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Interactions between an Anionic Porphyrin and Cationic Surfactants in Water

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Interactions between decyl-, dodecyl-, and tetradecyltrimethylammonium bromide (DeTAB, DTAB, and TTAB) and an anionic porphyrin, 5,10,15,20-tetrakis(4-sulfonatophenyl)porphine (H_2TPPS^{4-}), have been studied in water at 298.2 K. Precipitate formation constants between the surfactant cations and the H_2TPPS^{4-} anion have been obtained. The precipitates were resolubilized by a further addition of the surfactants at concentrations close to the critical micelle concentrations (cmc) in DeTAB, and below the cmc's in DTAB and TTAB solutions. Surface tension and conductance measurements show that the effects of H_2TPPS^{4-} on the cmc's are very small. The fluorescence of H_2TPPS^{4-} is quenched in both water and sodium dodecyl sulfate solutions by the methylviologen cation, but not in cationic surfactant solutions. The diffusion coefficients were measured in a system containing H_2TPPS^{4-} and TTAB; the results show the existence of large premicellar aggregates.

Because of their importance in biological and photochemical processes, porphyrins and metalloporphyrins have attracted much interest. Recently, water-soluble porphyrins have been shown to interact with 1,10-phenanthroline (phen) and pyridine derivatives,[1] amino acids,[2] and other ionic species.[3] Dimerization[4] and counterion-induced dimerization[5] of cationic and anionic porphyrins have been studied. Photoinduced electron-transfer and charge-separation processes have been studied extensively in microheterogeneous solutions including micelles and vesicles.[6–8] To understand these processes, an elucidation of the interactions of porphyrins with surfactants is essestial. Although there have been studies on the interactions between water-soluble porphyrins and polymers,[9,10] there have been no systematic studies on the interactions between ionic porphyrins and surfactants.

We report here on the interactions between an anionic porphyrin, 5,10,15,20-tetrakis(4-sulfonatophenyl)porphine (H_2TPPS^{4-}), and cationic surfactants in water. In acidic solutions, the predominant species of the porphyrin is H_4TPPS^{2-};[4b,9a] it tends to aggregate.[4a,4b] We have studied systems where H_2TPPS^{4-} is the predominant species. Measurements were made on precipitate formation and resolubilization concentrations, surface tension, conductance, fluorescence quenching , and diffusion coefficient. In a previous paper, we reported interactions between a metal chelate cation, $[Fe(phen)_3]^{2+}$, and anionic surfactants.[11] The present results are compared with the previous ones.

Experimental

Materials and Preparation of Solutions. H_6TPPS (Tokyo Kasei, specially prepared analytical reagent), sodium dodecyl sulfate (NaDS) (BDH, 99.0%), decyltrimethylammonium bromide (DeTAB), dodecyltrimethylammonium bromide (DTAB), and tetradecyltrimethylammonium bromide (TTAB) (Tokyo Kasei, guaranteed reagents) were used as received. Water was distilled twice. A stock solution of H_2TPPS^{4-} was prepared by neutralizing the H_6TPPS solution with NaOH. This solution was used to prepare buffered and nonbuffered solutions of the desired concentrations. The absence of H_4TPPS^{2-} was checked by the absorption spectrum, which showed a maximum at 413 nm, but no peak at 434 nm at the Soret bands.[12] Metalloporphyrin solutions were prepared by adding a trace amount of $Cd(NO_3)_2$ to the solution of H_2TPPS^{4-} as a catalyst,[13] and then adding equivalent amounts of the respective metal ions. The porphyrin and metalliporphyrin solutions were protected from light.

Measurements. All measurements were made at 298.2 K. For determining precipitate formation and the resolubilization concentrations, solutions of both H_2TPPS^{4-} and an alkyltrimethylammonium bromide were placed in a water thermostat controlled to ±0.1 K. After temperature equilibration, solutions of H_2TPPS^{4-} and the surfactant were mixed and replaced in the bath. The solubilization limit was determined by observing the presence or absence of precipitates, or turbidity. The absorption and fluorescence spectra were measured by using a Hitachi 228A spectrophotometer and a Hitachi F-2000 fluorescence spectrophotometer, respectively. The surface tensions of surfactant solutions were measured by using a De Nouy-type tensiometer (Furukawa Seisakusho). The solution conductivities were measured at 5 kHz by means of a linear-bridge conductometer (Huso Model 360 B) in an oil thermostat controlled to ±0.005 K.[11]

