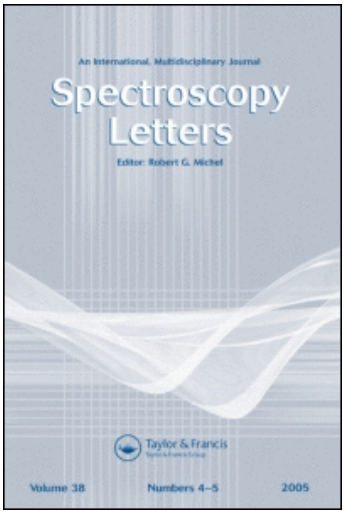

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ELECTRIC SPECTRA STUDY OF TETRA-HYDROPHENYL PORPHYRIN WITH TWO HEXADECYL CHAINS IN CTAB MICELLE AQUEOUS SOLUTIONS

Key Words: electric spectra, porphyrin, CTAB, micelle.

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ABSTRACT

UV-visible and fluorescence spectral studies shows that tetra-hydrophenyl porphyrin with two hexadecyl chains (P_2) could be solubilized in CTAB micelle, and that the hydrophilic ability of P2 increases with increasing bulk pH. The change in bulk pH lead to the changing of the solubilizing location of P_2 in the CTAB micelle. In neutral (pH 6.88) conditions, the hydrophilic head group of P_2 readily locates in the stern layer of CTAB micelle. However, the solubilizing location of P_2 takes a location change to the outer surface of the CTAB micelle with the bulk pH increasing up to 11.41. Furthermore, the CTAB micelle could provide a strong basic microenvironment (like 1.5 mol dm^{-3} NaOH aqueous solution) to P_2 in mild basic conditions; resulting in the deprotonation of the pyrrole nitrogen of the porphyrin moiety in a mile basic CTAB micelle solution.

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INTRODUCTION

The biomimetic chemistry of porphyrins is inspired by the central role of this molecule in important biological processes such as: light energy conversion, oxygen transport, and catalysis.[1-4] The diverse chemical and photophysical properties of porphyrins are in many cases due to the fact that these molecules are located in very different environments. Therefore, special incorporation of porphyrin molecule guests in biomimic membranes and their functions have been of great interest. Groves and Neumann [5] used a steroidal porphyrin to conduct a regio-selective epoxidation in phospholipid vesicles. Tsuchida and co-workers [6] introduced polymerizable porphyrins and phosphocholine porphyrins into polymerizable phospholipid vesicles, and examined their oxygen-carrier properties. By incorporating porphyrins in synthetic bilayers, Van Esch et. al. [7-8] investigated the location and orientation of them in the lipid bilayer. By selecting the anionic copper (II) porphyrins with different number negative charges, Ishikawa et. al. [9] has made it possible to insert them in host membranes with particular orientations.

So far, however, there is still no reported work about controlling porphyrin location in a membrane medium. In this paper, the prepared tetra-hydrophenyl porphyrin, with two hexadecyl chain P_2 (shown in Figure 1), was selected to be solubilized in CTAB micelle solutions. This kind of amphiphilic porphyrin shows an interesting property, in that the hydrophilic ability of hydrophenyl groups could be increased when they are deprotonized in basic conditions. Based on this property, we report a novel transfer process of porphyrin moiety from the inner, or stern, layer of CTAB micelle to the outer surface of CTAB micelle.

EXPERIMENTAL

Tetra-hydrophenyl porphyrin with a two hexadecyl chain (P_2) was prepared according to the previous literature.[10-12] Cetyltrimethyl ammonium bromide (CTAB) was the analytical reagent and was recrystallized twice from 90%

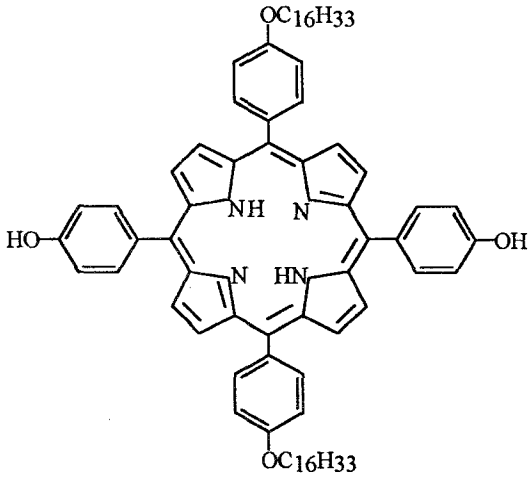

FIG.1. Structure of tetra-hydrophenyl porphyrin with a hexadecyl chain.

ethanol. Water was doubly distilled after passing through an ion-exchange resin column. All the organic solvents were analytical grade pure and were used without further purification.

CTAB micelle solution and 1.5 mol dm^{-3} NaOH aqueous solutions of P_2 were directly prepared from the porphyrin sample. In order to make P_2 completely soluble in the pure aqueous solution, and other organic-water mixtures (in order to measure the polarity effects on porphyrin electric spectra), solutions were prepared by injection of a specified amount of 2.5×10^{-3} mol dm^{-3} dioxane solution of P_2 to obtained 25 ml of total solution. Using this experimental condition, the volume ratio of dioxane and water or other mixture solvents was greater than 1000, so the effects of trace dioxane on the solution polarity could be neglected. After 20 min of sonication, the UV-visible spectra and fluorescence spectra of solutions were recorded on a Shimudu UV-3100 spectrophotometer and a Perkin-Elmer LS50B fluorescence spectrophotometer, respectively, by using a 1 cm quartz cell. The pH value of solutions were measured using a pH-

250 pH meter, and the solution pH was controlled by 1.5 mol dm^{-3} NaOH and 1:4 HCl aqueous solutions.

RESULTS AND DISCUSSION

1. Solubilizing of Tetra-hydrophenyl Porphyrin with Two Hexadecyl Chains in CTAB Micelle Solutions.

The amphiphilic porphyrin P_2 shown in Figure 1 is composed of: hydrophilic hydrophenyl groups, hydrophobic hexadecyl chains, and the porphyrin moiety. Figure 2 exhibits the UV-visible spectra of P_2 with a fixed concentration of 2.8×10^{-6} mol dm^{-3}, with different CTAB concentrations in aqueous solution. It can be seen from Figure 2 (1) that tetra-hydrophenyl porphyrin with two hexadecyl chains has a low solubility in pure aqueous solution, although it has two hydrophilic hydrophenyl groups and there is no obvious absorption peak that can be detected within the experimental region. However, with the concentration of CTAB increasing, the overall absorption of P_2 increases accordingly. When the concentration of CTAB increases up to 5.6×10^{-4} mol dm^{-3}, a strong characteristic soret band of P_2 at 431 nm (Figure 2 (4)) appears, indicating that P_2 can be solubilized in the CTAB micelle solution. With the concentration of CTAB increasing up to 2.6×10^{-3} mol dm^{-3}, the solubilizing behavior became more obvious and the absorbance at 431 nm of P_2 increased accordingly. Figure 3 shows the plot of absorbance at 431 nm against the concentration of CTAB. It can be seen from this figure that the soret band absorbance of P_2 increased abruptly around [CTAB]=5.6×10^{-4} mol dm^{-3}. Compared to the CMC of CTAB, as reported in the literature (9.2×10^{-4} mol dm^{-3})[13], the CMC of CTAB experiences some decrease in this system which may be induced by the porphyrin molecule. Mukejee et. al. [14] had investigated this decreasing mechanism of surfactant CMC induced by dye molecules. It concluded that the tetra-hydrophenyl porphyrin with two hexadecyl chains could be solubilized in CTAB micelle.

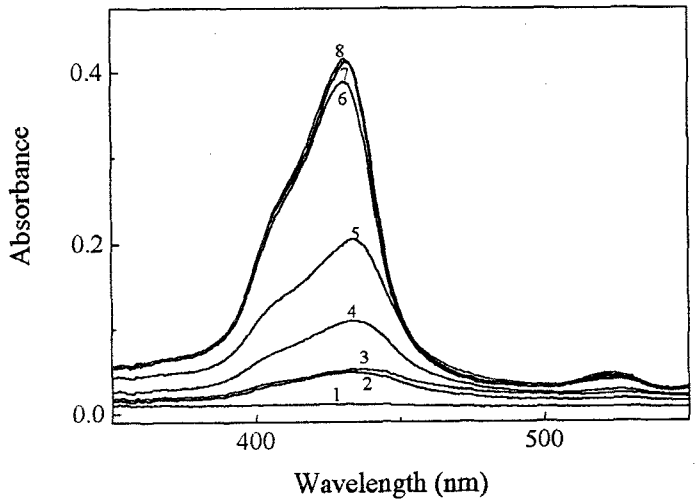

FIG. 2. UV-visible spectra of P_2 with fixed concentration of 1.6×10^{-5} mol dm^{-3} in different CTAB concentration aqueous solutions.
(1) [CTAB]=0 mol dm^{-3}; (2) [CTAB]= 1.0×10^{-4} mol dm^{-3}; (3) [CTAB]= 2.6×10^{-4} mol dm^{-3}; (4) [CTAB]= 4.2×10^{-4} mol dm^{-3}; (5) [CTAB]= 5.2×10^{-4} mol dm^{-3}; (6) [CTAB]= 7.8×10^{-4} mol dm^{-3}; (7) [CTAB]= 1.3×10^{-3} mol dm^{-3}; (8) [CTAB]= 2.6×10^{-3} mol dm^{-3}.

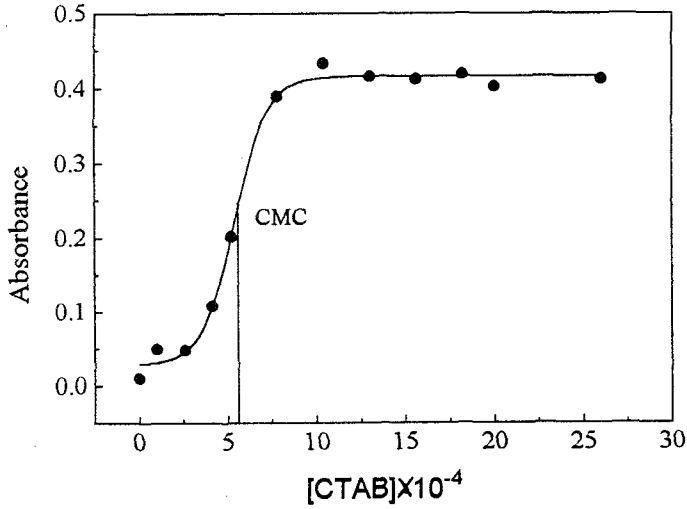

FIG. 3. Plot of absorbance of 431 nm of P_2 against the CTAB concentration.

2.UV-visible Spectra of Porphyrin in Different pH CTAB Micelle Aqueous Solutions.

It is known from Figure 2 (1) that P_2 has a low solubility in neutral aqueous solutions. However, it is found that the water solubility of P_2 can be increased with the bulk pH increasing, indicating that the hydrophilic ability of the hydrophenyl groups could be increased when they are deprotonized to form P_2^{-1}, P_2^{-2} and irons. Furthermore, P_2 becomes easily soluble in aqueous solutions under strong basic conditions, such as 1.5 mol dm^{-3} NaOH aqueous solution. The data of UV-visible spectra of P_2 are listed in Table 1, it can be seen from this Table that in 1.5 mol dm^{-3} NaOH aqueous solution, the half peak width of the soret band of P_1 increased markedly; and two new bands appeared at 585 nm and 675 nm, instead of the four Q bands of P_2 which occur in neutral aqueous solutions or organic solvents. These absorption characteristics, similar to that of metal porphyrins, indicate that the porphyrin moiety of P_2 has a symmetrical structure similar to that of metal porphyrins.[15] However, there is only one kind of metal ion (Na^+) that is difficult to complex. This indicates that in strong basic conditions, hydrogen atoms bonded to the pyrrole nitrogen atoms of porphyrin moiety may be deprotonized to form P_2^{-4}. So the porphyrin exhibits relatively strong hydrophilic ability and becomes easily soluble in water. The possible deprotonization process of P_2 is shown in Figure 4.

