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Protonation of 5, 10, 15, 20-Tetra(4-hydroxyphenyl)-porphyrin in SDS Micellar Solution

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Abstract: An amphiphilic porphyrin, 5, 10, 15, 20-tetra(4-hydroxyphenyl)-porphyrin (**P**) was solubilized in SDS micellar solutions. By taking advantage of protonation property of pyridine groups of amphiphilic porphyrin and the UV-Vis spectral sensitivity of Soret band and Q bands to the microenvironment of the porphyrin moiety, two-step protonation was studied in detail by means of UV-Vis spectroscopy. The free base, monocation and dication were described in detail in SDS micellar solution. The possibility of microphase transition was proposed to relate to the observation of two isosbestic points.

Keyword: Amphiphilic porphyrin, SDS, micellar solution, protonation.

Micelles, microemulsions and vesicles constitute a very active area of investigation for manifold implications in chemistry, physics, biology and materials sciences. In supramolecular chemistry, such organized noncovalent assemblies have been exploited to mimic membrane behavior[1]. Porphyrins, having photophysical and photochemical properties, have attracted much interest of many researchers for their location in the active site of many important biomolecules and in particular of enzymes. Spectroscopic characterization of both cationic and anionic porphyrins interacting with cationic, neutral and anionic micelles has been reported[2-5]. The protonation of porphyrins in different membrane systems is also an important topic of many researches[6,7]. Alsoph *et al.* have reported the protonation of porphyrin in 60% glacial acetic acid and 40% acetone[8]. They observed four, three, and two Q bands for the free base, monoprotonationated and biprotonationated porphyrins respectively. George *et al.* studied that in SDS or TX-100 micelles, H_2triP and its water insoluble N-methyl derivative had two porphyrin forms: the free base and the di-acid[9]. In this work, an attempt is made to gain more insight into the nature of amphiphilic porphyrin interactions with the biological mimetic system using the simplest model for membranes and potential reaction centers: aqueous ionic micelle. An amphiphilic porphyrin, 5, 10, 15, 20-tetra(4-hydroxyphenyl) porphyrin (**P)**, was solublized in micelle sodium sulfate (SDS) solutions. Such a porphyrin has the advantage of being amphiphilic, The big hydrophobic porphyrin moiety can be solubilized in organic solvents so as to in the nonpolar region of micelle. At the same

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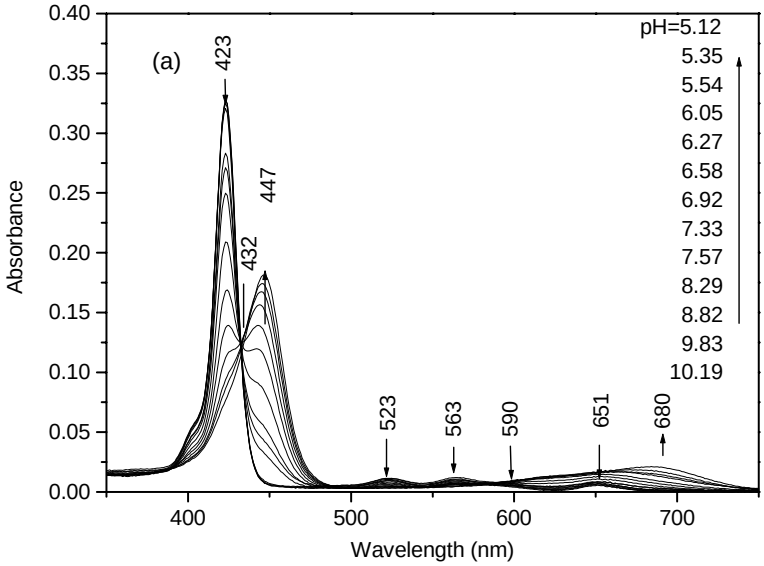
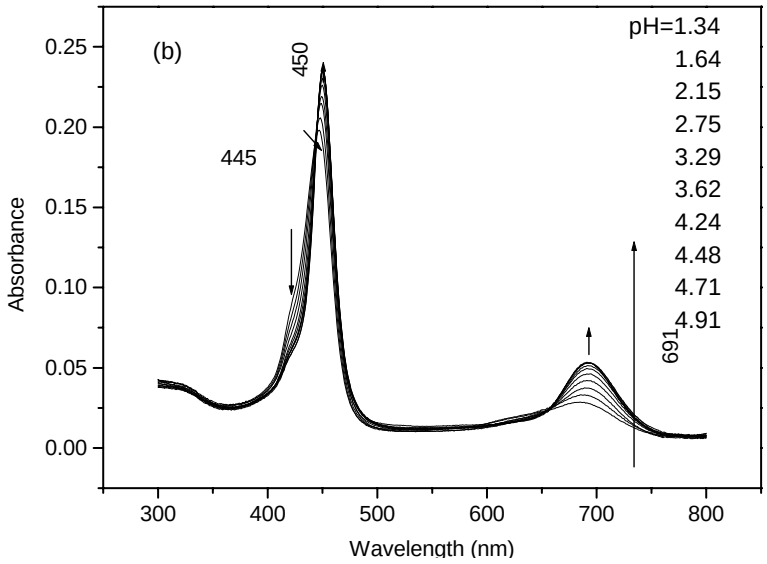
time, the four hydroxyphenyl groups have some hydrophilicity. Based on this property, the protonation of **P** in SDS micelle in the pH titration process will be discussed below.

