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Study of Adsorption of Water-Soluble Porphyrin at Glass–Solution Interface in the Presence of Cationic Surfactant Admicelles by Means of Total Internal Reflection Spectroscopy

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Total internal reflection (TIR) spectra were measured in the visible region at an interface between glass and an aqueous solution of 1.00×10^{-6} mol dm^{-3} 5,10,15,20-tetraphenylporphyrintetrasulfonic acid (TPPS) in the presence of admicelles of cetyltrimethylammonium bromide (CTAB). Comparison of the TIR spectra with transmission spectra of TPPS solutions with different CTAB concentrations revealed that the deprotonated ions, $TPPS^{4-}$, are simultaneously adsorbed at the interface as two complexes with $TPPS^{4-}/CTA^{+}$ ratios of 1 : 4 and 1 : 7. Interfacial concentrations of the 1 : 7 complex were estimated by using a linear relation between the absorbance and the interfacial concentration derived from a theory of TIR spectroscopy. The concentration data indicated that the adsorption of TPPS hardly occurs below pH 3, is saturated at pHs between 4 and 6, and continuously decreases above pH 6. Assuming an aggregative structure of the admicelle, the pH dependence of the adsorption was mathematically treated with a model including the dissociation, complex formation, and adsorption equilibria.

Because chemical reactions occurring at liquid–liquid and solid–liquid interfaces are essential to separation and concentration of chemical substances, many attempts have been made for understanding the interfacial reactions.[1,2] With a remarkable development of optical spectroscopy in recent years, the reaction mechanisms have been elucidated not only from a macroscopic viewpoint such as thermodynamics but also from a microscopic molecular one. That is to say, direct and in situ observations of chemical species existing in the interfacial region have been performed by using various spectroscopies, such as total internal reflection spectroscopy (TIRS),[3,4] non-linear spectroscopy (SHG and SFG),[5,6] and scanning microscopy (STM and AFM).[7,8] We have also applied TIRS to identifying chemical forms of Methylene Blue adsorbed at a glass–solution interface[9] and to determining the thickness of the adsorption layer.[10]

TIRS is a highly selective spectroscopy to the interfacial region, because the evanescent wave rapidly decays within a distance of one wavelength from the interface. In addition to such spatial selectivity, TIRS can be easily applied to in situ observation of any interfaces, such as liquid–liquid and solid–liquid interfaces, by choosing the angle of incidence properly. We can obtain information about a chemical form of an interfacial species from a TIR spectrum and can moreover estimate its interfacial concentration through the aid of a relation between the absorbance and the interfacial concentration. However, TIRS always suffers from low sensitivity because of the very short optical path per reflection. In spite of such a disadvantage, we did use a single-reflection TIR spectrometer with which the angle of incidence and the polarization condition of the light can be easily adjusted, because an exact measurement of the interfacial concentration was desired in this work. In addition, as will be shown later, the low sensitivity due to the single reflection leads to favorable selectivity between chemical species adsorbed on a glass surface and dissolving in a solution part of the interfacial region.

Porphyrins and metalloporphyrins have been widely studied in various fields of chemistry in connection with their vital functions such as photosynthesis and metabolism.[11,12] On the other hand, because of their planar structure and specific optical absorption in the visible region, the compounds have been investigated as optically functional material for molecular electric devices as well.[13] Thus it is important to examine an adsorption behavior of the porphyrin at liquid–liquid and solid–liquid interfaces. Water-soluble porphyrin used in this work (5,10,15,20-tetraphenylporphyrintetrasulfonic acid, TPPS) is an analytical reagent developed for a spectrophotometric analysis,[14] which exhibits a large molar absorption coefficient of ca. 5×10^{5} M^{-1} cm^{-1} (M = mol dm^{-3}).

The porphyrin used exists in anionic forms such as a protonated ion, H_2TPPS^{2-}, and a deprotonated one, $TPPS^{4-}$, in aqueous solution, depending on pH. On the other hand, the glass surface tends to be negatively charged when being in contact with aqueous solution. Thus it seems difficult for the porphyrin anion to be adsorbed on the negatively charged glass surface because of electrostatic repulsion between them. However, if cationic surfactants coexist in the interfacial region, even the porphyrin anion can be adsorbed on the glass surface. Indeed it has been shown in a previous paper[15] that the $TPPS^{4-}$ ion is adsorbed at a liquid–liquid interface in the presence of cetyltrimethylammonium bromide, CTAB.

At the liquid–liquid interface, it is expected that the surfactant ions form a uniform layer like a mono-molecular film because of electrostatic repulsion between charges on the head groups and dissolution of the hydrophobic alkyl chain into the organic phase. On the contrary, at a solid–liquid interface, the surfactant ions form an admicelle (an interfacial micelle) with a complicated structure.[8,16] In the present paper, the adsorption of TPPS at the glass-aqueous solution interface will be discussed in connection with the admicelle with a compactly aggregative structure.[17]

Experimental

TIR Spectrometer and Cell. Figure 1 illustrates a schematic diagram of the single-reflection TIR spectrometer. The spectrometer was specially designed and constructed by Unisoku Co. Light emitted from the source (Osram, HLX 64625,100 V, 12 W), after being monochromated with a diffraction grating, enters the cell through the polarizer (a Gran–Taylor prism) and the collimating lens. As shown by the broken line, the monochromatic light is totally reflected from a glass–solution interface in the cell and subsequently delivered to the photomultiplier through the condensing lens. On the total reflection, if there exists a light absorbing species in the interfacial region, light is absorbed by the species at a certain wavelength. Consequently, scanning the wavelength produces a TIR spectrum of the species. Two kinds of optical fibers were used for carrying the light between the two optical instruments. One had round slits of 1.8 mm in diameter at both ends and the other had a rectangular slit (0.4×7.0 mm) at one end. The fiber with the rectangular slit was used between the monochromator and the interface in the cell in order to minimize the divergence of the light rays entering the interface. In spite of the use of the rectangular slit and careful alignment of optical instruments around the cell, a measurement of the critical angle at the glass–distilled water interface indicated that the angle of incidence actually diverged from a value fixed with the goniometer by ±1.5°. Output signals from the photomultiplier were registered and stored along with the corresponding wavelengths in the personal computer through an A/D converter. Figure 2 displays an exploded view of the TIR cell. The cell body was made by drilling a hole of 15 mm in diameter into a block of poly(chlorotrifluoro ethylene) resin. The hemicylindrical prism, serving as a variable-angle internal reflection element for the single reflection, was made of glass (BK 7, $n_g = 1.529$ at 417.5 nm) and its surface was polished to optically flat. The prism was tightly attached to the cell body with an O-ring, two prism holders, and four screws, so that the hole of the cell body was blocked with a flat plane of the prism. Thus, pouring solution into the hole produces the glass–solution interface on the prism. The cell body was entirely kept at a constant temperature by surrounding it with the aluminium block in which thermostatic water was circulated.

