CHAPTER – 1

A BRIEF REVIEW ON THE STUDIES OF PORPHYRINS IN MICELLAR MEDIUM
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Most of the porphyrins studied in micellar medium are usually porphyrins that are soluble in aqueous medium. Therefore, most of the reported works in the literature are mainly the studies of porphyrins soluble in aqueous micellar medium. Advantage of such a system is that it can serve as a biological models for biomembranes1-3. The reactivity of a molecule in a micellar environment is more specific4,5. It is also known that naturally occurring porphyrins such as Protoporphyrin IX are readily solubilised in aqueous micelles3. Some of the studies of porphyrins in aqueous micellar systems /surfactants medium are reviewed in this chapter. A very brief review is presented here (citing only few) for comparison only. This is because we are not using aqueous micelles.

Dynamics of Porphyrin molecules in micelles. Pico – second time – resolved fluorescence anisotropy studies is reported6. In this study some Protoporphyrins IX derivatives are taken in aqueous micelles such as SDS, CTAB and TX – 100. It has been found that porphyrins are
solubilised as monomers in TX – 100 and CTAB near the interface. Further, the size of the micelle does not affect the molecular dynamics parameters.

Enhanced aggregation behavior of Antimony (V) porphyrins in poly fluorinated surfactants/clay hybrid micro environment is also reported\(^7\).

Intercalation behaviour of metalloporphyrins in poly fluorinated surfactant/clay hybrid compounds\(^8\) is reported. Intercalation and aggregation behavior of Sb(V) TSPP in sodium saponite clay layer and aggregation mechanisms are discussed. H- and J- type of Sb(V) TSPP dimer formation in the excess area of the hybrid compound is proposed.

Interaction of water – insoluble TPP with micelles probed by UV – Visible and NMR spectroscopy is also reported\(^9\). The methodology of incorporation of porphyrins (TPP derivatives) into micelles is discussed. To
established that the porphyrins are mono dispersed within the micelles, the soret band is examined. From the UV-Visible and NMR data obtained the mechanism of incorporation of porphyrin within the micelles are proposed. The incorporation depends on the nature of the substituent and the surfactant and the polarity of the substituent. Electrostatic interaction between the porphyrin and the micelle also plays important roles. It is also found that the porphyrin molecules diffused into the micellar solution are mono dispersed.

Electro chemistry of iron Protoporphyrin IX encapsulated in aqueous surfactant micelles is also reported\(^\text{10}\). The binding of the THF to iron porphyrin in SDS micelles stabilizes \(\text{Fe}^{2+}\) state. This has been characterized by \(67\text{mV}\) anodic shift in the voltammogram.

Gandini et. al.\(^\text{11}\) have reported the interaction of the \((\text{H}_2\text{TPP})^4^-\) with ionic surfactants: aggregation and location in micelles.
Kinetics of porphyrin metallation reaction in micellar medium is also reported\textsuperscript{12}.

The incorporation characteristics of tetra aryl porphyrins in bilayers formed from the synthetic surfactant are reported\textsuperscript{13}. UV-Visible and Fluorescence studies show that at low concentration the porphyrins are present in the bilayer in monomeric species. The location of these species depends on the nature of substituents on the porphyrin. At higher concentration, aggregation occurs. Aggregation of THPP causes splitting of the B band (soret band) into two bands one of which is lower in intensity.

Aggregation behaviour of (THPPH\textsubscript{2}) in the inner core and on the surface of CTAB micelles is also reported\textsuperscript{14}. Absorbance Vs. Concentration plot below the $1.0 \times 10^{-5}$ molL\textsuperscript{-1} obeys the Beer’s law but does not follow Beer’s law beyond $1.0 \times 10^{-5}$ mol L\textsuperscript{-1} indicating occurrence of porphyrin aggregation. The aggregation is reflected in the line width of the soret band. The line width of the soret band narrows
down. At higher concentration, the soret band position is also shifted and does not obey the Beer’s law indicating an aggregation of THPPH₂ on the outer surface of CTAB micelles. From the narrowing of the width of the soret band and the blue shift of the soret band it has been suggested that the aggregation is face-to-face H-type aggregation.

Porphyrrins in reverse micelles, the effect of the side-chain length on the aggregation has been studied by studying triplet-state life time. Longer excited life time indicating dominating monomer while shorter excited life time indicating aggregation. The high amphiphilic nature of porphyrins promotes the firm embedding of the porphyrin molecules in the interfacial region of reverse micelles. Such embedding may prevent the porphyrins from aggregation and exists as monomers in the reverse micelles.

Protonation of amphiphilic porphyrins in SDS micellar solution is also reported. The amphiphilic porphyrin taken is 5, 10, 15, 20-tetra (4-hydroxy phenyl)
porphyrin. Titration with HCl shows red shift of the band at 652nm to 691nm with an isosbestic point at 445nm. On the other hand titration with NaOH shows regeneration of free base and the band at 652nm disappears and an isosbestic point occurs at 432nm. Thus a microphase transition is observed.
REFERENCES


