Acid Dissociation of (5,10,15,20-Tetraphenylporphyrinato)zinc(II) in Cetyltrimethylammonium Chloride Reversed Micellar Solutions

Toshiyuki Nakashima, Ikuko Nishida, and Terufumi Fujiwara*

Department of Chemistry, Graduate School of Science, Hiroshima University,
1-3-1 Kagamiyama, Higashi-Hiroshima 739-8526

(Received January 22, 2002)

Acid dissociation of (5,10,15,20-tetraphenylporphyrinato)zinc(II), Zn(tpp) dispersed in reversed micellar media of cetyltrimethylammonium chloride (CTAC) in chloroform/water and chloroform–cyclohexane/water has been investigated using a stopped-flow spectrophotometer. When Zn(tpp) is mixed with the reversed micellar solution containing a concentrated acid, spectral data reveal that its dissociation, following immediate formation of the chloro-coordinated complex Zn(tpp)Cl^- in the interfacial phase of the reverse micelle, occurs rapidly to produce the diacid salt of 5,10,15,20-tetraphenylporphyrin, $H_4(tpp)^{2+}(Cl^-)_2$. The dissociation rate increases with an increase of acid concentration in the reversed micellar aqueous pool. At higher acid concentrations (> 3 mol dm^{-3} in the pool), the rate constant and the fraction of Zn(tpp)Cl^- formed increase in the order: $HNO_3 < HCl \leq H_2SO_4 < HBr < HClO_4$, and decrease with an increase in volume fraction of cyclohexane in the reversed micellar bulk solvent. These observations may be explained by assuming selective distribution of the Cl^- ion to the interfacial surfactant and bulk organic phases, which is affected by affinities of the acid anions for the surfactant head group and by the Cl^- solvation.

Using cetyltrimethylammonium chloride (CTAC) reverse micelles in 6:5 (v/v) chloroform–cyclohexane as micro-reactors in chemiluminescence (CL) analysis,[1–7] we have developed a flow injection method based on a reversed micellar-mediated CL detection following solvent extraction.[8–10] When mixed with the reverse micelle containing luminol, it has been found that the extracted neutral chelate complexes such as tris(8-quinolinolato)iron(III)[2,6] and bis(acetylacetonato)oxovanadium(IV)[5,7] are dissociated quickly to serve as a catalyst of the luminol CL reaction; the metals of these complexes can be thus transferred selectively from the bulk organic phase to the inner aqueous core or so-called water pool of the reverse micelle. Such behaviors in the metal uptake by the reverse micelles are an important aspect of the inorganic biochemistry because of a similarity to the behavior reported for the iron-store protein, ferritin micelle.[11] Since the neutral metal complexes are almost insoluble in water, it is interesting to elucidate the driving force responsible for the metal uptake by the reverse micelles. The reversed micellar interface may be regarded as significant in the uptake process. The incorporation of the oxovanadium(IV) complex into reverse micelles containing aqueous basic solution, required for an enhancement of the CL reaction, appears to arise from formation of the six-coordinate complex by an axial ligation of the hydroxide ion at the reversed micellar interface.[7] However, the nucleophilic attacks of such oxygen-containing ligands to the vanadium atom were reported to give small effects in the visible absorption spectrum of the complex,[12] and in fact, we obtained no observable spectral shift for the complex in the reversed micellar solutions. On the other hand, it has been observed that the CL emission with the iron(III)[6] and oxovanadium(IV)[5] complexes in reverse micelles containing aqueous acidic solution is enhanced, suggesting that the dissociation of the complexes is promoted by the dispersed acid. To clarify the metal uptake process involving dissociation of the neutral metal complexes at the reversed micellar interface, more work is thus required.

The (5,10,15,20-tetraphenylporphyrinato)zinc(II) complex, Zn(tpp) is especially well suited for spectrophotometric studies because of its large molar absorptivity at Soret band and axial ligation properties:[13] The four-coordinate complex accepts only one axial ligand to form a five-coordinate complex. Such adduct formation exhibits a systematic red shift with increasing charge and polarizability of the axial ligand. In our previous work,[14] the solubilization of the neutral Zn(tpp) complex in the interfacial region of the CTAC reverse micelles was studied as a model for the first step in the metal uptake process by the reverse micelles. We concluded that the coordination of the counter Cl^- ion of CTAC to the zinc atom of Zn(tpp) at the reversed micellar interface leads to an enhancement of its interfacial solubilization. Using aqueous basic solution as a reversed micellar aqueous pool, we observed that the interfacial solubilization of Zn(tpp) was promoted by the formation of the hydroxide ion adduct at the interface,[14] but subsequently no dissociation of Zn(tpp) occurs. On the other hand, acid dissociation reactions of the neutral zinc porphyrin complexes have been studied in various media such as methanol/hydrochloric acid system,[15] dimethylformamide/hydrochloric acid system,[16] and dodecane–aqueous acid interface.[17] The reaction rate and rate law are highly sensitive to the reaction media,[18] and it is thus interesting to examine the acid dissociation reaction of Zn(tpp) in the reversed micellar media.

In this work, the metal uptake process by the reverse micelles, which involves interfacial solubilization and subsequent acid dissociation of their complexes, is examined using the neutral Zn(tpp) complex as an appropriate model compound; a stopped-flow method is employed for monitoring rapid spectral changes in the dissociation reaction after mixing a Zn(tpp) solution with a CTAC reversed micellar solution containing a concentrated acid such as hydrochloric acid, hydrobromic acid, perchloric acid, nitric acid, sulfuric acid, or acetic acid. We also record the observed influences of added salts and the reversed micellar bulk solvents on the dissociation rates. The knowledge obtained from this work contributes to our understanding of the role of the interfacial phase of the reverse micelle in the metal uptake process.

Experimental

Reagents. The Zn(tpp) complex and 5,10,15,20-tetraphenylporphyrin, H_2(tpp) were purchased from Aldrich Chemical Co., Inc. (Milwaukee, WI, USA). The CTAC surfactant (> 98%) was obtained from Fluka (Buchs, Switzerland). Chloroform (> 99.7%, stabilized with pentene) and cyclohexane were of fluorescence reagent grade (Cica-Merck) and were obtained from Kanto Chemical Co., Inc. (Tokyo, Japan). By preliminary experiments, it was confirmed that the Zn(tpp) spectrum obtained in the reversed micellar solution is not affected by the presence of pentene.[14] Hydrochloric acid (36%, electronic grade), hydrobromic acid (47%, reagent grade), nitric acid (61%, analytical reagent grade), sulfuric acid (97%, analytical reagent grade) and acetic acid (99.7%, reagent grade) were purchased from Kanto Chemical Co., Inc., and perchloric acid (60%, analytical reagent grade) was obtained from Katayama Chemical Industries Co., Ltd. (Osaka, Japan). The nominal concentrations of the acids used were confirmed by a conventional acid–base titration. Lithium chloride and lithium perchlorate (> 99.0%, reagent grade) were obtained from Kanto Chemical Co., Inc., and Katayama Chemical Industries Co., Ltd., respectively. All chemicals were used without further purification. Distilled water (high-performance liquid chromatography reagent grade) was obtained from Kanto Chemical Co., Inc. and was used in the preparation of all aqueous solutions.

Apparatus. Kinetic measurements were carried out by using an Otsuka Densi model RA-2000 stopped-flow spectrophotometer, equipped with a four-jet mixer and a cylindrical quartz cell of 2.0 mm optical path length thermostated at 25.0 ± 0.1 °C. A photodiode array UV–visible detector (rapid-scan detection system) was used to measure the spectral change during the reaction. The water contents in the CTAC solutions were determined coulometrically using a Hiranuma model AQ-7 aquacounter.

Procedure. Stock concentrated acids (1.0–6.0 mol dm^{-3}) of HCl, HBr, $HClO_4$, HNO_3, H_2SO_4 and CH_3COOH were prepared by serial dilution of an undiluted acid with distilled water. Stock concentrated aqueous salt solutions (1.0–3.0 mol dm^{-3}) of LiCl and $LiClO_4$ were prepared in 3.0 mol dm^{-3} HCl. Chloroform and its mixture with cyclohexane were used as reversed micellar bulk solvents. Working reversed micellar solutions were prepared by dispersing an appropriate amount of the stock concentrated acids or the stock concentrated aqueous solutions in the reversed micellar bulk solvent containing the CTAC surfactant. By dissolving solid Zn(tpp) in chloroform or the mixed solvent of chloroform–cyclohexane, we could make the working solution of 1.0×10^{-5} mol dm^{-3} Zn(tpp). Both the working solutions were prepared daily to avoid chloroform decomposition.

The working Zn(tpp) solution and the working reversed micellar solution containing a concentrated acid or a concentrated aqueous salt solution in a couple of reservoirs of the stopped-flow apparatus were pushed through the four-jet mixer. After the mixing of the 1:1 volume ratio, the Zn(tpp) concentration was reduced to half its initial value, i.e., 5.0×10^{-6} mol dm^{-3} in the cell, where the flow was abruptly stopped. The progress of the acid dissociation reaction was monitored spectrally from 365 to 500 nm at 20 ms intervals over 2 s. The pseudo-first-order rate constants for the reactions were determined by analyzing the growth of the characteristic absorption band of the diacid salt of 5,10,15,20-tetraphenylporphyrin, $H_4(tpp)^{2+}(Cl^-)_2$ at 445 nm.

Results and Discussion

Kinetics of Acid Dissociation Reaction of Zn(tpp). In the absorption spectrum of Zn(tpp) as observed in our previous work,[14] two B (or Soret) bands at 419 and 433 nm, attributable to Zn(tpp) and a chloro-coordinated complex, Zn(tpp)Cl^-, respectively, appear in a CTAC reversed micellar solution, indicating that the following Zn(tpp)Cl^- formation is equilibrated much more rapidly:

$$\mathrm{Zn(tpp)} + \mathrm{Cl^-} \rightleftarrows \mathrm{Zn(tpp)Cl^-} \qquad (1)$$

On the other hand, an interesting spectral change was observed when a Zn(tpp) solution in chloroform was mixed with the reversed micellar solution containing 3.0 mol dm^{-3} HCl in the water pool (or the HCl concentration of 2.2×10^{-2} mol dm^{-3} in the final reversed micellar solution, calculated by taking into account a water pool to final total volume ratio), as shown in Fig. 1: A rapid decrease in these two peaks was produced, followed by the growth of a new band at 445 nm. Finally the former bands disappeared and the spectrum obtained is identical with that of the diacid salt of 5,10,15,20-tetraphenylporphyrin, $H_4(tpp)^{2+}(Cl^-)_2$ in chloroform,[19] indicating that the dissociation of Zn(tpp) into the acid form occurs completely without re-incorporation of the released Zn^{2+} ion. Furthermore, Fig. 1 shows the occurrence of a clear isosbestic point at 434 nm during the reaction, strongly suggesting that the Zn(tpp) and Zn(tpp)Cl^- complexes are always in a strictly constant ratio and the $H_4(tpp)^{2+}(Cl^-)_2$ salt alone is a product. This also means that Zn(tpp)Cl^- is in equilibrium with Zn(tpp) and

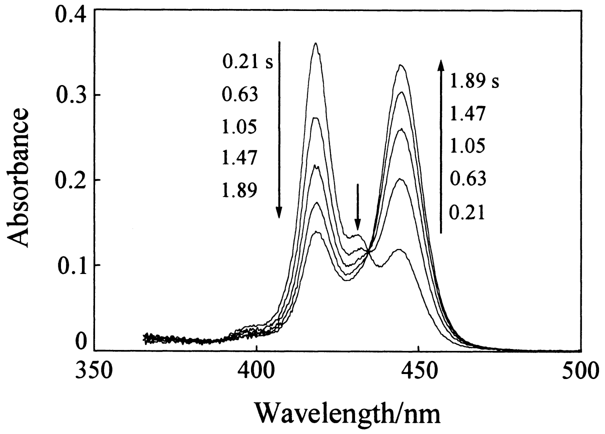

Fig. 1. Typical change in the rapid-scan spectra of Zn(tpp) observed in the chloroform/CTAC/HCl system at $R_w = 4$. [Zn(tpp)] = 5.0×10^{-6} mol dm^{-3}, [CTAC] = 0.10 mol dm^{-3}, [HCl] = 2.2×10^{-2} mol dm^{-3}, and t = 25.0°C.

