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Derivation of the explicit equation relating mass-transport-limited-current to voltage at the interface between two immiscible electrolyte solutions (ITIES)

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Abstract The potential drop between two immiscible electrolyte solutions consists of the sum of that across the double layer and the diffusion barrier layer. A relation between these components has been proposed by Indenbom. We extended his approach to give a relation between the current density and the overall potential drop between the two bulk solutions. The final expression is mathematically similar to the Butler–Volmer equation for classical electrode kinetics.

Keywords Polarizability · ITIES · Ion transfer

1 Liquid/liquid interfaces: background

The acronym ITIES, introduced for the first time by Koryta [1, 2], means the "Interface between two immiscible electrolyte solutions." The electrochemical cell used in such liquid/liquid interfaces has two reference electrodes (RE_1 and RE_2) and two platinum counter electrodes as current carriers (CE_1 and CE_2), connected to a four-electrode potentiostat which was successfully designed for the first time by Samec and Mareček [3]. The reference electrodes measure the potential difference between the tips of the reference Luggin capillaries, while the potentiostat adjusts the current between the two platinum counter electrodes

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such that the potential difference between the tips of the reference electrodes is equal to a chosen value. The solvents used to set up these interfaces must be immiscible, chemically compatible and with a different density so that a freestanding interface can be established.

Another condition must be their high relative permittivity (ε) so that supporting electrolytes and analytes dissolved in these solvents will dissociate and reasonable conductivity of the organic solution can be achieved. These requisites are fulfilled by solvents such as water ($\varepsilon = 78.58$), nitrobenzene ($\varepsilon = 34.82$), nitroethane ($\varepsilon = 30.3$), 1,2-dichloroethane ($\varepsilon = 10.36$) and several other organic solvents [1]. Decreasing the temperature or using mixtures of solvents of higher permittivity with very hydrophobic ions could be another way to reach the same effect [1, 4–8].

The sign convention with ITIES is '$E_{R.E.aq} - E_{R.E.org}$', so that the aqueous phase is more positive at the right hand side of a voltammogram with respect to the organic phase.

When the aqueous phase becomes sufficiently positive with respect to the non-aqueous phase, anions in organic (O)-phase, Y^-, will cross the interface to the water phase, while the transfer of the cations from the water (W)-phase, requiring generally a larger potential, are not usually seen in the voltammogram [1, 9, 10]. With increasing potential, the transport of the Y^- ion will become more pronounced and an increasing current will appear at the extreme right of the voltammogram. Upon reversal of the scan, this ion will return to its original phase, causing a negative current peak at the right, whose height depends on the switching potential and indicates the amount of ions being transported back to their original phase.

The extreme left is reached when the aqueous phase becomes progressively less positive and organic phase cations, X^+, will move into the aqueous phase, resulting in a negative current. As was the case for the inorganic cation

at the right side, the inorganic anions do not usually transfer to the organic phase at this potential. So, the general phenomenon observed at this extreme is the transfer of X^+ to the aqueous phase (a negative current minimum), and then their return during the sweep reversal, characterized by a positive current peak.

In these systems, two types of charge transfer reaction usually occur: (a) transfer of an ion with charge z through the interface, either on its own or facilitated by organic ligands, (b) electron transfer, that can be associated with the interchange between a donor-couple in the O phase and an acceptor-couple in the W phase and vice versa, leading to red–ox reactions at the interface.

Depending on the nature of the ions making up the electrolyte solutions, two different behaviours are possible as a consequence of the application of an electric field across the organic/water interface [4, 7]: non-polarizable and polarizable interfaces.

If both phases have only one, common, electrolyte the interface is non-polarizable. The potential difference across the interface is fixed by the concentrations of electrolytes on either side. The electrochemical equilibrium of the ion "i" located at the external boundaries of the double layer and between internal boundaries of the diffusion layers, is given by the following Nernst–Donnan equations [3]:

$$\Delta_O^W \Phi = \Delta_O^W \Phi_{X^+}^0 + \frac{RT}{F} \ln \frac{a_{X^+}^{s,O}}{a_{X^+}^{s,W}} \quad (1)$$

$$\Delta_O^W \Phi = \Delta_O^W \Phi_{Y^-}^0 - \frac{RT}{F} \ln \frac{a_{Y^-}^{s,O}}{a_{Y^-}^{s,W}} \quad (2)$$

where $a_i^{s,O}$ and $a_i^{s,W}$ = activity of ion "i" at the external boundaries of the electrical double layer $\Delta_O^W \Phi_i^0$ = standard ion transfer potential of the ion "i" from the organic solvent into water. This value can be related to the standard Gibbs transfer energy by the equation [9, 10]:

$$\Delta_O^W \Phi_i^0 = -\frac{1}{z_i F} \Delta G_{tr,i}^{0,O \to W} \quad (3)$$

If there are two immiscible solvents with the same salt X^+Y^- dissolved in both then X^+ cannot transfer without Y^- because of charge neutrality. In this case, for complete dissociation (e.g. very dilute solution) [4], the potential across the interface is given by:

$$\Delta_O^W \Phi = \frac{1}{2} \cdot \left(\Delta_O^W \Phi_{Y^-}^0 + \Delta_O^W \Phi_{X^+}^0 \right) = \frac{1}{2 \cdot F} \cdot \left(\Delta G_{tr,Y^-}^{0,O \to W} - \Delta G_{tr,X^+}^{0,O \to W} \right) \quad (4)$$

In other words, there is a liquid junction potential across the interface which ensures that any flux of anions, from one solution to the other, equals the flux of cations. Such a system is not useful to potentiometric studies, since the

potential across the interface is fixed: imposed currents only create iR drop in the solutions.

If the W phase contains a highly hydrophilic electrolyte MN and phase O contains a highly hydrophobic electrolyte XY, the interface behaves as an ideal polarised interface in a range of potential difference across the interface that is called the "polarizable potential range" or "potential window" of the organic/water interface.

As long as the potential difference at the interface does not exceed a certain range of positive or negative magnitude, the transfer of X^+ and Y^- from O to W and that of N^- and M^+ ions in the opposite direction should be negligible, since X^+ and Y^- ions are highly hydrophobic and N^- and M^+ ions are highly hydrophilic.

Since there is practically no current flow possible within the potential window, the interface behaves as a capacitor; the capacitance is that of the interfacial double-layer.

The clear-cut distinction between polarizable and unpolarizable interfaces is not respected in a real system where ions have a certain solubility in both aqueous and organic system. It is important to underline that ion transfer is basically an ionic transport process and not a chemical reaction as such: the only difference with a diffusion-migration process is the presence of the Gibbs energy gradient corresponding to the change of standard chemical potential across the mixed solvent layer [11].

The issue of reversibility of simple ion transfer at first sight seems to contradict the polarizability of ITIES. In ITIES, interfaces without a common ion are often called "blocked" and those with ions in common "unblocked". An unblocked interface is characterised by an unhindered exchange of ions between the two phases: therefore ionic equilibrium for all the species prevails throughout the system [12]. However, these distinctions should not be taken too literally. Current can cross even blocked interfaces if there are different species on each side which can make a redox reaction at the interface, transferring electrons instead of ions across the interface.

This leads to a threshold potential for current flows across the interface. In practice, one can assume:

(a) the low current at a polarizable interface between two supporting electrolytes is diffusion-limited following the creation of diffusion barrier layers each side of the interface [13];

(b) the heterogeneous step of the ion transfer is so fast that it may be considered as quasi-reversible [14].

This last assumption allows us to describe quantitatively the polarisation process of the interface between two supporting electrolyte solutions [13, 15]. Initially at the interface between organic solvent (O) and water (W), hydrophobic ions X^+ and Y^- are present only in the organic phase, whereas hydrophilic ions M^+ and N^- are
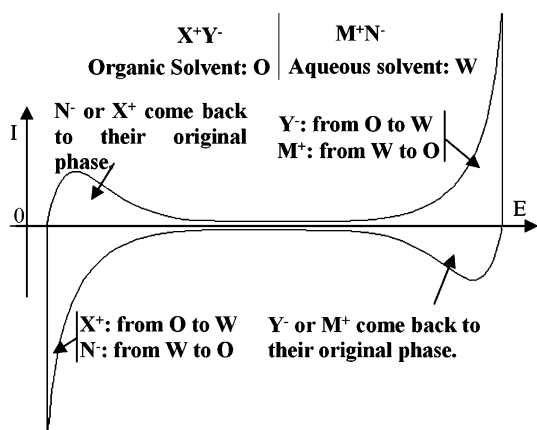
Fig. 1 Schematic cyclic voltammogram of ion transfer in ITIES

localised in the aqueous phase, but one of the four ions, e.g. X^+, can transfer to adjacent phase easier than the other ions (Fig. 1).

As the aqueous phase becomes progressively less positive with respect to the organic phase, X^+ transfer is enhanced and gives rise to a potential drop, $\Delta\Psi$ (Fig. 2) in the diffusion layer of the organic phase. To maintain charge neutrality X^+ can only transfer if there is a source and sink of ions at remote electrodes.

The comparison between the potential drop in the diffusion layer of the organic phase, $\Delta\Psi$ (Fig. 2) and the arising potential difference in the double layer, $\Delta_O^W\Phi$, determines the degree of polarizability. The potential difference can be found from three basic conditions, in the case of cation X^+ transferring from organic to water.

1. The Nernst–Donnan equation for the X^+ ion that will be transferred, in the form of Eq. 1.
2. Since Y^- cannot transfer, it must reach a steady-state concentration gradient such that its chemical potential gradient cancels the electrical gradient:

$$\Delta\Psi = \frac{RT}{F}\ln\frac{a_{Y^-}^{s,O}}{a_{Y^-}^{O}} = \frac{RT}{F}\ln\frac{\gamma^O c_{Y^-}^{s,O}}{\gamma^O c_{Y^-}^{O}} \qquad (5)$$

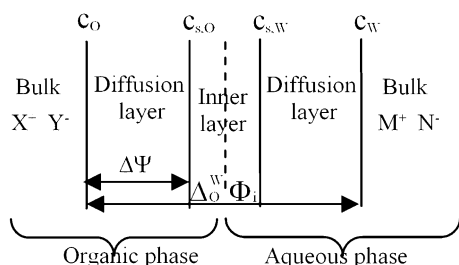3. Since the current, I, must be continuous across the interface, then:

Fig. 2 Symbols used at the interface

$$-I = \frac{2FD_{X^+}^O A}{\delta^O}(\gamma^O c_{X^+}^O - \gamma^O c_{X^+}^{s,O}) = \frac{FD_{X^+}^W A}{\delta^W}\gamma^W c_{X^+}^{s,W} \qquad (6)$$

where $D_{X^+}^O$ and $D_{X^+}^W$ = diffusion coefficients of X^+ ion in the organic phase and water.

A =	interfacial area.
δ^O and δ^W =	diffusion layer thickness in the organic and water phases, respectively.
γ^O and γ^W =	activity coefficient in the organic and water phase respectively.
c_i^{sO} and $c_i^{s,W}$ =	concentration of ion "i" at the external boundaries of the electrical double layer.
c_i^O =	concentration of ion "i" in the organic phase.

According to the electrochemical convention for ITIES, the current is considered to be negative during transfer of positive charges from the organic solvent to water. Furthermore the water phase volume in the cell is assumed to be sufficiently large that the concentration of X^+ ion in the bulk of water phase remains constant and negligible (compared to its concentration at the interface, $c^W = 0$) upon passage of the electric current. Finally, the coefficient "2" in the left side of Eq. 6 is conditioned by equal fluxes of diffusion and migration in the organic solvent in contrast to that in water, where migration is relatively unimportant.

The combination of the Eqs. 1, 5 and 6 yields the following equation for the relation between the potential drop across the boundary layer ($\Delta\Psi$) and the potential drop at the double layer at the liquid-liquid interface, $\Delta\Phi$:

$$\Delta\Psi = -\frac{RT}{F}\ln\left[1 + k\exp\left[-\frac{F(\Delta_O^W\Phi - \Delta_O^W\Phi_{X^+}^O)}{RT}\right]\right] \qquad (7)$$

where $k = \frac{D_{X^+}^O \delta^O}{2D_{X^+}^O \delta^W}$.

For two liquids with close viscosities it may be assumed that $k = 0.5$. The accuracy of the value should not essentially affect the result of the Eq. 7, because the coefficient k is only a pre-exponential factor.

This equation was put forward by Indenbom [13] although without its derivation or a discussion of simplifying assumptions used in its derivation (e.g. activity coefficients). He used it as a qualitative indication of the polarizability of the interface, demonstrating that if $\Delta_O^W\Phi_{X^+}^O < \Delta\Psi < \Delta_O^W\Phi_{Y^-}^O$, the potential drop in the diffusion layer is negligible (e.g. 10 mV). The potential drop across the interfacial double layer accounts for almost all the externally-applied potential difference. It means that the system behaves like an ideally polarised electrode at any potential ranging within the potential window and then the voltage is only used to charge the double layer

capacitor. It is then important to note that the polarizability of the interface beyond this potential range is dependent on the ion concentrations and diffusivities in the diffusion layer, rather than on the permeability of the double layer [13].

It would be useful to know the relationship between the current across the interface as a function of the total potential from one bulk solution to the other (i.e. I vs. $\Delta\Psi$), and this can easily be tested experimentally. Eliminating all the other variables, we derived an expression for the current as a function of the sum of the potential drops, for the typical case that the current is limited by transport in the barrier layer in the organic solvent. Figure 3 shows how this equation predicts the main features seen in experimental I-V plot; current rises exponentially when the total potential difference across the interface exceeds the potential required to transfer positive or negative ions across the interface. In this, it is mathematically similar to the Butler–Volmer equation for classical electrode kinetics.

2 Derivation of an equation relating mass transfer-limited-current to voltage across ITIES

As is conventional, the solution is conceptually divided into a bulk solution mixed by stirring or natural convection where the concentrations are constant, and a barrier-layer region where convection is absent. Even though there is a continuous transition between these regions, analysis made on the basis of an abrupt transition work well in practice [16].

In this region, the equations describing mass transport of electrolytes are [17]: (1) the flux equation; (2) the continuity equation; (3) the local electroneutrality assumption.

The transport of the ion i could be described in terms of the flux density, $\vec{J}_i$:

$$\vec{J}_i = c_i \vec{v}_i \tag{8}$$

where c_i = concentration of the ion i, v_i = velocity of the ion i.

In the linear approximation the mean velocity of the ion i is proportional to the thermodynamic driving force, which is defined by the gradient of the electrochemical potential (this assumption is valid being the difference between two potential states that are not too large, and applies to practically all ion transport processes):

$$\vec{v}_i = -u_i \vec{\nabla}\tilde{\mu}_i \tag{9}$$

where u_i = ion mobility = D_i/RT. $\vec{\nabla}\tilde{\mu}_i$ is the gradient of the electrochemical potential, defined as:

$$\vec{\nabla}\tilde{\mu}_i = \Delta\bar{\mu}_i + z_i F\vec{\nabla}\Phi = RT\vec{\nabla}\ln\gamma c_i + z_i F\vec{\nabla}\Phi \tag{10}$$

where $\Delta\bar{\mu}_i$ = chemical potential of the ion i.

Then the flux equation, assuming constant activity coefficient γ, becomes (in the assumption of Henryan

solution the activity coefficient is constant and cancels in the integration appearing in both terms of the fraction):

$$\vec{J}_i = -D_i\left(\vec{\nabla}c_i + z_i c_i \frac{F}{RT}\vec{\nabla}\Phi\right) \tag{11}$$

with the contribution of the diffusion and migration terms respectively. The first of them is related to the chemical energy gradient, while the latter is the motion of charged species moved by an electrical field $\vec{E} = -\vec{\nabla}\Phi$.

