The Behaviour of Surfactants in Binary Mixed Systems

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Téma práce:	**Chování surfaktantů v binárních směsích**

Zásady pro vypracování:

I. Teoretická část

1. Elaborate the literature search on the given topic. Focus on the issue of surfactant mixtures and summarize the latest findings related to this field.

II. Praktická část

1. In experimental part determine critical micelle concentration (CMC) of individual surfactants and their mixtures prepared in pre-defined ratios. For CMC determination, use surface tension measurements, densitometry and dynamic light scattering. Evaluate the influence of mixture composition on CMC and assess the mutual interactions of surfactants by choosing the appropriate physicochemical parameters. Based on the obtained results, formulate conclusions.

Rozsah diplomové práce: *91 stran*

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Forma zpracování diplomové práce: **tištěná/elektronická**

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[1] GOEL, A. Colloidal Chemistry. Discovery Publishing House, 2006, 254 p. ISBN 81-8356-171-3.

[2] SATAKE, M., HAYASHI, Y., MIDO, Y., IQBAL, S. A., SETHI, M. S. Colloidal & Surface Chemistry. 1st ed. Discovery Publishing House, 1996, 218 p. ISBN 81-7141-33-07.

[3] MYERS, Drew. Surfactant science and technology. 3rd ed. Hoboken, N.J.: J. Wiley, ? 2006, 380 p. ISBN 04-716-8024-9.

[4] ROSEN, Milton J. Surfactants and interfacial phenomena. 3rd ed. Hoboken: Wiley-Interscience, ?2004, 444p. ISBN 04-714-7818-0.

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ABSTRAKT

Diplomová práce se zabývá surfaktanty (*N*-lauroyl sarkosinát sodný, TWEEN$^{®}$20, TWEEN$^{®}$60), jejich binárními směsmi a popisuje jejich vlastnosti a využití. Pozornost je věnována stanovení kritické micelární koncentrace těchto látek a jejich směsí vybranými metodami (tenziometrie, konduktometrie, denzitometrie, měření dynamického rozptylu světla, sledování změn kontaktního úhlu smáčení). V teoretické i experimentální části je diskutováno chování a možnosti vzájemného ovlivňování surfaktantů ve směsi. Práce rovněž poskytuje srovnání výsledků vybraných metod, které lze ke stanovení kritické micelární koncentrace použít. V neposlední řadě jsou zohledněny aplikační možnosti směsí v souvislosti s vlivem na životní prostředí a finanční náklady při výrobě kosmetických výrobků a jiných produktů (výrobky spotřební chemie, léčiva) v nichž jsou povrchově aktivní látky obsaženy.

Klíčová slova: povrchově aktivní látka, binární směsi, kritická micelární koncentrace, interakční parametr

ABSTRACT

The diploma thesis deals with surfactants (*N*-lauroylsarcosine sodium salt, TWEEN$^{®}$20, TWEEN$^{®}$60) as well as their binary mixtures; and describes their properties and applications. Attention is paid to the critical micelle concentration of the surfactants and their mixtures determined by selected methods (tensiometry, conductometry, densitometry, dynamic light scattering, monitoring of the contact angle changes under wetting). In the theoretical and experimental part, the behaviour and possibilities of the surfactant interactions in the mixture are discussed. The thesis also provides comparison of the results given by the selected methods that can be used to determine the critical micelle concentration. Finally, the application potentials of the mixtures are considered in the context of their influence on the environment and financial costs of the production of cosmetics and other products (household chemical products, pharmaceuticals), in which the surfactants are present.

Keywords: surfactant, binary mixture, critical micelle concentration, interaction parameter

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My thanks belong as well to my family and to those who have supported me during my studies.

Motto:

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CONTENTS

INTRODUCTION

Various surfactants in mixtures interact strongly and show noticeable synergism. Their properties, such as efficiency to reduce surface tension, mixed micelle formation, wetting, foaming or solubilisation may be thus improved [1, p. 270, 407]. The surface properties of the surfactant mixtures are often more pronounced than those of the individual components. Due to the synergism, each of the surfactants in the mixture can be used in smaller amount than if used alone. Thus, the mixtures of surfactants present economic savings especially in production of daily used personal care products and cosmetics, as well as in development of the composition of medicines. Needless to say, due to lower concentration of surfactants the environment is less burdened. Moreover, the lower concentration of each surfactant leads to less mucous membrane and skin irritation [1, p. 95, 167, 379].

This thesis deals with mixtures of two non-ionic surfactants and anionic and non-ionic ones. The surfactants have been chosen with regard to the increasing interest for those that are not frequently studied and show possibilities of use in cosmetics, household products and pharmaceuticals.

The non-ionic surfactants are represented by polyoxyethylene (20) sorbitan monolaurate (TWEEN®20) and polyoxyethylene (20) sorbitan monostearate (TWEEN®60). They are both used in wide range of products and applications, for example in drug delivery microemulsion systems, as stabilising agents in nanoemulsions and there is also a study dealing with disruption of *E. coli* amyloid-integrated biofilm formation caused by a polysorbate surfactant. As the anionic surfactant, the *N*-lauroylsarcosine sodium salt was selected. Generally, *N*-acyl sarcosines and their salts are considered as mild, biodegradable surfactants. Their maximum surface activity is reached at slightly acidic pH, the range most compatible with human skin. Due to these properties they are believed to be suitable materials in cosmetic applications [2, p. 1, pp. 8−10].

Today's demands for ecology, raw-material sources and marketing have caused the follow-up to the research and development of such chemicals. Surfactants are one of the most versatile products of the chemical industry. They are a part of diverse products Zln personal care, pharmaceuticals, petroleum recovery processes, high-tech applications, and medicine [1, p. 1] [3, pp. 3 − 5].

I. THEORY

1 SURFACTANTS

Surfactants, or surface-active agents, are organic substances, whose most pronounced effect is a lowering of interfacial tension due to preferential sorption of their molecules at the interfaces, even in low concentrations of surfactants. In general, the adsorption results in the changes of the surface or interfacial properties of the system [1, p. 1] [3, p. 28] [4, p. 267] [5, p. 3].

1.1 Structure

The surfactant molecule is composed of hydrophilic group (the "head") and hydrophobic part (the "tail") [1, p. 3] [3, pp. 29–30] [4, p. 265]. This amphiphilic organisation provides molecule with suitable properties for surface activity. The hydrophobic group may be represented by a hydrocarbon, fluorocarbon, or short polymeric or siloxane chain. On the contrary the hydrophilic group is ionic or polar. In aqueous systems the hydrophilic group interacts with water molecules (solvent) and the hydrophobic group attaches non-polar particles (as non-polar fatty substances, non-polar surfaces or hydrophobic groups of other molecules of the surfactant). In non-polar solvents the hydrophilic and hydrophobic groups perform oppositely [1, p. 3] [3, pp. 29– 30].
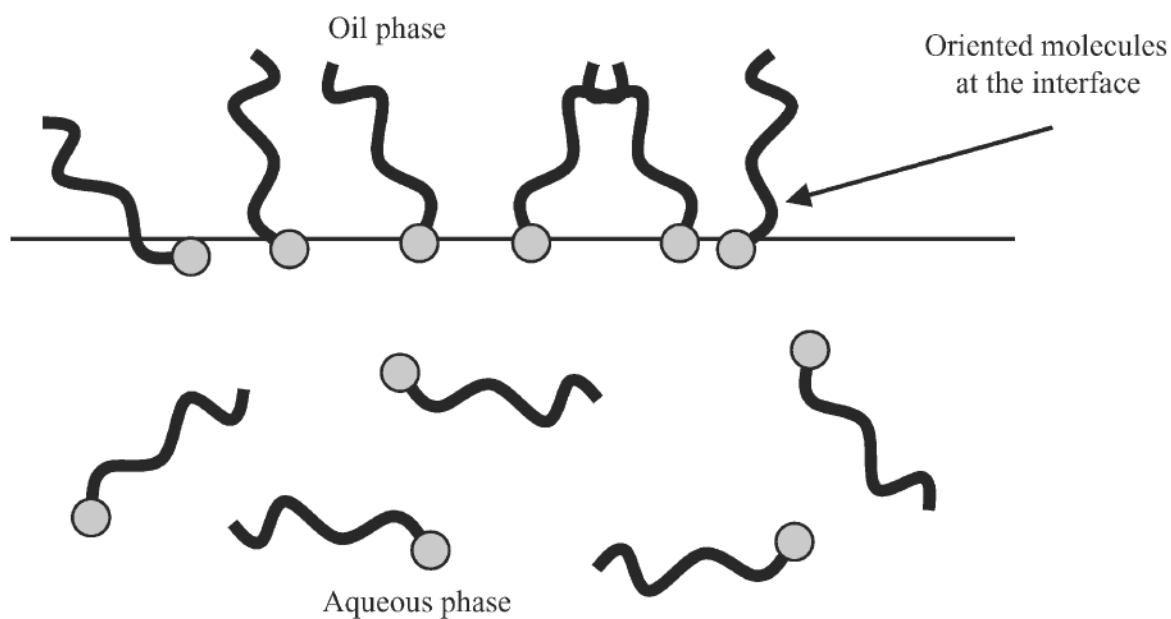

Fig. 1 The preferential orientation of surfactant molecules at the interface [3, p. 84]

1.2 Classification

Surfactants can be classified according to their composition from the two points of view, namely 1) according to the molar ratio of hydrophilic and hydrophobic part – the "hydrophilic-lipophilic balance" (HLB) [1, p. 321] [3, p. 30] and 2) on the basic of functional groups present in the surfactant molecule [3, p. 30].

The HLB value correlates with the effectiveness of surfactant acting as an emulsifier and when calculated, the HLB number is ranging from 0 to 20 [3, p. 30] or up to 40 [1, p. 321]. At the high end of the scale, the hydrophilic surfactants are situated. They stand for high water solubility and represent good solubilising agents, detergents, and stabilisers for "oil in water" (O/W) emulsions. At the opposite end of the scale there are surfactants with low water solubility, which act as "water in oil" (W/O) emulsion stabilisers. One of the determination of the HLB value is based on so called group contributions and can be calculated according to equation (1) [3, pp. 306– 307].

$$HLB = 7 + \sum (hydrophilic\ group\ numbers - \sum (hydrophobic\ group\ numbers) \qquad (1)$$

Some of the typical group contributions are listed in *Tab. 1*.

Tab. 1 Typical group contributions for calculation of the HLB values [3, p. 308]

group	HLB number	group	HLB number
hydrophilic		hydrophobic	
-SO$_4$Na	38.7	-CH-	-0.475
-COOK	21.1	-CH$_2$-	-0.475
-COONa	19.1	-CH$_3$	-0.475
-N (tertiary amine)	9.4	=CH-	-0.475
-COOH	2.1	Miscellaneous	
-OH (free)	1.9	-(CH$_2$CH$_2$O)-	0.33
-O-	1.3	-(CH$_2$CH$_2$CH$_2$O)-	-0.15

The application possibilities of surfactants according to the HLB value are presented in following table.

Tab. 2 The HLB ranges and general areas of application [3, p. 313]

HLB range	general applications
2–6	W/O emulsions
7–9	Wetting and spreading
8–18	O/W emulsions
3–15	Detergency
15–18	Solubilisation

According to the classification based on the character of hydrophilic group, the ionic and non-ionic groups of surfactants can be named.
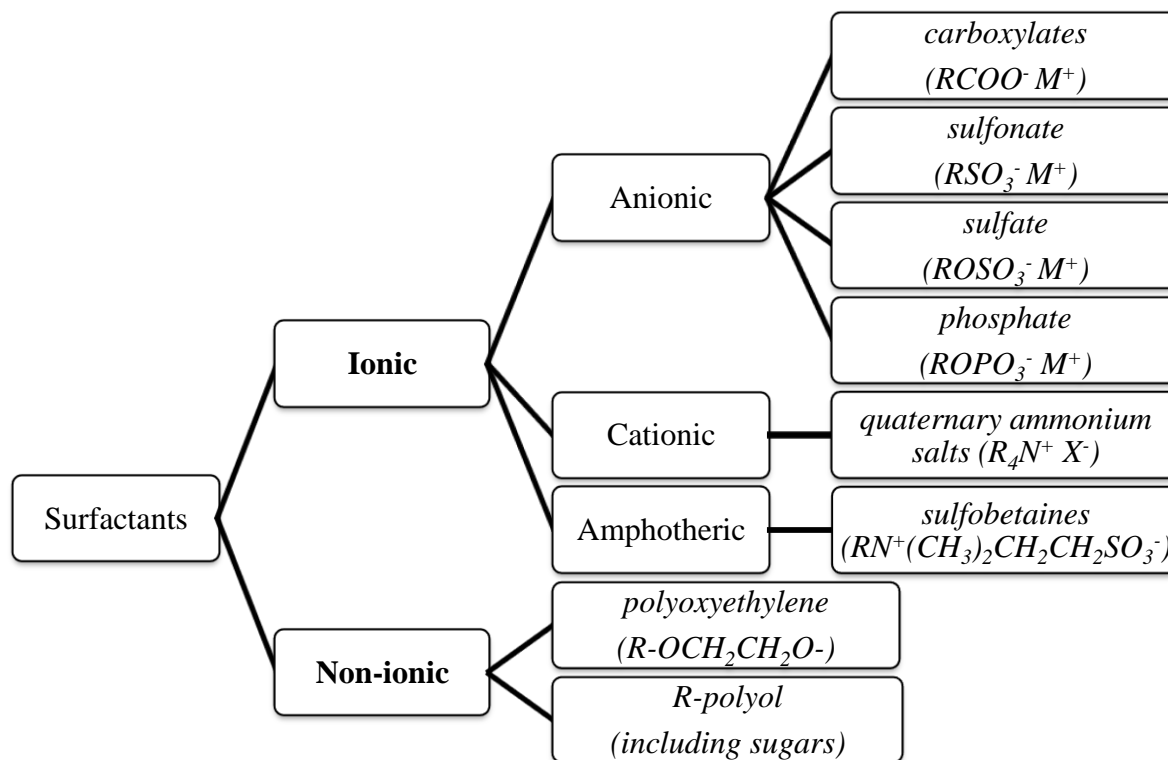

Fig. 2 The classification of surfactants according to their chemical structure

Anionic surfactants contain the negatively charged hydrophilic group. The positively charged hydrophilic group is present at cationic surfactants. In case the hydrophilic group has no charge and derives the water solubility from highly polar groups, the surfactants are called non-ionic. Finally, the amphoteric (zwitterionic) surfactant molecules can be named, which are composed of functional groups carrying both a negative and a positive charge [1, p. 5] [3, pp. 31– 32]. In general, the hydrophobic group (R) consists of long hydrocarbon chain; nevertheless its structure may vary with respect to the substitution and structure of the chain. Hence branched-chain alkyl groups (internal substitution), unsaturated alkenyl chains, alkylbenzenes, alkylnaphtalenes, perfluoroalkyl groups, high-molecular-weight polyoxypropylene glycol derivatives, polydimethylsiloxanes, or derivatives of natural and synthetic polymers can be encountered [1, p. 4] [3, pp. 31– 32]. The wide variety of structures provides possibility to choose an appropriate surfactant for certain application [3, p. 32].

1.3 Surfactant properties

Normally, reduction of surface tension (γ) is considered as one of the most common physical properties of surfactants. The surface tension depends directly on the replacement of molecules of solvent at the interface by molecules of surfactant, and therefore on the surface (or interfacial) excess concentration of the surfactant (Γ), as shown by the Gibbs equation (2), where $d\mu$ is the change in chemical potential of any component of the system [1, p. 208]:

$$d\gamma = - \sum_i \Gamma_i d\mu_i \tag{2}$$

The Gibbs adsorption isotherm is hence saying that if a substance adsorbs at an interface and its concentration is increased the interfacial tension decreases where $\frac{d\gamma}{dc}$ stands for surface activity of dissolved agent, R is the gas constant (8.314 J·mol^{-1}·K^{-1}) and T is the absolute temperature (K):

$$\Gamma = - \frac{c}{RT} \cdot \frac{d\gamma}{dc} \tag{3}$$

This process differentiates the various surfactant types and determines their utility in applications where surface tension lowering is important. In aqueous solutions, the

interface between the liquid and gas phases involves interactions between relatively densely packed, highly polar water molecules, and relatively sparse, non-polar gases. The fact results in an imbalance of forces acting on the surface molecules and there is high surface tension of water (72 mN/m) observed. With increasing extent of molecular interaction between the phases, by the introduction of polar groups, there the interfacial energy will be reduced. Therefore, addition of surfactant in water decreases surface tension of the solution, and the process continues till the interface becomes saturated with the monomeric form of surfactant [3, p. 94] [4, p. 266].

1.3.1 Adsorption

The impact of adsorption phenomena is relevant in numerous areas, such as cosmetics, cleaning and detergency, pharmaceuticals, food science, agriculture, mineral ore froth flotation, extraction of petroleum resources, surface protection and the use of paints and inks. These applications would be almost impossible without the effects of adsorbed surfactants and stabilisers at the solid–liquid interface [3, p. 323].

Because of the presence of hydrophilic and hydrophobic parts, the surfactant molecule is capable of the preferential orientation at interfaces and the adsorbed molecules are oriented in such way that the hydrophobic groups are directed away from the aqueous solvent phase [1, p. 34] [3, pp. 83– 84].

In the adsorption process, two aspects are considered: the kinetics of this process and the effect of the adsorbed species on the final equilibrium interfacial energy of the system. When interfacial adsorption occurs, the energy of the interface is being changed. To comprehend and predict the role of surfactant adsorption, it is necessary to determine the amount of material adsorbed at the interface. Changes in the interfacial energy of a system and the degree of adsorption of a species at the interface and the composition of the bulk phases are expressed by the Gibbs equation (3) [3, pp. 85– 86].

1.3.2 Solubilisation

Solubilisation is defined as a spontaneous process which leads to a thermodynamically stable solution of inherently insoluble or slightly soluble substance in a given solvent due to the addition of amphiphilic compounds that are in concentration above their critical micelle concentration [3, p. 193].

It is well known that the location of a substance to be solubilised in a micelle depends on the composition of the surfactant. Considering aqueous solutions, non-polar substances (e.g., hydrocarbons) are associated with the core of the micelle, whereas slightly polar materials (e.g., long-chain fatty acids and alcohols, esters, amides or nitriles) are usually located between the hydrophobic micelle core and the hydrophilic outer layer of the micelle [3, p. 194].
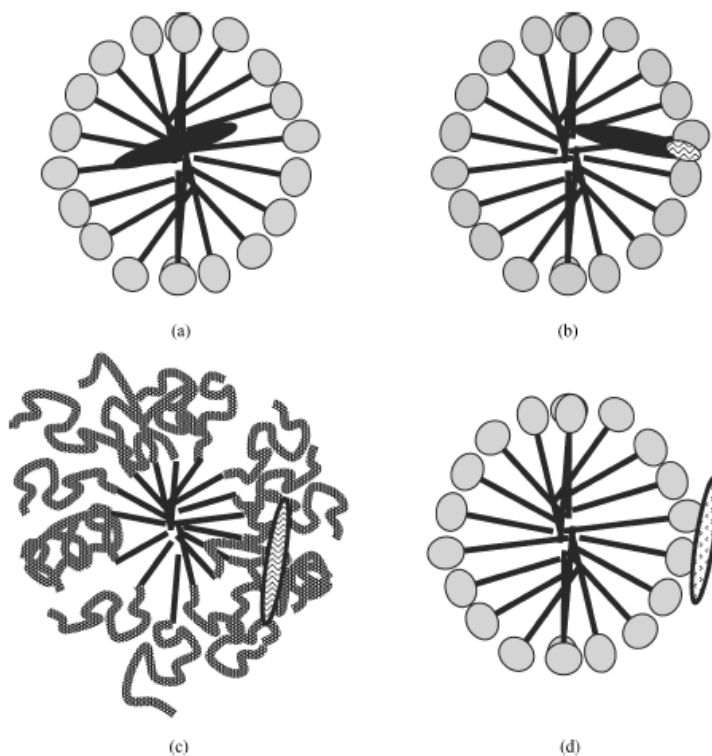

Fig. 3 The loci for the solubilisation of additives in micelles: (a) micelle core; (b) core-palisades interface; (c) surface region for non-ionics; (d) micelle surface for ionics [3, p. 194]

The solubilisation process is influenced by many factors; the most important are temperature, presence of electrolytes and polarity of solvent [1, p. 194].
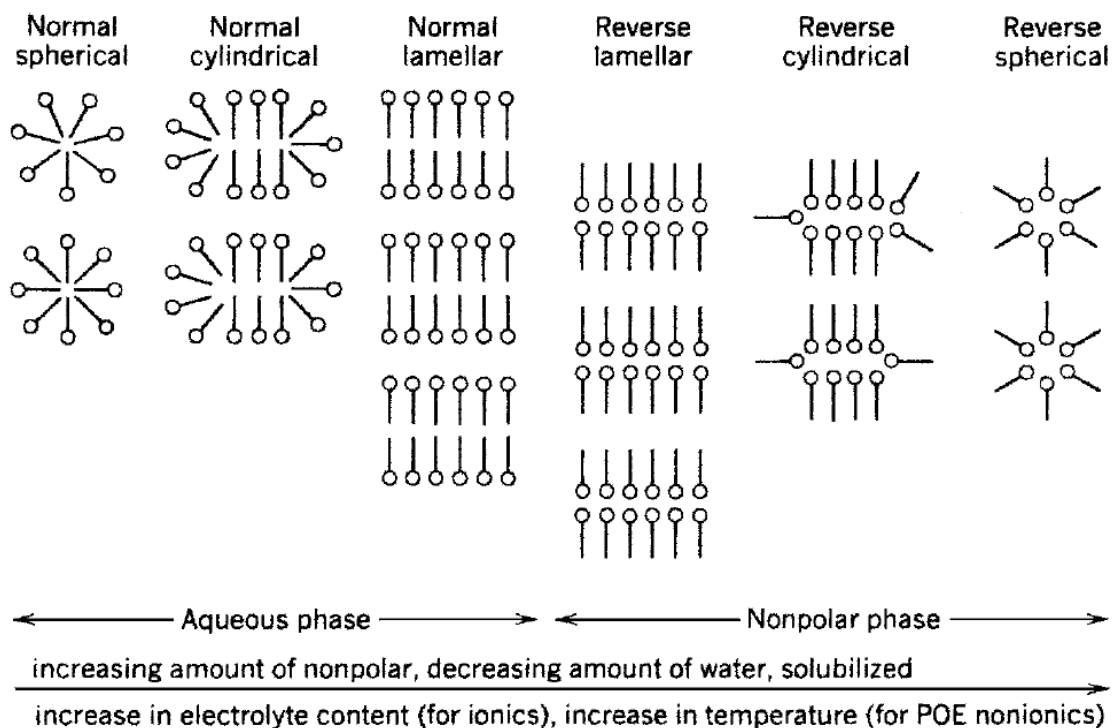

Fig. 4 Factors affecting micelle structure in solubilisation process [1, p. 194]

The ability to incorporate insoluble (or only slightly soluble) materials into a solvent system in a stable way may be applied in many important technological areas. The most important utilizations are new drug delivery systems, oil recovery methods and personal care products [3, p. 191].

Solubilisation can be also applied in micelle catalysis during the reaction of organic compounds. The effect of micelles can be attributed to electrostatic and hydrophobic interactions that affect the rate of a reaction; either by its effect on the transition state of the reaction or by its effect on the concentration of reactant placed close to the reaction site [1, p. 198].

1.3.3 Wetting

The wetting process is described as the situation when a solid surface is in contact with liquid and the liquid spreads to displace a second fluid (typically air) [3, p. 349]. This type of wetting is usually called spreading.

The spontaneity of spreading process is determined by the spreading coefficient ($S_{L/S}$), defined by equation (4).

$$S_{S/L} = \gamma_{SA} - (\gamma_{SL} + \gamma_{LA})$$ (4)

The spreading occurs spontaneously, if the spreading coefficient is positive; if it is negative, the liquid will not spread spontaneously over the substrate [1, p. 244].

Considering the solid surface, the spreading coefficient is evaluated by indirect means, as surface and interfacial tension of solid cannot be easily measured directly. Therefore the measurement of contact angle (θ) between the substrate and the liquid is involved [1, 246].
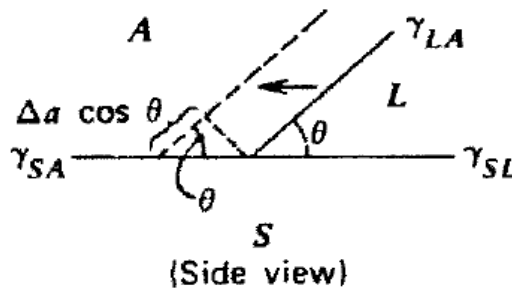

Fig. 5 The contact angle [1, p. 246]

The contact angle that the liquid makes when it is at equilibrium with the other phases is related to the interfacial free energies of those phases [1, p. 246]. This basic phenomenon is defined by Young equation (5). In practice, the γ_{SA} represents surface tension on the interface solid/air, γ_{SL} stands for surface tension on the interface of solid/liquid phases and γ_{LA} is surface tension on the interface liquid/air.

$$\cos \theta = \frac{\gamma_{SA} - \gamma_{SL}}{\gamma_{LA}}$$ (5)

The contact angle can be measured directly by use of a microscope fitted with a goniometric eyepiece or by taking the photos of the droplet [1, p. 247]. In the second type of wetting, adhesion wetting, a liquid not originally in contact with a substrate makes contact with that substrate and adheres to it. This type of wetting may be characterised as the work of adhesion, the reversible work required to separate the unit area of liquid from the substrate [1, p. 249], which is given by Dupré equation (6).

$$W_a = \gamma_{SA} + \gamma_{LA} - \gamma_{SL} \qquad (6)$$

The work of self-adhesion of a liquid (it means the work of cohesion) is defined as the work required producing two unit areas of interface from an original unbroken column of the liquid and is defined by equation (7).

$$W_c = 2\gamma_{LA} \qquad (7)$$

The difference between the work of adhesion of the liquid for the substrate and its work of cohesion equals the spreading coefficient [1, p. 250]:

$$W_a - W_c = \gamma_{SA} + \gamma_{LA} - \gamma_{SL} - 2\gamma_{LA} = \gamma_{SA} - \gamma_{LA} - \gamma_{SL} = S_{S/L} \qquad (8)$$

Come to the conclusion, if $W_a > W_c$, $S_{S/L} > 0$, $\theta = 0°$ the liquid spreads spontaneously over the substrate to form a thin film. On the contrary, if $W_a < W_c$, $S_{S/L} < 0$, $\theta > 0°$ the liquid does not spread over the substrate but forms droplets of lenses [1, p. 251].

1.3.4 Detergency and the cleaning process

Detergency is undoubtedly a phenomenon reflecting the physicochemical behaviour of matter at interfaces. This process of the removal of complex soils and oily mixtures from solid substrates depends on the mechanism of detergency, the chemical structure of the surfactants and other components present in formulations. The principle of detergency relies in the interaction between solid substrates and dispersed or dissolved materials. In most adsorption processes related to detergency, it is the interaction of the hydrophobic part of the surfactant molecule with the dispersed or dissolved soil and with the substrate that produces detergent action. The adsorption alters the chemical, electrical, and mechanical properties of the interfaces and depends strongly on the nature of each component. Generally, the soil may have liquid (oily) or

solid character; moreover it can have a complex composition and involve proteins, carbohydrates, fats, pigments etc. Naturally the mechanisms of soil removal should be complex as well. The adhesion of soils to solid substrates is influenced by variety of interactions, e.g. Van der Waals interactions, electrostatic forces, dispersion. Obviously, the cleaning process can be extremely complicated [3, pp. 355– 357].

During the removal of solid, particulate soils from a substrate in an aqueous cleaning bath there is involved the wetting of the substrate and soil by the cleaning bath followed by adsorption of surfactant at the substrate-liquid and soil-liquid interfaces. Ideally this process results in a reduction of the energy which is required to separate the two phases, and then an electrostatic or steric barrier is formed to prevent re-deposition of the soil onto the substrate. The solid dirt is usually removed without residues on the surface. The oily soils can be removed completely, if the contact angle between substrate and soil is above 90°. The problem occurs when the contact angle is lower than 90 °C. Then, the bulk of liquid soil is removed, however the residue of soil remains on the surface and it is necessary to prevent the re-deposition of separated soil until it is rinsed off. For the isolation of oily soils from the substrate, the micelle solubilisation or emulsification can be applied [3, pp. 356–359].

The correlations of surfactant structure and detergency could be summarised as follows: detergent power is increasing with the length of the hydrophobic chain; straight hydrophobic chains show better detergency than branched ones (assuming the same number of carbon atoms); non-ionic surfactant runs better in the solution which has the temperature above the cloud point of the surfactant; an increase in the length of the polyoxyethylene chain of non-ionic surfactant usually leads into a decrease in detergent power and the optimum detergency effect is achieved with 3−6 units of polyoxyethylene chain [3, p 362].

1.3.5 Emulsification

Emulsion formation and stabilisation is one of the most important areas of surfactant applications. An emulsion is defined as a heterogeneous system, consisting of at least one immiscible liquid dispersed in another in the form of small droplets with diameter of < 0.1 mm. Such systems have a tendency to disintegrate, thus addition of appropriate amphiphilic substance is required for its stabilisation [3, p. 280].

According to composition, emulsions can be described as either oil-in-water (O/W) or water-in-oil (W/O), where the first phase mentioned represents the dispersed phase and the second the continuous phase. Rarely, oil-in-oil (O/O) emulsions can be also found [3, p. 281].

1.4 Application

The common application for surfactants is their use as ingredients in soaps and detergents used in cleaning clothes, dishes, houses, etc. [3, p. 7] [4, p. 265]. Other areas where surfactants are widely applied are cosmetics, e.g., oral care products (toothpastes, mouthwashes), hair care products, skin care products (shower gels creams, lotions, shaving creams, make-up remover), as well as decorative cosmetics (lipstick, rouge, make-up, mascara), hair dyes and tints; also pharmaceuticals, such as drug-delivery systems have to be mentioned in this context [2, pp. 16−31] [4, p. 265]. Surfactants play an important role in textile-and-fibres industry especially in dyeing of textiles where they aid the uniform dispersion of the dyes in dying solution, the penetration of this solution into the fibre matrix and the proper deposition of the dyes and fixing to the fibre surface. The manufacture of leather and furs requires surfactants during leather tanning and dying. Obviously surfactants can be found in paints and lacquers and other coating products where a uniform dispersion stable to flocculation and coalescence is needed. In the papermaking industry, especially in production of coloured paper, surfactants have also their function. For example, the water-absorbing capacity of paper is frequently controlled by the addition of the appropriate surfactants. Surface-active agents are also involved in recycling paper process during the removal of the ink and pigments. Last but not least, mining and ore flotation, oilfield chemicals and petroleum production, metal-processing industries, plastics and composite materials, pharmaceuticals, agriculture (plant protection and pest control) and food industry cannot dispense with surfactants [3, pp. 7− 17].

1.5 Biodegradability

Surfactants are chemicals used in the products and processes affecting environment, and that is why biodegradability becomes their important parameter. Biodegradability increases with increasing linearity of the hydrophobic group and it is reduced by branching. Increasing number of oxyethylene groups in non-ionic surfactant mole-

cules also tends to hinder biodegradation process. Multiple substitution of quaternary ammonium surfactants decreases biodegradability as well [1, p. 31]. On the contrary, all sarcosinates show better biodegradability than frequently used sodium dodecyl sulphate (SDS) [2, p. 12].

Currently, more and more surfactants are produced from "natural" or renewable sources, mostly vegetable oils and animal fats [3, p. 8].

2 MICELLES AND CRITICAL MICELLE CONCENTRATION

Surfactant molecules have a specific structure that is responsible for their behaviour at interfaces where, due to their presence, the interfacial free energy (the surface tension) is reduced. If all interfaces are saturated with properly oriented surfactant molecules, the free energy is reduced through other mechanisms, such as crystallisation, precipitation or formation of surfactant aggregates – micelles [3, p. 105, 108] [4, p. 266]. Above certain concentration, called the critical micelle concentration (CMC), aggregates and free surfactant monomers coexist [19, p. 7173].

Micelles are spontaneous, thermodynamically driven self-associated structures in solution. Molecules of surfactant can also form highly ordered self-assembled structures such as vesicles, continuous bi-layered systems and multi-layer membranes [3, p. 107].

When micelles are formed in a solution, sudden change in properties, such as conductivity, turbidity, surface tension etc. is observed (*Fig. 6*) [3, pp. 105– 106, 117– 118]. This phenomenon is used for determination of CMC, the lowest concentration of surfactant at which micelles are formed and detected.
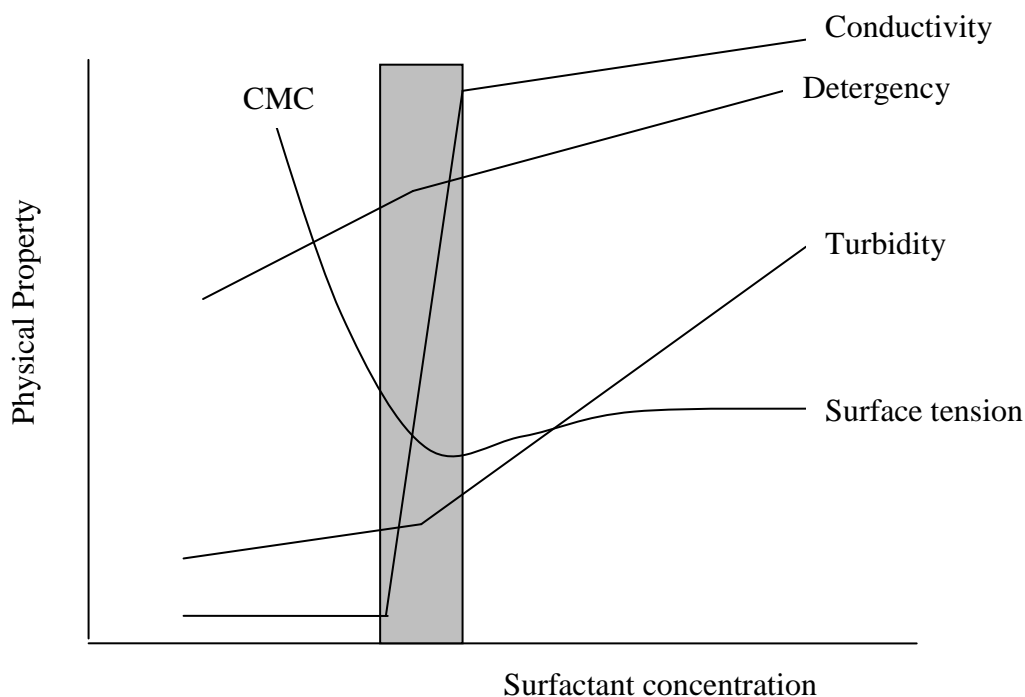

Fig. 6 The changes in surfactant measurable properties

Micelles can exist in various shapes and forms depending on surfactant concentration, temperature, additives and chemical structure of surfactant molecule [3, p. 108]. It is difficult to determine the exact shape of micelle, because micelles are not static species. The commonly used model of micelle is Hartley's spherical micelle, but this form is in fact an exception. More often, ellipsoidal, disk-shaped and rod-like structures are encountered [3, pp. 107–108] [4, p. 266] [7, pp. 119-121]. The micelle in aqueous media varies from spherical, cylindrical up to lamellar shape [3, p. 108]. One of the parameters describing the micelle is micelle aggregation number that is similarly as the micelle shape influenced by solvent, temperature and naturally by the chemical composition of the molecule of surfactant, especially the length of hydrophobic chain and the size of the hydrophilic group [3, pp. 113–119]. The parameters with impact on the CMC are summarised in *Tab. 3*. Micellisation process can be described by CMC/C_{20} ratio, where C_{20} is surfactant concentration required to decrease the surface tension of pure solvent by 20 mN/m [3, pp. 149 – 151].

Tab. 3 The factors affecting CMC

factor	decreasing CMC	increasing CMC
length and structure of hydro-carbon chain	increasing length of chain	branching of chain
	occurrence of benzene ring	occurrence of double bonds
properties of hydrophilic group	nonionic group	ionic group increasing length of polyoxyethylene chain
ion power	increasing ion power (occurrence of electrolytes)	n/a
other compounds	non-polar compounds	highly-polar compounds
temperature	increasing temperature (for non-ionic surfactants)	increasing temperature (for ionic surfactants)

2.1 Methods for determination the critical micelle concentration

Determination of CMC of surfactants is essential to scientists and technologists as a number of properties of a surfactant solution that suddenly change when the CMC is reached (*Fig. 6*). Around CMC phase transformation of monomeric surfactant solution to micelle solution occurs [4, p. 268]. The most conventional methods for CMC determination are tensiometry, conductometry and a method observing solubility of dyes. Other techniques are represented by fluorescence spectroscopy, densitometry, viscometry and methods using light scattering. Selected methods are described below.

2.1.1 Surface tension

In case of liquids, surface tension is a property caused by intermolecular forces near the surface leading to the apparent presence of a surface film and to capillarity.

