**Surface Activity and Micelle Formation**

Originally by Dr. Duncan Shaw, 1992, modified by T. Corcoran 2001, 2002

**Surface Active Agents (Surfactants)**

Substances such as short-chain fatty acids and alcohols are soluble in both water and oil (e.g. paraffin hydrocarbon) solvents. The hydrocarbon part of the molecule is responsible for its solubility in oil, while the polar -COOH or -OH group has sufficient affinity for water to drag a short-length non-polar hydrocarbon chain into aqueous solution with it. If these molecules become located at an air-water or an oil-water interface, they are able to locate their hydrophilic (water loving) head groups in the aqueous phase and allow the hydrophobic (water hating) hydrocarbon chains to escape from the water phase, as illustrated. This situation is energetically more favourable than complete solution in either phase.

![ Adsorption of surface-active molecules as an orientated monolayer at air-water and oil-water interfaces. The circular part of the molecules represents the hydrophilic polar head group and the zig-zag part represents the non-polar hydrocarbon chain.](image)

The strong adsorption of such materials at surfaces or interfaces in the form of an orientated monomolecular layer (or monolayer) is termed surface activity. Surface active materials (or surfactants) consist of molecules containing both polar and non-polar parts (amphiphilic). Surface activity is a dynamic phenomenon, since the final state of a surface or interface represents a balance between this tendency towards adsorption and the tendency towards complete mixing due to the thermal motion of the molecules.

**Surface tension of aqueous solutions of alcohols at 20°C**

The tendency for surface-active molecules to pack into an interface favours an expansion of the interface. This must be balanced against the tendency for the interface to contract under normal surface tension forces. If $\Pi$ is the expanding pressure (or surface pressure) of an adsorbed layer of surfactant, then the surface (or interfacial) tension will be lowered to a value

$$\gamma = \gamma_0 - \Pi$$  \[1\]

The above diagram shows the effect of lower members of the homologous series of normal fatty alcohols on the surface tension of water. The longer the hydrocarbon chain, the greater is the tendency for the alcohol molecules to adsorb at the air-water surface and, hence, lower the surface tension.

If the interfacial tension between two liquids is reduced to a sufficiently low value on addition of a surfactant, emulsification will readily take place, because only a relatively small increase in the surface free energy of the system is involved. If the interfacial tension is reduced to close to zero, a microemulsion will form.
Classification of Surfactants

The hydrophilic part of the most effective soluble surfactants (e.g. soaps, synthetic detergents, dyestuffs) is often an ionic group. Ions have a strong affinity for water owing to their electrostatic attraction to the water dipoles and are capable of pulling fairly long hydrocarbon chains into solution with them; for example, palmitic acid, $\text{C}_{16}\text{H}_{33}\text{COOH}$, which is virtually unionised, is insoluble in water, whereas sodium palmitate, which is almost completely ionised, is soluble.

It is possible to have non-ionic hydrophilic groups which also exhibit a strong affinity for water; for example, the monomer units in a poly(ethylene oxide) chain each show a modest affinity for water and the sum effect of several of these units in the polymer chain is an overall strong affinity for water.

Surfactants are classified as anionic, cationic, non-ionic or ampholytic according to the charge carried by the surface active part of the molecule. In addition, surfactants are often named in relation to their technological application; hence names such as detergent, wetting agent, emulsifier and dispersant.

### Surface-Active Agents

#### Anionic
- Sodium stearate
  - $\text{CH}_3(\text{CH}_2)_7\text{COO}^-\text{Na}^+$
- Sodium oleate
  - $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COO}^-\text{Na}^+$
- Sodium dodecyl sulphate
  - $\text{CH}_3(\text{CH}_2)_{11}\text{SO}_4^-\text{Na}^+$
- Sodium dodecyl benzene sulphonate
  - $\text{CH}_3(\text{CH}_2)_{11}\text{C}_6\text{H}_4\text{SO}_4^-\text{Na}^+$

#### Cationic
- Dodecylamine hydrochloride
  - $\text{CH}_3(\text{CH}_2)_{11}\text{NH}_3^+\text{Cl}^-$
- Hexadecyltrimethyl ammonium bromide
  - $\text{CH}_3(\text{CH}_2)_{15}\text{N(CH}_3)_3^+\text{Br}^-$

#### Non-ionic
- Polyethylene oxides
  - e.g., $\text{CH}_3(\text{CH}_2)_{7}\text{C}_6\text{H}_4(\text{OCH}_3\text{CH}_2)_{5}\text{OH}$
- Spans (sorbitan esters)
- Tweens (polyoxyethylene sorbitan esters)

#### Ampholytic
- Dodecyl betaine

### Thermodynamics of Adsorption: Gibbs Adsorption Equation

The extent of surfactant adsorption at a liquid surface is expressed in terms of its surface excess concentration, $\Gamma$. This is the amount of surfactant present per unit area of surface in excess of the amount which would be present if uniform surfactant concentration existed right up to the surface. Surface excess concentration is related to surface tension by the Gibbs equation, which for a non-ionic surfactant takes the form,

$$\Gamma = -\frac{c}{RT}\frac{d\gamma}{dc} = -\frac{1}{RT}\frac{d\gamma}{d\ln c}$$  \[2a\]

For a 1-1 ionic surfactant such as sodium dodecyl sulphate (SDS) this equation must be modified by a factor of two to allow for the fact that the sodium counter-ions, although themselves not surface active, also accumulate at the interface, paired off with the dodecyl sulphate ions.

$$\Gamma = -\frac{c}{2RT}\frac{d\gamma}{dc} = -\frac{1}{2RT}\frac{d\gamma}{d\ln c}$$  \[2b\]

Knowing $\Gamma$, it is easy to calculate the effective area occupied by each adsorbed surfactant molecule or ion.
Micelle Formation

Solutions of highly surface-active materials often exhibit unusual physical properties. In dilute solution the surfactant acts as a normal solute (and in the case of ionic surfactants, normal electrolyte behaviour is observed). At fairly well defined concentrations, however, abrupt changes in several physical properties, such as osmotic pressure, turbidity, electrical conductance and surface tension, take place. The rate at which osmotic pressure increases with concentration becomes abnormally low and the rate of increase of turbidity with concentration is much enhanced, which suggests that considerable association is taking place. The conductance of ionic surfactant solutions, however, remains relatively high, which shows that ionic dissociation is still in force.