The diffusion coefficients were measured by the Taylor dispersion method.[14] In this method a small amount of solution is injected into a solvent flowing through a capillary tube. The solute is dispersed along the tube. From the concentration profile at the end of the tube the difussion coefficient can be calculated. For tracer diffusion measurements, the solvent flowing through the capillary contained a specified amount of TTAB; the injected solution contained the same amount of TTAB and 10 μM ($1\ M=1\ mol\ dm^{-3}$) H_2TPPS^{4-}. Because the H_2TPPS^{4-} concentration was well below that of TTAB, the diffusion coefficient could be taken as the tracer diffusion coefficient. (Note that the concentration of the solute is further diluted as it flows through the capillary tube.) For interdiffusion between metalloporphyrins, the solvent flowing through the capillary contained a specified amount of TTAB and 50 μM $[Mn^{III}\text{-(tpps)}]^{3-}$; the injected solution contained the same amount of TTAB as the solvent and 50 μM $[M^{II}(\text{tpps})]^{4-}$, where M stands for Cu or Ni. This was possible because $[Mn^{III}(\text{tpps})]^{3-}$ has a weak absorption at 413 nm where $[Ni^{II}(\text{tpps})]^{4-}$ and $[Cu^{II}(\text{tpps})]^{4-}$ have an intense absorption. The concentration profile of the metalloporphyrin was monitored by spectrophotometric detectors, either Waters-490 or UVIDEC 100-IV. Other details concerning the measurements have been described.[11,15]

Results and Discussion

Precipitate Formation and Resolubilization. When a cationic surfactant was added to a fixed concentration of H_2TPPS^{4-}, a precipitate appeared, which was then resolubilized by a further addition of the surfactant. Figure 1 shows a phase diagram for precipitate formation and resolubilization for TTAB. Regions A and C correspond to clear solutions and region B corresponds to turbid (two-phase) systems. A similar phase diagram has been shown for the $[Fe(phen)_3]^{2+}$–DS^- system.[16] In an ammonium buffer (pH=8.0, I (ionic strength) =0.1 M), precipitate formation concentrations were larger and the resolubilization concentrations lower than in water. Figure 2 shows the effect of the surfactant chain length. With increasing surfactant chain length, both precipitate formation and resolubilization concentrations decrease. In Figs. 1 and 2, the cmc's of the surfactants determined from surface tension measurements are shown. For DTAB and TTAB, the resolubilization of the precipitate occurs at surfactant concentrations below their cmc's. This will be discussed later; we first examine the precipitate formation process. The precipitate formation reaction may be written as

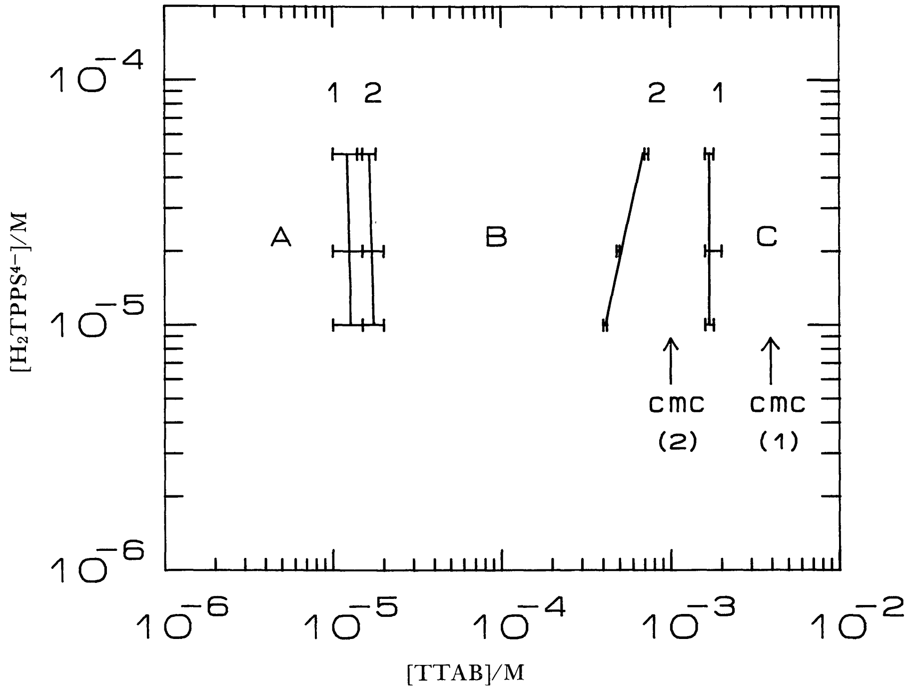

Fig. 1. Phase diagram for the precipitate formation and resolubilization for H_2TPPS^{4-} and TTAB at 298.2 K. Regions A and C correspond to the one-phase clear solutions and region B corresponds to the two-phase system. 1, In water (without added salt); 2, in ammonium buffer (pH=8.0, I=0.1 M). Arrows indicate cmc's of TTAB in water and in the ammonium buffer.

Table 1. Values of log K for the Precipitate Formation Reaction between C_nTA^+ and H_2TPPS^{4-} (Eq. 1) in Water at 298.2 K

Surfactant	log K		
	I=0.1 M[a]	No added salt	No added salt[b]
$C_{10}TAB$	18.19±0.12	19.82±0.17	13.37±0.36
$C_{12}TAB$	20.49±0.15	21.83±0.21	18.13±0.19
$C_{14}TAB$	23.71±0.38	24.32±0.45	22.20±0.34

a) Ammonium buffer (pH=8). b) The values for the reaction between C_nTA^+ and $[Fe(bpso)_3]^{4-}$ (Ref. 17).

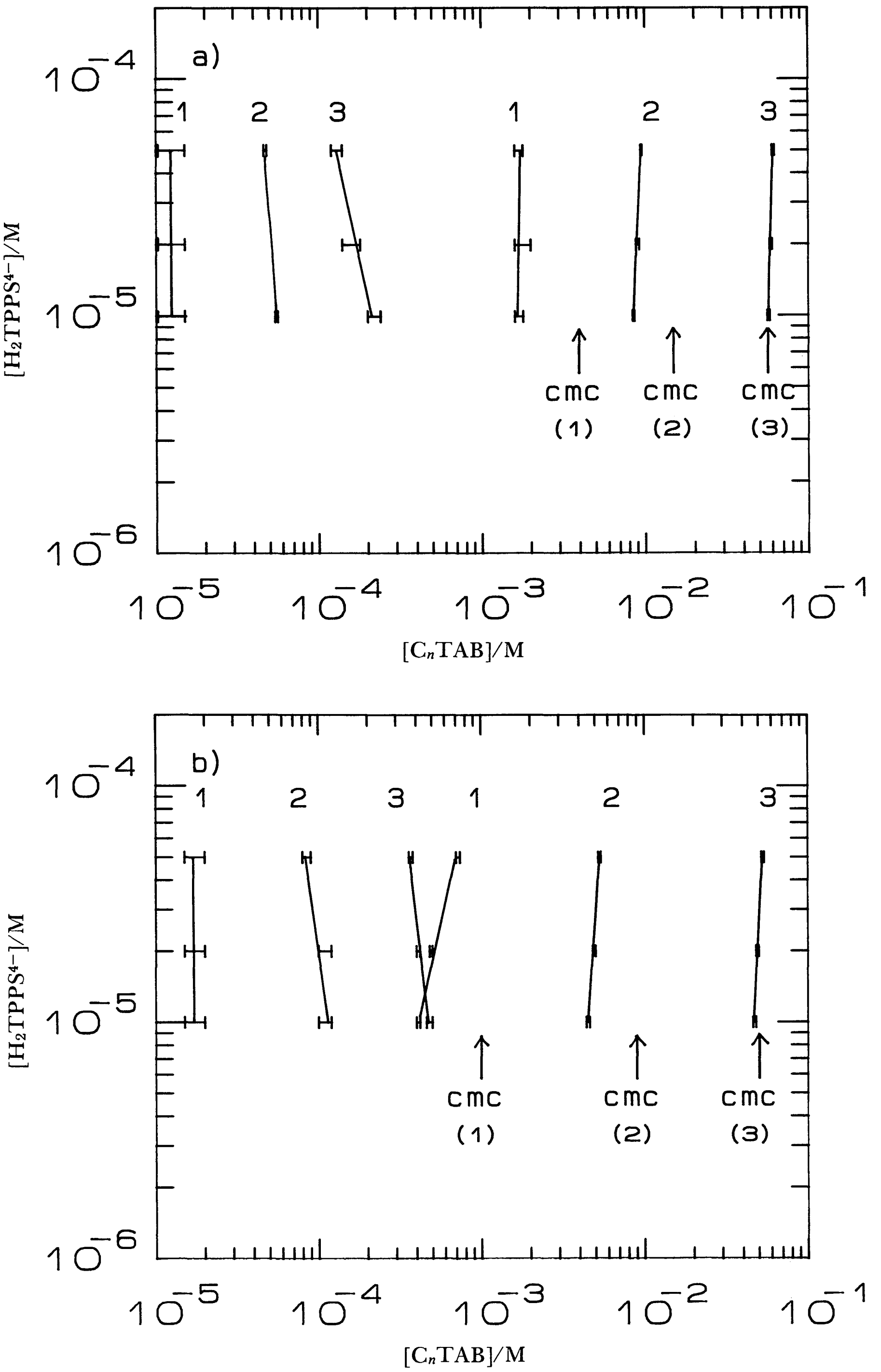

Fig. 2. Phase diagram for the precipitate formation and resolubilization for H_2TPPS^{4-} and TTAB (1), DTAB (2), and DeTAB (3) in water (without added salt) (a), and in ammonium buffer (pH=8.0, I=0.1 M) (b) at 298.2 K. Arrows indicate cmc's of the respective surfactants.

$$4C_nTA^+ + H_2TPPS^{4-} \overset{K}{\rightleftharpoons} (C_nTA)_4\cdot H_2TPPS, \qquad (1)$$

where C_nTA^+ stands for $DeTA^+$ (n=10), DTA^+ (n=12), or TTA^+ (n=14), and $K=1/\{[C_nTA^+]^4[H_2TPPS^{4-}]\}$.

Table 1 lists the values of log K. The standard Gibbs energy of transfer from the aqueous state to the solid state can be calculated as

$$\Delta G^\circ_{aq\rightarrow solid} = -RT\ln K, \qquad (2)$$

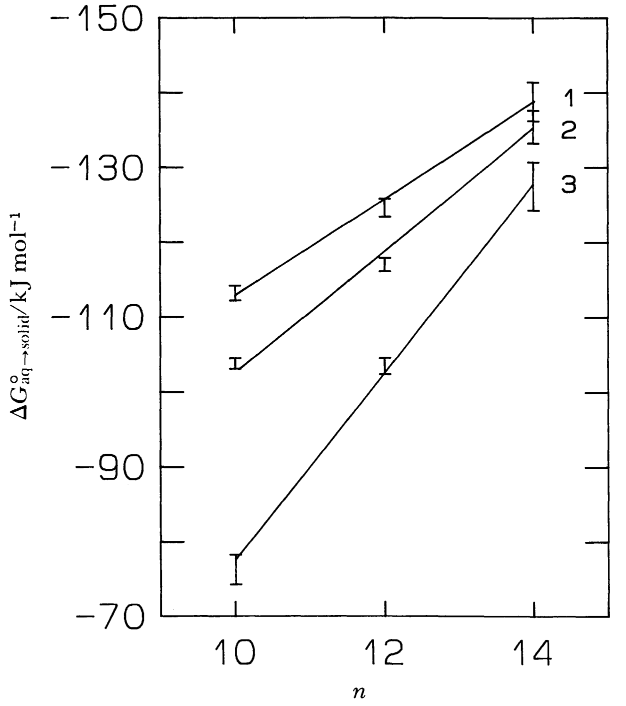

Fig. 3. Standard Gibbs energy of transfer of $(C_nTA)_4\cdot H_2TPPS$ and $(C_nTA)_4\cdot[Fe(bpso)_3]$ from the aqueous state to the solid state at 298.2 K. 1, $(C_nTA)_4\cdot H_2TPPS$ in water (without added salt); 2, $(C_nTA)_4\cdot H_2TPPS$ in ammonium buffer (I=0.1 M); 3, $(C_nTA)_4\cdot$[Fe(bpso)$_3$] in water (without added salt).

where R is the gas constant. In Fig. 3, the $\Delta G^{\circ}_{aq\to solid}$ values are plotted against the surfactant chain length. The results may be regarded as being linear within experimental uncertainties. From the slopes, the values for $\Delta G^{\circ}_{aq\to solid}$ per methylene group can be obtained, and are −6.4 and −7.9 kJ mol^{-1} in the cases of no added salt and I=0.1 M (ammonium buffer, pH=8), respectively. Also shown in Fig. 3 is the result for $[Fe(bpso)_3]^{4-}$ (bpso=4.7-diphenyl-1,10-phenanthroline-disulfonate).[17] The $\Delta G^{\circ}_{aq\to solid}$ value for the methylene group for this system is −12.8 kJ mol^{-1}; it is twice as large as that for the H_2TPPS^{4-} case. This difference reflects differences in the standard Gibbs energy in the two kinds of solids.

Surface Tension and Conductivity. The cmc values shown in Figs. 1 and 2 were determined from the break point of the surface tension vs. concentration curve. They are 57 mM, 16 mM, and 4.0 mM in water, and 50 mM, 9.0 mM, and 1.0 mM in the ammonium buffer for DeTAB, DTAB, and TTAB, respectively. Resolubilization of the precipitate occurs at surfactant concentration below their cmc's for DTAB and TTAB, though it occurs close to the cmc's for DeTAB. In order to determine whether the cmc's decrease in the presence of H_2TPPS^{4-}, surface tension measurements were made for DTAB and TTAB solutions in the presence of 5×10^{-5} M H_2TPPS^{4-}. The results showed that the presence of H_2TPPS^{4-} had negligible effects on the cmc values. Figure 4 shows the molar conductivities of TTAB in the presence (0.1 mM) and absence of H_2TPPS^{4-}. From the break point, the cmc of TTAB in water is found to be 3.8 mM, which is close to the value obtained from the surface-tension measurement (4.0 mM). As can be seen from the figure, the break point is not lowered, even in the presence of 0.1 mM H_2TPPS^{4-}. These results suggest that, at surfactant concentrations below the cmc's and above the resolubilization concentrations, there is no "normal" micelle, but there are premicellar aggregates which may be expressed as $(TTA)_x(H_2TPPS)_yBr_z^{(x-4y-z)+}$. Premicellar aggregates have been known for other ionic dyes, and are sometimes called "dye-rich induced micelles."[18—20]

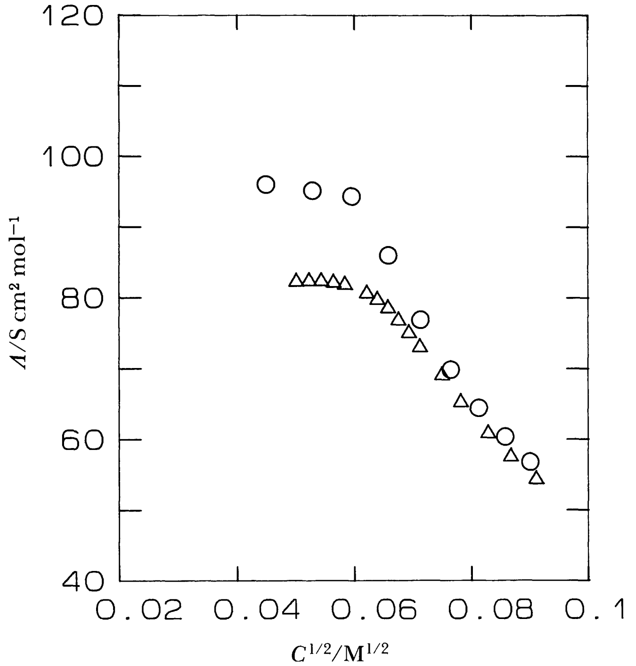

Fig. 4. Molar conductivities of TTAB in water (○) and in 0.1 mM H_2TPPS^{4-} solution (△) as a function of the TTAB concentration at 298.2 K.

Fluorescence Quenching. In order to obtain information about premicellar aggregates, fluorescence quenching experiments were carried out. If H_2TPPS^{4-} is associated with cationic surfactants, a cationic quencher may have difficulty in approaching the H_2TPPS^{4-} ion. In addition to cationic surfactant solutions, measurements were also made in water and in NaDS solutions; the results are shown in Fig. 5. In the case of no surfactant, the plot for the quenching of H_2TPPS^{4-} (maximum at 640 nm) by the methylviologen ion (MV^{2+}) does not give a straight line. This reflects the fact that there are ion pairs between MV^{2+} and the ground state H_2TPPS^{4-}, and that static quenching in addition to dynamic quenching ocurrs.[6] In fact, Schmehl and Whitten have obtained a value of 647 M^{-1} for the ion-pair formation constant between

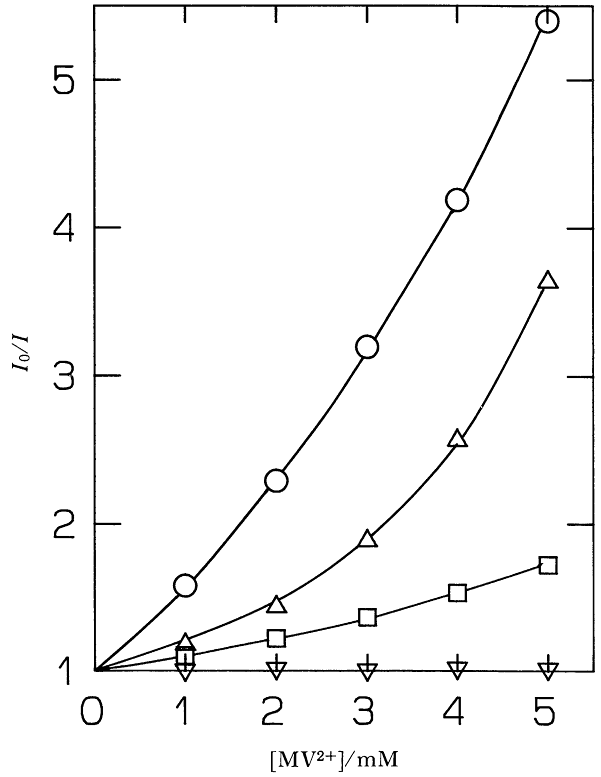

Fig. 5. Stern-Volmer plots for the quenching of H_2TPPS^{4-} by MV^{2+} in 0.1 M ammonium buffer (pH=8.0). ○, No surfactant; △, in 0.02 M NaDS; □, in 0.1 M NaDS; ▽, in 0.0005 M TTAB solutions at 298.2 K.

H_2TPPS^{4-} and MV^{2+} in 0.05 M NaCl.[6] In NaDS (0.02 M NaDS+0.05 M NaCl), although most of the MV^{2+} ions are bound to the micelles (>98%), they have estimated that the contribution to quenching is in the following order: static quenching>dynamic quenching by free MV^{2+}> dynamic quenching by micelle-bound MV^{2+}.[6] This makes plots in NaDS nonlinear also (Fig. 5). In 8 mM NaDS, the results were close to those in water (not shown in Fig. 5). With increasing NaDS concentration, the degree of quenching becomes smaller (Fig. 5), since more MV^{2+} ions are bound to the micelles.

In the case of 0.5 mM TTAB, fluorescence (maximum at 647 nm) is not quenched at all. It is unlikely that there are fewer free MV^{2+} ions in the TTAB solutions than in the NaDS solutions, since MV^{2+} ions must be less bound to TTA^+ ions than to NaDS micelles. The result therefore suggests that H_2TPPS^{4-} ions are associated with TTA^+ ions, and that the overall charge of an aggregate is positive. This prevents MV^{2+} ions from comming close to the H_2TPPS^{4-} ions and, as a result, electron transfer from the exited H_2TPPS^{4-} ion to the MV^{2+} ion does not occur. The results for 2 and 20 mM TTAB (above the cmc) and 10 mM DTAB (close to the cmc) also showed no quenching (not shown in Fig. 5).

Diffusion Coefficient. The final step in this study was to obtain information about the size of the aggregates. Figure 6 shows the tracer diffusion coefficients for H_2TPPS^{4-} and the interdiffusion

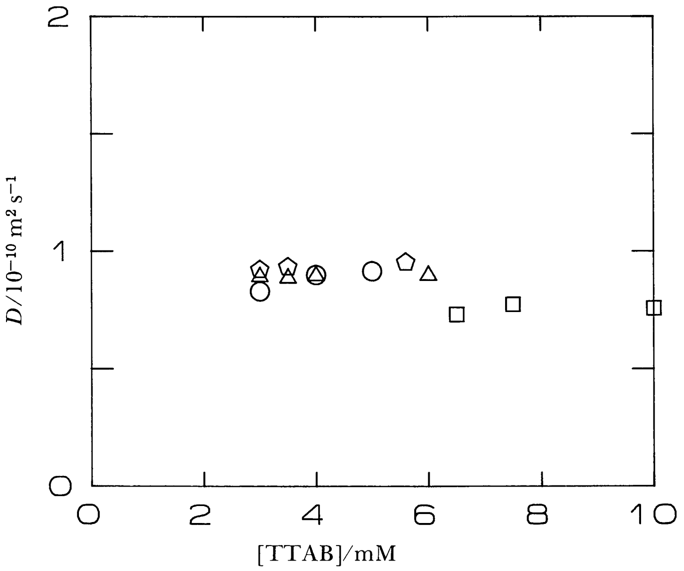

Fig. 6. Diffusion coefficients of H_2TPPS^{4-}, metalloporphyrins, and micelles in TTAB solutions at 298.2 K. ⬠, Tracer diffusion coefficients of H_2TPPS^{4-}; △, interdiffusion coefficients of $[Ni^{II}(tpps)]^{4-}$ and $[Mn^{III}(tpps)]^{3-}$; ○, interdiffusion coefficients of $[Cu^{II}(tpps)]^{4-}$ and $[Mn^{III}(tpps)]^{3-}$; □, tracer diffusion coefficients of the TTAB micelles.

coefficients for pairs of metalloporphyrins in TTAB solutions. When the TTAB concentration is zero, the tracer diffusion coefficient of the H_2TPPS^{4-} ion is $2.8\times10^{-10}\,m^2\,s^{-1}$ (not shown in Fig. 6), which was estimated from the limiting molar conductivity using the Nernst equation.[21] In 3—6 mM TTAB solutions, the tracer diffusion coefficient for H_2TPPS^{4-} is $(0.94\pm0.01)\times10^{-10}\,m^2\,s^{-1}$, and is significantly low when compared to the value in the absence of TTAB. The interdiffusion coefficient between $[M^{II}(tpps)]^{4-}$ (M=Cu or Ni) and $[Mn^{III}(tpps)]^{3-}$ in 3—6 mM TTAB is $(0.89\pm0.02)\times10^{-10}\,m^2\,s^{-1}$, and is close to the tracer diffusion coefficient for H_2TPPS^{4-}.[22] These values are compared with the tracer diffusion coefficient for the TTAB micelle, $(0.75\pm0.02)\times10^{-10}\,m^2\,s^{-1}$ at 6.5—10 mM, which was obtained by measuring the diffusion of pyrene solubilized in the micelle.

By a comparison of the diffusion coefficients of the aggregate and the micelle (Fig. 6), the value of x must be large but smaller than 70, which is the agreegation number of the TTAB micelle.[23] In the case of a 3 mM TTAB solution, the mole ratio of TTA^+ to H_2TPPS^{4-} is 300 at the time of injection, and increases with time for tracer diffusion measurements, while the mole ratio of TTA^+ to $[M(tpps)]^{n-}$ (n=3 or 4) is 60 throughout the measurement for the metalloporphyrin interdiffusion cases. In the tracer diffusion case, therefore, there are sufficient TTA^+ ions to bind with the H_2TPPS^{4-} ion and form large aggregates. For the interdiffusion case, however, the maximum value of x is 60, where all TTA^+ ions are bound to $[M(tpps)]^{n-}$ ions. This suggests that the value of y is larger than one. Such kinds of premicellar aggregates are, as mentioned before, sometimes called "dye-rich induced micelles".[18—20] As we have seen, the tracer diffusion coefficients of H_2TPPS^{4-} and the interdiffusion coefficients of the metalloporphyrins are very close in magnitude. This suggests that the size of the premicellar aggregates of H_2TPPS^{4-}, $[M^{II}(tpps)]^{4-}$, and $[Mn^{III}(tpps)]^{3-}$ are similar.

Comparison with Related Studies. Schmehl and Whitten have found that precipitate formation and resolubilization occurs for H_2TPPS^{4-} and hexadecyltrimethylammonium chloride (CTAC).[6] They have mentioned that, in the presence of H_2TPPS^{4-}, micellization of CTAC occurs significantly below the cmc of CTAC in the absence of added ions. Although we have not studied CTAC, our results suggest that in the presence of H_2TPPS^{4-} although the cmc is not significantly changed (i.e., there is no normal micelle), the premicellar aggregates, each having at least one H_2TPPS^{4-} ion, exist below the cmc.

In a previous study, we measured the tracer diffusion coefficients for the $[Fe(phen)_3]^{2+}$ ion in anionic surfactant solutions.[11] In solutions of sodium 1-dodecanesulfonate (NaDSO), no precipitate forms between $[Fe(phen)_3]^{2+}$ and DSO^-, at least when the $[Fe(phen)_3]^{2+}$ concentration is lower than 2 mM and the DSO^- concentration is lower than 7 mM. The tracer diffusion coefficient of $[Fe(phen)_3]^{2+}$ (which is the tracer diffusion coefficient of the aggregate $Na_z[Fe(phen)_3]_x(DSO)_y{}^{(y-2x-z)-}$) decreased monotonically with increasing concentration of NaDSO. When NaDS is added to a fixed concentration of $[Fe(phen)_3]^{2+}$, precipitates of $[Fe(phen)_3](DS)_2$ form, which are resolubilized upon further addition of NaDS below its cmc. In 3—8 mM NaDS (below the cmc), the tracer diffusion coefficient of $[Fe(phen)_3]^{2+}$ (which is the tracer diffusion coefficient of the aggregate $Na_z[Fe(phen)_3]_x(DS)_y{}^{(y-2x-z)-}$) was lower than the tracer diffusion coefficient of the NaDS micelle. Although the cases of H_2TPPS^{4-} and TTAB are similar to that of $[Fe(phen)_3]^{2+}$ and NaDS, in that in both systems a precipitate forms which is then resolubilized below cmc's of the surfactants, the tracer diffusion of H_2TPPS^{4-}, i.e., that of the $(TTA)_x(H_2TPPS)_yBr_z{}^{(x-4y-z)+}$ aggregates, is not smaller than that of the tracer diffusion coefficient of the TTAB micelles.

It would be of interest to see if the diffusion coefficient of the premicellar aggregates between $[Fe(bpso)_3]^{4-}$ and TTAB is larger or smaller than that of the TTAB micelles. However, the resolubilization of the $(TTA)_4[Fe(bpso)_3]$ precipitates occurs at a TTAB concentration close to its cmc,[17] and we have not been able to tell the difference in the diffusion coefficients of the premicellar aggregates and the micelles.

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12) When TTAB was added to an acidic solution containing H_4TPPS^{2-}, the absorption peak at 434 nm disappeared and the peak at 416—417 nm (2—4 mM TTAB), which corresponds to H_2TPPS^{4-}, appeared. It is worth noting that the total charge of the porphyrin increases in spite of the fact that the microscopic dielectric constant around the porphyrin decreases as a result of the interaction with TTAB. This means that what is important is microscopic charge of the central porphyrin ring, but not the total charge of the porphyrin. Similar result has been reported for the interaction of H_4TPPS^{2-} with poly(*N*-vinylpyrrolidone).[9a]

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22) If the Charges of the interdiffusing pair of metalloporphyrins are the same, the interdiffusion coefficient may be regared as the intradiffusion coefficient under the assumption that the diffusion coefficient is insensitive to the central metal ion.[11,15] However, we were unable to find a pair of tetraanionic metalloporphyrins which have sufficiently different absorption spectra so that the interdiffusion coefficient can be measured. For the definition of intradiffusion coefficient, see; R. Mills, *J. Phys. Chem.*, **69**, 3116 (1965).

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