Which mechanism operates in the electron-transfer process at liquid/liquid interfaces?

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We present a more general expression for the relationship of potential dependence, which implies that a change in the interfacial drop across the interface has little effect on the free energy of the reaction, but mainly affects the surface concentration of reactant in each phase. Abundant experimental results from several well-known groups are analyzed in great detail to confirm our conclusion. At the same time, we define a new parameter named Frumkin correction factor to describe this relationship of potential dependence, which expresses the thermodynamic effect of double diffuse layers within both phases in contrast with the so often suggested kinetic electron-transfer (ET) coefficient; we also find that it depends on two intimately related aspects: the charges of reactive species and the ratio of the diffuse layer potential to the total potential within each phase, so it is quite arbitrary to ignore the diffuse layer effect in the aqueous phase just because of its relatively small values. In addition, a fascinating question on the inverted region at liquid/liquid interfaces has been successfully interpreted by an opposite surface concentration effect, which was often considered as a kinetic Marcus inverse by most groups.

Introduction

There is a great deal of interest in the study of ET reactions at the interface between two immiscible electrolyte solutions (ITIES) because it was strongly suggested that these ET reactions open up the possibility of exploring heterogeneous electron exchange between redox centers in the absence of interfacial defects,† which is fairly appropriate to test and develop ET theory.‡ What is disappointing is that the mechanism of ET has been the subject of much argument over several decades and moreover the nature of ET is largely unknown until now. One of the most controversial issues is the dependence of the ET rate constant on the Galvani potential difference across the interface, which is also known as how the applied potential across the interface affects the observed rate constant.¶

At the beginning of ET investigations,§ with information lacking on the structure of the interface, these authors assumed that most of the applied potential occurs across a compact layer of oriented solvent molecules separating two diffuse layers. On the basis of this model and assumption, the traditional electrochemical theory of solid electrodes was transposed directly to describe the kinetics of the ET process. Soon according to the measurements of the solvent surface excess and the potential of zero charge by Girault and Schiffrin,⁵ it was noticed that no compact layer indeed is present at the interface. Instead, it was proposed that the interface should be regarded as a mixed solvent layer separating two diffuse layers with no preferential orientation of the dipolar solvent molecules, which can be penetrated partially by ions from both phases. This conclusion on the interfacial structure was further confirmed by Samec⁶b based on the analysis of the capacity measurements using the Gouy–Chapman theory, in which the authors revealed that contrary to the previous assumption a mixed solvent layer locates between the two diffuse layers and most of the potential drop across the interface mainly develops within these two diffuse layers. Accordingly, as stated clearly by the authors, the classical heterogeneous charge transfer theories extended directly to the case of ITIES were invalid. Afterward, in terms of their proposed model, Girault and Schiffrin⁶b developed an alternative theory to describe this ET process where they assumed that an interfacial precursor formed prior to the charge transfer step within the mixed solvent layer and also the formalism of homogeneous ET⁶ can be applied in this case. In this model, the conclusion indicated that the potential dependence of the observed rate constant involves two essential terms: (i) the potential drop between the redox species at the precursor level and (ii) the work term to bring the reactants from the bulk to form a precursor. Considering that the potential drop between the two redox species at the precursor...
level could be rather small, a variation of the observed rate constant with the applied potential cannot be attributed to changes in the ET Gibbs energy, but rather variations in the work term. Along this train of thought, a simulation based on lattice-gas modeling by Schmickler\textsuperscript{a,b} showed that as long as the electrostatic potential is extended over a distance much larger than the width of the interface, the potential drop between the reactants is not only rather small but also independent of the applied potential. Simultaneously, an interesting conclusion suggested by the author is that changes in the Galvani potential difference would have very little effect on the activation of ET but rather mainly affect the surface concentration of ionic species at the interface.

With the advent of recent progress in spectroscopic studies\textsuperscript{7} and molecular dynamics simulations\textsuperscript{1a,b} the results show that on the picosecond time-scale the interface is molecularly sharp with the solvent density profile extending in a region on the order of 1 nm. On the other hand, simulation of the ionic distribution based on more precise lattice-gas modeling\textsuperscript{9} indicates that the Debye lengths associated with the diffuse layers are on the order of 10 nm. In these cases, supposing that the distance separating the redox species is determined by the solvent density profiles, a similar conclusion is expected that a change of the potential difference between the two bulk phases will have little effect on the driving force for an ET reaction; however, it will change the concentration of ionic reactants at the interface. Therefore, the previous excellent works pioneered by Girault and Schillfrin\textsuperscript{a,b} and further developed by Schmickler\textsuperscript{c,e} seem reasonable for such an ET process at the ITIES.

But to our disappointment, this good idea has not been attached sufficient emphasis and the viewpoint of classical ET theory was still widely accepted by most groups to explain a number of experiments even when their observations presented a striking contrast\textsuperscript{3d,10} to the classical ET theory. So that, in the present condition of some new advances in the interfacial structure, it is rather imperative to further clarify which mechanism would operate in the ET process at the ITIES.

For this purpose, on the basis of a reasonable three-layer model we give our understanding for this confusion and put forward a more general expression for the relationship of the potential dependence, implying that a change in the interfacial structure, it is rather imperative to further clarify which mechanism would operate in the ET process at the ITIES.

Due to the potential drop across the inner layer driving ET, in terms of Butler–Volmer equation, the rate constant can be given as follows:

\begin{equation}
 k_f = k_f^\circ \exp\left(\frac{\alpha \Delta \phi}{RT}\right) \\
 k_b = k_b^\circ \exp\left[-\left(1 - \alpha\right)\Delta \phi\right]
\end{equation}

where $\Delta \phi$ is the potential drop across the inner layer, $k_f^\circ$ and $k_b^\circ$ are the corresponding forward and backward rate constants at $\Delta \phi = 0$. $\alpha$ is the ET coefficient and $f$ is equal to $F/RT$, where $F$, $R$ and $T$ have their usual meanings. By virtue of eqn (3) and (4), the flux of electron transfer can be expressed by the kinetic equation,

\begin{equation}
 v_e = k_f^\circ \omega_{f,2}^o - k_b^\circ \omega_{b,2}^o
\end{equation}

Theory

The structure of liquid/liquid interfaces has been a continually hot topic in scientific debate. Although the nature of the interface and the physical localization of the ET reaction remains problematic, here we still accept a simplified but quite reasonable three-layer model\textsuperscript{a,b} (see Scheme 1) for our discussion. As illustrated in Scheme 1, the inner layer is between $x_1^o$ and $x_2^o$ and the diffuse layer in the $x$ phase ($x = \text{water (w), oil (o)}$) is between $x_1^o$ and $x_2^o$, where $x$ is the coordinate perpendicular to the interface. Therefore, we define the potential $\phi$ and the concentration $c$ of species $i$ to be $\phi_1^i$, $\phi_2^i$, $\phi_1^o$, $\phi_2^o$, $\phi_{1i}$, $\phi_{12}$, $\phi_{2i}$ and $\phi_{22}$ at $x_1^o$, $x_2^o$, $x_1^i$ and $x_2^i$, respectively.

In addition, we define $\Delta \phi_1^i = \phi_1^i - \phi_2^i$, $\Delta \phi_2^i = \phi_2^i - \phi_1^i$, $\Delta \phi_1^o = \phi_1^o - \phi_2^o$, $\Delta \phi_2^o = \phi_2^o - \phi_1^o$, and $\Delta \phi = \phi_2^o - \phi_1^o$, which we assume that no adsorption occurs at each side of the interface, there is sufficient supporting electrolyte on both sides of the interface and the distance of double layer is not affected by the flow of current or ionic transport across the interface. Additionally, a number of experimental results from the published reports are discussed detailedly to verify our conclusion, which are all consistent with our theoretical description.
Considering the Frumkin effect within both phases the rate constant determined by experiments should be an apparent value at the position of $x_1^w$ and $x_1^o$, so that