Cl^- throughout the reaction and its formation constant is continually maintained. In this circumstances, it is likely that the above step of Eq. 1 is much more rapid than the following step:

$$Zn(tpp)Cl^- + Cl^- + 4H^+ \rightarrow H_4(tpp)^{2+}(Cl^-)_2 + Zn^{2+} \quad (2)$$

The negatively charged $Zn(tpp)Cl^-$ complex may be stabilized by forming an ion-pair like $Zn(tpp)Cl^-CTA^+$ in the interfacial and bulk organic phases that are low polar media.[14] The CTAC surfactant seems to serve as a phase transfer catalyst of Zn(tpp) from the bulk organic phase to the interfacial phase of the reverse micelle where the irreversible dissociation of Zn(tpp) may proceed.

In a comparative study, an acid dissociation of Zn(tpp) was examined in chloroform acidified with HCl, dispersed by using nitromethane as a solubilizing agent. The interaction between Zn(tpp) and nitromethane is expected to be small because of its relatively small donor number, DN = 2.7,[20,21] and in fact no spectral change was observed on the addition of small amounts of nitromethane. The dissociation of Zn(tpp) in the acidified chloroform occurs more rapidly to produce $H_4(tpp)^{2+}(Cl^-)_2$ and $Zn(tpp)Cl^-$, which may exist in an ion-pairing form, $Zn(tpp)Cl^-H^+$:[15] The 26% gain in $H_4(tpp)^{2+}(Cl^-)_2$ was obtained with 3.8×10^{-5} mol dm^{-3} HCl. However, the reaction reached an equilibrium and ceased immediately, so the Eq. 2 step may be reversible. In the CTAC reversed micellar medium, all runs have the common characteristic of an initial loss of the zinc porphyrins followed by a first-order dissociation process. The initial dissociation was too rapid to be monitored, because of the deadtime (90 ms) of the flow apparatus used. This kinetic behavior may be explained as follows: The reactants are in a more rapid equilibrium initially to give $H_4(tpp)^{2+}(Cl^-)_2$, likely due to the presence of the acid in mere trace and limited amounts in the bulk organic phase, that being the case in chloroform. Once the rapid equilibrium has been established, the subsequent dissociation reaction proceeds at a lower rate, probably in the interfacial phase of the reverse micelle. Thus, the starting absorbances are not obtained from the sum of the zinc porphyrins alone, but include a contribution from $H_4(tpp)^{2+}(Cl^-)_2$ initially produced. These results imply that uptake of the released Zn^{2+} ion by the reverse micelle into its water pool may play an important role in the irreversible dissociation of Zn(tpp). The stabilization of the Zn^{2+} ion due to hydration or water coordination in the water pool may propagate the reaction. In addition, the complexing Cl^- ion may facilitate the removal of Zn^{2+} ion from porphyrin ring in concert with the protonation of the porphyrin.[22]

For the determination of the rate law, we monitored the gain in $H_4(tpp)^{2+}(Cl^-)_2$, which is equivalent to the loss of total zinc porphyrins $[Zn(tpp)'] = [Zn(tpp)] + [Zn(tpp)Cl^-] = C_P - [H_4(tpp)^{2+}(Cl^-)_2]$, where C_P is the total concentration of porphyrins. In the presence of large excesses of CTAC and HCl compared to Zn(tpp) ($C_P = 5.0 \times 10^{-6}$ mol dm^{-3}), the reaction of the $H_4(tpp)^{2+}(Cl^-)_2$ formation was first order in total zinc porphyrins and thus can be accommodated by a rate law of the following form:

$$\frac{d[H_4(tpp)^{2+}(Cl^-)_2]}{dt} = \frac{d[Zn(tpp)']}{dt} = k_{obs}[Zn(tpp)'] \quad (3)$$

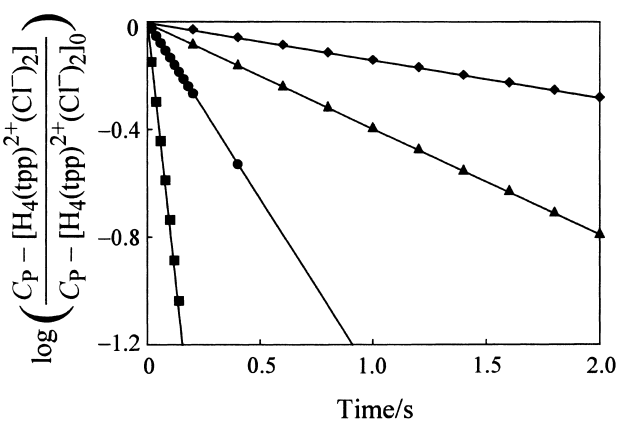

Fig. 2. Plots of log $[(C_P - [H_4(tpp)^{2+}(Cl^-)_2])/(C_P - [H_4(tpp)^{2+}(Cl^-)_2]_0)]$ vs time for the dissociation of Zn(tpp) at a fixed HCl concentration of 2.9×10^{-2} mol dm^{-3} on the basis of total volume of CTAC reversed micellar solutions at R_w = 3 (■, $[HCl]_{pool}$ = 5.3 mol dm^{-3}), 4 (●, $[HCl]_{pool}$ = 4.0 mol dm^{-3}), 5 (▲, $[HCl]_{pool}$ = 3.2 mol dm^{-3}), and 6 (◆, $[HCl]_{pool}$ = 2.7 mol dm^{-3}).

where k_{obs} is the pseudo-first-order rate constant and independent of C_P. The log $[(C_P - [H_4(tpp)^{2+}(Cl^-)_2])/(C_P - [H_4(tpp)^{2+}(Cl^-)_2]_0)]$ values, obtained from the spectral data at various molar ratios of water-to-surfactant ($R_w = [H_2O]/[CTAC]$) with a constant CTAC concentration of 0.1 mol dm^{-3}, were plotted against time in Fig. 2, where the designation $[H_4(tpp)^{2+}(Cl^-)_2]_0$ represents the aforementioned concentration of $H_4(tpp)^{2+}(Cl^-)_2$ initially produced. Furthermore, the fraction of the $Zn(tpp)Cl^-$ complex produced, $F_{Zn(tpp)Cl}$ (= $[Zn(tpp)Cl^-]/[Zn(tpp)']$) can be obtained from the spectral data using the respective molar absorptivities of Zn(tpp), $Zn(tpp)Cl^-$ and $H_4(tpp)^{2+}(Cl^-)_2$ in the same manner as reported in our previous paper.[14] No change in the value of $F_{Zn(tpp)Cl}$ with time was observed, confirming that $Zn(tpp)Cl^-$ is almost maintained in constant fraction throughout the reaction. The value will be related to k_{obs} as described below.

With an increase in R_w, an increase in the size of a reversed micellar water pool and changes in its physicochemical properties have been noted.[23–26] In the case with the water pool containing HCl at a fixed concentration, increasing the R_w value along with an increase in the water content at a constant CTAC concentration also causes an increase in the total amount of aqueous HCl dispersed in the reversed micellar solution. However, the rate observed for the first-order dissociation is gradually reduced as R_w increases. Since an increase in R_w results in a decrease in the Zn(tpp)-solubilizing ability of the reverse micelle, probably due to the Cl^- hydration in the interfacial phase,[14] this should be reasonable. On the other hand, a steep decrease in the dissociation rate was observed when the HCl concentration in the water pool, represented by the designation $[HCl]_{pool}$, was decreased with an increase in R_w or in the water content, but the total amount of HCl in the reversed micellar solution was kept constant ([HCl] = 2.9×10^{-2} mol dm^{-3}), as shown in Fig. 2. The concentrations in square brackets refer to the total volume of reversed micellar solution unless otherwise noted. Further, the influence of the number of water droplets in the reversed micellar bulk solvent on the dissociation rate was examined while changing both the CTAC and water concentrations at a fixed R_w value of 4. When 4.0 mol dm^{-3} HCl was dispersed as a reversed micellar aqueous core, an increase in the number of reverse micelles resulted in no change in the k_{obs} value. These observations suggest that the rate for the step of Eq. 2 is more sensitive to a change in the local concentration of HCl or the hydrogen ion, likely distributed to the interfacial phase, compared with its total concentration in the reversed micellar solution.

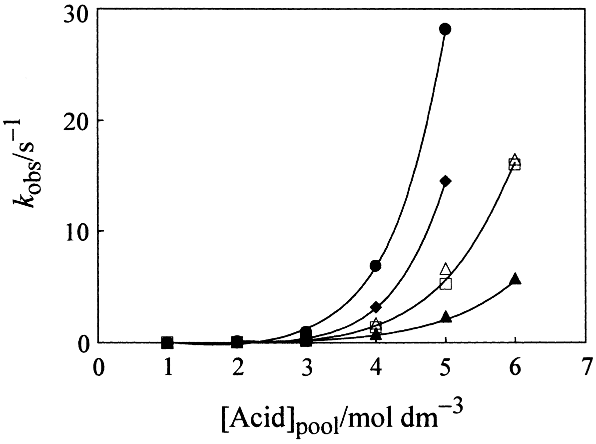

Fig. 3. Variations of k_{obs} for the dissociation reaction of Zn(tpp) with the concentrations of $HClO_4$ (●), HBr (◆), HCl (□), H_2SO_4 (△), and HNO_3 (▲) in the dispersed aqueous core of CTAC reverse micelles formed in chloroform at $R_w = 4$.

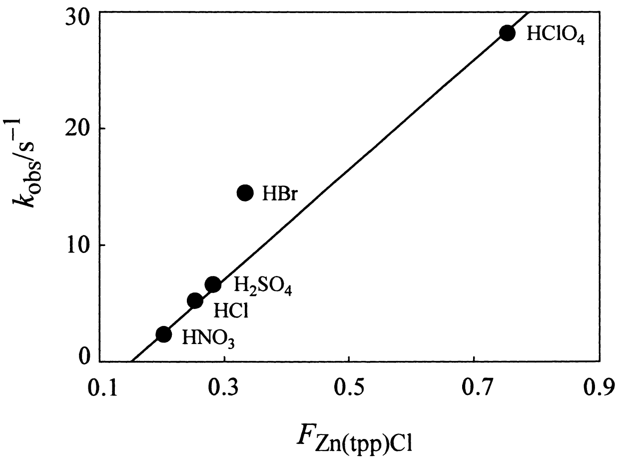

Fig. 4. Correlation between k_{obs} and $F_{Zn(tpp)Cl}$ for the dissociation reaction of Zn(tpp) observed with different acids dispersed as the aqueous core of the CTAC reverse micelle in chloroform at $R_w = 4$. [Acid] = 3.6×10^{-2} mol dm^{-3}.

Effect of Acid Anions. A comparative study for the aqueous acids used as the reversed micellar aqueous core was also carried out with various concentrations of acids such as $HClO_4$, HBr, H_2SO_4, HNO_3 and CH_3COOH. The use of CH_3COOH caused no acid dissociation reaction, probably due to its weak acidity. Despite differences in the acid anions, however, other initial spectra and changes in the spectra were similar to those obtained with HCl; for all the other acids, the two initial bands of Zn(tpp) and Zn(tpp)Cl$^-$ and the final band of $H_4(tpp)^{2+}(Cl^-)_2$ appeared. The Zn(tpp)Br$^-$ (434 nm) and $H_4(tpp)^{2+}(Br^-)_2$ (449 nm)[19] bands and the $H_4(tpp)^{2+}(ClO_4^-)_2$ (440 nm)[19] band may be expected but were not observed with HBr and $HClO_4$, respectively. These observations may reflect distribution of the Cl$^-$ ion alone outside the water pool, so it seems likely that almost the same situation arise in all the cases with acids. However, Fig. 3 reveals differences in an acceleration effect of acids on the reaction rate at higher acid concentrations ($[Acid]_{pool} > 3$ mol dm^{-3} in the water pool): The k_{obs} increased in the order: $HNO_3 < HCl \leq H_2SO_4 < HBr < HClO_4$ at each acid concentration. This sequence seems to lie in the order of increasing acidity of concentrated acid solutions for which the Hammett acidity functions are useful for comparing different acid media,[27] where no secondary dissociation of H_2SO_4 is considered to occur. On the other hand, the fraction of Zn(tpp)Cl$^-$, $F_{Zn(tpp)Cl}$ mentioned above is found to increase with an increase in the acid concentration and also with the acid in the same order at each acid concentration. Figure 4 illustrates a linear relationship between the k_{obs} and $F_{Zn(tpp)Cl}$ values obtained with different aqueous acids present in the respective reversed micellar water pools at the same concentration of 5.0 mol dm^{-3}. This experimentally obtained relationship is reproduced by the following equation:

$$k_{obs} = k_H F_{Zn(tpp)Cl} \tag{4}$$

where the rate constant k_H may be dependent on the hydrogen ion concentration as discussed below. Also, from Eqs. 3 and 4, $k_{obs}[Zn(tpp)'] = k_H F_{Zn(tpp)Cl} [Zn(tpp)'] = k_H [Zn(tpp)Cl^-]$, which may be obeyed by Eq. 2. This strongly suggests that the acceleration effect of acids on the reaction rate is attributed to an increase in the fraction of Zn(tpp)Cl$^-$, which may be caused by elevation in the activity of CTAC or the Cl$^-$ ion in the step of Eq. 1. This is likely due to an enhancement in the selective distribution of the Cl$^-$ ion to the interfacial and/or the bulk organic phase by the presence of the acid anions. A similar selectivity for Cl$^-$ was observed for location of a chromoionophore binding with anions in the hydrophobic layer of a cationic vesicle.[28] As reported previously,[14] an increase in the local Cl$^-$ concentration in the interfacial and bulk organic phases causes an enhancement in the Zn(tpp)Cl$^-$ formation, which would promote interfacial solubilization of the complex, presumably bringing about its dissociation. Therefore, the $F_{Zn(tpp)Cl}$ value may be used as a measure of the local Cl$^-$ concentration.

The observed trend in k_{obs} or $F_{Zn(tpp)Cl}$ appears to be fairly consistent with an increase in the relative binding ability of acid anions to normal CTA$^+$ micelles: The scales of CTA$^+$ affinity of anions[29] may be also correlated with a typical lyotropic series for anions:[30] $SO_4^{2-} < CH_3COO^- < Cl^- < Br^- < NO_3^-, ClO_4^- < I^- < SCN^-$. It seems likely that there is a competition between the counter Cl$^-$ ion and the acid anion for the positively charged head group of the CTA$^+$ surfactant at the reversed micellar interface. Since the micellar surface cannot be oversaturated by anions, it is postulated that, for more strongly CTA$^+$-bond anions such as the ClO_4^- ion, the Cl$^-$ ion is to some extent exchanged and transferred from the interface to both the surfactant hydrophobic layer and water pool of the

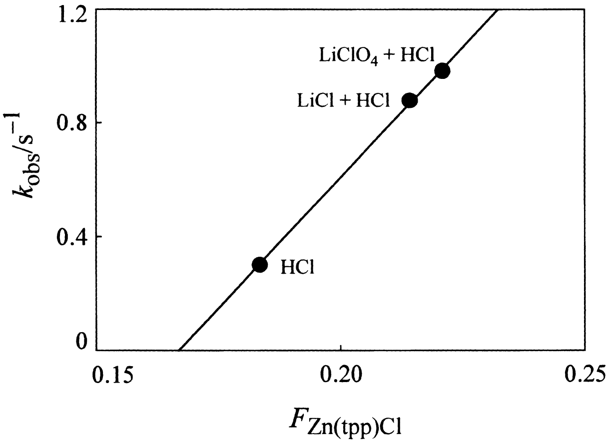

Fig. 5. Correlation between k_{obs} and $F_{Zn(tpp)Cl}$ for the dissociation reaction of Zn(tpp) observed with different salts (1.0 mol dm^{-3}) in 3.0 mol dm^{-3} HCl dispersed as the aqueous core of the CTAC reverse micelle in chloroform at R_w = 4.

reverse micelle; this may lead to an increase in the Cl^- concentration and thus to an increase in the fraction of $Zn(tpp)Cl^-$ in the hydrophobic layer and the bulk organic phase. Such an exchange equilibrium at the interface may be regarded as significant in the step of Eq. 1.

To investigate the anion effect on the reaction rate further, 3.0 mol dm^{-3} HCl containing a 1.0 mol dm^{-3} inorganic salt such as LiCl or $LiClO_4$ was dispersed as the reversed micellar aqueous core. The presence of the salt caused a pronounced enhancement in $F_{Zn(tpp)Cl}$ and the larger magnitude of the increase was obtained with $LiClO_4$ compared with LiCl as shown in Fig. 5. A similar trend in the anion effect on the $Zn(tpp)Cl^-$ formation was observed in the absence of the acid in the reversed micellar water pool.[31] Also, Figure 5 shows that there is a reasonable correlation of k_{obs} vs $F_{Zn(tpp)Cl}$ in agreement with that obtained with the different acids, supporting the above explanation.

