STUDIES ON THE STRUCTURAL TRANSITIONS
OF ORGANIZED ASSEMBLIES

DISSERTATION
SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS
FOR THE AWARD OF THE DEGREE OF
Master of Philosophy
IN
CHEMISTRY

BY
KRISHNA KUMARI

DEPARTMENT OF CHEMISTRY
ALIGARH MUSLIM UNIVERSITY
ALIGARH (INDIA)
1994
DEDICATED TO MY FATHER
The work embodied in the dissertation entitled, STUDIES ON THE STRUCTURAL TRANSITIONS OF ORGANIZED ASSEMBLIES is original work carried out by Miss KRISHNA KUMARI and is suitable for the consideration of the award of M.Phil. degree.

(PROF. KABIR-UD-DIN)
ACKNOWLEDGEMENTS

It gives me great pleasure to express my deep sense of gratitude to Dr. Kabir-ud-Din, Professor, Department of Chemistry, Aligarh Muslim University, Aligarh, for his supervision and guidance throughout my work. His constructive criticism with a lot of patience throughout the tenure of my work in this laboratory was a singular inspiration which made this work possible. I am also thankful to Dr. Sanjeev Kumar, Research Associate for his helpful comments; invaluable guidance, cooperation and encouragement at every stage of this work.

I am thankful to Prof. A. Aziz Khan, Chairman, Department of Chemistry, for providing the necessary research and seminar facilities.

I am extremely beholden to my father and all members of my family for their affectionate encouragement and interest in my academic pursuits.

I acknowledge the help offered to me by my friends, Miss Kirti, Miss. Sara Liz David and Mr. Rayees Ahmad Shah, among many others whom it would not be possible to mention individually.

(KRISHNA KUMARI)
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CHAPTER 1

GENERAL INTRODUCTION
There is considerable interest in the nature of the structural organisation of multimolecular assemblies of amphiphilic molecules. Recently, much effort has been directed towards the utilization of organized media to modify reactivity and regio-selectivity of products. Among the many ordered or constrained systems utilized to organize the reactants the notable ones are micelles, microemulsions, liquid crystals, monolayers and solid phases such as adsorbed surfaces and crystals. Judicious selection of a given organized system for a given application requires a sufficient understanding of the properties of the organized media themselves and those of the substrate interactions therein. Due to their widespread uses in many industrial applications there has been an increasing interest in the surfactant organized assemblies both from academic and applied point of views. A fundamental understanding of the physical chemistry of surfactant organized assemblies, their unusual properties and phase behaviour is essential for most industrial chemists.

1.1 **SURFACE ACTIVE AGENTS AND THEIR BEHAVIOUR IN SOLUTION**

The modification of surface characteristics of fluids in the presence of substances introduced from outside is of tremendous utility. Such type of foreign substances derived mostly from fatty acids, fatty alcohols,
alkyl phenols, alkylamines, mercaptans and from other variety of sources are known as surface active agents and surfactants. A surfactant molecule contains at least one polar hydrophilic part and at least one apolar hydrophobic unit, such as a hydrocarbon chain\(^1-\(^3\). Typical examples are soaps (sodium alkanoates) or phospholipids which form membranes. These molecules may be also called amphiphilic or tensioactive. Owing to the polarity of the distinct regions these substances have also been referred to as amphipathic, heteropolar or polar-nonpolar substances\(^4-\(^5\). The polar-nonpolar character is responsible for the unique properties of surfactant molecules in solutions which render possible applications in detergency, cleaning, wetting, floatation, emulsification, dispersion, foaming, etc.\(^6-\(^10\). The factors responsible for desired surface activity is the balance between lyophobic and lyophilic characteristics of the molecules\(^11\).

Aqueous solutions of surfactants at a minimum concentration, referred to as critical micelle concentration (CMC), associate dynamically to form normal micelles\(^10\) (some times called 'direct micelles'). Depending upon the nature of the hydrophilic head group, micelles can have either cationic, anionic, zwitterionic or nonionic surfaces. Some examples are given in Table 1.1. The number of monomers that aggregate to form a micelle is called the aggregation number (N). Typically the CMS's are in the range of
### TABLE 1.1

