Chapter 1

Introduction to Surfactants and Microemulsions

1.1 Surfactants

1.1.1 Definition of Surfactant

The word surfactant does not appear in most dictionaries. This is because it is not a technical term, but also a diminutive form of the phrase surface active agent. Surfactants or surface active agents, are materials that tend not only to accumulate at surfaces, but which, by their presence, change the properties of those surfaces. They are active at interfaces that can be between solid/liquid, liquid/liquid or liquid/gas pairs of phases. Most of the surfactants are soluble in at least one of the adjoining liquid phases, which may be any liquid. The most common solvent for surfactants is water, in presence of which surfactant exhibit the tendency of self association or aggregation.

![Structure of a Surfactant Molecule](image)

Figure 1.1: Structure of a Surfactant Molecule

Surfactants possess these characteristics because of their molecular structure is amphiphilic. The molecules have two distinct parts, one that has an affinity for solvent and the other that does not. In aqueous solutions, these two moieties are hydrophilic and hydrophobic, respectively. It is the tendency for
the hydrophobic parts of the molecules to aggregate because of mutual dislike of the solvent which is the driving force for the surfactant self-association.[Clint, 1992]

![Surfactant Orientation](image)

Figure 1.2: Orientation of Surfactant molecules at Interface

1.1.2 Types of Surfactants

Surfactant / Amphiphilic molecules have two parts namely hydrophilic and hydrophobic. Variety of chemical groups have been used exhibiting hydrophilic and hydrophobic nature, the following represent major classes of surfactants.

1.1.2.1 Hydrophilic groups

The hydrophilic group of a surfactant is usually referred to as the head group and is strongly polar or charged, that generally imparts water solubility to the surfactant molecule.[Myers, 2005]

A. Anionics

The hydrophilic is a negatively charged group such as carboxyl (RCO$_2^-$), sulfonate (RSO$_3^-$), sulfate (ROSO$_3^-$) or phosphate (-OPO$_4^-$). Majority of these find extensive applications in cleaning formulations. The major advantage of the sulfonates and sulfates over carboxylates is their greater tolerance of divalent metal ions in hard water.

B. Cationics

The hydrophilic bears a positive charge, such as the quaternary ammonium halides (R$_4$N$^+$), the four R group may or may not be same. The positive charge on the head group gives the surfactant a strong substantivity on negatively
charged fibers, such as cotton and hair. Thus, they are widely used as fabric and hair conditioners.

C. Nonionics

The hydrophilic has no charge, it derives its water solubility from highly polar groups such as polyoxyethylene -(OCH₂CH₂)ₙOH or R-polyol groups including sugars. They are used extensively in low-temperature detergency and as emulsifiers.

D. Amphoteric / Zwitterionic

The molecule generally contains both positive and negative charge, such as betaines (-N⁺(CH₃)₂CH₂CO⁻) or sulfobetaines (-N⁺(CH₃)₂CH₂SO₃⁻). These are comparatively more milder on skin as compared to anionics, thus they are used in toiletries and baby shampoo formulations.

1.1.2.2 Hydrophobic groups

The hydrophobic group is generally referred to as the tail group, nature of which significantly varies from that of hydrophilic group. Hydrophobic group is mostly a straight hydrocarbon chain CH₃(CH₂)ₙ-S (n = C₁₂- C₂₀ with terminal substitution of head group) or branched chain alkyl group, unsaturated alkenyl chains as those derived from vegetable oils CH₃(CH₂)ₙ-CH=CH(CH₂)ₘ-S.

Also, biodegradable linear alkyl benzene sulfonates CH₃(CH₂)ₙCH(C₆H₄)(CH₂)ₘCH₃ are being used as a substitute for branched alkyl benzene sulfonates thereby reducing their persistence in water after sewage treatment which is a cause of foaming of rivers. Keeping in mind safety and ecological considerations, more focus is towards tail groups with no aromatic groups.
1.1.3 Polyoxyethylene Based Nonionic Surfactants

Nonionic surfactants as earlier mentioned, are without any charge. There are many advantages of electrically neutral surfactant materials, including significantly lower sensitivity to the presence of electrolytes in the system, a reduced effect of solution pH and the synthetic flexibility of the ability to design the required degree of solubility into the molecule by careful control of the size of the hydrophilic group.

An interesting characteristic of many nonionic surfactants, especially the polyoxyethylene (POE) family, is that they exhibit inverse temperature-solubility relationship; that is, as the solution temperature is increased, their solubility in water decreases. The phenomenon is attributed to a disruption of specific interactions, in this case, hydrogen bonding, between the water and the POE units in the molecule. The temperature at which components of the POE surfactant begin to precipitate from solution is defined as the “cloud point”. In general, the cloud point of a given family of surfactants (with the same hydrophobic group) will increase with the average number of EO groups.

Of all the nonionic surfactant classes available, the polyoxyethylene based surfactants are of high technical importance. These materials have the general formula

\[ RX(CH_2CH_2O)_nH \]

Where, R is normally a typical surfactant hydrophobic group, but may also be a hydrophobic polyether such as polyoxypropylene, and X is O, N or another functionality capable of linking the POE chain to the hydrophobe. In most cases, n, the average number of OE units in the hydrophilic group ranges between (3-16 or higher). It is usually found that the properties of materials with the same hydrophobic group and varying POE chain lengths changes in a regular, predictable manner. The water solubility increases regularly as the number of OE groups is increased from 3 to 16, the surface tension of aqueous solutions of the materials decreases regularly over the same composition range. The other technologically important characteristics of these materials such as detergency, wetting powder, and dispersing ability are also found to vary with OE content.[Myers, 2005]
1.1.4 Hydrophile Lipophile Balance (HLB) Concept

The selection of different surfactants in the preparation of either O/W or W/O emulsions is often made on an empirical basis. A semi-empirical scale for selecting surfactants is the hydrophilic-lipophilic balance (HLB number) developed by Griffin [Griffin, 1954]. This scale is based on the relative percentage of hydrophilic to lipophilic (hydrophobic) groups in the surfactant molecule(s). For an O/W emulsion droplet the hydrophobic chain resides in the oil phase whereas the hydrophilic head group resides in the aqueous phase. For a W/O emulsion droplet, the hydrophilic group(s) reside in the water droplet, whereas the lipophilic groups reside in the hydrocarbon phase. [Tadros, 2005a]

The relative importance of the hydrophilic and lipophilic groups was first recognized when using mixtures of surfactants containing varying proportions of a low and high HLB numbers [Griffin, 1954]. The efficiency of any combination (as judged by phase separation) was found to pass a maximum when the blend contained a particular proportion of the surfactant with the higher HLB number.

The average HLB number may be calculated by additivity,

\[
HLB = x_1 HLB_1 + x_2 HLB_2
\]

where \(x_1\) and \(x_2\) are the weight fractions of the two surfactants with \(HLB_1\) and \(HLB_2\). Griffin developed simple equations to calculate the HLB number of relatively simple nonionic surfactants. For a polyhydroxy fatty acid ester

\[
HLB = 20 \left( 1 - \frac{S}{A} \right)
\]

where \(S\) is the saponification number of the ester and \(A\) is the acid number.

