Rate Constant for Ion Transfer in Inhomogeneous Media at the Interface of Immiscible Electrolytes

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An expression for the impedance due to ion transfer across the interface of immiscible electrolyte solutions (ITIES) is derived, assuming a continuous change of the ionic resolvation energy across an interfacial layer. The model is analogous to the Goldman constant field approximation. The result is practically identical to the one obtained assuming an activated step occurs during the transfer, i.e., the classical Butler−Volmer relationship, so that the standard rate constant k^0 in the Butler−Volmer theory is replaced by the quantity D/δ, where D is the average diffusion coefficient of the transferring ion inside the interfacial layer and δ is the thickness of the interfacial layer. At potentials close to the standard transfer potential, the apparent charge-transfer coefficient α takes the value of $^1/_2$. Combination of the charge-transfer impedance and an inner layer capacitance in parallel gives a complete semicircle in an impedance plot, characteristic of a parallel *RC* circuit.

Introduction

The mechanism of the ion transfer across molecular interfaces is still unclear partly because both the structure of these interfaces and the Galvani potential distribution present are still poorly understood. Different interfacial models have been proposed. In the original work of Gavach,[1] Buck et al.,[2] and Samec et al.,[3] a sharp boundary with two ion-free inner layers, one at each side of the interface, was proposed, similar to a modified Verwey−Niessen model. This was a direct transposition of the classical electrochemical formalisms for electron-transfer reactions at metallic electrodes. This interfacial model has been more recently applied to the study of interfacial electron-transfer reactions using the scanning electrochemical microscope.[4] In contrast to treating interfaces as molecularly sharp boundaries, a mixed solvent layer was suggested by Girault and Schiffrin.[5] More recently, comprehensive molecular dynamics simulations by Benjamin[6] indicate that these boundaries are highly disordered, with "fingering" phenomena prevailing. The possible influence of these interfacial structures on ion transfer has been evaluated.[6b]

The main question being discussed at present is whether ion transfer is a process containing an activated step corresponding, for instance, to resolvation or is it just a transport problem. If the former approach is accepted, the potential dependence of the transfer current will follow a classical Butler−Volmer relationship.[7] The difficulty with this model is the uncertainty regarding the potential distribution across the interfacial region. This is particularly important if it is considered that most of the potential drop normally occurs in the organic phase. When the Butler−Volmer model is applied to the analysis of experimental data, the standard rate constant, k^0, takes rather high values, on the order of 0.1 cm s^{-1}. Recently, Girault et al. measured the impedance of a microhole ITIES which facilitates the mass transfer on both sides of the interface, but could not find any charge-transfer resistance due to ion transfer, and concluded that k^0 has to take values on the order of at least 10 cm s^{-1}.[8]

A proposed alternative model considers the interfacial region as an inhomogeneous phase through which the trace ion is transferred. The solvent properties and salt concentrations of the adjoining phases are considered to vary continuously through this interfacial region. This model has been considered by Kakiuchi,[9] Kontturi et al.,[10] and Senda,[11] who integrated the Nernst−Planck equation across the interfacial region under steady-state conditions. The current−voltage characteristics thus obtained could be expressed as that of a first-order heterogeneous reaction, which enabled the comparison with the Butler−Volmer approach. The fundamental result of these analyses is that the Nernst−Planck model explains the salient features of the kinetic data, such as the nonlinear current−voltage characteristics and a value close to $^1/_2$ for the transfer coefficient α. Furthermore, the formal standard rate constant can be related to the diffusion coefficient of the transferring ion across the interfacial region and to its thickness. Quite recently, Aoki presented a more general theory of ion transfer[12] which includes these two approaches as its limiting cases. The comparison of the above two formalisms is not obvious for fast ion-transfer reactions.

