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## Microemulsions

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### ABSTRACT

Microemulsions are transparent or translucent mixtures of oil, water, electrolyte and one or more surfactants. They form spontaneously from the ingredients and are thermodynamically stable. *Microemulsions may be dispersions of very small water droplets in oil, or of oil droplets in water, or they may contain bicontinuous intertwinements of water and oil.* Equilibria between microemulsions and molecularly dispersed oil and/or water phases exist.

The surfactants promote a very low interfacial tension, and give the interfaces a certain stiffness against bending and a preferred radius of curvature. With these elements and the entropy of mixing of the microemulsion droplets with the medium a quantitative theory of microemulsion stability and of microemulsion phase equilibria can be formulated.

### INTRODUCTION

Oil and water do not mix. At best one can have *emulsions*, i.e. droplets of oil dispersed in water (O/W) or droplets of water dispersed in oil (W/O). Such emulsions are prepared by vigorous shaking or stirring or by cleverly letting the droplets grow molecule after molecule. The droplet size in emulsions is usually between 1  $\mu\text{m}$  and 10  $\mu\text{m}$ . Emulsions are very turbid, already at a droplet concentration of a fraction of a percent.

The large interfacial area contains a large amount of free energy, equal to  $\gamma \times A$ , where  $\gamma$  is the interfacial tension and  $A$  is the interfacial area. Emulsions therefore age by *coalescence* (flowing together of droplets when they make contact) and by *Ostwald ripening* (transfer of material via the medium from small droplets to larger ones) since these processes cause the interfacial area to decrease.

Coalescence can be prevented by coating the droplets with a layer that prevents contact. Such a layer may consist of proteins or of soaps or of similar materials. These *emulsifiers* (also called *stabilizers* or *protective agents*) must always be *surface active*, i.e. they must be spontaneously adsorbed at the interface.

A few examples of emulsions are:

*mayonnaise*, an emulsion of oil in water, stabilized by the lipids and proteins from egg-yolk,

*milk*, an emulsion of milkfats in an aqueous solution stabilized by proteins,

*latex*, an emulsion of rubber droplets in water, stabilized by proteins in the natural (fresh) state, by ammonium soaps in the transport state, and in the case of synthetic latices by ionic or non ionic soaps.

Both milk and latex are examples where the emulsion is not prepared by mechanical agitation, but by well regulated growth of the droplets.

In 1943 Hoar and Schulman described transparent or translucent mixtures of about equal masses of oil and water in the presence of large amounts of a combination of an *ionic surfactant* and a non ionic *cosurfactant*. Medium chain length alcohols are effective cosurfactants. A typical example contains (in weight percent)

oil	water	ionic surfactant	cosurfactant
34% toluene	33% water	23% K-oleate	10% hexanol

Light scattering, X-ray scattering and other physical properties show that the above mixture is a dispersion of aqueous droplets with a diameter of about 8 nm (80 Å) in the oil, most of the potassium oleate and the hexanol being at the interface between droplets and oil. The small size of the droplets explains the low turbidity of these systems, since in a first approximation the turbidity is proportional to the mass concentration times the mass of one droplet. In 1959–1960 (Schulman et al., Stoeckenius et al.) the term *microemulsion* has been proposed for these systems.

The most essential difference between microemulsions and ordinary emulsions is not in the size of the droplets or in the turbidity, but in the aspect that microemulsions form spontaneously, that their properties are independent of the way of mixing, that they do not age, and thus that they are *thermodynamically stable*, whereas ordinary emulsions require mechanical (stirring, shaking) or chemical (as in latex formation by emulsion polymerization) work in their formation, so that they are at best *kinetically stable* (i.e. protected against real contact at collisions between the droplets) and that they always change with time.

A great deal of research on microemulsions has been published between 1943 and 1960 but then the interest waned, to be resumed in the late sixties when it became clear that these systems might be important for enhanced oil recovery and in other applications. At present both fundamental and applied research is very lively in the microemulsion field.

In normal oil recovery wells become unproductive after only about half of the oil present in the formation has been brought to the surface. The remaining oil is present in the form of droplets. It cannot be pushed through the formation by waterflow, since the deformation of the droplets necessary to allow them to flow through narrow gaps requires too much interfacial energy water/oil. This is shown schematically in figure 1. A surfactant solution that can produce a microemulsion has necessarily a very low interfacial tension against oil. If such a solution is injected in the formation, it will allow the oil droplets to be deformed at very little energy cost and thus it may push them to the production well (Bansal and Shah, 1977). The process encounters many difficulties, such as high temperature, high salt content, channelling, adsorption of the expensive surfactant at the formation, and thus a great deal of research is still required.

Other areas of application of microemulsions are (Prince, 1977a): cutting oils, that provide cooling and lubrication in one fluid, floor and leather polishes that are O/W microemulsions and have a low viscosity and dry to a high shine. *Self emulsifiable oils* used in agricultural sprays (Moilliet et al., 1961) are often microemulsions in the concentrated state so that they can contain the relatively large amount of surfactants necessary to stabilize the emulsion of the active substance formed after dilution with water. A fairly recent application is the use of microemulsions in reactions between hydrophilic and oleophilic reactants. This allows among other things the use of watersoluble enzymes in reactions with oil soluble substrates. A nice example (Hilhorst et al., 1983, 1984) is the reduction of progesterone in oil by hydrogen gas which first reduces methylviologen in water with the aid of hydrogenase. The reduced methylviologen then reduces nicotineamide via lipoamid dehydrogenase. Finally the reduced nicotinamid reduces progesteron at the water/oil interface, using 20 $\beta$ -hydroxysteroid dehydrogenase as the catalyst.

