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# Characteristic Behavior of an Electron-Transfer Reaction across a Tributyl Phosphate Droplet/Water Interface: Micrometer Droplet-Size Effect

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An electron-transfer (ET) reaction between decamethylferrocene in a single tributyl phosphate (TBP) droplet and hexacyanoferrate(III) in the surrounding water phase was investigated by laser trapping, microspectroscopic, and electrochemical techniques. The interfacial ET rate constant ($k_{\mathrm{obs}}$) was inversely proportional to the droplet radius ($r$) at $>5$ μm, but deviated from a linear relationship between $k_{\mathrm{obs}}$ and $r^{-1}$ at $r<5$ μm. The characteristic droplet-size effect was independent of the Galvani potential between the TBP and water phases. The results are discussed in terms of the physical properties of the micrometer-sized TBP droplet/water interface.

Electron transfer (ET) and ion transfer (IT) at a liquid/liquid interface are worth studying both experimentally and theoretically in order to obtain an inside look at the mechanisms of vectorial charge-transfer processes in biological systems. Actually, charge-transfer processes across flat liquid/liquid interfaces have been studied on the basis of electrochemical and spectroscopic techniques.[1—8] These studies revealed factors governing the interfacial charge-transfer rate, including the free-energy change and Galvani potential dependencies of the rate. Also, the molecular dynamics of ET or IT at liquid/liquid interfaces has received current interest.[9] On the other hand, a spherical microscopic liquid (i.e., droplet)/liquid interface is very unique, since interfacial phenomena are strongly dependent on the droplet size. The characteristic behavior, different from that of a flat liquid/liquid interface, is expected for a charge-transfer process across a microdroplet/solution interface. An experimental study concerning the micrometer droplet-size dependence of the charge-transfer rate is very important to further elucidate the factors controlling the interfacial charge transfer. However, work along the line mentioned above has never been reported, owing to a lack of experimental methods for single microdroplets. In previous papers we argued that chemical processes across a single-microdroplet/water interface could be studied directly by laser trapping, microspectroscopic, and electrochemical techniques.[10—14] The method enables one to select and manipulate arbitrary-sized, single microdroplets in solution. Furthermore, since spectroscopic and electrochemical observations can be made for individual droplets simultaneously, various interfacial phenomena can be studied as a function of the droplet size.

A ferrocene (FeCp-H)/hexacyanoferrate(III) (Fe(III)) couple is a typical redox system, and has been extensively studied by various researchers.[15—19,12,14] In oil/water systems, however, it has been reported that IT of an FeCp-H cation (FeCp-H$^+$) from oil to water couples with ET between FeCp-H and Fe(III)[19,20] and that a side reaction between FeCp-H$^+$ and a supporting electrolyte such as a tetraphenylborate anion proceeds rapidly.[19,21] Furthermore, since FeCp-H in an oil distributes slightly to water, this also makes it difficult to analyze the interfacial ET reaction. Therefore, the FeCp-H/Fe(III) system may not be necessarily appropriate for studying interfacial ET.[19,20] Actually, metal diphthalocyanines, metal tetraphenylporphyrines and so forth, instead of FeCp-H, have been employed for studies of flat liquid/liquid interfacial ET reactions.[20,22,23] In the present study, however, these compounds could not be used, since single microdroplet measurements require a high solute concentration in oil droplets, and the solubility of the compound mentioned above does not meet the present conditions. Therefore, as the first demonstration of characteristic charge-transfer processes across a micrometer-sized droplet/solution interface, we selected a ferrocene derivative (FeCp-X)/Fe(III) system.

Our preliminary experiments indicate that the ET rate between ferrocene (FeCp-H) in a single tributyl phosphate (TBP) droplet and Fe(III) in water is inversely proportional to the droplet radius ($r$).[12,14] Such results are very important to further elucidate the characteristics of the interfacial ET. However, FeCp-H is not appropriate for studying the interfacial ET, as mentioned above. Therefore, we used a water-insoluble compound of decamethylferrocene (FeCp-DCM). It has been reported that the IT potential of the cation of FeCp-DCM (FeCp-DCM$^+$) in oil/water systems is more negative than that of FeCp-H$^+$ and a side reaction of FeCp-DCM$^+$ with an electrolyte is very slow in a 1,2-dichloroethane/water system.[19] Thus, the use of FeCp-DCM is more appropriate for studying ET across a microdroplet/water interface, and we expected that more reliable and accurate information could be obtained through such studies. In this paper we discuss a droplet-size effect on an ET reaction between FeCp-DCM in a single TBP droplet and Fe(III). The Galvani potential($\Delta_{\mathrm{O}}^{\mathrm{W}}\phi$) dependence between the TBP and water phases of the ET rate is also described.