For a simple alcohol ethoxylate, the HLB number can be calculated from the weight percent of ethylene oxide (E) and Polyhydric alcohol (P),

\[
HLB = \frac{E + P}{5}
\]

If the surfactant contains PEO as the only hydrophilic group, the contribution from one OH group can be neglected,

\[
HLB = \frac{E}{5}
\]

The above equations cannot be used for surfactants containing propylene oxide, butylene oxide. They also cannot be applied for ionic surfactants.
1.2 Behavior of Surfactant

1.2.1 Surface Activity

A surface or an interface may be described as the boundary between at least two immiscible phases. In any such system, the boundaries between the phases may be of primary importance in determining the characteristics and behavior of the system as a whole, although the bulk characteristics of each phase are, in theory, unaffected. The reality is that even very low levels of solubility among the phases can alter the bulk-phase characteristics to some extent. The viability of many scientific and commercial applications of multi-phase systems depends on an ability to control and manipulate phase boundaries or interfacial interactions.

Atoms or molecules at an interface will have a higher potential energy than those in the bulk of a material as a result of their “geography.” Their location at the interface means that they will experience a net asymmetric force field due to interactions with neighboring units significantly different from units in the bulk, as shown in Fig. 1.3. For two immiscible phases, surface or interfacial units will normally interact more strongly with identical units in the bulk rather than the “foreign” components in the adjacent phase. Because of the increased energy of units at the interface, thermodynamics demands that work be required to move them from the bulk phase to the surface. The minimum-energy rule for systems in equilibrium will therefore lead to surface conditions yielding minimum interfacial area, or minimum asymmetric interactions. Surface-active materials are compounds that, because of their characteristic molecular structures, are natural fence-sitters. Their split personalities drive them to reduce unfavorable energetic interactions by moving to more comfortable interfacial neighborhoods (adsorption), by getting together with their “own kind” (aggregation), or by simply getting out of town (precipitation or phase separation). When present in relatively low concentrations, such materials will preferentially adsorb at available interfaces, replace the higher-energy bulk-phase molecules, and result in a net reduction in the free energy of the system as a whole.
Materials that possess chemical groups leading to surface activity are generally referred to as being “amphipathic” or “amphiphilic.” When a material exhibiting the characteristics of surface activity is dissolved in a solvent (whether water or an organic liquid), the presence of the lyophobic group causes a distortion of the solvent liquid structure (and, in principle, that of a solid phase as well), increasing the overall free energy of the system. In an aqueous surfactant solution, for example, such a distortion of the water structure by the hydrophobic group increases the overall energy of the system and means that less work is required to transport a surfactant molecule to a surface or interface. The surfactant may therefore concentrate or preferentially adsorb at those locations, or it may undergo some other process to lower the energy of the system (e.g., aggregation or micellization). Since less work is required to bring surfactant molecules to the available interfaces, the presence of the surfactant decreases the work required to increase the interfacial area. The work per unit area required to form that new interface is the surface free energy or surface tension of the system, $\gamma$, usually reported in units of millinewtons per meter ($\text{mN/m}$) or dynes per centimeter ($\text{dyn/cm}$) in non-SI units. For solid surfaces, the convention is to use millijoules per square meter ($\text{mJ/m}^2$) or ergs per square centimeter ($\text{ergs/cm}^2$).

The presence of a lyophilic group on the surfactant molecule prevents or retards the complete expulsion of the solute molecules from the solvent as a separate phase, at least at low concentrations. The amphipathic structure of surfactant molecules not only results in their concentration at a liquid surface and consequent alteration of the surface tension but also causes orientation of the adsorbed molecules such that the lyophobic groups are directed away...
from the bulk solvent phase, as shown in Fig. 1.4. The resulting controlled molecular orientation produces some of the most important macroscopic effects observed for surface-active materials.

![Diagram of preferential orientation of surfactant molecules at interfaces.](image)

Figure 1.4: The preferential orientation of surfactant molecules at interfaces. [Myers, 2005]

### 1.2.2 Interface and Adsorption

The region of space forming the boundary between two immiscible phases is generally referred to as the “interface” and represents a transition region in which the chemical and physical characteristics of one bulk phase undergo an abrupt (on a macroscopic scale) change to those of the adjacent one. On a microscopic scale, however, that change must occur over the distance of at least one, but more often several, molecular distances. To quantitatively treat the phenomena related to surface activity, especially adsorption phenomena, it is necessary to mathematically define the location of the dividing line or surface at which the change is assumed to occur.

For convenience, it is usually assumed that a dividing surface can be defined as shown in Fig. 1.5a, where an ideal plane lies between phases 1 and 2. Such an ideal model is unrealistic, however, especially in the event of adsorption at the interface. Such an adsorbed interfacial film not only will possess a finite thickness related to the size of the adsorbed molecule but may also alter the nature of molecules of phases 1 and 2 located near the interface and result in an interfacial region in which the composition changes more or less continuously over a considerable distance Fig. 1.5b[Myers, 2005].
At this point it may be useful to reiterate that the general term “interface” refers to the above mentioned boundary between any two phases. In common usage, however, the term “surface” is used with reference to systems in which one phase is a gas, such as in the “surface tension” of a liquid. The use of “interfacial” will imply applicability to multiple types of boundary regions.

1.2.2.1 Thermodynamics of Adsorption

The surface tension of a liquid is related to the mechanical work required to create unit area of surface. A surfactant solution has a surface populated by adsorbed molecules in a state of lower free energy than those in the bulk solution. Therefore, less work will be needed to create unit area for pure solvent. In other words, the adsorption of surfactant should lower the surface tension of the liquid solvent. The thermodynamic relationship between quantity adsorbed per unit area and the change in the surface tension was first devised in 1878 by J. Willard Gibbs.

At constant temperature and pressure, for a surface phase it can be written that

$$-d\gamma = \sum_i \Gamma_i d\mu_i \quad (1.1)$$

which relates the change in surface tension $\gamma$ brought about by changes in chemical potential, $\mu_i$, for all species $i$, where $\Gamma_i$ is the number of moles of $i$ per unit area. For a solution with only two components, a solvent (1) and an unchanged surface active solute (2)
\[-d\gamma = \Gamma_1 d\mu_1 + \Gamma_2 d\mu_2 \quad (1.2)\]

The surface concentrations $\Gamma_i$ are strictly surface excesses defined as the
excess material present in the surface phase due to adsorption over and above
that which would be present if the bulk concentration were continued right up
to the interface.

The convention chosen by Gibbs was to define the position of the interface
to be such that the surface excess of the solvent $\Gamma_1$ is equal to zero. Then
equation 1.2 becomes 1.3

\[-d\gamma = \Gamma_2 d\mu_2 \quad (1.3)\]

Considering the changes in surfactant concentration,

\[d\mu_2 = RT.d\ln a_2 \quad (1.4)\]

where $a_2$ is the activity of component 2 in solution.