This seemingly anomalous behaviour can be explained in terms of organised aggregates, or micelles, of the surfactant ions in which the hydrophobic hydrocarbon chains are orientated towards the interior of the micelle, leaving the hydrophilic groups in contact with the aqueous medium. Except at very high concentrations, micelles are usually spherical in shape as illustrated below:

![Schematic representation of a spherical anionic micelle](image1)

![Physical properties of sodium dodecyl sulphate solutions at 25 °C](image2)

The fairly well defined concentration above which micelle formation becomes appreciable is termed the critical micelle concentration (c.m.c.). Micellisation is, therefore, an alternative mechanism to adsorption by which the interfacial energy of a surfactant solution might decrease.

Critical micelle concentrations can be determined by measuring any micelle-influenced physical property as a function of concentration. In practice, surface tension, electrical conductivity and dye solubilisation measurements are the most popular. The choice of physical property will slightly influence the measured c.m.c., as will the procedure adopted to determine the point of discontinuity.

**Experimental**

Make up 100 mL of stock solution of sodium dodecyl sulphate (MM = 288) (aq, approximately 0.02 mol dm$^{-3}$) using deionised and surfactant-free water. Use a magnetic stirrer to help the surfactant to dissolve. Do not shake the solution, since it is necessary to minimise foaming. Do this preparation right at the beginning of the session, since dissolution tends to be slow and time may be required to allow foam to subside. Placing the solution in a warm water bath (i.e., 45 °C) may help it dissolve, but be sure to let it return to room temp (e.g., place it in a 25 °C bath)
CMC 1: Conductivity measurements: Fill a burette with 50 mL of the SDS stock solution. Pipette 25.00 mL of distilled water into a beaker (preferably thermostatted, and having a magnetic stirrer). Measure the conductivity of the initial pure water, and record the initial burette volume, then add ~1 mL using the burette. Record the conductivity and the burette volume. Continue adding ~1mL aliquots in this way until you have reached the end of the scale on the burette.

CMC 2: Surface tension: In a second dry, clean 100 mL beaker again pipette 25.00 mL of distilled water, and refill the burette with SDS stock solution. This time perform surface tension measurements on the solution in the beaker, using ~2 mL aliquots until you reach the cmc (determined above).

Effect of Added Electrolyte on C.M.C.
Remeasure the c.m.c. of sodium dodecyl sulphate at 25 °C, but this time in NaCl solutions. Prepare 50.00 mL of a stock solution of 0.100 mol L\(^{-1}\) NaCl\((aq)\). Use this to prepare the solutions in the table below. Pipet the volumes of stock solution shown in the table into 50.00 mL volumetric flasks and dilute to the mark with distilled water.

<table>
<thead>
<tr>
<th>solution #</th>
<th>[NaCl] /mol L(^{-1})</th>
<th>[SDS] (approximately)</th>
<th>NaCl stock solution /mL</th>
<th>SDS stock solution /mL</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.010</td>
<td>0.0120</td>
<td>5.00</td>
<td>30.00</td>
</tr>
<tr>
<td>2</td>
<td>0.010</td>
<td>0</td>
<td>5.00</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>0.030</td>
<td>0.0080</td>
<td>15.00</td>
<td>20.00</td>
</tr>
<tr>
<td>4</td>
<td>0.030</td>
<td>0</td>
<td>15.00</td>
<td>0</td>
</tr>
</tbody>
</table>

Use the same method described above (CMC1 or CMC 2), but this time instead of water in the beaker, use solution 2, and fill the burette with solution 1 (note both solutions are 0.010 mol L\(^{-1}\) NaCl\((aq)\), therefore [NaCl] remains constant as you add surfactant. Repeat the measurements using 1 mL aliquots. Then, perform the measurement again using solutions 3 & 4. Using this data, redetermine the c.m.c. of sodium dodecyl sulphate in the solutions containing NaCl. Compare your c.m.c. with that in the absence of added electrolyte and suggest a qualitative explanation.

Other Possibilities
The temperature dependence of the c.m.c. is another possible area to study. Naturally this requires the ability to adjust the temperature of the samples. This can be arranged if you wish, discuss it with the instructor.

Processing of Results
Plot graphs of Λ versus \(c^{1/2}\) (CMC 1), or \(γ \) versus \(c\), and \(γ \) versus ln \(c\) (CMC 2). Determine a value for the c.m.c. (i.e. the concentration at which a discontinuity occurs) in each case and compare values. Compare your c.m.c. with that in the absence of added electrolyte and suggest a qualitative explanation, and compare all values to the literature.

If surface tension experiments are performed (CMC 2), use the Gibbs equation to calculate the surface excess concentration, \(Γ\) of SDS at the c.m.c. Hence calculate the average area occupied by each adsorbed dodecyl sulphate ion at the air-water interface. From your knowledge of bond lengths, estimate the cross-sectional area of a dodecyl sulphate ion and compare your experimental area with this value. (Molecular modeling is a useful tool here!)