Potential-Independent Electron Transfer Rate at the Liquid/Liquid Interface

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Abstract: Electron transfer (ET) from neutral zinc porphyrin (ZnPor) molecules in various organic solvents to aqueous redox species (e.g., $Ru(CN)_6^{3-}$) was probed by the scanning electrochemical microscope (SECM). Unlike previous studies in which organic redox species were charged, the ET rate was found to be essentially independent of the potential drop across the interfacial boundary. This difference is explained by diffuse double-layer effect predicted by known models of the liquid/liquid interface. The effect of solvent dynamics on the rate of ET at the liquid/liquid interface was observed for the first time. The high precision and sensitivity of the SECM allow one to detect complexity in an interfacial reaction that may not be obvious from other electrochemical measurements and select a suitable system for checking the ET theory.
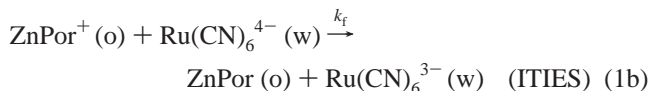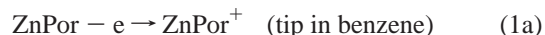
Introduction

The emerging interest in studies of electron transfer (ET) processes at the interface between two immiscible electrolyte solutions (ITIES) during last several years is due to its fundamental importance and a number of novel applications from artificial photosynthesis[1] to liquid redox extraction.[2] Several recently developed electrochemical[3,4] and spectro-electrochemical[5] techniques allow kinetic measurements and mechanistic studies of this process which were problematic just a few years ago.[6] One of fundamental questions addressed by these studies is about driving force for ET reaction. Following the approach of Schiffrin and co-workers,[7a] in many recent experimental studies one phase contained concentrated redox species and was considered to be metal-like. Similar to metal/solution electrochemistry, heterogeneous ET was assumed to be driven by the potential drop across the interfacial boundary (for the ITIES this is the difference of Galvani potentials of the organic and aqueous phases, $\Delta_w^o\varphi$[6]). Accordingly, the dependence of the ET rate constant on $\Delta_w^o\varphi$ should be exponential (Butler−Volmer kinetics) at low overpotentials and level off at much higher overpotentials according to Marcus theory.[8] This was either an explicit[7] or an implicit[8] assumption in most theoretical and experimental studies.

One should notice that the Butler−Volmer equation is applicable only if most of the interfacial potential drop occurs between the reacting redox moieties. This assumption is in conflict with a widely accepted three-layer model of the ITIES[9−11] proposed by Girault and Schiffrin and further developed by Schmickler. According to this model, the ET rate constant is essentially potential-independent because the potential drop across the compact part of the double-layer at the ITIES is small. The apparent dependence of the ET rate on $\Delta_w^o\varphi$ is due to the diffuse layer effect similar to Frumkin effect at metal electrodes.[12] Deviations from Butler−Volmer equation at the ITIES have been observed experimentally.[5,7b] However, only one group has previously reported potential-independent ET rate at the ITIES,[13] and those results are somewhat less reliable because of the transfer of ferrocenium ion that could occur simultaneously with ET.[6,7a]

Scanning electrochemical microscopy (SECM) was recently employed to probe ET at the ITIES.[3] In those experiments the ultramicroelectrode (UME) tip was positioned in the top, benzene (BZ), layer containing zinc porphyrin (ZnPor) and approached the bottom, aqueous, layer containing $Ru(CN)_6^{4-}$. The redox reactions at the tip and the ITIES were as follows:

$$ZnPor - e \rightarrow ZnPor^+ \quad \text{(tip in benzene)} \quad (1a)$$

$$ZnPor^+ (o) + Ru(CN)_6^{4-} (w) \xrightarrow{k_f}$$
$$ZnPor (o) + Ru(CN)_6^{3-} (w) \quad \text{(ITIES)} \quad (1b)$$

The ET rate constant of reaction 1b was evaluated from the tip

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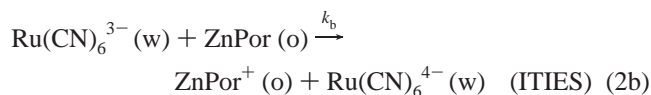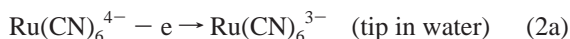
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current vs distance curves. The ln k_f vs $\Delta_w^o\varphi$ dependence obtained by varying $[ClO_4^-]_w$ was linear with a transfer coefficient, $\alpha = 0.5$, as expected from the Butler−Volmer model. However, the results of ref 3b do not allow one to unambiguously distinguish between the predictions of two models. According to Schmickler's model,[11] the observed increase in ET rate with the $\Delta_w^o\varphi$ can be attributed to accumulation of ZnPor$^+$ at the interface rather than to increasing driving force for ET.

