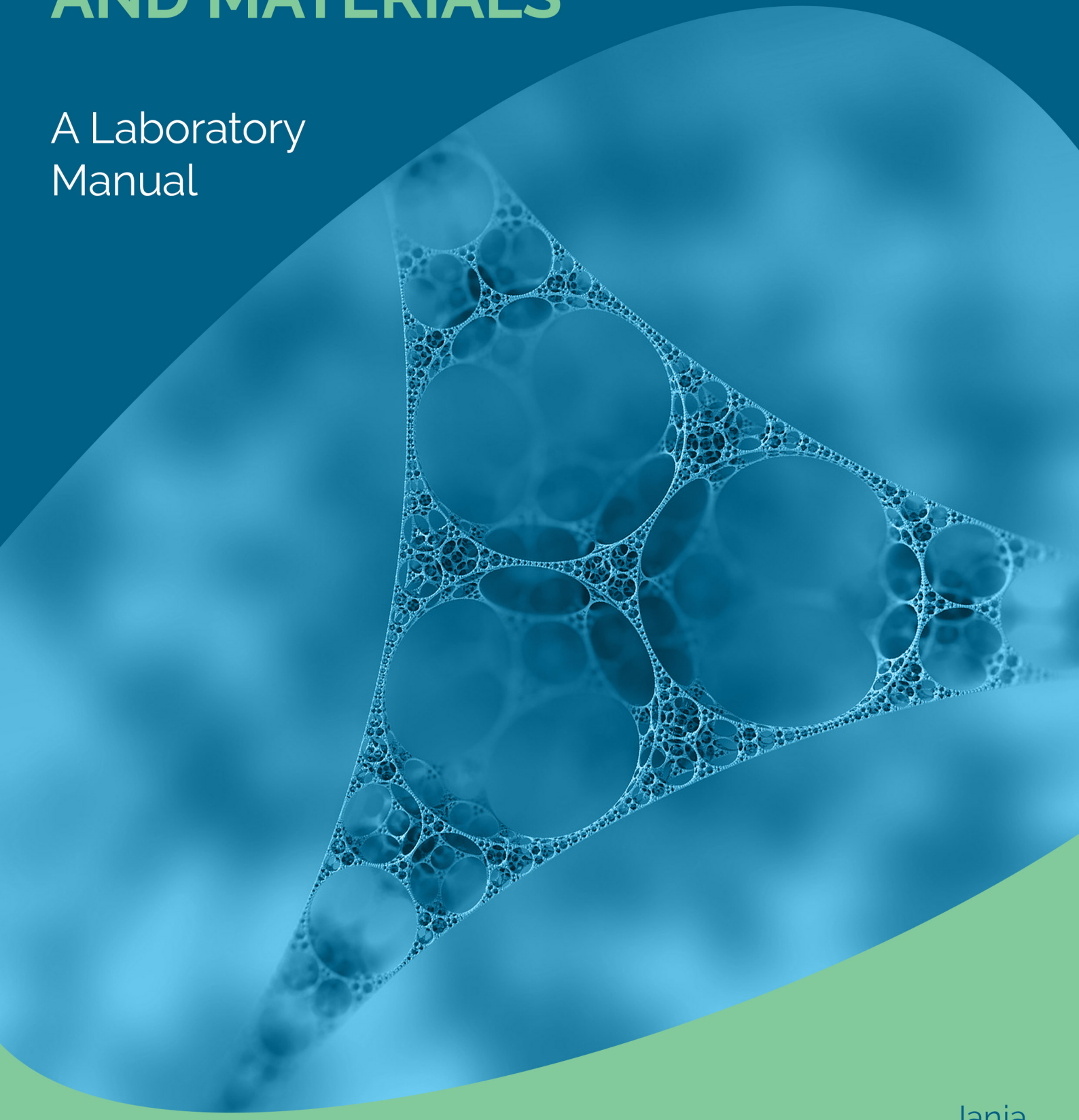
NANOCHEMISTRY
AND MATERIALS

A Laboratory Manual



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Faculty of Chemistry and Chemical Engineering

Nanochemistry and Materials

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Introduction

1.1 General instructions

Laboratory exercises are crucial for understanding the chemical properties of substances and the laws of physics and chemistry, so it is very important that the student must comes to the exercises well prepared. This means that he/she knows the procedure of the exercise and its theoretical background.

The assistant can check the student's readiness for an individual exercise in writing or orally before the exercise begins. Insufficient knowledge of an individual exercise may be a reason to discourage a student from doing a practical exercise.

1.2 Instructions for working in the laboratory

Before beginning the exercises, the students must familiarise themselves with the rules for working safely in the laboratory since work safety is extremely important in practical chemistry exercises.

The student must sign a statement at the beginning that he/she is familiar with these instructions. In case of an accident, it is necessary to inform the assistant and follow the instructions. After the exercise, the student must clean up the work area. It is necessary to wash and store the inventory in the agreed place and wipe down the workbench. He/she must take care of their own, common inventory and laboratory furniture.

1.3 Protective suit

During laboratory exercises, it is necessary always to wear protective clothing (a smock) and, when working with corrosive substances (acids, alkalis), also protective goggles and gloves.

In the laboratory, it is forbidden:

- to carry out experiments that are not part of the planned experimental procedure;
- to bring in and consume food and drinks;
- to use a mobile phones;
- to smoke.

1.4 The digester

The digester is a shelter where proper evaporation of vapours from the laboratory is assured. All reactions that produce irritating or toxic gases must be conducted in this room.

1.5 Waste chemicals

It is strictly forbidden to pour waste chemicals into ordinary troughs. All substances that, if discharged into the sewage system, could have harmful effects on the environment and humans (heavy metals, toxic substances, ...) are collected in special containers and later neutralised and taken to institutions where they are destroyed.

1.6 Aids and absence from exercises

The student must bring his/her calculator, a cloth to wipe the desk, and matches and dishwashing liquid if necessary.

Any absence from practice must be justified by a doctor's note, which the student must present to the assistant. In the case of early absence, the student must make an appointment with the assistant to attend the missed practice.

1.7 Laboratory diary

A properly written and equipped laboratory diary is also crucial for the final assessment of laboratory exercises. In it, the student writes his or her observations, calculations, measurements, and results clearly and legibly. The diary should be written in the 1st person singular in the past tense. If the assistant notices errors, he/she is obliged to correct them and mark them in the diary.

Exercises that are not done correctly must be repeated by the student; if the student cannot repeat the exercises on the same day, an appointment will be made with the assistant.

The exercises are completed when the student has all exercises signed off by the assistant. After the exercises, the diaries will remain in the archives of the Inorganic Chemistry Laboratory reviewed and signed.

Credit for the exercises will be given if the student completes the colloquium from the exercises in addition to the completed laboratory exercises successfully. The grade will be included in the overall grade of the examination in Nanochemistry and Materials.

