ABSTRACT

The present thesis describes a systematic study of microemulsions stabilized by anionic surfactants, using visible spectroscopic analysis of partition of two sulfonephthalein dyes, viz., phenol red (PR) and bromophenol blue (BPB) between different domains of the microemulsions. Emphasis was given to the acid-base equilibria in the media. The partition equilibria of the dyes have been utilized to study behavior of the microemulsions with respect to partition as well as loci of cosurfactant and buffer components between different domains in the microemulsions. Attempts have been made to apply the partition equilibrium approach to gain information on microemulsions.

The contents of the thesis have been presented in four chapters. In Chapter I, the general aspects of surfactants, surfactant aggregation, microemulsions, properties and applications of organized surfactant assemblies, interaction of dyes with surfactants and models for dye-surfactant systems pertaining to the subject of the thesis in particular have been briefly reviewed.

The sources and the methods of purification of the chemicals used in the study are described in Chapter II. The partition equilibria of two sulfonephthalein dyes, viz., phenol red (PR) and bromophenol blue (BPB) have been studied. While buffered water was used in all cases, benzene and toluene were used as oil. Sodium dodecyl sulfate (SDS), sodium dodecyl benzene sulfonate (SDBS) and aerosol OT (sodium bis(2-ethylhexyl)sulfosuccinate, abbreviated as AOT) were used as surfactants. A series of alcohols, viz., propan-1-ol, propan-2-ol, butan-1-ol, butan-2-ol, pentan-1-ol,
pentan-2-ol and pentan-3-ol as cosurfactant. The microemulsions were prepared by mixing appropriate amounts of the dye solution in buffered water, surfactant, cosurfactant and oil. They were kept overnight before recording the visible spectra on a Hitachi U 2001 UV-VIS spectrophotometer. The measured pH of the original aqueous buffered dye solution before mixing with other components to prepare microemulsions was used for the study.

The detailed experimental observations, their analysis and interpretations have been narrated in Chapter III. The chapter has been further segregated into six major sections, each of which deals with different aspects of the study.

A study of the effects of different alcohols on partition equilibrium of PR in micellar solutions of SDS and in o/w microemulsions of benzene in buffered water stabilized by SDS, has been reported in Section III.A. The alcohols used were propan-1-ol, propan-2-ol, butan-1-ol, butan-2-ol, pentan-1-ol, pentan-2-ol and pentan-3-ol. PR was chosen for this study because the dye does not precipitate in presence of anionic surfactants and shows color change in moderate pH range. The effects of alcohol on partition equilibrium of the dye in micellar solutions in the presence of alcohol were studied in order to compare the results with micellar solutions. The equilibrium constants, \( K_p \) of partition of the dye between different pseudophases in the micellar solutions and microemulsions have been determined from the spectral data. The effects of changing the oil volume fraction and surfactant-cosurfactant w/w ratio, \( r \) on \( K_p \) have been examined. The results have been correlated with incorporation of the alcohols to different regions in the micelles and oil-water interface and enhanced incorporation of the dye to the o/w interface with decreasing
droplet curvature. It has been inferred that preferred incorporation of alcohol in the interfacial head group region lowers $K_p$ initially up to $r$ of 1:1 in both micellar solutions and o/w microemulsions. The $K_p$ increased as the ratio exceeded 1:1 due to increased solubilization of the alcohol towards the hydrocarbon chain region of the surfactants rather than in the headgroup region. In the microemulsion systems, the $K_p$ increases with increase in oil volume fraction due to enhanced incorporation of the dye in the palisade layer of the oil-water interface with decreased droplet interface curvature. At a given volume fraction of oil, the $K_p$ increases on changing the alcohol in the order: propan-2-ol $<$ propan-1-ol $<$ butan-2-ol $<$ butan-1-ol $<$ pentan-3-ol $<$ pentan-2-ol $<$ pentan-1-ol. The trend has been attributed to synergistic surface activity between the surfactant and alcohol.

The effect of changing the surfactant on the partition equilibrium of PR in anionic micelles and in o/w microemulsions has been studied by using SDBS as the surfactant, which has been described in Section III.B. A comparison has been made between the partitions of the dye in o/w microemulsions stabilized by SDS with that stabilized by SDBS. The partition of the dye into the micelles or the o/w interface was higher in the case of SDBS than in SDS, which has been attributed to the higher hydrophobicity of SDBS than SDS.

Section III.C deals with the effect of buffer on the partition of PR, between oil-water interface, oil droplet core and the buffered bulk water in benzene/water/SDS/butan-1-ol o/w microemulsions with phosphate and Tris buffer systems. The $K_p$ of PR between oil-water interface and bulk water was found to increase with increase in the oil fraction. This has been attributed to incorporation of
the dye to the hydrocarbon region of the interface with decreasing droplet curvature. In Tris buffer system, the organic buffer component competes with the dye for incorporation to the interface.

In Section III.D, describes an attempt to calculate oil-water interfacial area and size of droplets in o/w microemulsions by partitioning of PR between oil-water interface and bulk water. The effects of changing the oil volume fraction surfactant concentration and surfactant-cosurfactant ratio on the droplet size have also been discussed. The predicted droplet sizes were within the range expected for microemulsions. The radius decreased with increase in the surfactant concentration and increased with increase in the oil fraction.

Section III.E contains a study of the partition behavior of another dye, viz., BPB in benzene-water-SDS-butan-1-ol o/w microemulsions. The dye showed an unusual electronic spectral behavior on increasing the concentration of the surfactant, at different fixed water pH and oil fractions. The dye shows absorption bands at 436 and 591 nm corresponding to the mono-negative (DH') and doubly negative (D^2-) form in water at the experimental pH 3.21 and 4.41. The DH' band at pH 3.21 initially increased with increase in [SDS] at the cost of the D^2- band as expected. But on increase in [SDS] above 0.128 mol dm^-3, the D^2- band, which is now red shifted to 600 nm recovers at the cost of the DH' band. This type of spectral behavior is so far observed only for BPB in micellar and microemulsions stabilized by surfactant of similar charge type. This unusual effect is augmented at the higher pH of 4.41, lower r and lower oil fraction. The behavior has been attributed to partition of the organic buffer component, viz., formic acid between different pseudophases. The unusual
spectral behavior arises due to increase in the pH of aqueous pseudophase, as a result of passing of formic acid into the oil pseudophase and oil-water interface.

The partition of BPB in different domains of w/o microemulsions of toluene/water/AOT has been studied at different water fraction and pH, which is described in Section III.F. The dye is partitioned between the oil-water interfaces and the water droplets in the microemulsions. The partition constants between the two pseudophases, \( K_p \) decreases considerably with increase in water fraction and pH. The observed decrease in \( K_p \) with the increase in water fraction has been attributed to increase in the oil-water interfacial area. The decrease in \( K_p \) with increase in pH has been attributed to lower tendency of the base form for association with the anionic oil-water interface compared to that of the acid form and to an increase in the negative charge density at the oil-water interface at higher pH.

The conclusions drawn from the entire work have been summarised in Chapter IV.

A major portion of the work described in the thesis has been already published in the form of four papers and the rest has been communicated for publication. The publications have been listed below: