There is a class of compounds called surfactants that decreases strikingly the surface tension or surface free energy of interfaces. This thesis is concerned exclusively with certain properties of the surfactants.

Surfactants generally consist of two distinct parts, a hydrocarbon portion and a polar or ionic portion in the same molecule. The hydrocarbon portion, which can be linear or branched, interacts only very weakly with water molecules in an aqueous environment. Moreover, the strong interactions between the water molecules arising from dispersion forces and hydrogen bonding act cooperatively to squeeze the hydrocarbon portion out of the water, hence the chain is usually called hydrophobic. The polar or ionic portion of the molecule, usually termed the head group, however, interacts strongly with the water via dipole–dipole or ion–dipole interactions and is solvated. Consequently, the head group is said to be hydrophilic.

Depending on the chemical structure of the hydrophilic moiety bound to the hydrophobic portion, the surfactants may be classed as cationic, anionic,
nonionic, or ampholytic (zwitterionic). Both the interfacial properties and bulk properties of solutions of surface active agents are consistent with the fact that at a certain concentration the surface active molecules associate to form longer units. These associated units are called micelles. The concentration at which this association phenomenon occurs is known as the critical micelle concentration (cmc). The value of cmc is dependent upon a large number of parameters like total carbon chain-length, additional polar groups, C=C bonds, chain branching of surfactants, various types of additives (polar and non-polar), electrolytes, temperature, and pressure.

While stupendous work on surfactants is reported in literature and today thousands of surfactants are available, studies are still underway to examine various factors responsible for their micellization and micellar growth and adsorption behaviour under different conditions. Several micellar systems have recently attracted considerable interest because of their potential uses in diverse fields. An interesting aspect of micellar solutions is that they show a large
change in viscosity on adding inorganic salts or organic cosurfactants. From a practical point of view, alcohols (as cosurfactants) have been used in tertiary oil recovery because they bring about a large decrease of viscosity, strongly accelerate the rate at which these systems reach equilibrium in the polyphasic range, and appear to decrease the adsorption of the surfactants in rock pores in the oil field, thereby increasing efficiency and decreasing cost. The viscous surfactant solutions are also of industrial importance because they enhance customer appeal and economy of various formulations. Usually, inorganic salts are used as thickening agents for concentrated surfactant solutions; the role of organic molecules as thickening agent is, however, not well studied.

The simplest possible aggregate of surfactant molecules is the micelle. At the molecular level, a balance of interfacial forces controls the curvature of the surfactant film which, in turn, determines the shape of the aggregates. It is now accepted that micelles are spherical near cmc. Transition of spherical to larger micelles for ionic surfactants
occurs upon a reduction of inter head group repulsion. It may be caused by salt or surfactant additions or solute solubilization. It is not clear if, at surfactant concentrations, micellar growth by increasing salt concentration is because of enhanced screening of the electrostatic interactions or due to change in "electrical charge per head group".

The solution viscosity responds to changes in both the structure of aggregates and their mutual interactions. In dilute solutions (where these interactions are minimized) the technique is sensitive to the shapes of particles in the solution. Transition from small to large micelles is accompanied by a significant increase in viscosity and appearance of anisotropic susceptibilities.

Due to solubilization properties, the micellar systems have several applications; thus a careful investigation of such properties is of paramount interest. The site of solubilization of different compounds within the micellar systems can be correlated with the structural organization of aggregates. A large body of work is available on solubilization of organic
compounds by surfactant micelles but structural changes produced by such additives have not been studied in much detail. Solubilization results of polar organic molecules are consistent with other physical evidences indicating that these molecules have their head group anchored in the polar/ionic outer region of typical ionic surfactants. Such molecules tend to solubilize at least partly within the hydrocarbon core of the micelle, although steric and substituent group effects may play important roles in modifying the structure and thermodynamic properties of "intermicellar solutions" of the organic solute in the micelles.

There has been considerable discussion in the literature about the location of organic solutes in ionic surfactant micelles. The aromatic hydrocarbons are intermediate in behaviour between moderately polar solutes (e.g., hydroxy substituted benzoates, organic acids, amines, medium chain alcohols, etc.) which are clearly intercalated in the micelle surface region and aliphatic hydrocarbons which preferentially solubilize in the micellar core region. These facts explain why the effect of organic additives on the properties of
micellar systems is a topic of importance.

In the thesis the first Chapter is "General Introduction". It is entirely based on up-to-date literature survey relating to the work described in preceding chapters.

Viscometric studies of the effect of added n-alcohols (C₃ - C₈OH) and n-amines (C₄, C₆ - C₈NH₂) on the micellar growth of cetylpyridinium chloride (CPC) in the presence and absence of potassium chloride (KCl) at four temperatures between 25 - 40°C are described in Chapter II. The presence of KCl or organic additive of lower chain-length (C₃OH, C₄OH or C₄NH₂) singly or jointly has little effect on the viscosity of the micellar solutions. With higher chain-length (C₅OH - C₈OH, C₆ - C₈NH₂) additives the viscosity increases as the additive concentration increases; magnitude being substantial in presence of KCl. Moreover, for equal chain-length additives the effect was greater for n-alcohols. An interesting observation was that in presence of KCl and with the additives C₅OH, C₆OH or C₇NH₂, the viscosity of CPC micellar solution increases with increase in the additive concentration (similar to
the case without KCl), reaches a maximum, and then decreases. In all probability, the other alcohols and amines, viz. C7OH, C8OH and C8NH2, would show the same phenomenon at higher additive concentrations, but studies were hampered as turbidity appeared at concentrations before such maxima could occur. These two effects show that a special phenomenon exists when 0.1M KCl and additives are present in the same system. The manifold increase in viscosity is the result of variation of different forces favorable for micellar growth. Addition of KCl to the CPC solution weakens the Coulombic repulsion between the micelles, and intercalation of higher chain-length additives decreases intramicellar Coulombic repulsive forces and increases hydrophobic forces among the monomers of the CPC micelle. As mentioned earlier, the decrease of Coulombic repulsion and/or increase in hydrophobic interactions are favorable conditions for micellar growth (either one of which exists if 0.1M KCl or organic additive is present singly).