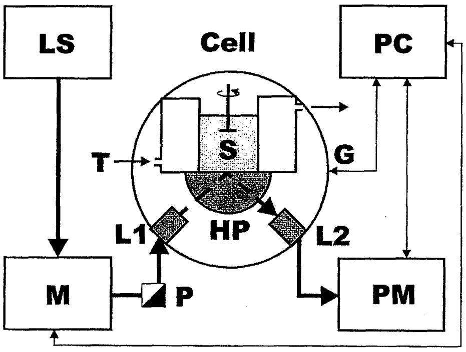

Fig. 1. Schematic diagram of the single-reflection spectrometer for total internal reflection spectroscopy (TIRS). LS, Light source; M, Monochromator; P, Polarizer; S, Sample solution; HP, Hemicylindrical glass prism; PM, Photomultiplier; PC, Personal computer; G, Goniometer; T, Thermostat. The thick lines indicate optical fibers carrying the light and the thin lines show a stream of electric signals. The broken line shows the light ray reflected totally from the glass–solution interface.

Reagents. 5,10,15,20-Tetraphenylporphyrintetrasulfonic acid (TPPS, Dojindo Laboratories) and cetyltrimethylammonium bromide (CTAB, Nacalai Tesque, guaranteed reagent, 99%) were used without further purification. All solutions were prepared with Milli-Q water (Millipore). The pHs of the TPPS solutions were adjusted with hydrochloric acid, sodium acetate, and sodium hydroxide. The ionic strength was between 0.005 and 0.01 M (1 M = 1 mol dm^{-3}). For a spectrophotometric determination of CTAB, Disulphine Blue (Patent Blue V, Tokyo Kasei) and chloroform (Nacalai Tesque, guaranteed reagent, 99%) were used as received.

Experimental Procedure. In order to prepare the surfactant admicelles on the glass surface prior to the TPPS adsorption experiment, 5.00×10^{-3} M CTAB aqueous solution was maintained in the TIR cell for at least 1 h at 36 °C under stirring; we took into account that the critical micelle concentration and the Krafft point are 0.92×10^{-3} M and 25 °C.[18] After removing the CTAB solution from the cell, the cell inside was once rinsed with blank solution and then 2 cm^3 of 1.00×10^{-6} M TPPS solution was added into the cell for recording the TIR spectra. While we tried to remove completely the CTAB solution from the cell in this procedure, the complete removal was difficult because rinsing the cell inside thoroughly damaged the admicelles. As an inevitable result, ca. 5×10^{-6} M CTAB was left in the bulk of solution, even when the adsorption attained equilibrium, as shown later in detail. After each experiment, the admicelles adsorbed on the glass surface and the cell wall were completely washed off with 1 M hydrochloric acid and Milli-Q water. the TIR spectra were recorded at time intervals of 15 min over several hours. During the adsorption experiment,

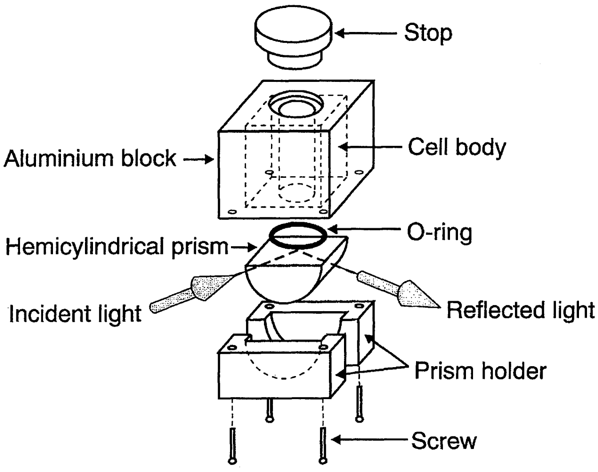

Fig. 2. Exploded view of the cell for TIRS.

the solution was stirred except for when the spectrum was recorded. The temperature of the cell was kept at 36 °C. Indeed we could obtain no spectral evidence that TPPS was adsorbed at 17 °C lower than the Krafft point. The incident light polarized in parallel to the plane of incidence was used and the angle of incidence was fixed at 70°C, which is much greater than the critical angle of 61.4° at 417.5 nm for the glass–water interface.