Here, we identify the origin of the apparent potential dependence of the ET rate by measuring the kinetics of the reverse ET reaction. In this case the tip UME is positioned in the aqueous phase containing $Ru(CN)_6^{4-}$ and approaches the organic layer containing ZnPor:

$$Ru(CN)_6^{4-} - e \rightarrow Ru(CN)_6^{3-} \quad \text{(tip in water)} \quad (2a)$$

$$Ru(CN)_6^{3-} (w) + ZnPor (o) \xrightarrow{k_b}$$
$$ZnPor^+ (o) + Ru(CN)_6^{4-} (w) \quad \text{(ITIES)} \quad (2b)$$

Unlike interfacial reaction 1b, the electron acceptor in eq 2b is anionic and the electron donor is a neutral species. If the Butler−Volmer model is operating, the k_b should increase exponentially when the organic phase is made more negative. However, the concentration of the neutral ZnPor at the interface is potential-independent, and the interfacial concentration of negatively charged $Ru(CN)_6^{3-}$ decreases with increasing negative value of $\Delta_w^o\varphi$. Since almost all interfacial voltage drops within the diffuse layer in organic solvent[5b] the effect of $\Delta_w^o\varphi$ on surface concentration of $Ru(CN)_6^{3-}$ is small. Therefore, Schmickler's model predicts that the rate of the reaction 2b is practically independent of $\Delta_w^o\varphi$.

Another question addressed below is the evaluation of suitability of an interfacial reaction as a model system for ET studies. Unlike heterogeneous ET at the electrode/electrolyte interface, analogous reactions at the ITIES are less directly accessible by electrochemical measurements. When the overall reaction is more complex than a simple second-order ET process, this may not be apparent from the voltammetric response. For example, Shi and Anson[4b] recently measured the rate constants for a number of ET reactions at the ITIES which appeared to be essentially independent of the difference between standard potentials of two redox couples (ΔE^o). Although a satisfactory explanation of these results has yet to be found, it was suggested that the mechanism of studied reactions may be more complex than cross-phase bimolecular ET. Here, we propose to use the SECM as the diagnostic tool for detecting mechanistic complexity of the interfacial reaction and selecting suitable model experimental systems for checking the ET theory at the ITIES.

Experimental Section

NaClO$_4$, NaCl, 5,10,15,20-tetraphenyl-21H,23H-porphine zinc (ZnPor), and 1,2-dichloroethane (DCE, 99.8% HPLC grade) from Aldrich (Milwaukee, WI), Na$_4$Fe(CN)$_6$ (Fisher Scientific, Fair Lawn, NJ) and decamethylferrocene (DMFc, Strem Chemicals, Newburyport, MA) were used as received. Tetrahexylammonium perchlorate (THAClO$_4$; Johnson Matthey, Ward Hill, MA) was recrystallized twice from an ethyl acetate/ether (9:1) mixture and dried under vacuum overnight at room temperature. Nitrobenzene (NB, >99%; Fluka Chemika, Switzerland) and benzene (BZ, spectrophotometric grade; Aldrich) solutions were washed with a larger volume of Milli-Q water several times before measurements to remove impurities from the organic phase. 7,7,8,8-
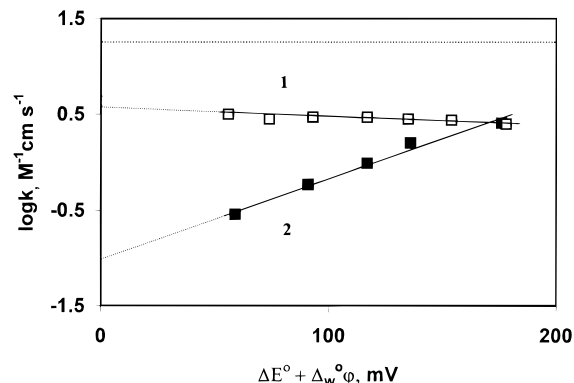
Figure 1. Potential dependence of the ET rate between ZnPor in BZ and $Ru(CN)_6^{3-}$ in water (curve 1) and an analogous dependence for the reverse ET reaction (curve 2, replotted from ref 3b,c). BZ contained (1) 2 mM ZnPor and 50 mM THAClO$_4$; and (2) 0.5 mM ZnPor and 0.25 M THAClO$_4$. The aqueous solution contained 0.01−2.0 M NaClO$_4$, 0.1 M NaCl and (1) 0.1 mM $Ru(CN)_6^{4-}$ or (2) 7 mM $Ru(CN)_6^{4-}$. The bimolecular rate constant, k, equals $k_b/[ZnPor]$ for reaction 2b and $k_f/[Ru(CN)_6^{4-}]$ for the reverse reaction 1b. ΔE^o is the difference between standard potentials of two redox couples. Horizontal dotted line shows the diffusion limit for the ET rate measurements by SECM under conditions corresponding to curve 1. The tip was biased at a potential corresponding to the plateau current of the oxidation wave of $Ru(CN)_6^{4-}$ (0.8 V vs Ag/AgCl; curve 1) or ZnPor (0.9 V vs Ag/AgCl; curve 2).

Tetracyanoquinodimethane (TCNQ) from Aldrich was recrystallized twice from ethyl acetate. All other chemicals were ACS reagent grade.

A three-electrode setup was employed with a 12.5-μm radius Pt UME tip, a Pt wire as the counter electrode, and a Ag/AgCl reference electrode. All electrodes were placed in the aqueous solution (top layer). The SECM apparatus and procedure and the electrochemical cell designed to keep a lower density solvent (BZ) under water were described previously.[3,14]

The potential drop across a nonpolarizable ITIES, $\Delta_w^o\varphi$, was determined by the concentrations of the common ion (e.g., ClO$_4^-$) in two phases. The concentration of perchlorate in the organic phase, $[ClO_4^-]_0 = 50$ mM was the same in most experiments, so $\Delta_w^o\varphi$ was governed by $[ClO_4^-]_w$:[3]

$$\Delta_w^o\varphi = \text{const} - S \log [ClO_4^-]_w \quad (3)$$

The slope, S, was found to be 56 mV/decade and 60 mV/decade for NB and DCE, respectively. A very similar (~60 mV/decade) slope was previously measured at the BZ/water interface.[3b] The use of the same potential scale allowed direct comparison of our results obtained in BZ to those in refs 3b,c. The driving force for ET reaction was expressed as $\Delta E^o + \Delta_w^o\varphi$. Although $\Delta_w^o\varphi$ cannot be found without an extrathermodynamic assumption,[6] the difference of two reversible half-wave potentials of organic and aqueous redox species measured with respect to the same Ag/AgCl reference electrode gives the absolute value of the driving force.[3c]

The concentration of ZnPor in organic phase ($\leq$5 mM) was limited by its solubility. The concentration of aqueous redox species was never higher than $[ZnPor]_0/20$ to avoid diffusion limitations in the bottom layer.[3] The dependencies of k_b on concentrations of redox species were measured and confirmed the first order of the interfacial reaction is both $Ru(CN)_6^{3-}$ and ZnPor.

Results and Discussion

Effects of $\Delta_w^o\varphi$ and ΔE^o on the Interfacial ET Rate. An experimental ln k_b vs $\Delta_w^o\varphi$ dependence obtained for reaction 2b at the BZ/water interface (curve 1 in Figure 1) fully confirms the prediction of the Schmickler's model. The k_b remained

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essentially constant within the limit of experimental error when the $\Delta_w^o\varphi$ was changed by about 120 mV. In contrast, the rate of the reverse reaction 1b increased more than 10 times over the same potential range (curve 2 in Figure 1[3b,c]). Both plots can be extrapolated to zero driving force ($\Delta E^o + \Delta_w^o\varphi = 0$) at which k_b and k_f should be equal in the absence of the double layer effect. The actual k_b/k_f ratio ($\sim$20) represents the magnitude of the diffuse layer effect on the ET rate constant at this potential.

While k_b is virtually independent of $\Delta_w^o\varphi$, it is expected to be a function of ΔE^o similarly to rate constants of homogeneous ET reactions.[8] Since the opposite observation was reported recently,[4b] we checked the dependence of the k_b on $\Delta_w^o\varphi$ by replacing $Ru(CN)_6^{4-}$ with $Fe(CN)_6^{4-}$. Because the formal potential of the $Fe(CN)_6^{3/4-}$ couple is $\sim$500 mV less positive, the replacement should result in about 4 orders of magnitude decrease in k. Accordingly, the interfacial reaction between ZnPor and $Fe(CN)_6^{3-}$ was immeasurably slow under our experimental conditions.

