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LEADING CONTRIBUTION

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Microemulsions in amphiphilic and polymer–surfactant systems

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Abstract Microemulsions may have very different microstructures: discrete water or oil droplets and bicontinuous – depending, inter alia, on the surfactant polarity, salinity, temperature, and co-surfactant. A review is given on structure determination of microemulsions of different systems and the conditions for occurrence of different structures. Polymer addition may dramatically influence microemulsion stability and structure and examples are given for different types of polymers and discussed on the basis of mixed solutions of polymers and surfactants in general.

Key words Microemulsions – polymers – phase behavior – osmotic stress

Surfactant-water-oil systems

Surfactant molecules are composed of two molecular blocks with strongly differing affinity towards water. The polar part of a surfactant is usually soluble in water, but shows a strong demixing with hydrocarbons, while the unpolar group exhibits an opposite behavior. The mixtures of surfactant, water and hydrocarbon (in microemulsion terminology, oil) form a variety of phases. In a state of thermodynamic equilibrium, all of them show spatial microheterogeneity, with relatively large (10–400 Å) oil and water domains. The surfactant molecules are located at the interface of those domains: the unpolar tails are immersed in oil, and the polar heads – into water. Since direct contact of oil and water is strongly disfavoured, the surfactant covers the interface of those domains without any holes, i.e., forms a monolayer at the O-W interface (Fig. 1).

Surfactant monolayer is the main construction block of the microemulsion phases: oil and water merely fill the space on both sides of the monolayer. The monolayer can acquire various topologies: spherical, cylindrical, planar, inverse spherical and inverse cylindrical, spongelike, etc. (Fig. 2). Each topology corresponds to a specific phase, which can be isotropic or anisotropic. During the last decade, it has become evident that the topology acquired by the monolayer is strongly dependent on its bending elasticity [1–3]. Not only stretching, but also bending the monolayer to some radii of curvature costs energy. Deviation of the monolayer curvature from some specific value, intrinsic for the given monolayer, increases the monolayer free energy according to the following Hookean equation [4]:

$$dG_c = (2\kappa(H - H_0)^2 + \bar{\kappa}K)\,dS \,. \qquad (1)$$

Here, $H = (c_1 + c_2)$ and $K = c_1c_2$ are the mean and Gaussian curvatures respectively, where c_1 and c_2 are the two principle curvatures, H_0 is the spontaneous curvature, dS is the surface area of the monolayer patch, κ is the bending modulus, and $\bar{\kappa}$ is the saddle splay modulus. The

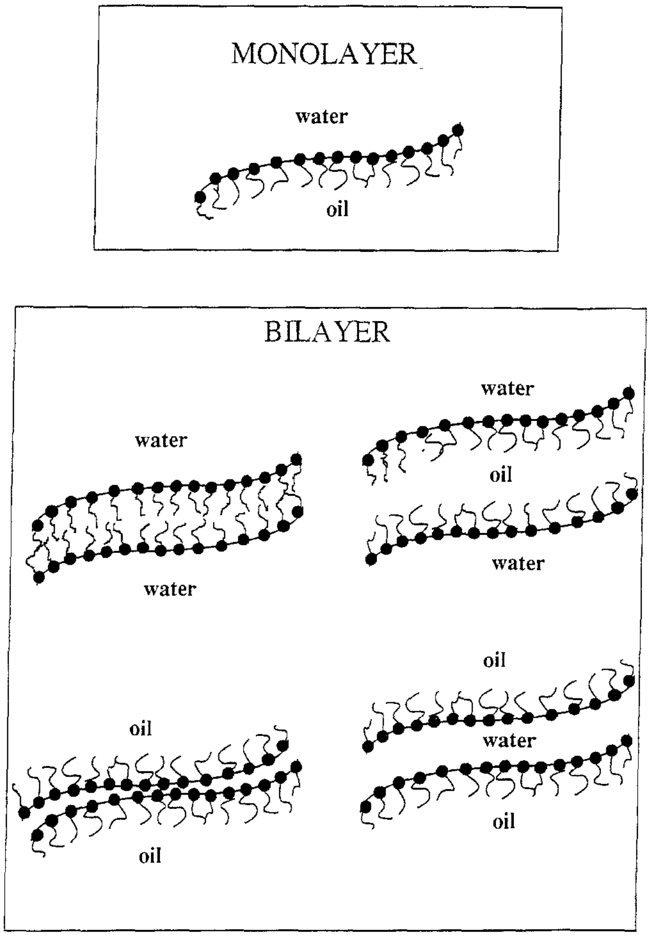


Fig. 1 Amphiphile–water–oil systems give a segregation into water and oil domains separated by amphiphile layers. They can be classified into monolayer and bilayer structures, the latter characterized by two correlated monolayers. Microemulsions have monolayer structures, while bilayer structures occur in lamellar liquid crystalline phases, in vesicles and in so-called sponge or L_3 phases

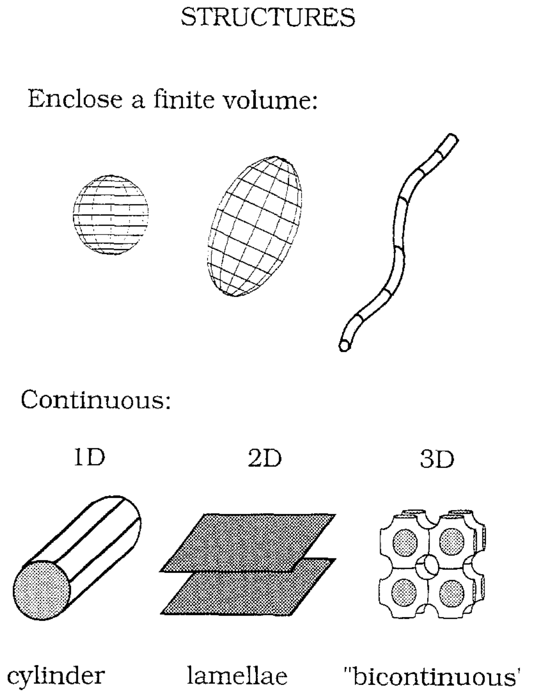


Fig. 2 Amphiphile layers can have many topologies. It is convenient to classify systems into structures where the amphiphile film encloses a finite volume (of oil or water) and those where it extends over macroscopic distances, which can be in one, two or three dimensions. Discrete particles can have many different shapes, here represented by spherical, prolate and thread-like micelles. Infinite domains are found, for example, in hexagonal (1 D), lamellar (2 D) and "bicontinuous" cubic (3 D) liquid crystalline phases. Bicontinuous microemulsions (see below) have a structure that locally resembles the latter but is disordered over larger distances

