Microemulsions
THEORY AND PRACTICE

Edited by

Leon M. Prince

Consulting Surface Chemist
Westfield, New Jersey

ACADEMIC PRESS, INC.   New York   San Francisco   London   1977

Academic Press Rapid Manuscript Reproduction

List of Contributors

Vinod K. Bansal
Departments of Chemical Engineering and Anesthesiology
University of Florida
Gainesville, Florida 32611

Stig Friberg
Department of Chemistry
University of Missouri-Rolla
Rolla, Missouri 65401
and the Swedish Institute for Surface Chemistry
Stockholm, Sweden

Hironobu Kunieda
Department of Chemistry
Faculty of Engineering
Yokohama National University
Yokohama, Japan

Leon M. Prince
Consulting Surface Chemist
7 Plymouth Road
Westfield, New Jersey 07090

Dinesh O. Shah
Departments of Chemical Engineering and Anesthesiology
University of Florida
Gainesville, Florida 32611

Kozo Shinoda
Department of Chemistry
Faculty of Engineering
Yokohama National University
Yokohama, Japan

Preface

Stable, opalescent "emulsions" had been on the market for thirty years when the term "microemulsions" was coined in 1958. "Microemulsions" describe the systems that Hoar and Schulman scientifically identified in 1943 as special colloidal dispersions. With this perspective, the book seeks to deal with both theory and practice regarding microemulsions so that the make-up of these unusual systems will be understandable to the practical chemist and the theoretician.

During the last five years, interest in microemulsions has expanded enormously, spawning a multitide of papers on every aspect of the subject. This circumstance has prompted the present book, which is the first text to be completely devoted to microemulsions, presenting both a history of the development of industrial emulsions and a sophisticated account of emulsion theory.

This book is at a crossroads in the development of the theory of these colloidal systems. During the past several years, there have been proposals that Schulman's fluid, translucent, isotropic dispersions of oil and water might not be emulsions at all but instead are swollen micelles, micellar solutions, or micellar emulsions. Such systems have been quantitatively defined by means of phase diagrams. This difference in terminology appears to be more than just a question of semantics and this book presents both sides of the controversy. The case for microemulsions vs micellar solutions was presented by Shinoda and Friberg in 1975 under the title "Microemulsions: Colloidal Aspects." The critical evaluation of the investigation of microemulsions stabilized by mixed films has certain areas of conflict with this review, which will require critical attention.

In addition to discussing theory, this book also sets forth the physics and chemistry of these systems in practical terms. It teaches a basic understanding of microemulsions, enabling the reader to follow the adsorption of molecular species to the interface between oil and water and to comprehend the interactions between them that determine the direction and degree of curvature of the interface and thus the type and droplet size of the resulting dispersions of liquids. HLB is only discussed briefly, since the reader is assumed to be familiar with this rating system for emulsifiers and oils. Although the references contained herein are comprehensive, covering most of the field, they are not complete. Many discussions of the theory of microemulsions have appeared in articles that deal with unrelated subjects. Finally, where primary references have been inadvertently omitted, they may usually be found in the papers to which such reference has been made.

Micellar solutions, which are usually described in terms of phase equilibria diagrams, are discussed, but again a primer course is not given. Enough basic material is presented to enable the reader to obtain a grasp of the subject.

Since the writing of this book certain aspects of the subject have undergone important changes. It has come to be understood that the phase equilibria diagram defines a very specific, narrow, and critical range of systems and requires much tedious and precise work to make. The use of phase maps is a much simpler device, which includes a broader range of experimental data that are much easier to accumulate. It is anticipated that future investigators will take the simpler route.

Within the past several months, there has been a realization on the part of the editor that some of the data on this subject might have been based on uncertain premises. Though a great deal is known about microemulsions, certainly we are just beginning to fully understand this phenomenon. The editor is reminded of the words of Gilbert N. Lewis:

> Science has its cathedrals built by a few architects and many workers . . . . The scientist builds slowly and with a gross but solid kind of masonry. If dissatisfied with any of his work, even if it be near the very foundation, he can replace that part without damage to the remainder.

Contents

Schulman's Microemulsions

LEON M. PRINCE

Consulting Surface Chemist
7 Plymouth Road
Westfield, New Jersey   07090

I.   INTRODUCTION

Three kinds of dispersions of oil, water, and surfactant will be considered in this book: microemulsions, micellar solutions, and the common variety of emulsions, which will be called macroemulsions. The last variety appears white and is characterized by its propensity to separate into its two original liquid phases on standing. Microemulsions and micellar solutions do not appear white; they are translucent or transparent and do not separate. Neither of the latter has been characterized well enough at this point to make possible a clear-cut differentiation between them. The writer has chosen to identify microemulsions as having droplet diameters in the range of 2000 A (0.2 µm) down to 100 A (0.01 µm) and micellar solutions as having aggregate diameters less than 100 A. In a sense, this is an extension of Becher's

1

definition (1) of an emulsion as an unstable heterogeneous
system in which the diameters of the dispersed droplets, in
general, exceed 1000 A. This writer's definition is by no
means a firm characterization and is open to legitimate dis-
pute. It is mentioned here simply to give the reader a rough
idea of, and the general range of, the area in question.

