Complex Formation between Water-Soluble Porphyrin and Cationic Surfactant below the Critical Micelle Concentration

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It was found that a visible absorption spectrum of 5, 10, 15, 20-tetraphenyl-21*H*, 24*H*-porphinetetrasulfonic acid (TPPS) drastically changes with concentration of cetyltrimethylammonium bromide (CTAB). This spectral change is due to the successive complex formation between them in aqueous solution (pH 7). The formation constants were determined by applying a factor analysis with equilibrium constraints (FAEC) to the spectra of TPPS solutions with different concentrations of CTAB.

Water-soluble porphyrins have been used as highly sensitive analytical reagents with large molar absorption coefficients (~5× 10^5 $\mathrm{M^{-1}cm^{-1}}$, M=$\mathrm{mol\,dm^{-3}}$) in spectrophotometry.[1,2] In addition, red fluorescence characteristic of the porphyrins has been also used for probing the nature of an interface and a micelle.[3-6] In particular, because the fluorescence is greatly influenced by the formation of a micelle, photoinduced redox reactions between the porphyrin and electron acceptors were investigated in aqueous solutions containing ionic surfactants.[5,6] In these investigations, it was very important to clarify the complex formation between the porphyrin and the surfactants. Tominaga et al.[6] reported that precipitation occurs between an anionic porphyrin and cationic surfactants and then the precipitate is resolubilized by a further addition of the surfactants below or close to the critical micelle concentrations (cmc). During our study on adsolubilization of TPPS at a glass/solution interface, we also found that a similar phenomenon, which accompanies a drastic change in a spectrum of TPPS, occurs between $\mathrm{TPPS^{4-}}$ and $\mathrm{CTA^+}$. In this letter, we will describe this spectral change due to the complex formation between them and report the formation constants determined by the FAEC.[7,8]

A uv-visible spectrophotometer (JASCO, V-550) equipped with a thermostat was used for measuring the spectra. Each measurement was carried out 15 min after fresh preparation of a test solution. The temperature was kept at 36 ℃, taking into account that the Krafft point of CTAB is 25 ℃.[9] TPPS (Dojindo Laboratories) and CTAB (nacalai tesque, guaranteed reagent, 99 %) were used without further purification. All test solutions contained 0.98×10^{-6} M TPPS and 0.01 M sodium acetate, and were prepared with purified water (Milli-Q, Millipore). The pHs of the test solutions were measured to be 7.0 ± 0.1, at which TPPS exists in an unprotonated form, $\mathrm{TPPS^{4-}}$.[3]

Figure 1 shows the spectra of TPPS solutions with different concentrations of CTAB in the Soret band region. The absorption band with a maximum at 413.5 nm, which is assigned to a free ion, $\mathrm{TPPS^{4-}}$, decreases in absorbance with increasing concentrations of CTAB till 10^{-5} M. The new band around 402.5 nm appears at the concentration range above 10^{-5} M and the band with a maximum at 417.5 nm develops with increasing concentrations from 5×10^{-5} to 1×10^{-3} M. At the concentrations above 1×10^{-3} M, though not shown in this figure, the maximum at 417.5 nm slightly shifted to a longer wavelength. The cmc of CTAB is reported to be 0.92×10^{-3} M.[9] Although it is known that the cmc decreases with increasing ionic strength, ionic strength of the test solutions, 0.01 M, influences the cmc of CTAB to a lesser extent.[10,11] Consequently, the spectral change shown in Figure 1 suggests that there exists some chemical interaction between $\mathrm{TPPS^{4-}}$ and $\mathrm{CTA^+}$ below the cmc. Further, the change indicates that at least three different species of TPPS exist in the solutions. The one is obviously the free ion, $\mathrm{TPPS^{4-}}$, and the others are expected to be complexes between $\mathrm{TPPS^{4-}}$ and $\mathrm{CTA^+}$, which show the spectra with the band around 402.5 nm and with the maximum at 417.5 nm. Twenty-three spectra of the test solutions were investigated by the FAEC. A number of the factor was reasonably determined to be 3 by the preliminary analysis. Based on this number, pure spectra, compositions, and formation constants for species corresponding to the factors were estimated, assuming the following equilibria:

$$\mathrm{TPPS^{4-}} + m\,\mathrm{CTA^+} \rightleftarrows [\mathrm{TPPS(CTA)}_m]^{(m-4)+},$$

$$K_1 = [\mathrm{TPPS(CTA)}_m{}^{(m-4)+}] / [\mathrm{TPPS^{4-}}][\mathrm{CTA^+}]^m \quad \text{and}$$

$$\mathrm{TPPS^{4-}} + n\,\mathrm{CTA^+} \rightleftarrows [\mathrm{TPPS(CTA)}_n]^{(n-4)+},$$

$$K_2 = [\mathrm{TPPS(CTA)}_n{}^{(n-4)+}] / [\mathrm{TPPS^{4-}}][\mathrm{CTA^+}]^n$$

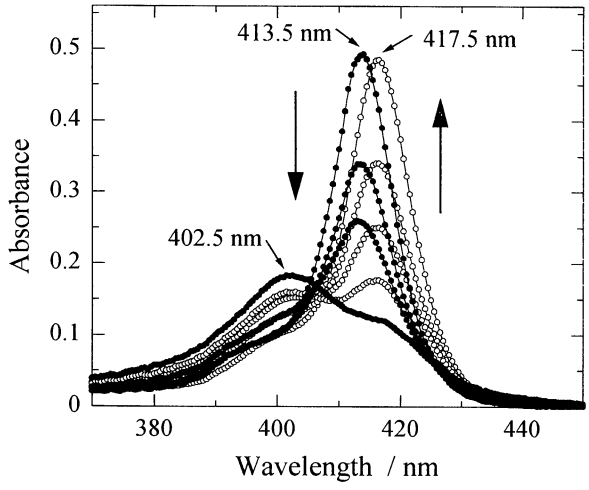

Figure 1. Visible absorption spectra of TPPS solutions with different concentrations of CTAB. The large arrows indicate increasing concentration of CTAB. The curves drawn with solid and open circles correspond to the spectra of TPPS solutions containing 0, 3.0×10^{-6}, 4×10^{-6}, 3.0×10^{-5} and 6.0×10^{-5}, 7.0×10^{-5}, 1.2×10^{-4}, 1.0×10^{-3} M CTAB.

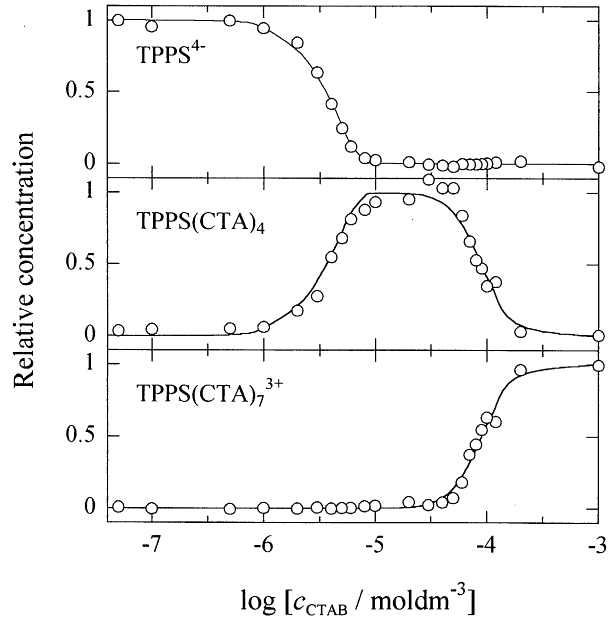

Figure 2. Relative concentration *vs.* log c_{CTAB}. The circles indicate observed values. The far left circles are observed values when $c_{CTAB} = 0$. The curves were calculated from the formation constants. The total concentration of TPPS^{4-} is 0.98 × 10^{-6} M.

for the first and second complex formations, respectively. The pure spectra corresponding to the three species were similar to those of the CTAB free solution and the solutions containing 3.0 × 10^{-5} and 1.0 × 10^{-3} M CTAB (see Figure 1). On the other hand, the FAEC nominated several candidates for a couple of integers, m and n (m<n), such as 3 and 6, 4 and 7 or 8, and 5 and 9. The couple of m=4 and n=7 was adopted as an optimal one, because this couple gave the smallest value as the error of the least-square method. Thus the three pure spectra correspond to a free ion, TPPS^{4-}, a 1:4 complex, TPPS(CTA)$_4$, and a 1:7 complex, [TPPS(CTA)$_7$]$^{3+}$. In addition, the formation constants, logK_1 and logK_2 were determined to be 23.2 and 35.4, respectively. Figure 2 illustrates existent fractions of TPPS^{4-}, TPPS(CTA)$_4$ and [TPPS(CTA)$_7$]$^{3+}$ as a function of the total concentration of CTAB when that of TPPS is 0.98 × 10^{-6} M. The solid curves in this figure were calculated from the formation constants. Significant deviations can be seen between the observed and calculated fractions of TPPS(CTA)$_4$ at concentrations of CTAB around 5 × 10^{-5} M. This is because the reproducibility of the spectra was rather poor in this concentration range because of the formation of a colloidal precipitate described below.[12]

Tyndall phenomenon, without the fluorescence, could be observed in solution containing 10^{-5} M TPPS and 10^{-4} M CTAB with the naked eye, which indicates that colloidal precipitation is caused by the complex formation between TPPS^{4-} and CTA$^+$. Because the 1:4 complex is expected to be formed in this solution (see Figure 2), the precipitate is ultimately assigned to the complex. (Hence the 1:4 complex should be denoted by [TPPS(CTA)$_4$]$_{solid}$ instead of [TPPS(CTA)$_4$].) In addition, this composition of the precipitate is also consistent with the fact that the electric neutrality holds when a ratio of TPPS and CTAB is 1 to 4. On the other hand, the red fluorescence was observed, when the concentration of CTAB was much lower or higher than that of TPPS. According to the assignment by the FAEC, it is clear that the fluorescence is emitted from the free ion and the soluble 1:7 complex. Namely, a continuous addition of CTAB to TPPS solution successively causes the colloidal precipitation and the complex formation of the soluble 1:7 complex, leading to quenching and the recovery of the fluorescence.

The spectrum of [TPPS(CTA)$_4$]$_{solid}$ is abnormally different from those of the free ion and the 1:7 complex. This difference implies a strong interaction between the free ions, such as stacking or aggregation, in the precipitate. Non-fluorescence of the precipitate may be attributed to self-quenching by an intermolecular energy transfer. On the contrary, the spectrum of the 1:7 complex is the same as that of the free ion except for a small shift of the absorption maximum (*ca.* 4 nm), indicating that the interaction is not very strong. An aggregate of CTA$^+$, which seems to be a precursor of the micelle, slightly changes a chemical environment or a solvation shell around the free ion.

The similar spectral change with concentration of CTAB has been found in a low pH region where TPPS exists in a protonated form, H$_2$TPPS^{2-}. The complex formation between water-soluble porphyrins and surfactants will provide basic information about adsolubilization at liquid/liquid and solid/liquid interfaces which play an important role in analytical separation techniques such as solvent extraction and chromatography.

References and Notes

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12 Because the precipitate formed fairly stable colloidal solutions, the spectra of the colloidal solutions could be treated by the FAEC in the same way as those of the other transparent solutions could be.