
Lab course 3.33

Surface Tension of Tenside decorated Interfaces

Advanced Lab Course
Section B

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Contents

1	Lab course description	4
2	Theory	5
2.1	Surface and Interfacial Tension	5
2.2	Surface active compounds - amphiphilic molecules	5
2.2.1	Properties	5
2.2.2	Micelle Formation	6
2.2.3	Types of Surfactants	6
2.3	Monomolecular films at the water/air interface	6
2.3.1	Generating monomolecular layers by spreading	6
2.3.2	Suitable substances for forming a monolayer on water	7
3	Methodology	8
3.1	Surface tension measurement using the du Noüy ring method	8
3.2	Determination of pressure-area isotherms using a film balance	10
4	Conducting experiments	12
4.1	Tensiometer	12
4.2	Langmuir trough	12
5	Experimental part	13
5.1	Safety instructions	13
5.2	General	13
5.3	Instructions for operating the tensiometer K11 from Krüss	14
5.3.1	Preparation	14
5.3.2	Measurement	14
5.4	Instructions for operating the film scale	15
5.4.1	Preparation	15
5.4.2	Measurement	15
6	Evaluation	16

1 Lab course description

Firstly, surface tension of aqueous surfactant solutions is measured at various concentrations. Using the obtained surface tension isotherms the critical micelle formation concentration, cmc, the surface tension, γ_{cmc} , associated with the cmc as well as the head group size, a_0 , and the packing parameter N_S of a particular surfactant can be determined.

Furthermore, pressure-area diagrams of monomolecular films consisting of water insoluble amphiphiles at the water/air interface are created. Different phase regions are interpreted and the space requirement A of a single molecule at the interface is determined.

2 Theory

2.1 Surface and Interfacial Tension

In condensed phases (liquid or solids), the molecules are attracted to one another due to attractive interactions with one another (e.g. van der Waals forces). This corresponds to the energetically favorable state and thus a minimum of free (Gibbs) energy. When an interface forms between two phases (if a phase is gaseous, it is called a surface), the interaction of a molecule at the interface with the other phase is reduced, so that a force perpendicular to the surface develops into its own phase (see particles B in Figure 1). This force is counteracted by the repulsive interaction from the Lennard-Jones potential. Work must therefore be done to bring molecules from the bulk phase to the interface and to enlarge it. This work dW is proportional to the increase in interface area dA . These experimental instructions are based on the textbooks [1, 2], that we recommend [4, 3] as further reading.

$$dW = \gamma dA \quad (1)$$

The proportionality factor will be referred to as the surface tension γ . It has the unit of energy per area ($\text{J}\cdot\text{m}^{-2}$) or force per length ($\text{N}\cdot\text{m}^{-1}$).

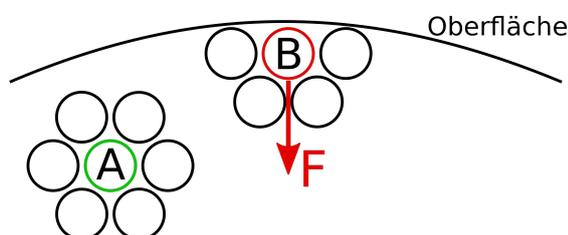


Figure 1: Interfacial tension as a consequence of the force on a molecule in the interface; a result of the asymmetry of intermolecular interactions. Particle A shows an isotropic force distribution with a vanishing net resultant force. In the case of particle B, the anisotropic force distributions results in a finite net force into the interior of the liquid.

The thermodynamic definition of surface tension uses σ as the formula symbol and is defined as the partial derivative of the free energy (Gibbs energy) G with respect to the area A . Since the Gibbs energy also depends on the pressure p as well as the temperature T , these must be kept as constant as possible during measurements.

$$\sigma = \left(\frac{\partial G}{\partial A} \right)_{p,T} \quad (2)$$

2.2 Surface active compounds - amphiphilic molecules

2.2.1 Properties

Dissolved substances, which lower the surface tension of a solvent are called surface active agents or in short, surfactants. One can also refer to them as amphiphiles due to their molecular structure containing both lipophilic and hydrophilic (non-polar and polar) parts (see Figure 2). Substances that act as surfactants in aqueous solutions are usually characterized by a hydrophilic head group and a lipophilic side chain. Examples of such compounds are explained in Section 2.2.3 “Types of Surfactants”.