Attributing the Butler–Volmer-type dependence of k vs $\Delta_w^o\varphi$ for ET involving charged organic redox species[3b] to the diffuse layer effect may be surprising because of the very small dielectric constant of BZ ($\sim$2.2). Under these conditions most ZnPor$^+$ species should be ion paired. However, this may not be so in the interfacial region. A recent work by Eisenthal and co-workers[15] showed that the polarity of the liquid/liquid interface is the arithmetic average of the polarities of two immiscible solvents. Thus, the BZ/water interface is much more polar than the bulk BZ, and the extent of ion pairing at the phase boundary should be significantly smaller. The observed dependence of the rate constant on $\Delta_w^o\varphi$ reflects the work of bringing the charged reactant species to the interface (w_p), according to[9]

$$k_{obs} = Z \exp\left(-\frac{w_p}{RT}\right)k_{et} \tag{4}$$

where k_{obs} is the observed rate constant, Z is the preexponential factor, and k_{et} is the first-order rate constant of the ET reaction within the precursor formed at the interface.

In contrast, the observation of the Marcus inverted region for long-range ET across a phospholipid monolayer[3c] suggests the true potential dependence of the rate constant. The difference is that the long-chain lipid molecules prevented ZnPor from coming very close to the phase boundary, and therefore interfacial potential dropped mostly between redox reactants.

In previously reported SECM experiments,[3] it was possible (albeit unlikely) that ZnPor$^+$ species produced at the tip was transferred into the aqueous solution in which ET occurred via a homogeneous bimolecular reaction. The apparent potential dependence of the rate constant in this case would represent ion transfer rather than ET reaction. Such a complication is excluded in the present work since the organic reactant (ZnPor) is a neutral species practically insoluble in water, and the transfer of $Ru(CN)_6^{3-}$ in organic phase is not possible under our experimental conditions.

Solvent Effect on the ET Rate. To investigate the effects of organic solvent on interfacial ET the k_b vs $\Delta_w^o\varphi$ dependencies were obtained in BZ, nitrobenzene (NB), and 1,2-dichloroethane (DCE) (Figure 2). For each of these solvents k_b is almost potential-independent. The slope of each k_b vs $\Delta_w^o\varphi$ curve reflects the competition between the concentration effect in water

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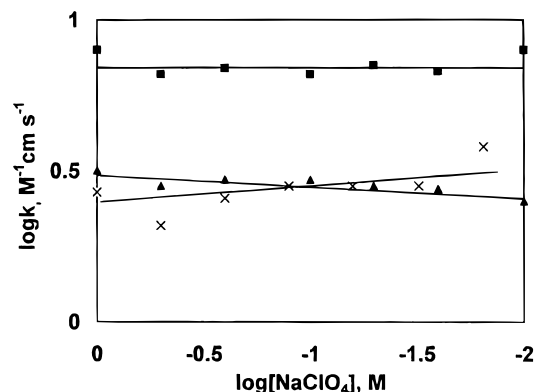
Figure 2. Solvent effect on the ET rate constant. The ET rate constants ($k = k_b/[\text{ZnPor}]$ for the reaction 2b) were measured at the interface between aqueous solution and BZ (▲), NB (×), and DCE (■). See Figure 1, curve 1 for compositions of the aqueous and organic phases. $\Delta_w^o\varphi$ is expressed in terms of log $[\text{ClO}_4^-]_w$.

Table 1. Optical (ϵ_{op}) and Static (ϵ_s) Dielectric Constants and Longitudinal Relaxation Times (τ_L) of NB and DCE[17]

solvent	ϵ_{op}	ϵ_s	$1/\epsilon_{op} - 1/\epsilon_s$	τ_L, ps
NB	2.40	34.8	0.388	5.3
DCE	2.08	10.4	0.385	1.6

(i.e., depletion of $Ru(CN)_6^{3-}$ at the ITIES at higher $[\text{NaClO}_4]$ corresponding to more negative $\Delta_w^o\varphi$) and change in driving force for ET produced by a small fraction of interfacial voltage dropping within the mixed layer. A very small negative slope for BZ/water interface indicates that diffuse layer effect in the aqueous phase in this case is very weak. This is not surprising because almost all $\Delta_w^o\varphi$ drops in BZ diffuse layer (for more polar DCE this fraction is about 95%;[5b] for less polar BZ is should be even larger).[9,11] With more polar DCE, the concentration effect in the aqueous phase is strong enough to counterbalance minor decrease in ET rate constant caused by a slightly smaller driving force at more positive $\Delta_w^o\varphi$. Hence a virtually zero slope of the k_b vs $\Delta_w^o\varphi$ curve. The diffuse layer effect on the aqueous side of the NB/water interface predominates and results in a small positive slope of the potential dependence.

