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Diffusion-controlled rate constant of electron transfer at the oil/water interface

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Abstract

In contrast to conventional electrode reactions, an electron transfer (ET) at an oil (O)/water (W) interface is a bimolecular reaction, so that the “microscopic” diffusion of a redox species in the immediate vicinity of an O/W interface should be not a linear one, but like a hemispherical diffusion. Accordingly, the second-order rate constant obtained from usual kinetic measurements involves such a bimolecular-reaction effect, having a certain upper limit determined by the microscopic diffusion process. In this study, the diffusion-controlled rate constant of ET at an O/W interface has been calculated in the analogy of the Smoluchowski–Debye theory for a bimolecular reaction in a homogeneous medium. It has been shown that when the heterogeneous ET process is very fast, the overall or observed rate constant may be restricted by the diffusion-controlled rate constant.

Keywords: Liquid/liquid interfaces; Electron transfer; Diffusion-controlled rate constant; Smoluchowski–Debye theory; Marcus theory

1. Introduction

Since Samec et al. [1] reported the first example of an electron transfer (ET) at the polarized oil (O)/water (W) (or liquid/liquid) interface, extensive studies have been carried out using several electrochemical techniques including cyclic voltammetry [1,2], current scan polarography [3], the ac impedance method [4,5], scanning electrochemical microscopy (SECM) [6–12], voltammetry with micro liquid/liquid interfaces [13], in situ spectroscopy in total internal reflection [14], laser trapping of a single oil droplet [15], etc (for reviews see [16,17]). It has been recognized through these studies that reaction mechanisms of ET at an O/W interface are 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 ferrocene (O)–ferricyanide (W) system, as the first example of a "heterogeneous" ET [1], has recently been found to come into the IT mechanism class, 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 [18]. A biomimetic ET system between ascorbate (W) and chloranil (O) [19] has also been shown to belong to the category of IT mechanism [20–23]. On the other hand, the ET mechanism corresponds to a heterogeneous ET across the O/W interface.

$$\mathrm{Red}_1\ (\mathrm{W}) + \mathrm{Ox}_2\ (\mathrm{O}) \rightleftharpoons \mathrm{Ox}_1\ (\mathrm{W}) + \mathrm{Red}_2\ (\mathrm{O}) \tag{1}$$

Such a "true" ET was first realized by Geblewicz and Schiffrin [2] who employed a highly hydrophobic, lutetium biphthalocyanine complex as the redox species in the O phase. In subsequent studies [24,25], other hydrophobic organometallic compounds were also claimed to show true ETs in the absence of possible IT. These experimental studies then stimulated theoretical studies by several researchers [26–34], and the applicability of the theory by Marcus [26–30] has been tested by means of the ac impedance method [5] and SECM [6–12].

In the previous kinetic studies the electrochemical measurements were usually performed by adding the redox couple in one phase in an excess amount compared with that in the other phase. Pseudo first-order rate constants were then determined by considering that the phase containing the excess redox species is a metal electrode in conventional electrochemical measurements. The mass transport process for the non-excess redox species in another phase was usually treated as a semi-infinite linear diffusion to a flat O/W interface. However, we should recognize that a heterogeneous ET at an O/W interface is a *bimolecular* reaction, and thus 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 as shown in Fig. 1. This situation is similar to that for an ultramicroelectrode array [35], which gives a steady-state current limited by the hemispherical diffusion of a redox species toward each electrode surface (while the diffusion layers of the individual electrodes are not overlapped). Similarly, the ET rate at an O/W interface could be affected by the microscopic hemispherical diffusion. In usual kinetic measurements the rate constant of the interfacial ET is determined by treating the mass transport process as a conventional, linear diffusion (for a flat interface). Therefore, the rate constant thus determined should involve the bimolecular-reaction effect, having a certain upper limit determined by the microscopic diffusion process.

In this study we have obtained theoretically the upper limit of the rate constant, i.e., the *diffusion-controlled* rate constant for ET at an O/W interface. The proposed theory is an analogy of the Smoluchowski–Debye theory [36–38] for diffusion-controlled bimolecular reactions in homogeneous solution. A somewhat different approach to the present issue has been advanced by Senda [39], who proposed a cylindrical-diffusion model to include the bimolecular-reaction effect.

