CHAPTER III

SCOPE AND OBJECTIVES OF THE PRESENT WORK

The usual properties of surfactants i.e. their abilities to form micelles and because of their use in chemical industry as solubilizing agents calls for systematic investigation of their properties in aqueous solutions. Further the presence of solutes and cosolvent significantly affect the physico-chemical properties of surfactant solutions. Surface and thermodynamic properties of aqueous surfactant solutions also provide a potential tool to investigate structural changes in these solutions. Again the review of literature has revealed that very limited number of studies\(^1\) have been made on the thermodynamics of micellization and of adsorption at air/liquid interface.

The studies of the micellar aggregates in aqueous solutions of detergent mixtures is important, not only because it may reveal the exact mechanism of micellization and their preferential micelle forming tendency but also because it has practical usefulness since commercial surface active agents mostly contain
impurities of some lower or higher homologs. Again, as the added cosolvent may alter the dielectric constant of the aqueous solution or form hydrates it would be of interest to explore the affect of such cosolvents on the micellar properties of both the pure detergents as well as their mixtures.

Further, although PVP + SDS system has been extensively studied in aqueous medium, yet there is considerable disagreement regarding the nature of interactions of PVP with SDS. While Fishman and Eirich\(^2\) maintained that there is little evidence of SDS adsorption on PVP coils at low SDS concentrations, Murata et al.\(^3\) inferred that at low SDS concentration, adsorption of SDS on PVP coils constitutes an important ingredient of the interaction of SDS with PVP. Further, while Rudd and Jennings\(^4\) maintain that PVP undergoes no conformational changes as a result of SDS adsorption, Fishman and Eirich have suggested a rapid expansion of polymer coils during polymer – surfactant interaction in aqueous medium. Again, while Rudd and Jennings infer that PVP does not undergo aggregation, Fishman and Eirich\(^5\) maintain that it is converted to a complex polyelectrolyte in water. Turro et al.\(^6\) from their spectrofluorometric studies have proposed the binding of premicellar associates to PVP, whereas Kresheek et al.\(^7\) from their calorimetric studies concluded the involvement of surfactant monomers during surfactant – polymer interaction. This calls for an extensive studies on this system.

In the present investigation, we have used Poly (N- vinyl-2-pyrrolidone) PVP, as one of the water soluble non-ionic polymers. PVP is a homopolymer of the monomer, N-vinyl-2- Pyrrolidone (I)
The official pharmaceutical name of PVP is 'Povidone'. The IUPAC name for PVP is: ethenyl-2-Pyrrolidinone polymer. The chemical abstracts registry number is (9003-39-8).

The monomer units of PVP have amphiphilic character (as it contains a highly polar amide group within the pyrrolidone ring), together with nonpolar parts comprising of 4 methylene and one methine groups and may undergo Keto-Enol tautomerism.

The $N$ and $O$ atoms of the amide linkage in PVP would then carry a fractional positive and negative charges respectively and while the oxygen end of PVP would
be exposed to the solvent medium, N end would be buried in the nonpolar region of the polymer backbone. As far as configuration of PVP is concerned, it is assumed to have linear, atactic configuration and the chain has very open flexible random coil conformation. Pereira et al.\textsuperscript{9}, using ultrasonic relaxation technique, have found that PVP has a structure similar to that of polystyrene, both existing in solution in a disordered random coil conformation. Both are semi-flexible polymer, capable of facile internal rotation about C=C bond is their chain backbone.

**Properties and uses of PVP**

1. PVP is a faintly yellow solid resembling albumin in appearance.
2. It is quite stable when stored under ordinary conditions.
3. It is soluble in water and alcohols. It is insoluble in aliphatic hydrocarbons and ether.
4. PVP is highly hydroscopic, about three water molecules being associated with one monomer unit\textsuperscript{10}.
5. The glass transition temperature is 448.15 K which is sharply reduced by small amounts absorbed moisture.
6. The intrinsic viscosity of aqueous PVP solution is found to be 22 ml g\textsuperscript{-1}. Molecular weight of PVP is calculated using Mark-Hauwink equation i.e.

\[
[\eta] = KM \phi^C
\]

and the constants for PVP in water at 25°C are

\[K = 5.65 \times 10^{-2} \text{ g dl}^{-1} \text{ and } \phi^C = 0.55\]

7. Aqueous solution of PVP has a very small value of conductance which is because of terminal carboxyl group\textsuperscript{12}.
8. It is used as blood plasma substitute\textsuperscript{13}.
9. It is useful as a thickening agent, emulsion stabilizer, desensitizer and dye solubilizer. These properties are utilized in Shampoos, hair tonics, shaving creams etc.

10. PVP has good adhesion to glass, metal and plastics and hence it is used in adhesive systems.

11. The presence of a tertiary amide group makes PVP a protein model.

12. It can be obtained in varying molecular weights.

Objectives

The present plan of work envisages

1. To determine from surface tension data the critical micelle concentration, maximum surface excess concentration, minimum area per molecule at the aqueous solution/air interface and surface pressure at the CMC and to calculate the standard thermodynamic parameters of adsorption and micellization for some anionic, cationic and non-ionic surfactants in aqueous solution and in water + dioxane mixtures with a view to understand structural variations in these surfactants in aqueous as well as mixed solvents.

2. To study surfactant - surfactant interactions in various binary surfactant mixtures (in aqueous solution as well as in mixed solvents) in order to understand the role of surfactant-surfactant interactions in the formation of mixed micelles and also to give molecular flavour to the interaction energies between the two surfactants.

3. To study a) surface and thermodynamic properties b) viscometric c) equilibrium dialysis d) ultra-sound velocity and absorption e) enthalpy change of mixing f) adsorption at solid/liquid interface for surfactants and polymers systems in order to assess i) the role of the charge both on
the polymer and on surfactant head group ii) the role of hydrophobic part of the surfactant (iii) Conformational changes induced in the polymer by the surfactant (iv) the role of polymer - surfactant mixed micelle formation in the surfactant polymer interactions.

4. To interpret the binding data of polymer - surfactant system in terms of various models of surfactant-polymer interaction.

5. To propose a new mechanism, if any, for surfactant polymer interactions.
REFERENCES