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# A True Electron-Transfer Reaction between 5,10,15,20-Tetraphenylporphyrinato Cadmium(II) and the Hexacyanoferrate Couple at the Nitrobenzene/Water Interface

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The ability of some metal complexes of 5,10,15,20-tetraphenylporphyrin (TPP) to give a voltammetric wave due to the heterogeneous electron transfer (ET) at a nitrobenzene (NB)/water (W) interface has been examined. The previously-proposed, electron-conductor separating oil-water (ECSOW) system has been successfully employed to find that the TPP complex with cadmium(II) added to NB gives a well-defined, reversible wave for the heterogeneous (*i.e.*, "true") ET with the hexacyanoferrate couple in W. A digital simulation analysis has entirely excluded the possibility of the ion-transfer mechanism due to the homogeneous ET in W. The *a.c.* impedance method has then been used to determine the kinetic parameters including the standard rate constant  $k_0 (= 0.10 \text{ cm M}^{-1} \text{ s}^{-1})$  and the transfer coefficient  $\alpha (= 0.53 \text{ at the half-wave potential})$ . These values are in good agreement with those predicted from the Marcus theory with the assumption that the heterogeneous ET due to molecular collision occurs at the "sharp" NB/W interface.

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## Introduction

Recently, increasing attention has been paid to the study of heterogeneous electron transfer (ET) at oil (O)/water (W) (or liquid/liquid) interfaces.<sup>1-4</sup> A variety of electrochemical techniques including cyclic voltammetry,<sup>5,6</sup> current scan polarography,<sup>7</sup> the *a.c.* impedance method,<sup>8</sup> scanning electrochemical microscopy (SECM),9-14 in situ total internal reflection,<sup>15</sup> and laser trapping of a single oil droplet<sup>16</sup> have been introduced in this field. These studies have shown that reaction mechanisms of ET at the O/W interface can be classified into two major categories: *i.e.*, the ion-transfer (IT) mechanism and the ET mechanism. The former involves an IT process of the ionic product of a homogeneous ET in one phase (usually, the W phase). The well-known ferrocene (O)-hexacyanoferrate (W) system<sup>5</sup> has recently been found to come into the IT mechanism, where the ET occurs "homogeneously" in the W phase and the IT of ferricenium cation as the reaction product is responsible for the current flowing through the interface.<sup>17</sup> A biomimetic ET system between ascorbate (W) and chloranil (O), first reported by Suzuki et al.,18 has also been shown to belong to the category of the IT mechanism.<sup>19-23</sup> In these ET systems that belong to the IT mechanism, redox species in the O phase do not seem to be very hydrophobic (usually, they have their partition coefficients into the O phase  $K_D < 10^4$ ), so that they may give rise to a homogeneous ET in the W phase, rather than a heterogeneous ET due to molecular collision at the O/W interface.

On the other hand, a highly hydrophobic redox species can show a heterogeneous ET at an O/W interface. Such a "true"

defined voltammetric wave for a plausible, heterogeneous ET at the O/W interface. In subsequent studies, other hydrophobic organometallic compounds including tin diphthalocyanine<sup>24</sup> and iron and ruthenium tetraphenylporphyrins<sup>25</sup> were also claimed to show true ET's in the absence of possible IT. These experimental studies then stimulated theoretical studies on the kinetics of ET at O/W interfaces.<sup>26-32</sup> Then, the applicability of the theory by Marcus<sup>26-30</sup> has been tested by means of the a.c.impedance method<sup>8</sup> and SECM.<sup>9-14</sup> Although these kinetic studies generally supported the Marcus theory, it seems premature to accept the validity of the theory, because there is not very much data, and because heterogeneous ET's at O/W interfaces are often complicated by unwanted reactions, such as the above-mentioned homogeneous ET's, decomposition reactions with supporting electrolytes, interfacial adsorption of redox species, etc.33

ET was first reported by Geblewicz and Schiffrin,6 who used an

extremely hydrophobic, lutetium diphthalocyanine complex as a redox species in 1,2-dichloroethane. They observed a well-

In this study, we focused on metal complexes of 5,10,15,20tetraphenylporphyrin (TPP) for redox species in the O phase. Since the TPP complexes are sufficiently hydrophobic, they were expected to give rise to a true ET at an O/W interface. Also, their redox potentials, in contrast to those of phthalocyanine metal complexes,<sup>34</sup> are very much dependent on the central metal ions.<sup>35</sup> We have thus tested some metal TPP complexes (MTPP; M = Co(II), Zn(II), Cd(II)) for their ability to give a voltammetric wave due to the heterogeneous ET at a polarized nitrobenzene (NB)/W interface. For this purpose, we have successfully used the electron-conductor separating oil-water (ECSOW) system, in which the O and W phases are separated by a metal phase.<sup>22</sup> The ECSOW system, where no mass transport occurs through the metal phase, has a very wide potential window, compared with the O/W interface. Taking

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this advantage, we easily found a true ET reaction between CdTPP and the hexacyanoferrate couple at the polarized NB/W interface. The kinetic parameters have also been determined by means of the *a.c.* impedance method.

