

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

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The interaction between the zinc(Ⅱ) complex of 5,10,15,20-tetraphenylporphyrin (Zn(tpp)) and cetyltrimethylammonium chloride (CTAC) at the interface of a CTAC reverse micelle in chloroform and 6:5 (v/v) chloroform–cyclohexane has been investigated spectrophotometrically. The spectra of Zn(tpp) in the CTAC reversed micellar solutions provide evidence of formation of the associated species Zn(tpp)CTAC; its Soret band is not influenced by solvent polarity. At a fixed molar ratio of water to surfactant ($R_w = [H_2O]/[CTAC]$), the absorbance at the maximum of the Zn(tpp)CTAC band increases with an increase in the CTAC concentration. In the slope of the plot a discontinuity was found, due to formation of reverse micelles at this CTAC concentration, taken as the critical micelle concentration (cmc). The variations of the spectral data were interpreted quantitatively by applying the pseudophase model. Increasing R_w causes a decrease in the Zn(tpp)-solubilizing ability of reverse micelles, implying that the nucleophilicity of Cl^- ion to the central zinc of the complex is dropped by the Cl^- hydration at the interface. Furthermore, the standard free energy of micellization, calculated from the cmc data, indicates that the micellization is promoted by the Cl^- hydration and by decreasing the chloroform fraction in the bulk organic phase.

A reverse micelle is a droplet of water surrounded by surfactant molecules dispersed in an organic solvent of low polarity, where their polar groups are concentrated in the inner aqueous core of the aggregate, while their hydrophobic moieties extend into the bulk organic solvent. The water pool, formed by water molecules included in the core of the reverse micelle, provides a unique and versatile reaction field, which is similar to the environment of biological systems, for example, the active sites of enzymes.[1–3] There has been also an increased interest in applications of reverse micelles in analytical methods.[4,5] It has been pointed out that the area with the most applications of reversed micellar media in spectroscopy may be that of analytical bioluminescence or chemiluminescence (CL) measurements.[5] Cetyltrimethylammonium chloride (CTAC) reverse micelles in 6:5 (v/v) chloroform–cyclohexane have been employed as micro-reactors in CL analysis.[5–11] We have developed a flow injection CL analytical method based on the combination of a reversed micellar-mediated CL detection with online solvent extraction.[12–14] Furthermore, the micro-reactor has the capability to transfer the 8-quinolinolatoiron(Ⅲ) complex[7] or the (acetylacetonato)oxovanadium(IV) complex[10] into the water pool easily, although the neutral metal complexes are almost insoluble in conventional aqueous solutions. At the surfactant–water pool interface, which was regarded as significant in the reversed micellar mediated CL reactions of luminol,[11,15] these complexes were observed to be dissociated immediately to catalyze the CL reactions.[7,10] Because an interfacial solubilization of the neutral complexes occurs in the uptake of the complexes by the CTAC reverse micelles into the water pools, it is important to understand the properties of the interface and it is desired to specify the factors governing the uptake processes.

Despite a considerable amount of information about the structure and properties of reverse micelles, very little has been known about the nature and the function of the reversed micellar interface where much chemistry occurs. In our previous work, the change in the polarization of water at the interfacial region in bis(2-ethylhexyl) sodium sulfosuccinate (AOT) reverse micelles was investigated using 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecanenickel(Ⅱ) ion as a probe.[16] The properties of water at the AOT reversed micellar interface and their variation with micelle size were examined with the molecular dynamics (MD) simulation technique.[17] On the other hand, CTAC is a positively charged surfactant, as opposed to AOT. Because of the CTAC headgroups carrying three methyl groups, the reversed micellar interface is a charged hydrocarbon surface, near which there are two competitive forces affecting the water–water hydrogen-bonded network: a breakdown of the network due to the charges and an enhancement due to the hydrophobic surface.[18] The first MD simulation of a reverse micelle, to our knowledge, was carried out by using a simplified model, in which the headgroups are positively charged.[19] In the simulation, the reversed micellar interface was described at the molecular level, although the effects of micelle size on the structural properties of the surfactant cation, counter-ion and water could not be assessed.

The (5,10,15,20-tetraphenylporphyrinato)zinc(II) complex, Zn(tpp) is a useful probe for estimating the local polarity of various media such as vesicles[20] and reverse micelles[21] because its absorption spectrum exhibits a pronounced dependence upon the solvent and donor environment. There have been numerous studies involving the Lewis acid–base interaction between Zn(tpp) and various donors in non-coordinating and nonpolar solvents.[22–24] Experimental evidence supports the fundamental description of the interaction as the following equilibrium: The four-coordinate

$$\mathrm{Zn(tpp)} + \mathrm{L} \rightleftarrows \mathrm{Zn(tpp)L} \quad (1)$$

Zn(tpp) complex accepts only one axial ligand to form a five-coordinate complex, Zn(tpp)L. The intense Soret absorption band shifts to longer wavelength side upon such adduct formation. Various investigators have compared the magnitude of the red shift to several chemical characteristics of the donor.[22–24] In addition, red shifts of the Soret band are generally caused by non-specific interactions or solvation.

