Introduction

Analyses of chemical and physical processes in water/oil interface systems are important for understanding such processes as separation by solvent extraction or reactions in oil-in-water emulsion systems. In these systems, the chemical and physical processes near the water/oil interface play important roles, and kinetic analyses of the interfacial processes are indispensable for mechanistic investigations. Kinetic analyses of the interfacial processes are necessary for kinetic analysis, because the interfacial processes often proceed during the formation of a water/oil interface. Rapid mixing of the water and oil phases and the use of spectroscopic measurements, polarographic measurements of droplets, and dynamic interfacial tension measurements have been used to analyze metal-complex formation across the water/oil interface. We have kinetically analyzed the extraction mechanisms of ferrocene derivatives in oil microdroplet/water systems by using single microdroplet manipulation, electrochemistry, and a microspectroscopic system. On the basis of quick electrolysis of the ferrocene derivative in an oil microdroplet contacting a microelectrode, the kinetics of interfacial mass transfer of the ferrocene derivative could be determined.

Experimental

Using a Cd-deposited microelectrode, an electrochemically generated Cd(II) ion in a micro-water phase was reacted with 5-octyloxymethyl-8-quinolinol (HC8Q) in 1,6-dichlorohexane. The fluorescence intensity of Cd(C8Q)2 near the water/oil interface (If) was analyzed under a confocal fluorescence microscope. The rate of decrease of If was independent of the HC8Q concentration and pH, but was influenced by the phase-boundary potential between the water and oil phases, suggesting that Cd(II) extraction is governed by Cd(C8Q)+ desorption at the interface.

Keywords: Confocal fluorescence microscope, liquid-liquid interface, microelectrode, solvent extraction, microdroplet

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microscope (Olympus, FV-1000D) (Fig. 1). The micro-water phase was cylindrical and the micro-water/oil interface was flat. An Ag/AgCl/3 M NaCl reference electrode and a Pt wire were inserted into the outer aqueous phase. Electrochemical measurements were performed with an electrochemical analyzer (DropSens, µStat 200). Three-dimensional spatially resolved fluorescence at a wavelength of 480 to 580 nm was measured under the confocal fluorescence microscope by using a CW diode laser (405 nm) and an objective lens (Olympus, LUCPlanFLN, 40×, NA = 0.6). The confocal aperture size was 80 μm. All measurements were performed at room temperature (≈298 K).

The phase-boundary potential between the water and 1,6-dichlorohexane phases (Δφ) was estimated by using the following equation:

Δφ = ΔφTAA+ + (RT/F)ln([TAA+(o)]/[TAA+(w)]),

where ΔφTAA+ is the standard ion-transfer potential of TAA+ between the water and oil phases. For TEA+, TBA+, and TPnA+ ions, the mid-point potential of TAA+ has been reported to be 42, −193, and −357 mV, respectively. The mid-point potential of TAA+ was assumed to be equal to ΔφTAA+. R is the gas constant, T is the absolute temperature, and F is the Faraday constant. [TAA+(w)] and [TAA+(o)] are the TAA+ concentrations in the water and oil phases, respectively.

Results

A 1:2 (Cd(II):quinolinol) complex is fluorescent, whereas a 1:1 (Cd(II):quinolinol) complex is non-fluorescent. The fluorescence maximum of Cd(C8Q)2 in 1,6-dichlorohexane occurred at a wavelength of 540 nm under conventional fluorescence spectroscopy. The micro-water/oil system was placed under the confocal fluorescence microscope. For quantitative fluorescence analysis, the Z (vertical direction) and Y (horizontal direction) axes were positioned on the micro-water/oil interface through the center of the circular interface (defined as the origin). The X axis was in a direction perpendicular to the micro-water/oil interface through the origin (Fig. 1). Cadmium on the microelectrode was oxidized to Cd(II) ion in the micro-water phase by using potential step electrolysis for 0.2 s at 0 V. After electrolysis, the fluorescence intensity (I0) of Cd(C8Q)2 was measured in the area of an ellipse with a major radius of 10 μm on the Y axis, a minor radius of 2.5 μm on the X axis, and the ellipse center at the origin. I0 rapidly increased and then decreased during ~10 s (Fig. 2a).

