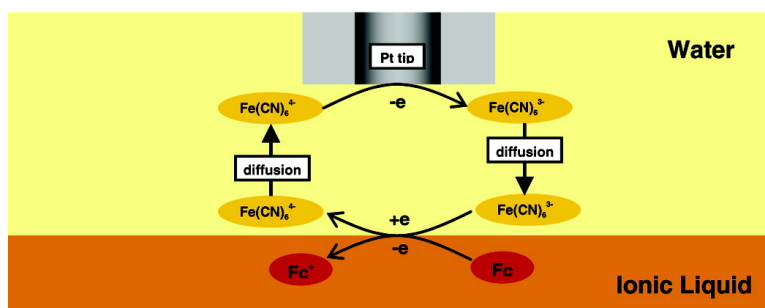


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Comparative Study of Electron Transfer Reactions at the Ionic Liquid/Water and Organic/Water Interfaces

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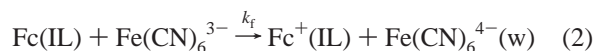
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We wish to report the first measurement of electron transfer (ET) kinetics at the interface between water and a hydrophobic ionic liquid (IL). All previous studies of charge-transfer processes at liquid interfaces were carried out at the water/organic solvent phase boundary. Therefore, our objective was to uncover the differences between ET kinetics at water/organic and water/IL interfaces. Scanning electrochemical microscopy (SECM) was used to measure standard bimolecular rate constant of the interfacial ET between ferrocene dissolved in IL and aqueous ferricyanide ($0.4 \text{ M}^{-1} \text{ cm s}^{-1}$), which was found to be more than 1 order of magnitude higher than the corresponding rate constant measured at the water/organic solvent interface. The Butler–Volmer-type driving force dependence of the ET rate was measured over a wide range of the interfacial potential drop values ($>200 \text{ mV}$). We also probed the ET reaction at the interface between aqueous solution and the mixture of the IL and 1,2-dichloroethane (DCE). By varying systematically the mole fractions in this mixture, one can investigate the transition from the water/organic to the water/IL interface.

The active current interest in IL is due to their applications in synthesis, separations, batteries, and fuel cells.^{1–3} The understanding of mechanisms of heterogeneous processes occurring at the IL/water interface is essential for these applications. The major differences between ILs and conventional organic solvents, i.e., significantly higher viscosity of and very high ionic concentrations in ILs,⁴ can be expected to influence the dynamics of interfacial ET reactions.

SECM has previously been employed to probe ET at the water/organic solvent interface.⁵ Using the feedback approach (Figure 1a), in our experiments the tip electrode was positioned in the top (aqueous) layer containing ferrocyanide and approached the bottom layer, i.e., 1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($\text{C}_8\text{mimC}_1\text{C}_1\text{N}$) containing ferrocene (Fc).⁶ The tip was biased at a potential where the oxidation of aqueous $\text{Fe}(\text{CN})_6^{4-}$ occurs at a diffusion-limited rate. The mediator was regenerated through the interfacial ET reaction 2:



The nonpolarizable IL/water interface was poised by the concentration of the common ion in water (i.e., either C_8mim^+ or $\text{C}_1\text{C}_1\text{N}^-$), providing a controllable driving force for the ET reaction.^{7a} With the constant concentrations of C_8mim^+ and $\text{C}_1\text{C}_1\text{N}^-$ in the IL phase, the interfacial potential drop ($\Delta_w^{\text{IL}} \varphi$) is^{8a}

$$\Delta_w^{\text{IL}} \varphi = \text{const} + 0.059 \log[\text{C}_8\text{mim}^+]_{\text{w}} \quad (3a)$$

or

$$\Delta_w^{\text{IL}} \varphi = \text{const} - 0.059 \log[\text{C}_1\text{C}_1\text{N}^-]_{\text{w}} \quad (3b)$$

The slopes of experimental dependences of the driving force for the interfacial ET vs $[\text{C}_8\text{mim}^+]_{\text{w}}$ and $[\text{C}_1\text{C}_1\text{N}^-]_{\text{w}}$ are 58.6 mV/decade and 58.2 mV/decade, respectively (Figure 1b).

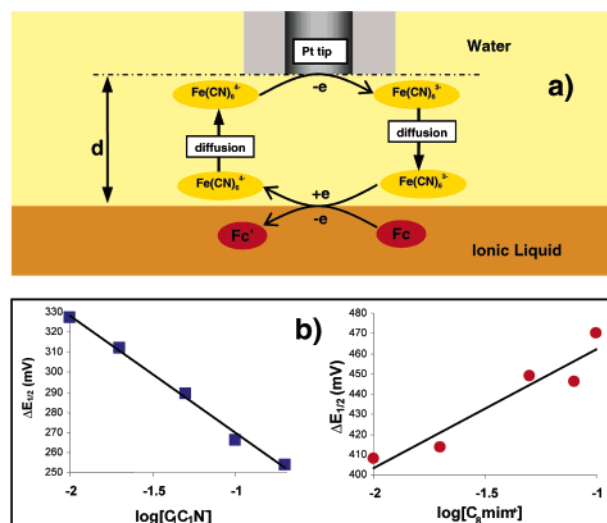


Figure 1. (a) Schematic diagram of SECM measurements of the kinetics of ET between Fc in IL and $\text{Fe}(\text{CN})_6^{3-}$ in water. (b) Dependence of the driving force on concentration of the common ion in the aqueous phase. The driving force for reaction 2 was evaluated as the difference of the half-wave potentials of ferrocyanide and Fc measured with respect to the same aqueous Ag/AgCl reference electrode.^{7a}

The rate constant of reaction 2 was extracted from the current vs tip-interface distance ($i_T - d$) curves.⁵ The driving force dependence of the effective bimolecular rate constant (Figure 2) was found to be linear over a wide potential range ($\sim 220 \text{ mV}$). One should notice that the k values obtained by varying either C_8mim^+ (green symbols) or $\text{C}_1\text{C}_1\text{N}^-$ (blue symbols) concentration in water lie on the same straight line. The orange point was obtained without adding any common ion to the aqueous phase, so that equal concentrations of C_8mim^+ and $\text{C}_1\text{C}_1\text{N}^-$ were generated by dissolution of $\text{C}_8\text{mimC}_1\text{C}_1\text{N}$ in water. The slope of the linear Butler–Volmer dependence in Figure 2 yields the transfer coefficient, $\alpha = 0.34$, which is similar to the values previously measured at the water/organic interface.⁵ Since the organic reactant (Fc) is a neutral species, the observed strong potential dependence of k suggests that a major fraction of the interfacial voltage drops between the electron donor and the acceptor. This could be expected because

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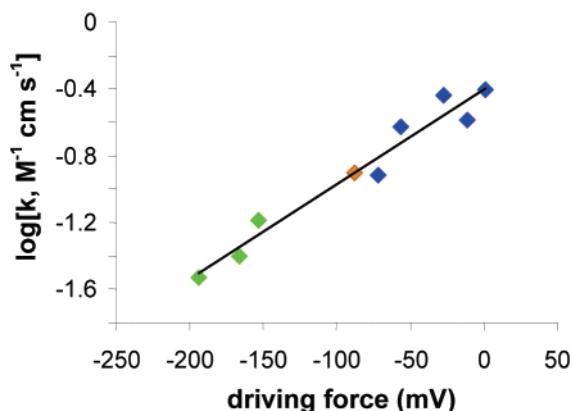


Figure 2. Potential dependence of the interfacial ET rate. IL contained 100 mM Fc. The aqueous solution contained 200 μM $\text{Fe}(\text{CN})_6^{4-}$. The tip was a 5.3- μm -radius Pt microdisk. The bimolecular rate constant, k , equals $k_t/[\text{Fc}]$.

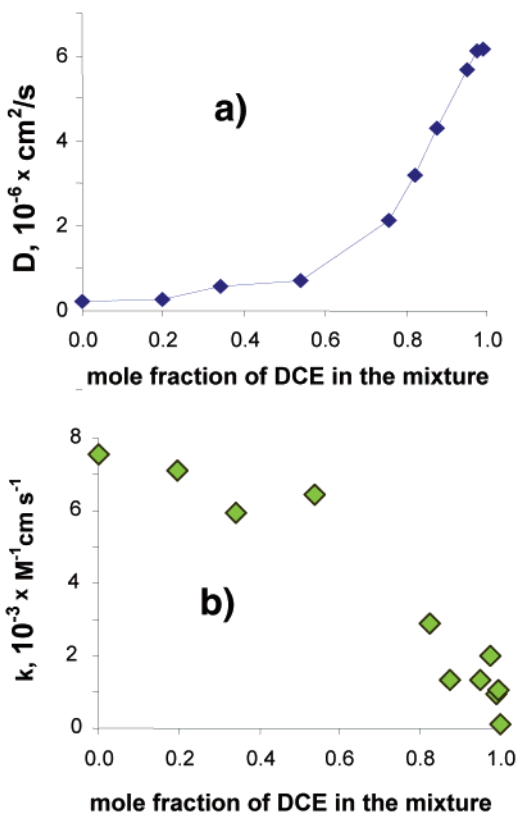


Figure 3. Dependences of the diffusion coefficient (a) and interfacial ET rate (b) on the mole fraction of DCE in its mixture with IL. The aqueous phase contained 200 μM ferrocyanide, 20 mM $\text{LiC}_1\text{C}_1\text{N}$, and 230 mM KCl; DCE/IL mixture contained 100 mM 1,1-diethylferrocene.

high ionic concentrations in IL should produce a relatively thin diffuse double layer, in contrast to a low-polarity organic phase (e.g., DCE).¹⁰

The standard rate constant value extracted from Figure 2 is more than 1 order of magnitude larger than that measured at the DCE/water interface. The larger rate constant may be related to significant differences in viscosity, polarity, or double layer properties in IL as compared to analogous parameters in DCE.^{10,11} The changes in viscosity and ET rate constant that accompany the transition from

the water/DCE to water/IL interface can be seen in Figure 3. The diffusion coefficient of 1,1'-diethylferrocene in the DCE/IL mixture increased monotonically with increasing mole fraction of DCE in the mixture (Figure 3a); the D value in DCE is ~ 45 times that in IL. At the same time, the k value obtained with a constant concentration of $\text{C}_1\text{C}_1\text{N}^-$ in water (i.e., without major changes in the driving force for ET) decreased by a factor of ~ 50 with increasing mole fraction of DCE (Figure 3b). This finding is in a sharp contrast with often observed direct correlation between the rate constant and diffusion coefficient values at the metal/liquid interface.¹² The k value at the IL/water interface should be proportional to the electrochemical rate constant measured for the same redox species in IL.¹¹ However, the electrochemical rate constant of Fc oxidation recently measured in a 1-alkyl-3-methylimidazolium-based ionic liquid was about 1 order of magnitude lower than the corresponding values obtained in various organic solvents.¹³ Therefore, one has to conclude that some interfacial factor (e.g., the thickness or the polarity of the phase boundary) makes the rate of the ET in the water/IL system faster than at the water/DCE interface. The observed dependences may also have been affected by adsorption of C_8mim^+ ^{8b} at the DCE/water interface or by ion pairing of Fc^+ with $\text{C}_1\text{C}_1\text{N}^-$.

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References

- (1) Rogers, R. D.; Seddon, K. R. *Science* **2003**, *302*, 792.
- (2) *Ionic Liquids in Synthesis*; Wasserscheid, P., Welton, T., Eds.; Wiley-VCH: Weinheim, Germany, 2003.
- (3) *Green Industrial Applications of Ionic Liquids*; Rogers, R. D., Seddon, K. R., Volkov, S., Eds.; NATO Science Series, Vol. 92. Kluwer: Dordrecht, The Netherlands, 2002.
- (4) Noda, A.; Hayamizu, K.; Watanabe, M. *J. Phys. Chem. B* **2001**, *105*, 4603.
- (5) Mirkin, M. V.; Tsionsky, M. In *Scanning Electrochemical Microscopy*; Bard, A. J., Mirkin, M. V., Eds.; Marcel Dekker: New York, 2001; p 299.
- (6) (a) A three-electrode setup was employed with a 5.3- μm -radius Pt UME tip, a Pt wire as the counter electrode, and a Ag/AgCl reference electrode. The denser ionic liquid formed a drop at the bottom of the electrochemical cell when the latter was filled with the aqueous solution. All electrodes were placed in the aqueous solution (top layer) except for the measurements of the formal potential of Fc in IL where the working electrode was immersed in IL. The SECM apparatus and procedure were described previously.⁷ $\text{C}_8\text{mimC}_1\text{N}$ was synthesized as described previously.^{8a} The room-temperature solubilities of IL in water and water in IL are 1.7 mM and 0.9 wt %, respectively.^{8a} The concentration of Fc in IL was limited by its solubility. The concentration of aqueous redox species was never higher than $[\text{Fc}]/500$ to avoid diffusion limitations in the bottom layer,⁹ and the concentration of KCl in the aqueous phase was adjusted to maintain a constant ionic strength of 250 mM. For more details of data analysis including the separation of ET and Fc partitioning processes see ref 6b. (b) Laforge, F. O.; Kakiuchi, T.; Shigematsu, F.; Mirkin, M. V. *J. Phys. Chem. B*, to be submitted for publication.
- (7) (a) Tsionsky, M.; Bard, A. J.; Mirkin, M. V. *J. Phys. Chem.* **1996**, *100*, 17881. (b) Liu, B.; Mirkin, M. V. *J. Am. Chem. Soc.* **1999**, *121*, 8352.
- (8) (a) Kakiuchi, T.; Tsujioka, N.; Kurita, S.; Iwami, Y. *Electrochem. Commun.* **2003**, *5*, 159. (b) Kakiuchi, T.; Shigematsu, F.; Kasahara, T.; Nishi, N.; Yamamoto, M. *Phys. Chem. Chem. Phys.* **2004**, *6*, 4445.
- (9) Barker, A. L.; Unwin, P. R.; Amemiya, S.; Zhou, J.; Bard, A. J. *J. Phys. Chem. B* **1999**, *103*, 7260.
- (10) (a) Girault, H. H.; Schiffrin, D. J. *J. Electroanal. Chem.* **1988**, *244*, 15. (b) Schmickler, W. *J. Electroanal. Chem.* **1997**, *428*, 123.
- (11) (a) Marcus, R. A. *J. Phys. Chem.* **1990**, *94*, 1050. (b) Marcus, R. A. *J. Phys. Chem.* **1990**, *94*, 4152. (c) Marcus, R. A. *J. Phys. Chem.* **1991**, *95*, 2010.
- (12) Zhang, X.; Leddy, J.; Bard, A. J. *J. Am. Chem. Soc.* **1985**, *107*, 3719.
- (13) Lagrost, C.; Carrié, D.; Vaultier, M.; Hapiot, P. *J. Phys. Chem. A* **2003**, *107*, 745.

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