So combining equations 1.4 and 1.3 gives 1.5

\[\Gamma_2 = -\left(\frac{1}{RT}\right) \cdot \left(\frac{d\gamma}{d\ln a_2}\right) \quad (1.5)\]

In case of dilute surfactant solutions, the activity of solute $a_2$ may be ap-
proximated to the concentration $c_2$ so that

\[\Gamma_2 = -\left(\frac{1}{RT}\right) \cdot \left(\frac{d\gamma}{d\ln c_2}\right) \quad (1.6)\]

This is the most commonly used form of the Gibbs equation. Here, it
has been assumed that the surfactant is a single component, that a dividing
surface can be defined for which the surface excess of solvent is zero and that
the activity of surfactant molecules is equal to concentration. [Clint, 1992]

### 1.2.3 Surfactant Solubility

The specific structure of surfactant molecules, having well-defined hydrophilic
and hydrophobic components, is responsible for their tendency to concentrate
at interfaces and thereby reduce the interfacial free energy of the system in
which they are found. The primary mechanism for energy reduction in most
cases will be adsorption at the available interfaces. However, when all interfaces
are or begin to be saturated, the overall energy reduction may continue through
other mechanisms as illustrated in Fig. 1.6. The physical manifestation of one
such mechanism is the crystallization or precipitation of the surfactant from
solution that is, bulk-phase separation such as that seen for a solution of any solute that has exceeded its solubility limit. In the case of surfactants, alternative options include the formation of molecular aggregates such as micelles and liquid crystal mesophases that remain in solution as thermodynamically stable, dispersed species with properties distinct from those of the monomeric solution.

Figure 1.6: Modes of surfactant action for the reduction of surface and interfacial energies.

[Myers, 2005]

Under a given set of conditions of solvent and temperature, and sometimes pressure, the solute has a specific solubility limit which, when passed, results in the formation of crystals or at least a distinct separate phase that can hypothetically be separated from the solvent or supernatant liquid by physical means. Surfactants and other amphiphiles, on the other hand, can exhibit a number of intermediate or mesophases in going from a dilute solution of individual or “independent” molecules to crystalline hydrates or anhydrous structures. A hypothetical “spectrum” of surfactant mesophases in aqueous solution is given in Fig. 1.7.
For ionic surfactants, the solubility of a material will often be observed to undergo a sharp, discontinuous increase at some characteristic temperature, commonly referred to as the Krafft temperature, $T_K$. Below that temperature, the solubility of the surfactant is determined by the crystal lattice energy and the heat of hydration of the system. The concentration of the monomeric species in solution will be limited to some equilibrium value determined by those properties. Above $T_K$, the solubility of the surfactant monomer increases to the point at which aggregate formation may begin, and the aggregated species (e.g., a micelle) becomes the thermodynamically favored or predominant form in solution. Nonionic surfactants, because of their different mechanism of solubilization, do not exhibit a Krafft temperature. They do, however, have a characteristic temperature-solubility relationship in water that causes them to become less soluble as the temperature increases. In some cases, phase separation occurs, producing a cloudy suspension of surfactant. The temperature (usually a range of temperature) at which the phases separate is referred to as the “cloud point” for that surfactant.
1.2.4 Self Association & Aggregation

When surfactant molecules pack together at an interface to form a monolayer, they do not act independently. Although the system is highly dynamic, with surfactant molecules arriving at and leaving the interface on a very rapid timescale, molecules at the interface interact with the neighboring molecules. Surfactant aggregation in water produces a wide variety of structures held together by physical interaction forces. Surfactant molecules are constantly joining and leaving an aggregate on a time scale that can be as rapid as microseconds. The result is that any one aggregate has a lifetime, which, can be a matter of milliseconds. Also, the differences in energy between various structural states are quite small, being dependent on physical forces of interaction. The consequence is that surfactants can often be transformed readily between the various types of aggregate simply by small changes in solution conditions such as temperature, concentration, pH or electrolyte strength.

1.2.4.1 Micelle Formation

The solution properties of surface-active materials, are unusual and could change dramatically over very small concentration ranges. The measurement of properties such as surface tension, electrical conductivity, or light scattering as a function of surfactant concentration produces property curves that normally exhibit relatively sharp discontinuities at comparatively low concentration, as shown in Fig. 1.8.

The sudden change in a measured property is interpreted as indicating a significant change in the nature of the solute species affecting the measured quantity. In the case of the measurement of equivalent conductivity (top curve), the break may be associated with an increase in the mass per unit charge of the conducting species. For light scattering (bottom curve), the change in solution turbidity indicates the appearance of a scattering species of significantly greater size than the monomeric solute. These and many other types of measurement serve as evidence for the formation of aggregates or micelles in solutions of surfactants at relatively well-defined concentrations.
Figure 1.8: Some important manifestations of micelle formation: abrupt changes in solution conductivity, a discontinuity in the surface tension-concentration curve; a sudden increase in solution turbidity.

[Myers, 2005]

The single-structure or Hartley model proposed spherical micelles with a diameter equal to approximately twice the length of the hydrocarbon chain, as shown in Fig. 1.9c. It was suggested that the structure was composed of 50-100 molecules and that the association should occurred over a relatively narrow concentration range. The interior of the micelle was described as being essentially hydrocarbon in nature, while the surface consisted of the charged head groups. The close proximity of the head groups required that some fraction be tightly bound to their counterions, thereby reducing repulsions between neighbors and reducing the overall mobility of the aggregated species in an electric field. Although the classical picture of a micelle is that of a sphere, most evidence indicates that spherical micelles are not the rule and may in fact be the exception. As a result of geometric packing requirements, ellipsoidal, disk-shaped, and rodlike structures may be the more commonly encountered shapes.
1.2.4.2 Molecular Geometry and Packing of Micelles

The effect of geometry on molecular aggregation and physical properties of surfactant like critical micelle concentration, aggregate size and shape is significant. Israelachivili and others have shown that the geometric factors that control the packing of surfactants into aggregated structures can be conveniently given by critical packing parameter or shape factor $P$, given by

$$P = \frac{v}{a_0 l_c}$$

Where, $v$ is the volume of the hydrophobic portion of the molecule, $a_o$ is the optimum head group area, and $l_c$ is the critical length of the hydrophobic tail. The value of the packing parameter will determine the type of association structure formed in each case. Depending on the critical packing parameter the following structural aggregates are expected,
<table>
<thead>
<tr>
<th>$P$</th>
<th>Expected Aggregate Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;0.33</td>
<td>Spherical or ellipsoidal micelles</td>
</tr>
<tr>
<td>0.33 - 0.5</td>
<td>Cylindrical or rod-shaped micelles</td>
</tr>
<tr>
<td>0.5 - 1.0</td>
<td>Vesicles and bilayer structures</td>
</tr>
<tr>
<td>1.0</td>
<td>Planar extended bilayer structures</td>
</tr>
<tr>
<td>&gt;1.0</td>
<td>Reversed or inverted micelles</td>
</tr>
</tbody>
</table>
1.3 Solubilization in Micelles

The term solubilization, refers to the phenomenon of dissolution of hydrophobic materials into water to an extent greatly exceeding their normal solubility in water. The interior of the micelle provides a hydrophobic environment in which non-polar compounds can be accommodated. Thus, solubilization can defined as a spontaneous process leading to a thermodynamically stable, isotropic solution of a substance (the additive) normally insoluble or only slightly soluble in a given solvent produced by the addition of one or more amphiphilic compounds, at or above their critical micelle concentration.

