Improving Solubilization in Microemulsions with Additives. Part III: Lipophilic Linker Optimization

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ABSTRACT: Polar oil additives are able to substantially improve the solubilization in surfactant-oil-water microemulsions through the so-called lipophilic linker effect. Long-chain alcohols (above C_8) and their low ethoxylation derivatives were found to produce such an improvement. A method is proposed to evaluate the lipophilic linker performance and to compare lipophilic linker candidates in different oil–surfactant systems. The best lipophilic linker was found to have a hydrophobe chain length as an average between that of the surfactant tail and the *n*-alkane oil. The experimental data agree with that obtained by using a simple model based on the estimation of molecular interactions.
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KEY WORDS: Additive, alcohol, microemulsion, optimization, solubilization, surfactant.

In the past 15 years, much work has been dedicated to improving the formulation of microemulsion systems, in particular their ability to cosolubilize oil and water. It was known that the best solubilization was associated with Winsor III type system, that happens at a so-called optimal formulation for three-phase behavior. Semiempirical correlations for the attainment of three-phase behavior have been reported for a variety of surfactant-oil-water systems containing different hydrocarbon oils and aqueous brines. On the other hand, the rules to enhance the amount of oil and water cosolubilized in the microemulsion were also investigated. Current techniques concerning solubilization can be found in a review monograph (1). A short pedagogical account for practitioners recently has been available as well (2).

All research done in the 1970s and 1980s was based on Winsor's premise (3), which states that any improvement in solubilization is due to enhanced interactions between the surfactant molecule adsorbed at interface and both the oil and water molecules located nearby on both sides of the interface.

Recently, a new way to improve the solubilization was reported that does not follow Winsor's premise. It was found that some very lipophilic amphiphiles, so-called lipophilic linkers (4,5), were significantly able to enhance oil solubilization in microemulsions without directly participating in the interfacial interactions. Unlike a cosurfactant which adsorbs at the interface, a lipophilic linker seems to be located inside the oil phase. However, experimental evidence indicates that it is probably segregated (6) in the vicinity of the interfacial layer because of its polarity. Since its predominant orientation is likely to be perpendicular to the interface, the lipophilic linker would favor ordering of the oil molecules in one or several layers next to the interface (5), and thus increasing the indirect interactions between the surfactant and bulk oil.

In part I (4) of this series, it was shown that addition of octylphenols with a low ethoxylation degree [0 to 1.5 ethylene oxide (EO) group per molecule] could substantially increase the solubilization originally produced by one containing 5 to 10 EO groups per molecule. Furthermore, it was found that solubilization increases linearly with additive concentration.

In part II (5), it was shown that long-chain alcohols ($>C_8$) behave as lipophilic linkers. Solubilization enhancement increased as the alcohol chain length increased, at constant alcohol molar concentration in the system. Moreover, it was shown that the effect depends upon the surfactant solubilization ability.

This third paper is dedicated to a practical goal: how to find the best lipophilic linker with the highest solubilization performance for a given oil and surfactant hydrophobe pair. Any optimization procedure requires an optimization criterion, i.e., a quantitative way to compare one system with another. This point will be addressed first.

OPTIMIZATION CRITERION

The criterion is based on the combination of two well-accepted results. The amount of oil and water solubilized in the microemulsion middle phase is essentially proportional to the amount of surfactant, as illustrated in Figure 1A, whenever the amount of surfactant is significantly higher than the critical micelle concentration (CMC). On the other hand, the lipophilic linker solubilization enhancement grows almost linearly with its concentration. Consequently, the slope of the variation of microemulsion volume vs. surfactant concentration increases as the

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