

Study of Electron Transfer across the Liquid/Ice-like Matrix Interface by Scanning Electrochemical Microscopy

Zhiquan Zhang,[†] Jinyou Ye,[‡] Peng Sun,[†] Yi Yuan,[†] Yuehong Tong,[†] Jiming Hu,[‡] and Yuanhua Shao^{*,†}

State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China, and College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, China

In this work, we report the findings of a study on scanning electrochemical microscopy (SECM) to investigate the interfacial electron-transfer (ET) reaction between the 7,7,8,8-tetracyanoquinodimethane radical anion (TCNQ^{•-}) in 1,2-dichloroethane and ferricyanide in an ice-like matrix (a mixture of insulating ice and conductive liquid) under low temperatures. Experimental results indicate that the formed liquid/ice-like matrix interface is superficially similar in electrochemical characteristics to a liquid/liquid interface at temperatures above $-20\text{ }^{\circ}\text{C}$. Furthermore, imaging data show that the surface of the ice-like matrix is microscopically flat and physically stable and can be applied as either a conductive or an insulating substrate for SECM studies. Perchlorate ion was selected as the common ion in both phases, the concentrations of which controlled the interfacial potential difference. The effect of perchlorate concentration in the DCE phase on interfacial reactions has been studied in detail. The apparent heterogeneous rate constants for TCNQ^{•-} oxidation by $\text{Fe}(\text{CN})_6^{3-}$ in another phase under different temperatures have been calculated by a best-fit analysis, where the experimental approach curves are compared with the theoretically derived relationships. Reaction rate data obey Butler–Volmer formulation before and after the freezing point, which is similar to most other known cases of ET reactions at liquid/liquid interfaces. However, there is a sharp change observed for heterogeneous rate constants around the freezing point of the aqueous phase, which reflects the phase transition. At temperatures below $-20\text{ }^{\circ}\text{C}$, surface-confined voltammograms for the reduction of ferricyanide were obtained, and the ice-like matrix became an insulating one, which indicates that the aqueous phase is really a frozen phase.

Charge (electron and ion) transfer across a liquid/liquid interface (L/L interface) or an interface between two immiscible electrolyte solutions (ITIES) is one of the fundamental physicochemical processes known to occur in nature. Consequently,

interfacial charge-transfer mechanisms have been investigated extensively during the past three decades.^{1,2} This field of electrochemistry has attracted broad research because of its application to many unsolved physicochemical problems associated with homogeneous and heterogeneous electron transfer (ET). The techniques developed are particularly useful in studies on pharmacokinetics and biomembrane research. The field is also directly relevant to the challenges facing the development of several classes of chemical sensor as well as phase-transfer catalysis.^{1b} As pointed out recently by Mirkin,³ one of the most intriguing questions about the liquid/liquid interface is its molecular structure. Basic issues yet to be resolved include the actual thickness of the interface as well as the distribution of electric potential across such interfaces. There are also troublesome questions relating to the adsorption and desorption behavior of surfactant species in the mixed-solvent layer. Fundamental structural information about this interface is certainly lacking and there is a need to draw on the resources of other microanalytical methods in order to gain a more detailed understanding. A few investigations that have been reported in the literature have attempted to make use of alternative experimental methods. However, published results have so far proven controversial.²

In the case of conventional electrochemistry at L/L interfaces, an external potential is applied to polarize the interface. This is analogous to measurements at electrode/electrolyte interfaces. Unfortunately, the typical experimental problems encountered with electrochemical measurements at an electrode/electrolyte interface are more severe in the case of liquid/liquid interfaces. Commonly cited examples are the difficulties in fully eliminating the iR drop across the cell, and the inability to distinguish between faradic current and charging currents, which are a consequence of interfacial ion transfer and redistribution.

Many ion-transfer (IT) processes are known to be fast and their kinetic parameters are not easily measured. The earlier studies of charge transfer across L/L interfaces with SECM, as advocated

* To whom correspondence should be addressed. E-mail: yhshao@ns.ciac.jl.cn.

[†] Changchun Institute of Applied Chemistry.

[‡] Wuhan University.

- (1) (a) Girault, H. H.; Schiffrin, D. J. in *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, 1989, Vol. 15, p 1. (b) 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.
- (2) Volkov, A. G.; Deamer, D. W., Eds., *Liquid/Liquid Interfaces*; CRC Press: Boca Raton, FL, 1996.
- (3) (a) Mirkin, M. V. *Anal. Chem.* **1996**, *68*, 177A–182A. (b) Mirkin, M. V. *Mikrochim Acta* **1999**, *130*, 127–153.

by Bard and co-workers in 1995, have been adopted and developed into a practical new tool for probing the mechanisms of charge-transfer reactions.^{4–6} The merits of SECM have been experimentally demonstrated in several key investigations with ideally nonpolarized L/L interfaces (characterized by the existence of a common ion in both phases). There are no limitations associated with the polarization window, which are routinely observed with ITIES, since all the electrodes in the measurement system are placed in the same phase. Moreover, SECM techniques are essentially free of experimental complications caused by *iR* drop and charging current, because scanning electrochemical microscopy (SECM) tips are usually of ultramicroelectrode (UME) dimensions.⁷ These technical advantages aid physical measurement and often mean that one can design experiments to distinguish between ET and IT processes that might be occurring simultaneously in some interfacial systems. Finally, SECM has shown itself to be a very versatile tool with broad application as a surface or interfacial probe. To date, studies with the technique have numbered many important substances and materials, including metals, polymers, semiconductors, L/L interfaces, and even biological specimens.

