

ABSTRACT

In this dissertation, detailed investigation of characteristics of molecular self-assembly of different surfactant systems have been explored via conductivity, UV-Visible spectroscopy, FTIR spectroscopy, fluorescence steady state emission spectroscopy, fluorescence anisotropy, Quantum chemical calculations, dynamic light scattering study (DLS), and high resolution transmission electron microscopic (HRTEM) study.

In **Chapter I**, the concept of molecular self-assembly has been introduced. The different types of molecular aggregates and the related systems have been presented. Applications of self assembled structures and important research advancements in related fields have been elaborately discussed.

In **Chapter II**, the scopes of research on molecular aggregates in the field of surface chemistry and the objectives of the present dissertation have been discussed.

In **Chapter III**, includes the extensive investigation on the self-assembly of didodecyldimethylammonium bromide ($D_{12}DAB$), didecyldimethylammonium bromide ($D_{10}DAB$) and ditetradecyldimethylammonium bromide ($D_{14}DAB$) in aqueous medium, which is severely restricted due to their insolubility. These surfactants are highly soluble in acetonitrile, which allows investigation in a wide range of concentrations. An unusual aggregation phenomenon is exhibited by double tailed cationic surfactants in acetonitrile, displaying multi-step breaks in conductivity-concentration profile in a wide concentration regime. These studies along with that of steady state fluorescence measurements indicate the presence of multi-step self-assembly phenomena to occur in the system. High resolution transmission electron microscopy (HRTEM) experiments show the presence of fascinating morphologies of the aggregates. The experimental observations are analyzed and the driving forces behind the phenomena are discussed.

In **Chapter IV**, involves micellization and related thermodynamic parameters of a double tailed cationic surfactant Didodecyldimethyl-ammonium bromide ($D_{12}DAB$) in various compositions of acetonitrile-water (ACN-W) mixed media have been studied at five temperatures ranging between 278K and 313K. Conductometric and fluorimetric experiments are done to obtain the parameters like critical aggregation concentration (c_{ac}), degree of counterion binding (β) and Stern-Volmer constant

(K_{SV}). Assuming mass-action model for micelle formation, various thermodynamic parameters are estimated from the temperature dependence of cac values. The inclusion of ACN causes an increase in cac of D₁₂DAB and low aggregation number of aggregates whereas the thermodynamic analysis shows that, although the micellization is not favorable compared to pure water, the process is spontaneous and exothermic.

In **Chapter V**, presents the report regarding the microstructural transition from aqueous to acetonitrile (ACN)-based non-aqueous reverse micelles (RMs) stabilized by cationic didodecyldimethyl-ammonium bromide (D₁₂DAB) and anionic sodium bis(2-ethylhexyl) sulfosuccinate (AOT) in cyclohexane. The synergistic solubilization capacity of corresponding polar solvent at a fixed composition and the nature of conductance plots in these RMs are markedly varied along with the composition of binary solvents (water and ACN at pure or mixed states) and the surfactant charge types (D₁₂DAB and AOT). The structural alteration in these RMs through water- and ACN-rich compositions are studied by FTIR, where the results are explained in terms of molecular states of water and ACN inside RMs. The differential binding affinity of both polar solvents with the two surfactants is shown using *ab initio* calculations. The subsequent appearance and disappearance of aqueous nano-pool is verified from UV-Vis technique using CoCl₂. The lack of H-bonding ability on going from aqueous to ACN-based RMs is evidenced from the temperature dependent DLS study along with the absorption profiles of 7-hydroxycoumarin. The results show how the microstructures and H-bonding interactions inside RMs are dramatically altered by simply changing polarity of the solvents or the surfactant charge types. This report could be useful to understand the formation mechanism of two class of RMs.

In **Chapter VI**, represents the fluorometric and uv-vis spectrometric measurements to explore the binding constants of 7-Hydroxy coumarin (7HC) with cationic surfactants didodecyldimethylammonium bromide (D₁₂DAB), didecyldimethyl-ammonium bromide (D₁₀DAB) and ditetradecyldimethylammonium bromide (D₁₄DAB) in the acetonitrile medium. The binding constants are found to be quite high in the first aggregation step. Series of spectral techniques like steady state fluorescence and fluorescence anisotropy study, UV-Vis study reveal the results of dye surfactant interaction in non-aqueous environment. Dye–surfactant interaction constants are

determined by UV-Vis spectroscopic study at different temperatures (293–323K) and subsequently the thermodynamic parameters, viz., ΔG^0 , ΔH^0 and ΔS^0 are evaluated using the binding constant.