$$v_e = k_{app}^{w} c_{O,1}^{w} r_{1}^{w} - k_{app}^{o} c_{O,1}^{o} r_{1}^{o}$$  \(6\)

with

$$k_{app}^{w} = k_{f}^{w} \exp(-z_{f}^{w}/\Delta \phi^{w} - z_{f}^{w}/\Delta \phi^{o})$$  \(7\)

and

$$k_{app}^{o} = k_{f}^{o} \exp(-z_{f}^{o}/\Delta \phi^{w} - z_{f}^{o}/\Delta \phi^{o})$$  \(8\)

where $\Delta \phi^{w}$ and $\Delta \phi^{o}$ denote the potential drop across the diffuse layer in each phase, respectively. Assuming that the ET process is in equilibrium state, $v_e = 0$, thus

$$k_{app}^{w} c_{O,1}^{w} r_{1}^{w} = k_{app}^{o} c_{O,1}^{o} r_{1}^{o}$$  \(9\)

At the position of $x_1^w$ and $x_1^o$, the concentration of each reactive species obeys the Nernst equation, which can be described as

$$\Delta \phi^{w} = \Delta \phi^{p} + 1/f \ln(c_{O,1}^{w}/c_{O,1}^{o})(c_{O,1}^{w}/c_{O,1}^{o})$$  \(10\)

where $\Delta \phi^{p}$ is $[E_{RHE}] - [E_{RHE}]$ being the standard ET potential of eqn (1). On the basis of eqn (9) and (10), we can easily derive

$$k_{app}^{o} \exp(z_{f}^{w}/\Delta \phi^{w} + z_{f}^{w}/\Delta \phi^{o})$$  \(11\)

Substituting eqn (7) and (8) into eqn (11), an important relationship will appear as

$$k_{b} = k_{f} \exp(z_{f}^{w}/\Delta \phi^{w} + z_{f}^{w}/\Delta \phi^{o})$$  \(12\)

In this case, we can define that $k_{f} = k_{b}$ at $\Delta \phi^{o}_{f} = \Delta \phi^{w}_{f}$. Then, with the aid of eqn (3) and (4), we can obtain

$$k^{o} = k_{f}^{o} \exp(z_{f}^{w}/\Delta \phi^{w} + z_{f}^{w}/\Delta \phi^{o})$$  \(13\)

which can also be written as

$$k^{o} = k_{f}^{o} \exp(-z_{f}^{w}/\Delta \phi^{w} + z_{f}^{w}/\Delta \phi^{o})$$  \(14\)

$$k^{o} = k_{f}^{o} \exp(-z_{f}^{w}/\Delta \phi^{w} - z_{f}^{w}/\Delta \phi^{o})$$  \(15\)

Then combining eqn (14) and (15) with eqn (3) and (4), respectively, we deduce

$$k_{f} = k_{f}^{o} \exp(z_{f}^{w}/\Delta \phi^{w} + z_{f}^{w}/\Delta \phi^{o})$$  \(16\)

$$k_{b} = k_{f}^{o} \exp(-z_{f}^{w}/\Delta \phi^{w} - z_{f}^{w}/\Delta \phi^{o})$$  \(17\)

Finally, according to eqn (16) and (17), eqn (7) and (8) can be rearranged as

$$k_{app}^{w} = k_{f}^{w} \exp(z_{f}^{w}/\Delta \phi^{w} + z_{f}^{w}/\Delta \phi^{o})$$  \(18\)

$$k_{app}^{o} = k_{f}^{o} \exp(-z_{f}^{w}/\Delta \phi^{w} - z_{f}^{w}/\Delta \phi^{o})$$  \(19\)