Since the neutral Zn(tpp) complex is almost insoluble in water, an interaction between Zn(tpp) and a reverse micelle occurs at the surfactant–water pool interface. In this work, Zn(tpp) has been thus used as an absorption probe to obtain information on the nature of the CTAC reversed micellar interface. We found a discontinuity in the slope of the absorbance vs CTAC concentration plot obtained under a fixed water-to-surfactant molar ratio (R_w = [H_2O]/[Surfactant]) condition. Beyond this CTAC concentration, a reverse micelle is probably formed and Zn(tpp) may be solubilized in its interfacial phase. We apply the pseudophase model[25,26] to examine quantitatively the influences of R_w and bulk organic solvents on the Zn(tpp)-solubilizing ability of the interfacial phase. The solubilizing ability reflects the competition between the hydration of the counter Cl^- ion of CTAC and its interaction with Zn(tpp) at the interface: If the coordination of Cl^- to Zn(tpp) at the interface dominates, an increase in the solubilizing ability will occur. If the Cl^- hydration at the interface dominates, the solubilizing ability will decrease. In addition, the anion hydration may be expected to make a substantial contribution to the stabilization energy of the micelle. In this work, the CTAC micellization energy is estimated by using the phase separation model[27,28] and its variation with R_w is also discussed. The knowledge obtained from this work contributes to our understanding of the properties of the water and ions, and of the interactions between complexes and ions at the reversed micellar interface.

Experimental

The Zn(tpp) complex was purchased from Aldrich Chemical Co., Inc. (Milwaukee, WI, USA). The CTAC surfactant (> 98%) was obtained from Fluka (Buchs, Switzerland). Tetra-*n*-butylammonium chloride (TBAC, ion-pair chromatography grade) was obtained from Tokyo Kasei Kogyo Co., Ltd. (Tokyo, Japan). Chloroform (> 99.7%, stabilized with pentene), cyclohexane, dichloromethane, and 1,2-dichloroethane were of fluorescence reagent grade (Cica-Merck) and were obtained from Kanto Chemical Co., Inc. (Tokyo, Japan). Preliminary experiments confirmed that no concentration effect of pentene on the Zn(tpp) spectrum occurred in the reversed micellar solution. 2-Morpholinoethanesulfonic acid (MES), 2-[4-(2-hydroxyethyl)-1-piperazinyl]ethanesulfonic acid (HEPES), *N*-cyclohexyl-2-aminoethanesulfonic acid (CHES) and *N*-cyclohexyl-3-aminopropanesulfonic acid (CAPS) were purchased from Dojindo Laboratories (Kumamoto, Japan). All chemicals were used without further purification. Deionized water was freshly collected from an Advantec Toyo (Tokyo) Model GSU-901 water purification apparatus and was used in the preparation of all aqueous solutions. A buffer solution (pH 6.0) containing 0.20 mol dm^{-3} MES and 0.08 mol dm^{-3} sodium hydroxide was prepared and used as the dispersed aqueous phase for preparation of the reversed micellar solution. Chloroform and 6:5 (v/v) chloroform–cyclohexane mixture were used as reversed micellar bulk solvents. A stock reversed micellar solution was prepared by dispersing an appropriate amount of the buffer aqueous solution in the reversed micellar bulk solvent containing the CTAC surfactant. By dissolving solid Zn(tpp) in chloroform or the mixed solvent of chloroform–cyclohexane, the stock solution of 1.2×10^{-5} mol dm^{-3} Zn(tpp) was made. Both the stock solutions were prepared daily to avoid chloroform decomposition. Working reversed micellar solutions of various concentrations of CTAC and water in chloroform or chloroform–cyclohexane at a constant R_w were made before use by serial dilution of the stock reversed micellar solution with the bulk solvent and addition of a certain amount of the stock Zn(tpp) solution, so that the Zn(tpp) concentration, calculated on a final volume total solution basis, was 1.2×10^{-6} mol dm^{-3} in the reversed micellar solutions.

To estimate the volume fraction of the bulk organic pseudophase described below, the density was evaluated by weighing 10 cm^3 of the working solution in a volumetric flask just before measuring the absorbance. Visible absorption spectra were recorded on a Shimadzu model UV-2200 double-beam spectrophotometer, equipped with 1.0 cm quartz cells thermostated at 25.0 ± 0.1 °C. The water contents in the CTAC solutions were determined coulometrically using a Hiranuma model AQ-7 aquacounter.