If a co-surfactant such as n-alkanol is added, the curvature of the micelle surface can be increased and a larger quantity of hydrophobic material can be solubilized. When the aggregates reach such a size that the dissolved hydrophobic material in the interior of the micelle has properties identical to that of the pure hydrophobe, the system would be referred to as a microemulsion.

1.3.1 Effect of Temperature on Solubilization

The ability of a given surfactant to solubilize an additive is intimately related to the characteristics of the micelle like size, shape etc. Changes in temperature are known to affect some of these characteristics, it can thus alter the solubilizing properties of surfactants as a result of modifications in micellar structure. Changes in temperature can affect the intermolecular interactions between solvent and solutes (e.g., hydrogen bonding), so the overall solvent properties of the liquid for surfactant and additive may be significantly altered.

With non-ionic surfactants, especially of the polyoxyethylene type, increasing temperature increases the micelle size and lowers the critical micelle concentration (CMC) so that the capacity to solubilize non-polar additives increases.
1.4 Microemulsions

Microemulsions are macroscopically isotropic mixtures of at least a hydrophilic, a hydrophobic and an amphiphilic component. Their thermodynamic stability and their nanostructure are two important characteristics that distinguish them from ordinary emulsions which are thermodynamically unstable. Microemulsions were first observed by Schulman [Schulman and Hoar, 1943] and Winsor [Winsor, 1968] in the 1950s. While the former observed an optically transparent and thermodynamically stable mixture by adding alcohol, the latter induced a transition from a stable oil-rich to a stable water-rich mixture by varying the salinity. In 1959, Schulman et al. introduced the term ‘microemulsions’ for these mixtures [Schulman et al., 1959][Stubenrauch, 2008].

The extensive research on microemulsions was prompted to optimise oil recovery, the oil reservoirs were flooded with a water–surfactant mixture. Oil entrapped in the rock pores can thus be removed easily as a microemulsion with an ultra-low interfacial tension is formed in the pores. Obviously, this method of tertiary oil recovery requires some understanding of the phase behaviour and interfacial tensions of mixtures of water/salt, crude oil and surfactant. These in-depth studies were carried out in the 1970s and 1980s, yielding very precise insights into the phase behaviour of microemulsions stabilized by non-ionic and ionic surfactants [Belloc et al., 1980; Langevin, 1986] and mixtures thereof [Kahlweit and Strey, 1988]. The influence of additives, like hydro- and lyotropic salts [Kahlweit et al., 1988a], short- and medium-chain alcohols (co-surfactant)[Penders and Strey, 1995] on both non-ionic and ionic microemulsions was also studied in detail. The most striking and relevant property of microemulsions in technical applications is the low or even ultra-low interfacial tension between the water excess phase and the oil excess phase in the presence of a microemulsion phase. The dependence of the interfacial tension on salt[Aveyard et al., 1986], the alcohol concentration and temperature [Scottmann and Strey, 1997] as well as its interrelation with the phase behaviour [Shinoda and Friberg, 1975; Schechter et al., 1985] can be regarded as well understood.

From the late 1980s onwards, the research on microemulsions turned to the understanding of the fascinating microstructure of these mixtures. Microemulsions are created by a surfactant film forming at the microscopic water/oil interface. Different methods such as NMR self-diffusion[Bodet et al., 1988; Lindman et al., 1989], transmission electron microscopy (TEM)[Bodet et al., 1988; Lindman et al., 1989; Jahn and Strey, 1988] and scattering techniques (small angle X-ray scattering (SAXS)[Licherfeld et al., 1986] and small angle
neutron scattering (SANS) [Chen, 1986] provided some of the larger pieces in the puzzle of the manifold structure of microemulsions.

Microemulsions have also become increasingly significant in industry. Besides their application in the enhanced oil recovery, they are used in cosmetics and pharmaceuticals, washing processes, chemical reactions (nano-particle synthesis), polymerizations and catalytic reactions. In practical applications, microemulsions are usually multicomponent mixtures. Salt solutions and other polar solvents or monomers can be used as hydrophilic component. The hydrophobic component, usually referred to as oil, may be an alkane, a triglyceride, a supercritical fluid, a monomer or a mixture thereof. Industrially used amphiphiles include soaps as well as medium-chained alcohols and amphiphilic polymers, respectively, which serve as co-surfactant.

1.5 Interfacial Tension

The most striking property of a microemulsion in equilibrium with an excess phase is the very low interfacial tension (IFT) between the macroscopic phases. In the case where the microemulsion coexists simultaneously with a water-rich and an oil-rich excess phase, the interfacial tension between the latter two phases becomes ultra-low [Kahlweit et al., 1988b]. This striking phenomenon is related to the formation and properties of the amphiphilic film within the microemulsion. Within this internal amphiphilic film the surfactant molecules optimise the area occupied until lateral interaction and screening of the direct water–oil contact is minimised [Prince, 1977a]. Low interfacial tensions play a major role in the use of microemulsions in technical applications [Schwuger et al., 1995] as, e.g. in enhanced oil recovery and washing processes.

The otherwise immiscible oil and water are made to mix by the action of amphiphiles. The immiscibility arises due to very high IFT between water and oil. From thermodynamic consideration, at a constant pressure and temperature, the IFT, \( \gamma = (\delta G/\delta A)T_P \). Since \( \gamma \) is positive, the Gibbs free energy change is also positive, and hence the mixing fails. Therefore to make the free energy change negative, the IFT or \( \gamma \) requires to be reduced to a very low value. Addition of surfactant and cosurfactant helps achieve this goal. The associated work process is given by the following energetic relation,

\[
\Delta G = \Delta H - T\Delta S + \gamma\Delta A
\]

where \( \Delta G, \Delta H, \Delta S, T, \) and \( \Delta A \) are the Gibbs free energy change, enthalpy change, entropy change, temperature in Kelvin, and change in interfacial area,
respectively. The enthalpy change when immiscible oil and water are mixed is negligible. Now, as the droplet size decreases, there is a positive change in entropy $(T \Delta S \gg \gamma \Delta A)$ causing negative $\Delta G$ for the system. Thus, the dispersion o/w or w/o becomes spontaneous and stable. By the action of surfactant, a constant but moderate IFT corresponds to a monolayer formation at the oil/water interface results. The addition of a cosurfactant brings down the IFT further to a very low value. For a multicomponent system, the change in IFT ($\gamma$) can be expressed by the relation

$$
\partial \gamma = - \sum_i \Gamma_i d\mu_i = - \sum_i \Gamma_i R T d \ln C_i
$$

where $\gamma_i$, $\mu_i$, and $C_i$ are the Gibbs surface excess, chemical potential, and the concentration of the $i$th component, respectively, and $R$ and $T$ have their usual significance.