Finally a completely different application of microemulsions is found in pure research. Microemulsions can behave to a large extent as suspensions of hard spheres (Caljé et al., 1977; Vrij et al., 1978). They can be used to investigate

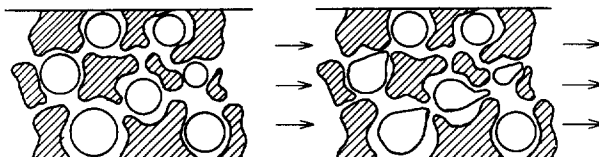


Fig. 1. Schematic picture of oil drops remaining in the formation and their deformation in flow from left to right.

light scattering, viscosity and other properties of such suspensions and even as models for fluids of spherical molecules, the droplets simulating the molecules and the continuous medium acting as a structureless background.

#### LOW INTERFACIAL TENSIONS

Since microemulsions contain a very large interface between oil and water, they can only be thermodynamically stable if the interfacial tension,  $\gamma$ , is very low, indeed so low that the positive interfacial free energy  $\gamma \times A$  ( $A$  is the area of the interface) can be compensated by the negative free energy of mixing ( $= -T \times$  entropy of mixing). The entropy of mixing per droplet is of the order of  $+k$ , where  $k$  is the Boltzmann constant.

Therefore

$$(1) \quad kT \approx 4\pi a^2 \gamma$$

with  $a$  = the radius of the droplets. If  $a = 10 \text{ nm}$ ,  $\gamma \approx 0.03 \text{ mNm}^{-1}$  ( $\text{dyne cm}^{-1}$ ).

The interfacial tension between oil and water is of the order of  $50 \text{ mNm}^{-1}$  and it is the role of the surfactants to lower this interfacial tension to close to zero. Because of the amphipolar nature of surfactants (they contain a polar part, often ionic, and a non polar part, often a fairly long hydrocarbon chain) they are adsorbed spontaneously at the water/oil interface, and this facilitates the extension of the interface, thus lowering the interfacial tension. Gibbs (1878) expressed this quantitatively in the equation (see also Adamson, 1967)

$$(2) \quad \frac{\partial \gamma}{RT \partial \ln c_i} = -\Gamma_i$$

where  $\Gamma_i$  is the amount adsorbed per unit area,  $c_i$  is the concentration of the surfactant,  $R$  is the gas constant and  $T$  the absolute temperature.

In figure 2 the interfacial tension,  $\gamma$ , (or surface tension) is plotted against the logarithm of the concentration of a soap or a similar surfactant.

According to eq. (2) the slope of that curve is proportional to the adsorption.

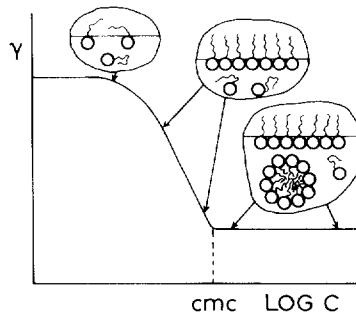


Fig. 2. Surface tension or interfacial tension,  $\gamma$ , plotted against the logarithm of the concentration,  $c$ , of a surfactant. cmc = critical micelle forming concentration. The polar group of the surfactant is represented as a circle, the hydrocarbon tail as a wavy line. Saturation adsorption often starts at 15–25% of the cmc.

At low concentrations the adsorption is small and  $\gamma$  decreases only slowly. At intermediate concentrations the adsorption is often found to be constant, especially in the presence of an excess electrolyte. Obviously the interface is full and *saturation adsorption* is reached (Van Voorst Vader, 1960). The interfacial tension decreases rapidly with increasing  $\log c$  until, over a very small concentration range,  $\gamma$  becomes virtually constant. Eq. (2) would require the adsorption to fall back to zero, which is utterly improbable. The correct explanation is that eq. (2) is an approximation.  $\ln c$  in the denominator should be  $\ln$  (activity) and although below the concentration marked cmc activity and concentration are nearly proportional, above it the activity remains constant although the concentration continues to grow. This behavior is explained by the formation of *micelles*, agglomerates of many (e.g. 50) soap molecules. On account of their amphipolar nature, surfactants are in a state of high free energy when individually dispersed and at a certain concentration, the *critical micelle forming concentration* (cmc), the individual molecules associate reversibly to particles that are large enough to hide all the non polar parts from the water with all polar parts at the surface and in contact with the strongly polar water molecules. Above the cmc the concentration of individually dissolved molecules remains constant (or nearly so) and thus the interfacial layer and the interfacial tension remain constant too.

