Electrode reactions at sub-micron oil | water | electrode interfaces

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Abstract

Our electrochemical system is a hemispherical droplet of nitrobenzene including ferrocene, which is mounted on a glassy carbon electrode in a sodium sulfate aqueous solution. It is composed of a hemispherical oil | water interface, a disk-shaped oil | electrode interface, a water | electrode interface and a ring oil | water | electrode interface. The voltammetric current of the droplet showed two anodic waves for the oxidation of ferrocene. The current at 0.5 V was proportional to the radii of the droplet and concentration of ferrocene, and was independent of the potential sweep rate as well as the concentration of sulfate. These facts indicate that the electrode reaction should occur at the thin ring on the electrode into which the water and the oil phase merge. A model of a microband electrode was suggested and was applied to the limiting current to evaluate the width of the three-phase interface. The evaluated width, 0.23 μm, is much larger than the molecular size.

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1. Introduction

There are some electrochemical systems in which an electrode is in contact with both a water phase and an oil phase, exemplified by electrochemical bio-sensors inserted into living tissues, carbon paste electrodes, and electrode reactions of emulsions [1–7]. Electroactive species in the water phase are usually of interest whereas the oil phase works as a blocking material, a support of immobilized chemicals, or a support of conducting materials. When an electroactive species is included even in the oil phase, electrode reactions in both phases are not only competitive but also as interactive [8,9] between the two phases through ion-transfer and/or electron transfer [10,11]. A simple system of the competitive behavior is the single oil droplet (ca. 50 μm in typical diameter) formed so carefully on a microelectrode (10–20 μm in diameter) in the water phase that the electrode may not be in contact with the water phase, developed by Nakatani et al. [9,12,13]. The product by the electrode reaction transfers through the oil | water interface in order to maintain electric neutrality. This mass transfer can be modeled as a series combination of the oil | electrode interface and the oil | water interface, and its kinetics have been analyzed by numerical computation [14]. The model is a modification of the cell configuration of the redox species–included oil-coated electrode immersed into water [15,16] from a viewpoint of mass transport.

A highly competitive system is the reaction at the three-phase boundary at which the electrode was exposed to both the oil and the water phase, explored by Scholz and coworkers [8,17,18]. It is composed of an oil droplet mounted on the electrode in an aqueous solution, as is shown in Fig. 1. Both electrode reactions and ion-transfer occur simultaneously at the three-phase junction (Fig. 1(A)) when the oil phase contains redox species such as ferrocene without deliberately added supporting electrolyte [8,19–21]. This three-phase reaction is based on the concept that the electrode reaction requires counterions, which are supplied only from the water phase to compensate the redox charge at the

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The proportionality of the lysis time owing to the gradual insertion of the anion to the area of the oil contrast, slow scan rates make the current proportional reaction, was observed at fast potential scan rates. In contrast, slow scan rates make the current proportional to the radii of the oil droplets. Although the proportionality to the radii has been demonstrated to be valid [8], the reaction domain extended to the whole oil | electrode interface with an increase in the electrolysis time owing to the gradual insertion of the anion into the oil phase [18,21,22]. The proportionality of the current with the radius, i.e. the three-phase boundary reaction, was observed at fast potential scan rates. In contrast, slow scan rates make the current proportional to the area of the oil | electrode interface, i.e., the two-phase boundary reaction [23]. Marken and coworkers [24,25] carried out the three-phase interface reaction for a redox liquid in aqueous solutions. This is an interesting system in that concentration of the redox species is extremely high. Although they have carried out the three-phase reaction in a redox liquid system.

The three-phase interface is expected to be as thin as molecular-size at the three-phase intersection. Thus, the three-phase interface may provide a steady-state current as in microelectrode behavior. Necessary conditions for forming the steady-state three-phase interface are

a) such high resistance of the oil phase that the electric field in the double layer at the oil | electrode interface is much lower than that at the water | electrode interface and the three-phase interface, and
b) the presence of an electroactive species only in the oil phase.