**Selected Surfactants**

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Structure</th>
<th>CMC (M)</th>
<th>t(°C)</th>
<th>Aggregation Number, N</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Anionic</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. Sodium dodecyl sulphate (SDS)</td>
<td>( \text{CH}_3(\text{CH}<em>2)</em>{11}\text{SO}_4^-\text{Na}^+ )</td>
<td>(8.1\times10^{-3})</td>
<td>25</td>
<td>62</td>
</tr>
<tr>
<td>2. Sodium dodecanoate</td>
<td>( \text{CH}_3(\text{CH}<em>2)</em>{10}\text{COO}^-\text{Na}^+ )</td>
<td>(2.4\times10^{-2})</td>
<td>25</td>
<td>56</td>
</tr>
<tr>
<td>3. Copper(II) dodecyl sulphate</td>
<td>( [\text{CH}_3(\text{CH}<em>2)</em>{11}\text{SO}_4^-]_2\text{Cu}^{2+} )</td>
<td>(1.2\times10^{-3})</td>
<td>30</td>
<td>85</td>
</tr>
<tr>
<td>4. Sodium hexadecyl sulphate</td>
<td>( \text{CH}_3(\text{CH}<em>2)</em>{15}\text{SO}_4^-\text{Na}^+ )</td>
<td>(5.2\times10^{-4})</td>
<td>40</td>
<td>-</td>
</tr>
<tr>
<td><strong>Cationic</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. Hexadecyl trimethyl ammonium bromide (CTAB)</td>
<td>( \text{CH}_3(\text{CH}<em>2)</em>{15}\text{N}^+(\text{CH}_3)_3\text{Br}^- )</td>
<td>(9.2\times10^{-4})</td>
<td>25</td>
<td>61</td>
</tr>
<tr>
<td>2. Hexadecyl pyridinium chloride (CPC)</td>
<td>( \text{CH}_3(\text{CH}<em>2)</em>{15}\text{N}^+\text{C}_5\text{H}_5\text{Cl}^- )</td>
<td>(9.0\times10^{-2})</td>
<td>25</td>
<td>95</td>
</tr>
<tr>
<td>3. Dodecylpyridinium chloride</td>
<td>( \text{CH}_3(\text{CH}<em>2)</em>{11}\text{N}^+\text{C}_5\text{H}_5\text{Cl}^- )</td>
<td>(1.5\times10^{-2})</td>
<td>25</td>
<td>-</td>
</tr>
<tr>
<td>4. Decyl trimethyl ammonium bromide</td>
<td>( \text{CH}_3(\text{CH}<em>2)</em>{9}\text{N}^+(\text{CH}_3)_3\text{Br}^- )</td>
<td>(6.5\times10^{-2})</td>
<td>25</td>
<td>48</td>
</tr>
</tbody>
</table>

Contd....
<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Structure</th>
<th>CMC(M)</th>
<th>t(°C)</th>
<th>Aggregat Number, N</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Nonionic</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. Polyoxyethylene(3) decanol</td>
<td>CH$_3$(CH$_2$)$_9$O(CH$_2$CH$_2$O)$_3$H</td>
<td>6.0x10$^{-4}$</td>
<td>25</td>
<td>-</td>
</tr>
<tr>
<td>2. N,N-dimethyldecylamine oxide</td>
<td>CH$_3$(CH$<em>2$)$</em>{11}$N(CH$_3$)$_2$</td>
<td>2.1x10$^{-3}$</td>
<td>27</td>
<td>-</td>
</tr>
<tr>
<td>3. Polyoxyethylene (9) hexadecanol</td>
<td>CH$_3$(CH$<em>2$)$</em>{15}$O(CH$_2$CH$_2$O)$_9$H</td>
<td>2.1x10$^{-6}$</td>
<td>27</td>
<td>279</td>
</tr>
<tr>
<td>4. Polyoxyethylene (6) dodecanol</td>
<td>(CH$_3$)(CH$<em>2$)$</em>{11}$O(CH$_2$CH$_2$O)$_6$H</td>
<td>8.7x10$^{-5}$</td>
<td>25</td>
<td>400</td>
</tr>
<tr>
<td><strong>Zwitterionic</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. 3(Dimethyldecylammonio)-propane-1-sulphonate</td>
<td>CH$_3$(CH$<em>2$)$</em>{11}$N$^+$(CH$_3$)$_2$CH$_2$CH$_2$SO$_3^-$</td>
<td>1.2x10$^{-3}$</td>
<td>25</td>
<td>-</td>
</tr>
<tr>
<td>2. 3(Dodecylmethylammonio)-propane-1-sulphonate</td>
<td>CH$_3$(CH$<em>2$)$</em>{11}$N$^+$/HCH$_3$CH$_2$CH$_2$CH$_2$SO$_3^-$</td>
<td>4.3x10$^{-3}$</td>
<td>25</td>
<td>-</td>
</tr>
<tr>
<td>3. N-Dodecyl-N,N-dimethyl-glycine</td>
<td>CH$_3$(CH$<em>2$)$</em>{11}$N$^+$(CH$_3$)$_2$CH$_2$COO$^-$</td>
<td>1.8x10$^{-3}$</td>
<td>23</td>
<td>-</td>
</tr>
<tr>
<td>4. C-Dodecyl-N,N-dimethyl-glycine</td>
<td>CH$_3$(CH$<em>2$)$</em>{11}$CH$^+$(CH$_3$)$_3$COO$^-$</td>
<td>1.3x10$^{-3}$</td>
<td>27</td>
<td>-</td>
</tr>
</tbody>
</table>
0.01-10.0 mM, with each micelle consisting of 40-180 monomers. Micelles do not exist at all concentrations and temperatures. For a given surfactant at a given temperature, there is a narrow concentration range below which aggregation to micelles is absent and above which association leads to micelle formation. In other words, certain amount of monomers can be accommodated in the cavities and any further addition of surfactant monomers provides a driving force to minimize contact of monomer hydrocarbon chains with water and resulting in the aggregation (micelle formation). This narrow concentration range during which micelle formation occurs is called the CMC.

The exact structure of an aqueous micelle is not known with certainty, although several intelligent guesses have been put forth. Figure 1 depicts some of these models. A conventional representation of micelle is that by Hartley (Fig.1.2) and is more acceptable and useful for visualization.

Though micelles provide a microscopically heterogeneous environment, they are generally small enough for the macroscopic properties to approximate those of truly homogeneous solutions. Moreover, the surfactant molecules are in dynamic equilibrium either between two micelles or between a micelle and bulk water. The hydrophobic interior of a micelle provides a restricted
Fig. 1.1: Various structural models for micelle formation.
Fig. 1.2: Schematic representation of a micelle: an excluded volume including an inner core with disordered hydrophobic chains and an outer shell with headgroups condensed counter-ions and hydration water.
volume of hydrophobic space in an aqueous environment.

Surfactant molecules can be considered as building blocks of micelles. It is possible to obtain various types of structures of surfactant molecules by simply increasing the concentration of surfactant in water (Fig.1.3) with a concomitant change in the size of the aggregates\textsuperscript{13}. The spherical micelles formed near the CMC become cylindrical ones which may be converted into a hexagonal packing of surfactant molecules to lamellar structures by increasing the concentration of surfactant in aqueous medium.

Certain physical properties such as conductivity, surface tension, osmotic pressure, chemical shift, etc., are plotted against the surfactant concentration, each shows a break point at the CMC. Light scattering has also been used to measure the CMC of surfactants. Density measurements can be used to show a change with concentration when micelle formation takes place. This is due to changes in partial molar volume of the surfactant. In the case of large spherical micelles, diffusion, viscosity and sedimentation velocity methods are used to collect information about size, shape and solvation of micelles. Ultrasonic absorption, SANS, SAXS and solution calorimetry are being considered as the most appropriate methods of studying structural transitions in micellar systems. A new technique, known as direct imaging (DI), has recently proven to be extremely
Fig. 1.3: Limit of sphericity of a micelle as given by Tanford. Large micelles cannot be of a spherical shape as a hole should occur at their centre.
powerful for surfactant related research. Since DI is able to make a clear distinction between connected and disconnected aggregates, it is likely that wide use will be made of this technique in structural studies in the future.

1.2 FACTORS AFFECTING CRITICAL MICELLE CONCENTRATION

1.2(a) Hydrocarbon Chain Length:

The critical micelle concentration depends on the length of the hydrocarbon chain. Generally, the CMC decreases as the hydrocarbon chain length increases. For the same head group, compounds containing longer hydrocarbon chains form micelles at lower concentrations than those containing short chains. For homologous series of surfactants, the CMC is related to the number (m) of carbon atoms in a straight hydrocarbon chain by

\[ \log \text{CMC} = A - Bm \]  

...(1)

Where A and B are constants for a homologous series and values of these constants were listed by Shinoda. Lengthening of the hydrocarbon chain causes an increase in the micelle size and aggregation number.

The position of the headgroup in hydrocarbon chain also affects the CMC. The closer the head group to the centre of the chain, the higher the CMC, due to the two branches of the chain partially shielding one another. The
presence of double bond in the chain also causes an increase in CMC.

1.2(b) **Temperature**

For ionic detergents the CMC first decreases with increasing temperature at low temperatures and increases at high temperatures\(^{15}\). Decrease in CMC in the low temperature is probably due to desolvation of parts of the monomer which make it more hydrophobic. The CMC increase is due to thermal agitation of molecules resulting in a decreasing adhesion between monomers and shifting the equilibrium in favor of the monomeric species.

For nonionic detergents the CMC decreases with increasing temperature\(^{16-17}\). Meguro et al.\(^{17}\) observed linear relation between log CMC and the reciprocal of temperature. The micelle size of the ionic detergents decreases\(^{18}\), and that of nonionic detergents increases\(^{19}\) with increase in temperature.

1.2(c) **Pressure**

The CMC has been found to increase upto a pressure of 1,000 atmospheres and decrease with further increase of pressure\(^{20-21}\). It has been suggested that the soap molecules when present in the micelle are in a more expanded condition than when present as the monomers in solution, so that the initial effects of pressure tend to compress the micelle and
mitigate against the increased freedom of the monomer in the micelle, thus giving a rise in CMC. The decrease in CMC on increasing the pressure above 1,000 atmospheres may be due to an increase in the dielectric constant of water, making less electrical work necessary to bring a monomer into a micelle.

1.2(d) **Additives**

Addition of polar and non-polar substances to solutions of surfactants may alter the aggregation behaviour such as CMC, aggregation number, size and shape of micelles.

