

Experiment 2 – Thermodynamics of micellisation

Ionic or polar derivatives of hydrocarbons are sometimes termed amphiphilic because they contain two parts, each of which has an affinity for a different phase:

1. The hydrophilic polar “head-group”, which has a high solubility in water. The head-group may be ionic or non-ionic.
2. The hydrophobic non-polar hydrocarbon “tail”, which has a low solubility in water, and a high solubility in non-polar solvents.

Most amphiphiles, when added to a mixture of oil and water move spontaneously to the oil/water interface, lowering the interfacial tension. The tail of the surfactant molecule partitions into the oil phase and the head-group into the aqueous phase. In aqueous solutions the molecules also self-aggregate into small globular structures called micelles. The tails of the surfactants lie inside the micelle away from the water, and the head groups are exposed to the water. Surfactant micelles may contain between around 50 and several thousand surfactant molecules.

A typical cationic surfactant is hexadecyltrimethylammonium bromide, abbreviated C₁₆TAB (see Figure 1). The head group is (CH₃)₃N⁺ which has associated with it Br⁻ as counterion, to maintain electrical neutrality. The hydrocarbon tail consists of a C₁₆H₃₃ alkyl group.

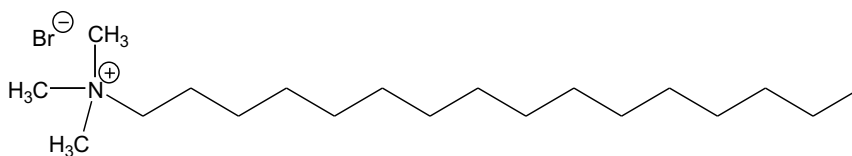


Figure 1. Hexadecyltrimethylammonium bromide, C₁₆TAB.

Micelle formation (*micellisation*) is an example of the hydrophobic effect, which lies at the heart of all the biological self-assembly processes, as well as surfactant aggregation. It arises from the unfavourable orientation which polar water molecules must take up around a non-polar hydrocarbon chain. In pure water, H₂O molecules are strongly hydrogen-bonded in a dynamic network. The presence of a hydrocarbon chain forces water to reorganise so that it does not have free H-bond sites around the alkyl group; this decreases its entropy and gives non-polar materials low solubilities in water.

When there are sufficient surfactant molecules present in the solution, rather than simply becoming insoluble, a more favourable situation for the water molecules is for the tails of the surfactant molecules to aggregate together into the core of the micelle, as shown in Figure 2. This occurs over a very narrow range of concentrations, and in practice is identified as the

critical micelle concentration (CMC). Favourable interaction with water and strong repulsions between head-groups lead to the unique arrangement of molecules in micelles.

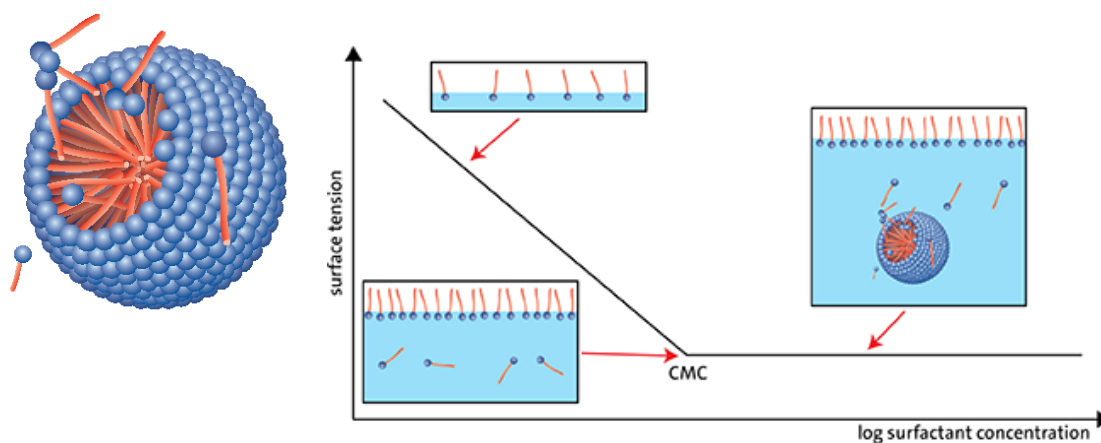


Figure 2. Scheme of a surfactant micelle (left) and plot of the surface tension as a function of the surfactant concentration (right). Adapted from dataphysics.de (tinyurl.com/y73aj237).

In this experiment, the critical micelle concentration (CMC) of a cationic surfactant in aqueous solution will be determined by conductivity. From measurements of the CMC, the Gibbs free energy of micellisation can be calculated. By comparing surfactants with different structures, it will be possible to compare the magnitude of head-group and tail effects on the CMC.

1. LEARNING OUTCOMES

After undertaking this experiment, you will have the following laboratory skills:

- Use of conductivity meters
- Preparation of diluted samples using volumetric glassware

After undertaking this experiment and writing the lab report, you will understand:

- The effect of head-group, counterion and tail structure on micellisation
- The use of Excel to fit data

2. CHEMICALS USED AND SAFETY DATA

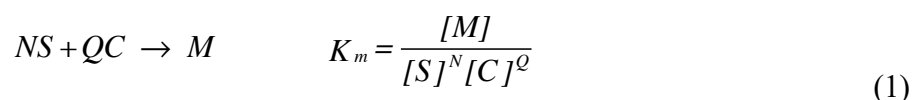
tetradecyltrimethylammonium bromide	corrosive
tetradecyltrimethylammonium chloride	corrosive
tetradecyltrimethylammonium formate	corrosive
dodecyltrimethylammonium bromide	corrosive
dodecyltrimethylammonium chloride	corrosive
dodecyltrimethylammonium formate	corrosive

All reagents used in this experiment can be disposed of in the sink.

3. BACKGROUND THEORY

3.1 Thermodynamic changes at the CMC.

The formation of a micelle (M) from the association of N individual surfactant molecules (denoted by S) and Q counterions (C) can be described by an equilibrium constant (K_m):



N is known as the *aggregation number* of the micelle.

For low aggregation numbers, N , the concentration of unaggregated (monomeric) surfactant changes only gradually; however, for large values of N (> 50), the curve describing monomeric surfactant concentration versus total surfactant concentration has two almost linear regions (see Figure 3): one in which the concentration of micelles is almost zero, and a second at higher concentrations where the concentration of monomeric surfactant is essentially constant. The point where the solution behaviour changes (i.e., at which micelles begin to form) is called the *critical micelle concentration (CMC)*. Above the *CMC*, further addition of surfactant results in an increase in the concentration of micelles, but the concentration of monomer remains essentially constant.

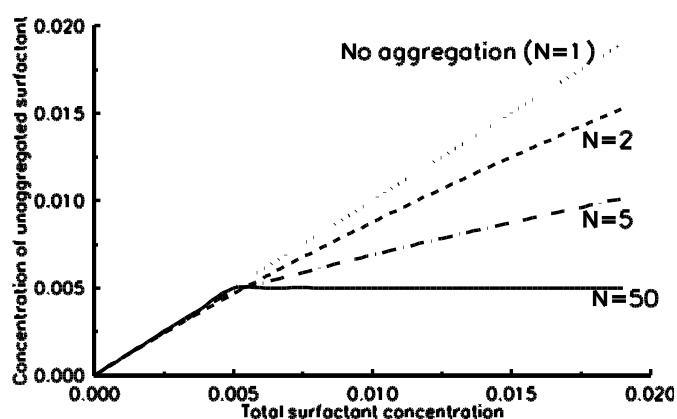


Figure 3. Variation of the monomeric (un-micellised) surfactant concentration with total surfactant concentration.

Q/N is the ratio of counterions to surfactant molecules per micelle. The quantity $1-Q/N$ represents the fractional charge on each surfactant molecule and is called the *fractional ionisation* of the micelle. (The total charge on the micelle is $N-Q$.)

The well-known thermodynamic result $\Delta G^\circ = -RT \ln K_m$ can be applied to Equation (1) to give the standard free energy of formation of one mole of *micelles*. The standard free energy of micellisation per mole of surfactant molecules is then given by

$$\Delta G_{mic}^\circ = RT \left(1 + \frac{Q}{N} \right) \ln(cmc) \quad (2)$$

where R is the gas constant and T is the absolute temperature. (ΔG_{mic}° is one N th of the free energy change for the formation of a mole of micelles; for derivation see references at the end of this experiment).

3.2 Determination of the CMC

The *conductivity* (κ) of the solution is a function of the concentration of electrolyte and the types of ions present. The conductivity is measured as a *resistance*, R , usually at an AC frequency of 1kHz across the solution between two plates of known area A separated by a distance l .

$$R = \frac{l}{\kappa A} \quad (3)$$

Thus, conductivity has the units $\text{ohm}^{-1} \text{cm}^{-1}$ (or S cm^{-1} , where S is the symbol for Siemens). Below the CMC, the surfactants are completely dissociated into positive surfactant ions and negative counterions. Thus, the conductivity increases approximately linearly with surfactant concentration as we approach the CMC.

Above the CMC, adding more surfactant ions causes micelles to be formed, which leads to an abrupt change in the conductivity behaviour. The conductivity continues to rise with total surfactant concentration since the concentration of counterions not bound to the micelles continues to increase. The (charged) micelles also still act as current carriers, but they are very large, and conduct poorly. Thus, when the surfactant concentration is raised above the CMC, the system continues to increase in conductivity, but the gradient of the κ vs conc graph will be much lower. The measured data above and below the CMC form two linear regions of different gradients. The intersection of the two lines of best fit is a good experimental determination of the value of the CMC.

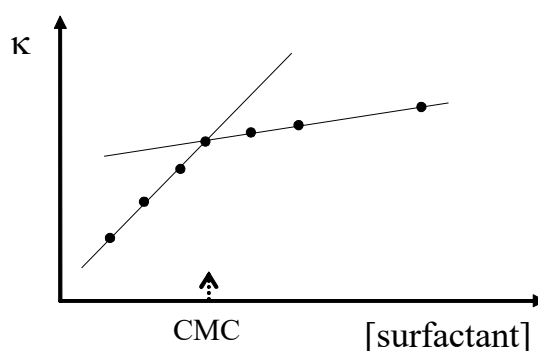


Figure 4: Variation of conductivity (κ) with surfactant concentration.