Since this symposium has been set up in memory of Professor Debye, it should be remarked here that, after earlier work on micelles by McBain (1913), Hartley (1936) and others, he has made important contributions to our understanding of micelles. In 1948 he developed a model for an ionic micelle, the size of which was determined by an equilibrium between the free energy decrease caused by the hiding of the non-polar parts from water and the free energy increase due to the accumulation of electric charge on the surface. Furthermore he showed in 1949 how the size (the *micellar molecular weight*) of the micelle could be determined from the light scattering (or turbidity) of the solution with a slight adaptation of an equation he had derived earlier (Debye, 1944, 1947) for the light scattering of polymer solutions.

In 1952 I met Prof. Debye for a short time, when we were both on a consulting visit with a U.S. firm. He drew figure 2 for me and asked me where I thought the surface would be saturated. Then he pointed out the remarkable fact that in the steep part of the curve the surface composition remains constant, whereas the surface tension or interfacial tension changes dramatically. That was a lesson I have never forgotten.

Back to the low and ultralow interfacial tensions now. Micelle formation usually prevents  $\gamma$  from reaching very low values. But, if a second surfactant, rather different from the first one, is added, then the effects of the two surfactants enhance one another, and the interfacial tension may become extremely low, as illustrated in figure 3. The Gibbs equation (2) can be extended to the case of two or more surfactants. It can be written

$$(3) \quad d\gamma = -\Gamma_1 RT d \ln c_1 - \Gamma_2 RT d \ln c_2 \text{ etc.}$$

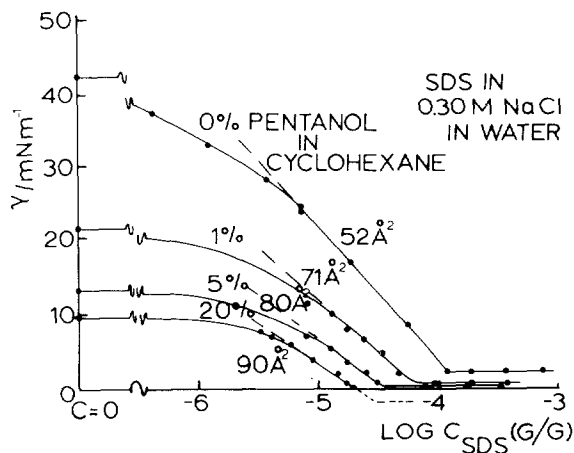


Fig. 3. Interfacial tension between solutions of sodiumdodecylsulphate (SDS) in aqueous 0.30 M NaCl and solutions of n-pentanol in cyclohexane. Pentanol (5%) decreases the interfacial tension already to about  $13 \text{ mNm}^{-1}$ . SDS can then bring the interfacial tension to nearly zero and with 20% pentanol zero interfacial tension is reached before micelles of SDS in water are formed. The area per SDS molecule, determined with eq. (2) increases from  $52 \text{ \AA}^2$  in the absence of pentanol to  $90 \text{ \AA}^2$  with 20% pentanol in the oil phase.

showing the effects of the two surfactants to be additive, as long as there is not too much interference between the two adsorptions and the concentrations are not spoiled by mixed micelle formation. With a mainly water soluble ionic surfactant and a mainly oil soluble cosurfactant the interfacial tension can become so low that further increase in concentration is not possible without making  $\gamma$  negative. A negative  $\gamma$  would imply that the interface expands spontaneously, taking up the excesses of surfactant and cosurfactant, thus bringing  $\gamma$  back to a positive value and in the meantime generating a microemulsion spontaneously. The curve for 20% pentanol in figure 3 is a case in point.

It should be mentioned that in a few cases very low interfacial tensions can be reached and microemulsions can be formed with a single surfactant without cosurfactant. This occurs in particular with double chain ionic surfactants and with some non-ionic surfactants in the fairly narrow temperature range where their oil solubility becomes comparable to their water solubility.

#### MODELS FOR MICROEMULSIONS

Figure 3 shows that one molecule of SDS (sodium dodecylsulphate, a much used surfactant with a  $\text{C}_{12}\text{H}_{25}$  chain and sulphate as the polar group) occupies  $80\text{--}90 \text{ \AA}^2$  in the range where microemulsions occur at 0.3 M NaCl. This area depends only weakly on the concentration and nature of the cosurfactant and on the electrolyte concentration. Thus one gram of this surfactant (molecular weight = 288) occupies about  $(1/288) \times 6.02 \times 10^{23} \times 85 \text{ \AA}^2 \approx 1780 \text{ m}^2$ .