2. Derivations of theoretical equations

Fig. 2 shows models for diffusion-controlled bimolecular reactions (a) in homogeneous solution and (b) at an O/W interface.

In homogeneous solution, molecule B can diffuse from all directions to react with molecule A. In a diffusion-controlled reaction, when the contact of molecules A and B immediately yields the product, the molar flux of B, J'_B (mol s^{-1}), across the spherical surface of the radius of r_{AB} (= $r_{\mathrm{A}} + r_{\mathrm{B}}$, i.e., the sum of the radii of molecules A and B) around the center of molecule A can be given by

$$J'_{\mathrm{B}} = 4\pi r_{\mathrm{AB}} D_{\mathrm{AB}}[\mathrm{B}], \tag{2}$$

where the bracket [ ] represents the molar concentration (mol cm^{-3}), and D_{AB} (cm^2 s^{-1}) is the relative diffusion coefficient that is assumed to be given by the sum of the diffusion coefficients of A and B

$$D_{\mathrm{AB}} = D_{\mathrm{A}} + D_{\mathrm{B}}. \tag{3}$$

This is because of the simultaneous movement of both molecules. On this basis, Smoluchowski [36] and later Debye [37] provided an equation for the diffusion-controlled second-order rate constant (cm^3 mol^{-1} s^{-1}) as

$$k_{\mathrm{D,hom}} = 4\pi r_{\mathrm{AB}} D_{\mathrm{AB}} L, \tag{4}$$

where L is Avogadro's number. However, this equation should be modified if both the reactants, A and B, are ions and thus have a long-range coulomb interaction [37,38,41]. The reaction rate will be increased when the signs of the ionic charges are opposite. This is the case for the interfacial reaction that is described below. For the sake of simplicity, however, we assume that at least one of the reactants is not an ion.

At an O/W interface, molecule B in the W phase can access molecule A staying in contact with the O-phase side of the interface, only from the W-phase side. It is here assumed that molecule B reacts with molecule A just when it reaches the "reaction surface", i.e., the part of the spherical surface of the radius of r_{AB} around the center of A which bulges out to the W phase (see the shadowed part in Fig. 2(b)). If the O/W interface is "rigid", this assumption is not valid, because molecule B can access the reaction surface only from the vertical direction. However, considering the "softness" of an O/W interface, the assumption may be adequate for simulating real reactions. The diffusion-controlled molar flux of B toward the reaction surface ($J'_{\mathrm{B,het}}$) would then be obtained by a simple extension of the Smoluchowski–Debye theory for a bimolecular reaction in a homogeneous medium. However, the relative diffusion coefficient D_{AB} in Eq. (2) should be replaced by the absolute diffusion coefficient of B in the W phase ($D_{\mathrm{B}}^{\mathrm{W}}$), because in this case, molecule A is regarded as staying at the interface for a reaction with B. Consequently, $J'_{\mathrm{B,het}}$ can be expressed as

$$J'_{\mathrm{B,het}} = 4\pi r_{\mathrm{AB}} \xi D_{\mathrm{B}}^{\mathrm{W}} [\mathrm{B}]. \tag{5}$$

Here, ξ is defined as the ratio of the reaction surface to the surface area of the sphere with the radius of r_{AB}, i.e.,

$$\xi = \frac{2\pi r^2{}_{\mathrm{AB}}(1-\cos\theta)}{4\pi r^2{}_{\mathrm{AB}}} = \frac{1-\cos\theta}{2}, \tag{6}$$

where θ is the angle shown in Fig. 2(b) and given by

$$\theta = \cos^{-1}\left(\frac{r_A}{r_{AB}}\right) = \cos^{-1}\left(\frac{r_A}{r_A + r_B}\right). \tag{7}$$

Next, let us estimate the interfacial reaction rate in an area of S (cm^2). The total flux of B to reach all A molecules in the area of S is expressed using the number of A in S, N(A):

$$J_{\mathrm{B,het}} = N(\mathrm{A})\, J'_{\mathrm{B,het}}\,. \tag{8}$$

Here, it is assumed that molecules A existing at the interface are fully isolated from each other so that diffusion layers of B are not overlapped. This assumption seems to be valid, so far as the concentration of A is not much higher than that of B.