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Experiment no. 1

Constructing a phase diagram in a system: Water phase/CTAB, 1-butanol/isooctane by the titration method

THEORETICAL BACKGROUND (1-3)

Microemulsions are isotropic, macroscopically homogeneous and thermodynamically stable solutions containing at least three components, namely, a polar phase (usually water), a nonpolar phase (usually oil) and a surfactant. On a microscopic level, the surfactant molecules form an interfacial film separating the polar and the nonpolar domains. This interfacial layer forms different microstructures, ranging from droplets of oil dispersed in a continuous water phase (o/w- microemulsion) over a bicontinuous "sponge" phase, to water droplets dispersed in a continuous oil phase (w/o-microemulsion). The latter can be used as nanoreactors for the synthesis of nanoparticles with a low polydispersity.

The microemulsion region is usually characterised by constructing ternary-phase diagrams. Three components are the basic requirements to form a microemulsion: An oil phase, an aqueous phase and a surfactant. If a cosurfactant is used, it may sometimes be represented at a fixed ratio to surfactant as a single component and treated as a single "pseudo-component". The relative amounts of these three components can be represented in a ternary phase diagram. Gibbs phase diagrams can be used to show the influence of

changes in the volume fractions of the different phases on the phase bahaviour of the system. A hypothetical phase diagram of a microemulsion is shown in Fig. 1-1.

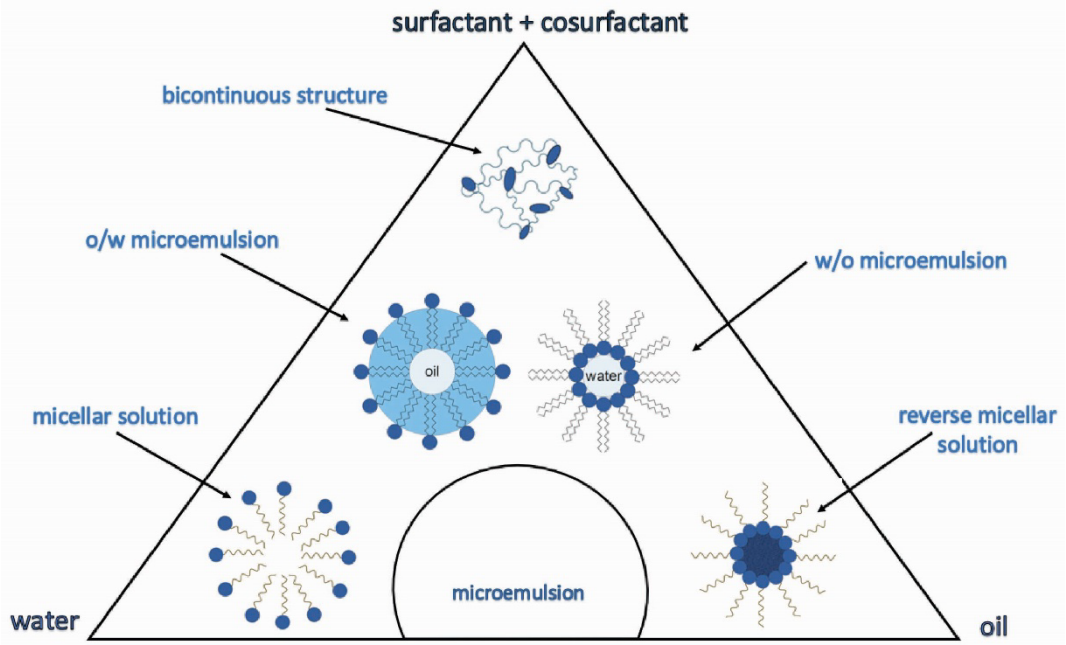

Figure 1-1: Hypothetical phase regions of a microemulsion system.
Source: own.

Three types of microemulsions are most likely to be formed, depending on the composition:

- oil in water microemulsions, wherein oil droplets are dispersed in the continuous aqueous phase;
- water in oil microemulsions, wherein water droplets are dispersed in the continuous oil phase;
- bi-continuous microemulsions, wherein the microdomains of oil and water are interdispersed within the system.

The three components composing the system are each found at an apex of the triangle, where their corresponding volume fraction is 100 %. Moving away from that corner reduces the volume fraction of that specific component and increases the volume fraction of one or both of the two other components. Each point within the triangle represents a possible composition of a mixture of the three components or pseudo-components, which may consist of one, two or three phases. These points combine to form regions with boundaries between them, which represent the "phase behaviour" of the system at

constant temperature and pressure. The Gibbs phase diagram, however, is an empirical visual observation of the state of the system and may or may not express the true number of phases within a given composition. Apparently, clear single-phase formulations can still consist of multiple iso-tropic phases. Since these systems can be in equilibrium with other phases, many systems, especially those with high volume fractions of both the two immiscible phases, can be destabilised easily by anything that changes this equilibrium, e. g. high or low temperature or the addition of surface tension modifying agents. A very convenient method for the preparation of a microemulsion and construction of a planer triangular phase diagram is the titration procedure. A surfactant is dissolved in an inaqueous (or organic) medium and is titrated with the organic (or aqueous) phase. The transition points are noted (turbid and transparent). The single-phased, optically transparent domains correspond to the microemulsions, whereas turbid zones are for multiphase systems. Almost all transition points can be noted by repeating the same procedure for different concentrations of surfactant solution. Thus, a triangular phase diagram can be drawn easily. Several other systems of water phase/oil phase/surfactant and/or cosurfactant are known, Table 1-1.

Table 1-1: Different systems of water/surfactant, cosurfactant/oil phase.

Water phase	surfactant	cosurfactant	Oil phase
Different water solutions of ions	CTAB (Cetyl trimethyl ammonium bromide) [$C_{19}H_{42}NBr$]	1-butanol [C_4H_9OH]	Isooctane [C_8H_{18}]
	CTAB (Cetyl trimethyl ammonium bromide) [$C_{19}H_{42}NBr$]	/	hexanol
	SDS (sodium dodecyl sulphate) [$NaC_{12}H_{25}SO_4$]	1-butanol [C_4H_9OH]	n-heptane [C_7H_{16}]
	AOT (sodium bis 2-ethylhexyl sulfosuccinate) [$C_{20}H_{37}NaO_7S$]	/	Isooctane [C_8H_{18}]
	AOT (sodium bis 2-ethylhexyl sulfosuccinate) [$C_{20}H_{37}NaO_7S$]	heptanol [$C_7H_{16}O$]	decane [$C_{10}H_{22}$]
	SDS (sodium dodecyl sulphate) [$NaC_{12}H_{25}SO_4$]	1-butanol [C_4H_9OH]	Ciklohexane [C_6H_{12}]

In Experiment 1, we will use the system of deionised water or different concentrated water phases of Fe^{2+} and Fe^{3+} ions (water phase), CTAB (surfactant), 1-butanol (cosurfactant) and isooctane (oil phase).

EXPERIMENTAL PROCEDURE

Inventory:

- 2x 50 mL Erlenmeyer flasks,
- 2x 100 mL volumetric flasks with stopper,
- 2x 50 mL glass beakers (for isooctane and butanol),
- 1x glass stick,
- 2x glass funnels,
- 2x byrettes,
- 2x glass beakers.

Laboratory Inventory:

- parafilm,
- 2x measuring pipettes (for isooctane and butanol),
- 2x pipetting balls,
- 2x magnetic stirrers,
- 2x magnetic stirrer mixers,
- 2x laboratory stands,
- 4x burette clamps,
- 4x bossheads.

