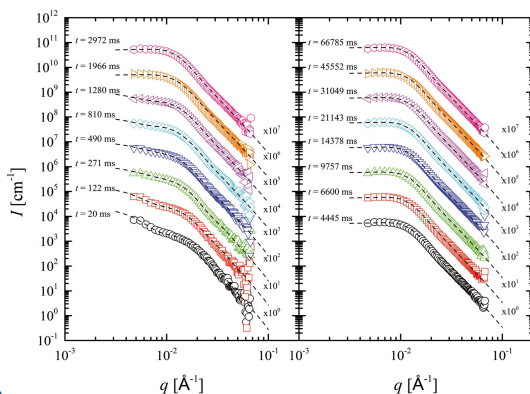




Helge F.M. Klemmer (Autor)
Amphiphilic Polymers in Microemulsions
The Influence on Structure and Formation Kinetics



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1 Introduction

Surfactant technology is of constantly growing scientific and industrial interest [1] although its origin dates back as far as the Babylonians in 2800 B.C. [2] and has been used by early societies in one form or another. They learnt to take advantage of the naturally occurring phenomenon and emulsified *e.g.* berry extracts and oil with eggs as paints or herbal extracts with solid fat and eggs to form ointments. In the present time surfactants are not only utilized in industrial and institutional cleaning, but also in the production of nanomaterials via *e.g.* template strategies [3-10], as nanoreactors in *e.g.* organic synthesis [11-21], in the pharmacological sector for *e.g.* drug delivery [22-27], in the food sector to *e.g.* reduce the caloric value of food [28-38], in the automobile industry to reduce emissions [39-41] and almost everywhere else, where two otherwise incompatible components would form an energetically disfavoured interface. Due to their amphiphilic structure surfactants adsorb at the interface enabling them to reduce the interfacial tension between the two components, thus reducing the surface energy stabilising the otherwise instable systems. If surfactant technology is to be utilized most efficiently both equilibrium and non-equilibrium properties of a surfactant system have to be considered. In the following these properties will be highlighted from a historical and application related viewpoint.

1.1 Surfactant Technology - History and Application

Dating back as far as the Babylonians in 2800 B.C. [2], surfactants have been used in an ever evolving way. For most of the last 5000 years detergency primarily served the purpose of cleaning either oneself or clothes. Soaps used were based on naturally occurring triglycerides that were hydrolyzed with either natron, potash or ammonium carbonate forming a mixture of mono- and diglycerides and sodium, potassium or ammonium salts of fatty acids [42-44]. As time passed, surfactant technology advanced and first emulsions, though unknowingly, were produced in the form of paints, salves (ointments) and foods - mostly stabilized by egg yolk [45]. First scientific approaches to investigate the driving force behind surfactant technology were performed by *Pliny the Elder* (23-79 AD, observation only) and *Benjamin Franklin* (experiment in 1757) [46]. Both realized, that disquiet water straightens, if small quantities of oil are placed on it. Although they observed surface tension between liquids, their findings were not discussed more thoroughly until *Lord Rayleigh* repeated the experiments in 1890 and calculated the thickness of the oil layer [47,



48]. At the same time, the autodidact *Agnes Luise Wilhelmine Pockels* observed that water in her kitchen sink behaves differently, if different amounts of soap or dirt are added. Without having studied at a university she constructed the first setup to measure surface tension with nothing more than scales, string and a button. She then developed the first slide trough, the *Langmuir* trough originates from. If not for her correspondence with *Lord Rayleigh* she would have been forgotten, but *Lord Rayleigh* ensured that she could publish her findings in *Nature* [49] resulting in her being the first scientist exploring surfactant technology followed by 40 more years of her passionate research. Based on her work *Langmuir* and *Blodgett* then developed the *Langmuir-Blodgett* trough proving among other things that a monolayer of surfactant covers the water - air interface to reduce the interfacial tension [50] resulting in a *Nobel* prize in 1932. Since then the key feature of surfactant technology was understood, the application of it exploded and it split into high and low surfactant load applications.

The introduction of mechanical energy, *e.g.* by shearing, into a mixture of a polar and a non-polar liquid containing low loads of surfactant can lead to the formation of kinetically stabilized emulsions which are structured on the micrometer-scale [45]. Depending on the nature of surfactant and temperature either oil-in-water (*o/w*) or water-in-oil (*w/o*) emulsions will occur [45]. Alternatively, double- or multiple-emulsions can be generated [45]. Such emulsion systems are generally favored by industry since they require low amounts of surfactants and are thus cost efficient. Well known examples are foods like milk (*o/w*-emulsion) and mayonnaise (*w/o*-emulsion), cosmetics like sun blocker, and pharmaceuticals like Propofol[®]. Nevertheless, emulsions are inherently thermodynamically unstable and will age after a limited time finally leading to complete phase separation. The most common aging mechanisms are *Ostwald* ripening [51] and coagulation followed by coalescence [51]. In case of *Ostwald* ripening larger droplets will grow at the expense of smaller droplets as matter is transported via monomeric diffusion. Coalescence takes place, if two or more droplets coagulate and fuse forming a larger one. Both mechanisms are driven by the reduction of the system's interfacial energy. By decreasing the surface to volume ratio and thus the overall interfacial area of the droplets the interfacial energy will decrease at constant surface tension.

