THERMODYNAMIC STUDIES OF SOME SURFACTANTS IN WATER AND AQUEOUS UREA AND ETHYLENE GLYCOL SOLUTIONS

by

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This is to certify that the thesis entitled "THERMODYNAMIC STUDIES OF SOME SURFACTANTS IN WATER AND AQUEOUS UREA AND ETHYLENE GLYCOL SOLUTIONS" being submitted by Mr. Rameshwar Jha to the Indian Institute of Technology, Delhi for the award of the degree of Doctor of Philosophy in Chemistry, is a record of bonafide research work carried out by him. Mr. Rameshwar Jha has worked under my guidance and supervision, and has fulfilled the requirements for the submission of this thesis which, to my knowledge, has reached requisite standard.

The results contained in this dissertation have not been submitted, in part or in full, to any other university or institute for the award of any degree or diploma.

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Rameshwar Jha.

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ABSTRACT

The present work describes the determination of the enthalpies of solution ($\bar{H}_2-H_2^o$) in pre- and post-CMC regions and therefrom the enthalpies of micellization ΔH_m of homogeneous nonionic surfactants polyoxyethylene mono n-decyl ether, $C_{10}E_n$ (n = 4,5,6 and 8) and octaoxyethylene mono-n-dodecyl ether, $C_{12}E_8$ and polydisperse Triton-X-100 in the temperature range 298.15 to 328.15 K, both in presence as well as in absence of cosolutes in water. The cosolutes used are urea and ethylene glycol at different concentrations. From the temperature variation of enthalpies of solution data, the heat capacities of monomeric and micellar forms as well as the heat capacities of micellization have been derived. The heat capacities of some pure liquid nonionic surfactants were measured on micro DSC, and combined with the monomeric heat capacities of solution, ΔCp_{mono}, to obtain the values of the partial molar heat capacities, $\bar{C}p_2^o$, at infinite dilution of these surfactants. The additivity rules have been tested by comparing these experimental values with the estimated values for the partial molar heat capacities, $\bar{C}p_2^o$. The apparent molar heat capacities, ϕ_c and apparent molar volumes, ϕ_v, of some nonionic and ionic surfactants in water have also been determined in post-CMC regions using Picker flow micro calorimeter and Anton Paar vibrating tube digital densitymeter.

It is evident from the enthalpies of solution ($\bar{H}_2-H_2^O$) data, that the thermodynamics of micellization is not only governed by the monomers but also by the state of aqueous solution in the post-micellar solution. The enthalpies of solution in pre-CMC region are found to be more exothermic than enthalpies of solution in the post-CMC region in water as well as in cosolvents except a few values of Triton X-100 in aqueous Ethylene Glycol solutions. All the ΔH_m values are found to be positive except a few values of Triton X-100 in aqueous Ethylene Glycol solutions.

The analysis of enthalpies of micellization values of polyoxyethylene alkyl ethers surfactants shows that the values of the enthalpies of micellization originate from the complete dehydration of 2 to 2.5 oxyethylene groups around 298.15 K.

The heat capacity of the surfactants in the pre-CMC region are highly positive reflecting strong interactions between monomeric surfactant and water. The heat capacities of micellar solution are positive but comparatively smaller in magnitude indicating relatively weaker interactions of micelles with the solvent water. The values of the heat capacities of micellization are relatively less negative compared to that in water. The analysis of the results of heat capacities of micellization indicates that there is an appreciable water penetration inside the micellar core.

The enthalpies and heat capacities of some $C_{10}E_n$ surfactants in monomeric and micellar states in 3 and 6M aqueous urea solutions have been determined. The enthalpies of micellization are comparatively less positive in magnitude in aqueous urea solution with respect to the corresponding values in water and there is a gradual decrease in enthalpies of micellization with increase in urea concentration and rise in temperature. The ΔCp_m of the surfactants are relatively higher in aqueous urea solutions. This has been attributed to the decreased hydration or structure around monomers in urea solutions and increased hydration of micelles due to a larger number of hydrogen bonding between ethylene oxide groups and urea molecules in aqueous urea solutions. The dominance of polyoxyethylene (hydrophilic) groups - urea interactions over the (decyl) hydrophobic group - urea interactions. The Hydrogen bond formation between oxyethylene groups and urea should also contribute significantly towards the negative values of transfer parameters.

The enthalpies of micellization at 298.15 and 308.15 K and heat capacities of micellization at 303.15 K have been determined for Triton X-100 in aqueous Ethylene Glycol (10 to 50% V/V) solutions.

The results indicate that the EG hydrocarbon interactions are more favourable than water hydrocarbon interactions i.e. the hydrocarbon chains of the Triton X-100 monomers are preferentially interacting with EG molecules. As the enthalpy of micellization becomes more negative with the increase in Ethylene Glycol concentration it is evident that with the increase in EG concentration the major contribution towards the free energy of micellization is that of the enthalpy of micellization rather than the entropy of micellization.

The values of $\bar{C}p_2^o$ of some nonionic surfactants have been estimated using group additivity rules and are found to be in good agreement with the experimental values. The ΔCp_m and ΔV_m obtained from the experimentally measured apparent molar heat capacities and volumes in post CMC region and estimated values of $\bar{C}p_2^o$ and $\bar{V}_2^o$ in pre-CMC region. These ΔCp_m are relatively less negative than those obtained from the enthalpies of micellization (Chapter III) data at different temperatures.

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