Manual for
Colloid Chemistry Practical Course

Pharmacy program 2017/2018
1st semester, 2nd year

Edited by Márta Berka, Levente Novák, Mónika Kéri, Dávid Nagy and Zoltán Nagy

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Department of Physical Chemistry

http://kolloid.unideb.hu/en/practice/

OPERATION OF THE LABORATORY

EXPERIMENTS
1. Rheological characterization of concentrated emulsions (creams)
2. Measurement of surface tension of solutions by Du Nouy tensiometer
3. Polymer’s relative molecular masses from viscosity measurements
4. Adsorption from solution
5. Solubilization
6. Determination of size distribution of a sedimenting suspension
7. Characterization of substances of different rheological properties by Brookfield DV-
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8. Steric and electrostatic stabilization mechanisms of colloidal dispersions
9. Determination of the critical micelle concentration of SDS
Appendix
OPERATION OF THE LABORATORY

THE COURSE
In the seven-week period assigned to the Colloid Chemistry Practical Course, six experiments have to be performed compulsorily, which are designed to be completed in four hours respectively. Each of the practices should be finished and the results should be evaluated in the laboratory. By the end of each lab session you must hand-in a report from the actual practice (the requirements how to write a report is described later). All experiments are preceded by a short written test. The short test consists of two questions: the first one is randomly chosen from the 8 equations below:

- Kelvin equation
- Einstein-Sokes equation
- Gibbs equation
- Langmuir isotherm
- Gouy-Chapman equation
- Stern equation
- The two equivalent definitions of surface tension
- Equation of the osmotic pressure

For each definition or equation the meaning of the symbols and the units of measurement must also be present.

The second question is related to the actual practice. You will receive a mark for each short test and another mark for each report. The average of short test marks and report marks will be calculated, your final mark will be given by the 2 to 1 weighted average of report marks and short test marks.

A student can’t have more than two failed marks (1) from the short test results and from the lab report results, respectively, in order to successfully accomplish the subject. One failed mark from lab reports can be corrected once during the semester, if a calculation error, plotting mistake or inappropriate conclusion is the reason of the unaccepted mark. The correction should be performed and the corrected lab report should be re-submitted until the end of the last practice week.

ATTENDANCE
The Colloid Chemistry laboratory is open from 14:00 to 18:00 on Monday and from 8:00 to 12:30 on Tuesday and Wednesday. You must arrive on time. Coats and bags should be left in
the corridor of the laboratory. The department does not accept responsibility for personal values (money, jewels, mobile phone, etc) left in the corridor; you should keep them with you.

**Do not leave valuable items in this area!**

If you are absent from a practical class (e.g. you are ill), you should report it to the administration (room D205, Mihály Szatmári) at the earliest opportunity to see whether the missed experiment(s) can be re-scheduled for an alternative date. Lack of attendance without good reason will result in a mark of zero.

**LABORATORY STAFF**

The academic staff member with overall responsibility for the Colloid Chemistry Practical Course is Prof. István Bányai (room D201). The Laboratory Managers are Mónika Kéri (Phone: 22385, room D202) on Monday and Levente Novák on Tuesday and Wednesday (Phone: 22437, room D205), the Technician in charge of the laboratory is Mihály Szatmári (room D205).

**EXPERIMENT BENCHES**

Each experiment has a bench assigned to it containing the apparatus and chemicals required for the particular experiment, except some chemicals or tools that are given by the Technician. As you will be doing a different experiment each week, it is essential that all the glassware involved are washed up by the end of a lab session first with tap water and then with distilled water and left clean in the correct cupboard for the next group’s use, the following week.

**PRE-LABORATORY WORK**

You must prepare pre-laboratory work before coming to the laboratory. A brief outline of the theory of the actual experiment should be written. (Usually it is enough to summarize the most important definitions, equations, relations, etc. in a half page extent). It should be followed by the description of the experiment, the detailed recipe that you have to follow to perform the experiment. On arrival in the laboratory you must show this work to a Demonstrator and get him/her to sign it. Failure to carry out the pre-laboratory work will result in the loss of marks. Pre-laboratory work should be carried out in your laboratory notebook.
ASSESSMENT

Your report should be organised into the following sections: Theory, Experimental, Results & Discussion and Conclusion.

The aspects taken into account for assessing your reports are the following:

• theoretical preparation, experimental skill, the quality of your data;
• the correct processing of data (e.g. correctness in calculations, accuracy in plotting graphs, inclusion of the appropriate units, labelling of axes, estimation of experimental uncertainties, etc.);
• correct answers to questions, the conclusion, the overall coherence of the report.

Failure to hand in work on time without good reason will result in downgrading. Exceptions will only be made if you have previously agreed with the academic staff member in charge of the laboratory (or have reported an illness to administration). If you get a “fail” (1) mark due to calculation errors or an inappropriate conclusion in your report, there is a second chance (only once in the course!) to correct the mistakes. In this case next week when you receive the report, you should bring back the corrected one until the end of that week (Friday, 12:00). The best mark you can get is “average” (3).

Final marks will be calculated from the marks of the written short tests weighted with a factor of one and those from the reports weighted with a factor of two:

\[
\text{final mark} = \frac{\text{average of tests} + 2 \times \text{average of reports}}{3}
\]

The calculated final mark will be rounded to the closest integer.

PLAGIARISM

Plagiarism means trying to pass off someone else’s work other than your own. The University takes very serious measures against students who have committed plagiarism in any context. This does not mean that you cannot discuss your laboratory work with other students. However, you can use only those primary data and other results in your report that you have measured yourself. If a student is found to be committing plagiarism, he or she will receive zero mark for the actual practice (when calculating your average the sum of the marks won’t grow, but 1 will be added to the divider).
LABORATORY NOTES

One of the objectives of the laboratory teaching is to introduce you to methods of recording results in a short and logical fashion. The ability to keep an accurate record of your laboratory work is of principal importance since your lab notes will be used as the basis for your lab report. You can print the theory part and/or the tables of the given experiment from this manual and you can put them together in your laboratory notebook or in your folder. It should become standard practice to record everything relevant directly into your laboratory notebook. This means you should record weights, data, calculations, rough graphs, reaction schemes and comments. Do not use scraps of paper with the idea of copying them more neatly later into your notebook. You should record your notes in ink, not pencil. Every page should have a clear heading which should include your name, the title of the experiment and the date at which it was carried out. The record of each experiment should begin with a brief statement of the experiment to be performed, and a brief plan of the experimental procedure. This should be done before you come to the lab. You can plot data manually on a mm scale paper or you can use database management systems like Microsoft Excel. In the latter case all the plotted graphs should be printed and attached to your report. The most important part of your report is the conclusion. First you should esteem the correctness and reliability of your results. (Did you get what you expected?) You should compare your results with literature data. You can find literature data on the internet or you can ask the supervisor/demonstrator for them. If the difference is significant, you should try to give explanations, possible reasons to it. Your laboratory notebook must be signed and dated by the demonstrator or supervisor when you have finished the experiment.

DAMAGE, REPARATIONS

Purchase of broken glassware, reparation of lost or defective utensils are at the charge of those who mishandled them. A written report form will be filled and signed by the person responsible for the damage and one of the supervisors. Reparation fee can be paid by cheques issued by the Department.

SAFETY INFORMATION

Emergency telephone numbers: First aid medical doctor number: 23009; Receptionist: 22300
There are First Aid Boxes in each Teaching Laboratory. In the event of a minor accident call the staff. External Numbers: Fire 9-105, Police 9-107, Ambulance 9-104

FIRE ALARMS
The alarms sound if a sensor detects flame, heat or smoke or if the break-glass alarm button is activated. Before activating the alarm you should size up the situation to avoid unnecessary fire alarms. In case of fire first you should inform the staff in charge, after that follow their instructions.

If you are in a practical class when the alarms sound, spend a few seconds for making your experiment safe, then leave the building by the nearest marked exit. Do not use the elevators! Do not attempt to enter the building until you have been told it is safe to do so!

LABORATORY SAFETY
Whilst working in the laboratory, it is your responsibility, by law:

• To take reasonable care for your own health and safety and for that of others in the laboratory
• To co-operate in matters of health and safety.
• Not to interfere with, or damage, any equipment provided for the purpose of protecting health and safety.

SAFETY DATA SHEETS
Before you commence any practical work you must familiarise yourself with the chemical hazards present in the experiment. No practical work can be undertaken without the presence of at least one staff member in the laboratory. If you have any queries or concerns about health and safety in the Teaching Laboratories you should direct these to the Departmental Safety Adviser.

EMERGENCY EQUIPMENT
You should make yourself familiar with the location of fire extinguishers and fire blankets. Training in the use of this equipment is given at the beginning of the year. A safety shower is located by the main door to the lab.

SAFETY PRECAUTIONS
Dress like a chemist. Wear clothing in the laboratory that will provide the maximum body coverage. When carrying out experimental work you MUST wear a fastened lab coat. In case of a large chemical spill on your body or clothes, remove contaminated clothing to prevent
further reaction with the skin. Every student has to have own safety glasses and to wear them when it is neccessary.

**Eating and drinking is strictly prohibited.** This includes chewing gum. Keep long hair tied back and ensure that long or large necklaces are safely tucked away. Mobile phones personal stereos etc. must be switched off when entering the laboratory. Anything that interferes with your ability to hear what is going on in the laboratory is a potential hazard. You are strongly advised not to wear contact lenses in the laboratory, even under safety glasses. After reading any warnings and recommendations, use all chemicals carefully whenever possible. Dispose solvents properly. Immediately return any chemicals you have used to the shelves for other students to use.

**Keep your work area tidy and clean up any spills, including water, on the floor.**

Report all accidents and dangerous incidents, no matter how trivial they may seem

**Wash your hands carefully when you leave.**

Work defensively!
EXPERIMENTS

1. Rheological characterization of concentrated emulsions (creams)

Theory

Rheology is the science of flow and deformation of body that describes the interrelation between force, deformation and time. Rheology is applicable to all materials, from gases to solids. Viscosity is the measure of the internal friction of a fluid. This friction becomes apparent when a layer of fluid is made to move in relation to another layer. The greater the friction, the greater the amount of force is required to cause this movement, which is called “shear”. Shearing occurs whenever the fluid is physically moved or distributed, as in pouring, spreading, spraying, mixing, etc. Highly viscous fluids, therefore, require more force to move than less viscous materials.

The viscosity of a fluid is a measure of its resistance to gradual deformation by shear stress. Viscosity is due to friction between neighboring parcels of the fluid that are moving at different velocities. The velocity gradient is the measure of the speed at which the intermediate layers move with respect to each other. It is also called “shear rate”. This will be symbolized as “\( D \)” in subsequent discussions. Its unit is reciprocal second, \( s^{-1} \). The force per unit area required to produce the shearing action is referred to as “shear stress” and will be symbolized by “\( \tau \)”. Its unit of measurement is \( \text{N/m}^2 \) (Newton per square meter). Using these simplified terms, viscosity may be defined mathematically by this formula:

\[
\eta = \frac{\text{shear stress}}{\text{shear rate}} = \frac{\tau}{D}
\]

The fundamental unit of viscosity measurement is Pas, Pascal-seconds. A material requiring a shear stress of one Newton per square meter to produce a shear rate of one reciprocal second has a viscosity of one Pas. (You will encounter viscosity measurements in “centipoise” (cP), but these are not units of the International System, SI; one Pascal-second is equal to ten poise; one milli-Pascal-second is equal to one centipoise.) Newton assumed that all materials have, at a given temperature, a viscosity that is independent of the shear rate. In other words twice the force would move the fluid twice as fast.

In rheology fluids are categorized in three groups:

- Newtonian fluids
- Non-Newtonian, time independent fluids
Non-Newtonian, time dependent fluids

The sub-categories and examples to the flow- and viscosity curves of these fluids is summarized in Figure 1. The detailed description of the categories can be found in the Appendix at the end of this supplementary material.

Figure 1. Flow and viscosity curves of newtonian and non-newtonian time-independent fluids

1. ideal (newtonian), 2. shear thinning or pseudoplastic, 3. shear thickening or dilatant, 4. ideal plastic (Bingham type), 5. plastic (pseudo-plastic type), 6. plastic (dilatant type)

What happens when the element of time is considered? This question leads us to the examination of “thixotropy” and “rheopexy”.

Thixotropic. A thixotropic fluid decreases in viscosity with time, while it is subjected to constant shearing, as you can find out from Figure 2. Rheoplectic. This is essentially the opposite of thixotropic behaviour, in that the fluid’s viscosity increases with time as it is sheared at a constant rate. See Figure 1. Both thixotropy and rheopexy may occur in combination with any of previously discussed flow behaviors, or only at certain shear rates. The time element is extremely variable; under conditions of constant shear, some fluids will reach their final viscosity in a few seconds, while others may take up to several days. Rheoplectic fluids are rarely encountered. Thixotropy is frequently observed in materials such as greases, heavy printing inks, and paints. When subjected to varying rates of shear, a thixotropic fluid will react as illustrated in Figure 2. A plot of shear stress versus shear rate was made increased to a certain value, then immediately decreased to the starting point. Note that the “up” and “down” curves do not coincide. This “hysteresis loop” is caused by the decrease in the fluid’s viscosity with increasing time of shearing (Figure 2.). Such effects may or may not be reversible; some thixotropic fluids, if allowed to stand undisturbed for a while, will regain their initial viscosity, while others never will.
Dispersions and emulsions, which are multiphase materials consisting of one or more solid (or liquid) phases dispersed in a fluid phase, can be affected rheologically by a number of factors. An emulsion is a mixture of two or more liquids that are normally immiscible. Based on the characteristics of the dispersed phase and the dispersion medium, the different types of emulsions are the following: oil in water (o/w), water in oil (w/o), oil in oil (o/o). Usually an o/w emulsion is more creamy, a w/o emulsion is more shiny and greasy to the touch. Emulsions can be diluted limitless with their own dispersion medium. Concentrated emulsions can be considered as coherent systems, they are called creams.

Chemicals
Type ungventum emulsificans nonionicum of base cream, water

Experimental procedure
In this practice, basic rheological terms and an interpretation on the relationship between rheological response and material structure have to be presented. A flow curve (shear rate $D$ versus shear stress $\tau$), and a viscosity curve (viscosity $\eta$ versus shear stress $\tau$), across a wide range of shear rates can provide important information about storage stability; optimal conditions for mixing, pumping, and transferring; and end-user applications. It also provides important information regarding the ways in which the structure changes to comply with the applied shear in different conditions, such as storage, processing, and application. The rheological behavior of the material may change as a result of these forces. If the shear rate...
changes during an application, the internal structure of the sample will change and the change in stress or viscosity can then be seen.

**Apparatus**

Rheometer LV (Brookfield torque range appropriate for measuring low viscosity materials; 100% torque = 673.7 dyne cm; dial reading viscometer with electronic drive), beaker, glass rod, spatula

The original Brookfield Dial Reading Viscometer is the lab standard used around the world. Easy speed control with convenient adjustable rectangular switch is on its side. The pointer can be stopped with a toggle behind the motor. Viscometers are supplied with a standard spindle set (LV-1 through LV-4).

*Put 150 cm³ of cream* (ointment or paste) into the measuring container by avoiding the formation of air bubbles or other inhomogeneity. *Screw* the appropriate spindle and observe the operation of the rheometer (*spindle must rotate centered*). When attaching a spindle, remember that it has a *left-hand thread* and must be screwed firmly to the coupling (for this operation always ask for the help of the supervisors). After attachment do not hit the spindle against the side of the sample container since this can damage the shaft alignment. When conducting an original test, the best method for spindle and speed selection is trial and error. The goal is to obtain a viscometer dial or display reading between 10 and 100 remembering that accuracy improves as the reading approaches 100. If the reading is over 100, select a slower speed and/or a smaller spindle. Conversely, if the reading is under 10, select a higher speed and/or a larger spindle. When conducting multiple tests, the same spindle/speed combination should be used for all tests. The *spindle should be immersed up to the middle* of the indentation in the shaft. We recommend inserting the spindle in a different portion of the sample than the one intended for measurement. The spindle may then be moved horizontally to the center of the sample container.
1. Immerse the spindle into the sample, and turn the rectangular screw on maximum speed \((RPM = 60, \text{ the actual speed is shown on the top of the screw})\), and allow it to run for 5 minutes then let it run at minimum speed \((RPM = 6)\) until a constant reading is obtained (or for about 15 minutes). (Homogenization) For measurement use every speed for 30 s.

2. Start the run with 6 RPM and read and write the value of display \(\alpha\) after 30 s running.

3. Increase the speed of rotation without stopping the motor and read the display again as before. If there is no dial or readable display or it is less than 5%, change spindle or speed. Repeat the measurement decreasing the speed from 60 RPM to 6 RPM, too.

4. After the measurement at all 4 speeds there and back, dilute the emulsion with 5 cm\(^3\) water and homogenize thoroughly with a glass rod. Repeat the measurement procedure from point 1 to point 3. Two more repetitions are needed following the instructions of point 4. (In total 4 times 5 cm\(^3\) deionized water will be added to the cream.)

Tabulate the data and plot rheology \((D \sim \tau)\) and viscosity \((\eta \sim \tau)\) curves.

**Calculation of the results**

Viscosity: \[\boldsymbol{\eta} \text{ (Pas)} = z \times \alpha/1000\] (1)

Shear stress: \[\tau \text{ (N/m}^2\text{)} = \eta \times D = z \times D \times \alpha/1000\] (2)

Shear rate: \[D \text{ (s}^{-1}\text{)} = RPM \times \text{constant}\]

Viscometer torque: \(\alpha\), displayed in \%

**Centimetre–gram–second system (CGS)** is a variant of the metric system of physical units. In rheology it is still widespread; Viscosity: 1 mPas = 1 cP Shear stress: 1 N/m\(^2\) = 10 dyne/cm\(^2\) Torque: 1 Nm = 10\(^7\) dyne cm.

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<tr>
<th>RPM</th>
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<td>12</td>
<td>0.2</td>
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<th>RPM/spindle no</th>
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**Determined Viscosity** (calculated from the average torques and $z$ using equation (1))

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<thead>
<tr>
<th>RPM</th>
<th>$\eta$ (cP)</th>
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**Determined shear stress** (calculated from the average torques, $z$ and $D$ using equation (2))

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<tr>
<th>RPM</th>
<th>$\tau$ (Pa)</th>
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Plot the flow ($D \sim \tau$) and viscosity ($\eta \sim \tau$) curves. Compare your 2 figures to Figure 1 and determine the rheology class of cream. **Explain how and why the $\tau_0$, $\eta_c$ and hysteresis loop change with dilution of the cream.**

**Discuss the results.**

Rheology and viscosity curves at different dilution of creams.

(This is only illustration, your results may differ from it depending on the temperature and the properties of the studied cream)

**Review questions**

Definition of viscosity. Rheological classification of materials, with their rheology and viscosity curves. Hysteresis loop.
2. Measurement of surface tension of solutions by Du Nouy tensiometer

Theory

The molecules at the surface of a liquid are subjected to an unbalanced force of molecular attraction as the molecules of the liquid tend to pull those at the surface inward while the vapor does not have as strong an attraction. This unbalance causes liquids to tend to maintain the smallest surface possible. The magnitude of this force is called the surface tension. When this lowest possible energetic state is achieved the surface tension acts to hold the surface together where the force is parallel to the surface. The symbol for surface tension is "gamma". Conventionally the tension between the liquid and the atmosphere is called surface tension while the tension between one liquid and another is called interfacial tension.

The specific surface free energy or surface tension of surface $\gamma$ is equal to the expenditure of work required to increase the net area of surface isothermally and reversibly way by unit of area, in J/m$^2$ (Joule per square meter); if the increase in the surface area is accomplished by moving a unit length of line segment in a direction perpendicular to itself, $\gamma$ is equal to the force, or "tension", opposing the moving of the line segment. Accordingly, it is usually expressed in units of N m$^{-1}$ (Newton per meter). Surface may be a free surface (exposed to air or vapor or vacuum) or an interface with another liquid or solid. In the event that the surface is an interface, this quantity is called interface tension. The value of surface tension is dependent on the nature of the liquid and also on the temperature (see Eötvös and Ramsay empirical rule). The temperature during the measurement of surface tension must be kept constant. It is found that the surface tensions of solutions are generally different from those of the corresponding pure solvents. It has also been found that solutes whose addition results in a decrease in surface tension tend to be enriched in the surface regions (positive surface concentration). The migration of solute either toward or away from the surface is always such as to make the surface tension of the solution (and thus the free energy of the system) lower than it would be if the concentration of solute were uniform throughout (surface concentration equal to zero). Equilibrium is reached when the tendency for free-energy decrease due to lowering surface tension is balanced by the opposing tendency for free-energy increase due to increasing nonuniformity of solute concentration near to the surface.