These requirements may be satisfied, for example, when an anion in the water phase cannot transfer into the oil phase and when the oil phase includes ferrocene without supporting electrolyte. Then no reaction occurs at the water | electrode interface because of the absence of electroactive species. No reaction occurs at the oil | electrode interface because of the absence of the double layer. Consequently, reactions should occur only at the three-phase interface. This interface may work as an extremely thin band electrode [23] rather than a cylinder electrode [27]. The current values can be predicted from the mass transport theory at the band electrode [28–30], exhibiting the proportional dependence of the current on the radii of the oil droplets and little dependence on potential scan rates in linear sweep voltammetry. Under this motivation, we generate in this paper the three-phase boundary by use of ferrocene-included nitrobenzene droplets in the Na2SO4-included water phase. The sulfate ion is selected in that its standard Galvani potential difference of ion-transfer is rather negative (−0.53 V) [31]. In order to evaluate the thickness of the interface, an approximate equation for the voltammetric peak current was derived as a function of the width and potential sweep rates on the basis of the band electrode model.

2. Experimental

The glassy carbon working electrode was fabricated with a GC-20S rod (Tokai Carbon, Tokyo) 6 mm in diameter by covering the side with a shrinkable polyfluoroethane tube so that the end of the tube was flush with the electrode surface. The electrode surface was polished with alumina powder and was sonicated in water. The electrochemical cell was a plastic spectroscopic cell (10 × 10 × 40 mm³), the bottom of which was drilled and plugged with the working electrode. The inserted working electrode was sealed with polytetrafluoroethane tape against a leakage of the aqueous solution (50 mM NaClO4 or 50 mM Na2SO4 (M: mol dm⁻³)). A nitrobenzene droplet was put on the electrode surface using a 5 mm³ syringe. A screw-driven plunger was installed in the syringe in order to control the volume of injection accurately. The volume of the aqueous solution was 3 cm³.

Photographs of the oil droplet were taken through a video microscope, VMS-1900 (Scalar Scopes, Tokyo). Diameters and amounts of oil droplets were evaluated from image analysis with computer software.

The reference electrode was Ag | AgCl in 3 M NaCl solution. The counter electrode was a platinum coil. The potentiostat was a μ-Autolab (Eco Chemie).

Nitrobenzene was purified with 30 volume% of alumina powder for a half day, and was separated by filtration. Ferrocene (Fc) (Wako, GR grade) was sublimated and collected in a cooling vacuum flask. Commercially available Na2SO4 was recrystallized.
3. Results and discussion

3.1. Features of voltammograms

Photographs of our electrochemical system are shown in Fig. 2. The oil droplet including ferrocene was mounted on the electrode in the 50 mM Na₂SO₄ aqueous solution before (A) and after (B). The droplet adhered so strongly on the glassy carbon surface that it could not be removed by mixing the aqueous solution or sucking the solution very close to the droplet by a syringe. The shape of the adhered droplet in the 50 mM Na₂SO₄ solution was a flattened hemisphere whereas that in the 50 mM NaClO₄ aqueous solution was a hemisphere [23]. Radii r₁ and r₂ (shown in Fig. 2), characterize the shape of the oil droplet, the former being defined by the radius of the circle on which the droplet meets the electrode, and the latter being the radius of the curvature with which the droplet is regarded as a part of a sphere. Values of r₁ and r₂ were determined by use of image analysis for droplets. The relation between r₁ and r₂ was almost proportional, as has been shown in Fig. 3 of Ref. [23]. Once the potential was scanned up to 0.9 V at 10 mV s⁻¹, the droplet became more flattened, as is shown in Fig. 1(B). This can be explained in terms of the decrease in the surface energy at the oil | water interface owing to the insertion of salt into the oil droplet, as will be described later.

Fig. 3 shows cyclic voltammograms of the ferrocene-included oil droplet to which 50 mM tetrabutylammonium perchlorate (TBAClO₄) was deliberately added. The voltammogram at the first scan showed a large anodic peak at 0.44 V (α), a cathodic peak at 0.34 V (α’) and a small cathodic peak at 0.16 V (β’). Waves (α) and (α’) are obviously a redox pair of ferrocene in the oil phase. The voltammogram at the second scan has not only waves (α), (α’) and (β’) but also a small anodic wave at 0.20 V (β). Waves (α) and (α’) decreased with an increase in the iterative potential scan, implying the reduction of concentration of Fc owing to the limited volume of the droplet. The reaction mechanism of the voltammetric behavior has already been described previously [23], and is explained here briefly with a help of the illustration in Fig. 1(B), as follows: Fc in the oil droplet is oxidized (wave (α)) at the electrode to yield ferricenium ion (Fc⁺) by compensating the positive charge with ClO₄⁻ in the droplet, as is shown in step (i) of Fig. 1(B). The perchlorate ion is supplied from the water phase (step (ii)) when the potential is over the Galvani ion transfer potential for ClO₄⁻. Ferricenium ion in the droplet is dissolved in the water phase (step (iv)) because it is dissolved more in water than in nitrobenzene. Then, the local concentration of Fc⁺ in the oil decreases. The Fc⁺ transferred to the water phase gives the reduction wave (β’) for which the potential is the same as the reported value [32]. The reduced ferrocene can be oxidized in the water phase to give wave (β) at the second and the succeeding positive scans (step (v)).

If Fc in the oil droplet is dissolved in the water phase by the oil | water partition equilibrium, the concentration of Fc and hence Iₚ may decrease even in the reduced state. In order to examine the possibility of the dissolution, we left a newly formed droplet for a given time, at most 30 min, in the reduced state and obtained Iₚ by linear sweep voltammetry. The dependence of Iₚ on the time, t, during which the droplet was left in the aqueous solution is shown in Table 1. The peak current is independent of the time, indicating a negligible amount of dissolution of Fc in the aqueous solution without electrochemical oxidation. The small amount of dissolu-
tion of Fc in the water phase was confirmed by the dependence of the voltammetric current on the volume (from 2 to 10 cm$^3$) of the water phase. No current-dependence was observed. Therefore, it is not necessary to take into account the dissolution of Fc in the reduced state.

When supporting electrolyte was not included in the oil droplet, the cyclic voltammograms were similar to the waves in Fig. 3 except for the slight potential shift in the positive direction as well as smaller peak currents [23]. The voltammetric behavior has been explained as follows [23]: since the oil droplet includes no salt before the potential application, Fc in the oil phase is electro-inactive at the oil | electrode interface. However, it is electroactive at the oil | water | electrode (three-phase) interface because of the formation of the double layer on the water side. Once Fc is oxidized at the three-phase interface (step (i) in Fig. 1A), perchlorate ion is transferred from the water phase into the oil phase close to the three-phase interface in order to compensate the positive charge of Fc$^+$ in the oil phase. Then a small domain in the oil droplet close to the three-phase interface becomes gradually ionic, and the double layer begins to be formed from the three-phase interface. As the perchlorate ion diffuses toward the center of the droplet, the reaction domain extends toward the center of the droplet (the arrow and step (iii)). This behavior has been demonstrated by the electrochemical microscopic technique [21]. Strictly speaking, the reaction only at the three-phase interface occurs immediately after the potential application [23]. Ferricenium ion accumulated in the oil phase transfers into the water phase (step (iv)), and is oxidized in the water phase at the second scan (step (v)).

A key factor in obtaining the steady-state reaction at the three-phase interface is to block the formation of the double layer at the oil | water interface or to block the transfer of anion (ClO$_4^-$) into the oil phase. In other words, an anion with a very negative value of the Galvani ion-transfer potential will realize the steady-state reaction at the three-phase interface. It is sulfate ion that has the most negative value of the available ion-transfer potentials [31]. We used Na$_2$SO$_4$ as a supporting electrolyte in the water phase. The cyclic voltammogram of the oil droplet containing ferrocene showed two anodic waves and three cathodic waves at the first scan, as is revealed in Fig. 4. Wave (c`) was not found when the potential scan was reversed at 0.3 V. Thus, it is due to the reduction of ferricenium ion in the water phase, and is the same as wave (β`) in Fig. 3. Waves (a) and (a`) are a redox pair because (a`) was also found when the potential scan was reversed at 0.55 V. A middle half-wave potential of (a) and (a`) is 0.43 V. Waves (b) and (b`) are also a redox pair because they were observed in the potential scan domain from 0.6 to 0.9 V. A middle half-wave potential of (b) and (b`) is 0.70 V. This potential is not inconsistent with the value predicted from the difference in standard ion-transfer potential at the NB | water interface, $E^\circ'(\alpha/\alpha') = [E^\circ'(\text{SO}_4^{2-}) - E^\circ'(\text{ClO}_4^-)] = 0.39 - (-0.53 + 0.094) = 0.82$ V [31]. The difference, 0.82–0.70 = 0.12 V, may be due to the difference in the interactions of Fe$^+$–ClO$_4^-$ and Fe$^+$–SO$_4^{2-}$. When a potential of 0.9 V was applied for a long time, the droplet turned from yellow to green. The color change indicates that ferrocene is oxidized to the ferricenium ion which is retained in the oil droplet. In contrast, no color change was found for the potential application of 0.5 V for a long time, probably because ferricenium ion is diffused away into the aqueous bulk phase.