One recurring difficulty with electrochemical studies at liquid/liquid interfaces is the limitation over the selection of organic solvents. Even with decades of research in this area, there are still few organic solvents discovered that satisfy the criteria proposed by Koryta and Vanysek.⁸ The list is short and comprises nitrobenzene (NB), 1,2-dichloroethane (DCE), and 2-nitrophenyl octyl ether (NPOE).⁹ The search for alternative organic solvents and improved electrolyte systems is highly necessary, and one that is still continuing. However, experiments with new kinds of interface can be found. Doe et al.¹⁰ demonstrated that the processes of charge transfer across a DCE/ice interface were similar in their electrochemical behavior to those studied at conventional L/L interfaces. Also, they found that a DCE/ice interface could be readily stabilized for experimental purposes at -15°C , by immersing a frozen electrolyte within a DCE solution, the temperature of the electrochemical cell being controlled by circulating the coolants.

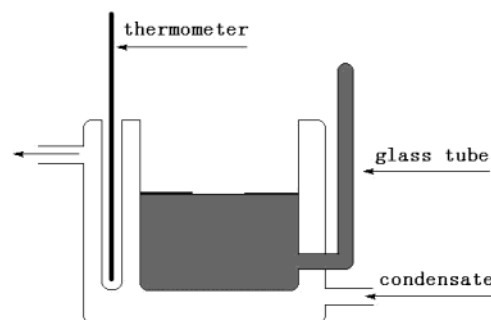


Figure 1. Schematic diagram of the electrochemical cell.

The freezing point for an electrolyte solution diminishes with the increase in the concentration of supporting electrolytes. Hence, for an aqueous phase containing 0.1 M KCl, the electrolyte begins to freeze at around -2.0°C , while the DCE phase remains in the liquid state (the freezing point for pure DCE is -36.7°C ¹¹). In this work, we have designed and described a low-temperature electrochemical cell for the purpose of making kinetic and structural measurements at a DCE/ice-like matrix interface using the techniques of SECM and UME. The temperature of the cell could be precisely controlled down to -35°C using a refrigeration cycle pump assembly, the basic arrangement of which is illustrated in Figure 1. We demonstrated experimentally for the first time that an ice-like matrix containing supporting electrolytes could be used as a substrate in SECM investigations. The formed interface is referred to as a liquid/ice-like matrix (a mixture of insulating ice and conductive liquid) interface. A potential difference at this interface can be readily controlled by a perchlorate ion placed in both phases. By employing this type of electrochemical cell, we have been able to investigate a novel experimental approach to the study of heterogeneous electron-transfer reactions. The ET between $\text{TCNQ}^{\cdot-}$ in 1,2-dichloroethane and ferricyanide in an ice-like matrix was examined by this low-temperature SECM approach. Apparent heterogeneous rate constants were evaluated by fitting the experimental approach curves with the established theory. The influence of reaction temperature on the ET kinetics has also been tested, as well as the variations of ClO_4^- concentrations in the organic electrolyte phases.

EXPERIMENTAL SECTION

Chemicals. The chemicals used were 1,2-dichloroethane (99.8%, HPLC grade, Tianjin Chemicals Co., Tianjin, China), KCl (99.8%), NaClO_4 (99.5%), and $\text{K}_3\text{Fe}(\text{CN})_6$ (99.5%) (all supplied by Beijing Chemicals Co., Beijing, China), TBAClO_4 (98%, Fluka), and 7,7,8,8-tetracyanoquinodimethane (TCNQ, 98%, Acros). All aqueous solutions were prepared from the Millipore water (Milli-Q, Millipore Corp.).

Electrodes and the Electrochemical Cell. Figure 1 shows the electrochemical cell, in which the temperatures can be controlled by use of a refrigeration cycle pump (Zhengzhou). The DCE/ice-like matrix interface was established inside this low-temperature cell. All electrochemical measurements were made

- (4) (a) Solomon, T.; Bard, A. J. *J. Phys. Chem.* **1995**, *99*, 17487–17489. (b) Wei, C.; Bard, A. J. *J. Phys. Chem.* **1995**, *99*, 16033–16042. (c) Tsionsky, M.; Bard, A. J. *J. Phys. Chem.* **1996**, *100*, 17881–17888. (d) Tsionsky, M.; Bard, A. J.; Mirkin, M. V. *J. Am. Chem. Soc.* **1997**, *119*, 10785–10792. (e) Delville, M. H.; Tsionsky, M.; Bard, A. J. *Langmuir* **1998**, *14*, 2774–2779.
- (5) (a) Shao, Y.; Mirkin, M. V. *J. Phys. Chem.* **1998**, *102*, 9915–9921. (b) Shao, Y.; Mirkin, M. V. *J. Electroanal. Chem.* **1997**, *439*, 137–143. (c) Shao, Y.; Mirkin, M. V. *J. Am. Chem. Soc.* **1997**, *119*, 8103–8104. (d) Shao, Y.; Mirkin, M. V. *Anal. Chem.* **1998**, *70*, 3155–3161. (e) Liu, B.; Mirkin, M. V. *J. Am. Chem. Soc.* **1999**, *121*, 8352–8355.
- (6) Zhang, J.; Unwin, P. R. *J. Phys. Chem.* **2000**, *104*, 2341–2347.
- (7) (a) Mirkin, M. V.; Richards, T. C.; Bard, A. J. *J. Phys. Chem.* **1993**, *97*, 7672–7677. (b) Bard, A. J.; Mirkin, M. V.; Unwin, P. R.; Wipf, D. O. *J. Phys. Chem.* **1992**, *96*, 1861–1868.
- (8) Koryta, J.; Vanysek, P. In *Advances in electrochemistry and electrochemical engineering*; Gerischer, H. Tobias, C. W., Eds.; John Wiley & Sons: New York, 1981; Vol. 12, p 113.
- (9) (a) Lee, H. J.; Beriet, C.; Girault, H. H. *J. Electroanal. Chem.* **1998**, *453*, 211–219. (b) Lee, H. J.; Beriet, C.; Girault, H. H. *Anal. Sci.* **1998**, *14* (2), 71–77. (c) Lee, H. J.; Beattie, P. D.; Seddon, B. J.; Osborne, D. D.; Girault, H. H. *J. Electroanal. Chem.* **1997**, *440*, 73–82. (d) Samec, Z.; Langmaier, J.; Trojanek, A. *J. Electroanal. Chem.* **1996**, 409–417.
- (10) (a) Doe, H.; Kobayashi, T.; Sawada, H. *J. Electroanal. Chem.* **1995**, *383*, 53–59. (b) Rahaman, M.; Doe, H. *J. Electroanal. Chem.* **1997**, *424*, 159–164.

(11) Kirk-Othmer Encyclopedia of Chemical Technology, 3rd ed.; John Wiley & Sons: New York, 1979; Vol. 5, p 725.

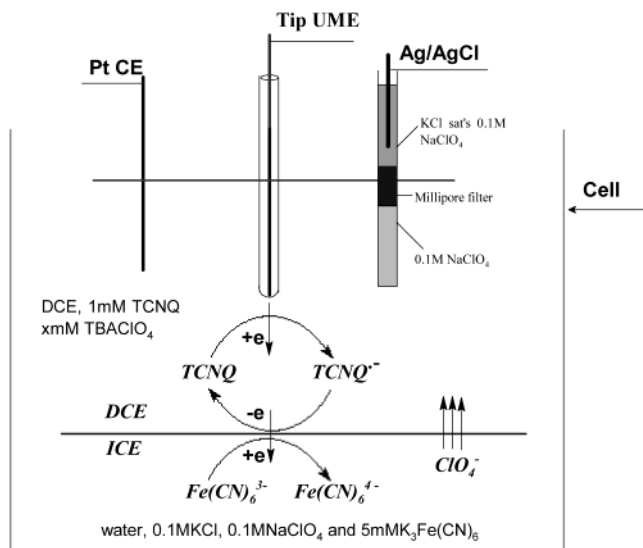


Figure 2. Schematic diagram of the application of SECM in the study of heterogeneous ET reactions at the liquid/liquid and the liquid/ice interfaces.

using a three-electrode arrangement as illustrated in Figure 2. A 10- μm -diameter Pt UME served as the working electrode (SECM tip). This UME was prepared using a procedure previously described in the literature.^{12,13} A BX-60 optical microscope (Olympus) was used to examine the microscopic structure and dimensions of the Pt ultramicroelectrode. The electrode tip was carefully polished before each measurement. A KCl-saturated, Ag/AgCl electrode served as the reference electrode with an ionic bridge (KCl and NaClO₄) between the reference electrode and organic phase. The three-electrode system was completed by a Pt wire counter electrode and the assembly positioned within the DCE phase. To make measurements of the heterogeneous rate constants for the reaction between TCNQ \cdot^- and Fe(CN) $_6^{3-}$, a CHI 900 SECM apparatus (CHI Instrument) was employed and a Pt UME as the tip. The tip potential was controlled at significantly negative values to reduce the TCNQ. A flat DCE/ice interface was established in the cell, between the DCE (top) phase and the aqueous phase (bottom) at low temperatures (-3 to -35 $^{\circ}\text{C}$). The experimental approach curves (tip current vs the distance between the tip and the ice-like matrix substrate) were then recorded. The aqueous phase contained 5 mM K₃Fe(CN) $_6$, 0.1 M KCl, and 0.01 M NaClO₄, while the DCE phase contained 1 mM TCNQ and 1–100 mM TBAClO₄.

RESULTS AND DISCUSSION

Steady-state voltammograms for K₃Fe(CN) $_6$ and TCNQ obtained on a 10- μm -diameter Pt UME are shown in Figure 3. These voltammetric waves were recorded with the SECM apparatus and correspond to the electrode reactions of the redox species in the aqueous and in the DCE phases at different temperatures. The voltammetric waves display the typical plateau currents expected for diffusion-controlled redox reactions at ultramicroelectrodes,

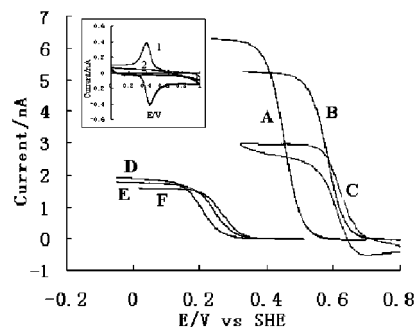


Figure 3. Cyclic voltammograms of TCNQ in DCE and K₃Fe(CN) $_6$ in aqueous phases at different temperatures. The DCE phase contained 1 mM TCNQ and 1 mM TBAClO₄ (D–F), and the aqueous phase contained 5 mM K₃Fe(CN) $_6$, 0.1 M KCl, and 0.01 M NaClO₄ (A–C). (A) and (D) are at 25 $^{\circ}\text{C}$, (B) and (E) are at -3 $^{\circ}\text{C}$, and (C) and (F) are at -15 $^{\circ}\text{C}$. The inset is the cyclic voltammograms K₃Fe(CN) $_6$ in aqueous phases at -26 (1) and -30 $^{\circ}\text{C}$ (2), and the potential (V·s) Ag/AgCl at the same temperature.