Chemicals:

- deionised water,
- isooctane,
- 1-butanol,
- CTAB (cetyl trimethyl ammonium bromide),
- $Fe_2(SO_4)_3 \cdot xH_2O$,
- $FeSO_4 \cdot 7H_2O$,
- 25 % NH_4OH.

In Experiment 1, we try to select a proper compositional range that would form a microemulsion in the water/CTAB, 1-butanol/isooctane system with the titration method. In this method, an aqueous solution is titrated in a mixture of the oil phase and surfactant/cosurfactant. With the addition of a small amount of aqueous solution, the oil-to-surfactant/cosurfactant, which has a milky appearance, turns into a clear, optically transparent liquid, signifying the formation of the microemulsion. The maximum amount of aqueous solution that can be solubilised is determined by the appearance of the permanent turbidity of a sample.

You will weigh the mass of surfactant, cosurfactant and oil phase in the Erlenmeyer flask; the masses are in Table 1-2. You will work at room temperature, with the mass ratio of surfactant:cosurfactant=1:1. The assistant will give you the concentration of the water phase.

Table 1-2: Ratio and masses of the surfactant, cosurfactant and oil phase.

pos.	$w_{isooctane}/w_{(CTAB+1\text{-}butanol)}$	m (isooctane)	m (CTAB+1-butanol)
1.	0,1/0,9	2,2g	10g+10g
2.	0,2/0,8	2,5g	5g+5g
3.	0,3/0,7	4,3g	5g+5g
4.	0,4/0,6	6,65g	5g+5g
5.	0,5/0,5	5g	2,5g+2,5g
6.	0,6/0,4	7,5g	2,5g+2,5g
7.	0,7/0,3	11,7g	2,5g+2,5g
8.	0,8/0,2	10g	1,25g+1,25g
9.	0,9/0,1	22,5g	1,25g+1,25g

You will titrate deionised water or aqueous solutions containing different concentrations of Fe^{2+} and Fe^{3+} (0.15 M, 0.25 M, 0.35 M) ions into the mixture with vigorous stirring from 1 to 9 (see Table 1-2). The molar ratio of Fe^{2+}:Fe^{3+} is 1.85:1. You will visually determine the compositional range of microemulsion stability and turbidity. First, you mix solutions without the water phase in the Erlenmeyer flask, and after 15 minutes, you will add the water phase drop by drop from the burette. Determine the volume when the microemulsion turn into a clear, optically transparent microemulsion, and continue with the titration of the water phase until the occurrence of permanent turbidity. You insert the results into the Laboratory report. When you finish with the titration method, the relative amounts of the water phase, surfactant, cosurfactant and oil phase are expressed in percentages of the selected parameter, such as:

$$w(m_1) = m_1/(m_1+m_2+m_3)\cdot 100\ \%$$

$$w(m_2) = m_2/(m_1+m_2+m_3)\cdot 100\ \%$$
$$w(m_3) = m_3/(m_1+m_2+m_3)\cdot 100\ \%$$
$$100\ \% = w(m_1)+w(m_2)+w(m_3)$$

m_1 … mass of the water phase
m_2 … mass of surfactant and cosurfactant
m_3 … mass of the oil phase
$w(m_1)$ … mass percentage of the water phase
$w(m_2)$ … mass percentage of surfactant and cosurfactant
$w(m_3)$ … mass percentage of the oil phase.

You insert the results of the titration method into the ternary phase diagram and determine the region of microemulsion stability.

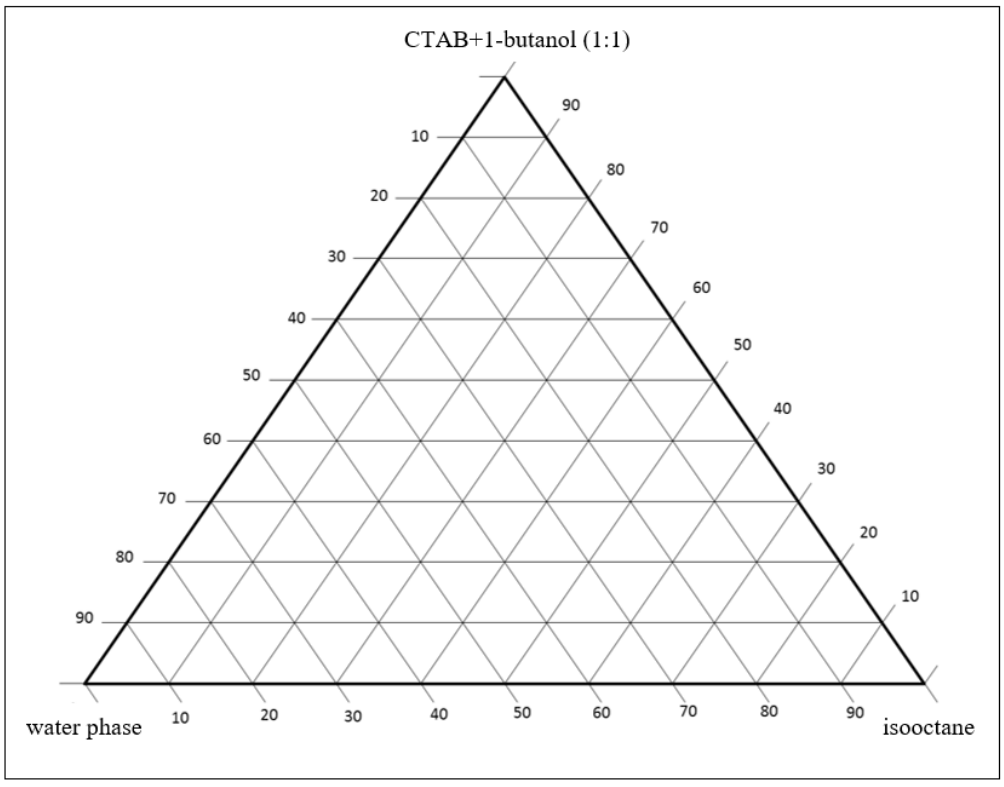

Figure 1-2: Ternary phase diagram of the water phase/ CTAB, 1-butanol/ isooctane.
Source: own.

Each group will titrate different concentrations of the water phase, and you have to put all the results on one diagram in the Laboratory report and comment on the results.

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Experiment no. 2

Co-precipitation in microemulsion: synthesis of maghemite nanoparticles

THEORETICAL BACKGROUND (2, 5-7)

The term microemulsion refers to a thermodynamically stable isotropically clear dispersion of two immiscible liquids, such as oil and water, stabilised by an interfacial film of surfactant molecules. A microemulsion is considered to be a thermodynamically or kinetically stable liquid dispersion of an oil phase and a water phase in combination with a surfactant. The dispersed phase typically comprises small particles of droplets with a size range of 5-200 nm and has a very low oil/water interfacial tension. Because the droplet size is less than 25 % of the wavelength of visible light, microemulsions are transparent. The microemulsion is formed readily and sometimes spontaneously, generally without high-energy input. In many cases, a cosurfactant or cosolvent is used in addition to the surfactant, the oil phase and the water phase.

The key difference between emulsions and microemulsions are that the former, whilst they may exhibit excellent kinetic stability, are fundamentally thermodynamically unstable, and will eventually phase separate. Another important difference concerns their appearance; emulsions are cloudy, while microemulsions are clear or translucent. In addition, there are distinct differences in their method of preparation since emulsions require a significant input of energy while microemulsions do not. The latter point has

obvious implications when considering the relative cost of commercial production of the two types of system.

Table 2-1: Comparison of the properties of emulsions and microemulsions.

properties	emulsion	microemulsion
appearance	cloudy	transparent, translucent
droplet size	150 nm- 100 μm	1.5 nm- 150 nm
formation	not spontanous	spontanous
thermodynamic stability	unstable	stable

The surface active agents or surfactant molecules are amphiphilic in character, i.e., they possess hydrophilic and hydrophobic regions in their molecules. They have a long hydrocarbon tail and a relatively small ionic or polar head group.

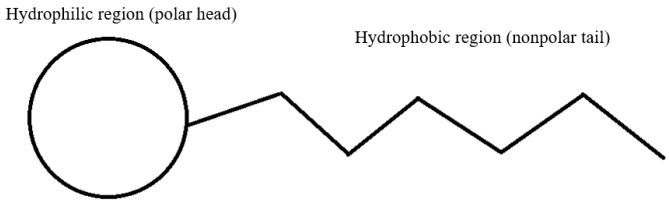

Figure 2-1: Schematic picture of a surfactant molecule.
Source: own.

Surfactants dissolved in organic solvents form spherical aggregates called reverse micelles. Reverse micelles can be formed both in the presence and absence of water. However, if the medium is completely free of water, the aggregates are very small and polydisperse. The presence of water is necessary to form relatively large surfactant aggregates. Water is incorporated readily into the polar core, forming a so-called "water pool", characterised by w_0, the water-surfactant molar ratio:

$$w_0 = [H_2O]/[\text{surfactant}]$$

w_0- molar ratio of the water/surfactant
$[H_2O]$- molar concentration of the water phase
[surfactant]- molar concentration of the surfactant.

The aggregates containing a small amount of water ($w_0 < 15$) are usually called "reverse micelles", whereas "microemulsions" correspond to droplets containing a large number of water molecules ($w_0 > 15$). Water-in-oil reverse micelles are transparent, isotropic and thermodynamically stable fluids in which nanometer-sized water droplets are dispersed in

a continuous oil phase. The droplet sizes are usually determined by the surfactants used for the reverse micelle and are known to be very uniform. Because of its size uniformity, a reverse micelle is considered a lucrative way to synthesise nanosize particles with a narrow size distribution.

The surfactants used to stabilise such a system may be: non-ionic, zwitterionic, cationic or anionic, depending on the nature of their head groups. A combination of these, particularly ionic and non-ionic, can be very effective at increasing the extent of the microemulsion region. Examples of non-ionics include polyoxyethylene surfactants such as Brij 35 (C12E35) or sugar esters. Phospholipids are a notable example of zwitterionic surfactants which exhibit excellent biocompatibility. Cetyltrimethylammonium bromide (cationic) provides a very flexible film, which gives rise to a high exchange dynamic of the micelles. The most widely studied anionic surfactant is probably sodium bis-2-ethylhexylsulphosuccinate (AOT), which is twin-tailed and is a particularly effective stabiliser of w/o microemulsions. In several important applications, ionic surfactants are used in conjunction with a co-surfactant such as a medium chain-length alcohol. The co-surfactant is an uncharged entity, and its adsorption is not impeded by the electric field. It, therefore, provides the additional lowering of interfacial tension necessary for microemulsion formation. Co-surfactants are usually alcohols or amines ranging from C4 to C10, and help in the formation and stabilisation of micelles/microemulsions. The co-surfactants provide a "dilution effect" in addition to that of the surfactant and cause a further decrease of the interfacial tension. Their short hydrophobic chain and terminal hydroxyl group are known to enhance the interaction with surfactant monolayers at the interface, which can influence the curvature of the interface and internal energy. The amphiphilic nature of co-surfactants could also enable them to distribute between the aqueous and oil phases.

Reverse micelles can be formed in the presence or absence of water. If the medium is free of water, then the aggregates are very small, while the presence of water makes large surfactant aggregates. Water is solubilised readily in the polar core and forms "water pool" contents. Depending on the proportion of the various components and the hydrophilic-lipophilic balance value of the surfactant used, the formation of microdroplets can be in the form of oil-swollen micelles dispersed in water as oil-in-water (o/w) microemulsion, or water-swollen micelles dispersed in oil as for water-in-oil (w/o) microemulsion, also called reverse microemulsion. These nanodroplets can be used as nanoreactors to carry out chemical reactions. In order to produce the nanoparticles, two microemulsions are mixed, carrying the appropriate reactants. A schematic picture of this process is

represented in Scheme 2-2. It can be seen that, after mixing both microemulsions containing the reactants, the interchange of the reactants takes place (here referred to as metal salt and reducing agent) during the collisions of the water droplets. The reaction then takes place inside the droplets (nucleation and growth), which controls the final size of the particles. Once the particles attain the final size, the surfactant molecules are attached to the surface of the particles, thus stabilising and protecting them against further growth.

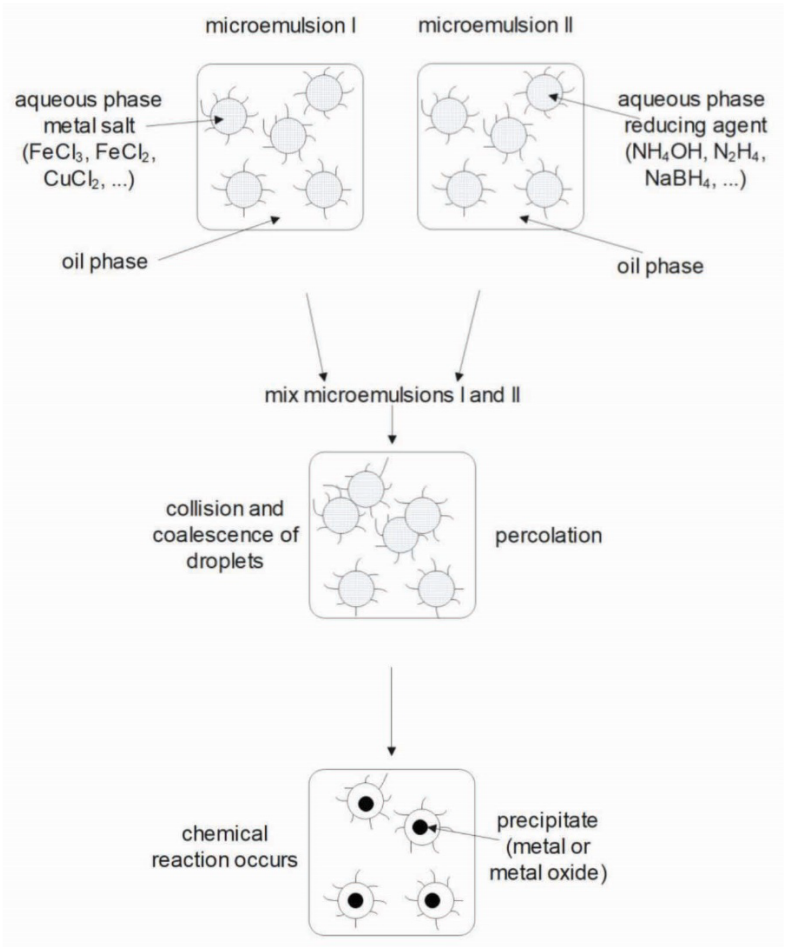

Figure 2-2: Proposed mechanism for the formation of metal particles by the microemulsion approach.
Source: own.

Microemulsion systems have been investigated for a broad range of technological applications - in enhanced oil recovery, as fuels, as coatings and textile finishing, as lubricants, cutting oils and corrosion inhibitors, in detergency, cosmetics, agrochemicals and pharmaceuticals. On the laboratory scale, microemulsions are a relatively simple process where the particles are obtained of the same size and shape. In Experiment 2, you will synthesise nanoparticles of maghemite with the microemulsion technique. The size of the synthesised maghemite nanoparticles will be determined by X-Ray powder diffraction.

EXPERIMENTAL PROCEDURE

Inventory:

- 2x 50 mL flasks (for isooctane and butanol),
- 2x measuring pipettes,
- 2x 50 mL volumetric flasks with stoppers,
- 1x 100 mL three-neck round-bottom flask,
- crystallising dish,
- 1x 50 mL Erlenmeyer flask,
- dropping funnel.

Laboratory Inventory:

- parafilm,
- 2x measuring pipettes (for isooctane and butanol),
- 2x pipetting balls,
- 2x magnetic stirrers,
- 2x magnetic stirrer mixers,
- 1x laboratory stand,
- 2x bossheads,
- 2x burette clamps,
- 2x 50 mL plastic centrifuge tubes,
- 1x thermometer,
- 1x cork flask stand,
- 1x condenser.

Chemicals:

- $Fe_2(SO_4)_3 \cdot xH_2O$,
- $FeSO_4 \cdot 7H_2O$,
- 25 % NH_4OH,
- isooctane (2,2,4 trimethylpentane),
- 1-butanol,
- CTAB (cetyl trimethyl ammonium bromide),
- ethanol,
- deionised water.

You will synthesise maghemite (γ-Fe_2O_3) nanoparticles by the microemulsion technique. The assistant will give you the point of the composition. You will prepare two microemulsions, A and B. Microemulsion A will contain a water phase of Fe^{2+} and Fe^{3+} ions/CTAB, 1-butanol/isooctane, and microemulsion B will contain a water phase of ammonium, but the other components will be the same as in microemulsion A. First, you will prepare a water solution of Fe^{2+} and Fe^{3+} ions in the molar ratio 1.85:1 (the assistant will give you the concentration) and a 1.5 M solution of ammonium in the 50 mL flask. Then you will weigh the calculated mass of surfactant (CTAB) into the 100 mL three-neck round bottom flask, cosurfactant (1-butanol) and oil phase (isooctane). You will prepare microemulsion A in the three-neck round bottom flask, whereas you will prepare microemulsion B in the Erlemeyer flask. You will mix microemulsions A and B for 15 minutes (the flasks are covered with parafilm). After 15 minutes, you will add the water phase; you will add in microemulsion A the water phase of Fe^{2+} and Fe^{3+} ions, and in microemulsion B 1.5 M ammonium with the help of the 1 mL pipette. Then you will cover the microemulsion A- three-neck bottom flask with the glass stopper, condenser and dropping funnel. You will turn on the condenser and will start with heating at 60 °C. When you reach 60 °C, you will add microemulsion B slowly to microemulsion A using the dropping funnel. Follow the colour changing! After adding the total amount of microemulsion B to microemulsion A, let the synthesis run for 2 hours to reduce the ions completely. Always maintain a constant temperature of 60 ° C. Clean the final product thoroughly by centrifugation and ethanol; centrifuge in two centrifuge tubes (50 mL, make up to 25 mL) at 6,500 rpm for 5 minutes, repeat the procedure 4 times and then dry the product in an oven at 80 ° C. Store the dried product in a plastic container and check the magnetism with a permanent magnet.

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Experiment no. 3

Synthesis of magnetic fluids-ferrofluids

THEORETICAL BACKGROUND (9, 10)

Magnetic fluids are colloidally stable suspensions of ferromagnetic particles, usually in the size of 10 nm, in a suitable carrier liquid. Magnetite (Fe_3O_4) or maghemite (γ-Fe_2O_3) are usually used as magnetic particles, and water, kerosene and other hydrocarbons as carrier fluids. It is characteristic of a magnetic fluid that the particles do not settle in the gravitational field or in the moderate gradients of the magnetic field, nor do they form agglomerates due to magnetic dipole interactions. Critical to the stability of magnetic fluids is an adequate surface treatment of the nanoparticles to prevent agglomeration due to van der Waals forces. Such protection can be achieved either by an electric charge on the surface of the nanoparticles or by producing a coating of long hydrocarbons on the surface of the nanoparticles. Such molecules are called surfactants and consist of a polar head that forms a bond with the surface of the nanoparticle and a long nonpolar tail that creates a reflection between the particles, preventing agglomeration while allowing compatibility of the nanoparticles and the carrier fluid. Figure 3-1 shows nanoparticles coated with surfactants schematically.

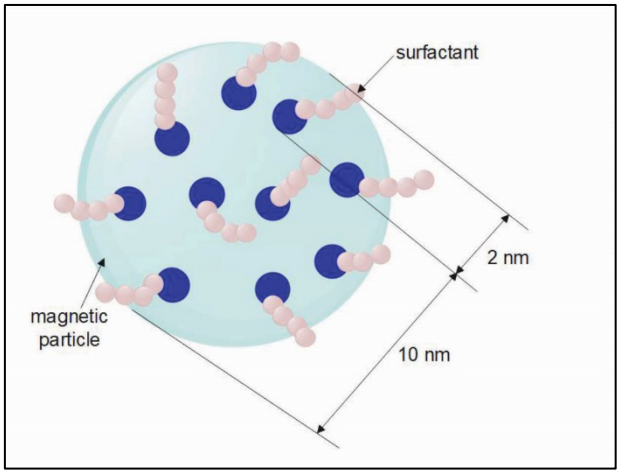

Figure 3-1: Schematic representation of coated nanoparticles in a magnetic fluid.
Source: own.

Such magnetic nanoparticles carry large magnetic moments, about 10^4 μB per particle. The initial susceptibility of magnetic fluids is about 10^4 higher than that of paramagnetic salt solutions. Since the force on the magnetic material caused by the magnetic field gradient is proportional to the magnetisation, relatively large forces on the particles can be obtained with moderate magnetic field gradients. Based on the above, we can control the current characteristics and properties of magnetic fluids using a magnetic field, which makes them extremely useful for various engineering and biomedical applications. Among the biomedical applications, the delivery of drugs to a specific location in the body stands out using a magnetic field. The purpose of this exercise is to synthesise a magnetic fluid, where the magnetic nanoparticles of maghemite (γ-Fe_2O_3) will serve as magnetic particles, and we will use water as the carrier fluid.

