

CHAPTER-VIII

Summary of the Works Done

The present dissertation has been divided into eight chapters.

Chapter I forms the background of the present work. After presenting a brief introduction of surfactants, some important aspects of micellar shape and size have been discussed. The importance and utility of various methods in the determination of critical micelle concentration (*cmc*) and the different factors affecting the micelle formation and the *cmc* have been described. The different models of thermodynamics of micelle formation¹⁻²² and their applications to both ionic and nonionic surfactants have been presented. The importance of mixed micelles and the theories of binary mixed micelle formation are highlighted. A brief account of the studies on micelle formations in nonaqueous solvents has been given stressing the importance of such work.

In chapter II the methods of purifications of different chemicals used in the study and the various experimental techniques for obtaining the results presented in the dissertation have been described.

Chapter III describes the micellization behavior of lithium dodecylsulfate in aqueous solution by using conductivity, density and adiabatic compressibility measurements. The critical micelle concentrations for the surfactant system have been determined by all these methods. The ionization degree of micelles, $\alpha = S_2/S_1$, at different temperatures were determined from the ratio of the mean gradients of the specific conductivity (κ) against concentration plots above (S_2) and below (S_1) the *cmc*²³⁻²⁶. The standard free energy change of micellization per mole of monomer, ΔG_m° , has been calculated considering the charge phase separation model²⁷ of micellization. The variation in standard enthalpy change upon aggregation has been determined by using Gibbs-Helmholtz equation. The changes of the apparent molar volume upon micellization of the surfactant have been calculated from density

measurements. Using density and ultrasound velocity measurements the apparent adiabatic compressibilities of the surfactant solutions have also been obtained.

In chapter IV the effect of some quaternary ammonium bromides R_4NBr ($R=H, CH_3, C_2H_5, C_3H_7$ and C_4H_9) on the micellar properties of lithium dodecylsulfate (LDS) micelles has been studied by conductometric and tensiometric techniques. The degree of the counterion binding, β , is found to increase with the increasing size of the alkyl chain length of the tetraalkylammonium ions. The thermodynamics of micelle formation of ionic surfactant LDS in the presence of 0.001M of different quaternary salts have been thoroughly assessed by the critical micelle concentration (*cmc*) measurement in the 288.15–318.15 K-temperature range at 10 K intervals conductometrically. Results show a shallow minimum of the *cmc* values typically between 300 to 305 K for LDS micelles in presence of various salts. The standard free energy of micellization has been found to decrease upon growth of temperature. The standard enthalpy change on aggregation was calculated by using the Gibbs–Helmholtz equation. Tensiometric results show a significant reduction in the solution surface tension with increasing electrolyte concentration. The surface excess of LDS and its minimum area at the air–water interface in the presence of different R_4NBr environment has been determined. The micellar solution of LDS has been found to exhibit a cloud point phenomenon in the presence of Bu_4NBr . The occurrence of cloud point phenomenon is accounted for in terms of the penetration of butyl chains at the surface layer of one micelle into another due to the hydrophobic effect^{28, 29}.

Chapter V describes the physicochemical studies on mixed micellization of the anionic surfactant, LDS and nonionic surfactants polyoxyethylene(23)laurylether (Brij-35) and polyoxyethylene(10)isooctyl phenylether (Titron-100) in aqueous media. Several parameters viz. *cmc*, degree of counterion binding, free energies of micellization and interfacial adsorption have been evaluated from conductometric, tensiometric and spectrophotometric methods. Established theories of Clint³⁰, Rosen³¹, Rubingh³², Motomura³³, Georgiev³⁴, Macda³⁵ and Blankschein^{36, 37} has been applied to evaluate the mole fractions of different components in the self-aggregated phase, the interaction parameter, free energy contributions and expected *cmc*.

In chapter VI Mixed micellization behavior of aqueous binary and ternary mixtures systems of cetylpyridinium chloride (CPC), tetradecyltrimethylammonium bromide (TTAB), and dodecylpyridinium bromide (DPC) has been studied at 298.15 K. Parameters like *cmc*, degree of counterion binding, free energies of micellization and interfacial adsorption have been evaluated from conductometric and tensiometric methods. Various existing theories^{30-37, 38} have been used and the results were compared with the experimental observations to obtain information on the interactions prevailing in the mixed surfactant systems.

In chapter VII micellization behavior of three alkyltrimethylammonium bromides *viz.*, hexadecyl-, tetradecyl-, and dodecyltrimethylammonium bromide (CTAB, TTAB, and DTAB, respectively) in ethylene glycol (EG) (1) + water (2) mixed solvent media with varying mass fractions of EG (w_1) has been studied by means of electrical conductivity and surface tension measurements. Temperature dependence of the critical micelle concentrations was also investigated in order to understand the micellar thermodynamics of these systems. The mass action model^{39, 40} of micelle formation was applied to obtain the thermodynamic parameters of micellization. Only small differences have been observed in the standard molar Gibbs energies of micellization over the temperature range investigated. The enthalpy of micellization was found to be negative in all cases whereas the entropic contributions were always positive, indicating that an enthalpy-entropy compensation effect is the governing factor for micellization. Surface tension measurements also provide information about the effects of the addition of ethylene glycol to water on the excess surface concentration, minimum area per surfactant molecule, the surface pressure at the critical micelle concentrations, and standard Gibbs energy of adsorption. The Gordon parameters⁴¹ for the EG (1) + water (2) mixtures were also estimated by means of surface tension measurements to assess the ability of EG (1) + water (2) mixtures to bring about the self-association of the surfactants investigated.

A summary of the works done has been given in chapter VIII.

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