Figure 1 UV-Vis spectra of **P** in SDS micelle at different conditions



(a) from pH10.19 to pH5.12;



(b) from pH4.91 to pH1.34.

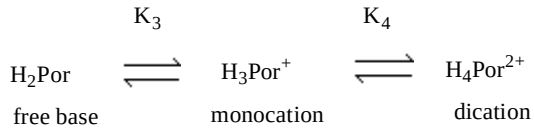
Results and Discussion

SDS solution containing 5,10,15,20-tetra(4-hydroxyphenyl)-porphyrin (**P)** was prepared by adding 10 μL of its 2.72×10^{-3} mol·L^{-1} tetrahydrofuran (THF) solution into 10 mL of 2.0×10^{-2} mol·L^{-1} SDS surfactant solution. The mixed solution was sonicated for 20 min. UV-visible absorption spectra were obtained by using TU-1901 spectrophotometer

Figure 1 shows the UV-Vis spectra of **P** in micellar SDS solutions at various bulk pH. At the first stage shown in **Figure 1 (a)**, starting from mild basic conditions (pH=10.19), the Soret band appears at 423 nm and four Q bands appear at 523, 563, 590, 651 nm respectively. With decreasing the pH value, the intensity of the Soret band at 423 nm decreases while a new Soret band at 447 nm appears and its intensity is increasing proportionately. At the same time, the intensities of the four Q bands all decreased to disappear. Instead, a new Q band with a wide half-width appears at 652 nm. With the decrease of bulk pH from 10.19 to 5.12, the new Q band shifts from 652 nm to 680 nm. Especially, an isosbestic point appears at 432 nm. Further addition of 1.5 mol·L^{-1} HCl to the SDS solution in **Figure 1 (b)**, *i.e.*, in the pH range of 4.91 to 1.34, the intensity of Q band at 691 nm continually increases. The Soret band appears at 450 nm and another distinct isosbestic point is shown at 445 nm.

In mild basic conditions (pH=10.19), these spectral characteristics of **P** in SDS micelle are as same as those of porphyrin monomer in organic solvent, which shows a Soret band at 419 nm and four Q bands at 518,556,595 and 649 nm, respectively. It suggested that the porphyrin moiety of **P** should be located in a weakly polar microenvironment in the inner core of the micelle near the surface of the SDS micelle as monomers. In strong acid conditions (pH=1.34), the number of Q bands changed from four to one. The overall absorption characteristics of **P** in pH 1.34 SDS solutions are similar to those of protonated **P** in 1.5 mol·L^{-1} HCl aqueous solution, indicating that **P** is protonated in a form of dications under this condition. The four Q bands and the shift of Soret band of **P** under neutral SDS conditions indicated that there is a new form for **P.** The Soret bands shifted from 423 to 447 nm due to the porphyrin monomers transformed from free base to a monocation. The isosbestic point at 432 nm results from the equilibrium of the free base and the monocation of **P**. It is noticed that the protonation of porphyrin could take place only under acidic conditions. The process of the formation of monocation under neutral condition indicates that SDS micelles could provide an acid surface microenvironment to **P**, although the bulk pH was not acidic. Fromherz and Masters[10] have found that the surface potential of SDS micelles is about –128 mV, which corresponds to a decrease of 2 units in the intrinsic pH value at the surface of SDS micelles compared to the bulk pH value. Therefore, it can be understood that a low pH value should exit at the surface layer of SDS micelles—similar to an aqueous acid solution.

One important fact is that there are two isosbestic points at 432 nm and 445 nm in the titration of **P.** Generally, the protonation of the porphyrins is considered to be described as follows[11, 12]:



In the most cases, due to the small difference between K_3 and K_4 (cooperative protonation), only two forms are observed by spectral methods: the free base H_2por and the dication H_4por^{2+} [11]. In our works, dissolution of **P** in neutral SDS micellar solution results in a new spectral form with a maximum absorbance at 652 nm, which has not been described before, we regard it as a sort of common effect of structure of **P** and its solubilizing site in SDS micelle. In order to identify this form, the solution was titrated with acid (HCl) and base (NaOH). With the addition of HCl, the new form (the 652 nm band) shifted to 691 nm, the isosbestic point was 445 nm, whereas deprotonation occurred on titration with NaOH, transformed this form into the **P** free base, absorbance at 652 nm disappeared and an isosbestic point was at 432 nm. These results allow to assign the new spectral form, which is spontaneously formed in neutral SDS and which is more acidic than the free base but less than the dication, to the monocation of **P**. Another interesting result is the sudden spectral change when the bulk pH decreases from pH5.54 to pH5.12, in other word, the isosbestic point at 432 nm only corresponds to the spectra in the pH range of higher than pH 5.54 while the isosbestic point at 445 nm just relates to the spectra of pH values lower than 5.12. We attribute it to a microphase transition related to the protonation process of **P** between pH 5.54 to 5.12.

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