Adsorption Kinetics of 5-Octyloxymethyl-8-Quinolinol at the Liquid-Liquid Interface

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Adsorption kinetics of 5-octyloxymethyl-8-quinolinol at liquid-liquid interfaces was investigated, and the factors which are expected to affect the interfacial reaction were discussed.

Liquid-liquid interfaces have been recognized to play an important role in solvent extraction,[1,2] photoinduced charge separation,[3] and synthesis of organic compounds.[4] As for the analytical methods for measuring the liquid-liquid interface, a high-speed stirring method[5] has been used. This method, however, has a disadvantage that the interfacial phenomena cannot be directly monitored. In contrast, interfacial tensiometry is useful for measuring the interfacial phenomena.

Complexation reaction at liquid-liquid interfaces has been recently paid a great attention in the solvent extraction chemistry.[1,2] However, only a few studies[6] have been reported on the complexation kinetics by the interfacial tensiometry, even on the adsorption kinetics of chelating reagents. In the present study, the adsorption kinetics of 8-quinolinol (Hqn) and 5-octyloxymethyl-8-quinolinol (Hocqn) at heptane-water and 1,2-dichloroethane(DCE)-water interfaces was investigated by a dynamic interfacial tension measurement. The purpose of this study is to propose a model for the adsorption kinetics at liquid-liquid interfaces.

Hqn (Wako, 99%), Hocqn (Wako, 99%), and other materials were used as received. Water was doubly distilled and deionized before use. Hqn or Hocqn was dissolved into heptane or DCE in the concentration range of 10^{-7} - 10^{-2} M (1 M = 1 mol dm^{-3}). Aqueous phase was an electrolyte solution with an ionic strength of 0.1 M. Dynamic interfacial tension $\gamma(t)$ was measured by a dynamic drop volume method.[6,7] The aqueous phase was dropped (heptane-water) or ascended (DCE-water) into the organic phase from a glass capillary at a dropping time of 3 - 100 s. All experiments were performed at 25 ± 0.5 °C.

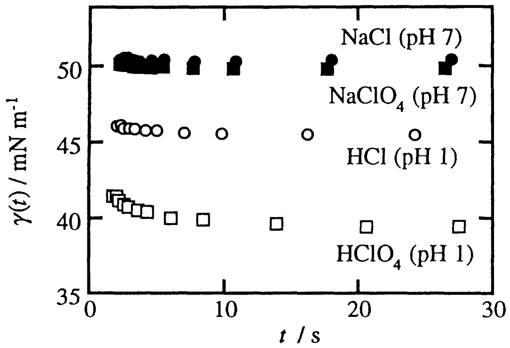

Figure 1. Dynamic interfacial tensions at the heptane-water interface.
Aqueous phase : 0.1 M electrolyte
Organic phase : 1.0×10^{-4} M Hocqn

Hocqn is an amphiphilic molecule which has both a hydrophilic group and a hydrophobic group. The pK_a values of Hocqn are 4.32 (NH^+) and 9.99 (OH).[8] Using a heptane-water system, dynamic interfacial tension was measured for solutions with different electrolytes, and the results are shown in Figure 1.

While the dynamic interfacial tension $\gamma(t)$ is almost constant at pH 7, $\gamma(t)$ decreases at low pH. This fact means that the interfacial adsorption of Hocqn occurs in the protonated form (H_2ocqn^+). The adsorptivity of H_2ocqn^+ is found to depend on counter anions in the aqueous phase as shown in Figure 1.

As for Hqn, it was found not to be adsorbed to the interface because the decrease in $\gamma(t)$ was not observed at pH 1 - 7. This different behavior in the interfacial adsorptivity between Hocqn and Hqn can be ascribed to the effect of a long alkyl chain substituent.

The dynamic interfacial tension reaches equilibrium within about 20 s as shown in Figure 1. The equilibrium interfacial concentration (Γ_e) of H_2ocqn^+ can be estimated by the following Gibbs equation:

$$\Gamma_e = -\frac{1}{RT}\frac{\partial \gamma_e}{\partial \ln [\mathrm{Hocqn}]_o} \qquad (1)$$

where γ_e is the equilibrium interfacial tension. From equation 1, Γ_e can be evaluated by plotting γ_e against the logarithm of Hocqn concentration in the organic phase, and the results are shown in Figure 2.

Figure 2 shows that the adsorptivity of H_2ocqn^+ clearly depends on counter anions in the aqueous phase. This dependence suggests that ion pair ($H_2ocqn^+X^-$) forms at the interface.