A surface-active molecule, also called a surface active agent or surfactant, possesses approximately an equal ratio between the polar and nonpolar portions of the molecule. When such a molecule is placed in an oil-water system, the polar group(s) are attracted to or oriented
toward the water, and the nonpolar group(s) are oriented toward the oil. This orientation of amphiphilic molecules is described by Hardy-Harkins principle of continuity. The surfactant is adsorbed or oriented in this manner, consequently lowering interfacial tension between the oil and water phase. When a surfactant is placed in a water system, it is enriched at the surface and lowers the surface tension between the water and air. When it is placed in a mixture of solid and liquid, it is enriched on the surface of the solid and lowers the interfacial tension between the solid and the liquid. Since the surfactant is adsorbed at the surface, it is logical that the concentration of surfactant at the surface would be greater than the concentration in the bulk solution. Mathematically such a relationship has been derived by Willard Gibbs. It relates lowering of surface tension to excess concentration of surfactant at the surface.

The **Gibbs equation** can be written as follows:

\[
\Gamma = -\frac{1}{RT} \frac{d\gamma}{d \ln c}
\]  

(1)

where \(c\) is the concentration (in mol m\(^{-3}\)) in the solution, \(T\) (K) the absolute temperature, \(R\) the gas constant (8.314 JK\(^{-1}\) mol\(^{-1}\)), \(\gamma\) (Nm\(^{-1}\)) the surface tension and \(\Gamma_c\) (mol m\(^2\)) is the surface excess concentration. It follows from Equation 1 that \(\Gamma_c\) is positive if \(d\gamma/dc\) is negative, that is the surface tension decreases with increasing solute concentration. On the basis of experimental surface tension vs. solute concentration function the \(d\gamma/dc\) can be determined and the \(\Gamma_c = f(c)\) adsorption isotherm (Eq. 2) can be calculated.

\[
\Gamma = \Gamma_\infty \frac{bc}{1 + bc}
\]

(2a)

\[
\frac{c}{\Gamma} = \frac{c}{\Gamma_\infty} + \frac{1}{b\Gamma_\infty}
\]

(2b)

where \(c\) is the bulk concentration of the analyte, \(b\) is a constant and \(\Gamma_\infty\) is the saturation (maximum) surface excess concentration.

The area (\(\phi_m\)) occupied per molecule is determined as: \(\varphi_m = \frac{1}{\Gamma_\infty N_A}\) where \(N_A\) is the Avogadro’s number (6\(\times\)10\(^{23}\) mol\(^{-1}\)). The \(\phi_m\) for alcohols are about 0.22 nm\(^2\) and for carboxylic acids about 0.25 nm\(^2\) extrapolated from the liquid condensed regions and \(\phi_m\) are about 0.20 nm\(^2\) extrapolated from the solid regions of two-dimensional isotherm of monolayer, independent of both the length of the hydrocarbon chain and the nature of the head.

**Apparatus**

Du Nouy tensiometer (this is a highly sensitive microbalance – a delicate instrument and you should use care when working with it), beakers, volumetric flask, pipettes
Chemicals
Deionized water, aqueous solution of alcohol or organic acids.

Experimental procedure
This tensiometer is capable of measuring the surface tension of liquids with the du Nouy ring. The du Nouy tensiometer consists of a platinum-iridium ring supported by a stirrup attached to a torsion balance. The force that is just requiring breaking the ring free of the liquid/liquid or liquid/air interface is proportional to the surface tension. The surface tension is displayed in mN/m, accurate to 0.1 mN/m. Attach the ring to the balance. Fill the test vessel with deionized water, and suspend the ring in the liquid and zero the instrument with the ring below the surface of the liquid. (For the first measurements ask for help from the supervisors). If you are making a surface tension measurement, begin to lower the platform that the wessel (petri dish) is on and add tension to the ring to maintain the ring in position until the ring breaks free of the liquid. Read off measurement when surface breaks. Then repeat the measurement as before. The ring can be cleaned with distilled water. Care must be taken not to touch or bent the ring with the fingers! The measured (apparent) surface tension for deionized water ($\gamma_{water \ measured}$) differs from literature water surface tension ($\gamma_{water}$) due to the different geometry of the rings. You can obtain the corrected values by multiplying the measured surface tensions with a correction factor=$\gamma_{water}/\gamma_{water \ measured}$. The correction factor is normally close to one.

Prepare 0.0, 0.10, 0.20, 0.50, 1.00, 1.50, 2.00 mol dm$^{-3}$ aqueous solutions of alcohol in 50 cm$^3$ volumetric flask, separately. The prepared solutions should be stored until the start of the measurement in the provided Erlenmeyer flasks sealed with the glass stoppers. Measure the surface tension of solutions with the tensiometer starting with the water and the more diluted solutions (take 3-5 measurements and take the average). After the measurement of each
solution rinse the vessel with the next (more concentrated) solution. (Table 1.) Do not discharge the solutions before you calculate the results.

Table 1.

<table>
<thead>
<tr>
<th>$c_1$ (mol dm$^{-3}$)</th>
<th>$\gamma_{c,1}$ (mN/m)</th>
<th>$\gamma_{c,2}$ (mN/m)</th>
<th>$\gamma_{c,3}$ (mN/m)</th>
<th>$\gamma_{c,\text{average}}$ (N/m)</th>
<th>$\gamma_{c,\text{corrected}}$ (N/m)</th>
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<tbody>
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<td>0</td>
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</table>

**Calculation of results**

Calibration with water: Correction Factor. It is necessary to apply a correction factor that takes into account the shape of the ring held up by the liquid (the ring is not perfectly flat and circular). It is bent and tilted. The liquid film (surface) will not be perfectly flat and the connection between the surface and the ring won’t be perfect, making the surface tension not even over the surface. We calibrate by measuring $\gamma$ for water. Take 5 measurements and take the average to be $\gamma_{\text{water}}$. The correction factor will be $[72.0/\gamma_{\text{water}}]$, where 72.0 mN/m is the literature value of surface tension of water and $\gamma$ is the experimental value. Multiply every future measurement by this correction factor.

Table 2

<table>
<thead>
<tr>
<th>$c$ (mol dm$^{-3}$)</th>
<th>$c$ (mol m$^{-3}$)</th>
<th>$\ln c$</th>
<th>$y_2$</th>
<th>$x_2$</th>
<th>$y_1$</th>
<th>$x_1$</th>
<th>$d\gamma/d\ln c$</th>
<th>$\Gamma_c$ (mol m$^{-2}$)</th>
<th>$c/\Gamma_c$ (m$^{-1}$)</th>
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</thead>
<tbody>
<tr>
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<td>2.00</td>
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</table>

Plot the corrected surface tensions ($\gamma_{c,\text{corrected}}$) against the natural logarithm of concentration ($\ln c$) according to Eq. (1). as shown in Figure 1. To determine $\Gamma$ for each concentration, $d\gamma/d\ln c$ should be determined by graphical differentiation of the curve. For this purpose draw
a tangent to a selected concentration and read the coordinates of two points \((x_1, y_1, x_2, y_2)\) on the tangent. To calculate \(\frac{dy}{d\ln c}\), use the following formula: \((y_2 - y_1)/(x_2 - x_1)\), than calculate \(\Gamma\) for each concentrations (it is in the order of \(10^{-6}\) mol m\(^{-2}\)). Repeat this procedure for each of the points.

Plot the Gibbs isotherm (Figure 2) and the linear representation of the isotherm, \(c/\Gamma = f(c)\) (Figure 3) and determine the value of \(\Gamma_\infty\) from the slope (1/slope = \(\Gamma_\infty\)). Calculate the area per molecule \(\varphi_m = \frac{1}{\Gamma_\infty N_A}\). Discuss the result and compare with literature results.

\[ \Gamma_\infty \]

**Figure 1.** Graphical differentiation of the curve of measured surface tension vs. natural logarithm of concentration \(\gamma = f(\ln c)\).

**Figure 2** Concentration dependance of surface excess concentration in case of capillar active material

**Figure 3** Linear representation of the isotherm, \(c/\Gamma = f(c)\)

**Review questions**

What is the surface tension? What is the capillary activity and inactivity effect? How does the surface tension change with the temperature?
3. Polymer’s relative molecular masses from viscosity measurements

Theory

Rheology is the science of flow and deformation of body and describes the interrelation between force, deformation and time. Rheology is applicable to all materials, from gases to solids. Viscosity is the measure of the internal friction in a fluid. This friction becomes apparent when a layer of fluid is made to move in relation to another layer. The greater the friction, the greater the amount of force required to cause this movement, which is called “shear”. Shearing occurs whenever the fluid is physically moved or distributed, as in pouring, spreading, spraying, mixing, etc. Highly viscous fluids, therefore, require more force to move than less viscous materials.

Isaac Newton defined viscosity by considering the model: two parallel planes of fluid of equal area “A” are separated by a distance “dx” and are moving in the same direction at different velocities “v₁” and “v₂”. Newton assumed that the force required maintaining this difference in speed was proportional to the difference in speed through the liquid, or velocity gradient. To express this, Newton wrote: $F/A = \eta \frac{dv}{dy}$ where $\eta$ is a constant for a given material and is called its “viscosity”. The velocity gradient, $dv/dy$, is a measure of the speed at which the intermediate layers move with respect to each other. It describes the shearing of the liquid experiences and is thus called “shear rate”. This will be symbolized as “$D$” in subsequent discussions. Its unit of measure is called the reciprocal second, $s^{-1}$. The term $F/A$ indicates the force per unit area required to produce the shearing action. It is referred to as “shear stress” and will be symbolized by “$\tau$”. Its unit of measurements is N/m² (Newton per square meter). Using these simplified terms, viscosity may be defined mathematically by this formula:

$\eta = \frac{\text{shear stress}}{\text{shear rate}} = \frac{\tau}{D}$

The fundamental unit of viscosity measurement is the Pas, Pascal-seconds. A material requiring a shear stress of one Newton per square meter to produce a shear rate of one reciprocal second has a viscosity of one Pas. (You will encounter viscosity measurements in “centipoise” (cP), but these are not units of the International System, SI; one Pascal-second is equal to ten poises, one milli-Pascal-second is equal to one centipoise.) Newton assumed that all materials have, at a given temperature, a viscosity that is independent of the shear rate. In other words twice the force would move the fluid twice as fast.
Viscosities of dilute colloid solutions. For most pure liquids and for many solutions and dispersions \( \eta \) is a well defined quantity for a given temperature and pressure which is independent of \( \tau \) and \( d\nu/dx \), provided that the flow is streamlined (i.e. laminar). For many other solutions and dispersions, especially if concentrated and/or if the particles are asymmetric, deviations from Newtonian flow are observed. The main causes of non-Newtonian flow are the formation of a structure throughout the system and orientation of asymmetric particles caused by the velocity gradient. Capillary flow methods

The most frequently employed methods for measuring viscosities is based on flow through a capillary tube. The pressure under which the liquid flows furnishes the shearing stress. The relative viscosities of two liquids can be determined by using a simple Ostwald viscometer. (Figure 1). 10 cm\(^3\) liquid is introduced into the viscometer. Liquid is then drawn up into the right-hand limb until the liquid levels are above A. The liquid is then released and the time, \( t \) (s) for the right-hand meniscus to pass between the marks A and B is measured. For a solution the relative viscosity:

\[
\eta_{rel} = \frac{\eta}{\eta_0} = \frac{t}{t_0} \tag{1}
\]

where \( t \) and \( t_0 \) are the flowing time for solution and solvent, respectively, \( \eta_0 \) and \( \eta \) are viscosity of pure solvent and solution. The specific increase in viscosity or viscosity ration increment: \( \eta_{spec} = \eta_{rel} - 1 \). The reduced viscosity (or viscosity number): \( \eta_{spec}/c \). The intrinsic viscosity (or limiting viscosity number):

\[
\left[\eta\right] = \lim_{c \to 0} \frac{\eta_{spec}}{c} = \lim_{c \to 0} \ln \frac{\eta_{rel}}{c} \tag{2}
\]

From expressions it can be seen that the reduced viscosities have the unit of reciprocal concentration. When considering particle shape and solvation, concentration is generally expressed in terms of the fraction of the particles (ml/ml or g/g) and the corresponding reduced and intrinsic viscosities are, therefore dimensionless.

Spherical particles. Einstein made a hydrodynamic calculation relating to the disturbance of the flow lines when identical, non-interacting, rigid, spherical particles are dispersed in a liquid medium, and arrived at the expression: \( \eta = \eta_0(1 + 2.5\phi) \). The effect of such particles on the viscosity of dispersion depends, therefore, only on the volume which they occupy and is independent of their size. For interacting, non-rigid, solvated or non-spherical particles the Einstein form is not applicable because the viscosity depends on these parameters. Viscosity measurements cannot be used to distinguish between particles of different size but of the same
shape and degree of solvation. However, if the shape and/or solvation factor alters with particle size, viscosity measurements can be used for the determination of particle size (for molar mass). The intrinsic viscosity of a polymer solution is, in turn, proportional to the average solvation factor of the polymer coils. For most linear high polymers in solution the chains are somewhat more extended than random, and the relation between intrinsic viscosity and relative molecular mass can be expressed by general equation proposed by Mark and Houwink:

\[ [\eta] = K M_\text{visc}^\alpha \]  

(3)

where \( K \) and \( \alpha \) are characteristic of the polymer-solvent system. Alpha depends on the configuration (stiffness) of polymer chains. In view of experimental simplicity and accuracy, viscosity measurements are extremely useful for routine molar mass determinations on a particular polymer-solvent system. \( K \) and \( \alpha \) for the system are determined by measuring the intrinsic viscosities of polymer fractions for which the relative molecular masses have been determined independently, e.g. by osmotic pressure, sedimentation or light scattering. For polydisperse systems an average relative molecular mass intermediate between number average \( (\alpha=0) \) and mass average \( (\alpha=1) \) usually results:

\[
M_\text{visc} = \left[ \frac{\sum M^{\alpha+1} dN}{\sum M dN} \right]^{1/\alpha}
\]

**Apparatus**

Ostwald viscometer, beaker, volumetric flask, pipette

**Chemicals**

2.5 g/100 mL aqueous stock solution of PVA.

**Experimental procedure**

By diluting the stock PVA solution (0.025 g cm\(^{-3}\)) with water, prepare a concentration series of polyvinyl alcohol having the following concentrations: 0, 0.0025, 0.005, 0.01, 0.015, 0.02, and 0.025 g cm\(^{-3}\). Use 10-10 cm\(^3\) from each solution for the measurement, start with the solvent and go on from the most diluted to the more concentrated solutions. Determine the relative viscosities of solutions by using the Ostwald viscometer.

Tabular the data and plot \( \eta_{\text{spec}}/c \) and \( \ln \eta_{\text{rel}}/c \) against concentration. Determine the intrinsic viscosity with extrapolation of the curves as Figure 2 shows. Calculate the molar mass from Equation 3, with \( K=0.018 \) and \( \alpha=0.73 \) for PVA.
Figure 1.
Ostwald viscometer.

Figure 2
Determination of the limiting viscosity number by extrapolation $c \rightarrow 0$ of reduced viscosity concentration curves

**Calculation of results**

<table>
<thead>
<tr>
<th>$c$ (g cm$^{-3}$)</th>
<th>$t$ (s)</th>
<th>$t$ (s)</th>
<th>$t$ (s)</th>
<th>$t_{\text{average}}$ (s)</th>
<th>$\eta_{\text{rel}}$</th>
<th>$\eta_{\text{spec}}$</th>
<th>$\eta_{\text{spec}}/c$</th>
<th>$(\ln \eta_{\text{rel}})/c$</th>
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<td>0</td>
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**Review questions**
Rheological classification of materials. The ideal chain mathematic model for linear polymer.
4. Adsorption from solution

Theory
Adsorption is the enrichment (positive adsorption, or briefly, adsorption) or depletion (negative adsorption) of one or more components in an interfacial layer. The material in the adsorbed state is called the adsorbate, while that present in one or other (or both) of the bulk phases and capable of being adsorbed may be distinguished as the adsorptive. When adsorption occurs (or may occur) at the interface between a fluid phase and a solid, the solid is usually called the adsorbent. Sorption is also used as a general term to cover both adsorption and absorption. Adsorption from liquid mixtures is said to have occurred only when there is a difference between the relative composition of the liquid in the interfacial layer and that in the adjoining bulk phase(s) and observable phenomena result from this difference. For liquids, accumulation (positive adsorption) of one or several components is generally accompanied by depletion of the other(s) in the interfacial layer; such depletion, i.e. when the equilibrium concentration of a component in the interfacial layer is smaller than the adjoining bulk liquid, is termed negative adsorption and should not be designated as desorption. Equilibrium between a bulk fluid and an interfacial layer may be established with respect to neutral species or to ionic species. If the adsorption of one or several ionic species is accompanied by the simultaneous desorption (displacement) of an equivalent amount of one or more other ionic species this process is called ion exchange.

It is often useful to consider the adsorbent/liquid interface as comprising two regions. The region of the liquid phase forming part of the adsorbent/liquid interface may be called the adsorption space while the portion of the adsorbent included in the interface is called the surface layer of the adsorbent. With respect to porous solids, the surface associated with pores communicating with the outside space may be called the internal surface. Because the accessibility of pores may depend on the size of the fluid molecules, the extent of the internal surface may depend on the size of the molecules comprising the fluid, and may be different for the various components of a fluid mixture (molecular sieve effect). In monolayer adsorption all the adsorbed molecules are in contact with the surface layer of the adsorbent. In multilayer adsorption the adsorption space accommodates more than one layer of molecules and not all adsorbed molecules are in contact with the surface layer of the adsorbent.

The surface coverage ($\theta$) for both monolayer and multilayer adsorption is defined as the ratio of $a$ the amount of adsorbed substance to $a_m$ the monolayer capacity (the area occupied by a
molecule in a complete monolayer); \( \theta = a / a_m \). Micropore filling is the process in which molecules are adsorbed in the adsorption space within micropores. The micropore volume is conventionally measured by the volume of the adsorbed material, which completely fills the micropores, expressed in terms of bulk liquid at atmospheric pressure and at the temperature of measurement. Capillary condensation is said to occur when, in porous solids, multilayer adsorption from a vapour proceeds to the point at which pore spaces are filled with liquid separated from the gas phase by menisci. The concept of capillary condensation loses its sense when the dimensions of the pores are so small that the term meniscus ceases to have a physical significance. Capillary condensation is often accompanied by hysteresis.

Adsorption from solution is important in many practical situations, such as those in which modification of the solid surface is of primary concern (e.g. the use of hydrophilic or lipophilic materials to realize stable dispersions in aqueous or organic medium, respectively) and those which involve the removal of unwanted material from the solution (e.g. the clarification of sugar solutions with activated charcoal). Adsorption processes are very important in chromatography, too.

The theoretical treatment of adsorption from solution is general, complicated since this adsorption always involves competition between solute(s) and solvent. The degree of adsorption at a given temperature and concentration of solution depends on the nature of adsorbent, adsorbate and solvent. Adsorption from solution behaviour can often be predicted qualitatively in terms of the polar/ nonpolar nature of the solid and of the solution components. A polar adsorbent will tend to adsorb polar adsorbates strongly and non-polar adsorbates weakly, and vice versa. In addition, polar solutes will tend to be adsorbed strongly from non-polar solvents (low solubility) and weakly from polar solvents (high solubility), and vice versa.

Experimentally, the investigation of adsorption from solution is comparatively simple. A known mass of adsorbent solid is shaken with a known volume of solution at a given temperature until there is no further change in the concentration of supernatant solution. This concentration can be determined by a variety of methods involving colorimetry, spectrophotometry, refractometry, surface tension, also chemical and radio-chemical methods where it is appropriate. The apparent amount of solute adsorbed per mass unit of adsorbent can be determined from the change of solute concentration in the case of diluted solution. The specific adsorbed amount can be calculated as follows:

\[
a = \frac{V}{m} \left( c_0 - c \right)
\]

(1)
where \( a \) is the specific adsorbed amount (mg/g) at constant volume, \( V \) is the volume of solution (dm\(^3\)), \( m \) is the mass of adsorbent (g), \( c_0 \) and \( c \) are the initial and equilibrium concentrations (mg dm\(^{-3}\)) of dissolved substance, respectively. In many practical cases it is found that the adsorption obeys an equation known as the Langmuir isotherm. This equation was derived for adsorption of gases on solids and assumes that:

1. the adsorption is limited to monolayer
2. and occurs on a uniform surface; i.e. all “sites” for adsorption are equivalent,
3. adsorbed molecules are localized,
4. there is no interaction between molecules in a given layer; independent stacks of molecules built up on the surface sites.

The Langmuir equation may be written as follows:

\[
a = \frac{a_m c}{1/b + c}
\]  

(2)

where \( a_m \) is the monolayer capacity or the amount adsorbed at saturation, \( c \) is the equilibrium concentration of solute and \( b \) is constant. The monolayer capacity can be estimated either directly from the actual isotherm or indirectly by applying the linear form of the Langmuir equation which is given by:

\[
\frac{c}{a} = \frac{c}{a_m} + \frac{1}{b a_m}
\]  

(3)

A plot of \( c/a \) against \( c \) must be a linear line with a slope of \( 1/a_m \) The surface area of the solid (usually expressed as square meters per gram) may be obtained from the derived value of \( a_m \) provided that the area occupied by the adsorbed molecule on the surface is known with reasonable certainty.

\[
A_{\text{surface}} = a_m N_A \phi_m
\]  

(4)

where \( N_A \) is Avogadro’s number and \( \phi_m \) is the cross-sectional area of an adsorbed molecule. Recall that the surface area determined by this method is the total area accessible to the solute molecules. If these are large (e.g. dyestuffs, long chain molecules) they may not penetrate the pores and cracks, and the area obtained may be only a fraction of the true surface area of the solid.
**Apparatus**
Spectrophotometer with 1 cm cells, volumetric flasks, beakers, volumetric pipettes, burette, measuring cylinder, laboratory vibrator

**Chemicals**
Adsorbent (aluminum oxide), dye solutions (indigo-carmine).

**Experimental procedure**
Prepare a concentration series of indigo carmine solutions from the stock solution and water in 50 cm³ volumetric flasks. Suggested concentrations are $1.0 \times 10^{-4}$, $1.5 \times 10^{-4}$, $2.0 \times 10^{-4}$, $2.5 \times 10^{-4}$, $3.0 \times 10^{-4}$, $4.0 \times 10^{-4}$ mol/dm³. From each of these solutions around 10-20 cm³ are required for the determination of the calibration curve and 25.00 cm³ for the determination of the adsorbed amount.

Clean six 250-ml Erlenmeyer flasks which should either have glass or rubber stoppers. Place $0.05000 \pm 0.0050$ g of aluminum oxide (weighed accurately between 0.0450 g and 0.0550 g to the nearest milligram in a weighing dish or on a weighing paper) into each flask. To each flask add accurately with a pipette 25-25 cm³ indigo carmine solution from the concentration series previously prepared and put the flasks on the laboratory shaker for at least 1 hr. While the solutions are being shaken, measure the absorbance $A$ of each calibrating solution with the spectrophotometer, then plot the absorbance values versus the respective concentration values. Draw the $A=f(c)$ curve (the calibration curve) which is the best fitting straight line passing through the data points.

<table>
<thead>
<tr>
<th>$c_0$, mol dm⁻³</th>
<th>0</th>
<th>$1.0 \times 10^{-4}$</th>
<th>$1.5 \times 10^{-4}$</th>
<th>$2.0 \times 10^{-4}$</th>
<th>$2.5 \times 10^{-4}$</th>
<th>$3.0 \times 10^{-4}$</th>
<th>$4.0 \times 10^{-4}$</th>
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<tbody>
<tr>
<td>$A$</td>
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</table>

After shaking the aluminum-oxide should be removed by sedimentation, letting the solutions to stand undisturbed on the bench for at least 5 minutes. Samples to be measured have to be taken with a 3 ml plastic pipette from the upper layer of the liquid, without disturbing the precipitated alumina. Measure the absorbance of the equilibrium solutions with the spectrophotometer. Determine the equilibrium concentrations with the aid of the calibration curve, see figure 1.
Figure 1. Determination of the equilibrium concentration of solutions after adsorption with the aid of the calibration curve (absorption vs. concentration).

**Calculation of results**

Calculate the adsorbed amounts with the equation (1). Fill in the table below! Plot the linearized form of Langmuir equation (3). Determine the slope of the line and calculate the $a_m$ monolayer capacity. Calculate the specific surface area of the adsorbent (equation 4); the area occupied by an indigo-carmine molecule on the surface is 1.34 nm$^2$ (recall that 1 nm = 10$^{-9}$ m).

<table>
<thead>
<tr>
<th>$c_0$ (mol/L)</th>
<th>1.0×10$^{-4}$</th>
<th>1.5×10$^{-4}$</th>
<th>2.0×10$^{-4}$</th>
<th>2.5×10$^{-4}$</th>
<th>3.0×10$^{-4}$</th>
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<tbody>
<tr>
<td>$A$ after adsorption</td>
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<tr>
<td>$c$ (mol dm$^{-3}$) after adsorption</td>
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<td>$m$ (g): mass of adsorbent</td>
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<tr>
<td>$a$ (mol/g): specific adsorbed amount</td>
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<tr>
<td>$c/a$ (g dm$^{-3}$)</td>
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</table>
Review questions

Definition of the adsorption. Isotherm types and the Langmuir isotherm.
5. Solubilization

Theory

It is widely observed that soluble amphipathic substances, both ionic and nonionic, show sharp changes in a variety of colligative physical chemical properties at a well-defined concentration which is characteristic to the solute in question. These phenomena are attributed to the association of solute molecules into clusters known as micelles. The concentration at which micellization occurs is known as the critical micelle concentration, generally abbreviated CMC. Figure 1 shows the superpositioned curves for a variety of properties (such as surface tension, electrical, specific and molar conductance, freezing-point depression, osmotic pressure, turbidity) versus concentration for sodium dodecyl sulfate solutions. Another interesting property of micelles is their ability to solubilize materials which otherwise are insoluble in aqueous solutions. Insoluble organic matter, for example, may dissolve in the interior of the micelle even though it shows minimal solubility in water. Certain oil-soluble dyes barely color water, but give vividly colored solutions above the cmc. This solubilization of organic molecules in micelles is known to play an important part in the process of emulsion polymerization.

Figure 1. Schematic illustration of a variety of properties (κ conductivity, π osmotic pressure, τ turbidity, γ surface tension, and λ equivalent conductivity) of sodium dodecyl sulfate versus concentration.

In discussing micellization, we have intentionally restricted attention to concentration near to cmc where the micelles are fairly symmetric in shape and they are far enough from each other.
to be treated as independent entities. At higher concentration, neither of these concentrations are met and more complex phase equilibria must be considered.

![Figure 2](image_url)

Figure 2. Pictorial representation of conformation of surfactant molecules (monomers) in a solution. Above the CMC concentration (a) micelles are formed. At higher surfactant concentration, the amphiphiles form a variety of structures, here illustrated with (b) a liquid crystalline lamellar single phase and (c) reversed micelles, an isotropic single phase.

The critical micelle concentration depends on the solvent (generally water), the structure of surfactant molecules, the salt concentration and the temperature. For charged micelles, the situation is complicated by the fact that the micelle binds a certain number of counterions with the remainder required for electroneutrality distributed in an ion atmosphere surrounding the micelle. The data show that as the salt concentration increases, the cmc decreases, the degree of aggregation increases, and the effective percent ionization decreases. The cmc of a nonionic surfactant generally decreases and the size of micelles increases with increasing temperature because of the decrease of solvation (hydrogen bond) with the temperature. The solubility of ionic surfactants shows a rapid increase from a certain temperature known as the Krafft point.

The study of solubilized systems obviously starts with the determination of concentration of solubilizate which can be incorporated into a given system with the maintenance of a single isotropic solution. This saturation concentration of solubilizate for a given concentration of surfactant is termed the maximum additive concentration, which shows the solubilization ability of the surfactant for the given solubilizate. The maximum additive concentration increases with increasing surfactant concentration. Above the maximum additive concentration a second phase of the matter appears. The maximum additive concentration or the solubilized amount depends on the hydrophilic-hydrophobic character of the organic matter. The organic molecule, depending on its structure, takes place in the micelle according to the equalization of polarities (Hardy-Harkins principle).
Apparatus

Volumetric flasks, beakers, volumetric pipettes, burette, magnetic stirrer or shaker.

Chemicals

Non-ionic surfactant (e.g. Tween 20 or 40), organic acids (e.g. salicylic acid, benzoic acid or dodecanoic acid), 0.02 M NaOH solution, absolute alcohol.

Experimental procedure

Prepare about 5% stock solution from 2.5 g surfactant in a 50 cm³ volumetric flask. Dilute from the stock solution 50-50 cm³ surfactant solutions with concentrations of 2%, 1%, 0.5%, 0.2%, 0.1% and 0% (carefully homogenize the solution to prevent foaming). Pour 50 cm³ from each solution into iodine value flasks and add approximately 0.5-0.5 g organic acid into each of these flasks. It is very important to grind the acid to a fine powder in a mortar before adding it to the flask. Place the flasks on the magnetic stirrer for 1 hour then separate the insoluble organic acid from the solution by filtration. Prepare 6 fluted folded filter papers for the filtration. Pipette 10-10 cm³ aliquots from the equilibrium solutions into Erlenmeyer flasks then add 5-5 cm³ of propanol and 2-3 drops of phenolphthalein indicator to each flask. Titrate the solutions with 0.02 M sodium hydroxide until the color of the solutions becomes pale pink.
**Calculation of the results**

Based on the titration, calculate the amount of acid (in grams) solubilized in 10 cm³ of surfactant solution. Plot the calculated amounts (in \( g_{\text{acid}}/10 \text{ cm}^3 \)) as a function of surfactant concentration (in \( g_{\text{Twee}}/10 \text{ cm}^3 \)) and fit a linear function to the experimental points. Determine the slope and the intersection of the line. The slope gives the amount of acid solubilized by 1 g of surfactant (\( g_{\text{acid}}/g_{\text{Twee}} \)).

