ABSTRACT

Surfactants due to their amphiphilicity and tendency to undergo self-association mimic biological systems. Interactions between surfactants and many substances such as proteins, dyes and polymers have been extensively investigated for contribution to elucidation of fundamental properties of surface-active agents and for extending their field of applications. The remarkable change in the spectral properties of visual indicators on addition of surfactants has been exploited since a long time due to the relevance of such dye-surfactant interaction to various analytical and biological applications. There is no dearth of literature on dye-surfactant interaction but still they are insufficient to provide a clear picture of the various types of interactive forces that governs such interactions. There is also paucity of information regarding dye-surfactant interactions near or below the critical micelle concentration (CMC) of the surfactants. Moreover, there are only a few quantitative reports available on the acid-base equilibrium of dyes in micelles of same charge and in polymer-surfactant systems.

So, an attempt has been made in this direction to fill up the gap. The present thesis contains spectroscopic and thermodynamic studies on the acid-base equilibrium of dyes in aqueous ionic and nonionic micellar solution, polymer-surfactant media and in submicellar systems. The content of the thesis have been presented in five chapters.
In Chapter I, the general aspects of surfactants, surfactant aggregates, properties and applications of organized surfactant assemblies, dye-surfactant interaction, polymer-surfactant interactions and models for dye-surfactant interactions pertaining to the subject of the thesis in particular have been briefly reviewed.

Chapter II deals with the study of acid-base equilibrium of sulphonephthalein dyes in anionic micellar systems. In this chapter a spectroscopic method has been reported which can be used to simultaneously determine partition equilibrium constant of anionic sulfonephthalein dyes between micellar pseudophase and aqueous phase, and CMC of the surfactants in buffered aqueous anionic surfactant systems. The method is based on two assumptions: (1) only one form of the dye goes into the micellar pseudophase, which holds for similarly charged dye–surfactant systems and (2) the activity terms for the conjugate acid and base forms of the dye can be combined in well-buffered solution. An absorption band, which decreases with addition of surfactant, is used for the analysis. The method has been found suitable to the systems of sulphonephthalein dyes, viz., bromophenol blue (BPB), bromothymol blue (BTB) and thymol blue (TB) with anionic surfactants, viz., sodium dodecyl sulfate (SDS), sodium dodecyl benzene sulfonate (SDBS) and sodium dodecyl sulfonate (SDSN). The partition equilibrium constant, $K_p$, has been found to be dependent on hydrophobicity of the dye and $pH$ of the solutions. The CMC’s have been found to increase with increase in $pH$ for a particular buffer system. The method can conveniently be used for study of
interactions in such dye–surfactant systems and to determine CMC of the anionic surfactants in buffered solutions.

Chapter III contains the results of the investigation on the acid-base equilibrium of sulphonephthalein dyes in aqueous nonionic micellar systems. The acid-base equilibria of the sulfonephthalein dyes, viz., BTB, TB and cresol red (CR) in aqueous nonionic micellar solutions of iso-octylpolyethoxy-ethanol (Triton X 100), polyoxyethylene (20) sorbitan monolaurate (Tween 20), polyoxyethylene (20) sorbitan monopalmitate (Tween 40), polyoxyethylene (20) sorbitan monostearate (Tween 60) and polyoxyethylene (20) sorbitan monooleate (Tween 80) have been investigated. The equilibrium constants, $K_p$ of the partition of the dyes between micellar and aqueous pseudophases have been determined spectrophotometrically at fixed $p$H using an iterative method developed for the purpose. The $K_p$ increased with changing the surfactants in the order Tween 80 < Tween 60 < Tween 40 < Tween 20 < TX 100. The effect of such associations on the $pK_{a2}$ of the dyes at various concentrations of surfactant has been studied. The $pK_{a2}$ of the dyes as a function of the concentrations of the surfactant were predicted from the equilibrium constants using a method developed to fit nonionic surfactant and were compared with experimental values determined directly. The $pK_{a2}$’s of the dyes predicted according to the present method have been found to be in good agreement with the experimental values.

In Chapter IV, the results of the spectroscopic and thermodynamic investigation on the interaction of anionic dyes with polymer-surfactant systems have been reported with special emphasis on the acid-base
equilibrium of the dyes. Acid-base equilibrium of three anionic sulphonephthalein dyes, viz., BTB, TB and CR were studied spectroscopically in aqueous media containing water soluble nonionic polymers polyvinyl alcohol (PVA) and polyethylene glycol (PEG) in the presence of the anionic surfactant, viz., SDS. A partition equilibrium method was utilized to determine the equilibrium constant of partition of the dyes between micellar pseudo phase and aqueous phase in the presence of PVA and PEG. The critical aggregation concentrations (CAC) of the surfactants in buffered aqueous systems containing the neutral polymers were also determined. The CAC’s of the polymer-surfactant systems is found to be lower than the CMC’s of such systems in the absence of polymer in otherwise identical conditions. The pH dependent association constants $K_p$ of the sulfonephthalein dyes with SDS-PVA system increases with the increase in molecular weight of the polymer. Interaction of the dyes with the aqueous SDS-PVA and SDS-PEG systems are found to be endothermic and entropy oriented. In the polymer domain the head group region of the micelles are more exposed but under excess polymer concentration they are increasingly shielded which impairs their electrostatic interactions with the dyes.

In Chapter V, the results of an investigation on the interaction of cationic dyes, Safranin O (3,7-diamino-2,8-dimethyl-5-phenylphenazinium chloride), Safranin T (3,6-diamino-2,7-dimethyl-5-phenylphenazinium chloride), Phenosafranin (3,7-diamino-5-phenylphenazinium chloride), Methylene blue (3,7-bis[dimethylamino]phenazothonium chloride) with SDS in the submicellar concentration range
have been reported. The variation in the visible absorption spectra of the
phenazinium dyes at concentrations of SDS slightly below CMC, were
attributed to the change in microenvironment of the chromophore of the dye on
incorporation into pre-micelles.

The work described in the thesis has been already published in
different journals: