

Microemulsions, Hydrotropic Solutions and Emulsions, a Question of Phase Equilibria¹

S. FRIBERG, The Swedish Institute for Surface Chemistry, Drottning Kristinas vag 47, S-114 28 Stockholm, Sweden

ABSTRACT

Investigations of phase equilibria in systems of water-surface active substances-organic compounds have related the properties of micellar liquid and liquid crystalline phases with the formation, existence and properties of microemulsions, hydrotropic solutions and emulsions.

INTRODUCTION

Emulsions and microemulsions have been treated as functions of the properties of the interface between two liquid phases, and hydrotropic solutions have been considered as a question of association into pre-micellar aggregates. This article is intended to show the common importance of association phenomena of surface active substances for all three materials.

Association of Surface Active Substances

Surface active substances associate into micelles and liquid crystalline phases. The composition region of the existence of these different phases has been thoroughly investigated by Luzzati (1), Lawrence (2), Ekwall and coworkers (3-6). The micelles exist as normal and reversed species, while the liquid crystalline phases show a great

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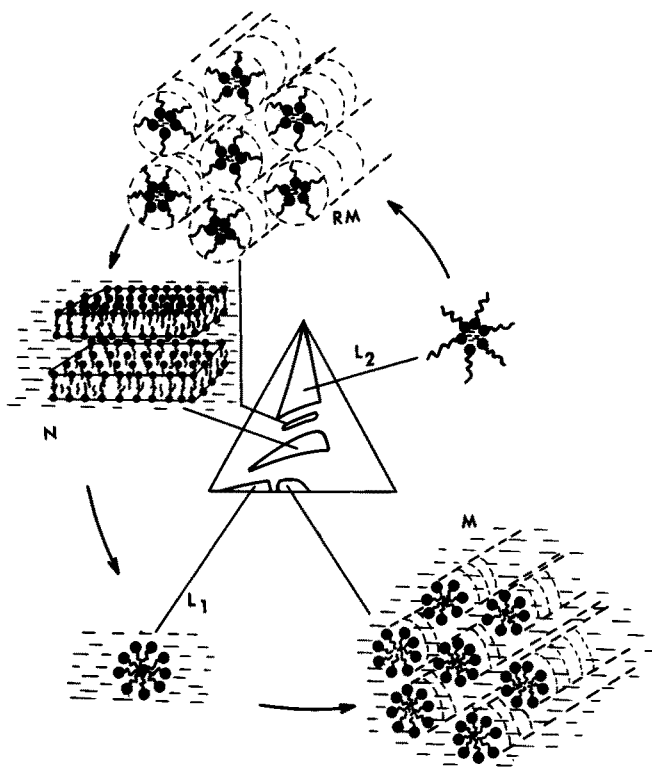


FIG. 1. Normal and reversed micelles and different liquid crystalline structures in a system of water-surface active substance-amphiphilic substance. L₁ and L₂ are liquids. M, RM and N are liquid crystals.

variety of structures. These structures have been investigated in great detail (7).

Figure 1 gives a simplified example of the structure conditions in different parts of a phase diagram of the three components water-surface active substances-amphiphilic substances. In the actual illustration the amphiphilic substance has such a pronounced interaction with water and the surface active substance as to permit the formation of reversed micelles. The association structures of the different regions shown in the figure consist of normal (L₁) and reversed micelles (L₂). The middle phase (M) consists of a hexagonal array of cylinders where the hydrocarbon chains are situated in the center of the cylinder, while the reversed middle phase (RM) consists of cylinders with aqueous centers. The neat phase (N) has a lamellar structure.

The following discussions intend to show how the properties of the media in the title are connected with these different association conditions.

Microemulsions

Microemulsions were first described by Schulman in 1948 (8). They were explained from the change of interfacial tension O/W, when a soap and subsequently an alcohol ($\sim C_6$) are added to an emulsion (9). As can be found in Figure 2 (9), the addition of a soap to the mixture reduces the interfacial tension. A consecutive addition of an alcohol causes a further reduction, which is linear, if plotted as a function of the logarithm of the alcohol concentration. Additions in excess of the concentration, marked A on the diagram, give a temporary negative surface energy, which is the result of the alcohol adsorption. This provides energy for an increase of the surface, which takes place by a reduction of the drop size. At the concentration

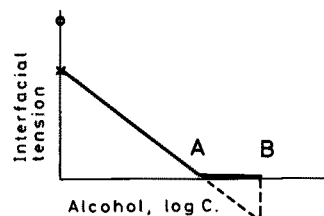


FIG. 2. The reduction of interface tension when a long chain alcohol is added to the system, water-oil-surface active substance. o, oil-water; x, oil-water with added surface active substance.

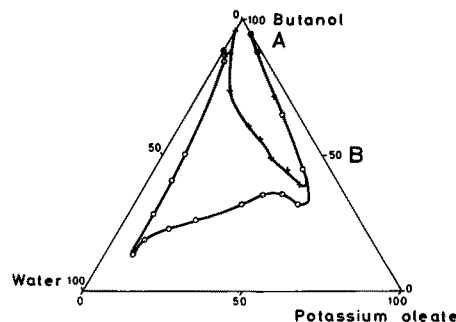


FIG. 3. Solubility region containing reversed micelles in the system, water-butanol-potassium oleate when benzene is added to the system (water + butanol + potassium oleate = 100%). o, 20 weight per cent benzene; x, 90 weight per cent benzene.

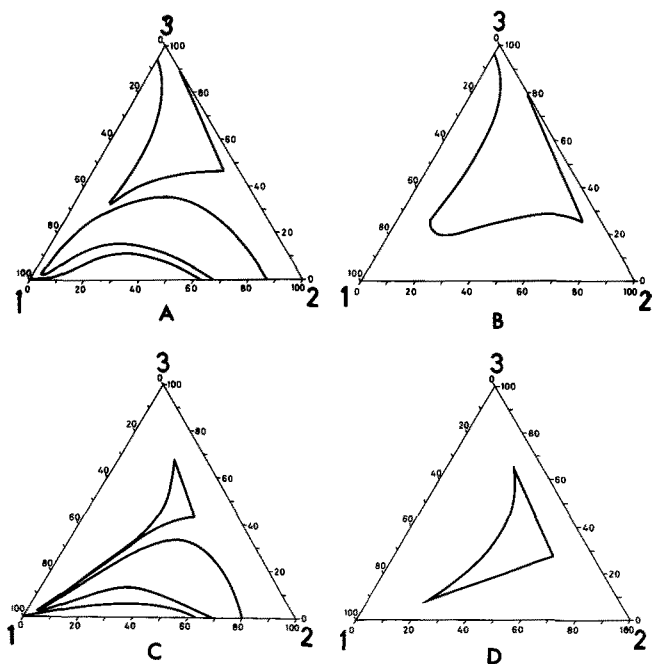


FIG. 4. Solubility region containing reversed micelles of a cationic substance under different conditions. 1, water; 2, octyl ammonium hydrochloride; 3, hexanol; A, no further addition; B, 40% benzene added; C, 1 M NaCl solution as the aqueous phase; D, B + C.

marked B in the figure, the size of the droplets is reduced to a level where they are not observable with optical means and the system is called a microemulsion.

The microemulsions can be related with the area L_2 in Figure 1. This region consists of an hexanol solution of water and soap, which latter are solubilized into reversed micelles at higher concentrations and possibly form association complexes of smaller dimensions at high concentrations of the alcohol. The alcohol solution can, as expected, dissolve a hydrocarbon and this solution forms a microemulsion.

The limits of the L_2 area for different amounts of benzene (10) form a suitable basis of information for the industrial application of microemulsions (Fig. 3). In the present example (10) the solubility regions give simple rules for the preparation of microemulsions, which have to withstand further dilution with water or oil. High amounts of water in the microemulsion are only possible in a narrow region towards the water corner. This means that in order to prepare a microemulsion which should be able to withstand dilution with water it is necessary to have an optimum ratio of soap to alcohol denoted by A in the

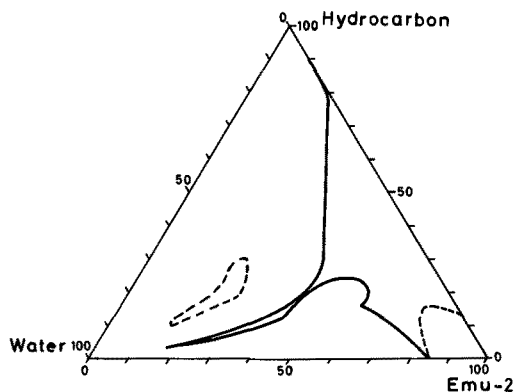


FIG. 5. The reversed micellar solution of systems water-hydrocarbon-nonionic emulsifier (commercial). —, *p*-xylene; ---, hexadecane.

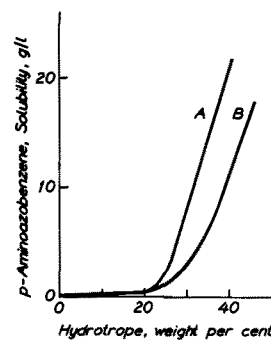


FIG. 6. Solubility increase due to the addition of hydrotrope. A, $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH}$; B, $\text{CH}_3 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_3$.

figure. This gives separation when 75% water is added. A composition denoted by B, not differing by more than 25% soap will give a separation at 20% water. On the other hand, a microemulsion, which should withstand high amounts of oil, must be prepared carefully to maintain the ratio of water to soap. The solubility region for 90% benzene shows that the optimum oil solubility is achieved with as small a percentage of water present as possible. An initial amount of less than 15% water or 40% alcohol will, however, not give any solubility of oil.

Ionic surface active substances will be influenced by the presence of salt. Figure 4 shows the influence on the solubility regions of added salt and water on cationic emulsions. The extension of the region containing a liquid crystalline phase should be observed. This liquid crystalline phase is the reason for the recent observation that microemulsions form "thick gels" unless salt is present (11).

An example of the fact that nonionic substances often form a continuous solubility region containing the surface active substance and the oil is given in Figure 5. It shows how water is solubilized up to about 80% in the organic solubility region (A). The properties of the oil are important. Replacing the *p*-xylene by hexadecane causes the phase diagram to change. One should observe the solubility "island" (B) in equilibrium with pure water and pure hydrocarbon. This phase is identical with the "detergent phase" introduced by Shinoda (12). The solubility regions of the nonionics do not show the dependence on the presence of salt as is characteristic for ionics, since the electric double layer has only a minor influence on the stability of the colloidal associations.

The practical applications of microemulsions as cleaning agents, in the cosmetic industry and in oil pollution

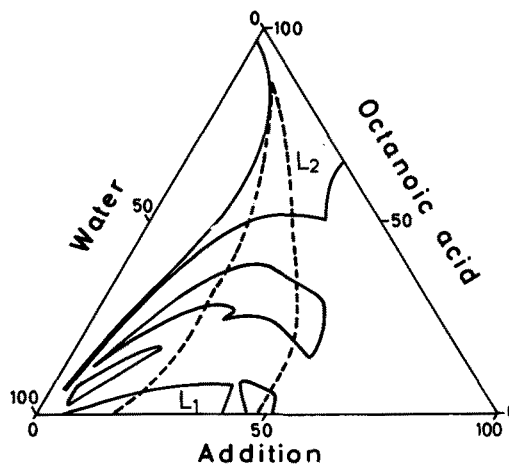


FIG. 7. A comparison of the phase equilibria in systems water-sodium xylene sulfonate-octanoic acid (----) and water-sodium octanoate-octanoic acid (—).

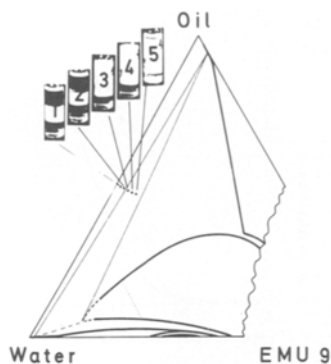


FIG. 8. The stability of water-*p*-xylene emulsions with a commercial nonionic emulsifier is suddenly increased when a liquid crystalline phase is present (emulsion No. 3).

treatment, are easy to visualize. It appears probable that the present approach, in giving rules for the stability of microemulsions, will be useful in their technical development.

Hydrotropic solutions

Hydrotropes are solubility-increasing agents which have been known for a long time. The first publication appeared in 1916 (13) and this has been followed by some 50 articles on the influence of different hydrophilic-lipophilic balances on the efficiency of solubility agents. A typical example of this treatment is presented in Figure 6 (14) which shows the increased solubility of *p*-aminoazobenzene in water due to the presence of high amounts of alcohols serving as hydrotropes. It is characteristic that rather high concentrations are needed to achieve this change of solubility.

The treatment of this phenomenon (14) at our institute has shown that the pronounced solubility increase is dependent on the presence of both normal and reversed micelles within the same solubility region. Figure 7 shows the solubility region of octanoic acid (broken line) in aqueous solutions of sodium-xylene sulfonate. From 17% hydrotrope in water the solubility increases from less than 1% to about 85% at 60% hydrotrope taken as percentage of the sum of water and hydrotrope only. The basis for this is the transformation from normal micelles at low content of octanoic acid to reversed micelles at high content of it in the same solubility region. Normal surface active substances, as represented by the sodium soap of the same acid (15), give a similar initial solubility increase of the acid (L_1) when the concentration of the soap reaches the critical micellization concentration. This solubility region does not, however, continuously pass over in the liquid region with reversed micelles (L_2). When the acid content exceeds 7% a liquid crystalline phase with a layer structure will be formed, thus creating an intermediate phase between the

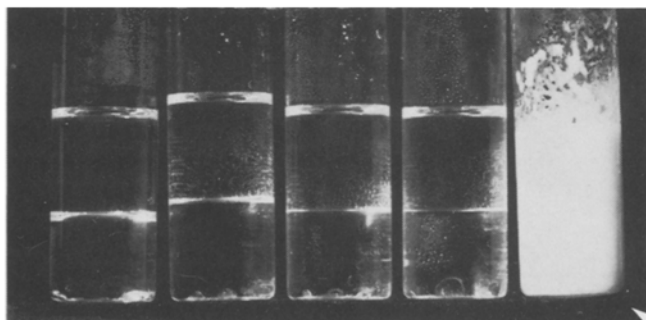


FIG. 9. The difference of stability is pronounced when a liquid crystalline phase is present (to the right) in emulsions of well-defined compounds.

