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## Micellar Solutions Versus Microemulsions

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## Micellar Solutions Versus Microemulsions

In a recent publication (1) an attempt has been made to distinguish between micellar solutions and microemulsions and a hypothetical "phase diagram" has been presented stating that such a phase diagram "was not contemplated by the proponents of the micellar solution terminology. The interactions needed to form phases of this diagram are of a higher order of complexity than those required for the phases of [the present] Refs. (2-8)." The article also stressed a negative interfacial tension as a main factor for the stability of microemulsions.

We do not accept these statements. Published phase diagrams (5, 6, 8, 9) have exemplified both W/O and O/W microemulsion systems and the importance of the different components of the interfacial free energy has been given an excellent treatment by Murphy (10). Furthermore, recent progress in the understanding of the stability of microemulsions (11) has demonstrated that other factors (11, 12) carry equal importance for their stability.

Against the background of the present intense interest in microemulsions we present an example of the isotropic liquid phase regions in a four-component system which gives microemulsions. We use this system

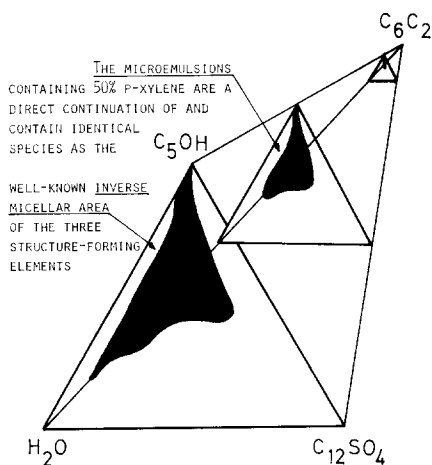


FIG. 1. The W/O microemulsions (middle height plane of the tetrahedron) are a direct continuation of the inverse micellar solution of the three structure-forming elements (base of the tetrahedron).

to point out what is incorrect in the hypothetical phase diagram (1) and to indicate the problems and dangers to which an oversimplified view will lead in the practical application.

The system consisted of water ( $H_2O$ ), *p*-xylene ( $C_6C_2$ ), sodium dodecyl sulfate ( $C_{12}SO_4$ ), and pentanol ( $C_5OH$ ). All materials were of the highest available purity and the water was twice distilled. The determination of the solubility areas was accomplished by titration and the results were checked by prolonged storage of selected compositions.

In agreement with previous workers (5, 7, 8), the results showed that the W/O microemulsions are a part of the inverse micellar regions (Fig. 1). The figure is in itself a good demonstration, and repetition of earlier facts is unnecessary. The advantages of phase diagrams, such as this one, have been described (13), and the diagrams have also been successfully applied (14).

The relation between O/W microemulsions and the normal micellar associations is less direct. The presentation in Fig. 2 is useful for understanding the important factors for obtaining an O/W microemulsion. The determining factor is the amount of ionic surfactant in the aqueous solution; the differences among the solubilization capacities of aqueous solutions containing 10, 15, and 20% of  $C_{12}SO_4$  are drastic and merit consideration.

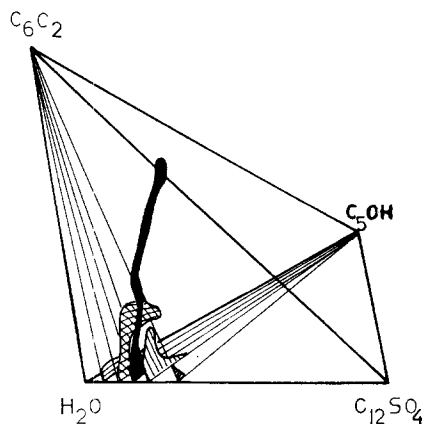


FIG. 2. The O/W microemulsions are a continuation of the aqueous solutions containing normal micelles.

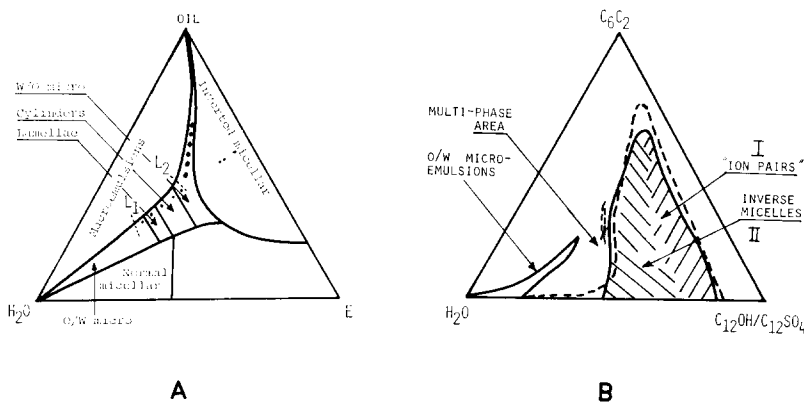


FIG. 3. Hypothetical (A) and correct (B) phase regions in a microemulsion system.  $C_5OH/C_{12}SO_4$ : —, 2; - - -, 3.5. (B) "Ion pairs" (Region II); inverse micelles (Region I).

The more common representation of phase equilibria in four component systems which is exemplified by Figs. 3A(1) and 3B (the present investigation) has a serious limitation; the phase regions are drastically modified by variation of the cosurfactant/surfactant ratio. Figure 3B is the diagram of the present model system. The differences between this and the hypothetical diagram (Fig. 3A) are important for the application of microemulsions and are briefly discussed.

The region to the right of the phase diagram in Fig. 3A, called "inverted micellar," does not exist. It has been amply demonstrated in the literature (15) that an ionic surfactant, such as potassium oleate or sodium dodecyl sulfate is insoluble in an alkanol or in an alkane/alkanol mixture (5); dissolution requires a strong hydrogen bond (16) or a multidentate liquid such as glycerol or water.

Furthermore, neither may Region I in Fig. 3B, which actually exists, be called micellar solution because no micelles exist in that part of the diagram. Several studies have shown that the solution contains small aggregates such as *ion pairs* of the surfactant each with a few associated water molecules. This part of the solubility region will disappear when high concentrations of saline solutions are encountered, which is important in tertiary oil recovery. Region II in Fig. 3B contains inverse micelles; the *alias* microemulsions may, of course, be used, but attempts to distinguish between inverse micelles and W/O microemulsions are not meaningful.

The difference from the transition region denoted "cylinders, lamellae" in Fig. 3A is even more pronounced. For the technical application it is of the utmost importance to realize that these "microemulsions" are multiphase systems of liquid crystals and solutions (17, 18). As pointed out by Ahmed *et al.* (8),

these systems may initially appear as isotropic liquids with no detectable birefringence, but prolonged storage inevitably leads to separation of the liquid crystalline phase.

The phase conditions in this part of the four-component systems are extremely difficult to clarify and it appears essential that when the nature of the phases is open to conjecture, it is presented as such.

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