## Experimental

**Chemical and Sample Preparations.** Potassium hexacyanoferrate(II) (Fe(II), Wako Pure Chemical Industries Ltd., GR grade), FeCp-DCM (Aldrich Chemical Co., Inc., 99+%), perylene (Pe, Aldrich Chemical Co., Inc., 99+%), tetrabutylammonium chloride ($\mathrm{TBA^+Cl^-}$, Tokyo Kasei Kogyo Co., Ltd., EP grade), and $MgSO_4$ (Kanto Chemical Co., Inc., G grade) were purified by recrystallizations from water, methanol, ethanol, acetone/diethyl ether, and water, respectively. Tetrabutylammonium tetraphenylborate ($\mathrm{TBA^+TPB^-}$) was prepared from sodium tetraphenylborate (Aldrich Chemical Co., Inc., 99.5%) and tetrabutylammonium bromide (Tokyo Kasei Kogyo Co., Ltd., EP grade), and then purified by recrystallization from acetone. TBP (Tokyo Kasei Kogyo Co., Ltd., GR grade) was purified by vacuum distillation. Water was used after deionization and distillation (Advantec Toyo Co., Ltd., GSR-200).

As an oil/water emulsion, TBP containing FeCp-DCM (20 mM, $1\ \mathrm{M} = 1\ \mathrm{mol\,dm^{-3}}$), Pe (0.5 mM), and $\mathrm{TBA^+TPB^-}$ (10 mM) was dispersed in an aqueous solution containing $\mathrm{TBA^+Cl^-}$ (1 or 100 mM), $MgSO_4$ (0.1 M), and Fe(II) (0.2 mM) with a 1/500 (oil/water) weight ratio. Under the present conditions, $\Delta_{\mathrm{O}}^{\mathrm{W}}\phi$ is determined by the distribution of $\mathrm{TBA^+}$ between the two phases, and is given by

$$\Delta_{\mathrm{O}}^{\mathrm{W}}\phi = \Delta_{\mathrm{O}}^{\mathrm{W}}\phi^0 + (RT/F)\ln(a_{\mathrm{O}}/a_{\mathrm{W}}), \qquad (1)$$

where $\Delta_{\mathrm{O}}^{\mathrm{W}}\phi^0$ is the standard Galvani potential in the TBP/water system, and $a_{\mathrm{O}}$ and $a_{\mathrm{W}}$ are the activities of $\mathrm{TBA^+}$ in the TBP and water phases, respectively. $R$, $T$, and $F$ are the gas constant, the absolute temperature, and the Faraday constant, respectively. Equation 1 indicates that the $\Delta_{\mathrm{O}}^{\mathrm{W}}\phi$ value can be controlled through the $a_{\mathrm{O}}/a_{\mathrm{W}}$ ratio. An increase in the $[\mathrm{TBA^+}]_{\mathrm{O}}/[\mathrm{TBA^+}]_{\mathrm{W}}$ ratio (assumed to be equal to $a_{\mathrm{O}}/a_{\mathrm{W}}$) from 0.1 to 10 leads to that in the $\Delta_{\mathrm{O}}^{\mathrm{W}}\phi$ value from ($\Delta_{\mathrm{O}}^{\mathrm{W}}\phi^0 - 59$ mV) to ($\Delta_{\mathrm{O}}^{\mathrm{W}}\phi^0 + 59$ mV), where $[\mathrm{TBA^+}]_{\mathrm{O}}$ and $[\mathrm{TBA^+}]_{\mathrm{W}}$ are the concentrations of $\mathrm{TBA^+}$ in the TBP and water phases, respectively.

**Individual Microdroplet Measurements.** All measurements were performed by laser trapping, microspectroscopic, and electrochemical techniques at ambient temperature (23±1 °C) (Fig. 1).[12] $SnO_2$ electrodes were gifts from Nissan Motor Co., Ltd. A sample emulsion was placed between an $SnO_2$ working electrode and a cover glass with a Teflon film (ca. 70 μm thickness) used as a spacer (optically transparent thin-layer electrochemical cell). The other $SnO_2$ electrode and an Ag/AgCl wire (diameter = 50 μm) were used as counter and reference electrodes, respectively. The electrolytic cell was set on the stage of an optical microscope (Nikon Co., Ltd., Optiphoto II). Bulk electrolysis of Fe(II) in the water phase was performed (800 mV vs. Ag/AgCl) by an electrochemical analyzer (BAS Inc., BAS100B/W).

For laser trapping-spectroscopy of single microdroplets, a 1064-nm beam from a continuous wave $\mathrm{Nd^{3+}}$ : YAG laser (Spectron Laser Systems Ltd., SL-902T, ca. 500 mW) was introduced to the microscope and focused on an oil droplet (spot size ≈ 1 μm) through an objective lens (×100, NA = 1.30). An increase in the temperature of the emulsion by laser irradiation was not observed under the present conditions. For fluorescence measurements, a Xe light beam (Hamamatsu Photonics Co., Ltd., C4264) was passed through glass filters (400—420 nm) and led to the microscope coaxially with the 1064-nm beam and irradiated to a laser-trapped droplet (spot size ≈ 5 μm). Fluorescence from Pe in the oil droplet was collected by the same objective lens and analyzed by a polychromator (Oriel Co., Multispec 257)—multichannel photodetector (Princeton Instruments, Inc., ICCD-576E/G) set.

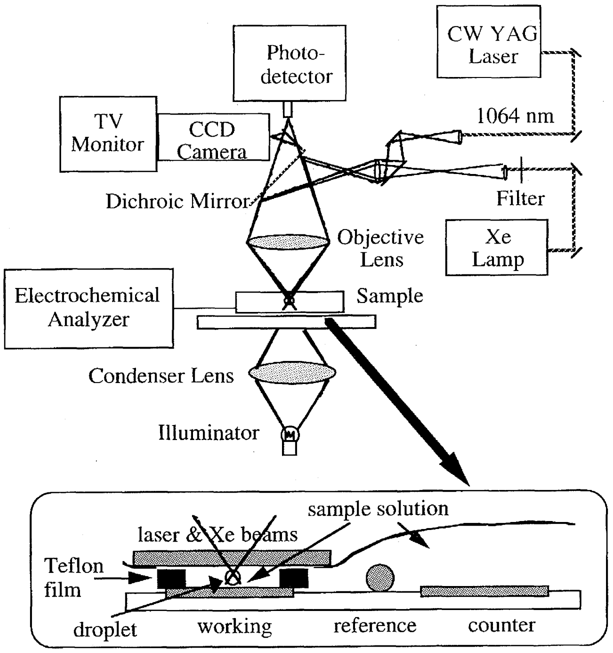

Fig. 1. Block diagram of a laser trapping-spectroscopy-electrochemistry system.

## Results and Discussion

**Kinetic Analysis of the ET Reaction across a Single-Droplet/Water Interface.** A single TBP droplet containing FeCp-DCM and Pe was laser-trapped and positioned above the working electrode without direct contact (Fig. 2). With the droplet being laser-trapped, Fe(II) in water was oxidized by potential-controlled bulk electrolysis. As characteristics of bulk electrolysis in a thin-layer cell, Fe(II) can be quickly and completely oxidized to Fe(III).[24,25] Indeed, the total electric charge increased rapidly with the electrolytic time ($t$), and was almost saturated at that point expected from complete oxidation of Fe(II) in the thin-layer cell ($t \approx 10$ s). Upon electrolysis, ET between FeCp-DCM in the droplet and Fe(III) in the water phase is induced, as illustrated in Fig. 2. Pe in the droplet acts as a fluorescence probe for the interfacial ET. Namely, the fluorescence of Pe in the droplet is quenched by FeCp-DCM, but is not by $\mathrm{FeCp\text{-}DCM^+}$ produced by the ET reaction. Therefore, the time course of the FeCp-DCM concentration in the oil droplet ($[\mathrm{FeCp\text{-}DCM}]_{\mathrm{O}}$) during the electrolysis of Fe(II) in water can be determined by that of the fluorescence intensity of Pe ($I_{\mathrm{F}}$). Although fluorescence quenching of Pe by Fe(II) or Fe(III) is also expected to take place at the droplet/water interface, such a contribution is neglected compared to the quenching by FeCp-DCM in the droplet interior, due to the short diffusion length of the excited singlet state Pe.[24]

Figure 3 shows the $t$ dependence of the fluorescence spectrum of Pe in a droplet ($r = 7.5$ μm). The fluorescence in-