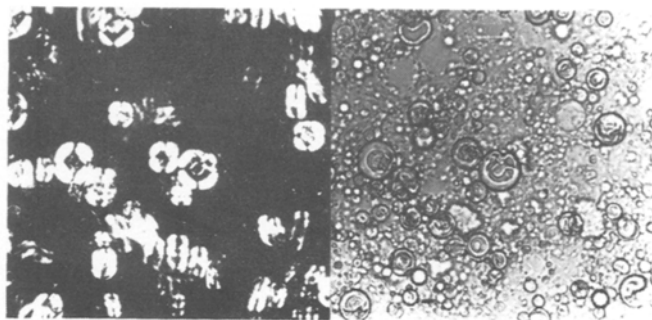


FIG. 10. The liquid crystalline phases are situated at the emulsion interfaces which can be observed in polarized light (to the right).

two liquid phases with normal and reversed micelles. This behavior has its source in the packing conditions of the hydrocarbon chains. The soap and the acid have chains of equal lengths which easily form a parallel pattern. Such conditions are prevented when the hydrotrope is added because of the difference of chain configuration. If two lines are drawn connecting the limits to the left and to the right of the liquid crystalline phases and the two liquid areas in the "soap diagram," a smooth solubility region similar to the hydrotropic one will be formed.

Emulsions

The treatment of emulsion properties has connected these with the droplet size distribution and the properties of the interface between two liquid phases (16,17). This, however, leaves some questions unanswered. Sherman, 1965, in a comment to a lecture (17), stated that sudden changes in the properties of the emulsion with increased emulsifier concentration still have to be explained; Davies (19) gave an example of two emulsions differing only in the composition of the hydrocarbon, but with different stability properties. The one containing benzene as the oil phase flocculated after long storage, but showed very little coalescence. In the other emulsion with petroleum ether as the oil component, no flocculated drops could be observed, but the wide size distribution gave evidence of an extensive coalescence having taken place.

The idea of liquid crystalline phases being present in emulsions and having an influence on the properties was put forward quite early (20-22). Work at our institute has shown that the equilibrium condition of systems containing water-oil-emulsifier (23) contain well defined liquid crystalline phases. The presence of these liquid crystalline phases has been shown to cause sudden changes of stability (Fig. 8) for commercial emulsifiers (24). Systems containing pure compounds (25) show a drastic increase of stability when the liquid crystalline phase is present (Fig. 9) and have also

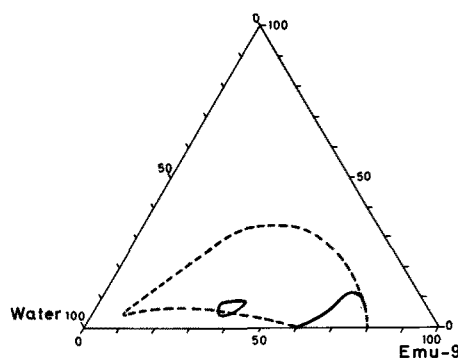


FIG. 11. The water-solubilizing capacity of the neat phase in *p*-xylene-(commercial)nonionic emulsifier-water (---) is of a different magnitude from the corresponding property of the system hexadecane-emulsifier-water (—).

made it possible to observe the location of the liquid crystals in the emulsion (Fig. 10).

These investigations have also shown the marked difference in the equilibrium phase conditions when an aromatic hydrocarbon is replaced by an aliphatic one (23). When adding *p*-xylene to the neat phase its water content is increased from 40% to a maximum of 85% (Fig. 11). Addition of hexadecane causes a reduction of the water content. Transformed to emulsion stability, this means that emulsions water-*p*-xylene (50/50) will be considerably more stable when the concentration of the emulsifier exceeds 4%. A similar increase of stability with the corresponding water hexadecane emulsions will take place first at 15% emulsifier due to the presence of an isotropic liquid crystalline phase. These results are related with the problem stated by Davies (19).

A sudden increase of viscosity followed by a slow decrease with time for certain emulsifier concentrations could also be explained with the disturbance of two liquid phases giving rise to a liquid crystalline phase (25). The formation of less viscous liquid crystalline phases at higher contents of the emulsifier explained the fact that the phenomenon was observed only at certain emulsifier concentrations.

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