Several possibilities exist for accommodating such a huge interface in microemulsions, as illustrated in figure 4. We may have droplets of oil in water or

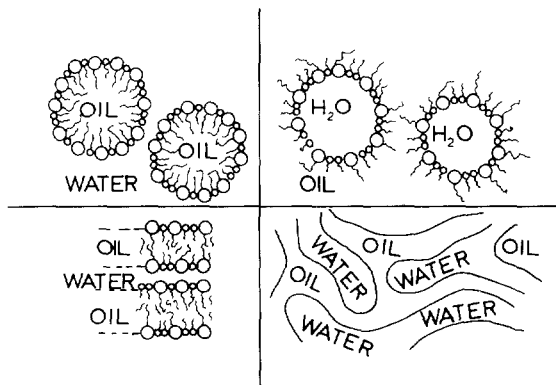


Fig. 4. Sketch of possible structures of microemulsions. Spherical droplets of W/O or O/W type, or liquid crystalline alternating oil and water layers, or an irregular bicontinuous structure. Most of the ionic surfactant and part of the cosurfactant is in the interface.

of water in oil, but there may also be ordered lamellar structures or more irregular bicontinuous structures. Light scattering and other experiments prove that many microemulsions contain indeed spherical droplets. In such cases the size of the droplets can be estimated from the composition of the microemulsion plus the area per surfactant molecule as determined from the interfacial tension. Nearly all the surfactant is in the interface, since the concentration in solution remains below the *cmc*. Consequently the total interfacial area,  $A$ , is nearly equal to the number of surfactant molecules,  $n_{sa}$  times the area per molecule,  $area_{sa}$ . For a W/O emulsion the total volume of the droplets,  $V$ , is nearly equal to the product of the number of water molecules,  $n_w$ , and the molecular volume of water  $v_w$ . With  $N_{dr}$  for the number of droplets and  $a$  for the droplet radius we have

$$(4) \quad N_{dr} \times 4\pi a^2 = A$$

$$(5) \quad N_{dr} \times \frac{4}{3} \pi a^3 = V$$

and thus

$$(6) \quad a = \frac{3V}{A} = \frac{3n_w v_w}{n_{sa} \times area_{sa}} = 1.06 \frac{n_w}{n_{sa}} \text{ \AA}$$

for  $area_{sa} = 85 \text{ \AA}^2$ .

#### THEORY OF MICROEMULSION STABILITY, FIRST STAGE

With the total composition and the character of the microemulsion (W/O or O/W) known, we can derive the size and the number of droplets from the eqs. (4)–(6). The only remaining freedom is the concentration of the surfactant ( $c < cmc$ ) in the aqueous part and the interfacial tension coupled to it via the  $\gamma$ - $\log(c_{sa})$  curve. Transfer of a small amount of surfactant between solution

and interface has only a minor influence on the area,  $A$ , but it may change  $c_{sa}$  and  $\gamma$  drastically.

The equilibrium situation is found by minimizing the free energy. This leads to a low positive interfacial tension and a small positive entropy of mixing (small, since the number of droplets is small compared with Avogadro's number).

But this cannot be the complete story. On this basis, there would be no upper limit to the droplet size (or to the water/surfactant ratio in the W/O case), if the interfacial tension can be close enough to zero. In fact, however, if one tries to raise the water/surfactant ratio at constant concentrations of cosurfactant and electrolyte above a certain maximum, the system splits into two macroscopic phases, one microemulsion containing all oil and nearly all surfactant and cosurfactant, but part of the water and the electrolyte form a separate non-colloidal phase.

#### PHASE EQUILIBRIA

In figure 5 phase equilibria are shown, prepared from equal volumes of an aqueous phase (water, SDS, NaCl) and an oil phase (cyclohexane, pentanol). At low concentrations pentanol O/W emulsions are found in equilibrium with excess oil; at high concentrations pentanol one finds W/O microemulsions plus an excess aqueous phase; in between three phase equilibria (W + microemulsion + O) occur at low amounts of SDS, but one phase microemulsions at higher amounts of SDS. Completely similar series of phase equilibria are found at constant concentration of pentanol but increasing concentrations of salt.

These equilibria are often described as *lower phase* or *Winsor I*, *upper phase* or *Winsor II*, *middle phase* or *Winsor III* equilibria and *single phase* or *Winsor IV* (Winsor, 1948, 1954, Robbins, 1977). Figure 6 shows the three phase region as a rather narrow closed area. It also shows that at 4% and smaller percentages

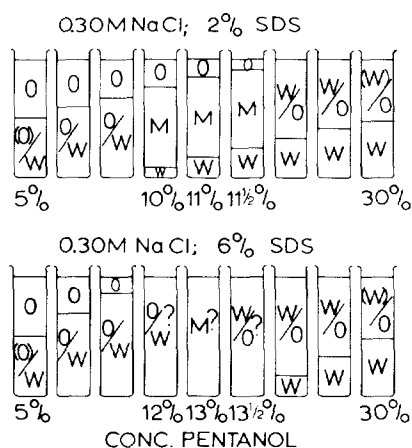


Fig. 5. Phase equilibria prepared from equal volumes of water,  $y\%$  in SDS and 0.3 M in NaCl and cyclohexane,  $x\%$  in pentanol. 25 °C.



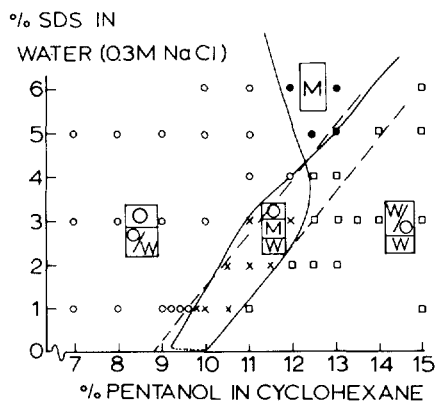


Fig. 6. Phase equilibria prepared as in figure 5. ○ = lower phase or Winsor I; × = middle phase or Winsor III; □ = upper phase or Winsor II; ● = single phase or Winsor IV.