Effect of Bulk Organic Solvent. In our previous studies, the formation of $Zn(tpp)Cl^-$ was found to be affected by the chloroform fraction in the reversed micellar bulk solvent. It has been reported that, in the core of an aggregate formed in CTAC–chloroform solution, chloroform molecules form hydrogen bonds directly with the counter Cl^- ions of CTAC.[32] Therefore, the effect of the bulk solvent due to hydrogen bonding may be expected to be responsible for the variation of the reaction rate with solvent composition. As shown in Fig. 6, where the data were obtained using 5.0 mol dm^{-3} HCl as the reversed micellar aqueous pool, obviously, the larger the chloroform fraction in the bulk solvent, the greater both the k_{obs} and $F_{Zn(tpp)Cl}$ values become. The plot is also linear, implying that the reaction process given by the aforementioned scheme is not altered by the change in solvent composition. The interaction between the counter Cl^- ion and chloroform may contribute to the selective distribution of the Cl^- ion to the surfactant hydrophobic layer and then to the bulk organic phase, thus leading to the increase in the Cl^- concentration in both the phases.

Mechanism of Acid Dissociation. The k_H value mentioned above was obtained from the slope of the linear plot of k_{obs} vs $F_{Zn(tpp)Cl}$ at each acid concentration used. The logarithmic relationship between the obtained k_H value and the acid concentration in the water pool is shown in Fig. 7. The fair agreement between the plots obtained with different acids and the different compositions of bulk organic solvent suggests that the reaction mechanism of Eq. 2 is independent of these differences. A slope of the linear plots is obtained as 3.4 ± 0.3, indicating that the rate law for Eq. 2 is third order in hydrogen ion.

Under the present experimental conditions (R_w = 4 and [CTAC] = 0.1 mol dm^{-3} in chloroform), our previous work[14] predicts that 26% of the $Zn(tpp)Cl^-$ complex will be solubilized in the interfacial phase. Since the molecular dynamics simulation of a model reverse micelle reveals the water distribution to the surfactant hydrophobic layer,[33] it may be reason-

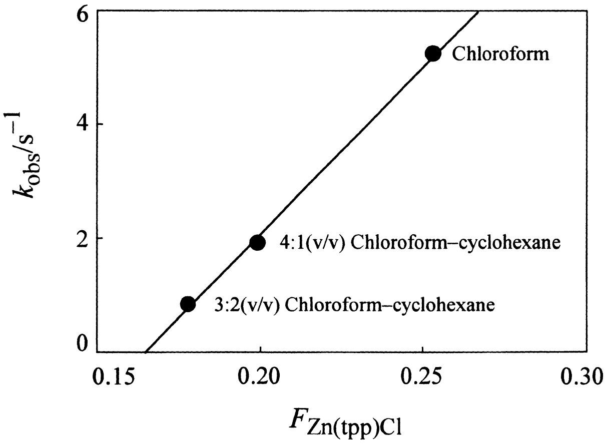

Fig. 6. Correlation between k_{obs} and $F_{Zn(tpp)Cl}$ for the dissociation reaction of Zn(tpp) observed with different volume ratios of chloroform to cyclohexane used as the CTAC reversed micellar bulk solvent at R_w = 4. [HCl] = 3.6 × 10^{-2} mol dm^{-3}.

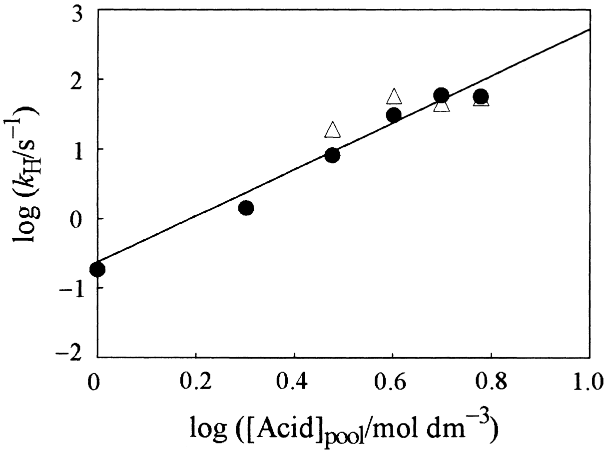

Fig. 7. Variations of k_H for the dissociation reaction of $Zn(tpp)Cl^-$ with the acid concentrations in the dispersed aqueous core of CTAC reverse micelles at R_w = 4. With the different acids (△) and the different compositions of the reversed micellar bulk solvent (●), the k_H values were obtained as slopes of the k_{obs} vs $F_{Zn(tpp)Cl}$ plots at respective acid concentrations.

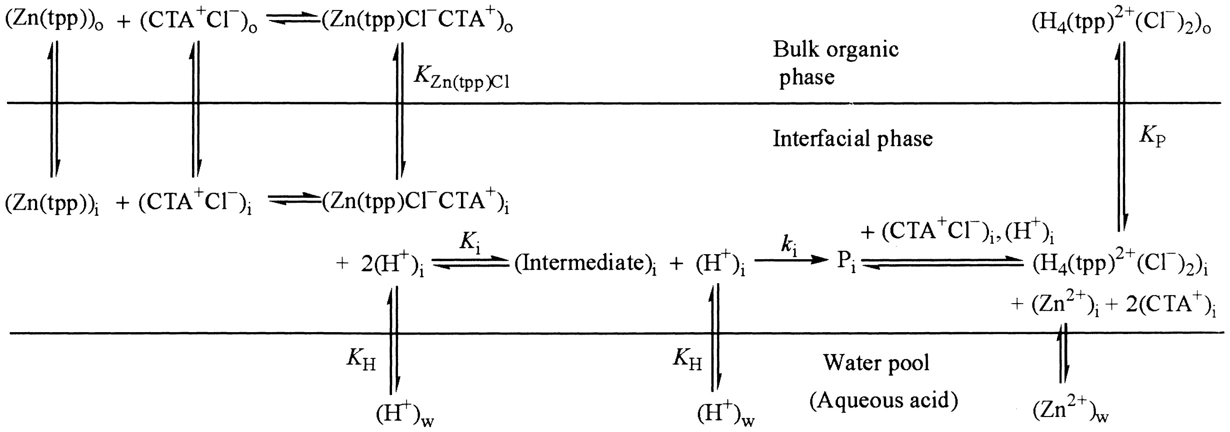

Fig. 8. Schematic representation of the acid dissociation reaction of Zn(tpp) in the interfacial phase of the CTAC reversed micellar system.

able to consider that hydration of the hydrogen ion should cause significant penetration of the hydrated proton into the interfacial phase, in which the Eq. 2 step proceeds. A quantitative model for the above situation may be constructed by applying the pseudophase model,[34] which was successfully used in our previous work.[14] With this model (Fig. 8), the reversed micellar media is assumed to be divided into three pseudophases, corresponding to the bulk organic phase, interfacial phase and water pool. In view of an amphiphilic characteristic of $H_4(tpp)^{2+}(Cl^-)_2$, this salt appears to be accumulated in the interfacial phase and thus it is assumed that the partition coefficient of $H_4(tpp)^{2+}(Cl^-)_2$, K_P between the interfacial and bulk organic phases is large enough.[35] Therefore, the observed pseudo-first-order rate constant can be obtained as follows:

$$k_{obs} = k_iK_iK_H^3[H^+]^3_{pool}f_iF_{Zn(tpp)Cl} \quad (5)$$

where k_i is the rate constant for the rate-determining step in the interfacial phase, K_i is the formation constant of (Intermediate)$_i$ in the interfacial phase, K_H is the partition coefficient of hydrated proton between the interfacial phase and water pool, and $f_iF_{Zn(tpp)Cl}$ is the concentration ratio of the solubilized $Zn(tpp)Cl^-$ relative to the total zinc porphyrins, i.e., $f_iF_{Zn(tpp)Cl} = [Zn(tpp)Cl^-]_i/[Zn(tpp)']$.[37] From Eqs. 4 and 5, $k_H = k_iK_iK_H^3f_i[H^+]^3_{pool}$. Since $f_i = 0.264$ under the experimental conditions used,[37] the value of $k_iK_iK_H^3$ for the dissociation in the interfacial phase is obtained as 0.84 dm^9 mol^{-3} s^{-1} from the intercept of the logarithmic plot as shown in Fig. 7.

It has been pointed out that the reaction order is highly sensitive to the reaction media.[18] In dimethylformamide acidified with HCl, the rate law for the dissociation of Zn(tpp) is second-order in hydrogen ion,[16] while in methanol acidified with HCl, the rate law for the zinc etioporphyrin(III) complex is third-order in HCl.[15] On the other hand, a first-order dependence of hydrogen ion concentration was obtained for the kinetics of the dissociation of Zn(tpp) at a dodecane–aqueous acid interface by using a centrifugal liquid membrane method.[17] In this work, the observed third-order behavior with increasing $[H^+]_{pool}$ suggests that the mechanism of Eq. 2 is similar to that for the zinc etioporphyrin(III) complex in the acidified methanol,[15] in which the zinc porphyrin•2HCl complex is considered to be a steady-state intermediate and the third attacking of HCl to the intermediate is the rate-determining step. Hence the mechanism of Eq. 2 is replaced by that shown in Fig. 8. In a comparative study with the reversed micellar solutions containing the acids, the protonation of the free base porphyrin, $H_2(tpp)$, to produce $H_4(tpp)^{2+}(Cl^-)_2$ was observed to be much faster than the acid dissociation of Zn(tpp) and to complete immediately, so that it was not monitored. This observation indicates that $H_2(tpp)$ is not formed prior to the rate-determining step in the Zn(tpp) dissociation process. The steady-state intermediate represented in Fig. 8 may be regarded as a sitting-atop (SAT) complex, in which the zinc(II) ion sits on the porphyrin plane and two N–H protons are present. The SAT complex has been reported to exist in the incorporation process of zinc(II) ion into 5,10,15,20-tetraphenylporphyrin.[38,39] Recently, we spectrophotometrically detected the SAT complex of copper(II) ion with 5,10,15,20-tetrakis[4-(*N*-trimethylammonio)phenyl]porphyrin in CTAC reversed micellar media,[40] and found that the interfacial phase plays an important role in formation of the SAT complex. As described above, on the other hand, the occurrence of the isosbestic point can imply that appreciable amounts of reaction intermediates such as an SAT complex are not present, but there may be very small stationary-state concentrations, presumably reflecting the stability of the SAT complex formed prior to the zinc atom dissociation following the third attacking of proton in the interfacial phase of the reverse micelle. This view may provide the reason for the observed third-order dependence of $[H^+]_{pool}$, although further investigations on the formation of the SAT complex in the reverse micelles are required.

Conclusion

Acid dissociation of Zn(tpp) occurs to produce a diacid salt, $H_4(tpp)^{2+}(Cl^-)_2$ in the CTAC reversed micellar solution containing concentrated acids. With the different acids, an increase in the dissociation rate with an enhancement in the formation of $Zn(tpp)Cl^-$ was observed. A good relationship between them suggests that the dissociation probably proceeds via the $Zn(tpp)Cl^-$ formation which promotes the interfacial solubilization of Zn(tpp). Also, the acid anions may play an important role in determining the acid dependence of the rate.

Acceleration effects of the anion and the reversed micellar bulk solvent may be attributable to an increase in the local Cl^- ion concentrations in the interfacial and bulk organic phases, in which selective distribution of the Cl^- ion may be influenced by the affinities of the anions for the surfactant head group and by the Cl^- solvation.

This work was partially supported by a Grant-in-Aid for Scientific Research No. 12640591, from the Ministry of Education, Science Sports and Culture.

References

1 T. Fujiwara, N. Tanimoto, J.-J. Huang, and T. Kumamaru, *Anal. Chem.*, **61**, 2800 (1989).

2 T. Fujiwara, N. Tanimoto, K. Nakahara, and T. Kumamaru, *Chem. Lett.*, **1991**, 1137.

3 Imdadullah, T. Fujiwara, and T. Kumamaru, *Anal. Chem.*, **63**, 2348 (1991).

4 Imdadullah, T. Fujiwara, and T. Kumamaru, *Anal. Chem.*, **65**, 421 (1993).

5 T. Fujiwara, TheingiKyaw, Y. Okamoto, and T. Kumamaru, *Anal. Sci.*, **13** (supplement), 59 (1997).

6 Theingi-Kyaw, T. Fujiwara, H. Inoue, Y. Okamoto, and T. Kumamaru, *Anal. Sci.*, **14**, 203 (1998).

7 TheingiKyaw, S. Kumooka, Y. Okamoto, T. Fujiwara, and T. Kumamaru, *Anal. Sci.*, **15**, 293 (1999).

8 T. Fujiwara, K. Murayama, Imdadullah, and T. Kumamaru, *Microchem. J.*, **49**, 183 (1994).

9 T. Fujiwara, I. U. Mohammadzai, H. Inoue, and T. Kumamaru, *Analyst*, **125**, 759 (2000).

10 T. Fujiwara, I. U. Mohammadzai, K. Murayama, and T. Kumamaru, *Anal. Chem.*, **72**, 1715 (2000).

11 J. K. Grady, J. Shao, P. Arosio, P. Santambrogio, and D. N. Chasteen, *J. Inorg. Biochem.*, **80**, 107 (2000).

12 K. Dichmann, G. Hamer, S. C. Nyburg, and W. F. Reynolds, *Chem. Comm.*, **1970**, 1295.

13 M. Nappa and J. S. Valentine, *J. Am. Chem. Soc.*, **100**, 5075 (1978).

14 T. Nakashima, T. Fujiwara, and T. Kumamaru, *Bull. Chem. Soc. Jpn.*, **75**, 749 (2002).

15 B. Shears, B. Shah, and P. Hambright, *J. Am. Chem. Soc.*, **93**, 776 (1971).

16 T. P. G. Sutter and P. Hambright, *Inorg. Chem.*, **31**, 5089 (1992).

17 H. Nagatani and H. Watarai, *Anal. Chem.*, **70**, 2860 (1998).

18 D. K. Lavallee, *Coord. Chem. Rev.*, **61**, 55 (1985).

19 J. Nishimoto, M. Tabata, T. Eguchi, and J. Takauchi, *J. Chem. Soc., Perkin Trans. 2*, **7**, 1539 (1998).

20 V. Gutmann, "The Donor–Acceptor Approach to Molecular Interactions," Plenum Press, New York (1978).

21 V. Gutmann, G. Resch, and W. Linert, *Coord. Chem. Rev.*, **43**, 133 (1982).

22 P. Hambright and E. B. Fleischer, *Inorg. Chem.*, **9**, 1757 (1970).

23 J. Lang and G. Mascolo, *J. Phys. Chem.*, **94**, 3069 (1990).

24 M. P. Pileni, "Structure and Reactivity in Reverse Micelles," ed by M. P. Pileni, Elsevier, Amsterdam (1989), pp. 44–49.

25 H. Kondo, I. Miwa, and J. Sunamoto, *J. Phys. Chem.*, **86**, 4826 (1982).

26 J. Nishimoto, E. Iwamoto, T. Fujiwara, and T. Kumamaru, *J. Chem. Soc., Faraday Trans.*, **89**, 535 (1993).

27 R. A. Cox and K. Yates, *Can. J. Chem.*, **61**, 2225 (1983).

28 T. Hayashita, T. Onodera, R. Kato, S. Nishizawa, and N. Teramae, *Chem. Commun.*, **2000**, 755.

29 M.-F. Ruasse, I. B. Blagoeva, R. C. L. Garcia-Rio, J. R. Leis, A. Marques, J. Mejuto, and E. Monnier, *Pure Appl. Chem.*, **69**, 1923 (1997).

30 J. W. Larsen and L. J. Magid, *J. Am. Chem. Soc.*, **96**, 5774 (1974).

31 T. Nakashima and T. Fujiwara, *Anal. Sci.*, **17** (supplement), i1241 (2001).

32 T. Kato and T. Fujiyama, *J. Phys. Chem.*, **81**, 1560 (1977).

33 D. Brown and J. H. R. Clarke, *J. Phys. Chem.*, **92**, 2881 (1988).

34 F. P. Cavasino, C. Sbriziolo, and M. L. T. Liveri, *J. Phys. Chem. B*, **102**, 3143 (1998).

35 As $K_P >> \phi_o/\phi_i$, we obtain the concentration of $H_4(tpp)^{2+}$-$(Cl^-)_2$ accumulated in the interfacial phase $[H_4(tpp)^{2+}(Cl^-)_2]_i = K_P[H_4(tpp)^{2+}(Cl^-)_2]/(K_P + (\phi_o/\phi_i)) \fallingdotseq [H_4(tpp)^{2+}(Cl^-)_2]$, where ϕ_o and ϕ_i are the volume fractions of the bulk organic and interfacial phases, respectively.

36 R. D. Lisi, S. Milioto, and R. E. Verrall, *J. Solution Chem.*, **19**, 665 (1990).

37 The f_i value is expressed as follows: $f_i = [Zn(tpp)Cl^-]_i/[Zn(tpp)Cl^-] = K_{Zn(tpp)Cl}/(K_{Zn(tpp)Cl} + (\phi_o/\phi_i))$, where $K_{Zn(tpp)Cl}$ is the partition coefficient of $Zn(tpp)Cl^-$ between the interfacial and bulk organic phases. Under the present experimental conditions, the f_i value of 0.264 is obtained by setting $K_{Zn(tpp)Cl} = 9.44$, $\phi_o = 0.947$ and $\phi_i = 0.0360$, which are estimated from the data of Refs. 14 and 36.

38 S. Funahashi, Y. Yamaguchi, and M. Tanaka, *Bull. Chem. Soc. Jpn.*, **57**, 204 (1984).

39 Y. Inada, Y. Nakano, M. Inamo, M. Nomura, and S. Funahashi, *Inorg. Chem.*, **39**, 4793 (2000).

40 T. Fujiwara, J. Saeki, T. Nakashima, and Y. Okamoto, *Anal. Sci.*, **17** (supplement), i1473 (2001).