<table>
<thead>
<tr>
<th>Surfactant concentration (%)</th>
<th>0</th>
<th>0.1</th>
<th>0.2</th>
<th>0.5</th>
<th>1.0</th>
<th>2.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surfactant concentration (g/10 cm³)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Added NaOH solution (ml/10 cm³)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Titrated acid (g/10 cm³)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

![Graph](image)

**Figure 3. Solubilized organic acid as a function of Tween amount**

**Review questions**

What is solubilization? What kind of ionic and non-ionic surfactants do you know?
6 Determination of size distribution of a sedimenting suspension

Theory
The size of a spherical homogeneous particle is unequivocally defined by its diameter. When the particle is irregular additional parameters are needed to correctly define its size. With some irregular particles so called derived diameters are determined by measuring a size-dependent property of the particle and relating it to a linear dimension. The most widely used of these are the equivalent spherical diameters. If an irregular shaped particle is allowed to settle in a liquid, its terminal velocity may be compared with the terminal velocity of a sphere of the same density settling under similar conditions. The size of the particle is then equated to the diameter of the sphere. That is to say we use the diameter of some consubstantial sphere that has the same sedimentation rate as the particle measured to represent the dimension of the actual particle. In the laminar flow region, the particle moves with random orientation, the free-falling diameter becomes the Stokes diameter.

Average diameters. The purpose of the average is to represent a group of individual values in a simple and concise manner in order to obtain an understanding of the group. It is important, therefore that the average should be representative of the group. All average diameters are a measure of central tendency which is unaffected by the relatively few values in the tails of distribution. The most commonly occurring values are the mode, mean and median. The mode the value at which the frequency density curve shows a maximum. For the mean:

\[ x = \frac{\sum xd\phi}{\sum d\phi} \], where \( \phi \) is the frequency function. \( \phi = \sum dN \) for a number distribution; \( \phi = \sum dW = \Sigma x^3 dN \) for a volume or weight distribution. The median is the value of 50 % frequency.
The principle of the sedimentation is the determination of the rate at which particles settle out of a homogeneous suspension. This may be determined by allowing the sediment to fall on to a balance pan and weighing it. In a sedimentation cylinder $h$ is the height of suspension above the balance pan in meter; the weight per cent $P(t)$ which has settled out at time $t$ is made up of two parts; $W$ consists of all particles with a free-falling speed greater than that of $r_{Stk}$ as given by Stokes’ law, where $r_{Stk}$ is the size of particle which has a velocity of fall $h/t$; the other consist of particles smaller than $r_{Stk}$ which have settled because they started off at some intermediate position ($h^*<h$) in the fluid column.
\[ v = \frac{h}{t} = \frac{2r^2(\rho - \rho_0)g}{\eta} \quad \text{hence} \quad r_{stk}^2 = \frac{9}{2} \frac{\eta h}{(\rho - \rho_0)gt} \quad \text{hence} \]

\[ r_{stk} = \sqrt{\frac{\text{cons}}{t}} ; \quad \text{cons} = \frac{9}{2} \frac{\eta h}{(\rho - \rho_0)g} \]  

(1)

Where \( r \) is radius of particles in meter; \( \rho \) and \( \rho_0 \) are the densities of the particle and medium; \( h \) is the height of suspension in meter; \( t \) is the time of the settling in second; \( \eta \)=0.001 Pas is the viscosity; \( g=9.81 \text{ m/s}^2 \). It can be shown that part of the smaller particles is \( t \frac{dP}{dt} \), so

\[ P(t) = W + t \frac{dP}{dt} \]  

(2)

Since \( P \) and \( t \) are known, it is possible to determine \( W \) using this equation by graphical differentiation as Figure 2 shows.

\[ \text{Figure 2. Determination of weight percentage oversize, } W(r) \text{ from a graph of weight of powder sedimented, } P(t) \text{ against time, } t. \]

\[ \text{Figure 2. Cumulative } W(r) \text{ and differential } \frac{dW}{dr} (r) \text{ distribution functions} \]

**Apparatus**

Sedimentation cylinder, sedimentation balance

**Chemicals**

4 g powder, deionized water

**Experimental procedure**

Measure the distance between the two signs on the sedimentation cylinder (the height of water column \( h \) in meters), then fill the cylinder with distilled water up to mark. Place the cylinder below the balance and hook up the balance pan to the balance. Start the Sediment program on the computer then zero the balance with the zero button. Add about 4 g of powder into the water, stir the suspension and let it about 10 minutes to wet. Stir the suspension thoroughly moving the balance pan up and down, put the cylinder to its place as fast as you can, set the
hook of the pan and start the sedimentation. The computer program read the settled weight ($P_t$, cg) against time ($t$). It is necessary to measure until the majority of the powder has settled out onto the balance pan, this can be assumed to happen when the weight doesn’t change for about 5-10 minutes. The last value is the maximum weight $P_{t=\infty}$ or 100%.

**Save the data and open it in excel.**

<table>
<thead>
<tr>
<th>$h$ (m)</th>
<th>$P_\infty$ (cg)</th>
<th>$\rho_{\text{medium}}$ (kg m$^{-3}$)</th>
<th>$\rho_{\text{solid}}$ (kg m$^{-3}$)</th>
<th>$\eta$ (Pa·s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1000</td>
<td>2600</td>
<td>0.001</td>
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</table>

**Calculation of the results**

<table>
<thead>
<tr>
<th>$t$ (s)</th>
<th>$r$ (m)</th>
<th>$W$ (%)</th>
<th>$t$ (s)</th>
<th>$r$ (m)</th>
<th>$W$ (%)</th>
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Plot the weight of settled suspension as a function of time, $P(t)$ in %. Determine the weight percentage oversize, $W(t)$ by graphical differentiation (see figure 1) from the $y$ axial intercepts of the tangents by 50 s scale units. Calculate the radius from the given times with Stokes’ law and fill the table above. Plot $W(r) = f(r)$ the cumulative percentage frequency curve (integral size distribution function). Determine the most commonly occurring value of particle size from the point inflexion of function of $W(r) = f(r)$, read particle sizes at the 16%; 50% and 84%; see Figure 2. Determine the difference between the size $r_{50\%}$ - $r_{84\%}$ and $r_{16\%}$ - $r_{50\%}$.

**Discuss the results**
Review questions
What is the Stokes’ radius? What is the advantage and disadvantage of this method? Characterize the normal distribution.
7. Characterization of substances of different rheological properties by Brookfield DV-II+ rotational viscosimeter

The theoretical background of rheology can be found in the description of Exercise 1 (Rheological characterization of concentrated emulsions) and in the Appendix. Please read the mentioned sections to prepare yourself for the short test.

**Principles of the measurement:**
The rheological properties of substances are studied in viscosimetry by rotating spindles. The studied substance exerts rolling friction toward the rotation of the spindle (cylinder), by this way reducing the rate of rotation. The rolling friction can be characterized by the strength of the friction or by the shear stress ($\tau$), that is a portion of strength of friction referred to the unit of area of the spindle. The cylinder can be rotated at different angular velocity and the related shear stress values can be determined. The spindle is connected to the rotatory shaft through a spiral spring driven by a synchronous motor. The rotation of the rotatory shaft is transferred to the spindle through the spiral spring. In the presence of viscous media the spring is stretched (wounded) due to the inertia of the spindle.

The viscometer measures the torque necessary to overcome the viscous resistance to the induced movement. The degree to which the spring is wound or deflected is proportional to the viscosity of the fluid. The spring deflection is measured with a rotary transducer. The revolutions per minute ($RPM$) of the rotatory shaft can be adjusted between 0 and 100 RPM through gears. The velocity gradient is proportional to the angular velocity of the motor.

**Execution of the measurements**
Switch on the rheometer with the switch at the back. Remove any spindle if mounted, then press any key. After the automatic zero, choose the appropriate spindle and mount it to the end of the shaft. For this procedure ask for the help of the instructors.

Mounting the spindle: fix the shaft with one hand, screw on the spindle (it is left-hand thread!), check the fixing.
Write the number of the spindle in your report sheet. When installing the spindle first immerse it to the sample, avoiding to hit it to the walls of the container. The beaker should be positioned so that the spindle is in the middle, and the spindle should be immersed below the surface of the sample by the mark on it. After this press any key on the instrument again.

When choosing the proper spindle for a measurement, the goal is that the viscosimeter torque, α displayed in % should be between 10 and 100. When the torque is greater then 100, EEEE overflow signal is displayed.

To start the measurements, chose the proper speed with the up and down arrows using table 1. When the speed is chosen, push set speed button until the RPM is flashing on the screen to apply the speed. After the measurement of the samples is started, always wait for the stabilization of α before reading the signal, then set the next speed. Ask for the help of the instructors to change the spindles for the next sample.

Necessary equations for the calculations:

\[
\eta \text{ (mPas)} = 100 \times TK \times SMC \times SRC \times \alpha / D
\]  

(1)

\[
D \text{ (s}^{-1}) = RPM \times SRC
\]  

(2)

\[
\tau \text{ (N m}^{-2}) = TK \times SMC \times SRC \times \alpha
\]  

(3)

Where α is the torque given in %, RPM is the revolutions per minute, TK is spring strength (for spindles of RV type it has the value of 1), SMC gives the viscosity equal to 1 unit of scale, SRC (Spindle Rate Constant) is a constant characteristic related to the geometry of the spindle (for cylindrical spindles it can be calculated or it is given in charts, otherwise take it to be 1).

<table>
<thead>
<tr>
<th>spindle data :</th>
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<tbody>
<tr>
<td>LV type*</td>
</tr>
<tr>
<td>TK=0.09373</td>
</tr>
<tr>
<td>Code</td>
</tr>
<tr>
<td>SMC</td>
</tr>
<tr>
<td>SF<em>N=100</em>SMC</td>
</tr>
<tr>
<td>*in 600 ml beaker</td>
</tr>
<tr>
<td>RV type *</td>
</tr>
<tr>
<td>TK=1</td>
</tr>
<tr>
<td>Code</td>
</tr>
<tr>
<td>SMC</td>
</tr>
<tr>
<td>SF<em>N=100</em>SMC</td>
</tr>
<tr>
<td>TK=1</td>
</tr>
<tr>
<td>Code</td>
</tr>
<tr>
<td>SMC</td>
</tr>
<tr>
<td>SF<em>N=100</em>SMC</td>
</tr>
<tr>
<td>TK=1</td>
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<tr>
<td>Code</td>
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<td>SMC</td>
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<tr>
<td>SF<em>N=100</em>SMC</td>
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<tr>
<td>SRC</td>
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<tr>
<td>SF<em>N=100</em>SMC</td>
</tr>
<tr>
<td>SRC</td>
</tr>
</tbody>
</table>

1 cP=1mPas
Samples to be measured:

1. **Rheological study of 10% wallpaper paste (Na carboxymethylcellulose)**

Before the start of the measurement, homogenize the sample by rotating the chosen spindle at 100 RPM for 5 minutes, after that wait for 10 minutes at 0 RPM to let the sample regain its unstrained structure. Thereafter, determine the torque values of the wallpaper paste at increasing and decreasing RPM values following the instructions given earlier. For data recording and evaluation, use table 1.