SDS no single phase region occurs. In other words, even the most favorable concentration of pentanol does not allow a higher water/SDS ratio than 25/1 on a weight basis, corresponding to a maximal radius of water droplets (or for that matter of oil droplets) of a little over 400 Å according to eq. (6).

Just in passing we mention that at and above 10% SDS the one phase region splits up in one phase and two phase regions, several with liquid crystalline properties.

Once it is realized that microemulsions can be in equilibrium with a liquid of the same nature as the interior of the droplets (O/W + O or W/O + W) it might be expected that the increased entropy of mixing for an increased number of droplets would blow most of the drops contents to the equilibrium liquid, thus generating a very large number of very small drops. Apparently the two extreme possibilities, very large and very small drops are prevented by a certain stiffness of the interface, a resistance against bending away from a *natural radius of curvature*. This natural radius depends on the concentrations of co-surfactant and salt, on the nature of the various components and – slightly – on the volume fraction. It may be positive, favoring W/O emulsions, negative, favoring O/W emulsions or very large positive or negative, leading to bi-continuous structures as sketched in figure 4.

The general idea of a preferred direction of bending of the interface is already quite old. It is frequently, but not always, worked out by assuming that the interfacial film forms a separate layer between oil and water with two interfacial tensions or spreading pressures parallel to one another but a finite distance apart. Bancroft (1913) and Clowes (1916) used it for ordinary emulsions, Winsor (1948) and Bowcott and Schulman (1955) applied it to microemulsions. Good reviews are given by Robbins (1977) and Prince (1977b). Mukherjee, Miller and Fort (1983, see also Miller and Neogi, 1980) stressed the need for characterizing the interface by at least two parameters, e.g. the interfacial tension and a *bending stress*. The approach by Ninham and co-workers

(e.g. Mitchell and Ninham 1981), who introduce a preferred shape of surfactant molecules, can be seen as another way to introduce an extra parameter in the description of the interface. In this paper we shall first deal with the interface in a rather qualitative way and later describe the mechanical properties of the interface by a curvature dependent interfacial tension and a bending stress parameter, a method, that goes back to Gibbs' work (Gibbs, 1878, p. 225–228).

#### THEORY, SECOND STAGE

The stiffness and the preferred curvature of the interface are a consequence of the rather close packing of the adsorbed molecules. As illustrated schematically in figure 7 the hydrocarbon tails of surfactant and cosurfactant are crowded together when the interface is curved around the oil phase. The counterions of the ionic surfactants are crowded together when the interface is hollow at the water side. Both effects increase the free energy of the interface (the interfacial tension) and thus the tails promote the formation of W/O emulsions, the ionic atmospheres promote O/W.

Now a number of influences on microemulsion formation fall into place.

1. *more cosurfactant* promotes W/O, since the tails become more tightly packed.

2. *more electrolyte* in the aqueous phase promotes W/O, since the thickness of the ionic atmospheres (Debye length,  $1/\kappa$ ) is inversely proportional to the square root of the ionic strength and a thinner ionic atmosphere can be more easily bent.

$$(7) \quad \text{Thickness of ionic atmosphere} \equiv \frac{1}{\kappa} = \left( \frac{\epsilon_r \epsilon_0 RT}{\sum_i c_i z_i^2 F^2} \right)^{1/2}$$

where  $\epsilon_r$  is the dielectric constant of water,  $\epsilon_0$  the permittivity of the vacuum,  $c_i$  and  $z_i$  are the concentration and charge number of the ions of type  $i$ , and  $R$ ,  $T$  and  $F$  have their usual meaning. Much of our insight in the properties of ionic atmospheres (also called: electric double layers) is due to Debye and Hückel's work on strong electrolytes (1923, 1924). Important older work on flat double

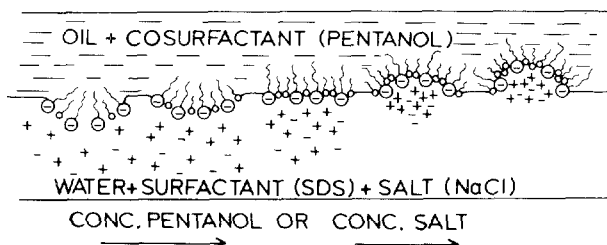


Fig. 7. Curvature of the oil-water interface changing under the influence of increasing concentrations of cosurfactant and/or salt from convex towards water to convex towards oil. More cosurfactant results in more crowding of the tails. More salt compresses the ionic atmosphere so that it can more easily be made concave to the water side.

layers is due to Gouy (1910, 1917) and Chapman (1913). Treatments of the influence of the curvature of the double layer are more recent and still in progress (Loeb, Overbeek and Wiersema, 1961, Levine and Robinson, 1972, Stokes, 1976, Overbeek, 1978, Mitchell and Ninham, 1983, Verhoeckx, 1985).

3. *Longer chain lengths* of surfactant and cosurfactant promote W/O, since the longer chains become more confined on bending.

4. *Longer chain length* of the oil promotes O/W since longer chains penetrate less easily between the chains of the surfactants.