EXPERIMENTAL PROCEDURE

Inventory:

- 1x cork stopper,
- 1x 10 mL measuring cylinder,
- 1x 250 mL measuring cylinder,
- 1x 100 mL Erlenmeyer flask,
- 2x 10 mL pipettes,
- 1x 100 mL flask,
- 1x 250 mL flask,
- 1x watch glass,

- 1x 100 mL volumetric flask with stopper,
- 1x 25 mL Erlenmeyer flask,
- 1x 25 mL volumetric flask with stopper,
- crystallisation dish,
- 1x 500 mL volumetric flask with stopper,
- laboratory spatula.

Laboratory Inventory:

- 1x magnetic stirrer,
- 1x magnetic stirrer mixer,
- 1x laboratory stand,
- 1x bosshead,
- 1x burette clamp,
- permanent magnet,
- thermometer,
- 6 centrifuge tubes,
- cork flask stand,
- pipetting ball,
- pH meter,
- 200 μL electronic pipette,
- pipette tips.

Chemicals:

- $Fe_2(SO_4)_3 \cdot xH_2O$,
- $FeSO_4 \cdot 7H_2O$,
- 25 % NH_4OH,
- Citric acid monohydrate,
- ethanol,
- deionised water.

Prepare a solution of Fe^{3+} (conc. 0.1 mol/L) and Fe^{2+} (conc. 0.12 mol/L) ions (solution A) in a 100 mL volumetric flask. Pour the prepared solution into a 250 mL beaker equipped with a magnetic stirrer and a thermometer and covered with a watch glass. Start heating the solution (stirring speed 400 rpm/min) on a heater equipped with a magnetic stirrer, and add 40 mL of 25 % ammonia solution when it reaches 80 °C.

Be sure to use protective equipment (goggles, protective gloves) and always work in a digester with the guard down. Maintain a constant temperature of 80 °C for 1 h. During this time, prepare a 0.5 M citric acid solution (solution B) in a 25 mL volumetric flask. Also prepare an ammonia solution (2.5 mL ammonia (25 %) in 10 mL deionised water) (solution C) in a 25 mL Erlenmeyer flask. Seal the conical flask with a cork stopper. Prepare alkaline water in a 500 mL volumetric flask for rinsing (add 150 μL of solution C to 500 mL of deionised water) (solution D).

After the synthesis is complete, cool the suspension to room temperature and remove the magnetic stirrer with a magnetic rod. Then place the cooled suspension on a permanent magnet and wait for the particles to settle, and then decant the liquid. Then add 50 mL of solution D and sonicate in an ultrasonic bath for 5 minutes, stirring the suspension occasionally with a spatula. After sonification, place the beaker back on the magnet to allow the particles to settle and decant the liquid. Repeat the rinsing process again. After the second rinsing of the particles, add 60 mL of solution D with a measuring roller and sonicate for 15 minutes (stirring several times with a spatula).

Next, 20 mL of solution B is placed in a 100 mL beaker, to which the magnetic solution is added slowly with vigorous stirring. Add citric acid to lower the pH, so raise it to pH= 5.1 with solution C using a pH meter. Add the prepared solution C using a 1-mL pipette. After reaching the pH of 5.1, pour the obtained magnetic liquid into a 100 mL conical flask without the magnetic stirrer, seal it with parafilm and sonicate it in an ultrasonic bath for 45 minutes. After sonification pour the given mixture into 6 centrifuge tubes, each containing about 15 mL and make up to 40 mL with ethanol. Place the mixture in the centrifuge tube and centrifuge at 5,000 rpm / 5 min.

After centrifugation, drain the supernatant and add 2 mL of water to each centrifuge tube and dissolve the settled mixture in this amount of water. Then transfer everything together into a single centrifuge tube so that there is as little loss as possible. Alkalise this solution with 400 μL of solution C to reach pH= 10. Then centrifuge at 6,500 rpm for 20 minutes. After centrifugation is complete, pour the liquid contents into a new centrifuge tube. Dry 5 mL of the final magnetic liquid in a centrifuge tube in an oven at 80 °C, as you will need the dried sample in exercise 5 (TGA characterisation).

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Experiment no. 4

Colloidal silver

THEORETICAL BACKGROUND (11)

Silver is known as a powerful natural antibiotic that has been used for thousands of years without any significant side effects. Even our great-grandmothers put a silver coin in milk to keep it from spoiling in the summer. The ancient Greeks knew its medicinal value. Kings, rulers, sultans, ... ate out of silver vessels and drank out of silver cups and rarely got sick, and no infections occurred as a result. It is an antibiotic that is said to be the only one that destroys all types of viruses, fungi and bacteria; it is completely harmless to human organs and only speeds up healing. Colloidal silver is not harmful to mammals, reptiles, plants and all living things that consist of more than one cell. Single-cell living things have a different system of oxygen metabolism. The advantage of colloidal silver is that it acts as a catalyst and does not interfere with chemical reactions in body tissues. If it is near viruses, bacteria or fungi, it destroys their oxygen-degrading enzyme immediately, causing them to suffocate and usually die within six minutes. The dead organism is then eliminated from the body by the immune and lymphatic systems. The advantage of colloidal silver is also that it does not destroy or inactivate important enzymes in the body as other antibiotics do but speeds up healing without negative consequences. In this exercise, you will learn about colloidal silver by its optical properties, which, of course, depend on the size of the individual particles. When we speak of bulk gold or silver, we immediately think of the characteristic yellow or silver colour. However, it is known that if you reduce the particle size of both metals to a size smaller than the wavelength of light, the particles of these will be coloured depending on their size, which you will demonstrate in your

experimental work. Electrons do not move around freely in small particles as they do in bulk materials because they are confined to a small space of the metal particle. The collective oscillation of conduction electrons within a single metal nanoparticle allows the scattering and absorption of light at a certain frequency, which depends on the volume of the particles and is reflected in different colours. Under the influence of light, the free conductive electrons of the metal start to oscillate according to the frequency of the incident light, and this is called Surface Plasmon Resonance (SPR).

EXPERIMENTAL PROCEDURE

Inventory:

- 1x byrette,
- 4x 25 mL flasks,
- 1x 100 mL volumetric flask with stopper,
- 2x 500 mL volumetric flasks with stoppers,
- 2x glass sticks,
- 1x glass funnel,
- 1x 10 mL volumetric flask with stopper,
- 1x 25 mL Erlenmeyer flask,
- 1x 100 mL flask,
- 9 cuvettes with stoppers,
- 1x 5 mL filling pipette.

Laboratory Inventory:

- 1x magnetic stirrer,
- 2x magnetic stirrer mixers,
- 1x laboratory stand,
- 2x bossheads,
- 2x burette clamps,
- 1 mL electronic pipette,
- pipette tips,
- 1x pipetting ball.