Results and Discussion

Absorption Spectra of Zn(tpp). The B (or Soret) band appears in the absorption spectrum of Zn(tpp) and is strongly solvent-dependent; in chloroform, the absorption maximum at 418.8 nm with a molar absorptivity of 6.25×10^5 dm^3 mol^{-1} cm^{-1} is observed: (a), shown in Fig. 1. When cetyltrimethylammonium chloride (CTAC) was added to the chloroform solution of Zn(tpp), the peak of Zn(tpp) at 418.8 nm decreased and a new peak at 432.6 nm appeared. In a comparative study with addition of CTAC, no change in the B band was observed for the (5,10,15,20-tetraphenylporphyrinato)copper(II) complex, which is expected to serve as a probe of detecting only non-specific interactions or solvation. Thus, the new band at 432.6 nm may be attributed to a specific interaction of Zn(tpp) with the counter Cl^- ion of CTAC, that is, to formation of the chloro-coordinated complex, Zn(tpp)Cl^-. The absorbance of this band reached a maximum with a molar absorptivity of 5.98×10^5 dm^3 mol^{-1} cm^{-1} around 1.3 mol dm^{-3} CTAC, (b) in Fig. 1, indicating that Zn(tpp)Cl^- was fully formed. An isosbestic point between the two peaks was obtained at 425.8 nm as the CTAC concentration increased. This implies the presence of only two spectroscopically different species, Zn(tpp) and Zn(tpp)Cl^-, dynamically in equilibrium in this medium. A similar change in the spectrum of Zn(tpp) was observed with the addition of tetra-*n*-butylammonium chloride, TBAC, to the

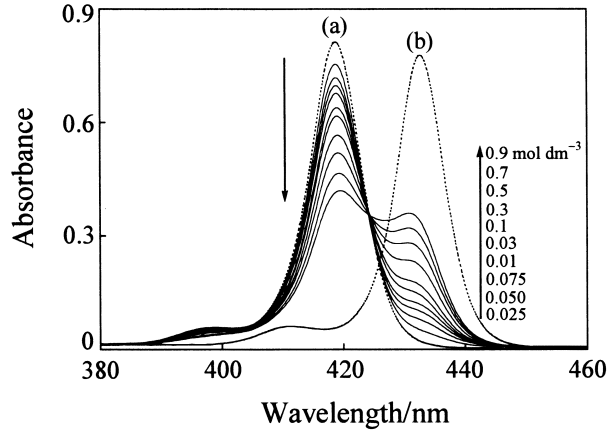

Fig. 1. Variation in the visible spectra of Zn(tpp) with CTAC concentration in the chloroform/CTAC/water system at R_w = 4. (a), Zn(tpp); (b), Zn(tpp)CTAC.

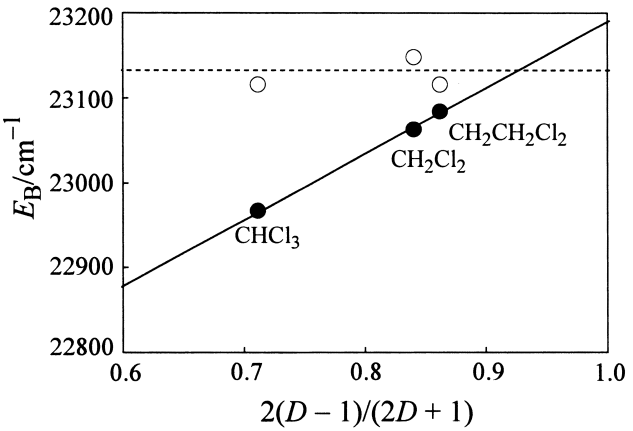

Fig. 2. Plots of the B band energy against the Onsager solvent polarity function of different solvents for Zn(tpp)-CTAC (○) and Zn(tpp)TBAC (●).

Zn(tpp) solution. In the limit (around 1.5 mol dm^{-3} TBAC), the spectrum is identical with that obtained in the 1.3 mol dm^{-3} CTAC solution but has a shift of 2.8 nm to the red, showing that it should be assigned to the Zn(tpp)Cl$^-$ species with a microenvironment different from that provided by the CTAC medium.

Such differences in the B band of Zn(tpp)Cl$^-$ between CTAC and TBAC media were also observed using other solvents. Figure 2 shows the plots of the B band energy, E_B of Zn(tpp)Cl$^-$ vs the Onsager solvent polarity function $f(D) = 2(D-1)/(2D+1)$,[29,30] where D is the dielectric constant of the solvent. A series of three selected solvents: chloroform, dichloromethane and 1,2-dichloroethane, have large variations in dielectric constants and small changes in their refractive indices. As shown in Fig. 2, the E_B of Zn(tpp)Cl$^-$ with TBAC increases linearly with $f(D)$, indicating that the Zn(tpp)Cl$^-$ complex is solvated enough to be influenced by solvent polarity. With CTAC, on the other hand, the E_B plot does not show such a dependence on $f(D)$. This may be explainable if it is assumed that an ion pair of Zn(tpp)Cl$^-$ with the positively charged surfactant (cetyltrimethylammonium, CTA$^+$) is the predominant entity in such low polar solvents, and if the CTA$^+$ removes solvents from Zn(tpp)Cl$^-$. The larger solvent removal effect of CTA$^+$ than that of tetra-*n*-butylammonium ion seems to be attributed to the predominant dispersion interaction of its longer hydrocarbon chain with the porphyrin ring. To denote this associated species, Zn(tpp)CTAC is used here. From Fig. 2, it should be predictable that Zn(tpp) in the associated species is in an apparently higher-polar microenvironment compared to the TBAC solutions; for the microenvironment provided by the polar CTAC molecule, the apparent dielectric constant of 18.5 is estimated from an intersection of the lines given by the E_B vs $f(D)$ plots with CTAC and TBAC.