Since the $J_{\mathrm{B,het}}$ given by Eq. (8) is regarded as the diffusion-controlled rate, we obtain from Eqs. (5) and (8):

$$\text{diffusion-controlled rate} = \frac{-\,\mathrm{d}n_{\mathrm{B}}}{\mathrm{d}t} = J_{\mathrm{B,het}}$$

$$= 4\pi r_{\mathrm{AB}}\xi D_{\mathrm{B}}^{\mathrm{W}}[\mathrm{B}]N(\mathrm{A}), \tag{9}$$

where n_{B} is the molar number (mol) of B existing in the area of S.

The rate equation for a bimolecular second-order reaction at an O/W interface is written as

$$\frac{1}{S}\left(-\frac{\mathrm{d}n_{\mathrm{B}}}{\mathrm{d}t}\right) = k_{\mathrm{het}}[\mathrm{A}][\mathrm{B}], \tag{10}$$

where k_{het} (cm^4 mol^{-1} s^{-1}) is the second-order rate constant for a unit area.

Although the estimate of N(A) in Eq. (9) is somewhat arbitrary, we assume that N(A) is the number of A existing in an interfacial layer of a thickness of $2r_{\mathrm{A}}$ (see Fig. 2(b)):

$$N(\mathrm{A}) = 2r_{\mathrm{A}}S[\mathrm{A}]L \tag{11}$$

Here, the concentration of A is assumed to be the same as the bulk concentration, [A], at any point in the layer. Although this assumption may lead to some overestimation of $N(\mathrm{A})$, the combination of Eqs. (9)–(11) yields an expression of the diffusion-controlled rate constant:

$$k_{\mathrm{D,het}} \;=\; 8\pi r_{\mathrm{A}} r_{\mathrm{AB}} \xi D_{\mathrm{B}}^{\mathrm{W}} L . \tag{12}$$

This equation has been derived by assuming that the reaction rate is limited by the diffusion of B in W. If the diffusion of A in O is the rate-determining step, we can obtain the following equation:

$$k_{\mathrm{D,het}} \;=\; 8\pi r_{\mathrm{B}} r_{\mathrm{AB}} \zeta D_{\mathrm{A}}^{\mathrm{O}} L \tag{13}$$

where $D_{\mathrm{A}}^{\mathrm{O}}$ is the diffusion coefficient of A in O, and ζ is given by

$$\zeta = \frac{2\pi r^{2}{}_{\mathrm{AB}}(1-\cos\omega)}{4\pi r^{2}{}_{\mathrm{AB}}} = \frac{1-\cos\omega}{2} \tag{14}$$

with

$$\omega \;=\; \cos^{-1}\left(\frac{r_{\mathrm{B}}}{r_{\mathrm{AB}}}\right) \;=\; \cos^{-1}\left(\frac{r_{\mathrm{B}}}{r_{\mathrm{A}} \;+\; r_{\mathrm{B}}}\right). \tag{15}$$

Thus, the diffusion-controlled rate constant for a bimolecular reaction at an O/W interface could be formulated using the model shown in Fig. 2(b). In the model, molecule B is assumed to diffuse to the “fixed” reaction point where molecule A is located. This approach would appear to be for a unimolecular reaction. However, the number of reaction points in a definite area of the interface is proportional to the concentration of A as shown in Eq. (11), though the value should be given by a statistical average because of the molecular motion of A. Consequently, the upper limit of the rate constant for the “bimolecular” reaction could be expressed by Eq. (12) or (13).

3. Discussion

3.1. Kinetic equation of the ET at an O/W interface

The diffusion-controlled rate constant thus estimated is related to the initial step of ET at an O/W interface:

$$\mathrm{A\,(O) + B\,(W)} \;\underset{k_{\mathrm{uni}}}{\overset{\substack{\text{diffusion}\\ k_{\mathrm{D,het}}}}{\rightleftharpoons}}\; \mathrm{A\cdots B} \;\overset{\substack{\text{ET}\\ k_{\mathrm{ET}}}}{\longrightarrow}\; \text{products} \tag{16}$$

where A···B represents the encounter complex of A and B, which is formed at the interface; k_{uni} is the dissociation rate constant of A···B; k_{ET} is the first-order heterogeneous rate constant of the intramolecular ET. In this manner, we consider the diffusion process and the ET process independently, and then assume that the forward rate constant of the diffusion process is approximated by $k_{\mathrm{D,het}}$. In general cases, however, the backward reaction for the diffusion process (i.e., k_{uni}) should be taken into account, because the concentration of B (alternatively, A) is not necessarily zero at the O/W interface.

On the analogy of a bimolecular reaction in homogeneous solution [40,41], the steady-state approximation method is here used to obtain an expression of the overall rate constant (k):

$$k = \frac{k_{\mathrm{D,het}}k_{\mathrm{ET}}}{k_{\mathrm{ET}} + k_{\mathrm{uni}}} = \frac{k_{\mathrm{D,het}}}{1 + (k_{\mathrm{uni}}/k_{\mathrm{ET}})}. \tag{17}$$

As is evident from this equation, $k_{\mathrm{D,het}}$ is the attainable maximum value of k; when $k_{\mathrm{ET}} \gg k_{\mathrm{uni}}$, the overall reaction becomes diffusion-controlled, i.e., $k = k_{\mathrm{D,het}}$. For slow reactions where $k_{\mathrm{ET}} \ll k_{\mathrm{uni}}$, the first step in the reaction scheme (16) is in equilibrium, i.e.,

$$k = Kk_{\mathrm{ET}} \tag{18}$$

with $K = k_{\mathrm{D,het}}/k_{\mathrm{uni}}$.

With a treatment similar to that for a homogeneous reaction in solution [40,41], we may relate k_{uni} (cm s^{-1}) to $k_{\mathrm{D,het}}$ (cm M^{-1} s^{-1}; M = mol dm^{-3}) as

$$k_{\mathrm{uni}} = \left(\frac{10^{-3}}{L}\right)\frac{k_{\mathrm{D,het}}}{\Delta V}, \tag{19}$$

where the volume ΔV (cm^3) contains the encounter complex and is approximately $(4/3)\pi r^3_{\mathrm{AB}}$.

The first-order heterogeneous rate constant, k_{ET}, for the intramolecular ET of A···B at the O/W interface would be estimated, based on transition state theory, in a similar manner as that for electrode reactions [42–44]:

$$k_{\mathrm{ET}} = \kappa Z_{\mathrm{het}} \exp\left(-\frac{\Delta G^{\ddagger}}{RT}\right) \tag{20}$$

where κ is the Landau-Zener non-adiabacity factor ($\kappa = 1$ for an adiabatic reaction); Z_{het} is the frequency factor; $\Delta G^{\ddagger}$ is the standard Gibbs energy of activation of the reaction; R and T have their usual meanings. The value of $\Delta G^{\ddagger}$ may be estimated using the theoretical equation by Marcus [26–30]:

$$\Delta G^{\ddagger} = w^{\mathrm{r}} + \frac{\lambda}{4}\left(1 + \frac{\Delta G^0 + w^{\mathrm{p}} - w^{\mathrm{r}}}{\lambda}\right)^2, \tag{21}$$

where w^{r} and w^{p} are the work terms, respectively, for bringing the reactants from infinite distance and for removing the products to the infinite distance; λ is given by the sum of the reorganization energy of “outer sphere”, i.e., the solvents (λ_{o}) and that of “inner sphere”, i.e., the intramolecular ligands (λ_{i}); and ΔG^0 is the standard Gibbs energy of the ET reaction (the forward reaction of Eq. (1)), which is expressed by the Galvani potential difference ($\Delta_{\mathrm{O}}^{\mathrm{W}}\phi$) of the O/W interface as $\Delta G^0 = nF(\Delta_{\mathrm{O}}^{\mathrm{W}}\phi - \Delta_{\mathrm{O}}^{\mathrm{W}}\phi^0)$ (where n is the number of electrons and $\Delta_{\mathrm{O}}^{\mathrm{W}}\phi^0$ is given by the difference between the standard potentials of the respective redox couples as $\Delta_{\mathrm{O}}^{\mathrm{W}}\phi^0 = E_{\mathrm{Ox_2/Red_2}}^{\mathrm{O}^0} - E_{\mathrm{Ox_1/Red_1}}^{\mathrm{W}^0}$ versus the same reference electrode). Accordingly, Eq. (21) is rewritten as

$$\Delta G^{\ddagger} = \Delta G^{0\ddagger} + \frac{1}{2} nF\left(\Delta_{\mathrm{O}}^{\mathrm{W}}\phi - \Delta_{\mathrm{O}}^{\mathrm{W}}\phi^0\right) + \frac{1}{4\lambda}\left\{n^2F^2\left(\Delta_{\mathrm{O}}^{\mathrm{W}}\phi - \Delta_{\mathrm{O}}^{\mathrm{W}}\phi^0\right)^2 + 2nF\left(\Delta_{\mathrm{O}}^{\mathrm{W}}\phi - \Delta_{\mathrm{O}}^{\mathrm{W}}\phi^0\right)\left(w^{\mathrm{p}} - w^{\mathrm{r}}\right)\right\} \tag{22}$$

where $\Delta G^{0\ddagger}$ stands for $\Delta G^{\ddagger}$ at $\Delta_{\mathrm{O}}^{\mathrm{W}}\phi = \Delta_{\mathrm{O}}^{\mathrm{W}}\phi^0$. If the work terms can be neglected, Eq. (22) is reduced to

$$\Delta G^{\ddagger} = \Delta G^{0\ddagger} + \frac{nF}{2}\left(\Delta_{\mathrm{O}}^{\mathrm{W}}\phi - \Delta_{\mathrm{O}}^{\mathrm{W}}\phi^0\right) + \frac{n^2F^2}{4\lambda}\left(\Delta_{\mathrm{O}}^{\mathrm{W}}\phi - \Delta_{\mathrm{O}}^{\mathrm{W}}\phi^0\right)^2 \tag{23}$$

with $\Delta G^{0\ddagger} = \lambda/4$ (cf. Eq. (21)). Substituting Eq. (23) to Eq. (20) and taking the logarithm yields

$$\ln k_{\mathrm{ET}} = \ln(\kappa Z_{\mathrm{het}}) - \frac{\lambda}{4RT} - \frac{nF}{2RT}\left(\Delta_{\mathrm{O}}^{\mathrm{W}}\phi - \Delta_{\mathrm{O}}^{\mathrm{W}}\phi^0\right) - \frac{n^2F^2}{4RT\lambda}\left(\Delta_{\mathrm{O}}^{\mathrm{W}}\phi - \Delta_{\mathrm{O}}^{\mathrm{W}}\phi^0\right)^2 \tag{24}$$

Accordingly, a plot of log k_{ET} against $\Delta G^0 = nF(\Delta_{\mathrm{O}}^{\mathrm{W}}\phi - \Delta_{\mathrm{O}}^{\mathrm{W}}\phi^0)$ should show an upward parabola with the apex at $\Delta G^0 = -\lambda$.

3.2. Application to experimental data

Previously, Bard's group [7,10] used SECM to determine bimolecular rate constants for heterogeneous ETs between the oxidized form of (5,10,15,20-tetraphenylporphyrinato)-zinc(II) ($\mathrm{ZnPor^+}$) and various aqueous reductants, which were claimed to show the driving-force (i.e., ΔG^0) dependence in accordance with the Marcus theory. In the theory, however, it is tacitly assumed that the above-discussed microscopic diffusion process is too rapid to affect the whole ET rate. In the following, we will try to examine the applicability of our proposed theory to the experimental data [10].

First, let us estimate the $k_{\mathrm{D,het}}$ value for the ET reaction between ZnPor^{+} (= A) in O and a reductant such as $\mathrm{Fe(CN)}_6^{-4}$ (= B) in W. The following parameters are here assumed: $r_{\mathrm{A}} = 8 \times 10^{-8}$ cm; $r_{\mathrm{B}} = 5 \times 10^{-8}$ cm; $D_{\mathrm{A}}^{\mathrm{O}} = 2.5 \times 10^{-6}$ cm^2 s^{-1}; $D_{\mathrm{B}}^{\mathrm{W}} = 1 \times 10^{-5}$ cm^2 s^{-1}. If the diffusion of B in W is the rate-determining step, we use Eqs. (6) and (7) to obtain $\xi = 0.192$. Substituting this value and some of the above parameters into Eq. (12), we obtain $k_{\mathrm{D,het}} = 302$ cm M^{-1} s^{-1}. If the diffusion of A in O limits the rate, we likewise obtain $\zeta = 0.308$ from Eqs. (14) and (15), and then $k_{\mathrm{D,het}} = 76$ cm M^{-1} s^{-1} from Eq. (13). Because the $k_{\mathrm{D,het}}$ value for the latter is smaller than that for the former, the diffusion-controlled rate constant for the present system should be considered as 76 cm M^{-1} s^{-1}.

The $k_{\mathrm{D,het}}$ value thus obtained enables us to calculate the k_{uni} value (= 1.4×10^{-5} cm s^{-1}) based on Eq. (19) with $\Delta V \approx (4/3)\pi r^3{}_{\mathrm{AB}} = 9.2 \times 10^{-21}$ cm^3. The overall rate constant k can then be evaluated from Eq. (17) using the values of $k_{\mathrm{D,het}}$ and k_{uni}. In Fig. 3, the thick solid line represents the dependence of k on the driving force $\Delta E_{1/2}$ (= $-\Delta G^0/nF = -(\Delta_{\mathrm{O}}^{\mathrm{W}}\phi - \Delta_{\mathrm{O}}^{\mathrm{W}}\phi^0)$); here, $n = 1$. In drawing the theoretical curve, we have treated the values of λ (= 0.8 eV) and κZ_{het} (= 9×10^{-5} cm s^{-1}) as adjusting parameters to fit the experimental data as well as possible. It should here be noted that the overall rate constant plateaus at the diffusion-controlled rate constant indicated by the broken straight line. The upward parabola shown by the broken line represents the value of Kk_{ET} that corresponds to the k value for $k_{\mathrm{ET}} << k_{\mathrm{uni}}$ (i.e., if the diffusion process was very fast). In Fig. 3 is also shown the theoretical curve (thin solid line) by Ding et al. [10], who did not consider the contribution of the diffusion process of interest. Neither their nor our theoretical curve, however, has an absolute advantage in fitting the experimental data showing considerable scatter. It should also be noted that both the theoretical curves have been drawn by neglecting the work terms, though the experimental data consist of those obtained with three different organic solvents and some different aqueous reductants. Further experimental verification seems to be desirable.

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Figure captions

Fig. 1. “Microscopic” hemispherical diffusion of redox species in the immediate vicinity of an O/W interface. This figure is drawn for the case when the redox species in the W phase diffuse toward the interface to react with redox species in the O phase.

Fig. 2. Models for diffusion-controlled bimolecular reactions (a) in homogeneous solution and (b) at an O/W interface. For details, see the text.

Fig. 3. Driving-force dependence of the second-order rate constant (log *k*) for heterogeneous ETs between ZnPor^+ and aqueous reductants: $\mathrm{Ru(CN)}_6^{4-}$, $\mathrm{Mo(CN)}_8^{4-}$, $\mathrm{Fe(CN)}_6^{4-}$, $\mathrm{W}(CN)_8^{4-}$, $\mathrm{Fe(EDTA)}^{2-}$, $\mathrm{Ru(NH_3)}_6^{2+}$, V^{2+}, and $\mathrm{Co(Sep)}^{2+}$ (Sep = sepulchrate). Thick solid line: from Eqs. (17) and (24) with $\lambda = 0.8$ eV and $\kappa Z_{\mathrm{het}} = 9 \times 10^{-5}$ cm s^{-1}. Thin solid line: the theoretical curve by Ding et al. [10]. The plots show their experimental data for the benzonitrile/W (●), benzene/W (■), dichloroethane/W (▲) interfaces. For further details, see the text.

