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# Direct Spectrophotometric Measurement of Demetalation Kinetics of 5,10,15,20-Tetraphenylporphyrinatozinc(II) at the Liquid−Liquid Interface by a Centrifugal Liquid Membrane Method

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**The equilibrium and kinetics of the protonation of 5,10,15,20-tetraphenylporphyrin ($H_2TPP$) and the demetalation of 5,10,15,20-tetraphenylporphyrinatozinc(II) (ZnTPP) at a dodecane−aqueous acid interface were investigated by means of a new in situ spectrophotometric method, the centrifugal liquid membrane method, which can provide the ultrathin two-phase liquid membrane system in a rotating glass cell. The consumption of $H_2TPP$ in the bulk dodecane phase and the production of the diprotonated aggregate, $(H_4TPP^{2+})_n$, adsorbed at the liquid−liquid interface were directly measured from the spectral change. The equilibrium constants of the interfacial aggregation of $H_4TPP^{2+}$ and the demetalation of ZnTPP were determined as $\log(K_{e1}/\mathrm{dm^6\ mol^{-2}}) = 2.14 \pm 0.07$ and $\log(K_{e2}/\mathrm{dm^9\ mol^{-3}}) = -6.05 \pm 0.04$ at 298 K, respectively. The observed rate constant of the demetalation of ZnTPP depended upon the first order of the acidity function, and it was suggested that the rate-determining step is the formation of the monoprotonated intermediate, $[ZnTPPH]^+$, at the liquid−liquid interface. The demetalation rate constant of ZnTPP was determined as $k_1 = (8.6 \pm 1.3) \times 10^{-5}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$ at 298 K. In the aggregation of $H_4TPP^{2+}$, the rate-determining step was controlled by molecular diffusion of $H_2TPP$ in the bulk dodecane phase.**

Only a limited number of methods and devices have been developed to study interfacial reactions and interfacial adsorption at liquid−liquid interfaces. Most of those methods are indirect, in that the interfacial phenomena must be estimated from concentration changes in the bulk phases, i.e., the high-speed stirring method, or from changes in interfacial energy, i.e., the interfacial tension methods.[1,2] The assignment of an interfacial species by these methods, therefore, is rather ambiguous. Previously, we reported the direct stopped-flow spectroscopic measurement of the diprotonation of 5,10,15,20-tetraphenylporphyrin ($H_2TPP$) at a liquid−liquid interface.[3] The two-phase stopped-flow spectrometry was very sensitive to detect the interfacial species and applicable to a fast interfacial reaction of submilliseconds, but the dispersed two-phase system formed was stable only for ~1000 ms. Thus, to establish the direct spectroscopic method of the interfacial kinetics, several requirements have to be resolved, including the stability of the two-phase system, the discrimination of overlapped absorption spectra of the bulk phase species, and the large specific interfacial area.

In this article, we propose a new in situ spectrophotometric method to study liquid−liquid interfacial reaction kinetics. The two ultrathin liquid membranes were made in a rotating optical cell, and the spectral change was directly observed.

The kinetics of the demetalation of metalloporphyrin are well studied in homogeneous systems.[4−6] However, the kinetics and liquid−liquid interfacial reaction mechanism of the metalloporphyrin have not been reported. Recently, we studied the adsorption behavior and reaction mechanism of several metalloporphyrins at the liquid−liquid interface.[7,8] 5,10,15,20-Tetraphenylporphyrinatozinc(II) (ZnTPP) is specifically adsorbed at the liquid−liquid interface, compared with other divalent metal complexes, e.g., those of cobalt, nickel, copper, and vanadyl. In the present study, the kinetics and mechanism of demetalation of ZnTPP at a dodecane−aqueous acid interface are investigated to demonstrate the advantages of the new method.

## EXPERIMENTAL SECTION

**Reagents.** 5,10,15,20-Tetraphenylporphyrinatozinc(II) (ZnTPP) was prepared from 5,10,15,20-tetraphenylporphyrin (Dojindo Laboratories) and zinc(II) acetate dihydrate (Wako Chemicals, >99.9%) in acetic acid by the conventional method.[9] ZnTPP prepared in acetic acid was extracted into dodecane and washed several times with Milli-Q water. Dodecane as an organic solvent was obtained from nacalai tesque, G.R., and purified by distillation after being washed with a mixture of fuming sulfuric acid (nacalai tesque, E.P., 25%) and sulfuric acid. The hydrochloric acid