With increasing concentration of surfactant in a solution the surface tension decreases. When the surfactant concentration corresponds to CMC and the micelles are formed, there is a break-point in tensiometric profile (usually the surface tension *vs.* surfactant concentration) [4, p. 269]. Common methods used for measuring the surface tension are the drop-weight method, du Noüy Ring or Wilhelmy plate method, maximum bubble pressure and spinning-drop method [11, pp. 122– 130].

In analysis part of this thesis, the Wilhelmy plate method is used and therefore it is described in more details below.

The Wilhelmy plate method is based on the measurements using a thin platinum (or platinum/iridium) plate placed on a micro-balance [11, p. 126]. The plate is put in a fixed position perpendicular to the liquid surface and dipped into the liquid whose surface tension is to be measured. The plate is gradually raised and the force at a point of the detachment of the plate from the liquid is recorded [12, pp. 3153– 3154].
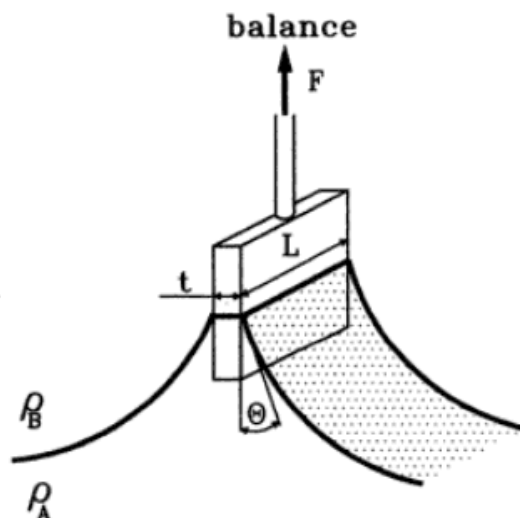
Fig. 7 The scheme of the Wilhelmy plate method [12, p. 3153]

The force (*F*) recorded on the balance is then used for γ calculation employing the Wilhelmy equation (9):

$$\gamma = \frac{F}{P \cos \theta} \tag{9}$$

$$P = 2(L + t) \tag{10}$$

In the calculation, parameter *P* stands for the wetted perimeter of the plate and *θ* is the contact angle. Modern instruments use plates of standard dimensions so that information on the plate size and weight are not required [12, p. 3154]. By cleaning the plate by burning it in the flame before each experiment, the contact angle is reduced to near-zero values, so the plate is completely wetted. The Wilhelmy plate method does not need any correction [11, p. 126]. The plate remains in contact with liquid during the entire cycle of interfacial tension measurement. A major source of experimental error arises from the adsorption of organic compounds from the laboratory environment or test solutions on the plate [12, p. 3154].

From tensiometric measurements, physicochemical parameters of the surfactant containing systems can be calculated, such as the excess concentration of surfactant Γ_{max}.

Another parameter evaluated form the tensiometric measurement is the efficacy of the surfactant monomer to populate the interface (usually air/solution) in the low concentration region, pC_{20} [4, p. 269].

$$pC_{20} = -\log C_{20} \tag{11}$$

The minimum area per molecule of surfactant related to the air/solution interface (A_{min}) can be also determined. The tendency of the surfactant adsorption at the interface relative to its tendency to participate in the micellisation process can be determined by the CMC/C_{20} ratio.

2.1.2 Conductivity

Conductivity is a physical quantity that can be measured with good reproducibility and high precision [14, p. 93]. Measurement of conductivity is meaningful only in ionic surfactant solutions. Their dissociation occurs in concentrations below CMC. In this concentration the molecules are in monomeric form and conductance increases with increasing surfactant concentration in solution. Due to electrostatic interaction (Coulombic forces) in the course of micellisation, counterions located inside the Stern layer condensate and the number of charged molecules decreases. This is reflected in the overall decline of conductivity that is presented as the decrease in the rate on increment in conductivity with increasing surfactant concentration [4, p. 269]. As a consequence, in conductometric profile, there is a noticeable which stands for CMC [4, p. 269].
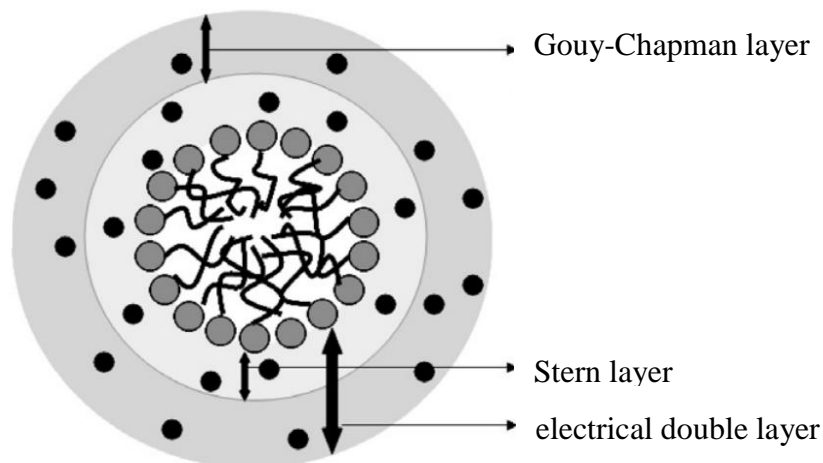
Fig. 8 The scheme of micelle microstructure of ionic surfactant
[4, p. 268]

In conductometric studies of ionic solutions, there is usually determined specific conductivity (κ), molar or equivalent conductivity (Λ), defined as κ/c, or differential conductivity, represented by $\Delta\kappa/\Delta c$. Conductivity method provides determination not only the CMC but also ionic constants of aggregates or complexes, such as aggregation number, equilibrium constant, amount of charge and ionisation degree [14, pp. 93– 94].

2.1.3   Light scattering

The dynamic light scattering is based on measurements of time-dependent fluctuations in the intensity of scattered light from the laser source, around its average value. These fluctuations are related to the interference, either constructive or destructive, of the scattered light at non-stationary particles that undergo a random Brownian motion [8, p. 431] [15, p. 1]. The time for fluctuation to return to the average value of scattered light intensity is described as the relaxation time (τ_c). Its value is related to the diffusion coefficient (D) of scattered particles.

That is explained by the equation (12), where Q represents the wave vector, whose value is determined by the wavelength of the primary light beam and by the angle, under which the intensity of the scattered light is measured [8, p. 431].

$$\tau_c = \frac{1}{DQ^2} \tag{12}$$

Due to Brownian motion, large particles move more slowly in comparison with small particles and, therefore, fluctuations of small particles caused by their movement disappear faster.
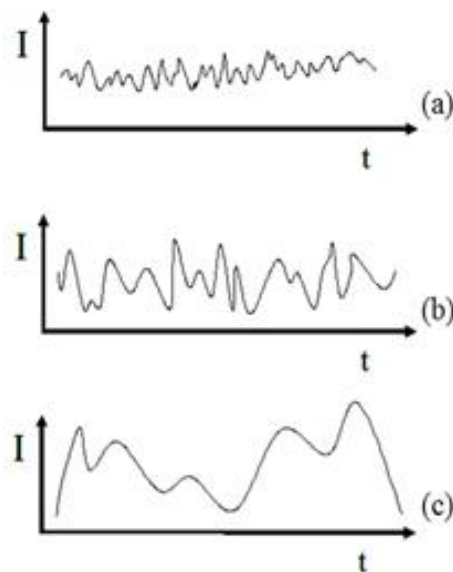

Fig. 9 The typical intensity fluctuations for small (a) and large (b, c) particles [16]

Finally, the diffusion coefficient D found by DLS is related to the hydrodynamic radius R_h via the Stokes-Einstein equation [15, p. 2].

$$R_h = \frac{k_b T}{6\pi\eta D_t} \tag{13}$$

Where k_b is Boltzmann's constant, T stands for thermodynamic temperature and η represents dynamic viscosity of dispersion medium.

The basic information obtained from a DLS measurement is intensity based particle size distribution [8, p. 431]. According to Rayleigh approximation, intensity of particle scattering is proportional to the sixth power of its diameter. From intensity distribution, volume and number distributions can also be generated [15, p. 5].
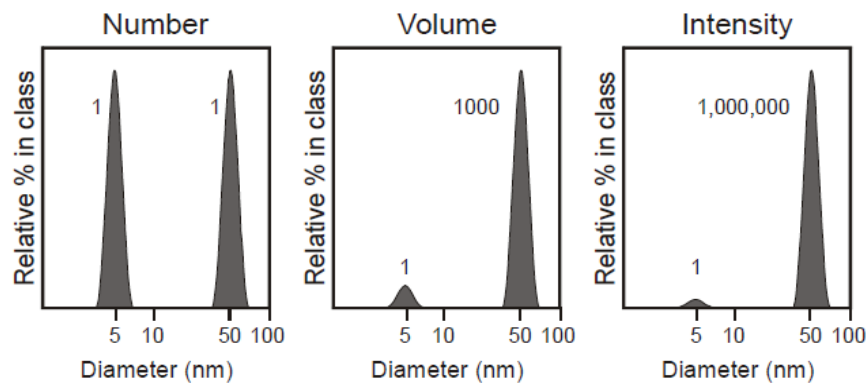
Fig. 10 The number, volume and intensity distribution (considering a sample containing only two sizes of particles with equal numbers of each size particle) [15, p. 5]

A typical DLS device consists of the following components (*Fig. 11*). Laser (1) is a light source to illuminate the sample within a cell (2). Intensity of the scattered light is measured by a detector (3). In theory, particles scatter the light in all directions, so the detector can be placed in any position. The most common detecting angles are 175° (A) or 90° (B). In order to avoid the detector overload with too much light detected, an attenuator (4) is used to reduce the scattering intensity. When measuring samples of low concentrations or very small particles, attenuator allows more light to pass through the sample. On the other hand, attenuator decrease amount of light that passes to the sample in case scattering of concentrated suspensions or large particles is too high. The appropriate attenuator position is automatically determined by the instrument during the measurement cycle. The scattering intensity signal for the detector is passed to a correlator (5), which compares the scattering intensity at a successive time intervals to derive the rate at which the intensity is varying. The correlated information goes to a computer (6), there software analyses the data and derive size information [15, pp. 6– 7].
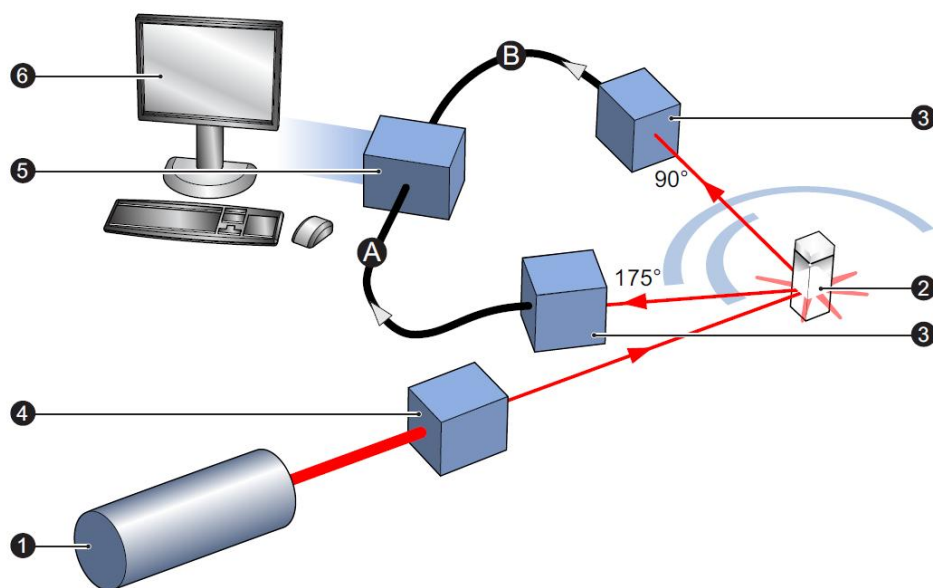
Fig. 11 The scheme of typical dynamic light scattering system [15, p. 6]

As mentioned above, the scattered light can be detected at two measuring angles. The optic with 175°detection is known as backscatter detection. This type of detection is advantageous as the incident beam does not have to travel through the entire sample, so that the pathway of the light through the sample is shorter. Therefore, higher particle concentrations can be measured and effects of multiple scattering and scattering caused by dust are reduced [15, pp. 7– 8].

Dynamic light scattering is used for particle size determination (0.3 nm – 5 μm) as well as determination of zeta-potential of colloids. It facilitates also measurement of molecular weight (down to 9 800 Da). DLS can also estimate the critical micelle concentration of surfactant solutions. Below CMC, the intensity of scattered light detected from each concentration is similar to that obtained from water. When the CMC is reached, the intensity of scattered light intensity due to the presence of micelles and the intercepts obtains higher [9, pp. 1– 2].

2.1.4 Density

Density of liquids can be determined by vibrating densitometers. Device can be based on the vibrating U−tube; the vibrating cylinder and straight tube; vibrating twin-tube or the vibrating fork [10, p. 4378] [27, p. 845]. The vibrating U−tube is used for the measurements in the analytical part of this thesis, therefore it is characterized further.

The measurement of density based on the oscillation U−tube method was invented by Dr. Hans Stabinger and Dr. Hans Leopold. During the measurements, the sample is injected into borosilicate glass U−tube that is being excited to vibrate at its characteristic frequency. Change of this frequency is depended on the density of the sample [24, p. 13].The period of oscillation of the U−tube is measured by optical pickups. Measurement is very much influenced by temperature. Values of density decrease with increasing temperature [17, p. 51]. Vibrating densitometer is calibrated with standard materials of known density. Accurate temperature compensation can become very demanding if measuring temperature rapidly changes [27, p. 845]. Extremely precise thermostating is provided by two platinum thermometers with Peltier elements [24, p. 14]. The fluid flows through U−tube section (diameter: 12.5 mm) welded at the node points. No air bubbles in U−tube during measurement are crucial. A pulsating current through the drive coil brings the U− tube into mechanical vibration. An armature and coil arrangement is provided to detect the vibration at the "pickup" end. The armature vibrates together with the U−tube and induces an alternating current (AC) voltage proportional to the fluid density in the pickup coil. This AC voltage is then converted into direct current (DC) in mV, which is more compatible with remote recorders or controllers [27, p. 848].
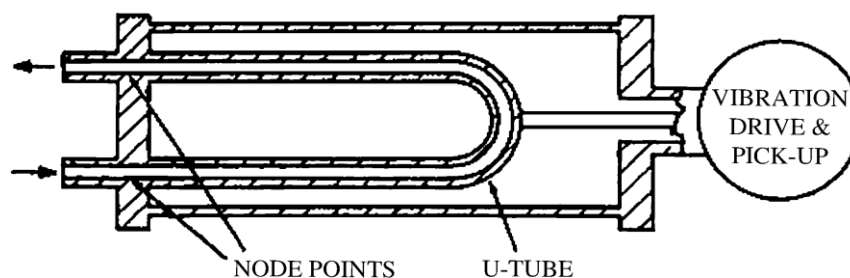

Fig. 12 The vibrating U-tube density detector [27, p. 848]

In the plot of density against concentration of solution, there is observed a sudden change in the aggregation of molecules, corresponding to the critical micelle concentration [17, p. 51– 52].

2.1.5 Viscosity

Micelles can pack together in a number of geometric arrangements known as liquid crystals that have the ordered molecular arrangement of solid crystals but the mobility of liquids. Due to this ordered arrangement of molecules, the viscosity of solution is increased considerably [1, p. 110].

Viscosity may be measured by various viscometers. In method using capillary viscometer, the efflux time of the defined volume of fluid passing through a capillary is measured. This viscometer is not suitable for characterisation of non-Newtonian fluids. The measurement with rolling-ball viscometer is based on Stokes' law. The sphere of known density is falling through a measured liquid and a time it takes the ball to passes through defined distance is measured. The third group of viscometers is rotational viscometers employing the principle that the torque required to turn a device in a fluid is a function of the viscosity of that fluid. They can be constructed in different geometries, for example as two concentric cylinders, or cone with plate [18, pp. 159– 160].

The microviscometer based on the rolling–ball principle is going to be described more closely. Usually, the device is able to measure dynamic, kinematic, relative and intrinsic viscosity of liquids especially in the low viscosity range. The method is based on filling the sample into a glass capillary in a temperature controlled capillary block, than the microviscometer is intended for measuring the rolling times of a ball in liquid samples and calculating the viscosities of samples from the obtained times. The relative viscosity and intrinsic viscosity can be calculated from the rolling times alone. On the other hand, determining a dynamic or kinematic viscosity requires adjusting the capillary and the ball. The sample's density and the density of the ball must also be known. The density of the sample may be provided with module measuring density [25, pp. 14–15], as it is possible with Anton Paar device.

3 BINARY SURFACTANT MIXTURES

The interfacial properties of the surfactant mixture are often improved in comparison with the individual components. Two surfactants in solution usually behave synergistically; therefore mixtures are used in many industrial processes and products rather than individual surfactants. The characteristic properties, such as wetting, foaming and solubilisation may be improved [1, p. 95, 167, 269−270, 379]. The tailoring of micelle properties may be also achieved by adding salts, organic solutes or, as mentioned above, a second type of surfactant forming the so-called mixed micelle system [20, p. 7188].