**(i) Effect of Salts**

Decrease in CMC of ionic detergents\(^{22-26}\) by addition of salts have been observed, presumably because the screening action of the simple electrolytes lower the repulsive forces between the polar head groups, and less electrical work is required in micelle formation. The micelle size increases\(^{27}\) with increased salt concentration due to the reduction in electrical repulsion affecting the balance of forces upon which the size of micelle depends. The effective charge on the micelles, \(p\) (the number of charge per micelle), increases with salt concentration, but the actual degree of dissociation \(p/N\), remains roughly constant.
The addition of salts in nonionic detergents have been found first to decrease and then increase the CMC. This may be due to a reduction in the hydration of the monomers, which increases their hydrophobicity and, consequently, their tendency to micellize. The effectiveness of salts in altering the CMC of nonionic surfactants approximately follows the lyotropic series, which for anions and cations, respectively, are:

\[ \text{SO}_4^{2-}, F^-, Cl^-, ClO_4^-, Br^-, NO_3^-, I^-, SCN^-, Na^+, K^+, Li^+, Ca^{2+} \]

The CMC of ionic surfactants in the presence of added univalent salts has been described by the equation:

\[ \log \text{CMC} = a \log C_i + b \quad \ldots (2) \]

where \( C_i \) represents the concentration of counterions and \( a \) and \( b \) are constants. The counterion concentration can be expressed as the sum of the concentration of surfactant CMC plus the concentration of added salts. The values of \( a \) and \( b \) were first estimated to be about -0.5 and -0.3. The coefficient \( a \) was later identified as \( -k_g \) by Shinoda as:

\[ \log \text{CMC} = \text{Const.} - k_g \log C_i \quad \ldots (3) \]

An alternate empirical equation was suggested by Yan and has the form

\[ \text{CMC'} = a' (\text{CMC} + C_i)^{\frac{1}{2}} + b' \quad \ldots (4) \]

A modified form of equation (4) was able to describe the effect of polyvalent salts on CMC.
(ii) **Effect of Non-electrolytes**

Non-electrolyte additives like urea and its derivatives increase the CMC of both ionic and nonionic surfactants\(^{37-39}\). Urea is generally believed to break the water structure\(^{37,38}\) and to decrease the structuring around the hydrocarbon chains, hence reducing the driving forces for micellization. This effect is generally greater for cationic micelles than for anionic micelles. The addition of urea to surfactant solutions containing a nonionic flourine labelled surfactant is reported to increase the micelle size\(^4^0\), although it decreases the micelle size for ionic sodium trifluorododecyl sulphate\(^4^1\).

Addition of acetamide and formamide decrease the CMC of surfactants\(^4^2\).

The addition of sucrose to nonionic surfactant solutions was found to promote a small lowering of CMC\(^4^3\). Addition of sucrose to alkylammonium bromide increases the CMC at all temperatures, while addition of glucose, may promote either CMC increase or decrease depending upon temperature. The hydrocarbon gases such as ethane and propane have been found to lower the CMC of dodecylamine hydrochloride and this effect increases with increasing chain length of hydrocarbons.

(iii) **Effect of Solvents**

CMC of surfactants were found to be lower in D\(_2\)O than in H\(_2\)O\(^{37,4^4}\). The suggestion was made\(^4^5\) that hydrophobic
bonds may be stronger in D$_2$O than in H$_2$O. Low concentrations of added alcohols reduce the CMC, but high concentrations tend to increase the CMC for nonionic and ionic surfactants. An increase in the CMC of polyoxyethylene nonylphenols and dodecyltrimethylammonium bromide was observed on the addition of 1,4-dioxane, ethylene glycol, and methanol due to the increase of monomer solubility in additive-water mixture. It was found that micelles disappear by the addition of some organic solvents to aqueous solution of surfactants.

1.3 STRUCTURAL TRANSITIONS IN MICELLAR SYSTEMS

At a higher concentration in many systems there is a transition to rod like micelles. As it is observed experimentally in the same manner as the primary CMC, it is referred to as the second CMC. Many studies, like light scattering, viscosity, conductivity, ultrasonic absorption, SANS, and solution calorimetry are employed to detect the structural transitions in micellar systems. Even at higher concentrations of surfactants, SANS measurements have shown that the rods of some systems shorten when their rotational volumes begin to overlap and undergo another transition to a different anisomeric form probably to that of a disk. Apart from temperature and concentration of surfactant solutions, there are some other factors such as electrolytes and co-surfactants which affect the shape of surfactant systems.
Packing considerations constitute a factor which involves the nature of the hydrophilic and hydrophobic groups of the surfactant. A critical ratio \( R_p \) with associated limits for several of the possible aggregation shapes has been devised by Ninham et al.\textsuperscript{72-73}

\[
R_p = \frac{V_h}{A_o l_c}
\]

where

- \( V_h \) = the volume of the amphiphile's hydrocarbon tail,
- \( A_o \) = the optimum cross-sectional area per amphiphile molecule, and
- \( l_c \) = the length of the fully extended hydrocarbon tail.

The optimum cross-sectional area per amphiphile molecule is observed experimentally by X-ray diffraction of bilayer system while the volume and length of the hydrocarbon tail may be calculated following Tanford\textsuperscript{74}

\[
V_h = (27.4 + 26.9 n) \text{Å}^3
\]

\[
l_c = (1.5 + 1.265 n) \text{Å}
\]

(n being the number of methylene groups in the hydrocarbon chain).

Considering the geometric dimensions, the volume and the surface area of each association structure yield critical conditions for the formation of various structures in the surfactant solutions (Fig.1.4). The \( R_p \) ratio depends on the surfactant chemical structure (\( l_c \) and \( V_h \)) and on surface repulsion between head groups (\( A_o \)). The desired
<table>
<thead>
<tr>
<th>$R_p = \frac{V_h}{A_0 l_c}$</th>
<th>Aggregate shape</th>
<th>Type of surfactant</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1/3$</td>
<td>Spherical micelles</td>
<td>Single chain ionic or zwitterionic</td>
</tr>
<tr>
<td>$1/2$</td>
<td>Cylinders (that may be flexible)</td>
<td>Single chain Non-ionic or ionic with added salt</td>
</tr>
<tr>
<td>$1$</td>
<td>Flexible lamella vesicles</td>
<td>Double chain</td>
</tr>
<tr>
<td></td>
<td>Lamellar phases</td>
<td>Double chain Small area per headgroup</td>
</tr>
<tr>
<td></td>
<td>Reverse micelles (in apolar solvents)</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 1.4: Schematic diagram of possible aggregate shapes according to the $V_h / A_0 l_c$ criterion (Israelachvili et al 1980). Note that reverse micelles are formed with an apolar solvent while all other cases refer to binary water–amphiphile solutions.
curvature (and thus, type of aggregate) may be obtained upon a correct choice of the surfactant molecule and solvent conditions (type of solvent, ionic strength, etc.), using the $R_p$ as guide. However, this ratio has to be used with caution as it accounts only for geometrical consideration.

Larger, less curved or even reverse structures of micelles are likely to be formed by amphiphiles with smaller inherent head group areas (high $R_p$). By addition of a counterion or a suitable cosurfactant in ionic surfactants, the same area-shrinking effect may be achieved. Lengthening or unsaturation of the hydrocarbon chain, particularly cis double bonds, leads to larger structures. In three and four component systems, by using this packing ratio, Fang explained a series of phase transitions (starting with normal micelles and ending with reverse micelles). The surface area occupied by the surfactant's polar head group should be large to form a spherical structure. If the heads are permitted to pack tightly, on the other hand, the aggregation number will increase and rod and disk-shaped micelles will be favored. The essential consideration pertaining to the area occupied by the heads is the work necessary to overcome the electrical repulsion experienced by heads of like charge. A surfactant carrying a large charge on a relatively small charge-bearing atom will inherently be more apt to form spherical micelles because of the high energy needed to overcome the prohibitive charge.
density of the head group. A surfactant with a high degree of counterion binding may overcome head group repulsion by holding the oppositely charged counterion between head groups of similar charge; head group repulsion is repressed and rod or disk-shaped micelles become favored.

1.3(a) Effect of Salts

Inorganic salts are usually used as thickening agents for concentrated solutions of surfactants. Addition of electrolyte ameliorates the electronic repulsion between surfactant head groups, increasing aggregation number, thus rod-shaped micelles will be favored. Salicylate\textsuperscript{76-77} and thiocyanate\textsuperscript{77} counterions have been shown to be extremely effective at promoting the transition when coupled with alkyltrimethylammonium and alkylpyridinium cationic surfactants, so effective that rod formation occurs at or near the CMC when the surfactant chain length is C\textsubscript{12} or longer\textsuperscript{77}.

Hayashi and Ikeda\textsuperscript{78} have shown by means of light scattering that the micelle of SDS changes its shape from spherical to rod-like when the concentration of added NaCl exceeds 0.45 M and the micelle concentration is $\sim$1 g dL$^{-1}$. Such an effect of added NaCl in the SDS micelle was also observed by Mazer and co-workers\textsuperscript{79-80} by the measurements of quasi-elastic and total-intensity light scattering. Corti and Degiorgio\textsuperscript{81-82} also observed large values of aggregation number and hydrodynamically equivalent radius of the SDS micelle in 0.6 M NaCl by using the same techniques.
In their subsequent work Ikeda et al. have demonstrated that the micelle of dodecyldimethyl ammonium chloride changes its shape from spherical to rod like when the NaCl concentration is higher than 0.8 M.

There are at least two factors responsible for determining such a transition of micellar shape in presence of salts. One is the electrostatic effect of simple salts due to the counterion binding on ionic micelles, and the other is the hydrophobic interaction between surfactant molecules or ions caused by the change in the hydrogen bonded structure of water. Many workers have discussed the effects of inorganic salts on ionic surfactant solutions in terms of electrostatic interactions, ionic hydratability, changes in the water structure, etc., and have classified ions as water structure breakers and promoters. It is now known that ionic solutions in aqueous solutions change not only their micelle size but also their shape, when simple salts are added. Generally, the micelle aggregation number of a surfactant increases with increasing salt concentration, irrespective of whether the micelle is spherical or rod like, and above a certain threshold salt concentration, surfactant micelles exist in two forms, i.e. spherical and rod like, that are in mutual equilibrium.

1.3(b) Effect of Nonpolar and Polar Additives

(i) Nonpolar Additives

Smith and Alexander have determined from
sedimentation and viscosity studies that methylcyclohexane when added to solution containing cetylpyridinium chloride (CPC) increases the aggregation number and viscosity only slightly and regularly, while additions of aromatic additives (toluene and trichlorobenzene) showed large increases of viscosity and aggregation number. These findings are interpreted in terms of aromatic hydrocarbons having the ability to promote rod formation and aliphatic hydrocarbons simply swelling the pre-existing spheres. Similar effects were found for benzene and cyclohexane with cetyltrimethylammonium bromide (CTAB) as surfactant. For micelles to maintain a spherical form some of the tails must be able to reach the centre of the micelle. At the center of micelle, there can be no vacuum, the structure of micelle must rearrange into a rod like shape when micellar size places an undue conformational stress on the surfactant tails to reach the center. Addition of an aliphatic hydrocarbon, generally thought to reside in the micellar core, relieves this requirement. Now the association structure can maintain spherical form containing the solubilized oil at a radius which was previously prohibitive. In this manner the aliphatic hydrocarbon retards the sphere-to-rod transition.