When water was added to the CTAC solutions of Zn(tpp) at a fixed molar ratio R_w (= 4), interesting spectral changes were observed, as shown in Fig. 1. An isosbestic point at 424.2 nm was obtained, but it is different from that (λ_{iso} = 425.8 nm) obtained in the absence of water in the CTAC solution. Thus, it is necessary to consider another minor band between the two main absorptions, although only a valley is observed in the experimental spectrum. The existence of this band can be confirmed by varying R_w. The isosbestic point shifts to shorter wavelengths as R_w is increased: e.g., λ_{iso} = 425.4 nm at R_w = 1; λ_{iso} = 423.4 nm at R_w = 8. On the basis of such shifts, the minor band may be assigned to the formation of the water-coordinated complex, Zn(tpp)(H_2O). When Zn(tpp) was dissolved in the water-saturated chloroform, a band at 424.0 nm (shoulder) appeared and the spectrum obtained by subtracting the Zn(tpp) spectrum in water-free chloroform, both normalized at 418.8 nm, could be assigned to Zn(tpp)(H_2O). Nagatani and Watarai reported the interfacial adsorption behavior of several metal complexes of 5,10,15,20-tetraphenylporphyrin at the dodecane/water interface and the preferential formation of Zn(tpp)(H_2O).[31] Its structure has been further confirmed in the solid state.[32] Thus, it seems likely that Zn(tpp)(H_2O) is formed in the reversed micellar interface. Furthermore, the pH in the reversed micellar water pool at R_w = 4 was changed in the range of 2 to 13 using sulfuric acid, sodium hydroxide and various Good's buffers such as MES, HEPES, CHES and CAPS. In the pH range 2–6.5, no significant spectral change was observed, while an increase in pH from 6.5 to 13 caused a significant increase in absorbance at 428.8 nm without any isosbestic point. Almost the same behavior in the spectral change with pH was observed using all the other buffers. These observations imply that at higher pH the hydroxide ion is coordinated to Zn(tpp), likely at the interface. Nappa and Valentine have concluded that the red shifts of the B band are principally correlated with the charge and polarizability of the axial ligands and their resulting ability to transfer charge to the porphyrin ring via the zinc atom.[24] Accordingly, the observed red shift, Zn(tpp) (418.8 nm) < Zn(tpp)(H_2O) (424.0 nm) < Zn(tpp)OH$^-$ (428.8 nm) < Zn(tpp)Cl$^-$ (432.6 nm), is evidence for increases in charge and polarizability which are responsible for the order of H_2O < OH$^-$ and OH$^-$ < Cl$^-$, respectively. In this work, the pH was kept at 6.0 using the MES buffer throughout the experiment to minimize the Zn(tpp)OH$^-$ formation effect. Under a fixed R_w and fixed pH conditions, the appearance of the isosbestic point (Fig. 1) indicates that the molar ratio of Zn(tpp)CTAC:Zn(tpp)(H_2O):Zn(tpp)OH$^-$ is kept constant. In the spectra obtained under the conditions used, the absorbances of Zn(tpp)(H_2O) and Zn(tpp)OH$^-$ made

negligibly small contributions to the absorption maxima of the Zn(tpp) and Zn(tpp)CTAC bands.

Interactions between Zn(tpp) and CTAC in a Reversed Micellar System. Figure 3 shows the changes in the absorbances at the maximum wavelengths of Zn(tpp) and Zn(tpp)CTAC as a function of CTAC concentration at a fixed R_w (= 4). A discontinuity in the slope of each curve is found at about 0.01 mol dm^{-3} CTAC concentration: Until the CTAC concentration in solution reaches this value, the absorbance of Zn(tpp)CTAC is increased rapidly with an increase in the amounts of CTAC, while on further addition of CTAC to the solution, it rises gradually. Beyond this concentration, referred to as the critical micelle concentration (cmc), reverse micelles may be formed. This finding may be taken as an indication of occurrence of the interfacial solubilization of Zn(tpp) as this behavior may arise by interaction between Zn(tpp) and CTAC at the reversed micellar interface or a displacement of Zn(tpp)CTAC from the bulk organic to the interfacial regions.

For interpreting the observed variation of the spectral data with the CTAC concentration, an important basis may be provided by the pseudophase model.[25,26] With this model (Fig. 4), the reversed micellar system is assumed to be divided into

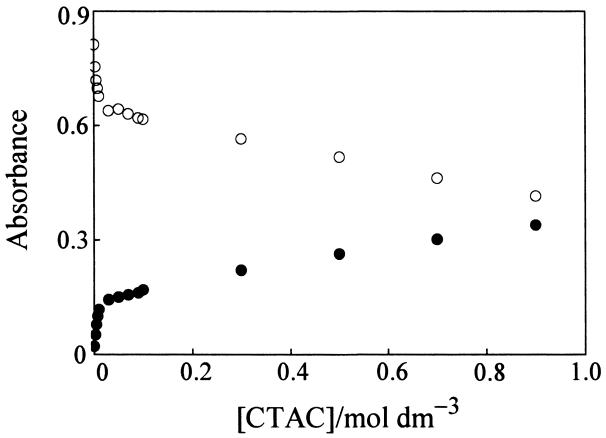

Fig. 3. Variations of absorbances of Zn(tpp) at 418.8 (○) and 432.6 (●) nm with CTAC concentration in the chloroform/CTAC/water system at R_w = 4.