from which estimates of diffusion coefficients (D) can be calculated by eq 1. For the TCNQ species in the DCE phase held at -3 $^{\circ}\text{C}$, with 0.01 M TBAClO₄ as the supporting electrolyte, D is equal to $9.17 \times 10^{-6} \text{ cm}^2/\text{s}$. Under the same electrolyte conditions, but at the higher temperature of 25 $^{\circ}\text{C}$, this value is raised slightly to $1.10 \times 10^{-5} \text{ cm}^2/\text{s}$. Equally, the ice-like matrix diffusion coefficient for K₃Fe(CN) $_6$, with 0.1 M KCl and 10 mM NaClO₄ as the supporting electrolyte, was calculated as $5.28 \times 10^{-6} \text{ cm}^2/\text{s}$, again a decrease compared to typical liquid-phase values. It is hard to obtain perfect cyclic voltammograms of the reduction of K₃Fe(CN) $_6$ when the temperatures are lower than -10 $^{\circ}\text{C}$ (See curve C in Figure 3). Moreover, we did not observe the so-called surface-confined behavior when the temperatures were higher than -20 $^{\circ}\text{C}$.¹⁴ This may indicate that the ice phase is not completely frozen and there exists liquid in the ice matrix and this is why we call it the ice-like matrix. The diffusion coefficients of both redox species decrease with decreasing temperature, and they are equal to 8.19×10^{-6} and $2.90 \times 10^{-6} \text{ cm}^2/\text{s}$ for TCNQ in the DCE and K₃Fe(CN) $_6$ in the ice phase at -15 $^{\circ}\text{C}$, respectively. The typical surface-confined voltammograms for the reduction of ferricyanide could be observed when the temperatures were below -20 $^{\circ}\text{C}$, which may indicate the aqueous phase is fully frozen (see the inset in Figure 3).

$$I_{ss} = 4nFDrc \quad (1)$$

where I_{ss} is the steady-state limiting current, n is the number of electron transferred, F is the Faraday constant, r is the radius of the UME, and D and C are the diffusion coefficient and the bulk concentration of redox species, respectively.

It can be noticed from these voltammetric waves that the half-wave potentials ($E_{1/2}$) for both TCNQ and K₃Fe(CN) $_6$ are shifted in a more positive direction at -3 $^{\circ}\text{C}$ compared with the $E_{1/2}$ at 25 $^{\circ}\text{C}$. The half-wave potential difference between them is 0.30 V

(12) Lee, C.; Miller, C. J.; Bard, A. J. *Anal. Chem.* **1991**, *63*, 78–83.

(13) (a) Slevin, C. J.; Unwin, P. R. *Langmuir* **1997**, *13*, 4799–4803. (b) Slevin, C. J.; Unwin, P. R. *Langmuir* **1999**, *15*, 7361–7371. (c) Zhang, J.; Slevin, C. J.; Unwin, P. R. *Chem. Commun.* **1999**, 1501–1502.

(14) (a) Stimming, U.; Schmickler, W. *J. Electroanal. Chem.* **1983**, *150*, 125–131. (b) Bond, A. M.; Svestka, M. *J. Electroanal. Chem.* **1991**, *301*, 139–154. (c) Bond, A. M.; Pfund, V. B. *J. Electroanal. Chem.* **1992**, *335*, 281–295.

Table 1. Effect of Temperature on the Half-Wave Potentials of ET Reactions between $\text{K}_3\text{Fe}(\text{CN})_6$ in the Aqueous and TCNQ in the DCE Phases^a

$T/^\circ\text{C}$	E^1/V	E^2/V	$\Delta E_{1/2}/\text{V}$
-26	0.55	0.25	0.30
-20	0.56	0.26	0.30
-15	0.58	0.28	0.30
-10	0.57	0.27	0.30
-3	0.56	0.26	0.30
0	0.44	0.21	0.23
5	0.43	0.20	0.23
10	0.43	0.20	0.23
15	0.42	0.20	0.22
20	0.42	0.20	0.22
25	0.41	0.20	0.21

^a The E^1 and E^2 are half-wave potentials for $\text{K}_3\text{Fe}(\text{CN})_6$ in the aqueous and TCNQ in the DCE phases, respectively. $\Delta E_{1/2} = E^1 - E^2$. The DCE phase contained 1 mM TCNQ and 10 mM TBAClO_4 . The aqueous phase contained 5 mM $\text{K}_3\text{Fe}(\text{CN})_6$, 0.1 M KCl, and 10 mM NaClO_4 .

at -3°C , which is larger than the value observed at 25°C .⁶ This means, thermodynamically at least, that it should be easier for $\text{K}_3\text{Fe}(\text{CN})_6$ to oxidize $\text{TCNQ}^{\cdot-}$ back to TCNQ at the DCE/ice-like matrix interface. As shown in Figure 3, the half-wave potentials for the electrode reactions of $\text{Fe}(\text{CN})_6^{3-}$ and TCNQ are based on the aqueous SHE scale. The method used to convert these experimental electrode potentials to the SHE scale has been described previously in the literature.¹⁵ Moreover, the effect of temperature variation on the half-wave potential ($E_{1/2}$ vs SHE) for $\text{Fe}(\text{CN})_6^{3-}$ and TCNQ electrode reactions are summarized in Table 1.

Potential Drop across the Liquid/Ice Interface. The potential drop across a liquid/liquid interface can be controlled in two ways. A liquid/liquid interface is normally described as an externally polarized liquid/liquid interface, which is the usual case for conventional electrochemistry at such interfaces. In this instance, an external electric potential can be applied in order to polarize the interface. An alternative way to control the potential drop across such interfaces is to employ a common ion in both phases, and this is usually called a nonpolarized liquid/liquid interface. So far, most studies on charge transfer across liquid/liquid interfaces using SECM techniques have employed the latter case. One noticeable advantage of this common ion method is that interfacial charge-transfer processes can be adjusted, or driven, in any particular direction to suit the requirements of the experiment. In our study, to simplify data analysis and compare results with existing literature, the ClO_4^- was chosen as the only common ion in the two phases. The ratio of the activities of ClO_4^- in the ice and the DCE phase would then determine the potential drop at the interface. Hence, at low concentrations, and approximating activities with concentrations, the potential drop, $\Delta_{\text{W}}^{\text{O}}\phi$ at the DCE/ice-like matrix interface should be governed by the concentration ratio $[\text{ClO}_4^-]_{\text{I}}/[\text{ClO}_4^-]_{\text{O}}$, of the potential-determining ion (ClO_4^-) in both phases.

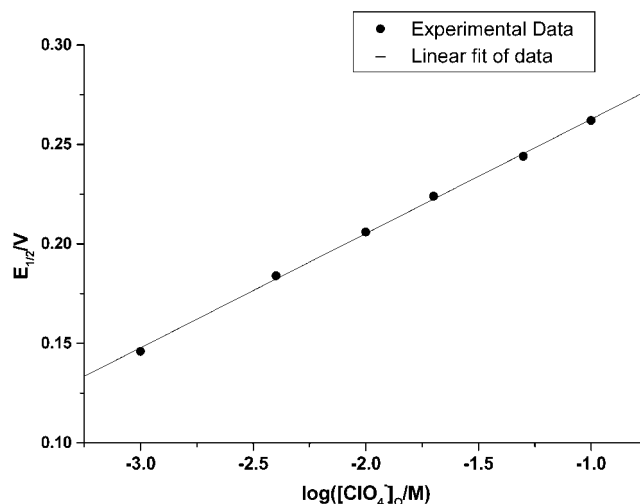


Figure 4. Dependence of the half-wave potential for the reduction of TCNQ on the concentrations of ClO_4^- in the DCE phase.

At 25°C and normal pressure, the following equation should hold:

$$\Delta_{\text{W}}^{\text{O}}\phi = \Delta_{\text{W}}^{\text{O}}\phi_{\text{ClO}_4^-}^0 + \frac{RT}{nF} \ln \frac{[\text{ClO}_4^-]_{\text{W}}}{[\text{ClO}_4^-]_{\text{O}}} \quad (2)$$

where $\Delta_{\text{W}}^{\text{O}}\phi_{\text{ClO}_4^-}^0$ is the standard transfer potential of ClO_4^- , with W and O as sub- or superscripts referring to the ice-like matrix and DCE phases, respectively. If the ratio of the concentrations of ClO_4^- in the ice-like matrix and DCE phase remains unchanged, the potential drop across their interface is constant. This kind of interface then serves as a convenient reference interface in studies on externally polarized interfaces.

Figure 4 is the dependence of half-wave potential for the reduction of TCNQ on the concentration of TBAClO_4 in the DCE phase. The essential linear dependence shows an approximately 120-mV change in the potential drop with an increase of $[\text{TBAClO}_4]_{\text{O}}$ from 1 to 100 mM, while the concentration of $[\text{ClO}_4^-]_{\text{W}}$ in the reference was kept the same. The slope of the line was 56 mV/decade, which is in good agreement with the theory.

Heterogeneous Rate Constants of the ET at the Liquid/Ice-like Matrix Interface. By using a common ion, the interfacial potential drop between the two phases could be adjusted over a certain range to control the ET reaction between the redox couples. The heterogeneous rate constant can be determined either from steady-state voltammetry or from analysis of the SECM i_T - d curve, where i_T is the current measured by the SECM tip and d is the distance between the tip and the substrate. Feedback mode is the main working arrangement for the quantitative analysis of SECM experimental data at present. For a tip near a conductive substrate, where $d < a$, the effective mass-transfer coefficient, m , is about D/d . By decreasing the tip-substrate distance, the mass-transfer rate can be increased sufficiently for a quantitative characterization of rapid electron-transfer kinetics.

In this experiment, we want to implement the following ET reaction at the liquid/ice-like matrix interface (see Figure 2):

(15) (a) Cheng, Y.; Schiffrin, D. J. *J. Chem. Soc., Faraday Trans.* **1994**, 90, 2517–2523. (b) Geblewicz, G.; Schiffrin, D. J. *J. Electroanal. Chem.* **1988**, 244, 27–37.

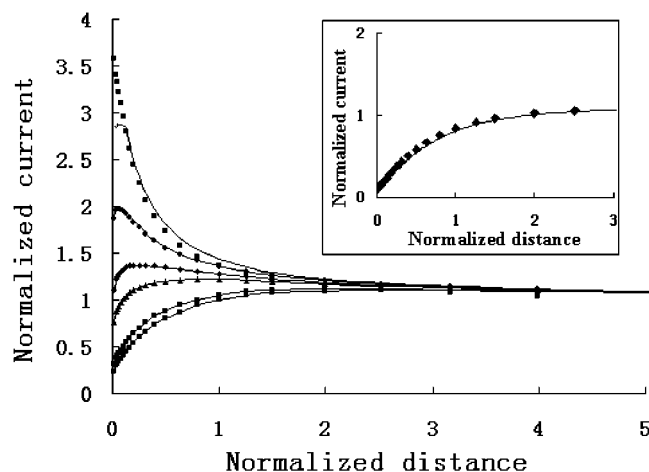
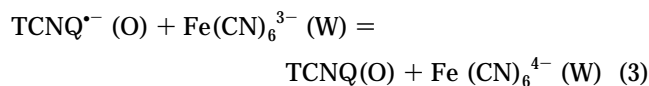
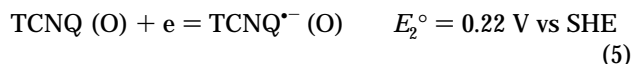
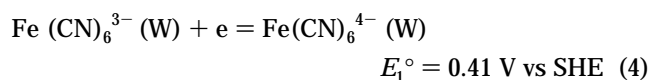