Clayton (2) had no such problem. His definition unmistak-
ably conveys the comprehensive insight into these systems that
workers in this field had 30 years ago. In fact, Clayton gra-
ciously acknowledged that F. Selmi quite clearly gave this
same definition almost 100 years earlier (3). Clayton's defi-
nition was "An emulsion is a system containing two liquid
phases, one of which is dispersed as globules in the other.
That liquid which is broken up into globules is termed the
dispersed phase, whilst the liquid surrounding the globules
is known as the continuous phase or dispersing medium. The
two liquids, which must be immiscible or nearly so, are fre-
quently referred to as the internal and external phases, re-
spectively." He further stated that when one of the liquids
is water and the other a water-insoluble liquid or "oil," two
sets of emulsions are theoretically possible, depending upon
whether oil is dispersed in water (o/w) or vice versa (w/o).
Also, he considered that there is no a priori reason why emul-
sions of any desired concentration should not be made of either
either liquid in the other.

In addition, there may be mixed emulsions in which both
o/w and w/o emulsions are present in the same system. The
oils may be different. One example is a margarine in which a
highly polyunsaturated oil-in-water emulsion of a very small
droplet size (0.5 to 1 μm) is the internal phase of a normal
w/o margarine (4), the dispersed droplets of water of which
are in the 20-25 μm range. This is called a double emulsion.
There may be more complicated systems.

In more modern terminology, an emulsion may be defined as
a dispersion of two (or more) mutually insoluble liquids, one
in the other. Because of the surface tension forces at play
between the two liquids, the dispersed phase consists of
spherical droplets. The state of the art at the time Clay-
ton promulgated his definition contemplated droplets only in
the diameter range of a few microns to a hundred microns. The
droplets of Schulman's microemulsions were very much smaller
than these and were, therefore, at first thought to be mi-
celles because of the way they scattered light and their sta-
bility. In the case of microemulsions and micellar solutions
one of the liquids is always water; in the case of macro-
emulsions, water is usually one of the liquids but there are
macroemulsions in which neither liquid is water (5).

Clayton's definition of an emulsion envisioned a system of

two mutually insoluble liquids, one dispersed in the other, (a) without any emulsifier, (b) with an emulsifier consisting of a single layer of finely divided powders situated at the interface between the two liquid phases, or (c) a single layer of discrete molecules adsorbed in highly oriented form at the interface. This oriented single layer is variously called a monolayer, a monomolecular film or layer, an interface or an interphase, the latter term suggesting that the single layer of highly oriented molecules constitutes a separate, third phase. All of Clayton's systems have a common denominator: mechanical work in the form of agitation, homogenization, ultrasonication, etc., must be put into the system in order to disperse one liquid in the other in the form of droplets.

The concept of a mixed film was part of (c) above. This was a monomolecular film consisting of two species, a soap or detergent and an alcohol (cosurfactant) which interacted with each other in the film in such a way as to greatly increase the stabilizing power of the interface by reducing droplet size. Input of work, however, was still required to form these systems. Schulman called the alcohol an amphiphile, a term that has gone into disrepute in recent years.

In the very year that Clayton's last edition appeared, 1943, Hoar and Schulman introduced a fourth situation. This was a mixed film which, in combination with certain oils, was capable of generating an emulsion of very small droplet sizes without the input of any work, i.e., the emulsion formed spontaneously. Such systems came to be called microemulsions.

Like macroemulsions, microemulsions are of the water-in-oil (w/o) type and oil-in-water (o/w) type and invert from one type to the other by adding more of one phase or by changing the type of emulsifier. It is in this area of inversion that Schulman's microemulsions display a peculiar phenomenon. Beginning with a fluid w/o microemulsion, as water is added, they pass through a viscoelastic gel stage. As more water is added, they invert to an o/w emulsion which is fluid again. This process is reversible. It has been determined that the viscoelastic gel stage (which can be almost solid) is comprised of an hexagonal array of water cylinders adjacent to the w/o stage and a lamellar phase of swollen bimolecular leaflets adjacent to the o/w emulsion. The phases of the gel stage are called liquid crystalline phases and this perhaps more than any other single factor is responsible for the controversy of microemulsion vs. micelle as discussed in Chapters 5 and 6.

It is relatively easy to recognize a commercial microemulsion of the Schulman type. Providing you know that oil, water, and surfactant are in the system, the chances are very good that the dispersion is a microemulsion if it is fluid,

optically clear (transparent) or opalescent (translucent) AND
when spun in a laboratory centrifuge for 5 minutes at 100 G's,
the dispersion does not separate. The reasons to support this
empirical definition are presented in some detail below. As
will be noted, these are essentially physical in nature. The
chemistry of the microemulsion upon which the formulation of
these extraordinary systems are critically dependent, is
treated in the third chapter.

     This chapter enumerates many of the microemulsions of com-
merce and describes methods for identifying them. The treat-
ment is as practical as possible consistent with the scienti-
fic principles involved.

II. MICROEMULSIONS OF COMMERCE

     Microemulsions are quite ubiquitous. We encounter them
frequently in our daily lives. When we arise in the morning
we find them as transparent essential oil-in-water (o/w) types
in our mouthwash or men's shaving lotion. At breakfast, homo-
genized milk contains microdroplets of fat dispersed in water,
and nonfat dried milk powers instantly form microemulsions
when stirred into water. Our clothing is returned from the
dry cleaners having been cleaned with transparent microemul-
sions of water dispersed in a dry cleaning fluid. There is a
good likelihood that the fat we eat for breakfast is absorbed
in our intestines via a microemulsion or micellar process. If
we wax the kitchen or family room floor, it is probably done
with an emulsion polymer latex that can be classified as a
microemulsion. Deodorizers and sanitizers to clean floors and
porcelain may be solubilized--another way of describing a
clear, transparent microemulsion. Flavors in pre-mix cake ic-
ings, ice cream, gelatin, desserts, as well as the flavors in
many beverages and fountain extracts are often solubilized.
Many food products contain or are entirely microemulsions.
Pomades of the "ringing gel" type are a form of microemulsion,
the viscoelastic gel stage. Cold creams and other cosmetic
products may be microemulsions. Microemulsions are used to
uniformly disperse the active principles of pharmaceutical
preparations (e.g., vitamins). Many industrial cleaners in
the janitor's supply trade are microemulsions. In recent
years slugs of w/o microemulsions have been used to recover
more oil from old wells (tertiary oil recovery). This is an
impressive list and one which is destined to become longer as
we learn how to microemulsify oils of different chemical
composition.

     For many years prior to 1959, before the term microemul-
sion was coined, colloidal dispersions of this kind were
called emulsions but they occupied a special niche in the

marketplace because their stability was measured in years. They were easily recognizable by their transparency or opalescence. Some of these systems were completely transparent but most of them were of the water-in-oil type. Such systems were considered unique because they looked and behaved differently than ordinary macroemulsions, which scattered white light and whose stability was measured in hours, days, or, at best, months. Among the prominent o/w microemulsions of this era were the Carnauba wax floor polishes, pine scrub soaps, cutting oils, chlordane emulsions, alkyd emulsions, all of the o/w type; only the cleaning fluids, which were also prominent, were of the w/o type. The evolution of these products is described in the next chapter. Suffice it to say here that of these pioneering products, only the cutting oils, pine scrub soaps, and cleaning fluids occupy an important place in today's marketplace. However, direct descendants of these products are gaining an ever-growing share of the market.

When Schulman called these systems microemulsions, he put them in their own niche, differentiating them from other classes of liquid/liquid systems. By doing this they could be viewed in a clearer scientific perspective, which enabled a number of advancements to be made in both the theory and art.

All microemulsions, however, cannot be classified as emulsions in accordance with Clayton's broad definition. The usual classification of microemulsions, or for that matter macroemulsions, as dispersions of oil and water is not strictly correct. As Clayton pointed out, an emulsion is a dispersion of any two insoluble liquids, one in the other. The fact that one is usually water is only a practical consideration. Neither liquid need be water. For example, glycerine is insoluble in olive oil, carbon tetrachloride, and amyl acetate, and emulsions have been made of these pairs of liquids (5). Many other mutually insoluble pairs of liquids can be emulsified and, depending on their relative indices of refraction and the emulsifying agent used, they may be transparent or chromatic while their droplets are in the micron size range. None of these systems have as yet made their debut on the market.

On the other hand, when water is one of the liquids, the definition of an oil is subject to a much broader definition than might be expected. For emulsification purposes an oil may be considered as any water-insoluble material that can be made liquid at a temperature at which water remains a liquid. By the use of pressure vessels, this means in practice that solids which melt as high as 220° to 250°F. can readily be emulsified with water. This encompasses high melting waxes, alkyds, polymers, and other amorphous substances as well as some crystalline ones. The range of solids may be increased

if they may conveniently be dissolved in a solvent that can be tolerated in the end use. A solid toxicant in deodorized kerosene or xylene as used in agricultural sprays for deposit by plane are commonplace examples of these.

