

PREPARATION OF MICROEMULSIONS
WITH IONIC SURFACTANTS

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I. INTRODUCTION

The microemulsions are transparent mixtures than concurrently contain large amounts of hydrocarbon and oil and which spontaneously form at contact between the components. They form an intriguing kind of materials with pronounced application potential (Friberg, 1976) and are at present the forms of intense and extensive research programs at several institutions.

The fact that they emanated from formulation activities (Prince, 1967) meant that their scientific introduction (Hoar and Shulman, 1943) and much of the subsequent treatment (Prince, 1975) focused on interfacial properties, disregarding other components of the free energy. In fact the notion of a negative interfacial tension was introduced.

Recent research on the thermodynamics of small dimension dispersed systems (Miller and Scriven, 1970; Ruckenstein and Chi, 1975; Eicke, 1979) has demonstrated this opinion to be premature. The thermodynamic stability of a dispersed system depends on several enthalpic terms; in addition the entropic contribution from the degree of dispersity is of similar importance.

The criteria for thermodynamic stability is of limited use in the formulation of microemulsions for such efforts the colloidal approach to microemulsion systems (Adamson, 1969; Gillberg, 1970; Shinoda, 1973; Ahmad, 1974; Shinoda, 1975; Friberg, 1976 and Sjoblom, 1978) is advantageous with its direct relation to the association structures of the chemical components. This article will give a short description of the common association structures of amphiphilic molecules and the mutual relations with the microemulsions.

II. MICELLAR AND MICROEMULSION PHASES

A microemulsion is water/hydrocarbon dispersion stabilized by an ionic surfactant such as a soap, alkyl sulphate or sulphonate and most often also contains a cosurfactant in the form of a medium chain length alcohol (pentanol). Of these four components water, surfactant and cosurfactant are called the structure forming elements since they form colloidal association structures similar to the microemulsions with no hydrocarbon present. The formulation and preparation of microemulsions is greatly enhanced by a knowledge of these composition dependent structures, hence an introductory description of them will be given.

A. Normal Micelles

The hypothesis of an aggregation of surfactants into micelles at concentrations in excess of the critical micellization concentration of the surfactant is old (McBain, Laring and Titlay, 1919; Jones and Bury, 1920 and Ekwall, 1927). The phenomenon can be empirically understood in the following manner.

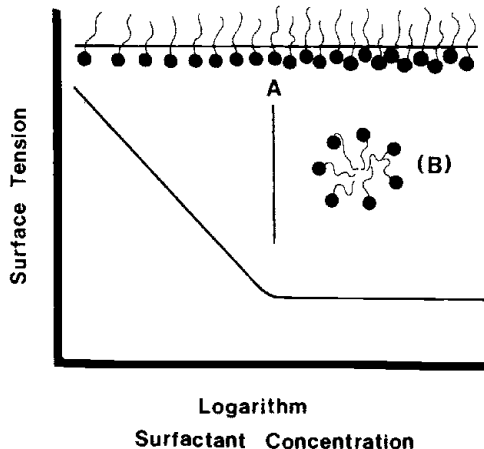


FIGURE 1. When the concentration of a surfactant is increased in an aqueous solution the molecules at the interface pack more closely (top) and the surface tension will be reduced (line). When the surface is saturated (concentration A) the further added surfactant molecules cannot reach the saturated interface; they form their own interface within the solution in the form of a micelle (B). The interfacial tension remains constant at concentrations higher than A.

Surfactant molecules added to water strongly absorb to the surface and the surface tension is reduced. At a certain concentration (A, Fig. 1) the surface is saturated, added surfactant molecules cannot reach the surface and the surface energy remains constant. The surfactant molecules added in excess of concentration A create an internal interface in the system by forming micelles; small spherical aggregates with a radius equal to the chain length of the surfactant. For this reason the concentration A is called the critical micellization concentration, cmc.

These micelles (B, Fig. 1) can in their hydrocarbon interior dissolve molecules otherwise insoluble in water e.g. hydrocarbons. This solubilization is limited to the magnitude of 10% per weight and the resulting solution is called a micellar solution and does not deserve the epithet microemulsion.

It is obvious that the combination water and surfactant with their micellization and solubilization is unable to explain the phenomenon of microemulsions. For an explanation the role of the cosurfactant must be understood. The next section will display the relationship with cosurfactant inverse micellar solutions and water-in-oil, W/O, microemulsions.

B. Inverse Micelles and Water-in-oil W/O Microemulsions

The cosurfactant, a medium chain length alcohol, may be considered a liquid of mainly "organic" nature. Hence an insignificant solubility of water and also of an ionic surfactant may be expected.

This condition is also experienced in reality. Figure 2 illustrates the conditions; the individual solubilities are small; the solubility of water is only 5% by weight. On the other hand the combinations of water and surfactant display pronounced solubilities. A surfactant/cosurfactant ratio of 0.3 gives rise to a solubility of water at 75 percent by weight. This pronounced solubility of water in predominantly organic solvent is the key to W/O microemulsion systems. Since hydrocarbons and the cosurfactant are mutually soluble, addition of a hydrocarbon to form a microemulsion appears reasonable. Before this step is taken a more suitable representation of the information in Fig. 2 in the form of a triangular diagram will be introduced.

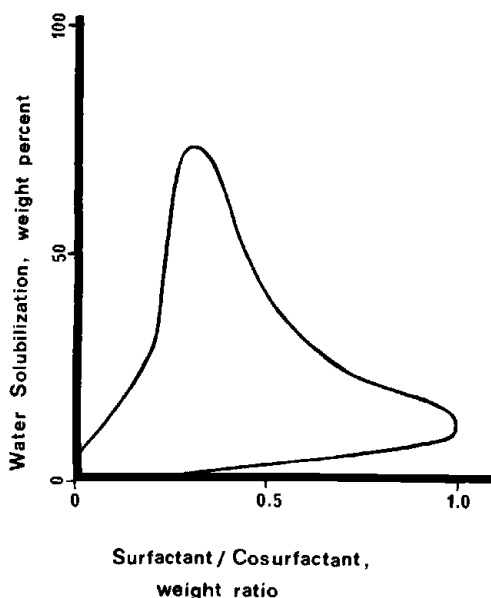


FIGURE 2. The solubility of water in pentanol (cosurfactant) shows a maximum for a certain surfactant/cosurfactant ratio.

Figure 3 gives a comparison between the Cartesian and the triangular coordinate system for the solubility curve in Figure 2. The letters A-D denote identical points in the upper and lower part. The maximum solubility of water 75 percent by weight as a weight fraction of 0.75 is now found at 0.75 of the distance from Q which corresponds to a surfactant/cosurfactant ratio of 0.33 (or fraction 0.25) to W which is 100% water.

In order to form a microemulsion hydrocarbon must be added and the triangular diagram now becomes a tetrahedron, Figure 4. The amount of hydrocarbon is now represented by the perpendicular distance from the base plate. The result is (Friberg, 1976) that the water solubilization counted on the three structure forming elements; water, surfactant and cosurfactant) remains constant. This means that point B representing 75 percent water in the base plane with zero hydrocarbon as point B" in the plane with 50% hydrocarbon represents 37.5 percent water. The total composition of point B" will be water 37.5%, hydrocarbon 50%, surfactant 3.125% and cosurfactant 9.375%. This is a water-in-oil microemulsion.

This manner of looking at the microemulsion systems is different from the traditional one (Prince, 1975; Rosano, 1974). It offers a systematic advantage in the preparation,

which will be described in the following section.

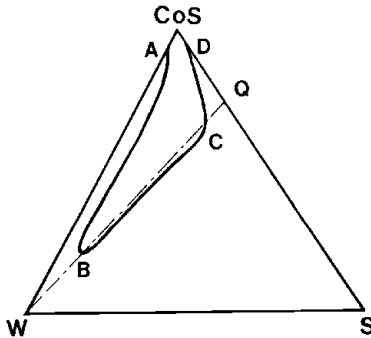
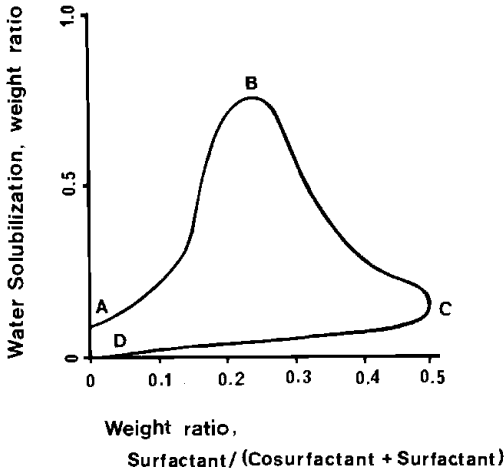


FIGURE 3. The solubility area of water (*W*) and surfactant (*S*) in the cosurfactant (*CS*) in a Cartesian (top) and triangular (bottom) coordinate system.

III. PREPARATION OF W/O MICROEMULSIONS

The preparation is initiated by the determination of the solubility area in the base-plane (Fig. 4). Surfactant/cosurfactant mixtures with increased accounts of surfactant are prepared and water is added. The percentage for the water amount when the mixture becomes transparent is marked on a triangular diagram forming the line *D-C* in Fig. 3. Continued addition of water leads to turbidity and the corresponding composition is

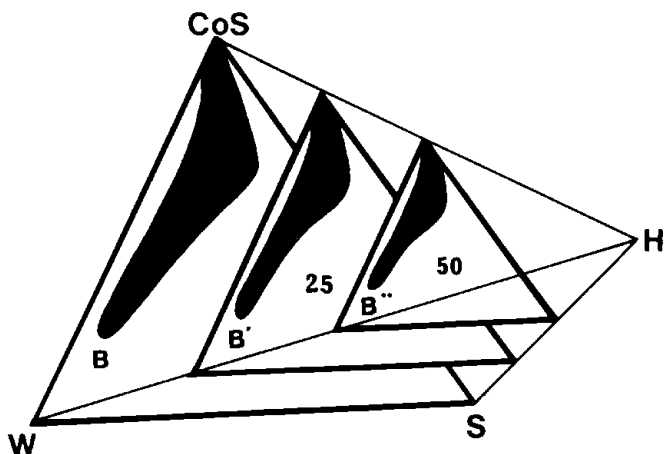


FIGURE 4. The microemulsion regions at 25 and 50 percent hydrocarbons are a direct continuation of the cosurfactant (CoS) solution (base plane) of water (W) and surfactant (S) with no hydrocarbons.

marked (the line A-B in Fig. 3). The line B-C finally is obtained by addition of cosurfactant to turbid mixtures of water and surfactant. The latter samples must be carefully mixed, since viscous liquid crystals appear during the addition.

The microemulsions are directly prepared by addition of hydrocarbon to compositions within the solubility area ABCD, Fig. 3. Compositions close to the solubility limit should be avoided; small changes of the area may be observed by the addition of hydrocarbon.

Hydrocarbon contents in excess of 50% by weight lead to rapidly reduced water solubilization. These conditions are more complex and the original literature (Friberg, 1976b; Sjoblom, 1978) should be consulted.

IV. THE STRUCTURE OF W/O MICROEMULSIONS

The common opinion (Prince, 1975) of the water being in the form of inverse micelles in the solubility area ABCD Figure 3 has after careful investigations been shown to be incorrect. Using NMR, electric conductance (Shah, 1971) dielectric measurement (Claude, 1976), light scattering and electron microscopy (Sjoblom, 1978) and positron annihilation technique (Ache, 1977) a change between smaller aggregates and inverse micelles was detected.

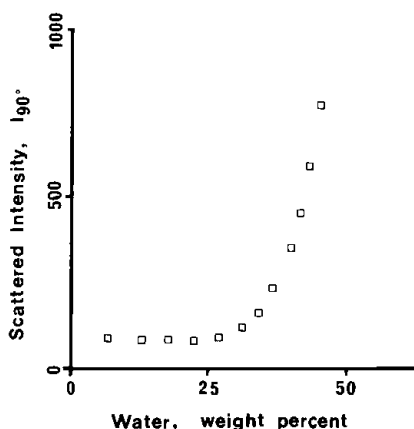


FIGURE 5. Light scattering curves show micellization first at 15% water per weight in a W/O microemulsion with 50% decane, stabilized by potassium oleate and pentanol (Sjoblom, 1978), (30% counted on water, surfactant and cosurfactant).

The typical light scattering curves (Sjoblom, 1978) show the increase of scattered intensity characteristic of micellar formation first at relatively high water concentrations. The example in Fig. 5 is from microemulsions with 50% by weight hexadecane stabilized by potassium oleate and pentanol (Sjoblom, 1978). The scattering intensity below a water concentration of 30% by weight (counted on water, surfactant,

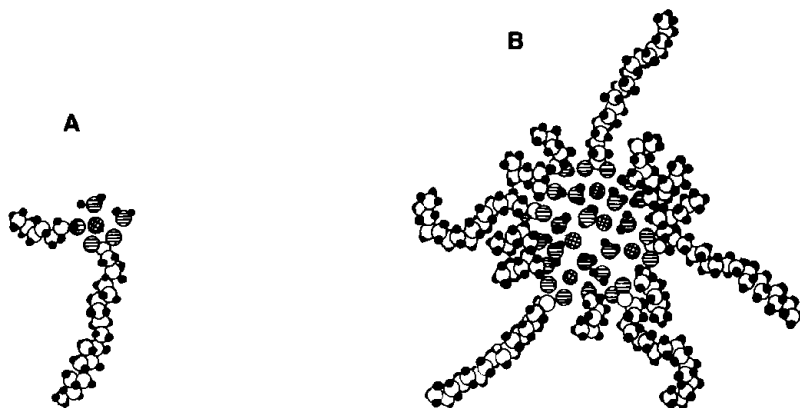


FIGURE 6. The W/O microemulsions contain small aggregates (A) at low water concentrations (Fig. 5) and inverse micelles (B) at higher concentrations.

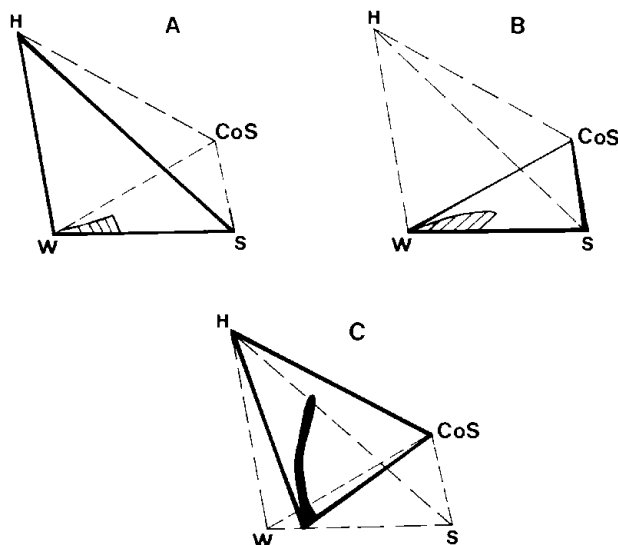


FIGURE 7. The solubilization of hydrocarbon is small in normal micelles (A) and so is the case for the cosurfactant (B). A combination of hydrocarbon and cosurfactant will give a microemulsion from an aqueous solution of optimum concentration of surfactant (C).

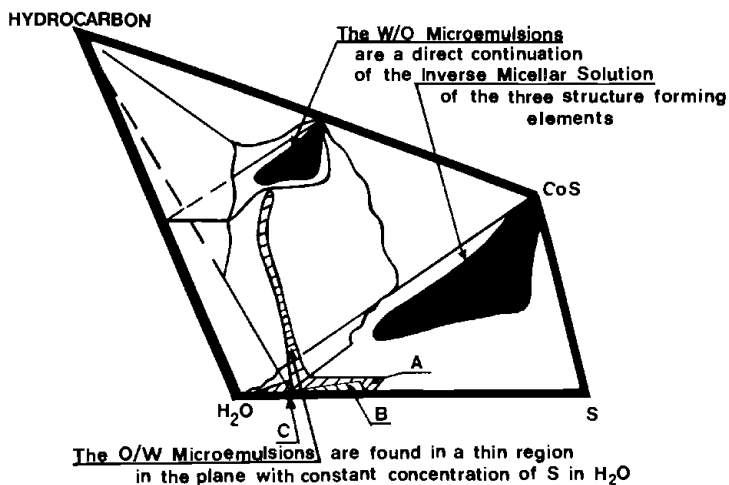


FIGURE 8. The relation between W/O and O/W microemulsion areas.

and cosurfactant alone, including the hydrocarbon = 15%) is lower than the one from pure benzene. It appears evident that the inverse micelles (= the microemulsion droplets) form first at high water concentrations.

These results and those using other methods (Shah, 1971; Clause, 1967; Ache, 1977) agree on the following interpretation. At low water concentration the surfactant molecules associate a few water and cosurfactant molecules around its polar part forming an aggregate such as the one in Fig. 6, A. With increasing water concentration a stepwise association to inverse micelles, Fig. 6, B, takes place (Eicke and Christen, 1974).

The transition to inverse micelles is important in microemulsions stabilized by a carboxylate, a soap. For these systems (Friberg, 1978) the presence of electrolyte in the water leads to a change of the solubility region; the minimum water content (CD, Fig. 3) will be enhanced and the maximum water solubilization (B, Fig. 3) will occur at higher surfactant/cosurfactant ratio.

