Interfacial Mass Transfer across a Single Microdroplet/Water Boundary. Laser Trapping and Generation-Collection Experiments at a Microelectrode Array

Kiyoharu Nakatani,* Norifumi Terui,† Kiyoshi Hasebe,† and Noboru Kitamura*
Division of Chemistry, Graduate School of Science, Hokkaido University, Kita-ku, Sapporo 060
†*Division of Material Science, Graduate School of Environmental Earth Science, Hokkaido University, Kita-ku, Sapporo 060*

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Mass transfer of 1-hydroxyethylferrocenium cation from a nitrobenzene microdroplet to the surrounding water phase was directly measured by a generation-collection mode of a microelectrode array combined with a laser trapping technique. The mass transfer time of the derivative across the droplet/water interface was analyzed for the first time by a potential scan rate dependence of cyclic voltammograms.

We reported recently mass transfer (MT) processes of a ferrocene derivative across a single nitrobenzene (NB) droplet / water interface on the basis of a laser trapping-electrochemistry (LTE) technique.[1-3] When the derivative in an NB droplet is electrolyzed at a microelectrode, the oxidized species undergoes quick exit to the surrounding water phase and, at a certain time after electrolysis, the derivative recovers to the electrolyzed droplet from the water phase to establish a distribution equilibrium between two phases (Figure 1a). Although the water-to-droplet MT process could be analyzed directly through a recovery time of the electric charge in the relevant cyclic voltammograms (CV) after electrolysis, the droplet-to-water MT process was too fast (< 1s) to follow by the technique. On the other hand, a generation-collection (GC) mode of a microelectrode array has been known to be highly potential for direct analyses of MT dynamics in solution,[4-7] so that GC experiments would provide information on the fast droplet-to-water MT process. In this letter, we report the direct observation of droplet-to-water MT of 1-hydroxyethylferrocenium cation ($FeCp^+$) through an application of GC mode experiments to the LTE method (Figure 1b).

An NB solution containing 1-hydroxyethylferrocene (FeCp) and tetra-n-butylammonium tetraphenylborate (0.10 M, 1 M = 1 mol dm^{-3}) was dispersed in an NB-saturated aqueous tetra-n-butylammonium chloride (1.0 mM) and $MgSO_4$ (0.10 M) solution. The concentrations of FeCp in the NB and water phases at the distribution equilibrium have been reported to be 0.077 M and 0.19 mM, respectively.[3]

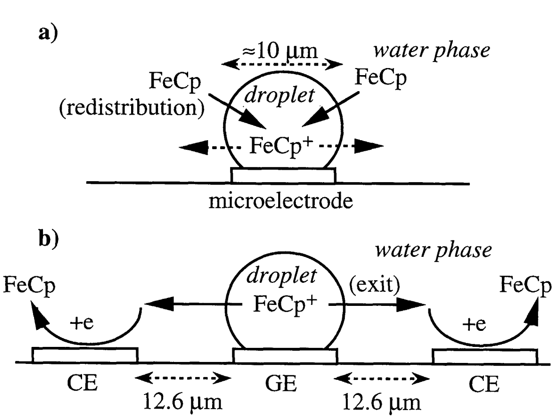

Figure 1. General schemes of mass transfer of $FeCp/FeCp^+$ across the single droplet/water interface in single microelectrode (a) and microelectrode array (b) systems.

Three microband electrodes (8.7 μm width x 60.0 μm long x 0.3 μm thickness), spaced in a 12.6 μm gap width, and a counter electrode (0.2 mm width x 3.5 mm long x 0.3 μm thickness) were fabricated on a sapphire plate by photolithography. Ag/AgCl(NaCl(sat.)) was used as a reference electrode. These electrodes were set on a slide glass as an electrolytic cell. The center and the side band-electrodes were used as generating (GE) and collecting electrodes (CE), respectively (Figure 1b). An LTE system has been reported in detail elsewhere.[2,3] Electrochemical responses were measured by a dual potentiostat system (BS-1, BAS) at room temperature (≈23 °C).

A single NB droplet (radius ≈ 5 μm) was contacted with GE by laser trapping, and currents at GE (I_g) and CE (I_c) were measured simultaneously without laser trapping, where the potential (E) of GE was swept between 0 and 0.68 V and that of CE was fixed at 0 V (Figure 2). As a general characteristics, a CV observed at a microelectrode shows a sigmoidal feature owing to cylindrical diffusion of a solute in solution. On the other hand, a CV of ferrocene in a single droplet exhibits only an anodic peak current and, cathodic current corresponding to reduction of the ferrocenium cation cannot be observed, analogous to a CV for irreversible oxidation in a thin-layer electrolytic cell.[2] In the present experiments, such two features are superimposed in the I_g-E curves. In Figure 2, namely, the I_g peaks at E = ≈200 and ≈400 mV (E scan rate (v) = 50 mV/s) correspond to oxidation of FeCp in the water phase (sigmoidal) and that in the droplet (anodic peak), respectively.[3] Analogous behaviour can be also seen in the I_c-E curve, where the sigmoidal (E = ≈200 mV) and peaked currents (E = ≈400 mV) are relevant to reduction of $FeCp^+$ originally distributed in the water phase and to that distributed from the electrolyzed droplet to the water phase, respectively. The collection efficiency ($\phi = I_c/I_g$) determined at E = ≈200 mV for the $FeCp/FeCp^+$ couple in the water phase was ≈0.4 (Figure 2). The value agreed well with