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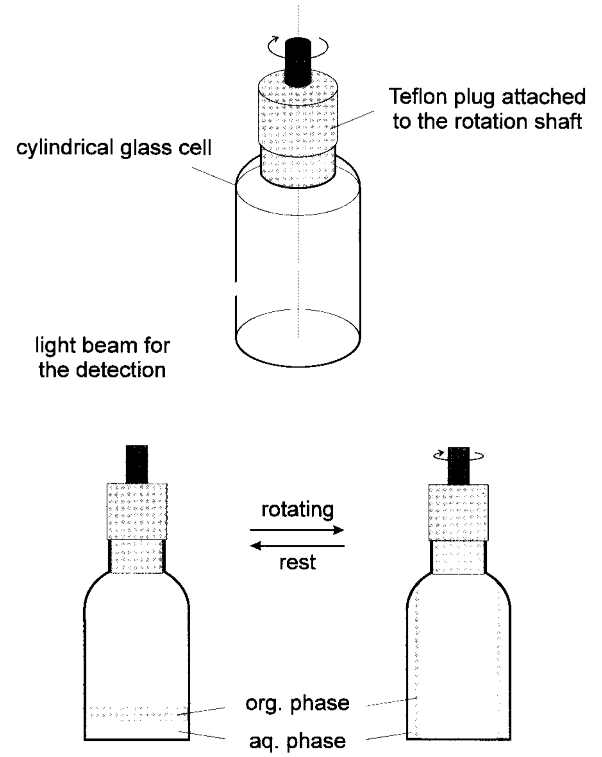

Figure 1. Schematic drawing of the centrifugal liquid membrane apparatus. The ultrathin two-phase liquid membrane system was stable at rotation speeds ranging from 6000 to 7500 rpm. In the present system, the organic phase, 0.150 $cm^3$, and the aqueous phase, 0.250 $cm^3$, were spread as an inner liquid membrane of 79-$\mu$m film thickness and an outer liquid membrane of 145-$\mu$m thickness, respectively. The transmission absorption spectrum was measured from the direction perpendicular to the rotation axis by the diode array spectrophotometer.

solution of various concentrations was used as an aqueous phase, and the ionic strength was kept at 2.0 by the addition of sodium chloride. All of the acids and sodium chloride were of reagent grade, nacalai tesque, G.R. The aqueous solutions used for the experiments were all prepared in Milli-Q water purified with Millipore Milli-Q SP.TOC.

**Centrifugal Liquid Membrane Method.** The centrifugal liquid membrane (CLM) method can form a stable, ultrathin two-phase liquid membrane by the centrifugal force produced by the rotation. The CLM apparatus is schematically shown in Figure 1. The organic phase, 0.150 $cm^3$, and the aqueous phase, 0.250 $cm^3$, were put into the cylindrical glass cell and stoppered by a Teflon plug attached to the rotation shaft of the high-speed motor (Hitachi GP 2SA). The rotation speed was regulated by a Toshiba Slidac SD105 and monitored by a digital tachometer (Ono Sokki HT-431). The inner diameter and inner height of the cylindrical cell were 19 and 29 mm, respectively. When the densities of organic and aqueous phases are different, the two-phase system is spread out at the inner wall of the cylindrical glass cell by high-speed rotation. The ultrathin two-phase liquid membrane system produced was stable in the rotation speed range of ~6000−7500 rpm and could be regarded just as coated liquid films. In the present system, the densities of dodecane used as an organic solvent and water at 298 K are 0.745 and 0.997 g $cm^{-3}$, respectively.[10] Thus, the dodecane was spread as an inner liquid membrane of 79-$\mu$m film thickness and the aqueous phase as an outer liquid membrane of 145-$\mu$m thickness, sandwiched between the dodecane layer and the cell wall. The interfacial area between the two phases, $S_i$, was 17 $cm^2$, and the specific interfacial area, $S_i/V_o$, was calculated as 113 $cm^{-1}$. The summation of the absorption spectra of both interfacial and bulk organic phase species was measured from the direction perpendicular to the rotation axis with Hewlett-Packard HP8452A diode array spectrophotometer. Thus, the light beam passed twice through the liquid−liquid interface and both bulk phases in the rotating optical cell. The typical transmission absorption spectra of the ultrathin two-phase liquid membrane systems are shown in Figure 2.

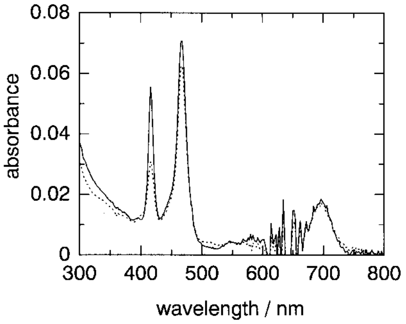

Figure 2. Typical transmission absorption spectra of the ultrathin two-phase liquid membrane system. The solid and dotted lines refer to the demetalation of ZnTPP and the protonation of $H_2TPP$, respectively. The absorption maximum wavelengths were 416 nm for ZnTPP and $H_2TPP$ in dodecane (79 $\mu$m in thickness) and 466 nm for $(H_4TPP^{2+})_n$ at the interface, respectively. The initial concentrations in dodecane of ZnTPP and $H_2TPP$ were $1.86 \times 10^{-5}$ and $1.71 \times 10^{-5}$ mol $dm^{-3}$, respectively. The concentrations of hydrochloric acid were 2.0 mol $dm^{-3}$ for the demetalation of ZnTPP and 0.17 mol $dm^{-3}$ for the protonation of $H_2TPP$.

