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Thermochromism of 5,10,15,20-Tetraphenylporphyrin in Acidic Aqueous Triton X-100

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Detergents have been used to monomerize and bring into aqueous solutions an insoluble porphyrin [1]. A nonionic detergent, Triton X-100 (C_8H_{17}-C_6H_4-$(OCH_2CH_2)_nOH$; $n = 9–10$), is widely used in protein studies. In the course of studies on the redox reaction of metalloporphyrins in detergents, we have found the thermochromism of 5,10,15,20-tetraphenylporphyrin (H_2tpp) in an aqueous solution in the presence of Triton X-100.

H_2tpp ($4.7–7.1 \times 10^{-6}$ M) prepared by the method in the literature [2] was solubilized in an aqueous Triton X-100 (2% *w/w* or 10% *w/w*) containing $NaClO_4$ and $HClO_4$ at $\mu = 0.10$ M and $[H^+] = 10^{-7}–7.0 \times 10^{-2}$ M. The solution was passed through a membrane filter (0.45 μ) before the spectroscopic measurements. The temperature was controlled within ±0.1 °C. H_2tpp decomposed slowly in a strong $HClO_4$ solution, but under the present experimental conditions the decomposition was negligible.

Figure 1a shows the temperature-dependent absorption spectra of H_2tpp in an aqueous Triton X-100 (2% *w/w*) solution containing 0.1 M $HClO_4$. As the temperature was raised, the absorbances at 420 nm, 515 nm and 547 nm increased and those at 440 nm, 598 nm and 653 nm decreased; three isosbestic points were observed at 429 nm, 470 nm and 560 nm. The green solution at lower temperatures turned brown at higher temperatures, reversibly.

Figure 1b shows the spectral change of H_2tpp with an increase in acidity at 9.0 °C, which is identical with the temperature-dependent spectra. Therefore, the thermochromism of the solution is ascribable to the change in the acid-base equilibria of H_2tpp with temperature:

$$H_4tpp^{2+} \underset{}{\overset{K_1}{\rightleftharpoons}} H_3tpp^+ + H^+ \tag{1}$$

$$H_3tpp^+ \overset{K_2}{\rightleftharpoons} H_2tpp + H^+ \tag{2}$$

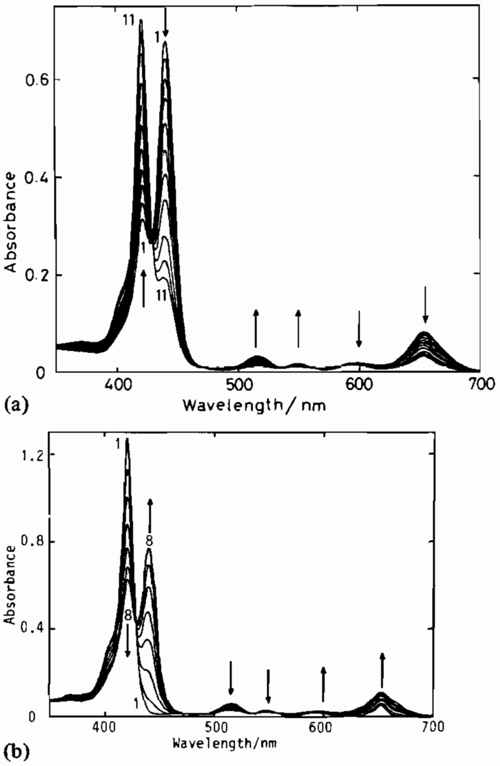

Fig. 1. (a): Temperature-dependent absorption spectra of H_2tpp (4.7×10^{-6} M) in aqueous Triton X-100 (2% *w/w*) solutions containing 0.10 M $HClO_4$. (1) 9.9 °C; (2) 12.0 °C; (3) 14.0 °C; (4) 15.9 °C; (5) 18.0 °C; (6) 20.5 °C; (7) 22.5 °C; (8) 25.0 °C; (9) 29.0 °C; (10) 32.0 °C; (11) 34.6 °C. (b): The spectral change of H_2tpp (7.1×10^{-6} M) with an increase in $[H^+]$ at 9.0 °C and $\mu = 0.10$ M ($NaClO_4$) in 2% Triton X-100 solutions. (1) $[H^+] = 10^{-7}$ M; (2) 10^{-2} M; (3) 2.0×10^{-2} M; (4) 3.0×10^{-2} M; (5) 4.0×10^{-2} M; (6) 5.0×10^{-2} M; (7) 6.0×10^{-2} M; (8) 7.0×10^{-2} M.

