Complexation Kinetics of 5-Octyloxymethyl-8-quinolinol with Ni(II) at the Heptane-Water Interface

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Complexation kinetics of 5-octyloxymethyl-8-quinolinol (Hocqn) with Ni(II) at the heptane-water interface was studied by measuring the dynamic interfacial tension. Decrease in the interfacial tension was caused by the adsorption of 1:1 complex formed at the interface. It was found that the complexation rate at the interface was 43 times faster than that in the bulk, and that the rate also depended on the counter-anion in the aqueous phase.

Liquid-liquid interface has been recognized to take an important role in many systems such as solvent extraction,[1-3] biomembranes,[4] photoinduced charge separation,[5] and synthesis of organic compounds.[6]

In order to study the adsorption / transfer kinetics at the liquid-liquid interface, interfacial tensiometry has been widely used,[2,7,8] however, no discussion has been made about the interfacial reaction by this technique. It is difficult to measure the interfacial phenomena directly by other techniques, such as a rapid-stirring apparatus[9] by which the contribution of the interfacial complexation was discussed.[1,3] In this respect, intefacial tensiometry has an advantage that it can be applied to analyze the interfacial reaction directly .

In this paper, metal ion (aqueous phase) - chelating reagent (organic phase) system was invetigated by measuring the dynamic interfacial tension. It was found that the reaction kinetics at the heptane-water interface shows remarkable differences compared with the kinetics in the bulk.

Hocqn (Wako, 99.0%) was used as received to prepare heptane solutions in the concentration range 2.5×10^{-5} - 2.5×10^{-4} M (1 M = 1 moldm^{-3}). Aqueous solutions contained 1.0×10^{-2} M NiX_2 (X^- = Cl^- or ClO_4^-). Ionic strength and pH were kept at 0.1 M and 5.0 (or 5.5) by adding NaX and HX. Since Hocqn does not adsorb to the interface in this pH range, it can be regarded that the decrease in the interfacial tension is caused by the adsorption of 1:1 complex ($Ni(ocqn)^+X^-$) formed at the interface. Dynamic interfacial tension ($\gamma(t)$) was measured by the dynamic drop volume method.[7] Throughout these measurements heptane was used without further purification and water was doubly distilled before use. All experiments were done at 25 °C.

The following reaction mechanism was derived by modifying the theory of Joos et al.[8] Since the diffusion of Hocqn to the interface is fast and the adsorption of $Ni(ocqn)^+X^-$ is equivalent to the complexation at the interface, it can be assumed that the complexation at the interface follows the Langmuir kinetics (1);

$$\frac{d\Gamma(t)}{dt} = k_1\,[Ni^{2+}]_a\,[Hocqn]_o\left(1 - \frac{\Gamma(t)}{\Gamma_{SAT}}\right) - k_2\,\frac{\Gamma(t)}{\Gamma_{SAT}} \qquad (1)$$

where, $\Gamma(t)$ is the interfacial concentration of $Ni(ocqn)^+X^-$, Γ_{SAT} the saturated interfacial concentration, k_1 the complexation rate constant at the interface, and k_2 the desorption rate constant of $Ni(ocqn)^+X^-$ into the aqueous phase. Subscripts a and o denote aqueous and organic phases, respectively. By integrating Eq.(1) and assuming that $d\Gamma$ is linearly dependent on $d\gamma$,[8] $\gamma(t)$ is given by Eq.(2).

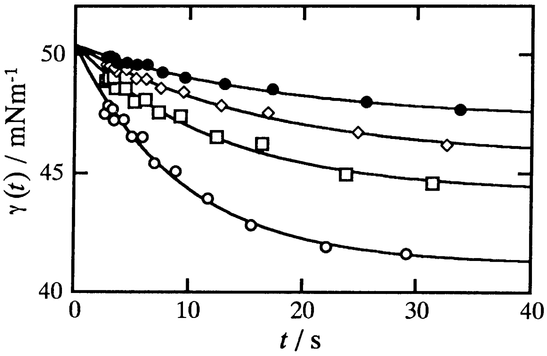

Figure 1. Dependence of $\gamma(t)$ on the Hocqn concentration. $[Hocqn]_o$ and calculated k values are; (○) 2.5×10^{-4} M, 12.8×10^{-2} s^{-1}; (□) 1.0×10^{-4} M, 9.4×10^{-2} s^{-1}; (◇) 5.0×10^{-5} M, 7.5×10^{-2} s^{-1}; (●) 2.5×10^{-5} M, 5.9×10^{-2} s^{-1}, respectively. Aqueous phase is 1.0×10^{-2} M $Ni(ClO_4)_2$ solution at pH 5.0.