2. **Rheological study of honey sample**

Repeat the previous measurement with the honey sample using the appropriate spindle. For data recording and evaluation, use table 1.

3. **Rheological study of 2.5% PVA (polyvinyl alcohol)–borax mixture**

Repeat the previous measurement with the PVA–borax mixture using the appropriate spindle. For the homogenization of the sample use 60 RPM instead of 100 RPM. For data recording and evaluation, use table 1.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Sample:</th>
<th>Spindle:</th>
<th>SMC:</th>
</tr>
</thead>
<tbody>
<tr>
<td>RPM (1/min)</td>
<td>α (%)</td>
<td>D (1/s)</td>
<td>τ (Pa)</td>
</tr>
<tr>
<td>0.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.6</td>
<td></td>
<td></td>
<td></td>
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<td>30</td>
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</tbody>
</table>
After all of the measurements have been performed, plot the viscosity curves $\eta = f(\tau)$ and flow curves $D = f(\tau)$ of the samples. The data points measured at increasing and decreasing RPM values should be plotted in the same graph (Thus you have to submit 6 graphs altogether). Determine the rheological class of the samples using figure 1 in Exercise 1. Decide if there is any hysteresis or not in the curves and give an explanation for these observations (see Exercise 1).

**Interpret the results.**
8. Steric and electrostatic stabilization mechanisms of colloidal dispersions

Theory

DVLO theory suggests that the stability of a colloidal system is determined by the sum of the van der Waals attractive (VA) and electrical double layer repulsive (VR) forces that exist between particles as they approach each other due to the Brownian motion. This theory proposes that an energy barrier resulting from the repulsive force prevents two particles to approach one another and to adhere. But if the particles collide with sufficient energy to overcome that barrier, aggregation may start.

DVLO theory assumes that the stability of a particle in solution is dependent upon its total potential energy function \( V_T \).

Lyophobic colloids can be stabilized kinetically by electrostatic or steric ways. In case of *electrostatic stabilization*, the repulsion of surface charges of sol particles hinder the frequent collision of particles, by this way the extent of sol aggregation is reduced. The surface charge depends on the property and quantity of positive and negative ions present in the solution, since the adsorption of different kind of ions to the surface of sol particles is variant. If the composition of the solution is such that the surface charge of colloid is zero (point of zero charge), the electrostatic repulsion ceases to exist and the coagulation of the sol is accelerated. Any increase in surface charge in whichever direction hinders the aggregation.

In case of *steric stabilization* the material adsorbed to the surface of the colloid particles (usually some kind of macromolecule or surfactant) *hinders* the direct contact of sol particles and by this way the aggregation, as well. If the macromolecule is adsorbed to the surface only in small concentration (thus one macromolecule is in connection with more than one sol particle), in contrast with the previously mentioned protecting effect, the sol particles will be *sensitized* to coagulation due to the so-called bridging flocculation mechanism.
Electrostatic (a) and steric stabilization (b) mechanisms of colloidal dispersions, and bridging flocculation (c).

The charge which is carried by surface determines its electrostatic potential. For this reason they are called the potential-determining ions. We can calculate the surface potential on the crystals of silver halids by considering the equilibrium between the surface of charged crystal and the ions in the surrounding solution:

$$\psi_0 = \frac{kT}{ze} \left( \ln a - \ln a_{pzc} \right)$$

For the ions involved:

$$\psi_0 = 60 \times (\log a_{Ag} - \log a_{Ag,pzc}) \quad \text{and} \quad \psi_0 = -60 \times (\log a_{Cl} - \log a_{Cl,pzc})$$

where $\psi_0$ is the surface potential, $a$ is the activity of the potential-determining ion (for dilute solutions $a \approx c$), $a_{ion,pzc}$ is the ion activity at the point of zero charge.

$\log a_{Ag,pzc} = -4.5$ ($[Ag_{pzc}] \approx 2.9 \times 10^{-5}$ M) and $\log a_{Cl,pzc} = -5.2$ ($[Cl_{pzc}] = 6.3 \times 10^{-6}$ M) and the solubility product for AgCl is $K_{sp} = 1.8 \times 10^{-10}$ mol$^2$ dm$^{-6}$.

**Chemicals**

0.05% PVA solution, 0.01 M AgNO$_3$ and 0.01 M KCl solution, deionized water.
The apparatus and experimental procedure

Cary 3 spectrophotometer, glass tubes, pipettes, optical cuvette.

Prepare 5.00-5.00 cm³ of solutions A and B according to the table below in polypropylene tubes equipped with caps. Take care of the proper use of automatic pipettes. If you are uncertain, feel free to ask for the help of the supervisors. After all of the components of the 6-6 A and B solutions are measured together, seal the tubes and mix their content thoroughly. Don’t mix the respective A and B solutions together, they have to be mixed in the cuvets inside the spectrophotometer.

<table>
<thead>
<tr>
<th>Solution number</th>
<th>Solution A</th>
<th>Solution B</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.05% PVA</td>
<td>0.01 M Cl</td>
</tr>
<tr>
<td>1</td>
<td>1.00 cm³</td>
<td>1.00 cm³</td>
</tr>
<tr>
<td>2</td>
<td>0.05 cm³</td>
<td>1.00 cm³</td>
</tr>
<tr>
<td>3</td>
<td>–</td>
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</tr>
<tr>
<td>4</td>
<td>–</td>
<td>1.10 cm³</td>
</tr>
<tr>
<td>5</td>
<td>–</td>
<td>0.95 cm³</td>
</tr>
<tr>
<td>6</td>
<td>–</td>
<td>0.90 cm³</td>
</tr>
</tbody>
</table>

Brief outline how to perform the measurements:

- Turn on the computer, then run the „Kinetics” module in the „Cary WinUV” folder
- Turn on the spectrophotometer with the red ON/OFF switch then turn on the thermostat as well.
- Under the „Kinetics” mode load „1cell-10m.MKN” (in the folder C:\Varian2\Cary WinUV2\Pharmacist)
- Place a PMMA cuve filled with deionized water to location 1 of the 6-cell sample holder of the spectrophotometer. Take care to place the cuvette with proper orientation. The triangle on the clear side of the cuvette should point to the right. Close completely the lid of the cuvette compartment.
- By clicking on the „Zero” button on the screen, the initial absorbance of the cuvette+solvent is set to zero
- Pour out the water from the cuvette thoroughly (it is not a problem when one or two small droplet remains), then pipette 1.5 cm³ of solution A to the cuvette.
- As soon as the temperature of the cuvette compartment is stabilized at 25.0 °C, start
the measurement with the „Start” button (leave the lid of cuvette compartment open).

- First give the sample name, then give the file name. After pressing OK, a 2 min countdown starts, the data acquisition will only starts at 0 min or when pressing OK.
- During the countdown pipette 1.5 cm³ from the corresponding solution B to the cuve placed in the photometer. Try to add the solution quickly, then mix it by drawing back and forth in the cone of the pipette, finally empty completely the contents of the pipette tip into the cuve. When ready, close immediately the lid of sample compartment and press enter to start the data collection.
- After the measurement wash the cuvette with deionized water.
- Repeat the measurement with the other solution pairs in the table, respectively.
- The six absorbance-time data pairs should be plotted in one graph in excel. For data transfer ask for help of the supervisors

<table>
<thead>
<tr>
<th>Solution No.</th>
<th>$c_{Ag}$</th>
<th>$\Psi_0$</th>
<th>Observation</th>
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<tbody>
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<td>1</td>
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**Discuss the results**

Compare and discuss the colloid stability of the six different AgCl sols. Calculate the surface potential of these sols and try to explain the results observed in the absence and the presence of PVA.

**Review questions**

Definition of the point of zero charge. What kind of relation is between the colloid stability and the zeta potential of lyophobic colloids? What is the origin of the charge of silver halide sols? What is the charge of silver chloride synthesized from stoichiometric quantities of Ag⁺ and Cl⁻?
9. Determination of the critical micelle concentration of SDS

Theory
Surfactants are amphiphilic molecules that possess both hydrophobic and hydrophilic properties. A typical surfactant molecule consists of a long hydrocarbon ‘tail’ that dissolves in hydrocarbon and other non-polar solvents, and a hydrophilic ‘headgroup’ that dissolves in polar solvents (typically water). Amphiphilic molecules can be found in a wide range of chemical structures, e.g. one or two hydrophobic chains as well as cationic, anionic or neutral polar heads. Anionic head groups are commonly found in soaps, as the strongly hydrophilic carboxyl and sulphonate groups increase their solubility in water. On the other hand, cationic head groups exhibit anti-bacterial properties, which find use in mild antiseptics and disinfectants.

If these molecules are dissolved in water, a large amount of solvent molecule is needed to keep them in the solution since the secondary interaction between the hydrophobic part and the water molecules is quite week. As a consequence less water molecules remain in the bulk solvent to form dipole-dipole interactions and H-bonds (entropy effect). Thus increasing the concentration of the surfactants, a point is reached where the formation of these hydrated molecules are not favorable considering the Gibbs free energy. At this particular concentration, which depends on the physical-chemical properties of both the surfactant and the solvent and the temperature, they have a tendency to form aggregates spontaneously, that is, surfactant molecules will arrange themselves into organized molecular assemblies, also called normal micelles. Above this concentration – which is called Critical Micelle Concentration (cmc) – the solvent molecules are excluded from the hydrophobic chains while the micelle “surface” becomes polar, hereby the solubility of the micelle is better than the monomeric species. Therefore less solvent molecule is needed for the solvation so the entropy of the bulk solution increases. The shape and size of a micelle is a function of the molecular geometry of its surfactant molecules and solution conditions such as surfactant concentration, temperature, pH, and ionic strength. Increasing the surfactant concentration the number of particles changes due to the micelle formation, the colligative properties, such as surface tension, conductivity, boiling point, osmotic pressure, etc. show a break around the cmc.
**Conductometric Determination of the cmc**

Below the cmc, the addition of ionic surfactant to an aqueous solution causes an increase in the number of charge and consequently, an increase in the conductivity. Above the CMC, further addition of surfactant increases the micelle concentration while the monomer concentration remains approximately constant (at the cmc level). Since a micelle is much larger than a monomer, it diffuses more slowly through solution and so it is a less efficient charge carrier. Thus, a plot of conductivity against surfactant concentration is expected to show a break around cmc.

**Apparatus:**
Consort multiparameter analyzer,
magnetic stirrer rod,
pipettes, tall vessel

**Chemicals:**
0.1 M SDS (Sodium dodecyl sulphate, an anionic surfactant) stock solution, MilliQ deionized water

**Experimental procedure**
Measure between 50 and 55 cm$^3$ of distilled water (note the exact volume added) then put a magnetic stirrer rod into a tall glass vessel. Wash the conductometric cell at least 3 times with fresh MilliQ water. As we want to measure only the conductivity change of the solution we do not need an accurate calibration. Put the vessel on the magnetic stirrer and immerse the electrode into the solution until the three black signs on the measuring cell get under the liquid surface. Switch on the stirrer and measure the conductivity of the distilled water. Switch on the Consort multiparameter analyser, and open the Data Information System software on the computer to registrate the measured values. Start data registration with the green button in the menu. This way you can manually save the measured value pressing the STORE button. Data will be registrated separately in two columns for the two electrodes. Measure 50-55 cm$^3$ of milliQ water to the measuring vessel. After measuring the conductivity of water, add given volumes of stock solution into the vessel, wait for the stabilization of the value and store the conductance. The displayed value shows up on the computer when the storage was successful. When you choose to plot the results manually on mm paper, add 0.4 cm$^3$ of stock solution 35 times. When you choose computer-aid data evaluation, add 0.2 cm$^3$ of stock solution 75 times. After the last reading please wash the glassware, the
sirring rod and the measuring cell accurately with distilled water and leave the electrode immersed in water. Fill the conductance values in the Table.

**Calculation:**
Calculate the derived conductivity ($\kappa'$), the molar conductivity ($\Lambda$) using the following equations:

$$\kappa' = \kappa_{\text{measured}} - \kappa_{\text{water}}$$

$$\Lambda = \frac{\kappa'}{c} \quad \text{(Calculate $\Lambda$ in SI units!)}$$

Plot the $c$-$\kappa'$ and $3\sqrt[3]{c}$-$\Lambda$ (Lottermoser-diagram) curves, find the breakpoints on the curves and calculate the CMC values from the two figures.

Determine the CMC value of SDS, and discuss it. (literature data: 0.008 mol dm$^{-3}$ at 25°C)

**Review questions**
What kind of ionic and non-ionic surfactants do you know? Define the critical micelle concentration! Describe the reasons of micelle formation!
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<th>$n$</th>
<th>$V_{\text{increments}}$ (cm$^3$)</th>
<th>$V_{\text{total added}}$ (cm$^3$)</th>
<th>$V_{\text{total}}$ (cm$^3$)</th>
<th>$c$ (mol dm$^{-3}$)</th>
<th>$c$ (mol m$^{-3}$)</th>
<th>$\kappa_{\text{measured}}$ (µS cm$^{-1}$)</th>
<th>$\kappa$ (µS cm$^{-1}$)</th>
<th>$\kappa$ (S m$^{-1}$)</th>
<th>$\sqrt[3]{c}$ (mol$^{1/3}$ m$^{-1}$)</th>
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Appendix

1. Basic concepts of rheology

Isaac Newton defined viscosity by considering the following model: two parallel planes of fluid of equal area “A” are separated by a distance “dy” and are moving in the same direction (x) at different velocities “v₁” and “v₂”. Newton assumed that the force required maintaining this difference in speed was proportional to the velocity gradient.

To express this, Newton wrote: \[ \frac{F}{A} = \eta \frac{dv}{dy} \] where \( \eta \) is a constant for a given material and is called its “viscosity”.

Rheological classification of materials

Fluids are normally divided into three different groups according to their flow behaviour:

**Newtonian fluids**

The viscosity of a Newtonian fluid is dependent only on temperature but not on shear rate and time.

Examples: water, milk, sugar solution, mineral oil.

**Non-Newtonian fluids, time independent**

The viscosity of a Non-Newtonian time independent fluid is dependent not only on temperature but also on shear rate.

Depending on how viscosity changes with shear rate the flow behaviour is characterized as:

- **shear thinning** or **pseudoplastic** - the viscosity decreases with increased shear rate
- **shear thickening** or **dilatant** - the viscosity increases with increased shear rate
- **plastic** - exhibits a so-called yield value, *i.e.* a certain shear stress must be applied before flow occurs

Examples of shear thinning fluids: paint, shampoo, slurries, fruit juice concentrates, ketchup,

Examples of shear thickening fluids: wet sand, concentrated starch suspensions

Examples of plastic fluids: tomato paste, tooth paste, hand cream, some ketchups, grease

**Non-Newtonian fluids, time dependent**

The viscosity of the fluid is dependent on temperature, shear rate and time.

Depending on how viscosity changes with time the flow behaviour is characterized as:

- **thixotropic** *(time thinning, *i.e.* viscosity decreases with time)* Examples: yoghurt, paint
- **rheopectic** *(time thickening, *i.e.* viscosity increases with time)* Examples: gypsum paste
Thixotropic fluids are quite common in chemicals as well as in food industry. Rheopectic fluids are very rare.

![Flow and viscosity curves of newtonian and non-newtonian time-independent fluids.](image)

1. ideal (newtonian), 2. shear thinning or pseudoplastic, 3. shear thickening or dilatant, 4. ideal plastic (Bingham type), 5. plastic (pseudo-plastic type), 6. plastic (dilatant type)

**Newtonian fluids.** The type of flow behaviour Newton assumed for all fluids is called, not surprisingly, “Newtonian”. It is, however, only one of several types of flow behaviour you may encounter. A Newtonian fluid is represented graphically in Figure 1, curve 1, which shows that the relationship between shear stress and shear rate is a straight line. In the other graph, curve 2 shows that the fluid’s viscosity remains constant as the shear rate is varied. What this means in practice is that at a given temperature the viscosity of a Newtonian fluid will remain constant regardless of which Viscometer model, spindle or speed you use to measure it. Newtonians are obviously the easiest fluids to measure – just grab your viscometer and go it. They are not, unfortunately, as common as that much more complex group of fluids, the non-Newtonians, which will be discussed in the next.

**Non-Newtonian fluids.** A non-Newtonian fluid is broadly defined as for which the relationship $\tau/D$ is not constant. In other words, when the shear rate is varied, the shear stress doesn’t vary in the same proportion (or even necessarily in the same direction). The viscosity of such fluids will therefore tend to change as the shear rate is varied. Thus, the experimental parameters of a Viscometer model, spindle and speed all have an effect on the measured viscosity called apparent viscosity of fluid, which is accurate only when explicit experimental parameters are furnished and adhered to.

Non-Newtonian flow is probably a mechanical proposition. As non-symmetrical objects pass by each other, as happens during flow, their size, shape, and cohesiveness will determine how much force is required to move them. At another rate of shear, the alignment of the objects may be different and more or less force may be required to maintain motion. By non-symmetrical objects, we refer to large molecules, colloidal particles, and other suspended materials such as clays, fibre, and crystals.
There are several types of Non-Newtonian flow behaviour, characterized by the way a fluid’s viscosity changes in response to variations in shear rate. The most common types of Non-Newtonian fluids you may encounter include:

**Pseudoplastic.** This type of fluid will display a decreasing viscosity with an increasing shear rate, as shown in Figure 1, curve 2. Probably the most common of non-Newtonian fluids, pseudoplastics include paints, emulsions, and dispersions of many types. This type of flow behaviour is sometimes called “shear-thinning”.

**Dilatant.** Increasing viscosity with an increasing shear rate characterizes the dilatant fluid. Although rarer than pseudoplasticity, dilatancy is frequently observed in fluids containing high levels of deflocculated solids, such as clay slurries, corn starch in water, and sand/water mixtures. Dilatancy is also referred to as “shear-thickening” flow behavior (in Figure 1, curve 3). Plastic. This type of fluid will behave as solid under static conditions. A certain amount of force must be applied to the fluid before any flow is induced; this force is called “yield value”. Tomato ketchup is a good example of this type of fluid; its value will often make it refuse to pour from the bottle until the bottle is shaken or struck, allowing the ketchup to gush freely. Once the yield value is exceeded and flow begins, plastic fluids may display Newtonian, pseudoplastic, or dilatant flow characteristics. See Figure 1, curve 4-6. So far we have only discussed the effect of shear rate on non-Newtonian fluids.

**Emulsions and creams**

One of the major characteristics to study is the state of aggregation of the sample material. Many pharmaceutical and cosmetic processes such as new ingredient selections, formulation preparations, material packaging, and shelf storage are associated with a complex flow behavior of these materials. The application and acceptance of pharmaceuticals and cosmetics are also dependent on the flow properties of the final product. Therefore, rheological measurements, an important route to reveal the flow and deformation behaviors of materials, cannot only improve efficiency in processing but can also help formulators and end users find pharmaceutical and cosmetic products that are optimal for their individual needs. In general, rheological measurements on pharmaceutical and cosmetic materials are performed for the following reasons: 1) to understand the fundamental nature of a system; 2) for quality control of raw materials, final products, and manufacturing processes such as mixing, pumping, packaging, and filling; and 3) to study the effect of different parameters such as formulation, storage time, and temperature on the quality and acceptance of a final product. Pharmaceutical and cosmetic materials range in consistency from fluid to solid. Semisolid products are the most difficult materials to characterize rheologically because they combine both liquid and solid properties within the same material. The majority of pharmaceutical materials are ointments, creams, pastes, and gels—all
semisolids. To understand these complex flows, commercial medical creams, shampoos, and e.g. children’s cough syrup are generally tested by rheometry.