We can see, therefore, that eqn (18) is divided into two essential terms: the first contribution is an ET kinetic-term, $k_{f}^{w} \exp(z_{f}^{w}/\Delta \phi^{w} + z_{f}^{w}/\Delta \phi^{o})$; the second contribution is a thermodynamic-term, $\exp(-z_{f}^{w}/\Delta \phi^{w} - z_{f}^{w}/\Delta \phi^{o})$, representing the surface concentration effect within double diffuse layers. In terms of little changes occurring at the potential drop across the inner layer, this $k_{app}/\Delta \phi$ response (eqn (18) and (19)) indicates that a variation of the applied potential is just equal to changing the surface concentration rather than activating ET at the position of $x_1^w$ and $x_1^o$.

When focusing on a forward-direction irreversible reaction as shown in Scheme 1, we easily obtain the relationship of the apparent rate constant,

$$k_{app}^{w} = k_{f,et} \exp(z_{f}^{w}/\Delta \phi^{w} + z_{f}^{w}/\Delta \phi^{o})$$  \(20\)

with

$$k_{f,et} = k^{o} \exp(-z_{f}^{w}/\Delta \phi^{w} - z_{f}^{w}/\Delta \phi^{o})$$  \(21\)

and

$$z_{f}^{w} = -z_{f}^{w}/\Delta \phi^{w} - z_{f}^{w}/\Delta \phi^{o} = -z_{f}^{w}/\Delta \phi^{w} + \Delta \phi^{p}/\Delta \phi^{o}$$  \(22\)

where $k_{f,et}$ is the defined ET kinetic-term keeping almost constant during the changes of $\Delta \phi^{w}_{f}$, $z_{f}^{w}$ is the corresponding Frumkin correction factor expressing the total diffuse layer effect within both phases. $z_{f}^{w} = -z_{f}^{w}/\Delta \phi^{w} - z_{f}^{w}/\Delta \phi^{o}$ being the corresponding Frumkin correction factor in each phase, respectively.

To understand eqn (20)–(22) more clearly, a concise expression should be performed by some definitions, as is also valid in any cases,

$$k_{app} = \text{const} + z_{f}^{w}(\Delta \phi_{f})$$  \(23\)

$$z_{f}^{w} = z_{f}^{w} + z_{f}^{o} = z_{f}^{w}(\Delta \phi^{w}/\Delta \phi^{o}) + z_{f}^{o}(\Delta \phi^{o}/\Delta \phi^{w})$$  \(24\)

where $\Delta \phi$ takes $\Delta \phi^{w}$ or $\Delta \phi^{o}$ when electron transfers from oil to water or from water to oil. The signs of $z^{w}$ and $z^{o}$ should be chosen according to this problem at hand: for a cation, the sign should be positive when acting as the oxidant and negative as the reductant; for an anion, it is just the other way around. Allowing for the reverse reaction, we define the reverse Frumkin correction factor $\beta_{FC}$ to it,

$$\beta_{FC} = \beta_{FC}^{w} + \beta_{FC}^{o} = (1 - z^{w})(\Delta \phi^{w}/\Delta \phi^{o}) + (1 - z^{o})(\Delta \phi^{o}/\Delta \phi^{w})$$  \(25\)

where $(1 - z^{w})$ and $(1 - z^{o})$ are the respective charges of the redox species in the aqueous and organic phases for the reverse ET reaction based on the above definition of signs. Then, the sum of $z_{f}^{w}$ and $\beta_{FC}$ can be calculated by the following relationship,

$$z_{f}^{w} + \beta_{FC}^{w} + \beta_{FC}^{o} = z_{f}^{w}(\Delta \phi^{w}/\Delta \phi^{o}) + z_{f}^{o}(\Delta \phi^{o}/\Delta \phi^{w}) + (1 - z^{w})(\Delta \phi^{w}/\Delta \phi^{o}) + (1 - z^{o})(\Delta \phi^{o}/\Delta \phi^{w}) = 1$$  \(26\)

which is very similar to the true ET coefficients $z_{f}^{w} = 1$. However, they are rather different from each other. In addition, $z_{f}^{w}$ and $\beta_{FC}$ are both functions of the applied potential but remain constant in a narrow potential region.

