Liquid-Junction Potential Dependence of the Electron Transfer Rate across a Single-Microdroplet/Water Interface

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An electron transfer (ET) reaction between ferrocene in a single oil droplet and hexacyanoferrate (III) in the surrounding water phase was investigated by laser trapping, spectroscopic, and electrochemical techniques. A droplet-size dependence of the ET reaction was studied as a function of a Galvani potential difference ($\Delta_o{}^w\phi$) between the droplet and water phases. The ET rate was shown to be highly dependent on $\Delta_o{}^w\phi$.

An interfacial potential dependence of electron transfer (ET) at an oil/water interface is worth to be elucidated experimentally and theoretically to obtain an inside look at mechanisms of vectorial ET in biological systems.[1] Previously, we showed that the ET rate between ferrocene (FeCp) in a single droplet and $Fe(CN)_6{}^{3-}$ (Fe(III)) in water could be determined on the basis of a laser trapping-fluorometry-electrochemistry technique.[2] However, we could not discuss the ET rate as a function of a Galvani potential difference ($\Delta_o{}^w\phi$) between the droplet and water phases owing to the use of an ionic surfactant as a stabilizer of the emulsion. Without a surfactant, an emulsion is easily separated into two phases so that experiments of single droplets are generally very difficult. Even in the absence of a surfactant, however, we recently succeeded in measuring the ET rate for the droplets with the diameter (*d*) of > 5 μm, by using relatively high laser power for trapping and a high sensitive photodetector. In this paper, we report for the first time a $\Delta_o{}^w\phi$ dependence of the ET rate across a single droplet/water interface.

Tri-n-butyl phosphate (TBP) containing FeCp (0.05 M, 1 M = 1 mol dm^{-3}), 9,10-diphenylanthracene (DPA; 0.01 M), and tetra-n-butylammonium tetraphenylborate (TBA^+TPB^-; 0.01 M) was dispersed in an aqueous solution of tetra-n-butylammonium chloride (TBA^+Cl^-; 10^{-1} - 10^{-3} M), $K_4Fe(CN)_6$ (Fe(II); 0.2 mM), and $MgSO_4$ (0.10 M) with a 1/500 weight ratio as an oil/water emulsion. The sample emulsion was placed between an SnO_2 working electrode (gifted from Nissan Motor Co. Ltd.) and a cover glass with the gap width of ≈70 μm. Ag/AgCl reference and counter electrodes were positioned near the working electrode. A droplet was trapped by a CW Nd^{3+}: YAG laser (Spectron, SL-902T, 1064 nm, ≈500 mW). An increase in temperature of the sample emulsion was not observed by laser irradiation to the SnO_2 electrode. Fluorescence from DPA in the droplet was analyzed by a polychromator (Oriel, Multispec 257)-multichannel photodetector (Princeton Instruments, ICCD-576E/G) set. Other experimental details have been reported elsewhere and all measurements were performed at ambient temperature (≈23 °C).[2]

Table 1. $[TBA^+]_w$ dependencies of $\Delta_o{}^w\phi$, ΔE and k_{ET}

$[TBA^+]_w$	$\Delta_o{}^w\phi$ / mV^a	ΔE / mV^b	k_{ET} / M^{-1} cm s^{-1} observed	k_{ET} / M^{-1} cm s^{-1} calculated^c
10^{-3}	-189	200	9.1×10^{-2}	5.1×10^{-3}
10^{-2}	-248	175	6.8×10^{-2}	1.8×10^{-3}
10^{-1}	-307	175	4.5×10^{-2}	9.5×10^{-4}

^{a}calculated as $a_o/a_w = [TBA^+]_o/[TBA^+]_w$. This leads to an error in determining $\Delta_o{}^w\phi$ to be ≈4 mV under the assumption that the activity coefficient of TBA^+ in water is equal to that of $(C_3H_7)_4N^+$ in water.[6]
^{b}determined from cyclic voltammograms of Fe(III) and 1-hydroxyethylferrocene in water. ΔE was slightly varied by the change in the activity of Fe(III).
^{c}calculated by the Marcus theory. See text and Ref. 7.

