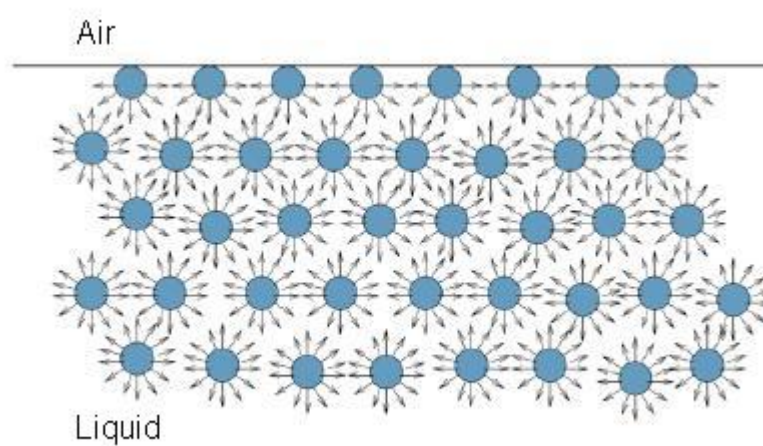# KEMS448 Physical Chemistry
Advanced Laboratory Work

Surfactants and Surface Tension

1   Introduction

Substances that lower the surface tension of a liquid or a solution are called surfactants. If this phenomenon is particularly powerful, the surfactant is called a tenside. For example, soaps are tensides. In this laboratory work, the surface tension of a tenside solution, as a function of concentration is measured with a tensiometer. From the results, the critical micelle formation concentration is determined and how the surface concentration Γ behaves as a function of concentration of the tenside.

2   Theory

2.1   Surface tension

Surface tension is a property of the liquid that makes it, when in contact with vapour or air, act like there is a strained film on the surface. The tension comes from the different force dynamics between the molecules completely inside the liquid when compared to the molecules near the surface. For molecules completely inside the liquid, the force of the same magnitude acts in every direction, but for molecules near the surface, the attractive forces act mostly from inside the liquid, and not from the air above the surface (see figure 1). Therefore, most of the molecules strive to get into a bulky phase, so for example in the case of a drop, the surface tends to curve. The ideal shape for liquid drops is a sphere because of its smallest ratio of surface area per used volume.

Surface tension is differentially defined as work dw required to change the surface area σ an infinitesimal amount

$$dw = \gamma \cdot d\sigma \tag{1}$$

The proportionality factor γ is called *surface tension* with units of $\frac{J}{m^2}$, but usually surface tension is stated in $\frac{N}{m}$. For water, the surface tension is $72,5 \frac{mN}{m}$ at $293\ K$. This value is fairly large and therefore for example detergents contain surfactants to lower the surface tension and enhance the results of washing.
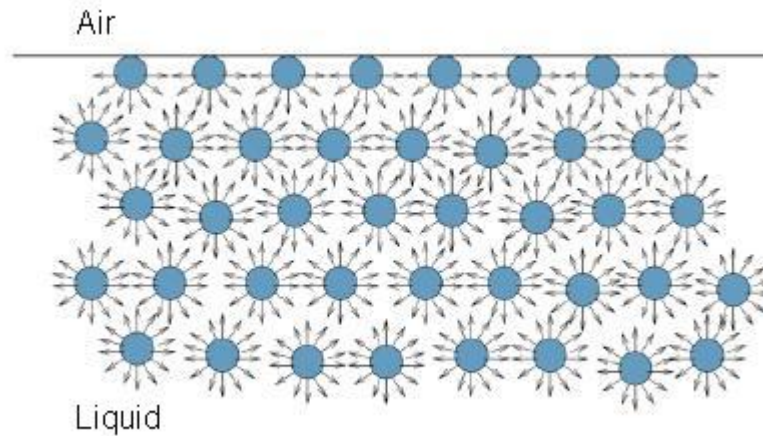
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Figure 1: *Molecular interactions in the liquid-air interface*

2.2 Tensides

Surfactants are substances that tend to accumulate at the interfase between two phases. The reason is the structure of these surfactants (tensides). Typically, tenside molecules have a hydrophilic and a hydrophobic end. The hydrophobic end is usually a carbon chain of roughly 8 to 20 carbom atoms, when the hydrophilic head contains a functional group (eg. $-COO^-$ or $-SO_3$). According to the functional hydrophilic group, tensides can be divided into subgroups: anionic, cationic, zwitterionic and neutral tensides.