In 1943 *Schulman* and *Hoar* reported the spontaneous, *i.e.* without input of mechanical energy, formation of water and oil emulsions if high surfactant loads were applied [52]. By using surfactant loads high enough to cover the whole interfacial area with surfactant molecules the interfacial tension between the polar and the non-polar phase can be driven to a minimum leading to the formation of a so called microemulsion [53]. *Winsor* described phase sequences of such systems as a function of temperature and composition in more detail in 1954 [54]. However, it was not until

1959 until the term microemulsion was used for such systems by *Schulman* [53]. Following the work of *Schulman*, who generated microemulsions with an ionic surfactant and co-surfactant (e.g. short chain alcohols) mixture, *Shinoda* introduced non-ionic surfactants of a general *n*-alkyl polyethylenoxide structure in 1967 [55-60]. These surfactants enabled *Kahlweit* and *Strey* from 1985 onwards to analyse the phase behaviour of microemulsions in a very sophisticated and detailed way. They realized, that the water-oil interfacial tension runs through an ultra-low minimum at the phase inversion temperature. Later on, *Strey* concentrated on the multifarious nanostructure and its link to the interfacial tension. For more details on microemulsions and their fundamental properties see chapter 2.1.

In the years to follow *Strey* and *Jahn* applied freeze fracture electron microscopy (*abbr.* FFEM) to image various microemulsion structures [61-63]. At almost the same time small angle neutron scattering (*abbr.* SANS) emerged as a complementary tool to determine the structural length scales [64-69]. Here groups like *Eastoe* [70], *Davis* [71-74], *Nallet* [75-79], *Langevin* [80-83], *Bassereau* [62, 84, 85], *Schubert* [64, 69, 86-91], *Glatzer* [88, 89, 91-93] and *Richter* [94-102] claim a cutting-edge role. Complementary to scattering techniques, self-diffusion NMR is facilitated by *Olsson* and *Wennerström* [76, 103-107] and *Söderman* [108-112] to determine the precise nature of the continuity of microemulsion phases and structures. The phase behaviour itself was thoroughly investigated by *Penders* [113], *Kunieda* [108, 114-120], and *Schomacker* [76, 121, 122]. Around the turn of the millennium, the so called "polymer-boosting effect" was introduced by *Jakobs et al.* [96]. They found that small amounts of amphiphilic block copolymers integrated into microemulsions improve the solubilization capacity of surfactants, vigorously. Fundamental systematic studies related to this effect have been performed, but not all phenomena are understood yet [96-98, 123-127].

A number of theoretical approaches were applied to describe the experimental findings. Worth mentioning here are theoreticians like *Gompper* [98, 128-130], *Schick* [128], *DeGennes* [131], *Safran*, *Tlusty*, *Pieruschka* and *Zilman* [132-146]. From various viewpoints they all related the interfacial energy and hence the curvature of the amphiphilic film to the equilibrium properties of microemulsions.

Owing to their outstanding solubilization capacity which is a consequence of the ultra-low interfacial tension and their tunable nanostructure, synonymous with their large interfacial area, microemulsions appear to be attractive for wide ranging industrial applications [1]. But, since high surfactant loads are required, the formation of microemulsions is costly. As a result of this, microemulsions are only utilized in otherwise unachievable or very specific applications. In

enhanced oil recovery oil residues trapped in porous rock can be mobilized using common or polymeric microemulsions and their ultra low interfacial tension [14, 147-150]. Microemulsions can furthermore be used as lubricants, cutting oils and anti-corrosives [151] where they primarily excel due to their thermal stability in comparison to macroemulsions [152]. Their ability to solubilize large quantities of otherwise incompatible liquids enables them to replace toxic solvent mixtures, making them perfect candidates as coating [153] and textile finishing agents [154] or to be used as reaction media [3-10, 14, 15, 17]. Since their nanostructure enables them to bypass the skin barrier, they are also facilitated in cosmetics [109, 155, 156] and pharmaceuticals [3-7, 28-32, 157, 158]. Nevertheless, their structural properties are not only used as stated above, but also in the food industry, to reduce caloric values [33, 34, 36-38], in biotechnology to *e.g.* immobilize or purify certain proteins or produce tailor-made membranes and bio-membranes [159-163]. The remarkable environmental potential of microemulsions is also highly valuable since they reduce the soot- and NO_x-emissions of diesel fuel [39-41], are suited to detoxify our environment [164-167] and most obviously to revolutionize the detergency industry [3-7, 28-32, 168-172]. While in some of the stated applications ready microemulsions are used, in other cases, water- or oil-rich surfactant mixtures are applied to solubilize either oil or water, respectively. In such applications a deeper knowledge about the *in situ* formation of microemulsions is required.

Despite the fact, that such a vast number of groups focus until this very day on the equilibrium states of microemulsion, very little work has been done with regard to the non-equilibrium states of microemulsions. While *Kahlweit* and *Strey* studied the formation of micelles in binary water - surfactant solution [173-176], most groups concentrated on the kinetics of structural transformations. *Egelhaaf* and *Schurtenberger* [177-184] as well as *Gradzielski* [185-193] studied the transformation from micelles to vesicles in aqueous anionic and cationic surfactant solutions. The transformation of lamellar phases to L₃ phases is investigated by *Strey* and *Olsson* [194-196], transitions from spheres to rods in binary water - surfactant mixtures by *Ilgenfritz* [197, 198]. *Fletcher* and *Binks* traced the exchange of solubilates between micelles or the swelling of such [199, 200]. Most of these experimental studies however only analyse the transitions between very closely related structures. The formation of microemulsions from unstructured solutions has not been tackled. However, for many applications understanding the primary formation kinetics of those systems is crucial. Regarding *i.e.* the load dependant use of water-diesel microemulsions [39] in diesel engines for the reduction of NO_x- and soot-emissions it is vital to know how fast the microemulsion forms when being mixed on-board right before combustion. Thus, a comprehensive study of the formation of microemulsions is overdue.

1.2 Objectives

Motivated by the above mentioned considerations the objective of this thesis is twofold: While one goal is the elucidation of the influence of newly derived amphiphilic polymers on the equilibrium properties of microemulsions, the other main goal is the investigation of the formation kinetics of oil-rich microemulsions.

Regardless of microemulsions' superiority over macro-emulsions with respect to thermodynamic stability, nanostructure, ultra-low interfacial tension and the related high solubilisation capacity they are not appealing for industry. The comparably high surfactant loads required for their formation are generally considered a major drawback as they significantly reduce the cost-efficiency. The *boosting effect* of amphiphilic block copolymers addresses this issue, but enhances the formation of liquid crystalline phases that cover the in the majority of cases desired isotropic one phase microemulsion regions. The molecular structure of the polymer, however, could be a promising parameter to control both the efficiency and the extension of the liquid crystalline phases. As a consequence the influence of a newly derived so called tapered diblock copolymers and structurally related copolymers on the phase behaviour and microstructure were to be studied in this thesis. As some applications, *e.g.* water-diesel microemulsions, require the efficient formulation of oil-rich microemulsions, the influence of amphiphilic polymers on non-ionic microemulsions of the type H_2O - alkane - C_iE_j was to be studied. A primary issue was if and to what degree technical diblock copolymers like poly(ethylenebutylene) - poly(ethyleneoxide) (PEB4.8-PEO4.8) affect the phase behaviour and particularly the extension of the *closed loop*. In order to examine the influence of the polymers on the cylinder/network transition the electric conductivity was to be measured systematically as a function of temperature, volume fraction of dispersed phase and polymer volume fraction.

Not only the equilibrium properties and an improved solubilization capacity are of great fundamental and technological relevance, but also the formation of microemulsions itself. Thus, the second objective of this thesis was to study the formation kinetics of microemulsions comprehensively. In order to be able to conduct appropriate kinetic studies an ultra-fast stopped-flow setup with the possibility to use transmitted light, scattered light and small angle scattering for detection was to be developed and calibrated. Based on the phase behaviour studies of H_2O - cyclohexane - C_{10}E_5 microemulsions the formation kinetics of water swollen micelles was to be studied using the ultra-fast stopped-flow setup at the new small angle neutron spectrometer D33 (Institute *Laue Langevin* (ILL), Grenoble). Selecting cyclohexane as oil both bulk and film contrast conditions were to be achievable. In the next step, the effect of amphiphilic diblock PEB4.8 - PEO4.8 on the formation kinetics of microemulsions was to be studied varying the polymer content and the scattering contrast and the mode of mixing systematically.



2 Fundamentals

In the following chapters the fundamentals of microemulsions, especially their phase behaviour, nanostructure and interfacial properties, amphiphilic block copolymers and their role in efficiency boosting, small angle neutron scattering in general and the models used to describe different structures, as well as general kinetics theory will be summarized briefly with emphasis on this thesis.

2.1 Microemulsions

By definition microemulsions are thermodynamically stable, macroscopically isotropic, nanostructured mixtures of at least three components [63, 201, 202]. To solubilize the mutually immiscible polar or hydrophilic (A) and non-polar or lipophilic components (B) in each other an amphiphilic component (C) is required. Due to its ambivalent structural nature one part of it is soluble in the polar and the other part in the non-polar component (compare Figure 2.1) and it can thus mediate the mixing of the incompatible components. Such an amphiphile or surface active substance (*abbr.* surfactant) is usually composed of a so called polar "head" group and a non-polar "tail". One can differentiate between non-ionic, cationic, anionic, zwitterionic and amphoteric surfactants based on the respective nature of the polar head group. A commonly used example for non-ionic surfactants are *n*-alkyl polyglycol ethers (*abbr.* C_iE_j , with *i* being the number of carbon atoms in the *n*-alkyl chain and *j* being the number of glycol units in the polar head group).

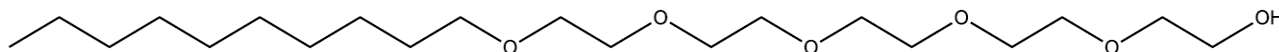


Figure 2.1: Example of a non-ionic amphiphilic substance. The depicted substance is an *n*-decyl pentaglycol ether or short $C_{10}E_5$.

Although they are macroscopically isotropic, there are well defined polar and non-polar domains to be found at microscopic level. The amphiphile adsorbs at the energetically disfavoured interface resulting in a surfactant monolayer that separates the polar from the non-polar domains. Depending on the nature of the surfactant and the competitive volume fractions of polar and non-polar component a wide variety of nanostructures may form. The adsorption of the amphiphiles at the interface furthermore results in a dramatic reduction of the interfacial tension between the

phases and allows the interfacial area to increase. As a function of temperature and composition such ternary mixtures exhibit a rich phase behaviour including one, two and three phase microemulsion states as well as lyotropic mesophases.

2.1.1 Phase Behaviour of Binary Mixtures

Although the term microemulsions was used by *Schulman* in 1959 [53] and *Shinoda* introduced temperature sensitive non-ionic surfactants in 1967 [55, 57-60] the first systematic studies on microemulsion phase behaviour were performed by *Kahlweit* and co-workers starting in 1985 [201] leading to the fundamental paper "*How to study microemulsions*" from 1987 by *Kahlweit* and *Strey* [108]. As shown by them, the fundamental properties of microemulsions can be derived from the ternary system H_2O (A) - *n*-alkane (B) - non-ionic surfactant (C) [201]. The phase behaviour of all such systems is generic and can be illustrated by a *Gibbs* phase prism at constant pressure p with a *Gibbs* phase triangle A - B - C at its base and with the temperature T as ordinate [108, 201, 203]. For better understanding of the complex ternary phase behaviour, the binary systems A - B, B - C and A - C, which are the three side face of the prism, have to be investigated (compare Figure 2.2, left).

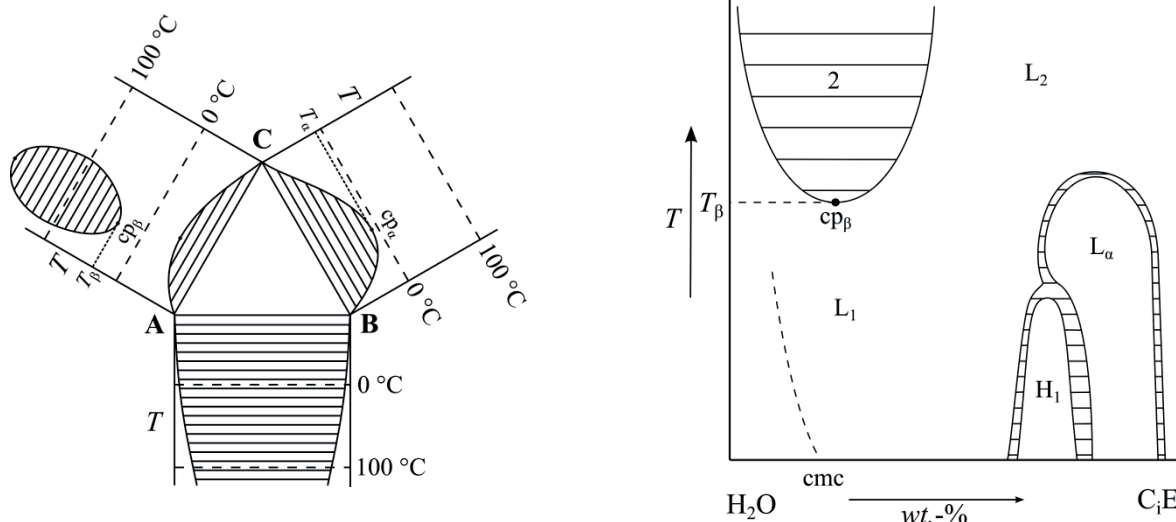


Figure 2.2: Left: Schematic drawing of the unfolded *Gibbs* phase prism of the system water (A) - *n*-alkane(B) - non-ionic surfactant (C). The phase diagrams shown are the three binary systems A - B, B - C and A - C (redrawn from [201]). Right: Schematic representation of the binary system A - C including the critical micelle concentration (cmc) and possible mesophases (redrawn from [204]).

The most simple binary phase diagram is of the mixture A - B, as both components are mutually immiscible. Consequentially, an extended miscibility gap is found over the whole accessible temperature range (0°C-100°C, the freezing and boiling point of liquid water at ambient pressure). The upper critical point of this gap is located above the boiling point of the mixture. The

system B - C commonly shows a lower miscibility gap at ambient temperature with an upper critical point cp_{α} . The critical temperature T_{α} strongly depends on the nature of the non-polar and the amphiphilic component, thus still spanning a wide temperature range. The binary mixture A - C shows the most complex phase behaviour [204] (compare Figure 2.2, right). As in the previous mixture a lower miscibility gap with an upper critical point occurs. At ambient pressure this gap is located far below the melting point of the mixture and will not be taken into further consideration. At elevated temperatures a closed miscibility gap with a lower critical point cp_{β} occurs at the critical temperature T_{β} . As with the other system the exact location of this point strongly depends on the nature of the amphiphile. The upper critical point lies above the boiling point of the mixture and will be disregarded. At amphiphile concentrations below the critical micelle concentration (cmc) only monomerically dissolved amphiphiles are present. Above the cmc micellar aggregates like spherical micelles start to form. At even higher concentrations hexagonal, lamellar and cubic mesophases are present.

2.1.2 The Phase Prism

Considering the three binary systems it is obvious that the complex phase behaviour of the ternary system is primarily based on the interplay of upper miscibility gap of the binary system A - C and the lower miscibility gap of the system B - C. (compare Figure 2.3). Accordingly, the whole phase behaviour is dependent on the inversion of the solubility of the amphiphile. At low temperatures the preferred solvent for the amphiphile is the polar phase, whereas the solubility of the amphiphile in the non-polar phase increases with temperature. This phenomenon is due to the partial dehydration of the amphiphile's head group [205]. Hence, at low temperatures $T > T_l$ a two phase coexistence between a oil-in-water (o/w)-microemulsion (a) and an oil excess phase (b) can be found. As the amphiphile-rich microemulsion phase in this situation usually has the higher density, this state is denoted with $\underline{2}$. As the slope of the tie-lines in the *Gibbs* phase triangles is negative the amphiphile-rich water phase coexists with an almost pure oil phase. As temperature increases the solubility of the surfactant in oil increases steadily. Upon reaching the temperature T_l , with its lower critical endpoint cep_{α} , the oil-in-water microemulsion separates into an amphiphile-rich middle phase (c) and a water excess phase (a) forming the three phase coexistence 3 together with the still persisting oil excess phase (b). Following the amphiphile solubility inversion, the composition of the amphiphile-rich middle phase changes from water-rich to oil-rich as temperature increases. Additionally, with rising temperature the composition of the oil excess phase (b) approaches that of the amphiphile-rich rich middle phase until at the temperature T_u of the upper critical endpoint cep_{β} these two phases obtain an equal composition and fuse

forming a two phase coexistence of an amphiphile-rich water-in-oil (w/o)-microemulsion (b) and a water excess phase (a). As now the density of the surfactant-rich phase is the lower, this state is denoted as $\bar{2}$.

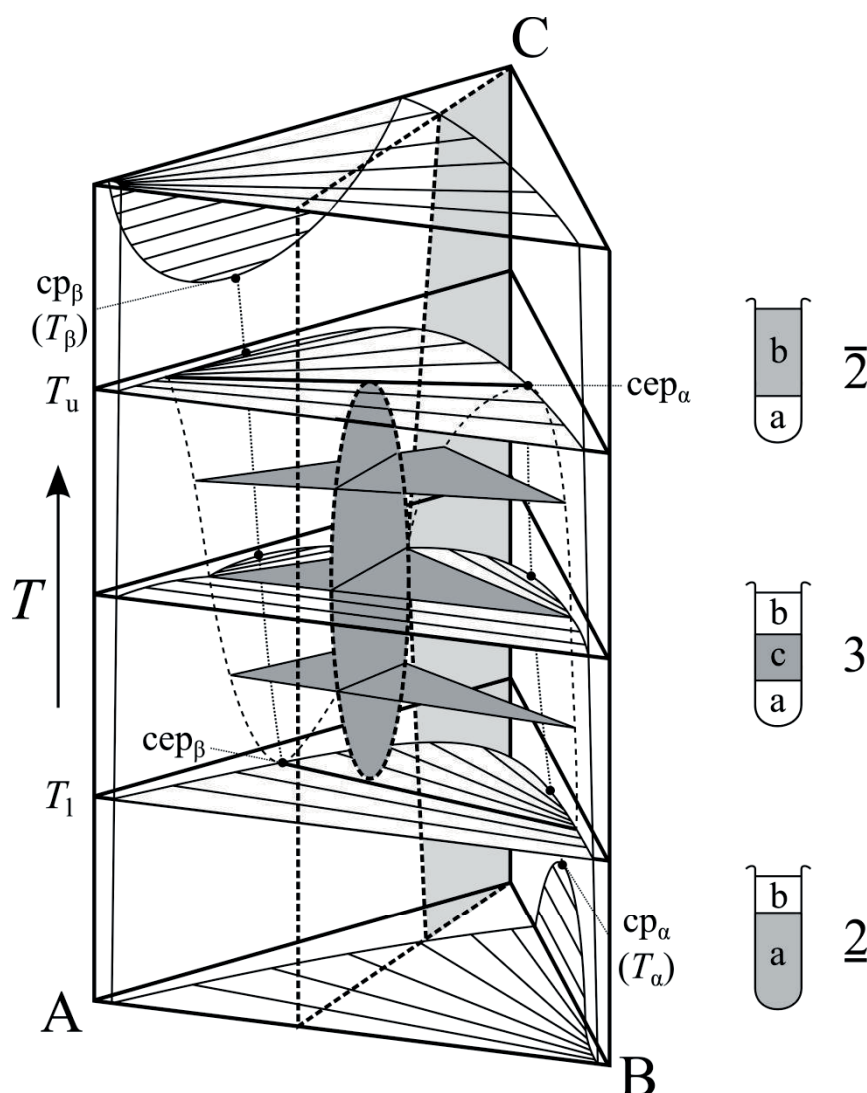


Figure 2.3. *Gibbs* phase prism of the system A - B - C with the temperature T as ordinate (redrawn from [201]). The test tubes display the corresponding phases.

Such a temperature driven phase sequence as depicted by the test tubes in Figure 2.3 is called phase inversion and typical for non-ionic surfactants.

2.1.3 Isoplethal Sections through the Phase Prism

Since it is extremely time-consuming to measure a complete phase prism it is common practice to perform isoplethal cuts through the prism. In this thesis two main cuts were performed: the $T(\gamma)$ -section and the $T(w_A)$ -section.

2.1.3.1 The $T(\gamma)$ -Section - the so called "Fish tail"-cut

One feasible way [201, 203, 206] to characterize the phase behaviour of a ternary system is a isoplethal cut at a constant oil weight fraction α in the oil and water mixture

$$\alpha = \frac{m_B}{m_A + m_B} \quad (1)$$

with m_A and m_B being the masses of either water (A) or oil (B).

The phase sequence is determined as a function of temperature T and the overall surfactant mass fraction γ

$$\gamma = \frac{m_C}{m_A + m_B + m_C} \quad (2)$$

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

Alternatively, the respective volume fractions ϕ and ϕ_C can be used if the densities of the corresponding components are known:

$$\phi = \frac{V_B}{V_A + V_B} \quad (3)$$

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

$$\phi_C = \frac{V_C}{V_A + V_B + V_C} \quad (4)$$

with V_A , V_B and V_C being the volumes of either water (A), oil (B) or surfactant (C).

A schematic representation of such a $T(\gamma)$ -section is depicted in Figure 2.4. For surfactant mass fractions below γ_0 unstructured oil and water phases including monomerically dissolved surfactant molecules coexist over the whole temperature range with monomeric surfactant adsorbing at the macroscopic interface until it is saturated. Upon reaching γ_0 the interface is

saturated and the excess surfactant preferentially dissolves in the water phase at low and the oil phase at high temperatures forming swollen aggregates resulting in an oil-in-water microemulsion in coexistence with an oil excess phase ($\underline{2}$) or in a water-in-oil microemulsion with a water excess phases ($\bar{2}$) respectively.

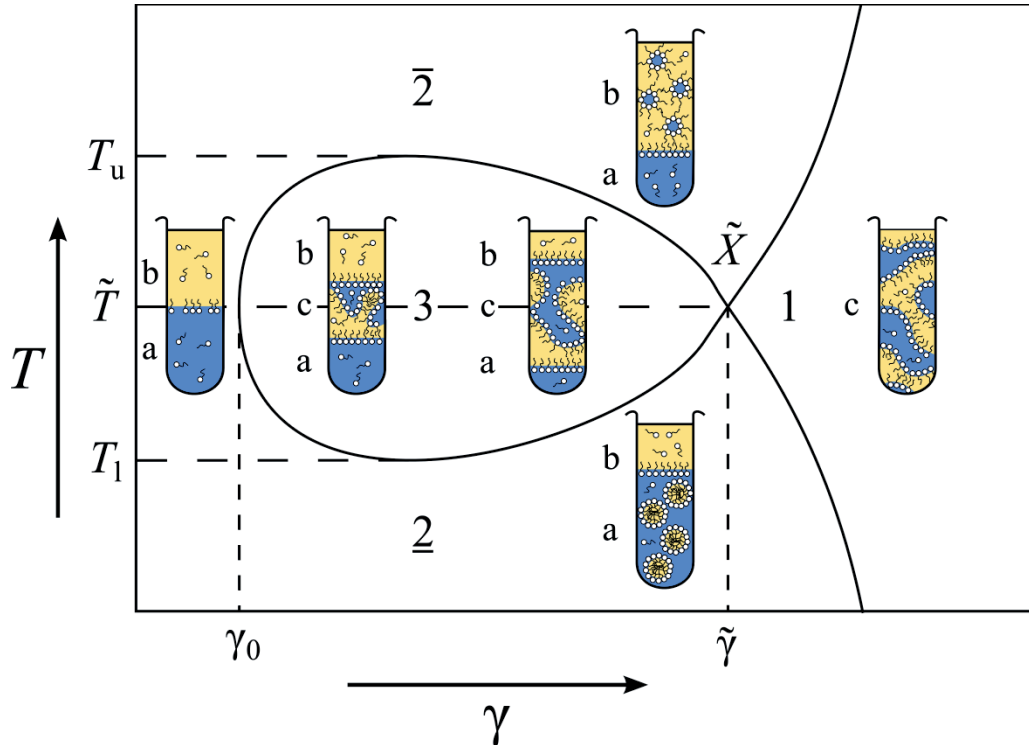


Figure 2.4. Schematic drawing of a $T(\gamma)$ -section through the ternary phase prism water - oil - non-ionic surfactant at a constant oil to oil and water volume fraction $\phi = 0.50$. At surfactant mass fractions $\gamma < \gamma_0$ only monomerically dissolved surfactant is present until at γ_0 the macroscopic interface is saturated with surfactant. For $\gamma_0 < \gamma < \tilde{\gamma}$ and intermediate temperatures between T_l and T_u a three phase region 3 forms. Above $\tilde{\gamma}$ the surfactant is able to solubilize water and oil completely in each other and a one phase region 1 forms. Depending on temperature different structures and continuities are present. At even higher surfactant mass fractions liquid crystalline mesophases are present (redrawn and modified from [63]).

At intermediate temperatures between T_l and T_u the surfactant is equally soluble in water and oil and a three phase state 3 composed of a balanced surfactant-rich microemulsion in coexistence with a water and an oil excess phase forms. As the surfactant mass fraction increases the volume of the surfactant-rich middle phase grows solubilizing more and more of the excess phases until upon reaching $\tilde{\gamma}$ the \tilde{X} -point describes the lowest amount of surfactant necessary to form a one phase microemulsion. In Figure 2.4 the one phase region is denoted as 1. Within this region close to the \tilde{X} -point bicontinuous sponge-like structures are present. At temperatures above \tilde{T} the continuity of the one phase region changes to oil-continuous, whereas it changes to water-continuous at temperatures below \tilde{T} . For even larger surfactant mass fractions the one phase region broadens and the structures within it change their nature. Close to the upper phase boundary water swollen

micelles in a continuous oil phase are present in contrast to the inverse at the lower boundary. In between for strong non-ionic surfactants with long n -alkyl chains dominant higher ordered liquid crystalline mesophases like lamellar L_α phases can be found. A more detailed view on the structures present in Figure 2.4 will be given in chapter 2.1.4.

2.1.3.2 The Optimal State

Each microemulsion system has its own unique \tilde{X} -point. Retaining a constant volume ratio ϕ , it defines the minimal amount of surfactant $\tilde{\gamma}$ necessary to completely solubilize oil and water at the corresponding temperature \tilde{T} , where the surfactant solubilization capacity is the highest. As depicted in Figure 2.3; the \tilde{X} -points for all volume fractions ϕ describe a parabola shaped line in the phase prism of the ternary mixture H_2O - n -alkane - non-ionic surfactant, that is called the trajectory of the middle phase [202]. Originating in the lower critical endpoint cep_α at the temperature T_l it ascends towards the upper critical end point cep_β at the temperature T_u . Hence, the composition of the middle phase of non-ionic microemulsions - defined by the position of the tip of the isothermal three-phase triangles - changes according to a rising curve from the water-rich to the oil-rich side of the phase prism. Common projections of the trajectory of the \tilde{X} -points are onto the A-B-C base and the A-B-T plane.

The mean temperature $T_m = (T_u - T_l) / 2$ describes the temperature, upon which the isothermal three-phase triangle extends maximally and is symmetric, implying the solubilization of equal amounts of water and oil in the microemulsion phase. In this state the microemulsion is considered balanced (from an hydrophilic-lipophilic balance HLB view point [207, 208]) or optimal [202]. Additionally, the \tilde{X} -point of this state accounts for the lowest amount of surfactant required to solubilize equal amounts of water and oil. Out of all \tilde{X} -points along the trajectory of the middle phase this point X_m proves the greatest challenge for a surfactant and can thus be considered a measure for the solubilization efficiency of a surfactant. The corresponding temperature T_m is a measure for the temperature at which the phase behaviour changes from the oil-in-water microemulsion to the water-in-oil and can be described as the phase inversion temperature. It is to be highlighted, that by scaling the trajectory of the middle phase for many different microemulsions of the type H_2O - n -alkane - C_iE_j with their temperatures T_m and their minimal amount of surfactant γ_m they can be united to a master trajectory [209] and that comparable scaling behaviour can be found for their structure size and the interfacial tension [209, 210]. Although the trajectory of the middle phase is scalable, the location of the optimal points strongly depends on the nature of the microemulsion components, like the hydrophobicity and amphiphilic strength of the surfactant. By plotting the X_m -points of various H_2O - n -octane - C_iE_j microemulsions ($\phi = 0.50$) as a function of



the surfactant mass fraction γ_m and the mean temperature T_m (compare Figure 2.5) this correlation is displayed best [211]. In the given systems both the hydrophilic and hydrophobic chain length of the surfactant were varied by choosing different parameters i (6 - 12) and j (2 - 7).

