UNI- AND BICONTINUOUS MICROEMULSIONS

U. OLSSON and B. LINDMAN,
Physical Chemistry 1,
Chemical Center,
Lund University,
P.O. Box 124,
S-221 00 Lund,
Sweden.

ABSTRACT. The structure of liquid surfactant-water-oil mixtures, so called microemulsions, is discussed. These solutions are microstructured into separate polar and apolar domains (typical length scales are of the order of 10-400 Å) separated by a monolayer of oriented surfactant molecules. The structure may be either uni- or bicontinuous. It is stressed that multicomponent self-diffusion measurements, most easily performed with the pulsed gradient FT NMR technique, is presently the most suitable technique for studying microemulsion structure. Molecular self-diffusion properties of uni- and bicontinuous microemulsion structure are presented. Various surfactant-water-oil systems are reviewed with emphasis on their liquid microstructure.

1. Introduction

Microemulsions [1-4] are thermodynamically stable liquid phases of oil, water (or an alternative polar solvent) and surfactant [5]. In many cases some additional component, cosurfactant and/or electrolyte, is needed for the formation of a microemulsion. Stable microemulsions form in a large variety of surfactant systems [6-21]. Very intriguing from both practical and theoretical points of view are microemulsions in which quite small amounts of surfactant molecules can mix comparable amounts of water and oil [22].

Of main concern when first introduced to a liquid phase in a surfactant(S)-water(W)-oil(O) system is the question of microstructure. In solution the surfactant molecules form a monolayer of oriented molecules that acts as dividing surface between water and oil domains. Depending on the conditions, such surfaces may enclose a finite volume, as in micelles, or be continuous in one, two or three dimensions. The interestingly rich phase behaviour of S/W/O systems is related to the numerous ways in which space may be divided into polar and apolar regions for a given surface to volume ratio. It is these properties of the surfactant monolayer we refer to when concerned with the liquid microstructure of microemulsions.
2. How To Study Microemulsion Structure

Several experimental techniques have been invoked in studies that address the structure of microemulsions. Scattering techniques [23-28] are well suited for determining structural dimensions in cases where the structure already has been determined, but has not yet been shown to discriminate between uni- and bicontinuous structures. Difficulties are associated with the simultaneous high volume fractions of water and oil, and the fact that, in contrast to many other colloidal solutions, dilution procedures are not appropriate for microemulsions: these structures are produced as a result of reversible self-assembly, which depends on the concentrations of all components in the system.

Electron micrographs of microemulsions are often plagued by artifacts, arising from the sample preparation procedure (for a critical review, see [29-31]). Another problem is obviously associated with the very long freezing time - of the order of several ms - compared to the estimated timescale for rearrangements of the surfactant films (\(\sim\mu s\)). In principle it is impossible to prove or disprove bicontinuity from a section of a three dimensional structure; bicontinuity cannot, in fact, exist in a plane. Nevertheless, micrographs of microemulsions, showing reliable structures, have been presented in recent years [32].

Probably, the technique that offers the most insight to the structure of microemulsions is by measuring the self-diffusion constants of the various components of the system. This technique easily discriminates between droplet and bicontinuous structures. The closely related technique of measuring conductivity can discriminate between water continuous and discontinuous structures. However, the strength of the self-diffusion technique is that it allows for measuring, simultaneously, the transport properties on the two sides of the surfactant monolayer (as well as in the surfactant film itself).

3. Self-diffusion

In an NMR FTPGSE experiment [33,34] one measures the mean squared displacement in one dimension. For Gaussian diffusion this is related to the diffusion constant, \(D\), and the observation time, \(\tau\), by

\[
< x^2 > = 2 D \tau
\]  

(1)

The observation time in the experiment is of the order of 100 ms and in typical microemulsions one measures a macroscopic root mean squared displacement of the order of \(1 - 10 \mu m\), which is usually much larger than any typical structural length scales in the solution. The validity of eq. (1), which may be verified experimentally, implies that nonrestricted diffusion [35] occurs on this time and length scale. We note, however, that restricted diffusion was observed in the very careful experiments of Bodet et al. [36] in a concentrated O/W microemulsion.

In the mid-1970s, the technique of NMR self-diffusion proved extremely valuable in establishing the bicontinuity of certain cubic I.c. phases, and the discreteness of certain other cubic phases [37]. In these self-diffusion studies, structural deductions are made from the restrictions in the long-range translational mobilities of the constituent molecules. The success of this method led us to apply the self-diffusion approach to microemulsion systems [38,39]. While in the first study a combination of radio-tracer and classical NMR spin-echo techniques was used [40], much of the progress can be referred to the development of the Fourier transform NMR technique [33] which