It is known that both K_1 and K_2 values are obtainable in nitrobenzene ($pK_1 = 4.38$ and $pK_2 = 3.85$) [3]. It is found, however, that the species having absorption maxima at 440 nm, 598 nm and 653 nm is H_4tpp^{2+} and that the species having absorption maxima at 420 nm, 515 nm and 547 nm is H_2tpp. The formation of the mono cation, H_3tpp^+, was negligible under the present experimental conditions, because the isosbestic points were observed at both a Soret and a visible region:

$$H_4tpp^{2+} \overset{K}{\rightleftharpoons} H_2tpp + 2H^+ \tag{3}$$

The acid-dissociation constant, K ($= K_1K_2$), was determined from the slope/intercept of the straight line of the plot of $1/|A - A_0|$ *vs.* $[H^+]^{-2}$:

$$\frac{1}{|A - A_0|} = \frac{1}{|A_\infty - A_0|} + \frac{K}{|A_\infty - A_0|} \times \frac{1}{[H^+]^2} \tag{4}$$

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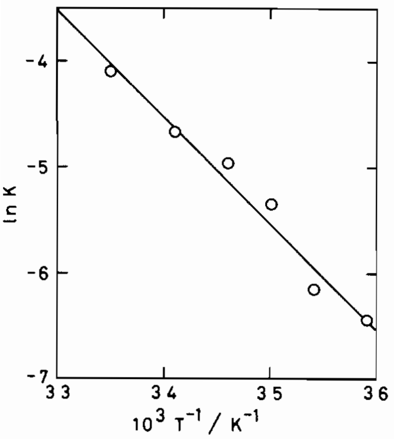

Fig 2. The plot of ln$K$ *vs* T^{-1} for the temperature-dependent acid-base equilibrium of H_2tpp at $\mu = 0.10$ M ($NaClO_4$)

where A is the observed absorbance and A_∞ and A_0 are the absorbances of H_4tpp^{2+} and H_2tpp, respectively. The values of pK obtained at four wavelengths (420 nm, 440 nm, 515 nm and 650 nm) and at six different temperatures decrease with the rise in temperature· 2.80 ± 0.06 at 5.2 °C, 2.67 ± 0.07 at 9.0 °C, 2.32 ± 0.09 at 12.8 °C, 2.16 ± 0.05 at 16.2 °C, 2.03 ± 0.11 at 20.0 °C and 1.78 ± 0.18 at 25.0 °C ($\mu = 0.10$ M). An equilibrated fraction of the neutral H_2tpp increases as the temperature is raised. The enthalpy and entropy changes were determined from the plot of ln$K$ *vs.* T^{-1} (Fig. 2): $\Delta H = 19.9 \pm 0.1$ kcal mol^{-1} and $\Delta S = 58.8 \pm 0.3$ cal K^{-1} mol^{-1}.

The spectrum in 2% sodium dodecyl sulfate (SDS) at pH 1 showed that of H_4tpp^{2+}. In 2% cetyltrimethylammonium bromide (CTAB) at pH 3 the spectrum showed that of H_2tpp. In methanol or 90% DMSO containing 0.1 M $HClO_4$ the spectrum showed that of H_4tpp^{2+}. These solutions did not show the thermochromism: the absorbance change with temperature was very small. This may arise from the fact that SDS and CTAB shift the equilibrium to H_4tpp^{2+} and to H_2tpp, respectively.

The critical micelle concentration (*cmc*) of Triton X-100 is reported to be 0.02% *w*/*w* at 23 °C and at $\mu = 0.01–0.10$ M [4]. Therefore, Triton X-100 forms a micelle under the present experimental conditions. The increasing concentration of Triton X-100 (10% *w*/*w*) at a constant temperature shifted the equilibrium in favor of H_2tpp. It is found that H_2tpp is more soluble in inorganic acids than in acidic Triton X-100. Therefore, it is suggested that Triton X-100 stabilizes H_2tpp rather than H_4tpp^{2+}. A plausible explanation of the thermochromism may involve changes with temperature in the partition coefficients for the micelle/aqueous environment partition equilibrium or for solubilization in different parts of the micelle.

References

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