In water, the molecules try to coordinate themselves, so that the hydrophilic end is in the water phase and the hydrophobic end faces towars another phase. Accumulation of the surfactant at the inteerface lowers the surface tension of water. As the concentration of surfactants in the solution is increased, more molecules are accumulating on the surface area and the surface tension decreases up until to a point, after which the surface tension is independent of concentration. At this point, no more tenside can be adsorbed on the phase boundary, since it is "full". For every system, a *critical micelle concentration (c.m.c.)* can be determined. In concentrations higher than that, the tensides begin to form dynamic aggregates, so called micelles, which are in an equilibrium with the surrounding solution (figure 2).

At the point of the critical concentration a clear discontinuation can be observed in the solution's physical properties such as molar conduction, surface tension, osmotic pressure and opacity (figure 3).
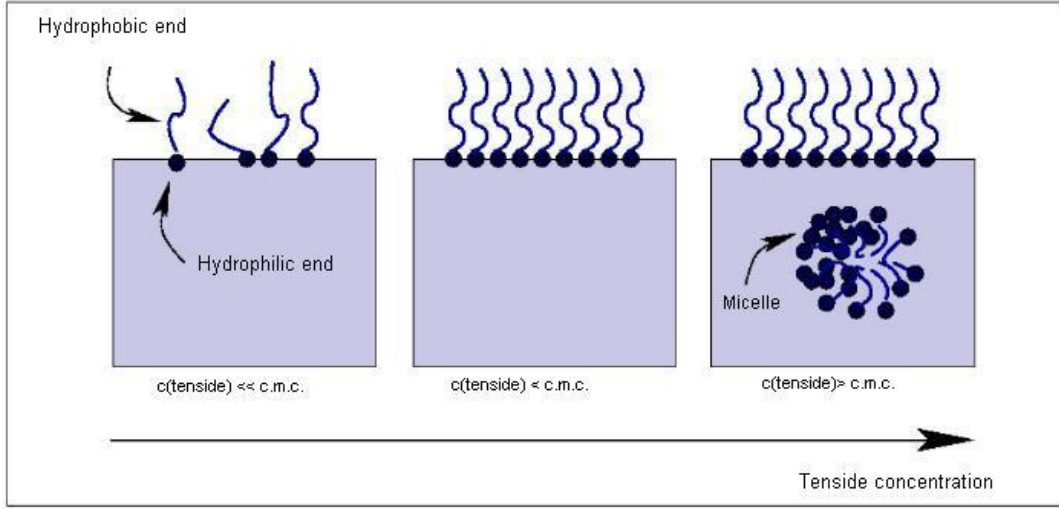
Figure 2: *A diagram of tenside molecules accumulating on the surface with different concentrations. Above the critical micelle concentration the tenside molecules start to form micelles.*

2.3 Surface concentration

In a system with two phases, the dissolved substance is not evenly distributed among the two phases, but some of it may concentrate at the interface. If the dissolved amount of substance J in the phase α is $n_J(\alpha)$ and in phase β, $n_J(\beta)$, the amount of dissolved matter in the surface layer σ is

$$n_J(\sigma) = n_J - n_J(\alpha) - n_J(\beta), \tag{2}$$

where n_J is the total concentration of the dissolved substance. The excess amount of matter in the surface of the liquid per area σ is called surface excess Γ:

$$\Gamma_J = \frac{n_J(\sigma)}{\sigma}. \tag{3}$$

Both n_J and Γ can be positive (substance is accumulated at the surface) or negative (less dissolved matter at the surface layer than in the bulk solution). The Gibbs isotherm defines the surface concentration's dependence on the chemical potential μ and the surface tension γ:

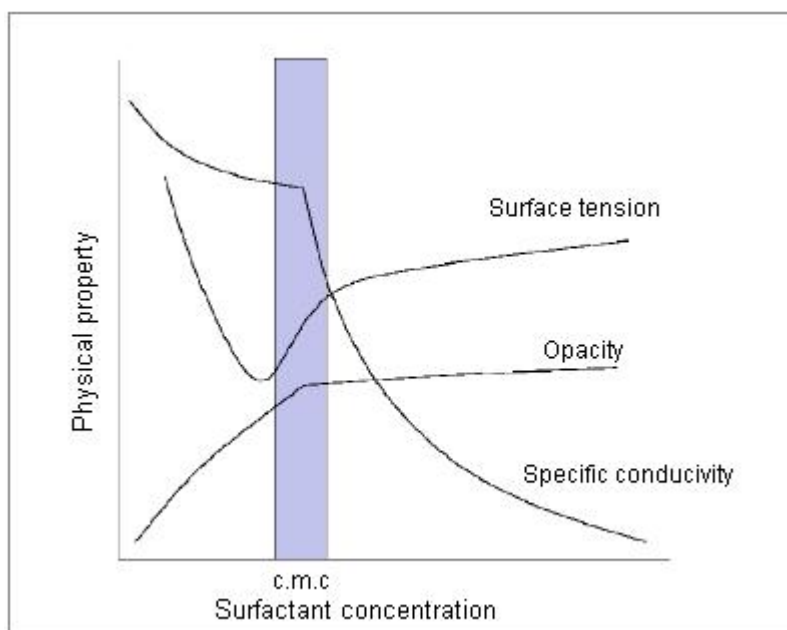$$\frac{d\gamma}{d\mu_J} = -\Gamma_J \tag{4}$$

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Figure 3: *Some physical properties and their behaviour as a function of the tenside concentration. The c.m.c. is seen as a discontinuity in the curves.*

In dilute solutions the approximation $d\mu \approx -RT\Gamma_J$ can be made, in which case equation 4 gets the form

$$\frac{d\gamma}{d\ln c_J} = -RT\Gamma_J, \tag{5}$$

where R is the molar gas constant, T the temperature and c_J the dissolved substance concentration. The surface concentration can therefore be determined from the slope of the curve $\gamma\, vs.\, \ln c_J$. Detailed derivation of the equation can be found in Atkins' *Physical Chemistry* (8th Ed. page 689).

2.4 The importance of surfactants

The ability of surfactants to lower surface tension is used in eg. soaps and detergents. When the solution's surface tension is lower, the surface that needs to be washed and the dirt particles on it get wet better. In addition, the hydrophobic ends of the tensides dissolve in oil and fat stains and remove the stains from the surface being washed.

An example of a biological tenside is the casein in milk. This phosphoprotein forms phosphate bonded micelli into the milk, inside which the fat in milk dissolve. As pH lowers, casein solubility decreases and it starts to precipitate, which can be seen when the milk goes sour.

3 Experimental methods

In this laboratory work, the surface tension of an anionic tenside molecule, sodium dodecyl sulphate (NDS), is measured as a function of concentration. From the results, the critical micelle concentration is determined and the behaviour of surface excess as a function of the concentration is examined. The measurements will be carried out with Sigma 7^{03} tensiometer usin *du Noyu ring process*, wherein the force required to separate the ring from the surface is measured. For measurements, a base solution of NDS is prepared, for example 500 mL of 0,1 M solution is enough. From the base solution, 20 differingly concentrated solutions are diluted into 100 mL volumetric flasks. The concentrations should be between $5 \cdot 10^{-4}$ M and $5 \cdot 10^{-2}$ M with emphasis around the c.m.c., which should be about $8 \cdot 10^{-3}$ M [1]. Use a magnetic stir when forming the base solution, because of the easily foaming tenside. Do not shake the bottle.

In surface tension measurements, the cleanness of the instruments is extremely important. Wash thoroughly all the volumetric flasks and their corks used, with ion-exchanged water. The Du Noyu tensiometer ring is platinum, with iridium as dopant. For the tensiometer to give out correct values, the ring must be planar and circular, so handle the ring with care. Before measurements, and between each different solution, the platinum ring must be cleansed with water, ethanol and heating it in the flame of a spirit lamp up to the point it becomes red-hot. When pulling the ring through the surface of the solution, surfactants may stick onto the ring, so this is a way to get rid of them. Also measure the temperature of each solution near the time of the surface tension measurements.

3.1 Using the tensiometer

Switch the tensiometer power on with the on/off switch (2) (figure 4). Hang the cleansed platinum ring on the hook (8). Check the measure mode (3) is on option R_c (= corrected ring process). Tare the value display with the adjuster (4) to show zero. Start the measurements with ion-exchanged water, and continue from there, from the most dilute solution all the way to the strongest. Between every measurement, rinse the sample container with ion-exchanged water, and with the solution you're going to measure next. Do not dry the sample container with paper.

The amount of sample solution does not matter (around $2 - 3$ cm will do), as long as the ring is completely submerged about 0,5 cm below the surface of the sample solution. Put the sample container on the stand (10) and raise it so that the ring is submerged properly. Start lowering the stand from the knob carefully, and at the same time follow the values changing in the tension display. As the ring
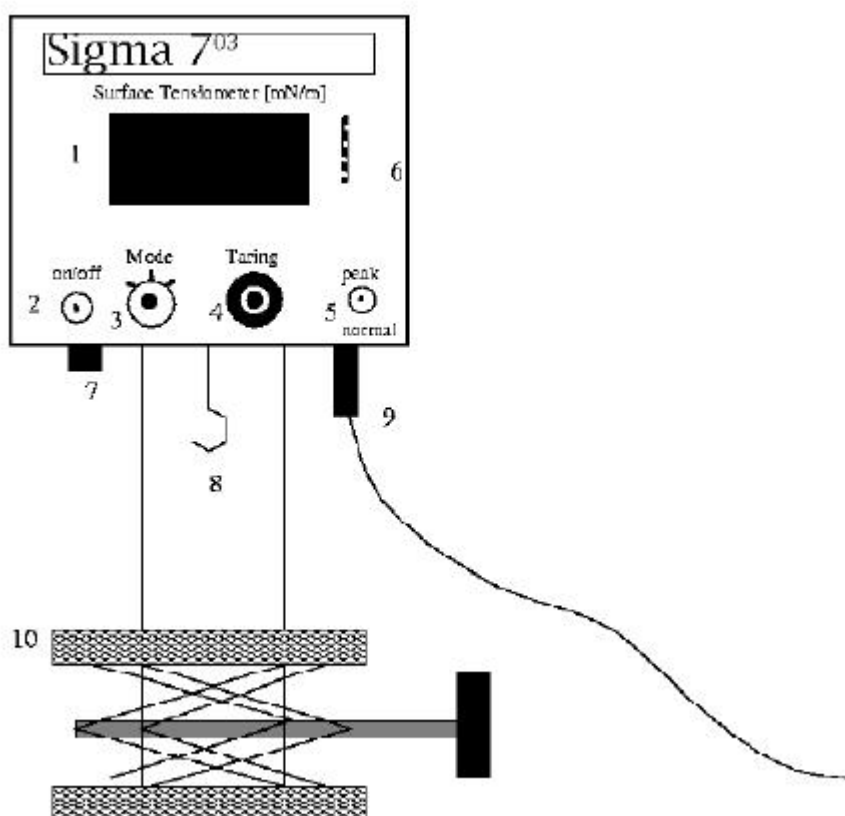

Figure 4: *Sigma* 7^{03} *Tensiometer*

starts to go above the surface, the tension on the ring starts growing. Document the maximum value the tension achieves (you can try lowering the stand multiple times to get a reasonable value). Take at least three similar values for surface tension for each of the sample solutions, and also document the temperature of the solution at the time of the measurements. The mean of these three values (of tension, temperature needs to be measured only once) is used in the calculations.

4   Results

Some liquid will always stick on the platinum ring in the measurements, which gives a systematic error to them. To the correction needed for the value of surface tension, the ratio of the platinum ring diameter and the ring thread thickness, and the difference between liquid and air densities, are noteworthy. In the measurements, the R_c-mode takes care of these all, so they do not need to be considered in the calculations.

Plot surface tension as a function of concentration ((c,γ)-graph), and as a function of the logarithmic concentration (($\ln c$,γ)-graph).

From the first graph, determine the critical micelle concentration, estimate errors for it from the graph and compare it with the literary value for sodium dodecyl sulphate. Tangents drawn into the second graph will give you a qualitative estimate of the surface excess changing as a function of the surfactant concentration. Report the maximum surface excess also in units of $\frac{molecules}{nm^2}$. Discuss the error effect of foam formation in the concentrations and thereby in the final results.

References

[1] Gui R., Tiauqing L., Weili Y., *Langmuir*, 1999, **15**, 624-630

[2] Atkins P.W., de Paula J., *Physical Chemistry*, 8th Edition (7th and 6th), Oxford University Press, pages 641-643, 685-689 (7th Ed.: pages 151, 755 and 758-759, 6th Ed.: pages 154, 702-709).

[3] Shaw L., *Introduction to Surface and Colloid Chemistry*, 4th Edition, Butterworth&Heinemann, Trowbridge, Wiltshire, L.K., **1991**, pages 65-84.