5. The influence of the *temperature* is often small. Adsorption and the structure of the ionic atmosphere are not very sensitive to the temperature, neither is the entropy of mixing. Only in the case of polyethyleneoxide type non-ionic surfactants, and with aerosol OT, where the temperature drastically changes the water/oil partition coefficient the temperature effects are large (Kuneida and Shinoda, 1980).

From the foregoing it will be obvious that the interfacial tension as a function of the curvature must have a minimum, since strong curvature either way increases the interfacial tension. The natural radius is located at the minimum of the interfacial tension, and due to the entropy of mixing the actual radius of the droplets is smaller than the natural radius. Figure 8 shows this schematically.

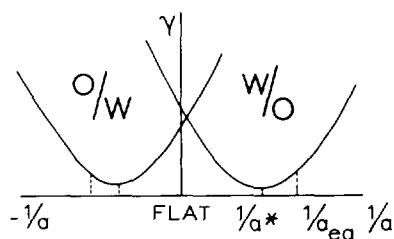


Fig. 8. Schematic representation of the interfacial tension,  $\gamma$ , between water and oil phases as a function of the curvature (more precisely half the curvature) of the interface. W/O corresponds to positive curvature (arbitrary choice), O/W to negative curvature.  $a^*$  = natural radius of curvature,  $a_{eq}$  = actual radius of the droplets of a microemulsion.

$1/a$  is chosen as the horizontal coordinate because then the transition between O/W and W/O is at  $1/a=0$ , where  $a \rightarrow \infty$ .

In most work on surfaces and interfaces the effects of curvature *on* the interfacial tension (not the effect of the curvature *of* the interface) may be neglected, because the radii involved are relatively large, say larger than  $1 \mu\text{m}$  and the interfacial tension is not extremely low. In microemulsions, however, the combination of a very low interfacial tension with a very strong curvature makes the curvature effects preponderant.

#### MIDDLE PHASE MICROEMULSIONS

Before going more deeply into the quantitative aspects of microemulsion theory, let us first consider the middle phase microemulsion more closely. The

middle phase microemulsion derives its name from the fact that it can be in equilibrium simultaneously with an oil phase and a water phase. From a model point of view it is a continuous transition between O/W and W/O microemulsions (see figures 5 and 6) and presumably a bicontinuous structure as sketched in the lower part of figure 4. Unfortunately there are no sharp experimental distinctions between O/W, bicontinuous and W/O types. Typical W/O microemulsions have a low electric conductivity, whereas O/W systems have a high conductivity. When going from W/O through middle phase to O/W the conductivity often starts to rise before the three phase region has been reached and continues to rise through the middle phase into the O/W region without any obvious breaks. This might mean that the middle phase covers a wider range of salt and cosurfactant concentrations than just the three phase region. It could also mean that close to the three phase boundary frequent Brownian encounters between droplets in W/O microemulsions allow enough charge (i.e. ions) transfer to increase the conductivity substantially.

However this may be, middle phase microemulsions have a limited water and oil content for a given interfacial area, since they can be simultaneously in equilibrium with water *and* with oil. Since the mean curvature of the interfaces in middle phase microemulsions must be small, the local thickness of water and oil regions must be limited, whatever the detailed bicontinuous structure. This can be interpreted as a consequence of the various interactions in these systems. The ionic atmospheres in the aqueous layers repel one another at distances of a few times the Debye length,  $1/\kappa$ . The hydrocarbon tails of the surfactants repel one another and prevent the oil layers from becoming too thin. On the other hand van der Waals attraction between the oil layers across the water gap and between the water layers across the oil tend to make the layers thinner. Thermal fluctuations will cause waviness of the interfaces and increase the average thickness of the layers. The combination of all these interactions will determine the oil content and water content of the middle phase microemulsions.

An interesting view on bicontinuous structures in micellar and microemulsion systems is given by Scriven (1977).

#### QUANTITATIVE ASPECTS OF THE THEORY

The discussion of the quantitative side of the theory will be limited to drop type microemulsions, since there the model is more explicit than for the middle phase type.

As mentioned earlier the Gibbs free energy of the microemulsion of a given total composition has to be minimized with respect to the distribution of the surfactants between droplet content, interface and dispersion medium. This results in a condition for *internal equilibrium*. Then we have to consider that part of the contents of the droplets may form a separate aqueous or oil phase in equilibrium with the remaining microemulsion. The minimal Gibbs free energy for this process gives the condition for *external equilibrium*. In certain cases, of course the free energy is minimal already without any second phase being formed.

The following elements enter into the formulation of the Gibbs free energy,  $G^M$  of the microemulsion.

1. The microemulsion contains amounts,  $n_i$  (in moles), of the components  $i$  ( $i$  = water, cyclohexane, SDS, pentanol, NaCl). If the droplets are not free to move around in the microemulsion we have the simple problem of the equilibrium of a number,  $N_{dr}$ , of drops of radius  $a$  with the surrounding medium. The chemical potentials,  $\lambda_i$ , are constant throughout the whole system. The pressure in the droplets is  $\Delta p$  higher than that in the medium. The total area of the interface is  $A$ , the interfacial tension,  $\gamma$ .

2. If the drops are free to move around, the free energy of mixing the drops with the medium has to be added. We use theoretical expressions for hard spheres (Percus and Yevick, 1958, Carnahan and Starling, 1969, 1970) that are valid up to quite high volume fractions,  $\phi$ .  $G^M$  then becomes (Overbeek, 1978, Verhoeckx, 1985).

$$(8) \quad G^M = \sum_i n_i \lambda_i - \Delta p V_{dr} + \gamma A + k T N_{dr} f(\phi, a)$$

$V_{dr}$  is the total volume of the drops. The term  $-\Delta p V_{dr}$  enters into eq. (8) because the droplets are at a pressure that differs from the ambient pressure. In eq. (8) the influence of the bending of the interface enters only implicitly through the dependence of  $\gamma$  on the radius,  $a$ . In the differential,  $dG^M$  it enters, however, explicitly.

$$(9) \quad dG^M = \sum_i \lambda_i dn_i - \Delta p dV_{dr} + \gamma dA + c A d\left(\frac{2}{a}\right) + k T d(N_{dr} f(\phi, a))$$

where  $c = (\partial\gamma/\partial(2/a))$  at constant chemical potentials. In eqs. (8) and (9)  $k T f(\phi, a)$  represents the free energy of mixing per droplet. The concentration dependent term is easily found (Overbeek, 1978), but the standard term is tricky. If the droplet would be just a small portion of the aqueous (for W/O) liquid, the standard term would already be included in the  $\lambda_i$ 's (Safran, 1983, Safran and Turkevich, 1983).  $f(\phi, a)$  would then be

$$(10) \quad f_S(\phi, a) = \ln \phi - 1 + \phi \frac{4 - 3\phi}{(1 - \phi)^2}$$

Reiss (1975, 1977), however, has pointed out, that a droplet in the laboratory frame has a fixed surface and a center of gravity that fluctuates around, whereas a droplet in the emulsion is described by its center of gravity moving around and contributing to eq. (10), whereas its surface fluctuates somewhat around that center of gravity. Using this model he finds that a term about equal to  $-\frac{3}{2} \ln(16a^3/v_w)$  has to be added to eq. (10), which is about  $-20$  for  $a = 100 \text{ \AA}$ . Accepting this argument we write

$$(11) \quad f_R(\phi, a) = \ln \phi - 1 + \phi \frac{4 - 3\phi}{(1 - \phi)^2} - \frac{3}{2} \ln \frac{16a^3}{v_w}$$

3. In the bending coefficient,  $c$ , in eq. (9) we need the Gibbs energy of the ionic atmosphere in (W/O) or around (O/W) a droplet as a function of the

radius,  $a$ . This requires the solution of the Poisson-Boltzmann equation for spherical symmetry and high potentials,  $\psi \gg RT/F$ . Overbeek (1978) has used a solution in the linear Debye-Hückel approximation valid for low potentials. Stokes (1976) has solved the problem as an expansion in powers of  $(1/a)$  for the O/W case. His solution can be adapted (Verhoeckx, De Bruyn and Overbeek, to be published) to the W/O case. The contribution of the ionic atmosphere,  $\gamma_{el}$ , to the interfacial tension is

$$(12) \quad \gamma_{el} = \gamma_{flat} + \frac{P_1}{\kappa a} + \frac{P_2}{(\kappa a)^2} + \frac{P_3}{(\kappa a)^3} + \text{etc.}$$

where  $\gamma_{flat}$ ,  $P_1$ ,  $P_2$  and  $P_3$  are known functions of the interfacial charge density.  $c_{el}$  then becomes

$$(13) \quad c_{el} = \left( \frac{\partial \gamma_{el}}{\partial (2/a)} \right)_{T, \lambda, x}$$

where  $x$  indicates that it has to be taken into account that the spherical surfaces corresponding to the interfacial charge (head groups of SDS), to the water volume ( $a$  as in eq. (5)) and to constant packing of the chains are separated by distances of a few Å. It turns out that a separation of only 2 Å between the charge surface and the constant packing surface has a considerable influence on  $c_{el}$  and on the phase equilibria connected with it.

4. We need also an expression for the influence of the hydrocarbon tails on  $\gamma$  and on  $c$ . In principle this can be found by an adaptation of the Flory-Huggins theory for polymer solutions (Flory, 1953). Huh (1983) has given the first terms of a series expansion in powers of  $(1/a)$  on this basis. Since this truncated series diverges for small  $a$  (small W/O drops) whereas one expects the effect of the radius to taper off for small  $a$ , we have used an empirical expression

$$(14) \quad \gamma_{tails} = L \exp(-l/a)$$

where  $L$  and  $l$  are adaptable parameters,  $L$  in the order of  $\text{mNm}^{-1}$  and  $l$ , in agreement with Huh of the order of a few times the length of the hydrocarbon chain.  $c_{tails}$ , the contribution of the tails to  $c$  is then

$$(15) \quad c_{tails} = -\frac{Ll}{2} \exp(-l/a)$$

The combination of eqs. (12) and (14) gives indeed for  $\gamma$  a curve of the type shown in figure 8.