The integrated form of Equation above for a two component system is then

$$
\gamma - \gamma_o = - R T \left[ \int \Gamma_1 d \ln C_1 - \int \Gamma_2 d \ln C_2 \right]
$$

where $\Gamma_1$ and $\Gamma_2$ are the surface excesses of the component 1 and 2, respectively at their concentrations $C_1$ and $C_2$, and $\gamma_o$ is the IFT between oil and water in absence of surfactant and cosurfactant. The microemulsion formation is a spontaneous process which is controlled by the nature of amphiphile, oil, and temperature. The mechanical agitation, heating, or even the order of component addition may affect microemulsification. [Stubenrauch, 2008]
1.6 Microemulsions, Macroemulsions and Micelles

The distinction between microemulsions and conventional emulsions is fairly clear. Although emulsions may be kinetically stable for long periods of time, they must, in the end, suffer the same fate: phase separation to attain a minimum in interfacial free energy. The actions of surfactants, polymers, and other stabilizing aids may shift the rate of droplet coalescence to extremely long times through decreased kinetic rate constants, but the thermodynamic driving force to minimize interfacial area of contact between immiscible phases remains unchanged. Microemulsions, on the other hand, appear to be thermodynamically stable compositions with essentially infinite lifetimes, assuming no change in such factors as composition, temperature, and pressure.

In addition to the thermodynamic distinction usually drawn between macro- and microemulsions, the two classes of colloids differ in several other more tangible characteristics, including the size of droplets formed and the mechanical requirements for their preparation. As far as droplet size is concerned, emulsions generally have relatively large particle diameters, meaning that such systems are usually quite turbid or opaque. Microemulsions, however, normally have droplet diameters of 100 nm or less, many of which are only slightly larger than those in micellar systems. Because those particles are much smaller than the wavelength of visible light, they are normally transparent or slightly bluish.

The energy requirements for the formation of emulsions can be quite substantial. The formation of small droplets requires that the system overcome both the adverse positive interfacial free energy between the two immiscible phases working toward drop coalescence and bulk properties of the dispersed phase such as viscosity. Microemulsions, on the other hand, form spontaneously with little or no agitation required when the proper composition of the system is reached.

If one constructs a “spectrum” of the possible situations for the dispersion of one liquid phase in another (e.g., oil in water), the possible sizes of the dispersed phase units range from the molecularly dispersed solution where “droplet” sizes are on the order of a few nanometers, to emulsions with droplet diameters of hundreds or thousands of nanometers, as shown in Fig. 1.10. Lying between the extremes are micelles (a few tens of nanometers), macromolecular solutions (tens to hundreds of nanometers), and colloids of several hundred to several thousand nanometers. The systems typically referred to as “microemulsions” will normally have particle sizes between 5 and 200 nm, generally well beyond the range of normal micelles in dilute solution. Classifications such as those illustrated in Fig.1.10 are certainly arbitrary in their
ranges and some overlap inevitably occurs; however, the physical differences encountered among most of the different groups are sufficient to obviate any controversy as to their general definitions.

The problem of the thermodynamic differentiation between micelles and microemulsions is less amenable to easy solution. While it is undoubtedly true that, in the smaller size ranges especially, many systems classed as microemulsions are almost indistinguishable from swollen micelles, it is equally true that the larger microemulsion systems far exceed the solubilizing capacity of micelles. Micelles will form under many circumstances, although the specifics of cmc, aggregation number, and other parameters may change with the environmental conditions. The formation of microemulsions, on the other hand, has been shown to have very specific compositional requirements.
1.7 Cosurfactant

The name “microemulsion” was first introduced by Hoar and Schulman in 1943 as the name for a clear or transparent system obtained by titration of a milky white emulsion with a medium-chain length alcohol (e.g., 1-pentanol or 1-hexanol) [Schulman and Hoar, 1943]. Molecules of an amphiphilic surfactant in a microemulsion system specifically arrange to form an interfacial area between the water component and the oil component, which are otherwise immiscible. Various cosurfactants can be added to the system in order to improve the oil solubilizing efficiency of the surfactant. Most frequently simple alcohols are used for this purpose. The effects of alcohols also strongly depend on their partition between the water phase, oil phase, and interface surfactant film. Their specific effects on the molecular organization in surfactant systems as a function of the molecular hydrocarbon chain length are thoroughly described for the case of different surfactant systems around the critical micelle concentration (CMC) in the review article of Zana [Zana, 1995] [Stubenrauch, 2008].

1.7.1 Role of Cosurfactant

In the microemulsion systems the primary alcohols are frequently considered as cosurfactants, which are usually weakly amphiphilic molecules that help the amphiphilic surfactants to reduce the surface tension of the interface between the immiscible components of the system. The alcohol co-adsorbs with the surfactant at the interface and thus changes the overall interaction of the amphiphilic film with the adjacent solvents. They usually enhance and emphasize the internal structure of the system at the colloidal level as shown in Fig. 1.11.

![Figure 1.11: Schematic representation of the enhanced packing efficiency of surfactants in the presence of polar additives.](Myers, 2005)
1.7.2 Short Chain & Medium Alcohols

Short-chain alcohols are actually well known to increase the critical micellar concentration of surfactants [Zana, 1995; Strey and Jonstromer, 1992; Caponetti et al., 1997]. Usually this is attributed solely to the effect of alcohol on water, assigning significant importance to the situation in alcohol/water systems. Namely, their presence increases the hydrophobicity of the system and correspondingly increases the surfactant solubility, thus the short-chain alcohols are usually addressed as good cosolvents. Some studies actually report short-chain alcohols to have the properties of structure breaking agents also at higher surfactant concentrations [Zana, 1995; Tomsic et al., 2006; Forland et al., 1998]—decreasing the size of the micelles or preventing some characteristic structures forming in a specific regime. Ethanol and 1-propanol as good cosolvents practically do not change the situation at these low alcohol and moderate surfactant concentrations in respect to the reference binary system. Both 1-butanol and 1-pentanol at these concentrations show a prevailing cosurfactant type behavior, decreasing the overall size of the micelles and concomitantly increasing the radius of the core [Tomsic et al., 2006].

1.7.3 Long Chain Alcohols

In case of higher alcohols, their hydrophobic nature becomes increasingly important and the interplay between their behavior as cosurfactant and the real oil phase starts to direct the structural situation in such ternary systems. The lipophilicity of the co-surfactant increases with the carbon chain length (n-butanol < n-pentanol < n-hexanol < n-heptanol). The longer the alcohol, the lower its tendency to act as co-surfactant, because it is rather solubilised in the oil phase, which is generally evident due to much bigger core radii. Consequently, the co-surfactant effect may be said to fade away, and to vanish for octanol or longer alcohols, depending of the nature of the oil phase.

