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Fluorometric and Coulometric Analyses of Electron Transfer across Microdroplet/Water Interface

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Electron transfer between ferrocene (FeCp) and Fe(III) across the droplet/water interface was studied by an optically transparent thin-layer electrode method. A time dependence of the FeCp concentration in the droplets caused by the interfacial electron transfer was discussed on the basis of coulometric analysis of Fe(II) or Fe(III) in the water phase and fluorometric analysis of FeCp in the droplets.

Chemical reactions in heterogeneous systems such as oil/water or water/oil emulsions are in general very complicated, so that discussions on mass transfer (MT) and subsequent reactions in emulsions should be made separately for those in each phase and across the oil/water interface. In oil/water emulsions, although a solute(s) distributes to both phases, MT and/or electron transfer (ET) in the water phase can be studied electrochemically, since direct ET across the oil droplet/electrode interface is restricted by the presence of a stabilizer (i.e., surfactant) and protective colloids.[1] On the other hand, chemical reactions in oil droplets can be followed by absorption/fluorescence spectroscopy. When one employes an optically transparent thin-layer electrode,[2] therefore, chemical reactions in emulsions can be elucidated quantitatively by both electrochemical and spectroscopic techniques. In this letter, we show ET between ferrocene (FeCp) and $Fe(CN)_6^{3-}$ (Fe(III)) in an oil/water emulsion system, and discuss the rate of ET across the droplet/water interface based on both coulometric and fluorometric analyses of the FeCp concentration in the oil droplets during electrolysis of $Fe(CN)_6^{4-}$ (Fe(II)) in the water phase.

As an oil/water emulsion, tri-n-butyl phosphate (TBP; 0.10 g) droplets containing FeCp (0.10 or 0 M; 1 M = 1 mol dm^{-3}), 9,10-diphenylanthracene (DPA; 0.010 M), and tetra-n-butylammonium tetraphenylborate (0.010 M) were dispersed in an aqueous electrolyte solution (19.80 g; tetra-n-butylammonium chloride (0.010 M), $MgSO_4$ (0.10 M), $K_4Fe(CN)_6$ (2.0 x 10^{-4} or 0 M)) and a 3.0 wt% aqueous sodium dodecylsulfate (SDS) solution (0.10 g). The diameter (*d*) of the droplets in the emulsion was in the range of 0.5 - 40 μm (average $d \approx 4$ μm) as determined under an optical microscope. The concentrations of FeCp in the TBP droplets ([FeCp(o)]) and the water phase ([FeCp(w)]) were determined to be 6.8 x 10^{-2} M and 1.6 x 10^{-4} M, respectively, from extraction experiments of FeCp in a macroscopic TBP/aqueous SDS solution system. DPA or Fe(II) was almost distributed in the TBP (0.010 M) or water (2.0 x 10^{-4} M) phase, respectively.

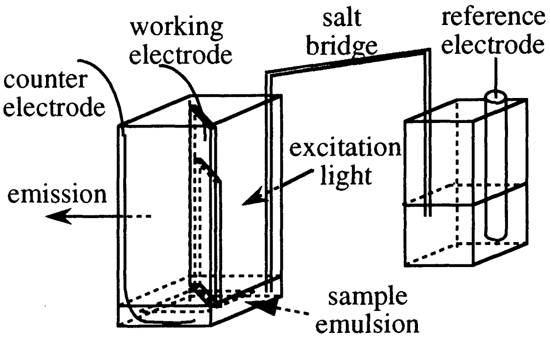

Fig. 1. Electrolytic cell system.

An electrolytic cell used in this study is shown in Fig. 1. As a thin-layer working electrode, an SnO_2 electrode (effective electrode area; 8 mm wide x 26 mm long) was covered by a glass plate with a Teflon film ($\approx$ 70 μm thickness) being placed in between as a spacer. The working electrode was set in a quartz cuvette (optical path length = 1 cm) containing the sample emulsion and the thin-layer electrode was filled with the sample by capillarity. A Pt wire and an Ag/AgCl were used as counter and reference electrodes, respectively. Electrochemical measurements were accomplished by a potentiostat (HA-301, Hokuto Denko) and a function generator (HB-104, Hokuto Denko). Fluorescence from DPA was measured by a spectrofluorometer (MPF4, Hitachi; excitation wavelength = 374 nm). The measurements were performed under aerated conditions at room temperature ($\approx$ 292 K).

The oxidation potential of FeCp in TBP is known to be 230 mV (vs. Ag/Ag^+). However, FeCp in the droplets dispersed in an aqueous SDS solution was not oxidized directly at the electrode in the potential range of 0 - 800 mV, indicating that the redox reaction of $FeCp^+$/FeCp ($FeCp^+$; ferrocenium cation) at the droplet/electrode interface was inhibited by the presence of SDS.$^{1)}$ FeCp solubilized in the water phase ([FeCp(w)] = 1.6×10^{-4} M) was not electrolyzed under the conditions mentioned above, either. FeCp will be solubilized in micells or microemulsions ($d < 0.5$ μm) so that no electrochemical reaction of FeCp proceeds in the water phase. Therefore, we explore to oxidize FeCp in the droplet via a redox reaction of an electron mediator in the water phase. Actually, when Fe(II) in the water phase was oxidized to Fe(III) at 800 mV by a controlled potential coulometric method, the relevant current (i) - time (t) curve was dependent on the absence or presence of FeCp in the droplets. In the absence of FeCp (Fig. 2(a)), oxidation of Fe(II) was almost completed within $t \approx 20$ s, while that proceeded until $t \approx 100$ s for [FeCp(o)] = 6.8×10^{-2} M (Fig. 2(b)). The total electric charge flowing at the electrode is much larger in the presence of FeCp in the droplet as compared with that without FeCp, demonstrating ET from FeCp to Fe(III) at the droplet/water interface.

Simultaneous measurements of DPA fluorescence from the FeCp droplets during electrolysis were also performed. Although the spectral band shape of the DPA fluorescence was unchanged, its intensity (I^F) increased upon electrolysis of Fe(II) in the water phase (Fig. 2(c)). It is noteworthy that an increase of I^F is not observed in the absence of Fe(II) so that I^F is governed by the redox reaction in the water phase. Furthermore, fluorescence quenching of DPA by Fe(II) or Fe(III) at the droplet/water interface can be neglected, since a diffusion length (l) of the excited singlet state of DPA (DPA^*) within the lifetime ($\tau_0 = 1/k_0 = 6.7$ ns; including O_2 quenching in the absence of FeCp) is very short (l = 3 nm) compared with d ($\approx$ 4 μm), as estimated from $l = (2\,D\,t)^{1/2}$, where D is the diffusion coefficient of DPA

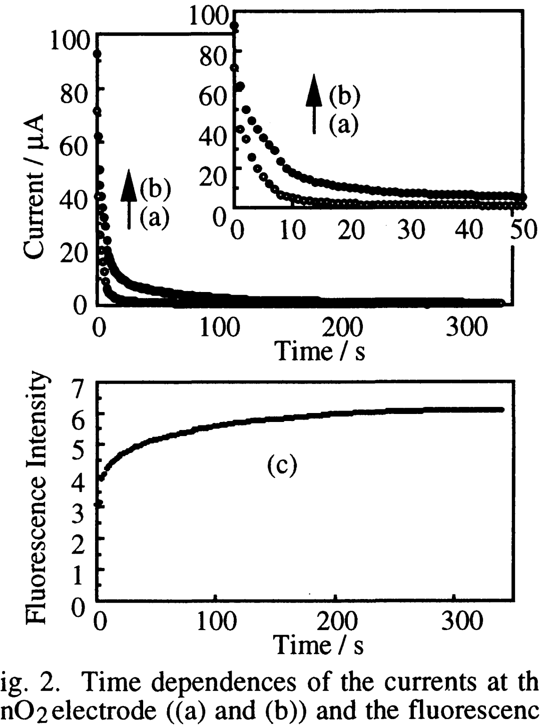

Fig. 2. Time dependences of the currents at the SnO_2 electrode ((a) and (b)) and the fluorescence intensity from the DPA/FeCp droplets (c) during electrolysis of Fe(II) in water (800 mV).
(a); [FeCp(o)] = 0, (b) and (c); [FeCp(o)] = 6.8×10^{-2}M.