**Equilibrium Measurements.** The equilibrium constants of the interfacial protonation of $H_2TPP$ and the demetalation of ZnTPP in the dodecane−hydrochloric acid system were determined by the CLM method in a thermostated room at 298 ± 2 K. The concentrations of $H_2TPP$ and ZnTPP were $1.71 \times 10^{-5}$ and $9.7 \times 10^{-6}$ mol $dm^{-3}$, respectively.

**Kinetic Measurements.** A stable, two-phase liquid membrane system in the rotating optical cell was established at ~4 s after the beginning of the rotation. The kinetic measurement of protonation and aggregation of $H_2TPP$ in the dodecane−hydrochloric acid system was carried out by using the dodecane solution of $H_2TPP$ ranging in concentration from $3.23 \times 10^{-5}$ to $5.9 \times 10^{-6}$ mol $dm^{-3}$, and the demetalation of ZnTPP was studied by using $8.9 \times 10^{-6}$ mol $dm^{-3}$ ZnTPP in dodecane. The absorbance changes at the absorption maximum wavelengths were recorded at 1.0-s intervals, with an integration time of 1.0 s. The typical kinetic profiles obtained in the CLM measurements are shown in Figure 3. The kinetic measurements were carried out in a thermostated room at 298 ± 2 K.

## RESULTS AND DISCUSSION

**Protonation and Aggregation of $H_2TPP$.** The kinetic measurement of protonation and aggregation of tetraphenylpor-

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(10) Riddick, J. A.; Bungel, W. B.; Sakano, T. K. *Organic Solvents*, 4th ed.; John Wiley & Sons: New York, 1986; pp 74, 132.

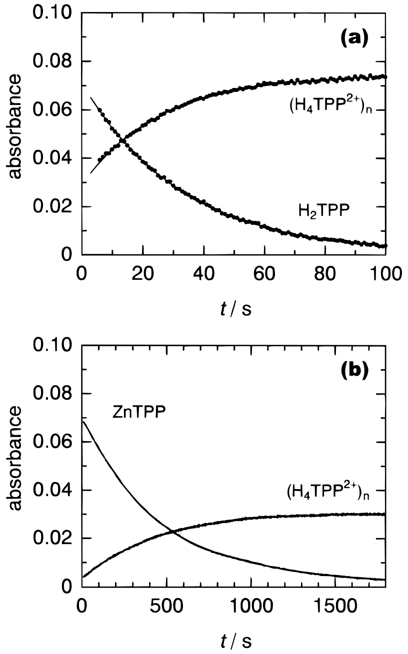

Figure 3. First-order kinetic profiles observed from the CLM measurements in the diprotonation of $H_2TPP$ (a) and the demetalation of ZnTPP (b). The solid line is the fitting curve obtained by the first-order analysis. The initial concentrations of $H_2TPP$ and ZnTPP were $1.71 \times 10^{-5}$ and $8.9 \times 10^{-6}$ mol dm$^{-3}$, respectively. The concentration of hydrochloric acid was 2.0 mol dm$^{-3}$.

phyrin ($H_2TPP$) in the dodecane–hydrochloric acid system was carried out by applying the centrifugal liquid membrane method. When the dodecane solution of $H_2TPP$ was contacted with the aqueous acidic solution, $H_2TPP$, which was hardly adsorbed at the interface, was protonated, and the diprotonated species formed, $H_4TPP^{2+}$, was changed to the aggregate, $(H_4TPP^{2+})_n$, at the interface,

$$H_2TPP_o + 2H^+ \rightarrow H_4TPP^{2+}{}_i \tag{1}$$

$$nH_4TPP^{2+}{}_i \rightarrow (H_4TPP^{2+})_{ni} \tag{2}$$

where the subscripts o and i refer to the bulk organic phase and the interface, respectively. The overall reaction was represented by