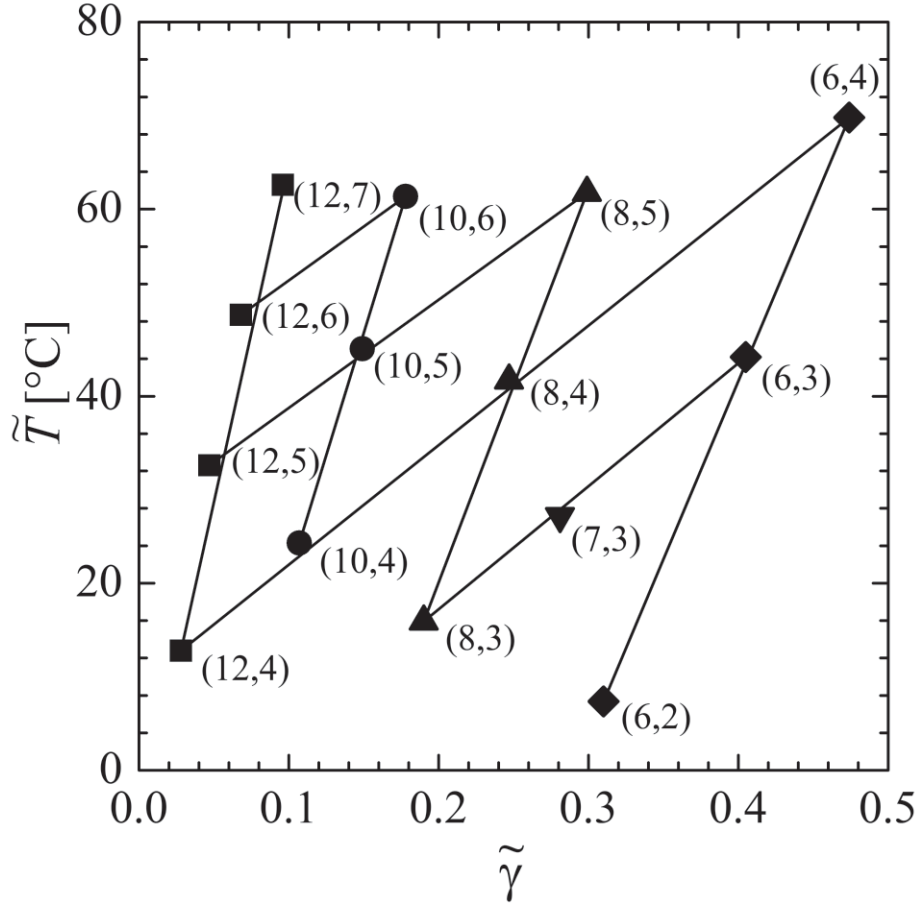


Figure 2.5: X_m -points of multiple H_2O - n -octane - C_iE_j microemulsions plotted as a function of the surfactant mass fraction γ_m and the phase inversion temperature T_m . The nature of the surfactant is given the values (i,j) . While i mainly influences the efficiency of the microemulsion, j affects the phase inversion temperature T_m . Redrawn from [211].

As the hydrophobic chain length increases, so does the solubilization efficiency of water and n -octane by the surfactant resulting in a decreasing γ_m . In addition, the increasing hydrophobicity leads to a slight decrease of T_m and lower temperatures are needed to drive the surfactant from the water to the oil phase. In the same fashion, T_m increases when the hydrophilic chain length j increases and is accompanied by a minor decrease of the solubilization efficiency (compare chapter 2.1.4.2).

On the whole, the \tilde{X} -points are not only affected by the nature of the surfactant, but also by the size of the n -alkane as to be seen in Figure 2.6 for various H_2O - n -alkane (C_kH_{2k+2}) - C_iE_j microemulsions ($\phi = 0.50$) [121, 211]. With increasing chain length of the n -alkane k for a given surfactant γ_m increases steadily, *i.e.* the oil is harder to solubilize. Simultaneously, the phase

inversion temperature increases, as the solubility of a surfactant with a fixed hydrophobic chain length is lower in an alkane with a larger chain length. Accordingly, higher temperatures are required to drive the surfactant from the water into the oil phase. This finding correlates with the increase of the critical temperature T_α of the binary n -alkane – surfactant mixture.

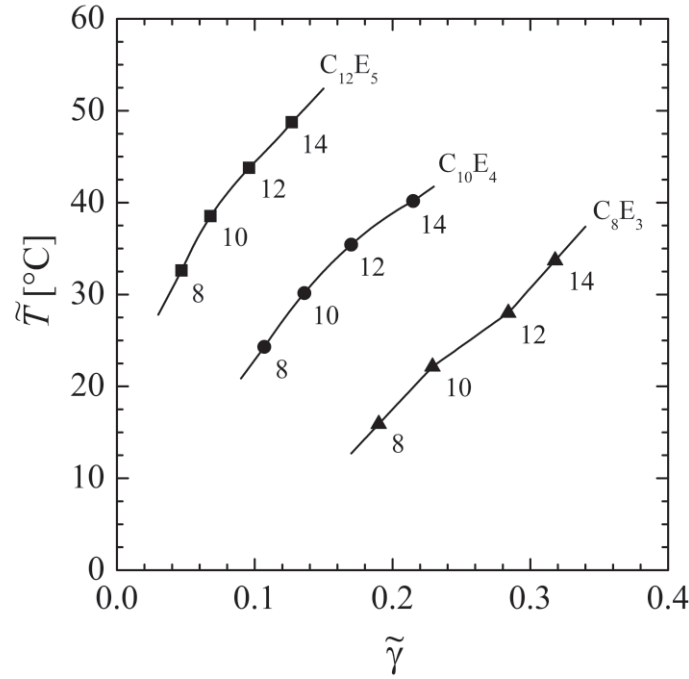


Figure 2.6: Influence of the n -alkane chain length on the X_m -point of multiple H_2O - n -alkane (C_kH_{2k+2}) - C_iE_j microemulsions ($\phi = 0.50$). The chain length of the n -alkane is given by the number k . With increasing k the X_m -point steadily shifts to higher surfactant weight fractions γ_m and higher phase inversion temperatures T_m . (redrawn from [211]).

2.1.3.3 The $T(w_A)$ -Section - Oil-rich Microemulsions

As with the $T(\gamma)$ -section for balanced microemulsions, the $T(w_{A/B})$ -section is the most convenient way to study the phase behaviour of oil- or water-rich microemulsions, respectively. As in this thesis only oil-rich microemulsions are studied, only these will be discussed here. To study the phase behaviour in this manner small amount of water are added to a fixed oil - surfactant mixture. Within this mixture the surfactant mass fraction γ_b is defined as:

$$\gamma_b = \frac{m_C}{m_B + m_C} \quad (5)$$

with being m_B and m_C being the masses of oil (B) and surfactant (C), respectively. Furthermore the overall water mass fraction w_A is defined as: