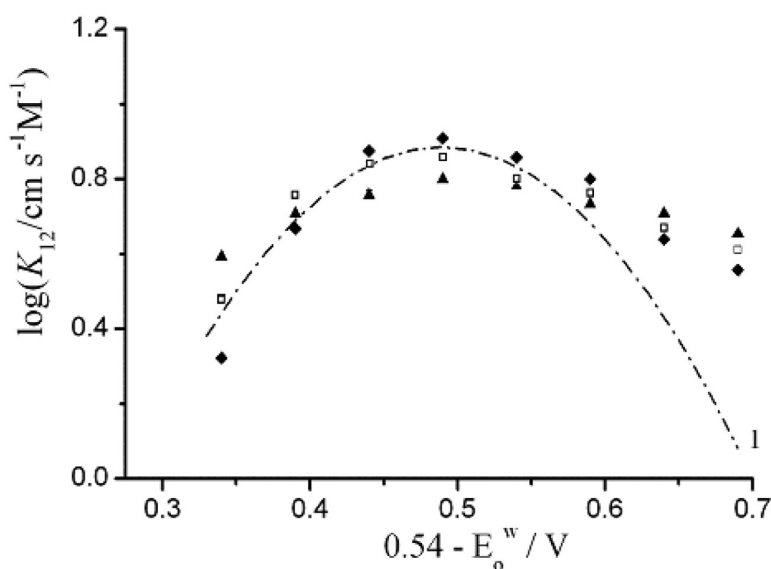Communication

Observation of the Marcus Inverted Region of Electron Transfer Reactions at a Liquid/Liquid Interface

Peng Sun, Fei Li, Yong Chen, Meiqin Zhang, Zhiquan Zhang, Zhao Gao, and Yuanhua Shao

More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 7 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

View the Full Text HTML

Observation of the Marcus Inverted Region of Electron Transfer Reactions at a Liquid/Liquid Interface

Peng Sun,[†] Fei Li,[†] Yong Chen,[†] Meiqin Zhang,[†] Zhiquan Zhang,[†] Zhao Gao,[†] and Yuanhua Shao*,[†,‡]

State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry of the Chinese Academy of Sciences, Changchun 130022, China, and College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

Received May 20, 2003; E-mail: yhshao@chem.pku.edu.cn

Because of the recent developments in scanning electrochemical microscopy (SECM), and spectroscopic and photoelectrochemical techniques, considerable progress has been made in studies of heterogeneous electron transfer (ET) reactions at an interface between two immiscible electrolyte solutions (ITIES) or at a liquid/liquid (L/L) interface.[1−5] The ability to precisely measure the rate constants of ET reactions makes it possible for one to seek experimental verifications of the Marcus theory and, in particular, to explore whether the Marcus inverted region actually exists at an ITIES.[4−8] The Marcus theory predicts that the rate constant of an ET reaction increases when the driving force is low and decreases when the driving force is high.[9] Bard et al. demonstrated the existence of a Marcus inverted region at a lipid modified ITIES by SECM.[4] They further extended the study of the Marcus inverted region to very exothermic ET reactions at an ITIES by a combination of SECM and electrogenerated chemiluminescence.[5] Recently, Girault et al. reported the study of the Marcus inverted region for a photoinduced ET at an externally polarized ITIES by analysis of the obtained photocurrents.[8]

Despite that several reports provided the observation of the Marcus inverted region, the mechanism of action of the Galvani potential difference, $\Delta\phi$, which is part of the driving force, has been an issue of debate.[4−8,10,11] Some experimental results demonstrate that $\Delta\phi$ mainly concentrates on the organic diffuse layer. Thus, both the potential dependence and the independence phenomena have been observed when different systems were used in the organic phase.[10,11] This problem is even more complicated when one probes the Marcus inverted region because almost all of the interfacial ET reactions studied by SECM have been carried out at a nonpolarized ITIES, where a common ion is used in both phases to control the $\Delta\phi$ at the ITIES.[2−7] This results in a rather limited controllable range of $\Delta\phi$. To increase the driving force, different redox couples in the aqueous phase have to be used to tune ΔE^0.[6,8] Thus, the reorganization energy and solvation structure are varied, making data analysis complicated.

We report here a new approach to investigate heterogeneous ET reactions at an ITIES. This approach involves the use of SECM with a three-electrode setup and adjustable concentration ratio of redox species in both phases. One of the important features of this approach is that the ITIES is externally polarized and a potential window of about 0.5 V is readily obtained when the supporting electrolytes are properly chosen.[12] As will be demonstrated below, for the two opposite heterogeneous ET processes being studied at the externally polarized water/1,2-dichloroethane (W/DCE) interface, the values of $\Delta\phi$ can be quantitatively controlled in a wide range, allowing precise measurements of the rate constants of the ET reactions. Meanwhile, the concentration ratio of the redox
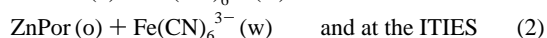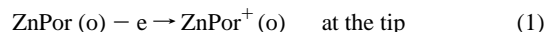
species in both phases can be adjusted to facilitate the analysis of the resultant data.

Scheme 1
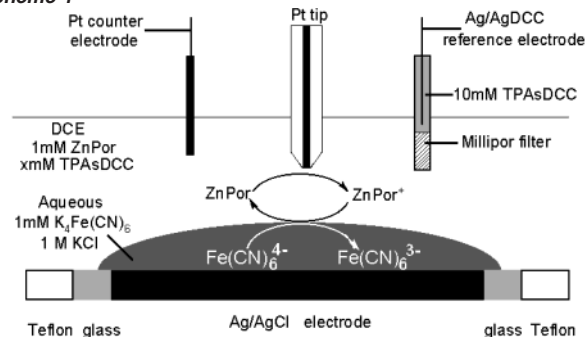
In our study, both 5,10,15,20-tetraphenyl 21*H*,23*H*-porphyrin zinc (ZnPor, O)/Fe(CN)$_6^{4−}$ (W) and TCNQ (O)/Fe(CN)$_6^{3−}$(W) are chosen as the redox couples in each phase as model systems. The former process undergoes first an oxidation at the SECM tip, and then it can be regenerated at the ITIES via the bimolecular reduction, whereas in the later case the reactions occur in the opposite direction. An Ag/AgCl electrode covered with the aqueous droplet containing 1 mM K$_4$Fe(CN)$_6$ (or K$_3$Fe(CN)$_6$) and 1 M KCl is immersed in DCE phase containing supporting electrolyte (tetraphenylarsonium cobaltdicarborane, TPAsDCC) and 1 mM ZnPor (or TCNQ) (the experimental setup is shown in Scheme 1). The W/DCE interface is polarized externally by the bipotentiostat of the SECM (CHI 900, CH Instruments) and scanned by a SECM tip (25 μm-diameter Pt disk tip, RG = 3[13]).

When the tip approaches the L/L interface and the potentials of the tip and the ITIES are properly controlled, the reactions both at the tip and at the ITIES can be summarized as follows:[4]

$$\text{ZnPor (o)} - \text{e} \rightarrow \text{ZnPor}^+ \text{(o)} \quad \text{at the tip} \quad (1)$$

$$\text{ZnPor}^+ \text{(o)} + \text{Fe(CN)}_6^{4-} \text{(w)} \rightarrow$$
$$\text{ZnPor (o)} + \text{Fe(CN)}_6^{3-} \text{(w)} \quad \text{and at the ITIES} \quad (2)$$

The relationship between the rate constant of a second-order ET, κ_{12}, and the energy of activation, $\Delta G^{\ddagger}$, can be written as follows:[4,6]

$$\kappa_{12} = \text{const} \exp(-\Delta G^{\ddagger}/RT) \quad (3)$$

For a lower overpotential, a Butler−Volmer type approximation can be employed:

$$\Delta G^{\ddagger} = -\alpha F(\Delta E^0 + \Delta\phi) \quad (4)$$

where α and F are the transfer coefficient and the Faraday constant, respectively. $\Delta E°$ is the difference between the standard potentials of the two redox couples in both phases.
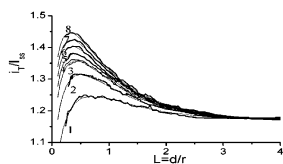
Figure 1. Normalized experimental approach curves fitted with theoretical values. As shown in Scheme 1, where $x = 10$ mM. Tip potential is 0.85 V, the substrate potentials are (1) 0.2 V, (2) −0.15 V, (3) −0.1 V, (4) 0.15 V, (5) −0.05 V, (6) 0.1 V, (7) 0.0 V, and (8) 0.05 V, respectively.
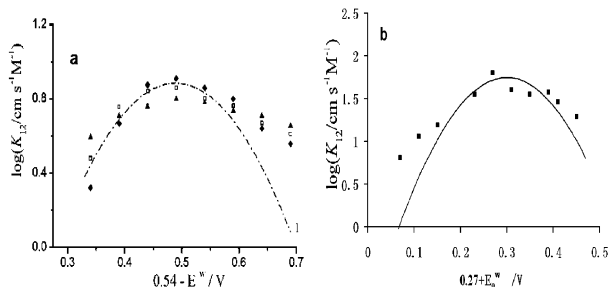

Figure 2. (a) Tafel plots for the system of ZnPor/Fe(CN)$_6^{4-}$ at different concentrations of organic electrolyte and the Marcus theoretical curve (1); the concentrations are (▲) 10 mM, (□) 50 mM, and (◆) 100 mM, respectively. (b) Tafel plot for the system of TCNQ/Fe(CN)$_6^{3-}$.

According to the Marcus theory, the energy of activation for an ET reaction can be simplified when the overpotential is high:[4,6]

$$\Delta G^{\ddagger} = (\lambda/4)(1 + \Delta G^0/\lambda)^2 \qquad (5)$$

where λ is the reorganization energy, and ΔG° is given by

$$\Delta G^0 = -F(\Delta E^0 + \Delta\phi) \qquad (6)$$

In this work, $\Delta E^0 + \Delta\phi$ is equal to $0.54 - E_o^w$ and $0.27 + E_o^w$ for the reduction of ZnPor$^+$ and oxidation of TCNQ$^-$ via the bimolecular reaction at the ITIES, respectively. E_o^w is the externally applied potential (see Supporting Information).

The experimental SECM approach curves (normalized tip currents vs the normalized distances between the tip and the substrate) fitted with theoretical values (the theoretical approach curves are calculated using the program provided by Dr. P. R. Unwin, et al.) at various potentials of the ITIES are shown in Figure 1. The shape of the approach curve is a peak when the tip is close to the ITIES and is similar to what was obtained at a nonpolarized ITIES for small K_r ($K_r = C_{Red2}/C_{Red1}$, in our cases $K_r = 1$).[7] Thus, it is possible to probe the same point in the whole experiment because the tip is not needed to touch the ITIES, and the rate constants can be evaluated by the best-fit of experimental data with theoretical values. The dependence of the $\log(\kappa_{12})$ on $\Delta E^0 + \Delta\phi$ is shown in Figure 2a. At lower applied potentials ($0.54 - E_o^w < 440$ mV), the Tafel plot increases sharply. When the applied potential is set at >440 mV, the values of $\log(\kappa_{12})$ in Figure 2a are increased slowly and reached a maximum at about 500 mV. They start to decrease slowly when the driving force exceeds 600 mV. These behaviors can only be explained by the Marcus theory.[9] A reorganization energy, λ, obtained from the best-fitting of the experimental curve, is 47.2 kJ/mol. These data are considered to be reliable on the grounds that the reproducibility of these experiments is excellent and 5−10% changes of rate constant can be clearly distinguished by SECM. There are deviations which may be due to the coupling reactions with supporting electrolyte in the DCE phase when the applied potentials are close to the ends of potential windows (for Figure 2a when $0.54 - E_o^w > 600$ mV, and for Figure 2b when $0.27 + E_o^w < 150$ mV).

It is likely that the concentration of organic supporting electrolyte may have some significant effect on ET reactions under study.

Because both the cation (ZnPor$^+$) and the anion (DCC$^-$) of the supporting electrolyte are large molecules, we have to make sure whether the ion pair (ZnPor$^+$DCC$^-$) formation can seriously affect our kinetic analysis. Our results demonstrate that the ion pair effect can be ignored (more information can be obtained in the Supporting Information). Figure 2a also provides the Tafel plots for different concentrations of the organic supporting electrolyte. As the concentration of organic supporting electrolyte increases, a Marcus inverted region becomes more evident, where $\log(\kappa_{12})$ varies with the potential drop across the ITIES. This is probably because the thickness of the diffuse layer becomes smaller and the ratio of the potential drop of the mixed layer to the potential drop across the ITIES becomes larger.

We also observed the Marcus inverted region for the ET reaction between TCNQ in DCE and Fe(CN)$_6^{3-}$ in the aqueous phase. The plot of $\log(\kappa_{12})$ versus the applied potential is shown in Figure 2b. In this system, the processes are just opposite to those studied in the ZnPor case. TCNQ is first reduced at the tip and then regenerated via the bimolecular reaction at the interface. The reorganization energy, λ, obtained from the best-fitting of the experimental curve, is 28.9 kJ/mol. This confirms that the ZnPor/Fe(CN)$_6^{4-}$ system is not a special case.

In conclusion, we have employed SECM with a three-electrode setup to investigate ET processes at an ITIES and have demonstrated unambiguously the observation of the Marcus inverted region for two totally different systems at a bare L/L interface. The only variable of the driving force is the interfacial potential difference, which can be precisely controlled externally. These preliminary results demonstrate that the newly developed approach is versatile, easy to implement, and potentially applicable to other systems.

Supporting Information Available: Experimental details for evaluation of the relation between the driving force and applied potential, and the determination of ion-pair formation (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Girault, H. H. In *Modern Aspects of Electrochemistry*; Bockris, J. O'M., Conway, B. E., White, R. E., Eds.; Plenum Press: New York, 1993; Vol. 25, p 1. (b) Reymond, F.; Fermin, D. J.; Lee, H. J.; Girault, H. H. *Electrochim. Acta* **2000**, *45*, 2647−2662.
(2) Amemiya, S.; Ding, Z.; Zhou, J.; Bard, A. J. *J. Electroanal. Chem.* **2000**, *483*, 7−17.
(3) Bard, A. J.; Mirkin, M. V. *Scanning Electrochemical Microscopy*; Marcel Dekker: New York, 2001.
(4) Tsionsky, M.; Bard, A. J.; Mirkin, M. V. *J. Am. Chem. Soc.* **1997**, *119*, 10785−10792.
(5) Zu, Y.; Fan, F.; Bard, A. J. *J. Phys. Chem. B* **1999**, *103*, 6272−6276.
(6) Ding, Z.; Quinn, B. M.; Bard, A. J. *J. Phys. Chem. B* **2001**, *105*, 6367−6374.
(7) Barker, A. J.; Unwin, P. R.; Amemiya, S.; Zhou, J.; Bard, A. J. *J. Phys. Chem. B* **1999**, *103*, 7260−7269.
(8) Eugster, N.; Fermin, D. J.; Girault, H. H. *J. Phys. Chem B.* **2002**, *106*, 3428−3433.
(9) (a) Marcus, R. A. *J. Phys. Chem.* **1990**, *94*, 4152−4155. (b) Marcus, R. A. *J. Phys. Chem.* **1991**, *95*, 2010−2013.
(10) Liu, B.; Mirkin, M. V. *J. Am. Chem. Soc.* **1999**, *121*, 8352−8355.
(11) Liu, B.; Mirkin, M. V. *J. Phys. Chem. B* **2002**, *106*, 3933−3940.
(12) (a) Zhang, Z.; Yuan, Y.; Sun, P.; Su, B.; Shao, Y.; Girault, H. H. *J. Phys. Chem. B* **2002**, *106*, 6713−6717. (b) Sun, P.; Zhang, Z.; Gao, Z.; Shao, Y. *Angew. Chem., Int. Ed.* **2002**, *41*, 3445−3448.
(13) RG is defined by *Rg/a*, where *Rg* and *a* are the radii of insulator glass and tip, respectively.

JA0362297