Kinetic Analysis of the Solvent Extraction of Cadmium(II) Complexes Using a Cadmium-deposited Recessed Microelectrode and Confocal Fluorescence Microscope

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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 (*I_F*) was analyzed under a confocal fluorescence microscope. The rate of decrease of *I_F* 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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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.^{1,2} In metal-complex formation and solvent-extraction systems, quick generation of a reactant near the water/oil interface is 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,³⁻⁶ polarographic measurements of droplets,^{7,8} and dynamic interfacial tension measurements^{9,10} 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.¹¹⁻¹⁵ However, the solvent extraction of another metal complex could not be demonstrated, because the metal complex was not easily electrolyzed in the oil microdroplet. Here, Cd deposited on a recessed microelectrode was oxidized to Cd(II) ion in a micro-water phase, and extraction of Cd(II) with 5-octyloxymethyl-8-quinolinol (HC₈Q) across the micro-water/oil interface was kinetically analyzed under a confocal fluorescence microscope.

Experimental

5-Octyloxymethyl-8-quinolinol (HC₈Q, Wako Pure Chemical, >99.0%), tetraethylammonium chloride (TEA⁺Cl⁻, Tokyo Kasei Kogyo, >98%), tetrabutylammonium chloride (TBA⁺Cl⁻, Tokyo Kasei Kogyo, >98%), and tetrapentylammonium chloride (TPenA⁺Cl⁻, Tokyo Kasei Kogyo, >98%) were used without further purification. Tetraalkylammonium tetrakis(pentafluorophenyl)borate (TAA⁺TPFPB⁻, TAA⁺ = TEA⁺, TBA⁺ or TPenA⁺) was prepared from TAA⁺Cl⁻ and lithium tetrakis(pentafluorophenyl)borate (Li⁺TPFPB⁻, Tokyo Kasei Kogyo, >70%) in a methanol/water (2:1) solution, and then purified by recrystallization from an acetone/n-hexane (1:3) solution.

A gold microdisk electrode (20 μm in diameter) was electrochemically etched in HCl (2 M) and a recess with a depth (*d*) of 10 μm and a diameter of 20 μm was produced.^{15,16} Copper was deposited on the gold microelectrode surface by the reduction of Cu(II) ion in a CuSO₄ (1 mM) and NaCl (5 mM) solution at -1.20 V (vs. Ag/AgCl/3 M NaCl electrode) for 5 s. Cd was then deposited on the Cu/Au microelectrode by the reduction of Cd(II) ion in a CdCl₂ (10 mM) solution at 10 nA for 360 s.

Water-saturated 1,6-dichlorohexane (200 μL) containing HC₈Q (10, 50 mM) and TAA⁺TPFPB⁻ (1 to 50 mM) was poured into an aqueous TAA⁺Cl⁻ solution (1 to 50 mM, 25 mL) of pH = 2 (13 mM HCl, 47 to 96 mM KCl) or 7 (31 mM KOH, 70 mM KCl, 72 mM *N,N*-bis(2-hydroxyethyl)taurine) and contacted onto a glass plate that had been treated with dichlorodimethylsilane. The ionic strength of the aqueous solution at pH = 2 was adjusted to 0.11 M with KCl. The recessed Cd/Cu/Au microelectrode was inserted into the oil phase, and a micro-water phase of the same aqueous solution of pH = 2 or 7 was injected into the recess of the microelectrode by using a microcapillary injection and manipulation system (Narishige, IM-11-2/MN-151) under a confocal fluorescence

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Fig. 1 Schematic illustration of the electrolytic cell under a confocal fluorescence microscope.

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, μ Stat 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 $\times$, NA = 0.6). The confocal aperture size was 80 μ m. All measurements were performed at room temperature ($\sim$ 298 K).

