



SPECTROSCOPIC CHARACTERIZATION OF INTERACTION WATER-SOLUBLE CATIONIC PORPHYRAZINE AND ANIONIC SURFACTANTS WITH DIFFERENT ALKYL CHAIN LENGTH

Hamid Dezhampahah^{[a]*} and Roghaye Firouzi^[a]

Keywords: Water-soluble porphyrazine; Surfactant; Premicellar aggregate; Micellized monomer, Anionic surfactant; hydrophobic interaction.

Interactions of cationic tetrakis (N, N', N'', N''')- tetramethyltetra-3, 4-pyridinoporphyrinatozinc (II) [Zn (tmtppa)] with various anionic micelles of surfactants n- alkyl sulfonate and sulfate (n=11, 12, 14) have been investigated spectrophotometrically at 25 °C in premicellar and postmicellar region. The results have shown that with increasing the alkyl chain length of surfactants, the maximum absorbance of Zn (tmtppa) shifted to a higher wavelength and binding affinity of Zn (tmtppa) to anionic micelles increases. This confirms that the surfactant micelle, which has a longer alkyl hydrocarbon chain, enables greater solubilization of porphyrazine. Thus, the hydrophobic interaction of the porphyrazine with micelles increases in the order: C₁₁H₂₃SO₃Na < C₁₂H₂₅SO₄Na < C₁₄H₂₉SO₃Na..

* Corresponding Authors

Tel: + 98-131-3243630-5

Fax: + 98-131-3233262

E-Mail: h.dpanah@guilan.ac.ir, h_dpanah@yahoo.com

[a] Laboratory of physical Chemistry, Department of Chemistry, Faculty of Science, University of Guilan P.O. Box 1914, Rasht 0098, Iran:

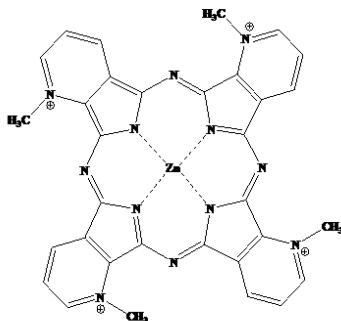
length; sodium 1-decansulfonate (C₁₁H₂₃SO₃Na), sodium dodecylsulfate (C₁₂H₂₅SO₄Na), sodium tetradecylsulfonate (C₁₄H₂₉SO₃Na) surfactants in aqueous solutions. Spectrophotometric method is used to investigate this interaction at the concentration below and above their critical micelle concentration (CMC).

Introduction

The aggregation of porphyrin and metalloporphyrin provides an insightful information in understanding the fundamental processes of living organisms and has been extensively studied in order to explain the biosynthetic formation and biological activity of naturally occurring compounds.¹ Under appropriate conditions with controlled ionic strength and protonation, porphyrins form highly ordered aggregates, namely J- or H-aggregates. J-aggregate is side-by-side arrangement of the porphyrin rings with absorption band red-shift, while H-aggregate is face-to-face arrangement of the porphyrins with absorption band blue-shift compared with porphyrin monomer. In the aggregation complex, the adjacent porphyrin molecules interact by hydrophobic interaction or electrostatic attraction.^{2,3}

Cationic tetra-azaporphyrins, or porphyrazines, represent an alternative and highly developed class of cationic porphyrinic compounds. Macrocycles based on the porphyrazine core, including phthalocyanines, but the replacement of the meso methylene carbons of porphyrins with nitrogen in porphyrazines creates profound differences.⁴ For example, porphyrazines absorb more strongly at longer wavelengths, a critical feature in biological and medical applications.^{4,5}

The objective of the current work is to understand and characterize the role of the hydrophobicity on the interaction between tetrakis(N,N',N'',N''')-tetramethyltetra-3,4-pyridinoporphyrinatozinc(II) [Zn(tmtppa)] (scheme 1) and a series of anionic surfactants with different alkyl chain