Finally, to facilitate the understanding of eqn (23) and (24), we give an example on reaction systems Fe(CN)$_3$$^+$/TCNO$^-$. In this case, owing to Fe(CN)$_3$$^+$ and TCNO$^-$ being the anion oxidant and reductant, $\Delta \phi^{w}$ takes $\Delta \phi^{o}$ as electron transfers from oil to water. $z^{w} = -3$ and $z^{o}$ take $-3$ and $1$, respectively. Thus,

$$z_{f}^{w} = z_{f}^{w} + z_{f}^{o} = -3(\Delta \phi^{w}/\Delta \phi^{o}) + (\Delta \phi^{o}/\Delta \phi^{w})$$  \(27\)
Table 1  Theoretical $z_{FC}$ for several redox systems reported in previous studies

<table>
<thead>
<tr>
<th>Redox systems$^a$</th>
<th>$z^o / z^w$</th>
<th>$z_{FC}^o$</th>
<th>$z_{FC}^w$</th>
<th>$z_{FC}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoL-H/RBr$_2$</td>
<td>0.0</td>
<td>=0</td>
<td>=0</td>
<td>=0</td>
</tr>
<tr>
<td>Fe(CN)$_6^{3-}$/DMFC</td>
<td>-3.0</td>
<td>&lt;0</td>
<td>=0</td>
<td>&lt;0</td>
</tr>
<tr>
<td>Ru(CN)$_6^{3-}$/ZnPor</td>
<td>-3.0</td>
<td>&lt;0</td>
<td>=0</td>
<td>&lt;0</td>
</tr>
<tr>
<td>Fe(CN)$_6^{3-}$/TCNQ</td>
<td>4.0</td>
<td>&gt;0</td>
<td>=0</td>
<td>&gt;0</td>
</tr>
<tr>
<td>Ru(CN)$_6^{3-}$/ZnPor$^+$</td>
<td>4/1</td>
<td>&gt;0</td>
<td>&gt;0</td>
<td>&gt;0</td>
</tr>
<tr>
<td>Fe(CN)$_6^{3-}$/DMFC$^+$</td>
<td>4/1</td>
<td>&gt;0</td>
<td>&gt;0</td>
<td>&gt;0</td>
</tr>
<tr>
<td>Fe(CN)$_6^{3-}$/TCNQ$^+$</td>
<td>-3/1</td>
<td>&gt;0</td>
<td>&gt;0, &lt;0</td>
<td>&gt;0, &gt;0</td>
</tr>
</tbody>
</table>

$^a$ Co-L-H: a protonation product of Co(II) form of vitamin B$_12$. RBr$_2$: trans-1,2-dibromocyclohexylborane. ZnPor: zinc meso-tetraphenylporphine. TCNQ: 7,7,8,8-tetracyanoquinodimethane. DMFC: decamethylferrocene. $^b$ The signs of $z^o$ and $z^w$ can be taken in terms of the definition. $^c$ The sign of $z_{FC}$ is uncertain in the redox systems of Fe(CN)$_6^{3-}$/TCNQ. When $|z_{FC}^o| < |z_{FC}^w|$, the total value of $z_{FC}$ will be positive indicating that the case of accumulation in the organic phase plays a dominant role; when $|z_{FC}^o| > |z_{FC}^w|$, it will be negative showing that the depletion in the aqueous phase plays another dominant role. More detailed analysis could be seen in the Results and discussion section.