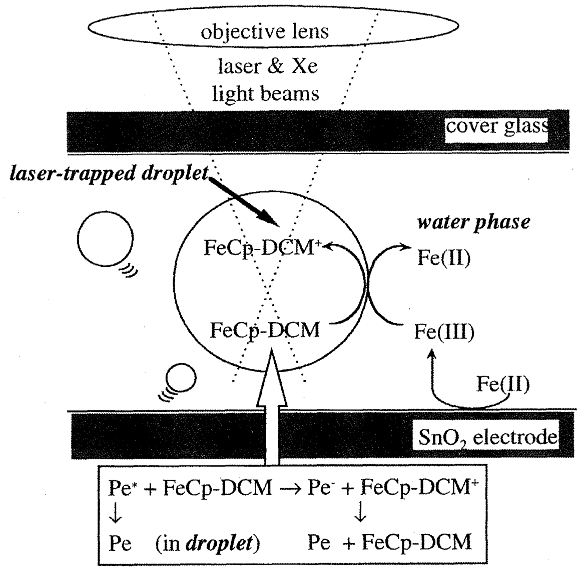

Fig. 2. Reaction scheme of electron transfer between FeCp-DCM and Fe(III) across the droplet/water interface. FeCp-DCM; decamethylferrocene, FeCp-DCM$^+$; a cation of FeCp-DCM, Pe; perylene, Pe$^-$; radical anion of Pe, Fe(II); $Fe(CN)_6^{4-}$, Fe(III); $Fe(CN)_6^{3-}$.

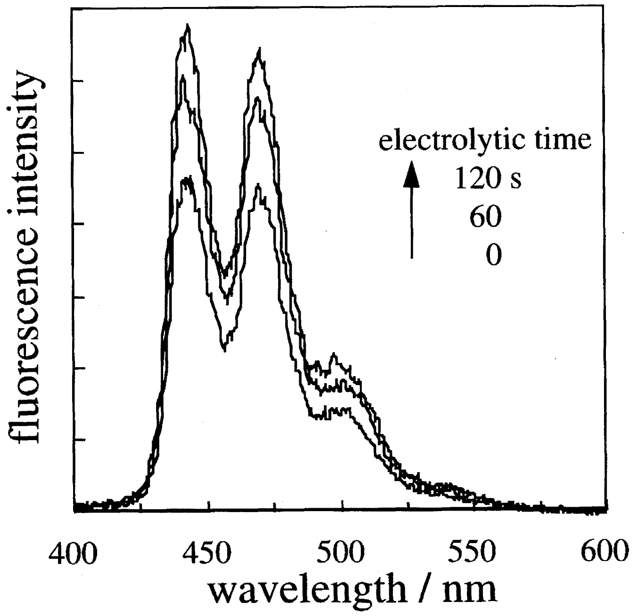

Fig. 3. Electrolytic time dependence of the fluorescence spectrum of Pe (400—420 nm excitation) in a single droplet with $r$=7.5 μm. TBA$^+$TPB$^-$; 10 mM, TBA$^+$Cl$^-$; 1 mM. The droplet was laser trapped during the experiments (laser power at 1064 nm; ca. 500 mW).

tensity of Pe ($I_F$) in the droplet increased with $t$ without any change in the spectral band shape.[26] This result indicates that ET between Fe(III) in the water phase and FeCp-DCM in the droplet takes place as expected from Fig. 2.

The time dependence of $I_F$ ($I_F(t)$) can be converted to that of [FeCp-DCM]$_O$ ([FeCp-DCM($t$)]$_O$) on the basis of the Stern–Volmer relation,[12]

$$I_{F0}/I_F(t) = 1 + k_q\tau_0[\text{FeCp-DCM}(t)]_O, \qquad (2)$$

where $I_{F0}$ is $I_F$ at [FeCp-DCM]$_O$ = 0; $k_q$ and $\tau_0$ are the fluorescence quenching-rate constant of Pe by FeCp-DCM ($7.3\times10^9$ M$^{-1}$ s$^{-1}$) and the fluorescence lifetime of Pe in the absence of FeCp-DCM (4.7 ns).

In a micrometer-sized droplet since the diffusion time of FeCp-DCM in the droplet is very short (<ca. 1 s), the diffusion of FeCp-DCM in the droplet is not the rate-determining step.[12] The total amount of Fe(III) produced in the water phase at $t\approx 10$ s by bulk electrolysis is 4.5-times larger than that of FeCp-DCM in the droplets, and the electrolysis is continued during the $I_F$ measurement. Therefore, the rate-determining step is neither the mass transfer of Fe(II) nor the bulk electrolysis of Fe(II) in water. When the rate-determining step is ET between FeCp-DCM in the droplet and Fe(III) in water (discussed later), the reaction rate at $t>10$ s can be analyzed on the basis of a pseudo-first-order reaction (Fe(III) concentration; [Fe(III)] = 0.2 mM). [FeCp-DCM($t$)]$_O$ is given as in Eq. 3 under the boundary condition of [FeCp-DCM]$_O$ = [FeCp-DCM(0)]$_O$ at $t=0$,

$$\ln([\text{FeCp-DCM}(t)]_O/[\text{FeCp-DCM}(0)]_O) = -k_{obs}[\text{Fe(III)}]t, \qquad (3)$$

where $k_{obs}$ is the observed second-order rate constant of the ET reaction. Combining Eq. 2 with Eq. 3, we obtain the kinetic equation:

$$\ln\{(I_{F0}/I_F(t)) - 1\} = -k_{obs}[\text{Fe(III)}]t + \ln(k_q\tau_0[\text{FeCp-DCM}(0)]_O). \qquad (4)$$

Figures 4a and 4b show the $t$ dependencies of $I_F$ and $\ln\{(I_{F0}/I_F(t))-1\}$, respectively. Upon the electrolysis of Fe(II) in the water phase, the $I_F$ value increased with time, and saturated at a certain value (Fig. 4a). The saturated $I_F$ value was used as $I_{F0}$ for a given experiment. As predicted from Eq. 4, the $\ln\{(I_{F0}/I_F(t))-1\}$ value decreased linearly with $t$ (Fig. 4b). The result indicates that the assumption of pseudo-first-order reaction kinetics (Eq. 4) is valid in the present system. It is noteworthy that the slope of the $\ln\{(I_{F0}/I_F(t))-1\}$ vs. $t$ plot in Fig. 4b, corresponding to the ET rate ($k_{obs}$, having a dimension of M$^{-1}$ s$^{-1}$), was smaller for a larger-sized oil droplet. Namely, the interfacial ET proceeds rather quickly for a smaller droplet.

**Specific Interfacial Area Effect on the ET Reaction in a Droplet/Water System.** A droplet-size dependence of the ET rate has been suggested. We therefore studied the $r$ dependence of $k_{obs}$ under various conditions. Figure 5 shows the $r$ dependence of $k_{obs}$ at $\Delta_O^W\phi = (\Delta_O^W\phi^0+59$ mV) (closed triangles; [TBA$^+$Cl$^-$]$_W$ = 100 mM) or ($\Delta_O^W\phi^0-59$ mV) (open triangles; [TBA$^+$Cl$^-$]$_W$ = 1 mM). The reaction rate across a droplet/solution interface is expected to be dependent on the interfacial area ($A = 4\pi r^2$)/volume ($V = (4/3)\pi r^3$) ratio of a droplet. When this is the case, $k_{obs}$ should be linearly proportional to the inverse of $r$,[12] as in

$$k_{obs} = (A/V)k_{ET} = (3/r)k_{ET}, \qquad (5)$$

where $k_{ET}$ (having a dimension of cm M$^{-1}$ s$^{-1}$) is the ET

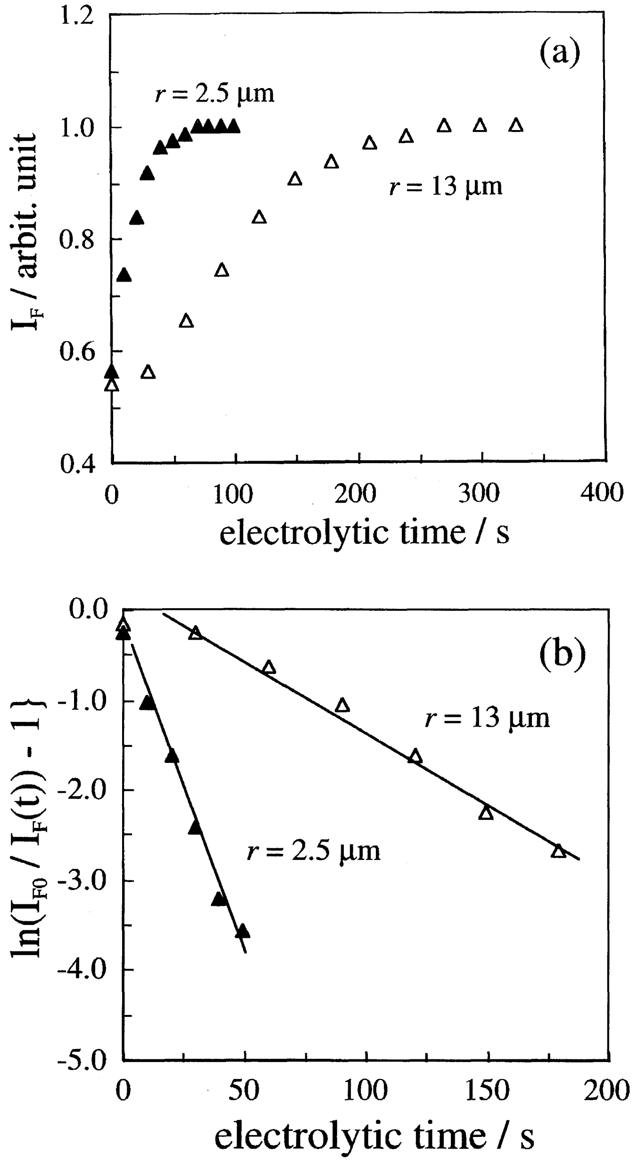

Fig. 4. Electrolytic time dependencies of $I_F$ (a) and $\ln\{(I_{F0}/I_F(t))-1\}$ (b) in single droplets with $r = 2.5$ and 13 µm. $TBA^+TPB^-$; 10 mM, $TBA^+Cl^-$; 1 mM.

rate constant per unit interfacial area of a single droplet. In an FeCp-H/Fe(III) system, $k_{obs}$ was reported to be proportional to $r^{-1}$ at $r>5$ µm and $k_{ET}$ was determined to be ca. $10^{-2}$ cm $M^{-1}$ $s^{-1}$,[14)] which was in good agreement with that reported for the same redox couple at a flat water/nitrobenzene or water/1,2-dichloroethane interface.[27)] In the present FeCp-DCM/Fe(III) system, $k_{ET}$ was determined to be 0.04 $M^{-1}$ cm $s^{-1}$ at $r>5$ µm (Fig. 5). Since the redox potentials of the FeCp-DCM/FeCp-DCM$^+$ and FeCp-H/FeCp-H$^+$ couples in TBP were 113 and 506 mV (vs. Ag), respectively, the ET rate of FeCp-DCM should be faster than that of FeCp-H. Nonetheless, the ET rate between FeCp-DCM and Fe(III) was almost the same as that of the FeCp-H/Fe(III) system (ca. $10^{-2}$ $M^{-1}$ cm $s^{-1}$).[14,27)] Since FeCp-DCM is a bulky molecule, a relatively long electron-transfer distance compared with that between FeCp-H and Fe(III) would be a possible reason.[19)] At $r<5$ µm, on the other hand, it is noteworthy that $k_{obs}$ does not fall on the linear relationship between $k_{obs}$ and $r^{-1}$. Namely, the interfacial ET rate is not governed by the $A/V$ ratio alone for a droplet smaller than $r = 5$ µm. Thus, the factor(s) governing the ET rate is different between below and above $r \approx 5$ µm (discussed later).

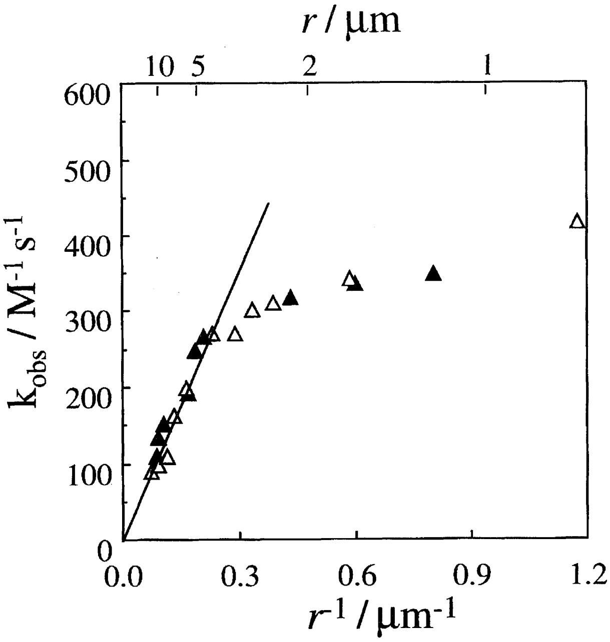

Fig. 5. Droplet-size dependence of $k_{obs}$ at $\Delta_O^W\phi = \Delta_O^W\phi^0-59$ or $\Delta_O^W\phi^0+59$ mV. $TBA^+TPB^-$ (10 mM), $TBA^+Cl^-$ (1 or 100 mM).

