

# Study of Electron-Transfer Reactions across an Externally Polarized Water/1,2-Dichloroethane Interface by Scanning Electrochemical Microscopy

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Received: December 5, 2001

A novel method to study electron-transfer (ET) reactions between ferrocene in 1,2-dichloroethane (DCE) and a redox couple of  $\text{K}_3\text{Fe}(\text{CN})_6$  and  $\text{K}_4\text{Fe}(\text{CN})_6$  in water using scanning electrochemical microscopy (SECM) with a three-electrode setup is reported. In this work, a water droplet that adheres to the surface of a platinum disk electrode is immersed in a DCE solution. The aqueous redox couple serves both as a reference electrode on the platinum disk and as an electron donor/acceptor at the polarized liquid/liquid interface. With the present experimental approach, the liquid/liquid interface can be polarized externally, while the electron-transfer reactions between the two phases can be monitored independently by SECM. The apparent heterogeneous rate constants for the ET reactions were obtained by fitting the experimental approach curves to the theoretical values. These rate constants obey the Butler–Volmer theory; i.e., they are found to be potential dependent.

## Introduction

Studies of charge (electron and ion) transfer across a liquid/liquid interface (L/L interface) or across an interface between two immiscible electrolyte solutions (ITIES) by scanning electrochemical microscopy (SECM) have been reported for many systems since the pioneering work of Bard et al. in 1995.<sup>1–4</sup> It has been shown that SECM has several advantages to investigate an ideally nonpolarized interface. First, there are no limitations associated with the polarization window of an L/L interface. Second, SECM measurements are essentially free of complications caused by  $iR$  drop and the charging current as with conventional voltammetric techniques.<sup>5</sup> Also, electron-transfer (ET) and ion-transfer (IT) could be distinguished.

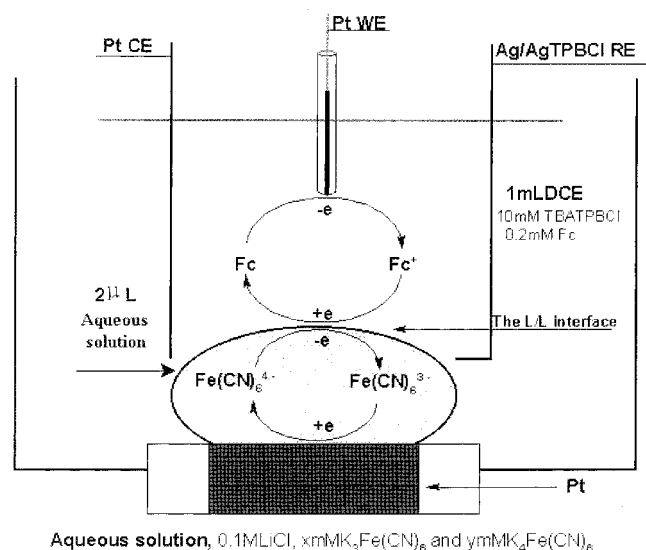
We can distinguish two kinds of liquid/liquid interfaces. One is the so-called ideally nonpolarized interface, for which the interfacial potential is controlled by a common ion in both phases. Almost all the investigations of charge transfer across L/L interfaces by SECM have so far been carried out using externally nonpolarized interfaces. The adjustable interfacial potentials controlled by the distribution of a common ion are practically limited to  $\pm 120$  mV, which is a rather small interfacial polarization to study the potential dependence of ET and IT reactions. The second class of L/L interface is the externally polarized interface, for which the aqueous phase contains a strongly hydrophilic supporting electrolyte and the organic phase contains a strongly lipophilic salt. This type of interface can be polarized within a so-called potential window. Charge-transfer reactions can then be investigated by external control of the applied potential difference, and in this way thermodynamic and kinetic information for electron- and ion-transfer or facilitated ion-transfer reactions can be obtained. A

major experimental difficulty is associated with uncompensated  $iR$  drop that can be quite large with the nonaqueous solvent. In the present paper, we combine conventional electrochemical control of the applied potential difference across a liquid/liquid interface and the SECM methodology.

In recent years, micro- and nano-L/L interfaces, which have the advantages of ultramicroelectrodes (UMEs), have also been studied with a two-electrode setup.<sup>2c,6–9</sup> Another important issue related to L/L interfaces is the phase ratio, as recently addressed by Kakiuchi,<sup>10</sup> and various thin liquid films method have also been used to study charge transfer across liquid/liquid interfaces.<sup>11–13</sup> Recently, Ulmeanu et al. have developed a new approach to study ion transfer across a liquid/liquid interface with a three-electrode setup using the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  redox couple to fix the potential at the Pt electrode. The Gibbs energies of transfer of alkylammonium cations across the water/DCE interface could be evaluated by this arrangement,<sup>14</sup> and the results obtained were in good agreement with the data obtained with a four-electrode setup.

In this work, we demonstrate that the combination SECM and conventional electrochemistry of charge transfer across L/L interfaces can be realized successfully. The gist of the approach is to simplify the four-electrode system to a three-electrode setup. We selected a small volume of aqueous solution that adhered to the surface of a platinum electrode, which contained a redox couple of  $\text{Fe}(\text{CN})_6^{3-/4-}$ . A bipotentiostat is employed to polarize the liquid/liquid interface and at the same time to control the tip potential of SECM. The approach curves ( $i_T - d$ ) were recorded at different applied potential differences across the liquid/liquid interface. The apparent heterogeneous rate constants were obtained by fitting the experimental approach curves with theoretical values. The external addition of the potentials can block the interfacial ET reaction and decrease the apparent heterogeneous rate constants. The effect of the

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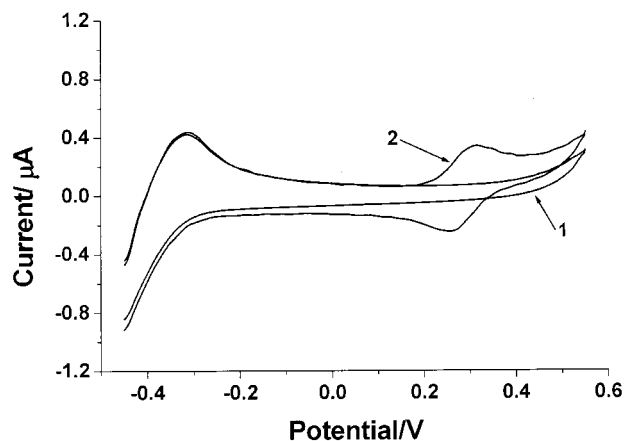
**Figure 1.** Schematic diagram of the application of SECM in the feedback mode measurement of the kinetics of ET between Fc in the DCE and a redox couple of  $\text{K}_3\text{Fe}(\text{CN})_6$  and  $\text{K}_4\text{Fe}(\text{CN})_6$  in the aqueous phase.

concentration ratios of the redox couple for this process was also investigated in detail.

### Experimental Section

1,2-Dichloroethane (DCE; HPLC grade) was supplied by Tianjin Chemicals Co., China. LiCl (AR),  $\text{K}_4\text{Fe}(\text{CN})_6$  (98%), and  $\text{K}_3\text{Fe}(\text{CN})_6$  (98%) were supplied by Beijing Chemicals Co., China. Tetrabutylammonium chloride (TBACl; 98%) was supplied by Fluka, and potassium tetrakis(4-chlorophenyl)borate (KTPBCl; 98%) was supplied by Aldrich. Ferrocene (Fc; 98%, ACROS) was used without further purification. All aqueous solutions were prepared from deionized water (Milli-Q, Millipore Corp.). Tetrabutylammonium tetrakis(4-chlorophenyl)borate (TBATPBCl) was prepared using the method described in the previous paper.<sup>15</sup>