1.7.4 Branched Alcohols

Branched alcohols such as sec-butanol and ter-pentanol, are relatively neutral as far as their affinity for the oil and water is concerned and have essentially no effect modifying the formulation. These alcohols are however used because they do adsorb at the interface thus decreasing its rigidity and inhibiting the formation of lamellar liquid crystals, which are likely to be generated at opti-
mum formulation because of the zero curvature. This effect is often used with ethoxylated fatty alcohol non-ionic surfactants (unless the EON distribution is broad which automatically suppresses highly ordered phases). Branched alcohols such as sec-butanol and tert-pentanol are particularly useful to mix with linear chain surfactants because their branching increases the average area of the surfactant in the interfacial layer. The driving force to adsorb at the interface is the neutral affinity for oil and water. Hence, these alcohols provide more spacing between surfactant molecules, and consequently they are the best to decrease cohesion and rigidity. However, they are poor as far as their stabilization performance is concerned.
1.8 Mean Curvature of the Amphiphilic Film

The curvature tendencies of the interfacial film plays a major role in phase behavior of surfactants, there is a strong correlation between surfactant type, oil and water phase behavior. The possibility that the preferred curvature of the surfactant interfacial films influences emulsion type was conjectured several decades ago by Sutheim. It was known that hydrophilic agents preferentially dissolve (as micelles) in the aqueous phase and tend to promote O/W emulsions and that hydrophobic agents preferentially dissolve (as inverse micelles) in the oil phase. It was speculated that in an emulsion, because of the strong curvature preference of the sheet-like microstructure evident in a micellar solution, “Whereby the interfacial film will develop curvature convex to the water and concave to the oil” in the case of hydrophilic agents. Sutheim conjectured just the opposite curvature tendency in the case of hydrophobic agents [Davis, 1994]. The mean curvature of the amphiphilic film is given by,

\[ H = \frac{1}{2} (c_1 + c_2) \]

where \( c_1 = 1/R_1 \) and \( c_2 = 1/R_2 \) are the principal curvatures at a certain point on the film. By definition curvatures are positive if the amphiphilic film tends to enclose oil (o/w-microemulsions) and negative if it tends to enclose water (w/o-microemulsions). Parameters on which the curvature of the amphiphilic film depends are the temperature, the composition of the amphiphilic film, the salinity, etc. The mean curvature \( H \), which can be determined experimentally by scattering techniques, is closely related to the spontaneous curvature \( H_0 \), which is the curvature the interfacial film will adopt if no external forces, thermal fluctuations or conservation constraints exist. Both \( H_0 \) and the Gaussian curvature \( K = c_1c_2 \) are important parameters in Helfrich’s bending energy.

Fig. 1.12, schematically shows the variation of the mean curvature \( H \) of the amphiphilic film for the temperature-sensitive ternary water-oil-CiEj systems by means of a wedge-shaped representation. For temperature-sensitive ternary systems one finds oil-in-water (o/w) microemulsions at low and water-in-oil (w/o) microemulsions at high temperatures due to a change of the mean curvature \( H \) of the amphiphilic film. At low temperatures the size of the surfactant head group is larger than that of the hydrophobic chain which curves the amphiphilic film around the oil. With increasing temperature, the size of the surfactant head group shrinks due to a dehydration, whereas the size of the hydrophobic chain increases due to an increasing number of chain conformations and the increasing penetration of oil molecules. Thus, \( H \) changes
gradually from $H > 0$ to $H < 0$, i.e. from oil-in-water (o/w) to water-in-oil structures (w/o) structures via a locally planar amphiphilic film, i.e. $H = 0$.

Figure 1.12: Mean curvature $H$ of a non-ionic surfactant film at the water/oil interface as a function of temperature $T$. The decrease in $H$ with increasing $T$ is mainly due to the shrinking size of the head group. In order to illustrate this behaviour, a wedge-shaped representation has been chosen.

[Stubenrauch, 2008]
1.9 Phase Behaviour of Microemulsions

1.9.1 Introduction

Microemulsions are spontaneously forming, thermodynamically stable, homogeneous low viscous, and optically isotropic solutions. These macroscopic homogeneous mixtures are heterogeneous on a nanometer scale [Moulik and Paul, 1998; Kumar and Mittal, 1999; Sjoblom et al., 1996]. Reverse or inverse microemulsions have nanoscopic water droplets dispersed in a pseudocontinuous phase of oil, and the low radius of curvature in this case has opposite sign to the radius of curvature in the oil-in-water (o/w) example. Due to their unique properties, microemulsions have been used in a variety of technological applications. The determinations of the phase behavior of water/surfactant/oil system quantitatively is of eminent significance for further investigation and possible applications. The study of the phase behavior of nonionic surfactants in water and oil demonstrated that the amount of surfactant present at the water–oil interface determines the extent of water and oil mutual solubilization [Kunieda and Yamagata, 1993; Pes et al., 1995; Kunidea et al., 1995]. This amount of surfactant depends on factors like surfactant’s chemical structure and hydrophilicity, the monomeric solubility of surfactants in oil and water, and the presence of additives.

The structure of microemulsions can be idealized as a set of interfaces dividing polar and apolar domains. Mixtures of water, oil, and surfactant exhibit a rich variety of microstructures, ranging from spherical micelles, rodlike micelles, and bicontinuous microemulsions to ordered liquid crystalline phases, as shown in Fig. 1.13. Depending on the composition of the system of oil, water, and surface-active agent(s), the microstructure of a microemulsion may exist as w/o droplets, o/w droplets, or a bicontinuous structure [Davis, 1994; Tomsic et al., 2006; Bumajdad et al., 1999; Kaler, 1988; Glatter et al., 2000; Fanun, 2008].
1.9.2 Phase behaviour of Ternary Non-ionic Microemulsions

The primary aim of microemulsion research is to find the conditions under which the surfactant solubilises the maximum amounts of water and oil, i.e. the phase behaviour has to be studied. As the effect of pressure on the phase behaviour is (in general) rather weak [Sassen et al., 1992], it is sufficient to consider the effect of the temperature. Furthermore, it has been shown that simple ternary systems consisting of water, oil and non-ionic n-alkyl polyglycol ethers (C\textsubscript{i}E\textsubscript{j}) exhibit all properties of complex and technically relevant systems. The complex phase behaviour of microemulsions can be better understood by considering the phase diagrams of the corresponding binary base systems. In the case of ternary non-ionic microemulsions these are the three binary systems: water (A)–oil (B), oil (B)–non-ionic surfactant (C) and water (A)–non-
ionic surfactant (C). For thermodynamic reasons, each of these systems shows a lower miscibility gap with an upper critical point.

