Chapter-II

Experimental
The chemicals used throughout the study are listed in Table 2.1 which also includes their abbreviated names, chemical formulas, sources and purities. All the surfactants (SDS, CTAB and Triton X-100) and hydrotrope (NaSal) were used as received.

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 P₂O₅. Other inorganic salts were used as received.

All the organics were used as supplied. The water used to prepare the solutions was demineralized and double distilled in an all-glass (Pyrex) distillation set up. The specific conductivity of water was in the range 1-2x10⁻⁶ S cm⁻¹. For the small-angle neutron scattering experiments, D₂O of 99.4% purity was supplied by the Heavy Water Division, Bhabha Atomic Research Centre (BARC), Mumbai.

Special care was taken while cleaning the glasswares (by immersing successively in 1M NaOH ethanol and 1M nitric acid baths and then by rinsing with double-distilled water.

Stock solutions of surfactants (in water containing either a fixed concentration of salt or no salt) were prepared by weight.

To see the additive effects, sample solutions were made by taking requisite amounts or volumes of additives (depending on their physical state) in standard volumetric flasks and making up the volumes with the stock solution. When required, more samples were prepared by dilution. After proper mixing, the sample solutions were kept overnight for equilibration. To avoid evaporation, the containers were kept properly stoppered during equilibration and measurement.

**Conductivity Measurements**

A Philips conductivity meter (model 9500) equipped with platinized electrodes (cell constant: 1.02 cm⁻¹) was use for conductivity measurements.
Table 2.1- Name and structural formulas of the chemicals used

<table>
<thead>
<tr>
<th>Name</th>
<th>Abbreviation</th>
<th>Structural Formula</th>
<th>Make</th>
<th>% Purity</th>
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<tbody>
<tr>
<td><strong>A. Surfactants</strong></td>
<td></td>
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<tr>
<td>Sodium dodecyl sulfate</td>
<td>SDS</td>
<td>CH(_3)(CH(<em>2))(</em>{11}) OSO(_2)(^-)Na(^+)</td>
<td>Fluka (Switzerland)</td>
<td>99</td>
</tr>
<tr>
<td>Cetyltrimethylammonium bromide</td>
<td>CTAB</td>
<td>C(<em>{16})H(</em>{33}) (CH(_3))(_3) N(^+)Br(^-)</td>
<td>Merck (Germany)</td>
<td>99</td>
</tr>
</tbody>
</table>
| Poly(ethylene glycol)-
  -octyphenyl ether | TX-100       | \(t\)-C\(_8\)H\(_{17}\)-C\(_6\)H\(_4\)-(OCH\(_2\)CH\(_2\))\(_n\)OH | Fluka             | ~99     |
| **B. Hydro trope**                        |              |                                           |                  |         |
| Sodium salicylate                         | NaSal        |                                           | Fluka            | 99      |
| **C. Inorganic salts**                    |              |                                           |                  |         |
| Sodium bromide                            | -            | NaBr                                      | Merck            | 99      |
| Sodium chloride                           | -            | NaCl                                      | Merck            | 99      |
| **D. Quaternary salts**                   |              |                                           |                  |         |
| Tetra-
  -n-butyrammonium bromide              | Bu\(_4\)Br   | \((n\)-C\(_4\)H\(_9\))\(_4\)NBr\)          | Fluka            | ≥99     |
| Tetra-
  -n-butylyphosphonium bromide           | Bu\(_4\)PBr  | \((n\)-C\(_4\)H\(_9\))\(_4\)PBr\)          | Fluka            | ≥99     |
| **E. Vitamin**                            |              |                                           |                  |         |
| Riboflavin (B2)                           |              |                                           | Sigma (USA)      | ≈98     |

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<table>
<thead>
<tr>
<th>F. Ureas</th>
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</tr>
</thead>
<tbody>
<tr>
<td>Urea</td>
<td>U</td>
<td>NH₂CONH₂</td>
<td>BDH (England)</td>
</tr>
<tr>
<td>Monomethylurea</td>
<td>MMU</td>
<td>CH₃NHCONH₂</td>
<td>Sigma</td>
</tr>
<tr>
<td>Dimethylurea</td>
<td>DMU</td>
<td>(CH₃)₂NCONH₂</td>
<td>Fluka</td>
</tr>
<tr>
<td>Tetramethylurea</td>
<td>TMU</td>
<td>(CH₃)₂NCON (CH₃)₂</td>
<td>Fluka</td>
</tr>
<tr>
<td>Thiourea</td>
<td>TU</td>
<td>NH₂CSNH₂</td>
<td>s.d.fine (India)</td>
</tr>
<tr>
<td>Tetramethylthiourea</td>
<td>TMTU</td>
<td>(CH₃)₂NCSN (CH₃)₂</td>
<td>TCI (Japan)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>G. Alcohols</th>
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<tbody>
<tr>
<td>n-Propanol</td>
<td>PrOH</td>
<td>CH₃(CH₂)₂OH</td>
<td>BDH</td>
</tr>
<tr>
<td>n-Butanol</td>
<td>BuOH</td>
<td>CH₃(CH₂)₃OH</td>
<td>BDH</td>
</tr>
<tr>
<td>n-Pentanol</td>
<td>PeOH</td>
<td>CH₃(CH₂)₄OH</td>
<td>Merck</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>H. Solvents</th>
<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetonitrile</td>
<td>AN</td>
<td>CH₃CN</td>
<td>Qualigens (India)</td>
</tr>
<tr>
<td>Dimethylsulfoxide</td>
<td>DMSO</td>
<td>(CH₃)₂SO</td>
<td>Merck</td>
</tr>
<tr>
<td>Methyl cellosolve</td>
<td>MC</td>
<td>CH₃OCH₂CH₂OH</td>
<td>BDH</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>EG</td>
<td>CH₂(OH) CH₂OH</td>
<td>BDH</td>
</tr>
</tbody>
</table>
For a typical measurement the sample solution was taken in a Pyrex glass container and the conductivity cell was introduced into it, which was then allowed to attain thermal equilibrium at the desired temperature (bath was designed and assembled in the laboratory with commercially available components). The conductivity was then noted. The solvent correction was made by deducting the conductivity of solvent from that of the sample solution.

**Viscometry**

All fluids may be considered to be consisting of molecular layers arranged one over the other. When a shearing force is applied to a liquid, it flows. However, the forces of friction between the layers offer resistance to this flow. Viscosity of a liquid is a measure of its frictional resistance. Viscosity is expressed as dyne-seconds per cm$^2$ or poise. In practice, smaller units centipoise and milipoise are used.

There are a number of methods of different kinds for measuring viscosity, $\eta$. The method commonly employed is based on Poiseuille's law which is given by,

$$\eta = \pi pr^4t/8lv$$

(2.1)

where $v$ is the volume in cm$^3$ of the liquid flowing in $t$ seconds through a narrow tube of $r$ cm under a hydrostatic (driving) pressure of $p$ dynes cm$^{-2}$.

It is not possible to find the absolute coefficient of viscosity ($\eta$) straight away from Poiseuille's equation as experimental measurement of $p$, $r$, $l$, and $v$ offers considerable difficulty. Hence, viscosity of a liquid is determined with respect to another liquid, usually water. This is called relative viscosity ($\eta_r$).

Let $t_1$ and $t_2$ be the times of flow of a fixed volume $v$ of the two liquids through the same capillary. The expression for relative viscosity ($\eta_r$) can be derived from Eq. (2.1)

$$\eta_r = \frac{\eta_1}{\eta_2} = \frac{\pi pr^4t_1}{\pi pr^4t_2} = \frac{8lv}{8lv} = \frac{p_1t_1}{p_2t_2}$$

(2.2)

Since the pressure is proportional to the density, we have
\[ \eta_r = \frac{d_1 t_1}{d_2 t_2} \]  

(2.3)

where \(d_1\) and \(d_2\) are the densities of the solution and solvent. Ozeki and Ikeda\(^1\) found density corrections to be negligible, \(\eta_r\) values may therefore, be calculated using equation

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

(2.4)

In the present study the viscosities of the solutions were measured at 25 °C by an Ubbelohde viscometer, thermostated at the experimental temperature. The temperature was controlled within ±0.1 °C in the thermostated water bath. The flow times always exceeded 150 s, and no kinematic corrections were necessary.

**CP Measurements**

The CP’s were obtained by placing several Pyrex tubes, each containing different volume percentage of non aqueous solvents at fixed [SDS] with fixed [salt], into the temperature controlled bath. The temperature was ramped at the rate of 0.1 °C/min near the CP. Onset of turbidity (visual observation) was taken as the CP. However, the temperature was oscillated slowly through the CP until it was reproducible.

Similar CP measurements were made by using different [SDS] with fixed [salt] and different [SDS] with different salts.

The CP measurements with TX–100 + urea were performed by following the same procedure.

**Small–Angle Neutron Scattering: Technique and Measurements**

Small-angle neutron scattering (SANS) covers a length scale, where most of the micelle structures starting from spherical to rod-like or disk-like shapes and sizes are formed\(^2,^3\). SANS gives information about the shapes and sizes of
the micelle and interactions between the micelles. SANS is thus an ideal technique for studying the structural aspects of micellar solutions.

In a typical neutron scattering experiment, a monochromatic beam of neutrons is incident on the sample being studied and intensity of the neutrons scattered by the sample is then measured as a function of scattering angle. The data acquisition consists of counting the number of neutrons scattered at various angles normalized by either total fixed number of neutrons incident on the sample or normalized with time.

SANS experiment is a diffraction experiment which involves scattering of a monochromatic beam of neutrons from the sample and measuring the scattered neutron intensity as a function of the scattering angle. The wave-vector transfer, \( Q = \frac{4 \pi \sin \theta}{\lambda} \), where \( \lambda \) is the incident neutron wave length and \( 2\theta \) is the scattering angle) in these experiments is small, typically in the range of \( 10^{-3} \) to \( 1.0 \) Å\(^{-1}\). The wave length of neutrons used for these experiments are usually 4-10 Å. Since smallest \( Q \)-values occur at small scattering angle (\( \sim 1^\circ \)) the technique is called small-angle neutron scattering. SANS measurements were performed using a spectrometer with the following details:

- mean wave length (\( \lambda \)) of the BeO filtered beam = 5.2 Å
- angular divergence of the incident neutron beam = ± 0.5°
- beam size of the sample position = 1.5 cm x 1.0 cm
- accessible wave-vector transfer range = 0.018-0.32 Å\(^{-1}\)

The scattered neutrons were detected in an angular range of 1-15° using a linear He\(^3\) position-sensitive gas detector (PSD). The PSD is made up of a stainless steel tube filled with He\(^3\) gas at 30 psi and Kr at 15 psi pressure. To have good contrast between micelles and solvent, samples for SANS measurements were prepared in D\(_2\)O. Scattered neutron intensity in a SANS experiment depends on the square of the difference between the average scattering-length densities of the micelle (\( \rho_m \)) and the solvent (\( \rho_s \)), \((\rho_m - \rho_s)^2\); this is called the contrast factor. Intensity of scattered neutrons from micellar solutions increases considerably when D\(_2\)O is used in place of water as the
scattering length of hydrogen is negative ($= -0.3723 \times 10^{12}\text{ cm}$) and that for the deuterium is positive ($= 0.6674 \times 10^{12}\text{ cm}$). The contrast between the micelle and the solvent can be increased by deuterating either the solvent or the surfactant. The properties of most of the systems usually do not change on replacing $\text{H}_2\text{O}$ to $\text{D}_2\text{O}$. PSD allowed for the simultaneous recording of data over the full $Q$-range.

The samples were held in a 0.5 cm path-length quartz cell. The cell was properly stoppered and thermostated at various temperatures. The raw data were corrected for the background, empty-cell scattering and sample transmission. The corrected intensities were normalized to absolute cross-section units, and thus the coherent differential scattering cross section, $d\Sigma/d\Omega$, vs. $Q$ was obtained.

Data from the position sensitive detector are stored in a multichannel analyzer as intensity vs. channel number. There is a one-to-one correspondence between the channel number and the distance $R$ between the point of neutron detection and the centre of the incident beam at the detector. The scattering angle is given by $2\theta = \tan^{-1}(R/L_s)$, where $L_s$ is the distance between the sample and the detector. Thus, each channel of the multichannel analyzer is related to the corresponding $Q$ value. SANS experiment involves recording the three SANS distributions. These are, (i) intensity distribution $I_s(Q)$ from the micellar solution ($\text{D}_2\text{O} + \text{surfactant}$), (ii) intensity distribution $I_e(Q)$ from pure $\text{D}_2\text{O}$ and the container, and (iii) intensity distribution $I_b(Q)$ of the background (no sample and the neutron beam is blocked). The measured intensity from the sample $I_s(Q)$ is corrected for these contributions. The corrected scattered intensity $I(Q)$ of interest from the sample is given by

$$I(Q) = \left[ \frac{I_s(Q) - I_e(Q)}{T_s} - \frac{I_s(Q) - I_b(Q)}{T_e} \right] T_e,$$  

where $T_s$ is the sample transmission and $T_e$ is the transmission of the empty sample holder. $I_b(Q)$ and $I_e(Q)$ in Eq. (2.5) correspondence to the same monitor counts.
In a SANS experiment, the sample is generally taken in the form of a plate (circular or rectangular), so that it has uniform thickness over the beam area. If \( d\Sigma d\Omega(Q) \) is the differential scattering cross-section per unit volume of the sample, the measured scattered intensity can be represented as

\[
I(Q) = KT_i \frac{d\Sigma}{d\Omega}(Q)
\]

(2.6)

where \( t \) is the sample thickness and \( K \) is a constant which depends on instrumental specifications, incident neutron flux, detector efficiency, solid angle subtended by detector element at sample position. By combining Eqs. (2.5) and (2.6), we get the following expression for the scattering cross-section of the sample:

\[
\frac{d\Sigma}{d\Omega}(Q) = \frac{I(Q)}{Kt} \left[ \frac{I_s(Q) - I_s(Q)}{T_s} - \frac{I_s(Q) - I_s(Q)}{T_s} \right]
\]

(2.7)

The instrumental constant \( K \) is determined by recording the data from a standard sample (e.g., H\(_2\)O, vanadium, etc.). The measurement thus provides \( d\Sigma/d\Omega(Q) \) in absolute units, namely cm\(^{-1}\).

**SANS data analysis**: The experimental data points were fitted by adopting the routines as described by Hayter and Penfold\(^{10-12}\) and Chen and coworkers\(^{13,14}\). The data have not been corrected for resolution effects. The residuals in the fitting were negligible.

For monodisperse interacting micelles of volume \( V_m \) present at a number density \( n_m \) and of scattering-length density \( \rho_m \) dispersed in a solvent of scattering-length density \( \rho_s \), \( d\Sigma d\Omega \) may be written as\(^4,10,11,14\)

\[
\frac{d\Sigma}{d\Omega} = n_m V_m^2 (\rho_m - \rho_s)^2 \left\{ \langle F^2(Q) \rangle + \langle F(Q) \rangle^2 \{S(Q) - 1\} + B \right\}
\]

(2.8)

Eq. (2.8) for non-interacting micelles \( S(Q) = 1 \) can be reduced to

\[
\frac{d\Sigma}{d\Omega} = n_m V_m^2 (\rho_m - \rho_s)^2 \langle F^2(Q) \rangle + B
\]

(2.9)
Here $F(Q)$ is the single particle form factor, $S(Q)$ is the interparticle structure factor, and $B$ is a constant term that denotes the incoherent scattering which mainly arises due to hydrogen in the object. The micelle aggregation number $n_s$ is related to $V_m$ by

$$V_m = n_s v_h$$

(2.10)

where $v_h$ is the volume of a surfactant monomer obtained with the help of Tanford's formula. For an ellipsoidal micelle

$$\langle F^2(Q) \rangle = \int_a^b [F(Q, \mu)]^2 d\mu$$

(2.11)

$$\langle F(Q) \rangle^2 = \left\{ \int_a^b [F(Q, \mu)] d\mu \right\}^2$$

(2.12)

$$F(Q, \mu) = \frac{3(\sin x - x \cos x)}{x^3}$$

(2.13)

$$x = Q[a^2 \mu^2 + b^2 (1 - \mu^2) \right)^{1/2}$$

(2.14)

were $a$ and $b$ are, respectively, the semi-minor and semi-major axes of the ellipsoid and $\mu$ is the cosine of the angle between the axis of revolution and $Q$.

For a rod-shaped micelle of length $L = 2l$ and radius $R (= a)$

$$\langle F^2(Q) \rangle = \frac{\gamma}{\int_0^{\pi/2} \sin^2 (Q \cos \phi) \frac{4 J_1(Q R \sin \phi)}{Q^2 R^2 \sin^2 \phi} \sin \phi d \phi}$$

(2.15)

($\phi$ is the angle between the axis of the rod and bisectrix, and $J_1$ is the Bessel function of the order unity.) In this analysis, the rod is fitted with a fixed radius equal to the length of surfactant monomer ($=a$), varying the other dimension.

$S(Q)$ is the Fourier transform of the radial distribution function $g(r)$ for the centers of mass of the micelles. In the analysis, $S(Q)$ has been calculated using the mean spherical approximation. The fractional charge $\beta (= Z/n_s$, where $Z$ is the micellar charge) is the additional parameter in the calculation of $S(Q)$.

In this analysis, the only unknown parameters to calculate $d\Sigma/d\Omega$ are the $\beta$ and $n_s (= 4\pi a^2 b/3v)$. 

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The data (corresponding to 0.3 M SDS + 0.2 M Bu₄NBr with and without urea/thiourea) were analyzed using the above method. The minor axis \( a = 16.7 \text{Å} \), which is the length of the extended SDS monomer, was obtained from Tanford’s formula\(^{16}\). \( n_\text{a} \) and \( \beta \) were taken as parameters of the fit.

**Surface Tension (\( \gamma \)) Measurements**

Surface tension (\( \gamma \)) measurements were made by the well known drop-volume method.

A drop of liquid is allowed to form at the lower end of a capillary tube. The drop is supported by the upward force of surface tension acting at the outer circumference of the tube. The weight of the drop (\( mg \)) pulls it downward. When the two forces are balanced, the drop breaks. Thus, at the point of breaking

\[
mg = 2\pi r \gamma
\]  

(2.16)

where \( m = \) mass of the drop,

\( g = \) acceleration due to gravity, and

\( r = \) outer radius of the tube.

The apparatus employed was a glass pipette with a capillary at the lower part. This is called a stalagmometer or drop pipette. It was cleaned, dried and filled with the experimental liquid up to the mark. The number of drops were counted. Similarly, the pipette was filled with the reference solution and number counted. Let \( n_1 \) and \( n_2 \) be the number of drops produced by the same volume \( V \) of the two liquids, then

- volume of one drop of liquid 1 = \( V/n_1 \),
- mass of one drop of liquid 1 = \( (V/n_1) \rho_1 \),

where \( \rho_1 \) is the density of liquid 1.

Similarly, the mass of one drop of liquid 2 = \( (V/n_2) \rho_2 \). Then –

\[
\frac{\gamma_1}{\gamma_2} = \frac{(V/n_1)\rho_1}{(V/n_2)\rho_2} = \frac{n_2\rho_1}{n_1\rho_2}
\]  

(2.17)
The value of $\rho_1$ was determined with a pyknometer. Knowing $\rho_2$ and $\gamma_2$ from reference tables, $\gamma_1$ was calculated.

**Spectrophometry**

Solubilization of riboflavin in aqueous solutions containing NaSal + additives was checked by recording spectra using a UV-vis Spectrophotometer (Cintra 5, GBC Scientific Equipment, Australia).
References