Chapter 1

Introduction

Nowadays, surfactants play a significant role in both private and industrial sectors. Due to their amphiphilic nature they interact with hydrophilic as well as hydrophobic components which enables a broad spectrum of applications. In general, by thinking of surfactants first of all cleaning processes comes to the mind.[1–3] But also in drug delivery[4–9], as food additive[10–12] or for size control of nanoparticles[13–16] surfactants have become indispensable. Furthermore, they make a valuable contribution to the enhanced oil recovery. By flooding oil reservoirs with aqueous surfactant solutions, the oil is displaced from the rock pores by overcoming the existing capillary forces and reduction of the interfacial tension. In combination with other techniques such as low salinity injection, the oil production can be drastically increased.[17–20] In order to further optimize the field of application, the development of new surfactants and investigation of their mode of action is consequently of constant interest.

A fundamental milestone contributed *Langmuir* and *Blodgett* in the investigation of the surface tension reduction between water – air by surfactant monolayers which was awarded with the Nobel prize in 1932 ”for his discoveries and investigations in surface chemistry”.[21] Later *Schulman et al.* described that surfactants can also reduce the interfacial tension between a polar and non-polar phase whereby a so called microemulsion is formed.[22;23] In the following, *Winsor et al.* investigated more detailed the phase sequence of those systems in dependence of temperature and composition.[24] So far, microemulsions were formulated by ionic surfactants in combination with *e.g.* short-chain alcohols as co-surfactant exclusively. This was changed by *Shinoda et al.* who introduced polyethylene glycol *n*-alkyl ethers as efficient non-ionic surfactants.[25–29] Based on these initial findings, *Kahlweit* and *Strey* investigated precisely the phase behaviour of different compositions of microemulsions as well as their manifold nanostructures.[30–34] In this way, the fundament for the various applications of microemulsions was created.

Nevertheless, the aggregation of surfactants in micellar and microemulsion systems still raises some issues. An opportunity to better clarify these processes is offered by fluorescence labeling methods. It started first by the addition of different fluorescent probes to aqueous surfactant solutions. These additives are only sparingly soluble in water but much better in the lipophilic environment of the micelle interior. Due to this, the critical micelle concentration could be determined by monitoring the fluorescence shift of the additives.[35–37] This method was improved by the use of pyrene-end-labeled polyethylene glycols to mimic surfactant behaviour in polar solvents by studying their concentration-dependent eximer formation.[38–40] It is only logical that consequently surfactants which themselves contain a fluorophore have been developed in order to investigate aggregation independently of additives. So compared *Sakomura et al.* different distributed pyrene-labeled fatty acids in their behaviour in Langmuir-Blodgett films.[41] As pyrene is a well established fluorophore, numerous surfactants with this motif were designed and their aggregation properties investigated.[42–44] Nevertheless, fluorescent surfactants were only barely used in microemulsion as they are mostly to bulky and inefficient to monitor a sufficient emission with at low surfactant loadings. To this end, the design of suitable fluorescent surfactants for the better understanding of microemulsions is of steady interest as they play an important role in many applications.

Due to their ultra low interfacial tension and tunable nanostructure microemulsions are frequently used in polymerization processes.[45–49] *Santana et al.* studied their advantage for enhanced oil recovery.[50–52] Extensive investigations were performed by *Capek et al.*[53–55] as well as *Eastoe et al.*[56,57] in the shape and size distribution of nanomaterials. Microemulsions also offer a great potential as reaction medium in organic synthesis due to their outstanding property of solubilizing hydrophilic and hydrophobic reacting species completely in each other. Here, different types of reactions like hydroformylation[58], oxidation[59,60] or nucleophilic substitution[61,62] could be improved in a microemulsion as reaction medium. *Holmberg et al.* showed that regioselectivity can be induced in the microemulsion environment due to the highly structured amphiphilic film.[63,64]
Furthermore, *Wielpütz et al.*[65] and also *Anderson et al.*[66] demonstrated that reaction rates can be significantly increased in a microemulsion compared to common organic solvents. This is related to the extremely large internal interface of a mi-

croemulsion. Hitherto, reaction rates are improved by catalysts such as enzymes or organocatalysts. Consequently, the combination of microemulsion and catalyst would result in a boost of the reaction rate. As enzyme catalysis is mostly restricted to mild reaction conditions and non-toxic solvents, microemulsions are nowadays well established and can be regarded as ultimate microreactors due to their tunable composition.[67–72] In contrast, in the field of organocatalysis still conventional solvents are frequently used. Here, the use of microemulsions would be particularly suitable for large polarity differences or targeted product removal.

In today's organocatalytic chemistry N-heterocyclic carbenes (NHCs) are of great interest as they provide unique properties by inverting the polarity of carbonyl compounds.[73,74] After *Arduengo et al.* succeeded in the isolation of the first stable NHC, their use in organocatalysis was on the rise.[75] In this context, the isolation and characterization of the Breslow intermediate by *Berkessel et al.*[76], which was postulated by *Breslow*[77] as the key intermediate in the benzoin reaction, was a breakthrough in the understanding of the mechanism in NHC catalysis. Despite their sensitivity towards air and moisture, N-heterocyclic carbenes are used in numerous transformations like benzoin reaction, Stetter reaction or redox esterification.[78–80]
Although the reaction properties of Breslow intermediates in organocatalysis has been widely studied, hardly anything is known about the coordination behaviour to transition metals. Here, investigations would be beneficial for a better understanding in cooperative catalysis. Findings from the structurally related N-heterocyclic olefins (NHOs) could be transferred here. These deoxy-Breslow intermediates have well established over the last decades in organocatalysis[81–83], CO_2 fixation[84] or polymerisation reactions[85–87]. Beside that, many investigations have been carried out on NHO-metal-complexes which may provide initial evidence towards metal complexes of Breslow intermediates.[88–91]

1.1 Objectives

It is well-known that aromatic surfactants have a superb efficiency boosting effect in cleaning processes, the origin of this effect however is still unknown. Thus, a better understanding of the intermolecular interactions of those surfactants at the amphiphilic film, with special focus on the aromatic part, is of high interest. To this end, new surfactants were to be synthesized with special properties. The requirements were to design a non-bulky fluorescent surfactant with the fluorophore as linker between hydrophilic headgroup and hydrophobic tail. This should ensure that the fluorophore is maximally affected during the aggregation. Alteration in fluorescence by formation or curvature change of an amphiphilic film were to be monitored by interfacial tension measurements and fluorescence spectroscopy. Further, the intermolecular interactions of the surfactants were to be investigated by crystal structures. The knowledge of the surfactant class was to be exploited to generate structurally related surfactants which should have a high solubilization potential. The new surfactants were to be compared with known ionic surfactants such as sodium alkyl sulfates and sulfonates. For this purpose, the influence on the phase behaviour of a microemulsion system was to be investigated. Since the physiological properties of these new compounds will be unknown, the influence on eukaryotic cell cultures was to be examined.

Further, the inherent vast interfacial area of microemulsions was to be utilized for reactions across the interface catalyzed by an N-heterocyclic carbene (NHC). Here, decomposition attempts of glucose for the release of formaldehyde were of particular interest. To this end, the individual impacts of the reactants on a microemulsion were to be investigated and consequently a suitable reactive system was to be formulated.

The aldehyde adducts of NHCs (Breslow intermediates) are of great importance in organocatalysis. However, little is known about their coordination behaviour with transition metals. To investigate this more in detail, stable Breslow intermediates were to be reacted with cobalt compounds of different oxidation states. For this purpose, crystal structures were to be formed and analyzed. Additionally, the steric and electronic influences of the aldehydes on the complexation properties were to be studied and compared.

Chapter 2

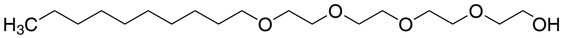
Fundamentals

2.1 Microemulsions

Microemulsions are thermodynamically stable, macroscopically isotropic, nonostructured mixtures of at least three components.[30,33,92] The hydrophilic (lipophobic) component (A) forms a polar phase (a), whereas the hydrophobic (lipophilic) component (B) generates a non-polar phase (b). To solubilize both mutually immiscible phase the amphiphilic component (C) is required as it consists of a hydrophilic (headgroup) and a hydrophobic (tail) domain. Due to this ambivalent nature the amphiphile or rather surface active agent (*abbr.* surfactant) is miscible with component A as well as with B.[23] In a ternary mixture A – B – C the amphiphile adsorbs at the internal interface between polar and non-polar phase resulting in a significant decrease of the surface tension. The formulated microemulsion shows a diverse phase behaviour with a variety of nanostructures in dependence of composition and temperature.[25–28,93,94]

2.1.1 Phase Behaviour

To get insight into microemulsions it is essential to understand their phase behaviour.[95] All ternary microemulsion systems of the type water (A) – oil (B) – non-ionic surfactant (C) follow the same general pattern by the interplay of the three binary systems A – B, A – C and B – C. An example for non-ionic surfactants is compound **1** which belongs to the class of polyethylene glycol monoalkyl ethers ($\mathrm{C_iE_j}$) which consist of a hydrophilic polyethylene oxide chain and a hydrophobic alkyl chain (figure 2.1).



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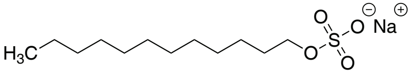
Scheme 2.1: Tetraethylene glycol monodecyl ether ($C_{10}E_4$, **1**) as an example for the non-ionic surfactant class C_iE_j.

According to this, microemulsions with ionic surfactants (D) like compound **2** which can be subdivided in amphotheric, zwitterionic, cationic and anionic surfactants consist of three binary systems (A – B, A – D and B – D) as well.



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Scheme 2.2: Sodium dodecyl sulfate ($NaC_{12}SO_4$, **2**) as an example for an anionic surfactant.

A change of the surfactant properties in terms of headgroup and/or alkyl chain length as well as addition of further components have a strong impact on the phase behaviour of the overall system which will be discussed later in this chapter.

2.1.1.1 Binary Systems

The complex nature of a ternary microemulsion system can be understand better by examining the three binary systems first (figure 2.1).

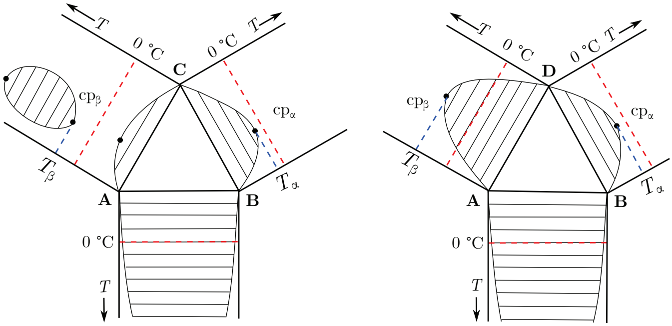

Figure 2.1: Illustration of the binary systems with non-ionic (left) and ionic (right) surfactant as unfolded Gibbs phase prism. Schematically redrawn from [32].

The most simple system water (A) – oil (B) shows a distinct miscibility gap which extends over almost the entire measuring range (0–100 °C). The upper critical point is far above 100 °C and therefore above the boiling point of water. In the system of water (A) – non-ionic surfactant (C) a lower miscibility gap with a critical point occurs often at temperatures far below 0 °C and plays therefore a minor role in the measuring range. Further, an upper closed miscibility gap is present with the lower critical point cp_β at the critical temperature T_β. The molecular structure of the surfactant directly influences the expression of the miscibility gaps. As the surfactant becomes more hydrophilic its solubility in water increases resulting in a smaller upper miscibility gap and vice versa.[34] Contrary to this, the system of water (A) – ionic surfactant (D) only shows a lower miscibility gap with its critical point cp_β above 0 °C. Last but not least, in the binary system oil (B) – non-ionic surfactant (C) or oil (B) ionic surfactant (D) respectively a lower miscibility gap occurs with the critical point cp_α at the critical temperature T_α. Depending on the nature of the oil and surfactant the position of the critical point may lie in the measuring range.

2.1.1.2 Ternary Systems

In a ternary system A – B – C the more complex phase behaviour depends strongly on the interplay of the upper miscibility gap of the binary system A – C and the lower miscibility gap of the binary system B – C. Consequently, the overall phase behaviour is determined by the inversion of the solubility of the surfactant which can be investigated in a Gibbs phase prism (figure 2.2).

Here, the corners represent the pure components water (A), oil (B) and non-ionic surfactant (C). Each side of the phase prism displays a binary system with the temperature T as ordinate. At low temperatures an oil-in-water (o/w)-microemulsion (a) coexists with an oil excess phase (b). This state is denoted as $\underline{2}$. With increasing temperature the solubility of the surfactant in the polar phase decreases due to partial dehydration of the hydrophilic headgroup. Consequently, its solubility in the non-polar increases.[96] By passing the temperature T_l with its lower critical endpoint cep_α the oil-in-water microemulsion separates into water excess phase (a) and a surfactant-rich middle phase (c). With the still persisting oil excess phase (b) a three-phase state (3) is formed. Upon reaching the temperature T_l with its upper critical endpoint cep_β the surfactant-rich middle phase (c) and oil excess phase (b) fuse by forming a water-in-oil (w/o)-microemulsion (b) in coexistence with the water excess (a) phase. This state is denoted as $\overline{2}$. The temperature-depending phase transition of a (o/w)-microemulsion into a (w/o)-microemulsion, which means $\underline{2} \rightarrow 3 \rightarrow \overline{2}$, is referred to as phase inversion.

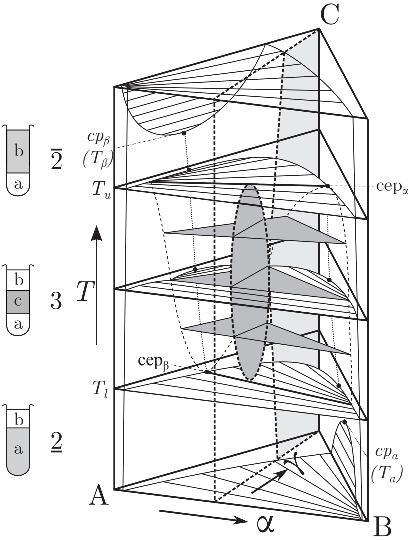

Figure 2.2: Display of the temperature-dependent phase behaviour of the ternary system water (A) – oil (B) – non-ionic surfactant (C) as Gibbs phase prism. On the left side the two- and three-phase states are illustrated corresponding to the phase behaviour as test tubes. Schematically redrawn from [33].

2.1.1.3 The $T\gamma$-Section

Since it is extremely complex to measure a complete Gibbs phase prism it is common practice to perform an isoplethal cut through the prism[30,32,97] at a constant pressure and volume fraction ϕ of the hydrophilic and hydrophobic components,

$$\phi = \frac{V_\mathrm{B}}{V_\mathrm{A} + V_\mathrm{B}}. \tag{2.1}$$

V_A = Volume of hydrophilic component A
V_B = Volume of hydrophobic component B

Alternatively, a cut at a constant mass fraction α of the components is well-established,

$$\alpha = \frac{m_\mathrm{B}}{m_\mathrm{A} + m_\mathrm{B}}. \tag{2.2}$$

m_A = Mass of hydrophilic component A
m_B = Mass of hydrophobic component B

The resulting $T(\gamma)$-section (figure 2.3) displays the phase behaviour of a microemulsion system as the function of surfactant mass fraction γ and temperature T,

$$\gamma = \frac{m_\mathrm{C}}{m_\mathrm{A} + m_\mathrm{B} + m_\mathrm{C}}. \tag{2.3}$$

m_C = Mass of amphiphilic component C

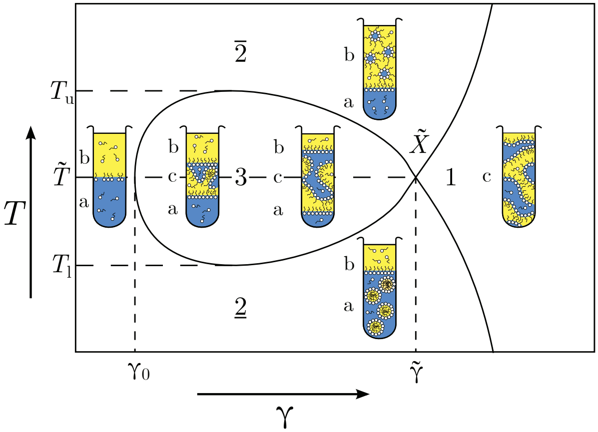

Figure 2.3: $T(\gamma)$-section through the Gibbs phase prism of the system water (A) – oil (B) – non-ionic surfactant (C) at $\phi = 0.50$. The test tubes illustrate the one-, two- and three-phase states in dependence of the temperature T (ordinate) and surfactant mass fraction γ. Schematically redrawn from [33].

At low surfactant mass fractions the surfactant is monomerically dissolved in a coexisting water and oil excess phase (2) and adsorbs at their internal interface. By reaching γ_0 the macroscopic interface is saturated with surfactant molecules resulting in the formation of temperature-dependent aggregates. Consequently, the monomeric solubility of the surfactant can be determined directly from γ_0.[98] At low temperatures ($T < T_\mathrm{l}$) an (o/w)-microemulsion coexists with an oil excess phase ($\underline{2}$). Whereas at high temperatures ($T > T_\mathrm{u}$) a (w/o)-microemulsion coexists with a water excess phase ($\overline{2}$). Between T_l and T_u a three-phase state (3) is formed in which the surfactant-rich middle phase (c) expands with increasing surfactant concentration to the $\tilde{X}$-point. At this point, defined by the surfactant mass fraction $\tilde{\gamma}$ and the temperature $\tilde{T}$, the minimal amount of surfactant is needed to solubilize water and oil completely in each other by forming a macroscopically isotropic one-phase state

(1). Here, various microstructures occur in dependence of surfactant concentration and temperature.

2.1.1.4 The Optimal State

By definition, the less surfactant is needed to solubilize water and oil completely in each other, the more efficient it is. Consequently, the efficiency of a surfactant can be determined by its $\tilde{X}$-point.
As already shown, a surfactant is divided into a hydrophilic headgroup and a hydrophobic tail. For non-ionic surfactants of the class C_iE_j its amphiphilicity can be directly adjusted by variation of the alkyl chain length or the degree of ethoxylation respectively which has a direct effect on the phase behaviour of a microemulsion and therefore the efficiency (figure 2.4).

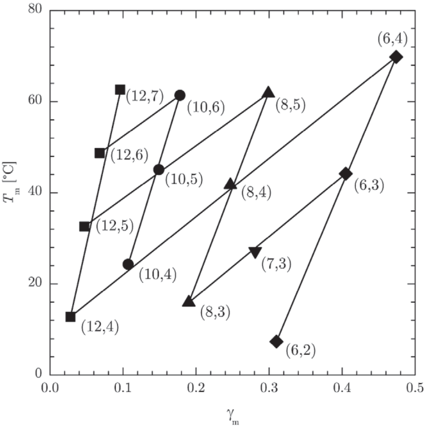

Figure 2.4: Overview of the $\tilde{X}$-points of the system H_2O – *n*-octane – C_iE_j at $\phi = 0.50$, demonstrating the effect of the structure of the amphiphile (alkyl chain length and degree of ethoxylation) on the phase behaviour. Redrawn from [33].

From this, the two following relationships can be derived:

- *Variation of the degree of ethoxylation j, at constant alkyl chain length i.*
  By increasing the degree of ethoxylation the surfactant becomes more hydrophilic. Accordingly, the phase boundaries are shifted to higher temperature and is getting slightly inefficient.

- *Variation of the alkyl chain length i, at constant degree of alkylation j.*
  If the alkyl chain is getting longer the surfactant becomes more hydrophobic.