Different Aggregation Behaviors of Tetra- (4-hydroxyphenyl) Porphyrin ($THPPH_2$) in the Inner Core and on the Surface of CTAB Micelles

Chen MA, Yun Hong ZHANG*, Chang Song FU, Qian Shu LI

School of Chemical Engineering and Materials Science,
Beijing Institute of Technology, Beijing 100081

Abstract: The UV-Vis spectra of $THPPH_2$ in CTAB micelles at pH7.2 and pH11.0 were analyzed to study the effect of micellar environments on the aggregation behaviors of this porphyrin.

Keywords: $THPPH_2$, CTAB micelles, aggregation, UV-Vis spectra.

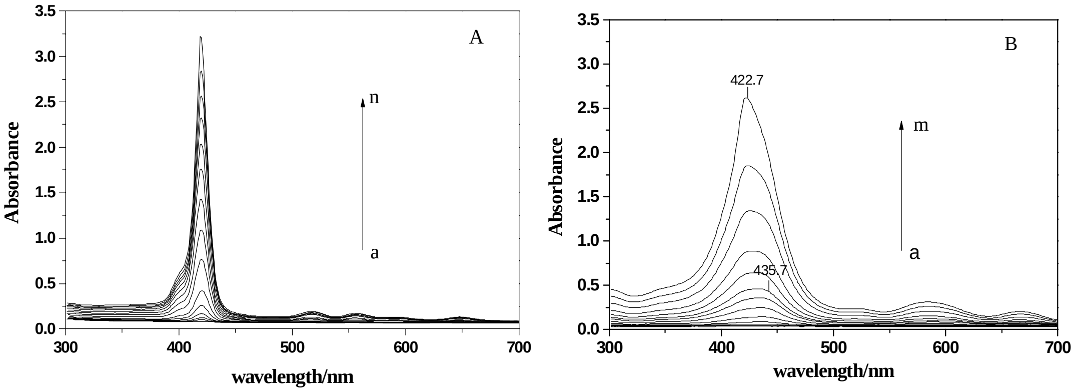
It is hard to study the effects of different microenvironments on porphyrin aggregation because of its complex substituted groups. A trans-membrane process was realized by controlling bulk pH values for an amphiphilic porphyrin from the inner core to the surface of CTAB micelles[1]. Thus it is posible to study the different aggregation actions of the porphyrin in the inner core and on the surface of micelle.

Results and Discussion

The absorption spectra of $THPPH_2$ at pH 7.2 have four Q bands at 516.8nm, 555.7nm, 589.7nm and 649nm in **Figure 1**(A), with the maxma of the Soret band (λ_{max}) at 420.4nm. When the porphyrin concentration is below 1.0×10^{-5}mol.L^{-1}, the half band width of the Soret band is 14.3nm, which is reduced to 12.3nm above 1.0×10^{-5}mol.L^{-1}. $THPPH_2$ follows Beer's law in **Figure 2**, indicating that $THPPH_2$ is solubilized in the inner core of CTAB micelles[1]., the absorbance *vs* concentration plot does not follow Beer's law above 1.0×10^{-5}mol.L^{-1}, indicating the occurrence of porphyrin aggregation[2]. The effect of aggregation on the absorption spectra often exhibits a change of the half band width[3] and a shift of the Soret band[4]. There is no shift of the Soret band in **Figure 1**(A), but the narrowing of the half band width suggests the formation of highly ordered porphyrin aggregate[3]. This aggregate may be some kind between H- and J-aggregate, in which the monomeric molecules arrange in a dimension that the angle between the transition moment and the line joining the molecular centers is 54 degrees in **Figure 3** (A), resulting in the constant gap of the energy level of the Soret band[3].

$THPPH_2$ has two Q bands at 585nm and 667nm in **Figure 1** (B), suggesting that the two N atoms on the pyrrole rings are also deprotonized, and the porphyrin molecules have transferred from the inner core to the outer surface of CTAB micelle[1]. λ_{max} is 435.7nm at lower porphyrin concentrations. At 1.28×10^{-5}mol.L^{-1}, there is a plateau of the Soret band, and $A_{422.7}$ is slightly higher than $A_{435.7}$, suggesting the aggregate formation although it still seems to follow Beer's law (**Figure 2**). At higher concentrations, the Soret band has gradually shifted to 422.7nm, and the plot does not follow Beer's law, which consistent with an aggregation of $THPPH_2$ on the outer surface of CTAB micelles. This aggregate might be considered a face-to-face H-aggregate[3] from the narrowing and the blue shift of the Soret band in **Figure 3** (B).

Figure 1. UV-Vis spectra of $THPPH_2$ in CTAB solutions



(A) at pH 7.2, 10^{-7}c[$THPPH_2$]/(mol.L^{-1}): *a.* 1; *b.* 2; *c.*4; *d.* 8;*e.* 16; *f.* 32; *g.* 48; *h.* 64;*i.* 80;*j.* 96; *k.* 104;*l.* 112; *m.*120; *n.*128, and (B) at pH11.0, 10^{-7}c[$THPPH_2$]/ (mol.L^{-1}):*a.* 1; *b.* 2; *c.* 4; *d.* 8; *e.* 16; *f* 32;*g.*48; *h.* 64; *i.* 96; *j.* 128; *k.* 192; *l.* 256; *m.* 320.

Figure 2. Dependence of $THPPH_2$ concentration at pH7.2 (■,λmax=420.4nm) and pH11.0 (▼, λ_1=422.7nm;□, λ_2=435.7nm)

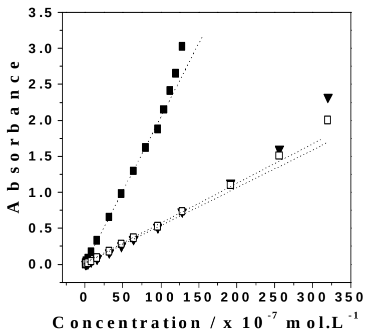
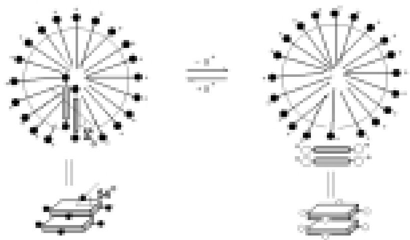


Figure 3. Aggregation behaviors of $THPPH_2$ in the inner core (A) and on the surface (B) of CTAB micelles



A B

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