Voltammetric measurements were carried out for renewed droplets at various potential scan rates, $v$, various sizes of the droplets, and various concentrations of ferrocene. The renewal is significant because ferricenium ion diffuses into the water phase and leads to depletion of ferrocene in the oil droplet. With an increase in the scan rates and with a decrease in droplet size, waveforms especially of wave (b) became vague. We evaluated the limiting current of wave (b) by extracting a contribution of wave (a) in terms of the graphical background subtraction, as is shown in Fig. 4. Fig. 5 shows dependence of the limiting current of wave (a) and (b), respectively ($I_{L,a}$) and ($I_{L,b}$), on the concentration of ferrocene, $c_{Fc}$, in the logarithmic scale. The current values fall on the line with a unity slope, except for $c_{Fc} < 0.5$ mM. The proportionality of ($I_{L,a}$ and

<table>
<thead>
<tr>
<th>$t$/min</th>
<th>$I_p$/μA</th>
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<tbody>
<tr>
<td>0</td>
<td>1.33 ± 0.08</td>
</tr>
<tr>
<td>1</td>
<td>1.20 ± 0.18</td>
</tr>
<tr>
<td>15</td>
<td>1.30 ± 0.16</td>
</tr>
<tr>
<td>30</td>
<td>1.35 ± 0.04</td>
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Potential scan started $t$ min after the droplet was formed on the electrode in the aqueous solution.
Fig. 5. Logarithmic dependence of the limiting currents of wave (a) (circles) and wave (b) (triangles) on the logarithmic concentration for oil droplets whose radii ranged from 0.50 to 0.63 mm in 50 mM Na_2SO_4 aqueous solution. Voltammograms were obtained at 5 mV s^{-1}. The regression line with unity slope was drawn for currents of wave (a).

\( \text{I}_b \) to \( c_{Fe} \) supports the proposal that the current is due to the oxidation of ferrocene. The finding, \( \text{I}_a / C_30 / \text{I}_b \), in Fig. 5 seems to be by chance in selecting variables, \( v \) and \( r_1 \).

3.2. Voltammograms at the three-phase interface

Fig. 6 shows variations of the limiting current of wave (a) with both the radius and the area of the oil | electrode interface. The proportionality to \( r_1 \) indicates that the reaction occurs at the circumference of the oil | electrode interface, i.e., at the three-phase interface. The proportionality to \( r_1 \) was also observed at fast scan rates by Scholz’s group [8] and Aoki’s group [23], independently. In order to find the time-dependence of the current, especially at long-time behavior, we carried out voltammetry at some slow scan rates before 0.6 V, and show some waves in Fig. 7. Wave (a) was almost independent of the scan rates. Wave (a’) at the backward scan had a waveform similar to the wave (a). This similarity as well as the scan-rate independence is a feature of steady-state voltammograms, as is known in microelectrode behavior. In contrast, wave (c’) was enhanced with an increase in the scan rate, implying a reduction at the water | electrode interface. In order to examine the steady-state feature quantitatively, we plotted the limiting current of wave (a) against the scan rate in Fig. 8. Values of the limiting currents were independent of the scan rates even at \( v = 0.5 \text{ mV s}^{-1} \), supporting the finding that the reaction at the three-phase interface is at the steady-state. Consequently, the reaction domain in Fig. 1(A) does not extend to the whole oil | electrode interface but is localized at the three-phase interface.