### **Experimental**

#### Chemicals

The metal TPP complexes were prepared as reported previously,36 and were purified by triple recrystallization from acetone. An aqueous solution of Li<sub>3</sub>Fe(CN)<sub>6</sub> was prepared from a 0.5 M aqueous solution of Na<sub>3</sub>Fe(CN)<sub>6</sub> by ion exchange with a cation exchange resin (Dowex, 50W-4). The concentration of Li<sub>3</sub>Fe(CN)<sub>6</sub> was determined by coulometry with a flow column electrolytic cell (Hokuto Denko Co., HX-203). Tetraoctylammonium salt of 12-tungstophosphate ((TOcA)<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>), which was used as the supporting electrolyte in NB, was prepared as described elsewhere.<sup>37</sup> The tetrapentylammonium salt ((TPnA)<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>) was prepared in a similar manner, but tetrapentylammonium bromide was substituted for tetraoctylammonium bromide. Tetrapentylammonium tetrakis-(4-chlorophenyl)borate (TPnATClPB) was prepared as reported previously.38 An aqueous solution of tetrapentylammonium chloride (TPnACl; Tokyo Kasei) was treated with silver chloride to remove iodide ion (a possible impurity); the concentration was determined by potentiometric titration with a standard silver nitrate solution. An amount of analytical grade nitrobenzene (Wako) was treated before use with activated alumina for column chromatography (Wako; 200 mesh). All other reagents were of analytical grade and were used as received.

#### Electrochemical measurements

Cyclic voltammetric measurements with the ECSOW system<sup>22</sup> were performed using a microcomputer-controlled fourelectrode potentiostat (Hokuto Denko, HS1010mM1S), which was equipped with a positive feedback circuit for ohmic drop compensation.<sup>39</sup> Unless noted otherwise, the electrolytic cell used can be expressed as



where the electron-conductor (EC) phase consisted of two gold disk electrodes (each surface area, 0.071 cm<sup>2</sup>) which were connected with an electric wire. For each measurement, the electrode surfaces were freshly polished with a 0.25  $\mu$ m diamond slurry and then rinsed with distilled water or acetone in an ultrasonic field. The hexacyanoferrate ions were added to the W phase as potassium salts. The two reference electrodes (RE1 and RE2) were immersed in the NB and W phases by means of Luggin capillaries whose tips were located near the respective boundaries of the EC phase. The solution resistance (ca. 8 k $\Omega$ ) was compensated for by means of the positive feedback circuit. The interface between phases I and II was formed in the Luggin capillary. Although the respective phases contained no common ion, the Galvani potential difference was found to be practically time-independent at least for several hours after preparation of the reference electrode (the reproducibility of electrode potential was  $\pm 5$  mV). Two platinum coil electrodes were immersed in the respective phases and served as counter electrodes. The NB and W phases were purged with  $N_2$  gas prior to voltammetric measurements. Other details were described previously.<sup>22</sup>

Cyclic voltammetric measurements with the O/W interface were performed in a similar manner to the ECSOW system. However, phases II and IV in Cell A were not separated by the EC phase and were put directly in contact to form a test O/W interface (area, 0.095 cm<sup>2</sup>) in the previously reported fourelectrode electrolytic cell.<sup>39</sup> The test interface was renewed for each record of a voltammogram. The counter electrode for the NB phase was a Ag/AgCl/4 mM TPnACl + 20 mM MgSO<sub>4</sub> (W) electrode, whereas that for the W phase was a Pt/0.1 M LiCl (W) electrode. The hexacyanoferrate ions were added as lithium or sodium salts in order to obtain a wider potential window.

For *a.c.* impedance measurements, the four-electrode system had yielded no satisfactory frequency response, so the previously reported two-electrode system<sup>40</sup> was then adopted. The electrolytic cell used is expressed as



where the interface between phases II and III is the test O/W interface (area, 0.095 cm<sup>2</sup>). An *a.c.* voltage (1 – 10 Hz; 10 mV peak to peak), being superimposed on a linear sweep voltage (5 mV s<sup>-1</sup>), was applied to the test interface using the potentiostat (Hokuto Denko, HS1010mM1S) in the two-electrode mode. Real (in-phase) and imaginary (out-of-phase) components of the *a.c.* current were measured by means of a lock-in amplifier (NF, LI5640) and recorded against the linear sweep voltage. For each measurement, the test interface was renewed and the solution resistance (*ca.* 8 k $\Omega$ ) was accurately determined by means of a conductivity meter (Yanaco, MY-9). Usually, 95% of the solution resistance was compensated for by a positive feedback circuit, and the rest was corrected for by calculation. The electrolytic cell was reported previously.<sup>40</sup>

All the electrochemical measurements were performed at  $25 \pm 0.1^{\circ}$ C.