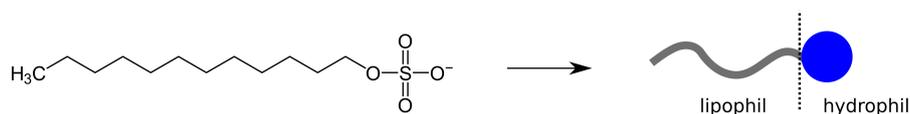


Figure 2: Chemical structure of sodium dodecyl sulfate (SDS) as well as a schematic sketch to illustrate the amphiphilic character.

Due to their special molecular structure, surfactants do not accumulate in a random distribution in aqueous solutions but preferentially accumulate at the water/air interface. The hydrophilic head group is in the aqueous phase while the lipophilic side chains protrude into the gas phase. This disrupts the interaction of the water molecules at the interface and reduces the surface tension as the surfactant concentration increases until the surface is saturated with surfactant molecules.

2.2.2 Micelle Formation

After the surface is saturated with surfactant molecules, additional molecules are randomly distributed in the solution until a limiting concentration is reached. Above this concentration there is no precipitation because the molecules exhibit the ability to form self-aggregating systems (association colloids). During aggregation, spherical micelles often form spontaneously (see Figure 3). In these spherical constructs, the lipophilic side chains are assembled and the hydrophilic head group points outwards. As the surfactant concentration increases additional structures, such as rod-shaped micelles, vesicles or lamellar phases can be observed.

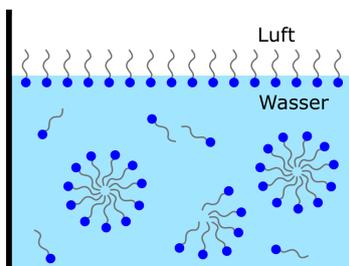


Figure 3: Schematic representation of a solution above the cmc. The surface is saturated with surfactant molecules. Self-aggregated structures form in solution.

The concentration at which micelles form is characteristic for each surfactant and is referred to as the critical micelle concentration (cmc).

2.2.3 Types of Surfactants

While the lipophilic side chain is usually a hydrocarbon chain of various lengths, there are a variety of different head groups. Surfactants are therefore classified based on the type and charge of the head group:

- *Non-ionic Surfactants*: exhibit a very polar but not charged head group. These are often polyethers (e.g. polyoxethylene $-O-CH_2-CH_2-O-$) or polyglucosides. Non-ionic surfactants show high surface activity and have a small cmc.
- *Anionic Surfactants*: exhibit a negatively charged head group. These are usually carboxylates ($-COO^-$), sulfates ($-OSO_3^-$) or sulfonates ($-SO_3^-$).
- *Cationic Surfactants*: exhibit a positively charged head group. They are almost exclusively quaternary ammonium compounds ($-NR_4^+$). Compared to non-ionic surfactants, ones with charged head groups (i.e. anionic and cationic surfactants) show a much higher cmc.
- *Amphoteric Surfactants*: also known as zwitterionic surfactants, i.e. their head group has both a positive and a negative charge resulting in a neutral net charge. The best-known representatives are the naturally occurring phospholipids (phosphatidylcholines), which make up the cell membrane.