physical meaning of the spontaneous curvature is related to the shape of surfactant molecules: if the polar "head" of the surfactant molecule is larger than the unpolar "tail", it prefers to pack into spheres with the unpolar core inside. The spontaneous curvature in this case is large ($H_0 \approx 1/a$, where a is the molecular size) and, according to the sign convention, positive. If the tail and the head are of the same size, the spontaneous curvature is close to zero. In this case, the monolayer forms planar or saddle like (with equal in absolute value and opposite in sign principal curvatures) surfaces, e.g., lamellar and cubic liquid crystals, and sponge phases. If the head is smaller than the tail, then the surfactant packs into spheres with the water core inside and the spontaneous curvature $H_0 \approx -1/a$ is large in absolute value and negative.

The bending modulus κ is always positive, has a dimension of energy and reflects how flexible is the monolayer. If κ is large in comparison with the thermal energy $k_B T$, the monolayer is rigid, and more ordered liquid crystalline phases are favoured. If the bending modulus becomes comparable with $k_B T$, new highly disordered phases appear (spongelike bicontinuous microemulsion phase, highly swollen lamellar phase). The bending modulus depends on the interactions acting between the surfactant chains. For similar surfactants (e.g., in homologous series), the bending modulus increases with the length of the surfactant molecule.

The saddle splay modulus also has a dimension of energy and can take on positive and negative values. It couples with the surfactant film topology. If $\bar{\kappa}$ is positive, the saddle like surfaces are favoured with respect to planar ones and one may expect formation of "sponges" and cubic phases. If $\bar{\kappa}$ is negative, formation of separate particles is preferred.

In the following, we briefly describe the phase behavior of microemulsion systems prepared from different types of surfactants. Although the trends are very much similar, each surfactant group has its own specificity.

Polyethylene oxide-based surfactants

Historically, the first microemulsion systems were prepared from four or five component mixtures (usually, a mixture of oil, water, ionic surfactant, alcohol and, sometimes, an inorganic electrolyte [5]. For obvious reasons, it was very difficult to rationalize the phase behavior of those systems. Only recently it has become evident that the main features of the microemulsion phase behavior could be reproduced by using merely three-component mixtures. The basic contributions in this field are due to pioneering studies of Shinoda and Kunieda [6–8] and following systematic studies of Kahlweit's group [9–11]. Oligo(ethylene oxide)-based surfactants, in particular, polyethoxylated alcohols, turned out to be the best suited for these purposes. Surfactants of this type contain a hydrophobic tail and a polar head composed of several ethylene oxide units (C_mE_n), where m and n are the numbers of carbon atoms in the alkyl chain and the number of the ethylene oxide groups, respectively. The C_mE_n monolayers formed at the oil-water interface are very flexible, due to a high degree of solvent penetration into the surfactant "brush": the bending modulus is usually of the order of k_BT. The spontaneous curvature of these surfactants depends on the relative length of alkyl and polyethylene oxide units. It can be also effectively varied by changing temperature. Raising temperature makes water a poor solvent for poly(ethylene oxide); this leads to a collapse of oligo(ethylene oxide) polar heads and the monolayer bends towards water [12]. As a consequence, the phase diagrams of water–oil–C_mE_n ternary systems are strongly temperature dependent.

Figure 3 shows a simplified representation of the microemulsion phase equilibrium as a function of temperature. At low temperatures, the surfactant monolayer has a large positive spontaneous curvature. The surfactant molecules self-assemble into spherical micelles with the oil solubilized in the unpolar core. The excess of oil coexists with spherical micelles in a two-phase equilibrium. Raising temperature reduces the monolayer spontaneous curvature (i.e., increases the radius of preferred curvature) and micelles absorb more oil. At a certain temperature, the spontaneous curvature becomes close to zero. This curvature is no longer compatible with a spherical shape and a spongelike bicontinuous microemulsion phase with a peculiar topology is formed. The volume fractions of oil and water in this phase are comparable. The phase consists of relatively large (~300 Å) interconnected and highly disordered oil and water domains, separated by the film of the surfactant monolayer. The phase equilibrium pattern also changes: in contrast to micellar phase, coexisting with excess oil in a two phase equilibrium, bicontinuous microemulsion phase coexists both with excess of oil and water in a three-phase equilibrium. At higher surfactant concentrations, the bicontinuous microemulsion phase co-exists with the liquid crystalline lamellar phase. Raising temperature further makes the spontaneous curvature negative. The surfactant molecules self-assemble into spherical aggregates with the polar core inside, i.e., form so-called reverse micelles. Again, in analogy with the case of oil-n-water micelles, the micellar phase co-exists with excess water in a two-phase equilibrium. The same trend (the transition O/W micelles – bicontinuous microemulsion – W/O micelles) can be found with many nonionic surfactants of C_mE_n type, the nature of surfactant (and, to a less degree, oil) affecting only the respective temperature range.

