

Improving Solubilization in Microemulsions with Additives.

1. The Lipophilic Linker Role

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Very lipophilic additives are able to substantially improve the solubilization in surfactant-oil-water microemulsions. The so-called lipophilic linker effect is studied, and its role is discussed.

Introduction

Since the enhanced oil recovery research boom in the mid-1970s, a lot of work has been aimed at improving the formulation of microemulsion systems. Semi-empirical correlations for the attainment of so-called optimum formulation for three-phase behavior have been reported for anionic and nonionic surfactant systems containing a variety of hydrocarbon oils and aqueous brines (1). On the other hand, the guidelines to improve the quality of an optimum formulation, i.e., the interactions between the surfactant and its physicochemical environment, were also found. The up-to-date knowledge on these topics has been gathered in a recent monograph (2).

As far as applications are concerned, the microemulsion systems are not made of pure components, but rather of mixtures of different surfactants, different oils, and complex brines; as a matter of fact, the behavior of such systems is not yet fully understood, and additional work is required.

A way to simplify the conceptual approach to complex systems is to use the so-called pseudophase model, which considers that a microemulsion may be split into an interfacial pseudophase, an oil pseudophase, and an aqueous pseudophase (3). The interfacial pseudophase is essentially made of surfactant species and may also contain other substances which are associated in some way with the surfactant; these include amphiphilic molecules or oil molecules which are preferentially extracted from the bulk oil phase (4). This pseudophase then includes all the materials which are associated with the interfacial layer and which differ from those of the bulk oil and aqueous pseudophases. It is worth noting that the oil and aqueous phases may contain substantial amounts of dissolved surfactant species, the composition of which generally differs from that of the interfacial pseudophase because of the so-called partitioning phenomena (5).

In this paper, we will show that the presence of some proper additive at or near the interface may considerably alter the solubilization properties of the surfactant.

We have compared the microemulsification of a hydrocarbon oil and a polar oil of similar molar volume in different physicochemical environments containing nonionic surfactants with variable alkyl group length and poly(ethylene oxide) chain size. The length distributions on both hydrophilic and lipophilic groups result in fractionation phenomena with interesting effects on the solubilization. An anomalous behavior leads us to show that the presence of a lipophilic amphiphile may considerably improve the solubilization. The effect is studied with different additives.

A model for the role of this additive, called the lipophilic linker, is proposed, and the experimental results are interpreted according to the location of the different species in the gradient of polarity that exists through the interfacial region.

Materials and Experimental Procedures

The nonionic surfactants used are polyethoxylated alkylphenols with a Poisson distribution of the ethylene oxide chain length (6). Their linear alkyl chains contain 8, 10, 12 (Huls products), 14, and 16 (Texaco products) carbon atoms, with average ethylene oxide numbers (EON) of 3, 5, 7, and 9. Intermediate EON values are obtained by mixing neighboring species assuming a linear mixing rule on a mole fraction basis.

Isooctane, hexadecane, and n-alcohols are purum grade Fluka reagents. Ethyl oleate is a pharmaceutical grade (98% minimum) product manufactured by Laserson-Sabetay.

The phase equilibrium experiments are carried out according to a standard procedure (7). The aqueous (respectively oleic) surfactant solution is poured into an elongated graduated test tube together with the oil (respectively brine) phase in the required proportions. The volumic water-to-oil ratio (WOR) is 1.

The test tubes are sealed and placed in a constant-temperature bath. They are gently shaken twice a day during a week, and then are left to equilibrate during two months. The phase behavior is noted, and the phase volumes are recorded to compute the solubilization parameters.

Experiments are generally carried out by scanning a single formulation variable in a sequence of tubes; the value of the scanned variable which corresponds to the optimum formulation is noted with an asterisk.

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