Synthesis and study of macroemulsions

Theoretical background: D. Fennell Evans, Hakan Wennerström: *The colloidal domain*, Chapter 11.3 (pp: 568-590), Wiley-VCH, 1999.
Type of practice: Pairwise.
Purpose of practice: Synthesis and characterization of macroemulsions, and the measurement of interfacial tension at different emulsifier concentrations across the oil – water interface.

1 Introduction

Emulsions have been defined as heterogeneous systems of one liquid dispersed in another in the form of droplets, where the two liquids are immiscible or partially miscible and chemically unreactive. It is common to name one of the liquid pairs (of apolar character) oil and the other one (polar) water. Since the diameter of the dispersed liquid drops is usually greater than 1 μm, these so-called macroemulsions are coarse dispersions. There are also emulsions containing droplets smaller than the above size, the so-called microemulsions, but in this practice we only deal with the investigation and properties of macroemulsions.

An emulsion can be prepared by dispersing a liquid in another one, e.g., by simply shaking two immiscible liquids together. A variety of mechanical techniques are available commercially for preparation of emulsions both on the laboratory and industrial scales (e.g., high-speed stirrers, colloidal mill and ultrasonic agitator). In theory, the amount of work required to break the liquids into droplets (w_e) is proportional to the interfacial tension between the two liquids (γ_{ow}) – oil (o) and water (w) - and to the specific surface area (a_S) calculated from the surface and mass of the dispersed droplets formed:

$$w_e = \gamma_{ov} \cdot a_S \ .$$

The work required to prepare emulsions can be reduced by using surfactants (emulsifiers or emulsifying agents), as they reduce the value of γ_{ow}. Unless emulsifying agent is present, the emulsions are unstable, and the liquids separate into two phases. Therefore, to maintain the sufficient stability, the use of emulsifiers is essential. These compounds are typically of amphiphilic character meaning that they possess a polar or hydrophilic (i.e., lipophobic or water soluble) part and a non-polar or hydrophobic (i.e., lipophilic or non-water soluble) part, thus they accumulate at the o/w interface, providing a continuous transition between the two phases. The emulsifying agent forms an adsorbed film around the dispersed droplets, therefore it decreases the interfacial tension and forms a barrier to hinder the coalescence of the globules. In this way, emulsifiers lower the interfacial tension between the oil and water phases, stabilizing the droplets and preventing them from coalescing. Surfactants, macromolecules (proteins) and solid grinds (surface modified clay minerals) can also act as emulsifiers.

1.1 Emulsion types

In all emulsions, there is a continuous phase that disperses the droplets of the other material, which is called the dispersed phase. In an oil-in-water emulsion (o/w), the continuous phase is the water and the dispersed phase is the oil, while in a water-in-oil emulsion (w/o) the oil is the continuous phase. The type of emulsion, which is formed once a given pair of immiscible liquids are homogenized, depends greatly on the physical-chemical properties of the emulsifier. The Hydrophilic-Lipophilic Balance (HLB) represents the oil and water solubility of an emulsifier and it can be used to classify them. Surfactants with an HLB value between 12–20 promote formation of o/w emulsions, while emulsifiers with an HLB value between 2–8 tend to induce the formation of w/o emulsions. The type of emulsions can be determined by the following methods:

***Dilution test*:**

It is based on the fact that each emulsion can be diluted with a liquid of the same or similar polarity as the liquid forming the continuous phase. It can be tested by putting a drop of emulsion into a test tube

containing water and oil separately and then, shaking gently. A drop of an aqueous emulsion dissipates completely in water, but continues to form a drop in oil. In the case of w/o emulsions, the situation is reversed.

***Colouring test*:**

In this probe, an emulsion is mixed with a water soluble dye (methylene blue) and observed macroscopically. If the continuous phase appears blue, it means that the emulsion is o/w type as water is in the continous phase and the dye will dissolve in it to give colour. If the dispersed globules appear blue and continuous phase colourless, then it is w/o type. Similarly, if an oil soluble dye (Sudan III) is added to an emulsion and the continuous phase appears to be red, then the emulsion is w/o type.

***Cobalt(II) chloride test*:**

For this test, one uses a filter paper, which is impregnated with an aqueous solution of 20 g/dm^3 $CoCl_2$ and dried in an oven at 80 °C. During such a thermal treatment, the pink hydrous $CoCl_2$ turns to the blue, which is the colour of its anhydrous form. If a few drops of o/w emulsion are added to the blue filter paper, a pink coloration can be seen on the back, which can be explained by the re-uptake of water by $CoCl_2$. If the emulsion is w/o type, only a yellow oil stain will appear on the back of the filter paper.

Probably the most important physical property of an emulsion is its stability. The term "emulsion stability" can be used with reference to three essentially different phenomena, creaming (or sedimentation), coagulation and breaking of the emulsion due to droplet coalescence (Figure 1.). Creaming originates from the density difference between the two phases, i.e., the liquid forming the dispersed phase is of lower density than the continuous phase. Emulsions are not thermodynamically stable systems, since reduction of the surface area of oil in contact with water will always result in coalescence of the droplets. Non-stabilized emulsions coalescence rapidly, while stabilized emulsions can retain a highly dispersed internal phase for months or years.

The type of emulsion, which tends to form, depends on the balance between the hydrophilic or lipophilic properties of the emulsifier. For example, in the case of surfactants, it depends on the HLB values. If the lipophilicity of the emulsifier (e.g., the HLB value of the surfactants) is modified, the character or type of the emulsion also changes. This process is called emulsion phase inversion. As stated by the Bancroft rule, the liquid, in which the emulsifier is more soluble, will be the continuous phase of the emulsion.

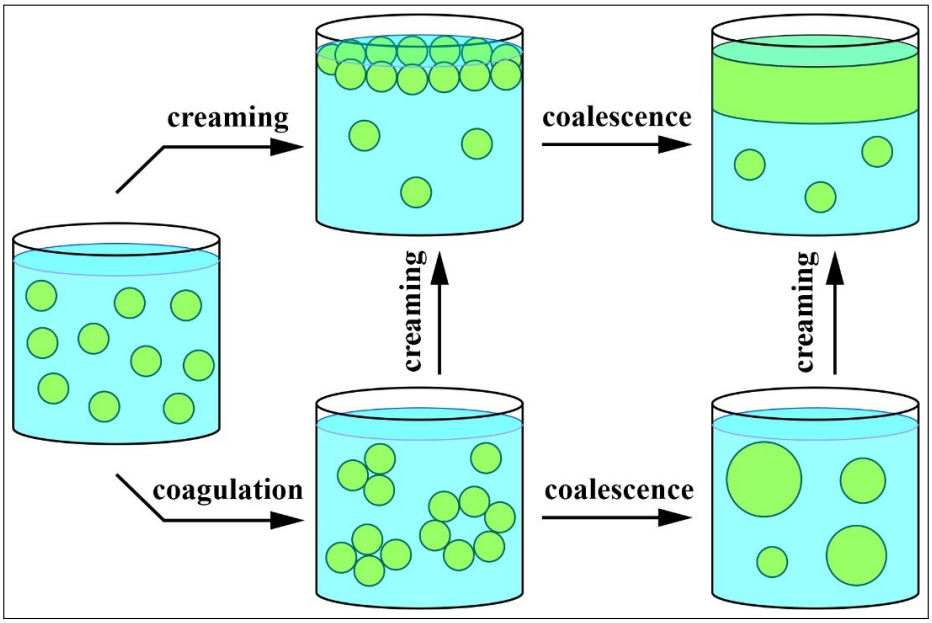

Figure 1: Possible scenarios for emulsion breakage.

For instance, the daily used general soaps (Na-soap) stabilize the o/w type emulsions, since it exhibits polar nature due to complete dissociation to Na+ cations and surfactant anions. However, if Na-soap is converted to Ca-soap by adding an appropriate amount of $CaCl_2$, phase inversion of the emulsion occurs due to the negligible dissociation of the Ca-surfactant compound and thus, the emulsion type will change to w/o.

1.2 Interfacial tension between two liquids

The interfacial tension between two non-miscible liquids is an important parameter for the characterization of the emulsion. It can be determined via drop counting method, for example. Since the decrease in the interfacial tension is a key factor in emulsification, sufficient methods to follow this quantity are necessary to apply. If one counts the drop number of an oil in water (n_0) and in an aqueous surfactant solution of a given concentration (n) and the pure water/oil interfacial tension ($\gamma_{ow,0}$) is given, the interfacial tensions can be calculated at the corresponding surfactant solution. The $\gamma_{ow,0}$ is 30 mN/m at the interface of vegetable oil and water. Since the density of dilute surfactant solutions does not differ significantly from the density of water, their quotient can be taken as $\sim$1 and hence, γ_{ow} can be calculated with the following relation:

$$\gamma_{ov} = \frac{n_0}{n} \cdot \gamma_{ov,0} \ .$$

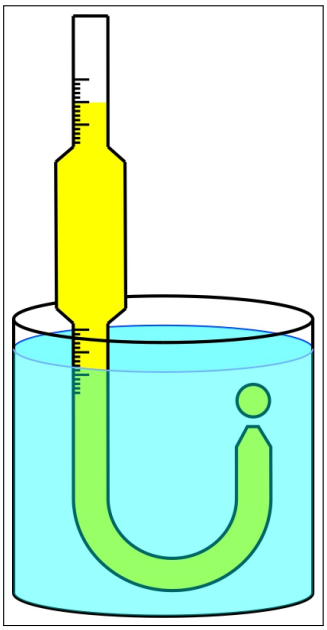

Figure 2: Schematic illustration of the Donnan pipette.

The above-mentioned drop numbers can be determined using Donnan pipette (Figure 2.). The principle of this method is the determination of the number of oil droplets, formed from equal volumes of the oil drawn into the pipette, in aqueous surfactant solutions of different concentrations. At the point the oil droplet is detached from the pipette, the buoyancy force is equal to the force acting due to the interfacial tension at the edge of the pipette.

2 Experimental procedure

Tasks 2.1 and 2.2 are performed by two students independently, using different surfactants given by the teaching assistant.

2.1 2.1. Effect of surfactant on oil/water interfacial tension

2.1.1 Implementation of the exercise

From one of the provided stock solutions (200 mmol/dm^3 NaDS (M_r=288,4), 50 mmol/dm3 NaDBS (M_r=348,5) or 50 mmol/dm^3 Na-oleate (Mr=304.5)), dilute a series of 8 samples of 250 cm^3 in the concentration range of 2–20 mmol/dm^3 (NaDS) or 0.2–5 mmol/dm^3 (NaDBS or Na-oleate). If there are no specific instructions, NaDS surfactant must be used. Choose the concentrations so that their logarithmic values vary nearly equally over the given range. This is necessary because the logarithm of the concentrations will be included in the evaluation. Prior to experimental work, all necessary calculations concerning the dilutions must be carried out and shown in the laboratory exercise book and the assistant must validate them. Start the measurement with distilled water and move from diluted solutions to more concentrated ones.

Fix the Donnan pipette - cleaned and dried previously - in the vertical position to a burette holder. Attach the infusion set to the top of the pipette. Immerse the Donnan pipette in the beaker containing the oil and

draw oil into the pipette to a level above the upper scale. Make sure that there are no air bubbles in the oil and that the oil does not enter the rubber tube. After the filling, close the tap, pull out the pipette by lowering the beaker, allow the oil to drain and carefully wipe off the excess with a paper towel. Do not touch the end of the pipette. Place a tall beaker containing 250 cm^3 of distilled water on the Bunsen stand and immerse the oil-filled pipette, so that the bended end should be 1.5–2 cm below the water level at the center of the beaker. Start the oil dropping by opening the infusion set and adjust the flow rate to a speed, when one drop forms in each 3–5 seconds.

Determine the number of oil droplets formed from the same volume of oil in water and in solutions with different surfactant concentrations. In each case, select scale sections of the Donnan pipette within the middle parts of the upper and lower scales, and then use them consistently for each measurement. Since it is unlikely that an integer number of drops will be formed from the same volume, the scale of the pipette must be calibrated, i.e., the relation between scale marks corresponding to 1 drop must be determined. During the drop counting, record the position of the meniscus at the beginning (upper scale) and at the end (lower scale) of the procedure, while counting how many whole drops were formed from the given volume of fluid. From the recorded upper and lower marks, use the above discussed calibration values to calculate the fraction of droplets. It is strongly advised that you consult with the teaching assistant regarding the proper use of the Donnan pipette.

The calibration and the drop counting can be performed in the same measurement. At the end of each experiment, close the infusion set roller, lower the beaker, and carefully wipe the pipette with a paper towel, then refill it with oil and repeat the measurement with distilled water, then measure the next sample. Unless the assistant orders otherwise, the droplet number in the surfactant solutions needs to be determined only once. The drop number increases with increasing surfactant concentration and a critical value can be obtained, at which the oil flows out of the pipette in a jet. This sample and the ones of higher surfactant concentrations can no longer be investigated by this method.

2.1.2 Evaluation of the measured data

- Observe the stability of the oil droplets floating on the surface of the solutions and in Table 1, give the approximate time (t), at which a continuous oil layer is formed from the individual droplets floating on the surface at a given surfactant concentration.
- Calculate the interfacial tension of the solutions at each surfactant concentration ($c_{surfactant}$) and summarize the measured and the calculated data in Table 1.
- Plot the obtained interfacial tension values as a function of the logarithm of surfactant concentration and interpret the observed changes. Based on the intersection of the obtained two fits performed on different sections of the graph, give the critical micelle concentration, above which the surfactant forms micelles.

Table 1: Summary of the measured and calculated data.

$c_{surfactant}$ (M)	$\lg\left(\frac{c_{surfactant}}{M}\right)$	n (db)	γ_{ow} (mN/m)	t (min)

2.2 Investigation of phase inversion of emulsions

2.2.1 Implementation of the exercise

Carefully clean the shaker measuring cylinder before the experiment, but do not use soap or detergent for cleaning, since these substances are emulsifiers and as a contaminant, their presence even in small amount leads to false results. Prepare one of the oil/aqueous soap mixtures in 15/35, 20/30 or 25/25 volume ratio

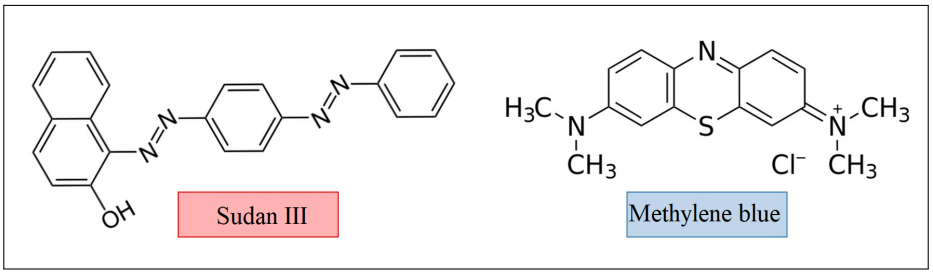

Figure 3: Chemical structure of Sudan(III) and methylene blue used for the colouring test.

(vegetable oil cm^3/aqueous surfactant solution (10 g/dm^3 Na-stearate or Na-oleate solution) cm^3) in the shaker cylinder. If there are no specific instructions, choose the 25/25 volume ratio and use Na-stearate. First, measure the aqueous phase directly into the mixing cylinder and then layer the vegetable oil on it. Prepare the emulsion by strong shaking.

Titrate the emulsion with the $CaCl_2$ solution in accordance with the calculation carried out in section 2.2.2 Start the titration with 1 cm^3 CaCl2 solution and then, near the calculated theoretical phase inversion point, use 0.5 cm^3 $CaCl_2$ doses. Continue the titration until phase inversion. After this titration point, add 1 cm^3 of titrant to the emulsion for final characterization.

Shake the cylinder after each $CaCl_2$ portion, then follow the change of emulsion type after 1–2 minutes of standing. Determine the nature of the emulsions. Unless otherwise specified by the assistant, the characterization test must be performed before the addition of the titrant, at each titration point and at the end of the titration. First use the colouring test (methylene blue and Sudan (III), Figure 3) and then the cobalt(II) chloride method. Make sure that you pipette only 1 drop of emulsion for the tests using a Pasteur pipette to keep appropriate volume of the sample in the mixing cylinder.

2.2.2 Evaluation of the measured data

- Considering the chemical reaction, calculate the volume of 0.1 mol/dm^3 $CaCl_2$ solution necessary to stoichiometrically form Ca-soap from Na-soap (either Na-stearate (M_r=306,5) or Na-oleate (M_r=304.5)).
- Based on the structural formulas shown in Figure 3, explain in a few sentences why methylene blue is suitable for the detection of aqueous continuous phase and why Sudan (III) dye can be used for the oily phase.
- In the table below, indicate the observations (colour, foaming, density and number of visible phases) for different volumes (V) of added $CaCl_2$ solutions.

Table 2: Summary of the measured data

V (cm^3)	$\Phi^{\star}_{foam}$	Number of phase**	Relative viscosity***	Type of emulsion

Notes:

* To characterize the foam volume (Φ_{foam}), read or estimate the total volume of the system if it exceeds the scale of the mixing cylinder. From this information, and knowing the total volume of the liquid phase, the volume fraction of the dispersed gas phase can be estimated.

** One considers separated phase as the phase after creaming or one-phase oil layer.

*** A relative scale is used to characterize the viscosity. It is assumed that the internal friction is inversely proportional to the flow time of the emulsion on the wall of the measuring cylinder. After shaking, the

flow time of the liquid film along the wall of the mixing cylinder can be well estimated by following the downward movement of a visible bubble for 2–3 seconds. From this, calculate a „scale part/time" flow rate for each composition from which the ratio of the reciprocals of the velocities - which corresponds to the relative viscosity - can be calculated by considering the initial emulsion's value as 1.

Test questions

1. What is macroemulsion? How can it be prepared?
2. What substances are called emulsifiers and what is their role in the production of emulsions?
3. Explain the interfacial tension modifying effect of surfactants.
4. How do you calculate the interfacial tension of surfactant solutions from the known water/oil interfacial tension and the number of droplets counted in water or in surfactant solution?
5. Do macroemulsions have thermodynamic or kinetic stability? What materials can be used to increase their stability?
6. What types of emulsions do you know?
7. How does the type of the emulsion depend on the hydrophilicity / hydrophobicity of the emulsifiers?
8. Why does the type of Na-soap-stabilized emulsions change after adding sufficient amount of Ca(II)-salt solution?
9. How can you determine the type of emulsions? Describe the main principle of the methods discussed in the lab manual.
10. Calculate the number of drops of the liquid leaving the $5\,cm^3$ Donnan pipette in the form of regular spherical droplets with a radius of 3 mm?