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Absorption Complex between Porphyrin and Phenothiazine in Reverse Micelles

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Abstract: The interaction between amphiphilic porphyrin and phenothiazine in AOT/isooctane/ water reverse micelle was investigated by UV-Vis spectra. A new absorption complex between the two species is formed in such circumstances, which is ascribed to the enrichment of the components by the reverse micelle. The fluorescence quenching of CHTTP by PTH becomes more efficient after the formation of the absorption complex.

Keywords: Porphyrin, phenothiazine, absorption complex, reverse micelle.

Porphyrin derivatives attract much more interest in photodynamic therapy (PDT). Their importance as therapeutic drugs and targeting agents has been widely recognized[1], and many of the efforts have been put towards crafting new porphyrin-based molecular entities to achieve enhanced tumor localization, better tissue penetration and increased singlet oxygen quantum yield[2]. The states of porphyrins in tissue models such as micelles, lipid bilayers are extensively investigated focusing more or less on the aggregation of porphyrins and their interaction with surfactants or DNA[3-5]. While the interaction of porphyrins with other biological molecules in such circumstances was seldom involved. Here we used the simplest model, reverse micelle, for membranes and protein reaction centers to gain more insight into the interaction of porphyrins in biological structures with adjacent molecules. In view of the low ionization potential of phenothiazine, it was applied to represent the highly reductive molecules[6].

Results and Discussion

The amphiphilic porphyrin herein used is 5-[4-(6-carboxyhexoxy)phenyl], 10, 15, 20-tris (4-methylphenyl)porphyrin (CHTTP); the phenothiazine is 10H-phenothiazine (PTH); and the surfactant, S, is aerosol-OT [AOT, bis (2-ethylhexyl) sodium sulfosuccinate]. The water-surfactant molar ratio (w = $[H_2O]/[S]$) was kept at 10 with a concentration of AOT in isooctane (IOA) being 0.1 $mol \cdot L^{-1}$ throughout this paper. The absorption spectra were measured with Shimadzu UV-1601PC UV-Visible spectrophotometer and the fluorescence spectra with Hitachi F-4500 Fluorescence spectrophotometer.

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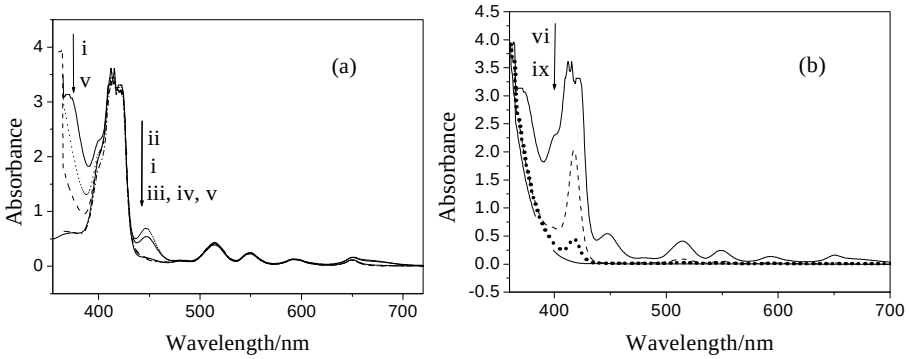
Figure 1 shows the absorption spectra of CHTTP and PTH with varied concentration. When increasing the concentration of PTH in CHTTP (2.3×10^{-5} mol·L^{-1}) AOT/IOA/water reverse micelle solution to 5×10^{-3} mol·L^{-1}, a new absorption at 447 nm emerges. As the concentration of PTH increased further, the height of the peak at 447 nm decreases compared to a lower concentration of PTH and another new peak in a strong absorption at 369 nm appears (see **Figure 1** (a)). The appearance of the absorption at 447 nm is concentration dependent not only on PTH but also on CHTTP. **Figure 1** (b) shows the absorption of PTH (1×10^{-2} mol·L^{-1}) with varied concentration of CHTTP. The absorption at 447 nm can appear only when both the concentrations of CHTTP and PTH get high enough. The observation of a new band at 447 nm is characteristic of the absorption complex of CHTTP and PTH but neither of CHTTP nor of PTH[7]. The concentration dependence of the new absorption band, as shown above, also confirms the formation of absorption complex.

Figure 1 Absorption spectra of CHTTP and PTH in AOT/IOA/water reverse micelles.



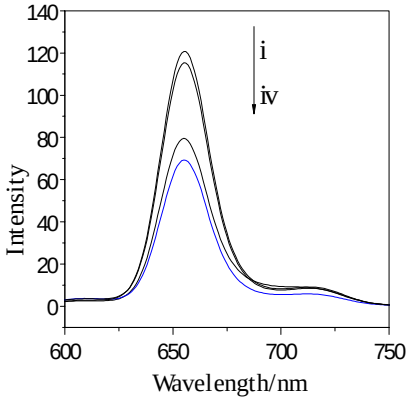
(a) The concentration of CHTTP was 2.3×10^{-5} mol·L^{-1}**;** the concentration of PTH varied to, in mol·L^{-1}, (i) 1×10^{-2}, (ii) 5×10^{-3}, (iii) 2.3×10^{-3}, (iv) 2.3×10^{-4}, (v), 0. (b) The concentration of PTH was 1×10^{-2} mol·L^{-1}**;** the concentration of CHTTP varied to, in mol·L^{-1}, (vi) 2.3×10^{-5}, (vii) 4.6×10^{-6}, (viii) 9.2×10^{-7}, (ix), 0.

The formation of such an absorption complex is ascribed to the enrichment of the reverse micelle. The saturated solution of PTH in IOA is *ca.* 2.5×10^{-3} mol·L^{-1}, and that of CHTTP is *ca.* 1.3×10^{-5} mol·L^{-1}; in such concentrations there was no new absorption band observed in IOA. The solubility of the two species in IOA is much improved by application of the reverse micelle. Considering the very poor solubility of PTH and CHTTP in water, the two components must predominantly localize in the interfaces between the hydrophobic zone and the polar aqueous interior of the micelle.

Intermicelle transfer of PTH or CHTTP is banned. When PTH and CHTTP were dissolved in the stock reverse micelle solution separately and then blended together at the same concentration to form the reverse micelle solution, no new absorption was observed. This fact indicates that once the component has localized in the reverse micelle, the

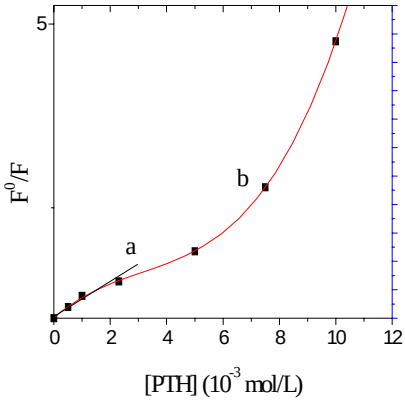
molecules are anchored in the micelles. The absorption spectra of the blended solution remained unchanged even though the blended solution was kept for three days at room temperature or sonicated for an hour. The poor ability of the components to transfer from one micelle to another may result from the low solubility in IOA. Such a phenomenon is concerned with the techniques of pharmacy.

Figure 2 Emission spectra of CHTTP (2.3×10^{-5} mol·L^{-1}) in reverse micelles; excitated at 434 nm with different concentrations of PTH.



(i) 0, (ii) 2.3×10^{-3}, (iii) 5×10^{-3}, (iv) 1×10^{-2} mol·L^{-1}.

Figure 3 Stern-Volmer plots quenching of CHTTP (2.3×10^{-5} mol·L^{-1}) by PTH. Excitation wavelength 413 nm.



The B band of CHTTP is a little blue-shifted by a new strong absorption (412 nm) abutting against the original band (417 nm) (see **Figure 1** (b)), which appears that the B band has broadened and such a shift can be attributed to the formation of H-aggregates[8].

$$R_w\ (\text{Å}) = 1.5\ w$$

Since the water pool radius follows the relation[9] and the apparent molar volume of Solubilized water in AOT/IOA/water reverse micellar solution is 56.8 mol·L^{-1} at 24°C[10], the reverse micelle concentration in the solution is *ca.* 2.1×10^{-3} mol·L^{-1}, nearly two orders of magnitude higher than the concentration of CHTTP in solution (2.3×10^{-5} mol·L^{-1}), which may disfavor the aggregation of CHTTP greatly because in such case the possibility of two CHTTP in one micelle will be not more than 1×10^{-4} according to Poisson population[12]. The formation of aggregate of CHTTP, however, was indeed observed, which further support the conclusion obtained above that the intermicelle transfer of CHTTP is banned, because the intermicelle transfer of CHTTP will facilitate the scattering of CHTTP among the micelles.

The fluorescence spectra of CHTTP are shown in **Figure 2**. The quenching of CHTTP by PTH becomes more efficient when the concentration of PTH has increased high enough to form the absorption complex, and further increase of the concentration of PTH gives little contribution to the efficient quenching of CHTTP.

Linear Stern-Volmer plots were obtained in the quenching of CHTTP in the concentration of PTH below 2.3×10^{-3} mol·L^{-1} (see **Figure 3**, a). Upward curving is produced by increasing the concentration of PTH, which suggests the formation of a probe-quencher complex, *i.e.* the absorption complex between PTH and CHTTP (see **Figure 3**, b)[11].

In summary, the interaction of an amphiphilic porphyrin, CHTTP, with phenothiazine was investigated in AOT/IOA/water reverse micelles by UV-Vis spectra. A new absorption complex formed in such circumstances because of the enrichment of solutes by the reverse micelles, and fluorescence quenching of CHTTP by PTH became more efficient after the formation of absorption complex.

Acknowledgments

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