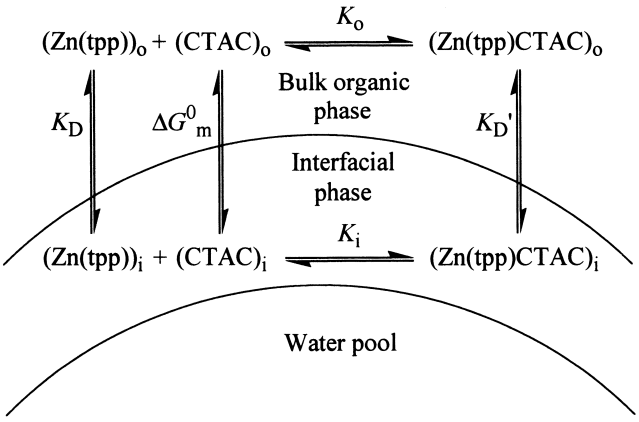

Fig. 4. Schematic representation of the interactions between Zn(tpp) and CTAC in a reversed micellar system.

three phases corresponding to the bulk organic region (o), the surfactant interfacial region (i), the water pool (w), each of which is considered as being uniformly distributed in the total volume of the reversed micellar solution. The volume fractions of these pseudophases can be estimated by Eqs. 2–4:[25,26]

$$\phi_o = V_o[\text{Solvent}] \quad (2)$$

$$\phi_i = V_i[\text{CTAC}]_i \quad (3)$$

$$\phi_w = 1-(\phi_o + \phi_i) \quad (4)$$

where V_o is the molar volume (dm^3 mol^{-1}) of the bulk organic solvent and V_i may be considered either the molar volume of micellized CTAC or an "effective" volume[33] (per mole of CTAC) of interfacial pseudophase. $[\text{CTAC}]_i$ is the micellized CTAC concentration; $[\text{CTAC}]_i = [\text{CTAC}]_{total}-[\text{CTAC}]_o$, where $[\text{CTAC}]_{total}$ is the total CTAC concentration and $[\text{CTAC}]_o$ is the concentration of CTAC monomer dispersed in bulk organic phase. The concentrations in square brackets refer to the total volume of reversed micellar solution.

In view of the solubility characteristics of Zn(tpp), its amount in the water pool may be neglected compared with those in the other phases. Thus, the distribution equilibrium of Zn(tpp) between the interfacial and the bulk organic phases is given by the following partition coefficient, and in the bulk

$$K_D = \frac{[\text{Zn(tpp)}]_i/\phi_i}{[\text{Zn(tpp)}]_o/\phi_o} \quad (5)$$

organic and interfacial phases, the respective formation constants of Zn(tpp)CTAC are given by the following expressions: Above cmc, the local CTAC concentration $[\text{CTAC}]_o/\phi_o$ in the bulk organic phase

$$K_o = \frac{[\text{Zn(tpp)CTAC}]_o}{[\text{Zn(tpp)}]_o([\text{CTAC}]_o/\phi_o)} \quad (6)$$

$$K_i = \frac{[\text{Zn(tpp)CTAC}]_i}{[\text{Zn(tpp)}]_i([\text{CTAC}]_i/\phi_i)} \quad (7)$$

may be saturated with the CTAC monomer and remain a constant value C_S. Thus, the distribution equilibrium of Zn(tpp)-CTAC between the two pseudophases is also expressed by $K_D' = K_DK_i/K_oC_SV_i$.

Since the spectrum of Zn(tpp)CTAC is almost independent of solvent polarity, probably due to the solvent removal effect of CTAC, as mentioned above, the associated species $(\text{Zn(tpp)CTAC})_o$ and $(\text{Zn(tpp)CTAC})_i$ present in the bulk organic and interfacial phases, respectively, can be regarded as the spectroscopically identical species. On the contrary, shifts of the respective spectra of $(\text{Zn(tpp)})_o$ and $(\text{Zn(tpp)})_i$ in the bulk organic and interfacial phases may be expected to occur according to their distinct environments, e.g., as λ_{max} = 418.8 nm in chloroform and λ_{max} = 416.6 nm in dodecane.[31] As shown in Fig. 1, however, the spectrum of the Zn(tpp) species (λ_{max} = 418.8 nm) in the reversed micellar solution is practically identical to that in a homogeneous solution of chloroform. This indicates that the concentration of $(\text{Zn(tpp)})_i$ is negligibly small as compared to that of $(\text{Zn(tpp)})_o$ and thus the total concentration $[\text{Zn(tpp)}]_{total}$ is nearly equal to $[\text{Zn(tpp)}]_o$. As