A 11  $\mu\text{m}$  diameter Pt microelectrode ( $\text{RG} < 3$ ;  $\text{RG} = b/a$ , where  $a$  is the radius of the electrode and  $b$  is the radius of the electrode plus the thickness of the insulating layer) was used as the working electrode (SECM tip), and it was made using the procedure described in ref 16. An Olympus BX-60 optical microscope was used to check the quality of the electrode. A 0.2 mm diameter Ag wire coated with AgTPBCl was used as a reference electrode in the organic phase, and a 0.125 cm diameter Pt wire was used as the counter electrode. All of the electrodes were placed in the DCE phase. The small-volume water phase was placed on the surface of a platinum disk electrode (diameter 0.2 cm). A mixture of  $\text{K}_3\text{Fe}(\text{CN})_6$  and  $\text{K}_4\text{Fe}(\text{CN})_6$  was used as the aqueous redox couple. The dual purpose of the aqueous redox couple was to control the polarization of the platinum/water interface and function as the aqueous-phase reference electrode to control the interfacial potential difference between the ITIES, and at the same time, a liquid/liquid interface could be formed when it was immersed in the DCE phase. All electrochemical and SECM measurements were performed using a CHI 900 system (CHI Instrument) (Figure 1). The tip was positioned just right on the top of the droplet. The coordinate of the L/L interface ( $d = 0$ ) was determined from the sharp increase (or decrease) of the tip current that occurred when the tip touched the ITIES. All of the experiments were carried out at room temperature ( $22 \pm 2$  °C).



**Figure 2.** Potential window and the ET reaction across the W/DCE interface: (1) 0.01 MTBTPBCl in the DCE phase, and 10 mM  $\text{K}_3\text{Fe}(\text{CN})_6$  + 10 mM  $\text{K}_4\text{Fe}(\text{CN})_6$  + 0.1 M LiCl in the aqueous phase; (2) experimental conditions the same as in (1) and 0.2 mM Fc in the DCE phase. The scan rate was 5 mV/s.

**TABLE 1: Effect of the Concentrations of the Redox Couple in the Aqueous Phase on the Peak Potential  $E_p$  and the Half-Peak Potential  $E_{1/2}$  vs SHE<sup>a</sup>**

$c_{\text{Ox}}/\text{mM}$	$E_p/\text{V}$	$E_p'/\text{V}$	$E_{1/2}/\text{V}$	$\Delta E/\text{V}$
0.2	0.317	0.227	0.272	0.090
0.5	0.317	0.239	0.278	0.078
1	0.317	0.250	0.284	0.067
2	0.317	0.255	0.287	0.062
5	0.319	0.257	0.288	0.061
10	0.320	0.261	0.290	0.059

<sup>a</sup> All of the concentrations ratios of  $\text{K}_3\text{Fe}(\text{CN})_6$  to  $\text{K}_4\text{Fe}(\text{CN})_6$  were 1:1 in the aqueous phase, and the concentration of Fc in DCE was 0.2 mM. The scan rate was 10 mV s<sup>-1</sup>.

### Results and Discussion

**Electron Transfer across the Liquid/Liquid Interface between Fc in the DCE Phase and  $\text{Fe}(\text{CN})_6^{3-}$  in the Aqueous Phase.** Figure 2 shows the cyclic voltammograms obtained at the water/DCE (W/DCE) interface supported at the Pt electrode covered with an aqueous droplet (2  $\mu\text{L}$ ) immersed in the DCE phase (1 mL). The droplet contains a 10 mM  $\text{K}_3\text{Fe}(\text{CN})_6$  and 10 mM  $\text{K}_4\text{Fe}(\text{CN})_6$  redox couple and 0.1 M LiCl as supporting electrolyte, and the DCE phase contains 10 mM TBATPBCl as supporting electrolyte. With these electrolyte solutions, the voltammetric response (curve 1 in Figure 2) is the classical potential window observed with conventional electrochemistry at the water/DCE interface using a four-electrode potentiostat. The positive limit is the transfer of  $\text{K}^+$  from the aqueous to the DCE phase, whereas the negative side is limited by  $\text{TBA}^+$  transfer from the DCE to the aqueous phase. This voltammetry is here carried out with a three-electrode potentiostat.<sup>6</sup> When the organic phase contains 0.2 mM Fc (Figure 2, curve 2), we can observe the electron-transfer reactions associated with the oxidation of ferrocene as would be observed with a classical four-electrode setup at a large interface:<sup>17</sup>

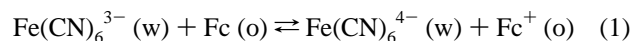


Table 1 illustrates that the voltammetric characteristics when the concentrations of the redox couple are varied. It can be observed that the  $\Delta E_p$  (peak to peak) increases when the concentrations of the redox couple are decreased. These results are in good agreement with the theoretical simulation developed by Stewart et al.<sup>18</sup>

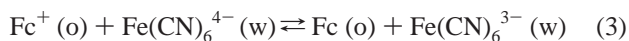
To determine the diffusion coefficient of Fc in DCE, a steady-state cyclic voltammogram for Fc oxidation has been measured on a 11  $\mu\text{m}$  diameter Pt microdisk electrode. From the plateau current, the diffusion coefficient of Fc in the DCE phase was calculated using eq 2

$$I_{T,\infty} = 4nFDac \quad (2)$$

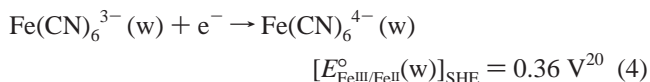
and is equal to  $1.21 \times 10^{-5} \text{ cm}^2/\text{s}$  when 1 mM Fc is in the DCE phase and 0.01 M TBATPBCl is used as the supporting electrolyte. In eq 2,  $I_{T,\infty}$  is the steady-state limiting current,  $n$  is the number of electrons transferred,  $F$  is the Faraday constant,  $D$  is the diffusion coefficient,  $a$  is the radius of the UME, and  $c$  is the bulk concentration of Fc. The value obtained is similar to that reported in the literature.<sup>19</sup> According to the literature,<sup>20c</sup> the standard transfer potential of  $\text{Fc}^+$  across this interface should be about 160 mV more negative than that of the heterogeneous ET reaction. However, we did not observe the transfer of  $\text{Fc}^+$  within the potential window under our experimental conditions.

**Heterogeneous Rate Constants of the ET at the Water/DCE Interface.** Feedback mode is the main working mode in quantitative analysis of SECM experimental data at present. The SECM can be used to determine the magnitude of heterogeneous electron-transfer rates between a tip and a substrate surface. The heterogeneous rate constant can be evaluated from the fitting of the experimental (tip current)  $i_T - d$  (the distance between the tip and the substrate) curve (or called an approach curve) with theoretical values. For the 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 quantitative characterization of rapid electron-transfer kinetics.

In this work, we implement the following ET reaction at the W/DCE interface:



The half-reactions in both the water and DCE phases are as follows:



where

$$[E_{\text{Fc}^+/\text{Fc}}^\circ(\text{o})]_{\text{SHE}} = [E_{\text{Fc}^+/\text{Fc}}^\circ(\text{w})]_{\text{SHE}} + \Delta_o^w \phi_{\text{Fc}^+}^\circ - \Delta G_{\text{tr,Fc}}^{\circ, \text{w} \rightarrow \text{o}}/F \quad (6)$$

From eqs 4 and 5, we can define the standard Galvani potential difference for the heterogeneous electron-transfer reaction:

$$\Delta_o^w \phi_{\text{ET}}^\circ = [E_{\text{Fc}^+/\text{Fc}}^\circ(\text{o})]_{\text{SHE}} - [E_{\text{FeIII/FeII}}^\circ(\text{w})]_{\text{SHE}} = 0.28 \text{ V} \quad (7)$$

Using the experimental arrangement of Figure 1, we actually measured a value equal to 0.55 V. To convert the experimental potential difference to the Galvani potential difference, tetraethylammonium ( $\text{TEA}^+$ ) chloride was added as an internal reference ion, and its half-wave potential is about 285 mV. According to eq 8 and with  $\Delta_o^{\text{wo}} \phi_{\text{TEA}^+}$  equal to 19 mV,<sup>17f</sup> the Galvani potential difference of the heterogeneous ET is at about 284 mV, which is in good agreement with the value obtained by eq 7. This value corresponds to the half-wave potential for the cyclic voltammogram of Figure 2.

$$\Delta_o^w \phi_{\text{ET}}^\circ - \Delta_o^w \phi_{\text{TEA}^+}^\circ = \Delta_o^w \phi_{\text{ET}}^{1/2} - \Delta_o^w \phi_{\text{TEA}^+}^{1/2} \quad (8)$$

We control externally the potential difference between the two phases to control the above ET reaction by the three-electrode potentiostat. At the same time, the heterogeneous rate constant can be extracted from analysis of the  $i_T - d$  curve.<sup>1b</sup>

$$I_T^k = I_S^k (1 - I_T^{\text{ins}}/I_T^c) + I_T^{\text{ins}} \quad (9)$$

$$I_S^k = 0.78377/L(1 + 1/\Lambda) + (0.68 + 0.3315 \exp(-1.0672/L))/(1 + F(L, \Lambda)) \quad (10)$$

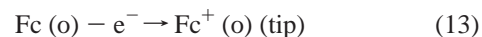
where  $I_T^k$  represents the normalized tip currents for finite substrate kinetics controlled regeneration of a redox mediator,  $I_S^k$  is the kinetically controlled substrate current,  $\Lambda = k_{\text{rd}}/D_R$  ( $D_R$  is the diffusion coefficient of the reduced mediator in DCE), and  $F(L, \Lambda) = (11 + 7.3\Lambda)/(\Lambda(110 - 40L))$ .  $I = i_T/i_{T,\infty}$  and  $L = d/a$  are the normalized tip current and the normalized distance, respectively.

$$I_T^c = 0.78377/L + 0.3315 \exp(-1.0672/L) + 0.68 \quad (11)$$

$$I_T^{\text{ins}} = 1/(0.15 + 1.5358/L + 0.58 \exp(-1.14/L) + 0.0908 \exp((L - 6.3)/(1.017L))) \quad (12)$$

where  $I_T^c$  and  $I_T^{\text{ins}}$  represent the normalized tip currents for diffusion-controlled regeneration of a redox mediator and insulating substrate. Figure 3 shows the family of working curves ( $I_T^k$  vs  $k$ ) for different values of  $L$  along with the simulated data.

When the ET reaction taking place at the liquid/liquid interface is controlled by external addition of potentials, the reactions occurring at the tip of the microelectrode and at the surface of the platinum disk holding the aqueous droplet are as follows:



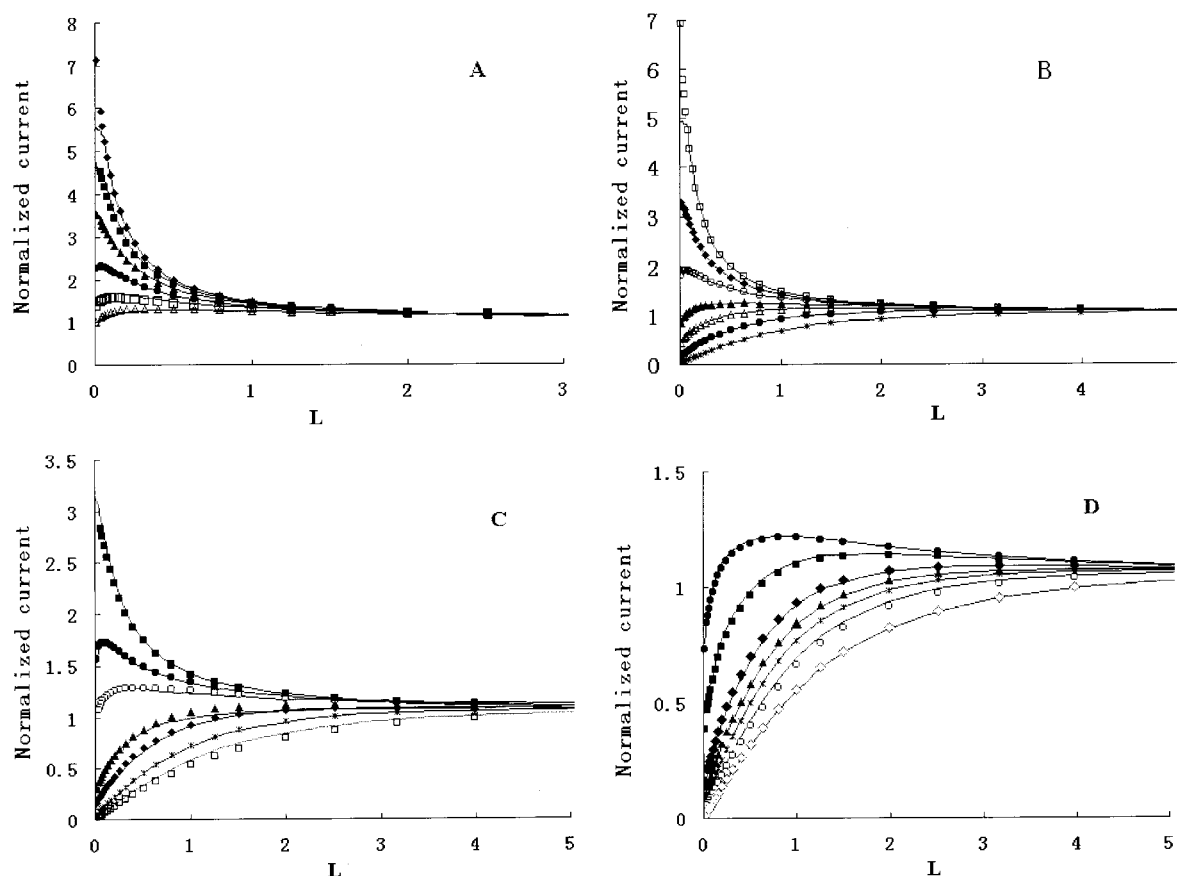
For the pseudo-first-order electron-transfer reaction at the W/DCE interface, we can use in a first instance a Butler-Volmer formalism<sup>21</sup> which can generally be written as

$$I = nFAk^\circ [c_{\text{R1}}^w c_{\text{O2}}^o e^{-\alpha n F(\Delta_o^w \phi - \Delta_o^w \phi^\circ)/RT} - c_{\text{R2}}^w c_{\text{O1}}^o e^{(1-\alpha)n F(\Delta_o^w \phi - \Delta_o^w \phi^\circ)/RT}] \quad (15)$$

and we can define the forward rate constant for the reduction of ferricinium as

$$k_f = k^\circ c_{\text{Fe}(\text{CN})_6^{4-}} \exp(-\alpha n F(\Delta_o^w \phi - \Delta_o^w \phi^\circ)/RT) \quad (16)$$

where  $k^\circ$  is the standard bimolecular rate constant. Figure 3A shows the experimental  $i_T - d$  curves fitted with theoretical values while there is no applied potential at the W/DCE interface. The positive feedback decreases with the decrease of the concentrations of the redox couple in the droplet. Parts B-D of Figure 3 show the feedback decrease with the increase of externally applied potentials at the W/DCE interfaces with different concentrations of the redox couples in the water droplet. Table 2 lists the kinetic rate constants of the ET at the different potentials added externally under various concentrations of the redox couple in the water droplet. They decrease with the increase of the applied potential difference.

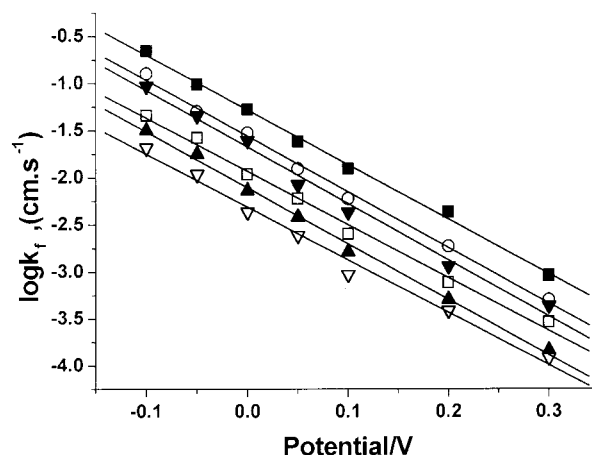


**Figure 3.** Experimental approach curves (symbols) fitted with theoretical values (lines). The DCE phase contained 0.01 M TBATPBCl and 0.2 mM ferrocene. The aqueous phase contained 0.1 M LiCl +  $x$  M  $\text{K}_3\text{Fe}(\text{CN})_6$  +  $y$  M  $\text{K}_4\text{Fe}(\text{CN})_6$ . For (A) there was no external potential and  $x = y = 10, 5, 2, 1, 0.5$ , and  $0.2$  mM, respectively, for (B)  $x = y = 10$  mM, for (C)  $x = y = 2$  mM, and for (D)  $x = y = 0.2$  mM. From top to bottom, the external potentials were  $-0.10, -0.05, 0, 0.05, 0.10, 0.20$ , and  $0.30$  V. All of the approach rates were  $1 \mu\text{m/s}$ .