On the basis of the above results, we take into account detailed mechanisms of three-phase interface reaction. The oil phase does not include any salt because of insufficient potentials of transfer of \( SO_4^{2-} \) into the oil phase for \( E_{B} / \text{0.6 V} \), whereas the water phase does. Therefore, the double layer responsible for the electrode reaction is not formed at the oil | electrode interface. It is at the oil | water | electrode interface and/or at the water | electrode interface that ferrocene is oxidized. Two possible reaction mechanisms can be suggested as follows:

A) Charge transfer followed by the transfer (Fig. 9(A)): the double layer at the water | electrode interface seeps out to the oil | electrode interface by at least a molecular sized domain even without the transfer of \( SO_4^{2-} \) into the oil phase, and hence it is formed at the three-phase interface. When ferrocene reaches the three-phase interface, it is oxidized to ferrice-
Fc(O) → Fc(W)

Fc(W) → Fc⁺(W) + e⁻  \hfill (1)

This mechanism is similar to a CE reaction. This partition equilibrium should give rise to a potential shift by \((RT/F) \ln(7000) = 0.22 \text{ V}\) from the redox reaction of ferrocene in the water phase (e.g. the cathodic wave at 0.16 \text{ V} in Fig. 4(c')). However, wave (a) in Fig. 4 is more positive than the predicted value, 0.16 + 0.22 = 0.38 V. Therefore, mechanism (B) can be excluded from the possibilities.

The mechanism suggested is the oxidation of ferrocene at the three-phase interface with the help of sulfate in the water phase. This oxidation requires sulfate ion to participate in forming the double layer, and can be expressed by

\[
\text{Fc(O)} | \frac{1}{2} \text{SO}_4^{2-}(W) \rightarrow \text{Fc}^+(W) + \frac{1}{2} \text{SO}_4^{2-}(W) + e^- \hfill (2)
\]

where | denotes the three-phase interface. The sulfate ion adjoining the interface behaves as if it were to react with Fc(O) stoichiometrically in order to maintain electrical neutrality. It is predicted that a lower concentration of either \(c_{\text{Fc}}\) or \(c_s\) determines the rate of reaction (2). We obtained the limiting currents of wave (a) at various concentrations of Na₂SO₄ and plotted them in Fig. 10. Although lower concentrations less than 0.1 mM made the voltammograms broad owing to high solution resistance, the limiting currents could be evaluated with good reproducibility. Contrary to our expectation, the limiting current was independent of the concentrations of Na₂SO₄ in the domain of 0.002 < \(c_s\) / \(c_{\text{Fc}}\) < 5.0. This result indicates that sulfate ion does not work as a reactant but participates in forming the double layer as well as maintaining the electric neutrality. A question may arise about why \(c_s < c_{\text{Fc}}\) can satisfy the electric neutrality. When the sulfate ion employed for electrical neutrality (on the left hand side of reaction (2)) diffuses to the three-phase interface, it works again to catalyse the formation of the double layer. Therefore, the oxidation at the three-phase interface occurs at low concentrations of Na₂SO₄.

3.3. Model of microband electrode

The three-phase interface may be a very thin ring on the GC electrode. Ferrocene in the oil phase is consumed at the ring interface, and ferricenium ion is dispersed from the ring into the bulk of the water phase. Therefore the ring three-phase interface behaves as if it were a usual electrode for redox reactions. An image of the ring interface is illustrated in Fig. 9(A), where \(w\) is the width of the ring. An interesting feature of this ring model is that the electrode surface is mostly electro-inactive except for the ring. We shall evaluate the width from the limiting currents in order to understand the structure of the three-phase interface.

The diffusion layer developed at a given point on the ring (e.g. at the right edge in Fig. 1(A)) does not overlap with the diffusion layer at the faced point on the ring (e.g. at the left edge in Fig. 1(A)) in the present voltammetric time scale because the diameter of the droplet (ca. 1 mm) is larger than the diffusion thickness (0.3 mm) at 100 s. It is reasonable to assume that the curvature of the ring has a negligible contribution to

![Fig. 9. Two possible mechanisms of the oxidation of ferrocene in the oil droplet without supporting electrolyte and in the Na₂SO₄ aqueous solution.](image)