In the present system, $\Delta_o{}^w\phi$ betweeen TBP and water is determined by both the standard Galvani potential difference ($\Delta_o{}^w\phi^0$) and the activities of TBA^+ in the TBP (a_o) and water (a_w) phases as given by: $\Delta_o{}^w\phi = \Delta_o{}^w\phi^0 + (RT/F)\ln(a_o/a_w)$ (R, T, and F; usual meanings).[1] A Gibbs free energy change of the ET reaction is given by $\Delta G = -F(\Delta_o{}^w\phi + \Delta E)$, where ΔE is the energy gap between the redox potentials of the two reactants. $\Delta_o{}^w\phi$ and ΔE are summerized in Table 1. In the present experiments, the TBA^+ concentration in TBP ($[TBA^+]_o$) was

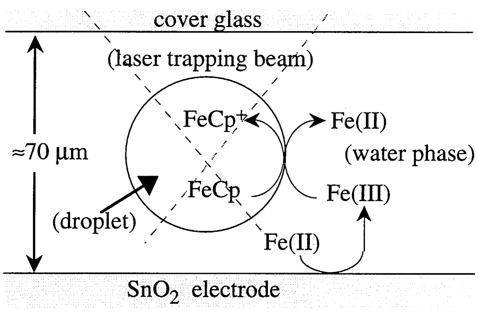

Figure 1. Reaction scheme of ET between FeCp and Fe(III) across the droplet/water interface.

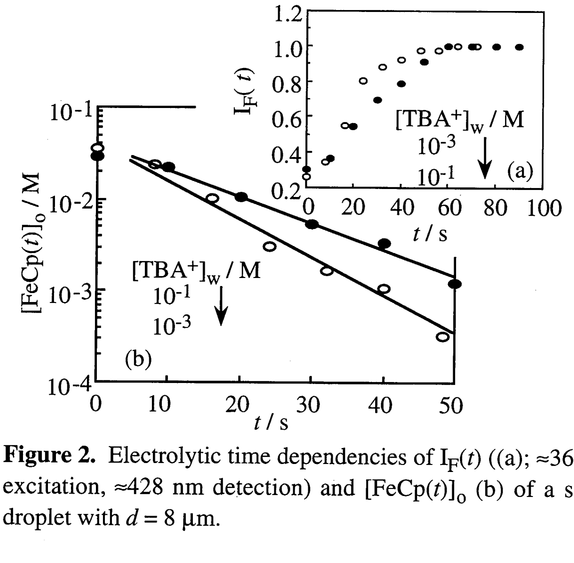

Figure 2. Electrolytic time dependencies of $I_F(t)$ ((a); ≈360 nm excitation, ≈428 nm detection) and $[FeCp(t)]_o$ (b) of a single droplet with *d* = 8 μm.

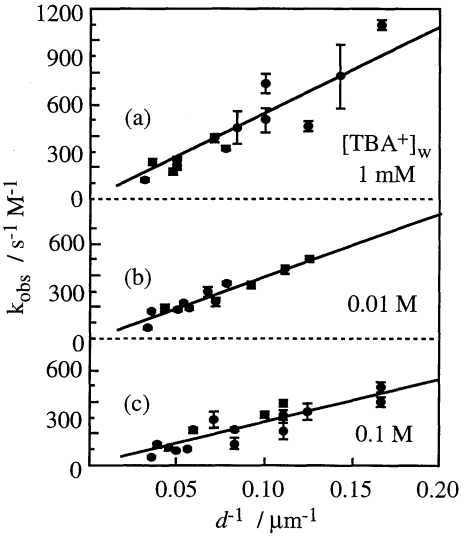

Figure 3. Droplet-size dependence of the ET rate.

fixed constant at 0.01 M and that in water ($[TBA^+]_w$) was varied from 10^{-1} to 10^{-3} M. Therefore, ΔG can be varied through $[TBA^+]_o/[TBA^+]_w$.

A single droplet was laser-trapped and positioned above the electrode without direct contact (Figure 1). With the droplet being laser-trapped, Fe(II) in the water phase was oxidized by a potential step method (800 mV vs. Ag/AgCl). As characteristics of bulk electrolysis in a thin-layer cell, Fe(II) can be oxidized almost completely to Fe(III) during the first ≈10 s.[2] Upon electrolysis, an ET reaction between FeCp in oil droplets and Fe(III) in the water phase can be induced (Figure 1). The time course of the FeCp concentration in the droplet ($[FeCp(t)]_o$) during electrolysis of Fe(II) in water was determined by fluorometry. In the droplet, namely, fluorescence from DPA is quenched by FeCp, but not by ferrocenium cation ($FeCp^+$). Therefore, the fluorescence intensity of DPA in the droplet during electrolysis ($I_F(t)$) can be used as a measure of $[FeCp(t)]_o$.[2]