Results and discussion

Large numbers of experimental results reported by some well-known groups will be discussed as below, all of which reveal that the apparent rate of ET dependence on the potential is only due to the diffuse layer effect or surface concentration effect in contrast to ET theory suggested by most groups. As illustrated in Scheme 2, when the redox species are charge neutral, therefore no surface concentration effect occurs, it can be concluded that the apparent rate will remain constant during the changes of the applied potential (as shown in Table 1). The previous experimental result$^{10c}$ (Co-LH/RBr$_2$) indicated that the overall rate of the interfacial reaction was independent of the interfacial potential drop and the authors suggested that the bimolecular ET reaction was not the rate-limiting step and the interfacial reaction could not be described fully by a simple second-order rate law. However, we consider that it is just a normal situation not involving the diffuse layer effect. So the observation of Co-LH/RBr$_2$ gives a direct evidence for this thermodynamic behavior when changing the applied potential, which could not be explained by typical ET theory. Similar to the above manner, the results$^{10d,11}$ in Table 2 including Fe(CN)$_6^{3-}$/TCNQ and Fe(CN)$_6^{3-}$/DMFC reaction systems also demonstrate such a diffuse layer effect. For instance, when the ion-strength in the aqueous phase varies from 0.1 M (NaCl) to 2 M (NaCl), the thickness of the diffuse layer in the aqueous phase becomes smaller, and the ratio of the diffuse layer potential in the aqueous phase to the total potential becomes much smaller too. As can be seen from eqn (24), the theoretical $z_{FC}$ will get smaller and the appearing results in Table 2 from 0.68 to 0.39 or from −0.44 to −0.10 due to a variation of the ratio of the diffuse layer potential in the aqueous phase from 17% to 9% or from 11% to 4% at the water/1,2-dichloroethane interface seem reasonable for such a diffuse layer effect. Consequently, the ion-strength effect offers another convicive evidence to confirm this thermodynamic manner.

As described in Scheme 3, the redox systems are the negative oxidant/electroneutral reductant, such as Fe(CN)$_6^{3-}$/DMFC, Ru(CN)$_6^{3-}$/DMFC, IrCl$_6^{3-}$/DMFC and Ru(CN)$_6^{3-}$/ZnPor. In this case, their manners are quite similar: as the defined potential ($\Delta_{\phi}$) increases, the surface concentration of the negative oxidant in the aqueous phase decreases with little changes in the organic phase. Thus, the apparent rate constant decreases reversely with the increase of the applied potential. Obviously, the $z_{FC}$ will display a negative value (as shown in Table 1). From previous reports,$^{10d,12}$ the results of $z_{FC}$ including Fe(CN)$_6^{3-}$/DMFC at the water/1,2-dichloroethane interface and Ru(CN)$_6^{3-}$/ZnPor at the water/benzene interface are both negative being −0.44 and −0.05, respectively, which agrees well with the above analysis. Why does the $z_{FC}$ of Ru(CN)$_6^{3-}$/ZnPor reaction systems approach zero? It can be found that it is quite reasonable because the low dielectric constant of the organic solvent of benzene leads to low ratio of the diffuse layer potential drop in water (i.e., ca. 2%).

![Scheme 2](image1.png)  
**Scheme 2** Illustration of the absence of the surface concentration effect when the species are charge neutral. $C_i^{\uparrow}$ ($i = O, W$) is the surface concentration in the $i$ phase. $\uparrow$ refers to increase and $\leftrightarrow$ means constant. In other schemes, $\uparrow \downarrow$ refers to further increase, $\uparrow$ and $\downarrow \downarrow$ have the opposite meanings.

![Scheme 3](image2.png)  
**Scheme 3** Illustration of depletion of surface concentration in water.
Sometimes, although the experimental results on the negative $\varepsilon_{FC}$ were ascribed to the Marcus inverted region by ET theory or others, it is suggested more reasonably as a simple diffuse layer effect.

