1 Introduction

"*Opposites attract.*" In the case of ions and colloidal chemistry this is certainly true (and sometimes also in daily life) but then again "*Birds of a feather flock together*" is true even more often. Water and oil, or more precisely hydrophilic and hydrophobic components, do not like each other: they are immiscible substances. Yet, we come across water and oil mixtures every day in the form of milk, butter, margarine, sauces, but also in cosmetics (e.g. lotions), cleaning products and colors. We have to know the structure of milk or egg yolk to understand how nature solves the problem of solubilizing otherwise immiscible components. Milk is essentially a mixture of oil droplets in water. The oil droplets are stabilized by emulsifiers consisting of a hydrophilic part that attracts water and a hydrophobic part that attracts oil, which is why they are called *amphiphiles* from the Greek *amphis* ("both") and *philia* ("love"). These amphiphiles are able to reduce the interfacial tension between water and oil by absorbing to the liquid-liquid interface, thus allowing previously immiscible phases to merge. Life could not exist without amphiphiles stabilizing cell membranes, most importantly phospholipids. In everyday products several classes of emulsifiers, or *surfactants*, are applied. Phospholipids and alkyl glucosides are the most commonly used ones in cosmetics, cleaning, foods and health care products. These products are often oil-in-water (o/w) or water-in-oil (w/o) emulsions, which are thermodynamically unstable.

Microemulsions, on the other hand, are thermodynamically stable, macroscopically isotropic, nano-structured mixtures of at least three components: a hydrophilic (A), hydrophobic (B), and amphiphilic one (C) [1-4]. In fact, the applied microemulsions often consist of more than three components such as co-surfactants (D) [5, 6] and salt (E) [5, 7]. One special feature of microemulsions is the diversity of different phases, such as lamellar, bicontinuous, or droplets, which can occur as a function of composition, pressure, temperature and number of components. Typically, the structure size ranges within the nanometer scale, which is why microemulsions have been studied and discussed extensively over the last two decades. Various studies mainly focused on the properties of the amphiphilic film [8-10]. Especially, through the work of several groups, most notably *Olsson* and *Wennesström* [11, 12], *Bellocq* and *Roux* [13, 14], *Langevin* and *Meunier* [15], *Binks et al.* [16], *Friberg*, *Shinoda*, and *Kunieda* [17, 18], *Kahlweit* and *Strey* [19, 20], the connection between the phase behavior and amphiphilic film became clear. Furthermore, the low interfacial tension ranging from 50 mN/m in water-oil to 10^{-4} mN/m [3] in water – oil – surfactant is a well studied feature of microemulsions [21-23]. However, the suitability of microemulsions in daily life is still not completely understood, even though food-grade and bio-compatible microemulsions are promising delivery systems for a number of high-potential applications in pharmaceutics, health care, cleaning and food, where they could improve the availability of bioactive compounds, the solubility, and the texture.

1.1 Applications of microemulsions

1.1.1 Detergency

Global warming has become an important issue in recent years. By decreasing the production temperature, for example in washing applications, energy is saved and thus leads to lower greenhouse gas emissions. Therefore, improved surfactant systems for detergency applications have to be investigated, whereas detergency can be defined as the removal of unwanted substances, so called soil, from a solid surface using a liquid [24]. This process depends on several different factors, such as nature of additives and solid surface, hydrodynamic conditions, concentration of surfactants or temperature [25]. It turned out that the occurring of lamellar phases in an at least three component system, plays an important role in improving soil removal during the detergency process [26, 27]. Furthermore, it is observed that the detergency efficiency reached the optimum at the HLB temperature in ternary systems. This indicates that microemulsions are formed and thus are the best choice in efficient detergency applications [28].

In textile cleaning, raw wool scouring and skin degreasing the main components are chlorinated solvents and flammable ones like low-molecular-weight hydrocarbons [29]. This is a major disadvantage due to the health risk of said solvents. Therefore suitable detergency with bio-compatible surfactants has to be investigated, such as alkyl glucosides. The main advantages of microemulsions are that water and oil soluble soils can be removed in one step. Several studies of the suitability of microemulsions in industrial cleaning were published [30-32]. It turns out, that they are more efficient compared to commercially liquid detergent solutions [30, 31], because no additional energy input was needed, which leads to a lower energy requirement during the industrial process [31] (CO_2 reduction). However, these systems have to improve regarding required surfactant mass fraction and biocompatibility.