![Fig. 10. Variation of the limiting current of wave (a) with concentrations of Na₂SO₄ aqueous solution, observed for oil droplets (ca. \(r_1 = 0.5\) mm) including 5 mM ferrocene at \(v = 5\) mV s⁻¹.](image)
diffusion because the perimeter of the ring is much longer than \( w \). Consequently, the mass transport of the system is regarded as diffusion at a band electrode \( 2\pi r_1 \) long and \( w \) wide. According to the theory of linear sweep voltammetry at a microband electrode [28–30], the diffusion-controlled current, \( I \), at potential, \( E \), is expressed by

\[
I = \frac{DnFE^*}{nFc}D(2\pi r_1) = \frac{(\theta/\pi)}{\int_0^\theta f(Du/w^2)[1 + e^{-3(\theta-\phi)}]^{-1}d\phi}
\]

with

\[
\zeta(t) = nF[E(t) - E^\prime]/RT = nF[\theta t + E_c - E^\prime]/RT
\]

where \( E_c \) is the initial potential, \( f \) is the function

\[
f(z) = 2\pi[(\ln z + 3)^{-1} - 0.577(\ln z + 3)^{-2}
- 1.312(\ln z + 3)^{-3} - \cdots]
\]

and \( \theta \) is the contact angle of the oil droplet, as is shown in Fig. 9(A). Eq. (5) is the asymptotic expansion for large values of \( z \), the original form of which is given by the integral of the combination of modified Bessel functions [28]. On the assumption of a very negative value of \( E_c \), Eq. (3) can be rewritten as

\[
I/20nFc\!*Dr_1 = \frac{\int_0^{\zeta^*} \frac{1}{1 + e^{-3(\zeta_0 - \zeta)}} f(DRTz^2/w^2nFv) d\zeta}{4}
\]

\[
= \frac{1}{4} \int_0^{\zeta^*} \sec^2\left(\frac{\zeta - \zeta_0}{2}\right) f(\zeta p^{-2}) d\zeta
\]

where

\[
p = (nFv^2/RTD)^{1/2}
\]

\[
\zeta_0 = nFE/RT
\]

The predicted value of \( p \) is \( 2 \times 10^{-5} \) for \( w = 1 \) nm and \( v = 0.01 \) V s\(^{-1}\). Therefore, a value of \( \zeta p^{-2} \) in Eq. (6) is of the order of \( 10^8 \) for \( \zeta < 0.04 \) (or \( E = 1 \) mV at \( 25 \) °C). For these values of \( \zeta p^{-2} \), the second and the third term in Eq. (5) contribute to values \( f(z) \) with 2.2 and 0.2% errors, respectively.

We carried out numerical computation of the integration of Eq. (6) for various values of \( \zeta^* \) and \( p \), and plotted the values against \( E - E^\prime \) in Fig. 11. These curves are equivalent to normalized linear sweep voltammograms. The following features are addressed: the almost steady-state voltammograms with an ambiguous peak and little dependence on \( p \), i.e. \( v \) or \( w \). Therefore, experimentally obtained voltammograms should show a steady-state sigmoid curve without a peak. This can be seen in the curves of Fig. 7. Their limiting currents should not vary with \( v \), as has been demonstrated experimentally in Fig. 8. The proportionality of the current to \( r_1 \), which is predicted from Eq. (6), has also been demonstrated in Fig. 6.

In order to evaluate the peak current, \( I_p \) readily, for known values of \( v \), \( w \), \( r_1 \) and \( D \), we obtained an approximate equation for \( I_p \). The curves in Fig. 11 indicate that the peak potentials are close to \( n(E_p - E^\prime) = 0.12 \) V. Values of \( \zeta p^{-2} \) in Eq. (6) are so large that the asymptotic expansion (Eq. (5)) is valid except for \( \zeta^* \) close to zero, because values of \( p \) are very small. For values of \( \zeta^* \) at which Eq. (5) may not hold, values of \( \sec((\zeta_0 - \zeta)/2) \) are almost zero. These variations lead to the following approximation:

\[
I_p/20nFc\!*Dr_1 = \frac{1}{4} \int_0^{\zeta^*} \sec^2\left(\frac{\zeta - \zeta_0}{2}\right) f(\zeta p^{-2}) d\zeta
\]

\[
\approx \frac{1}{4} f(\zeta_0 p^{-2}) \int_0^{\zeta^*} \sec^2\left(\frac{\zeta - \zeta_0}{2}\right) d\zeta
\]