Chemicals:

- $AgNO_3$,
- poly (sodium styrenesulfonate),
- ascorbic acid ($C_6H_8O_6$),
- trisodium citrate ($Na_3C_6H_5O_7$),
- sodium borohydride ($NaBH_4$),
- deionised water .

The goal of this exercise is to synthesise silver nuclei that will grow using different concentrations to form silver nanoparticles of varying sizes in the form of nanoprisms, which you will observe in rainbow-coloured solutions. Prepare a 10 mM solution of ascorbic acid in a 100 mL flask, a 25 mM solution of trisodium citrate in a 500 mL flask, and a 10 mM sodium borohydride solution also in a 500 mL flask. Weigh the masses on slips of paper on an analytical balance and transfer them to a small beaker. Then transfer to flasks and dilute to the mark. A solution of silver nitrate and poly (sodium styrenesulfonate) will be prepared in advance by your assistant. Also prepare a 2.5 mM trisodium citrate solution. To help yourself, pipette 1 mL of the 25 mM trisodium citrate solution into a 10 mL flask and fill up to the mark with deionised water. Once you have all the solutions ready, start preparing the silver grains first. In a 25 mL conical flask prepare a solution consisting of 5 mL of 2.5 mM trisodium citrate solution, 250 μL of 500 mg/L aqueous solution of poly(sodium styrenesulfonate), and 300 μL of 10 mM sodium borohydride. Mix the resulting solution with a magnetic stirrer. Finally, add a 5 mL 0.5 mM silver nitrate solution to this mixture using a burette at a drip rate of 2 mL/min. After adding all the $AgNO_3$, stir for 2 more minutes and then close the conical flask with parafilm. Next, pour the $AgNO_3$ solution into a 50 mL burette. Then add 10 mL of deionised water, 2 mL of the prepared ascorbic acid solution, and 5 mL of synthesised silver grains to a 100 mL beaker. Mix the mixture with a magnetic stirrer and start the titration with $AgNO_3$ from the burette. Add $AgNO_3$ dropwise, and, after 3 mL addition, pipette 1 mL of the sample from the beaker into the cuvette and add 0.5 mL of 25 mM trisodium citrate. Then pipette the sample after adding 6 mL, 9 mL, 12 mL, 18 mL, 21 mL, 24 mL, 30 mL, and 39 mL of $AgNO_3$ from the burette. Add 0.5 mL of trisodium citrate to each pipetted sample. Store the samples in cuvettes and measure their sizes on a DLS (Exercise 5). Annotate the results obtained accordingly and compare them with each other.

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Experiment no. 5

Characterisation of nanoparticles with the XRD, TGA and DLS methods

THEORETICAL BACKGROUND (12-14)

The final products prepared by various synthesis methods like microemulsions, coprecipitation, hydrothermal synthesis, microwave synthesis, the sol-gel method and mechanical comminution can be characterised by various methods. We will learn about three of them, namely, X-ray powder diffraction (XRD), thermogravimetric analysis (TGA) and dynamic light scattering (DLS).

XRD is a method by which we can analyse granular, crystalline materials qualitatively and quantitatively, and it can also be used to analyse coarse materials. It is one of the most important methods for characterisation in solid state chemistry. X-rays are electromagnetic waves and cause the electron incident on them to vibrate. Electromagnetic waves, on the other hand, propagate concentrically, with a source frequency that we call scattering. Interference of scattered light occurs in crystals, where atoms and, thus, electrons are arranged periodically. From this point of view, X-rays are suitable for determining the structure of crystals because the rays scatter, and if the geometrical conditions are fulfilled (Bragg's law), a deflecting ray is produced, the intensity of which strikes the detector. We express Bragg's law as:

$$(n \cdot \lambda) = (2 \cdot d \cdot \sin\theta)$$

where: n is a natural number,

- λ- wavelength of the X-rays,
- d- distance between planes in the crystal lattice,
- θ- angle between the direction of the incident light and the grid plane.

In powder X-ray analysis, the sample under study is usually in the form of a fine powder so that the crystals are oriented randomly. For X-ray deflection to occur, a portion of the powder crystals must be oriented so that their crystal planes form the angle θ with the incident beam, thus satisfying Bragg's law. The obtained deflected beam forms a Bragg angle or 2θ-angle with the incident beam. The basis of the apparatus implementation of the diffractometer method is that the sample is placed in the centre of the measuring circle, and the detector detects the deflected X-rays on this circle. The sample on the measuring circle rotates at half the speed of the detector, so that the angle of incidence of the beam is constantly changing. The result is a diffractogram, showing the intensity of the light as a function of the angle of deflection. From the shape of the diffractogram, one can judge at a glance whether the substance is amorphous, semi-crystalline or crystalline. Using the database from the diffractogram, we can determine which substance it is based on the same position of the peaks.

Thermogravimetric analysis (TGA) is a method for determining the physical and chemical properties of samples of all types - inorganic, organic, plastic, ceramic, glass, ... The method tracks the mass of the sample, which is subjected to a controlled heating programme. Using thermogravimetric curves, we show the change in mass of the sample on the y-axis as a function of temperature or time on the x-axis. The mass can be expressed in milligrams or in % of weight loss. The main features of thermal analysis are:

- the sample can be in a solid or liquid state, gel, ...
- it evaluates physical changes - melting, sublimation, evaporation, ... as well as chemical changes - oxidation, reduction, decomposition, polymerisation, ...
- use a small sample volume (vessels with a volume of 70 or 150 μL)
- the measurement takes place in the chosen atmosphere (air, nitrogen, argon, ...)
- the time of analysis and the temperature step can be determined precisely.

The shape of the curve is, thus, influenced by several factors, the composition of the substance, the heating rate in K/min, the atmosphere, etc.. As already mentioned, decomposition can take place in different atmospheres. It is important to know the substances well because many organic substances oxidise when heated in air, and chemical decomposition takes place in an inert atmosphere. Decomposition can also cause volatiles to escape from the sample, changing the atmosphere in direct contact with the sample, and, thus, allowing the possibility of slowing further decomposition. The optimal conditions that will give us the best results in the thermal analysis are difficult to determine, but we can help ourselves with a small sample volume, an open crucible, a dynamic inert atmosphere and a low heating rate.

Dynamic Light Scattering (DLS) is one of the most popular methods for determining particle size by measuring Brownian motion in suspension. The laser illuminates the particles, then the intensity of the motion in the scattered light is analysed. Suspended particles in a liquid are never in a steady state as they are constantly in motion, which is expressed as Brownian motion. A very important feature of Brownian motion for DLS is that small particles move very fast while large particles move more slowly. Therefore, if we have large particles moving slowly, their intensity of fluctuation also seems to be slow. If small particles are moving fast, their intensity of motion or fluctuation also appears to be very fast. So the DLS instrument measures the speed of the intensity of particle motion and then converts that motion to the particle size of interest using a function.

The method of measuring particle size using DLS has several advantages. It is a very fast method, almost everything is automated, and, thus, not much prior knowledge is required to make the measurement.

EXPERIMENTAL PROCEDURE

Material:

- dried product of the 2nd exercise for X-ray characterisation,
- dried sample of magnetic fluid synthesised by the 3rd exercise for TGA characterisation,
- 4 or 5 differently stained solutions of the 4th exercise for DLS characterisation.