When two surfactants are in the mixture, mixed aggregates/micelles form and the CMC becomes a function of the surfactant composition. Assuming an absence of interaction between two surfactants (the ideal mixing), the theoretically calculated CMC of the mixture ($CMC*$) can be computed using Clint equation (14). Thus the $CMC*$ value may be calculated at any value of molar fraction of surfactant 1 (α) in mixture from the CMC values of pure surfactant 1 and 2 [1, pp. 167− 168] [10, p. 4379] [19, p. 7173] [21, p. 3340].

$$\frac{1}{CMC*} = \frac{\alpha}{CMC_1} + \frac{1-\alpha}{CMC_2} \tag{14}$$

Respectively:

$$CMC^* = \frac{CMC_1 \cdot CMC_2}{CMC_1 \cdot (1-\alpha) + CMC_2 \cdot \alpha} \tag{15}$$

However, there are observed synergistic effects in many surfactant mixtures resulting in the CMC deviation from the ideal behaviour [19, p. 7173]. The observed synergism can be attributed to non-ideal mixing in micelles, which may result in considerably smaller value of CMC and interfacial tensions, than would be expected on basis of individual characteristics of the surfactants. The non-ideal mixing relies on electrostatic interactions between the hydrophilic parts of different surfactant molecules. These molecules are randomly aggregated in micelle formation [5, p. 3]. In mixtures, two types of behaviour around CMC value can exist. Either the CMC of the mixture determined experimentally (CMC_{mix}) lies always between those of two components (CMC_1, CMC_2), or surfactants can interact in such way that CMC_{mix} (at certain

ratio between the two surfactants) is lower than either CMC_1 or CMC_2. If the latter situation occurs, the system is said to be the synergistic. In the case the CMC_{mix} at certain ratio of the two surfactants is higher than either CMC_1 or CMC_2, the system is considered to be negatively synergic, antagonistic [1, p. 167, 400]. The behaviour of regular mixtures is evaluated through interaction parameter β, which indicates the strength and nature of interactions among different component of the mixed micelle [1, p.167] [19, pp. 7173–7174] [21, p. 3341]. The deviation of β from zero is commonly assumed to result from specific interactions between surfactant head-groups [1, p. 167] [19, pp. 7173–7174]. Positive value of β indicates that upon mixing the two surfactants undergo either less attraction or greater repulsion upon mixing than before mixing. In contrast, negative interaction parameter shows that upon mixing surfactants exhibit greater attraction or less repulsion than before [1, pp. 379–380] [19, p.7174]. It indicates the existence of synergistic interaction between molecules of surfactants in the mixed state [21, p. 3341]. The β values with the largest magnitude observed experimentally have been found for mixtures of an anionic and a cationic surfactant where β is of the order −20 or even less. For mixtures of a monovalent ionic and a non-ionic surfactants, the β values are, as a rule, considerably smaller and fall in the range $-5 < \beta < -1$. For mixtures of two non-ionic surfactants, β is usually either small ($-1 < \beta < 0$) [19, p. 7174]. However, it may also happen that β value can be close to zero, thus little or no change in interactions upon mixing occur [1, pp. 379–380].

The molecular interaction parameter for mixed micelle formation by two different surfactants is defined by equation (16) based on Rubingh theory and related to the experimental CMC_{mix}, where x_m is the mole fraction of the surfactant 1 in the mixed micelle [1, p. 381] [10, p. 4379] [21, p. 3341].

$$\beta = \frac{\ln\left(\frac{\alpha \cdot CMC_{mix}}{x_m \cdot CMC_1}\right)}{(1 - x_m)^2} \tag{16}$$

The mole fraction of the surfactant 1 in the mixed micelle is given by equation (17) [1, p. 381] [21, p. 3340]:

$$\frac{x_m{}^2 \cdot \ln \dfrac{CMC_{mix} \cdot \alpha}{CMC_1 \cdot x_m}}{(1 - x_m)^2 \cdot \ln \dfrac{CMC_{mix} \cdot (1 - \alpha)}{CMC_2 \cdot (1 - x_m)}} = 1 \tag{17}$$

Interaction parameter is influenced by variation in the chemical structures of the tw surfactants and by the environment, such as pH, temperature and ionic strength of the solution [1, pp. 384−385]. A decrease in attractive interactions is commonly caused by increasing temperature in the range of 10−40 °C [1, p. 397]. Synergistic effects are believed to be caused by entropy contributions to the free energy of aggregation rather than by the specific interactions among the surfactant head-groups [19, p. 7174].The interaction between the two surfactants is mainly affected by electrostatic forces. Their strength decreases in the order anionic− cationic > anionic–zwitterionic capable of accepting a proton > cation–zwitterionic capable of losing a proton > anionic–POE non-ionic > cationic–POE non-ionic. Particularly weak interactions are observed in mixtures of surfactants of the same charge type (anionic–anionic, cationic–cationic, non-ionic–non-ionic, zwitterionic–zwitterionic), at the aqueous solution–air interface, although they can show significant interaction at other interfaces. Two oppositely charged surfactants decrease β towards large negative values because of attractive electrostatic interaction while mixed. Steric effects are also important. Branching near the hydrophilic group seems to reduce the negative value of β. Increasing number of oxyethylene groups in POE non-ionic surfactants results in sharp increasing the negative value of β in mixtures of sodium anionic and POE non-ionic. This phenomenon is not observed in cationic−POE non-ionic mixtures [1, p. 385].

Some of the other variables used for the characterisation of surfactant mixtures are provided below in text.

The surface excess concentration (Γ_{max}) at the CMC for the individual and the mixed surfactant systems can be determined using equation (18) based on Gibbs equation (3).

$$\frac{d\gamma}{d\ln c} = -nRT\Gamma_{max} \tag{18}$$

In equation (18), n is the number of species at the interface. For characterisation of pure anionic surfactant the value of n is 2, whereas n value of 1 is used for the non-ionic surfactants. For mixtures of anionic and non-ionic surfactants, the value of n is $(2 - \alpha_2)$, where α_2 is the mole fraction of the second component in the mixture [21, p. 3343].

The minimum surface area per molecule (A_{min}) at the air/water interface for the pure surfactant as well as for surfactant mixtures is given by equation (19), where N_A is Avogadro's constant ($6.022\,141\,79 \cdot 10^{23}$ mol^{-1}) [21, p. 3343]:

$$A_{min} = \frac{1}{\Gamma_{max}\, N_A} \tag{19}$$

The relation between synergism (and antagonism) is the fundamental characteristic of mixed monolayer formed at an interface of a mixed micelle in solution. Synergism in various practical applications of surfactants is still a relatively unexplored area [1, p. 405].

Moreover, the activity coefficients of both components in the mixed micelle f_1 and f_2, are often published. These parameters can be obtained from the following equations [22, p. 683].

$$f_1 = exp[\beta \cdot (1 - x_M)^2] \tag{20}$$

$$f_2 = exp[\beta \cdot (x_M)^2] \tag{21}$$

3.1   Mixture of two ionic surfactants

The same charge type surfactant mixtures (anionic–anionic, cationic–cationic) show only very weak interaction (negative β values of 1 or less) at the aqueous solution–air interface, although they can show significant interaction at other interfaces. The self-repulsion of the ionic surfactants can be reduced after mixing with non-ionic surfactant [1, p. 385]. Frequently, scholarly literature deals with binary anionic mixture. The combinations of two cationic surfactants are scarce. It may be concluded that equally charged surfactants can possess both ideal and non-ideal behaviour in micelle forming solutions [26, p. 701].

Oppositely charged surface-active components belong also to less extensively studied mixtures. Because of ion pairing of the two surfactants, such mixtures may often result in precipitation. Consequently, the surface activity and properties such as solubilisation, wetting, detergency etc. then disappear. Nevertheless, very carefully combined surfactants with opposite charge can turn out into systems with interesting characteristics, showing for example lowering surface tension due to close ion-pairs formation in the surface monolayer [1, p.407] [3, p. 152]. The large negative β values observed in the cases of two oppositely charged surfactants are consequence of the attractive electrostatic interactions [1, p. 385].

3.2   Mixture of ionic and non-ionic surfactants

Mixed micelles formed of ionic and non-ionic surfactants have been a topic of several investigations owing to their extended use in technical, pharmaceutical and biological fields. The reason is their better performance compared to pure micelles composed of single surfactants [20, p. 7188]. Ionic surfactants in mixtures with non-ionic ones are used to improve the solubility of substances [1, p. 270] [20, p. 7188]. For example, the limited solubility of non-ionic polyoxyethylenes (POE) in water (< 0.25 g/L) stands for poor textile wetting power. Owing to interaction of these poorly soluble, non-ionic surfactants and soluble, ionic surfactants in mixture, the wetting improves. Moreover, the addition of a POE has proved to increase wetting properties of some anionic surfactants and decrease wetting of cationic ones. [1, p. 270].

The synergism would result in reduction of the repulsion between the surfactant ionic head groups originating from electrostatic stabilisation caused by intercalation of

non-ionic surfactant and the head groups of ionic surfactant, so-called shielding [20, p.7189] [21, p. 3340] [23, p. 5008]. Consequently, enhancement of the hydrophobicity of the formed mixed micelle system initiates micelle formation at lower surfactant concentration [21, p. 3340]. Such mixed systems with positive synergism and enhanced surface active properties can be used as smart materials for surfactant applications. As polyethoxylated surfactants are biodegradable, such mixed systems are expected to be ecologically safer than the pure anionic surfactants [21, p. 3347]. Additionally, the interactions between anionic and non-ionic POE surfactants are stronger than those formed between cationic and POEs. The reason can be found in a presence of a partially protonated oxygen atoms in POE resulting in a partial positive charge on the non-ionic surfactant. Considering the molecular structure of ionic and non-ionic surfactants, their interactions may depend on ion-dipole intermolecular forces between the head groups of the two types of surfactants. Upon the aggregation of mixed ionic/non-ionic surfactants, hydration, electrostatic, and steric interactions are important driving forces that cannot be ignored in models predicting their interaction. Further, these non-ideal mixtures generally deviate extremely from the properties of ideal micelle solutions [23, p. 5008]. Most common cationic surfactants contain tetravalent nitrogen atoms carrying the positive charge. Due to the presence of this charge, cationic molecules are allowed to adsorb strongly to most surfaces, and these types of surfactants are often used in surface modification. In addition, cationic surfactants show higher toxicity in aqueous systems than other typical surfactants [23, p. 5009].

3.3 Mixture of two non-ionic surfactants

POE represents an important model of amphiphilic self-assembly. The molecular structure of this type of surfactant may be systematically changed, that provide possibility to control its HLB. The most significant driving forces for the formation of aggregates in solution of two non-ionic surfactants are the hydrophobic interactions; it is not necessary to consider electrostatic interactions [23, p. 4980]. Micellisation is affected by internal factors (such as the number of POE groups and the length of the alkyl chain), as well as external factors (temperature and concentration). Owing to all these factors, micelle shape, size and aggregation number are changed. The length of alkyl chain plays a more effective role than the head groups [23, p. 4983].

Theoretically, binary mixtures of POE homologues in aqueous solutions may be considered as ideal mixed systems [23, p. 5002]. However, different chemical structures of non-ionic surfactant molecules exhibit non-ideal mixing behaviour caused by steric repulsion in surfactant microstructures. Studies of non-ideal mixtures of non-ionic surfactants in aqueous solution are not frequent in comparison with the two above mentioned groups and have been, for example, focused on the formation and the rheological behaviour of viscoelastic solutions of their micelles [23, p. 5003].

4   THE STATE OF THE ART

Scientific articles looking into the studies of mixed surfactants have been focused on characterisation of micelles and the micellisation process. Studies dealing with the thermodynamics of micellisation and adsorption, counterion binding, polarity, and aggregation number have been reported, but systematic studies are not so common. The most frequently observed parameters are critical micelle concentration, molecular interaction parameter, and standard free energy of micellisation. Many studies deal with evaluation of micelle size and composition, such as critical chain length, volume of hydrophobic chain, surface of polar head group or packing parameters and radius. Some studies go further in physicochemical characterisation of binary surfactant mixtures, and describe parameters such as the standard enthalpy and entropy of the micellisation. [21, p. 3342–3343].

In general, the most frequent methods applied for the characterisation of surfactants and their mixtures are tensiometry and conductometry. Quite often, fluorescence spectroscopy connected with solubility of dyes and calorimetry is used as well. The rarely applied techniques then include densitometry and light scattering.

The crucial parameter occurring in all the studies dealing with surfactants is the CMC. Therefore, the published CMC values of individual surfactants used in the experimental part of the thesis (*N*-lauroylsarcosine sodium salt, TWEEN®20, TWEEN®60), measured by various techniques, are provided in *Tab. 4, Tab. 5* and *Tab. 6.* The CMC values reported in the tables were chosen with regard to similar experimental conditions, which were set in this thesis, namely un-buffered aqueous systems without the addition of salts and temperature close to 25 °C. The information about the CMC of the surfactant mixtures studied in the thesis has not been published yet. Therefore, any previous experimental data cannot be provided in this work.

Tab. 4 The values of the CMC of N-lauroylsarcosine sodium salt (SLSa) obtained from the data published in scientific articles with regard to the methods used for measurement (n. p. not provided)

method	CMC$_{SLSa}$ [mM]	temperature [°C]	reference
tensiometry	2.7	n. p.	[2, p. 3]
(Wilhelmy plate)	3.65	20	[30, p. 128]
conductometry	13.0	25	[31, p.137]
	12.7	25	[32, p. 134]
dynamic light scattering	10.0	n. p.	[30, p. 129]
density	2.4	20	[30, p. 128]

The literature search has shown that the tensiometry is the main method used for determination of the CMC. For ionic surfactants, the conductometry is frequently applied as well. For non-ionic surfactants, the surface tension measurement is almost the only technique that is reported; results from other techniques are published only rarely.

Tab. 5 The values of the CMC of TWEEN®20 obtained from the data published in scientific articles with regard to the methods used for measurement

method	CMC$_{T20}$ [mM]	temperature [°C]	reference
tensiometry	0.0169	20	[33, p. 1244]
	0.011	22	[34, p. 55]
(Wilhelmy plate)	0.06	n.p.	[35, p. 2346]
	0.0804	21	[40, p. 390]
dye micellisation	0.042	22	[34, p. 55]

Tab. 6 The values of the CMC of TWEEN®60 obtained from the data published in scientific articles with regard to the methods used for measurement

method	CMC$_{T60}$ [mM]	temperature [°C]	reference
tensiometry	0.0055	22	[34, p. 55]
(Wilhelmy plate)	0.022	n.p.	[35, p. 2346]
dye micellisation	0.022	22	[34, p. 55]

II. ANALYSIS

5 THE AIM OF THE WORK

The aims outlined in the diploma thesis can be summarized in the following points:

- Elaborate the literature search on the given topic with the focus on the surfactant mixtures and summarize the latest findings related to this field.

- Experimentally determine CMC of used individual surfactants (N-lauroylsarcosine sodium salt, TWEEN$^®$20, TWEEN$^®$60) and their mixtures prepared in pre-defined ratios. For CMC determination, use surface tension measurements, conductivity, densitometry, dynamic light scattering, or another relevant method.

- Evaluate the influence of mixture composition on CMC and assess the mutual interactions of surfactants by choosing the appropriate physicochemical parameters.

- Estimate the accuracy, advantages and disadvantages of the methods used for CMC determination.

6 MATERIALS AND METHODS

6.1 Chemicals

In the thesis, the following surfactants are used.

N-Lauroylsarcosine sodium salt

$CH_3(CH_2)_9CH_2$ — N(CH_3) — CH_2 — C(=O) — ONa
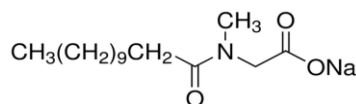
Synonyms:	Sarkosyl NL
	N-Dodecanoyl-N-methylglycine sodium salt
Formula:	$C_{15}H_{28}NNaO_3$
Formula weight:	293.38 g/mol
Density:	1.141 g/mL (20 °C)
CMC:	14.6 mM (20– 25 °C)
HLB [2, p. 2]:	acid: 13.1
	sodium salt: 29.8
Brand:	Sigma-Aldrich
CAS-No.:	137-16-6

TWEEN®20
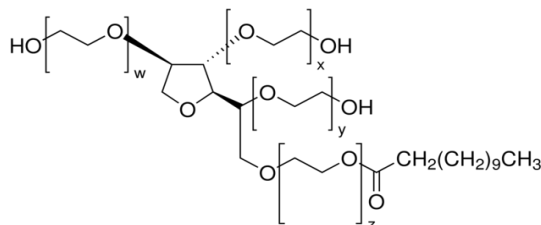
Synonyms:	Polyoxyethylenesorbitan monolaurate
	Polyethylene glycol sorbitan monolaurate
Formula:	$C_{58}H_{114}O_{26}$
Formula weight:	1228 g/mol
Density:	1.095 g/mL (25 °C)
CMC:	0.06 mM (20– 25 °C)
HLB:	16.7
Brand:	Sigma-Aldrich
CAS-No.:	9005-67-8

TWEEN®60
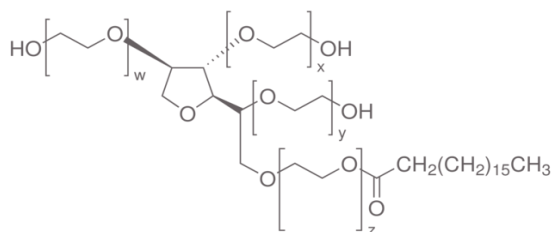
| Synonyms: | Polyoxyethylenesorbitan monostearate |
| | Polyethylene glycol sorbitan monostearate |

Formula: $C_{64}H_{126}O_{26}$

Formula weight: 1309 g/mol

Density: 1.044 g/mL (25 °C)

CMC: 0.02 mM (20– 25 °C)

HLB: 14.9

Brand: Sigma-Aldrich

CAS-No.: 9005-67-8

Data was given by Sigma-Aldrich.

Commercial products were used without further purification.

Furthermore, deionised water, acetone and ethanol were used.

6.2 Instruments and devices

Tensiometer

Name: EasyDyne

Type: K20

Brand: KRÜSS

Measuring range: 1 – 999 mN/m

Resolution: 0.1 mN/m

Components: tempering bath
temperature sensor
glass bowl
platinum plate (PL21)

Thermostat

Name:	HAAKE
Type:	C10 (control panel)
	P5 (bath with heating system)
Brand:	THERMO electron corporation
Components:	thermometer, inlet and outlet fluid temperature control system

Conductivity meter

Type:	HI 8733
Brand:	HANNA
Measuring range:	0 – 199.9 mS
Resolution:	0.1 μS
Components:	magnetic stirrer HI 190 M

Particle size analyzer

Type:	Zetasizer Nano ZS90 (and Zetasizer Nano ZS)
Brand:	Malvern
Measuring range:	0.3 nm to 5.0 μm (0.3 nm to 10.0 μm)
Accuracy:	particle size: 2 %
Repeatability s. d.:	particle size: 2 %
Minimum sample volume:	20 μL (12 μL)
Temperature control range:	0 to 90 °C
Light source:	He-Ne laser 633nm, max 4mW, Class 1
Measuring angle:	90 ° (173°)

Density Meter

Type:	DMA 5000 M
Brand:	Anton Paar
Measuring range:	density: $0 - 3$ g/cm^3
Accuracy:	density: 0.000005 g/cm^3
Repeatability s. d.:	density: 0.000001 g/cm^3
Minimum sample volume:	1 mL

Digital microscope camera

Type:	AM7013MT Dino-Lite Premier
Brand:	DINO LITE
Resolution:	5 M pixels (2592 x 1944)
Magnification:	20x ~ 50x, 200x
Components:	holder for digital microscope camera, movable table, light source (standard fluorescent tube), metal shield, PARAFILM$^®$M

Laboratory scales

Name:	KERN EW420-NM
Brand:	Kern & Sohn
Measuring range:	0.02 – 420 g
Accuracy:	0.001 g

Pippetes

Name:	Eppendorf Research
Brand:	Eppendorf
Volume range:	100 – 1000 μL and 0.5 – 10 μL
Name:	-
Brand:	Plastomed
Volume range:	20 – 200 μL

It was also used laboratory glassware, polystyrene cuvettes, plastic pipette tips and other common laboratory equipment.

