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Title of the Thesis: ***Thermodynamic and Transport Studies of Amino acid – Surfactant and Surfactant – Surfactant Interactions in Aqueous Medium***

Abstract

It is well known that the thermodynamic behaviour and the state of solvation of proteins and peptides in solution rely heavily on interactions of water with various functional groups of the protein. However biological fluids are not pure water as they contain many organic and inorganic salts. These co-solutes/ co-solvents affect proteins in different ways, acting as effective probes of their conformations in solutions. Investigations of these conformational changes provide valuable information on the role of solvent/co-solute/co-solvent in maintaining of native, intermediate, and denatured states of the proteins. Surfactants may interact with proteins directly by binding to them, thereby, inducing substantial changes into proteins conformation, thus leading to alterations in functional characteristics of proteins. However details of surfactants-proteins interactions are yet to be investigated. Therefore it would be important to understand the original nature of protein-surfactant interactions in aqueous medium. As the complex conformational factors affect the structure of proteins in various solutions, the direct study of proteins-surfactant interaction is very difficult. Thus in order to understand these interactions, interactions of building block proteins (amino acids) with surfactants should be studied owing to the complex structure of biological macromolecules (proteins). The knowledge in thermodynamic properties of amino acids, surfactant interactions in aqueous medium will be helpful for the development and design of new separation and purification processes of bio-molecules in pharmaceutical industry, food industry and bio-technology and other fields.

Chapter 1. This is an introductory chapter and it embodies the scope and objective of the proposed work. Various aspects of the work have been explained. To illustrate the work being carried out in this field, an up to date literature survey has been presented.

Chapter 2. Materials and experimental techniques, which have been used in the present investigations, are presented in this chapter. Conductometry, tensiometry, and fluorescence were used to investigate the interactions taking place in amino acid-surfactant and surfactant-surfactant systems. The standard operating procedures for the apparatus and instruments used have been explained in detail.

Chapter 3. Micellization behavior of hexadecyltrimethylammonium bromide (HTAB) was investigated conductometrically in aqueous and in 0.02 m (mol kg^{-1}) aqueous glycine (Gly), diglycine (Gly-Gly), and triglycine (Gly-Gly-Gly) as a function of surfactant concentration at different temperatures. The values of CMC and the degree of counterion dissociation of the micelles were utilized to evaluate the standard free energy for transferring the surfactant hydrophobic chain out of the solvent to the interior of the micelle, ΔG_{HP}^0, free energy associated with the surface contributions, ΔG_S^0, standard free energy, ΔG_m^0, enthalpy, ΔH_m^0, and entropy, ΔS_m^0 of micellization were also calculated. The CMCs obtained by fluorometric method are in close agreement with those obtained conductometrically. Furthermore, decrease in the I$_1$/I$_3$ ratio of pyrene intensity suggests the solubilization of the additives by the surfactant micelles and that this solubilization increases as the hydrophobicity increases from Gly to Gly-Gly-Gly.

Chapter 4. The critical micelle concentration (CMC) of sodium dodecyl sulphate (SDS) in pure water and in the presence of amino acids (0.01, 0.02, and 0.03 mol. kg^{-1}), L-valine (Val) and L-leucine (Leu)

were determined from conductometric and fluorometric methods using pyrene as luminescence probe. Highest negative value of ΔH_m^0 in 0.01 m Val, with lowest CMC value, shows that 0.01 m aqueous Val is the most suitable medium favouring the micellization of SDS. Decrease in I_1/I_3 from Val to Leu confirms the relative hydrophobicity of two amino acids. The observed values of the packing parameter, P, of SDS in water and in aqueous amino acids suggested that micelles formed were spherical in nature.

Chapter 5. Pseudophase ion exchange model was employed with Krafft temperature (T_K) measurements of hexadecylpyridinium bromide (HPyBr) in pure water as well as in presence of glycine (Gly) and potassium bromide (KBr) using conductivity measurements. The Krafft tememperature values of HPyBr were observed to increase with the increase in concentration of Gly as well as KBr. The Krafft temperature increases with increase in the counterion concentration because the solubility of the surfactant is reduced at a faster rate than the CMC. Krafft temperature measurements were employed to find the interaction between HPyBr and glycine.

Chapter 6. In this chapter, different mole fractions of cetrimide and SDS were investigated which showed nonideal behaviour as the experimental CMC`s were less than the calculated values by using the Clint equation. The activity coefficients calculated were also less than unity, suggesting the interaction between cetrimide and SDS which were observed to decrease with increasing the mole fraction of cetrimide in the mixture. Negative values of interaction parameter, β, indicate the synergism between the surfactant mixtures. The negative β values and $|\beta| > |\ln(CMC_1/CMC_2)|$ clearly indicated the synergism that is attractive interaction in mixed micelle formation. The more negative ΔG_{ex} and ΔH_{mix} values of the mixed systems at different bulk mole fractions showed the same trends as β and f values, because more negative favouring the formation of stable system. For pure surfactants and surfactant-surfactant systems, the ΔG_m^0 and ΔH_m^0 values were negative, become more negative with increasing temperature, indicating the process to be spontaneous and exothermic. The ΔS_m^0 values observed were positive for all the studied mole fractions and at all the temperatures indicating the spontaneity of the system.

Chapter 7. Conductometric and Surface tension techniques were employed to study the different mole fractions of nonionic surfactants (TX-100 and Brij-35) with cetrimide. The standard Gibbs energies of micellization (ΔG_m^0) and the Gibbs energies of transfer (ΔG_{trans}^0) in the mixture of surfactants were also calculated and the micellization becomes more spontaneous on increasing the amount of non-ionic surfactants in the mixture. It was observed that the values of Γ_{max} in surfactant mixtures decrease in comparison to the pure surfactants but the values of A_{min} increase in surfactant mixtures than in the pure ones. It was also observed that the interaction parameter, β values are negative at all mole fractions. A gradual decrease in β with temperature is observed indicating the synergism between the two components and is attributed to the decrease of the electrostatic repulsion between the charged heads of the cationic surfactant as the nonionic surfactant is being intercalated into the micelle. The activity coefficients were found out to be less than unity confirming nonideality of the system and the negative values of excess free energy of mixing confirm that the mixed micelles formed were stable.