Chapter 1

Introduction

Surfactants were and still are our inconspicuous companions at macroscopic but more often at microscopic scale. Many technologies are only possible due to surfactant applications, which are of constantly growing scientific and industrial interest for approximately 100 years [1]. Hence, since its definition 'micro emulsion' by *Schulman* [2] optically isotropic surfactant formulations and their variations have become a significant part in today's society. In nowadays' most popular sector of nanomaterials surfactants are utilised for productions of such via template strategies [3–10]. Organic synthesis benefits from the immensely huge interfacial area of microemulsions resulting in bigger yields which were not possible before [11–21]. Closely related to organic synthesis, pharmaceutical industries enjoy the benefits of drug delivery via e.g. vesicels which play a major role during drug transport into the blood stream [22–27]. Simpler application of surfactants were reported 1984 where cationic surfactants were utilised as stabiliser for antibiotics [28]. Concerning healthier and conscious nutrition microemulsions are applied for reduction of the caloric value of food [29–39]. Also, to contribute to environmental protection exhaust emissions can be reduced by introducing water and surfactants into fuels [40–42]. Surfactant systems or in most cases microemulsions are very adaptable and can therefore be utilised in their most different states. This chapter gives an insightful introduction into the world of microemulsions.

1.1 Surfactants: A Short History of Today's Detergents

Today's microemulsions or surfactant-rich/-based systems as we know them experienced their development and popularity beginning with *Schulman* and *Hoar* [43]. The researchers used high surfactant loads and could report a spontaneous formation of isotropic water and oil emulsions. At sufficiently high amphiphile concentrations the whole interfacial area between water and oil could be covered with surfactant molecules leading to a drastic decrease of interfacial tension resulting in the coining of the term 'micro emulsion' [2, 44]. In 1954 *Winsor* could describe a phase sequence of different kind appearing when studying the composition of a specific system as a function of temperature [45]. Whereas *Schulman* and co-workers concentrated their studies on systems with ionic surfactants using co-surfactants, e.g. alcohols, *Shinoda* could show for the first time an analogue system with non-ionic surfactants only [46–51]. These studies became a stepping stone for systematic and detailed analyses of phase behaviour of microemulsions by *Kahlweit* and *Strey* as we know them now. Years to follow many discoveries concerning structures and their sizes within the one-phase region using e.g. freeze fracture electron microscopy (FFEM) [52, 53] or small angle neutron scattering (SANS) [54–58] were made. Concerning SANS researchers like *Langevin* [59–61], *Glatter* [62–65], *Schubert* [54, 58], *Bassereau* [53, 66, 67] and many more contributed their efforts and knowledge. Also for more exact characteristics concerning the continuity of the structures experiments using self-diffusion NMR were performed by *Söderman* [68–70] and *Olsson* and *Wennerström* [71–76].

The most important and remarkable feature of microemulsion, being the reason for this work for that matter, is its ultra-low interfacial tension emphasised by *Kahlweit* and *Strey* from 1985 onwards specifically at the phase inversion temperature (please refer for further details to section (2.7)). This fundamental feature explains various observations which can be made in everyday life.

As a prestage to the ultra-low interfacial tension, in 1891 the autodidact *Agnes Luise Wilhelmine Pockels* could observe surface tension in her everyday life by noticing different behaviour of water running down the kitchen sink if various amounts of soap or dirt were added. Following that, she constructed a simple yet effective set-up for surface tension measurements using scales, string and a button. Based on it, she developed first slide trough, on which the *Langmuir* trough is based. If it had not been for *Lord Rayleigh*, who corresponded with *Pockels* about her observations, the contribution of *Pockels* would have been abandoned to oblivion. He ensured her publications in *Nature* [77] on 12. March, 1891 noting to the editor that her findings "seem to me very suggestive, raising, if they do not fully answer, many important questions". In the following *Langmuir* and *Blodgett* developed the *Langmuir-Blodgett* trough based on the work of *Pockels* and recieved 1932 a *Nobel* prize for prove of existing surfactant monolayer on the water – air interface [78] resulting in reduced interfacial tension. After 1932 *Pockels* recieved an honorary doctorate in engineering from the Department of Mathematics and Physics of Polytechnical University of Brunswick as well as *Laura Leonard* Prize from the *Colloid Society.* At the time, *Ostwald* included an article in *Kolloid-Zeitschrift* testifying importance of her work [79].

Though the first surface tension measurements are roughly 100 years old, without being aware of it, the Babylonians in 2800 B.C. made use of the reduction of surface or interfacial tension using soaps [80]. Like the Romans after them, they used water and bone ashes (alkali) in combination with oil of *cassia* for very sophisticated cleaning processes [81]. In 1500 B.C. the Egyptians with their bathing-rich culture made soaps from vegetable or animal fats with alkali salts [82]. *Pliny the Elder* mentioned combination of ashes with sebum for soap formation. He also noticed the straightening of disquiet water, if small oil droplets are placed in it [83]. *Aelius Galenus* wrote about using sodium hydroxide for soap-making [84].

Despite the general importance of hygiene and mainly due to the Dark Ages until the late 20th century nothing new happened concerning soap production. Until then hard soap bars were used to wash textiles. In 1890 two washing powders were very popular and heavily advertised for. *Gold Dust Washing Powder* by *Fairbank* which used hydrogenation processes during production and *Rinso* by *Hudson*. However, these were nothing more than soap flakes or pulverised soap [85]. *Rinso* became the leader of the two due to the usage of better sodium silicate as a builder instead of commonly used sodium carbonate. The *Hudson* company was later acquired by *Lever Brothers*, who founded in 1930 *Unilever* [86]. However, the *Rinso* brand is distributed until today in Indonesia [87].

With *Persil*, the first 'self-acting' detergent, an innovation was introduced in 1907 by *Henkel & Cie.*, founded 1876 [88]. The formulation contained hydrogen peroxide and sodium silicate which allowed washing of textiles in an odourless and more gentle way than any other bleach (chlorine mostly) at that time [85].

Following the raising development of chemical industry during World War I first synthetic detergents were invented in Imperial Germany due to the shortcomings of natural fats for soap-making [89]. These replacements were introduced in detergent formulations in form of branched chain alkyl benzene sulfonates and short chain alkyl naphthalene sulfonates. The very first synthetic detergent was introduced by *Boehme* (later subsidiary of *Henkel*) in 1932 under the trading name *Fewa* and is distributed until today in Austria [88, 90]. Later a synthetic detergent containing phosphate builder was launched in 1946 by *Procter & Gamble* marketed as *Tide* [91]. On the German market the *Persil* formulation was improved with visual brighteners in 1950 and synthetic anionic surfactants in combination with a foam enhancer and perfume agents in 1959 [88].

All these developments, be they intentional or forced, had an immense influence on our environment. The common use of hardly biodegradable tetrapropylene benzene sulfonate (TPS) showed its consequences: severe foam generation in aquatic environment was inevitable leading to German law restrictions about detergents and cleaning agents in 1961 [92]. It was later modified as an answer to excessive algae growth due to usage of phosphates in washing formulations in 1975 [93]. Finally, a law modification was implemented at EU level quite recently [94].

Since these laws emerged modern washing detergents can contain up to 16 components [95] where TPS is already replaced by linear alkyl benzene sulfonates (LAS) which are biodegradable. Phosphates found their replacement in various components, most important of which are zeolites (for further details concerning components of washing formulations please refer to chapter (5), table (5.1)).

The judicative changes were more than necessary considering the sheer amount of detergents used. As to be seen in figure (1.1), the left part depicts German market share of detergents. All-purpose detergents are most sold with 59%. In the right part of the figure going to lower amounts of detergents used the development and evolution of washing detergents is observable. Nowadays washing detergents consist of lesser filling material - the consumer needs 80 g of powder detergent or 67 g of super-concentrate detergent per 4.5 kg dry textiles [96] which is already a satisfying improvement in comparison with data from over 30 years back.

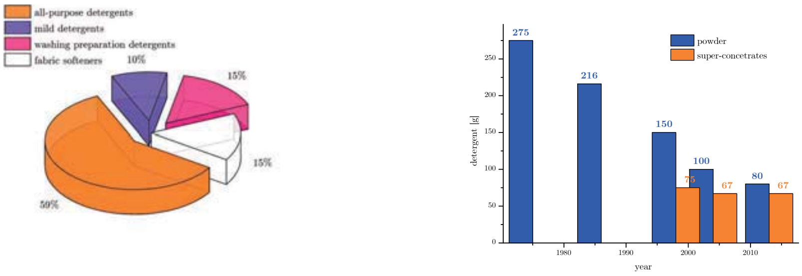

Figure 1.1: Washing detergents on German market in 2013. Left: washing detergents of all kinds sold at retail prices. Right: compacting washing detergents (both redrawn and modified from [96]).

This correlates with the growing environmental consumer awareness as well as stricter laws resulting in adjusted formulations.

However, with future in mind these achievements must be outperformed. Sustainability is the key word of today and tomorrow concerning not only detergency but the reduction of the overall carbon footprint of manufacturers. Meanwhile the implementation of great objectives takes place at large companies, like e.g. *Henkel*, where a plan of '*Faktor 3*' must be completed until 2030 [97]. It stipulates the increase of the overall company efficiency in relation to their carbon footprint. Also, 2010 *Unilever* came up with its *'Unilever Sustainable Living Plan'* in which the company plans to reduce the environmental impact and to improve health and well-being by 2020 [98]. This trend is also followed by *Procter & Gamble* in the *'P&G Report Card: Progress toward 2020 Sustainability Goals'* campaign [99].

Additional positive notice equally concerns the automotive industry. There, formerly used organic solvents which are classified as 'toxic' (T) like, e.g. 1-methyl-2-pyrrolidone, make way for water-rich emulsions. These are used as strippers for protective grease coatings during the production of car bodyworks. Fine optics manufacturers are in the process of similar adjustment for the removal of protective lacquer layer [100].

Hence, the washing formulations must be adjusted accordingly. They should contain less components which should additionally be biodegradable. Lowering the washing temperature is also an important agenda item as well as the reduction of water used. For implementation of these goals an understanding of washing formulations, more specifically the interactions between the components used, as well as their impact on washing processes and textiles is crucial.

However, mere understanding is not enough. Dirt like grease, oils, or other hydrophobic substances on textile fibres or other surfaces must be detached and then mobilised in form of stable mixtures or dispersions in order to prevent reprecipitation. For the remainder of this thesis the term "dirt" will be used meaning all impurities and dirt of non-polar nature. Modern washing detergents work on basis of emulsions which are known for their marginal surfactant input. Microemulsions were frowned upon for a long time due to the erroneous belief of need of high surfactant loads. One important quality of microemulsions has been omitted and completely overlooked. The ultra-low interfacial tension of microemulsions allows oil-water interactions like they never can be found in an emulsion state. The ultra-low interfacial tension is always present – be it a one-phase region or three-phase region of a microemulsion. Its impressive meaning becomes clear when observing a striking correlation of the ultralow interfacial tensions and dirt removal which was pointed out by *Kahlweit* and *Strey* in 1985 depicted in figure (1.2).

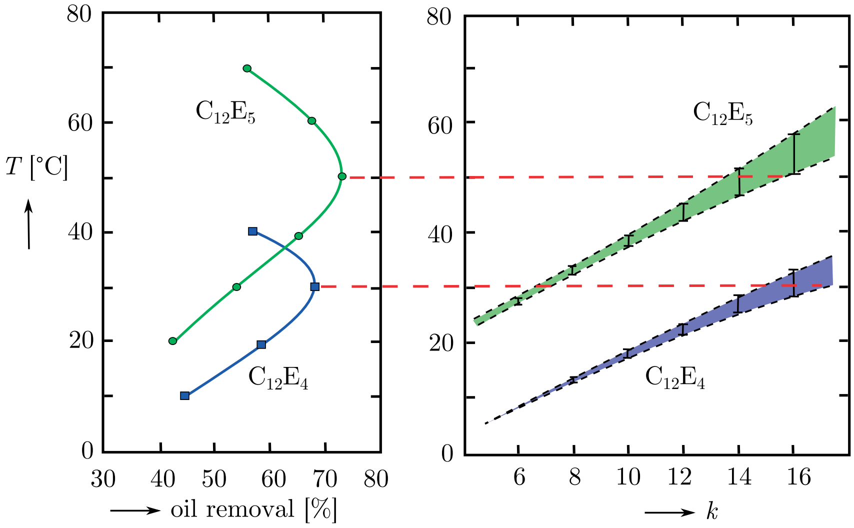

Figure 1.2: Left: Dirt removal from textile blends. Right: Position of the three-phase region on the temperature scale. Note the correlation of maximum dirt removal of mineral oil with the occurrence of the three-phase system for hexadecane (redrawn from [101] and [102] as in [103]).

To take advantage of the ultra-low interfacial tensions we suggest the non-polar dirt to be mixed into the microemulsion. To ensure this, the oil-continuous subphase of the microemulsion is made continuous with the non-polar dirt, i.e. the microemulsion is made lipophilic (the state $\overline{2}$ introduced in chapter (2)). Then the dirt is removed by slipping through the bicontinuous sponge-like structure with its associated ultra-low interfacial tension, e.g. during a dilution-induced phase inversion. This way an optimal removal can be ensured. Obviously the cleaning is made possible by a sponge in a double sense. First the oil is taken up as with a household sponge and second the sponge-structure passed, for which reasons we call this procedure the *lipophilic sponge* for the remainder of this thesis.

With various changeable parameters at hand and knowledge of phase behaviour microemulsion systems can be tuned to one‘s liking depending on applications. Microemulsions can be delivered as such on the soiled surface or they can be formed in situ as soon as contact with dirt to be removed is ensured. Therefore the study of microemulsion systems for washing or general common cleaning processes is advantageous concerning increase of washing i.e. cleaning efficiency as well as usage of small surfactant loads when operating in a three-phase region or in a properly adjusted one-phase region.

1.2 Objectives

In contrast to the use of emulsions or water-rich surfactant solutions, microemulsions allow the advantage of ultra-low interfacial tension which is a necessary prerequisite for the best cleaning efficiency possible. Mainly, microemulsions can be formulated in three different ways. Water-rich microemulsions contain water and marginal oil amounts with according surfactant load. Oil-rich systems are mirror-images of water-rich systems. Balanced microemulsions, e.g. mixtures of equal oil and water amounts are more challenging with respect to effective higher oil and water loads which must be solubilised in each other. Hence, the primary aim of this thesis was the development of a general guideline on how to formulate an optimised microemulsion within the limits of given projects, whereupon this guideline was to be applied in different projects.

Textile detergency at domestic scale has always been a matter of washing suds, i.e. water solutions of surface active agents. The primary role of a washing detergent is the removal of dirt, which mostly consists of oils with broad distribution of alkyl chain lengths. Therefore, a system must be formulated which is capable of effective oil absorption. For that purpose the novel *lipophilic sponge* concept was developed which provides this property at the very first contact of textile fibres with the active washing formulation. This concept also describes the interaction of ultra-low interfacial tension of the microemulsion used with the oil-containing dirt allowing for the best possible washing efficiency (see chapter (4), figure (4.1)). Not only the achievement of best washing results is desirable but also a low surfactant load should be possible. After dirt removal the mobilised oil droplets should remain in solution without reprecipitation on the textile surface. This is managed by nanoemulsions which are formed during the dilution step in a washing process. Based on the surface charge of the resulting oil droplets covered with ionic surfactant molecules the droplets experience repulsive forces resulting in a stable solution.

Another application of microemulsions proposes the use in an oil-rich environment due to easily corroding metal parts which are to be cleaned. Here the maintenance of the one-phase region is of great importance for a ready product. Therefore, a temperature-invariant system was aimed for. This was ensured by combination of ionic and nonionic surfactants. At a specific point the ionic to nonionic ratios result in a one-phase region which extends over the whole temperature axis. Additionally, this oil-rich microemulsion is capable of high supplementary water permeation which is a necessary feature for the use of the microemulsion in countries with high air humidity.

Finally, a balanced microemulsion was to be formulated. It should replace the toxic organic solvents during fine optics productions leading to environmentally friendly and healthier working space. Along low manufacturing costs this microemulsion should cleanse high quantities of fine optics from protective lacquer layers.

All these applications had to comply with the procedure and formulation guideline developed in the beginning of this thesis.

Chapter 2

Fundamentals

Every washing process regardless its terms, restrictions or area of application implies the use of surface active agents, polar and non-polar components. It may seem as a very simple process. However underneath it lies a deep understanding of interaction between these three main components.

This chapter includes theory about microemulsions, very specifically their phase behaviour, nanostructure and interfacial properties. Also the influence and interactions between ionic and non-ionic surfactants are explained, as well as the one of additives.

2.1 Binary Systems and Phase Prisms

It is commonly known that water and oil do not mix. However, the addition of a surface active agent (C) to the two otherwise immiscible polar or hydrophilic (A) and non-polar or lipophilic (B) components leads to the formation of emulsions and microemulsions depending on the surfactant concentration. In contrast to the inherently unstable emulsions, microemulsions are thermodynamically stable, macroscopically isotropic and nanostructured mixtures of at least three components [104–106]. The miscibility is possible given the ambivalent structural nature of the surface active substance (surfactant). Two kinds of surfactants can be distinguished: non-ionic and ionic surfactants. The latter ones are subdivided in cationic, anionic, zwitterionic and amphoteric surfactants. Despite their nature they all consist of a polar ‘head’ group and non-polar alkyl chain ‘tail’ (see figure (2.1)).

The nature of the ionic surfactants is determined by the chemical structure of

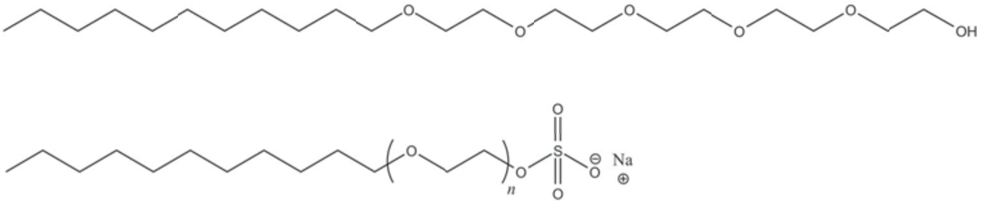

Figure 2.1: Examples of a non-ionic surfactant, here $C_{12}E_5$ (n-dodecyl pentaglycol ether) and an ionic sodium lauryl ether sulfate (SLES), here with n-degree of ethoxylation.

their polar head groups. The non-ionic surfactants as well as ionic ones come with various alkyl chain lengths and degree of ethoxylation. For non-ionic surfactants it is common to use C_iE_j nomenclature, where i is the number of carbon atoms in the alkyl chain and j the number of glycol units in the polar head group.

Notwithstanding their nature the advantage of surface active substances lies in their ability of adsorbing at the energetically disfavourable interface existing between polar and non-polar domains. Following the adsorption a simultaneous decrease in interfacial tension is observable leading even to the formation of more interface. Considering parameters like temperature, surfactant concentration etc. multiple phases may form up to lyotropic mesophases.

The term ‘micro emulsion’ or microemulsion nowadays was first introduced by *Schulman* and *Bowcott* in 1955 after performing titrations with a co-surfactant and inverting a two-phase emulsion into an optical isotropic mixture[2] which was confirmed 2004 by *Giustini* and co-workers [107] using pulsed gradient spin-echo NMR. The first report of transparent water-in-oil dispersions was published in 1943 by *Schulman* and *Hoar* [43]. In 1967 *Shinoda* investigated temperature sensitive non-ionic surfactants [46, 48–51]. Systematic study of microemulsions however was done by *Kahlweit* and co-workers starting in 1985 [108] resulting two years later in the seminal paper ‘How to study microemulsions’ by *Kahlweit* and *Strey* and co-workers [109]. According to this paper, the phase behaviour of all general microemulsions can be derived from the ternary system H_2O (A) – n-alkane (B) – non-ionic surfactant (C) which can also be explained by a *Gibbs* phase prism at constant pressure p with a *Gibbs* phase triangle A – B – C at its base and with the temperature as ordinate [108–110].

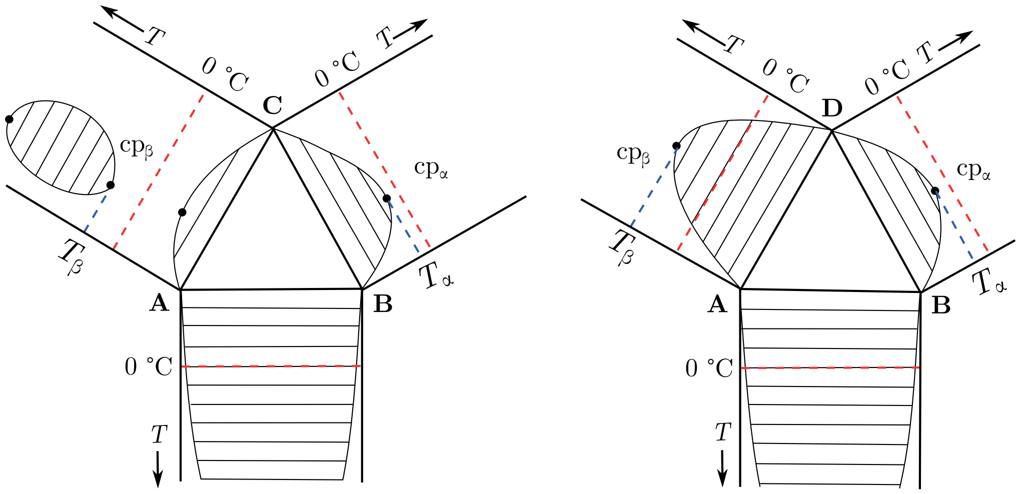

Figure 2.2: Unfolded phase prisms of binary systems with non-ionic surfactant (left) and ionic surfactant (right) (redrawn from [110], schematic). All binary systems are comparable except for A – C and A – D systems.

The phase behaviour of microemulsions of at least three components is based on the interactions between the binary systems: water (A) – oil (B), water (A) – surfactant (C/D) and oil (B) – surfactant (C/D), whereat C is for non-ionic surfactant and D stands for ionic surfactant (see figure (2.2)). The most simple binary system is the A – B system. For almost the whole temperature range oil and water are immiscible. Just towards higher temperatures a marginal miscibility at low percentage of oil in water or water in oil is exhibited respectively. The upper critical point of this system is located way above the boiling point of the mixture.

The binary systems B – C or B – D respectively either with non-ionic or ionic surfactant exhibit a lower miscibility gap below 0 ℃ in this schematic drawing with an upper critical point cp_α. The position of this critical point and its associated temperature T_α is strongly dependent on the nature of the surfactant and oil used. Therefore, this point may lie way beyond the 0 ℃ mark in both directions of the ordinate. The most interesting and especially complex system of all is the A – C binary system [111]. Like the B – C system it also has the lower miscibility gap with an upper critical point. For further discussion in case of non-ionic surfactant it will not be taken into consideration due to its position far below the melting point of the mixture at ambient pressure. In addition, the binary system A – C exhibits an upper closed miscibility gap with its lower critical point cp_β positioned at critical temperature T_β. The upper critical point lies above the boiling point of the mixture and is regarded non-substantial. In case of A – D (right) only a lower miscibility gap can be found. Its critical point cp_β lies above 0 ℃ contributing herewith to the formation of a one-phase region of microemulsions.

By positioning each of the binary systems vertically a corresponding *Gibbs* phase prism can be constructed with temperature T as ordinate. Here, like previously, one can differentiate between systems with non-ionic (left) and ionic surfactant (right) (see figure (2.3)).

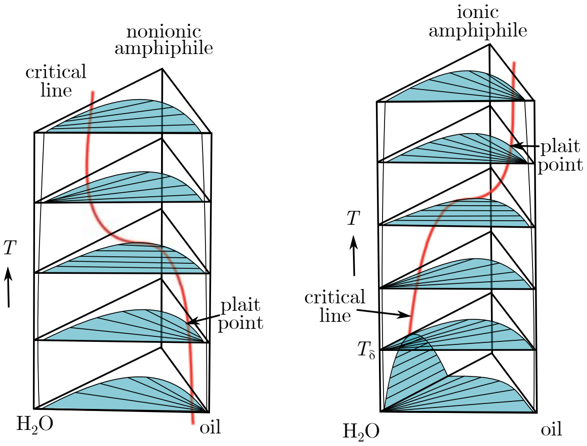

Figure 2.3: Schematic *Gibbs* phase prisms for ionic (left, redrawn from [112]) and non-ionic (right, redrawn from [113]). The critical lines in both prisms exhibit mirror-image-like progression underlining the resulting inverse phase behaviour of systems.

The phase prisms consist of stacked *Gibbs* triangles which cut the phase prisms isothermally. The triangles display binodals in form of curves and the straight lines represent the tie lines which specify the composition at equilibrium state between the existing phases. The phases reach equal composition at the plait point. The critical line connects all plait points in a phase prism as function of temperature. In case of ionic surfactants the critical line goes from water-rich towards the oil-rich side of the phase prism. An inverse behaviour is observable in the phase prism with non-ionic surfactant. In this case both systems, ionic and non-ionic, happen to be in a prestage of presence of tricritical point which is the reason for absence of the three-phase region [102].

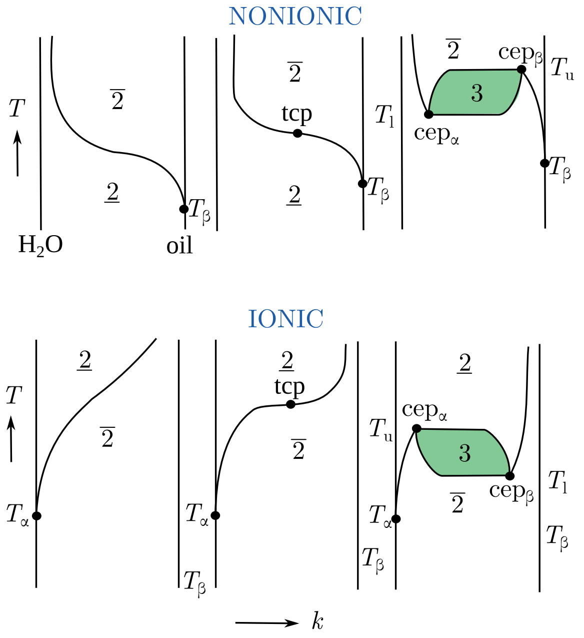

Figure 2.4: Formation of the three-phase region by means of 'breaking' the corresponding critical lines at tricritical points (tcp) as function of oil alkyl chain length k, for non-ionic (top) and ionic system (bottom) [112].

When changing the nature of oil or hydrophibicity of the surfactant used at some point a tricritical point may emerge. Here, the critical line can break leaving place for formation of a three-phase region. Its formation is dependent on the size of the B – C gap and the strength of the A – C loop [102]. The formation of the three-phase region occurs when both miscibility gaps of systems B – C and A – C happen to overlap.

A schematic formation of a three-phase region is depicted in figure (2.4) during a variation of alkyl chain length of an oil. Here, the critical line is projected schematically at the front side of the previously seen phase prisms (figure (2.3)).

The increase of alkyl chain length k initiate the growth of the B – C miscibility gap. As consequence, T_α increases also forcing more non-ionic surfactant into the non-polar phase. Simultaneously the inflexion point of the critical line rises higher increasing herewith its 'bending tension'. At one specific alkyl chain length the critical line breaks at a tricritical point (tcp), leaving a three-phase region in its place with cep_β at T_l and cep_α at T_u. In case of ionic surfactants the elevation of T_α in B – D gap results in gradual repositioning of ionic surfactant into the polar phase. Here the tricritical point leads to formation of cep_β at T_u and cep_α at T_l, the opposite of the non-ionic case.

A more detailed depiction of the *Gibbs* phase prism for non-ionic surfactants is to be seen in figure (2.5).

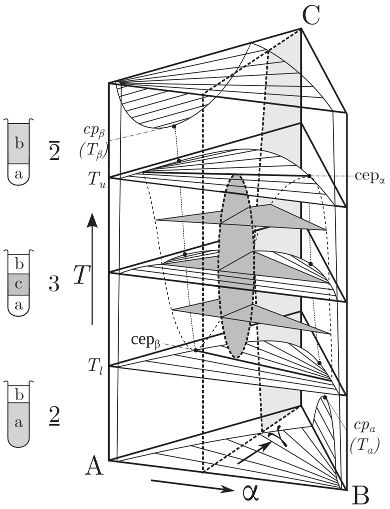

Figure 2.5: *Gibbs* phase prism of a non-ionic system A – B – C with temperature T as ordinate displaying the corresponding three binary systems, isothermal triangles and breaking of the critical line with the formation of the three-phase body (redrawn from [108]). The test tubes illustrate optical appearances and the phase states of the microemulsion.

At its base the phase prism has the ternary system A – B – C as a triangle. The phase behaviour is temperature dependent and the properties of the interfacial amphiphilic film (see subsection (2.6.1)) change according to the temperature T positioned on the ordinate. With increasing temperature a phase inversion takes place. The o/w - state (oil droplets in continuous water phase a with oil excess phase b) shifts to the formation of the three-phase region as depicted in the middle test tube. Here the separation of the both excess phases water a (bottom) and oil b (top) is clearly visible. The middle phase c is the microemulsion phase which contains bicontinuous structures. There, oil and water are equally dispersed in each other with a separating amphiphilic film between them. Raising temperature even higher the three-phase region vanishes leaving w/o - state (water droplets in continuous oil phase b with water excess phase a) in its place. This phase sequence is called phase inversion and is typical for non-ionic surfactants. For ionic surfactant applies inverse phase behaviour.

The phase prism displays the immensily complicated interaction between at least three components and accordingly their binary systems. To study phase behaviour many sections through the phase prism can be undertaken. The most convenient of them would be the $T(\gamma)$-section or so-called ‘fish tail’ cut at constant oil to water ratio. This cut is depicted schematically in the *Gibbs* phase prism by medium dashed lines. Its three-phase ‘head’ and temperature-variant ‘tail’ remind of a fish or whale which is where the name comes from. There are also other sections which depending on desired application or result can be made. Some of them additionally to the $T(\gamma)$-section are discussed in the next chapter.

2.2 Sections Through the Phase Prism

The measurement and exhibition of the whole phase prism is time consuming and for the most applications not relevant. Therefore, it is common practise to perform isoplethal cuts through the phase prism according to one's needs. For this work two sections find their application: the $T(\gamma)$-section and the $T(w_A)$-section.

2.2.1 The $T(\gamma)$-Section, so Called 'Fish tail'-Cut

One of the most practical and classical ways to study phase behaviour of interest is performing a $T(\gamma)$-section through the phase prism at constant oil to oil and water ratio α as constant weight fraction [108, 110, 114]:

$$\alpha = \frac{m_B}{m_A + m_B} \tag{2.1}$$

where m_A and m_B are masses of water (A) and oil (B) respectively.

The $T(\gamma)$-section represents the phase behaviour as a function of the surfactant mass fraction γ and temperature T

$$\gamma = \frac{m_C}{m_A + m_B + m_C} \tag{2.2}$$

with m_A, m_B and m_C being the masses of water (A), oil (B) and surfactant (C).

In order to have the possibility of measuring symmetric phase diagrams it is advisable to use the volume fractions Φ and Φ_C given that the densities of the components used are known:

$$\Phi = \frac{V_B}{V_A + V_B} \tag{2.3}$$

with V_A and V_B being the volumes of water (A) and oil (B),

$$\Phi = \frac{V_C}{V_A + V_B + V_C} \tag{2.4}$$

where V_A, V_B and V_C are the volumes of water (A), oil (B) and surfactant (C) respectively.

An example of such a symmetrical $T(\gamma)$-section as a function of temperature T is depicted in a schematic representation in figure (2.6). For small surfactant mass fractions which are located below γ_0 oil and water phases include monomerically dissolved surfactant molecules without building up any kind of microscopic structures over the whole temperature range. Going further to higher surfactant mass fractions the energetically undesired interface between oil and water is saturated with surfactant molecules which are positioning themselves between the two immiscible phases until the interface is completely filled.

As the surfactant mass fraction increases and the boundary of γ_0 is overcome small aggregates consistent of arranged surfactant molecules containing either oil or water, micelles or inverse micelles respectively, are starting to gain number at lower and higher temperature values. These are two states which are permanently present around the 'fish' head and also its 'tail'. At lower temperatures below T_l this is the state $\underline{2}$ where micells filled with oil are distributed in a water continuous phase in coexistence with an oil excess phase (o/w).

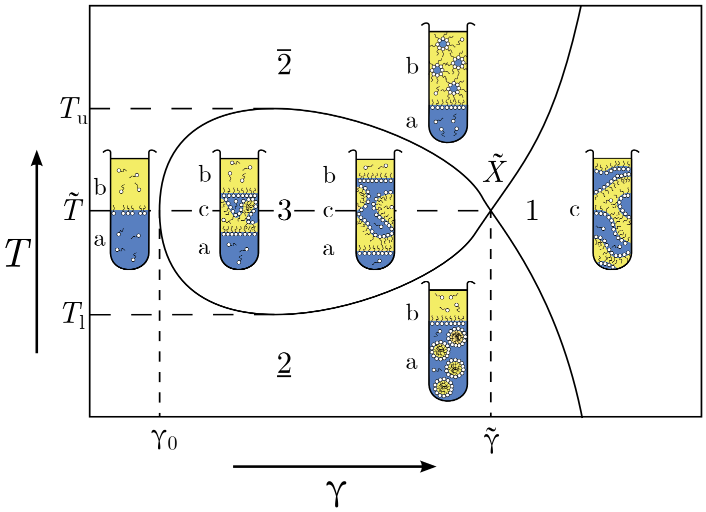

Figure 2.6: Schematic depiction of a $T(\gamma)$-section through the *Gibbs* phase prism of a ternary system water – oil – non-ionic surfactant at a constant oil to oil and water volume fraction $\Phi = 0.50$. At small surfactant mass fractions below γ_0 the macroscopic interface gets saturated with monomerically dissolved surfactant molecules. Above this concentration between $\gamma_0 < \gamma < \tilde{\gamma}$ at temperatures between T_l and T_u a three-phase region with its bicontinuous aggregates forms. Upon reaching surfactant mass fractions above $\tilde{\gamma}$ the formation of the one-phase region takes place with its various types of structures (redrawn and modified from [104]). Above and below the three-phase and one-phase regions w/o (water in oil) and o/w (oil in water) micelles and their corresponding excess phase are present, which form in oil continuous or water continuous phases, respectively.

Above T_u the inverse state $\bar{2}$ contains water-swollen droplets shielded by surfactant molecules in form of inverse micelles from the oil continuous phase which is found to be in coexistence with a water excess phase. At intermediate temperatures localised between T_l and T_u and at higher surfactant mass fractions than γ_0 the surfactant is equally soluble in water in oil. At these temperatures small amounts of oil can gradually be solubilised in water forming a three phase state 3 where a balanced surfactant-rich microemulsion (c) coexists with the remaining oil (b) and water (a) excess phases. With increasing surfactant mass fraction further amounts of oil and water can be integrated into the microemulsion phase until the so-called $\tilde{X}$-point located at $\tilde{\gamma}$ and $\tilde{T}$ is reached. The $\tilde{X}$-point gives the efficiency of a system as it is the minimal amount of surfactant required in order to solubilise equal amounts of oil in water resulting in a formation of an optically isotropic one-phase region denoted as 1. Within this region close to the $\tilde{X}$-point bicontinuous sponge-like structures are present. Going to higher temperatures above T_u this bicontinuous structure changes its nature towards the oil-continuous state, where in comparison the continuity below T_l turns water-continuous.

At even higher surfactant mass fractions the one-phase region broadens and the nanostructures within evolve due to energetic and geometrical reasons to water swollen micelles close to the upper phase boundary and oil swollen micelles present at the lower phase boundary respectively. Depending on the nature of surfactant used, e.g. long dominant n-alkyl chains, a formation of higher ordered liquid crystalline mesophases like lamellar phase (L_α) can be observed.

2.2.2 The Optimal State

Depending on the nature of components used to form a microemulsion the resulting system can require more or less surfactant. Each specific system has its own efficiency. Efficiency of a microemulsion is defined by means of minimal surfactant mass which is needed in order to completely solubilise oil in water forming herewith an one-phase region - a microemulsion. The point in question is the $\tilde{X}$-point and its position including its coordinates provides information about the efficiency of the microemulsion. In general, microemulsions considered efficient require as low surfactant mass fraction as possible at the $\tilde{X}$-point. Temperature is a tunable parameter which is specific for later application. When observing the *Gibbs* phase prism of the ternary system H_2O – n-alkane – C_iE_j in figure (2.5) a parabolic run, called the trajectory of the middle phase [106], of the $\tilde{X}$-points is present for all volume fractions Φ or mass fractions α (see figure (2.7)). Starting at the lower critical endpoint cep_α at the temperature T_u the line ascends towards the upper critical endpoint cep$_\beta$ at the temperature T_l. Along with the run of the line the composition of the microemulsion changes from oil-rich to water-rich. Schematic trajectories of such composition change are common in the A – B – C base and the A – B – T plane.

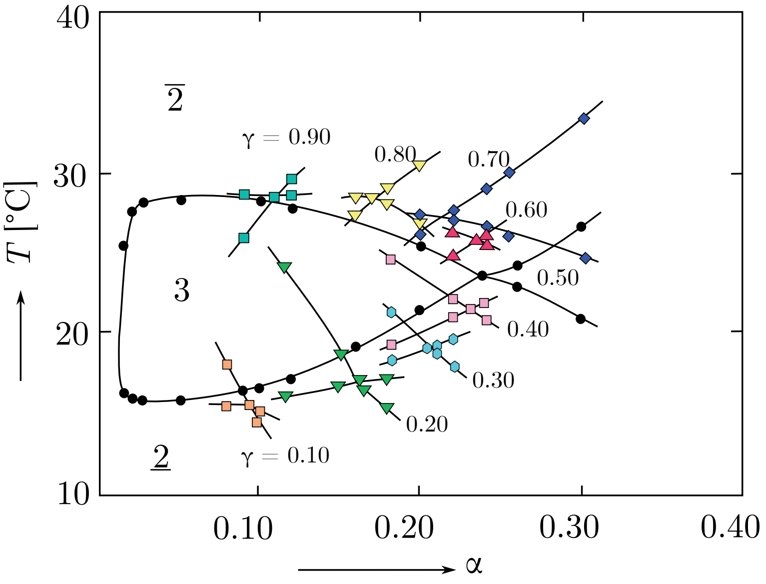

Figure 2.7: System H_2O – n-decane – C_8E_3 at various α values projecting a trajectory of $\tilde{X}$-points. $\tilde{T}$ decreases systematically beginning with $\alpha = 0.90$ from the oil-rich to the water-rich side at $\alpha = 0.10$ (redrawn from [109]).

A balanced microemulsion, taking hydrophilic-lipophilic balance into consideration [115, 116], is formed given the isothermal three-phase triangle extends maximally and is symmetric, implying the solubilisation of equal amounts of oil and water in the microemuslion phase. The temperature at which this balanced or optimal [106] state occurs is the mean temperature $T_m = \frac{T_u - T_l}{2}$. In comparison to other $\tilde{X}$-points on the trajectory X_m-point delivers the most best performance in solubilisation of equal amounts of oil and water and therefore can be regarded as the measure or bench mark of the efficiency of the corresponding microemulsion.

Starting from below X_m up the temperature scale the nature of the microemulsion turns from oil-in-water to water-in-oil, making this point the phase inversion temperature. As shown in [117, 118], there is a general trend to be observed when scaling the trajectory of the middle phase for microemulsions of type H_2O – n-alkane – C_iE_j with their temperatures T_m and minimal surfactant amount γ_0 needed for the formation of the one-phase region. How strongly or weakly this scaling is pronounced in other systems depends on the nature of the components used. An effective overview [119] of distribution of γ_m-points as a function of T_m is given in figure (2.8) where various systems of type H_2O – n-octane – C_iE_j at $\Phi = 0.50$ are plotted.

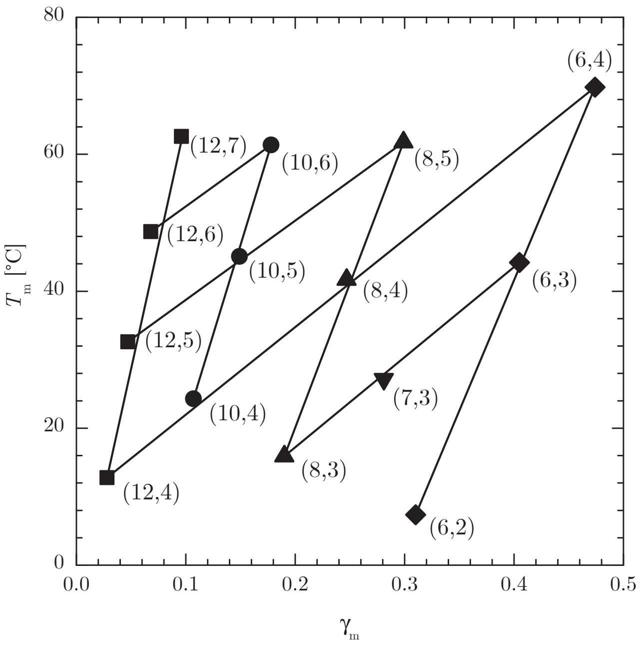

Figure 2.8: X_m-points of system H_2O – n-octane – C_iE_j at $\Phi = 0.50$ where C_iE_j ranges from C_6E_2 to $C_{12}E_7$ as a function of the surfactant mass fraction γ_m and the inversion temperature T_m. Two effects are observable: the increase of hydrophily of the head groups j affects the phase inversion temperature T_m. The changes to the alkyl chain length i of the surfactant in question influence the efficiency of the overall system (redrawn from [119]).

Variations of polar head groups as well as of alkyl chain length are possible and can be used to one's advantage. So, the increase of the non-polar alkyl chain of the surfactant results in a more pronounced hydrophobic nature of the surfactant implying the corresponding upper miscibility gap of the binary system A – C with its lower critical point cp_β becomes more dominant causing the phase boundaries of the whole system to shift down the temperature scale towards smaller T_m-values.

In the whole, the solubilisation efficiency of water and n-octane increases along with the growing alkyl chain length resulting in decreasing γ_m. On the contrary, T_m increases along the increase of the hydrophilic chain legth j which is accompanied by the decrease of the solubilisation efficiency.