*Application of the equilibrium conditions.*

Applying the condition for internal equilibrium in the form

$$(16) \quad (dG^M)_{p, T, \text{all } n_i} = 0$$

leads to

$$(17) \quad \gamma + \frac{2c}{a} = \frac{3kT}{4\pi a^2} \{-f(\phi, a) + z_1\}$$

where  $-f(\phi, a)$  is of the order of  $+20$  according to eq. (11) and  $z_1$  is a term of the order of  $-2$ , involving the adsorption of salt and the surfactants, the volume fraction and the droplet size. Similarly the condition for external equilibrium leads to

$$(18) \quad \Delta p = \frac{2\gamma}{a} - \frac{2c}{a^2} = \frac{3kT}{4\pi a^3} \{z_2\}$$

where  $z_2$  is a term similar to  $z_1$  varying from about  $+1$  to  $-10$ . From eqs. (17) and (18) it is found that

$$(19) \quad \gamma = \frac{kT}{4\pi a^2} \{-f(\phi, a) + z_3\}$$

and

$$(20) \quad c = \frac{kT}{4\pi a} \{-f(\phi, a) + z_4\}$$

with  $z_3$  between  $-1$  and  $-12$  and  $z_4$  between  $-2$  and  $+3$ .

When the effects of the free energy of mixing are neglected,  $\gamma$ ,  $c$  and  $\Delta p$  are all zero, the droplets have the natural radius  $a^*$  and the composition inside the droplets (far from the interface) is the same as in the equilibrium liquid.

The free energy of mixing causes  $\gamma$  and  $c$  to be positive,  $\Delta p$  to be negative in most cases, and  $a$  to be smaller than  $a^*$ , whereas the compositions of the droplets and the equilibrium liquid remain very close to being identical.

With eqs. (13) and (15) the bending parameter,  $c$ , can be expressed in the salt-concentration (via  $1/\kappa$ ), in  $l$ ,  $L$  and the distance  $x$  between the charge surface and the constant packing surface. With  $c$  known,  $a^*$  can be found from  $c=0$ . The actual radius can be found from eq. (20) when the volume fraction,  $\phi$ , is known. The interfacial tension between the drops and the medium can be found from eq. (19) and the interfacial tension between the macroscopic phases by a simple integration.

$$(21) \quad \gamma(\text{flat}) = \gamma(a) - \int_{1/a=0}^a c(a) d(2/a) + \sum_i \int_{\lambda_i}^{\mu_i} \left( \frac{\partial \gamma}{\partial \mu_i} \right)_{1/a=0} d\mu_i$$

where  $\mu_i$  is the chemical potential of component  $i$  in the final system. It may be expected that  $l$  and  $x$  are much less dependent on the cosurfactant concentration than  $L$ . If we assume  $l$  and  $x$  to be constant, we can find the relation between  $L$  and the cosurfactant concentration from the experimental relation between the radii,  $a$ , and the cosurfactant concentration.  $L$  increases with  $c_{co}$  as expected from the model.

Now we can plot  $a$  and  $\gamma$  against the cosurfactant (or salt) concentration. We find curves as sketched in figure 9 in agreement with experiments if we chose

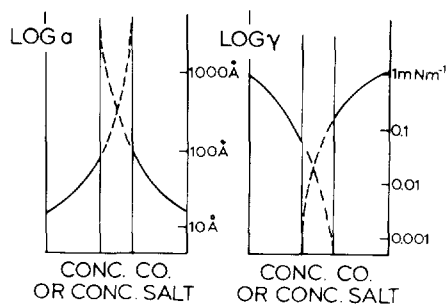


Fig. 9. Influence of the concentration of cosurfactant or salt on the particle radius,  $a$ , and on the interfacial tension,  $\gamma$ , between the microemulsion and the equilibrium oil and/or water phases. From left to right; O/W + O, O + M + W, W/O + W. Observed curves and curves calculated from the theory are in reasonable semi-quantitative agreement, even though the droplet model is not realistic in the middle phase region.

the parameters  $x$ ,  $l$  and  $L$  within reasonable limits.  $x = 2 \text{ \AA}$ ,  $l = 20 \text{ \AA}$  and  $L = 4$  to  $5 \text{ mNm}^{-1}$  work well.

The work is still in progress, but the results look promising. The main test will be how well the influence of the salt concentration and the volume fraction (or the surfactant concentration) is predicted.

#### CONCLUSIONS

A theory for droplet type ionic microemulsions is available and works reasonably well. Even in the middle phase region, where the model must be defective, the interfacial tensions follow the theoretical predictions.

The composition of the interface varies little in a wide range of conditions. The surfactant adsorption is saturated. The interfacial tension is widely adaptable through variation in the surfactant concentration, which remains below the cmc. The interfacial tension is mainly determined by the droplet radius (eq. 19).

Subtle effects govern the existence and the properties of microemulsions. Of these effects the bending stress of the interface is perhaps the most important. It is controlled by the crowding of the hydrocarbon tails and of the ionic atmosphere on bending of the interface.

A great deal of work still has to be done, especially in collecting more and better data on interfacial tensions and adsorptions and on the distribution of various components between the phases. In particular a better theoretical description of the middle phase is desirable.

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