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MICROEMULSIONS

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SUMMARY

Microemulsions are apparently homogeneous mixtures of water and oil with large amounts of surfactants. Microemulsions form spontaneously, are thermodynamically stable and contain particles that are so small that turbidity is low. The surfactants create an extremely low interfacial tension between oil and water, which promotes emulsification. In many, but not all cases, microemulsions can be regarded as rather monodisperse droplets of water-in-oil or oil-in-water. They may be in equilibrium with excess oil, excess water or both. Phase equilibria in these multicomponent systems are quite complicated. Often only two-dimensional cross-sections through the complete phase diagrams are used. Droplet size in microemulsions appears to be limited and this may be explained by the effect of curvature on the interfacial tension.

Most of this chapter deals with the combination of ionic surfactants and simple nonionic cosurfactants such as pentanol, but attention is also given to microemulsions stabilized by nonionic polyethylene oxide derivatives. Application of microemulsion systems in enhanced oil recovery and other applications are mentioned.

INTRODUCTION

Oil and water do not mix, but if some soap or another micelle forming surfactant is added, a small amount of oil is solubilized (Vold and Vold, 1983a) in the micelles and after vigorous shaking or stirring turbid emulsions are formed (Vold and Vold, 1983b). These emulsions are never really

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stable. The free energy contained in the interfacial area between the droplets and the continuous phase tends to destroy this interface and thus emulsions coarsen by Ostwald ripening (growth of large droplets at the expense of smaller ones) and coalescence.

In 1943 Hoar and Schulman described transparent or translucent systems, formed spontaneously when oil and water were mixed with relatively large amounts of an ionic surfactant combined with a cosurfactant, e.g. a medium size alcohol. These systems are dispersions of very small drops (radius of the order of 10 nm) of water-in-oil (W/O) or of oil-in-water (O/W). Since for small particles light scattering is proportional to the square of the volume of the scattering particle and obeys the equation (Rayleigh, 1871; Kerker, 1969)

$$I(\mathrm{scatt}) = I_0 f n V^2 \qquad (1)$$

these systems scatter little light and are not turbid. In equation (1) $I(\mathrm{scatt})$ is the intensity of the scattered light, I_0 that of the incident light, n the number of particles in the scattering volume, V the volume of one particle and f a factor which takes into account the refractive indices of the particles and their surroundings, the angle between incident and scattered light, the planes of polarization, and the lack of ideality of the dispersion.

These systems have been called microemulsions (Schulman *et al.*, 1959; Prince, 1977a). They differ from ordinary emulsions not only in their lack of turbidity but, more essentially, in being thermodynamically, i.e. indefinitely, stable. Because continuous transitions occur from molecular solutions via swollen micelles (or inverse micelles) to microemulsions, the transition from swollen micelles to microemulsions can only be located arbitrarily at a radius of the order of 3 nm.

In recent years microemulsions have attracted a great deal of attention because, if oil and water can be made to mix spontaneously, there may be hope of enhanced oil recovery by water flooding of dried up oil wells (Bansal and Shah, 1977).

REASON FOR COMBINING SURFACTANT AND COSURFACTANT

Spontaneous formation of an emulsion with decrease of the free energy can only be expected if the interfacial tension is so low that the remaining free energy of the interface can be overcompensated by the entropy of dispersion of the droplets in the medium. Surfactants do lower the interfacial tension, but in most cases the c.m.c. or the limit of solubility is reached before the interfacial tension is close to zero. Addition of a second surfactant of a completely

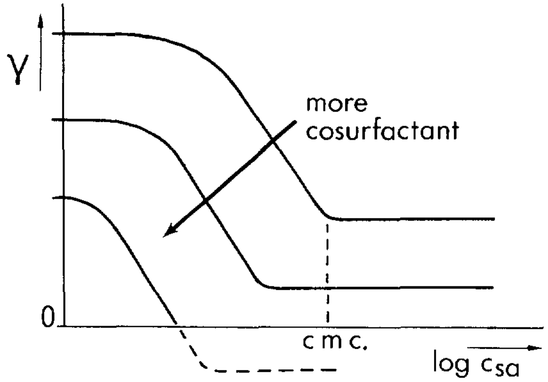

Fig. 1. Interfacial tension, γ, plotted against the logarithm of the surfactant concentration for three different concentrations of cosurfactant. The dotted part, below γ = 0, cannot be realized.

different nature then lowers the interfacial tension further and very small, even transiently negative values, may be reached, as illustrated in Fig. 1.

The well-known Gibbs adsorption equation for a two-component system (Adamson, 1967)

$$\left(\frac{\partial \gamma}{\partial \mu_{\text{solute}}}\right)_{p,T} = -\left(\frac{\partial n_{\text{solute}}}{\partial A}\right)_{p,T,n_1} = -\Gamma^{1}_{\text{solute}} \qquad (2)$$

can be extended to multicomponent systems to yield

$$d\gamma = -\sum_i \Gamma_i d\mu_i \simeq -\sum_i \Gamma_i RT d\,\ln c_i . \qquad (3)$$

In these equations γ is the surface tension or interfacial tension, μ_i is the chemical potential of component i, c_i its concentration, n_i its amount, Γ_i the amount of i adsorbed per unit area (= the surface excess), and A the surface or interfacial area. Component 1 is the solvent. Equation (3) shows that the addition to the system of a new surfactant which is positively adsorbed will always cause a further lowering of γ.

If γ were to become negative, as suggested by the dotted line in Fig. 1, the interface would expand, adsorb surfactants, until their concentration is lowered enough to make γ positive again.

In some cases single surfactants will lower γ far enough for microemulsion formation to become possible. Examples are: AOT (sodium diethylhexylsulphosuccinate) and many nonionic

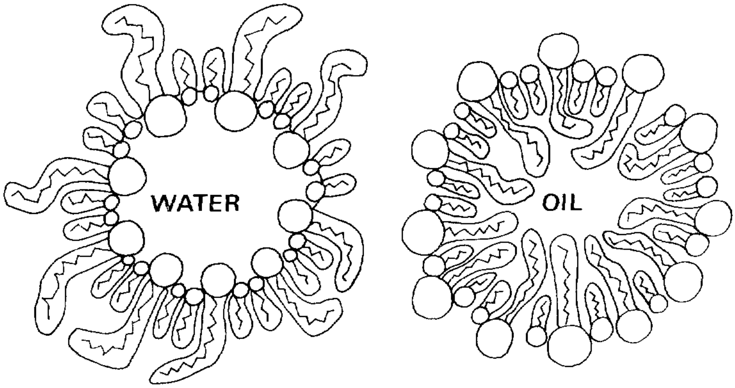

Fig. 2. Schematic pictures of a W/O and an O/W droplet with a long surfactant and a short cosurfactant. It should be clear that the polar heads are more crowded in W/O whereas the hydrocarbon tails are more crowded in O/W.

surfactants near the temperature where they change from being water-soluble to being oil-soluble.

MODEL CONSIDERATIONS

As a typical example of a microemulsion system we consider a combination of sodium dodecylsulphate (SDS), the surfactant ("sa"), pentanol, the cosurfactant ("co"), water with or without NaCl ("w") and a hydrocarbon, e.g. n-hexane, cyclohexane, hexadecane or toluene, the oil ("o").

To begin with, we assume that a microemulsion contains spherical droplets of uniform size. Fig. 2 gives a schematic picture of W/O and O/W droplets. The crowding of surfactant and cosurfactant in the surface as shown corresponds to reality.

In a microemulsion the concentration of sa in the aqueous phase is at or below the c.m.c. Most of the sa is therefore at the interface. The cosurfactant will be distributed more evenly between the oil phase and the interface, with a small but finite concentration in the water phase. The surface excesses of surfactant and cosurfactant can be found from measurements of the interfacial tension between macroscopic water and oil phases and application of the Gibbs adsorption equation (2,3). In the concentration ranges occurring in microemulsions the adsorptions show saturation behaviour in the sense that $\partial\gamma/\partial \ln c_i$ is constant (Van Voorst Vader, 1960),

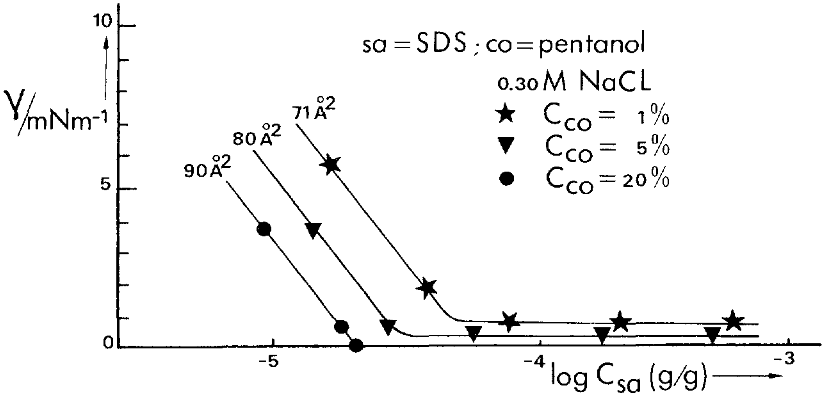

Fig. 3. Interfacial tensions between 0.30 M aqueous NaCl and cyclohexane, containing SDS in the aqueous phase and pentanol, mostly in the oil phase. From the slopes of the lines below the c.m.c. the area per SDS molecule is found, using equation (4). At 20% pentanol any excess of SDS above $c_{sa} = 2 \times 10^{-5}$ *g/g was taken up in the oil phase.*

but the value of Γ_{sa} depends on c_{co}, and Γ_{co} depends on c_{sa}. Fig. 3 shows surface excesses, Γ_{sa}, as from

$$\Gamma_{sa} = - \ [\partial\gamma/(RT\partial \ln c_{sa})]_{c_{co}} \tag{4}$$

in the presence of excess NaCl. These values may be assumed to equal those in the microemulsion, which cannot be easily determined. Depending on c_{co} and c_{NaCl} the area per SDS molecule is found to vary between 70 Å^2 and 110 Å^2. Under conditions where W/O microemulsions form the area per pentanol molecule is about 30 Å^2. These values mean that every 90 Å^2 of interface contains about one SDS molecule plus three pentanol molecules.

The model now becomes much more precise. In a W/O emulsion, the total volume, V, of the droplets is equal to the volume of water + salt, the total interfacial area, A, is equal to

$$A = n_{sa}/\Gamma_{sa} \simeq n_{sa} \times N_{Avog} \times 90 \text{ Å}^2 \tag{5}$$

where n_{sa} is the amount of surfactant. With volume and area known, the radius of the droplets, a, is then

$$a = 3 \times \frac{4}{3} \pi a^3/4\pi a^2 = 3V/A. \tag{6}$$

With $V = n_{\text{water}} \times 18\ \text{cm}^3\text{mol}^{-1}$ and $A = n_{\text{sa}} \times N_{\text{Avog}} \times 90\ \text{Å}^2$ equation (6) transforms into

$$a = (n_{\text{water}}/n_{\text{sa}})\,\text{Å}. \tag{7}$$

These surprisingly simple expressions give quite good values for the droplet radius. Other methods for the determination of the droplet size are: Rayleigh and dynamic light scattering (Vrij *et al.*, 1978), X-ray diffraction (Schulman and Riley, 1948), small angle neutron diffraction (M. Lagües *et al.*, 1978; Cebula *et al.*, 1982). These various methods lead to slightly different values for a, since equations (6) and (7) give the water radius, whereas the other methods also include a smaller or larger part of the adsorbed sa and co.

For O/W microemulsions, usually formed at lower concentrations of co, analogous equations are valid. The number of cosurfactant molecules per sa in the interface is smaller, perhaps 2 rather than 3.

Of course the actual numbers given in this section will be different if other components are chosen.

PHASE EQUILIBRIA

If the spontaneous formation of a large interface would be the only essential requirement for microemulsion formation, there would be no preference for O/W over W/O or the reverse.

However, the entropy of mixing of the droplets with the continuous phase would favour the phase with the smaller volume to form the droplets since, at a given interfacial area, the number of droplets is inversely proportional to the square of their total volume and a larger number of droplets leads to a larger entropy of mixing.

Moreover, experiment shows that microemulsions of either type may become saturated with respect to the droplets, long before a volume fraction of one half is reached. If more of the internal liquid is presented, such microemulsions form an equilibrium with the excess aqueous (for W/O emulsions) or oily (for O/W emulsions) phase and even three-phase equilibria, water-microemulsion-oil, exist although in that case our droplet model is suspect.

The understanding of such phase equilibria is an essential test of our understanding of microemulsions. Before proceeding further we must first consider whether microemulsions are to be treated as one- or two-phase systems.

ARE MICROEMULSIONS ONE- OR TWO-PHASE SYSTEMS?

A phase may be defined as a region of space filled homogeneously with matter. But it depends on the fineness of the grid that we use to determine homogeneity whether a solution, a colloidal suspension or a microemulsion are homogeneous or heterogeneous. This point of view seems to give difficulties with the phase rule. If we change arbitrarily the number of phases by one, then the phase rule tells us that we also change the number of degrees of freedom by one. And that cannot be correct.

The problem is already an old one and has been reviewed by Hermans (1952). The phase rule can be written:

$$f = n - p + 2 \tag{8}$$

where f is the number of degrees of freedom, n the number of components, and p the number of phases of the system. The number 2 refers to the independent variables temperature and pressure. One may consider $(n-p)$ in equation (8) as the number of concentrations that can be varied independently. In suspensions or emulsions one deals not only with the concentrations of the low molecular weight components but one must also consider the concentration of the particles, c_p. In a coarse suspension or emulsion this, however, is a "negligible variable" (Tolman, 1913) but in a microemulsion it affects the thermodynamic properties of the system, e.g. the chemical potential of the suspending liquid.

There are therefore two legitimate, equivalent but different ways to describe a microemulsion. It is a one-phase system, obeying equation (8) with $(n-1)$ independently variable concentrations; or, it is a two-phase system with $(n-2)$ independent concentrations plus an independently variable concentration of droplets, and thus again $(n-1)$ degrees of freedom.

The one-phase point of view is often the more obvious choice, especially in considering equilibria with other phases, but in calculating properties of microemulsions from their composition the two-phase approach is often preferable.

PHASE DIAGRAMS

Phase equilibria in microemulsions are best described with more or less schematic phase diagrams. Such phase diagrams are bound to be complicated, as we have to deal with four or five components and because the two-component water-surfactant phase diagram is already often complicated. Even at constant temperature and pressure, a four-component system can only be represented in three dimensions, e.g. in a tetrahedron. For simplicity we shall start with some three-component and pseudo-three-component diagrams.

Figure 4 shows schematically a phase diagram of a system containing only water (+ salt), sa, co, but no oil (Friberg, 1977; Danielsson *et al.*, 1982). The cosurfactant fulfils the

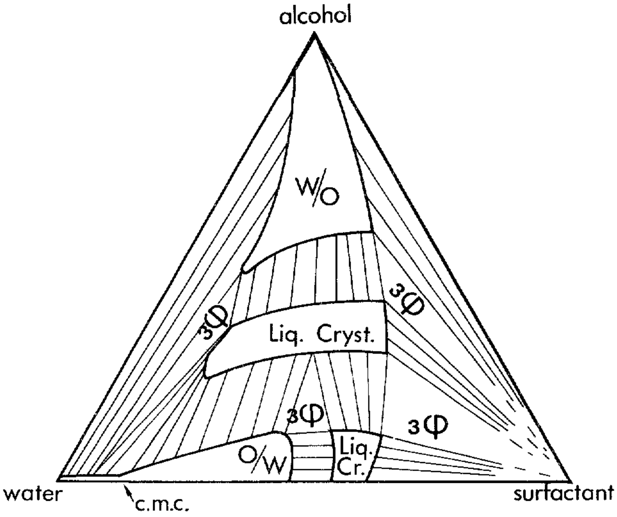

Fig. 4. Schematic three-component phase diagram for a water, surfactant, cosurfactant combination. It shows four one-phase regions, four three-phase (3φ) regions and a number of two-phase regions with tie-lines. The surfactant corner has been left vague. There may be hydrates, and/or further mesomorphic phases.

double role of co and oil. The diagram contains four one-phase regions, first a W/O microemulsion growing out from the region of true solubility of water in the alcohol. At the left-hand border (high water-surfactant ratio, large droplets, equation (7)) this phase is in equilibrium with a dilute sa solution in water, at the right-hand border with solid surfactant, and at the lower border (high droplet concentration) with a birefringent mesomorphic phase (assumed to be lamellar), itself the second one-phase region. An (inverted) hexagonal phase between the lamellar phase and the W/O region has been left out for simplicity.

A third phase is the isotropic O/W microemulsion, extending from the water corner as a molecular solution below the c.m.c. and with alcohol solubilized in the surfactant micelles above it.

The fourth one-phase region is again mesomorphic presumably containing hexagonally-packed cylinders, and growing out of the "middle soap" region in the water-surfactant phase diagram.

Between the various one-phase regions, two-phase regions

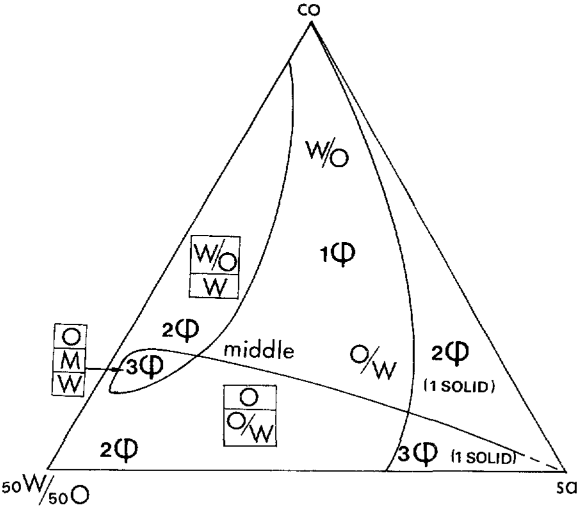

Fig. 5. Schematic cross-section through the complete three-dimensional phase diagram, with equal quantities of oil and water in one corner and co and sa in the other corners. In the two- and three-phase regions the kind of equilibria are indicated, but tie-lines cannot be shown since they are not in the plane of the figure. Middle refers to middle-phase microemulsion. For further details see text.

occur where the phases in equilibrium are connected by tie-lines, and triangular three-phase (3ϕ) regions, having zero degrees of freedom at constant p and T in a three-component system.

Addition of a small amount of oil, miscible with the cosurfactant, but not with water and the surfactant, changes the phase diagram only slightly, but addition of more oil leads to more fundamental changes as illustrated in Fig. 5 in which the boundaries are shown of one-phase, two-phase and three-phase regions for a system containing equal volumes of oil and water. Tie-lines are not shown, since they are not in the plane of this figure.

Near the co corner the changes as compared to Fig. 4 remain small, but the O/W microemulsion near the water-sa axis is now not in equilibrium with the lamellar phase, but with a non-colloidal oil + cosurfactant phase. If co is added to such a two-phase equilibrium at fairly high sa concentration all oil is taken up and a one-phase microemulsion appears.

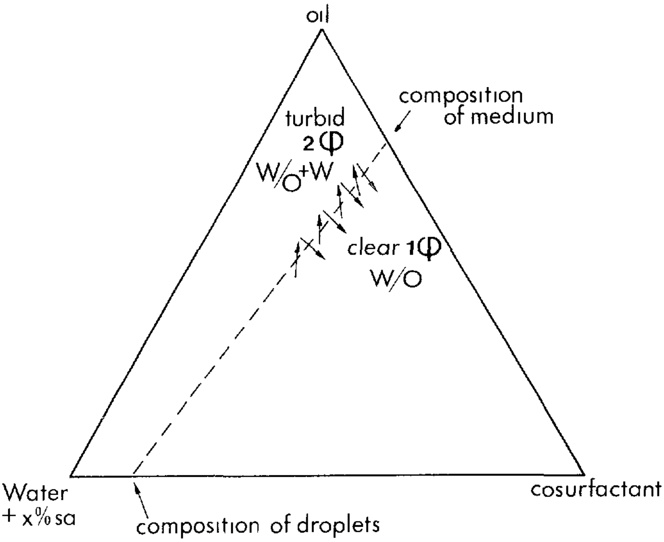

Fig. 6. Illustrates the titration procedure, which allows dilution of the microemulsion without changing the composition of the droplets.

But addition of co at low sa concentration may lead to separation of an excess aqueous phase before all oil is taken up in the microemulsion. A three-phase system is formed, containing a microemulsion that cannot be clearly identified as W/O or O/W and that presumably is similar to the lamellar phase swollen with oil or to a still more irregular intertwining of aqueous and oily regions. We have called this a middle-phase microemulsion.

The interfacial tensions between the three phases are very low, between 0.1 and 0.0001 mNm^{-1} or even lower than that. Further addition of co to the three-phase system makes the oil phase disappear and leaves a W/O microemulsion in equilibrium with a dilute aqueous sa solution. In the large one-phase region continuous transitions from O/W to middle-phase to W/O microemulsions are found.

