Summary
Interest in research on self-assemblys in solutions is increasing day-by-day. This is not only because of their wide variety of applications in industries, but also due to the development of new and more powerful experimental and theoretical tools for probing the microscopic behavior of these systems.

A surface active agent, i.e., surfactant, is a substance that, when present at low concentration in a system, has the property of adsorbing onto the surface or interface of the system and altering to a marked degree the surface or interfacial free energies.

Many types of substances act as surfactants, but all share the property of amphipathy; the molecule is composed of nonpolar hydrophobic portion and apolar hydrophilic portion. The polar part of the molecule is called hydrophilic group and the nonpolar part hydrophobic group.

Classifying the surfactants on the basis of hydrophilic group, one differentiates anionic, cationic, nonionic, and zwitterionic surfactants.

It is well known that the surfactant molecules form self-organized aggregates known as micelles above a certain concentration, which is known as the critical micelle concentration, cmc. The cmc depends upon the nature of polar group, the surfactant counterion, the length and the structure of the hydrophobic chain, solvent polarity and type, temperature, pressure, pH, etc.

McBain and Hartley from their preliminary research work had concluded that the micelles are spherical or roughly spherical in their shape. Upon increasing the concentration of surfactant, spherical micelles become cylindrical and subsequently the cylindrical structures become hexagonally
packed. If concentration is further increased, the lamellar structures are formed. Further increase in concentration results in a hexagonal packing of water cylinder. It is possible to induce transition from one structure to another by changing the physicochemical conditions such a temperature and addition of salts, etc.

Simple geometric arguments are effectives for predicting the micellar structure. The so-called packing factor $R_p = \frac{v_h}{a_o l_c}$ allow the prediction of the micellar structure with three adjustable parameters, the optimum head group area ($a_o$), volume of surfactant monomer ($v_h$), and the length of the surfactant molecule ($l_c$). When $R_p$ is less $1/3$, spherical micelles are favored and when $1/3 < R_p < 1/2$ infinite rodlike micelles are preferred. The packing factor indicates that the formation of elongated micelles is promoted by lowering the head group area ($a_o$) or by increasing the volume of hydrocarbon chain ($v_h$).

Addition of electrolyte or cosurfactant results in elongated micelle formation by reduction in $a_o$ because of screening effect. Addition of certain organic compounds also promotes the sphere-to-rod transition and the continued growth of the rods to an extent at which point some of the rods apparently revert back to spheres or convert to disks.

Cloud Point

Upon heating, aqueous solutions of many nonionic surfactant become turbid at a temperature known as the cloud point (CP), above which there is a separation of the solution into two phases. Phase separation results from the competition between entropy, which favors miscibility of micelles in water,
and enthalpy, which favors separation of micelles from water. Depending on the variation of these two contributions with temperature, either a lower or an upper consolute point can result.

The temperature at which the CP phenomena occurs depends on the structure of surfactants.

Clouding phenomenon can be exploited in separation science for the development of extraction, purification and preconcentration schemes for desired analytes. Since the addition of just a small amount of an appropriate surfactant to the aqueous sample solution is required, this approach is convenient and fairly benign, eliminating the need for the use of organic solvents as in conventional liquid-liquid or solid-liquid extraction.

**Hydrotropy**

Over 90 years ago, the phenomenon of ‘hydrotropy’ was discovered by Neuberg. The class of compounds that normally increase the aqueous solubility of sparingly-soluble solutes are called hydrotropes. Besides solubilization, hydrotropes have uses in vesicle preparation and selective separation, as stabilizer of o/w microemulsion, viscosity modifiers and as clearing agents in cloudy detergent formulation. The classification of hydrotropes on the basis of molecular structure is difficult, as examples include diverse type of compounds, like aromatic alcohols, alkaloids, ionic surfactants, etc.

The concentration above which hydrotropic action is observed may be referred to operationally as the *minimal hydrotropic concentration (MHC)*.
Hydrotropes exhibit noticeable similarities and differences in properties with surfactants. The hydrotropes are amphiphilic in character, have short hydrophobic regions and thus differ from classical surfactants.

The work described in the thesis deals with studies on surfactant systems in presence of various additives.

In the General introduction (Chapter I) a detailed account of the behavior of surfactants and the various phenomena exhibited by them, for example, micellization, causes of micellization, factors affecting cmc and micellar size, the effect of additives, etc. are described. The phenomena of clouding occurring in surfactant solutions and hydrotropy are also presented. An up-to-date literature survey related to the work embodied in subsequent chapters is also included.

Chapter II deals with the experimental details which have been followed in study. Materials used, their purities, make, etc., are given in tabular form.

Studies on the effect of addition of urea and other family members on micellization and related phenomenon like sphere-to-rod transition in a typical ionic micellar system and its possible implications in protein folding are described in Chapter III. Evidence has been collected on the basis of critical micelle concentration (cmc, obtained from conductometry), \([n\)-pentanol] needed for s→r transition (obtained from viscometry), aggregation number (obtained from small- angle neutron scattering) and cloud point measurements. All of these effects are attributed to urea-assisted aggregation up to certain
concentration, which depends upon the nature and presence of number of methylene groups in a particular urea. The results are explained on the basis of influence of the additive on solvent water, adsorption on head group and hydrocarbon tail and size of the additive.

It was seen that cmc’s of SDS and CTAB decrease up to certain concentration of the additive and then an increase was observed on continued additions. For each urea analogue there exists a minimum in the cmc value, which is dependent on nature and number of methyl groups in the additive.

It is well known that repulsive forces between similar charges vary inversely with the dielectric constant of the medium. Therefore, the decreased electrostatic repulsion between head groups of the micelle on urea addition contribute to the predominance of the hydrophobic interactions and to the decrease in the cmc at low concentrations of different ureas. At moderately higher concentration of ureas, the additive molecule gets adsorbed onto charged surfactant monomer ions and lead to repulsion between them. Also, the arrest of surfactant monomer ions among urea (or similar molecules) would decrease the hydrophobic interactions. The increase in cmc of SDS or CTAB at higher [urea] may be a resultant of the above two effects.

In order to have more evidences regarding the above urea effects in low concentration range, we carried out SANS measurements on 0.3 M SDS + 0.2 M Bu₄NBr system. Aggregation number ($n$) increased with the addition of both urea and thiourea, but the $n$ increase was more with the later which
indicates that thiourea is more effective in increasing the aggregation
tendencies as was observed from the cmc data.

The above interpretation for the low concentration region of ureas found
further support by viscometry and cloud point measurements. (i) Viscometry
was performed on 3.5% SDS (w/v) + 0.28 M NaCl + n-pentanol system to find
[n-pentanol] needed to bring s→r transition. The concentration of n-pentanol,
obtained for each [urea], was found to first decrease and then increase with the
continuous addition of each member of urea family. Thus, s→r transition is
prepond initially with lower concentration regime of different urea family
members supporting the cmc and SANS data. (ii) The CP results of TX-100
solutions with added urea also showed first a decrease, followed by an increase
with progressive urea addition. The initial CP decrease indicates that the
dehydration of the TX-100 micelle has taken place by the addition of urea (in a
low-concentration regime). The decrease in the CP is not remarkable but
enough to that urea does influence the amphiphile properties, which, in turn,
depend on the [urea] itself.

Chapter IV is concerned with the effect of different polar nonaqueous
solvents (acetonitrile, AN; dimethylsulfoxide DMSO; methylcellosolve, MC;
and ethylene glycol. EG) on the clouding behavior of SDS + quaternary
bromide (Bu₄NBr/Bu₄PBr) systems. The CP was found to decrease with initial
increase in the volume percent of the above solvents in mixtures (with water).
After a minimum in CP vs. volume percent plots, further increase in volume
percent caused increase in CP, followed by near constancy region. The data
have been discussed on the basis of the effect of above solvents on the two
types of water present in the system: hydrated water and bulk water. The
limited cmc data also run parallel to CP results. This seems a very important
result which hints towards a modification of hydrophobic interactions at such a
low volume percent.

We can say that the clouding in ionic surfactant solutions can be
facilitated to certain volume percents of polar nonaqueous solvents (mixed with
water) which are reported to postpone micellization.

Chapter V describes that association tendency of hydrotropes can be improved
by the addition of salts, n-alkanols, and ureas. Urea decreases or increases the
MHC depending on whether the urea content is lower or higher (e.g., the
increased solubility of sparingly soluble riboflavin corroborates the increase in
the hydrotropic properties of the system). In the present work, the association
tendencies of sodium salicylate (a well known hydrotrope), sodium dodecyl
sulfate, and sodium bromide were compared. Conductivity measurements have
been used to study the aggregations phenomena. The data suggest that the
behavior of NaSal reflects neither a normal uni-univalent electrolyte (like
NaBr) nor a classical micellar system (like SDS). The increased association of
NaSal in the presence of salts may thus be due to the screening action of salts,
which lower the repulsive force between the polar head groups. The association
tendency is increased by the presence of n-alkanols. The results have been
explained on the basis of increased hydrophobic interactions owing to the
presence of alkyl moieties in the additive molecules. Our conductance results at
low urea and thiourea concentrations show that urea has a tendency to improve NaSal association up to a certain concentration, after which it shows regular destabilization of the hydrotrope. This is explained by the fact that urea and thiourea are known to enhance the hydrophobic interactions initially, followed by preferential adsorption on hydrophilic surface which causes repulsion between the molecules and leads to rise in MHC.

References


