

Enhancing Solubilization in Microemulsions—State of the Art and Current Trends

Jean-Louis Salager^a, Raquel E. Antón^a, David A. Sabatini^{b,*},
Jeffrey H. Harwell^c, Edgar J. Acosta^c, and Laura I. Tolosa^a

^aLaboratorio de Formulación, Interfases, Reología y Procesos (Lab. FIRP), Chemical Engineering School, University of The Andes, Mérida, 5101 Venezuela, and ^bCivil Engineering & Environmental Science and ^cChemical Engineering and Material Science Departments, University of Oklahoma, Norman, Oklahoma 73019

ABSTRACT: Along a formulation scan, solubilization is maximal when a bicontinuous microemulsion is in equilibrium with both oil and water excess phases in a so-called Winsor III system. The logical way to enhance solubilization is to increase the interaction of the surfactant for both the oil and water phases, which can be easily attained by increasing the size of both the head and tail groups. However, this approach is limited by solubility constraints. Additional solubilization enhancement can be attained by introducing a molecule(s) that bridge the bulk phase and the adsorbed surfactant layer; this can be accomplished by using the so-called lipophilic and hydrophilic “linker effect” or by using block copolymer additives. In either case, the goal is to modify an extended zone in the oil and water domains close to their boundary. The intramolecular grafting of a linker group between the hydrophilic and lipophilic moieties in a surfactant results in a so-called “extended” surfactant structure, which produces enhanced solubilization, as does the surfactant/linker combination, but with the added benefit that the self-contained extended surfactant structure does not undergo selective partitioning. We conclude that an improvement in solubilization is directly related to the presence of a smooth, blurred, and expanded transition across the interfacial region from polar to apolar bulk phases.

KEY WORDS: Extended surfactants, future trends, interfacial tension, lipophilic and hydrophilic linkers, microemulsions, solubilization, state of the art.

MICROEMULSIONS

Microemulsions are thermodynamically stable mixtures of oil and water that are stabilized by surfactants. Although several books have been written on the subject (1–7), they are not al-

ways advisable as introductory reading for the uninitiated researcher because they are symposium proceedings or assemblages of articles with a variety of authors on a variety of concepts that are not always well integrated. The exception is the contribution of Bourrel and Schechter (8), which was written in a pedagogical manner for practitioners, although it might be too complex as a first reading on microemulsions. Several review papers with a pedagogical approach are more convenient for a first contact with the topic, although the presentation approach varies from author to author (9–12). The present monograph seeks to provide such an introductory treatment of the microemulsion as a high-solubilization medium.

Interest in the application of microemulsions continues to grow. Figure 1A presents the number of publications per year on microemulsions, beginning with the original paper by Hoar and Schulman in 1943 (13) and continuing through 2003 (14). Figure 1A shows that microemulsions attracted only limited attention from 1940 to 1970, but that in the mid-1970s, a greater interest in microemulsions emerged because of their potential use in enhanced oil recovery (EOR). Although microemulsion-based EOR proved to be technically feasible, declining oil prices in the late 1980s discouraged its use for economical reasons. However, intensive surfactant research greatly improved our understanding of microemulsion systems, which in turn helped promote their use in a wide variety of applications. Figure 1B illustrates the range of applications that were made possible by advances resulting from the earlier EOR research.

It is worth pointing out that the term “microemulsion” is a misnomer, since, with the exception of some borderline cases, microemulsions cannot be considered tiny droplets dispersed in a continuous phase (15), i.e., a microemulsion is not really a “special case” of a regular emulsion or macroemulsion. In fact, regular emulsions and microemulsions are fundamentally different. Unfortunately, the well-entrenched terminology of “macroemulsions” and “microemulsions” emphasizes similarities that do not really exist. The most fundamental difference between them is that microemulsions exist in a state of thermodynamic equilibrium. In contrast, macroemulsions are metastable two-phase systems in which the coalesced state is the actual state

*To whom correspondence should be addressed at 202 W. Boyd, Rm. 334, University of Oklahoma, Norman, OK 73019.
E-mail: sabatini@ou.edu

Current address of fifth author: Chemical Engineering and Applied Chemistry Department, University of Toronto, Ontario, Canada.

Abbreviations: ACN, alkane carbon number; EO, ethylene oxide; EON, ethylene oxide number; EOR, enhanced oil recovery; HLB, hydrophilic-lipophilic balance; HLD, hydrophilic-lipophilic deviation; LC, liquid crystals; OW, oil/water; S+A, surfactant + alcohol; SAD, surface affinity difference; SAOW, surfactant–alcohol–oil–water; SOW, surfactant–oil–water; WOR, water-to-oil ratio.