**Galvani Potential Dependence of the ET Rate.** A Gibbs free-energy change of the ET reaction ($\Delta G$) is given by $\Delta G = -F(\Delta_O^W\phi+\Delta E)$, where $\Delta E$ is the energy gap between the redox potentials of FeCp-DCM and Fe(III). The increase in $\Delta_O^W\phi$ renders a more negative shift of $\Delta G$ and, therefore, $k_{ET}$ should increase with increasing $\Delta_O^W\phi$.[28)] In the FeCp-DCM/Fe(III) system, however, the data on $k_{obs}$ at both $\Delta_O^W\phi = (\Delta_O^W\phi^0+59$ mV) and $(\Delta_O^W\phi^0-59$ mV) fall on the same curve (Fig. 5). Furthermore, the ET reaction proceeds efficiently even in the absence of $TBA^+TPB^-$ and $TBA^+Cl^-$, and the absolute $k_{obs}$ values were analogous to those at $\Delta_O^W\phi = (\Delta_O^W\phi^0\pm59$ mV) (Fig. 5), as shown in Fig. 6. Therefore, $k_{obs}$ (i.e., $k_{ET}$) is independent of $\Delta_O^W\phi$. These results suggest that the ET reaction between FeCp-DCM and Fe(III) does not proceed at a sharp liquid/liquid boundary.

Although it has been reported that an interfacial layer between two immiscible solutions, such as nitrobenzene/water and 1,2-dichloroethane/water, is very thin (ca. 1 nm),[9,30,31)] the solubility of water in TBP (4.67 wt%) is much larger than that in nitrobenzene (0.24 wt%) or 1,2-dichloroethane (0.15 wt%).[32)] Therefore, the interfacial layer between TBP and water is expected to be thicker than 1 nm. If the interfacial layer is very thick compared to the molecular size of FeCp-DCM or Fe(III) ($\gg$1 nm), the ET reaction will take place in the interfacial TBP/water mixed layer. Furthermore,

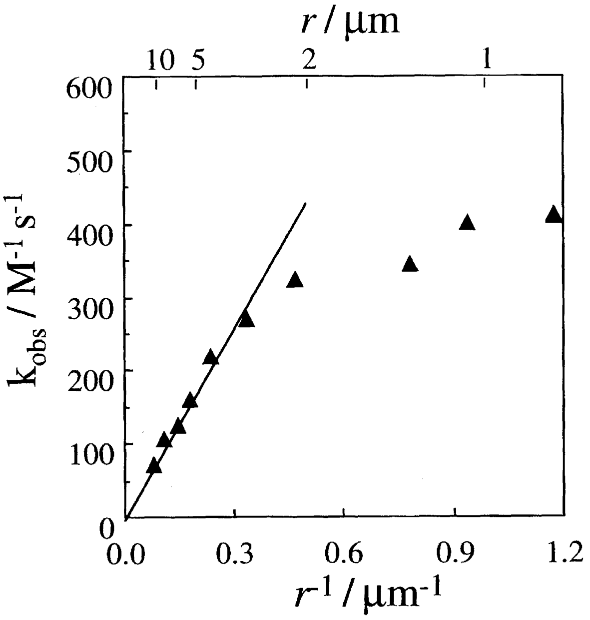

Fig. 6. Droplet-size dependence of $k_{obs}$ in the FeCp-DCM/Fe(III) system in the absence of $TBA^{+}TPB^{-}$ and $TBA^{+}Cl^{-}$.

although it has been reported that the ET reaction between FeCp-DCM and Fe(III) does not take place at a 1,2-dichloroethane/water interface,[19] the reaction does occur at the TBP/water interface, even in the absence of an electrolyte in the TBP droplet (Fig. 6). This will also be explained by assuming a relatively thick interfacial TBP/water mixed layer.

**Characteristic Behavior of the Interfacial ET Rate at $r < 5$ μm.** An observation of the droplet-size dependence of $k_{obs}$ at $r < 5$ μm (Figs. 5 and 6) is quite important to analyze the characteristics features of a micrometer-sized spherical liquid/liquid interface; its possible origin is worth discussing in detail.

Firstly, the ET rate becomes more or less faster with decreasing $r$ through an increase in the $A/V$ ratio, so that the experimental and analytical conditions/assumptions may not necessarily be warranted for droplets with $r < 5$ μm. However, our experimental setup enables one to determine $k_{obs}$ faster than $10^3$ $M^{-1}$ $s^{-1}$,[14] so that the leveling-off of $k_{obs}$ with an increase in $r^{-1}$ is not an experimental artifact.