($\approx 5 \times 10^{-6}$ cm^{2}s^{-1}) and $t = \tau_0 = 6.7$ ns. These results indicate that the enhancement of I^F upon electrolysis is primarily ascribed to a decrease in the fluorescence quenching yield of DPA by FeCp. A reaction scheme is as follows.

$$\mathrm{Fe(II)} \xrightarrow{k_1} \mathrm{Fe(III)}$$ at electrode in water

$$\mathrm{Fe(III)} + \mathrm{FeCp} \xrightarrow{k_2} \mathrm{Fe(II)} + \mathrm{FeCp}^+$$ at droplet/water interface

$$\mathrm{DPA} \xleftarrow{k_0} \mathrm{DPA}^* + \mathrm{FeCp} \xrightarrow{k_3} \mathrm{DPA}^{\cdot -} + \mathrm{FeCp}^+ \rightarrow \mathrm{DPA} + \mathrm{FeCp}$$ in droplets

k_1 and k_2 are the rate constants of bulk electrolysis of Fe(II) at the electrode and ET between Fe(III) and FeCp across the droplet/water interface, respectively. When both FeCp and DPA coexist in the droplet as in the case for the droplet before electrolysis, DPA* is efficiently quenched by FeCp3) (rate constant : k_3). Upon electrolysis, FeCp is oxidized by Fe(III) to FeCp$^+$, and FeCp$^+$ is ejected into the water phase,3) which leads to the enhancement of I^F owing to a decrease in [FeCp(o)]. Therefore, I^F increases with the electrolytic time as demonstrated in Fig. 2(c). The total amount of FeCp is 2.5 times higher than that of Fe(II), so that Fe(II) reproduced by ET with FeCp at the droplet/water interface sholud be oxidized again to Fe(III) at the electrode (i.e., redox cycle) to fulfill complete oxidation of FeCp in the droplets.

The above discussion indicates that the curve given by subtracting the i - t curve in the absence of FeCp (Fig. 2(a)) from that for [FeCp(o)] = 6.8×10^{-2} M (Fig. 2(b)), i^{sub} - t curve, should correspond to a time dependence of the oxidation of FeCp in the droplets, and is proportional to that of [FeCp(o)]. Figure 3(a) shows the log i^{sub} - t curve thus obtained. The total electric charge calculated by integrating the i^{sub} - t curve at $t < 150$ s was $\approx 7 \times 10^{-4}$ C, which was in good agreement with that estimated from the total amount of FeCp in the droplets (7×10^{-4} C). The results explicitly prove that FeCp in the droplets are oxidized via the redox cycles of Fe(II)/Fe(III) in the water phase. Close inspection of Fig. 3(a) indicates that, although log i^{sub} decreases almost linearly with t, that deviates from the linearity in the initial stage of electrolysis ($t < 20$ s). This particular time range corresponds to that of the sharp decrease in i in Fig. 2(a) or 2(b). At $t < 20$ s, the phenomena seem to be very complicated (discussed later again), so that we focus our discussion on the results at $t > 20$ s.

[FeCp(o)] can be estimated from the observed I^F data under the assumption of the Stern-Volmer relation: $I^F{}_0 / I^F = 1 + k_3 \tau_0$ [FeCp(o)],4) where $I^F{}_0$ is I^F for [FeCp(o)] = 0 and assumed to be equal to I^F at $t \approx 300$ s. k_3 was determined to be 3.1×10^9 M^{-1}s^{-1} by fluorescence decay measurements. Knowing I^F at various t, a time dependence of log [FeCp(o)] was simulated (Fig. 3(b)). The time course of [FeCp(o)] is