Scheme 4 shows the behavior of redox systems of Fe(CN)$_6^{3-}$/TCNQ. With the increase of the applied potential ($\Delta^0\phi$) the surface concentration in the aqueous phase also increases without any changes in the organic phase. So the $\varepsilon_{FC}$ will be positive (as shown in Table 1). As reported in ref. 11, the $\varepsilon_{FC}$ of this reaction systems is 0.68 in the condition of ion-strength being 0.1 M (NaCl) in water. In this case, the ratio of the diffuse layer potential in the aqueous phase to the total potential is given at 17%, suitable for the potential distribution at the water/1,2-dichloroethane interface. Although the nature of this system has been often considered as a typical ET manner, it should be more reasonable as a thermodynamic behavior as described above.

Scheme 5 shows the accumulation of the surface concentration in each phase with the increase of the applied potential ($\Delta^0\phi$) among these redox systems, such as ZnPor$^+$/Ru(CN)$_6^{4-}$, Fe$^+$/Fe(CN)$_6^{4-}$ and DMFC$^+$/Fe(CN)$_6^{4-}$. Thereby the $\varepsilon_{FC}$ will be a positive value (as shown in Table 1). From the previous report about ZnPor$^+$/Ru(CN)$_6^{4-}$ at the water/benzene interface, the slope of the relationship is 0.5; another report including Fe$^+$/Fe(CN)$_6^{4-}$ and DMFC$^+$/Fe(CN)$_6^{4-}$ at the polarized water/o-nitrophenyl octyl ether interface is 1.62 and 1.09, respectively, whose signs are all in accord with our analysis. However, on the basis of eqn (24), suppose that an appropriate ratio of the diffuse layer potential in benzene to the total potential is $\approx 0.5$, which distinguishes largely from the experimental result of 0.5. We surmise that it may originate from the experimental error by curve fitting. On the similar hypothesis, the results (1.62 and 1.09) at the polarized water/o-nitrophenyl octyl ether interface are really close to the theoretical $\varepsilon_{FC}$ of 1.3. Clearly, such large values can be perfectly interpreted by the thermodynamic mechanism unimaginable for kinetic manner.

For the reaction systems Fe(CN)$_6^{3-}$/TCNQ, the situation can be shown in Scheme 6: as the applied potential ($\Delta^0\phi$) increases, the surface concentration of Fe(CN)$_6^{3-}$ decreases but that of TCNQ$^-$ increases. When in a low range of the applied potential, the case of accumulation in the organic phase will play a dominant role meaning a positive $\varepsilon_{FC}$ (as shown in Table 1); when in a high range of the applied potential, the depletion effect on the surface concentration in the aqueous phase will play another dominant role showing a negative $\varepsilon_{FC}$ (as shown in Table 1). The previous report about these reaction systems exhibited an inverted region, which was considered to be a kinetic inverse as Marcus predicted. However, we consider that it is not a so-called kinetic behavior but just an opposite diffuse layer effect. A detailed analysis can be given as follows: when the ratio of the diffuse layer potential in the aqueous phase to the total applied potential varies from 15% to 30% on changing the applied potential, according to eqn (24) the $\varepsilon_{FC}$ will vary from 0.4 to $-0.2$ resulting in a thermodynamic inverted region. The hypothesis on this changing ratio (from 15% to 30%) is also in accordance with the electrostatic theory and simulation based on Gouy–Chapman theory. So the observation from ref. 15 should be ascribed to the opposite surface concentration effect. So far, we only find two true kinetic inverses reported by Unwin et al. and Bard et al., where the authors changed the standard potentials of a variety of species in the aqueous phase instead of changing the applied potential.

Conclusions

All in all, owing to the particular structure of ITIES, a variation of the applied potential cannot change the driving force of ET, which is totally different from the manner at metal/solution interfaces. The truth of variations of the applied potential at the ITIES is a thermodynamic behavior called diffuse layer effect, just like Schmickler said: “If the main arguments of our work are correct, we cannot hope to learn much about ET reactions at liquid/liquid interfaces by studying their potential dependence, since this mainly amounts to changing the concentration. On the other hand, it should then be possible to use a redox reaction as a probe to explore the distribution of the potential at the interface.”

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Notes and references