where \( \zeta_0 \) is such an adjustable value that \( f(\zeta p^{-2}) \) can be regarded to show negligible variations with \( \zeta^* \). We took \( \zeta_0 \) to be 8.6, corresponding to \( n(E_p - E^\prime) = 0.22 \) V. This value is equivalent to the potential domain from the current-rising potential to the peak potential. Then the approximate equation is given by

\[
I_p = 4\pi \theta nFc\!*Dr_1/[\ln(8.6RTD/nFv^2) + 3]
\]

to which only the first term in Eq. (5) was applied. This equation holds within 10% for \( p < 0.34 \) or \( (w < 17 \mu m, D = 10^{-5} \text{ cm}^2 \text{ s}^{-1}, v = 0.01 \text{ V s}^{-1} \text{ at } 25 \text{ °C}) \).

We inserted experimental values of the slopes for \( I_L \) versus \( r_1 \) curve in Fig. 6 into Eq. (8), where \( I_L \) was regarded as \( I_p \). We took \( \theta \) to be 0.36\( \pi \) (65°) from the photographs. The value of \( D (5.08 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}) \) was obtained from the slope of voltammetric peak currents of ferrocene versus \( v^{1/2} \) in nitrobenzene solution at the glassy carbon electrode without the water phase. Extracting the logarithmic term in Eq. (8) for known values of the slopes, \( e^* \) and \( D \), we obtained \( \ln(8.6RTD/nFv^2)+3 = 15.3 \), where the correlation coefficient of the proportional line in Fig. 6 was 0.982, equivalent to errors of 1.8%. For \( v = 0.01 \text{ V s}^{-1} \), we obtained \( w = 0.23 \)
μm. This value is much larger than the molecular width for the three-phase boundary, predicted intuitively from the illustration in Fig. 9. The error of 1.8% does not mean \( w = 0.226 \pm 0.226 \times 0.018 \) μm but \( \ln(8.6RTD/\pi Fw^2) + 3 = 15.3 \pm 15.3 \times 0.018 \). Then, values of \( w \) range from 0.22 to 0.31 μm. Three reasons for the larger value can be considered, as is illustrated in Fig. 12.

A) The first is due to microscopic fluctuation at the oil | water interface such as capillary waves. The fluctuation makes the length of the three-phase interface larger than \( 2\pi r_1 \) (Fig. 12(A)). If the effective length of the boundary is twice the value of \( r_1 \), the value of \( w \) takes a molecular size (0.5 nm). The twofold length corresponds to the waveform of \( 3.3 \sin(x) \) if the capillary wave is expressed by a sinusoidal form, where \( x \) is the length along the boundary. The ratio of the amplitude (3.3) to the wavelength is \( 3.3/2\pi = 0.52 \), which is too large for capillary waves. Therefore, it is difficult to explain the sub-micron dimension of the width only in terms of the fluctuation of the boundary length.

B) The oil | water interface may not be essentially a sharp boundary but may have a locally continuous domain at which oil is mixed with water in an emulsion form. Then the three-phase interface is obscure (in Fig. 12(B)), and its thickness may have a macroscopic scale. The continuity of the boundary was suggested by Kakiuchi et al. [33,34] as an ion-transfer model based on Goldman-type theory in order to explain the potential dependence of the transfer coefficient.

C) The potential application up to 1.0 V renders the oil droplet visibly flattened, as is shown in Fig. 2. This is partly because \( \text{SO}_4^{2-} \) transferred into the oil phase decreases the oil | water interfacial energy owing to the oil phase becoming more ionic and partly because potentials more positive than the capillary maximum decrease the oil | water interfacial energy. Then the oil phase near the three-phase interface overhangs the electrode, as is shown in Fig. 12(C), and the effective thickness of the boundary becomes of micron order especially when effect (A) participates in the disturbance.

D) If there are hydrophobic pores on the glassy carbon surface, nitrobenzene may penetrate into them. However, observation of the glassy carbon surface through the microscope showed no pores within the resolution (0.5 μm). Even if pores of 0.23 μm in diameter were to be detected, we could not identify whether they were hydrophobic or not. Therefore, we can only include up this possibility.

In Fig. 6 we estimated \( w \) from the slope by use of known and given values of \( \varepsilon^*, D \), and \( \varepsilon \). We could not use the variation of \( I_t \) with \( t \) (Fig. 8) for estimation of \( w \), because the variation was much smaller than experimental errors. It is expected that chronoamperometric curves over a wide time domain allow us to estimate \( w \) by applying the theory of chronoamperometric curves at the band electrode. The chronoamperometric curve responding to 0.50 V is shown in Fig. 13(A). It has actually a steady-state current at \( t > 20 \) s. The transient current at \( t \) is expressed by [29]

\[
I = F\varepsilon^*D(2\pi r_1)(\theta/\pi)f(Dt/w^2)
\]

(9)

Retaining the first term of Eq. (5) for \( f(Dt/w^2) \) and taking the inverse of Eq. (9) gives

\[
1/I = (\ln t + \ln Dw^{-2} + 3)/4\pi\theta F\varepsilon^*Dr_1
\]

(10)

Variation of \( 1/I \) with \( \ln t \) should have a linear relation. Fig. 13(B) shows this variation, demonstrating the linear variation in the domain of \( 2 < \ln(t)/s < 3.8 \) (10 < \( t < 50 \) s). The lower deviation (larger current) at a short time is due to capacitive current and the Cottrell component.

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Fig. 12. Illustrations of the enlarged width of the three-phase interface by (A) capillary waves, (B) substantially continuous oil | water interfaces, and (C) the flattened droplet which covers the electrode over a macroscopic distance.

Fig. 13. Chronoamperometric curve (A) of the oil droplet of \( r_1 = 0.4 \) mm at the potential step to 0.50 V and plot (B) of the inverse current against \( \ln(t) \) of the curve. The straight line was obtained by a linear regression. The oil phase contained 5 mM ferrocene whereas the water phase contained 50 mM Na₂SO₄.
An upper deviation (lower current) at a long time was sometimes observed. Therefore the slope is underestimated whereas the intercept is overestimated. Values of \([\text{slope}]/[\text{intercept}]\) equal to \(\ln(D_{w}^{-2}) + 3\) were found, from which we obtained \(v = 0.46 \text{ mm}\). This is twice the value evaluated from the slope of Fig. 6. Although the chronoamperometry gave the microelectrode behavior at the thin ring interface, the reproducibility was worse than that of the linear sweep voltammetry.

4. Conclusion

We described in the previous paper [23] that the three-phase interface could be observed only at a short time partly because the effective electroactive surface for Fe is limited to the domain in which anion is transferred from the water phase and partly because the anion in the oil phase diffuses toward the center of the electrode. In other words, the electroactive domain for the \(\text{ClO}_4^-\) system spreads from the ring line to the whole area of the oil | electrode interface. This concept is illustrated in Fig. 14(A) by use of predicted concentration profiles. We used here \(\text{SO}_4^{2-}\) instead of \(\text{ClO}_4^-\) in order to block the anion transfer to the oil phase. Then, the voltammetric current at 0.5 V was proportional to the radii of the droplet and independent of the potential sweep rate as well as the concentration of sulfate. These facts support strongly the proposition that the electrode reaction occurs at the very thin ring on the electrode into which the water and the oil phase merge. There is no \(\text{SO}_4^{2-}\) in the oil phase. Even a low concentration of \(\text{SO}_4^{2-}\) in Fig. 14(B)) gives the same value of the diffusion controlled current as that for high concentrations, probably because of the catalytic contribution to both the electric neutralization and formation of the double layer, as is shown in Eq. (2). When the potential was greater than 0.6 V, sulfate ion could transfer into the oil phase, yielding the same behavior as for \(\text{ClO}_4^-\) (Fig. 14(A)) or wave (b) in Fig. 4.

We presented a convenient equation for the voltammetric current at an extremely thin ring electrode. Application of this equation to the linear variation in Fig. 6 yielded 0.23 \(\mu\text{m}\) for the thickness of the ring. This submicron value is unexpected from the geometry of the three-phase interface. We suggested two possible reasons for the submicron value: the continuous variation at the oil | water interface and the spread of the three-phase interface by the overhung oil droplet. At present, we have no evidence to identify the reason.

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