Chapter II

Experimental
The materials used throughout the study are given in the Table 2.1, including their abbreviated names, chemical formulas, make and purities.

The quaternary salts were dried for at least 72h before use in a vacuum drying oven. The temperature during drying was maintained according to the thermal stability and fusion point of the salt. The dried salts were stored over P$_2$O$_5$. All other chemicals were used as received.

**Synthesis of tetra-n-butylammonium dodecyl sulfate (TBADS)**

TBADS was prepared by mixing equimolar solutions of SDS and TBAB, followed by stirring for 64h. TBADS was extracted with dichloromethane (DCM), which was separated and washed repeatedly with water. The solvent DCM was then evaporated which left a colorless viscous mass (TBADS) at room temperature. The surfactant was characterized by $^1$H NMR, IR and mass spectrometry. The purity of the surfactant was further ensured by absence of minimum in surface tension vs. [TBADS] plot. The cmc of the surfactant (~1mM), determined by conductivity measurements was in agreement with the literature value.

**Synthesis of bis(hexadecyldimethylammonium)butane dibromide (16-4-16)**

The bis(hexadecyldimethylammonium)butane dibromide was synthesized and characterized by adopting Scheme 2.1.

Scheme 2.1: i: C$_{16}$H$_{33}$N(CH$_3$)$_2$ (2.1 equiv.), Dry Ethanol, Reflux, 48h.
A 1:2.1 equivalent mixture of 1,4-dibromobutane with \textit{N}, \textit{N}-dimethylhexadecylamine in dry ethanol was refluxed (at \textasciitilde 80°C) for 48h. The progress of reaction was monitored by using TLC technique. The solvent was removed under vacuum from the reaction mixture and the solid thus obtained was recrystallized several times from hexane and ethyl acetate mixture to obtain the compound in pure form. The overall yield of the surfactant was \textasciitilde 80\%. Purity of the gemini surfactant was checked on the basis of C, H, N analysis and surface tension measurements\textsuperscript{1} which was further characterized by \textsuperscript{1}H NMR, mass and IR spectroscopy\textsuperscript{4,6}.

The water used to prepare the solutions was demineralized and double distilled in all glass (Pyrex) distillation set-up. The specific conductivity of the water was in the range 1-2 x 10\textsuperscript{-6} S cm\textsuperscript{-1}.

Special care was taken for cleaning the glasswares. The glassware was properly washed with freshly prepared chromic acid and distilled water then rinsed with acetone and kept in oven for drying before use.

\textbf{Viscosity Measurements}

Viscosity implies resistance to flow. It is the measure of the internal friction of a fluid. It is developed in liquids because of the shearing effect of moving one layer of the liquid past another.
The fundamental unit of viscosity is the ‘Poise’ (1 Poise = 1 dyne.sec. cm²).

There are a number of methods of different kind for measuring viscosity, \( \eta \). The method commonly employed is based on Poiseuille’s law, which is given by

\[
\eta = \frac{\pi r^4 P}{8vl}
\]  

(2.1)

where \( v \) is the volume (cm³) of the liquid flowing in \( t \) seconds through a narrow tube of radius \( r \) cm and length \( l \) cm under a hydrostatic (driving) pressure of \( P \) dynes per square centimeter.

The usual procedure is to determine the viscosity of a liquid with reference to that of water. This is termed as relative viscosity (\( \eta_r \)). If \( t_1 \) and \( t_2 \) are times of flow of the same volume of water and the liquid, respectively, then

\[
\eta_r = \frac{\eta_1}{\eta_2} = \frac{\pi r^4 P_1}{8vl} / \frac{\pi r^4 P_2}{8vl} = \frac{t_1 P_1}{t_2 P_2}
\]  

(2.2)

Since the pressure head is proportional to density (\( \rho \)) of the liquid, we have

\[
\eta_r = \frac{t_1 \rho_1}{t_2 \rho_2}
\]  

(2.3)

Ozeki and Ikeda⁷ found density corrections to be negligible, \( \eta_r \) values may, therefore, be calculated using equation

\[
\eta_r = \frac{t_1}{t_2}
\]  

(2.4)
Aqueous surfactant solutions containing spherical micelles are of low viscosity. Addition of salts and organic additives usually changes the shape/size of the micelles, which is often reflected by the change in viscosity. Micellar growth is accompanied by a distinct rise in viscosity while a solution of swollen micelles has distinctly less viscosity. In view of the fact that shape/size is sensitive of the microscopic objects in a homogeneous suspension, one can expect the evolution of micellar shape to be reflected in the viscosity variation.

Stock solutions of surfactant in distilled water (containing either a fixed concentration of the salt or no salt) were prepared by weight. Sample solutions were made by taking requisite volumes of additives with the help of micropipette (Hamilton) in standard volumetric flasks and making up the volumes with the stock solutions. After proper mixing the sample solutions were left overnight for equilibration. To avoid evaporation, the flasks/viscometer were kept properly stoppered and sealed.

The temperature was controlled within \pm 0.1 \degree C in a thermostatic water bath, which was designed and assembled in the laboratory with commercially available components.

In the present investigation, viscosities of the solutions were obtained by using an Ubbelohde viscometer thermostated at particular temperature. The method is simple, reliable and provides information related to micellar size. As the viscosities of certain systems were highly dependent on the rate of flow, it was necessary to obtain values under Newtonian flow conditions. For this
purpose, the following modification was made in the Ubbelohde viscometer. A wide U-tube containing water was connected to one of the limbs of the viscometer, which is open to the atmospheric pressure under normal operation conditions. Thus the pressure, $P$, can be varied under which the solution flows. The viscosity values at different rates of flow can be obtained from the slopes of the straight lines $P$ vs. $1/t$.

**Cloud Point Measurements**

Cloud points (CP) of TBADS solutions were obtained in pure as well as in presence of different additives. For the purpose, different samples in Pyrex glass tubes were suspended in a water bath. The temperature at which the CP phenomenon occurs was determined by the method reported by Carvalho and Briganti. The method is based on the visual observation of the separation of phases in the micellar solution. The initial solution was heated in a water bath at temperatures well above its CP (turbid solution). Then the solution was cooled gradually with constant stirring and kept at a stable temperature at which the solution became clear. To verify the results, the opposite process was carried out by gradually heating the clear solution until turbidity appeared. The reported value is the average of four determinations.
Reference

   


### TABLE 2.1:

Names and structural formulas of the chemicals used.

<table>
<thead>
<tr>
<th>Name</th>
<th>Abbreviation</th>
<th>Structure/Formula</th>
<th>Make</th>
<th>% Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Surfactants</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium dodecyl sulfate</td>
<td>SDS</td>
<td>$\text{CH}_3(\text{CH}<em>2)</em>{11}\text{OSO}_3^-\text{Na}^+$</td>
<td>Sigma (USA)</td>
<td>99</td>
</tr>
<tr>
<td>Bis(hexadecyldimethylammonium)</td>
<td>16-4-16</td>
<td>$\text{Br}^-$ $\text{Br}^-$ $n\text{-C}<em>{16}\text{H}</em>{33}\text{Me}_2\text{N}(\text{CH}_2)<em>4\text{Me}<em>2n\text{-C}</em>{16}\text{H}</em>{33}$</td>
<td>Self Synthesized</td>
<td>—</td>
</tr>
<tr>
<td>butane dibromide</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tetra-$n$-butylammonium dodecyl</td>
<td>TBADS</td>
<td>$\text{CH}_3(\text{CH}<em>2)</em>{11}\text{OSO}_3^+\text{N}(\text{C}_4\text{H}_9)_4$</td>
<td>Self Synthesized</td>
<td>—</td>
</tr>
<tr>
<td>sulfate</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Inorganic bromides</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lithium bromide</td>
<td>LiBr</td>
<td></td>
<td>Loba Chemie (India)</td>
<td>99</td>
</tr>
<tr>
<td>Sodium bromide</td>
<td>NaBr</td>
<td></td>
<td>Loba Chemie (India)</td>
<td>99</td>
</tr>
</tbody>
</table>

Contd...
Potassium bromide  
Ammonium bromide  
Lithium nitrate  
Sodium nitrate  
Potassium nitrate  
Ammonium nitrate  
Magnesium nitrate  
Calcium nitrate  
Strontium nitrate  

**Quaternary bromides**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Abbreviation</th>
<th>Formula</th>
<th>Supplier</th>
<th>Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetraethylammonium bromide</td>
<td>TEAB</td>
<td>(C₂H₅)₄NBr</td>
<td>Fluka (Switzerland)</td>
<td>≥97</td>
</tr>
<tr>
<td>Tetra-n-propylammonium bromide</td>
<td>TPAB</td>
<td>(C₃H₇)₄NBr</td>
<td>Fluka (Switzerland)</td>
<td>≥98</td>
</tr>
<tr>
<td>Tetra-n-butylammonium bromide</td>
<td>TBAB</td>
<td>(n-C₄H₉)₄NBr</td>
<td>Fluka (Switzerland)</td>
<td>≥98</td>
</tr>
</tbody>
</table>

**Organic salts**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Abbreviation</th>
<th>Structure</th>
<th>Supplier</th>
<th>Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anilinium hydrochloride</td>
<td>AHC</td>
<td><img src="image" alt="Anilinium Hydrochloride" /></td>
<td>Fluka (Switzerland)</td>
<td>≥99</td>
</tr>
<tr>
<td>Ortho-toluidine hydrochloride</td>
<td>oTHC</td>
<td><img src="image" alt="Ortho-toluidine Hydrochloride" /></td>
<td>Fluka (Switzerland)</td>
<td>≥98</td>
</tr>
</tbody>
</table>

Contd...
**Para-toluidine hydrochloride**  
*p*THC  
\[
\text{NH}_2\text{HCl}
\]

Fluka (Switzerland)  
≥99

**Sodium salicylate**  
NaSal  
\[
\text{COONa}
\]

CDH (India)  
99.5

**Sodium benzoate**  
NaBen  
\[
\text{COONa}
\]

Merck (India)  
99.5

**Sodium anthranilate**  
NaAn  
\[
\text{COONa}
\]

CPC (USA)  
98

Contd...
<table>
<thead>
<tr>
<th>Ureas</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Urea</td>
<td>U</td>
<td>NH₂CONH₂</td>
<td>BDH (India)</td>
<td>99</td>
<td></td>
</tr>
<tr>
<td>Monomethyl urea</td>
<td>MMU</td>
<td>CH₃NHCONH₂</td>
<td>Merck (Germany)</td>
<td>&gt;97</td>
<td></td>
</tr>
<tr>
<td>Dimethyl urea</td>
<td>DMU</td>
<td>(CH₃)₂NCONH₂</td>
<td>Fluka (Switzerland)</td>
<td>~97</td>
<td></td>
</tr>
<tr>
<td>Tetramethyl urea</td>
<td>TMU</td>
<td>(CH₃)₂NCON(CH₃)₂</td>
<td>Fluka (Switzerland)</td>
<td>≥99</td>
<td></td>
</tr>
<tr>
<td>Thiourea</td>
<td>TU</td>
<td>NH₂CSNH₂</td>
<td>s. d. fine (India)</td>
<td>99</td>
<td></td>
</tr>
<tr>
<td>Dimethylthiourea</td>
<td>DMTU</td>
<td>(CH₃)₂NCSNH₂</td>
<td>Lancaster (England)</td>
<td>98</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sugars</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>D(+)Xylose</td>
<td></td>
<td></td>
<td>s.d. fine (India)</td>
<td>99</td>
<td></td>
</tr>
</tbody>
</table>

Contd...
L(+)Arabinose

D(+)Mannose

D(-)Fructose

Sigma (USA)

s.d. fine (India)

Merck (India)

Contd...
L(-)Sorbose

Amino acids

L-Glutamic acid

L-Histidine

Aliphatic alcohols

Methanol

C₄OH

CH₃OH

Fluka (Switzerland)

Sisco (India)

Loba Chemie (India)

Ranbaxy (India)

Contd...
<table>
<thead>
<tr>
<th>Alcohol</th>
<th>Molecular Formula</th>
<th>Structure</th>
<th>Supplier</th>
<th>Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Propanol</td>
<td>C₃OH</td>
<td>CH₃CH₂CH₂OH</td>
<td>BDH (England)</td>
<td>99.5</td>
</tr>
<tr>
<td>n-Butanol</td>
<td>C₄OH</td>
<td>CH₃(CH₂)₂CH₂OH</td>
<td>S. M. Chemicals (India)</td>
<td>95</td>
</tr>
<tr>
<td>n-Pentanol</td>
<td>C₅OH</td>
<td>CH₃(CH₂)₃CH₂OH</td>
<td>Fluka (Switzerland)</td>
<td>≥99</td>
</tr>
<tr>
<td>n-Hexanol</td>
<td>C₆OH</td>
<td>CH₃(CH₂)₄CH₂OH</td>
<td>BDH (England)</td>
<td>99</td>
</tr>
<tr>
<td>n-Heptanol</td>
<td>C₇OH</td>
<td>CH₃(CH₂)₅CH₂OH</td>
<td>BDH (England)</td>
<td>99</td>
</tr>
</tbody>
</table>

**Aliphatic amines**

<table>
<thead>
<tr>
<th>Amine</th>
<th>Molecular Formula</th>
<th>Structure</th>
<th>Supplier</th>
<th>Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylamine</td>
<td>C₂NH₂</td>
<td>CH₃CH₂NH₂</td>
<td>Fluka (Switzerland)</td>
<td>70 (in water)</td>
</tr>
<tr>
<td>n-Propylamine</td>
<td>C₃NH₂</td>
<td>CH₃CH₂CH₂NH₂</td>
<td>Fluka (Switzerland)</td>
<td>≥99</td>
</tr>
<tr>
<td>n-Butylamine</td>
<td>C₄NH₂</td>
<td>CH₃(CH₂)₂CH₂NH₂</td>
<td>Riedel-de-Haen (Germany)</td>
<td>98</td>
</tr>
<tr>
<td>n-Pentylamine</td>
<td>C₅NH₂</td>
<td>CH₃(CH₂)₃CH₂NH₂</td>
<td>Fluka (Switzerland)</td>
<td>≥99.5</td>
</tr>
<tr>
<td>n-Hexylamine</td>
<td>C₆NH₂</td>
<td>CH₃(CH₂)₄CH₂NH₂</td>
<td>Merck (Germany)</td>
<td>&gt;98</td>
</tr>
</tbody>
</table>

Contd...
<table>
<thead>
<tr>
<th>Hydrocarbons</th>
<th>Fluka (Switzerland)</th>
<th>s. d. fine (India)</th>
<th>Merck (India)</th>
<th>Fluka (Switzerland)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n$-Heptylamine</td>
<td>CH$_3$(CH$_2$)$_6$CH$_2$NH$_2$</td>
<td>C$_6$H$_4$</td>
<td>C$_7$H$_8$</td>
<td>C$<em>8$H$</em>{18}$</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>C$_6$H$_6$</td>
<td>C$<em>7$H$</em>{16}$</td>
<td>C$<em>8$H$</em>{18}$</td>
<td></td>
</tr>
</tbody>
</table>