**TABLE 2: Kinetic Rate Constant of the ET Reaction (cm/s) at Different Potentials**

$c$ ratio/mM	nonpolarized	$E = -0.1$ V	$E = -0.05$ V	$E = 0$ V	$E = 0.05$ V	$E = 0.1$ V	$E = 0.2$ V	$E = 0.3$ V
0.2:0.2	0.029	0.021	0.011	0.0044	0.0025	0.00090	0.00040	0.00012
0.5:0.5	0.040	0.032	0.018	0.0074	0.0039	0.0016	0.00051	0.00015
1:1	0.067	0.045	0.026	0.011	0.0061	0.0024	0.00073	0.00029
2:2	0.11	0.094	0.046	0.024	0.0085	0.0043	0.0012	0.00044
5:5	0.17	0.12	0.047	0.030	0.012	0.0061	0.0019	0.00070
10:10	0.23	0.22	0.090	0.053	0.024	0.010	0.0024	0.00092

Thus, the dependence of the plot of  $\log(k_f)$  vs  $\Delta_o^w\phi$  for different concentrations of  $\text{Fe}(\text{CN})_6^{4-}$  should be linear with a slope proportional to  $\alpha$ , and  $\log(k_f)$  decreases with the externally applied potential difference. The latter is confirmed by the plots of  $\ln k_f$  vs  $\Delta_o^w\phi$  (see Figure 4). As shown in Figure 4, similar electron-transfer coefficients can be found from the linear portions of the Tafel plots, and  $\alpha = 0.38, 0.36, 0.39, 0.37, 0.38$  and  $0.35$ , respectively. These values are close to  $0.5$ , which indicates that conventional ET theory such as for the metal/solution interface is applicable to heterogeneous reactions at the ITIES such as this one. It is clearly shown that the adjustable polarization is at least  $400$  mV and is larger than in the cases where common ions are employed to control the potential differences between ITIES. Indeed, this driving force (polarization) would depend on the available potential window too. It should be rather easy to understand why the obtained heterogeneous rate constants of the above ET reaction decrease with the increase of the applied potentials because it would be more difficult to maintain the recycle (see Figure 1) when more positive potentials were applied.



**Figure 4.** Dependence of the effective heterogeneous rate constants on the externally applied potential across the W/DCE interfaces. The ratios of the concentration of  $\text{K}_3\text{Fe}(\text{CN})_6$  to that of  $\text{K}_4\text{Fe}(\text{CN})_6$  in the aqueous phase from top to bottom were  $10 \text{ mM}:10 \text{ mM}$ ,  $5 \text{ mM}:5 \text{ mM}$ ,  $2 \text{ mM}:2 \text{ mM}$ ,  $1 \text{ mM}:1 \text{ mM}$ ,  $0.5 \text{ mM}:0.5 \text{ mM}$ , and  $0.2 \text{ mM}:0.2 \text{ mM}$ , respectively. The concentration of Fc in the DCE phase was  $0.2 \text{ mM}$ .



## Conclusions

We demonstrated for the first time experimentally that the combination of the conventional electrochemistry at liquid/liquid interfaces with SECM could be achieved successfully. Here the L/L interface functions similarly to a conductive solid substrate. The heterogeneous electron transfer between two immiscible phases can be affected by external addition of potentials. This opens a novel way to investigate charge transfer across liquid/liquid interfaces by SECM.

**Acknowledgment.** We thank the Chinese Academy of Sciences (CAS), the National Natural Science Foundation of China (NSFC), the Third World Academy of Sciences (TWAS), and the State Key Laboratory of Electroanalytical Chemistry of the CAS for the financial support of this work.

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