Effects of aromatic hydrocarbon additives is different for cationic surfactant than for anionic surfactant system. Aromatic hydrocarbon have ability to stimulate rod growth in case of cationic surfactant which
may stem from interaction of the delocalized \( \pi \)-electron cloud of the benzene ring with the positive charges of the surfactant head groups, this behaviour is very similar to that of a cosurfactant counterion. The resulting reduction of head group repulsion favors rods by shrinking the surface area occupied per amphiphile, thereby allowing the aggregation number to increase. The apparent increase of rod promotion with longer side chains on benzene emanates from the increase of aggregation number associated with an increase of radius.

Benzene, toluene and ethylbenzene show a tendency to destabilize spheres in SDS micelles, then there is a trend towards increasing stabilization of the spherical form with subsequent methylene additions to the side chain (e.g., with n-propyl and n-butylbenzene). It was observed that the \( \pi \)-electrons of the benzene ring do not have as strong an effect when positioned at the anionic SDS micellar surface as in the cationic case. With increasing length of the alkyl chain, the aromatic molecule acts more like a saturated hydrocarbon, with apparently a higher preference for the center of micelle. Residence at the micellar core then promotes the spherical form by relieving the requirement of the surfactant chains to reach the center of the structure.

(ii) Polar Additives

Wormuth and Kaler\textsuperscript{96} treated the hydrophilic ranking of amines, alcohols and carboxylic acids in terms of the
partitioning behaviour between micellar and aqueous pseudophases. The authors also noted that amines hydrophilicity was lower than they expected when coupled with anionic surfactant. In their studies on the effect of n-alkylamines \( \text{C}_6-\text{C}_{16} \) on tetradecyltrimethylammonium bromide (TTAB) and SDS, Lindemuth and Bertrand have observed that amines are more effective in the SDS system than in the TTAB. It indicates a specific interaction between the amine and the anionic head group at the micellar interface. It was further seen that the amine head group has the ability to sit deeper in the SDS micelle than other polar additives relieving the requirement of the surfactant tails to reach the center of the micelle at a shorter alkyl chain length. Primary amines were shown to have a synergistic effect with the interface of anionic micelles, while the same hold true for carboxylic acids in cationic surfactant.

1.4 APPLICATIONS OF MICELLAR SOLUTIONS

Micelles provide several unique properties which make their extensive use in many disciplines and have many practical applications in analytical chemistry, enhanced oil recovery, and in many other areas. The solubilization capacity of micelles makes them more useful in a variety of chemical and photophysical processes. An over simplified artistic conception of a cross section of an aqueous normal micelle with different solubilization sites is shown in Fig.1.5. Several other unique abilities and
Fig. 1.5: A cross section of an aqueous normal micelle with different solubilization site. A and B represent same and opposite charge solute to the micelle while C and D represent the nonpolar and amphiphilic solutes.
properties possessed by micelles are their capability to concentrate, compartmentalize, organize and localize reactants/solutes; alter effective microenvironments (such as polarity, dielectric constant, viscosity) about solubilized solutes; alter chemical pathways and rates; alter spectral parameters of solubilizates; alter photophysical pathways and rates; solubilize reactants, intermediates and products; alter quantum efficiencies; alter the position of equilibrium (such as dissociation constants); alter redox properties (potentials); maintain product and/or reactant gradients; separate products (charges); alter drastically transparent photophysically inactive; and on the whole relatively "nontoxic".

1.5 IMPORTANCE OF RESEARCH PROBLEM

Increasing attention is being devoted to the study of the "incorporation" or solubilization of neutral organic molecules into micelles in aqueous solutions. Some of the most studied solubilizates are alcohols because of the important role they have in preparation of microemulsion. It is generally accepted that the medium chain length alcohols intercalate between the surfactant ionic head groups to decrease the micellar surface charge density. This effect is correlated with modification of the growth and shape of the micelles.

Visualizing the significance of micellar structure transitions and their dependence on the nature of the
electrolytes\textsuperscript{108-109}, temperature and, in some cases, the influence of organic additives\textsuperscript{110}, it was thought worthwhile to pursue a study of the effect of aliphatic alcohols on concentrated micellar solutions in aqueous sodium bromide (NaBr). Compared with other techniques, the capillary viscometry method is simple and reliable and can provide a large body of important information with respect to the investigation of the increase in micelle size\textsuperscript{111}. The result of studies on the effect of the addition of various aliphatic alcohols on the viscosity of 0.3 m SDS + 0.3 m NaBr solutions are presented herein. From the temperature dependence of the viscosity, the activation free energies ($\Delta G^*$), enthalpies ($\Delta H^*$) and entropies ($\Delta S^*$) for the viscous flow have also been calculated.
REFERENCES


CHAPTER - 2

EFFECT OF ALCOHOLS AND TEMPERATURE ON THE VISCOSITY BEHAVIOUR OF SODIUM DODECYL SULPHATE MICELLES IN AQUEOUS SODIUM BROMIDE SOLUTIONS
2.1 INTRODUCTION

Several papers have recently been published on the structural transitions in aqueous ionic micellar solutions\textsuperscript{1-4}. The interesting aspect of the micellar solutions is that they show a large change in viscosity on adding simple salts\textsuperscript{4}. The same phenomenon is observed on adding aliphatic alcohols and amines to concentrated surfactant solutions\textsuperscript{1,5}. Depending on the nature of the alcohol the viscosities of micellar solutions are found to increase or decrease. The sphere-to-rod transition for sodium dodecyl sulphate (SDS) in aqueous, micellar solutions was reported to occur at a concentration of 1.16 mol kg\textsuperscript{-1} \textsuperscript{6}. An extensive study of the phase diagrams of SDS/l-pentanol/water/NaCl was made by Guerin and Bellocq\textsuperscript{7}; especially in the water rich region. This study has shown that various phases and critical points are present in the system depending on the NaCl concentration and temperature. It was also reported that the addition of 0.1 M NaCl to solutions of SDS in pure water and to aqueous solutions of 0.2 M SDS + 0.6 M l-pentanol increases aggregation number from about 65 to 93 \textsuperscript{8,9} and from 47 to 197 \textsuperscript{10}, respectively. This indicates a clear cut increase in aggregation number when salt and alcohol are present jointly in the same micellar solution.

Unfortunately, in the semidilute region light scattering experiments measure quantities which are independent of the mean degree of aggregation of micelles.
and therefore do not test the growth of the micelles. Viscosity and self-diffusion experiments are more appropriate as they are sensitive to the mean degree of aggregation and shape of the micelle, irrespective of the surfactant concentration\textsuperscript{11-13}. Till fairly recent time, it seems that there has been very few reports which directly concern the effect of alcohols on SDS micelles in aqueous salt solutions\textsuperscript{14}. Therefore, the investigation of this subject is of practical and theoretical importance. The capillary viscometry method is simple and reliable and can provide a large body of important information with respect to investigation of the change in micellar shape\textsuperscript{13,15}. Visualizing the significance of micellar structure transitions and their dependence upon the nature of electrolyte, temperature and, in some cases, the influence of organic additive, it was thought worthwhile to pursue a systematic study of the influence of medium chain aliphatic alcohols on concentrated micellar systems in aqueous salt solutions. We present here the results of a study on the effect of alcohol concentration on the viscosities of 0.3 m SDS + 0.3 m NaBr solutions. This particular concentration of starting sample was chosen by the study of effect of NaBr concentration on 0.3 m SDS aqueous solution (Fig. 2.1). Figure 2.1 shows that there is a distinct rise in viscosity at 0.3 m NaBr concentration which is a possible indication of rod-like micelles in the solution\textsuperscript{16}. The value of energy of activation for the viscous flow, $E_a$, was found to be 37.56
Fig. 2.1: Effect of NaBr concentration on the relative viscosity of 0.3 m SDS micellar solution at 298.16 K.
kJ/mole for the present system which, in conjunction with the above pointed transition, clearly indicates the presence of rod-like micelles in the solution (Eₐ value for spherical micelles is <17 kJ/mole). From the temperature dependence of the viscosity of SDS solutions in presence of NaBr and alcohols, the activation free energies (ΔG*) and enthalpies (ΔH*) for viscous flow have been calculated.

2.2 EXPERIMENTAL

Materials

"Specially pure" grade sodium dodecyl sulphate (SDS) was obtained from BDH, Poole, UK, while sodium bromide (NaBr) was a Merck "pro analysi" grade. All alkanols were of BDH high purity chemicals. All the solvents were used as supplied and water was distilled twice in all glass still.

Measurements

The viscosities of the solutions were measured in Ubbelohde viscometer thermostated at a fixed temperature (25, 30, 35 or 40°C). The temperature of the bath was controlled to an accuracy of ± 0.1°C. The method of measurement of viscosities under Newtonian flow conditions was the same as described by other workers. Density corrections were not made, since it was found that these were negligible.
2.3 RESULTS AND DISCUSSION

Figure 2.1 shows the variation of relative viscosity \( \eta/\eta_o \) of 0.3 m SDS solution with the NaBr concentration (\( \eta \) and \( \eta_o \) represent the viscosities of solution and solvent water, respectively). At a given SDS concentration, addition of NaBr induces a strong screening of the repulsive forces which decreases the intermicellar interactions and favors the growth of the micelles. The two effects lead to a sharp rise in \( \eta/\eta_o \) around 0.3 m NaBr which indicates the formation of non-spherical micelles: this being the reason of choosing 0.3 m SDS + 0.3 m NaBr system for the detailed study of the effect of alcohols and temperature.