Figure 5. Experimental approach curves of the system (line) and the theoretical curves (dot). The ice phase contained 5 mM $\text{K}_3\text{Fe}(\text{CN})_6$, 0.1 M KCl, and 0.01 M NaClO_4 . The DCE phase contained 1 mM TCNQ. From top to bottom, the concentrations of TBAClO_4 in DCE phase were 1, 4, 10, 20, 50 and 100 mM, respectively. The rates of electron transfer $k/(\text{cm}\cdot\text{s}^{-1}\cdot\text{M}^{-1})$ were 12.2, 7.9, 4.6, 3.2, 1.3, and 0.97. The inset shows the approach curve at -26°C with 1 mM TBAClO_4 in the DCE phase. All of the approach rates were $1\ \mu\text{m/s}$.



The half-reactions in the aqueous and the DCE phases are as follows.⁴



From eqs 4 and 5, we can obtain $\Delta E^\circ = E_1^\circ - E_2^\circ = 0.19\ \text{V}$. Clearly, a heterogeneous ET reaction between $\text{Fe}(\text{CN})_6^{3-}(\text{W})$ and $\text{TCNQ}^{\bullet-}(\text{O})$ is thermodynamically favored at the aqueous and the DCE interface. As stated, the half-wave potential difference measured experimentally was 0.30 V at -3°C , signifying that interfacial reaction 3 is very highly favored. The methodology presented by Bard et al.⁴ was applied in this work to determine the kinetic parameters of reaction 3, from the experimental i_T - d data and a best-fit analysis with the theoretical values. Figure 5 illustrates the family of working curves (i_T^k vs k) for different values of L along with the corresponding simulated data. Where, i_T^k and k are the theoretical values for the feedback tip current and rate constant, respectively, and L is the normalized distance between the tip and the substrate.

The interfacial reaction 3 can be considered as a first-order ET process in which $\text{TCNQ}^{\bullet-}$ is oxidized at the ice-like matrix surface. The following equations can therefore be assigned to analyze the experimental data.¹⁶

(16) (a) Marcus, R. A. *J. Phys. Chem.* **1990**, *94*, 1050–1055. (b) Marcus, R. A. *J. Phys. Chem.* **1990**, *94*, 4152–4155. (c) Marcus, R. A. *J. Phys. Chem.* **1991**, *95*, 2010–2013.

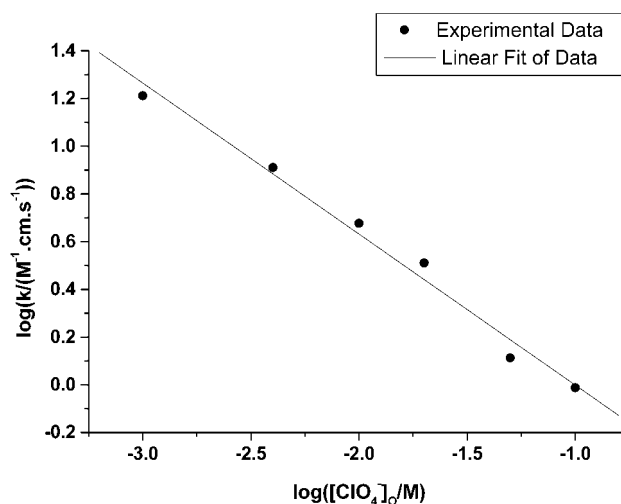


Figure 6. Dependence of k on the concentration of ClO_4^- in the DCE phase. The data are taken from Figure 5.

$$k_f = \text{const}[\text{Fe}(\text{CN})_6^{3-}] \exp(-\Delta G^\ddagger/RT) \quad (6)$$

$$\Delta G^\ddagger = -anF(\Delta E^\circ + \Delta_{\text{W}\phi}^\circ) = \text{const} + 0.059aF \log[\text{ClO}_4^-]_{\text{O}} \quad (7)$$

$$k_f = \text{const}[\text{Fe}(\text{CN})_6^{3-}] \exp[-(\text{const} + 0.059aF/RT \log[\text{ClO}_4^-]_{\text{O}})]$$

$$\log k_f = \text{const} - 2.303a \log[\text{ClO}_4^-]_{\text{O}} \quad (8)$$

where k_f is the first-order rate constant for the oxidation of $\text{TCNQ}^{\bullet-}$ at the DCE/ice-like matrix interface and $[\text{Fe}(\text{CN})_6^{3-}]$ and $[\text{ClO}_4^-]$ are concentrations terms for ferricyanide and perchlorate, respectively.

With these relationships and a knowledge of the $\text{K}_3\text{Fe}(\text{CN})_6$ concentration, an effective bimolecular rate constant, $k = k_f/[\text{Fe}(\text{CN})_6^{3-}]$ ($\text{M}^{-1}\cdot\text{cm}\cdot\text{s}^{-1}$), for reaction 3 can also be calculated. Obviously, when $[\text{Fe}(\text{CN})_6^{3-}]$ is constant, $\log k$ is proportional to $\log([\text{ClO}_4^-]_{\text{O}})$ and $\alpha = 0.32 \pm 0.02$ can be calculated from the slope of this plot from Figure 6 (see eq 8). Moreover, by this best-fit analysis, the experimental data confirm that eq 8 can be applied to explain the effects of TBAClO_4 concentration in the DCE phase on the ET reaction between $\text{TCNQ}^{\bullet-}$ and $\text{Fe}(\text{CN})_6^{3-}$ at the liquid/ice-like matrix interface. At temperatures lower than -20°C , negative feedbacks were obtained (see the inset in Figure 5), which is consistent with the surface-confined behavior observed using cyclic voltammetry. The rate constant decreases significantly at -20°C (see Figure 9).