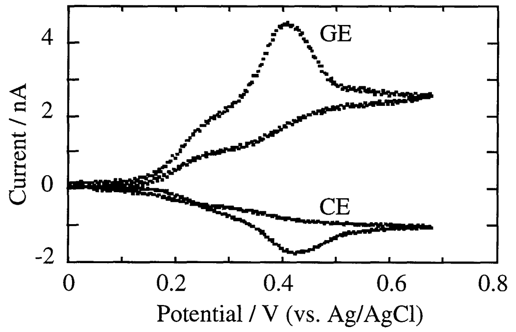

Figure 2. Cyclic voltammograms of an $FeCp/FeCp^+$ couple observed at GE and CE. The potential at GE was swept between 0 and 680 mV (50 mV/s) while that at CE was set 0 V.

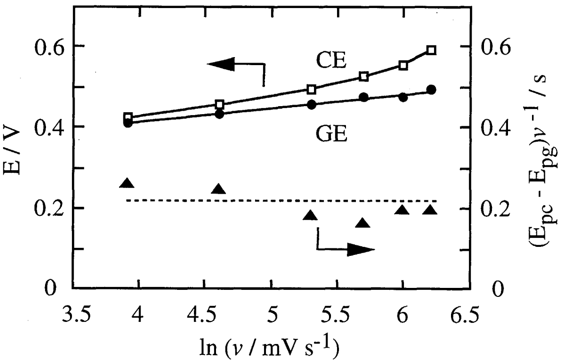

Figure 3. Logarithmic v dependencies of E_{pg} (●), E_{pc} (□) and $(E_{pc} - E_{pg})v^{-1}$ (▲).

that obtained for an $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ couple in an aqueous solution. Furthermore, ϕ of the FeCp/FeCp$^+$ couple defined as the ratio of the total electric charge in the symmetrical peak at GE to that at CE (E = ≈400 mV) was calculated to be ≈0.4. These results proved that FeCp$^+$ distributed from the electrolyzed droplet was collected at CE. The droplet-to-water MT processes can be thus analyzed by the present approach.

I_g- and I_c-E curves were recorded repeatedly for the single droplet, in which the experiments were performed at every ~1 min after the previous potential scan to allow the distribution reequilibrium of FeCp between two phases.[1-3] We found that the peak potentials at GE (E_{pg}) and CE (E_{pc}) were highly dependent on v. As shown in Figure 3 the E_{pg} value was proportional to ln (v), indicating irreversible oxidation of FeCp in the droplet at the electrode/droplet interface.[2] On the other hand, although E_{pc} increased with increasing v, the values did not fall on a straight line. We consider that the v dependence of E_{pc} is governed by the MT time of FeCp$^+$ from GE to CE. In the case of diffusion-limited MT, the diffusion time (t_d) of FeCp$^+$ from GE to CE can be calculated by the equation, $t_d = d^2/(2D)$, where d and D are the diffusion distance and the diffusion coefficient of FeCp$^+$, respectively. The D value of FeCp in water or NB was determined to be 6×10^{-6} or 4×10^{-6} cm^2 s^{-1}, respectively, by cyclic voltammetry. Since FeCp$^+$ diffuses in both the NB and water phases, we take D of FeCp$^+$ as an average of these two values (5×10^{-6} cm^2 s^{-1}). Furthermore, we assume that the sum of a quarter width of GE (2.2 μm) and the interelectrode distance between GE and CE (12.6 μm) is equal to d (14.8 μm).[6] Using these values, t_d was calculated to be 0.22 s. Experimentally, a time dependence of the concentration of FeCp$^+$ around GE or CE upon electrolysis can be analyzed by E_{pg}/v or E_{pc}/v, respectively. Thus, the value of $(E_{pc} - E_{pg}) / v$ is regarded as a measure of the MT time of FeCp$^+$ between GE and CE, which has been estimated to be ≈0.2 s irrespective of v (Figure 3). The value is in good agreement with the calculated MT time (t_d). A potential difference across the NB/water interface ($\Delta\phi$) is determined by the concentrations of tetra-n-butylammonium cation dissolved in both phases, and calculated to be -131 mV on the basis of the Nernst equation.[2] Therefore, the MT time of FeCp$^+$ from GE to CE is not limited by quick exit of positively charged FeCp$^+$ at the droplet/water interface.[2] Diffusion of FeCp$^+$ in the NB and water phases is thus concluded to be the rate-determining step of MT from GE to CE across the droplet/water interface.

We demonstrated a potential means of the laser trapping and microelectrode array methods to study quick MT processes between a droplet and the surrounding solution phase. In the present case, MT of FeCp$^+$ was shown to be limited by diffusion of the compound in both phases. Generally, however, interfacial MT processes are influenced by $\Delta\phi$, the size of a droplet, and so forth. These aspects will be also elucidated directly by the present approaches, which are the next target of the research.

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