Table 1: k and k values at [TBA+(w)] = [TBA+(o)] = 10 mM

| pH   | [HC8Q(o)] = 10 mM | [HC8Q(o)] = 50 mM |
|------|-----------------|------------------|
| pH = 2 | 5 ± 1           | 3 ± 1            |
| pH = 7 | 7 ± 2           | 6 ± 2            |

From the total electric charge (~3 μC), the total concentration of the Cd(II) ion generated in the micro-water phase by the electrolysis was estimated to be ~5 mM. The concentration of HC8Q in the oil phase ([HC8Q(o)], 10 to 50 mM) was greater than that of Cd(II) ion in the micro-water phase. The volume of the oil phase (200 μL) was much larger than that of the micro-water phase (3 μL), so that Cd(C8Q)2 is considered to be completely extracted into the oil phase. Moreover, the change in [HC8Q(o)] was negligibly small. The formation process of 1:1 (Cd(C8Q)+) or the 1:2 (Cd(C8Q)2) complex can be assumed to be a pseudo-first-order reaction. The time (t) dependence of I0 after electrolysis was analyz

The time (t) dependence of I0 after electrolysis was analyzed by using the equation:

\[ I_t = I_0\exp\{-k_0(t + t_0)\} - \exp\{-k(t + t_0)\}, \]

where \( I_0 \) is the pre-exponential factor and \( t_0 \) is an adjustable parameter relevant to the time resolution of our experiments (0 < t0 < 0.2 s); \( k_0 \) and \( k \) are rate constants for the increase and decrease, respectively, in \( I_t; \ t = 0 \) is defined as the time after electrolysis for 0.2 s. \( I_t \) was successfully fitted to Eq (2) (Fig. 2b). Table 1 summarizes the \( k_0 \) and \( k \) values for various [HC8Q(o)] values and pH in the water phase at Δφ = −193 mV ([TBA+(w)] = [TBA+(o)] = 10 mM). \( k_0 \) had large experimental
errors and will not be discussed in detail, because $1/k_d$ was comparable with the time resolution (~0.2 s). The $k_d$ value was independent of the [HC8Q(o)] and pH. On the other hand, $k_d$ was independent of the TBA-TPFPB- concentration in the oil phase at $\Delta \phi = -193$ mV, whereas $k_d$ depended significantly on $\Delta \phi$ (Fig. 3).

Discussion

Rate-determining step for increase and decrease in $I_f$

In our system, Cd(C8Q): fluorescence was observed alone and rate-determining steps were expected to exist regarding the increase and decrease in $I_f$. One was an elementary process before Cd(C8Q)+ formation, and the other was an elementary process after Cd(C8Q)+ formation. The diffusion time ($t_{d1}$) from the electrode surface to the micro-water/oil interface was estimated at 0.07 s by using the equation $t_{d1} = D_h (2D_o)$, where $D_h$ is the diffusion coefficient of Cd(II) ion in water ($7 \times 10^{-6}$ cm$^2$ s$^{-1}$). The $t_{d1}$ value was smaller than $1/k_d$ or $1/k_e$ (Table 1), so the diffusion of Cd(II) ion in the micro-water phase was not the rate-determining step. Cd(C8Q)+ diffusion between the micro-water/oil interface and the bulk oil phase was also fast. Under the assumption of the diffusion coefficient of Cd(C8Q)+ ($D_o$), where $D_o = 8 \times 10^{-7}$ cm$^2$ s$^{-1}$, which is the reported coefficient of diffusion of a 1:1 complex (Cd(Q)+) between Cd(II) ion and 8-quinolino (HQ) in nitrobenzene, the diffusion time ($t_{d2}$) from the measuring area to the outer area was estimated. The fluorescence was measured in the area of a semi-ellipse with a major radius of 10 µm and a minor radius of 2.5 µm on the oil-phase side. Since the diffusion length ($L$) was assumed to be the minor radius (2.5 µm) plus a spatial resolution value (~2 µm ($L = 5$ µm), $t_{d2} = L^2/(2D_o)$) was roughly estimated to be ~0.2 s, which agreed with $1/k_d$ (Table 1). The fluorescence of Cd(C8Q)+ could disappear from the measuring area only as a result of the diffusion of Cd(C8Q)+; therefore, the rate of Cd(C8Q)+ diffusion from the measuring area was expected to be the rate-determining step after Cd(C8Q)+ formation.

The reported dissociation constants of H$_2$C8Q$^+$ and HC8Q in water are 10$^{-4.32}$ and 10$^{-9.39}$, respectively. When the interfacial tension at the water-droplet/1,6-dichlorohexane interface was measured by using a pendant drop method, the interfacial tension values were 20 to 23 mN m$^{-1}$, independent of the HC8Q concentration (0, 10, and 50 mM) in 1,6-dichlorohexane and the pH (2 and 7) of the water phase. We considered that the amount of HC8Q or H$_2$C8Q$^+$ adsorbed at the water/oil interface was negligibly small. HC8Q and H$_2$C8Q$^+$ are scarcely dissolved in the water phase. Therefore, the processes of Cd(C8Q)+ and Cd(C8Q)$_2$ formation proceed at the micro-water/oil interface, or near to the interface; $k_d$ was independent of the [HC8Q(o)] and pH in the water phase (Table 1), so the rate-determining step for $k_d$ was not the Cd(C8Q)+ or Cd(C8Q)$_2$ formation and interfacial transfer of H$^+$ generated during the Cd(II) complex formation. The interfacial transfer of Cd(C8Q)$_2$+ should depend on $\Delta \phi$, although that of Cd(C8Q)+ (neutral species) is independent of $\Delta \phi$. However, the rate-determining step is not related to ion-pair formation of Cd(C8Q)$^+$ with TPFPB$^-$ because $k_d$ was independent of the TBA-TPFPB- concentration (Fig. 3a). The use of a dynamic interfacial tension measurement technique has revealed that a 1:1 complex between a divalent metal ion (M$^{2+}$) and HC8Q is quickly adsorbed onto a water/oil interface. An electrochemical investigation of the transfer of Cd(Q)+ as a monovalent ion at a water/nitrobenzene interface has shown that the standard ion transfer potential of Cd(Q)$^+$ is ~0.04 V. Cd(C8Q)$^+$ is more hydophobic than Cd(Q)$^+$, suggesting that the standard ion transfer potential of Cd(C8Q)$^+$ ($\Delta \phi_{\text{Cd(C8Q)O}}$) is smaller than ~0.04 V. In our system, $\Delta \phi$ ranged from ~0.357 to ~17 mV; these values are comparable to $\Delta \phi_{\text{Cd(C8Q)O}}$. If $k_d$ is directly related to the ion transfer rate constant of Cd(C8Q)$^+$ across the water/oil interface, then $k_d$ should increase with increasing $\Delta \phi$. However, $k_d$ did not increase with increasing $\Delta \phi$ (Fig. 3b). The adsorption of surface-active ions becomes a maximum at around the standard ion-transfer potential, indicating that the desorption rate of surface-active ions is at a minimum at about the standard ion-transfer potential. We considered that $\Delta \phi_{\text{Cd(C8Q)O}}$ was between ~0.25 and ~0.04 V, and that $k_d$ was the desorption rate constant of Cd(C8Q)$^+$ at the water/oil interface. Therefore, $k_d$ decreased with increasing $\Delta \phi$ for $\Delta \phi < \Delta \phi_{\text{Cd(C8Q)O}}$.

Extraction mechanism in the Cd(II)-HC8Q system

Previous reports have discussed the adsorption and transfer of M(C8Q)$^+$ and M(Q)$^+$ at the water/oil interface. However, the rates of M(C8Q)$^+$ and M(C8Q)$_2$ as a final extracted species had not been clarified kinetically. From the above results, we propose a mechanism for the extraction of Cd(II) with HC8Q (Fig. 4). The process of Cd(C8Q)$^+$ formation from the Cd(II) ion and HC8Q (or H$_2$C8Q$^+$) is fast, and Cd(C8Q)$_2$+ is adsorbed onto the micro-water/oil interface. However, the reaction with HC8Q (or H$_2$C8Q$^+$) of Cd(C8Q)$_2$+ that has been adsorbed onto the water/oil interface may be strongly suppressed, because the central atom (Cd(II)) of Cd(C8Q)$_2$+ is likely to be located near the interface of the water-phase side. The rate of desorption of Cd(C8Q)$^+$ from the interface into the oil phase is thus a rate-determining step (rate constant, $k_d$). Once Cd(C8Q)$^+$ is desorbed, it reacts rapidly with HC8Q to form Cd(C8Q)$_2$. Cd(C8Q)$_2$
diffusion is also a rate-determining step (rate constant, $k_2$). In this model, the [Cd(C8Q)$_2$] concentration in the oil phase near the interface ([Cd(C8Q)$_2$]) corresponding to $I_F$ is given by the equation

$$[\text{Cd(C8Q)$_2$}] = \frac{k_1 [\text{Cd(C8Q)}^+]_0}{k_2 - k_1} \times \{\exp(-k_1 t) - \exp(-k_2 t)\},$$

(3)

where $[\text{Cd(C8Q)}^+]_0$ is the Cd(C8Q)$^+$ concentration at the water/oil interface at $t = 0$. In Eq. (3), because $k_2$ is greater than $k_1$, the pre-exponential factor for $\exp(-k_1 t)$ is a positive value and that for $\exp(-k_2 t)$ is a negative value. Therefore, Cd(C8Q)$_2$ diffusion from the measuring area near the water/oil interface into the bulk oil phase is the increasing component of $I_F$ ($k_2 = k_r$), and the desorption of Cd(C8Q)$^+$ from the water/oil interface into the oil phase is the decreasing component of $I_F$ ($k_1 = k_d$).

Conclusions

The kinetic analysis of the extraction of Cd(II) with HC8Q in a micro-water/oil system could be performed by using a Cd-deposited microelectrode and confocal fluorescence microscope. We consider that this approach based on the characteristics of mass transfer in a micrometer-sized region has sufficient potential for use in the analysis of chemical and physical processes across water/oil interfaces.

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