

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

Kiyoharu NAKATANI,<sup>†</sup> Naoki SAWADA, and Tatsumi SATO

*Division of Chemistry, Faculty of Pure and Applied Sciences, University of Tsukuba, 1-1-1 Tennoudai, Tsukuba, Ibaraki 305-8571, Japan*

Using a Cd-deposited microelectrode, an electrochemically generated Cd(II) ion in a micro-water phase was reacted with 5-octyloxymethyl-8-quinolinol (HC<sub>8</sub>Q) in 1,6-dichlorohexane. The fluorescence intensity of Cd(C<sub>8</sub>Q)<sub>2</sub> 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 HC<sub>8</sub>Q 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(C<sub>8</sub>Q)<sup>+</sup> 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.<sup>1,2</sup> 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,<sup>3-6</sup> polarographic measurements of droplets,<sup>7,8</sup> and dynamic interfacial tension measurements<sup>9,10</sup> 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.<sup>11-15</sup> 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 (HC<sub>8</sub>Q) across the micro-water/oil interface was kinetically analyzed under a confocal fluorescence microscope.

### Experimental

5-Octyloxymethyl-8-quinolinol (HC<sub>8</sub>Q, Wako Pure Chemical, >99.0%), tetraethylammonium chloride (TEA<sup>+</sup>Cl<sup>-</sup>, Tokyo Kasei Kogyo, >98%), tetrabutylammonium chloride (TBA<sup>+</sup>Cl<sup>-</sup>, Tokyo Kasei Kogyo, >98%), and tetrapentylammonium chloride (TPenA<sup>+</sup>Cl<sup>-</sup>, Tokyo Kasei Kogyo, >98%) were used without further purification. Tetraalkylammonium tetrakis(pentafluorophenyl)borate (TAA<sup>+</sup>TPFPB<sup>-</sup>, TAA<sup>+</sup> = TEA<sup>+</sup>, TBA<sup>+</sup> or TPenA<sup>+</sup>) was prepared from TAA<sup>+</sup>Cl<sup>-</sup> and lithium tetrakis(pentafluorophenyl)borate (Li<sup>+</sup>TPFPB<sup>-</sup>, 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.<sup>15,16</sup> Copper was deposited on the gold microelectrode surface by the reduction of Cu(II) ion in a CuSO<sub>4</sub> (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 CdCl<sub>2</sub> (10 mM) solution at 10 nA for 360 s.

Water-saturated 1,6-dichlorohexane (200 μL) containing HC<sub>8</sub>Q (10, 50 mM) and TAA<sup>+</sup>TPFPB<sup>-</sup> (1 to 50 mM) was poured into an aqueous TAA<sup>+</sup>Cl<sup>-</sup> 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

<sup>†</sup> To whom correspondence should be addressed.  
E-mail: nakatani@chem.tsukuba.ac.jp

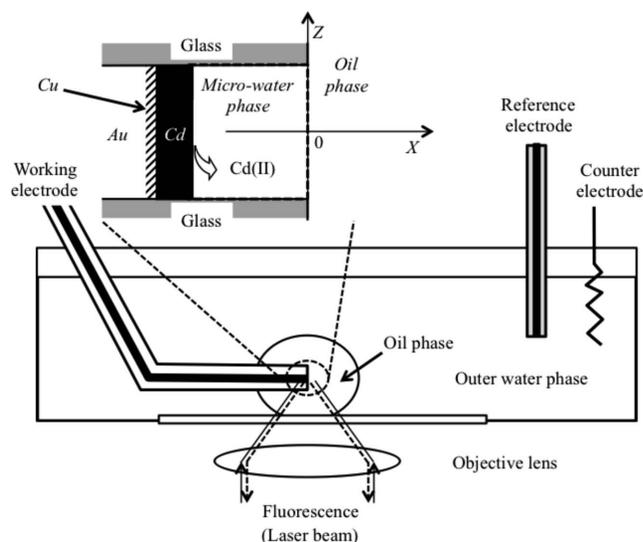


Fig. 1 Schematic illustration of the electrolytic cell under a confocal fluorescence microscope.

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,  $\mu$ 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  $\mu$ 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:<sup>2</sup>

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

where  $\Delta\phi_{\text{TAA}^+}^{\circ}$  is the standard ion-transfer potential of TAA<sup>+</sup> between the water and oil phases. For TEA<sup>+</sup>, TBA<sup>+</sup>, and TPenA<sup>+</sup> ions, the mid-point potential of TAA<sup>+</sup> has been reported to be 42, -193, and -357 mV, respectively.<sup>17</sup> The mid-point potential of TAA<sup>+</sup> was assumed to be equal to  $\Delta\phi_{\text{TAA}^+}^{\circ}$ .  $R$  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<sup>+</sup> 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.<sup>18</sup> The fluorescence maximum of Cd(C<sub>8</sub>Q)<sub>2</sub> 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

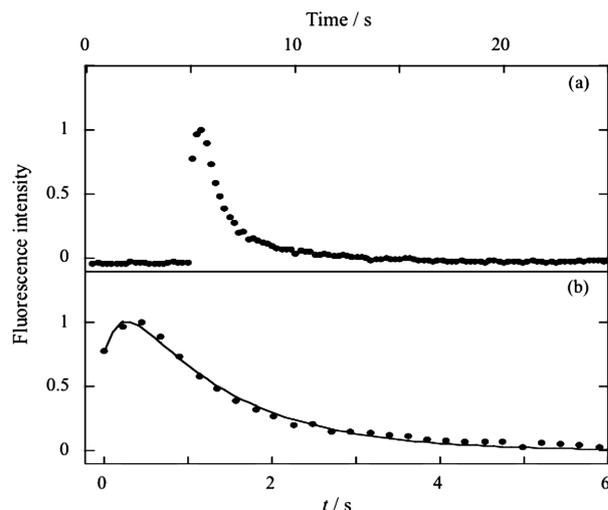


Fig. 2 Time dependence of the fluorescence intensity (a) before and after electrolysis and (b) after electrolysis at pH = 7,  $[\text{HC}_8\text{Q}(\text{o})] = 50$  mM, and  $[\text{TBA}^+(\text{w})] = [\text{TBA}^+(\text{o})] = 10$  mM. The solid line represents the results of calculations using Eq. (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
$k_r/\text{s}^{-1}$	$5 \pm 1$	$5 \pm 3$	$7 \pm 2$	$6 \pm 2$
$k_d/\text{s}^{-1}$	$1.2 \pm 0.3$	$1.3 \pm 0.3$	$0.8 \pm 0.3$	$0.8 \pm 0.2$

(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 ( $I_F$ ) of Cd(C<sub>8</sub>Q)<sub>2</sub> was measured in the area of an ellipse with a major radius of 10  $\mu$ m on the Y axis, a minor radius of 2.5  $\mu$ 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 Cd(II) ion generated in the micro-water phase by the electrolysis was estimated to be  $\sim$ 5 mM. The concentration of HC<sub>8</sub>Q in the oil phase ( $[\text{HC}_8\text{Q}(\text{o})]$ , 10 to 50 mM) was greater than that of Cd(II) ion in the micro-water phase. The volume of the oil phase (200  $\mu$ L) was much larger than that of the micro-water phase (3  $\mu$ L), so that Cd(C<sub>8</sub>Q)<sub>2</sub> 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 (Cd(C<sub>8</sub>Q)<sup>+</sup>) or the 1:2 (Cd(C<sub>8</sub>Q)<sub>2</sub>) 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

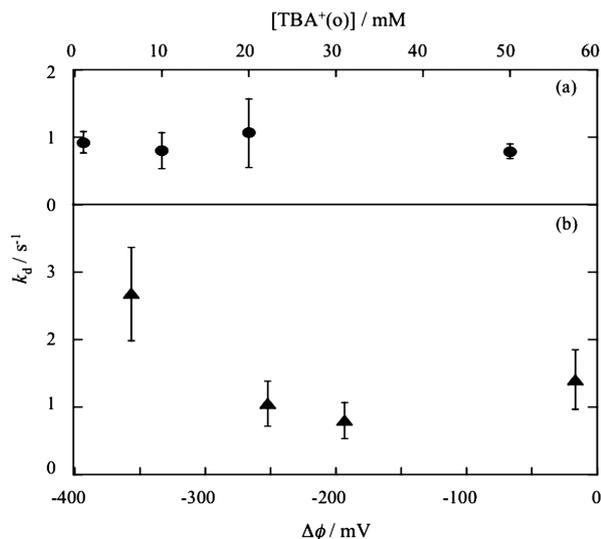


Fig. 3  $k_d$  for various (a)  $[TBA^+(o)]$  ( $= [TBA^+(w)]$  at  $\Delta\phi = -193$  mV) and (b)  $\Delta\phi$  values at pH = 2.

errors and will not be discussed in detail, because  $1/k_r$  was comparable with the time resolution ( $\sim 0.2$  s). The  $k_d$  value was independent of the  $[HC_8Q(o)]$  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,  $Cd(C_8Q)_2$  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  $Cd(C_8Q)_2$  formation, and the other was an elementary process after  $Cd(C_8Q)_2$  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 ( $7 \times 10^{-6}$  cm<sup>2</sup> s<sup>-1</sup>).<sup>19</sup> 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.  $Cd(C_8Q)_2$  diffusion between the micro-water/oil interface and the bulk oil phase was also fast. Under the assumption of the diffusion coefficient of  $Cd(C_8Q)_2$  ( $D_o$ ), where  $D_o = 8 \times 10^{-7}$  cm<sup>2</sup> s<sup>-1</sup>, which is the reported coefficient of diffusion of a 1:1 complex ( $Cd(Q)^+$ ) between Cd(II) ion and 8-quinolinol (HQ) in nitrobenzene,<sup>7</sup> 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  $\mu$ m and a minor radius of 2.5  $\mu$ m on the oil-phase side. Since the diffusion length ( $L$ ) was assumed to be the minor radius (2.5  $\mu$ m) plus a spatial resolution value ( $\sim 2$   $\mu$ m) ( $L \approx 5$   $\mu$ m),  $t_{d2}$  ( $= L^2/(2D_o)$ ) was roughly estimated to be  $\sim 0.2$  s, which agreed with  $1/k_r$  (Table 1). The fluorescence of  $Cd(C_8Q)_2$  could disappear from the measuring area only as a result of the diffusion of  $Cd(C_8Q)_2$ ; therefore, the rate of  $Cd(C_8Q)_2$  diffusion from the measuring area was expected to be the rate-determining step after  $Cd(C_8Q)_2$  formation.

The reported dissociation constants of  $H_2C_8Q^+$  and  $HC_8Q$  in water are  $10^{-4.32}$  and  $10^{-9.99}$ , respectively.<sup>10</sup> When the interfacial tension at the water-droplet/1,6-dichlorohexane interface was measured by using a pendant drop method, the interfacial

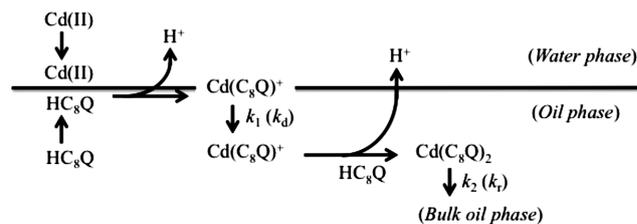


Fig. 4 Extraction mechanism of Cd(II) with  $HC_8Q$ .

tension values were 20 to 23 mN m<sup>-1</sup>, independent of the  $HC_8Q$  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  $HC_8Q$  or  $H_2C_8Q^+$  adsorbed at the water/oil interface was negligibly small.  $HC_8Q$  and  $H_2C_8Q^+$  are scarcely dissolved in the water phase.<sup>10</sup> Therefore, the processes of  $Cd(C_8Q)^+$  and  $Cd(C_8Q)_2$  formation proceed at the micro-water/oil interface, or near to the interface;  $k_d$  was independent of the  $[HC_8Q(o)]$  and pH in the water phase (Table 1), so the rate-determining step for  $k_d$  was not the  $Cd(C_8Q)^+$  or  $Cd(C_8Q)_2$  formation and interfacial transfer of  $H^+$  generated during the Cd(II) complex formation.

The interfacial transfer of  $Cd(C_8Q)^+$  should depend on  $\Delta\phi$ , although that of  $Cd(C_8Q)_2$  (neutral species) is independent of  $\Delta\phi$ . However, the rate-determining step is not related to ion-pair formation of  $Cd(C_8Q)^+$  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  $HC_8Q$  is quickly adsorbed onto a water/oil interface.<sup>10</sup> 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.<sup>7</sup>  $Cd(C_8Q)^+$  is more hydrophobic than  $Cd(Q)^+$ , suggesting that the standard ion transfer potential of  $Cd(C_8Q)^+$  ( $\Delta\phi_{Cd(C_8Q)^+}^0$ ) is smaller than  $-0.04$  V. In our system,  $\Delta\phi$  ranged from  $-357$  to  $-17$  mV; these values are comparable to  $\Delta\phi_{Cd(C_8Q)^+}^0$ . If  $k_d$  is directly related to the ion transfer rate constant of  $Cd(C_8Q)^+$  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,<sup>20</sup> indicating that the desorption rate of surface-active ions is at a minimum at about the standard ion-transfer potential. We considered that  $\Delta\phi_{Cd(C_8Q)^+}^0$  was between  $-0.25$  and  $-0.04$  V, and that  $k_d$  was the desorption rate constant of  $Cd(C_8Q)^+$  at the water/oil interface. Therefore,  $k_d$  decreased with increasing  $\Delta\phi$  for  $\Delta\phi < \Delta\phi_{Cd(C_8Q)^+}^0$  (Fig. 3b).

### Extraction mechanism in the Cd(II)- $HC_8Q$ system

Previous reports have discussed the adsorption and transfer of  $M(C_8Q)^+$  and  $M(Q)^+$  at the water/oil interface.<sup>7,10</sup> However, the fates of  $M(C_8Q)^+$  and  $M(C_8Q)_2$  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  $HC_8Q$  (Fig. 4). The process of  $Cd(C_8Q)^+$  formation from the Cd(II) ion and  $HC_8Q$  (or  $H_2C_8Q^+$ ) is fast, and  $Cd(C_8Q)^+$  is adsorbed onto the micro-water/oil interface. However, the reaction with  $HC_8Q$  (or  $H_2C_8Q^+$ ) of  $Cd(C_8Q)^+$  that has been adsorbed onto the water/oil interface may be strongly suppressed, because the central atom (Cd(II)) of  $Cd(C_8Q)^+$  is likely to be located near the interface of the water-phase side. The rate of desorption of  $Cd(C_8Q)^+$  from the interface into the oil phase is thus a rate-determining step (rate constant,  $k_1$ ). Once  $Cd(C_8Q)^+$  is desorbed, it reacts rapidly with  $HC_8Q$  to form  $Cd(C_8Q)_2$ .  $Cd(C_8Q)_2$

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  $I_F$  ( $k_2 = k_i$ ), 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 Cd(II) with  $\text{HC}_8\text{Q}$  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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