![Phase behaviour of binary systems](image)

Figure 1.14: Schematic view of the phase behaviour of the three binary systems water (A)–oil (B), oil (B)–non-ionic surfactant (C), water (A)–non-ionic surfactant (C) presented as an ‘unfolded’ phase prism. The most important features are the upper critical point $c_p\alpha$ of the B–C miscibility gap and the lower critical point $c_p\beta$ of the binary A–C diagram. Thus, at low temperatures water is a good solvent for the non-ionic surfactant, whereas at high temperatures the surfactant becomes increasingly soluble in the oil. The thick lines represent the phase boundaries, while the thin lines represent the tie lines.

[Stubenrauch, 2008]

Fig. 1.14 shows the unfolded phase prism with schematic diagrams of the three binary systems. The phase diagram of the binary water (A)–oil (B) system is the simplest of the three. The upper critical point of its lower miscibility gap lies well above the boiling point of the mixture, i.e. water and oil are almost immiscible between the melting and boiling point. The phase diagram of the binary oil (B)–non-ionic surfactant (C) system is almost as simple. Its upper critical point $c_p\alpha$ usually lies not far from the melting
point of the mixture and depends on the nature of both oil and surfactant. In
general, the lower the more hydrophilic the oil is and the more hydrophobic the
surfactant is. The phase diagram of the binary water (A)–non-ionic surfactant
(C) system is the most complex of the three. At ambient temperatures and
above the critical micelle concentration (cmc) the surfactant molecules self-
assemble. At higher temperatures most of the systems show an additional
upper (closed) miscibility gap with a lower critical point \( cp_\beta \). The shape of
this loop depends on the nature of the surfactant and plays an important role
in the phase behaviour of the ternary system [Stubenrauch, 2008].

1.9.2.1 Microemulsions with technical-grade non-ionic surfactants

In industrial applications, technical-grade surfactants which are usually mix-
tures of homologues and (or) isomers are used instead of pure surfactants.
Common non-ionic technical-grade surfactants are ethoxylated alcohols or etho-
xylated alkyl phenols. In contrast to the pure \( C_i E_j \) surfactants, the technical-
grade surfactants have a broad distribution of the ethoxylation degree and
a residual amount of non-reacted alcohol. However, the chain length of the
alcohol is rather narrowly distributed. Several studies on microemulsions for-
mulated with technical-grade surfactants have shown that surfactant blends
can be treated as a single (pseudo) component [Kunieda and Ishikawa, 1985;
Graciaa et al., 1983; Kunieda and Shinoda, 1985].

In order to show the effect of technical-grade surfactants on the phase
behaviour of microemulsions, \( T(\gamma) \)-sections of the systems \( H_2O - n-octane - C_{12}E_6 \) and the technical grade analogue DA-6 (dodecyl-alcohol-6) were studied
for comparison [?]. It was observed that the technical-grade DA-6 system
solubilized water and n-octane slightly more efficiently than the pure \( C_{12}E_6 \)
surfactant [Stubenrauch, 2008].

1.9.3 Phase Inversion

It can be anticipated from Fig. 1.14, that the temperature-dependent phase
behaviour of the ternary system is a result of the interplay between the lower
miscibility gap of the B–C mixture and the upper miscibility gap of the A–C
mixture. At low temperatures the non-ionic surfactant is mainly soluble in
water, while it is mainly soluble in oil at high temperatures. Thus, an increase
in temperature turns a non-ionic surfactant from hydrophilic into hydrophobic.
[Stubenrauch, 2008] Fig. 1.15, shows this behaviour in the form of the related
Gibbs phase triangles.
Figure 1.15: Isothermal Gibbs triangles of the system water (A)–oil (B)–non-ionic surfactant (C) at different temperatures. Increasing the temperature leads to the phase sequence 2 (left) - 3 - 2 (right). A large miscibility gap can be found both at low and high temperatures. While at low temperatures a surfactant-rich water phase (a) coexists with an oil-excess phase (b), a coexistence of a surfactant-rich oil phase (b) with a water-excess phase (a) is found at high temperatures. At intermediate temperatures the phase behaviour is dominated by an extended three-phase triangle with its adjacent three two-phase regions. The test tubes illustrate the relative change in phase volumes.

[Stubenrauch, 2008]

At low temperatures the phase behaviour is dominated by a large miscibility gap. The negative slope of the tie lines indicates that a non-ionic surfactant-rich water phase (a) coexists with an oil-excess phase (b). This situation is denoted as 2 or Winsor I, Fig. 1.15 left. Increasing the temperature one observes an extended three-phase triangle with its adjacent three two-phase regions as shown in Fig. 1.15 center. Within the three-phase triangle (denoted as 3 or Winsor III) a surfactant-rich microemulsion (c) coexists with an excess water (a) and oil phase (b). The symmetric form of the triangle implies the stabilization of equal amounts of water and oil. A further increase of the temperature again leads to the formation of an extended miscibility gap as shown in Fig. 1.15 right. Here, the positive slope of the tie lines indicates that a non-ionic surfactant-rich oil phase (b) coexists with a water-excess phase (a). This situation is denoted as 2 or Winsor II. The test tube shown below each Gibbs phase triangle illustrates the relative change in phase volumes for mixtures containing equal volumes of water and oil [Stubenrauch, 2008].
Stacking the isothermal Gibbs triangles on top of each other results in a phase prism as shown in Fig. 1.16(a), which represents the temperature-dependent phase behaviour of ternary water–oil–non-ionic surfactant systems. As discussed above, non-ionic surfactants mainly dissolve in the aqueous phase at low temperatures (2). Increasing the temperature one observes that this surfactant-rich water phase splits into two phases (a) and (c) at the temperature $T_1$ of the lower critical endpoint $cep_\beta$, i.e. the three-phase body appears. Subsequently, the lower water-rich phase (a) moves towards the water corner, while the surfactant-rich middle phase (c) moves towards the oil corner of the phase prism. At the temperature $T_u$ of the upper critical endpoint $cep_\alpha$ a surfactant-rich oil phase is formed by the combination of the two phases (c) and (b) and the three-phase body disappears. Each point in such a phase prism is unambiguously defined by the temperature $T$ and two composition variables. It has proved useful [6] to choose the mass fraction of the oil in the mixture of water and oil

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

and that of the surfactant in the mixture of all three components

$$\gamma = \frac{m_C}{m_A + m_B + m_C}.$$  

Knowing the densities of the components for calculating the volumes one can also use the volume fractions $\phi$ and $\phi_c$, respectively. A simple and extremely useful procedure to obtain an overview of the phases occurring in such a phase prism is to measure the phase diagram at a constant oil/water ratio as a function of the temperature $T$ and the surfactant mass fraction $\gamma$ ($T(\gamma)$-section). Such a section through the phase prism is highlighted in Fig. 1.16(a) (3 phase region = dark grey, 1 phase region = light grey) and shown schematically in Fig. 1.16(b). It permits easily to determine the phase inversion temperature (PIT), at which the hydrophilic-lipophilic balance (HLB) is achieved.
Figure 1.16: (a) Schematic phase prism of the system water–oil–non-ionic surfactant showing the temperature-dependent phase behaviour. A convenient way to study these systems is to measure the phase behaviour at constant oil/(water + oil) ratios as function of temperature $T$ and surfactant mass fraction $\gamma$ (3 phase region = dark grey, 1 phase region = light grey). (b) Schematic $T(\gamma)$-section at a constant oil/(water + oil) volume fraction of $\phi = 0.5$. Assigned are the minimal mass fraction $\tilde{\gamma}$ of surfactant needed to solubilize water and oil, the mass fraction $\gamma_0$ of surfactant which is solubilised monomerically in water and oil, the lower ($T_L$), upper ($T_U$) and mean ($\tilde{T}$) temperature of the three-phase body. Again the test tubes illustrate the relative volume of the phases.