The phase-boundary potential between the water and 1,6-dichlorohexane phases ($\Delta\phi$) was estimated by using the following equation:²

$$\Delta\phi = \Delta\phi_{\text{TAA}^+}^0 + (RT/F)\ln([TAA^+(\text{o})]/[TAA^+(\text{w})]), \quad (1)$$

where $\Delta\phi_{\text{TAA}^+}^0$ is the standard ion-transfer potential of TAA^+ between the water and oil phases. For TEA^+ , TBA^+ , and TPenA^+ ions, the mid-point potential of TAA^+ has been reported to be 42, -193, and -357 mV, respectively.¹⁷ The mid-point potential of TAA^+ was assumed to be equal to $\Delta\phi_{\text{TAA}^+}^0$. R is the gas constant, T is the absolute temperature, and F is the Faraday constant. $[TAA^+(\text{w})]$ and $[TAA^+(\text{o})]$ 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.¹⁸ The fluorescence maximum of $\text{Cd}(\text{C}_8\text{Q})_2$ in 1,6-dichlorohexane occurred at a wavelength of $\sim$ 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. 2 Time dependence of the fluorescence intensity (a) before and after electrolysis and (b) after electrolysis at pH = 7, $[\text{HC}_8\text{Q}(\text{o})] = 50$ mM, and $[\text{TBA}^+(\text{w})] = [\text{TBA}^+(\text{o})] = 10$ mM. The solid line represents the results of calculations using Eq. (2).

Table 1 k_r and k_d values at $[\text{TBA}^+(\text{w})] = [\text{TBA}^+(\text{o})] = 10$ mM

Rate constant	$[\text{HC}_8\text{Q}(\text{o})] = 10$ mM		$[\text{HC}_8\text{Q}(\text{o})] = 50$ mM	
	pH = 2	pH = 7	pH = 2	pH = 7
k_r/s^{-1}	5 ± 1	5 ± 3	7 ± 2	6 ± 2
k_d/s^{-1}	1.2 ± 0.3	1.3 ± 0.3	0.8 ± 0.3	0.8 ± 0.2

(Fig. 1). Cadmium on the microelectrode was oxidized to $\text{Cd}(\text{II})$ ion in the micro-water phase by using potential step electrolysis for 0.2 s at 0 V. After electrolysis, the fluorescence intensity (I_F) of $\text{Cd}(\text{C}_8\text{Q})_2$ was measured in the area of an ellipse with a major radius of 10 μ m on the Y axis, a minor radius of 2.5 μ m on the X axis, and the ellipse center at the origin. I_F rapidly increased and then decreased during $\sim$ 10 s (Fig. 2a). From the total electric charge ($\sim$ 3 nC), the total concentration of the $\text{Cd}(\text{II})$ ion generated in the micro-water phase by the electrolysis was estimated to be $\sim$ 5 mM. The concentration of HC_8Q in the oil phase ($[\text{HC}_8\text{Q}(\text{o})]$, 10 to 50 mM) was greater than that of $\text{Cd}(\text{II})$ ion in the micro-water phase. The volume of the oil phase (200 μ L) was much larger than that of the micro-water phase (3 μ L), so that $\text{Cd}(\text{C}_8\text{Q})_2$ is considered to be completely extracted into the oil phase. Moreover, the change in $[\text{HC}_8\text{Q}(\text{o})]$ was negligibly small. The formation process of 1:1 ($\text{Cd}(\text{C}_8\text{Q})^+$) or the 1:2 ($\text{Cd}(\text{C}_8\text{Q})_2$) complex can be assumed to be a pseudo-first-order reaction.

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

$$I_F = I_{F0}[\exp\{-k_d(t + t_0)\} - \exp\{-k_r(t + t_0)\}], \quad (2)$$

where I_{F0} is a pre-exponential factor and t_0 is an adjustable parameter relevant to the time resolution of our experiments ($0 < t_0 < 0.2$ s); k_r and k_d are rate constants for the increase and decrease, respectively, in I_F ; $t = 0$ is defined as the time after electrolysis for 0.2 s. I_F was successfully fitted to Eq. (2) (Fig. 2b). Table 1 summarizes the k_r and k_d values for various $[\text{HC}_8\text{Q}(\text{o})]$ values and pH in the water phase at $\Delta\phi = -193$ mV ($[\text{TBA}^+(\text{w})] = [\text{TBA}^+(\text{o})] = 10$ mM). k_r had large experimental

Fig. 3 k_d for various (a) [TBA⁺(o)] (= [TBA⁺(w)]) at $\Delta\phi = -193$ mV and (b) $\Delta\phi$ values at pH = 2.

errors and will not be discussed in detail, because $1/k_r$ 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)₂ 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)₂ formation, and the other was an elementary process after Cd(C₈Q)₂ 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 $t_{d1} = d^2/(2D_w)$, where D_w is the diffusion coefficient of Cd(II) ion in water (7×10^{-6} cm² s⁻¹).¹⁹ The t_{d1} value was smaller than $1/k_r$ or $1/k_d$ (Table 1), so the diffusion of Cd(II) ion in the micro-water phase was not the rate-determining step. Cd(C₈Q)₂ 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)₂ (D_o), where $D_o = 8 \times 10^{-7}$ cm² s⁻¹, which is the reported coefficient of diffusion of a 1:1 complex (Cd(Q)⁺) between Cd(II) ion and 8-quinolinol (HQ) in nitrobenzene,⁷ 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 μ m and a minor radius of 2.5 μ m on the oil-phase side. Since the diffusion length (L) was assumed to be the minor radius (2.5 μ m) plus a spatial resolution value (~ 2 μ m) ($L \approx 5$ μ m), t_{d2} ($= L^2/(2D_o)$) was roughly estimated to be ~ 0.2 s, which agreed with $1/k_r$ (Table 1). The fluorescence of Cd(C₈Q)₂ could disappear from the measuring area only as a result of the diffusion of Cd(C₈Q)₂; therefore, the rate of Cd(C₈Q)₂ diffusion from the measuring area was expected to be the rate-determining step after Cd(C₈Q)₂ formation.

The reported dissociation constants of H₂C₈Q⁺ and HC₈Q in water are $10^{-4.32}$ and $10^{-9.99}$, respectively.¹⁰ When the interfacial tension at the water-droplet/1,6-dichlorohexane interface was measured by using a pendant drop method, the interfacial

Fig. 4 Extraction mechanism of Cd(II) with HC₈Q.

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 H₂C₈Q⁺ adsorbed at the water/oil interface was negligibly small. HC₈Q and H₂C₈Q⁺ are scarcely dissolved in the water phase.¹⁰ 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)⁺ should depend on $\Delta\phi$, although that of Cd(C₈Q)₂ (neutral species) is independent of $\Delta\phi$. However, the rate-determining step is not related to ion-pair formation of Cd(C₈Q)⁺ with TFPB⁻ 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 (M²⁺) and HC₈Q is quickly adsorbed onto a water/oil interface.¹⁰ 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.⁷ Cd(C₈Q)⁺ is more hydrophobic than Cd(Q)⁺, suggesting that the standard ion transfer potential of Cd(C₈Q)⁺ ($\Delta\phi_{\text{Cd(C8Q)+}^0}$) is smaller than -0.04 V. In our system, $\Delta\phi$ ranged from -357 to -17 mV; these values are comparable to $\Delta\phi_{\text{Cd(C8Q)+}^0}$. 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,²⁰ indicating that the desorption rate of surface-active ions is at a minimum at about the standard ion-transfer potential. We considered that $\Delta\phi_{\text{Cd(C8Q)+}^0}$ 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 $\Delta\phi < \Delta\phi_{\text{Cd(C8Q)+}^0}$ (Fig. 3b).

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.^{7,10} However, the fates 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 H₂C₈Q⁺) is fast, and Cd(C₈Q)⁺ is adsorbed onto the micro-water/oil interface. However, the reaction with HC₈Q (or H₂C₈Q⁺) of Cd(C₈Q)⁺ that has been adsorbed onto the water/oil interface may be strongly suppressed, because the central atom (Cd(II)) of Cd(C₈Q)⁺ 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_1). 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 $\text{Cd}(\text{C}_8\text{Q})_2$ concentration in the oil phase near the interface ($[\text{Cd}(\text{C}_8\text{Q})_2]_i$) corresponding to I_F is given by the equation

$$[\text{Cd}(\text{C}_8\text{Q})_2]_i = \{k_1[\text{Cd}(\text{C}_8\text{Q})^+]_{i0}/(k_2 - k_1)\} \times \{\exp(-k_1t) - \exp(-k_2t)\}, \quad (3)$$

where $[\text{Cd}(\text{C}_8\text{Q})^+]_{i0}$ is the $\text{Cd}(\text{C}_8\text{Q})^+$ 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 $\exp(-k_1t)$ is a positive value and that for $\exp(-k_2t)$ is a negative value. Therefore, $\text{Cd}(\text{C}_8\text{Q})_2$ 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 $\text{Cd}(\text{C}_8\text{Q})^+$ 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 $\text{Cd}(\text{II})$ with HC_8Q 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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