In this exercise, you will learn about characterising particles or products obtained during the exercises. The methods you will use to characterise or analyse are X-ray powder diffraction, thermal analysis, and dynamic light scattering.

You will use X-ray powder diffraction to verify that you really synthesised the desired product maghemite (γ-Fe_2O_3), and you will help yourself with the characteristic points from the database. You will record an X-ray powder diffractogram on a Siemens-Bruker-D-5005 diffractometer. In a diffractogram, an X-ray beam falls on a pattern that rotates on its own axis. The detector, which records the intensity of the deflected beams, rotates about the same axis as the sample, only at twice the angular velocity. The device uses CuKα radiation (λ= 0.1542 nm).

The powder sample will first be sprayed onto a SiO_2 support and placed in a diffractometer. You will measure in the range 2θ= 20 ° to 80 °, the measurement step will be 2θ= 0.0358 °, and the step time will be 30 s. The whole measurement will take about 16 hours. As a result, you will obtain a diffractogram, with which you can check whether the characteristic deflection points correspond to the maghemite compound, and with which you can estimate the particle size using the Sherrer equation:

$$d_x = \frac{(0.94 \cdot \lambda)}{(\beta \cdot \cos\theta)}$$

where:

- d_x- particle diameter
- λ- characteristic wavelength
- β- width of the slope at half height
- θ- diffraction angle.

You will determine the average particle size d_x as the average of the individual particle sizes obtained at the deflection widths for different levels.

Using thermal analysis (TGA), you will determine how much citric acid the particles in the magnetic fluid are coated with. We will be measure on a Mettler Toledo TGA/SDTA 851^e. The instrument consists of a precision balance on which we will place a pot of Al_2O_3 with a sample using tweezers, an oven with temperature programming and a computer recording of the data. Temperatures can range from 25 °C to 1600 °C, but you will measure in the temperature range from 30 °C to 700 °C, with a temperature step of 10

K/min under an air atmosphere with a flow rate of 100 mL/min. The measurement will take 67 minutes.

As a result you will obtain a diagram in which the mass loss of the sample is plotted on the y-axis and the temperature or the measurement time is plotted on the x-axis. You annotate the temperature-dependent mass loss curve with the aid of an assistant, and, thus, determine the amount of citric acid bound to the particles in the magnetic fluid.

As a third characterisation you use dynamic light scattering (DLS). Using this method you determine the particle size in individual coloured silver particle synthesis products. You place the sample in the apparatus and use an assistant to measure the particle size of the individually coloured solution. You will compare the size with 4 or 5 differently coloured solutions and record and annotate the results accordingly.

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NANOCHEMISTRY AND MATERIALS
A LABORATORY MANUAL

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Abstract The publication contains instructions for laboratory work in the subject Nanochemistry and Materials. Students are introduced to the experimental principles of nanochemistry in the laboratory. They learn about various synthesis and characterization methods, in conjunction with magnetic nanoparticles useful in biomedical and engineering applications. They learn about the safety of nanoparticles and their effects, impact on technology, and contribution to improving life on many levels when used properly. The instructions are written in English as they are intended for foreign students who choose the mentioned subject.

Keywords: magnetic nanoparticles, coprecipitation, microemulsion technique, X-Ray powder diffraction, dynamic light scattering

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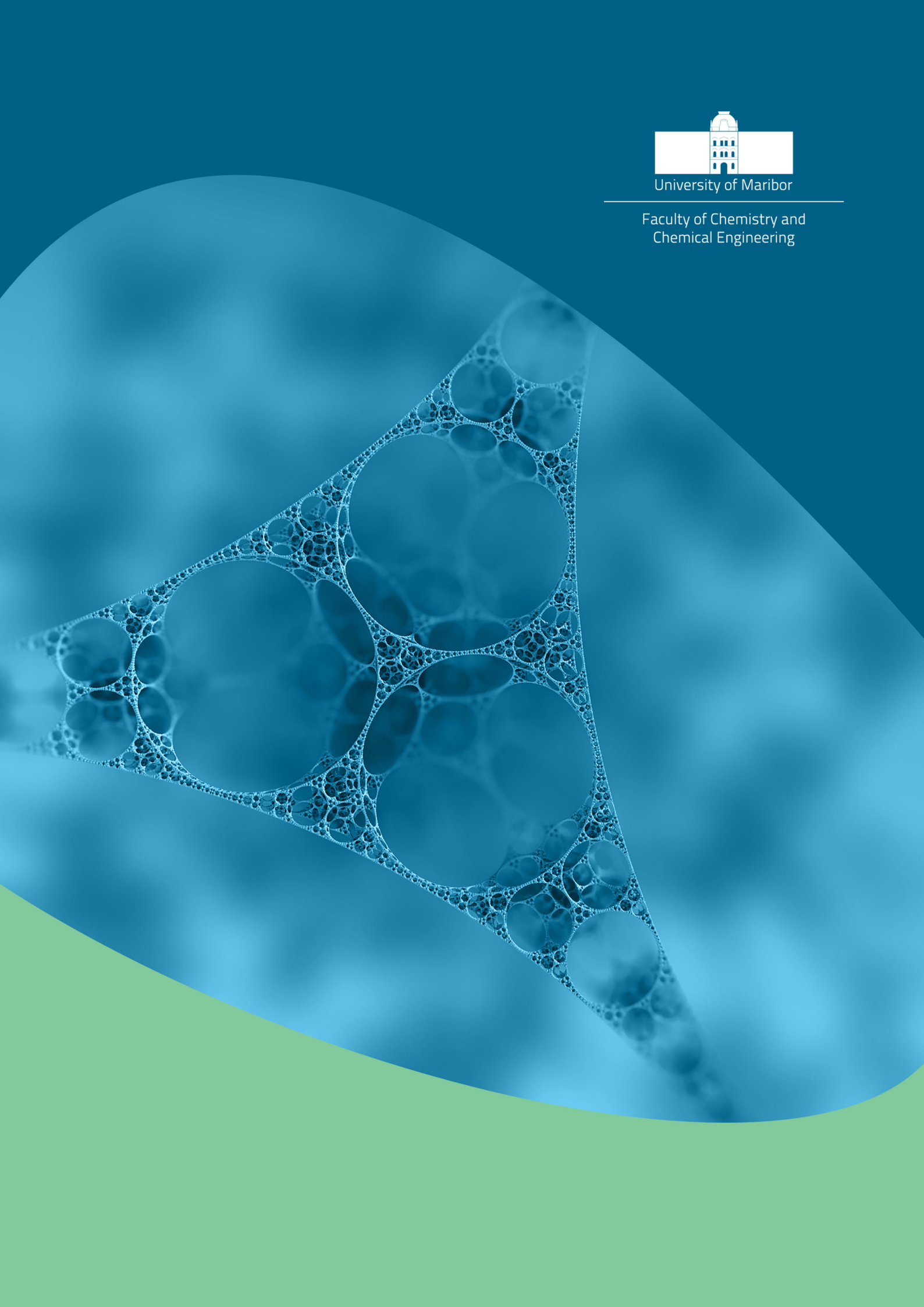

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