V. O/W MICROEMULSIONS

The solubilization of hydrocarbons in normal micelles (Vide ante) was not sufficient to justify the name microemulsion and a role of the cosurfactant was envisioned as necessary. This is also the case (Rance, 1977). These microemulsions are found in the plane that connects the hydrocarbon and cosurfactant corners with one point on the water/surfactant axes, Fig. 7. The concentration of surfactant in the aqueous solution is the critical factor; higher and lower concentrations fail to produce the large solubilization area.

Contrary to the case of W/O systems some of the O/W microemulsions are not stable. This has been found true for high hydrocarbon content; stability has been found for compositions with less than 30% hydrocarbon.

VI. SUMMARY

The relations between micellar solutions and microemulsions has been reviewed for microemulsion systems with ionic surfactants. The W/O microemulsions are a direct continuation of the cosurfactant inverse micellar solution. At low water content no surfactant association takes place; the surfactant molecules form small aggregates with a few water and cosurfactant molecules. The W/O microemulsions are thermodynamically stable.

The O/W microemulsions emanate from the aqueous micellar solutions in a more complex manner. They are stable only for low ($< \approx 30\%$ by weight) hydrocarbons.

ACKNOWLEDGMENTS

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REFERENCES

- Adamson, A. W. (1969). *J. Colloid Interface Sci.* 29, 261.
- Ahmad, S. J., Shinoda, K. and Friberg, S. E. (1974) *Ibid.* 47,32
- Clausse, M. and Rayer, R. (1976). *M. Colloid and Interface Science II"* (M. Kerker, ed.), p. 217, Academic Press New York.
- Eicke, H. F. and Christen, H. (1974). *J. Colloid Interface Sci.* 48, 281.
- Eicke, H. G. (1979), *Ibid.* 68, 440.
- Ekwall, P. (1927). *Acta Acad. Aboensis (Mat et Phys)* 4, 1.
- Friberg, S. E. (1976). *Chem. Tech.* 6, 12 Y.
- Friberg, S. E. and Buraczewska, T. (1978), *Prog. Colloid Polymer Sci.* 63, 1.
- Gillberg, G., Lehtinen, H. and Friberg, S. E. (1970) *J. Colloid Interface Sci.* 33, 40.
- Hoar, T. P. and Schulman, J. H. (1943). *Nature* 152, 102.
- Jean, Y. C. and Ache, H. J. (1977). *J. Am. Chem. Soc.* 99,7504.
- Jones, E. R. and Bury, C. R. (1920). *Phil. Mag.* 4, 841.
- McBain, J. W., Laring, M. E. and Titley, A. F. (1919). *J. Chem. Soc.* 115, 1279.
- Miller, C. A. and Scriver, L. E. (1970). *J. Colloid Interface Sci.* 33, 360.
- Prince, L. (1967). *Ibid.* 23, 165.
- Prince, L. (1975). *Ibid.* 52, 182.
- Rosano, H. (1974). *J. Soc. Cosmetic Chem.* 25, 609.
- Rance, D. G. and Friberg, S. E. (1977). *J. Colloid Interface Sci.* 60, 207.
- Ruckenstein, E. and Chi, J. C. (1975). *J. Chem. Soc. Faraday Trans. II*, 71, 1690.
- Shah, D. O. and Hamlin, R. M. (1971). *Science* 171, 483.
- Shinoda, K. and Kunieda, H. *J. Colloid Interface Sci.* 42, 381.
- Shinoda, K. and Friberg, S. E. (1975). *Adv. Colloid Interface Sci.* 4, 281.
- Sjoblom, E. and Friberg, S. E. (1978). *J. Colloid Interface Sci.* 67,16.

ADDENDUM

The discussion centered on the behavior of the system nonionic surfactants, water and hydrocarbon with the speaker and Dr. Thomas as participants.

Nonionic surfactants with pronounced hydrophilic character behave like ionic surfactants; they show a normal micellar formation in the aqueous phase with a hydrocarbon non-micellar phase in equilibrium. Higher surfactant concentrations give rise to liquid crystalline phases with a structure dependent on the length of the hydrophilic part of the surfactant.

With increased temperature or shortened hydrophilic chain length the cloud-point will be exceeded, the surfactant will become oil soluble and inverse micelles form consecutively when the water concentration is increased.

At high concentrations of the surfactant anisotropic aggregates are formed which may be considered as precursors to a liquid crystalline phase.