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Abstract. We present experimental results on microemulsions made with water–alkane non-ionic surfactant systems that confirm the close relationship between the maximum characteristic size in the microemulsion and the persistence length of the surfactant layer. The microemulsion structures are found with surfactants that form films of small bending elasticity. When the bending elasticity is too large, ordered lamellar phases are obtained. When it is too small, the surfactant film cannot form, and the medium is a structureless molecular mixture. This evolution is associated with a wetting transition.

1. Basic concepts

Microemulsions are thermodynamically stable mixtures of oil and water, stabilized by surfactant molecules [1, 2]. Their structure is frequently made of droplets, either of oil or water, surrounded by a surfactant monolayer. This is because the surfactant layer has a preferred curvature C_0: if C_0 is positive (negative), the layer tends to curve towards water (oil) and an oil in water (o/w) (a water in oil, w/o) microemulsion is obtained if the amount of oil (water) is small. The droplet radius is given by:

$$R = 3\varphi/C_s\Sigma \tag{1}$$

where φ is the dispersed phase volume fraction, C_s the surfactant concentration (number of molecules per unit volume) and Σ the area per surfactant molecule in the monolayer. It has been experimentally found that Σ is relatively constant for a given surfactant: this supports the assumption that the surfactant layer is compact and rather incompressible [1].

When the amount of oil (water) is increased, the droplet radius increases according to (1), and eventually reaches the spontaneous radius of curvature $R_0 = |C_0^{-1}|$. At this point, when more oil is added, this oil is rejected in an excess phase. This is called the emulsification failure [3]. In some cases, phase separation occurs earlier: when the droplet radius increases, attractive interactions between the droplets can become important, and a phase separation between two microemulsion phases is observed. The behaviour is analogous to the liquid–gas transition in simple fluids.

When the spontaneous curvature C_0 is small, different types of structure are obtained. In some cases, the structure is lamellar: oil and water layers separated by surfactant monolayers. This structure possesses long-range orientational order and is distinct from a microemulsion, which is a disordered phase: first-order transitions are

currently observed between microemulsions and lamellar phases. In other cases, a microemulsion phase is obtained for small C_0 values: as a droplet microemulsion, it is an isotropic phase. Unlike lamellar phases, this particular microemulsion is continuously connected to the droplet microemulsion phases. But it has a random, sponge-like, continuous oil and water structure, i.e. it is a bicontinuous phase. From random space-filling models, the mean size ξ of the oil and water microdomains can be calculated. With a cubic lattice:

$$\xi = 6\varphi_0 \varphi_w / C_S \Sigma \tag{2}$$

where φ_0 and φ_w are respectively the oil and water volume fractions. ξ increases with φ_0 and φ_w and reaches a maximum ξ_0, above which the oil and water are rejected as excess phases: a generalization of the emulsification failure concept.

For a given set of conditions (temperature, chemical potential, composition), the fact that the system displays well defined structures (w/o, o/w, bicontinuous, lamellar) can be explained by considering the properties of the interfacial layer. Its bending energy per unit area can be written as [4]

$$F = \tfrac{1}{2}K(C_1 + C_2 - 2C_0)^2 + \bar{K}C_1C_2 \tag{3}$$

where C_1 and C_2 are the local principal curvatures of the surfactant layer and K and $\bar{K}$ are respectively the splay and the gaussian bending elastic moduli. In the following, $\bar{K}$ will be assumed to be zero unless stated otherwise.

When C_0 is large in absolute value, we have seen that the maximum droplet size is close to $1/C_0$. But when $C_0 \sim 0$ and K is of the order of kT, this is no longer true. In this case, the monolayers are locally flat but strongly undulated due to thermal motion. The cut off wavelength of the thermal fluctuations is the persistence length [1]:

$$\xi_K = a \exp(2\pi K/kT) \tag{4}$$

a being a molecular length. ξ_K is the correlation length for the normals to the layer, i.e. the distance over which the layer remains flat.

Experiments show that bicontinuous microemulsions are not completely random: there is a rather well defined characteristic distance between the oil and water micro-structural elements. This distance corresponds to the mean size in the space filling models, as given by (2). There are now two types of theories attempting to give a physical significance to ξ_0, the maximum value of ξ. Indeed, because of the strong thermal fluctuations, ξ_0 is more likely to be related to ξ_K than to C_0^{-1}.

In the first type of theories, the free energy of the system is calculated by incorporating the dispersion entropy, the interfacial energy and the bending energy (3). Since the bicontinuous microemulsions can coexist with both excess oil and water, these theories have to account for three phase equilibria. This can be done by assuming that the surfactant film is not fully incompressible (the interfacial energy accounts for the Σ variations) [5, 6]. The relationship between ξ_0 and ξ_K obtained in this way is rather indirect. A second approach can be made by assuming that the surfactant monolayer is incompressible but that the elastic constant varies with the scale, as recently demonstrated [7, 8]. In this way, ξ_0 is found to be proportional to ξ_K [9].

The second type of theories are lattice theories, in which the treatment of the system free energy is more rigorous [10–12]. However, a phenomenological microscopic bending elasticity has to be used and the connections between the results and the macroscopic notion of persistence length is still far from clear. However, when the degree of amphiphilicity of the surfactant, i.e. its probability to sit at the oil-water

interface increases, an evolution from a structureless (molecular) mixture to a micro-emulsion and finally to a lamellar phase is predicted. The evolution predicted by the phenomenological theories is similar. Indeed, the degree of amphiphilicity as well as the elastic modulus K increase with chain length.

In one of the recent lattice models, Gompper and Schick [12] predict that the asymptotic form of the correlation function for $r \to \infty$ is proportional to $\exp(-r/\xi_1)$ $\sin(2\pi r/\xi_2)/r$. This form has been used by Teubner and Strey to fit small angle x-ray and neutron scattering spectra of a number of different bicontinuous microemulsion systems [13]. The transition between structureless mixtures and bicontinuous structures corresponds in the model to $\xi_2 \to \infty$. In structureless mixtures, the correlation function should indeed decay exponentially without oscillations, as in ordinary liquid phases. More recently, Gompper and Schick [14] used a Ginzburg–Laundau theory to show that this transition should be associated to an unusual wetting transition. It is known that bicontinuous microemulsions fail to wet the o/w interface [15, 16]. The model predicts that when $\xi_2 \to \infty$, i.e. when the peak of the scattering spectra disappears, the surfactant rich middle phase will wet the o/w interface.

In this paper, we will present experimental determinations of microemulsion micro-structures and of interfacial properties made with a series of non-ionic surfactants of increasing chain length. We will explore the boundaries with molecular mixtures on one side and lamellar phases on the other.

2. Experimental details

The microemulsions studied here are mixtures of water, alkanes and non-ionic surfac-tants, alkyl polyglycol ethers (C_iE_j). Four surfactants of increasing chain lengths have been chosen in order to vary the bending elastic constant of the surfactant layer: C_6E_2 and C_8E_3 (from Bachem), $C_{10}E_4$ and $C_{12}E_5$ (from Nikko Chemicals). The corresponding alkanes are hexadecane, decane, octane and hexane respectively. In this way, the temperatures at which middle phase microemulsions are obtained fall in the same range. For $T < T_l$ one obtains an o/w microemulsion coexisting with excess oil and for $T > T_u$ a w/o microemulsion coexisting with excess water. For $T_l < T < T_u$, a middle phase microemulsion coexisting with both excess oil and water is obtained [17]. This phase transition when the temperature is increased is due to dehydration of the ethylene oxide groups, leading to a decrease in the bulkiness of the surfactant polar moitie, i.e. to a decrease in C_0.

The width of the three phase region becomes very large for C_6E_2, from below 18 °C (freezing point of pure hexadecane; in the presence of dissolved surfactants and water, the freezing point is found to be 15–16 °C) to 63 °C. In this system, a wetting transition has been observed by Robert and Feng at $T_w = 49$ °C [18]. Below T_w, the middle phase forms a lens at the oil–water interface, above T_w, it wets this interface.

In this study, neutron scattering experiments have been performed on the middle phase microemulsions. Typical experimental spectra are shown in figure 1. They have been fitted with the Teubner and Strey form [13]:

$$I(q) = A/(1 + aq^2 + bq^4) \tag{5}$$

q being the scattering wave vector, A, a and b, three adjustable parameters. They are related to the characteristic lengths of the correlation function ξ_1 and ξ_2 through:

$$\xi_1 = (2\sqrt{b})^{1/2}/(1 + a/2\sqrt{b})^{1/2}$$
$$\xi_2 = 2\pi(2\sqrt{b})^{1/2}/(1 - a/2\sqrt{b})^{1/2} \tag{6}$$

The corresponding values of ξ_1 and ξ_2 are reported in table 1. The quality of the fits
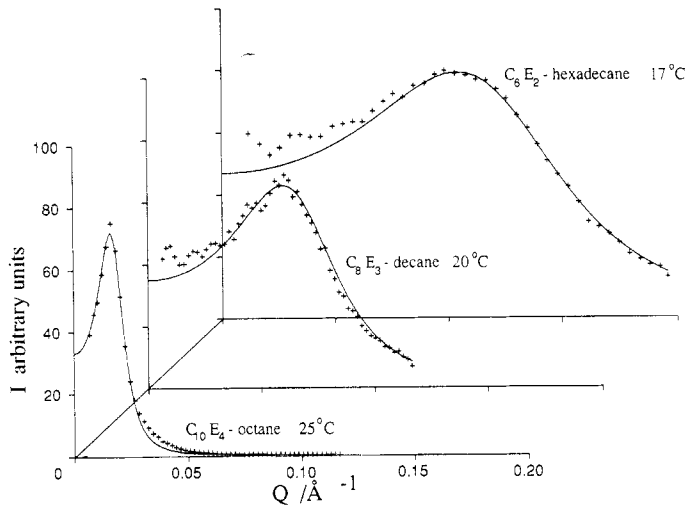
Figure 1. Typical neutron scattering spectra for the microemulsions made with the different surfactants. The lines have been fitted using equation (5).

Table 1. Measured sizes and calculated persistence lengths.

| System	T (°C)	$\xi_0 = \pi/q_{\max}$ (Å)	ξ_1 (Å)	ξ_2 (Å)	ξ_2/ξ_1	ξ_k (Å)
C_6E_2	17	31	17	53	3.1	
C_8E_3	20	54	38	99	2.6	69
$C_{10}E_4$	25	196	151	361	2.39	211

at large q is not very good, but this is not surprising since (5) is the Fourier transform of the asymptotic form of the correlation function for $r \to \infty$. For $C_{12}E_5$, no peak is observed in the spectra. This is probably because the characteristic sizes are too large and the peaks corresponding to these correlation lengths occur at q values smaller than the range of q used in this study. In table 1, we also give the values of the persistence length calculated from independent determination of K using ellipsometry [19]. As expected, the characteristic lengths increase rapidly with surfactant chain length and the ratio ξ_2/ξ_1 decreases.

Figure 2 shows the evolution of the scattering spectra for C_6E_2 versus temperature. Contrary to the predictions of Gompper and Schick [14], the peak is not displaced towards $q = 0$ at the wetting transition. Rather, it moves towards larger values when the temperature is increased. This discrepancy with the theory could be due to the role of long range forces [20]. Indeed the wetting transition seems to be first order rather than second order, according to the measurements of the contact angle [21].

Further work is currently under way to understand the transition towards the lamellar phases.

3. Conclusion

We have studied a series of bicontinuous microemulsions made with surfactants of different chain length. At a critical chain length, the wetting transition predicted by
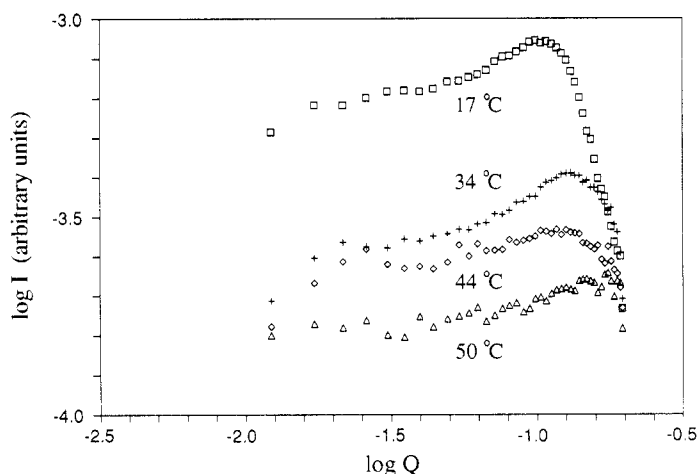
Figure 2. Neutron scattering spectra for the microemulsions made with C_6E_2 versus temperature.

theory is observed: the middle phase microemulsion does not wet the o/w interface below the wetting transition temperature; above this temperature, wetting occurs. The peaks of the scattering spectra do not move towards the origin as predicted by the theory. This could be due to the role of long-range forces which have not been taken into account in this theory but which are necessary to produce a first-order wetting transition. Although the oscillatory part of the correlation function does not disappear at the wetting transition, the scattered intensity decreases, indicating that the microemulsion structure is becoming more disordered.

The characteristic sizes in the microemulsion increase with increasing chain length and are comparable to the persistence length of the surfactant layer. This is also observed in other systems made with ionic surfactants [22]. The ratio of the periodicity ξ_2 of the oscillations of the correlation function to the damping length ξ_1 decreases. For longer chain surfactants, lamellar structures are observed.

Acknowledgments

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