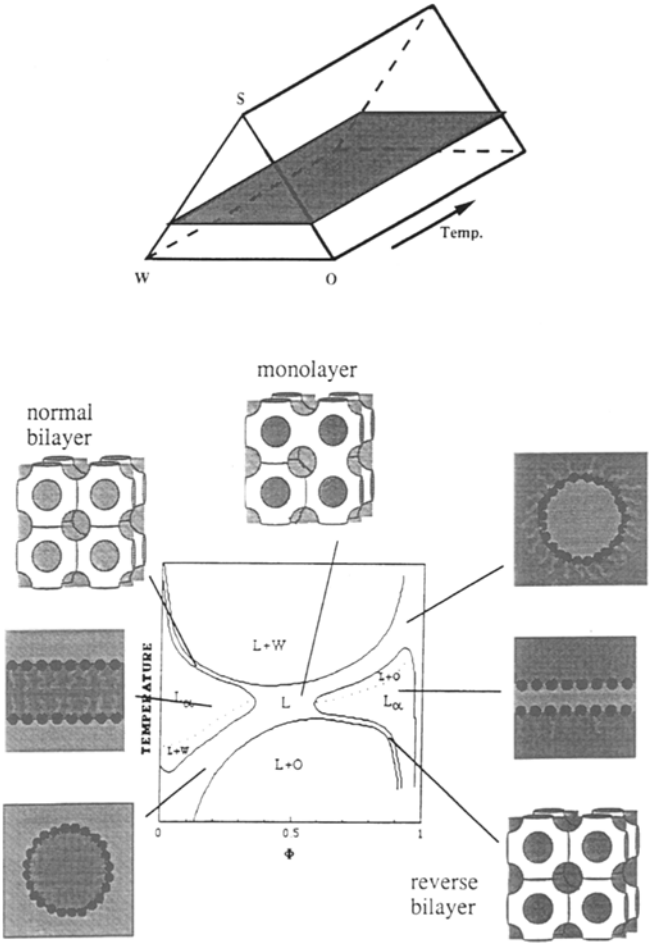


Fig. 3 For a nonionic surfactant, the phase behaviour is much influenced by temperature and it is convenient to represent the phase diagram of a surfactant(S)–water(W)–oil(O) system by a cut at constant surfactant concentration in the phase prism. In the phase diagram the temperature is plotted as a function of the volume fraction of oil in the solvent mixture. Phases are indicated as follows: L, microemulsion; W, water-rich solution phase; O, oil-rich solution phase; L_α, lamellar liquid crystalline phase. In the figure are indicated the microstructures found under different conditions

Ionic surfactants

As it follows from the previous section, to prepare a microemulsion with a high solubilization of components in each other, one has to i) reduce the (absolute value of) spontaneous curvature and ii) to decrease the monolayer bending modulus. For polyethoxylated surfactants, temperature is the most effective tool for controlling the spontaneous curvature. With conventional ionic surfactants this can be done by adding inorganic electrolytes and/or by mixing the surfactant with a alcohol (cosurfactant) or a surfactant having different H_0. Inorganic salts screen electrostatic repulsion between the soap polar heads; as a result, the monolayer bends towards water. In the case of mixed surfactant or surfactant/cosurfactant films, H_0 can be tuned by varying the mixing ratio.

The bending elasticity is more difficult to control. It depends on details of headgroup-headgroup and chain-chain interactions, but a general rule is that it increases with an increasing surfactant film thickness [13]. Hence, adding a short or medium chain alcohol to a surfactant film normally increases the film flexibility in addition to the spontaneous curvature effect.

Ionic surfactant systems generally show only a weak temperature dependence. The general trend is that H_0 increases with increasing temperature, i.e. opposite to the nonionics. One exception, however, is the branched double chained ionic surfactant AOT (sodium bis(2-ethylhexyl) sulfosuccinate), where a strong temperature dependence is observed, in particular in the presence of salt [14, 15]. The AOT molecule is asymmetric with the two chains being inequivalent. The origin of this temperature dependence appears to derive from a significant temperature dependence in the packing of the asymmetric surfactant in the film, with additional complexity arising from three chiral centers in the molecule [16].

Phospholipids

Phospholipids play a very important role in nature, because they constitute the main component of cell membranes. Phospholipids from various sources differ in the length and the degree of saturation of the hydrocarbon tail, and in the structure of the polar head. Spontaneous curvature of phospholipid molecules is close to zero and they usually pack into bilayers, forming liquid crystalline lamellar phases. At high dilutions, lamellar phase transforms into vesicles – spherical bilayer "bubbles" with the water pools inside. Rising temperature usually produces a shift in the monolayer spontaneous curvature to negative values, although the effect is much weaker than with the polyethoxylated surfactants. This results in formation of cubic and reverse hexagonal phases at high temperatures [17–19].

Solvent penetration into the phospholipid monolayer formed at the interface between oil and water is low. As a result, phospholipid monolayers are considerably more rigid than, e.g., those formed by oligo(ethylene oxide) surfactants: κ is larger by, at least, two orders of magnitude (~ 10–$100\,k_BT$) [18]. This means that phospholipids do not form microemulsions per se. Adding a small amount of short-chain alcohols, however, makes the monolayer much more flexible and one can observe a typical microemulsion phase behavior [20].

Microemulsion microstructure

The microemulsion structure is very difficult to study. The transitions in the shape of the surfactant film and the relevant changes in oil and water domains continuity has become evident only during the last few years, due to application of such techniques as NMR FT-PGSE [21], freeze fracture electron microscopy [22] and small-angle scattering [23], in particular neutron scattering with contrast variation [24, 25]. The first method allows one to measure the diffusion coefficients of all the microemulsion components, and thereby, to prove the oil and water continuity of the phases. For the component, confined to spherical droplets, the diffusion coefficient is orders of magnitude smaller than that of the neat liquid. Therefore, in an O/W micellar solution, the diffusion coefficient of oil is small and that of water is large. In an inverse W/O micellar solution, with water pools inside the particles, the water diffusion coefficient is small and that of the oil is high. In bicontinuous microemulsion phase, both the oil and water diffusion coefficients are high and comparable to those of the neat liquids. Experimental studies performed on different microemulsion systems proved those trends, see e.g. [3, 26–29].

Polymer–surfactant mixtures. Basic aspects

As a background to the discussion of the role of polymers in microemulsions we will firstly briefly consider some basic aspects of polymer–surfactant interactions. Thereafter, an introduction to the phase behaviour of ternary systems polymer/surfactant/water will be given. This will serve as a basis for our discussion of the systems with oil as a fourth component.

One of the most important practical aspects of polymer–surfactant systems is the possibility to control rheology over very wide ranges. Surfactant molecules that bind to a polymer chain generally do so in clusters which closely resemble the micelles formed in the absence of polymer. (For reviews of the field, see refs. [30–36].) If the polymer is less polar or contains hydrophobic regions or sites, there is an intimate contact between the micelles and the polymer chain. In such a situation the contact between one surfactant aggregate and two polymer segments will be favourable. The two segments can be in the same polymer chain or in two different chains, the former being the typical case for a dilute polymer solution and the latter for more concentrated solutions with extensive chain overlap. The cross-linking of two or more polymer chains can lead to network formation and dramatic rheological effects.

For so-called hydrophobe-modified (HM) polymers, the cross-linking that may be induced by surfactant aggregates is shown in Fig. 4. The polymer molecules show a weak self-association in the absence of surfactant, which may be strongly enhanced by the formation of surfactant aggregates around hydrophobic centers from two or more polymer molecules. As has been demonstrated for many systems of a nonionic polysaccharide and an ionic surfactant [37–40] this may increase the viscosity by several orders of magnitude.

Surfactant–polymer interactions may be treated in different ways, the appropriateness of approaches depending strongly on the polymer. In one model, one analyzes the surfactant binding to a polymer. The binding isotherms obtained typically indicate a strong cooperativity in binding and the onset of binding is quite well-defined and a critical association concentration (cac) is introduced. Cac varies strongly with the system and decreases for example strongly with increasing chain length of the surfactant. The latter observation suggests the alternative model, which is to analyze the effect of a polymer on surfactant micellisation, a polymer affecting the stability of a micelle by short- or long-range (electrostatic) interactions much in the same way as low molecular weight cosolutes (weak amphiphiles, electrolytes) [41].

The main driving force for surfactant self-assembly in polymer–surfactant systems is generally the hydrophobic interaction between the alkyl chains of the surfactant molecules. Ionic surfactants often interact significantly with both nonionic and ionic polymers, which can be attributed to the unfavourable contribution to the energetics of micelle formation from the electrostatic effects and their partial elimination due to charge neutralisation or lowering of the charge density. For nonionic surfactants, there is little to gain in forming micelles in the presence of a polymer and they, therefore, in general, do not interact strongly with polymers. If the polymer molecules contain hydrophobic segments or groups, like in block copolymers and hydrophobe-modified polymers, a hydrophobic polymer–surfactant interaction will be significant. Consequences of this are a higher specificity in the interaction leading to a lower cac, a lower cooperativity and lower aggregation numbers.

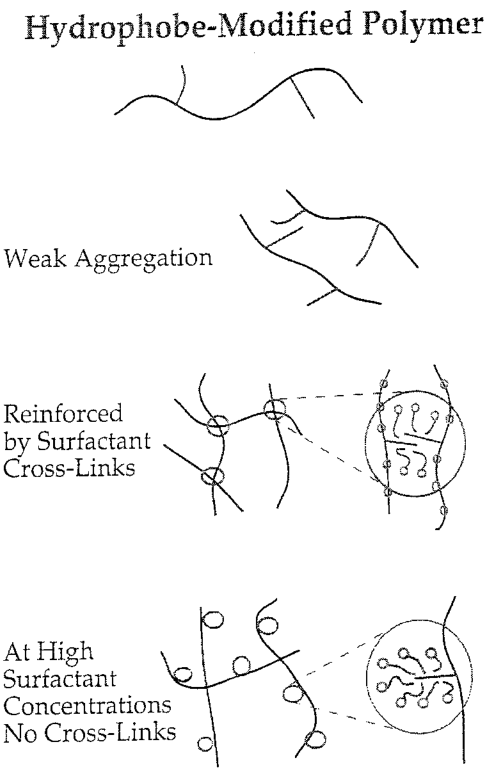


Fig. 4 Schematic picture of possible association processes in solutions of a surfactant and a polymer with hydrophobic centers

Phase behaviour of surfactant–polymer mixtures

There is thus a considerable current interest in the properties of aqueous mixtures of polymers and surfactants. Most studies of such mixtures focus on the *association* of polymer and surfactant, and tend to concentrate on the incipient association processes, which take place in more-or-less dilute one-phase solutions. (The surfactant concentration is typically kept below or equal to the cmc of the polymer-free surfactant solution.) Recently, however, increasing attention has been paid to phase-separation phenomena in more concentrated systems [42–53], and has drawn attention to the analogies, with respect to phase behaviour, between aqueous polymer/surfactant mixtures and mixtures of dissimilar polymers.

Since the surfactant molecules in a polymer solution in general occur in a strongly self-assembled form, it is a natural starting-point to treat the surfactant micelles as a second polymer and use the quite good understanding of polymer-polymer-solvent systems [54–56] as a basis, as we recently have reviewed [57].

What are then the important differences between a polymer and a surfactant aggregate? Both polymers and surfactant aggregates may respond to changes in the solution conditions by changing their conformation in some way, resulting in global changes in size and local changes in the balance between exposed hydrophobic/hydrophilic groups, distances between charged groups, etc. These responses differ in detail between a polymer and a surfactant aggregate. However, the principal way in which a surfactant aggregate differs from a polymer is that the "*degree of polymerisation*" of the former may vary, essentially between one and infinity, depending on the solution conditions.

The entropy of mixing is a comparatively weak thermodynamic force in a multicomponent polymer system. In the binary polymer/solvent mixture, this manifests itself in the inherently lower solubility of a polymer, compared to that of the corresponding monomer. In a ternary polymer/polymer or surfactant/solvent mixture, which is in focus here, the low entropy of mixing can, depending on the balance between the various monomer-monomer and monomer-solvent pair interactions, result in two main types of liquid-liquid phase separation phenomena [58–60] (cf. Fig. 5), which may both be understood in the context of the Flory–Huggins theory of polymer mixtures [61, 62]. In the first type, both of the separating phases contain cosolutes of a comparable total concentration, but the cosolute composition is strongly asymmetrical, so that each phase is enriched in one of the cosolutes. This kind of phase separation, which is often called "polymer incompatibility", will here be referred to as a *segregative* phase separation. Segregation results when the effective interaction between unlike cosolutes is repulsive, and/or when the two cosolutes differ in their affinity towards the solvent [55, 56, 58, 62].

The second type of phase separation is when a phase concentrated in *both* cosolutes separates from a phase which essentially contains only solvent. This phenomenon is often referred to as "complex coacervation" [59, 60]. We will here refer to the latter type of phase-separation as an *associative* phase separation. The term is here taken to include all cases when there is a sufficiently strong effective attraction between different cosolutes so as to result in the associative phase separation.

Inasmuch as the analogy between a finite surfactant aggregate and a polymer chain is a valid one, we expect that the phase behaviour of aqueous polymer/surfactant mixtures should conform to the patterns displayed by polymer/polymer mixtures. As a rule, *mixtures of nonionic surfactants with nonionic polymers* show no strong, mutual effective attraction [30, 31, 35]. For this reason, such mixtures have generally attracted little attention. The analogies between surfactant/polymer and polymer/polymer mixtures suggest, however, that sufficiently concentrated mixtures should display a segregative phase separation. Results from our laboratory [36] support this prediction. Mixtures of $C_{12}E_8$ or $C_{12}E_5$ with dextran at 10 °C and at 25 °C thus display a phase behaviour similar to that of the analogous dextran/poly(ethylene oxide) mixture. The two-phase area is largest for the $C_{12}E_5$ surfactant, which is known to form larger micelles than $C_{12}E_8$ [63]. The temperature dependence is also revealing: For $C_{12}E_8$, where no micellar growth is expected, the phase diagrams at the two temperatures are virtually identical. For $C_{12}E_5$, on the other hand, where substantial micellar growth with increasing temperature is known to take place already at room temperature, a significant increase of the two-phase region is seen at the higher temperature. The experiment thus confirms the expected effect on the phase behaviour of the "degree of polymerisation" of the surfactant. (A similar effect on the phase behaviour was also seen when the degree of polymerisation of the dextran component was altered.)

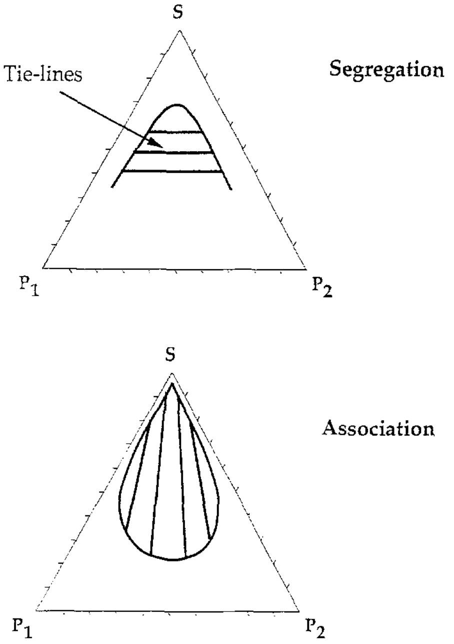


Fig. 5 Schematic illustration of segregative and associative phase separation for a system of a solvent and two polymers. With good approximation, the micelles in a polymer–surfactant mixture can be modelled as a second polymer

A fundamental difference between surfactant/surfactant and polymer/polymer solutions is that the surfactant monomers may mix and form mixed aggregates. Since the identity of the micelles is not kept, we may thus not use directly the reasoning for polymer-polymer systems to account for the phase behaviour of mixed solutions of surfactants. Indeed, the phase behaviour of surfactant/

surfactant systems is quite different from that of polymer/polymer systems. In particular, a segregation behaviour is encountered only on a microscopic scale in special cases, and then generally only within a one-phase solution. Segregation into different macroscopic phases would require a very strong incompatibility between different surfactant molecules, leading to quite complete microscopic segregation into separate micelles, and has, to our knowledge, not been observed.

The phase diagrams that are available today support the notion of a close correspondence between the phase behaviour of aqueous polymer/surfactant mixtures, on the one hand, and aqueous polymer/polymer mixtures, on the other, while surfactant/surfactant mixtures behave differently [57]. Recent experiments reveal a particularly rich behaviour in ionic mixtures, which may be qualitatively understood in terms of the entropy of mixing of the counterions [57].

A factor which complicates the analysis of polymer/surfactant mixtures is that the aggregation number of the surfactant aggregate is variable. Moreover, the effect of the polymer on the aggregation number of the surfactant may be substantial, particularly in systems of the associating type (no added salt). In principle, however, it should be possible to predict the equilibrium association number of the surfactant using the same approaches as have been established for aqueous surfactant solutions in the absence of polymer. By utilising these well-known ways to vary the aggregation number of the surfactant and/or the interaction between the polymer and the (mixed) surfactant aggregate it should be possible to tailor phase-separating polymer/surfactant systems according to specified needs. In particular, it should be possible to design systems which change their phase characteristics (from monophasic to biphasic or *vice versa*) in response to changes in system variables such as the concentrations of added salt or cosurfactant.

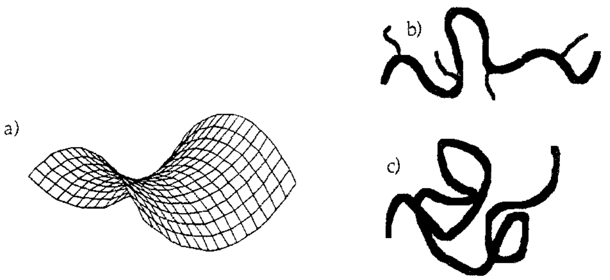


Fig. 6 We are considering mixtures of flexible surfactant films (a) and polymers which may adsorb onto the films by hydrophobic "stickers" (b) or non-adsorbing polymers which interact with the films only by excluded volume (c)

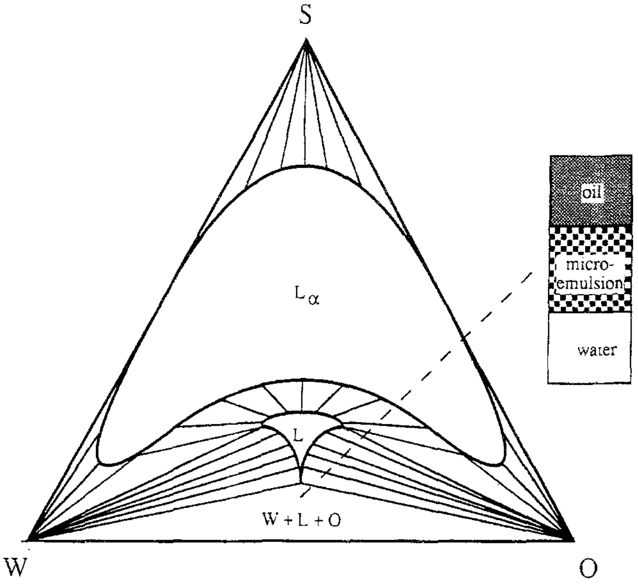


Fig. 7 Under balanced conditions a surfactant(S)–water(W)–oil(O) system contains a liquid microemulsion phase (L) and a lamellar liquid crystalline phase (L_α) in addition to the phases of the three individual components, respectively. The temperature of the balanced condition is strongly dependent on surfactant and less strongly dependent on the oil used

Polymers in bicontinuous microemulsions

Below we will discuss a part of a recent project concerning the investigation of mixed systems of adsorbing (associating) or non-adsorbing (segregating) polymers in various phases of flexible surfactant films (Fig. 6). We will describe the effects of water soluble homopolymers and hydrophobically modified water soluble polymers on the phase equilibrium of a balanced microemulsion. The homopolymers are non-adsorbing while a hydrophobically modified polymer adsorbs onto a surfactant film by means of its hydrophobic "stickers" [64]. Note that while we restrict ourselves here to water soluble polymers, the effects are expected to be essentially symmetric with respect to water–oil exchange. In the following discussion we will refer to some recent studies by Kabalnov et al. [65, 66] who used, as a model microemulsion, the water–$C_{12}E_5$–decane system, where $C_{12}E_5$ denotes the nonionic surfactant pentaethyleneoxide dodecylether. As non-adsorbing polymers they studied for example dextran, and ethyl (hydroxyethyl)cellulose (EHEC), while as an adsorbing polymer they used hydrophobically modified EHEC (HM-EHEC). The bicontinuous microemulsions can also be seen as interesting model systems for porous media. Analysing the thermodynamic response of a bicontinuous microemulsion to added polymer thus offers a possibility to study general polymer properties in a porous medium.

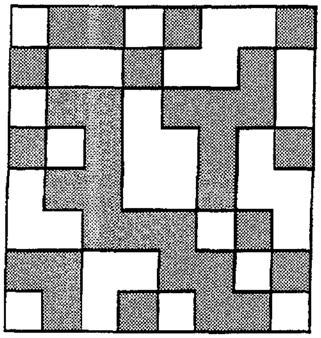


Fig. 8 A schematic two-dimensional representation of the structure of a balanced bicontinuous microemulsion

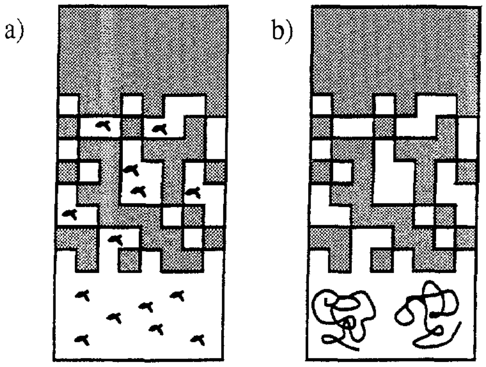


Fig. 9 Small oligomers are soluble in the microemulsion phase (a), whereas coils that are larger than the pore size of the microstructure are insoluble in the microemulsion phase and confined to the excess water phase (b)

A balanced microemulsion contains equal volumes of water and oil and has a disordered bicontinuous microstructure with a zero average mean curvature of the surfactant film. The sponge-like microstructure has an average "pore-size", ξ, which is determined by the interfacial area per unit volume, i.e., the surfactant volume fraction, Φ_S. In the balanced case, the water and oil domain pore-sizes are equal and for the $C_{12}E_5$–water–decane system given approximately by $\xi = (25/\Phi_S)$ Å.

A balanced microemulsion has a limited swelling capacity with water and oil. When saturated with water and oil and having a maximum "pore-size", it is in a three phase equilibrium with excess water and oil phases. A schematic phase diagram of a surfactant–water–oil system under balanced conditions is shown in Fig. 7. In Fig. 8 we show a schematic two-dimensional representation of the structure of a balanced bicontinuous microemulsion.

Solubility of homopolymers in bicontinuous microemulsions

Here we consider the partitioning of added polymer between a balanced microemulsion and the excess water phase in a three phase equilibrium (Fig. 9). Small oligomers partition essentially uniformly between the two phases. Large polymer coils with a radius of gyration, $R_g \gg \xi$ are on the other hand insoluble in the microemulsion. For an intermediate coil-size, the polymer shows a partitioning between the microemulsion and the excess water phase, characterised by a partitioning coefficient, P, which we can define as:

$$0 < P = \frac{C_p^{me}}{C_p^{w}} < 1 \tag{2}$$

where C_p^{me} and C_p^{w} are the polymer concentrations in the microemulsion and excess water phases, respectively, where C_p^{me} is the local aqueous concentration within the water domains. In Fig. 10 we show the partition coefficient P for dextran between the microemulsion and the excess water phase in the balanced $C_{12}E_5$–water–decane system, plotted as a function of the average end-to-end distance of the polymer coil. P decreases rapidly with the end-to-end distance, and levels off at an essentially zero value for end-to-end distances larger than ≈300 Å, which is about the same size as the pore size of the microstructure. (The finite value of P for larger end-to-end distances is due to low molecular weight impurities).

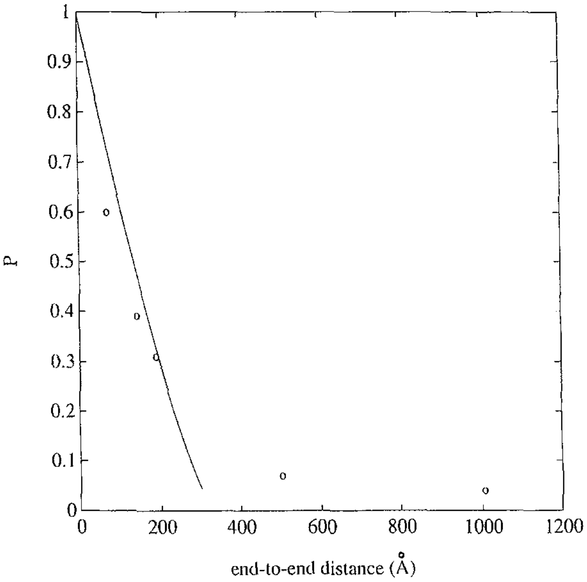


Fig. 10 Variation of the partition coefficient for dextran with the unperturbed end-to-end distance between the balanced microemulsion and the excess water phase in $C_{12}E_5$–water–decane system. The solid line is a partitioning calculated on the basis of Eq. (5). The parameters are: $\Phi_s = 0.07$, $\Phi_w = 0.465$, $\langle H \rangle = 0$ (balanced state), $\langle K \rangle = 1.78\,(\Phi_s/l_s)^2$ and $R_g = r/\sqrt{6}$, where r is the average polymer end-to-end distance. The Gaussian curvature term comes from describing the surfactant film as the Schwartz D minimal surface [69], where Φ_s/l_s is the interfacial area per unit volume