$$H_2TPP_o + 2H^+ \xrightarrow{k_0} (H_4TPP^{2+})_{ni} \tag{3}$$

where $k_0$ (s$^{-1}$) is the pseudo-first-order rate constant. This aggregate existed only at the interface, and the counterions for the diprotonated species were postulated as chloride ions. The diprotonation and aggregation were indicated by the large red-shift of the Soret band of $H_2TPP$ as shown in Figure 2, in which the transmission absorption spectra of $H_2TPP$ in the dodecane phase and $(H_4TPP^{2+})_n$ at the interface were depicted. The isosbestic point was observed at ~430 nm, and the absorption maximum wavelength, $\lambda_{max}$, was 416 nm for $H_2TPP$ in dodecane and 466 nm for $(H_4TPP^{2+})_n$, respectively. The diprotonated monomer, $H_4TPP^{2+}$, at the interface was obtained at 440 nm in the initial stage of the aggregation; however, it disappeared rapidly, accompanied by the formation of $(H_4TPP^{2+})_n$ at 466 nm. The broad absorption peak at 698 nm is the Q-band of $(H_4TPP^{2+})_n$. The molar absorptivities, $\epsilon$, at $\lambda_{max}$ were $4.33 \times 10^5$ dm$^3$ mol$^{-1}$ cm$^{-1}$ for $H_2TPP$ in dodecane and $3.06 \times 10^5$ dm$^3$ mol$^{-1}$ cm$^{-1}$ for $H_4TPP^{2+}$ forming the aggregate at the interface, respectively. Previously, we studied the interfacial diprotonation and aggregation of $H_2TPP$ by the two-phase stopped-flow method in the dispersed dodecane–hydrochloric acid system. It was concluded that the diprotonation process from $H_2TPP$ to $H_4TPP^{2+}$ is faster than the aggregation process from $H_4TPP^{2+}$ to $(H_4TPP^{2+})_n$, and $\lambda_{max}$ is 440 nm for $H_4TPP^{2+}$ and 457 nm for $(H_4TPP^{2+})_n$. It is noted that the $\lambda_{max}$ for $(H_4TPP^{2+})_n$ is not consistent between the two-phase stopped-flow experiment, 457 nm, and the CLM experiment, 466 nm. This disagreement may be attributable to the different conditions of the interface, i.e., the interface of droplets in the stopped-flow system is appreciably perturbed during the measurement, but the interface in the CLM system is not perturbed. Since the larger red-shift of the Soret band in the aggregate of $H_4TPP^{2+}$ corresponds to the larger aggregation number,[11,12] it can be concluded that the aggregation of $H_4TPP^{2+}$ in the stopped-flow system proceeds less than that in the CLM system.

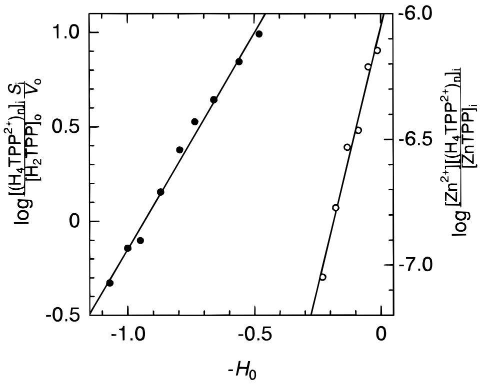

Figure 4. Logarithmic plot of $[(H_4TPP^{2+})_n]_i S_i/[H_2TPP]_o V_o$ and $[Zn^{2+}][(H_4TPP^{2+})_n]_i/[ZnTPP]_i$ against the acidity function of hydrochloric acid, $-H_0$. The closed and open circles refer to the diprotonation of $H_2TPP$ and the demetalation of ZnTPP, respectively. The slopes of the straight lines were 2.3 for the protonation and 4.1 for the demetalation systems, respectively. The equilibrium measurements were carried out in a thermostated room at 298 ± 2 K.

The equilibrium constant of the interfacial diprotonation of $H_2TPP$, $K_{e1}$ (dm$^6$ mol$^{-2}$), was defined as

$$H_2TPP_o + 2H^+ \rightleftharpoons (H_4TPP^{2+})_{ni} \tag{4}$$

$$K_{e1} = \frac{[(H_4TPP^{2+})_n]_i S_i / V_o}{[H_2TPP]_o [H^+]^2} \tag{5}$$

The value of log $K_{e1}$ was determined as 2.14 ± 0.07 from the intercept of the logarithmic linear function shown in Figure 4, and the slope, which means the reaction order of hydrogen ion was 2.29 ± 0.08. Since the concentration of hydrogen ion in the aqueous acid phase was in large excess over that of $H_2TPP$, the

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(11) Barber, D. C.; Freitag, R. A.; Whitten, D. G. *J. Phys. Chem.* **1991**, *95*, 4074–4086.

(12) Jin, R.-H.; Aoki, S.; Shima, K. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 3945–3953.

absorbance changes at $\lambda_{max}$ of $H_2TPP$ and $(H_4TPP^{2+})_n$ were analyzed by a pseudo-first-order rate law written as follows:

$$-\frac{d[H_2TPP]_o}{dt} = \frac{d[(H_4TPP^{2+})_n]_i}{dt}\frac{S_i}{V_o} = k_0[H_2TPP]_o \qquad (6)$$

The typical first-order kinetic profiles are shown in Figure 3a and the rate constant, $k_0$ ($s^{-1}$), were determined by least-squares curve-fitting of the absorbance change at each $\lambda_{max}$. The diprotonation and aggregation attained equilibrium after ~100 s, and the values of $k_0$ did not depend on the concentrations of $H_2TPP$ in the dodecane phase and of hydrogen ion in the aqueous phase. The values of the observed rate constants were $(3.9 \pm 0.4) \times 10^{-2}\ s^{-1}$ for the decrease of $H_2TPP$ and $(4.4 \pm 0.4) \times 10^{-2}\ s^{-1}$ for the increase of $(H_4TPP^{2+})_n$, respectively, and the average value was $(4.1 \pm 0.5) \times 10^{-2}\ s^{-1}$. Thus, it was suggested that the interfacial diprotonation of $H_2TPP$ in the present system proceeded by the diffusion-controlled mechanism as concluded in the two-phase stopped-flow experiments.[3] The rate law for the diffusion-controlled protonation of $H_2TPP$ at the interface is derived from Fick's first law as follows:[13]

$$-\frac{dC_\delta}{dt} = \frac{D_o}{\delta_o}\frac{S_i}{V_o}(C_\delta - C_i) \qquad (7)$$

where $C_\delta$, $C_i$, $D_o$, and $\delta_o$ are the concentration of $H_2TPP$ in dodecane at a distance $\delta_o$ from the liquid−liquid interface, the concentration of $H_2TPP$ at the interface, the diffusion coefficient of $H_2TPP$ in dodecane[3] ($3.5 \times 10^{-6}\ cm^2\ s^{-1}$), and the thickness of the diffusion layer in dodecane with a linear concentration gradient, respectively. The thickness of the diffusion layer is assumed to be equal to the thickness of the organic liquid membrane, $d_o$ (cm), in the present system, because the two-phase liquid membrane system formed by the CLM method is the ultrathin unstirred system, and the mass transfer is expected to be carried out only by molecular diffusion. For $t = 0$ s, the initial concentrations are all same, $C_\delta = C_i$. Since the intrinsic protonation rate of $H_2TPP$ is much faster than the mass-transfer rate, the value of $C_i$ becomes to zero soon after the start of the reaction, and the concentration of $H_2TPP$ in the organic layer decreases from $C_\delta$ to zero with a linear gradient. In this situation, the concentration of $H_2TPP$ observed in the CLM measurement is the mean concentration of the organic layer,

$$[H_2TPP]_o = \frac{C_\delta - C_i}{2} \simeq \frac{C_\delta}{2} \qquad (8)$$

From eqs 6−8, the rate constant, $k_0$, is expressed as

$$k_0 = \frac{D_o}{\delta_o}\frac{S_i}{V_o} \qquad (9)$$

where $D_o$ and $S_i$ are constant value. Equation 9 shows that $k_0$ is a function of $V_o$ and $\delta_o$ ($=d_o$). When $V_o$ is decreased, $k_0$ should be increased according to eq 9. The values of $k_0$ and $d_o$ were determined in several conditions of $V_o$ with a constant aqueous phase volume, 0.250 $cm^3$. The calculated mass transport constant, $k_{calc}$ ($s^{-1}$), was obtained from eq 9 replacing $\delta_o$ by $d_o$. The values of $k_0$ and $k_{calc}$ are summarized in Table 1. The values of $k_0$ are ~10−30% smaller than $k_{calc}$; however, it is thought that $k_0$ agreed with $k_{calc}$ within experimental errors. Thus, it was confirmed that the diprotonation of $H_2TPP$ in the CLM system is governed by the diffusion-controlled mechanism, and $k_0$ is mass transport constant. It was also shown that the thickness of the diffusion layer can be easily regulated by changing the organic phase volume, and the values of $k_0$ correspond to the limiting value of mass transfer rate in the present two-phase liquid membrane systems.

Table 1. Rate Constants for the Diprotonation of $H_2TPP$ Determined at Several $V_o$ Conditions[a]

| conditions | | | rate constants | |
|---|---|---|---|---|
| $V_o$, $10^{-3}$ $cm^3$ [b] | $S_i/V_o$, $cm^{-1}$ [c] | $d_o$, $10^{-4}$ cm[d] | $k_0$, $10^{-2}$ $s^{-1}$ [e] | $k_{calc}$, $10^{-2}$ $s^{-1}$ [f] |
| 100 | 170 | 53 | 9.9 ± 3.4 | 11.3 |
| 150 | 113 | 79 | 4.4 ± 0.7 | 5.0 |
| 200 | 85 | 100 | 2.1 ± 0.1 | 3.0 |
| 250 | 68 | 132 | 1.5 ± 0.3 | 1.8 |

[a] The kinetic measurements were carried out at a constant aqueous phase volume of 0.250 $cm^3$. The concentration of HCl and the ionic strength were 1.0 mol $dm^{-3}$ and 2.0, respectively. [b] The organic phase volume introduced into the rotating glass cell. [c] $S_i$ is a constant value, 17 $cm^2$. [d] The thickness of an organic liquid membrane. [e] Experimental rate constants at 298 K. [f] Calculated mass transport constants.