The plots in Figure 2 were well fitted by the following

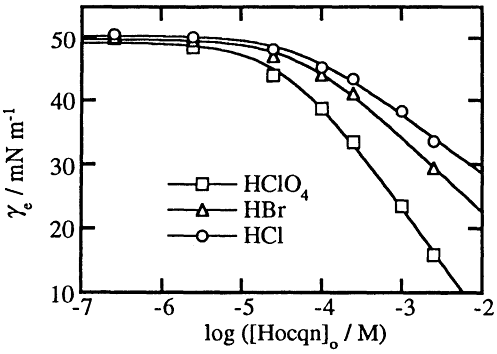

Figure 2. Effect of counter anions on the adsorption of H_2ocqn^+ at the heptane-water interface.
Aqueous phase : 0.1 M acid
Organic phase : Hocqn

Table 1. Parameters on the adsorption of H_2ocqn^+ at the liquid-liquid interfaces

Organic phase	Counter anion	a / 10^{-5} M	Γ_{sat} / 10^{-10} mol cm^{-2}	Area / Å^2
Heptane	ClO_4^-	3.3	3.1	54
	Br^-	4.9	2.1	79
	Cl^-	4.7	1.6	102
DCE	Cl^-	32	0.62	268

Szyszkowski equation:[9]

$$\gamma_0 - \gamma_e = R T \Gamma_{sat} \ln\left(1 + \frac{[\mathrm{Hocqn}]_o}{a}\right) \qquad (2)$$

where γ_0 is the interfacial tension without chelating reagents, Γ_{sat} is the saturated interfacial concentration, and a is the Langmuir-von Szyszkowski constant. The parameters estimated from the fitting were summarized in Table 1.

It is recognized in Table 1 that the a value depends not on counter anions but remarkably on the organic solvent. This result is consistent with the fact that the a value corresponds to the free energy for the adsorption. On the other hand, the Γ_{sat} values are dependent on both counter anions and the organic solvent. The effect of counter anions can be explained as follows: H_2ocqn^+ would be adsorbed to the interface with the hydrophilic group (*i.e.* quinolinol moiety). However, the area per molecule shown in Table 1 is larger than that of 8-quinolinol (42 Å^2).[10] This is caused by the electrostatic repulsive interaction between the H_2ocqn^+ ions adsorbed at the interface. The ability of ClO_4^- to neutralize cations in the hydrophobic environment, such as organic solvent and liquid-liquid interface, is greater than those of Br^- and Cl^-. This property is reflected upon a high selectivity coefficient in an anion-exchange resin. The ion pair H_2ocqn^+ ClO_4^-, which is considered to be most neutralized at the interface, can be adsorbed to the interface most stably.

The effect of the organic solvent on the adsorptivity of H_2ocqn^+ is caused by the partition coefficient of Hocqn. Because the partition coefficient is larger in the DCE-water system ($10^{5.0}$) than in the heptane-water system ($10^{4.6}$), the Γ_{sat} of H_2ocqn^+ becomes large in the heptane-water system.

The interfacial tension decreases within about 20 s. By analyzing the decay curves in Figure 1, we can discuss not only the adsorption equilibria but also the adsorption kinetics. When the adsorption kinetics is diffusion-controlled, the dynamic interfacial tension $\gamma(t)$ obeys following equation 3:[7]

$$\gamma(t) - \gamma_e = \frac{R T \Gamma_e^2}{[\mathrm{Hocqn}]_o} \sqrt{\frac{\pi}{4 D t}} \qquad (3)$$

where D is the diffusion coefficient. The $\gamma(t)$ should be linearly dependent on $t^{-1/2}$ in case of the diffusion-controlled based on equation 3, and the results are shown in Figure 3.

From Figure 3, it can be said that the adsorption kinetics of $H_2ocqn^+X^-$ is diffusion-controlled. The D values calculated from the slopes of the curves are about 10^{-10} cm^2 s^{-1}, which is a reasonable value, and is independent of counter anions in the aqueous phase and Hocqn concentration in the organic phase. The diffusion-controlled adsorption means that the rate of protonation and ion pair formation at the interface is fast.

In conclusion, the adsorption kinetics of Hocqn can be expressed by Figure 4. The adsorption of neutral species was not considered since the decrease of interfacial tension was negligibly small. The factors governing the interfacial adsorptivity of chelating reagents are the partition coefficient P, acid dissociation constant K_a, adsorption constant K_{ads}, and ion pair formation constant K_{IP}. From the factors mentioned above, it is expected that complexation kinetics at liquid-liquid interfaces are affected by; (i) long alkyl chain substituent which controls the adsorptivity and the orientation of chelating reagents at the interface; (ii) counter anions and pH in the aqueous phase; (iii) organic solvent which controls the environment of the interface, such as the permittivity, in addition to P and K_{ads}.

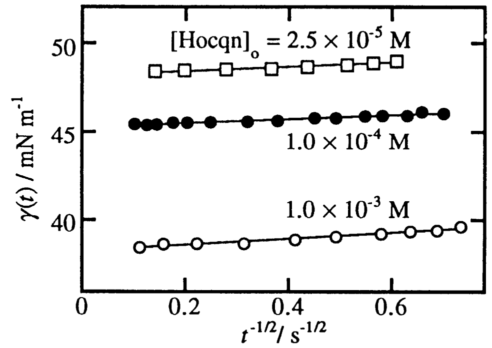

Figure 3. Dynamic interfacial tensions at the heptane-water interface.
Aqueous phase : 0.1 M HCl
Organic phase : Hocqn

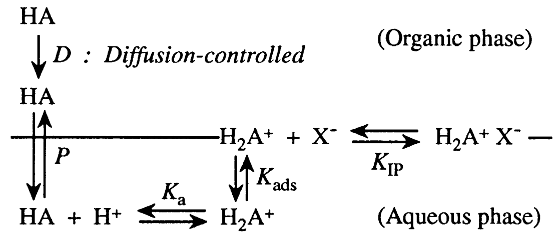

Figure 4. Adsorption kinetics at the liquid-liquid interface.

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