[Stubenrauch, 2008]

Fig. 1.16(b) shows such a $T(\gamma)$-section at a constant oil/ (water + oil) volume fraction of $\phi = 0.5$. As can be seen, the phase boundaries resemble the shape of a fish. Starting with the binary water–oil system, two phases, namely a pure water phase and a pure oil phase, coexist over the entire experimentally accessible temperature range. Small amounts of added surfactant molecules dissolve monomerically in the two phases. Being amphiphilic, the surfactant molecules preferentially adsorb at the macroscopic interface. At a mass fraction $\gamma_0$ both excess phases and the macroscopic interface are saturated with the surfactant molecules and the amphiphilic molecules are forced into the microscopic water/oil interface leading to topologically ordered interfacial films in solutions, i.e. the ‘real’ microemulsions. Looking at these mixtures microscopically, we find at low temperatures an amphiphilic film that forms oil-swollen micelles in a continuous water phase (a). This oil-in-water (o/w) microemulsion coexists with an oil-excess phase (b) (2). At high temperatures
the inverted situation (2) is found. Here, a water excess phase (a) coexists with a water-in-oil (w/o) microemulsion in which the amphiphilic film forms water-swollen micelles in a continuous oil phase (b). At intermediate temperatures the surfactant is almost equally soluble in both solvents and a locally planar amphiphilic film is formed. Here, three phases (3), i.e. a surfactant-rich bicontinuously structured phase (c), an excess oil and water phase coexist. Microscopically, the observed trend of the phase behaviour from 2 over 3 to 2 with increasing temperature can be attributed to a gradual change of the mean curvature \( H \) of the amphiphilic film. While at low temperatures the film is curved around the oil (\( H > 0 \)) it curves around water at high temperatures (\( H < 0 \)) as shown in Fig. 1.12.

Considering now the variation of the phase behaviour with increasing mass fraction \( \gamma \) of surfactant one can see that the volume of the respective microemulsion phase increases (test tubes in Fig. 1.16(b)) until the excess phases vanish and a one-phase microemulsion is found. The optimal state of the system is the so-called \( \tilde{X} \)-point where the three-phase body meets the one-phase region. It defines both the minimum mass fraction \( \tilde{\gamma} \) of surfactant needed to solubilize water and oil, i.e. the efficiency of the surfactant, as well as the corresponding temperature \( \tilde{T} \), which is a measure of the PIT.

### 1.9.4 Effect of Temperature on Phase Behavior of Nonionic systems

The phase equilibria for nonionic surfactants, will be mostly governed by the clouding of the nonionic surfactant. For hydrophobic nonionics with a low cloud point the phase behaviour is dictated by the capacity of the surfactant dissolved in the nonpolar solvent to take up water and form reversed micelles. In parallel the capacity of the liquid crystalline phase to hold a nonpolar additive will be decisive for the major features of the phase diagram. More hydrophilic nonionics (with higher cloud points) form micelles, and hence the solubilization into these micelles will govern at lower temperatures while the water solubilization into reversed aggregates will be the conspicuous feature at higher temperatures.

Depending on the solubilizing capacity of the nonionic surfactant one can refer to either weak amphiphiles with a limited solubilizing capacity or strong amphiphiles as efficient solubilizers. Their phase equilibria with water/oil will be quite different as will their internal structures be depending on the requirements set by the volume of the solubilizate. [Sjoblom et al., 1996]
1.10 Formulation of Microemulsions

1.10.1 Significance of Formulations

Formulation is of significant importance because the properties of surfactant-oil-water systems in general and the formation of microemulsions in particular, are very sensitive to it and slight deviations from a ‘proper’ formulation may result in drastic changes of the properties. Consequently, formulation has to be controlled accurately, which is quite challenging because of the high number of degrees of freedom in any practical case.

Formulation essentially relates to the content of the systems and generally not to the way it is attained if thermodynamically stable systems are considered. The simplest microemulsion system would contain an organic oil phase (O), an aqueous phase generally referred to as water (W), and a surfactant (S) at a given temperature (T) and pressure (p). This means that at least five variables are required to describe the system. In practice, the situation is much more complicated. Water always contains electrolytes. Moreover, oils as well as nearly all commercial surfactants are mixtures. In many cases, a co-surfactant (e.g. an alcohol (A)) is added, among other functions, to reduce the rigidity of the surfactant layer and thus to prevent the formation of gel-like mesophases.

When mixtures are dealt with, some approximations allow to decrease the number of variables. For instance, if a commercial surfactant contains substances all of which behave similarly, then a so-called pseudo-component may be used to describe it. However, this is not the general case and in many instances so-called fractionation phenomena take place and the different components behave independently of each other. In this case, the actual number of components could be larger than three or four. Aside the nature of each of the components of the SOW and eventually the SOWA system, T and p also influence the properties, sometimes to quite a large extent. Note that all variables describing the nature of the components as well as T and p are intensive, i.e. they do not depend on the quantities the reason for which they have been called formulation variables. On the other hand, the relative amount of the different substances present in the system are also likely to change the properties, and are often referred to as composition variables; they are expressed as weight or volume fraction, percentage, or proportion. If n components are included, (n - 1) independent composition variables are required to quantitatively describe the contents of the system. In the simplest SOW ternary case, the two composition variables are often selected to be the surfactant concentration and the
water-to-oil ratio (WOR).

In a practical case with water, cosurfactant, a natural oil, and a commercial surfactant, the actual number of variables, thus of degrees of freedom, would be high. If a random trial and error procedure is taken as a method to test formulation, as often the case, the number of experiments to be carried out could be extremely high. This is of course quite a problem in practice, and non-random trial techniques would of course be very valuable. This is why a numerical handling of the formulation is so important in practice, to reproduce cases, to compare formulations, to compensate effects and to predict new recipes.

An accurate formulation handling is extremely useful not only to make microemulsion and to adjust their properties such as their stabilization ability, or to attain a low interfacial tension to ease emulsification. Formulation has been shown to be also directly linked with emulsion properties such as their type, stability, viscosity, drop size and with the efficiency of the emulsification protocol [Perez et al., 2002; Salager et al., 2009].