**Demetalation Kinetics of ZnTPP.** In the acidic systems, ZnTPP adsorbed at the interface was decomposed to zinc ion and free base porphyrin by the attack of hydrogen ions.

$$ZnTPP_o \rightarrow ZnTPP_i \qquad (10)$$

$$ZnTPP_i + 2H^+ \rightarrow Zn^{2+} + H_2TPP_i \qquad (11)$$

Immediately, $H_2TPP$ was diprotonated, and the aggregate of $H_4TPP^{2+}$ was produced at the interface (cf. eqs 1 and 2). The overall demetalation of ZnTPP can be written,

$$ZnTPP_o + 4H^+ \rightarrow Zn^{2+} + (H_4TPP^{2+})_{ni} \qquad (12)$$

where $(H_4TPP^{2+})_{ni}$ refers to the unit porphyrin constructing the aggregate. The demetalation represented in eq 12 was observed from the significant spectral change, since $\lambda_{max}$ at the Soret band was changed from 416 nm for ZnTPP to 466 nm for $(H_4TPP^{2+})_n$. The molar absorptivity of ZnTPP in dodecane was $4.98 \times 10^5\ dm^3\ mol^{-1}\ cm^{-1}$ at 416 nm. The equilibrium constant of the interfacial demetalation of ZnTPP, $K_{e2}$ ($dm^9\ mol^{-3}$), was defined as

$$ZnTPP_i + 4H^+ \rightleftharpoons Zn^{2+} + (H_4TPP^{2+})_{ni} \qquad (13)$$

$$K_{e2} = \frac{[Zn^{2+}][(H_4TPP^{2+})_n]_i}{[ZnTPP]_i[H^+]^4} \qquad (14)$$

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(13) Danesi, P. R. In *Principles and Practices of Solvent Extraction*; Rydberg, J., Musikas, C., Choppin, R. G., Eds.; Marcel Dekker: New York, 1992; Chapter 5.

The logarithmic values of $[Zn^{2+}][(H_4TPP^{2+})_n]_i/[ZnTPP]_i$ were plotted against the acidity function of hydrochloric acid, $-H_0$,[14] as shown in Figure 4. The intercept, $\log K_{e2}$, and the slope of the linear plots were determined as $-6.05 \pm 0.04$ and $4.1 \pm 0.3$, respectively. At initial concentrations of ZnTPP higher than $\sim 1.3 \times 10^{-5}$ mol dm$^{-3}$ in the acidic conditions, $-H_0 \geq 0$, the final amount of $(H_4TPP^{2+})_n$ produced at the dodecane−water interface was saturated, giving an absorbance value of $0.067 \pm 0.004$ at 466 nm. In this situation, the dodecane−water interface was completely occupied by the monolayer of the diprotonated aggregates, and the remaining ZnTPP in the bulk organic phase cannot be demetalated any more. Therefore, this limiting value refers to the saturated interfacial concentration, $a$ (mol cm$^{-2}$), of $H_4TPP^{2+}$ forming the aggregate at the interface, and the value of $a$ can be evaluated from

$$a = \frac{A_{\mathrm{sat}}}{2}\frac{1}{10^3\epsilon} \tag{15}$$

where $A_{\mathrm{sat}}$ and $\epsilon$ are the saturated absorbance at 466 nm and the molar absorptivity of the monomer unit in $(H_4TPP^{2+})_n$ at 466 nm ($3.06 \times 10^5$ dm$^3$ mol$^{-1}$ cm$^{-1}$), respectively. The saturated interfacial concentration and the occupied area per molecule were determined as $(1.10 \pm 0.06) \times 10^{-10}$ mol cm$^{-2}$ and $(1.51 \pm 0.08)$ nm$^2$, respectively. Taking into account that the molecular area occupied by $H_4TPP^{2+}$ is predicted to be $\sim 1.9$ nm$^2$ from the molecular mechanics (MM2) calculation, the experimental value is $\sim 20\%$ smaller than the predicted value. We have already observed that $\lambda_{\max}$ of the aggregate was red-shifted from 440 nm of $H_4TPP^{2+}$ to 466 nm. Therefore, it was suggested that $H_4TPP^{2+}$ is adsorbed as J-aggregates at the dodecane−hydrochloric acid interface. The tilting angle of the pyrrole ring plane from the interface and the overlapped area of the monomers were estimated as less than 27° and 40%, respectively.

The absorbance decrease at $\lambda_{\max}$ of ZnTPP was analyzed as pseudo-first-order kinetics, since the concentration of hydrogen ion in the aqueous acid phase was in large excess. The rate law of the demetalation of ZnTPP represented by eq 12 was described as

$$-\frac{\mathrm{d}[\mathrm{ZnTPP}]_{\mathrm{T}}}{\mathrm{d}t} = k_{\mathrm{obs}}[\mathrm{ZnTPP}]_{\mathrm{i}}\frac{S_{\mathrm{i}}}{V_{\mathrm{o}}} \tag{16}$$

where $k_{\mathrm{obs}}$ (s$^{-1}$) is the observed rate constant and $[\mathrm{ZnTPP}]_{\mathrm{T}}$ is the total or initial concentrations of ZnTPP dissolved in the bulk organic phase, which equals the sum of the ZnTPP concentrations in the organic phase and at the interface.

$$[\mathrm{ZnTPP}]_{\mathrm{T}} = [\mathrm{ZnTPP}]_{\mathrm{o}} + [\mathrm{ZnTPP}]_{\mathrm{i}}\frac{S_{\mathrm{i}}}{V_{\mathrm{o}}} \tag{17}$$

The rate constants were obtained by least-squares curve-fitting of the absorbance change at $\lambda_{\max}$ of ZnTPP. The values of $k_{\mathrm{obs}}$ depended on the concentration of hydrochloric acid, and the logarithmic values of $k_{\mathrm{obs}}$ were linearly correlated with the acidity function of hydrochloric acid, as shown in Figure 5. The slope of the linear plots was calculated as 0.95, and a first-order reaction for the hydrogen ion was suggested. Since $k_{\mathrm{obs}}$ of the demetalation of ZnTPP was much smaller than $k_0$ of the protonation of $H_2TPP$, it was suggested that the rate-determining step of the demetalation at the dodecane−water interface is the protonation of the pyrrole ring, as shown in eq 18.

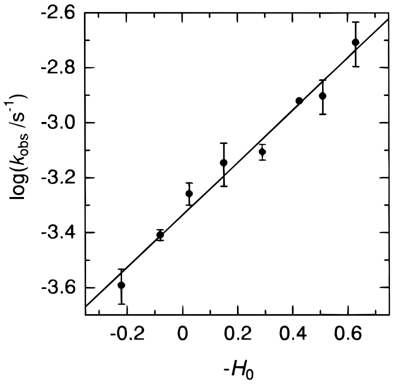

Figure 5. Logarithmic plot of the observed demetalation rate constants of ZnTPP, $k_{\mathrm{obs}}$ (s$^{-1}$), vs acidity function of hydrochloric acid, $-H_0$, at 298 K. The slope of the straight line is 0.95. The concentration of ZnTPP was $8.9 \times 10^{-6}$ mol dm$^{-3}$, and the ionic strength was maintained at 2.0.

$$\mathrm{ZnTPP}_{\mathrm{i}} + \mathrm{H}^+ \xrightarrow{k_1} [\mathrm{ZnTPPH}]^+_{\mathrm{i}} \tag{18}$$

$$[\mathrm{ZnTPPH}]^+_{\mathrm{i}} + \mathrm{H}^+ \xrightarrow{k_2} \mathrm{Zn}^{2+} + \mathrm{H_2TPP}_{\mathrm{o}} \qquad (k_2 \gg k_1) \tag{19}$$

Thus, it can be thought that the second attack of hydrogen ion shown in eq 19 is a very fast process, and the rate constant of the second step, $k_2$ (dm$^3$ mol$^{-1}$ s$^{-1}$), is much larger than the rate constant of the first step, $k_1$ (dm$^3$ mol$^{-1}$ s$^{-1}$). In this case, the rate law of the demetalation is described as follows:

$$-\frac{\mathrm{d}[\mathrm{ZnTPP}]_{\mathrm{i}}}{\mathrm{d}t}\frac{S_{\mathrm{i}}}{V_{\mathrm{o}}} = k_1[\mathrm{H}^+][\mathrm{ZnTPP}]_{\mathrm{i}}\frac{S_{\mathrm{i}}}{V_{\mathrm{o}}} \tag{20}$$

From eqs 16, 17, and 20, the value of $k_1$ can be calculated by

$$k_1 = \frac{k_{\mathrm{obs}}}{(1 + (1/K')(V_{\mathrm{o}}/S_{\mathrm{i}}))[\mathrm{H}^+]} \tag{21}$$

where the adsorption constant of ZnTPP in the dodecane−water system, $K'$, is defined as

$$K' = \frac{[\mathrm{ZnTPP}]_{\mathrm{i}}}{[\mathrm{ZnTPP}]_{\mathrm{o}}} \tag{22}$$

and the value of $K'$ in the dodecane−water system was determined as $2.1 \times 10^{-4}$ dm.[7] Therefore, the rate law of the overall reaction can be rewritten as

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[14] Cox, R. A.; Yates, K. *Can. J. Chem.* **1981**, *59*, 2116−2124.