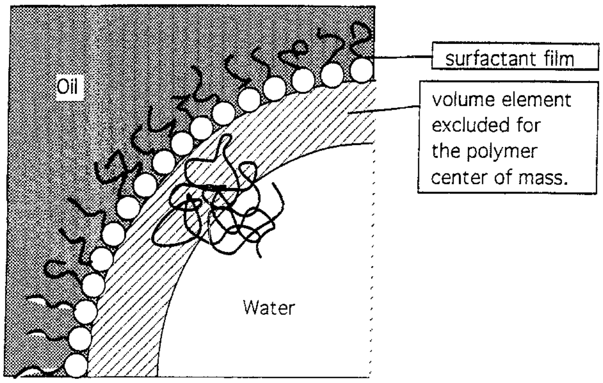


Fig. 11 In the water domains of the microemulsion, the polymer centre of mass is excluded from a volume element of thickness $\approx Rg$ from the surfactant film

This coil-size dependence on the partitioning can be understood in terms of an excluded volume effect. As illustrated in Fig. 11, the center of mass of the coil is excluded from a certain volume element out from the surfactant film. This volume element can be seen as a water layer adjacent to the film of thickness $\approx R_g$. In the case of only excluded volume interactions, the partition coefficient is given by:

$$P = 1 - \frac{V_{\mathrm{excl}}}{V} \tag{3}$$

where V_{excl} is the excluded volume and V the total volume. If we consider for example a spherical cavity of radius R (applicable to a partitioning between water-swollen reverse micelles and an excess water phase), the partition coefficient becomes:

$$P = \left(1 - \frac{R_g}{R}\right)^3 . \tag{4}$$

More generally, the relative excluded volume depends on the average mean and Gaussian curvatures of the surfactant film. Within the parallel surface model [67, 68] the partition coefficient becomes:

$$P = 1 - \frac{\Phi_s}{\Phi_w l_s} R_g \left(1 + \langle H \rangle R_g + \frac{\langle K \rangle R_g^2}{3}\right) . \tag{5}$$

Here, $\langle H \rangle$ and $\langle K \rangle$ are the area averaged mean and Gaussian curvatures, respectively, of the surfactant film, and l_s is the effective surfactant length, defined as the volume-to-area ratio of the surfactant molecule.

Note that (5) reduces to (4) for the spherical case. For a spherical reverse micelle the radius of the water core depends on the enclosed volume-to-area ratio, and can be ritten as:

$$R = \frac{3\Phi_w l_s}{\Phi_s} . \tag{6}$$

Furthermore, we have $H = -1/Rd$ and $K = 1/R^2$, which inserted together with the relation (6) in Eq. (5), gives Eq. (4).

In the simple planar case (lamellar phase), $\langle H \rangle = \langle K \rangle = 0$, and Eq. (5) reduces to:

$$P = 1 - \frac{\Phi_s}{\Phi_w l_s} R_g = 2\frac{R_g}{d_w} \tag{7}$$

where $d_w = 2\Phi_w l_s/\Phi_s$ is the water layer thickness in the lamellar phase structure.

In Fig. 10, partitioning data of dextran in the balanced $C_{12}E_5$–water–decane system [65] are compared with a calculated partition coefficient based on Eq. (5). The values of the various parameters are given in the figure caption. As is seen, a reasonable agreement is found with this simple model.

A balanced or near balanced bicontinuous structure can be seen as voids of size ξ connected by slightly more narrow necks. Equation (5) is expected to be a good description only in the limit of small coils ($R_g \ll \xi$). When the polymer coils are excluded from the necks, but still fits inside the voids, P is expected to be given by a formula similar to Eq. (4): $P = A(1 - R_g/\xi)^3$, where A is the relative void volume. The partition relations discussed above, relies also on the assumption that the composition of the microemulsion or lamellar phase does not respond to the partition of polymer. Hence, we consider the microemulsion to behave as "solid" porous medium. In a general thermodynamic treatment of the phase equilibria we need to equate chemical potentials, where we will find a contribution from the osmotic work performed by the excess polymer solution when $P \ll 1$. The limiting case when $P = 0$, is discussed in the following section below.

Large polymer coils: osmotic stress experiments

A large water soluble polymer, being insoluble in the middle phase microemulsion, is confined to the excess water phase. There, the addition of polymer results in a an osmotic pressure increase (lowering of the water chemical potential). The middle phase microemulsion responds by also expelling some oil to the excess oil phase. A typical variation in the phase volumes, as a function of added polymer is shown in Fig. 12. The shrinkage of the middle phase is slightly asymmetric; it expels more water than oil.

The composition of the excess oil phase remains essentially unaltered. This implies that the shrinkage of the microemulsion takes place under a constant oil chemical potential. Hence, the composition of the middle phase microemulsion follows a trajectory in the ternary phase diagram corresponding to the phase boundary of the

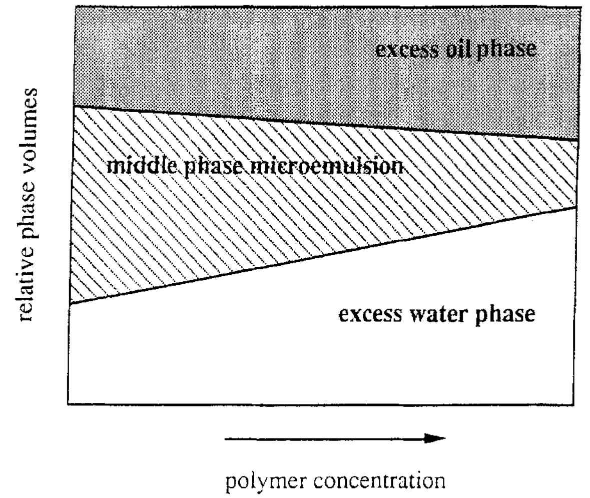


Fig. 12 Typical variation of the relative phase volumes with the polymer concentration for a non-adsorbing large molecular weight polymer

