



Bimolecular-reaction effect on the rate constant of electron transfer at the oil/water interface as studied by scanning electrochemical microscopy

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ABSTRACT

Two interfacial electron transfer (ET) systems, *i.e.*, the decamethylferrocene (DcMFC)–Fe(CN)₆^{3−} system and the MTPP⁺–Fe(CN)₆^{4−} system (M = Zn or Cd; TPP = 5,10,15,20-tetraphenylporphyrin) at oil/water interfaces were studied by means of scanning electrochemical microscopy. The second-order rate constants (*k*) for the ET systems could be accurately determined at different “standard” Gibbs energies (ΔG°) by changing the nature and concentration ratio of a common ion added to both phases. The driving force dependence, *i.e.*, the $\log k$ vs. ΔG° plot did not show a simple upward parabola, with the *k* values being limited in a certain range of ΔG° . This clearly suggested that there should be a bimolecular-reaction effect, as predicted previously [T. Osakai, H. Hotta, T. Sugihara, K. Nakatani, *J. Electroanal. Chem.* 571 (2004) 201–206]. However, the observed diffusion-controlled rate constants are typically one-order smaller than the theoretical ones, and have shown only small dependence on the viscosity of organic solvents for the DcMFC–Fe(CN)₆^{3−} system. These results were unexpected from the previous model based on “microscopic diffusion” of a redox species in the vicinity of the interface, and then suggested an alternative model, in which the rate-determining step is “interfacial diffusion” of a redox species across the oil/water interface.

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1. Introduction

The study of electron transfer (ET) at the interface between two immiscible electrolyte solutions (ITIES) or the so-called oil/water (O/W) interface is useful for understanding not only catalytic reactions in two phase systems (liquid membranes, microemulsions, micelles, *etc.*) but also biological processes occurring at lipid membranes (*e.g.*, respiratory chain, photosynthesis, and antioxidative activity) [1,2]. Since Samec *et al.* [3] reported the first example of an ET reaction at a polarized O/W interface, a variety of interfacial ET systems have been studied by means of electrochemical techniques, which include cyclic voltammetry (CV) [3–8], *ac* impedance method [8,9], current scan polarography [10], CV with micro O/W interfaces [11], scanning electrochemical microscopy (SECM) [12–24], and electrolysis with a single micro O- or W-droplet [25–28]. These experimental studies have shown that reaction mechanisms of ET at O/W interfaces are classified into two categories, *i.e.*, the ion-transfer (IT) mechanism and the ET mechanism [2]. The former involves an IT process of the ionic product of a homogeneous ET in one phase (ordinarily, the W phase). The ferrocene (O)–hexacyanoferrate (W) system, as the first example of a “heterogeneous” ET

[3], has been found to come into the IT-mechanism class. The ET mechanism, *i.e.*, a “true” ET reaction can be realized by using a sufficiently hydrophobic redox species in the O phase, *e.g.*, metal complexes of biphthalocyanine [4,5] and 5,10,15,20-tetraphenylporphyrin (TPP) [8].

In the early 1990s, Marcus presented a general theory of ET rates across O/W interfaces [29–33]. An expression was given for the second-order ET rate constant (*k*). When one can neglect the so-called “work terms”, *k* is given approximately by

$$\ln k = \ln Z - \frac{\lambda(1 + \Delta G^\circ/\lambda)^2}{4RT} \quad (1)$$

where *Z* is the frequency factor; λ is the reorganization energy; ΔG° is the “standard” Gibbs energy defined by Eq. (8) shown below; *R* and *T* have their usual meanings. Before and after the Marcus's study, similar but somewhat different theoretical studies were undertaken by other researchers [34–38]. A parabolic dependence of $\log k$ on ΔG° , as predicted from Eq. (1), was first claimed by Bard and coworkers, who used SECM to determine the *k* values for the ET reactions between the oxidized zinc complex of TPP (ZnTPP⁺) and various aqueous reductants [16,19]. However, the experimental $\log k$ vs. ΔG° plot showed considerable scatter from the theoretical curve, probably because of the use of the reductants having different intramolecular reorganization energies.

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More recently, our group [39] pointed out that an ET reaction at the O/W interface is a bimolecular reaction, so that the “microscopic” diffusion of a redox species in the immediate vicinity of the O/W interface should be not a linear one, but like a hemispherical diffusion. Therefore, we predicted that the k value obtained from kinetic measurements would involve such a bimolecular-reaction effect, having a certain upper limit determined by the microscopic diffusion process. In the previous paper [39], the diffusion-controlled rate constant (k_D) of ET at an O/W interface was formulated in the analogy of the Smoluchowski–Debye theory [40,41] for a bimolecular reaction in a homogeneous medium. If the rate-determining step is the microscopic diffusion of a redox species in the O phase (as expected in ordinary cases), then k_D is given by [42]

$$k_D = 4\pi r_A r_B D_A N \quad (2)$$

where r_A and r_B are the radii of redox species, A and B, added to the O and W phases, respectively; D_A is the diffusion coefficient of A in O; N is Avogadro's number. It is here assumed that species A reacts with species B just when it reaches the “reaction surface” that is shown by shadow in Fig. 1. We then predicted that if the ET process is very fast, the overall or observed rate constant should be restricted by the diffusion-controlled rate constant. This prediction was not inconsistent with the previous kinetic data [19], however no decisive conclusion could be reached because of the scatter of experimental data points. We would like to add that Senda [43] also reported a theory of the bimolecular-reaction effect using a cylindrical-diffusion model.