Secondly, the ET reaction rate might be influenced by the diffusion of Fe(III) in water, depending on $r$. If the rate-determining step is the diffusion of Fe(III), the relevant rate ($v_{diff}$) is given as $v_{diff} = D_W[\mathrm{Fe(III)}]\{(\pi D_W t)^{-1/2} + r^{-1}\}$,[25] where $D_W$ is the diffusion coefficient of Fe(III) in water ($5\times10^{-6}$ $cm^2$ $s^{-1}$, determined by cyclic voltammetry). Since the contribution of $(\pi D_W t)^{-1/2}$ to $v_{diff}$ is negligibly small compared to that of the $r^{-1}$ term at $r < 10$ μm and $t > 10$ s, the diffusion-limited rate constant ($k_{diff} = D_W/r$) is calculated to be $5\times10^{-2}$, $1\times10^{-2}$, and $5\times10^{-3}$ cm $s^{-1}$ at $r = 1$, 5, and 10 μm, respectively. The $k_{ET}[\mathrm{FeCp\text{-}DCM}(t)]_O$ value at $t$—0 is determined to be $8\times10^{-4}$ cm $s^{-1}$ and decreases with $t$. Clearly, the $k_{ET}[\mathrm{FeCp\text{-}DCM}(t)]_O$ value is much smaller than $k_{diff}$ at $r < 10$ μm. Therefore, the droplet-size effect does not originate from the diffusion process.

Thirdly, the photochemistry/photophysics of Pe, itself, may be dependent on $r$. If this is the case, the fluorescence intensity of Pe before the electrolysis of Fe(II) should be dependent on $r$ through an $r$ effect on $k_q$ and/or $\tau_0$. Nonetheless, since the ET rate is determined from the slope of an $\ln\{(I_{F0}/I_F(t)) - 1\}$ vs. $t$ plot, the $k_{obs}$ value is not influenced by variations of $k_q$ and $\tau_0$ (Eq. 4). Therefore, this possibility is also neglected.

These discussions indicate that factors other than those mentioned above influence the ET process. We consider that the characteristic droplet-size effect originates from the ET reaction in the thick interfacial layer, as discussed above. For relatively large droplets, the interfacial layer is thin enough compared with the droplet radius, so that the interfacial ET rate is determined by the $A/V$ ratio ($r > 5$ μm). On the other hand, the contribution of the interfacial layer to the overall reaction rate becomes important along with a decrease in $r$. Below a certain droplet radius, namely, the rate will deviate from that expected due to the $A/V$ effect. If $r$ is comparable to the thickness of the interfacial layer, $k_{obs}$ will be independent of $r$. Qualitatively, this is what was observed in the present experiments. Such a model is not unrealistic, since analogous droplet-size effects have been reported (not single-droplet measurements) for a dye formation reaction between a quinonediimine derivative in water and a naphthol derivative in oil droplets: The rate is dependent on $r$ at $r >$ca. 0.1 μm, but is not at $r <$ca. 0.1 μm.[33] In separate experiments for the FeCp-H/Fe(III) system, $k_{obs}$ was proportional to $r^{-1}$ at $r > 5$ μm,[14] while the rate deviated from a linear relationship between $k_{obs}$ and $r^{-1}$ at $r < 5$ μm, similar to the droplet-size effect on $k_{obs}$ in the FeCp-DCM/Fe(III) system. Although the interfacial ET reaction between FeCp-H and Fe(III) is complicated due to a droplet-to-water mass transfer and a side reaction of $\mathrm{FeCp\text{-}H^{+}}$, the result can be also explained by assuming relatively thick interfacial layer.

## Conclusions

The ET rate between FeCp-DCM and Fe(III) across the TBP-droplet/water interface was determined for individual microdroplets. We found two classes of the droplet-size effect on the ET rate: the $A/V$ ratio effect ($r > 5$ μm) and the characteristic droplet-size effect ($r < 5$ μm). The droplet-size effect was independent of $\Delta_O^W \phi$. The present findings are very important, since the characteristic features of a spherical micro-liquid/liquid interface were observed experimentally for the first time. We expect that further detailed and systematic studies will reveal new insights concerning microdroplet chemistry. Finally, it is worth pointing out that a study of the droplet-size dependence of the reaction rate is indispensable for elucidating detailed mechanisms of the reaction in emulsion systems.

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