To a good approximation, the *ratio of the slopes* of conductivity versus concentration above and below the CMC can be equated to the *fraction* of free counterions in solution above the CMC, $1-Q/N$. Thus, from conductivity measurements it is possible to obtain both the quantities needed to calculate the Gibbs free energy of micellisation (Equation (2)).

4. PROCEDURE

This experiment is to be conducted in pairs.

Collect the necessary clean, dry glassware from the ovens in the laboratory. Allow them to cool for a few minutes before preparing your solutions.

Preparation of Cationic Surfactant Solutions

You will be assigned a cationic surfactant to study. Note its chemical name and the stock solution concentration on the results sheet provided in the lab, which you should paste into your laboratory notebook.

Prepare 12 different concentrations of the stock solution according to Table 1 on the Results Sheet. Once you have prepared the solutions, place the beakers in a water bath to equilibrate to 25 °C. **Do not attempt to adjust the temperature of the water bath yourself.**

You will be provided with a conductivity meter that has already been calibrated. Place the conductivity probe in the **most dilute** (i.e. pure water) of the solutions to be measured. It is important that each surfactant's conductivity behaviour be determined separately, since mixing even small quantities of surfactant will affect the CMC. Swirl the solution gently with the probe to ensure equilibration at the electrodes. Adjust the scale settings on the front panel of the instrument to maximise the resolution of the readout. Leave the probe in the solution until the value stabilises. (This may take a couple of minutes for dilute concentrations). See a demonstrator if it takes longer than this. Record the value of the conductivity for that solution on your results sheet.

Remove the probe and gently remove as much excess solution as possible with a tissue. Place the probe in the next most dilute solution and repeat until series is complete. When complete, rinse the probe thoroughly with distilled water. Pour your surfactant solutions down the sink and wash all glassware with water followed by ethanol.

Make sure you plot your data as you go to ensure that any potential problems are picked up early. Do not discard any of your solutions until you have confirmed with your demonstrator that your results are satisfactory.

Plot the conductivity, κ , against surfactant concentration. Determine the CMC by fitting the two linear regions and calculating the intersection of the two straight lines. Use regression analysis to determine i) the CMC and error, ii) Q/N and error, and iii) ΔG°_{mic} for your assigned surfactant.

After you have completed your calculations, fill in your three values for your assigned surfactant on the table on the whiteboard. Copy all the values (from all groups) onto your results sheet, to include in your report.

5. DATA ENTRY

Before you leave the lab, you must submit your results on the online system on one of the computers. You will be asked to identify your surfactant and enter your experimental CMC (in mM) and Q/N, and your calculated ΔG°_{mic} (kJ mol⁻¹). You may have more than one attempt, but repeated data entry attempts will be recorded and will incur a mark penalty.

6. ORAL PRESENTATION

This experiment is assessed by a five-minute oral presentation with your partner, which must be presented as five (PowerPoint) slides:

1. Title, author(s), and aim of your experiment. Your title should identify the specific surfactant you examined in your study here.
2. Your primary results: A graph of conductivity versus concentration for your assigned surfactant, including the two fitted lines showing how the CMC was determined. You should compare your experimental CMC with a value from the scientific literature. (In oral presentations, references are presented as a footnote at the bottom of the slide where the information appears.)
3. Calculation of ΔG°_{mic} (with errors) from CMC and Q/N for your surfactant.
4. A table comparing your CMC, Q/N and ΔG°_{mic} (with errors) results with those collected by others in your group for various surfactants. Discussion of effects of chain length and counterion.
5. Your summary and conclusions from this experiment.

Each group will also be expected to answer 2-3 questions about the experiment and the interpretation of your results from assessors and other students at the end of your presentation. In preparation for this you should read relevant sections of the suggested references below, paying particular attention to i) different experimental techniques for measuring CMCs, and ii) how solution conditions and surfactant structure affect CMC, as well as ΔG°_{mic} , ΔH°_{mic} , and ΔS°_{mic} .

Oral presentations are assessed by a combination of peer and instructor marking to make up 50% of the overall experiment (see table on page 2). Your participation in peer marking and asking (at least) one question during oral presentations contributes to your individual report mark for this experiment. The oral mark breakdown is: academic and demo mark (25%), student peer marks (15%) and student asking one question (10%).

One member only of your group must upload your presentation (in pdf or PowerPoint form) to the correct Canvas dropbox before 12:30 pm on the day of your presentation. Detailed feedback and marks breakdown will be provided to this file after your presentations; you should share this feedback with your partner.

7. REFERENCES & SUGGESTED READING

1. Principles of Colloid and Surface Chemistry, P.C. Hiemenz, Marcel Dekker, NY.
2. Introduction to Modern Colloid Science, R.J. Hunter, Oxford University Press
3. Surfactants and Interfacial Phenomena, M.J. Rosen, Wiley