For verification of our proposed theory [39], we employed CV with a single micro W-droplet to determine the k value for ET between decamethylferrocene (DcMFC) in 2-nitrophenyl octyl ether (NPOE) and $\text{Fe}(\text{CN})_6^{3-}$ in the W droplet [27]. In this measurement, ΔG° was varied by changing not the aqueous metal complex but the common ion, which was added to both phases to control the Galvani potential difference ($\Delta\phi \equiv \phi^W - \phi^O$) between the O/W interface. As expected, an upper limit of k was confirmed when ΔG° was decreased, however further experimental verification was needed.

In this paper, we have employed SECM to perform accurate determination of k for two ET systems, i.e., the $\text{MTPP}^+(\text{M} = \text{Zn}, \text{Cd})\text{--Fe}(\text{CN})_6^{4-}$ system and the $\text{DcMFC--Fe}(\text{CN})_6^{3-}$ system. In the later system, several organic solvents were used, including 1,2-dichloroethene (DCE), 1,6-dichlorohexane (DCH), nitrobenzene (NB), and NPOE. In these measurements, ΔG° was varied by changing the nature and concentration ratio of a common ion added to both phases. Based on the $\log k$ vs. ΔG° plots prepared for various ET systems, the validity of our theory has been examined comprehensively.

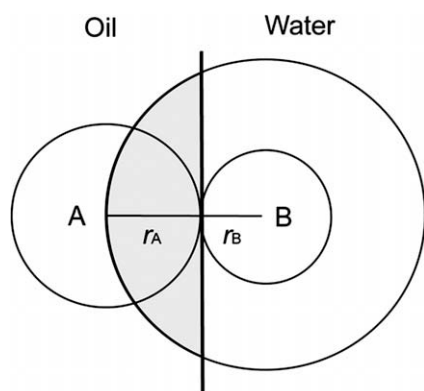


Fig. 1. Previous model for the formulation of a diffusion-controlled rate constant of ET at an O/W interface [39].

2. Experimental

2.1. Reagents

CdTPP was prepared as reported previously [44] and purified by triple recrystallization from acetone. ZnTPP, DcMFC, and potassium hexacyanoferrate(II) ($\text{K}_4\text{Fe}(\text{CN})_6$) were purchased from Wako Pure Chemical Industries and used as received.

Tetraphenylborate salts of tetraethyl-, tetrapropyl-, tetrabutyl-, and tetrapentylammonium (TAATPB with TAA = TEA, TPrA, TBA, TPnA) were prepared by metathesis of the corresponding chlorides (all available from Tokyo Chemical Industry) in ethanol with sodium tetraphenylborate (Dojindo Laboratories) in methanol; the resultant crude salts were washed five times with deionized water, followed by recrystallization from acetone–ethanol (1:1). In a similar manner, perchlorate salts of tetrabutyl- and tetrapentylammonium (TBAClO_4 and TPnAClO_4) were prepared with sodium perchlorate (Aldrich), followed by recrystallization.

DCE for HPLC was purchased from Wako and used without further purification. DCH (98%; Aldrich) was purified by a modified previous method [45]. The purchased reagent was shaken in a separatory funnel with conc. sulfuric acid, and the upper DCH layer was then mixed with activated alumina (Wako; 200 mesh for column chromatography), followed by filtration. This purification process was repeated several times until either the sulfuric-acid layer or the activated alumina were not colored in brown by impurities. The resultant DCH containing some sulfuric acid was shaken successively with deionized water (emulsification occurred), 10 M sodium hydroxide, and deionized water again, and was finally treated with activated alumina. NB (Wako; analytical grade) and NPOE (Dojindo) were treated before use with activated alumina. All other reagents were of the highest grade available and used as received.

2.2. Apparatus and procedures

The SECM measurements were performed with a commercially available system (HV-402E; Hokuto Denko Co.) combined with a potentiostat (HA1010mM1A). A glass-coated platinum ultramicro-electrode (UME; a 10 μm diameter disc electrode with a glass sheath of 100 μm outer diameter) was used as the probe. For further details of the SECM apparatus, see the previous paper [24]. The SECM measurements were performed in an air-conditioned room at 23 ± 2 °C.

Two types of the electrolytic cells used in SECM are schematically shown in Fig. 2. In Cell A for the $\text{DcMFC--Fe}(\text{CN})_6^{3-}$ system, the O phase solvent was DCE, DCH, NB, or NPOE. In Cell B for the $\text{MTPP}^+\text{--Fe}(\text{CN})_6^{4-}$ system, the O phase solvent was NB. Since NB is heavier than water, the test O/W interface in the latter system was prepared at the end of a glass tube of 8 mm inner diameter. To ensure the physical stability of the test interface, the inner glass wall, which should be in contact with the O phase, was siliconized in advance with dimethyldichlorosilane vapor. The O and W solutions were deaerated with nitrogen gas prior to the SECM measurements.

In SECM, the steady-state UME current (I^k) was monitored by moving the UME tip toward an O/W interface at $1.0 \mu\text{m s}^{-1}$. A touch of the UME tip to the interface was usually detected by a sudden change of the current. Using the thus-estimated distance (d) between the UME tip and the interface, the plot of I^k against d , a so-called “approach curve” was obtained. The simulation of approach curves was made by using a theoretical model reported previously [12,22]. The UME used in this study is suitable for the simulation, being characterized by $RG = r_g/a = 10$ (r_g = the radius of the glass sheath; a = the radius of the electrode disc) [46].

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