The nature of organic solvent can affect the value of the ET standard rate constant at the ITIES in two ways: (i) through the Pekar factor, $1/\epsilon_{op} - 1/\epsilon_s$, where ϵ_{op} and ϵ_s are the optical and static dielectric constants of organic phase; and (ii) through longitudinal solvent relaxation time, τ_L. Solvent effects have previously been reported for homogeneous and electrochemical ET reactions[16] but not for ET at the ITIES. The Pekar factor values are similar for NB and DCE[17] (Table 1). In contrast, the relaxation time for DCE is significantly smaller (Table 1) and the measured rate constant is about three times higher, as can be expected from the theory.[8,16] A direct comparison of this results to those obtained in BZ is difficult because for the latter solvent ϵ_{op} and ϵ_s are similar and no relaxation data is available.

Precision of SECM Measurements and the Choice of a Suitable Model System for ET Studies. The rate constant values in Figures 1 and 2 were obtained from the best fit of the experimental tip current vs distance curves to the previously developed theory.[3a] A typical experimental curve (symbols) and the corresponding to theoretical dependence (solid line 1) are shown in Figure 3A. A very good fit between the experimental

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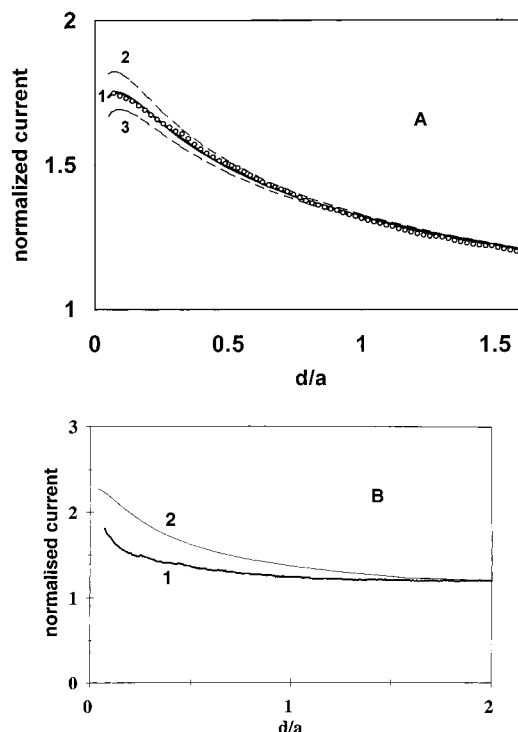
Figure 3. Theoretical and experimental approach curves for ET reactions at the ITIES. A 12.5-μm radius Pt tip UME in aqueous solution was scanned at 1 μm/s. (A) NB was 2 mM in ZnPor and 0.05 M in THAClO$_4$. The aqueous solution contained 0.1 M NaCl, 60 mM NaClO$_4$, and 0.1 mM Na$_4$Ru(CN)$_6$. The tip potential was held at 0.8 V vs Ag/AgCl, corresponding to the plateau current of first oxidation of Ru(CN)$_6^{4-}$. Solid curve 1 represents the best theoretical fit obtained with k_b = 0.0055 cm/s. Curves 2 and 3 were calculated using the k_b values 5% larger (i.e., 0.00577 cm/s) and 5% smaller (i.e., 0.00522 cm/s) than the k_b found from the best fit. (B) Curve 1, DCE was 10 mM in TCNQ and 10 mM in tetrabutylammonium tetraphenylborate (TBATPB). The aqueous solution contained 0.1 M KCl, 50 mM TBACl, and 0.5 mM K$_3$Fe(CN)$_6$. The tip potential was held at 0.04 V vs Ag/AgCl, corresponding to diffusion-controlled reduction of Fe(CN)$_6^{3-}$. Curve 2 is the theory for k_b = 0.016 cm/s.

and theoretical curves results in a low uncertainty in calculated rate constants. The differences between experimental data and theoretical curves calculated using a 5% larger (curve 2) or smaller (curve 3) rate constant value are very significant. Each rate constant value in Figures 1 and 2 was obtained by averaging the results of at least five experiments, and the relative uncertainty is always no more than 5%.