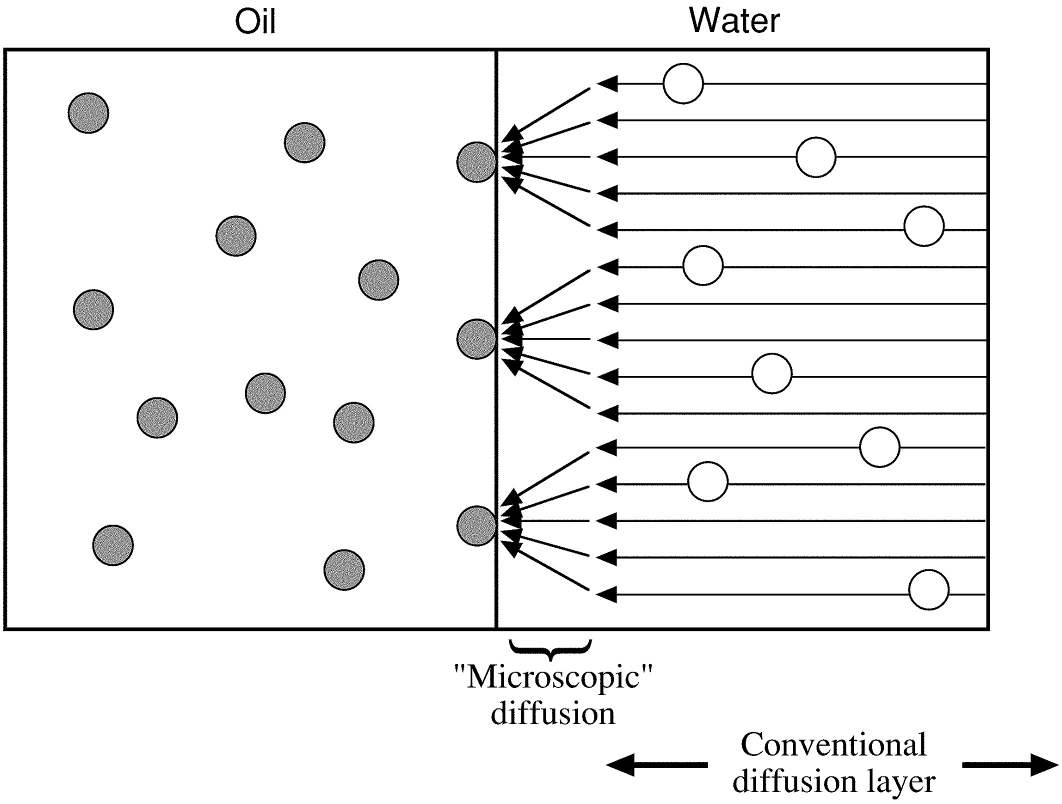
Oil
Water
"Microscopic" diffusion
Conventional diffusion layer

Fig. 1

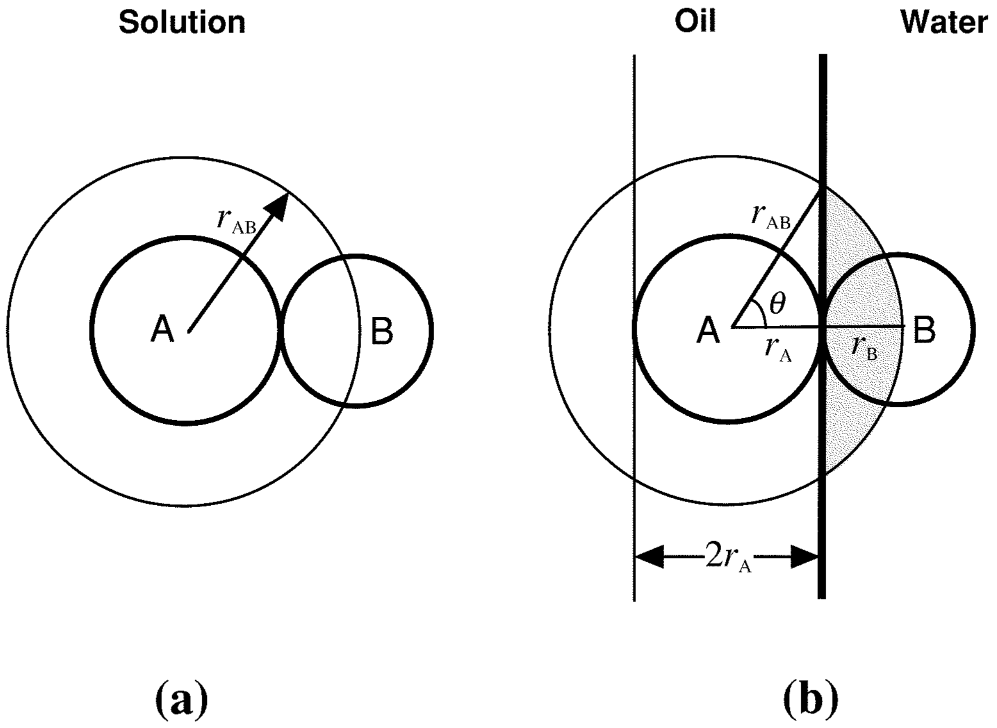

Fig. 2

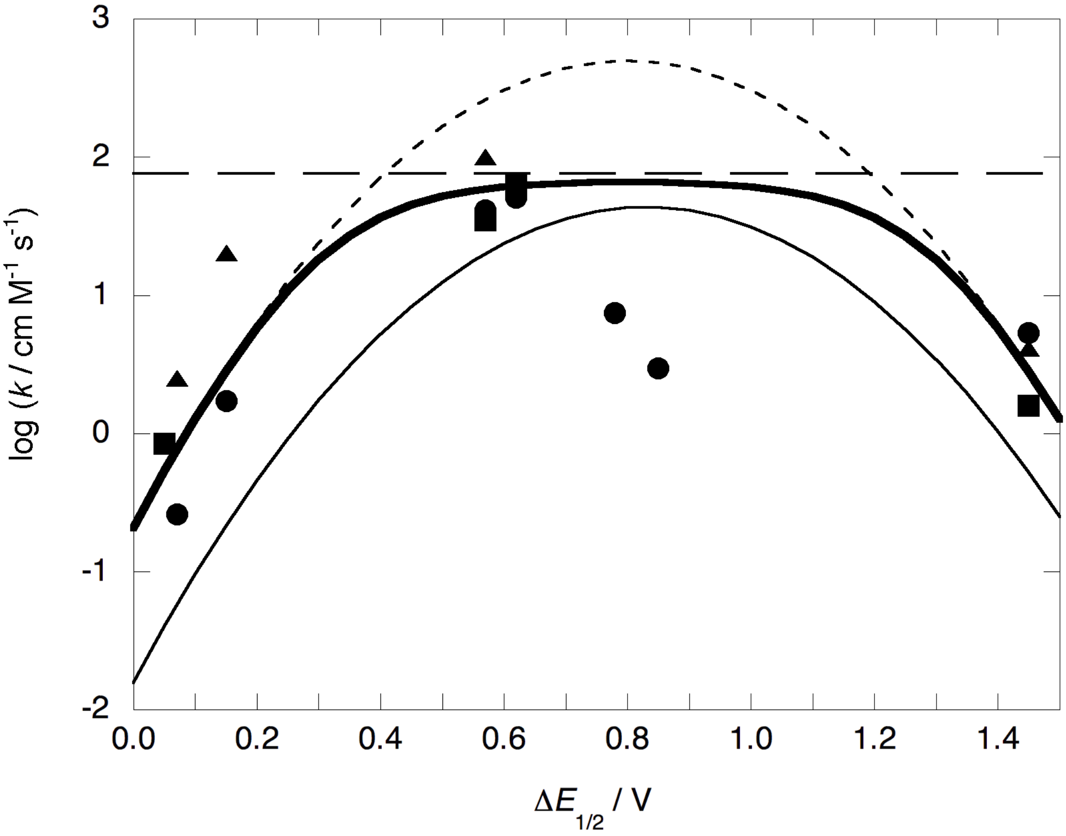

Fig. 3