In ITIES application the geometry of the cell should ensure that the current is perpendicular to the interface. Thus:

$$J_i = -D_i\left(\frac{dc_i}{dx} + z_i c_i \frac{F}{RT}\frac{d\Phi}{dx}\right) \tag{12}$$

The ion i is moving into the water phase, where its concentration is much lower than the other ions present (i.e. it is in a supporting electrolyte), so that in the bulk water phase $c_i^w = 0$.

The presence of a supporting electrolyte means that the contribution of the migration term in the transport equation is negligible compared to the diffusion term. So the integration can be done with respect to the diffusion term:

$$J_i = -D_i^W \frac{dc_i}{dx} = \frac{D_i^W c_i^{s,W}}{\delta_w} \tag{13}$$

In the organic phase, the current is carried only by the X^+ ion since Y^- could not cross the interface, meaning zero flux. The electrochemical potential difference of Y^- across the boundary layer is then zero, so:

$$\vec{\nabla}\tilde{\mu}_{Y^-} = 0 \tag{14}$$

$$F\Delta\Psi = \Delta\bar{\mu}_{Y^-} = RT\ln\frac{c_{Y^-}^{S,O}}{c_{Y^-}^O} \tag{15}$$

$\Delta\Psi$ being the potential drop in the diffusion boundary layer of the organic phase.

Charge neutrality says that the concentration of X^+ and Y^- are the same: so too must be their chemical potentials, in the case of large monovalent ions having approximately equal γ. The electrical potential drop across the boundary layer is obviously also the same for both ions; the only difference is the charge sign, which inverts the sign of the electrical part of the electrochemical potential.

For Y^- the chemical potential exactly opposes the electrical potential, whereas for X^+ the two potentials are equal and reinforcing, doubling the driving-force for transport to the interface:

$$\vec{\nabla}\tilde{\mu}_{X^+} = \vec{\nabla}\bar{\mu}_{X^+} + F\vec{\nabla}\Psi = 2\vec{\nabla}\bar{\mu}_{X^+} \tag{16}$$

which means that:

Fig. 3 Potential drop in the diffusion layer, flux and current for X^+ (**a**, **c**, **e**) and Y^- (**b**, **d**, **f**); potential drop in the diffusion layer and current for transfer of both ions (**g**, **h**) (all graphs are drawn versus the potential drop across the interface)
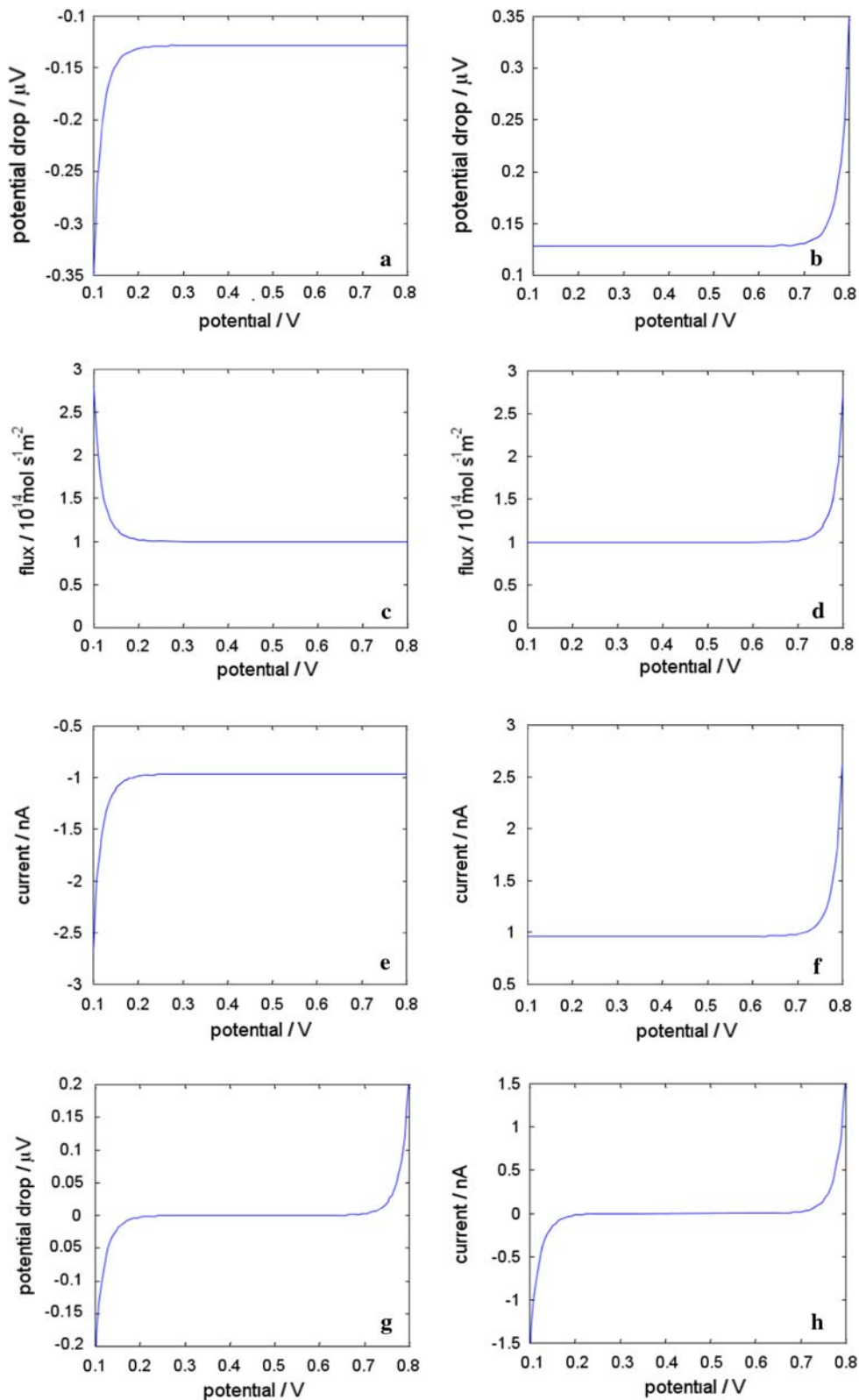
$$J_{X^+} = -2D_{X^+}^O \frac{dc_{X^+}}{dx} = -2D_{X^+}^O \frac{(c_{X^+}^{s,O} - c_{X^+}^O)}{\delta^O} \qquad (17)$$

and for the condition of charge neutrality applied to Eq. 15:

$$c_{X^+}^{s,O} = c_{X^+}^O \exp\left(\frac{F}{RT}\Delta\Psi\right) \qquad (18)$$

The current I is the sum of the contribution of all the fluxes of the ions:

$$\vec{I} = F \sum_i z_i \vec{J}_i \qquad (19)$$

and then the continuity of the current at the interface allows us to write (the current I is the sum of the contribution of all the fluxes of the ions, $I = F\Sigma z_i J_i$, but in the case of only one ion crossing the interface, the equality of currents means equality of fluxes):

$$-2D_{X^+}^O \frac{(c_{X^+}^{s,O} - c_{X^+}^O)}{\delta^O} = \frac{D_{X^+}^W c_{X^+}^{s,W}}{\delta_W} \qquad (20)$$

From Eqs. 18 and 20 together with the Nernst equation for liquid/liquid interfaces (Eq. 1), we obtain (with the assumption of activity coefficient constant in both phases or equal to unity it is possible to substitute the activity with the concentration and then to use the other expressions for the concentrations) the expression for the potential drop across the interface as a function of the potential drop on the diffusion layer $\Delta\Psi$:

$$\Delta\Psi_{X^+} = \Delta\Psi$$
$$= -\frac{RT}{F} \ln\left\{ 1 + k \exp\left[-\frac{F}{RT}\left(\Delta_O^W \Phi - \Delta_O^W \Phi_{X^+}^0\right)\right] \right\} \qquad (21)$$

where $k = \frac{D_{X^+}^W \delta_O}{2D_{X^+}^O \delta_W}$

In ITIES the current is considered to be positive during the transfer of positive charges from water to organic phase, but here X^+ transfers in the opposite direction $(\vec{I} = -I_X)$.

Thus $-I_x = FJ_x$ and, finally, for the left part of the diagram, will result in:

$$I_{X^+} = \frac{2FD_{X^+}^O c_{X^+}^O}{\delta_O} \left(\exp\left(\frac{F}{RT}\Delta\Psi_{X^+}\right) - 1\right) \qquad (22)$$

The same equations can be written for Y^-, using the same assumptions. It is then possible to relate $\Delta\Psi = f(\Delta_O^W \Phi)$ and $I = f(\Delta_O^W \Phi)$, using "Matlab" software. $\Delta\Psi_{X^+}$, J_{X^+} and I_{X^+} are shown in Fig. 3a, c, e. The final equations obtained for Y^-, $\Delta\Psi_{Y^-}$ and I_{Y^-} (shown in Fig. 3b, f) are the following ($J_{Y^-} = -\frac{1}{F}I_{Y^-}$ is shown in Fig. 3d):

$$\Delta\Psi_{Y^-} = \Delta\Psi$$
$$= \frac{RT}{F} \ln\left\{ 1 + k \exp\left[\frac{F}{RT}\left(\Delta_O^W \Phi - \Delta_O^W \Phi_{Y^-}^0\right)\right] \right\} \qquad (23)$$

$$I_{Y^-} = \frac{2FD_{Y^-}^O c_{Y^-}^O}{\delta_O} \left(\exp\left(\frac{F}{RT}\Delta\Psi_{Y^-}\right) - 1\right) \qquad (24)$$

The complete window for $\Delta\Psi$ and I as a function of $\Delta_O^W \Phi$ is shown on Fig. 3g, h (see Appendix for the assigned values).

3 Conclusions

An expression relating the current density and the overall potential drop between two bulk solutions has been expanded from the work of Indenbom [13].

The theory assumes that most of the solution is stirred, that the mean velocity of the ion 'i' is proportional to the thermodynamic driving force and that the potential gradient is developed only in the x direction. The theory correlates well with experimental results. In fact, the observed linear relation between $\Delta\Psi$ and $\Delta_O^W \Phi_i$ at large potentials (both positive and negative) (e.g. [13]) is consistent with the exponential relation between I and $\Delta_O^W \Phi_i$.

Appendix

The following values have been assigned to the variables in the correlations

Faraday Constant: $F = 96{,}485/C \text{ mol}^{-1}$; Gas Constant: $R = 8.314/J \text{ mol}^{-1} \text{ K}^{-1}$; Absolute temperature: $T = 298/K$; Standard transfer potential of the X ion: $\Delta_O^W \Phi_{X^+}^0 = 0.100/V$; Standard transfer potential of the Y ion: $\Delta_O^W \Phi_{Y^-}^0 = 0.800/V$; Diffusivity of the ion X in water: $D_{X^+}^W = 10^{-15}/\text{m}^2 \text{ s}^{-1}$; Diffusivity of the ion X in the organic phase: $D_{X^+}^O = 10^{-10}/\text{m}^2 \text{ s}^{-1}$; Diffusivity of the ion Y in water: $D_{Y^-}^W = 10^{-15}/\text{m}^2 \text{ s}^{-1}$; Diffusivity of the ion Y in the organic phase: $D_{Y^-}^O = 10^{-10}/\text{m}^2 \text{ s}^{-1}$; Bulk concentration of ion X in the organic phase: $c_{X^+}^O = 10^{-6}/\text{mol m}^{-3}$; Diffusion layer thickness in the organic phase: $\delta_O = 10^{-7}/\text{m}$; Diffusion layer thickness in the water phase: $\delta_W = \delta_O$; Charge of the ion X: $zX = 1$; Charge of the ion Y: $zY = -1$.

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