Actually, Figure 2(a) demonstrates an increase in $I_F(t)$ (d = 8 µm) with an electrolytic time (t) owing to consumption of FeCp by the interfacial ET. For kinetic analyses, $I_F(t)$ was converted to $[FeCp(t)]_o$ on the basis of the Stern-Volmer relation: $I_{F0} / I_F(t) = 1 + k_q\tau_0 [FeCp(t)]_o$ where I_{F0} is $I_F(t)$ at $[FeCp(t)]_o = 0$.[2] k_q and τ_0 are the fluorescence quenching rate constant and the fluorescence lifetime of DPA in the absence of FeCp ($k_q = 9 \times 10^{10}$ M^{-1} s^{-1}, τ_0 = 9 ns), respectively.[3] Figure 2(b) shows the relation between $[FeCp(t)]_o$ and t thus calculated by the Stern-Volmer equation with the data in Figure 2(a). At both $[TBA^+]_w$ = 10^{-1} and 10^{-3} M, $\ln[FeCp(t)]_o$ was shown to decrease linearly with t. When the rate-determining step is the interfacial ET process, the $[FeCp(t)]_o$ - t curve can be analyzed as a pseudo-first-order reaction due to [Fe(III)] = ≈0.2 mM (see also above) and, therefore, the slope of the plot corresponds to the observed ET rate constant (k_{obs}), as reported previously.[2] Furthermore, k_{obs} is related to the rate constant of ET per unit surface area of a single droplet (k_{ET}) through $k_{obs} = (6/d)k_{ET}$, where the $(6/d)$ term is originated from the surface area/volume ratio of the droplet.[2] This indicates that k_{ET} can be determined directly by the slope of a k_{obs} - d^{-1} plot. The k_{obs} values were determined for individual droplets with various d and several $[TBA^+]_w$. Figure 3 clearly demonstrates that the slope of the plot is larger at a lower $[TBA^+]_w$. A decrease in $[TBA^+]_w$ from 10^{-1} to 10^{-3} M leads to an increase in $\Delta_o{}^w\phi$ from -307 to -189 mV under the assumption of $\Delta_o{}^w\phi^0$ = -248 mV (a value of a nitrobenzene/water system)[1] and, therefore, to a more negative shift of ΔG (= $-F(\Delta_o{}^w\phi + \Delta E)$). This agrees well with the experimental observations in Figure 3, where k_{ET} increases with decreasing $[TBA^+]_w$.

The results were compared with the prediction from the liquid/liquid interfacial ET theory by Marcus.[4,5] In the present system, the variation of ΔG is caused by that of $\Delta_o{}^w\phi$ alone, so that the k_{ET} value at given $[TBA^+]_w$ can be calculated on the basis of the relevant ΔG and the ΔG dependence of the activation free energy for ET.[7] The calculated and observed k_{ET} values are summerized in Table 1. Although k_{ET} was predicted to increase with increasing $\Delta_o{}^w\phi$ (i.e., normal region), the calculated k_{ET} was 10 - 10^2 times smaller than observed one. In the present case, $FeCp^+$ produced in the droplet is slightly dissolved in the water phase, so that the interfacial ET process is supposed to be influenced by mass transfer of $FeCp^+$.[1] Furthermore, correct evaluations of the outer-sphere reorganization energy and the electrostatic works for ET at a liquid/liquid interface are very difficult. Qualitatively, however, we suppose that the $\Delta_o{}^w\phi$ dependence of k_{ET} is explained within the frame work of the Marcus theory.

At the present stage of investigation, the ΔG range examined is very limited, so that we cannot make enough theoretical discussion. Nonetheless, since the number of the work on the interfacial ET and the relevant theoretical discussion are still limited, the present approach is quite unique and potential enough for studying interfacial ET. Further studies are now in progress in our laboratory and detailed discussion will be reported in a separate publication.

References and Notes

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7 k_{ET} was calculated as reported in Ref. 4. Following values were used for the calculation: outer-sphere reorganization energy = 65.7 kJ mol^{-1}, inner-sphere reorganization energies of the Fe(II)/Fe(III) and $FeCp/FeCp^+$ couples = 39.7 and 0.6 kJ mol^{-1}, respectively, electrostatic works to bring the reactants together and to separate the products = 7.22 and 6.49 kJ mol^{-1}, respectively.