Rate constants are conveniently measured by perturbation techniques, such as ac impedance spectroscopy.[7a] Unfortunately, the classical analysis based, for example, on a Randles-type equivalent circuit, *includes explicitly a particular potential dependence of the rate constant, in all cases, given as the Butler−Volmer equation*. The question is whether the rate constant derived from transient techniques is uniquely related to the use of a specific kinetic model or, indeed, no particular kinetic equation for ion transfer needs to be assumed and all the kinetic information obtained from these techniques is simply a consequence of the diffusion and migration characteristics of an ion in an inhomogeneous region as described by the Nernst−Planck equation. Previous theoretical ac impedance analysis in systems related to the present one has been carried out by

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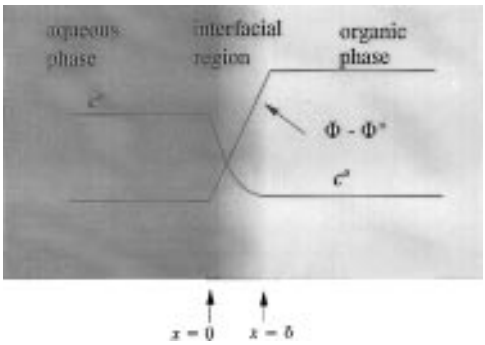

Figure 1. Schematic presentation of the interfacial region.

Buck et al.[13a,b] More recently, this analysis has been extended by the same authors by the use of transmission lines to the study of ion- and electron-transfer reactions in membranes.[13c,d] The numerical analysis by Buck[13a] referred to the membrane case, in which activated ion transfer at the membrane−solution boundary takes place.

The purpose of the present work is to analyse the ac response for ion transfer across the interface of immiscible electrolytes and compare the results derived from the solution of the diffusion and migration problem with those for which an activated step process (the Butler−Volmer approach) was considered. In particular, it was regarded important to be able to ascertain if the observation of an ac response containing a classical charge-transfer resistance would be equally well derived from the phenomenological migration and diffusion description of ion transport.

Theory

The case considered here is that of a cation from the aqueous phase transferring across the interface. The concentration of the cation is c^w in the aqueous phase and c^o in the organic phase. Concentration polarization is neglected so that interfacial concentrations are equal to those in the bulk; the effect of the concentration polarization was studied in ref 10. The reason for doing this is to highlight the nature of interfacial ion transfer. The diffusional components (Warburg impedance) in both adjoining phases can be simply taken into account in much the same way as is usually done in the impedance theory for metal electrodes.[14] The Warburg impedance can then be subtracted from the experimental data.[15] Furthermore, it is assumed that the entire changes of the Galvani potential and standard chemical potential of the ion take place in the interfacial region, the thickness of which is denoted by δ; see Figure 1. The latter assumption may not be quite correct; that is, the change of Galvani potential probably extends over a wider distance than δ. Refining the model accordingly would, first, bring about unnecessary mathematical complications and, second, have only a minor effect on the final result, as we have shown in ref 10. The analysis is carried out assuming the presence of supporting electrolytes in both phases. Two different cases will be considered: (i) equilibrium impedance and (ii) overpotential impedance.

Solution of the General Problem. The ion transfer is described as an electrodiffusion problem, and the flux of the transferring ion, J, follows the phenomenological equation[16]

$$J = -\frac{Dc}{RT}\frac{\mathrm{d}\tilde{\mu}}{\mathrm{d}x} \tag{1}$$

where D and c are the diffusion coefficient and concentration of the ion being transferred and $\tilde{\mu}$ is its electrochemical potential; R and T have their usual significance. For a cation transfer and considering that the activity coefficient of the tracer ion is independent of concentration, the flux is given by

$$J = -D\left[\frac{\partial c(x)}{\partial x} + c(x)f\frac{\partial(\Phi(x) - \Phi^0(x))}{\partial x}\right] \tag{2}$$

where $c(x)$ is the concentration of the tracer ion a distance x from the aqueous phase boundary (taken as the origin of coordinates), $f = zF/RT$, and $\Phi^0(x) = -\mu^0(x)/zF$. $\mu^0(x)$ is the standard chemical potential of the tracer ion for the solvent composition at point x. The quantity $\mu^0(x)$ recognizes that ion transfer occurs across an inhomogeneous interfacial region, in which not only potential changes but also the chemical solvation energy gradient must be considered.[17] The inner potentials given in eq 2 are absolute quantities, but integration across the interfacial region leads to more convenient relative quantities expressed with reference to the either of the phases. Here, we use the convention $\Delta_o^w\Phi = \Phi(0) - \Phi(\delta)$ and $\Delta_o^w\Phi^0 = \Phi^0(0) - \Phi^0(\delta)$. Hence, the more positive $\Delta_o^w\Phi - \Delta_o^w\Phi^0$ is made, the more the cation flux from the aqueous to the organic phase is accelerated.

The solution of eq 2 under steady-state conditions (ss) is dependent on the assumptions made on the electrical and standard chemical potentials gradient in the interfacial region. For membrane or confined regions, the Goldman constant field assumption is commonly employed to describe the potential distribution.[18] This approximation implies that no space charges are present in the interfacial phase. However, even in cases where the potential distribution deviates significantly from linearity, there is little difference in the calculated values of the current−voltage response.[10,19] The latter observation is very important, since it shows that the fine details of the interfacial potential distribution have a small effect on the calculated values of the rate constants for ion transfer. Similar arguments apply to the chemical potential contribution to the driving force for interfacial ion transfer,[10,19] and therefore, (2) becomes

$$J_{ss} = -D\left[\frac{\mathrm{d}c_{ss}(x)}{\mathrm{d}x} + c_{ss}(x)G_{ss}\right] \tag{3}$$

where J_{ss} and $c_{ss}(x)$ are the steady-state flux and ion concentration at x. G_{ss} is defined as

$$G_{ss} = -\frac{f(\Delta_o^w\Phi_{ss} - \Delta_o^w\Phi^0)}{\delta} \tag{4}$$

Direct integration of (3) between $x = 0$ and $x = \delta$ leads to

$$J_{ss} = DG_{ss}\frac{c^w - c^o e^{G_{ss}\delta}}{e^{G_{ss}\delta} - 1} \tag{5}$$

From (3) and (5) the concentration distribution of the cation is in the interfacial region accordingly given by

$$c_{ss}(x) = \frac{c^w(e^{G_{ss}(\delta - x)} - 1) - c^o(e^{G_{ss}(\delta - x)} - e^{G_{ss}\delta})}{e^{G_{ss}\delta} - 1} \tag{6}$$

Note that eq 6 leads to correct limits $c_{ss}(0) = c^w$ and $c_{ss}(\delta) = c^o$. The system is perturbed by applying an ac potential difference to the interfacial region in addition to the steady-state value: $\Delta_o^w\Phi = \Delta_o^w\Phi_{ss} + \Delta_o^w\Phi_{ac}$. This results in a perturbation of the steady-state cation distribution within the interfacial region, $c(x,t) = c_{ss}(x) + c_{ac}(x,t)$, which leads to an ac current. In the present analysis, however, the boundary concentrations remain unchanged since no mass-transfer limitation outside the interfacial region is considered here.[10] Hence,

$c_{ac}(0,t) = c_{ac}(\delta,t) = 0$. In what follows, for the sake of simplicity, $c_{ss}(x)$ and $c_{ac}(x,t)$ are denoted as c_{ss} and c_{ac}, respectively.

Let us rewrite eq 2, in a form that makes explicit reference to the deviation of the flux from its steady-state values, J_{ss}, by the applied ac signal, J_{ac}:

$$J = J_{ss} + J_{ac} = -D\left[\frac{d}{dx}(c_{ss} + c_{ac}) + (c_{ss} + c_{ac})(G_{ss} + G_{ac})\right] \tag{7}$$

where $G_{ac} = -f\Delta_o^w\Phi_{ac}/\delta$. From (3) and (7), and neglecting the second-order ac term, the ac component of the flux is given by

$$-J_{ac} = D\left[\frac{dc_{ac}}{dx} + c_{ss}G_{ac} + c_{ac}G_{ss}\right] \tag{8}$$

The ac component of the concentration in the case of a sinusoidal potential perturbation, $\Delta_o^w\Phi_{ac} = \Delta_o^w\hat{\Phi}e^{j\omega t}$, can be expressed as $c_{ac} = \hat{c}e^{j\omega(t+\theta)}$, where $\Delta_o^w\hat{\Phi}$ is the peak potential perturbation, θ the phase angle with respect to the exciting potential function, and ω its angular frequency; j is the imaginary unit. As it will be seen, it is not necessary to calculate θ to obtain the impedance. The continuity condition of the flux is then given by

$$-\frac{\partial J_{ac}}{\partial x} = \frac{\partial c_{ac}}{\partial t} = j\omega c_{ac} \tag{9}$$

Applying (9) into (8) and after minor arrangements,

$$\frac{\partial^2 c_{ac}}{\partial x^2} + G_{ss}\frac{\partial c_{ac}}{\partial x} - \frac{j\omega}{D}c_{ac} = -G_{ac}\frac{\partial c_{ss}}{\partial x} \tag{10}$$

where it has been assumed that $\partial G_{ac}/\partial x = \partial G_{ss}/\partial x = 0$ according to the Goldman constant field approximation. The total electric current is given by[13a]

$$I = A\left(FJ - \epsilon\frac{\partial^2\Phi}{\partial x\,\partial t}\right) \tag{11}$$

where the first term inside the parentheses is the current due to cation transfer (faradaic current) and the second term is the Maxwell's displacement current (capacitive current). A is the interfacial area and ϵ the mean permittivity of the interfacial region. Thus, even though J is position dependent, the total current I is position independent. Since no information of the time variation of the electric field inside the interfacial region can be obtained from our theoretical model, an alternative approach must be followed.

Integration of (11) with respect to the spatial coordinate from $x = 0$ to $x = \delta$ gives

$$I\delta = A\left(F\int_0^\delta J\,dx + \epsilon\frac{\partial}{\partial t}\Delta_o^w\Phi\right) \tag{12}$$

so that in the case of a sinusoidal perturbation it must be satisfied that

$$\frac{I_{ac}}{AF} = \frac{1}{\delta}\int_0^\delta J_{ac}\,dx + j\omega\frac{\epsilon}{\delta F}\Delta_o^w\Phi_{ac} \tag{13}$$

where I_{ac} is the ac component of the current. From (8)

$$\int_0^\delta J_{ac}\,dx = -D[G_{ss}\int_0^\delta c_{ac}\,dx + G_{ac}\int_0^\delta c_{ss}\,dx] \tag{14}$$

Hence, inserting (14) into (13), the impedance of the system can be calculated for different boundary conditions.

(i) Equilibrium Impedance. At equilibrium, no steady-state current flows through the interface and $J_{ss} = 0$. Therefore, the steady-state concentration is equal to the equilibrium concentration, i.e., $c_{ss} = c_{eq}$, which can be calculated from (3):

$$c_{eq}(x) = c^w e^{-G_{eq}x} \tag{15}$$

where G_{eq} corresponds to (4) in the absence of current. Taking, as discussed above, $c_{ac}(0) = c_{ac}(\delta) = 0$, the solution of (10) is

$$\frac{c_{ac}}{\frac{D}{j\omega}G_{ss}G_{ac}c^w} = \frac{e^{r_1x + r_2\delta}(1 - e^{r_1\delta}) - e^{r_1\delta + r_2x}(1 - e^{r_2\delta})}{e^{r_2\delta} - e^{r_1\delta}} - e^{(r_1+r_2)x} \tag{16}$$

where $r_{1,2}$ are the roots of the characteristic function

$$r_{1,2} = -\frac{G_{eq}}{2} \pm \sqrt{\left(\frac{G_{eq}}{2}\right)^2 + \frac{j\omega}{D}} \tag{17}$$

From (16) and (17) and, after some rearrangements,

$$\int_0^\delta c_{ac}\,dx = \frac{DG_{ac}G_{eq}c^w}{j\omega}\frac{r_1^2(e^{r_2\delta} - 1)^2e^{r_1\delta} - r_2^2(e^{r_1\delta} - 1)^2e^{r_2\delta}}{r_1r_2(r_1 + r_2)(e^{r_2\delta} - e^{r_1\delta})} \tag{18}$$

$$= -\frac{G_{ac}c^w\delta^2e^{-G_{eq}\delta/2}}{\sinh((r_2 - r_1)\delta/2)}\left[\frac{\cosh(r_1\delta) - 1}{(r_1\delta)^2} - \frac{\cosh(r_2\delta) - 1}{(r_2\delta)^2}\right]$$

Expanding $\cosh x \approx 1 + x^2/2 + x^4/24$, $\sinh x \approx x + x^3/6$ and using the binomial expansion $(1 + x)^{-1} \approx 1 - x$, after lengthy algebra (18) can be approximated to

$$\int_0^\delta c_{ac}\,dx \approx -\frac{G_{ac}G_{eq}c^w\delta^3e^{-G_{eq}\delta/2}}{12} \tag{19}$$

Also, the second integral term on the right-hand side of (14) can be expanded to give

$$\int_0^\delta c_{eq}\,dx = c^w\delta\frac{1 - e^{-G_{eq}\delta}}{G_{eq}\delta} = c^w\delta e^{-G_{eq}\delta/2}\left(1 + \frac{(G_{eq}\delta)^2}{24} + ...\right) \tag{20}$$

Therefore (see eq 14),

$$G_{ac}\int_0^\delta c_{eq}\,dx + G_{eq}\int_0^\delta c_{ac}\,dx \approx G_{ac}\delta c^w e^{-G_{eq}\delta/2}\left(1 - \frac{(G_{eq}\delta)^2}{24} + ...\right) \tag{21}$$

Finally, from (13), (14), and (21) it is found that

$$I_{ac} = \left[\frac{AF^2Dc^w}{RT\delta}e^{-G_{eq}\delta/2} + j\omega\frac{\epsilon A}{\delta}\right]\Delta_o^w\Phi_{ac} \tag{22}$$

The two contributions inside the brackets are admittance components corresponding to a parallel *RC* combination. In this case, the resistance corresponds to the charge-transfer

resistance, R_{ct},[14] and the capacitance to that of the interfacial region of thickness δ. Therefore, at equilibrium

$$R_{ct} = \frac{RT\delta}{AF^2Dc^w}\exp\left[-\frac{f}{2}(\Delta_o^w\Phi_{eq} - \Delta_o^w\Phi^0)\right] \qquad (23)$$

and the interfacial layer capacitance takes the form $C = \epsilon A/\delta$; $\epsilon = \epsilon_r\epsilon_0$, where ϵ_r is the relative permittivity of the interfacial layer and $\epsilon_0 = 8.854 \times 10^{-14}$ F cm^{-1}.

(ii) Overpotential Impedance. In this case a steady-state current is flowing across the interface. Considering external potential polarization in terms of an overpotential, η, it is found that $G_{ss} = G_{eq} + G_{ov}$ where $G_{ov} = -\eta/\delta = -f(\Delta_o^w\Phi - \Delta_o^w\Phi_{eq})/\delta$. In order to solve (14), c_{ss} (eq. 6) has to be integrated across the interfacial region between 0 and δ. This gives

$$\int_0^\delta c_{ss}\,dx = \frac{(c^w - c^o)\delta}{G_{ss}\delta} - \frac{(c^w - c^o e^{G_{ss}\delta})\delta}{e^{G_{ss}\delta} - 1}$$

$$= c^w\delta e^{-G_{eq}\delta/2}\left[\frac{2\sinh(G_{eq}\delta/2)}{G_{ss}\delta} + \frac{\sinh(G_{ov}\delta/2)}{\sinh(G_{ss}\delta/2)}\right]$$

Expanding the sinh term, this can be approximated to

$$\int_0^\delta c_{ss}\,dx \approx c^w\delta e^{-G_{eq}\delta/2}\left[\frac{G_{eq}\delta\left(1 + \frac{(G_{eq}\delta)^2}{24} + ...\right)}{G_{ss}\delta} + \frac{G_{ov}\delta\left(1 + \frac{(G_{ov}\delta)^2}{24} + ...\right)}{G_{ss}\delta\left(1 + \frac{(G_{ss}\delta)^2}{24} + ...\right)}\right] \qquad (25)$$

$$\approx c^w\delta e^{-G_{eq}\delta/2}\left[1 + \frac{G_{eq}(G_{eq} - 2G_{ov})\delta^2}{24} + ...\right]$$

The solution of (10) is here omitted, but the corresponding integral in (14) takes the form

$$\int_0^\delta c_{ac}\,dx = \frac{G_{ac}(c^w - c^o)\delta^2}{\cosh(r_2\delta) - \cosh(r_1\delta)} \times \left[\frac{\cosh(r_1\delta) - 1}{(r_1\delta)^2} - \frac{\cosh(r_2\delta) - 1}{(r_2\delta)^2}\right] \qquad (26)$$

$$\approx -\frac{G_{ac}(c^w - c^o)\delta^2}{12}\left[1 + \frac{1}{20}((r_1\delta)^2 + (r_2\delta)^2) + ...\right]$$

where r_1 and r_2 correspond to (17) replacing G_{eq} with G_{ss}. Neglecting the last term inside the brackets, (26) simplifies to

$$\int_0^\delta c_{ac}\,dx \approx -\frac{G_{ac}c^w\delta^2 e^{-G_{eq}\delta/2}}{12}2\sinh(G_{eq}\delta/2) \approx -\frac{G_{ac}G_{eq}c^w\delta^3 e^{-G_{eq}\delta/2}}{12} \qquad (27)$$

From (13) and (14) it follows that the interfacial admittance is given by

$$\frac{I_{ac}}{\Delta_o^w\Phi_{ac}} = \frac{AF^2Dc^w e^{-G_{eq}\delta/2}}{RT\delta}\left[1 - \frac{1}{24}G_{eq}(G_{eq} + 2G_{ov})\delta^2 + ...\right] + j\omega\frac{\epsilon A}{\delta} \qquad (28)$$

The form of the admittance in this case is similar to that for the equilibrium case, as shown in (22), and therefore, the charge-transfer resistance is given by

$$R_{ct} = \left\{\frac{RT\delta}{AF^2Dc^w}\exp\left[-\frac{f}{2}(\Delta_o^w\Phi_{eq} - \Delta_o^w\Phi^0)\right]\right\} \times \left[1 + \frac{1}{24}G_{eq}(G_{eq} + 2G_{ov})\delta^2 + ...\right] \qquad (29)$$

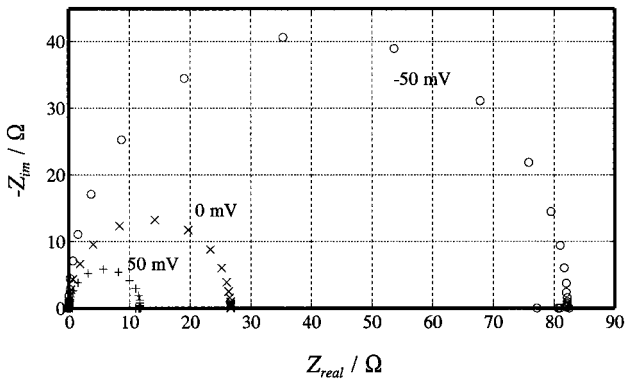

Figure 2. Numerical simulation of the equilibrium impedance. $\epsilon_r = 40$, $\delta/A = 10^{-7}$ cm^{-1} and $Dc^w = 10^{-15}$ mol cm^{-1} s^{-1}. $f = 0.01-100$ kHz, 5 points per decade. Numerical values indicate values of $\Delta_o^w\Phi_{eq} - \Delta_o^w\Phi^0$ used.

Results and Discussion

The approximations implicit in the series expansions made above may seem to restrict the present analysis to potentials close to the standard potential, while in practice the equilibrium potential can be varied in a range of several hundred millivolts by varying the concentration ratio of the potential-determining ion between the two phases. Therefore, the validity of the approximations made have been examined with numerical simulations. Computations were carried out with Matlab for Windows in a Pentium processor personal computer. A simulation of the equilibrium impedance is presented in Figure 2, using the complete forms of the integrals of (18) and (20). As can be seen, the impedance plot is similar to that of a parallel *RC* circuit. The potential dependence of R_{ct} for this case is shown in Figure 3; R_{ct} was obtained from the intercept of the impedance diagram with the real impedance axis at the low-frequency limit. A similar plot for R_{ct} in the overpotential case ii is shown in Figure 4, using the corresponding complete integrals given in (24) and (26).

Equations 23 and 29 describing the charge-transfer resistance are important results. Firstly, since this is only a resistive component, its combination in parallel with the interfacial capacitance leads to a semicircle in the impedance plots *indistinguishable* from an activated charge-transfer reaction.[14] Secondly, the potential dependence of R_{ct} is identical to that predicted from the Butler−Volmer ($^{B-V}$) formalism:[14]

$$R_{ct}^{B-V} = \frac{RT}{AF^2k^0c^w}\exp[-\alpha f(\Delta_o^w\Phi_{eq} - \Delta_o^w\Phi^0)] \qquad (30)$$

with a transfer coefficient $\alpha = {}^1/_2$. The apparent charge-transfer

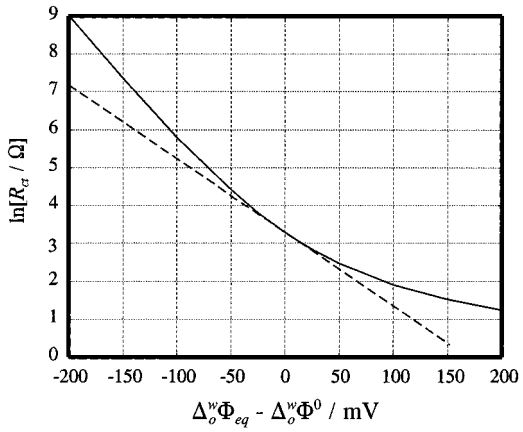

Figure 3. Potential dependence of the equilibrium charge-transfer resistance. Straight line corresponds to (23). Parameters are the same as in Figure 2.

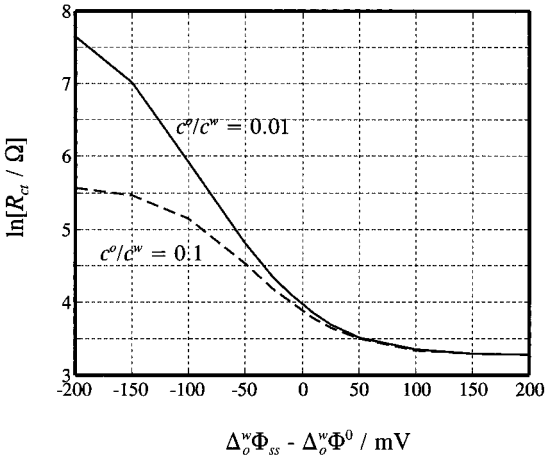

Figure 4. Potential dependence of the charge-transfer resistance at the concentration ratios $c^o/c^w = 0.01$ (—) and 0.1 (- - -), corresponding to equilibrium potentials $\Delta_o^w\Phi_{eq} - \Delta_o^w\Phi^0 = -118$ and -59 mV, respectively. Parameters are the same as in Figure 2.

coefficient derived from the present work is given by

$$\alpha = -\frac{RT}{F}\frac{\mathrm{d}\ln R_{ct}}{\mathrm{d}\Delta_o^w\Phi_{eq}} \qquad (31)$$

and from the potential dependence of the simulation results shown in Figure 3, a value of $\alpha = {}^1/_2$ can be calculated at potentials close the equilibrium potential. This is strictly in agreement with the theoretical calculations presented in (23) and (29). It should be stressed, though, that the physical meaning of α from the Butler−Volmer and from the solution of the Nernst−Planck equations is quite different. In the former case, the transfer involves a single activated step, which could be, for instance, a potential dependent ionic resolvation process.[17] However, in the Nernst−Planck case, $\alpha = {}^1/_2$ occurs as a natural consequence of the form of the diffusion and migration equation combined with the symmetry of the Goldman approximation. The similarity between (23) and (30) holds as long as the equilibrium potential is close to the standard transfer potential. However, since the potential dependence of R_{ct} is different in the two formalisms, the comparison is not straightforward at other potentials, while keeping the apparent standard rate constant defined as $k^0 = D/\delta$.

Although the two formalisms lead to identical relationships between the charge-transfer resistance and the potential, the physical models underlying the two approaches are very different. As mentioned above, the idea behind the Butler−Volmer equation is that in the transition from water to the organic phase a potential dependent rate-determining step is present. In contrast, the treatment of ion transfer as a diffusion and migration problem does not make any assumptions regarding the individual steps occurring during transfer, but rather treats it as a continuous migration and diffusion through an interfacial region.[9−12] The average diffusion coefficient for this process contains, in this case, the information on resolvation phenomena, through the incidence of an average friction coefficient that incorporates resolvation energy considerations.

To give an idea of the order of magnitude of the quantities discussed, for $k^0 = 0.22$ cm s^{-1},[15] (for example, for the tetraethylammonium transfer across the water−nitrobenzene interface), $D = 10^{-7}$ cm^2 s^{-1} for $\delta = 4.5$ nm. The value of D estimated in the interfacial region for this value of k^0 is lower than that in the adjoining phases, as expected if a resolvation process occurs during the transfer. The difference with the activated step approach is mainly in the possibility that resolvation occurs continuously during transfer. However, the recent results of Girault et al.[8] for ion transfer across the water/1,2-dichloroethane interface give values of D much closer to those in the bulk phases. This gives additional support to the idea of treating the structure of these liquid/liquid interfaces as a mixed solvent layer.[5] Of course, the value of its thickness, δ, is arbitrarily chosen, and future work is required to understand the dynamics of resolvation. A lead in this direction is the advanced molecular dynamics simulations of Benjamin et al.[6] These nonequilibrium calculations for ion transfer indicate that surface roughness due to the phenomena of "fingering"[6] and the associated transfer of water of hydration into the organic phase are responsible for the increased friction coefficient for ionic movement. This implies that the solvent exchange process occurs at a much faster rate than ionic migration through the thickness δ.

Conclusions

It has been shown that the ac impedance technique, commonly employed to obtain rate constants for charge-transfer reactions across immiscible interfaces, gives values that are indistinguishable for an activated step, or from a migration and diffusion model. The apparent charge-transfer coefficient takes the value of $^1/_2$ at potentials close to the standard transfer potential. This shows that it is not necessary to interpret these rate constants as resulting from a single rate-determining step, but a resolvation model affecting the average diffusion coefficient (or friction coefficient) of the transferred ion across the interfacial region can account for the measured rate constants.

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