$[Zn(tpp)CTAC]_{total} = [Zn(tpp)CTAC]_o + [Zn(tpp)CTAC]_i$, the concentration ratio of Zn(tpp)CTAC to Zn(tpp) is obtained by using Eqs. 2–7 as follows:

$$\frac{[Zn(tpp)CTAC]_{total}}{[Zn(tpp)]_{total}} = K_D K_i \frac{[CTAC]_{total}}{\phi_o} + C_s(K_o - K_D K_i). \quad (8)$$

Below cmc or C_S, on the other hand, the following expression is obtained by using Eq. 6 alone, since reverse micelles are absent and thus $[CTAC]_o = [CTAC]_{total}$.

$$\frac{[Zn(tpp)CTAC]_{total}}{[Zn(tpp)]_{total}} = K_o \frac{[CTAC]_{total}}{\phi_o} \quad (9)$$

Since the absorbances are the sums of the contributions of Zn(tpp) and Zn(tpp)CTAC at the respective main bands, the total concentration ratio can be obtained from the spectral data using the respective molar absorptivities of Zn(tpp) and Zn(tpp)CTAC.

When the $[Zn(tpp)CTAC]_{total}/[Zn(tpp)]_{total}$ ratios are plotted as a function of $[CTAC]_{total}/\phi_o$ for the chloroform/CTAC/water system, indeed straight lines denoted by (a) and (b) in Fig. 5, corresponding to the respective regions above and below C_S, are obtained with the slopes $K_D K_i$ and K_o, respectively, as predicted by Eqs. 8 and 9. Also, the intersection of the lines (a) and (b), i.e., C_S, is calculated from the values of $K_D K_i$, K_o, and the intercept of the plot (a), $C_S(K_o - K_D K_i)$. Table 1 assembles the data obtained with both the chloroform/CTAC/water and 6:5 (v/v) chloroform–cyclohexane/CTAC/water systems, providing support to the validity of the pseudophase model and the equilibrium treatment employed in this work.

As seen in Table 1, an increase in R_w causes only a slight change in K_o, implying that the Cl^- ion of CTAC in bulk organic phase is negligibly hydrated. The K_o values in the 6:5 (v/v) chloroform–cyclohexane/CTAC/water system were about 6 times larger than those in the chloroform/CTAC/water system, implying that lowering the chloroform fraction in the bulk solvent increases the affinity of CTAC for Zn(tpp). This may be also attributed to the high solvation ability of chloroform toward the Cl^- ion and Zn(tpp). It was concluded that CTAC

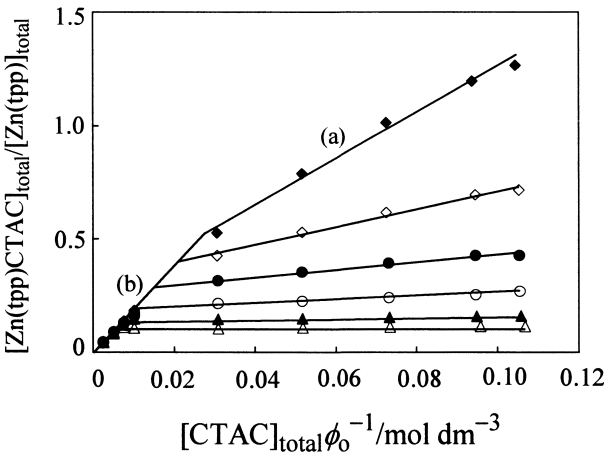

Fig. 5. Plots of $[Zn(tpp)CTAC]_{total}/[Zn(tpp)]_{total}$ against $[CTAC]_{total}/\phi_o$ in the chloroform/CTAC/water system at R_w = 1 (◆), 2 (◇), 3 (●), 4 (○), 6 (▲), and 8 (△). Straight lines (a) and (b) are predicted by Eqs. 8 and 9, respectively.

dissolves in chloroform by forming hydrogen bonds with several chloroform molecules.[34] In gas phase, the hydrogen bonding between a chloroform molecule and a Cl^- ion has been also confirmed.[35] The Cl^- solvation, probably due to the considerable acidity of chloroform (acceptor number, AN = 23.1[36,37]), leads to masking the nucleophilicity of the Cl^- ion to Zn(tpp). In addition, the hydrogen bonding between chloroform and nitrogen heterocycles of Zn(tpp) has been queried.[22] The access of chloroform molecules also hinders the Cl^- attack on the central metal of Zn(tpp).

The $K_D K_i$ values may be used as a measure of the Zn(tpp)-solubilizing ability of the interfacial phase, although we cannot obtain any information about the partition coefficient K_D. Assuming that the penetration of Zn(tpp) into the interfacial region, i.e., K_D is not appreciably affected by R_w, we can reasonably consider the variation of $K_D K_i$ to be due to a change in K_i with R_w. The MD simulation for a cationic surfactant reverse micelle reveals that there is anion distribution in the interfacial phase and that penetration of water into the region is caused by

Table 1. Parameters Obtained by Applying the Pseudophase Model for Reversed Micellar Solutions of CTAC in Chloroform/Water and 6:5 (v/v) Chloroform–Cyclohexane/Water at Various R_w (t = 25 °C)

R_w	K_o[a]/dm^3 mol^{-1}	$K_D K_i$[b]/dm^3 mol^{-1}	$C_s(K_o - K_D K_i)$[c]	C_s/mmol dm^{-3}	$\Delta G°_m$[d]/kJ mol^{-1}
			Chloroform/CTAC/water		
1	18.4 ± 0.1	10.6 ± 0.6	0.22 ± 0.04	28.3	−15.1
2	17.1 ± 0.2	4.2 ± 0.2	0.30 ± 0.02	23.6	−15.5
3	16.6 ± 0.4	1.76 ± 0.06	0.260 ± 0.004	17.6	−16.3
4	15.0 ± 0.6	0.67 ± 0.01	0.189 ± 0.001	13.1	−17.0
6	14.7 ± 0.9	0.246 ± 0.005	0.1349 ± 0.0004	9.36	−17.8
8	13 ± 1	0.1956 ± 0.0005	0.09769 ± 0.00003	7.73	−18.3
			6:5 (v/v) Chloroform–cyclohexane/CTAC/water		
1	102 ± 1	21.0 ± 0.9	0.89 ± 0.06	11.0	−17.1
2	100 ± 3	5.1 ± 0.1	0.487 ± 0.005	5.16	−19.0
3	96 ± 2	1.751 ± 0.007	0.2662 ± 0.0005	2.81	−20.5
4	93 ± 2	0.940 ± 0.004	0.1416 ± 0.0003	1.53	−22.0

a) Slope (Eq. 9). b) Slope (Eq. 8). c) Intercept (Eq. 8). d) Calculated using Eq. 10 with the V_o values of 0.0802 and 0.0909 dm^3 mol^{-1} for chloroform and 6:5 (v/v) chloroform–cyclohexane, respectively (see text).

the anion hydration.[19] Thus, a significant decrease in K_i with increasing R_w may be ascribed to an increase in hydration number of the Cl^- ion at the interface as nucleophilic attack of the Cl^- ion to Zn(tpp) is hindered by the hydration. The quantity $K_D K_i$ in the chloroform system is slightly smaller than that in the 6:5 (v/v) chloroform–cyclohexane system at each R_w. This observation may be connected with the variation of K_D with the chloroform fraction in the bulk solvent. The solvation of Zn(tpp) by chloroform appears to suppress the penetration of Zn(tpp) into the interfacial region.

Standard Free Energy of Micellization. The free energy change for the transfer of 1 mol of surfactants from ideal solution to the micellar phase, referred to as the standard free energy of micellization, $\Delta G°_m$, is given by the following expression[27,28] assuming that the phase separation

$$\Delta G°_m = RT \ln (X_S) \quad (10)$$

model (equilibrium between monomers and micelles) is an adequate representation in the CTAC micellizations at various R_w. In Eq. 10, R is the gas constant, T is the absolute temperature and X_S is the C_S expressed in mole fraction units, i.e., $X_S = V_o C_S/(1 + V_o C_S)$. By assuming the additivity of the molar volumes of chloroform and cyclohexane, the chloroform to cyclohexane volume ratios in the bulk solvents dictate the V_o values, which are 0.0802 and 0.0909 $dm^3\ mol^{-1}$ for chloroform and 6:5 (v/v) chloroform–cyclohexane mixture, respectively. As given in Table 1, all the $\Delta G°_m$ values are negative, indicating that thermodynamically stable micelles are formed spontaneously by CTAC in chloroform and in its mixture with cyclohexane. In Fig. 6, the data of $\Delta G°_m$ are plotted against R_w, showing that the $\Delta G°_m$ values decrease linearly with increasing R_w in both the systems. From the intercept of this plot, the standard free energy $\Delta G°_{m0}$ at $R_w = 0$ can be evaluated for the micellization or formation of CTAC aggregates in the absence of water; the $\Delta G°_{m0}$ values of -14.1 and -16.0 kJ mol^{-1} corresponding to the cmc values $X_S = 0.0034$ and 0.0016 were obtained for the chloroform and 6:5 (v/v) chloroform–cyclohexane systems, respectively. For the CTAC surfactant in the water-free chloroform using a light scattering method without use of any probe, Kato and Fujiyama have reported the cmc value $X_S = 0.003$,[38] which is in good agreement with the cmc value of 0.0034 mole fraction obtained in this work. In addition, it has been noted that the formation of micelles of cetyltrimethylammonium bromide in dichloromethane is favored in the presence of a porphyrin compound.[39] However, this agreement indicates that such a contribution to micellar stabilization energy that comes from the binding of Zn(tpp) to CTAC micelles should be negligible as the Zn(tpp) concentration (1.2×10^{-6} mol dm^{-3}) used is too low to affect the micellization. In fact, we confirmed no change in the cmc caused by reducing the Zn(tpp) concentration to half the concentration. It has been pointed out that the aggregation of surfactants in low polar solvents is hindered by solvent–surfactant interactions.[40] The $\Delta G°_{m0}$ values obtained here indicate a lowering of the micellar stabilization in the chloroform system compared to the 6:5 (v/v) chloroform–cyclohexane system. The increased solvation of CTAC by chloroform may lead to suppressing the transfer of CTAC from the bulk phase to the micellar phase.