7 PREPARATION OF SOLUTIONS

7.1 Stock surfactant solutions

For the purposes of each measurement, stock solutions of TWEEN[®]20 (T20), TWEEN[®]60 (T60), *N*-Lauroylsarcosine sodium salt (SLSa) and their mixtures (T20:T60, T20:SLSa, T60:SLSa) in appropriate molar ratios (20:80; 30:70; 50:50; 70:30; 80:20) were prepared as follows: each stock solution was prepared by weighing the pre-calculated amount of surfactant into a volumetric flask. Then the surfactant was dissolved in warm deionised water with occasional stirring (circle moving with the flask) and the flask was filled up to volume. Stock solutions were equilibrated before the further dilution for approximately 17 hours at laboratory temperature.

7.2 Working solutions

Working solutions were prepared by proper dilution of the stock solution with deionised water. Concentrations of individual solutions were chosen according to values of the CMC published by surfactant supplier, Sigma-Aldrich. In the case of mixtures, the concentration range covered a wide area around CMC of both individual surfactants in mixture. From the stock solution, the required volume calculated according to the mixing equations was taken to another volumetric flask and filled up to volume with deionised water. The prepared surfactant solutions were equilibrated for 5 hours at laboratory temperature.

Tab. 7 The published values of the CMC; Sigma-Aldrich [36] [37] [38]

surfactant	CMC [mM]
N-lauroylsarcosine sodium salt	14.6
TWEEN[®]20	0.06
TWEEN[®]60	0.02

To get reproducible results, the samples were prepared with care and by the same way every time.

8   METHODS

8.1   Measurement of surface tension

The surface tension was measured by Tensiometer KRÜSS EasyDyne 20 using Wilhelmy plate. As a reference substance, deionised water was employed. Tabulated surface tension of 72 mN/m at 25 °C was used and the accuracy of the instrument was verified prior each measurement series [28, p. 39].

Surfactant solution (of about 25 mL) was poured into a glass bowl and placed in a tempering unit. During measurement, the temperature was kept at 25.0 ± 0.2 °C. The platinum Wilhelmy plate connected to highly sensitive tensiometric balances was submersed in a solution. After stabilising, the plate was pulled out of the solution and the force required was used to determine surface tension. The instrument performed automatically five readings of surface tension and temperature; then the mean values were read from the display. After that, the bowl was thoroughly washed with water, rinsed with deionised water and acetone; and then dried in laboratory oven. The platinum plate was carefully rinsed with deionised water, acetone and flamed over in a Bunsen burner. Each one solution was measured at least three times (3 x 25 mL), each time in a perfectly clean, dry glass bowl.

The evaluation of measured data was based on the plotting of surface tension, γ [mN/m], against concentration of surfactants in solution, c [mM]. The CMC was then determined by the intersection of the two regression straight lines passing through the pre- and the post- CMC region. The first line goes through the concentrations below CMC, where surfactant monomers are presented in solution. This line is characterised by a rapid decrease with increasing concentration. When micelles occur in solution, the straight line changes its slope and the surface tension is only slightly changed with increasing surfactant concentration [28, p. 39].

8.2   Measurement of conductivity

For measuring conductivity, the conductivity meter HANNA HI 8733 was used. The conductivity of deionised water should be minimal, practically 1.2 µS, which signifies that the water is ion-free.

The sample (100 mL) was slowly poured along the glass wall (to avoid bubbles) into a 100 mL beaker. Then, the conductivity probe was inserted into the solution and the air bubbles were removed from the probe by gently tapping. The appropriate speed of magnetic stirrer was set. The device was adjusted to the suitable measuring range. The measurement was completed after stabilisation of the conductivity value on the instrument display, which took approximately 30 seconds to 1 minute. Each of the solutions was measured at least twice.

The measured data were evaluated by the plotting the conductivity, κ [mS], against concentration of surfactants in solution, c [mM]. The intersection between the two regression straight lines, passing through the pre- and the post- CMC region stands for the CMC value. The line representing pre-CMC region has positive slope. When micelles occur in solution, the line posing the post-CMC area changes its slope slightly, resulting in retaining a positive slope, but the conductivity is not increasing so steeply with increasing surfactant concentration.

8.3 Measurement of light scattering

Measurements of intensity of scattered light were accomplished with Zetasizer Nano ZS90 and Zetasizer Nano ZS. The solution in volume of 1 mL was slowly pipetted into a polystyrene cuvette and closed with a cap. The sample was equilibrated for approx. 30 minutes at laboratory temperature. The instrument was turned on and left for 30 minutes to stabilize the laser. The Zetasizer software was started and supplied with data needed for calculations. The instrument software was set to perform three measurement cycles at 25 °C. By pressing the metallic button, the lid to the Zetasizer was opened; cuvette was inserted and covered with a protective black lid to maintain the set temperature in the measuring cell. The main lid was closed and the measurement was started. The intensity of scattered light (λ = 633 nm) was observed at scattering angle of 90° (ZS90) and of 173° (ZS). After measurement was completed, the data were automatically saved and used for calculation. Measurements of hydrodynamic radius of micelles were expressed as intensity-weighed z-average particle diameter.

Data evaluation was based on the published procedure, where intensity of scattered light measured in counts [kcps] or hydrodynamic diameter of micelles [nm] were obtained for various surfactant concentrations [9, p. 24].

8.4 Measurement of density

Density measurements were conducted on DMA 5000 M by Anton Paar. Correspondingly to conductivity measurements, also prior to density measurement, a water-check was performed.

The prepared sample of surfactant was sucked by a hollow needle into the glass U–tube of the measuring cell. Real time monitoring of filling process and automatic detection of filling errors and bubbles helped to obtain accurate and reproducible results. Density of the sample was repeatedly measured until the set temperature (25 °C) was reached and the steady-state density value was obtained. Each surfactant concentration was measured only once because of high repeatability of the measurements provided by the instrument (0.000001 g/cm^3). After measurement was completed, the density value was recorded from the display and the U–tube was rinsed through flushing with the next surfactant solution to be measured. Before turn off, the instrument was rinsed by deionised water at least five times and by ethanol at least twice. Finally, ethanol was evaporated by a stream of air for 5 minutes.

The density values were plotted against concentration of surfactant in solution.

8.5 Measurement of contact angle

The contact angle of surfactant solution drops on a hydrophobic PARAFILM®M surface was observed on movable table by digital microscope camera AM7013MT Dino-Lite Premier. To keep the surface of PARAFILM®M smooth, the film was gently stretched and fixed on both sides of the table with an adhesive tape. The sample volume of 3 μL was dropped on the PARAFILM®M surface and the photo of the drop was taken without any time delay to prevent its evaporation, the shape change and distortion of the contact angle. There were taken 10 photos of 10 different drops of each surfactant concentration in solution, which means that each concentration was measured ten times.

The evaluation of the contact angle was performed by FTA32 Video 2.1 software. For calculation of the limit contact angle, which theoretically corresponds to the CMC, the minimum of polynomial function fitted through the dependence contact angle *vs.* surfactant concentration close of this point was determined.

9 CALCULATIONS

The value of the CMC, given by tensiometry and conductometry, represented by the intersection of the regression lines passing through the pre- and the post-CMC region was calculated from a system of the two equations with two unknown parameters. CMC for TWEEN®20 from tensiometry was, for example, calculated from the following equations:

$$\gamma = -129{,}35c + 50{,}53 \text{ (pre- CMC)}$$

$$\gamma = -1{,}1429c + 39{,}87 \text{ (post- CMC)}$$

The solution of these two equations provided the value of 0.0832 mM.

In order to determine the interactions between both non-ionic surfactants (TWEEN®20 and TWEEN®60) as well as interactions between each of the TWEENs and anionic SLSa, the following calculations were performed.

Theoretical *CMC** values of studied surfactant mixtures, representing the ideal mixing, were determined by calculation according to Clint equation (15). For the calculation, the CMC values of individual surfactants determined experimentally in this thesis were used (refer to Section 10.1).

For example, the determination of *CMC** for the mixture of TWEEN®20 and TWEEN®60 in a ratio of 20:80 is shown below (15).

$$CMC^* = \frac{CMC_1 \cdot CMC_2}{CMC_1 \cdot (1 - \alpha) + CMC_2 \cdot \alpha}$$

$$CMC^* = \frac{0.0832 \cdot 0.0265}{0.0832 \cdot (1 - 0.2) + 0.0265 \cdot 0.2}$$

Where *CMC₁* and *CMC₂* represent critical micelle concentrations of T20 and T60, respectively and α is a molar ratio of T20 in the mixture.

The mole fraction of surfactant in the mixed micelles x_m and the interaction parameter β were calculated using equations (16) and (17) by an in house written iterative computer program in Microsoft Excel application.

10 RESULTS AND DISCUSSION

Among various factors affecting the CMC value of ionic surfactants, the presence of additional substances in the surfactant solution, such as electrolytes that causes lowering of CMC, is crucial. On the contrary, CMC of ionic surfactants may be increased or entirely inhibited by highly polar substances.

During the thorough literature search it was found out that determination of CMC for anionic surfactant SLSa is not a straight forward issue. The problem related to CMC of this surfactant is namely its known pH dependence of surface tension. In the *Fig. 13*, there is shown the variation in surface tension of 0.1% solution of the SLSa with pH. Evidently, the minimum in γ values is reached between pH value of 5 and 7, where only minor variation of γ was observed with pH change. Below pH 5, precipitation of surfactant from the solution was reported due to predominance of insoluble acid form. The surface tension then rapidly increased at pH above 8.5 [2, p. 4].
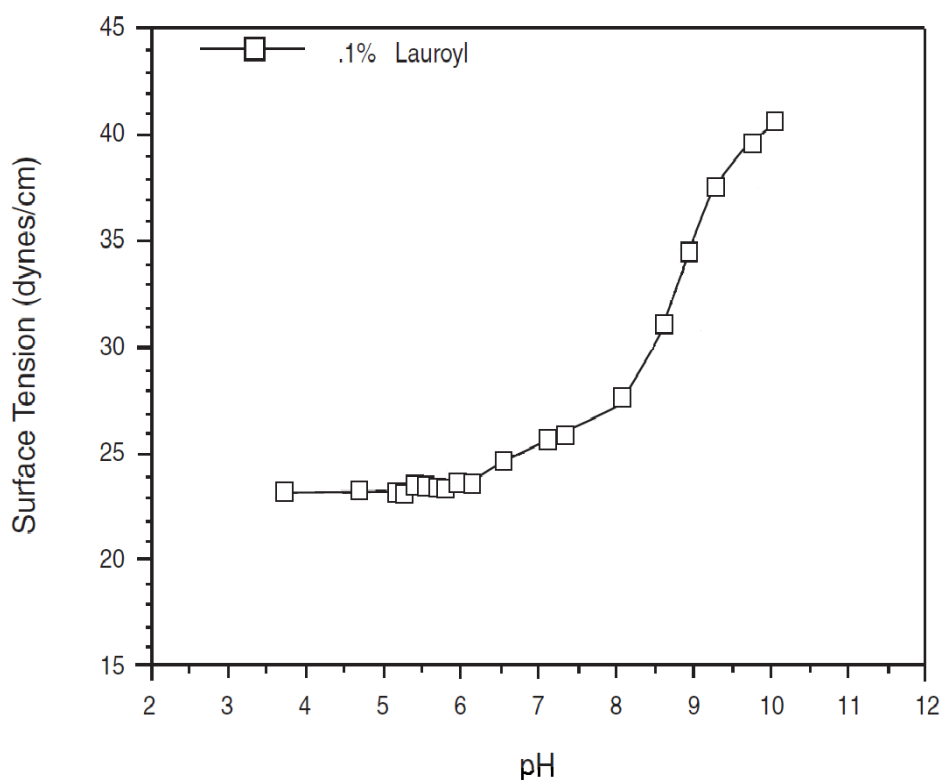
Fig. 13 The dependence of surface tension vs. pH of anionic surfactant N-Lauroyl sarcosinate [2, p. 4]

It was experimentally verified that the measured concentrations of SLSa in solution used for determination of CMC were in the pH range of 5.5 to 6.5, hence in the range where the surface tension was not significantly changed. It was also confirmed that the CMC values of buffered and un-buffered SLSa solutions in the concentration range used for CMC determination did not differ considerably. Therefore, the solutions used in the experiment were not adjusted to specific pH value.

Moreover, in cosmetic applications it is not recommended to modify pH of the solutions/formulations outside of the physiological values due to potential thread of skin irritation. Since the pH of SLSa solution with concentration close to CMC is almost identical to the pH of human skin, the unbalance of the pH of epidermis under these conditions does not occur.

The data applicable for the CMC determination provided by tensiometry and conductometry are statistically reliable. Therefore, the results from these two most frequently published methods are used for CMC determination intended for further calculations of interaction parameters for surfactants in mutual mixtures.

The remaining methods listed in part 8 of the thesis are mainly used with the aim to find out whether the CMC values determined using these procedures differ from those reported in literature, which are rather scattered. Records relating to monitoring the contact angle are shown only briefly with the purpose to reveal the further possibilities of this method.

10.1 Determination of CMC of individual surfactants

10.1.1 Tensiometry

The variation of surface tension γ *vs.* concentration c of individual surfactants is shown in *Fig. 14*, *Fig. 15* and *Fig. 16*. The CMC values are summarized in *Tab. 8*. In the table, there are also values of surface tension determined at the CMC (γ_{CMC}). The CMC for *N*-lauroylsarcosine sodium salt was of 2.62 ± 0.08 mM with surface tension at this point being of $\gamma_{CMC} = 28.7$ mN/m. The average CMC for TWEEN®20 is of 0.083 ± 0.0006 mM and surface tension at this point was lowered to $\gamma_{CMC} = 39.8$ mN/m. For TWEEN®60, the average CMC was of 0.027 ± 0.0002 mM and at this concentration, the surface tension decreased towards 47.7 mM.

The CMC values determined for non-ionic TWEENs and anionic SLSa roughly correspond with the CMC reported in the literature. However slight differences with respect to published data were observed that may be caused by the possible presence of impurities in the individual surfactants and by the variation in the conditions of methods used by authors of scientific articles (refer to *Tab. 4, Tab. 5, Tab. 6* and *Tab. 7*).

The intersections of the two regression straight lines passing through the pre- and post- CMC region in surface tension measurements, reflecting the aggregation of surfactant monomers into micelles is clearly seen, thus the determination of CMC is considered as reliable. The trend of γ *vs. c* dependence corresponds to data in published studies dealing with determination of CMC by tensiometry.

The data presented in *Tab. 8* corroborate theoretical assumptions saying that in comparison, the non-ionic surfactants (T20, T60) have much lower CMC than ionic ones (SLSa). Expressed in numerical values, the difference is up to two orders of magnitude. This variation is typical for such types of surfactants and consistent with the literature findings.

Comparing the two non-ionic TWEENs studied in the thesis, the micelle formation of T60 occurs at a lower concentration than the micelle formation of T20, as can be judged from the CMC values. It can be also concluded, that T20 reduces the surface tension more than T60, i.e. γ_{CMC} of T20 is lower than γ_{CMC} of T60. Interestingly, γ_{CMC} of SLSa is lower in comparison with both non-ionic surfactants

(28.7 *vs.* 39.8 and 47.7 mN/m), however micelle formation occurs at significantly higher surfactant concentration.

Tab. 8 The values of the CMC and γ_{CMC} for individual surfactants determined using tensiometry

surfactant	CMC [mM]	SD$_{CMC}$ [mM]	γ_{CMC} [mN/m]	SDγ_{CMC} [nM/m]
SLSa	2.62	0.08	28.7	0.3
T20	0.0832	0.0006	39.8	0.7
T60	0.0265	0.0002	47.7	0.5

SD…standard deviation

reference for T20 and T60 data [39, p. 6]
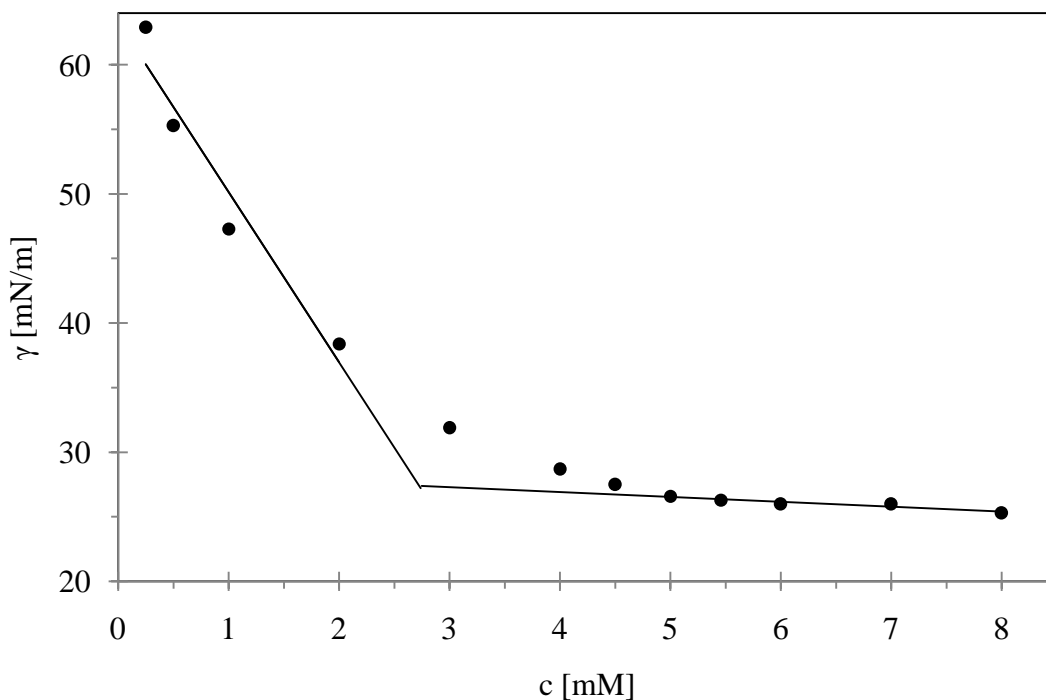
Fig. 14 The dependence of surface tension vs. concentration of anionic surfactant SLSa determined using tensiometry
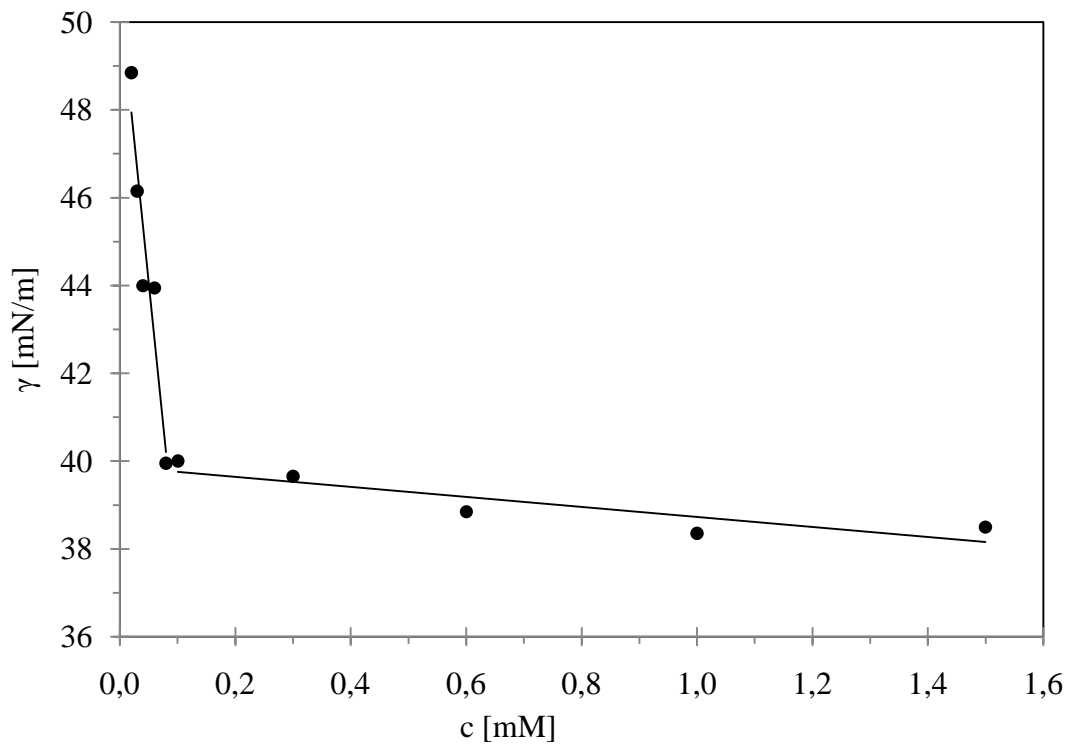
Fig. 15 The dependence of surface tension vs. concentration of non-ionic surfactant TWEEN®20 determined using tensiometry [28, p. 42]
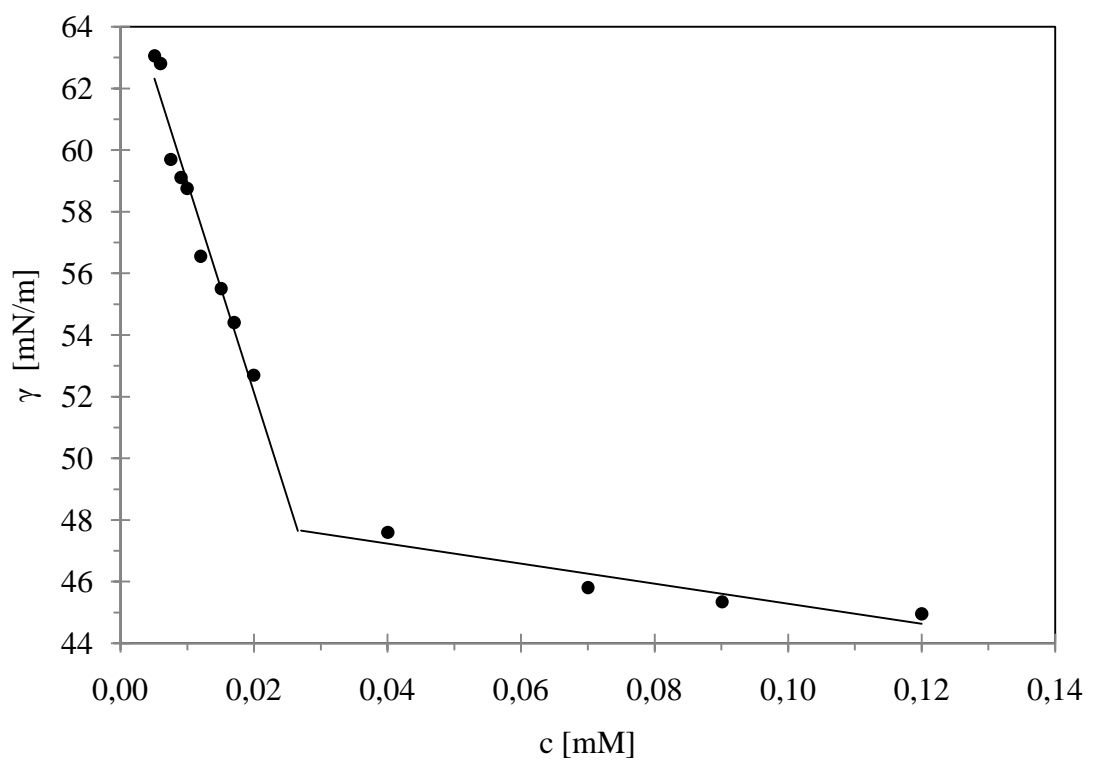
Fig. 16 The dependence of surface tension vs. concentration of non-ionic surfactant TWEEN®60 determined using tensiometry [28, p. 43]

10.1.2 Conductometry

Naturally, using conductivity, the CMC value can be determined only for the anionic SLSa, for non-ionic surfactant this method is not applicable. The correlation between conductivity κ and concentration c of SLSa is shown in *Fig. 17*. The CMC value and the value of conductivity read at CMC (κ_{CMC}) are presented in *Tab. 9*. The average CMC for N-lauroylsarcosine sodium salt was of 11.96 ± 0.08 mM with conductivity at this point 0.776 mS.

The CMC value determined with this method corresponded with CMC reported in the literature (CMC = 14.6 mM) [36], (see also *Tab. 4*).

The deviations from reported value is not as significant as in the case of surface tension measurements, however it may be attributed to the possible impurities present in the surfactant solutions, to minor concentration of Na^+ and/or Ca^{2+} ions in deionised water and, possibly slightly different measurement conditions used by authors of the scientific article.

The intersections of the two regression straight lines passing through the pre- and post- CMC region reflecting limit for forming the micelles are based on reliable determination of conductivity of concentration series prepared for SLSa. Therefore, the results of these measurements may be also considered as reproducible.

Tab. 9 The values of the CMC and κ_{CMC} for SLSa determined using conductometry

CMC	SD$_{CMC}$	κ_{CMC}	SDκ_{CMC}
[mM]	[mM]	[mS]	[mS]
11.96	0.08	0.776	0.003
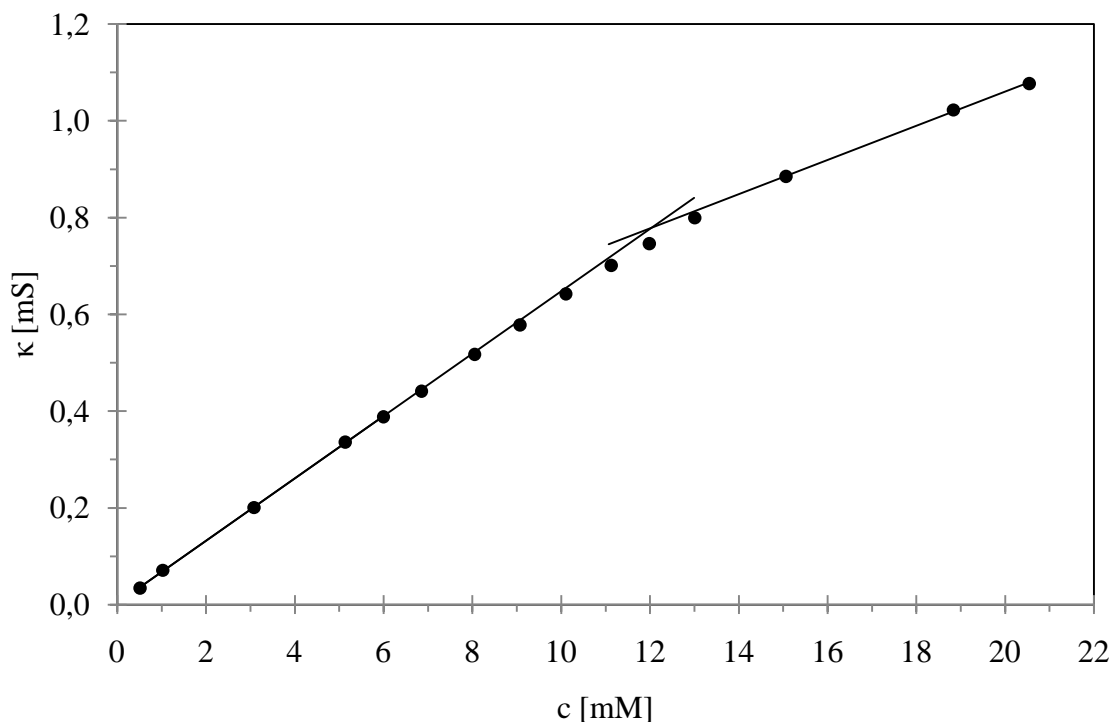
Fig. 17 The dependence of conductivity vs. concentration of anionic surfactant SLSa determined using conductometry

10.1.3 Densitometry a dynamic light scattering

Densitometry and dynamic light scattering measurements did not provided reproducible data and will not be used either for determination of the CMC or for the calculation of interaction parameters.

To illustrate the reasons for these conclusions, the measured densitometry data are presented in *Fig. 18*. It can be seen that region of the possible occurrence of the CMC is of about 6 mM. Here, similarly as for the two above methods, the sudden change of the regression line in the pre- and the post-CMC area should be visible. However, the statistical evaluation of the measured data was not unambiguous, and other possible areas with the CMC occurrence seem to be present in the plot (about 12 mM and/or 14 mM).
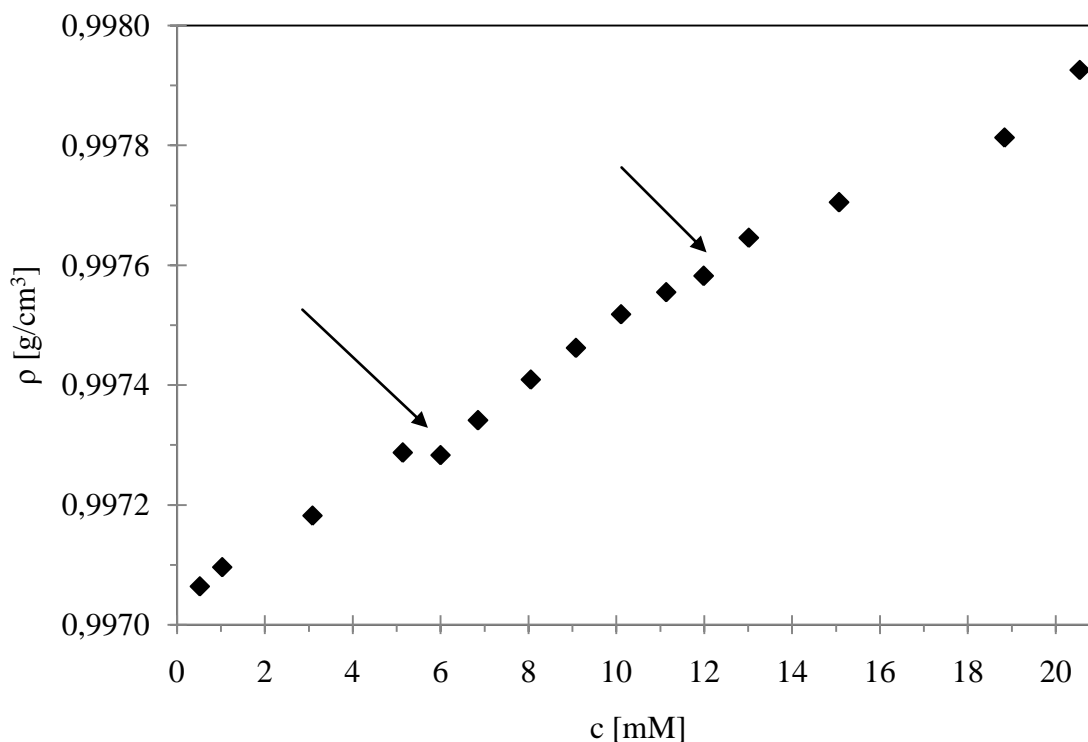
Fig. 18 The dependence of density vs. concentration of anionic surfactant SLSa determined using densitometry

During the literature search it was also found that the CMC determined by densitometry is not clearly interpreted in scientific papers, either [30, p.129]

By theory, dynamic light scattering is a method capable of determining the CMC. The procedure consists of measurements of a concentration range of a respective surfactant dissolved in deionised water. Below the CMC, the intensity of scattered light, expressed in kilo counts [kcps] detected from each surfactant concentration should be similar to that detected from water and no information about particle size should be obtained. When the CMC is reached and micelles occur, the intensity of scattered light increases. Hence, plotting the intensity or micelle size *vs.* surfactant concentration should provide dependence with a sudden change of the measured parameter, which corresponds to CMC.

Unfortunately, any of the measurements performed within the diploma thesis did not provide the results with corresponding quality as published in the literature. In any of the graphs (intensity *vs.* concentration; hydrodynamic diameter *vs.* concentration), no statistically provable area of sudden changes that would clearly refer to the CMC

was observed. Thus, this method was found to be inconclusive for determining CMC of selected surfactants and their mixtures. However, measurements of DLS afforded micelle sizes of studied surfactants measured at sufficiently high concentration of 0.6 mM for TWEENs and 18 mM for SLSa.
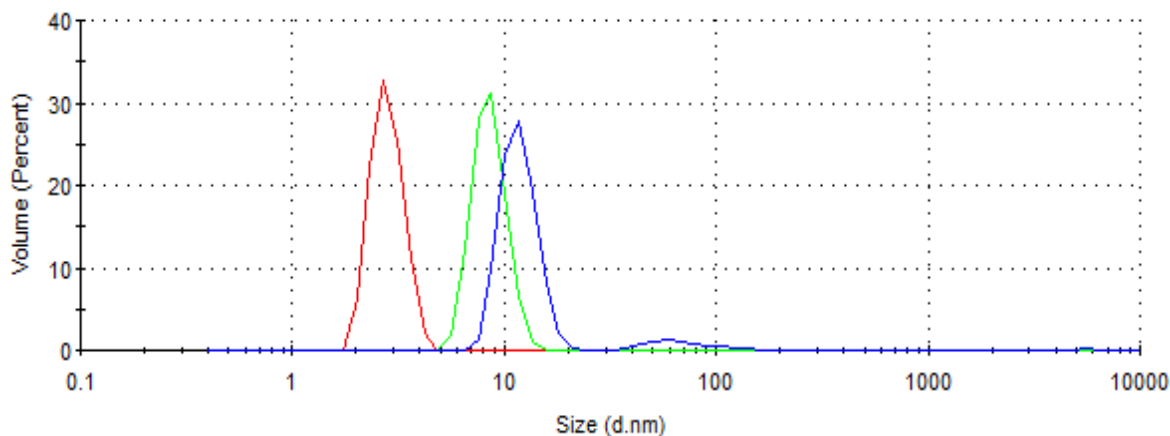
Fig. 19 The size distribution, by volume, of anionic surfactant SLSa (red line), T20 (green line), T60 (blue line) determined using dynamic light scattering with 90° detection

As shown in the *Fig. 19*, and as summarised in the *Tab. 10*, the size of micelles of individual surfactants are clearly distinguishable. The smallest micelles are formed by SLSa (2.87 ± 0.19 nm in diameter), larger micelles are provided by the non-ionic surfactant T20 (8.46 ± 0.13 nm) and even larger aggregates are formed by T60 molecules (12.99 ± 0.09 nm). The difference between micelle sizes of T60 and T20 is in good agreement with the variation in their structure.

Tab. 10 The values of the size of micelles for individual surfactants determined using dynamic light scattering with 90° detection

surfactant	micelle size [nm]
SLSa	2.87 ± 0.19
T20	8.46 ± 0.13
T60	12.99 ± 0.09

10.1.4 Contact angle measurements

Although, the contact angle of droplets and its change around the CMC has a good theoretical background, this technique applied for determining the CMC is rarely found in scientific publications. However, the experiments in this thesis showed that the method is capable of providing interesting results, which are worth mentioning.

When the formation of micelles occurs, a decrease in contact angle of the drop is observed; which means in practice that the drop of aqueous solution containing surfactant in contact with the hydrophobic surface behaves differently under and above the CMC. In post-CMC area, the increasing surfactant concentration can lead to slight increase of the contact angle. With further growth of surfactant concentration in solution the contact angle may be constant or slightly declined. For the time being, the evaluation of the CMC using this method was based on the finding the minimum of a polynomial function fitted through the measured points in the near vicinity of the CMC. The values of the CMC and the contact angle corresponding to the CMC (θ_{CMC}) are summed up in *Tab. 11*. In the graphs presented in *Fig. 20*, *Fig. 21* and *Fig. 22*, the data points marked with a cross are used in the polynomial function, from which the minimum corresponding to the CMC was calculated.