Figure 5 shows the UV-visible spectra of P_2 in CTAB micelle solution at various bulk pH, and Figure 5 (a) and (b) are the soret band and Q bands of P_2, respectively. It is clear from this picture that it takes a great change on maximum absorbance, half peak width of the soret band, as well as Q bands of P_2 with the bulk pH increasing, indicating that the structure and the location of the microenvironment of

P_2 solubilizing in CTAB micelle are also changed accordingly.[16] In order to make the comparison, the data of the UV-visible spectra of P_2 in different solutions, together with the relative spectral data of Figure 5, are all listed in Table 1. It can be seen from this table that in pH 6.88 CTAB aqueous solution, the soret band of P_2 shows a maximum at 431 nm, and the half peak width is relatively narrow;

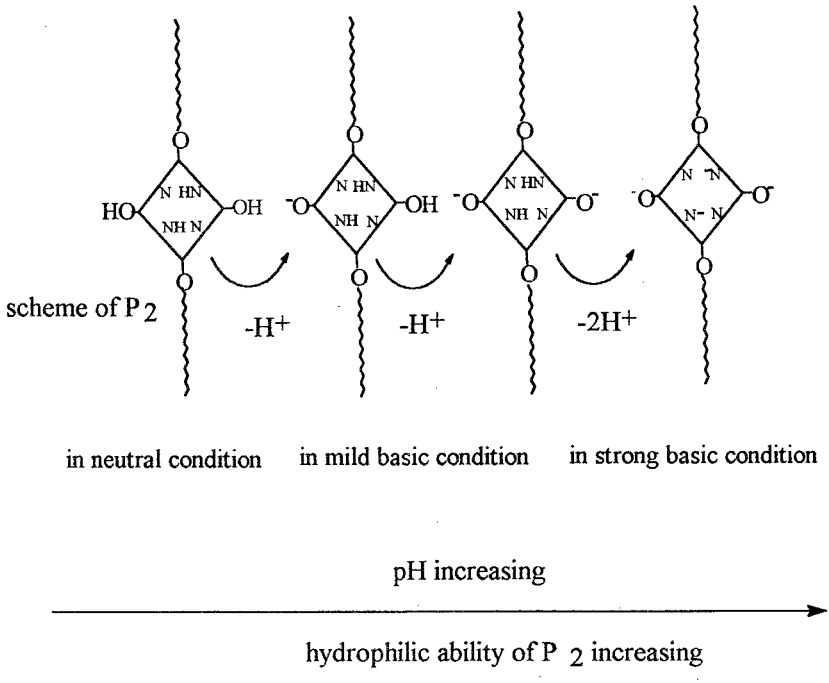

FIG. 4. Deprontonation process of P_2 with the pH of solution increases.

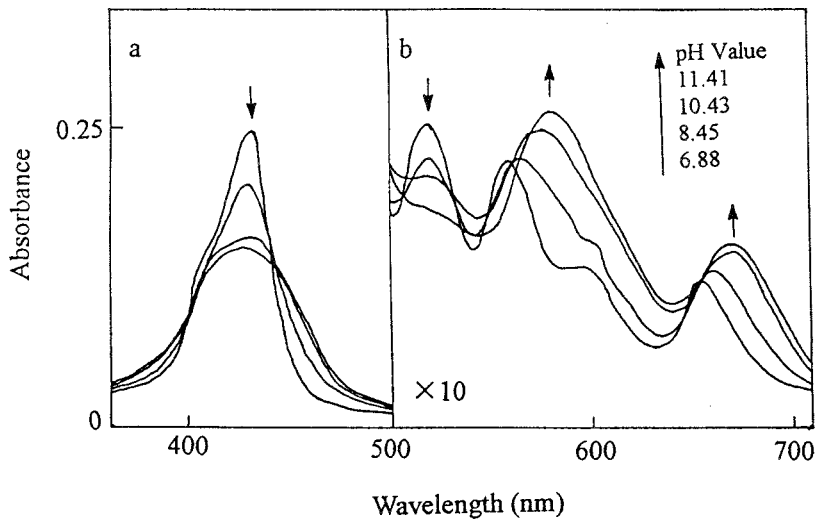

FIG. 5. UV-Visible spectra of P_2 in different pH CTAB micelle aqueous solutions.

$[P_2]= 1.6\times10^{-6}$ mol dm^{-3}; $[CTAB]= 2.6\times10^{-3}$ mol dm^{-3}.

TABLE 1.

The UV-Visible Spectra Data of P2 in Different Solutions.[a]

Solutions	pH	Soret Band λ_{max} (nm)	ε (L/mol.cm)	$W_{1/2}$ (nm)	Q Bands Q_1	Q_2	Q_3	Q_4 (nm)
CTAB Auqeous Solution	6.88	431	1.89×10^5	35	520	560	595	653
2-propanol	-----	421	4.73×10^5	17	507	546	591	648
CTAB Aqueous Solution	11.42	433	1.23×10^5	66	583			671
Aqueous Solution[b]	6.20	437	0.31×10^5	50	523	564	594	657
Aqueous Solution[b]	11.19	438	0.28×10^5	70	526	565	597	658
1.5 mol dm^{-3} NaOH Aqueous Solution	Strong Basic	433	0.77×10^5	70	585			675

a: $[P_2]=1.6\times10^{-6}$ mol dm^{-3}; $[CTAB]=2.6\times10^{-3}$ mol dm^{-3}.
b: Preparation of the solutions was described in experimental section.

four Q bands appear at 520, 560, 595, and 653 nm respectively. These absorption characteristics are similar to those of P_2 in organic solvent 2-propanol, rather than in aqueous solutions. It suggests that P_2 should locate in the inner core of the CTAB micelle with a polarity microenvironment like 2-propanol. Nevertheless, in a pH 11.41 CTAB micelle aqueous solution, the UV spectra of P_2 is greatly changed. The soret band of P_2 decreases and experiences obvious broadening. Furthermore, two new bands appear at 583 nm and 671 nm, instead of the four Q bands of P_2 in neutral condition. These spectral characteristics are similar to that of P_2 in strong basic solutions, such as 1.5 mol dm^{-3} NaOH aqueous solutions ([CTAB]=0). This indicates that P_2 may be completely deprotonized to form P_2^{-4} as shown in Figure 4. In pH 11.41 CTAB micelle aqueous solution, and influenced by the strong hydrophilic ability of P_2^{-4}, the solubilizing location of P_2 may transfer from the inner core of the micelle to the stern layer of the micelle; which could provide a relatively strong polarity microenvironment.

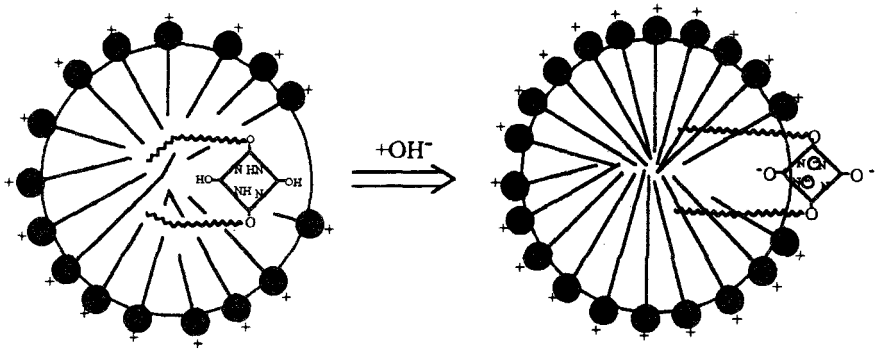

FIG. 6. The changing of solubilizing location of P_2 in CTAB micelle with bulk pH increasing.

The above investigations are focused on the solubilizing location of P_2 in a CTAB micelle at two special pH value (6.88 and 11.41). The UV-visible spectra of P_2 as shown in Figure 5, suggests that P_2 solubilizes in the hydrophobic inner CTAB micelle under neutral conditions. With the pH of solution increasing, the hydrophilic ability of P_2 increases accordingly, and the porphyrin macrocycle will approach to or even transfer out of the stern layer of the micelle as the hydrophenyl groups and porphyrin moiety are being deprotonized. This transfer process could be represented as in Figure 6.

It should be pointed out that the deprotonization of pyrrole nitrogen atoms of porphyrin moiety could take place only in strong basic aqueous solutions (such as 1.5 mol dm^{-3} NaOH aqueous solution). While in mild basic conditions, as pH 11.19 pure aqueous solution ([CTAB]=0), the UV-visible spectrum of P_2 still exhibits four Q bands, and no obvious change could be detected (see Table 1). However, in a pH 11.41 CTAB micelle solution, P_2 shows an absorption spectrum similar to that of P_2 in strong basic solution and could be completely deprotonized under such a low pH condition. This indicates that the CTAB micelle could provide a strong basic surface microenvironment to P_2 although the bulk pH is not too high. This function of CTAB micelle is based on the surface

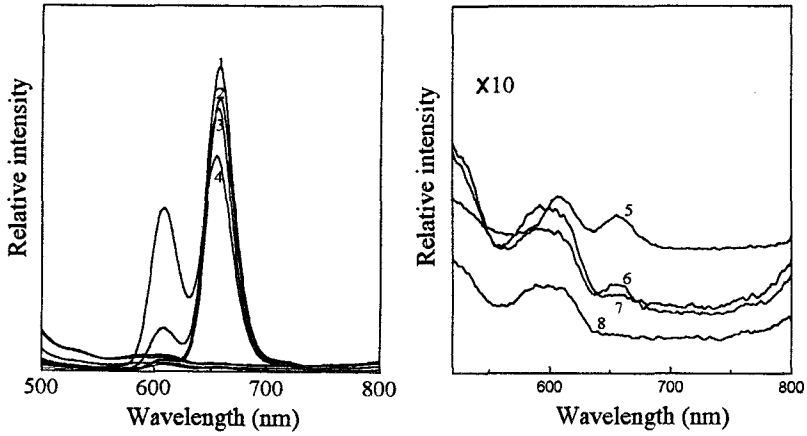

FIG. 7. Fluorescence spectra of P_2 in different solutions.
(1) dioxane; (2) tetrahydrofuran; (3) 2-propanol; (4) methanol; (5) 70% MeOH-H_2O; (6) 50% MeOH-H_2O; (7) 20% 2-propanol-H_2O; (8) H_2O.

potential property of the micelle. The relationship between surface potential and surface effective concentration of H^+ of the micelle is shown by the following Equation.[17]

$$\alpha_H^i = \alpha_H^w \, e^{-F\Psi/RT} \qquad (1)$$

Where α_H^i and α_H^w are the effective concentration of H^+ in the micelle surface and bulk aqueous phase respectively, F is Faraday constant, Ψ is surface potential of the micelle, T is degrees Kelvin temperature, and R is the Boltzman constant. As we know, the cation surfactant CTAB micelle exhibits a positive surface potential ($\Psi>0$), so $\alpha_H^i \ll \alpha_H^w$ according to Equation (1). This means that the pH value of the CTAB micelle surface is much greater than that of the bulk aqueous phase. Thus, the CTAB micelle could provide a strong basic surface microenvironment under mild basic conditions, and make P_2 completely deprontonized to form hydrophilic P_2^{-4}.

3. Fluorescence Spectra of Porphyrin in CTAB Micelle Solutions.

It is well accepted that the inner core of the spherical micelle has shown low polarity; and the effective dielectric constants of the stern layer are approximately 36~46.[18] The outer surface of the micelle, as well as the nearby bulk aqueous phase, exhibit strong polarity. Thus, the polar microenvironment of the micelle could be represented by the dielectric constant (ε) as in following:

$$\varepsilon_{\text{hydrophobic inner core}} < \varepsilon_{\text{stern layer}}\ (36\sim46) < \varepsilon_{\text{outer surface and nearby aqueous phase.}} \quad (2)$$

In other words, the more distance there is from the hydrophobic center of micelle, the greater polarity the microenvironment exhibits.

Previous studies showed that the fluorescence spectra of porphyrins were greatly effected by the polarity of the solvents. [19-20] In general, fluorescence intensity increased when the polarity of the solvents decreased, and vice verse. Figure 7 illustrates the fluorescence spectra of P_2 in different solvents. It can be seen from this Figure that in the low polarity solvent of dioxane (ε=2.3), P_2 exhibits a very strong fluorescence band at 660 nm and a relatively weak shoulder band at around 610 nm, respectively. While in a 50% water-methyl mixture, where solvents exhibit a dielectric constant of 54.9, the fluorescence band at 660 nm decreases markedly. Moreover, the 660 nm fluorescence band is almost quenched in a pure aqueous solution (ε=78.5). However, with the polarity of solvents increasing, the fluorescence band at 610 nm is not changed as fast as that of the band at 660 nm (it even increased by comparison). Based on this behavior, the polar microenvironment of P_2 can be represented by the fluorescence intensity ratio of 610 nm and 660 nm A_{610}/A_{660} of P_2. Figure 8 shows the plot of A_{610}/A_{660} of P_2 against the dielectric constants of different solvents. It can be seen from this plot that in the low polarity regions, with dielectric constants (ε) lower than 22, the plot is flat. This indicates that no obvious change in the intensity ratio A_{610}/A_{660} appears, especially the fluorescence intensity of 660 nm of P_2. However, when the dielectric constant of

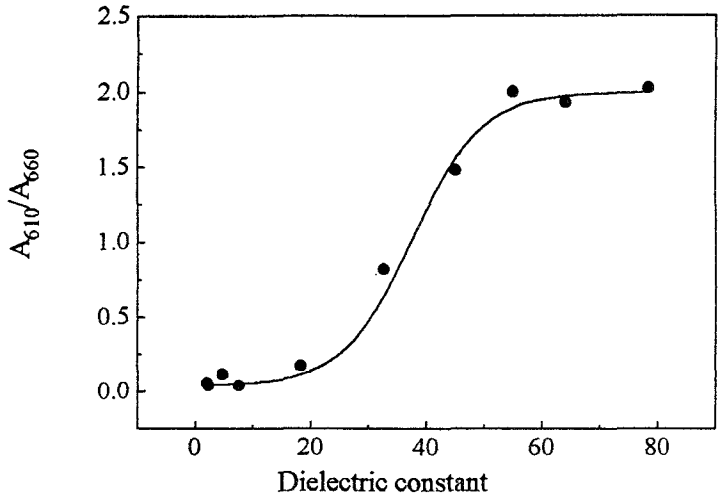

FIG. 8. Plot of intensity ratios of 610 nm and 660 nm of P_2 against the dielectric constants of solvents.

The solvents and their dielectric constants used in this experiment from left to right are:[20-21] dioxane (2.3); chloroform (4.8); tetrahydrofuran (7.6); 2-propanol (18.3); 95% ethanol (26.1); methanol (32.6); 70% MeOH-H_2O (45.0); 50% MeOH-H_2O (54.9); 20% 2-propanol-H_2O (64.1); H_2O (78.5).

solvent increased to greater than 22, the intensity ratio of P_2 increased rapidly, corresponding to the quenching of the fluorescence band at 660 nm. This quenching behavior may be due to the solvent effects as described above. Furthermore, according to Table 1, the UV-visible spectra of P_2 show some red shift, and lower absorbance and broader half peak width, in strong polar solutions. So P_2 may form different kinds of non-fluorescence multimers instead of monomer or other ordered and single aggregates.[23-24] This effect leads to the fluorescence quenching of P_2.

Figure 9 displays the fluorescence spectra of P_2 in CTAB micelle solutions with different bulk pH values. It can be seen from this picture that in bulk pH 6.88 solution, P_2 exhibits a strong fluorescence band at 660 nm and a weak shoulder band at around 610 nm, respectively. With the bulk pH value increasing,

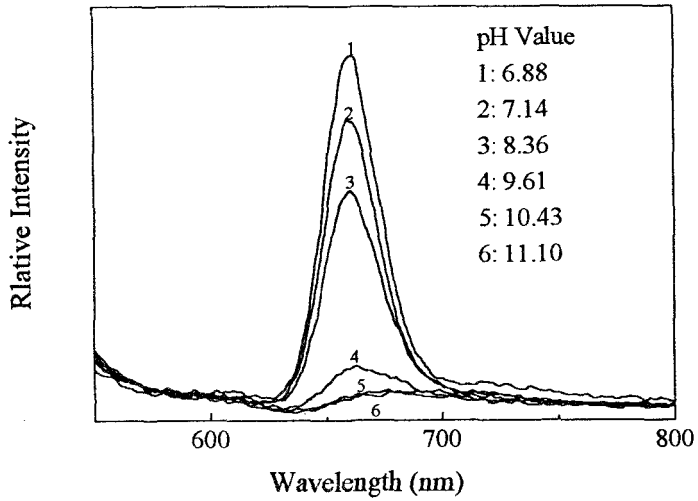

FIG. 9. Fluorescence spectra of P_2 in different pH CTAB micelle aqueous solutions.
$[P_2]= 1.4\times10^{-6}$ mol dm^{-3}; $[CTAB]= 2.6\times10^{-3}$ mol dm^{-3}.

the fluorescence band at 660 nm decreases rapidly, and red shifts to around 690 nm gradually. Nonetheless, the shoulder band at 610 nm shows little effect on the changing of the bulk pH. Contrasted with the similar behavior of Figure 7 and Figure 8, it allows the conclusion that the polar microenvironment of P_2 solubilizing in the CTAB micelle changes greatly with the bulk pH increasing. In pH 6.88 CTAB micelle solution, the intensity ratio A_{610}/A_{660} of P_2 is similar to that of P_2 in solvent with a dielectric constant of 14. According to the polar microenvironment relationship (2) of the micelle, the porphyrin hydrophilic head group was located in the inner core of CTAB micelle in the bulk pH 6.88 condition. With the bulk pH of the solution increasing up to 11.10, the hydrophilic ability of P_2 increased accordingly, which make the porphyrin hydrophilic moiety transfer towards the stern layer of the micelle. So the fluorescence band of P_2 decreased and the intensity ratio A_{610}/A_{660} of P_2 increased accordingly. The red shift of the 660 nm band to 690 nm indicates that the electric

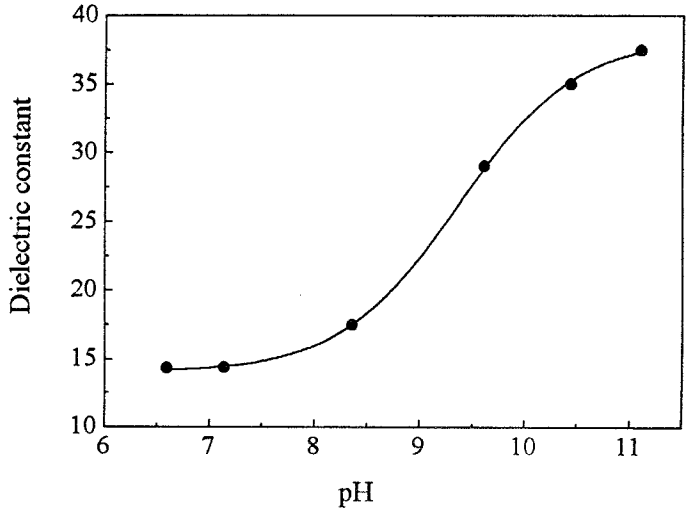

FIG. 10. Plot of dielectric constants against the pH value of CTAB micelle solutions of P_2.

state of P_2 changed as the deprotonation of hydrogen phenyl groups and pyrrole nitrogen atoms of porphyrin moiety occurred under basic conditions. The plot of the intensity ratio A_{610}/A_{660} of P_2 in different bulk pH CTAB micelle solutions against the corresponding polar microenvironment (dielectric constants) obtained from Figure 8 is shown in Figure 10. It is clear from this plot that bulk pH is a controlling factor in the transfer process of solubilizing location of P_2 in CTAB micelle. The porphyrin moiety was transfer from the stern layer of micelle with low polar microenvironment of ε=14 to the outer surface of micelle with strong polar microenvironment of ε=38. This pH controlled transfer process of P_2 in CTAB micelle is corresponding to the same results obtained by the UV-visible spectra study described above.

CONCLUSIONS

According to the UV-visible and fluorescence spectra of P_2, it can be

concluded that P_2 could be solubilized in CTAB micelle. It can also be concluded that the CTAB micelle could also provide a strong basic microenvironment (i.e., 1.5 mol dm^{-3} NaOH aqueous solutions) to P_2 in mild basic conditions. This results in the deprotonation of pyrrole nitrogen of porphyrin moiety in mile basic CTAB micelle solution. Furthermore, the hydrophilic ability of P_2 increases with the bulk pH increasing, which leads to the changing of the solubilizing location of P_2 in the CTAB micelle. In neutral (pH 6.88) conditions, the hydrophilic head group of P_2 is easily located in the hydrophobic inner core of the CTAB micelle; and the solubilizing location of P_2 takes a change to the stern layer of the CTAB micelle with the bulk pH increasing up to 11.49.

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