The pHs of the TPPS solutions were measured with a Horiba F-16 pH meter. The spectrophotometric determination of the CTA^+ ion was carried out with a JASCO V-550 spectrophotometer, according to a Disulphine Blue method in which the surfactant ion is extracted as an ion-pair into chloroform.[19]

Results and Discussion

TIR Spectra of TPPS Adsorbed at the Glass–Solution Interface. Figure 3 shows TIR spectra of 1.00×10^{-6} M TPPS solution at the glass–solution interface in the presence (a) and absence (b) of the CTA^+ admicelles at pH 5.9. As can be seen in this figure, two absorption bands were observed at 402.5 and 417.5 nm in the presence of the admicelles, whereas no bands appeared in the absence. These facts indicate that TPPS is adsorbed at the interface only when the admicelles exist on the glass surface. In addition, the two bands belong to the Soret band of the deprotonated TPPS, $TPPS^{4-}$, because the $TPPS^{4-}$ ion is a major species in the bulk of solution at pH 5.9. On the other hand, the fact that no bands appeared in the absence of the admicelles means that the TIR spectrum is insensitive to optical absorption by the $TPPS^{4-}$ ions in a solution part of the interfacial region where the evanescent wave is still vivid. This insensitivity, coming from a lack of sensitivity due to the single reflection, is very important in this work, because only the absorption bands for TPPS adsorbed at the interface can appear in the TIR spectrum. In particular, when formulating a relation between the absorbance and an interfacial concentration of TPPS, it will simplify the relation.

In order to assign the two bands appearing at 402.5 and 417.5 nm, a series of transmission spectra for 0.98×10^{-6} M TPPS solutions with different CTAB concentrations were treated by a factor analysis with equilibrium constraints.[20] Figure 4 shows component spectra resulting from the analysis. These spectra correspond to three chemical forms of TPPS: namely, spectrum (a) corresponds to a free $TPPS^{4-}$ ion, and spectra (b) and (c) to two complexes between $TPPS^{4-}$ and CTA^+ with ratios of 1 : 4 and 1 : 7, respectively. The 1 : 4 complex forms colloidal particles because of its electric neutrality and the 1 : 7 is thought to be a *dye-rich induced micelle*, which is cooperatively produced by dye and surfactant molecules.[21] Comparison between the TIR spectrum in Fig. 3 and the component spectra in Fig. 4 shows that the absorption bands at 402.5 and 417.5 nm in the TIR spectrum should be assigned to the 1 : 4 and 1 : 7 complexes, respectively. In fact, as shown in Fig. 5, we could mathematically synthesize a spectrum similar to the TIR spectrum from the two component spectra. Thus it is concluded that the $TPPS^{4-}$ ions exist in two chemical forms of the 1 : 4 and 1 : 7 complexes at the interface in the presence of the CTA^+ admicelles.

Change of the TIR Spectrum with Time. Figure 6(a) shows the TIR spectra which were recorded at time intervals of 1 h after the TPPS solution had been added into the cell. The absorption bands at 402.5 and 417.5 nm continue to grow with time and converge on a steady spectrum after several hours. Every TIR spectrum recorded was mathematically separated into the two component spectra of the 1 : 4 and 1 : 7 complexes, and absorbance at $\lambda_{\max}$ of each component spectrum was plotted against the passing time, as

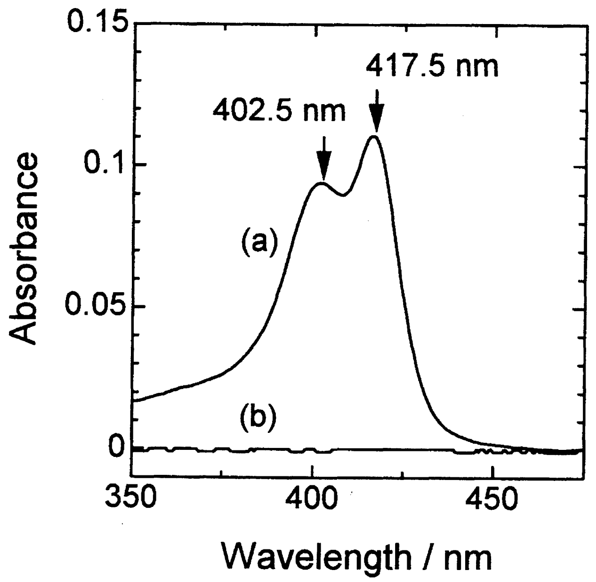

Fig. 3. TIR spectra of TPPS at the glass–solution interface. (a) and (b) are the spectra for 1.00×10^{-6} M TPPS aqueous solution in the presence and absence of the CTA^+ admicelles, respectively.

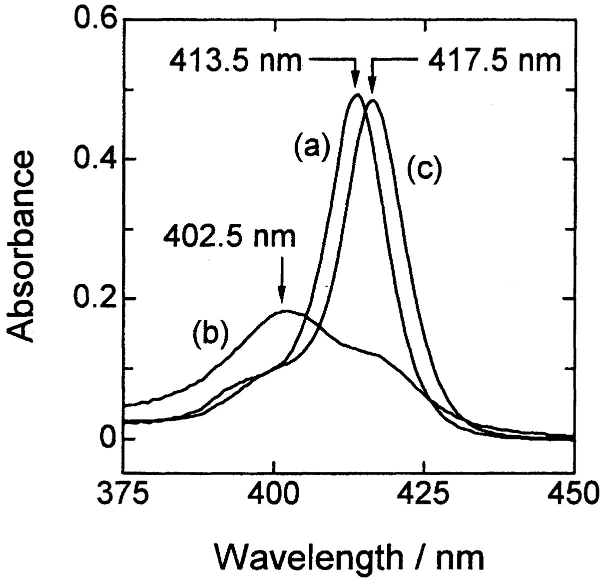

Fig. 4. Three component spectra resulting from the factor analysis.[20] The spectra (a), (b), and (c) correspond to the free $TPPS^{4-}$ ion and the 1 : 4 and 1 : 7 complexes formed between the $TPPS^{4-}$ and CTA^+ ions, respectively.