#### Determination of the partition coefficient of CdTPP

The partition coefficient ( $K_D$ ) of CdTPP from W to NB was determined by back extraction: CdTPP was initially added to 20 mL of NB so that the concentration became 1 – 5 mM and then distributed to 75 mL of W. After standing overnight at 25°C, CdTPP in the W phase (70 mL) was back-extracted into 15 mL of NB. The concentration of CdTPP in the NB phase was determined spectrophotometrically (molar absorption coefficient:  $\varepsilon = 245000$  at 427 nm). The  $K_D$  value obtained from this distribution experiment was  $2.0 \times 10^5$ ; this is in good agreement with the value of  $1.7 \times 10^5$  which was calculated from the saturated concentrations in NB and W (*i.e.*,  $6.7 \times 10^{-3}$  M and  $3.9 \times 10^{-8}$  M, respectively).

#### **Results and Discussion**

#### Electrode reactions of metal TPP complexes

Electrode reactions of metal TPP complexes have so far been studied in various solvents that contained supporting electrolytes such as tetrabutylammonium perchlorate or

Table 1 Reversible oxidation potentials of metal TPP complexes in NB

MTPP	$E^{\circ\prime}$ /V vs. Fc <sup>+</sup> /Fc			
	1st	2nd	3rd	
CoTPP	0.249ª	0.631	0.916	
ZnTPP	0.362	0.718		
CdTPP	0.170			
H <sub>2</sub> TPP	0.552			

a. Quasi-reversible.

hexafluorophosphate.<sup>41</sup> However, these common supporting electrolytes are not suitable for the present experiments with the O/W interface, because they contain somewhat hydrophilic anions. Thus we studied voltammetric behaviors of the metal TPP complexes in NB containing (TOcA)<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> or TPnATClPB as the supporting electrolyte. As an example, cyclic voltammograms of CdTPP obtained at a gold disk electrode are shown in Fig. 1. When TPnATClPB was used, a well-developed, one-electron oxidation peak of CdTPP was observed at ca. +0.2 V vs. Fc+/Fc (Fc = ferrocene) on the first anodic scan; however, the corresponding reduction peak did not appear on the reverse scan. This is probably because of the oxidation of TCIPB- by the oxidation product of CdTPP. The final rise from +0.3 V is due to the oxidation of TCIPB- at the electrode. On the other hand, when using (TOcA)<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>, a well-defined, one-electron reversible wave was obtained. The anodic and cathodic peaks correspond to the one-electron oxidation-reduction of CdTPP:35

$$[Cd(II)TPP] \stackrel{\sim}{\longleftrightarrow} [Cd(II)TPP]^{+}$$
(1)

The measurements using  $(TOcA)_3PW_{12}O_{40}$  were then extended to other metal TPP complexes and also the free base (H<sub>2</sub>TPP). For the respective cases, one reversible wave and two or three successive waves (not shown) were obtained for the following electrode reactions:<sup>35,42</sup>

$$[Co(II)TPP] \stackrel{-e^-}{\longleftrightarrow} [Co(III)TPP]^+ \stackrel{-e^-}{\longleftrightarrow} [Co(III)TPP]^{.2+}$$
$$\stackrel{-e^-}{\longleftrightarrow} [Co(III)TPP]^{3+} (2)$$

$$[Zn(II)TPP] \stackrel{-e^-}{\longleftrightarrow} [Zn(II)TPP]^{+} \stackrel{-e^-}{\longleftrightarrow} [Zn(II)TPP]^{2+}$$
(3)

$$[H_2 TPP] \stackrel{\neg e}{\longleftrightarrow} [H_2 TPP]^{+}$$
(4)

The reversible oxidation potentials estimated from the midpoint potential of each reversible wave are summarized in Table 1.

#### Cyclic voltammetry with the ECSOW system

In the ECSOW system,<sup>22</sup> no ion transfer occurs across the EC phase, and thus we can obtain a much larger potential window than in the O/W interface. Accordingly, we may easily know, by a simple measurement, at what potential a wave due to a heterogeneous ET should appear in the corresponding O/W interface. Figure 2 shows cyclic voltammograms obtained with the ECSOW system for the ET's between MTPP (M = Co, Zn, Cd) and the hexacyanoferrate couple. For CoTPP and ZnTPP, three or two successive waves were obtained. The respective waves correspond to the oxidation-reduction reactions in Eq. (2) or (3) occurring at the gold electrode in the NB phase. At the other gold electrode in the W phase, the concurrent reduction-oxidation reactions of Fe(CN)<sub>6</sub><sup>3-</sup> added in excess should be taking place:



Fig. 1 Cyclic voltammograms of 0.5 mM CdTPP at a gold disk electrode in NB. Supporting electrolyte: ( $\longrightarrow$ ) 6.6 mM (TOcA)<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>; ( $\cdots$ ) 20 mM TPnATClPB. Scan rate: 100 mV s<sup>-1</sup>.



Fig. 2 Cyclic voltammograms obtained with the ECSOW system. The NB phase contained 0.5 mM CoTPP, ZnTPP, or CdTPP, whereas the W phase contained 100 mM Fe(CN)<sub>6</sub><sup>3-</sup> and 1.0 mM Fe(CN)<sub>6</sub><sup>4-</sup>. The dashed lines for CoTPP and ZnTPP show the voltammograms obtained with the corresponding NB/W interface under the same conditions. The dashed line for CdTPP shows the base current at the NB/W interface. Scan rate: 100 mV s<sup>-1</sup>.

$$\operatorname{Fe}(\operatorname{CN})_{6^{3-}} \stackrel{+e^{-}}{\longleftrightarrow} \operatorname{Fe}(\operatorname{CN})_{6^{4-}}$$
 (5)

As shown in Fig. 2, however, these successive waves appeared out of the potential window of the corresponding O/W interface, and thus would not be observed at the O/W interface. However, CdTPP having a lower oxidation potential gave a welldeveloped oxidation current within the potential window of the O/W interface, though the anodic peak appeared at around the



Fig. 3 Cyclic voltammograms obtained with (A) the ECSOW system and (B) the corresponding NB/W interface. (A) The NB phase contained 0.5 mM CdTPP, whereas the W phase contained 1.0 mM Fe(CN)<sub>6</sub><sup>4-</sup> and (a) 5, (b) 50, and (c) 500 mM Fe(CN)<sub>6</sub><sup>3-</sup>. (B) The NB phase contained (d) 0.5 mM CdTPP or (e) none, whereas the W phase contained 1.0 mM Fe(CN)<sub>6</sub><sup>4-</sup> and 500 mM Fe(CN)<sub>6</sub><sup>3-</sup>. Scan rate: 100 mV s<sup>-1</sup>.

positive end of the window. The electrode reaction occurring at the gold electrode in the NB phase is represented by Eq. (1). We then changed the concentration of  $Fe(CN)_6^{3-}$  to observe the wave just within the potential window of the O/W interface. As expected, the wave shifted to more negative potentials with increasing the  $Fe(CN)_6^{3-}$  concentration, as shown in Fig. 3A. The degree in the potential shift was *ca.* –68 mV per decade change in the concentration, being close to the –60 mV value expected from a digital simulation analysis.<sup>17</sup> Based on these measurements with the ECSOW system, we successfully observed a well-defined voltammetric wave within the potential window of the O/W interface, as shown in Fig. 3B.

#### Cyclic voltammetry for the ET of CdTPP at the O/W interface

The cyclic voltammogram thus obtained for the ET of CdTPP at the NB/W interface is shown again in Fig. 4. In the figure and the following ones, the potential axis is expressed by the Galvani potential difference,  $\Delta_0^W \phi$ , which has been estimated by referring to the midpoint potential (= 0.315 V in Cell A without the EC phase, or 0.367 V in Cell B) for the reversible transfer of tetraethylammonium ion whose standard potential is -0.055 V.<sup>43</sup> In Fig. 4, curve (c) represents the base-current corrected voltammogram. The anodic and cathodic peaks may correspond to the

$$[Cd(II)TPP] (NB) + Fe(CN)_{6^{3-}} (W)$$
  
$$\rightleftharpoons [Cd(II)TPP]^{+} (NB) + Fe(CN)_{6^{4-}} (W) \qquad (6)$$

in which one electron is involved. The peak separation was *ca*. 68 mV in the scan rate range between 10 and 100 mV s<sup>-1</sup>. As is also shown by solid circles in Fig. 4, the voltammogram could be well reproduced by digital simulation based on the reversible



Fig. 4 Cyclic voltammograms obtained with the NB/W interface in the (a) presence and (b) absence of 0.5 mM CdTPP in the NB phase. The W phase contained 500 mM Fe(CN)<sub>6</sub><sup>3-</sup> and 1.0 mM Fe(CN)<sub>6</sub><sup>4-</sup>. Curve (c) represents the base-current corrected voltammogram. Solid circles show the regression data obtained by assuming the reversible ET reaction. Scan rate: 100 mV s<sup>-1</sup>.

ET reaction.<sup>17</sup> The plots of the anodic peak current against both the CdTPP concentration and the square root of scan rate showed straight lines (data not shown), suggesting that the observed current was limited by diffusion of CdTPP in the NB phase. Thus, the interfacial ET of interest was considered as a reversible process in *d.c.* cyclic voltammetry. When the ET reaction is in equilibrium,  $\Delta_0^w \phi$  should be given by

$$\Delta_{\rm O}^{\rm W}\phi = \Delta_{\rm O}^{\rm W}\phi_{\rm ET}^{\circ} + \frac{RT}{F}\ln\frac{[\rm Fe(\rm CN)_6^{4-}]_{\rm W}[\rm CdTPP^+]_{\rm O}}{[\rm Fe(\rm CN)_6^{3-}]_{\rm W}[\rm CdTPP]_{\rm O}}$$
(7)

where []<sub>w</sub> and []<sub>o</sub> denote the concentrations of hexacyanoferrate ions in W and of the complex ions in O, respectively, *R*, *T*, and *F* have their usual meanings, and  $\Delta_O^W \phi_{ET}^{\omega}$  is the formal potential defined by the difference between the formal redox potentials of the respective redox couples in O and W:

$$\Delta_{\rm O}^{\rm W}\phi_{\rm ET}^{\circ\prime} = E_{\rm CdTPP^{+}/CdTPP}^{\circ\prime} - E_{\rm Fe(CN)_6^{3-}/Fe(CN)_6^{4-}}^{\circ\prime}$$
(8)

Here,  $E_{CdTPP'/CdTPP}^{\circ'}$  and  $E_{Fe(CN)s^{L}/Fe(CN)s^{L}}^{\circ'}$  should be expressed on the same potential scale. As shown in Table 1,  $E_{CdTPP'/CdTPP}^{\circ'}$  is +0.17 V vs. Fc<sup>+</sup>/Fc; a value that corresponds to +0.70 V vs. NHE (cf.  $E_{Fe'/Fe}^{\circ'} = +0.53$  V vs. NHE<sup>3,4</sup>). Since  $E_{Fe(CN)s^{L}/Fe(CN)s^{L}}^{\circ'}$  is +0.41 V vs. NHE, <sup>3,4</sup>  $\Delta_{0}^{\circ}\phi_{ET}^{\circ'}$  is then evaluated to be +0.29 V.

#### Exclusion of the IT mechanism by digital simulation

The above-mentioned voltammetric measurements with the O/W and ECSOW systems suggest that the ET mechanism operates for the CdTPP-hexacyanoferrate system. By way of precaution, however, we have examined the possibility of the IT mechanism using a digital simulation technique.<sup>17</sup> In this simulation, the experimentally-determined value of  $2.0 \times 10^5$  was used for the  $K_D$  of CdTPP. The homogeneous ET rate constant,  $k_1$ , in the W phase was assumed to be the diffusion-controlled value ( $7.3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ), which was estimated by the Smoluchowski-Debye theory.<sup>44,45</sup> In this estimation, the radius of CdTPP, r (= 0.62 nm), was obtained by using the approximated equation:<sup>46</sup>  $r = (r_1r_2r_3)^{1/3}$  with  $r_i$  (i = 1, 2, 3) being the radii along the perpendicular axes (*i.e.*,  $r_1 = 0.89 \text{ nm}$ ;  $r_2 = 0.89 \text{ nm}$ ;  $r_3 = 0.3 \text{ nm}$ ; estimated using the MM3 method).

The above assumption that  $k_1$  is the diffusion-controlled value would be the most favorable for the IT mechanism. However, the simulation result has shown that the current due to the IT



Fig. 5 (A) Real and (B) imaginary components of the admittance at 1 Hz for the NB/W interface in the presence (-----) and absence (-----) of 0.4 mM CdTPP in NB. The W phase contained 500 mM  $Fe(CN)_6^{3-}$  and 2.0 mM  $Fe(CN)_6^{4-}$ .

mechanism cannot be observed if the difference between  $\Delta_0^W \phi_{ET}^{er}$  (= +0.29 V) and the standard ion-transfer potential of CdTPP<sup>+</sup> ( $\Delta_0^W \phi_{CdTPP^*}^{or}$ ) is more than +0.6 V. However, a previous semiempirical theory<sup>43</sup> predicts that  $\Delta_0^W \phi_{CdTPP^*}^{or}$  is approximately -1.4 V. Therefore, the difference,  $\Delta_0^W \phi_{ET}^{or} - \Delta_0^W \phi_{CdTPP^*}^{or}$ , is *ca.* +1.7 V, showing the impossibility of the IT mechanism.

#### A.C. impedance measurements

Thus, the above results clearly show that the CdTPP-hexacyanoferrate system is a "true" ET. We then determined the rate constant by means of the a.c. impedance method. Figure 5 shows the real and imaginary components of the admittance at 1 Hz for the NB/W interface, in the presence and absence of 0.4 mM CdTPP in NB. As seen in the figure, a well-defined bell-shaped curve was obtained for both the real and the imaginary components. Using a common equivalent circuit,<sup>40</sup> in which the charge-transfer impedance is expressed by a series combination of resistance  $(r_s)$  and capacitance  $(c_s)$ , we determined the values of  $r_s$  and  $1/\omega c_s$  ( $\omega = 2\pi f$ ; f being the a.c. frequency). In Fig. 6 these values are plotted against  $\omega^{-1/2}$  at  $\Delta_0^{W}\phi = -0.092$  V. Both plots are straight lines with a common slope, which gives the diffusion coefficient of CdTPP in NB:  $D_{\text{R1}} = (2.5 \pm 0.7) \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ . Similar parallel plots were obtained at other potentials and for other CdTPP concentrations (0.2 and 0.3 mM). According to the usual procedure,<sup>40</sup> the kinetic parameter  $\lambda$  defined by the following equation was then evaluated.