The high precision of measurements of ET rates by SECM and its sensitivity to surface reactions allow one to use this technique for selecting experimental systems suitable for kinetic measurements at the ITIES. A few interfacial ET reactions previously probed by voltammetry (either conventional[7a] or thin layer based[4]) or impedance methods[5,7b] are supposed to be mechanistically simple and suitable as model experimental systems. Those include oxidation of decamethylferrocene (DMFc) by ferricyanide[4b] and reduction of 7,7,8,8-tetracyano-quinodimethane (TCNQ) by ferrocyanide.[5a,18] Probing both reactions by SECM revealed additional complexity in their mechnisms. Figure 3B shows our attempt to fit a typical current/distance curve for TCNQ/Fe(CN)$_6^{4-}$ reaction to the theory. Clearly, the curvature of the experimental curve is different and no satisfactory fit can be obtained (cf. Figure 3A). We obtained a number of approach curves for this system using different

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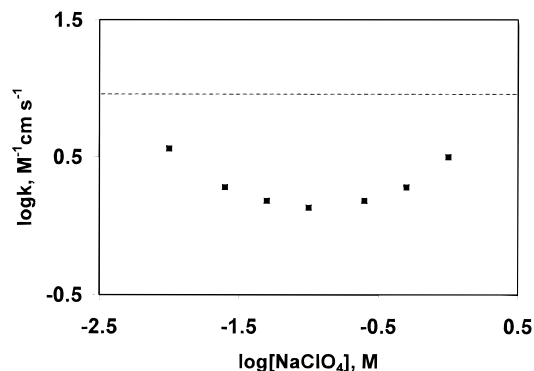
Figure 4. Potential dependence of the ET rate between DMFc in DCE and Fe(CN)$_6^{3-}$ in water. DCE contained (1) 2 mM DMFc and 50 mM THAClO$_4$. The aqueous solution contained 0.01−1.0 M NaClO$_4$, 0.1 M NaCl, and 0.1 mM Fe(CN)$_6^{4-}$. Horizontal dashed line shows the diffusion limit for the ET rate measurements.

solvents (NB, DCE) and different concentrations of redox species and supporting electrolytes. Under no conditions was it possible to fit experimental data to the theory for a simple heterogeneous reaction.

In the case of the ET from DMFc to Fe(CN)$_6^{3-}$ the experimental approach curves fit the theory reasonably well. However, the k vs $\Delta_w^o\varphi$ dependence (Figure 4) is at variance with known ET theories and models of the ITIES. The appearance of a minimum in this curve (confirmed by repeated measurements in NB and DCE) indicates additional complexity of the mechanism and suggests that one has to be very cautious using this reaction as a model system for ET studies at the ITIES.

Conclusions

Our results indicate that the rate constant of ET across the ITIES is essentially independent of interfacial potential drop when the organic redox reactant is a neutral species. This result is in agreement with the widely accepted three-layer model of the ITIES.[9−11] The Butler−Volmer-type dependence of k vs $\Delta_w^o\varphi$ for ET involving charged organic species[3b] may be attributed to the diffuse layer effect. However, when a spacer (e.g., a molecular monolayer of a long-chain lipid[3c]) prevents the reactants from coming very close to the phase boundary, the interfacial voltage drops between the aqueous and organic redox species, and the true potential dependence of the rate constant can be observed.

The solvent dynamics effect on ET at the ITIES was observed for the first time. The rate of the ET from ZnPor to Ru(CN)$_6^{3-}$ at the DCE/water interface was about three times as fast as the analogous reaction at the NB/water interface.

The choice of mechanistically simple processes for probing ET at the ITIES is less obvious than for studies of homogeneous ET reactions in solution or heterogeneous ET at metal electrodes. Some processes previously expected to be one-step bimolecular reactions (e.g., DMFc/Fe(CN)$_6^{3-}$ or TCNQ/Fe(CN)$_6^{4-}$) were probed by SECM and exhibited more complex behavior. They may not be suitable as model experimental systems. Work is in progress to clarify the origins of interfacial complexity in these systems.