2.3 Monomolecular films at the water/air interface

2.3.1 Generating monomolecular layers by spreading

The term spreading (or wetting) refers to the spreading of a liquid volume phase on a surface, to decide whether a liquid spreads on a surface the so-called spreading coefficient S is used.

$$\Pi_S = \gamma_1 - (\gamma_2 + \gamma_{12}) \quad (3)$$

Here, γ_1 corresponds to the surface tension of the subphase (e.g. H_2O), γ_2 corresponds to the surface tension of the spreading solution against air and γ_{12} corresponds to the interfacial tension of the spreading solution against the subphase. If the spreading coefficient is positive, spreading occurs due to a reduced surface energy as a result of wetting. Substances with a high γ_1 value, such as water or mercury, are therefore suitable as a substrate on which spreading should take place. A high surface tension corresponds to a high surface energy. Since all systems want to minimize their energy, high-energy surfaces wet better than low-energy surfaces.

Using a spreading agent as a solvent, it is also possible to create monomolecular layers even if a substance does not actually spread on the substrate. To do this, the substance is dissolved in a suitable solvent (e.g. a fatty acid in chloroform) which spreads and is almost insoluble in the subphase (e.g. water). After the spreading solution has been dripped onto the substrate, a monomolecular layer is formed. The solvent evaporates and a kind of two-dimensional "skeletal layer" is left behind (see Figure 4).

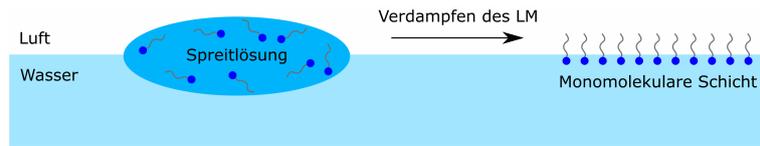


Figure 4: After applying the spreading solution the solvent evaporates and a monomolecular layer forms.

When studying the properties of monomolecular films on a surface their insolubility in the substrate is a crucial property because otherwise the molecules could desorb from the surface.

2.3.2 Suitable substances for forming a monolayer on water

Lipids and phospholipids are particularly suitable for investigating the compression behavior of monomolecular layers at the water/air interface - e.g. long-chain fatty acids, fatty alcohols, amines, fatty acid esters, lecithins, cholesterol and substances with a similar structure (see Figure 5).

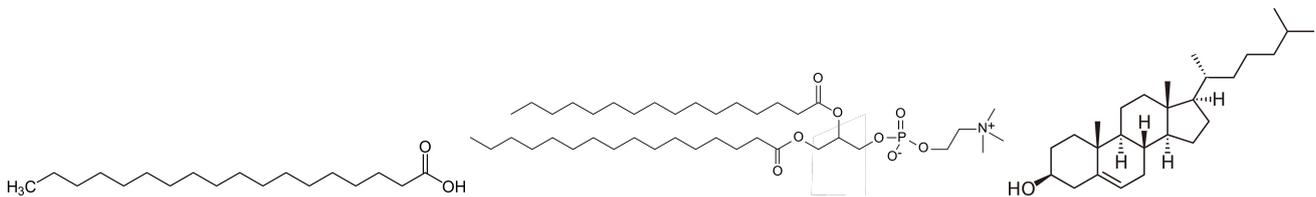


Figure 5: Chemical structure of stearic acid (left), cholesterol (middle) and phosphatidylcholine (right).

3 Methodology

3.1 Surface tension measurement using the du Noüy ring method

The surface tension is determined from directly measurable forces. So-called demolition methods, in which the force necessary to increase the liquid surface is measured, are common here. The methods used in this experiment, the ring method according to du Noüy and the vertical plate method according to Wilhelmy (see film balance section) can be classified as such. The Wilhelmy plate method can only be used to determine the surface tension of non-ionic surfactants, as it assumes a contact angle of zero, which is only given for non-ionic surfactants.