$$\lambda = \frac{k_{\rm f}'}{\sqrt{D_{\rm R1}}} + \frac{k_{\rm b}'}{\sqrt{D_{\rm O1}}} \tag{9}$$



Fig. 6 Plot of the real ( $r_s$ ) and imaginary ( $1/\omega c_s$ ) components of the ET impedance against  $\omega^{-1/2}$  for the CdTPP-hexacyanoferrate system (at  $\Delta_0^{\rm eV}\phi = -0.092$  V). The concentration of CdTPP in NB was 0.4 mM.



Fig. 7 Plot of  $\ln[\lambda/(1 + \exp(-\xi))]$  against  $\xi [= F(\Delta_0^W \phi - \Delta_0^W \phi_{1/2})/RT]$  for three different CdTPP concentrations: (O) 0.4; ( $\Delta$ ) 0.3; and ( $\Box$ ) 0.2 mM. The error bars for the data points (O) show the standard deviations for five independent measurements. The solid line shows the regression curve for 0.4 mM CdTPP.

Here,  $k_{\rm f}'$  and  $k_{\rm b}'$  are the pseudo first-order rate constants, respectively, for the forward and backward ET reactions in Eq. (6);  $D_{\rm R1}$  and  $D_{\rm O1}$  are the diffusion coefficients for CdTPP and CdTPP<sup>+</sup> in NB. In Fig. 7, the value of  $\ln[\lambda/(1 + \exp(-\xi))]$  is plotted against  $\xi [= F(\Delta_{\rm N}^{\rm W}\phi - \Delta_{\rm O}^{\rm W}\phi_{1/2}')/RT$ , where  $\Delta_{\rm O}^{\rm W}\phi_{1/2}'$  is the reversible half-wave potential being approximated by the midpoint potential in cyclic voltammetry] for the three different CdTPP concentrations. For every concentration, the plot shows an upward convex curve. The solid line represents the regression curve for 0.4 mM CdTPP, which has been obtained using the fitting equation:<sup>40</sup>

$$\ln[\lambda/(1 + \exp(-\xi))] = \ln \Lambda' + \alpha' \xi \ln(D_{01}/D_{R1})^{1/2} + (\alpha_0 + \alpha' \xi) \xi \qquad (10)$$

with

$$\Lambda' = k_{\rm s} \left(\frac{1}{\sqrt{D_{01}}}\right)^{\alpha_0} \left(\frac{1}{\sqrt{D_{\rm R1}}}\right)^{1-\alpha_0} \tag{11}$$

In this analysis, it has been assumed that the transfer coefficient,  $\alpha$ , for the forward ET reaction is linearly dependent on the potential, *i.e.*,  $\alpha = \alpha_0 + \alpha' \xi$ . It has also been assumed that  $D_{\text{R1}} = D_{01}$ . The values of the standard rate constant ( $k_s$ ),  $\alpha_0$ , and  $\alpha'$ obtained as adjusting parameters in the curve fitting are summarized in Table 2. As seen, these kinetic parameters show

Table 2 Kinetic parameters for the CdTPP (NB)-hexacyanoferrate (W) system at 25°C

[CdTPP] <sup>*a</sup> /mM	$k_{\rm s}/10^{-3}{\rm cm~s^{-1}}$	$lpha_0$	ά
0.2	2.7	0.43	-0.26
0.3	3.2	0.60	-0.04
0.4	2.5	0.55	-0.08
Average	$2.8 \pm 0.3$	$0.53\pm0.07$	$-0.13\pm0.09$

a. Bulk concentration of CdTPP in NB.

no significant dependence on the CdTPP concentration. The  $k_s$  value thus obtained should be related to the second-order rate constant,  $k_0$ , as<sup>8</sup>

$$k_{\rm s} = k_0 (C_{\rm O2})^{1-\alpha_0} (C_{\rm R2})^{\alpha_0} \tag{12}$$

where  $C_{02}$  and  $C_{R2}$  are the bulk concentrations of Fe(CN)<sub>6</sub><sup>3-</sup> and Fe(CN)<sub>6</sub><sup>4-</sup>, respectively. Using Eq. (12) with  $k_s = 2.8 \times 10^{-3}$  cm s<sup>-1</sup>,  $\alpha_0 = 0.53$ ,  $C_{02} = 500$  mM and  $C_{R2} = 2$  mM, we obtain  $k_0 = 0.10$  cm M<sup>-1</sup> s<sup>-1</sup>.

Additionally, we have employed the *a.c.* impedance method to investigate the adsorptivity of CdTPP at the NB/W interface. However, an addition of 0.5 mM CdTPP to the NB phase did not cause any significant change in the double-layer capacity of the interface, showing that CdTPP is not specifically adsorbed at the NB/W interface.

#### Verification of the Marcus theory

The rate constant determined above has been compared with that predicted from the Marcus theory.<sup>26-30</sup> In the theory, the second-order rate constant for heterogeneous ET at a "sharp" O/W interface is given by an Arrhenius-type general kinetic equation:

$$k = Z \exp\left(\frac{-\Delta G^{\ddagger}}{RT}\right) = 2\pi (a_1 + a_2) \kappa \nu (\Delta l)^3 \exp\left(\frac{-\Delta G^{\ddagger}}{RT}\right)$$
(13)

where  $\Delta G^{\ddagger}$  is the standard Gibbs energy of activation of the reaction,  $a_1$  and  $a_2$  are the molecular radii of the reactants in O and W, respectively,  $\kappa$  is the transmission coefficient ( $\kappa = 1$  for a perfect adiabatic ET), v is the frequency for molecular motion, and  $\Delta l$  is the parameter appearing in an exponent for the dependence of the ET rate [ $\propto \exp(-l/\Delta l)$ ] on separation distance l. As typical values,  $\kappa v = 10^{12} \text{ s}^{-1}$  and  $\Delta l = 0.1$  nm were adopted by Marcus.<sup>29</sup>

The activation energy  $\Delta G^{\ddagger}$  is related to the standard Gibbs energy of ET  $[\Delta G^{\circ} = -F(\Delta_{O}^{W}\phi - \Delta_{O}^{W}\phi_{ET}^{\circ}); \Delta_{O}^{W}\phi_{ET}^{\circ})$  being the standard potential]:<sup>26</sup>

$$\Delta G^{\ddagger} = w^{\mathrm{r}} + \frac{\lambda}{4} \left( 1 + \frac{\Delta G^{\circ} + w^{\mathrm{p}} - w^{\mathrm{r}}}{\lambda} \right)^{2}$$
(14)

where  $w^{r}$  and  $-w^{p}$  are the work terms for bringing the reactants from the distance between two reactants  $(d) = \infty$  and for removing the products to  $d = \infty$ , respectively. The values are given by<sup>26</sup>

$$w^{r} = \frac{N_{A}e^{2}}{4\pi\varepsilon_{0}} \left[ -\left(\frac{(z_{1}^{r})^{2}}{4d_{1}\varepsilon_{1}^{s}} - \frac{(z_{2}^{r})^{2}}{4d_{2}\varepsilon_{2}^{s}}\right) \left(\frac{\varepsilon_{2}^{s} - \varepsilon_{1}^{s}}{\varepsilon_{2}^{s} + \varepsilon_{1}^{s}}\right) + \frac{2}{l} \frac{z_{1}^{r}z_{2}^{r}}{\varepsilon_{1}^{s} + \varepsilon_{2}^{s}} \right] (15)$$

and

$$w^{\rm p} = \frac{N_{\rm A}e^2}{4\pi\varepsilon_0} \left[ -\left(\frac{(z_1^{\rm p})^2}{4d_1\varepsilon_1^{\rm s}} - \frac{(z_2^{\rm p})^2}{4d_2\varepsilon_2^{\rm s}}\right) \left(\frac{\varepsilon_2^{\rm s} - \varepsilon_1^{\rm s}}{\varepsilon_2^{\rm s} + \varepsilon_1^{\rm s}}\right) + \frac{2}{l} \frac{z_1^{\rm p} z_2^{\rm p}}{\varepsilon_1^{\rm s} + \varepsilon_2^{\rm s}}\right] (16)$$

where  $N_A$  is the Avogadro constant, e is the elementary charge;  $\varepsilon_0$  is the permittivity of vacuum;  $\varepsilon_i^{s}$  is the static dielectric constant of solvent i (i = 1 for O; i = 2 for W);  $z_1^{r}$  or  $z_1^{p}$  is the charge number of the reactant or product in solvent i (here,  $z_1^{r} =$ 0;  $z_2^{r} = -3$ ;  $z_1^{p} = +1$ ;  $z_2^{p} = -4$ ); and  $d_i$  is the distance from the center of the reactant or product to the interface. It is here assumed that  $d_1 = a_1 = 0.62$  nm,  $d_2 = a_2 = 0.44$  nm,<sup>47</sup> and  $l = a_1 + a^2 = 1.06$  nm.

In Eq. (14),  $\lambda$  is the reorganization energy given by the sum of the contributions of "outer sphere", *i.e.*, solvents ( $\lambda_{out}$ ), and that of "inner sphere", *i.e.*, the intramolecular ligands ( $\lambda_{in}$ ). Marcus<sup>26,27</sup> gave the equation for  $\lambda_{out}$ :

$$\lambda_{\text{out}} = \frac{N_{\text{A}}(ne)^{2}}{4\pi\varepsilon_{0}} \left[ \frac{1}{2a_{1}} \left( \frac{1}{\varepsilon_{1}^{\text{op}}} - \frac{1}{\varepsilon_{1}^{\text{s}}} \right) + \frac{1}{2a_{2}} \left( \frac{1}{\varepsilon_{2}^{\text{op}}} - \frac{1}{\varepsilon_{2}^{\text{s}}} \right) - \frac{1}{4d_{1}} \left( \frac{\varepsilon_{2}^{\text{op}} - \varepsilon_{1}^{\text{op}}}{\varepsilon_{1}^{\text{op}}(\varepsilon_{2}^{\text{op}} + \varepsilon_{1}^{\text{op}})} - \frac{\varepsilon_{2}^{\text{s}} - \varepsilon_{1}^{\text{s}}}{\varepsilon_{1}^{\text{s}}(\varepsilon_{2}^{\text{s}} + \varepsilon_{1}^{\text{s}})} \right) - \frac{1}{4d_{2}} \left( \frac{\varepsilon_{1}^{\text{op}} - \varepsilon_{2}^{\text{op}}}{\varepsilon_{2}^{\text{op}}(\varepsilon_{1}^{\text{op}} + \varepsilon_{2}^{\text{op}})} - \frac{\varepsilon_{1}^{\text{s}} - \varepsilon_{2}^{\text{s}}}{\varepsilon_{2}^{\text{s}}(\varepsilon_{1}^{\text{s}} + \varepsilon_{2}^{\text{s}})} \right) - \frac{2}{l} \left( \frac{1}{\varepsilon_{1}^{\text{op}} + \varepsilon_{2}^{\text{op}}} - \frac{1}{\varepsilon_{1}^{\text{s}} + \varepsilon_{2}^{\text{s}}} \right) \right]$$
(17)

where  $\varepsilon_i^{\text{op}}$  refers to the optical dielectric constant of solvent *i*.

Using Eqs. (15) - (17) with  $\varepsilon_1^s = 34.7$ ,  $\varepsilon_2^s = 78.3$ ,  $\varepsilon_1^{op} = 2.4$ ,<sup>48</sup>  $\varepsilon_2^{op} = 1.8$ ,<sup>48</sup> and the above-mentioned parameters, we obtain:  $w^r = 3.5$  kJ mol<sup>-1</sup>,  $w^p = -3.7$  kJ mol<sup>-1</sup>, and  $\lambda_{out} = 66.4$  kJ mol<sup>-1</sup>. Regarding  $\lambda_{in}$ , the contribution from Fe(CN)<sub>6</sub><sup>3-</sup> is known as  $\lambda_{in}$ (Fe(CN)<sub>6</sub><sup>3-</sup>) = 0.11 eV (= 10.6 kJ mol<sup>-1</sup>),<sup>49</sup> and the contribution from the large CdTPP complex may be approximated to be zero:  $\lambda_{in}$ (CdTPP)  $\approx 0$  kJ mol<sup>-1</sup>, so that  $\lambda_{in}$  is evaluated to be 10.6 kJ mol<sup>-1</sup>. Thus,  $\lambda$  is estimated as  $\lambda = \lambda_{out} + \lambda_{in} = 77.0$  kJ mol<sup>-1</sup>.

Substituting  $\Delta G^{\circ} = 0$  and the estimated parameters,  $w^{r}$ ,  $w^{p}$ , and  $\lambda$ , into Eq. (14) yields  $\Delta G^{\ddagger} = 19.3 \text{ kJ mol}^{-1}$  at  $\Delta_{O}^{W}\phi_{ET}^{\circ'}$  ( $\approx \Delta_{O}^{W}\phi_{ET}^{\circ'}$ ). Accordingly, the rate constant at  $\Delta_{O}^{W}\phi_{ET}^{\circ'}$  is obtained using Eq. (13) as  $k_{0} = 0.17 \text{ cm M}^{-1} \text{ s}^{-1}$ .

The transfer coefficient can be obtained from the relation:<sup>17</sup>

$$\frac{1}{2}\left(1+\frac{w^{p}-w^{r}}{\lambda}\right) = 1-\alpha$$
(18)

Using the values of  $w^{\rm r}$ ,  $w^{\rm p}$ , and  $\lambda$ , we obtain  $\alpha = 0.55$ .

The kinetic parameters thus predicted from the Marcus theory are close to the experimental values:  $k_0 = 0.10 \text{ cm } \text{M}^{-1} \text{ s}^{-1}$  and  $\alpha_0$ = 0.53. This suggests the validity of the above theoretical prediction, which assumes that the heterogeneous ET reaction occurs due to molecular collision at the "sharp" O/W interface. However, further experimental as well as theoretical work seems to be needed to reach a comprehensive understanding of the heterogeneous ET at O/W interfaces.

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