The observed viscosity decrease at higher concentrations with the aforementioned additives is
possibly due to the fact that they may be salted-out by the added 0.1M KCl and start dissolving in the micellar core rather than remaining in the vicinity of interfacial region; therefore the requirement of the surfactant chains to reach the centre of the micelle become relaxed. It is, thus, possible that at high additive contents the larger micelles disintegrate to smaller ones and form the basis of the viscosity decrease. The solubility and packing constraints do not allow C7OH, C8OH or C8NH₂ to do so as there is not a sufficient amount of these additives available to form the core of the micelle (solubilized system).

Thus, it was concluded that the presence of a salt and an organic additive in the system produce favorable conditions for micellar growth. The electrostatic effect produced by additives at the micellar surface is the governing factor in addition to the hydrophobic part of the additives. In case of additives of equal chain-length, its efficacy of decreasing effective head group area at micellar surface (A₀) decides the potential of the additive for structural growth. Temperature dependence of the viscosity was used to
compute the free energy of activation, $\Delta G^*$, for the viscous flow.

In Chapter III, the effects of the addition of aliphatic $n$-amines (C$_4$, C$_6$, C$_7$ and C$_8$NH$_2$) and temperature on the shape of cetyltrimethylammonium bromide (CTAB) in 0.1M KBr, studied by viscosity measurements, are described. The data show that transition of rod-shaped micelles to larger aggregates is induced by addition of higher amines (C$_6$ - C$_8$NH$_2$) upto a certain concentration, a further increase in concentration produced the opposite effect. With C$_4$NH$_2$, the viscosity decreased gradually right from the beginning. Activation free energies ($\Delta G^*$, computed from the temperature dependence of the viscosity) were higher for larger aggregates than for smaller ones. The data were interpreted in terms of solubilization / incorporation (decrease of micellar surface charge density) of amines at various sites of micelles.

The shear viscosities of CTAB micellar solutions in presence of aromatic compounds (sodium salicylate, NaSal, sodium benzoate, NaBen, salicylic acid, SA, and anthranilic acid, AA) at different temperatures were
measured which are given in Chapter IV. A Brookfield viscometer (model DV - I+) with cone / plate geometry was used to obtain the viscosities at different shear rates. The data were collected for fixed CTAB concentrations (0.05, 0.10 and 0.20 M) with varying concentrations of the additives. For all the systems, the viscosities were highly dependent on the rate of shear (non-Newtonian flow) and exhibit viscoelastic character. The zero shear viscosity ($\eta_{G=0}$) vs $[NaSal]$ plots showed a two-peak structure. Similar behaviour was obtained with NaBen. It was also seen that the $\eta_{G=0}$ slightly decreased with temperature but positions of the maxima and minimum remained unaltered. With SA and AA, only a single peak (though broad) was observed which broadened and shifted to higher [additive] as the [CTAB] was increased.

With the addition of NaSal in 0.1M CTAB, while intermicellar correlation diminishes (owing to the electric shielding), the micellar size or rod length increases and these long micelles entangle with each other. This is the reason for initial steep rise in $\eta_{G=0}$ values as we increase the amount of NaSal.
Penetration of Sal$^-$ into micelles increases the $R_p$ (Sal$^-$ binds strongly to CTA$^+$ cation which could reduce $A_0$). Also, the phenyl moiety of the salicylate might be embedded into the micellar hydrophobic region. The result then is the trend short rod-shaped micelles $\rightarrow$ large wormlike micelles and hence a steep rise in the viscosity was observed. Beyond first maximum, further addition of NaSal destroys intermicellar correlation (entanglement to disentanglement) owing to the electric shielding effect. As a result, the rheological character diminishes in opposition to micellar growth, and the $\eta_C=0$ is decreased. With the addition of excess NaSal {$>[\text{CTAB}]$}, the specific adsorption and penetration are promoted which accelerate the growth of rodlike micelles and the viscosity rises unto the second maximum due to entanglement. As the concentration is increased further, the excess adsorption and penetration of Sal$^-$ allow the micelles to charge negatively and to diminish destructively to smaller sizes because of the electrostatic repulsion (the micelles are now negatively charged). Similar behaviour was observed with NaBen.
Interestingly, only a single peak was observed with both the AA and SA and thus the behaviour of these acids was different than the NaSal or NaBen. This may be due to the fact that with these acids electrostatic interactions are not that strong as the case with NaSal or NaBen.

These acids interact, in the first approximation, due to a combined effect of electrostatic and hydrophobic forces with the micelle and, after saturating the palisade layer, they can get adsorbed at the surface of the micelle. This is responsible for the fall of viscosity. It was further observed that, at equal concentrations of SA and AA, the viscosities were higher with the former. It may be due to the fact that \(-\text{NH}_2\) group (of AA) is less effective in transferring electron cloud to the charged acidic group. It is, therefore, concluded that the chemical structure of the additive has an important role to play for such micellar growth processes.

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