{A''} = 0.5$, $D_K^O = D_{A''}^O = 10^{-6}$ cm^2 s^{-1}, $D_K^W = D_{A''}^W = D_{A'}^W = 2 \cdot 10^{-6}$ cm^2 s^{-1}, $\Delta_O^W \varphi_K^0 = -0.343$, $\Delta_O^W \varphi_{A''}^0 = 0.372$, $^b c_S^O = 0.1$, and $^b c_S^W = 0.02$ mol dm^{-3}. C_{dl}'s at both interfaces were set equal to 20 μF cm^{-2}. The values for $\Delta_O^W \varphi_i^0$ were taken corresponding to those for TPnA$^+$ and TPB$^-$ ions, respectively. The equivalent circuit is represented as circuit b in Fig. 1. In the calculation, the solution resistance was assumed to be zero, since it can be compensated for experimentally. Figure 6 at 50 Hz and $t = 1\ 000$ s shows that, when the area of the reference interface, A_r, is smaller than that of the working interface, A_w, both Eqs (*44*) and (*45*) underestimate C_{dl} even in the middle part of the potential window. The frequency dependence of the estimated C_{dl} values is shown in Fig. 7 at $\Delta_O^W \varphi = -0.1$ V and $t = 1\ 000$ s. Again, when $A_r/A_w < 1$, the C_{dl} dramatically decreases at higher frequencies. This behavior has been found experimentally in C_{dl} measurements with a two-electrode system, when the reference interface was made using a sintered glass[34], where the effective area of the interface could be much smaller than the geometrical area of the sintered glass frit. In order that the interference from the reference interface is to be negligible in the estimation of C_{dl} up to 200 Hz, A_r/A_w should be larger than 10. One can see from Fig. 7 that even when

$A_r/A_w < 1$, the C_{dl} value calculated from Eq. (44) extrapolated to infinitely small frequency gives a good estimate of C_{dl}, e.g. Eq. (44) is applicable to wider range of $\Delta_O^W \varphi$ than Eq. (45).

Table I shows that the effect of the impedance of reference interface is much more profound on the real part than on the imaginary part of the admittance. The real

TABLE I

Effect of the ratio of the areas of working and reference interfaces, A_r/A_w, on real and imaginary parts of admittance for circuit b in Fig. 1a

A_r/A_w	Y'^b	Y''^b
1/10	$5 \cdot 43 \cdot 10^{-4}$	$1 \cdot 53 \cdot 10^{-3}$
1/3	$1 \cdot 91 \cdot 10^{-4}$	$1 \cdot 73 \cdot 10^{-3}$
1	$7 \cdot 20 \cdot 10^{-5}$	$1 \cdot 76 \cdot 10^{-3}$
10	$1 \cdot 08 \cdot 10^{-5}$	$1 \cdot 77 \cdot 10^{-3}$
∞	$3 \cdot 94 \cdot 10^{-6}$	$1 \cdot 77 \cdot 10^{-3}$

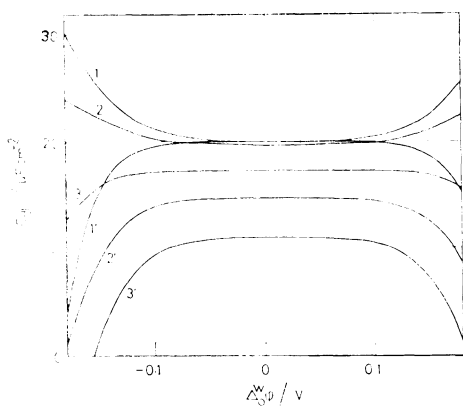^{a} See text for the parameters used in calculation; ^{b} unit is $[\Omega A^b c_S^O]^{-1}$.

FIG. 6

Apparent C_{dl} vs $\Delta_O^W \varphi$ curves calculated from Eqs (44) $(1', 2', 3')$ and (45) $(1, 2, 3)$ at 50 Hz and $t = 1\ 000$ s using the equivalent circuit b in Fig. 1. The reference interface is $0 \cdot 02\text{M-}KA'(W)/0 \cdot 1\text{M-}KA''(O)$. $A_r/A_w = 10 (1\text{ and }1')$, $1 (2\text{ and }2')$, and $1/3 (3\text{ and }3')$. See text for other parameters
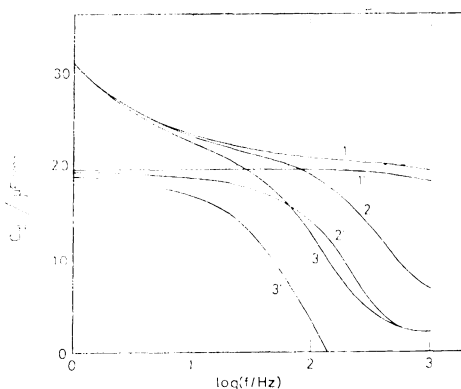
FIG. 7

Apparent C_{dl} vs frequency curves calculated from Eq. (44) $(1', 2', 3')$ and (45) $(1, 2, 3)$ at $\Delta_O^W \varphi = 0 \cdot 100$ V. $A_r/A_w = 10$ $(1\text{ and }1')$, $1 (2\text{ and }2')$, and $1/3 (3\text{ and }3')$. Other conditions and parameters are the same as in Fig. 6

part increases more than twofold when $A_r/A_w = 0 \cdot 1$. This is caused by the change in phase angle, aside from the increase in the total impedance, introduced by the reference interface. This increase in the real part of the admittance appears to be able to explain at least partly the residual real part of the admittance observed experimentally when using the cell with the reference oil–water interface made through a sintered glass[6].

Effect of Nonpolarized Interface on the Determination of Kinetic Parameters of Charge Transfer

Similarly, by using the equivalent circuit c in Fig. 1, we have estimated the influence of the reference interface on the evaluation of the kinetic parameters of charge transfer from impedance measurements. The ion transfer process of ion i whose kinetic parameters were to be determined was assumed to have the true values, $k_i^0 = 2 \cdot 87 \cdot 10^{-2}$ cm s^{-1} and $\alpha = 0 \cdot 5$, besides the standard ion transfer potential, $\Delta_o^w \varphi_i^0 = 0 \cdot 00$ V, and the diffusion coefficients, $D_i^o = 3 \cdot 92 \cdot 10^{-6}$ and $D_i^w = 7 \cdot 84 \cdot 10^{-6}$ cm^2 s^{-1}. The parameters for calculating Z_b, Z_{ref}, C_{d1} and $C_{d1'}$ are the same as in Figs 6 and 7. The apparent value of cot φ_i for the transfer of ion i was calculated from the real and imaginary components of the apparent ion-transfer admittance, which were calculated by subtracting the real and imaginary components of the admittance of the circuit b in Fig. 1 from the corresponding components of the total admittance of the circuit c in Fig. 1. The solution resistance was again neglected. The resultant cot φ_i(app) vs $\Delta_o^w \varphi$ curves were plotted in Fig. 8 when $A_r/A_w = 1/2 \cdot 8$ and in Fig. 9 when $A_r/A_w = 1$, at several different concentrations of ion i in the aqueous phase. Two important features are discernible in Figs 8 and 9. First, cot φ_i(app) is singnificantly higher than the true cot φ_i over the entire range of $\Delta_o^w \varphi$ examined and the discrepancy between the true and apparent values becomes greater with smaller A_r/A_w. Second, cot φ_i(app) increases with the concentration of ion i. This tendency has been observed experimentally, when the cell with sintered glass was employed[34]. Thus, the interference from the reference interface gives rise to higher cot φ values, i.e., slower rate of charge transfer than the actual. A comparison of Fig. 9 with Fig. 7 indicates that the effect of the reference interface on the determination of cot φ_i is more serious than on C_{d1} measurements. The variation of cot φ_i with $\omega^{1/2}$ is plotted in Fig. 10 for $A_r/A_w = 1$ and $\Delta_o^w \varphi = \Delta_o^w \varphi_i^0$. The impedance of the reference interface markedly bends the curves upwards, as if there remains uncompensated solution resistance[35]. The interference due to the reference interface persists, even when $A_r/A_w = 10$. For obtaining reliable kinetic parameters, A_r/A_w should be of the order of several tens. If the standard rate constant to be measured is faster than that used in the present calculation, as reported recently[12,36], the interference of the reference interface should be more serious. As can be seen from curve 3 in Fig. 10, the increase in the concentration of KA' in W to $0 \cdot 1$ mol dm^{-3} somewhat alleviates the interference.

FIG. 8

Apparent $\cot \varphi$ vs $\Delta_O^W \varphi$ curves calculated assuming the equivalent circuits b and c in Fig. 1, when $A_r/A_w = 1/3$ and the concentration of a depolarizer ion is 0·5(1) and 1·0(2) mmol l^{-1}. The reference interface is 0·02M--KA'(W)/0·1M-KA''(O). See text for other parameters. The broken line indicates true $\cot \varphi$
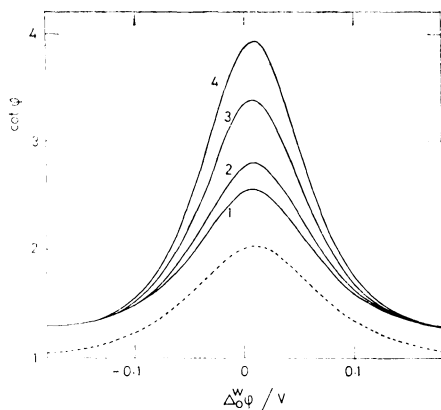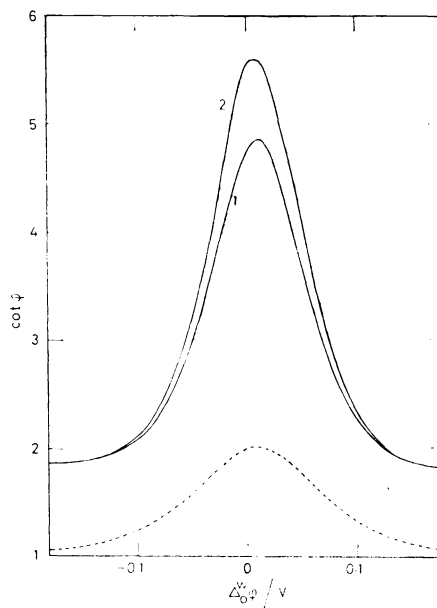

FIG. 9

Apparent $\cot \varphi$ vs $\Delta_O^W \varphi$ curves when $A_r/A_w =$ = 1 and the concentration of depolarizer is 0·2(1), 1(2), 3(3), and 5(4) mmol l^{-1}. The conditions and parameters are the same as in Fig. 8. The broken line indicates true $\cot \varphi$
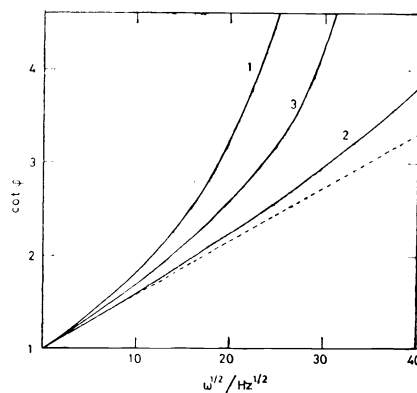

FIG. 10

Apparent $\cot \varphi$ vs $\omega^{1/2}$ curves at $\Delta_O^W \varphi =$ = $\Delta_O^W \varphi_i^0$ calculated assuming the equivalent circuits b and c in Fig. 1, when A_r/A_w is 1(1) and 10(2) for the reference interface: 0·02M-KA'(W)/0·1M-KA''(O), and $A_r/A_w =$ = 1 for the reference interface: 0·1M--KA'(W)/0·1M-KA''(O)

In conclusion, it is important to check the frequency dependence of the experimentally observed C_{dl} values and to check the frequency dependence and depolarizer-concentration dependence of the kinetic parameters to estimate the degree of the interference associated with the non-ideal behavior of working and reference interfaces. A reference oil–water interface with larger effective area is highly recommended. The above estimations have been done on some typical sets of parameters. In actual cases, the lower concentration of a supporting electrolyte in oil phase, e.g., $0\cdot01$ mol cm^{-3}, has often been used. In this case, the requirement for A_r/A_w would be more stringent.

REFERENCES

1. Samec Z., Mareček V., Homolka D.: J. Electroanal. Chem. Interfacial Electrochem. *126*, 121 (1981).
2. Hundhammer B., Solomon T., Alemu H.: J. Electroanal. Chem. Interfacial Electrochem. *149*, 179 (1983).
3. Mareček V., Samec Z.: J. Electroanal. Chem. Interfacial Electrochem. *149*, 185 (1983).
4. Hájková P., Homolka D., Mareček V., Samec Z.: J. Electroanal. Chem. Interfacial Electrochem. *151*, 277 (1983).
5. Homolka D., Hájková P., Mareček V., Samec Z.: J. Electroanal. Chem. Interfacial Electrochem. *159*, 233 (1983).
6. Osakai T., Kakutani T., Senda M.: Bull. Chem. Soc. Jpn. *58*, 370 (1984).
7. Silva F., Moura C.: J. Electroanal. Chem. Interfacial Electrochem. *177*, 317 (1984).
8. Reid J. D., Vanýsek P., Buck R. P.: J. Electroanal. Chem. Interfacial Electrochem. *161*, 1 (1984).
9. Osakai T., Kakutani T., Senda M.: Bull. Chem. Soc. Jpn. *58*, 2626 (1985).
10. Kakutani T., Nishiwaki Y., Osakai T., Senda M.: Bull. Chem. Soc. Jpn. *59*, 781 (1986).
11. Wandlowski T., Mareček V., Samec Z.: J. Electroanal. Chem. Interfacial Electrochem. *242*, 29 (1988).
12. Wandlowski T., Mareček V., Holub K., Samec Z.: J. Phys. Chem. *93*, 8204 (1989).
13. Seno M., Iwamoto K., Chen Q.: Electrochim. Acta *35*, 127 (1990).
14. Grahame D. C., Whitney R. B.: J. Am. Chem. Soc. *64*, 1548 (1942).
15. Kakiuchi T., Senda M.: Bull. Chem. Soc. Jpn. *56*, 2912 (1983).
16. Kakiuchi T., Senda M.: Bull. Chem. Soc. Jpn. *56*, 1322 (1983).
17. Samec Z., Mareček V.: J. Electroanal. Chem. Interfacial Electrochem. *200*, 17 (1986).
18. Pang Z., Cheng C. A., Wang E.: J. Electroanal. Chem. Interfacial Electrochem. *234*, 71 (1987).
19. Pang Z., Wang E., Chang C. A.: Electrochim. Acta *33*, 1291 (1988).
20. Homolka D., Mareček V.: J. Electroanal. Chem. Interfacial Electrochem. *112*, 91 (1980).
21. Wiles M. C., Schiffrin D. J., VanderNoot T. J.: J. Electroanal. Chem. Interfacial Electrochem. *278*, 151 (1990).
22. Koryta J.: Electrochim. Acta *24*, 293 (1979).
23. Hung L. Q.: J. Electroanal. Chem. Interfacial Electrochem. *115*, 159 (1980).
24. Kakiuchi T., Senda M.: Bull. Chem. Soc. Jpn. *60*, 3099 (1987).

25. Melroy O. R., Buck R. P., Stover F. S., Hughs H. C.: J. Electroanal. Chem. Interfacial Electrochem. *121*, 93 (1983).
26. Melroy O. R., Bronner W. E., Buck R. P.: J. Electrochem. Soc. *130*, 373 (1983).
27. Melroy O. R., Buck R. P.: J. Electroanal. Chem. Interfacial Electrochem. *151*, 1 (1983).
28. Hundhammer B., Solomon T.: J. Electronal. Chem. Interfacial Electrochem. *157*, 19 (1983).
29. Osakai T., Kakutani T., Nishiwaki Y., Senda M.: Anal. Sci. *3*, 499 (1987).
30. Samec Z., Mareček V., Colombini M. P.: J. Electroanal. Chem. Interfacial Eleltrochem. *257*, 147 (1988).
31. Heyrovský J., Kůta J.: *Principles of Polarography*, p. 65. Academic Press, New York 1966.
32. Underkofler W. L., Shain I.: Anal. Chem. *37*, 218 (1965).
33. Smith D. E. in: *Electroanalytical Chemistry* (A. J. Bard, Ed), Vol. 1, Chap. 1. Dekker, New York 1966.
34. Kakiuchi T., Senda M.: Unpublished results.
35. Milner D. F., Weaver M. J.: J. Electroanal. Chem. Interfacial Electrochem. *222*, 21 (1987).
36. Kakiuchi T., Noguchi J., Kotani M., Senda M.: A paper presented at the *35th Annual Meeting on Polarography, Nov. 1989 (Tokushima)*; abstract: Rev. Polarogr. (Kyoto) *35*, 55 (1989).