1.1.2 Cosmetics

In recent years anti aging products became more and more interesting for the cosmetic industry. However, skin-care products, like moisturizers and antioxidant agents have a poor percutaneous absorption due to the barrier of the skin. Microemulsions cause a fast penetration and permeation of the cosmetic substances into the skin [33-35]. In addition several studies have shown that ingredients dissolved in microemulsions are able to penetrate the skin at higher amounts than in conventional creams and lotions [36, 37, 34, 38]. They exhibit a high solubilization power, because they offer the possibility to incorporate hydrophilic and hydrophobic substances. The thermodynamical stability provides a long shelf-life. Microemulsions are also useful for essential lotions like sunscreens, as they provide a good skin feel, easy spread, and water proof effects [39].
Some desired ingredients have a low photo-stability to ultraviolet B irritation. Using microemulsions as delivery systems, the stability compared to aqueous solutions is increased [40]. Accordingly, due to all these advantages of microemulsions in cosmetics, more than 6000 patents related to cosmetics exist [41]. However, they require a larger amount of surfactant than emulsions, leading to a higher probability of skin irritation and toxicity. To prevent this problem the efficiency of the applied systems has to increase and bio-compatible and non-toxic surfactants have to be used.

1.1.3 Pharmaceutics

In recent decades numerous studies have brought increasing attention to microemulsions as potential drug delivery systems [42-45, 35]. They can be used either as vehicle for topical applications or as bioavailability enhancers for poorly water-soluble active pharmaceutical substances, because of their unique solubilization capabilities [33, 34].

Especially o/w microemulsions provide protection from hydrolyses oxidation of the drug, because it is not exposed to water or air [46]. The most advantageous way of drug delivery is transdermal, but it is difficult for most drugs to be delivered into the skin in order to act because the skin barrier is very high. Studies carried out by *Sintov et al.* have shown that the transdermal delivery of diclofenac has an eight-fold permeation of diclofenac when using microemulsions rather than ordinary available gels [47]. Moreover, they are able to improve delivery, efficiency and bioavailability of several drugs like ketoprofen [48, 49] and diclofenac [50, 51, 47]. The dermal absorption of local anaesthetic agents like lodocaine is also improved more than eight-fold compared to commercial available emulsions [52]. Furthermore, the temperature over which the microemulsions exhibit a single phase can be rather wide, thus the phases do not separate and the drug delivery system is stable.

Until now there are no dermal or transdermal microemulsion formulations on the market for pharmaceutics, but Neroal® (oral Route), is already available [53] . There are various numbers of review papers and studies on this field, but there is no systematical study investigating the interactions of drugs and components of the used system.

1.1.4 Food

Foodstuffs are the soft matter we eat every day. In fact, they make up some of the most complex examples within this research area [54]. This field has rarely been investigated by soft matter scientists. Apart from the scientific curiosity of understanding the complex structure and physical behavior of food, edible carrier systems are of growing interest in food applications.

Obvious possible applications of microemulsions in food are incorporation of flavors, nutrients, aromas, colors and achievement of food stability. But the use of them in food is limited by the choice of components, especially food-grade surfactants. Many emulsifiers are non-permissible in foods or only allowed at low amounts. Moreover, forming microemulsions within polar oils such as triglycerides bear a particular challenge because they are difficult to solubilize [55, 56]. Thus, there exist many food-grade studies [57-61], mostly by the research group at the Casali Institute of Applied Chemistry, Jerusalem. Almost all of these studies include non-edible components such as alcohols and only a few contain both phospholipids and triglycerides [62-65]. Furthermore, the studies were carried out formulating w/o or even less o/w systems, but the research of bicontinuous microemulsions is totally neglected. *Leser et al.* even claimed that it is not possible to formulate a bicontinuous microemulsion containing triglycerides [66].

1.2 Surfactants

The correct selection of components is the principal factor when formulating bio-compatible or food-grade microemulsions suitable for the application areas introduced above. The two promising classes of surfactants are the alkyl glucosides and phospholipids (E 322) [35]. Both feature efficient solubilization of water and oil, but co-surfactants such as short chain alcohols or 1,2-diols are needed to obtain bicontinuous microemulsions [67, 68]. To develop tools for tuning these kind of surfactants, *Penders and Strey* [6] have clarified in detail the effect of adding an alcohol to a ternary system. *Kahlweit et al.* have done several investigations to formulate non-toxic microemulsions [69] using alkyl glucosides [68, 70] or lecithins [71, 72]. The first phospholipid based microemulsion was studied by *Shinoda et al.* in 1989 [73]. In the following years, *Shinoda et al.* investigated several lecithin based systems [67, 74] and a few alkyl glucosides [75].

A selection of further surfactants, which are permissible in food is presented in Tab. 1.1. These surfactants can be used as co-surfactants to improve a system regarding the required surfactant mass fraction or to tune the temperature range.

Tab. 1.1: Selection of surfactants permissible in food.

type	***in this work***	***E number***
lecithin	soybean and egg yolk phospholipids	E 322
mono- and diglycerides	Paalsgard291	E 471
sucrose esters of fatty acids	sucrose laurate (L-1695)	E 473
polyglycerol ester	sugin 475	E 475
polyglycerol polyricinolate	PGPR	E 476

1.2.1 Alkyl glucosides

Green chemicals are produced from renewable resources, because of the increasing awareness of the impact surfactants may have on the environment. One of the most significant green surfactants belongs to the class of alkyl glucosides, often abbreviated as C_mG_n [76], also referred to as sugar surfactants. Here, *m* represents the length of the hydrophobic alkyl chain - the hydrophobic part (*e.g.* tail) of the surfactant molecules, while *n* equals to the number of glucose groups – the hydrophilic part (*e.g.* head-group) of the surfactant molecule. C_mG_ns belong to the group of nonionic surfactants and are extracted from carbohydrates such as sugars and fatty alcohols [75]. The main reason C_mG_ns are considered more "environmentally friendly" surfactants is their head-group. The ethylene oxide head-groups of the non-ionic polyethylene oxide surfactants take a long time to be decomposed under natural conditions, but C_mG_ns break down into fatty alcohols and glucose directly [77], which both naturally occur in the environment and are already metabolized by many living organisms. Another interesting attribute of linear alkyl glucosides is the ability to form stable foams. At the same time alkyl glucosides with branched tails are poorly foaming surfactants [78, 79]. This is particularly interesting for dishwashing processes, because it is difficult to get rid of the produced foam. But alkyl glucosides are not only *green chemicals*, but also bio-compatible [77]. They also have good dermatological properties and are efficient surfactants. Therefore they are of particular interest as a component in delivery systems in cosmetics and pharmaceutical industries. So it is no surprise that more than 1000 papers related to alkyl glucosides in cosmetic and pharmaceutical applications exist [80, 35, 41].

1.2.2 Phospholipids

Phospholipids are an important class of bio-amphiphiles, because they are fundamental building blocks in cell membranes and thus necessary for living organisms [81]. They are edible and widely used in every day products such as in food, cosmetics and pharmaceutics [82]. They consist of a diglyceride, one phosphate group (switter ionic polar head-group) and a linker molecule like choline. Often pure phospholipids are abbreviated by $(C_m)_2$PC, whereas m describes the C-chain length of the tails and PC stands for the type of head-group (here Phosphadylcholine) [67]. Phospholipids are strong surfactants [67] and show no skin irritation even when used in lotions, creams or gels at high concentrations [83]. They can be easily extracted from egg yolks and soy beans and therefore are widely used in science and industrial applications [84, 28]. Although the phase behavior of phospholipid systems is rather complex, there exist more than 9000 patents related to phospholipid microemulsions [41].

1.3 Task description

Food-grade microemulsions are suitable delivery systems in various applications such as detergent, cosmetic, pharmaceutical, and food industry. To achieve suitable microemulsions for any kind of application, the effects of the desired components, hydrophilic (sugar), hydrophobic (triglycerides) and amphiphilic (edible surfactants) on the characteristics of microemulsions have to be determined first.

Almost every kind of food contains sugar or sweetener. So water, which is inherent in the well known microemulsion systems H_2O/NaCl – *n*-decane – C_iE_j, has to be stepwise substituted by different types of sugar or sweetener. The same model systems are applied to replace *n*-decane systematically by triglycerides, which are the favorable edible oils in food industry, as nearly all fats are composed of them.

Phospholipids are the most promising food-grade surfactants, because they exhibit the ability to solubilize water and oil at rather low mass fractions compared to ordinary surfactants. Phase behavior investigations on several kinds of phospholipids should be performed in *n*-alkane and triglyceride systems, to gain more information about their phase behavior in such systems. Additionally, small angle neutron scattering (SANS) technique will be used to investigate the structure of phospholipid microemulsions.

Another important class of bio-compatible surfactants is alkyl glucosides, which are composed of a long C-chain and a sugar-head (C_mG_n). Even the simple ternary system D_2O – *n*-octane – C_8G_1 is not fully understood, yet. Thus nuclear magnetic (NMR) and small angle X-ray diffraction (SAXD) are used to elucidate the phase behavior of the ternary system in a close collaboration with the group of Prof. Olle Söderman at the University of Lund.

Finally, food-grade microemulsions are formulated based on the gained knowledge with the previous measurements. The structure of these types of microemulsions is to be investigated by SANS measurements.