Scheme 1. The structure of tetrakis (N, N', N'', N''')- tetramethyltetra-3, 4-pyridinoporphyrinatozinc(II) [Zn (tmtppa)]

Materials

The Zn (tmtppa) was prepared and purified according to literature methods.⁶ Sodium 1-decansulfonate, sodium dodecylsulfate, sodium tetradecylsulfonate were Sigma chemicals and were used without further purification. All experiments were run in phosphate buffer of pH=7.2. spectrophotometric measurements a series of dye-surfactant solution by constant concentration of porphyrazine (1×10⁻⁵ M) and various concentration of surfactant was prepared and the absorption spectra of these solutions were recorded at 25 ± 0.1 °C. The absorbances were measured on the double beam absorbance spectrophotometer Cary 500 scan UV-vis, using a matched pair of quartz cells (1 cm path length) at 25.0 °C. The mixed solutions were prepared instantly and the absorbance was measured after thermostatation.

Results and discussions

The UV-vis absorption spectra of Zn(tmtppa) in aqueous solution in the presence and the absence of $C_{14}H_{29}SO_3Na$ are displayed in Figures 1A and 1B. It is observed that the addition of $C_{14}H_{29}SO_3Na$ changes the position, width, and intensity of the absorption spectra of Zn(tmtppa) at different ratio of $[C_{14}H_{29}SO_3Na]/[Zn(\text{tmtppa})]$ (R). The interaction process can be divided into two successive stages. At the first stage ($R = 0\text{--}52.5$), with the increase of the concentration of $C_{14}H_{29}SO_3Na$, remarkable hypochromicity accompanied by broadening of Q -band is observed. At $R = 52.5$, was observed, which is blue shifted compared to the monomer peak at 681 nm. The occurrence of 53 nm blue shift and significant decreasing of Q -band indicate the aggregation of porphyrazine. We assume that a new type Zn(tmtppa)– $C_{14}H_{29}SO_3Na$ aggregate formed in the solution, which can be classified as H-aggregate.

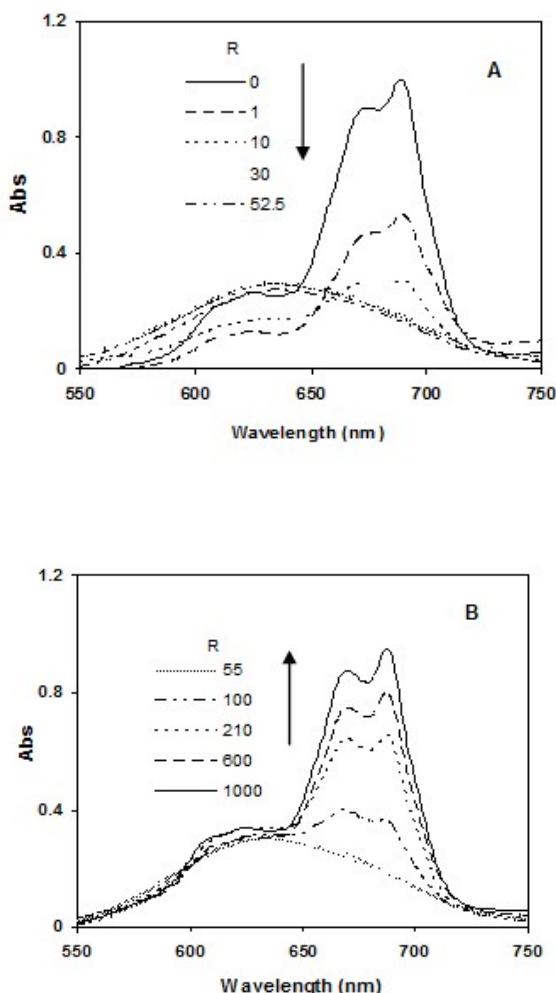


Figure 1. The UV-vis spectra of Zn(tmtppa) in the presence of various $C_{14}H_{29}SO_3Na$ concentrations: (A) at low concentrations; (B) at high concentrations.

In the second stage ($R > 52.5$), when $R = 55\text{--}1000$, a gradual hyperchromicity and red shift of Q -band can be observed. The structure of J-aggregate changes slightly along with increase in the concentration of $C_{14}H_{29}SO_3Na$ ($R > 55$). When $R = 1000$, the hyperchromicity and red-shift of Q -band to 678 nm, suggesting that the aggregates are broken partially after

further interaction with $C_{14}H_{29}SO_3Na$. We assume that the porphyrazine-surfactant complex formed at high concentration of $C_{14}H_{29}SO_3Na$, which is much lower than the CMC of $C_{14}H_{29}SO_3Na$, is the micellized monomer. The intensity and position of Q band (681 nm) is almost unchanged until R is more than 1000, which implies that almost all Zn(tmtppa) molecules become micellized monomer. Similar spectral change was observed in the case of the others surfactants.

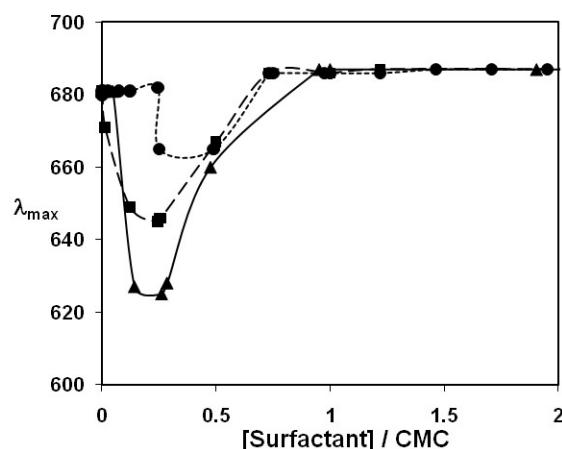


Figure 2. The Wavelength absorbance change of 1×10^{-5} mol/L Zn(tmtppa) (below and above the CMC) with the concentration of $C_{11}H_{23}SO_3Na$ (●), $C_{12}H_{25}SO_4Na$ (■) and $C_{14}H_{29}SO_3Na$ (▲).

The absorbance change of 1×10^{-5} mol L⁻¹ Zn(tmtppa) (below and above the CMC) with the concentration of $C_{11}H_{23}SO_3Na$, $C_{12}H_{25}SO_4Na$ and $C_{14}H_{29}SO_3Na$ are shown in Figure 3. The absorbance of Zn(tmtppa) initially decreased with increasing the surfactant concentrations well below the CMC and reached a minimum value and then increased again with further increasing of surfactant concentrations above the CMC. This indicates that the bound Zn(tmtppa) to micelles increases with the lengthening of the alkyl chains of the surfactants. This implies an increase in equilibrium distribution of the porphyrazine molecules that are transferred into the micellar phase more favorably with the increase in their hydrophobicity, as observed also in other cases.⁷

Acknowledgment

We gratefully acknowledge the Research Council of University of Guilan for supporting this work.

References

- Ibrahim, H., Kasselouri, A., You, C., Maillard, P., Rosilio, V., Pansu, R., Prognon, P. *J. Photochem. Photobiol. A: Chem.*, **2011**, 217(1), 10.
- Paulo, P. M. R.; Costa, S. M. B., *Photochem. Photobiol. Sci.*, **2003**, 2, 597.
- Gouterman, M. In: *The porphyrins*, Vol. 3, Dolphin D. (Ed.) Academic Press: New York, **1978**;
- Suchetti, C. A. Duranini, E. N., *Dyes Pigments* **2007**, 74, 630.
- Thamae M. and Nyokong, T., *J. Electroanal. Chem.*, **1999**, 470, 126.

⁶Schenning, A. P. H. J., Hubert, D. H. W. Feiters, M. C. Nolte, R. J. M., *Langmuir*, **1996**, *12*, 1572.

⁷Maiti, N. C. Mazumdar, S. Perisamy, N., *J. Phys. Chem. B*, **1998**, *102*, 1528.

Received: 22.05.2013.

Accepted: 11.06.2013.