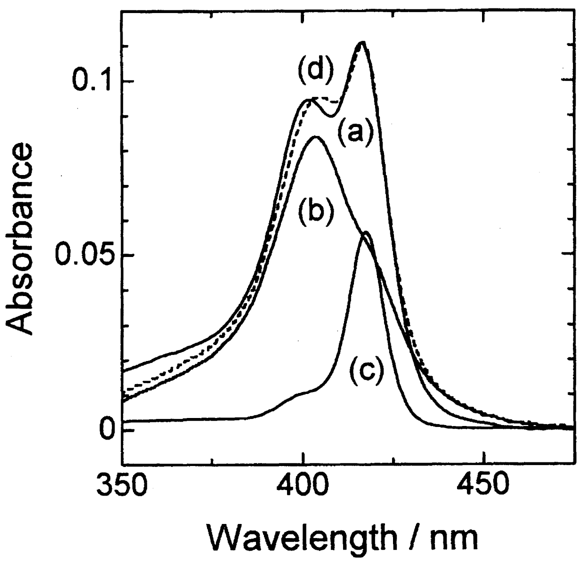

Fig. 5. Comparison of the TIR spectrum with a spectrum synthesized from the two component spectra for the 1 : 4 and 1 : 7 complexes. (a) TIR spectrum observed (the solid curve), (b) component spectrum for the 1 : 4 complex, (c) component spectrum of the 1 : 7 complex, (d) spectrum synthesized from the two component spectra (the broken curve). The spectrum (d) was synthesized with a ratio of 1 to 4.36 between the component spectra for the 1 : 7 and 1 : 4 complexes.

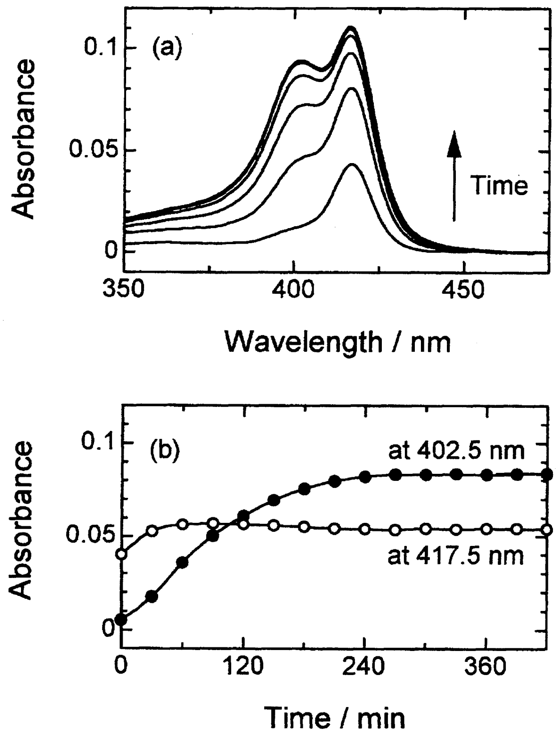

Fig. 6. Change of the TIR spectrum with time (a) and a plot of absorbance at λ_{max} of each component spectrum against the passing time (b). The TIR spectra were recorded at time intervals of 1 h after the addition of TPPS solution. Every TIR spectrum was mathematically separated into two component spectra for the 1 : 4 (λ = 402.5 nm) and 1 : 7 complexes (λ_{max} = 417.5 nm).

shown in Fig. 6(b). The absorbance at 417.5 nm levels off soon after the addition of TPPS solution. This fact predicts the existence of the admicelle with a specific structure with which the $TPPS^{4-}$ ion can instantly form the 1 : 7 complex, namely, the structure consisting of seven CTA^+ ions. Gu et al.[17] have suggested from an adsorption isotherm for the CTA^+ ion on fumed silica (Aerosil 200) that the CTA^+ ions produce a compact aggregate with the aggregation number of 6.7 on the silica. This incidental agreement between the ratio of 1 : 7 and the aggregation number strongly supports the above prediction. As described later, the existence of the admicelle with such a structure will be also confirmed from a mathematical treatment of a pH dependence of the adsorption. On the contrary, the absorbance at 402.5 nm ultimately attains a constant value of absorbance after several hours. This fact implies that the $TPPS^{4-}$ ion once forms the 1 : 4 complex with the CTA^+ ions, which have been left in the preparation procedure of the admicelle, in the bulk of solution and then the complex is adsorbed at the interface. Indeed it can be shown that the 1 : 4 complex preferentially exists in the bulk at the CTA^+ concentration in the cell, being approximately 5×10^{-6} M.[20] In addition, while the change in absorbance at 417.5 nm was reproducible, that at 402.5 nm greatly varied in each experiment. The latter experimental observation is probably due to variance of a volume of CTAB solution left in the preparation procedure. Figure 7 schematically illustrates the adsorption mechanism of TPPS in the presence of the CTA^+ admicelles. The admicelles consisting of seven CTA^+ ions in this figure are drawn on the basis of a shape of the compact aggregate proposed by Gu et al.[17,22] Note that this figure includes several chemical equilibria discussed later. The above discussion has proved that the TIR spectroscopic observation is very effective in identifying chemical species adsorbed at the interface and in elucidating the adsorption mechanism.

Derivation of a Linear Relation between Absorbance and an Interfacial Concentration (an A–Γ Relation). Another feature of TIRS is that a concentration of a species adsorbed at the interface can be easily obtained from a value of absorbance measured through the A–Γ relation. Here let us derive the A–Γ relation for the present interfacial system. According to a theory by Hansen,[23] at the interface consisting of the glass prism, the admicelle layer including the 1 : 7 complex,[24] and the TPPS aqueous solution, the absorbance measured, A is strictly expressed as

$$A = \frac{1}{n_g \cos\theta} \times \left[n_{ad}\alpha_{ad}\langle E^2\rangle_{ad} h_{ad} + n_s(\varepsilon c)\langle E^2\rangle_s d \right]. \qquad (1)$$

Here θ denotes the angle of incidence. Refractive indices of the prism, the admicelle layer, and the solution are represented by n_g, n_{ad}, and n_s, respectively. α_{ad} is an absorption coefficient of the admicelle layer in cm^{-1}, ε and c are a molar absorption coefficient of the $TPPS^{4-}$ ion and its concentration in the bulk. $\langle E^2\rangle$ is the mean square electric field, that is, the intensity of light, in each phase. The thickness of the admicelle layer and the penetration depth of the evanescent