In Fig. 6 still a further way of looking at the four-component system is given. Here a fixed water-surfactant ratio is shown in one corner, the other corners being co and oil. This figure also illustrates the titration procedure (Bowcott and Schulman, 1955), by which the composition of the droplets and of the continuous medium can be determined. A microemulsion (W/O in this case) is just at the border between the one-phase

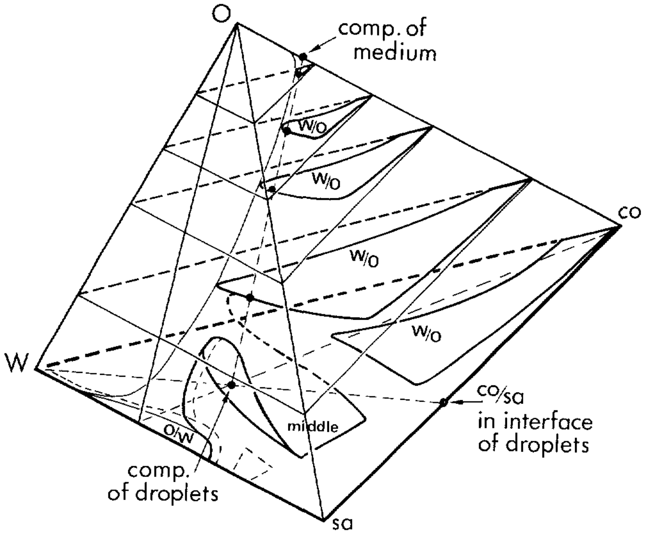

Fig. 7. Schematic four-component phase diagram. The merging of the W/O, O/W and middle-type one-phase regions is indicated. A titration plane as given in Fig. 6 is drawn in.

and the two-phase region. Oil and cosurfactant can be added alternately while just straddling the borderline, on one side of which the system is transparent, on the other side markedly turbid. The ratio of oil and co added in this process gives the composition of the continuous medium. Extrapolation of the borderline thus found to the w/sa-co axis gives the composition of the droplet and also, since the cosurfactant is hardly water-soluble and most of the sa is in the interface, the ratio of sa to co in the interface.

By using this titration procedure one can dilute a microemulsion without changing the droplet composition. It is assumed implicitly that this composition is hardly affected by the droplet concentration.

Finally a very schematic phase diagram in a four-component tetrahedron is shown in Fig. 7. On addition of oil to the w, sa, co system, the one-phase W/O region expands, changes shape, retracts again and disappears at high oil contents. The one-phase O/W region disappears already at modest oil contents from the o, w, sa triangle, but shifts to the inside of the tetrahedron, and may form a continuous microemulsion region with the middle and the W/O microemulsion. In this tetrahedron a titration triangle as given in Fig. 6 is drawn showing a dilution curve in its three-dimensional location.

It hardly needs to be mentioned that given the freedom to change surfactant, cosurfactant, oil and salt content large variations in the phase diagrams may occur. Nevertheless Figs 4 to 7 have their utility as a qualitative mnemonic device.

THERMODYNAMICS OF MICROEMULSIONS

Considering the complicated phase behaviour of microemulsions, we are left with a number of questions and few answers. A low interfacial tension O/W appears to be essential for the formation of a microemulsion, but we do not understand why O/W, W/O or still another structure is formed nor how the phase equilibria are controlled.

These and other questions may find their answers in thermodynamics. We therefore choose a model, minimize its calculated free energy and check whether the model explains typical phase equilibria.

Such programmes have been carried out by several authors of whom we mention Adamson (1969), Ruckenstein *et al.* (1975, 1979, 1980), Reiss (1975), Wagner (1976), Overbeek (1978), Miller and Neogi (1980), Mukherjee *et al.* (1983), Mitchell and Ninham (1981). None of the results so far obtained is completely satisfactory. We shall therefore give a rather simplified treatment of the W/O case, just to show which factors are involved. We use the model of spherical drops of equal size, large enough to make the description, as a drop of constant composition with a surface layer of adsorbed surfactants, acceptable. We "prepare" the emulsion in a number of steps and for each step calculate the Helmholtz energy, F, involved. The Helmholtz energy is chosen because the pressure inside the drops is higher by the Laplace pressure, $2\gamma/a$, than the pressure in the continuous medium.

First step Prepare the oil phase in its <u>final</u> concentration

$$F_1 = \sum_i n_i'\mu_i' - p_1V_1 \tag{9}$$

where n_i' and μ_i' are the amount and chemical potential of oil and cosurfactant in the continuous phase, without droplets being mixed in. p_1 is the atmospheric pressure, and V_1 the volume of the oil phase.

Second step Prepare the aqueous phase in its final concentration

$$F_2 = \sum_i n_i'\mu_i' - p_1V_2$$

where i are now water, surfactant and salt and V_2 is the volume of the water phase.

Third step Form the water phase into droplets, close packed in the oil phase, and add all the adsorbed material.

$$F_3 = \gamma A + \Gamma_{sa} A(\mu'_{sa} + \frac{2\gamma}{a} \overline{V}_{sa}) + \sum_i \Gamma_i A \mu'_i \tag{11}$$

where i refers to cosurfactant and oil. The oil must be negatively adsorbed in order to keep the volume of the adsorption layer zero, in accordance with the assumption of a Gibbs dividing plane. It is assumed in equation (11) that the Gibbs plane, the surface of tension in this case (see Hill, 1968), lies close enough to the surface, where $\Gamma_{water} = 0$.

Fourth step We allow the close packed emulsion to expand to its final concentration, thus generating the Helmholtz energy of mixing

$$F_4 = n_{dr} RT \, f(\phi) \tag{12}$$

where n_{dr} is the amount of droplets (in moles) and $f(\phi)$ is a function of the volume fraction, ϕ, of the droplets, most simply written ($\ell n \, \phi - \ell n \, 0.74$) and, more accurately, using the Percus-Yevick-Carnahan Starling (1969) approximation for hard spheres as

$$\begin{aligned} f(\phi) &= \ell n \, \phi + \phi \frac{4-3\phi}{(1-\phi)^2} - \ell n \, 0.74 - 0.74 \frac{4 - 3 \times 0.74}{(1-0.74)^2} \\ &= \ell n \, \phi + \phi \frac{4-3\phi}{(1-\phi)^2} - 19.25. \end{aligned} \tag{13}$$

The constant term, -19.25, deviates from the one given earlier (Overbeek, 1978), because now the free energy of mixing of droplets and medium is assumed to be zero at close packing, rather than deriving the standard chemical potential of the droplets from an assumed behaviour at high dilution.

Combining equations (9) to (13) gives the Helmholtz energy, F of the complete emulsion. The F is minimized with respect to a change in the interfacial area, A. This involves transfer of adsorbed components to or from the interface, thereby changing the bulk concentrations and thus γ. The result is then that

$$\gamma = -\text{const.} \times \frac{1}{a^2} \times g(\phi) \tag{14}$$

where $g(\phi)$ is similar to but not identical with $f(\phi)$. Since the radius, a, has to fit both equations (6) and (14), and γ is the most easily varied quantity in these equations, the correct value of γ is obtained by adaptation of c_{sa}. So far we have used the two-phase approach with n_{dr} (equation (12)) as the extra variable. We now switch over to the one-phase approach by calculating μ_w, μ_{sa}, μ_{salt} for the complete microemulsion ($\mu_i = \partial G/\partial n_i$, where $G = \sum_i^4 F_i + p_i(V_1+V_2)$) and check under which conditions these μ_i combine to an equilibrium solution.

It is at this stage that difficulties are encountered which point to inadequacies in the model. According to equation (14) any value of a is allowed in the accessible range of γ. In particular if γ can be close to zero very large radii, i.e. very large water/sa ratios are allowed, but in the phase diagram such large w/sa ratios lead to demixing.

It appears necessary to add an explicit influence of the radius of curvature on the interfacial tension to the model and thus to give the interfacial layer a limited range of curvatures that are acceptable. Notions of this nature have been introduced by several authors. Bowcott and Schulman (1955 suggested that the interfacial layer may have two different interfacial tensions, one at the water side and one at the oil side, which would cause the film to bend (duplex film theory). Mitchell and Ninham (1981) have extended the idea, that the limitations to the shape of close packed surfactants determine the shape of micelles and vesicles, to microemulsions. Mukherjee *et al.* (1983) have made fairly elaborate calculations of the free energy of mixing of the hydrocarbon tails of surfactant and cosurfactant with the oil molecules for curved surfaces and the free energy of the electric double layer is also curvature dependent (Overbeek, 1978).

If we look at Fig. 2 and consider the actual numbers for the surface area per surfactant, we see that the ionic headgroups are not close packed (100 Å^2, whereas if present alone they pack to about 50 Å^2, (Van Voorst Vader, 1960)). With about three cosurfactant molecules per surfactant, the chains are nearly close-packed over the length of the co-chains (4 chains per 100 Å^2) and the outer fringe is again very open. The packing of the short chains and the packing of the polar heads will favour W/O curvature with a ratio of 3 or more for co/sa and favour O/W with a co/sa ratio of 2 or less with an uncertain region in between. A longer chain alcohol will promote W/O. The double layer free energy is always in favour of O/W, the more so the lower the electrolyte concentration. This double layer effect can be expressed quantitatively (Overbeek, 1978) and contributes a term: const/ac to the interfacial tension, where c is the total electrolyte concentration.

To give a quantitative expression for the crowding effect of the chains is more difficult.

The main conclusion at this stage must be that the thermodynamic theory is still developing. A few qualitative conclusions can nevertheless be drawn.

1) O/W microemulsions need less cosurfactant than W/O ones.
2) The formation of W/O microemulsions requires more cosurfactant, not only to decrease γ, but also to promote the curvature with its convex side towards the oil. This effect is expected to be more pronounced with longer chain cosurfactants.
3) Electrolyte promotes W/O.
4) Since γ depends explicitly on the radius a, there is a tendency towards monodispersity.
5) Low volume fraction (ϕ) microemulsions have a lower free energy of formation than high ϕ ones, since the entropy of mixing is relatively more important for low ϕ and small a.
6) At about 40 to 50% water volume in W/O emulsions ϕ (which includes the hydrocarbon tails at the interface) gets close to 74%. The advantage of forming droplets disappears since the free energy of mixing becomes very small. Then a lamellar (or hexagonal) phase is preferred, because in such a phase the hydrocarbon tails can be better packed. This occurs at a smaller water volume for small particles than for large ones, since the extra tail volume makes a relatively larger contribution with small droplets. This explains why the W/O microemulsion can take up most water at the lowest sa/w ratio, i.e. at the largest possible radius (see Figs 4 and 7).

NONIONIC SURFACTANTS

Nonionic surfactants e.g. polyoxyethylene (POE) alkylphenylethers also may form microemulsions. When these microemulsions are compared with ionic ones two striking differences are found:

1) No cosurfactant is needed even with pure specimens of nonionics (very often nonionics are mixtures with a range of chain lengths).
2) Since the solubility of nonionic surfactants is highly temperature dependent the temperature plays an essential role in microemulsion behaviour.

A POE-alkyl surfactant is soluble in water at low temperature and forms micelles of increasing size over a fairly wide

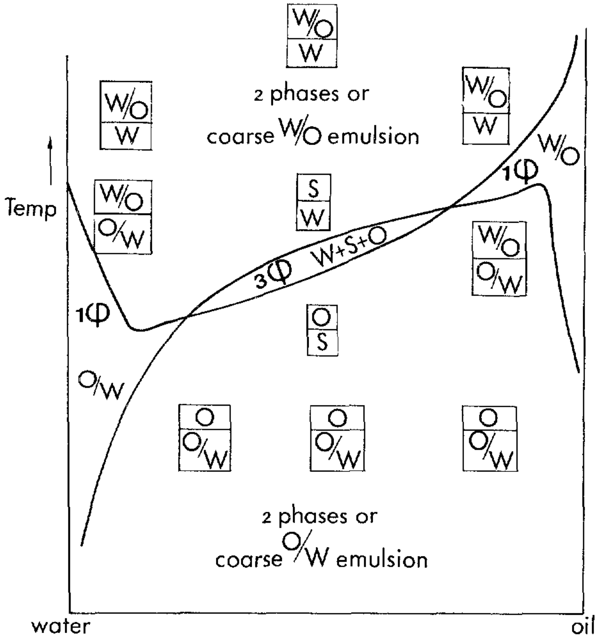

Fig. 8. Schematic phase diagram for a nonionic surfactant e.g. POE(n~9)-nonylphenylether in a fixed concentration e.g. 10% in mixtures of water and oil as a function of the temperature. The various one-, two- and three-phase regions are indicated. S is a "surfactant phase".

concentration region. At higher temperature the solubility of the POE moiety decreases until separation occurs in two liquid phases (cloud point). In hydrocarbon oil, on the contrary, the solubility is high at high temperature but decreases towards lower temperature.

The transition temperature depends on the hydrophilic-lipophilic balance (HLB) of the surfactant. A schematic phase diagram is given in Fig. 8 for an oil-water system containing a fixed percentage e.g. 10% of such a surfactant.

On the water side, at the lowest temperature, the surfactant solution solubilizes little oil; excess oil may be emulsified in a coarse O/W emulsion. At somewhat higher temperature the solubilization increases and fairly concentrated e.g. 10-20% O/W microemulsions may be formed. At still higher temperatures the solubility in water of the surfactant decreases rather suddenly and the system separates in a dilute O/W microemulsion and an oil phase, in which some water is solubilized in an oil-surfactant solution.

At the oil side of the diagram essentially the inverse processes occur.

But if oil and water are present in comparable amounts a narrow (in the temperature direction) three-phase region is found with a "surfactant phase" between surfactant-poor oil and water phases. In this middle region interfacial tensions are extremely low.

Microemulsions with a clear W/O or O/W character contain presumably spherical droplets (Robbins, 1977), but the surfactant phase may well be a bicontinuous structure, lamellar or otherwise.

Nonionic microemulsions are less sensitive to electrolyte than ionic ones, but the hydrophilic group is salted out by electrolyte and thus an addition of electrolyte works in the same direction as increasing the temperature or as switching to a more lipophilic surfactant (Robbins, 1977).

TECHNIQUES FOR CHARACTERIZATION OF MICROEMULSIONS

Microemulsions have been studied with a great variety of techniques, many of which are discussed in Prince's book (1977b). Here we only give a brief survey.

Phase diagrams are an indispensible tool in the study of microemulsions. The boundaries of the one-phase regions can be found from simple observation of mixtures of known composition or by a titration technique as depicted in Fig. 6. Determination of tie-lines in two-phase regions requires analysis of the phases. Given the small driving force for equilibrium, for example small differences in density, equilibration times are long and often run into many days, rather than hours or minutes.

The polarization microscope is needed to determine whether phases are anisotropic or not.

Interfacial tension measurements are required since low interfacial tension is a typical asset of microemulsions, but also to determine the area per surfactant or cosurfactant molecule and from there, using equation (6), $a = 3V/A$, the radius of the droplets. Low interfacial tensions require special techniques. The spinning-drop technique (shape of a drop in a cylindrical capillary rotating around its axis) is popular. Maintaining the temperature constant during the time needed for the freshly formed interface to come to equilibrium is one of the problems (Cayias *et al.*, 1975; Chatenay *et al.*, 1982).

Classical light scattering with a dilution technique which maintains the identity of the droplets gives the particle size and the interaction between particles. A hard sphere model is a good first approximation, but it needs refinements (Caljé *et al.*, 1977, Vrij *et al.*, 1978). Monodispersity or a narrow size distribution fits the data. The smallness of the particles usually allows the Rayleigh approximation ($a < \lambda/20$) to be used. In the transition region between O/W and W/O microemulsions critical phenomena accompanied by critical opalescence (Cazabat *et al.*, 1982) have been observed.

Dynamic light scattering or photon correlation spectroscopy has been used to determine diffusion coefficients (and thus the hydrodynamic radius of the particles) and their concentration dependence (Vrij *et al.*, 1978).

Small angle X-ray scattering (SAXS) has already been used by Schulman *et al.* (1948, 1951) to obtain information about particle size and shape. Small angle neutron scattering (SANS) allows separate information to be obtained about droplet core and surfactant layer by selective deuteration of water, surfactants or oil, since D scatters thermal neutrons much more than H (Fletcher *et al.*, 1982).

Viscosity with the use of Einstein's equation for the relative viscosity, η_r

$$\eta_r = 1 + 2.5\phi \tag{16}$$

or extensions thereof gives a check on the total hydrodynamic volume of the particles. More generally rheology and streaming birefringence are useful for determining hydrodynamic and other interactions and deviations from the sperical shape.

Sedimentation and ultracentrifugation rates and equilibria lead to hydrodynamic radii and particle mass (Hwan *et al.*, 1979, Dvolaitzky *et al.*, 1978).

Electrical conductivity is one of the classical methods to distinguish between O/W (high cond.) and W/O (low cond.) emulsions. In the microemulsion field the situation is more complex, since not too dilute W/O systems may show an increased conductivity as an indication of exchange of ions between droplets or of so-called "percolative behaviour", as a step towards a bicontinuous surfactant phase (Bennett *et al.*, 1982; Lagües *et al.*, 1978).

Measurements of dielectric dispersion give similar information (Boyle *et al.*, 1982; Boned *et al.*, 1979).

NMR measurements and self diffusion measurements, using radioactive labelling (Lindman *et al.*, 1982) give information on the mobility of various components. Slow diffusion indicates that a component is present in individual non-connected slowly moving particles. With NMR the complication arises that sharp signals, indicating high mobility, may be due to mobility within the entities just mentioned. A special NMR pulsed gradient spin-echotechnique allows, however, the diffusion coefficient to be obtained (Stibbs and Moseley, 1979; 1980).

Finally electronmicroscopy should be mentioned. Prince (1977a) shows small droplets of an O/W microemulsion after staining with OsO_4, but given the danger of artifacts (Biais *et al.*, 1981) electronmicroscopy is at best a tricky tool in this field.

APPLICATIONS

Applications of microemulsions are furthered by their spontaneous formation, their thermodynamic stability and thus their lack of aging. Applications may be based on the low interfacial tensions, on the possibility of preparing nearly homogeneous mixtures of oil- and water-soluble substances and also on the near uniform droplet size which occurs in several microemulsions.

The most spectacular use of microemulsions is found in the tertiary oil recovery (Bansal and Shah, 1977). In this application the low interfacial tension is essential. It allows residual oil in the reservoir to be pushed through the reservoir capillary structure without being hampered by the pressure drop at a curved oil-water interface with a normal interfacial tension, as schematically shown in Fig. 9. The method is still under development, but its huge potential in terms of money probably explains a good part of the very wide interest in microemulsions in the last ten years or so. The process is not simple on account of reservoir temperature, high salt content in the underground water, loss of expensive surfactant by adsorption in the reservoir, and by incomplete recovery.

Other applications (Prince, 1977d) are cutting oils (O/W), providing cooling and lubrication in one fluid, and dry-cleaning fluids (W/O) in which both oil- and water-soluble

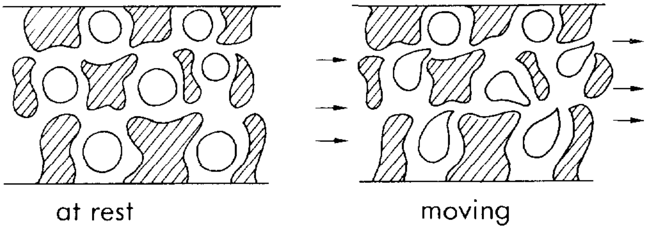

Fig. 9. In a porous oil bearing formation stagnant oil drops are spherical. In flow through narrow pores the drops must be deformed. This requires interfacial energy and an extra pressure drop, unless γ is very close to zero.

contaminants dissolve.

"Self emulsifiable oils" (Moilliet *et al.*, 1961) as used in agricultural and horticultural sprays, are possibly not strictly microemulsions at the final dilute O/W stage but they are often W/O microemulsions at the concentrated stage.

Probably the first commercial use of microemulsions - *avant la lettre* - is the use of Carnauba wax floor polishes in the 1930s (Prince, 1977e) prepared as a high temperature W/O microemulsion, which then is inverted into a translucent O/W type. The attraction of such emulsion-based floor and leather polishes is that they are easily applied (low viscosity) and dry to a high shine without the need for buffing.

Many cosmetic and pharmaceutical preparations are microemulsions.

The possibility of contacting oil- and water-soluble reactants at a large interface offers the possibility of greatly accelerating heterogeneous reactions, e.g. with lipids and water-soluble enzymes (Hilhorst *et al.*, 1982).

A completely different kind of application is found in pure science, where the (near) monodispersity is important (Agterof *et al.*, 1976; Caljé *et al.*, 1977; Vrij *et al.*, 1978). The droplets in such a monodisperse emulsion may be considered as huge molecules and the macroscopic behaviour of concentrated microemulsions can be used to test theories of hard or soft sphere fluids, where due to the size of the particles scattering and diffraction of visible light replaces X-ray techniques used for small molecules.

CONCLUSION

Microemulsions still offer worthwhile scientific challenges for many scientists and at the same time have a potential for applications which is by no means exhausted.

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