Imaging. Most of the published SECM images were made using the technique in a constant-height mode,^{17,18} in which the tip is scanned across the substrate in the x - y plane and tip current monitored as a function of tip location. By this means, a three-dimensional image of the substrate can be converted to a plot of

(17) (a) Turyan, I.; Matsue, T.; Mandler, D. *Anal. Chem.* **2000**, *72*, 3431–3435. (b) Selzer, Y.; Turyan, I.; Mandler, D. *J. Phys. Chem.* **1999**, *103*, 1509–1517.
(18) (a) Shiku, H.; Takeda, T.; Yamada, H.; Matsue, T.; Uchida, I. *Anal. Chem.* **1995**, *67*, 312–317. (b) Shiku, H.; Uchida, I.; Matsue, T. *Langmuir* **1997**, *13*, 7239–7244.

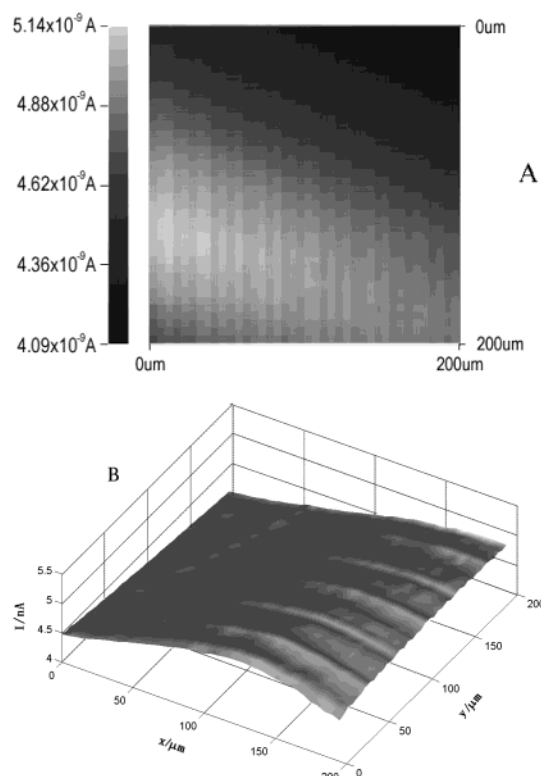


Figure 7. Constant-height mode gray scale images of the liquid/ice interface, (A) is a 2D image of the experiment and (B) is a 3D image of the same experiment. The DCE phase contained 1 mM TCNQ and 1 mM TBAClO₄. The tip scan speed rate was 5 μm/s. The ice phase contained 0.1 M KCl, 0.01 M NaClO₄, and 5 mM K₃Fe(CN)₆.

z-distance between tip and substrate versus *x*–*y* position for any conducting or insulating substrate. In this experiment, we also used the SECM in a constant-height mode to image the liquid/ice-like matrix interface. The SECM probe employed to image the structure of the ice-like matrix surface from within the DCE phase consisted of a 10-μm-diameter Pt UME with a TCNQ mediator. Figure 7 shows the conductive surface of the ice-like matrix containing 0.1 M KCl, 10 mM NaClO₄, and 5 mM K₃Fe(CN)₆ at –3 °C. These images clearly define the liquid/ice-like matrix interface and reveal that this layer is microscopically flat. The reproducibility of the imaging data also demonstrates that an electrolytic ice matrix is stable and can be used as a novel SECM substrate. The existence of a linelike structure that is regularly spaced over the images indicates regions where the SECM tip had contacted the substrate when scanning across the ice-like matrix surface. This suggests that the ice interface may well be soft or not fully frozen. There is whether a liquidlike layer (LLL) existed between an ice and an organic solvent and how thick are they are generally interested questions. Previous studies indicated that there are LLL in existence on an ice surface or between an ice and an organic solvent.¹⁹ This LLL usually is less than 100 nm, and its physical properties, such as conductivity, viscosity, and diffusion coefficient, differ from those of ordinary supercooled water by orders of magnitude.^{19,20} Indeed, the effect

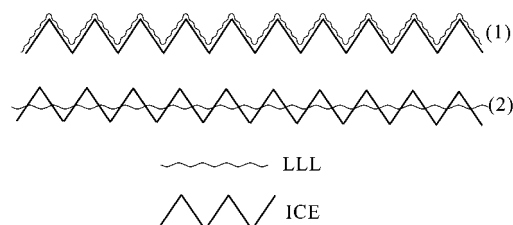


Figure 8. Schematic diagram of the possible coverage of the LLL on ice surface.

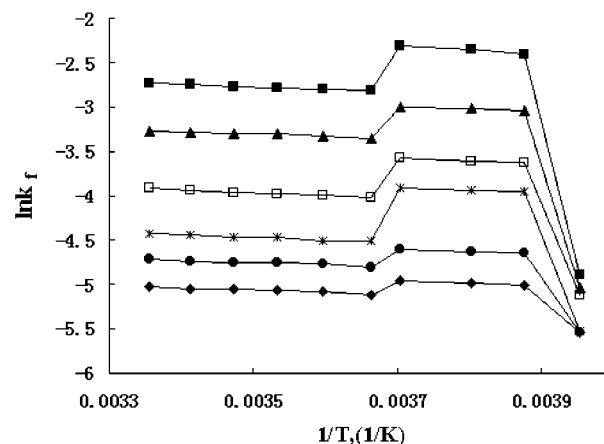


Figure 9. Plots of $\ln k_f$ vs $1/T$. The temperature ranged from 253 to 298 K. The DCE phase contained 1 mM TCNQ, and from top to bottom, the concentrations of TBAClO₄ in DCE phase were 1, 4, 10, 20, 50, and 100 mM, respectively. The aqueous phase contained 5 mM K₃Fe(CN)₆, 0.1 M KCl, and 10 mM NaClO₄.