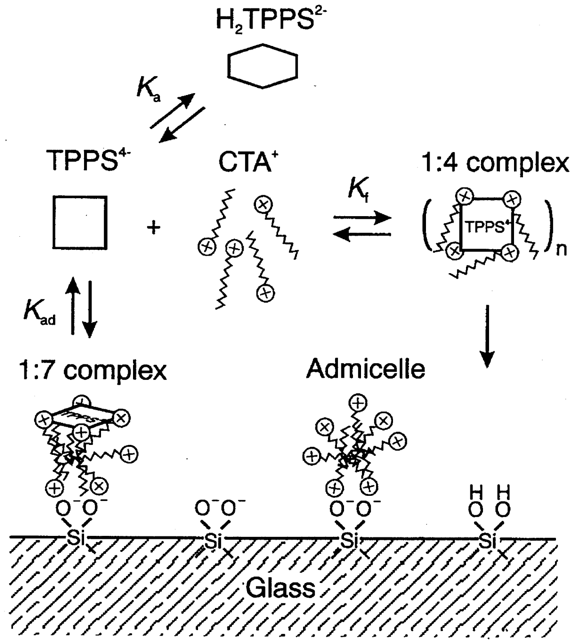

Fig. 7. Schematic illustration of the adsorption mechanism of TPPS at the glass–solution interface in the presence of the CTA^+ admicelles. The admicelles consisting of seven CTA^+ ions are drawn on the basis of a shape of the compact aggregate proposed by Gu et al.[17,22] Note that this figure includes several chemical equilibria discussed later.

wave are represented by h_{ad} and d. As already mentioned, optical absorption by the TPPS solution can be neglected. Moreover not only is the admicelle layer much thinner than the penetration depth, but also its optical absorption is not so strong. In fact, a value of d is calculated to be 65 nm at 417.5 nm for this interface and h_{ad} is thought to be less than twice of a length of the cetyl group, ca. 5 nm, according to the compact aggregate model by Gu.[17] Under such optical conditions, the absorbance for the 1 : 7 complex in the admicelle layer can be approximately written by the following expression:

$$A \simeq 1000 \times \varepsilon' \times \left(\frac{n_{ad}\langle E^2\rangle^{\circ}_{ad}}{n_g \cos\theta}\right) \times \Gamma_c \equiv b_{eff} \times \Gamma_c, \qquad (2)$$

where Γ_c is the interfacial concentration of the 1 : 7 complex in mol cm^{-2} and $\langle E^2\rangle^{\circ}_{ad}$ means the mean square electric field when all the three phases are optically transparent. The molar absorption coefficient of the 1 : 7 complex in the admicelle layer, ε', was assumed to be the same as that of the 1 : 7 complex in the bulk expected from the factor analysis (see Fig. 4), that is, 5.0×10^5 M^{-1} cm^{-1}, because both 1 : 7 complexes in the admicelle layer and the bulk are essentially identical. The absorption coefficient and the thickness of the admicelle layer is seemingly eliminated from Eq. 1 by substituting $\alpha_{ad}\times h_{ad}$ to $1000\times\varepsilon'\times\Gamma_c$. Because a value of n_{ad} was not available, we calculated b_{eff} with n_{ad} from 1.342 for water[25] to 1.378 for 25% cetyltrimethylammonium chloride (CTAC) aqueous solution[26] in order to evaluate a maximum error resulting from a choice of n_{ad}. As the result, the b_{eff} ranged from 3.064×10^9 for the CTAC solution to 3.283×10^9 mol^{-1} cm^2 for water. This result leads to the maximum error of 6.7% in the interfacial concentration. As shown later, this error is not so large in comparison with standard deviations of absorbance observed in the adsorption experiment. In this work, we adopted 1.378 for the CTAC solution as n_{ad}. Thus, the interfacial concentration of the 1 : 7 complex can be directly obtained from the absorbance through the aid of Eq. 2.

pH Dependence of the Adsorption. In order to understand the adsorption of TPPS in the presence of the admicelles in more detail by using the A–Γ relation, the pH dependence of the adsorption was examined. We will first discuss the dependence over the pH region examined and then mathematically treat that in the pH region of interest. Figure 8 shows the pH dependence of the adsorption of TPPS in the presence of CTA^+ admicelles. A scale on the right-hand side of this figure indicates the interfacial concentration of the 1 : 7 complex calculated from Eq. 2. As can be seen in this figure, the adsorption profile is divided into three pH regions: below 3, between 3 and 6, and above 6. The smaller absorbance or the lower interfacial concentration at pHs below 3 indicates that little adsorption takes place in this pH region. At pHs below 3, a major species in the bulk is the protonated TPPS, H_2TPPS^{2-}. As shown in the previous work,[15] the H_2TPPS^{2-} ion is only slightly adsorbed at a liquid–liquid interface in the presence of CTAB, probably due to its distorted structure. Similarly, the ion may be slightly adsorbed at the glass–solution interface. On the other hand, it is reported that a charge density on silica asymptotically approaches zero at pHs below 4.[27] Because a similar behavior of the charge density is likely on a surface of the

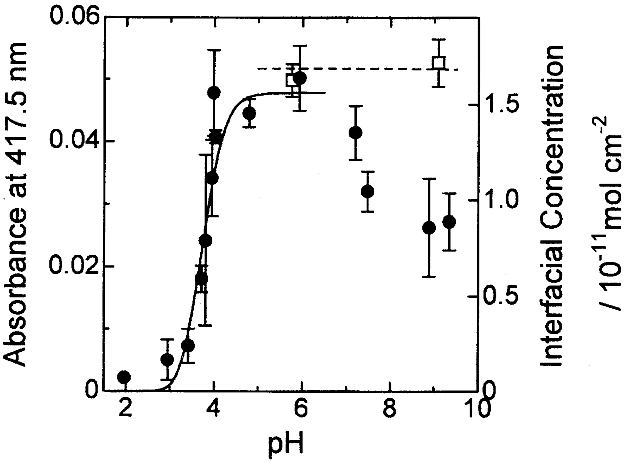

Fig. 8. pH dependence of the adsorption of TPPS at the glass–solution interface in the presence of the CTA^+ admicelles. Every absorbance was measured after the adsorption attained equilibrium, that is, after about 6 h. The error bars indicate standard deviations for three or four measurements. The squares show results of the experiment using 1×10^{-5} M TPPS solution. The solid curve was drawn by using Eq. 5 with the constants determined in this work. The broken line merely shows that the absorbance is nearly constant in the pH region between 6 and 9.