Tab. 11 The values of the CMC and θ_{CMC} for individual surfactants determined using measurement of contact angle

surfactant	CMC [mM]	θ_{CMC} [°]
SLSa	9.95	41.25
T20	0.084	80.60
T60	0.022	99.23
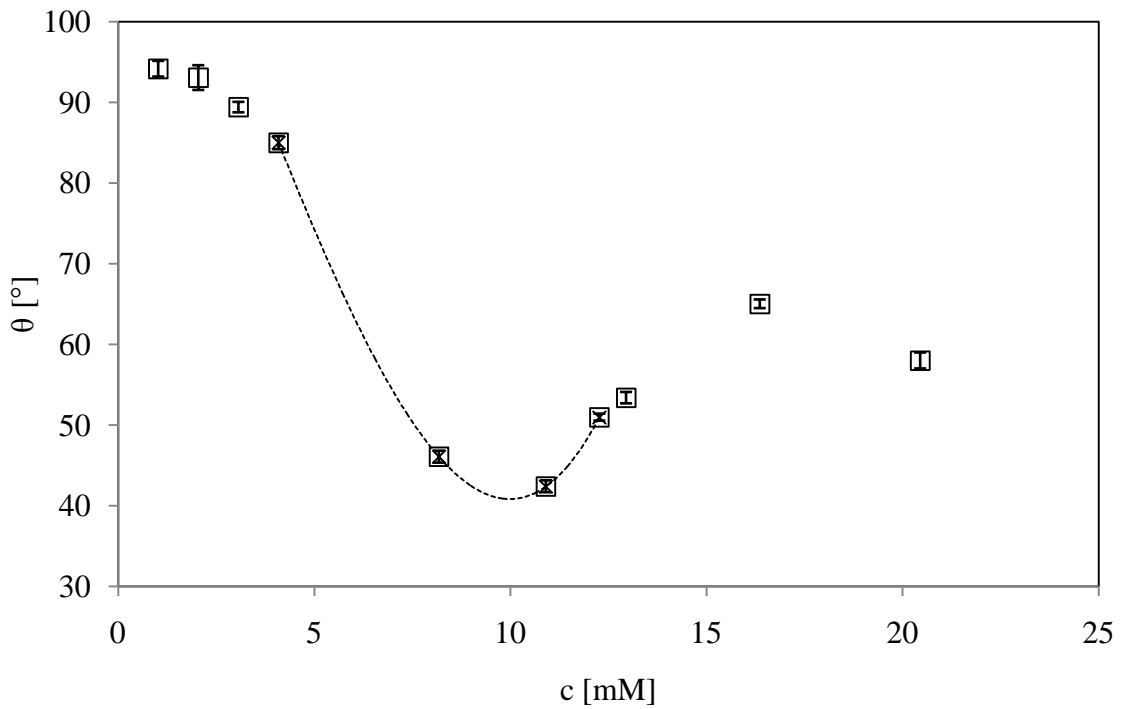
Fig. 20 The dependence of contact angle vs. concentration of anionic surfactant SLSa determined using measurement of contact angle
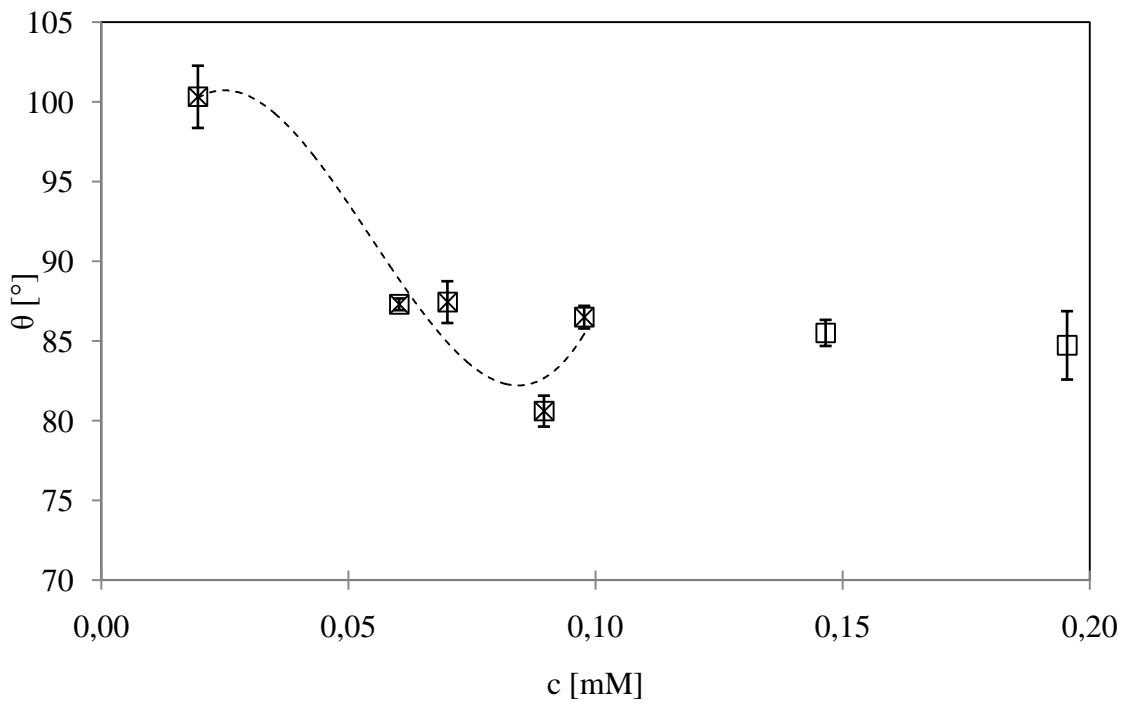
Fig. 21 The dependence of contact angle vs. concentration of non-ionic surfactant TWEEN®20 determined using measurement of contact angle
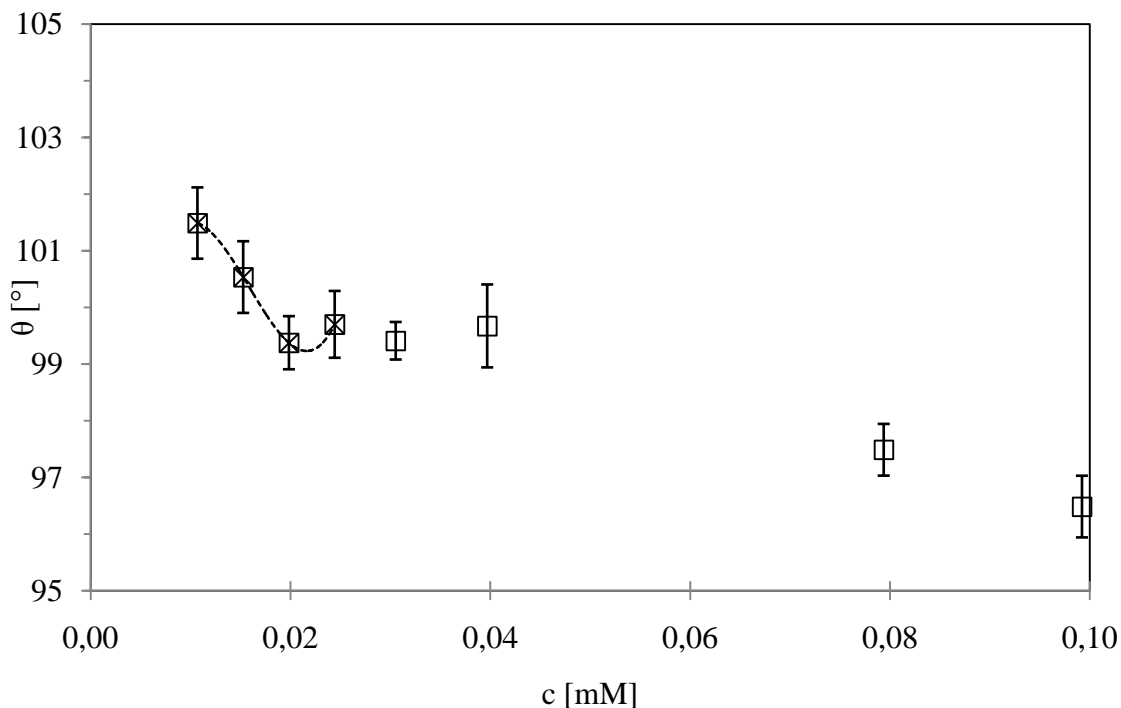
Fig. 22 The dependence of contact angle vs. concentration of non-ionic surfactant TWEEN®60 determined using measurement of contact angle

As it is obvious from *Tab. 12*, the CMC values of both non-ionic TWEENs provided by tensiometry and contact angle are in fairly good agreement. The CMC value of ionic surfactant (SLSa), given by conductometry, corresponds better to the CMC from contact angle determination. Regarding SLSa, the CMC from tensiometry is significantly lower than the values determined by the two remaining methods. This phenomenon might be explained by the fact that the surface tension is influenced by the very low concentrations of surfactants in the solution due to characteristic molecular orientation at air/water interface. Moreover, surface tension measurement is known to be considerably influenced by even small amount of impurities.

Tab. 12 The summary of the CMC values determined on studied surfactants by methods tested in the diploma thesis

surfactants	CMC_γ [mM]	$SD_{CMC\gamma}$ [mM]	CMC_κ [mM]	$SD_{CMC\kappa}$ [mM]	CMC_θ [mM]
SLSa	2.62	0.08	11.96	0.08	9.95
T20	0.0832	0.0006	n/a	n/a	0.0843
T60	0.0265	0.0002	n/a	n/a	0.0216

10.2 CMC of surfactant mixtures

10.2.1 Two non-ionic surfactants TWEEN®20 and TWEEN®60

The values of CMC_{mix} and $\gamma_{CMC(mix)}$ determined for mixtures of T20:T60 are listed in *Tab. 13*. Additional parameters are presented in *Tab. 14.* The average values of CMC_{mix} were plotted against molar fraction of T20, x_{T20} (*Fig. 23*, dashed line). In this figure, the full line connecting the points is also plotted and stands for the theoretical CMC^* values for particular molar fraction of T20 in the mixture (for calculation see equation (15)). The figure clearly illustrates that the measured values of CMC_{mix} are located below the line relating to theoretical CMC^* and follow its increasing trend. The deviation between the theoretical and measured values may be explained by the existence of differences in the efficiency of micellisation in real situation and important role plays also synergistic effects [39, p. 7]. The presence of these effects during formation of mixed micelles is also confirmed by negative values of interaction parameter (*Tab 13*). As mentioned in reference [19, p. 7174], the β *f*or mixtures of two non-ionic surfactants is usually in range from −1 to 0. From the slopes of the linear plots γ *vs. c*, the surface excess (Γ_{max}) concentrations were calculated at the CMC_{mix} points (refer to equation (18)). The minimum area per head group (A_{min}) of the surfactants at CMC_{mix} at the saturated interface was obtained from the equation (19). The activity coefficients of both components in the mixed micelle f_1 and f_2 were obtained from the equations (20) and (21).

Tab. 13 The values of CMC$_{mix}$, $\gamma_{CMC(mix)}$, x_m and β; mixture of T20 and T60 determined using tensiometry

x_{T20}	CMC* [mM]	CMC$_{mix}$ [mM]	SD$_{CMC(mix)}$ [mM]	$\gamma_{CMC(mix)}$ [mN/m]	SD $\gamma_{CMC(mix)}$ [mN/m]	x_m	β
0	0.0265		0.0002	47.7	0.5	n/a	n/a
0.2	0.031	0.030	0.0014	46.0	1.4	0.08	−0.17
0.3	0.034	0.026	0.0013	45.0	1.7	0.25	−1.66
0.5	0.041	0.034	0.0012	46.0	1.5	0.30	−0.80
0.7	0.052	0.039	0.0020	45.9	1.4	0.45	−1.06
0.8	0.059	0.046	0.0012	43.5	1.2	0.54	−0.99
1.0	0.0832		0.0006	39.8	0.7	n/a	n/a

Tab. 14 The values of f_1, f_2 Γ_{max} and A_{min}; mixture of T20 and T60 determined using tensiometry

| x_{T20}	f_1	f_2	Γ_{max} [10^{-6} mol/m^2]	A_{min} [nm^2]
0	n/a	n/a	5.30	0.31
0.2	0.87	0.99	2.45	0.68
0.3	0.39	0.90	1.80	0.92
0.5	0.68	0.93	2.79	0.59
0.7	0.73	0.81	3.25	0.51
0.8	0.81	0.75	2.52	0.66
1.0	n/a	n/a	6.46	0.26
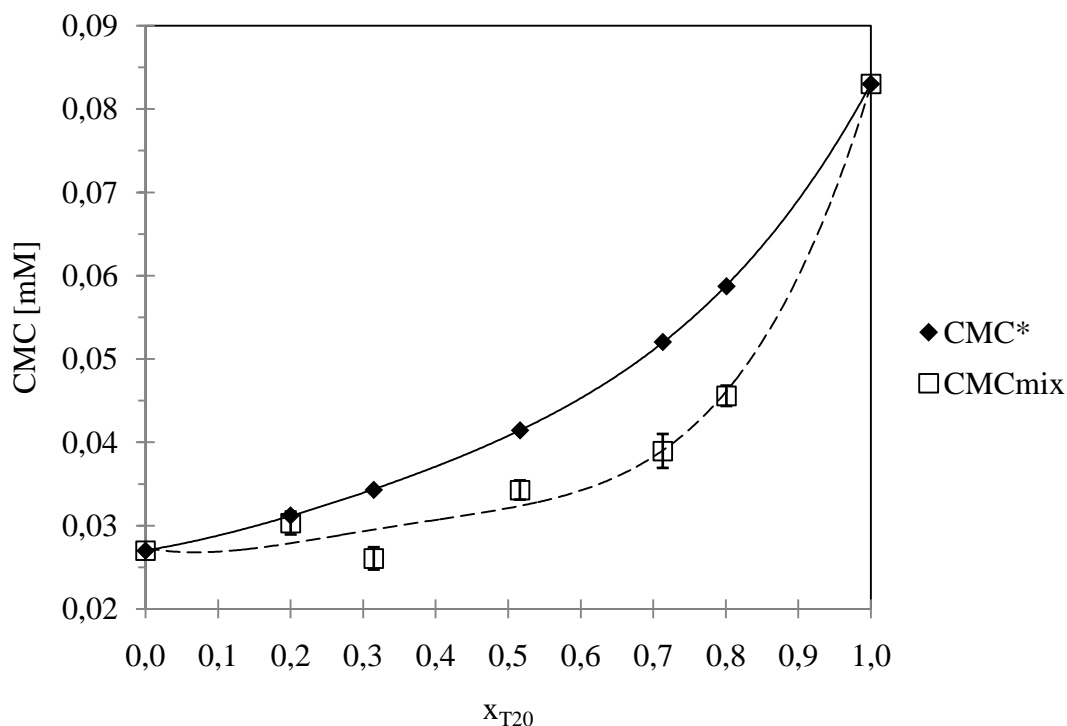
Fig. 23 The dependence of theoretically calculated CMC* and experimentally determined CMC$_{mix}$ vs. x_{T20}; mixture of T20 and T60 determined using tensiometry [39, p. 8]

The selected non-ionic surfactants have very similar structure of molecules. Molecule of T60 has longer hydrophobic chain and lower CMC than T20. It can be assumed, that mixed micelles formed at a lower surfactant concentrations are richer in T60 than the aggregates created at a higher concentration of surfactants. The hydrophilic parts of both surfactants are identical, thus it can be suggested that the mixing is influenced predominantly by the hydrophobic parts of the molecules [39, p. 9].

10.2.2 Non-ionic and anionic surfactant TWEEN®20 and SLSa

The values of CMC_{mix} and $\gamma_{CMC(mix)}$ as well as the parameter β determined for mixture T20:SLSa are listed in *Tab. 15*. The average values of CMC_{mix} (dashed line) obtained from tensiometry and the theoretical $CMC*$ (full line) were plotted against x_{T20} (*Fig. 24*). The figure shows that the measured values for mixtures (CMC_{mix}) are located above the theoretical $CMC*$ and the behaviour of the system can be considered as non-synergistic, which is also proven by numerical values of parameter β. Considering surfactant mixtures with SLSa, the parameter x_M was calculated , however it is not

listed. The reason is that x_m was too high and constant, probably due to the fact that in micelles SLSa is most likely present in predominant amount. Other parameters (Γ_{max}, A_{min}, f_1 and f_2) exhibited also unusual trends/results in terms of large variations of their values. The reason might lie in various effects, such as counter ion binding, chain length mixmatch, ionic strength variation, etc. However, the behaviour of surfactant mixtures with SLSa seems to be so complicated and complex that it requires more detailed study.

Tab. 15 The values of CMC_{mix}, $\gamma_{CMC(mix)}$ and β; mixture of T20 and SLSa determined using tensiometry

| x_{T20}	CMC* [mM]	CMC_{mix} [mM]	$SD_{CMC(mix)}$ [mM]	$\gamma_{CMC(mix)}$ [mN/m]	SD $\gamma_{CMC(mix)}$ [mN/m]	β
0	2.62		0.29	28.7	0.3	n/a
0.2	0.37	1.156	0.120	38.4	0.2	10.2
0.3	0.259	0.909	0.230	39.1	0.1	10.4
0.5	0.162	0.241	0.017	39.8	0.2	9.6
0.7	0.118	0.133	0.008	40.2	0.3	9.3
0.8	0.103	0.126	0.012	40.0	0.4	9.4
1.0	0.0832		0.0006	39.8	0.7	n/a
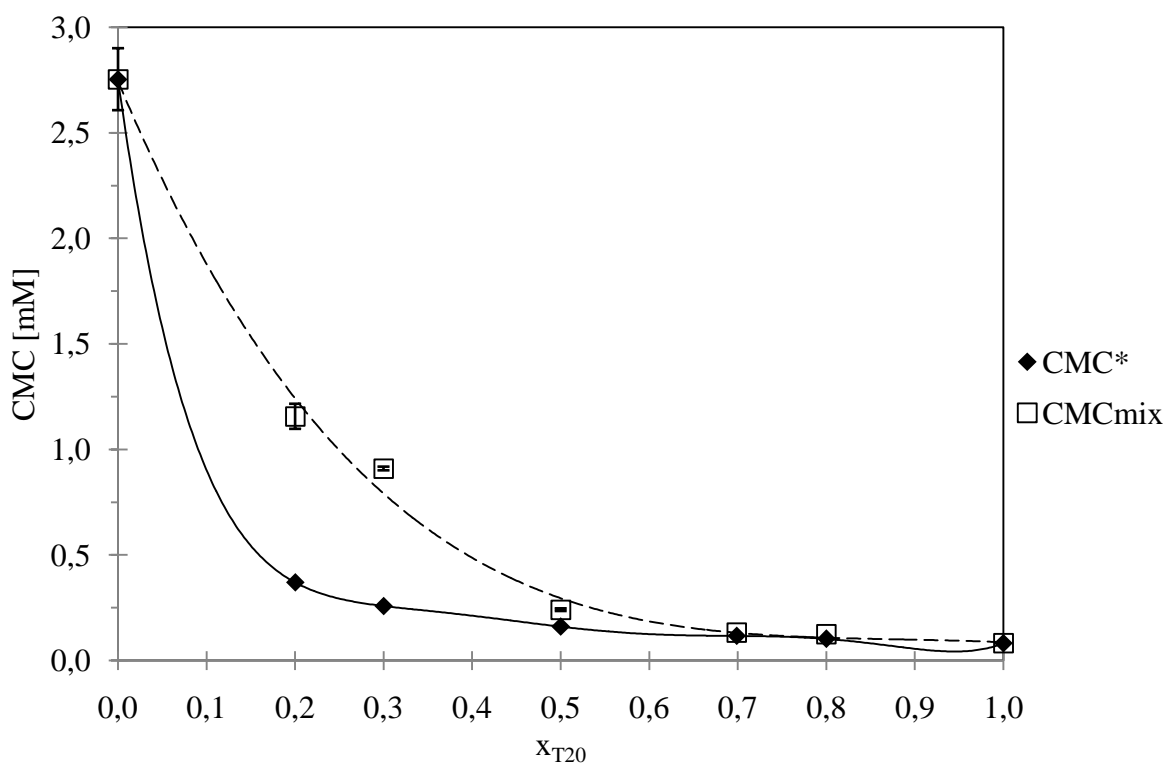
Fig. 24 The dependence of theoretically calculated CMC* and experimentally deter-mined CMC_{mix} vs. x_{T20}; mixture of T20 and SLSa determined using tensiometry

The conductometric data for mixtures of T20:SLSa, in terms of CMC_{mix}, $\kappa_{CMC(mix)}$ and β, are listed in *Tab. 16*. In *Fig. 25*, the average values of CMC_{mix} and the theoretical *CMC** values for respective molar ratio of T20 in the mixture are presented. The data plotted in the *Fig. 25* show non-synergistic behaviour occurring during the surfactant micellisation, which is confirmed by parameter β (*Tab. 16*). In the theoretical trend (*CMC* vs. x_{T20}*), the significant difference between the CMC values of individual surfactants is seen. In practice, the influence of SLSa seems to be more dominant and the decreasing trend in CMC_{mix} values is not as rapid as the decrease of theoretical *CMC**. It can be also noticed that even a low mole fraction of TWEEN[®]20 in the solution induces a notable decrease in the CMC, since the non-ionic surfactant has significantly lower CMC than the ionic one.

Tab. 16 The values of CMC_{mix}, $\kappa_{CMC(mix)}$ and β; mixture of T20 and SLSa determined using conductometry

x_{T20}	CMC* [mM]	CMC_{mix} [mM]	$SD_{CMC(mix)}$ [mM]	$\kappa_{CMC(mix)}$ [mN/m]	$SD\ \kappa_{CMC(mix)}$ [mN/m]	β
0		11.95	0.08	0.776	0.003	n/a
0.2	0.40	9.38	0.14	0.473	0.006	12.3
0.3	0.27	5.38	0.03	0.249	0.0003	12.2
0.5	0.17	5.76	0.33	0.194	0.009	12.6
0.7	0.12	6.88	0.28	0.141	0.005	13.3
0.8	0.10	4.43	0.22	0.071	0.003	13.0
1.0		0.0832	0.0006	n/a	n/a	n/a
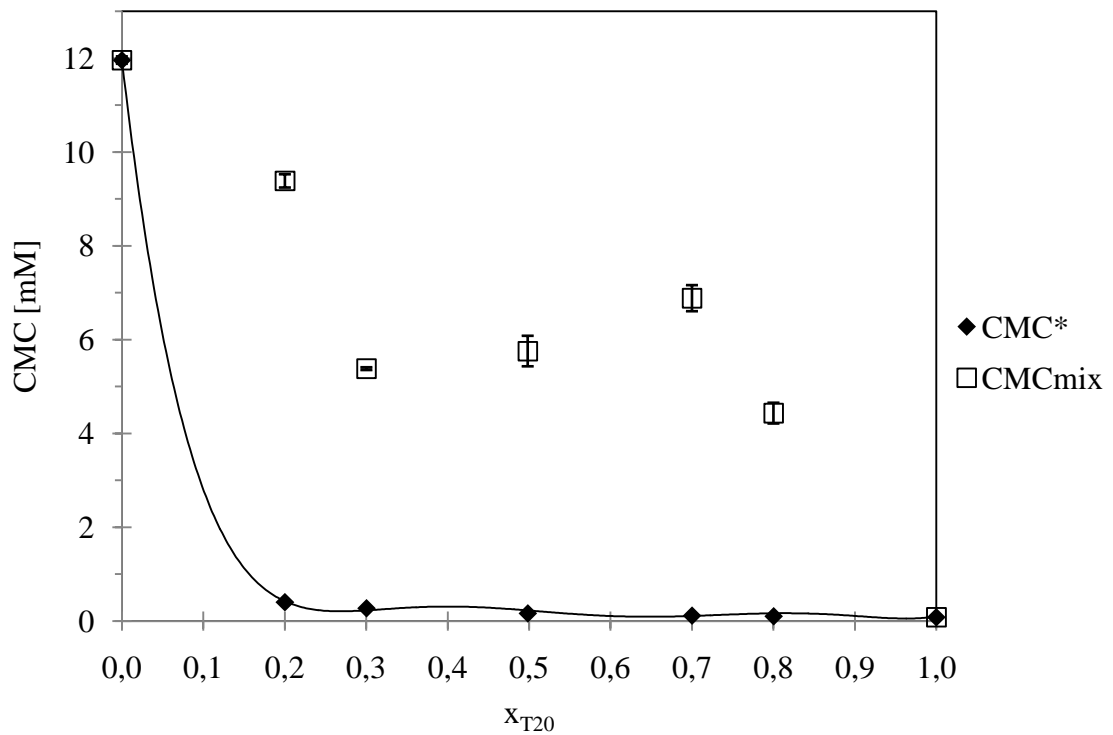
Fig. 25 The dependence of theoretically calculated CMC* and experimentally deter-mined CMC_{mix} vs. x_{T20}; mixture of T20 and SLSa determined using conductometry

10.2.3 Non-ionic and anionic surfactant TWEEN[®]60 and SLSa

Finally, the mixtures of non-ionic TWEEN[®]60 and SLSa were tested with respect to their behaviour during mixing. The values of CMC_{mix} and $\gamma_{CMC(mix)}$, as well as the parameter β recorded by tensiometry are presented in *Tab. 17.* In the *Fig. 26*, the average values of CMC_{mix} and the theoretical CMC^* were plotted against molar fraction of TWEEN[®]60 (x_{T60}). According to the results shown in this figure, the non-synergistic phenomena during micellisation process may be expected; which is also indicated by the values of parameter β.

Tab. 17 The values of CMC_{mix}, $\gamma_{CMC(mix)}$ and β; mixture of T60 and SLSa based on tensiometry

x_{T60}	CMC* [mM]	CMC_{mix} [mM]	$SD_{CMC(mix)}$ [mM]	$\gamma_{CMC(mix)}$ [mN/m]	SD $\gamma_{CMC(mix)}$ [mN/m]	β
0	2.62		0.08	28.7	0.3	n/a
0.2	0.13	0.95	0.03	36.7	0.19	11.2
0.3	0.09	1.04	0.12	36.3	0.16	11.7
0.5	0.05	0.24	0.03	39.6	0.4	10.7
0.7	0.04	0.10	0.02	36.3	0.05	10.2
0.8	0.03	0.15	0.03	37.6	0.18	10.7
1.0	0.0265		0.0002	47.7	0.5	n/a
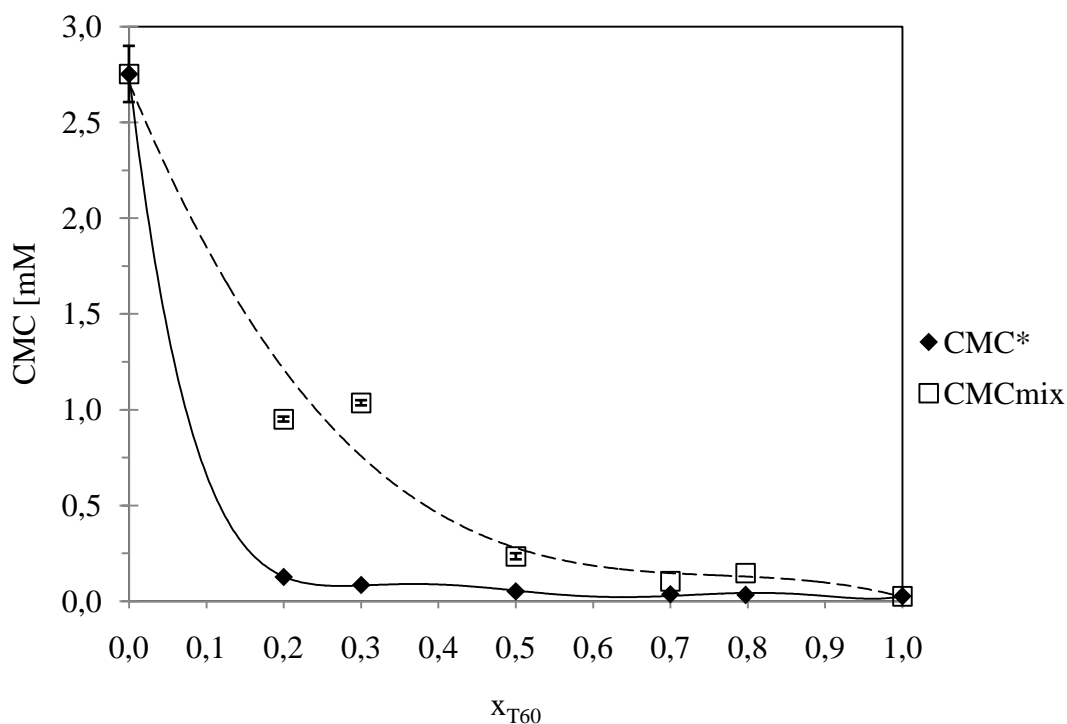
Fig. 26 The dependence of theoretically calculated CMC* and experimentally determined CMC$_{mix}$ vs. x_{T60}; mixture of T60 and SLSa determined using tensiometry

The data from conductometry obtained for mixture T60:SLSa (CMC$_{mix}$, $\kappa_{CMC(mix)}$ and β) are given in *Tab. 18*. In the *Fig. 27*, the average values of *CMC$_{mix}$* and the theoretical *CMC** values for molar ratio of T60 in the mixture are shown. As it is apparent from the figure, non-synergistic behaviour is observed and verified by β in *Tab. 18*. As in the previous mixture (T20:SLSa), the CMC values of individual surfactants in theoretical trend differ highly. In real situation, the SLSa affects the properties of the mixture far more than it would be expected from the theoretical calculation. The behaviour of mixture can be considered as constant for $x_{T20} > 0.7$, in terms of the CMC value.

Tab. 18 The values of CMC$_{mix}$, $\kappa_{CMC(mix)}$ and β; mixture of T60 and SLSa based on conductometry

x_{T60}	CMC* [mM]	CMC$_{mix}$ [mM]	SD$_{CMC(mix)}$ [mM]	$\kappa_{CMC(mix)}$ [mN/m]	SD $\kappa_{CMC(mix)}$ [mN/m]	β
0		11.96	0.08	0.776	0.003	n/a
0.2	0.14	8.41	0.016	0.432	0.0003	13.3
0.3	0.09	5.84	0.15	0.301	0.006	13.4
0.5	0.06	3.18	0.03	0.142	0.002	13.3
0.7	0.04	0.58	0.04	0.045	0.004	11.9
0.8	0.03	0.76	0.003	0.052	0.0003	12.3
1.0		0.0265	0.0002	n/a	n/a	n/a
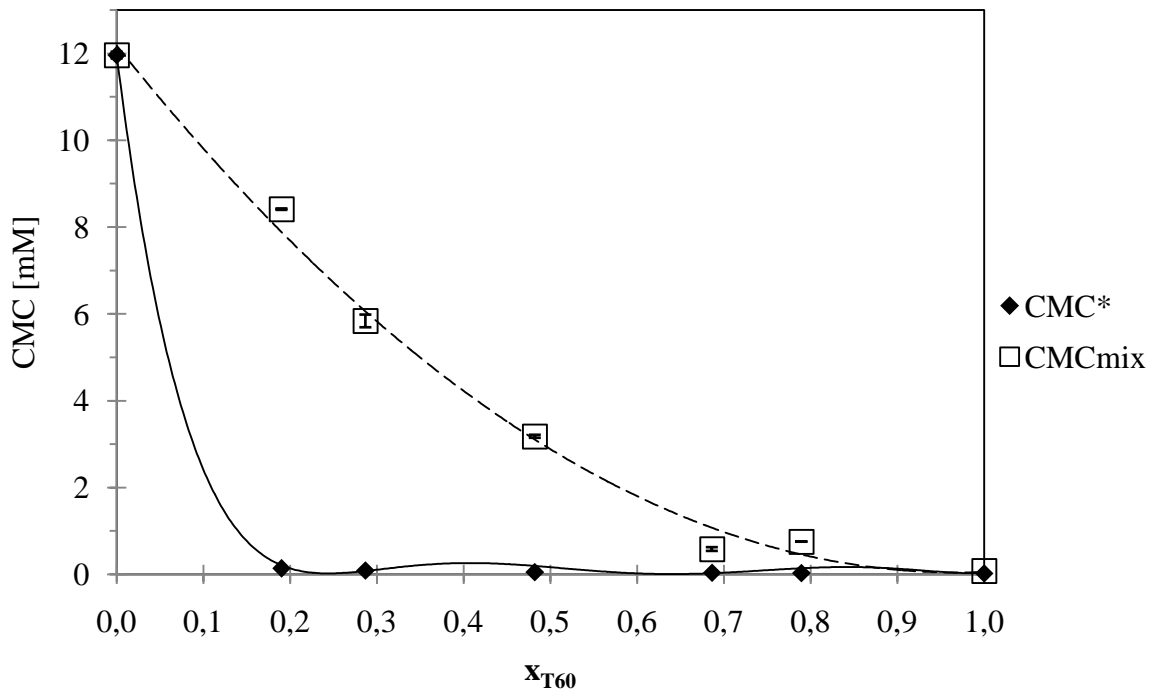
Fig. 27 The dependence of theoretically calculated CMC and experimentally determined CMC$_{mix}$ vs. x_{T60}; mixture of T60 and SLSa determined using conductometry*

The behavior of T20:SLSa and T60:SLSa mixtures upon mixing determined by tesiometry and conductometry gave similar results only in terms of the presence of antagonism during mixing. In a more detailed evaluation of both methods, the differences can be found in how each of them describes surfactant behavior in mixture. Generally, tensiometry provided more consistent results with minor differences between measured CMC_{mix} and calculated CMC^*. TWEEN$^®$60 in mixture with SLSa reduced value of CMC_{mix} more notably compared to TWEEN$^®$20, however both systems showed CMC_{mix} trend more or less following the line calculated for ideal mixing (CMC^*). Conductometry, on the other side, provided CMC_{mix} differing more notably from CMC* which is more visible in the case of T20:SLSa mixture. Here, values of CMC_{mix} for molar ratio of TWEEN$^®$20 $x_{T20} = 0.7$ and 0.8 do not show expected drop to lower values and remain as high as 5.88 and 4.43 mM, respectively. In this context, behaviour of the second mixture, T60:SLSa, is more predictable. Regarding $β$ values, interaction parameters of T20:SLSa ($β$ in range from 12.2 to 13.3) are close to T60:SLSa ($β$ in range from 11.9 to 13.4) and the mixtures showed similar antagonistic effects.

The behaviour of studied surfactant systems show that mixtures of anionic and non-ionic surfactants are important not only from the theoretical point of view, but also from the application standpoint. They namely exhibit non-ideal behaviour during mixing and presented interactions can lead to lowering the CMC of the mixed surfactants in comparison with SLSa alone. As it is published [23, p. 5008], these non-ideal mixtures extremely deviate from the properties of ideal micelle solutions. This is important characteristic as anionic surfactants are frequently used in cosmetics formulation and lowering of their CMC is the way how to decrease the surfactant amount in the products and contribute to the protection of the environment as well.

CONCLUSION

The diploma thesis deals with the determination of the critical micelle concentration of individual non-ionic (TWEEN[®]20, TWEEN[®]60) and anionic (*N*-lauroylsarcosine sodium salt) surfactants through selected methods (tensiometry, conductometry, densitometry, dynamic light scattering and contact angle measurement).

By tensiometry, the CMC for N-lauroylsarcosine sodium salt of 2.62 ± 0.08 mM was measured and corresponded to the literature data [30, p. 128]. The CMC for TWEEN[®]20 (0.083 ± 0.0006 mM) and TWEEN[®]60 (0.027 ± 0.0002 mM) also comply with references [40, p. 390] and [35, p. 2346], [38]. The values of CMC for *N*-lauroylsarcosine sodium salt determined using conductometry (11.96 ± 0.08 mM) are in good agreement with data published in references [31, p.137], [32, p. 134] [36]. However it should be stressed that the CMC values for SLSa determined by different methods differ significantly.

Monitoring of the CMC by a change in the contact angle performed reasonably as well. The CMC values determined by this method (SLSa: 9.95 mM; T20: 0.0843 mM; T60: 0.0216 mM) corresponded to CMC values determined by other methods applied in this work. Nevertheless, the statistical background for this method is complicated and more effort is needed to verify the obtained data. However, monitoring of contact angle may be suitable procedure for determination of CMC for commercial surfactant mixtures, especially in the production of detergents, since the wetting is the crucial characteristic of the cleaning process. Moreover, countless variations in terms of the surface on which the drop can be observed are possible. Thus, the wetting of different materials can be easily monitored.

Tensiometry and conductometry were also confirmed as the most suitable methods for the determination of CMC providing reproducible and statistically reliable results. The techniques measuring density and dynamic light scattering are also worth paying attention. However, the conditions for these measurements should be optimised.

By the analysis of the three mixtures (T20:T60; T20:SLSa; T60:SLSa), the synergistic or antagonistic behaviour during micellisation was observed. The mixture of

non-ionic surfactants was confirmed as synergic while forming micelles. The binary mixtures of non-ionic and anionic surfactants exhibited less attraction, which means higher repulsion upon mixing. The CMC_{mix} of the mixed surfactants was lower than the CMC of piscine SLSa. It can be concluded, that use of the last mentioned surfactant pairs in the mixture is more efficient than the use of single SLSa only. Application of such mixed systems in cosmetics or household products may then result in a lower impact of these chemicals on the environment as well as in cost savings.

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LIST OF ABBREVIATIONS

SLSa	N-lauroylsarcosine sodium salt
T20	TWEEN$^{®}$20
T60	TWEEN$^{®}$60
HLB	hydrophilic lipophilic balance
O/W	oil in water emulsion
W/O	water in oil emulsion
O/O	oil in oil emulsion
γ	surface tension
Γ_{max}	excess concentration of surfactant
R	gas constant
T	absolute temperature
$S_{L/S}$	spreading coefficient
γ_{SA}	surface tension on the interface solid/air
γ_{SL}	surface tension on the interface solid/liquid
γ_{LA}	surface tension on the interface liquid/air
θ	contact angle
W_a	work of adhesion
W_c	work of cohesion
SDS	sodium dodecyl sulphate
CMC	critical micelle concentration
κ	specific conductivity
Λ	molar or equivalent conductivity
τ_c	relaxation time
D	diffusion coefficient

Q	wave vector
R_h	hydrodynamic radius
k_b	Boltzmann's constant
η	dynamic viscosity of dispersion medium
CMC*	theoretically calculated CMC of mixture
α	molar fraction of surfactant 1
CMC_{mix}	experimentally determined CMC of mixture
β	interaction parameter
x_m	mole fraction of the surfactant 1 in the mixed micelle
A_{min}	minimum surface area per molecule (hydrophobic part)
N_A	Avogadro's constant
f_1, f_2	activity coefficients

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