of the existing LLL for the ET reactions is a rather complicated and profound scientific matter. The ET reaction may occur at the LLL/DCE interface and the ET rate constant should have some relation to the thickness of the LLL. There are two possibilities (see Figure 8): (1) The ice surface is fully covered with very thin LLL; and (2) The interfacial boundary consists of patches of crystalline ice and LLL because the ice surface is in micrometer scale (see Figure 7) and the LLL is in nanometer scale. It is useful to test the dependence of the ET rate constant on the temperatures.

Effect of Temperature on the Heterogeneous Rate Constant of the ET Reaction at the Liquid/Liquid Interface. To understand the effect of temperature on the heterogeneous rate constant of the ET reaction at the water/DCE and the DCE/ice-like matrix interfaces, the experimental approach curves were investigated at temperatures from –20 to 25 °C. The ET reaction rate could be obtained by fitting the experimental curves with the theoretical SECM relationships. At a given concentration of Fe(CN)₆^{3–} and K_p , where $K_p = [\text{LiClO}_4]/[\text{TBAClO}_4]$, the apparent rate constant depends on the temperature of reaction. One can see from Figure 9 that the apparent ET rate constant is reduced as temperatures decrease just before the freezing point. There is clearly a sharp change around this point and then the apparent ET rate constant decreases again as the temperatures decrease. This reflects the aqueous-phase change from liquid to ice-like matrix and then the ET rate constant depends on the thickness of the LLL on the ice surface. Apparently, the thickness of the LLL is reduced with the temperature decreases. The dependence of k_f on the temperature can be written as followed:

(19) (a) Doppenschmidt, A.; Butt, H. *Langmuir* **2000**, *16*, 6709–6714. (b) Petrenko, V. F. *J. Phys. Chem. B* **1997**, *101*, 6276–6281.
(20) Mizuno, Y.; Hanafusa, N. *J. Phys. C1* **1987**, *48* (3), 511.

Table 2. Data of the Slopes and α Evaluated from Figure 8^a

$[\text{ClO}_4^-]_0/\text{mM}$	slope ₁	α_1	slope ₂	α_2
1	353	0.19 ± 0.01	462	0.25 ± 0.03
4	350	0.19 ± 0.02	453	0.25 ± 0.02
10	380	0.21 ± 0.02	444	0.24 ± 0.02
20	370	0.20 ± 0.03	414	0.23 ± 0.03
50	346	0.19 ± 0.02	438	0.24 ± 0.04
100	360	0.20 ± 0.03	456	0.25 ± 0.03

^a Slope₁ and α_1 were taken from 0 to 25 °C and slope₂ and α_2 taken from -3 to -15 °C.

$$k_f = \text{const}[\text{Fe}(\text{CN})_6^{3-}] \exp\left[-aF\left(-\Delta E^\circ + \frac{RT}{F} \ln[\text{ClO}_4^-]_0\right)/RT\right]$$

$$\ln k_f = \text{const} + aF\Delta E^\circ/RT - a \ln([\text{ClO}_4^-]_0) \quad (9)$$

Figure 9 shows the plots of $\ln k_f$ versus $1/T$ for different ratios of common ion in both phases. The slopes of these plots were closely separated for different TBAClO₄ concentrations in the DCE phase, the only variation in the data being that they have different intercepts. Table 2 provides the data on α calculated from Figure 9. The rather small values of α may indicate that the eqs 7 and 9 oversimplify the analysis of the driving force in this heterogeneous ET reaction.^{16,21,22} The k_f decreases markedly after -20 °C, which means that there may not be any LLL on the ice surface.

- (21) (a) Girault, H. H.; Schiffrin, D. J. *J. Electroanal. Chem.* **1988**, *244*, 15–26.
 (b) Samec, Z. *J. Electroanal. Chem.* **1979**, *99*, 197–205.
 (22) Ding, Z.; Quinn, B. M.; Bard, A. J. *J. Phys. Chem. B* **2001**, *105*, 6367–6374.

CONCLUSIONS

ET reactions between TCNQ^{•-} in 1,2-dichloroethane and ferricyanide in an ice-like matrix can be investigated by application of new techniques in microelectrochemistry. The liquid/ice-like matrix interface under study was stabilized in a low-temperature electrochemical cell, which was found suitable for comprehensive investigations by SECM. The apparent heterogeneous rate constants were obtained by fitting the experimental approach curves with the theoretical values at various K_p s and the temperatures.

The experimental results demonstrated that the aqueous solution containing supporting electrolyte and ferricyanide could be cooled to an ice-like matrix with a water network below -3 °C, and it can be used as a conductive SECM substrate. It can only be fully frozen when the temperatures are below -20 °C, and the so-called surface-confined phenomenon can be obtained. Under these conditions, the frozen aqueous phase can be used as an insulating SECM substrate.

ACKNOWLEDGMENT

The authors thank the Chinese Academy of Sciences (CAS), the National Natural Science Foundation of China (NSFC), and the Third World Academy of Sciences (TWAS) for their assistance and financial support. The authors also thank one of the reviewers for the suggestions for lower temperature experiments. Y.S. also thanks Professors Donghang Yan and Guoyi Zhu of the Changchun Institute of Applied Chemistry for their constructive discussions.

Received for review January 12, 2001. Accepted January 2, 2002.

AC010056R