Measured relative viscosities \( \eta/\eta_o \) of 0.3 m SDS + 0.3 m NaBr in presence of various concentrations of n-alcohols at different temperatures are given in Table 2.1. Plots of \( \ln (\eta/\eta_o) \) versus concentration of alcohols are shown in Figure 2.2. It is seen from Figure 2.2 that \( \eta/\eta_o \) changes abruptly with n-pentanol and n-hexanol. It is also interesting to note that \( \eta/\eta_o \) for n-butanol and n-pentanol increase up to a certain concentration and then decrease as the concentration of added alcohol increased. However, no such fall in viscosity could be observed in the case of n-hexanol up to its solubility limit. The viscosity increments at low concentrations of higher alcohols (C₄-C₆) can be interpreted in terms of the formation of larger micellar aggregates owing to their incorporation into the micelles. The decrease in the viscosity of micellar solutions on a
TABLE - 2.1

Relative viscosities, activation free energies and enthalpies for the viscous flow of 0.3 m SDS + 0.3 m NaBr solution in the presence of n-alkanols and correlation coefficients (r) for the linear variation of ln (n/n₀) with 1/T.

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Fig. 2.2: Logarithms of relative viscosities of 0.3 m SDS + 0.3 m NaBr solutions as a function of added n-alcohols at 298.16 K.
further addition of n-pentanol and n-butanol is a result of the breaking of larger aggregates into small rods. The preceding discussion indicates that alcohols with chain length > C₅ only promote the growth of rods in the presence of electrolytes. Similar behaviour has been reported for aqueous CTAB micellar systems in the presence of salts and higher chain length alcohols¹,¹⁹.

It is further seen that n-propanol decreases the viscosity of 0.3 m SDS + 0.3 m NaBr solution. This is because short-chain alcohols are mainly hydrophilic molecules with an excellent solubility in water, and are partitioned more in the aqueous phase than in the micellar phase; hence they affect the water structure more efficiently and cause the larger micelles to break into smaller ones. Such transitions from rod-to-sphere by the addition of lower alcohols to dodecyltrimethylammonium bromide-sodium salicylate micelles have been reported from light scattering measurements²⁰.

Figure 2.3 shows the ln (η/ηₒ) vs. 1/T plots for micellar solutions in presence of various concentrations of n-pentanol. Similar plots were obtained with other alcohols. The observed linearity in the plots of ln (η/ηₒ) vs. 1/T can be interpreted in terms of the equation¹³

\[ \ln \left( \frac{\eta}{\eta_o} \right) = \ln A + \frac{\Delta G^\ast}{RT} \]  

where A is a constant and \( \Delta G^\ast \) is the activation free energy of viscous flow. The densities of the solutions were very close to the density of water, hence by neglecting kinematic
Fig. 2.3: Variation of \( \ln(\eta/\eta_0) \) with \( 1/T \) for 0.3 m SDS + 0.3 m NaBr solutions in the presence of various concentrations of n-pentanol mentioned in ( ).
corrections, values of $\Delta G^*$ were calculated from the slopes of straight lines shown in Fig. 2.3. These values are also recorded in Table 2.1.

From the temperature dependence of $\Delta G^*$ and using the well known equation

$$\frac{\partial (\Delta G^*/T)}{\partial (1/T)} = \Delta H^*$$

$\Delta H^*$ values were obtained from the slopes of $\Delta G^*/T$ vs. $1/T$ plots (Fig. 2.4). Similar plots were obtained for other alcohols and the $\Delta H^*$ values for other systems were also calculated. Table 2.1 records all these values. The data show that $\Delta H^*$ nearly covers total contribution and, accordingly, the entropic contribution is negligible (Table 2.1). In addition, the observed linearity in the $\ln \eta/\eta_\infty$ vs. $1/T$ plots (Fig. 2.3) also implies that the enthalpic and entropic Contributions, to $\Delta G^*$ are independent of temperature. The variation of $\Delta H^*$ with concentration of various alcohols are shown in Figure 2.5. The energy involved in the transition from larger aggregates to smaller ones is reflected by the $\Delta H^*$ values, which seems to be more important contribution related to the rupture of larger micelles to give smaller aggregates.

The dependence of $\Delta G^*$ and $\Delta H^*$ on the nature and concentration of added alcohols is reflected from the data recorded in Table 2.1. From the magnitude of these thermodynamic parameters for various alcohols it may be seen that addition of n-hexanol promotes the micelles to larger aggregates (elongated rods) as the $\Delta H^*$ values are higher.
Fig. 2.4: Gibbs-Helmholtz plots for 0.3 m SDS + 0.3 m Na Br in the presence of various concentrations of n-pentanol mentioned in ( ).
Fig 2.5: Variation of activation enthalpy ($\Delta H^*$) for the viscous flow of 0.3 m SDS + 0.3 m NaBr solutions as a function of added n-alcohols.
for this alcohol, whereas n-propanol breaks the initially present rod shaped micelles into spherical micelles. However, in the case of n-butanol and n-pentanol the size of the micelle initially increases, and then, at a certain concentration of the alcohol, the micelles break up to give smaller aggregates. The behaviour of these alcohols is due to the combined influence of two opposite effects; namely, hydrophobic interactions and nature of solvent. At higher alcohol concentrations having chain length < 6 carbon atoms, the latter effect dominates and is responsible for breaking of rod shaped micelles with a concomitant decrease in $\Delta H^*$ values.
REFERENCES