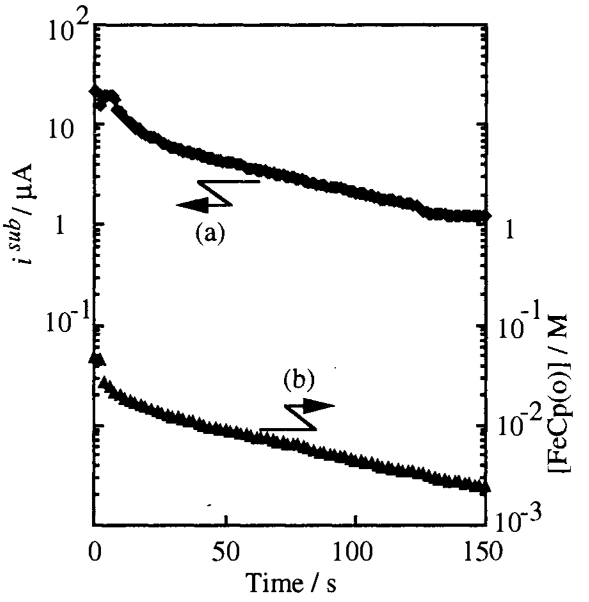

Fig. 3. Time dependences of i^{sub} (a) and [FeCp(o)] (b) during electrolysis.

very similar to that of i^{sub} at $t > 20$ s. If MT of Fe(II) or Fe(III) between the droplets and the electrode is the rate-determining step for the FeCp oxidation, the time profile of i^{sub} will not agree with that of [FeCp(o)]. Indeed, the diffusion time of Fe(II) or Fe(III) ($D = \approx 7 \times 10^{-6}$ cm^{2}s^{-1}) necessary to pass the electrolytic cell (thickness $\approx$ 70 μm) is calculated to be 3.5 s. The value is very short as compared with the observed electrolytic time. On the other hand, MT of FeCp in the droplet will be also very fast because d of the droplet is of the order of μm. Therefore, the rate-determining step is ET between Fe(III) and FeCp across the dropet/water interface. As seen in Figure 3, the time profile of i^{sub} or [FeCp(o)] at $t > 20$ s can be analyzed as a pseudo first-order reaction and k_2 is determined to be 80 M^{-1}s^{-1} when [Fe(III)] is assumed to be 2.0×10^{-4} M. This corresponds to the rate constant per unit area at the interface ($k_2' = (V / A)\, k_2$) of $\approx 5 \times 10^{-3}$ M^{-1}cm s^{-1} for $d = 4$ μm, where A and V are the surface area ($4\pi(d/2)^2$) and volume ($(4/3)\pi(d/2)^3$) of the droplet, respectively. An ET rate constant at a macroscopic liquid/liquid interface has been reported to be 0.01 - 1 M^{-1}cm s^{-1}.5) In the present system, the droplets are stabilized by SDS and the actual physical structures of the droplet/water interface will be complicated as compared with that at the macroscopic liquid/liquid interface. If one takes such circumstances of the present system into account, the observed k_2' value is considered to be comparable to the reported value and will be regarded as the rate constant of ET across the droplet/water interface.

Fluorometric and coulometric analyses were successful to elucidate a rate-determining step of chemical reactions in the emulsion system. Since d of the droplets and the thickness of the electrolytic cell are in μm dimension, the contributions of MT of a solute(s) in both the water and oil phases to the total reaction are very small and, therefore, ET across the droplet/water interface can be directly observed. In the present study, d was distributed in 0.5 - 40 μm and the experiments were performed based on spatially-unresolved measurements for a number of the droplets. The fast decay component(s) observed in the time dependence of i^{sub} or [FeCp(o)] at $t < 20$ s is therefore likely to be originated by contributions from very small droplets. Furthermore, k_2' may depend on d through effects of an interfacial potential and surface tension of the droplet. Recently we developed spatially-resolved spectroscopic and electrochemical techniques for studying individual droplets.3,6) Application of such new technique to the present system will reveal further detailed mechanisms and the work along the line including a d dependence of the ET rate for individual droplets is now in progress in this laboratory.

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