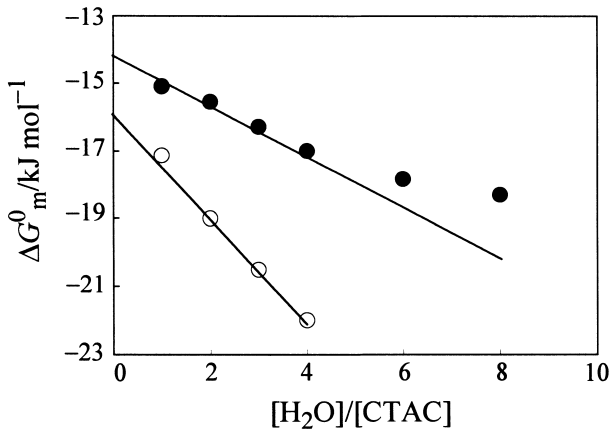

Fig. 6. Variations of the standard free energy of micellization with R_w in the chloroform/CTAC/water (●) and 6:5 (v/v) chloroform–cyclohexane/CTAC/water (○) systems.

The slope ($\Delta\Delta G°_m$) of the plot shown in Fig. 6 corresponds to the micellar stabilization energy gained by increasing the mole of water molecule per CTAC molecule or Cl^- ion; $\Delta\Delta G°_m$ of -0.72 and -1.5 kJ mol^{-1} are obtained for the chloroform/CTAC/water and 6:5 (v/v) chloroform–cyclohexane/CTAC/water systems, respectively. It has been noted that the presence of traces of water is critical to the formation of surfactant aggregates and that the water molecules can bridge the surfactant headgroups through hydrogen bonding.[40] However, hydrogen bonding between the water molecules and the CTA^+ headgroup is unlikely since the headgroup carries hydrocarbon groups as mentioned above. In the MD simulation study,[19] it has been suggested that an anion hydration effect may have some relevance to the role of cosurfactants in stabilizing micelle formation. This is supported by the present results indicating that the micelle formation is promoted by the Cl^- hydration, which should be enhanced with increasing R_w. Furthermore, decreasing the chloroform fraction in the reversed micellar bulk solvent causes an increase in the absolute value of $\Delta\Delta G°_m$, that is, the micellar stabilization energy gained. This may be relevant to a difference in the activity of water at the interface between these systems explained by assuming the inward migration of chloroform into the interfacial region and its interaction with water in the region. In addition, it is interesting to note that the linear plot for the chloroform/CTAC/water system breaks at R_w of around 5. Recently, the infrared spectra recorded by vibrational predissociation spectroscopy for the gas-phase anionic clusters of $Cl^-(H_2O)_n$ provided evidence of water–water hydrogen-bonding networks in $n = 4$ and 5, while for $n = 2$ and 3, Cl^- ion is hydrated without hydrogen bonding between the waters.[41] Up to $n = 4$, no break in the stepwise hydration enthalpies of the $Cl^-(H_2O)_n$ clusters was observed by using high-pressure mass spectrometer.[42] Therefore, with an assumption that the structure formed by water molecules about the Cl^- ion at the reversed micellar interface closely resembles that in the gas-phase clusters, the break in the $\Delta G°_m$ vs R_w plot may be related to the occurrence of water–water hydrogen-bonding in competition with the Cl^- hydration at the interface, although further investigations are required to clarify this phenomenon.

Conclusions

The absorption spectra of Zn(tpp) in the CTAC solutions provide evidence of the Zn(tpp)CTAC formation, due to an interaction between Zn(tpp) and the counter Cl^- ion of CTAC. In the slope of the absorbance plot against the CTAC concentration at a fixed R_w, a discontinuity appears at a concentration corresponding to cmc. It is demonstrated that, in the CTAC reversed micellar system, the process of the interfacial solubilization of Zn(tpp) may involve the Zn(tpp) distribution between the bulk organic and the interfacial phases, and the subsequent Zn(tpp)CTAC formation at the interface. By increasing R_w, a decrease in the Zn(tpp)-solubilizing ability of the interfacial phase is caused, probably due to the Cl^- hydration effect at the interface. Furthermore, the standard free energy of micellization was evaluated from the cmc data at each R_w value, and it was confirmed that the cmc value obtained for the CTAC surfactant in the water-free chloroform in this work was in good agreement with the previously reported value determined by a light scattering method without use of any probe. The micellization is promoted by an increase in the water ratio R_w and a decrease in the chloroform fraction in the reversed micellar bulk solvent, implying that an enhancement of anion hydration and poor solvation of CTAC may be essential for the micellar stabilization.

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