A Microvoltammetric Study of Transport Process through a Nitrobenzene / Water Interface

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Transport of ferrocenylmethanol and $Co(phen)_3^{2+}$ through a nitrobenzene/water interface was examined by an electrochemical method using a microelectrode. The transfer rate of $Co(phen)_3^{2+}$ through nitrobenzene / water interface was determined to be 0.05 cm/s by digital simulation analysis. Transfer of ferrocenylmethanol was very fast, with the transfer rate estimated to be larger than 0.1 cm/s.

Since the interface between two immiscible electrolyte solutions has been suggested as a simple model for biological membrane, transfer phenomena such as mass transport and charge transport across liquid/liquid interface has been studied extensively. Ion and charge transport across a liquid/liquid interface has been investigated by electrochemical methods.[1,2] However, application of the usual electrochemical methods to transport of neutral solutes is difficult. Recently, microelectrode techniques have been widely applied to monitor phenomena occurring at various kinds of interfaces, such as enzyme reactions at solid/liquid interface,[3-5] charge transfer across the liquid/liquid interface,[6-10] and permeation and ion transfer through membranes.[11,12] Kitamura and coworkers examined the transport rate of ferrocene derivatives across a nitrobenzene-microdroplet/water interface by an electrochemical method.[13-15] They measured the time dependence of the amount of ferrocene derivatives in the nitrobenzene microdroplet by voltammetry with a microelectrode contacting the droplet and found that the mass transport from water to nitrobenzene was diffusion-limited. They also reported that adsorption as well as diffusion in the water was governed by the transfer rate for amphiphilic ferrocene derivatives.

As reported herein, we have examined the transfer rate across the interface of ferrocenylmethanol and $Co(phen)_3^{2+}$ using the microvoltammetric technique. Kitamura and coworkers observed the transfer rate from water to nitrobenzene, whereas, in this investigation, we have observed the transfer rate from nitrobenzene to water by voltammetry in the water phase. Specifically, FMA was oxidized to FMA^+ at a microelectrode located near the interface perturbing partition equilibrium and causing transport of FMA from nitrobenzene to water. The transfer rate across the interface was quantitatively analyzed using digital simulation of the oxidation current.

Ferrocenylmethanol (purchased from Tokyo Kasei Co.) was recrystallized from hexane solution. $Ru(NH_3)_6(ClO_4)_3$ [16] and $Co(phen)_3(ClO_4)$ [17] were synthesized using methods described in the literature. All aqueous solutions were prepared with water purified by a Milli-Q Jr (Millipore Co.) water purification system.

A nitrobenzene solution containing 57 mM ferrocenylmethanol or 50 mM $Co(phen)_3(ClO_4)_2$ was mixed with an equal volume of 2.2 mM $Ru(NH_3)_6(ClO_4)_3$ in 0.1 M KCl, 0.05 M Tris/Cl (pH 7.5). The mixture solution was shaken for few minutes to accomplish full partitioning of ferrocenylmethanol or $Co(phen)_3^{2+}$ between water and nitrobenzene.

Cyclic voltammetry was carried out using a two-electrode configuration. Current was amplified with a Keithley Model 427 amplifier. The working electrode was a 5.5 μm radius platinum wire mounted in soft glass. The tip radius of the electrode including the insulator part was ~15 μm. The electrode surface was polished with fine emery paper (Sumitomo 3M Co.), followed by a thorough rinse with water in an ultra sonic bath. The counter electrode (Ag/AgCl) was directly immersed in the aqueous phase. The tip of the microelectrode was placed near the nitrobenzene/water interface. Micromovement of the electrode was performed by means of a motor driven XYZ stage (Chuoseiki Co.).

The distance between the electrode and the interface was estimated from the decrease in the reduction current of $Ru(NH_3)_6^{3+}$. Digital simulation was used to analyze the currents. In the simulation, the solution is considered as to be an assembly of discrete volume elements.[18] The concentrations can be calculated by taking into account diffusion, mass transfer though liquid/liquid interface, and electron transfer at the electrode. The contributions of diffusion and electron transfer to the concentration profile are described in the literature.[5] The concentration changes (ΔC) of the elements on both side of the nitrobenzene/water interface caused by mass transfer through the interface at a certain time interval (Δt) are:

$$\Delta C_w = \frac{\Delta t}{\Delta x} \quad (k_{-1}C_o - k_1C_w)$$

$$\Delta C_o = \frac{\Delta t}{\Delta x} \quad (k_1C_w - k_{-1}C_o)$$

where C_w and C_o are the concentrations of the FMA or $Co(phen)_3^{2+}$ in the volume element adjacent to the interface on water and nitrobenzene, respectively. Δx is a length of the volume elements on both sides of the interface. The mass transfer rate constants from water to nitrobenzene and from nitrobenzene to water are k_1 and k_{-1}, respectively.

Figure 1 shows the cyclic voltammograms of FMA and $Ru(NH_3)_6^{3+}$ taken at different distances between the microelectrode and the liquid/liquid interface. The voltammograms show the reduction waves for $Ru(NH_3)_6^{3+}$ and oxidation waves for FMA. The oxidation and reduction currents are normalized by division by the steady state oxidation and reduction currents at the electrode located far from the interface. The concentration of FMA in the aqueous phase was found to be 0.30 mM by voltammetry at the microelectrode located far from the interface and the concentration of FMA in the nitrobenzene was 57 mM; consequently, the partition coefficient for FMA was 1.9×10^2. A remarkable decrease in the reduction current was observed as the tip of the microelectrode approached the interface. On the other hand, the oxidation current increased as the tip of the microelectrode approached the interface. Since $Ru(NH_3)_6^{3+}$ is highly hydrophilic, the concentration of $Ru(NH_3)_6^{3+}$ in the

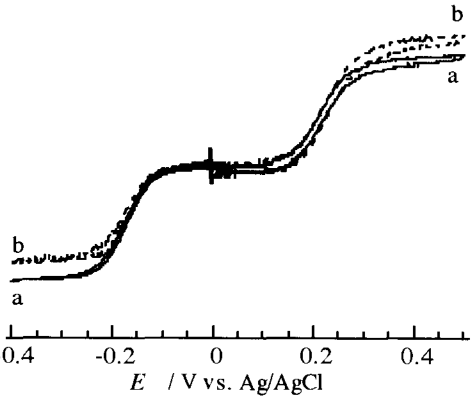

Figure 1. Cyclic voltammograms of FMA and $Ru(NH_3)_6^{3+}$ on Pt microdisk electrode (radius = 5.5 μm) at a scan rate of 0.05 V/s. The currents were normalized by division by the steady state current when the electrode tip was far from the interface.
a, microelectrode was located far from the interface.
b, microelectrode was located at 11.5 μm from the interface.

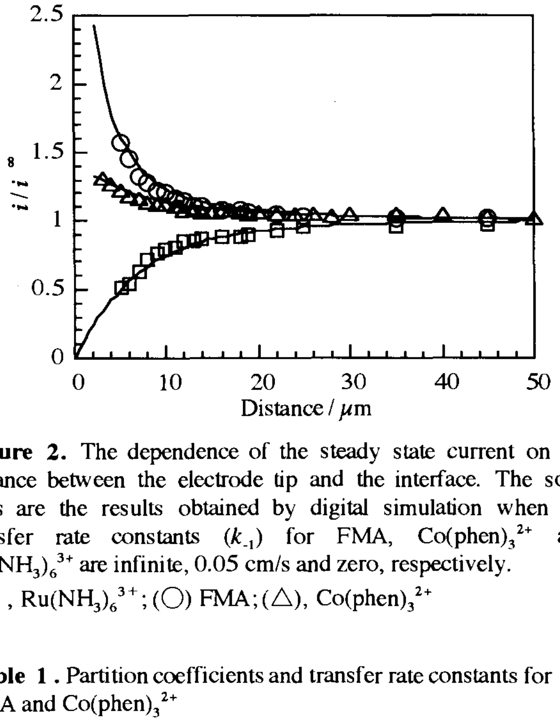

Figure 2. The dependence of the steady state current on the distance between the electrode tip and the interface. The solid lines are the results obtained by digital simulation when the transfer rate constants (k_{-1}) for FMA, $Co(phen)_3^{2+}$ and $Ru(NH_3)_6^{3+}$ are infinite, 0.05 cm/s and zero, respectively.
(□) , $Ru(NH_3)_6^{3+}$; (○) FMA; (△), $Co(phen)_3^{2+}$

Table 1. Partition coefficients and transfer rate constants for FMA and $Co(phen)_3^{2+}$

	Partition coefficient	k_1 / cm/s	k_{-1} / cm/s
$Co(phen)_3^{2+}$	$5.3x10^2$	27	0.050
FMA	$1.9x10^2$	>19	>0.1

nitrobenzene phase was negligible. The interface acts as a wall for $Ru(NH_3)_6^{3+}$. The partition equilibrium of FMA was perturbed due to oxidation of FMA to FMA^+ at the microelectrode, therefore, FMA is transferred from nitrobenzene to the aqueous phase. The dependence of steady state oxidation and reduction currents on the distance is depicted in Figure 2. The voltammetry was also carried out in a $Co(phen)_3^{2+}$ solution. The partition coefficient for $Co(phen)_3^{2+}$ is given in Table 1. The steady state oxidation current for $Co(phen)_3^{2+}$ as a function of the distance between electrode tip and the interface is plotted in Figure 2.

The solid lines in Figure 2 are the results obtained by digital simulation when the transfer rate constants for FMA, $Co(phen)_3^{2+}$ and $Ru(NH_3)_6^{3+}$ are infinite, 0.05 cm/s and zero, respectively. Good agreement between measurement and simulation could be obtained with non-zero values for k_{-1}. Transfer of FMA from nitrobenzene to the aqueous phase is controlled by diffusion under the present experimental conditions.

To estimate the minimum value of k_{-1} for FMA, further digital simulations were performed by assuming various values for k_{-1} ranging from 0 to 0.1 cm/s. Simulation curves with k_{-1} larger than 0.1 cm/s were almost identical to that using the infinite k_{-1}. The minimum transfer rate of FMA from nitrobenzene to the aqueous phase is therefore 0.1 cm/s.

We could not derive a definite value for the transfer rate of FMA in this study. Considering the reported transfer rates of alkyl ammonium ions[2], we can estimate the transfer rate of FMA to be around 0.1 cm/s. Investigations with a much smaller electrode allow determination of FMA transfer rate.

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