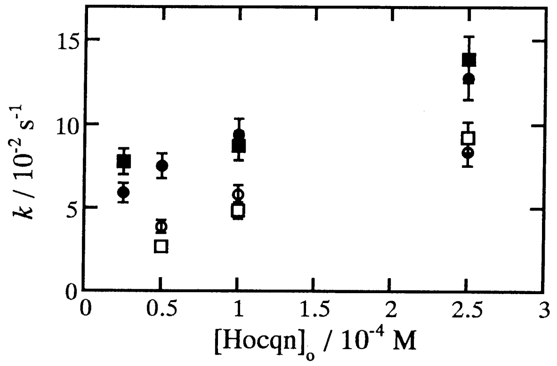

Figure 2. Dependence of k on the Hocqn concentration. Counter-anion in the aqueous phase is; (○) Cl^- at pH 5.0; (●) ClO_4^- at pH 5.0; (□) Cl^- at pH 5.5; (■) ClO_4- at pH 5.5.

$$\gamma(t) = \gamma_e - \left(\gamma_e - \gamma_0\right)\exp\left(-k\,t\right) \qquad (2)$$

where γ_e and γ_0 are the equilibrium interfacial tension and the interfacial tension of pure solvent, respectively. The rate constant k is given by the following equation:

$$k = \frac{1}{\Gamma_{SAT}}\left(k_1[Ni^{2+}]_a[Hocqn]_o + k_2\right) \qquad (3)$$

Figure 1 shows the dependence of $\gamma(t)$ on the Hocqn concentration in the organic phase. In Figure 1 plots were fitted by Eq.(2), and k was elucidated. It is clear that the observed k value depends on the Hocqn concentration. This fact means that Eq.(3) is adequate to evaluate the complexation rate constant k_1 for the system in question.

In order to obtain k_1, it is required to examine the dependence of k on the Hocqn concentration. The results are shown in Figure 2. It can be seen that k depends linearly on the Hocqn

Table 1. Parameters related to the complexation of Hocqn with Ni(II) at the heptane-water interface

X^-	k_i / 10^{-5} $ms^{-1}M^{-1}$	Γ_{SAT} / 10^{-10} mol cm^{-2}
Cl^-	2.2	1.0
ClO_4^-	4.0	1.4

concentration, and that k does not depend on pH. From these facts, the main reaction at the heptane-water interface can be described as follows (subscript i denotes interface):

$$Ni^{2+}{}_a + HL_i \xrightarrow{k_i} NiL^+{}_i + H^+{}_a \qquad (4)$$

The calculated k_i values are summarized in Table 1 as well as the Γ_{SAT} values which were estimated by the Gibbs isotherm.

From Table 1, it is found that k_i is larger in case of ClO_4^-, than in case of Cl^-. This may be caused by that reaction products (i.e. $Ni(ocqn)^+X^-$) adsorbed at the interface may have some influences on the successive reaction. For example, Ni^{2+} and $Ni(ocqn)^+$ have +2 and +1 charge, respectively. So, it is considered that the higher the interfacial concentration, the slower the reaction rate because of the electrostatic interaction, and that Ni^{2+} will participate in the reaction more easily in case of ClO_4^- than in case of Cl^- because $Ni(ocqn)^+ClO_4^-$ would be more neutralized.

Next, we compared the complexation rate at the heptane-water interface with that in the bulk. As for the rate constant of Hocqn in the bulk, the value for 8-quinolinol was used, because it is expected that there will be only a slight difference in the reaction rate in the bulk between Hocqn (with alkyl chain) and 8-quinolinol (without alkyl chain).

In our system of ClO_4^-, k_i, $[Hocqn]_o$ and $[Ni^{2+}]_a$ are 4.0×10^{-5} m $s^{-1}M^{-1}$, 1.0×10^{-4} M and 1.0×10^{-2} M, respectively. The initial complexation rate at the heptane-water interface is given as a product of the above three values, and is calculated as 4.0×10^{-8} $mols^{-1}m^{-2}$.

On the other hand, the complexation rate constants (k_L and k_{HL}) of 8-quinolinol in the bulk are defined as follows:

$$Ni^{2+} + L^- \xrightarrow{k_L} NiL^+ \qquad (5)$$

$$Ni^{2+} + HL \xrightarrow{k_{HL}} NiL^+ + H^+ \qquad (6)$$

where HL and L represent the neutral form and the dissociated form of 8-quinolinol, respectively. Dietz et al.[3] reported that $k_L = 2.88 \times 10^8$ $mol^{-1}cm^3s^{-1}$ and $k_{HL} = 9.33 \times 10^5$ $mol^{-1}cm^3s^{-1}$. We have only to take k_{HL} into consideration because the main reaction at the interface is caused by neutral species. It is also necessary that k_{HL} should be converted as the formation rate per second and per area. Carpenter and Hehre[10] estimated that the thickness of the hexane-water interface is 10 ± 3 Å by molecular dynamics simulation study. Accordingly, it can be assumed that molecules in the space having a thickness of d = 10 Å around the interface can participate in the reaction. Thus the complexation rate is given by the product of k_{HL}, $[Hocqn]_a$ (= 2.3×10^{-9} M), $[Ni^{2+}]_a$, and d. It is calculated as 2.1×10^{-14} mol $s^{-1}m^{-2}$, and this value is about 10^{-6} times as small as that at the interface. This may be caused by the fact that $[Hocqn]_a$ is extremely small at this pH. However, even if we assume that $[Hocqn]_a$ is equal to $[Hocqn]_o$ (i.e. 1.0×10^{-4} M), the complexation rate is calculated as 9.3×10^{-10} mol $s^{-1}m^{-2}$, which is still 43 times as small as that at the interface.

The result that the rate constant is larger at the interface than in the bulk, can be explained as follows; first, the heptane-water interface is regarded as a phase which has a solvent gradient from heptane to water. So, the dielectric constant at the heptane-water interface is smaller than that of water, and reactions involving neutralization can easily occur. Secondly, Hocqn molecules will be oriented at the heptane-water interface with the chelate group toward the aqueous phase and the long alkyl chain toward the heptane phase. Accordingly it can be expected that metal ion can easily react with Hocqn.

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