According to du Noüy's ring method, which can also be used to measure ionic surfactants, a metal ring (usually made of a platinum-iridium alloy) is immersed in to the liquid to be determined. When pulled out through the water/air interface a lamella forms between the ring and the liquid (see Figure 6). The force that has to be applied to pull the ring higher (and thus increase the surface area of the lamella) depends on the surface tension of the liquid (as well on the mass of the lamella) and increases with increasing height. This force decreases again after passing through a maximum shortly before the lamella tears off.

$$\gamma = \frac{F_{max}}{2U} = \frac{F_{max}}{4\pi r} \quad (4)$$

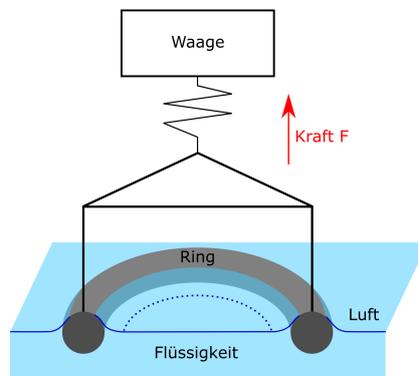


Figure 6: Schematic representation of the measurement of surface tension using the ring method.

The Krüss tensiometer used here is calibrated so that after the measurement it directly indicates the surface tension γ in the common unit $\text{mN}\cdot\text{m}^{-1}$. However, it should be noted that working with the ring method, the force obtained must be corrected using two factors which the control program has already implemented in this experiment.

- The first source of errors are inaccuracies in the ring geometry, such as deformations and weld seams on the ring suspension.
- The second source of error relates to the finite diameter of the wire. The volume of liquid located vertically beneath the wire exerts a hydrostatic force on the ring. This must be subtracted from the measured force.

These sources of error are taken into account by the correction term according to Huh and Mason so that the value displayed on the tensiometer is already corrected.

Description of surface tension isotherms

The obtained data are plotted in a γ - $\ln(c)$ diagram. Since the measurements are carried out at a constant temperature it can also be referred to as the adsorption isotherm. The following information can be obtained from this plot (see Figure 7):

- **Critical micelle formation concentration cmc** and the associated surface tension γ_{cmc}

The cmc is characterized by a distinctive kink in the γ - $\ln(c)$ diagram. An intersection point can be determined by fitting the linear areas.

- **Head group space requirement of a surfactant** at the interface

The shape of the curve can be described by the Gibbs adsorption isotherm Γ :

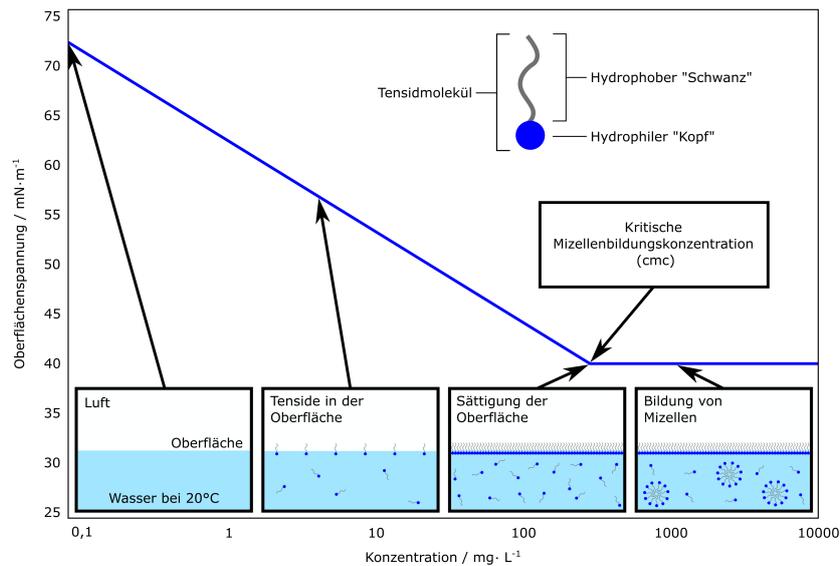


Figure 7: Representation of the surface tension of a surfactant solution with increasing concentration. The figure was freely adapted from:
<https://www.kruss-scientific.com/de-DE/know-how/glossar>

$$\Gamma = -\frac{1}{RT} \cdot \left(\frac{\partial \gamma}{\partial \ln(c)} \right)_T \quad (5)$$

This equation applies to non-ionic surfactants. For ionic surfactants complete dissociation of the head group must be assumed, so the equation must be modified to the following:

$$\Gamma = -\frac{1}{2RT} \cdot \left(\frac{\partial \gamma}{\partial \ln(c)} \right)_T \quad (6)$$

With the help of the adsorption isotherms, the maximum possible surfactant adsorption on the surface, the excess concentration Γ_{max} can be determined. To do this you need the absolute temperature T , the gas constant R and the slope of the isotherms below the cmc. The head group space requirement a_0 of a surfactant molecule can then be estimated from the calculated excess concentration.

$$a_0 = \frac{1}{N_A \cdot \Gamma_{max}} \quad (7)$$

Here, N_A is the Avogadro constant.

- **Packing parameter of a surfactant**

The form in which surfactants aggregate can be estimated using the packing parameter N_S . In Figure 8 the different aggregation forms are assigned to the respective packing parameters. This can be calculated using the head group space requirement a_0 as well as taking the molecular geometry into account.

$$N_S = \frac{v_c}{(l_c \cdot a_0)} \quad (8)$$

In above mentioned equation v_c and l_c describe the volume and length of the hydrophobic side chain. If the side chain is a pure hydrocarbon chain, both values can be calculated using the number of carbon atoms n_c in the chain.

$$v_c \approx (0,029 + n_c \cdot 0,027) \text{ nm}^3 \quad (9)$$

$$l_c \approx (0,15 + n_c \cdot 0,127) \text{ nm} \quad (10)$$

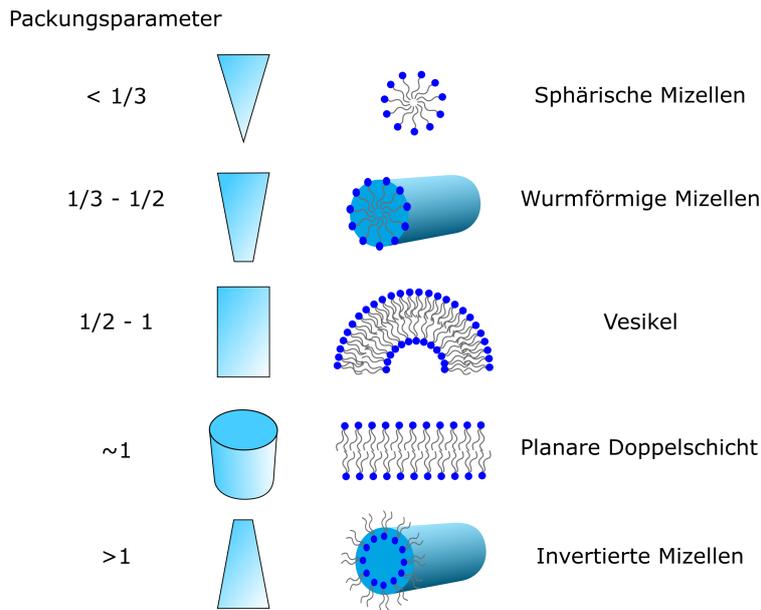


Figure 8: Different forms of aggregation can be assigned to a specific packing parameter.

3.2 Determination of pressure-area isotherms using a film balance

The phase behavior of monomolecular films - also called Langmuir films - is determined experimentally using a film balance. This technology, going back to Langmuir and Pockels, practically corresponds to a two-dimensional compression piston with the help of the available area per molecule which can be continuously reduced.

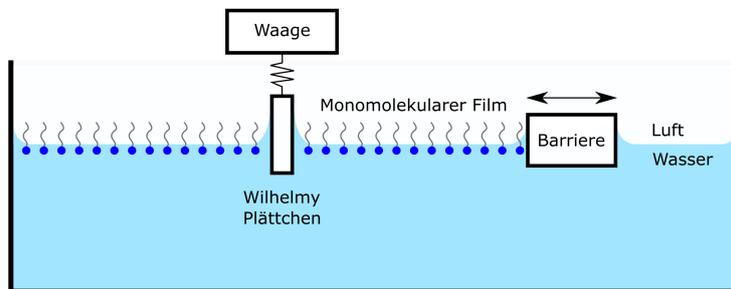


Figure 9: Schematic representation of the measurement of surface pressure in the film balance.

In this experiment, a Langmuir trough is first filled with water. The solution containing the substance to be spread is then gently tapped onto the surface of the water. After the spreading agent has evaporated and the monolayer has formed, the area available to the monolayer can be reduced by the movable shear barrier. The change in surface pressure Π depending on the film area is measured. Π is the difference between the surface tension of pure water γ_W without film and the film-covered water surface γ_F .

$$\Pi = \gamma_W - \gamma_F \quad (11)$$

Various measuring methods are available to measure surface pressure. For practical reasons, the film scale does not use the ring methods according to du Noüy but rather the vertical plate method according to Wilhelmy. After the calibration has already been carried out, the surface pressure is displayed directly in $\text{mN}\cdot\text{m}^{-1}$.

Description of the Π -A isotherms

The values obtained should be plotted in a pressure-area ($\Pi - A$) diagram, where A represents the average area of a molecule. This plot can be used to describe the compression properties of monolayers.

Figure 10 shows an idealised shear surface isotherm. The isotherm is typically divided into the following areas:

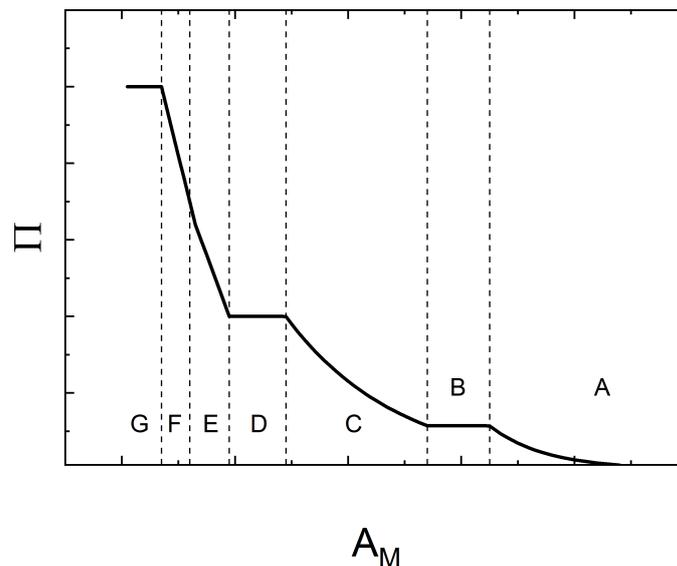


Figure 10: Idealised shear surfaces isotherm.

- **Area A:** The spread molecules have a lot of surface area available resulting in a large average distance and small intermolecular interactions. Due to the low interaction energy, this state is called a gas-analog phase. For most surfactants this phase ends at lateral pressures around 0,1 mN/m. Since a resolution better than 0,1 mN/m cannot be achieved with typical film scales, the investigation of shear surface isotherms usually begins here.
- **Area B:** In this area the lateral pressure does not change as the area continues to sink. This region can be interpreted as a two-dimensional phase transition from a gas-analog to a liquid-analog phase.
- **Area C:** Here, the film pressure increases again with further compression which indicates a higher interaction energy between the individual molecules. The hydrophobic chains of fatty acid molecules begin to straighten up here. This phase is called the liquid-expanded phase.
- **Area D:** In this transition area between the liquid-expanded and liquid-condensed phase (area E), the hydrophobic chains of the surfactants straighten up to an increasing extent. Ideally, this transition also does not lead to an increase in lateral pressure but due to the already very long relaxation times of the film, a slight increase in lateral pressure is typically observed in this area.
- **Area E:** In the liquid-condensed phase, the hydrophobic chains of the surfactants are straightened but can still be inclined towards the surface normal and still have a certain spatial leeway.
- **Area F:** With even greater compression, the solid-condensed phase finally forms. The transition between the liquid-condensed and solid-condensed phases is characterized by a break point in the isotherm. If this part of the isotherm is extrapolated to $\Pi = 0$, a statement can be made about the molecular cross-sectional area for fatty acids, for example (see evaluation).
- **Area G:** Further compression eventually leads to a film collapse. Individual parts of the monolayer are pushed over one another and multilayers are formed.

The $\Pi - A$ isotherms can look very different, i.e. different curve branches with different curvatures and slopes can appear in a diagram. The existence or absence of various phases described above depends on many parameters such as the sample examined and the temperature. Further $\Pi - A$ diagrams including descriptions of the different phases can be found in the literature source [1]. The relevant section of this book (5.6 Filmpolymorphie monomolekularer Schichten) is also accessible in digital form via the University and State Library website. To do this use the link "Kapitel 1" under the heading "Hinweise zum Inhalt".

4 Conducting experiments

4.1 Tensiometer

- In order to check that the tensiometer is functioning correctly the surface tension of pure water is initially measured. (Reference: $\gamma_{H_2O} = 72,80 \text{ mN}\cdot\text{m}^{-1}$ (20°C); $72,13 \text{ mN}\cdot\text{m}^{-1}$ (25°C))
- A stock solution of sodium dodecyl sulfate (SDS) with a concentration of $40 \text{ mmol}\cdot\text{L}^{-1}$ (= 40 mM) is provided. This should be diluted with ultrapure water (also: miliQ water) to produce 11 solutions concentrations ranging from 0.5 mM, 0.8 mM, 1 mM, 2 mM, 3 mM, 5 mM, 8 mM, 10 mM, 20 mM, 30 mM to 40 mM. The total volume of the solution should be 25 mL. Calculate the volumes for the dilution **before** starting the experiment.
- After the various solutions have been prepared they will be measured with the tensiometer with increasing concentration.

4.2 Langmuir trough

- Before using the film scale the device is checked using a test measurement. For this purpose the surface tension of ultrapure water is measured again. It should be noted, that the surface pressure is displayed by the apparatus. If this value for ultrapure water is $0 \text{ mN}\cdot\text{m}^{-1}$ the Langmuir trough is ready for use.
- Two solutions of fatty acids (arachidic acid with $M = 312,54 \text{ g}\cdot\text{mol}^{-1}$ and myristic acid with $M = 228,38 \text{ g}\cdot\text{mol}^{-1}$) in chloroform are used and will be provided ($c_{\text{arachidic acid}} = 3,763 \text{ mM}$, $c_{\text{myristic acid}} = 4,07 \text{ mM}$). Approx. $20 \mu\text{L}$ (for arachidic acid) and approx. $17,5 \mu\text{L}$ (for myristic acid) of the spreading solution will be put onto the water surface in the film balance, afterwards allowing the solvent to evaporate for about 10 minutes to form a monomolecular film.
- After the monomolecular film is created a Π -A diagram can be recorded. Both fatty acids must be measured.

5 Experimental part

5.1 Safety instructions

- Dangerous substances are used in this experiment. Those carrying out the experiment must therefore deal with the dangerous substances before the experiment begins. Any possible ambiguities must be clarified with the supervisor.

Safety aspects must be taken into account for the following substances. The fatty acids used are not subject to any labelling with a hazard symbol.

Chemicals	Hazard symbols
Sodium dodecyl sulfate solution	
Chloroform	

- Eating and drinking is prohibited in the lab. Lab coats, safety glasses and gloves are provided.

5.2 General

- With the two measuring methods presented even tiny traces of contamination can cause serious errors. All parts must therefore be kept as clean as possible. This is even more important because fats (e.g. from fingers and hair) accumulate at the water/air interface.
- In the clean room it is necessary to remove dirt and dust from the shoes on an adhesive sheet before entering the room. Shoe covers are then provided and must be worn over the shoes throughout the entire stay in the clean room. This minimizes the entry of contaminants into the clean room.
- **All practical activities in this experiment that have to do with handling samples and open measuring instruments must therefore be carried out with gloves and tweezers!**

5.3 Instructions for operating the tensiometer K11 from Krüss

5.3.1 Preparation

- The Teflon trough into which the measuring solution is placed must be cleaned before the measurement. To do this it is rinsed thoroughly with milliQ water, isopropanol and again with milliQ water and then dried using a stream of nitrogen. The trough can then be filled. Before each measurement the solution is tempered for 5 minutes at the desired measuring temperature (25,0°C).
- The platinum-iridium measuring ring must also be cleaned before each measurement. After dipping the ring several times in a solution of water and isopropanol and then drying it with a clean room cloth, it is swirled in the flame of a gas burner until it begins to glow. This serves to remove organic residues. The ring should only glow for a very short time to prevent deformation or damage. The clean ring can then be hooked into the tensiometer, and the housing cleaned.
- **The Pt-Ir ring is very sensitive to mechanical damage. It must therefore not be touched with your hands or placed on the Teflon trough!**
- **The ring may only be inserted or removed from the tensiometer very carefully, as the weighing device is very sensitive and can otherwise be damaged!**

5.3.2 Measurement

After the solution and the ring have been placed in the tensiometer, the measurement can be carried out. To do this, open the "KRÜSS Laboratory Desktop" program on the associated measuring computer. The measurement is then carried out according to the following scheme:

- First, the surface must be moved close to the measuring ring. This is done manually using the control wheel on the tensiometer panel. Raise the trough manually so that the surface is close to the ring (the surface must not be wet here yet!).
- Further settings are made directly in the panel software. Coordinate this with the supervisor and start the measurement.
- After the measurement is finished, export the obtained data by right-clicking on the diagram (/export/file/text). This is needed for the evaluation.
- Manually remove the Teflon trough from the ring and clean the ring and the Teflon trough.

5.4 Instructions for operating the film scale

5.4.1 Preparation

- Before the actual experiment can begin, the film balance must be cleaned. The trough of the film scale is made of a highly water-repellent material (Teflon) that can be easily cleaned. Cleaning is done by wiping with a laboratory cloth that has previously been soaked in chloroform. The trough is then rinsed twice with exactly 130 mL of ultrapure water and vacuumed again.
- After a measurement the solution must first be sucked from the surface. Remaining contamination is removed by wiping with a chloroform-soaked laboratory cloth.
- Ultrapure water is used as the subphase. Before each experiment the purity of the water used and the apparatus must be checked using a blind sample.
- To form the monolayer, the substance dissolved in chloroform is applied dropwise to various parts of the water surface using a Hamilton syringe. Make sure that the drops do not hit the surface of the water from too high a height, otherwise the formation of a monomolecular layer can be made more difficult. After spreading you have to wait about 10 minutes until the solvent evaporates and the system is ready for measurement.
- **It is important to ensure that the barrier does not touch the Wilhelmy tile.**

5.4.2 Measurement

- Specific instructions for operating the film scale will be given by the supervisor on the day of the experiment.

6 Evaluation

- Create a γ - $\ln(c)$ diagram of the surface tension measurements obtained and use this to determine the following properties:
 - The cmc and the associated surface tension γ_{cmc}
 - The slope of the area below the cmc
 - The headgroup space requirement a_0
 - The packing parameter N_S
- Then discuss different areas in the curve and compare the cmc obtained with a literature value (cite correctly!). What are possible sources of error? What form of aggregation do you expect for the surfactant?
- Plot the data obtained for both fatty acids on a Π -A diagram and discuss the different observable areas.
- Determine in both cases the space required by a single fatty acid molecule at the interface by extrapolation for $\Pi \rightarrow 0$ in the condensed solid film. Compare both values and discuss them.

Note: The raw data from the measurements with the Langmuir trough are given in a tabular form. The assignment of the individual columns is as follows:

#	t/s	$A_{\text{ges}}/\text{cm}^2$	$A_{\text{Molekül}}/\text{Å}^2$	$\Pi/\text{mN m}^{-1}$	N.N.	N.N.	T/°C
...

The 4th and 5th columns are relevant for the evaluation.

References

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