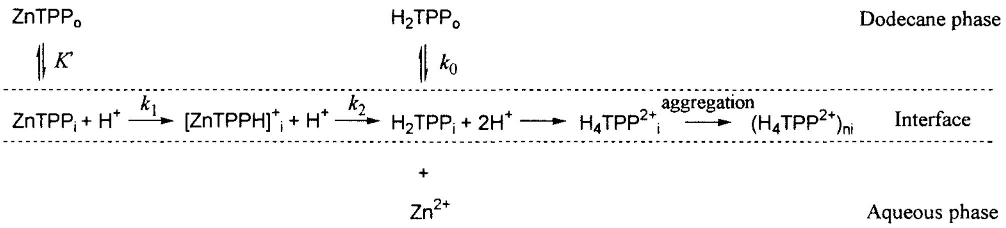

Figure 6. Schematic drawing of the demetalation mechanism of ZnTPP in the dodecane−hydrochloric acid system. ZnTPP distributes between the bulk dodecane phase and the interface with the adsorption constant defined in eq 22. At first, ZnTPP is monoprotonated at the interface and changed to the intermediate, $[ZnTPPH]^+$. Instantly, $[ZnTPPH]^+$ is further protonated, and the free base $H_2TPP$ is produced. The rate-determining step of the interfacial demetalation of ZnTPP is the first attacking step of a hydrogen ion with the rate constant, $k_1 = (8.6 \pm 1.3) \times 10^{-5}$ dm$^3$ mol$^{-1}$ s$^{-1}$ at 298 K. The diprotonation of $H_2TPP$ in the present conditions is much faster than the demetalation of ZnTPP, and at the end of reaction, the diprotonated aggregate, $(H_4TPP^{2+})_n$ is formed at the interface.

$$-\frac{d[\mathrm{ZnTPP}]_T}{dt} = k_1(1 + (1/K')(V_o/S_i))[\mathrm{H}^+][\mathrm{ZnTPP}]_i\frac{S_i}{V_o} \quad (23)$$

The averaged value of $k_1$ was $(8.6 \pm 1.3) \times 10^{-5}$ dm$^3$ mol$^{-1}$ s$^{-1}$, and the parameters obtained in the present study are summarized in Table 2.

The demetalation mechanism of ZnTPP in the dodecane−hydrochloric acid system was schematically shown in Figure 6. In homogeneous systems, a second-order hydrogen ion dependence has been reported for the demetalation of various metalloporphyrins.[15−19] However, a first-order dependence of hydrogen ion concentration was obtained in this work. This discrepancy suggests the unique property of the liquid−liquid interface as a reaction field. Since zinc atom is a relatively positive part in the ZnTPP molecule and located out of the plane of the pyrrole ring in its structure, it is expected that the zinc atom side of the adsorbed complex faces the aqueous phase.[7] It may be difficult for the hydrogen ion to approach the nitrogen atom of the pyrrole ring in the ZnTPP molecule, which is somewhat solvated by dodecane. Once the zinc complex is monoprotonated by a hydrogen ion, it will become more hydrophilic than the neutral compound, ZnTPP, and the produced intermediate, $[ZnTPPH]^+_i$, will be adsorbed at the interface closer to the aqueous phase. Thus, the second protonation at the pyrrole ring can easily proceed. Thus, the rate-determining step of the demetalation of ZnTPP at the interface is ascribable to the first attacking step of a hydrogen ion.

Table 2. Parameters of Protonation and Demetalation Determined in the Dodecane−Hydrochloric Acid System at 298 K

| system | log $K_c$[a] | rate constants | $a$, mol cm$^{-2}$ [b] |
|---|---|---|---|
| interfacial protonation of $H_2TPP$ | $2.14 \pm 0.07$ | $(4.1 \pm 0.5) \times 10^{-2}$ s$^{-1}$ | |
| interfacial demetalation of ZnTPP | $-6.05 \pm 0.04$ | $(8.6 \pm 1.3) \times 10^{-5}$ dm$^3$ mol$^{-1}$ s$^{-1}$ | $(1.10 \pm 0.06) \times 10^{-10}$ |

[a] The logarithmic values of equilibrium constants, $K_{e1}$ (dm$^6$ mol$^{-2}$) and $K_{e2}$ (dm$^9$ mol$^{-3}$), refer to the diprotonation and the demetalation equilibria, respectively. [b] The saturated interfacial concentration determined by direct spectrophotometric measurements.

## CONCLUSIONS

A new spectrophotometric method to study the interfacial reaction, named the centrifugal liquid membrane (CLM) method, was established in this study. By using this method, a kinetics study of the demetalation of ZnTPP in a dodecane−hydrochloric acid system was done, and it was confirmed that the rate-determining step is the first attack of hydrogen ion on ZnTPP at the interface. The specific interfacial area of the CLM method is a constant value, regardless of the kind of solute species. The value of 113 cm$^{-1}$ in the present study is sufficiently large in comparison with other direct spectrophotometric methods to study the interfacial reaction in the liquid−liquid system, e.g., 20 cm$^{-1}$ of the Teflon capillary plate method, 67 cm$^{-1}$ of the optical stir cell method,[20] and 777 cm$^{-1}$ of the two-phase stopped-flow method.[3] Thus, the CLM method is a sensitive and reliable method for the study of the interfacial kinetics and the adsorption equilibria. When the volume of the organic phase is reduced, the liquid membrane becomes thinner, and the specific interfacial area can readily be increased. Furthermore, the applicability of the CLM method is not restricted by the presence of surfactant and the properties of an organic solvent, e.g., polarity, viscosity, and refractive index. A difference in the densities of both phases is only necessary for the operation of the CLM method. This method may possibly be combined with other spectroscopic techniques, such as fluorescence and Raman spectrometries.

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