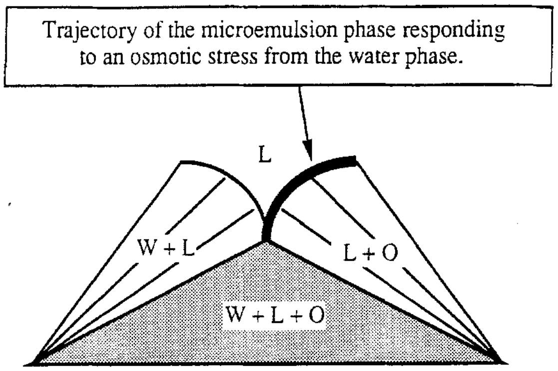


Fig. 13 The trajectory of the middle phase microemulsion composition when subject to an osmotic stress from the excess water phase

L-phase with excess oil, as illustrated in Fig. 13. The lowering of the water chemical potential is balanced by an increase in the surfactant chemical potential according to the Gibbs–Duhem relation:

$$\sum_i n_i \, d\mu_i = 0 \, . \tag{8}$$

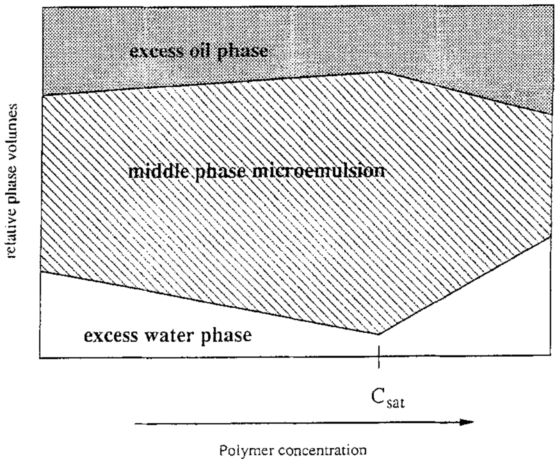
From knowing the concentration dependence of the osmotic pressure of the polymer solution it is possible to determine the chemical potentials of all three microemulsion components along the phase boundary towards excess oil. Such an osmotic stress experiment performed on the balanced $C_{12}E_5$–water–decane system [65] revealed that the variation in the water chemical potential along the excess oil phase boundary is of the order of 10^{-5} k_BT per molecule.

Adsorbing polymers

Adsorbing polymers of large molecular weight can be solubilized in a bicontinuous microemulsion. In a recent study [66], Kabalnov et al. compared the effects of EHEC (non-adsorbing) and hydrophobically modified HM-EHEC on the phase equilibria of a balanced microemulsion (EHEC stands for ethyl(hydroxyethyl) cellulose). The effects of EHEC followed the same trends as described for dextran above. HM-EHEC on the other hand, showed a strong partitioning to the microemulsion phase, resulting in an initial swelling of the microemulsion phase with water. Figure 14 describes schematically the variation of the relative phase volumes with the polymer concentration.

The solubility of the hydrophobically modified polymer in the microemulsion phase is however finite. The finite solubility can be seen as reaching a saturation of the surfactant film. However, if the thickness of the adsorbed polymer layer is not small compared to ξ, the steric interaction between two facing polymer layers is also expected to influence the solubility. Above the solubility limit, the excess polymer is squeezed out to the excess water phase. There, the excess polymer has the same effect as a homopolymer, i.e., it will exert an osmotic stress on the microemulsion phase. Hence increasing the polymer concentration above the solubility limit, the swelling of the microemulsion phase is abruptly reversed, and the microemulsion contracts, expelling water to the excess water phase (Fig. 14).

Fig. 14 Typical variation of the relative phase volumes with the polymer concentrations for an adsorbing polymer. The initial swelling of the middle phase microemulsion is reversed at higher polymer concentrations when the middle phase has become saturated with polymer. Additional polymer above C_{sat} is solubilized in the excess water phase where the osmotic pressure results in a contraction of the microemulsion phase



The adsorbed polymer layer affects the curvature properties of the surfactant film. Under good solvent conditions the polymer layer wants to be highly swollen making the surfactant film to curve away from water, i.e., increases the spontaneous curvature of the film (Fig. 15). In addition to the change in spontaneous curvature which causes an increase in the water-to-oil ratio of the microemulsion phase, there is also a general swelling of the microemulsion phase (decrease of the surfactant concentration). In the $C_{12}E_5$–water–decane system, the change in spontaneous curvature can be balanced by a small temperature increase in order to bring the system with adsorbed polymer back to balanced conditions. If the polymer effects on the spontaneous curvature are in this way counter-balanced by a simultaneous temperature increase, one finds that the middle phase microemulsion swells upon addition of adsorbing polymer. The swelling capacity of a balanced microemulsion is expected to increase with increasing bending rigidity of the surfactant film. While the swelling observed in the $C_{12}E_5$–water–decane system is consistent with an increased film rigidity due to polymer adsorption, one also has a contribution from interactions of overlapping polymer layers inside the water domains of the bicontinuous microemulsion.

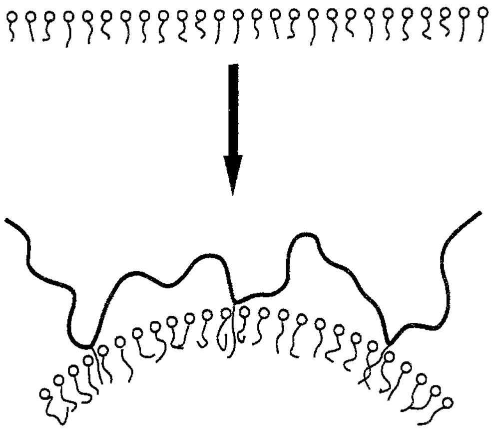


Fig. 15 Under good solvent conditions, the adsorption of polymer on the surfactant film results in an increase in the film spontaneous curvature away from water

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