glass containing 72 mol% SiO_2 (BK 7), the surfactant cations find it difficult to be adsorbed on the glass surface through Coulombic forces at pHs below 3. Moreover, if the glass surface is strongly hydrated, the adsorption is also difficult due to an hydrophobic interaction between the glass surface and an alkyl chain of the surfactant ion. Consequently, the admicelle is not developed enough to incorporate the $TPPS^{4-}$ ion, leading to the little adsorption of TPPS at pHs below 3. Both low adsorptive properties of the H_2TPPS^{2-} ion at the interface in the presence of CTAB and the CTA^+ ion on the glass surface are probably responsible for the low adsorption, though it is unclear which cause is dominant. The steep increase in absorbance around pH 4 is due to an acid dissociation from H_2TPPS^{2-} to $TPPS^{4-}$. Because the H_2TPPS^{2-} ion is expected to be a major species in the bulk around pH 4 from the pK_a values (pK_{a1} = 4.60 and pK_{a2} = 5.17[15]), it seems strange that the 1 : 7 complex containing the $TPPS^{4-}$ ion exists considerably even at pHs around 4. However, this is only because the acid dissociation from H_2TPPS^{2-} to $TPPS^{4-}$ is influenced by the existence of the admicelle, and consequently the pK_a values apparently shift to a lower pH region at the interface compared with in the bulk. Indeed the TIR spectra observed around pH 4 were the same in shape as that at pH 5.9 shown in Fig. 1, though a transmission spectrum for the H_2TPPS^{2-} ion shows an absorption band around 435 nm. In the pH region between 4 and 6, the absorbance takes a constant value of ca. 0.05. Figure 9 shows a plot of the absorbance at 417.5 nm against a logarithm of a total concentration of TPPS, $[TPPS]_t$, at pH 5.9. As can be seen in this figure, the absorbance of 0.05 corresponds to a saturated interfacial concentration of the 1 : 7 complex. It is therefore expected in this pH region that the admicelle layer is saturated with the complexes. The adsorption behavior in the pH region between 3 and 6 will be mathematically analyzed later.

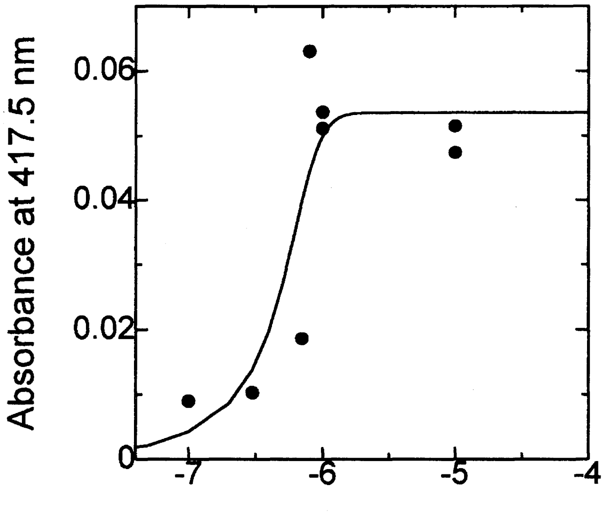

Fig. 9. Relationship between the absorbance at 417.5 nm and a logarithm of the total concentration of TPPS at pH 5.9. The solid curve was drawn by using Eq. 4 with the constants determined in this work.

With increasing pH above 6, the absorbance continuously decreases, namely, the adsorption decreases. A few causes are possible for explaining the decrease. One is a decrease of a surface concentration of the admicelle. However, because the glass surface is negatively charged at pHs above 6,[27] the admicelle can be formed enough through Coulombic forces between the glass surface and the CTA^+ ions. Further, in the adsorption experiment with 1.00×10^{-5} M TPPS solution, usually 1.00×10^{-6} M, such a decrease in absorbance was not found even at pH 9. (see open squares in Fig. 8) This fact also supports the conclusion that the admicelle is maintained at the surface concentration similar to that in the pH region between 4 and 6 until pH 9 at least. If the admicelles serving as an adsorption site for the $TPPS^{4-}$ ion decreased in concentration, the decrease in absorbance would be found even at the higher TPPS concentration of 1.00×10^{-5} M. Thus, the decrease of the interfacial concentration of the complex is not associated with the surface concentration of the admicelle. Instead, a certain chemical equilibrium should be considered in the interfacial system. One possibility is an ion-exchange equilibrium between the hydroxide ion and the $TPPS^{4-}$ ion in the complex. Such ion exchange is unlikely, because the hydroxide ion is rather exchanged with any other anions on an ion exchanger, as is generally known. In particular, because the solution contains acetate ions in large excess compared with the hydroxide ions, a preferential ion exchange of the hydroxide ion with the $TPPS^{4-}$ ion is not acceptable. Although a curve fitting including the ion exchange model apparently explained the pH dependence in this pH region, an exchange ratio expected from the fitting, which was 1 to 0.5 between the $TPPS^{4-}$ and hydroxide ions,[28] is difficult to explain with reasonable chemical reality. On the other hand, an increase in concentration of the hydroxide ion with increasing pH induces more negative charges on the glass surface.[27] As the result, the $TPPS^{4-}$ anion tends to have an affinity with the bulk of the solution rather than with the electrically negative interface. Treiner et al.[29] proposed in a study of coadsorption of salicylate anions in the presence of cationic surfactants that a similar decrease with increasing pH is due to negative sites on a silica surface. Although no one has clarified yet how the $TPPS^{4-}$ ion in the complex is influenced by the negatively charged glass surface, we suggest that the continuous decrease of the adsorption above pH 6 is caused by more negative charges induced on the glass surface by the increase in pH.

Mathematical Treatment of the pH Dependence. Here only the pH dependence of the adsorption in the pH region between 3 and 6 is mathematically analyzed by considering the following equilibria.

$$H_2TPPS^{2-} \rightleftharpoons TPPS^{4-} + 2H^+$$

$$\left(K_a = \frac{[TPPS^{4-}][H^+]^2}{[H_2TPPS^{2-}]} = 10^{-9.77}\right)^{15)}$$

and

$$TPPS^{4-} + 4CTA^+ \rightleftharpoons TPPS(CTA)_4$$

$$\left(K_\mathrm{f} = \frac{[\mathrm{TPPS(CTA)_4}]}{[\mathrm{TPPS^{4-}}][\mathrm{CTA^+}]^4} = 10^{23.2}\right)^{20)}$$

in the bulk of solution, and

$$\mathrm{TPPS^{4-}} + (\mathrm{CTA^+})_\mathrm{ad} \rightleftarrows \mathrm{TPPS(CTA^+)_{ad}}$$

$$\left(K_\mathrm{ad} = \frac{\Gamma_\mathrm{c}}{[\mathrm{TPPS^{4-}}][(\mathrm{CTA^+})_\mathrm{ad}]}\right)$$

at the interface. The first and second formulas express the acid dissociation equilibrium of TPPS and the complex formation equilibrium of the 1 : 4 complex, $\mathrm{TPPS(CTA)_4}$, in the bulk. In the adsorption equilibrium expressed by the last formula, it is assumed that seven $\mathrm{CTA^+}$ ions associate with each other on the glass surface to form the admicelle, $(\mathrm{CTA^+})_\mathrm{ad}$. By considering the fact that the adsorption is saturated at the total TPPS concentration of 1.00×10^{-6} M (see Fig. 9), we can express the absorbance as follows:

$$A = \frac{b_\mathrm{eff}K_\mathrm{ad}\Gamma_\mathrm{max}[\mathrm{TPPS^{4-}}]}{1 + K_\mathrm{ad}[\mathrm{TPPS^{4-}}]}. \tag{3}$$

Here $\Gamma_\mathrm{max}=[(\mathrm{CTA^+})_\mathrm{ad}]+\Gamma_\mathrm{c}$. Because A/b_eff corresponds to Γ_c, Eq. 3 is rearranged to

$$\frac{[\mathrm{TPPS^{4-}}]}{\Gamma_\mathrm{c}} = \frac{1}{K_\mathrm{ad}\Gamma_\mathrm{max}} + \frac{[\mathrm{TPPS^{4-}}]}{\Gamma_\mathrm{max}}. \tag{4}$$

The equilibrium concentration of $\mathrm{TPPS^{4-}}$ in the bulk, $[\mathrm{TPPS^{4-}}]$, can be calculated from the following expression:

$$[\mathrm{TPPS^{4-}}] = \frac{[\mathrm{TPPS}]_\mathrm{t}}{1 + \dfrac{[\mathrm{H^+}]^2}{K_\mathrm{a}} + K_\mathrm{f}[\mathrm{CTA^+}]^4}.$$

Here $[\mathrm{TPPS}]_\mathrm{t} = [\mathrm{H_2TPPS^{2-}}] + [\mathrm{TPPS^{4-}}] + [\mathrm{TPPS(CTA)_4}] + \Gamma_\mathrm{c}\times(1000\times S/V)$, where S and V are an area of the interface (1.77 cm^2) and a volume of the TPPS solution (2.00 cm^3). Values of $[\mathrm{CTA^+}]$ were obtained at various pHs by resolving a quintic equation with coefficients normalized with the concentrations determined experimentally. Figure 10 shows the concentrations determined and a curve including solutions of the quintic equation. Equation 4 indicates that Γ_max and K_ad can be determined from a plot of $[\mathrm{TPPS^{4-}}]/\Gamma_\mathrm{c}$ vs. $[\mathrm{TPPS^{4-}}]$. Figure 11 shows the plot. The straight solid line in this figure was obtained from a least-square method for five points in the $\mathrm{TPPS^{4-}}$ concentration range between 4 and 14×10^{-9} M. From the slope and the intercept, Γ_max and K_ad were determined to be 1.72×10^{-11} mol cm^{-2} and 6.78×10^8 dm^3 mol^{-1}. The reciprocal of Γ_max suggests that one admicelle, strictly one 1 : 7 complex, occupies an area of 9.65 nm^2 on the glass surface. According to the compact aggregate model,17) the diameter of an admicelle is limited within one to two times the length of the surfactant ion. Because the length of the $\mathrm{CTA^+}$ ion was estimated to be 2.3 nm by Molecular Mechanics 2 (MM2),30) the occupied area is predicted to be between 4.2 and 16.6 nm^2. The occupied area obtained from the plot is approximately an average of the area predicted. This result confirms that the admicelle is a compact aggregate and that one $\mathrm{TPPS^{4-}}$ ion is incorporated with the aggregate to form the 1 : 7 complex. Because of Coulombic forces between negative and positive charges on the $\mathrm{TPPS^{4-}}$ ion and the admicelle surface, the $\mathrm{TPPS^{4-}}$ ion probably resides at the admicelle periphery (see Fig. 7).

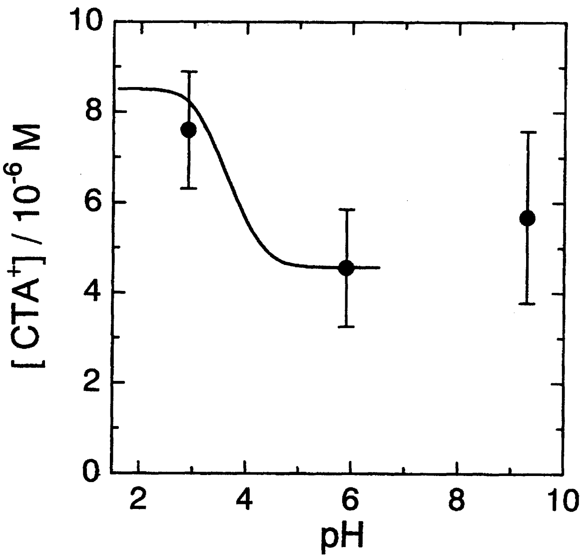

Fig. 10. pH dependence of the $\mathrm{CTA^+}$ concentration in the bulk of solution. The error bars indicate standard deviations for three measurements. The curve shows solutions of the quintic equation for $[\mathrm{CTA^+}]$ (see text). The concentrations were measured after the adsorption attained equilibrium.

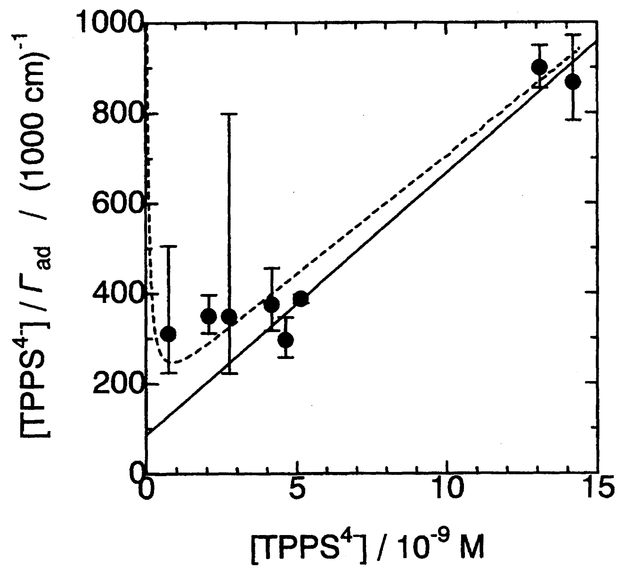

Fig. 11. Plot of $[\mathrm{TPPS^{4-}}]/\Gamma_\mathrm{c}$ vs. $[\mathrm{TPPS^{4-}}]$. The straight line was obtained from a least-square method for five points in the $\mathrm{TPPS^{4-}}$ concentration between 4 and 14×10^{-9} M. The broken curve was drawn by using Eq. 5 when $x=2$ and $K_\mathrm{ex} = 1\times10^{-29}$ M^5.

In Fig. 11, disagreement between the straight line and the experimental values can be seen in the $\mathrm{TPPS^{4-}}$ concentration range below 3×10^{-9} M. Such low $\mathrm{TPPS^{4-}}$ concentrations are found in the solutions with pHs below 4. Because little adsorption of the surfactant ion takes place at pHs below 4, the disagreement is thought to be due to low formation of the admicelle on the glass surface in the acidic region. This can be explained in terms of ion exchange between the CTA^+ ions in the admicelle and hydrogen ions of a silanol group on the glass surface. Coupling the ion exchange equilibrium,

$$\{Si(-O^-)_x \cdot (CTA^+)_{ad}\}^{7-x} + xH^+ \rightleftharpoons Si(-OH)_x + 7CTA^+,$$

with the above equilibria changes Eq. 4 to the next expression,

$$\frac{[TPPS^{4-}]}{\Gamma_c} = \frac{1}{K_{ad}\Gamma_{max}}\left(\frac{K_{ex}[H^+]^x}{[CTA^+]^7} + 1\right) + \frac{[TPPS^{4-}]}{\Gamma_{max}}. \qquad (5)$$

Here

$$K_{ex} = \frac{[Si(-OH)_x][CTA^+]^7}{[\{Si(-O^-)_x \cdot (CTA^+)_{ad}\}^{7-x}][H^+]^x}.$$

Further $Si(-O^-)_x$ and $Si(-OH)_x$ denote the dissociated and neutral silanol groups on the glass surface. When x was equal to 2, the fitting was fairly good (the broken line in Fig. 11). It is apparently contradictory with electric neutrality in an ion exchange equilibrium that two hydrogen ions, which belong to the same silanol group, ion-exchange with seven CTA^+ ions of the admicelle. However, an idea that the compact aggregate can interact with the glass surface only through a few CTA^+ ions (see Fig. 7) may accept the result that x is equal to 2. The solid line in Fig. 8 shows a theoretical curve calculated from Eq. 5 when x and K_{ex} are equal to 2 and 1×10^{-29} M^5. The curve is fairly fitted with the experimental values, indicating that the pH dependence between pH 3 and 6 is successfully explained by the present treatment.

The adsorption constants of the $TPPS^{4-}$ ion at liquid–liquid interfaces were determined in the presence of CTAB.[15] The constants were 45 cm at the toluene–water interface and 1.2 cm at the bis(2-ethylhexyl) phthalate–water interface. The constant determined in this work is estimated to be 11.7 cm ($=\Gamma_{max} \times K_{ad}$), which is similar to those at the liquid–liquid interfaces. This implies that the interaction between the $TPPS^{4-}$ and CTA^+ ions is essentially identical at the glass–liquid and liquid–liquid interfaces, namely, the interaction is merely electrostatic at both interfaces. However, the structural shape of the admicelle is greatly dependent on the interface. Because the glass surface is strongly hydrated, the hydrophobic alkyl chains associate with each other to produce the compact aggregate at the glass–solution interface. On the other hand, at the liquid–liquid interface, a uniform layer can be easily formed because of dissolution of the alkyl chains into the organic phase.

Concentration and separation of electrically neutral species have been studied by using surfactant admicelles adsorbed on a solid substrate.[2,31] These studies mainly rely on a hydrophobic part of the admicelle. However, as shown in this work, the admicelle is available for concentrating ionic species. The admicelle will therefore become a more important phase in separation chemistry.

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