Systems of this kind are called emulsions or microemulsions, depending on droplet size, because they are formed by an emulsification process. Upon cooling, of course, the solid-in-water system is, in the strictest sense, a dispersion. Obviously, the terms wax emulsion, polymer emulsion, or Lindane emulsion are commonplace, and we know what is meant.

As opposed to macroemulsions, microemulsions command a premium in the marketplace. Even though they may not be recognized as such--the transparent ones may be called solubilized systems, micellar solutions, or just solutions--their attributes contribute special value to the product in one or more ways. The most obvious is stability. In the case of wax or polymer emulsions (for floor polish and paint), fine particle size ensures high gloss and film integrity. The opalescence or transparence of cosmetic systems may add an aesthetic touch to their sales appeal. Uniformity of dosage in pharmaceutical preparations is another important contribution of microemulsions. Finally, the rheological properties (cf. C. below) of microemulsions can be adjusted easily so that viscous or fluid systems can be obtained almost at will.

III. PHYSICAL PROPERTIES

There are two reasons for wanting to know about the physical properties of microemulsions. The first is to be able to recognize such systems when they are met. This involves identification by the naked eye and, at least, a minimum comprehension of the kind of colloidal system one will have to deal with. The second has to do with the ability to understand the performance of the systems and what measures can be taken to modify their performance attributes to your benefit. Some of this material has already been presented in unified form (6).

Among the physical measurements that are useful for identifying microemulsion systems are light scattering, optical birefringence, sedimentation, centrifugation, rheology, conductivity, and very recently, nuclear magnetic resonance (NMR). Each measurement tells us something about the system. Consideration of two or more measurements together goes a long way in firmly classifying these oil and water systems. The several measurements are described below in simplified form. All of these techniques are within the purview of the practical chemist or biologist. More scientific discussions of

these techniques are considered in other chapters, where their
greater complexity is relevant.

A. Light Scattering

The most obvious property of systems of very small aggre-
gates is the way they scatter light. In aqueous dispersions
this is apparent to the naked eye as the Tyndall Effect.   It
is that portion of the scattered light that is polarized.
Thus, microemulsions appear blue to reflected light and
orange-red to transmitted light.   Dilution of the dispersion
accentuates this effect.   On the other hand, certain systems
will appear transparent in concentrated form and then display
opalescence on dilution.
Light is scattered by all molecules or components of them.
Particles that are large in comparison with the wavelength of
light (white light, λ, averages 5600 A) reflect and refract
light in a regular manner and thus appear white, whereas par-
ticles that are small in comparison with the incident light
waves scatter light in all directions.   This scattered light
is plane polarized, each particle becoming the source of a
new wave front.   When the droplets of an emulsion are less
than $1/4$ λ (ca. 1400 A) in diameter, white light can pass
through the dispersion and it becomes translucent or opales-
cent.   Depending on the relative index of refraction of the
oil and water, such systems appear transparent to the naked
eye when the droplets are about 100 A in diameter.   (Trans-
lucent is the general term and includes transparent, which
may be called very translucent.)
This phenomenon is not restricted to solutions.   Freshly
formed cigar smoke will scatter blue light and transmit
orange red.   Moreover, if one watches a tall exhaust stack
spewing out its smoke, the same phenomenon will be observed
close to the outlet; after a few feet, however, the particles
aggregate into larger ones and then scatter white light.
Lord Rayleigh (J. W. Strutt) ascribed the blue of the sky
and the orange red of the sunset to these same phenomena, but
the aggregates in his system were molecules of oxygen and ni-
trogen.   Although the ocean of air above us extends almost
1000 miles high, the bulk of the gases exist less than 50
miles from the surface of the earth.   Sunlight passes through
these gases and is reflected by the surface of the earth.
This reflected light is scattered by the 50 mile thick layer
of gas.   Rayleigh developed an equation that showed that the
shortest wavelengths of the mixture that is called white
light (λ = 4000-7000 A) are scattered most.   Thus, blue light
is scattered more than the longer red wavelengths and our eyes
see the sky as blue.   As the sun lowers in the sky and we are
able to look almost directly at it, we see the orange-red

hues transmitted by the gases and by the very fine particles
of dust close to the earth. We can see only these two basic
colors in the sky. Were it not for this phenomenon of
nature, we would see a black sky behind the sun as the astro-
nauts did on the moon.

It is noteworthy that it takes 50 miles of scattering to
produce the basic colors of the sky when the scatterers
(chiefly oxygen and nitrogen molecules) are only an Angstrom
unit or two in size. In our beakers and bottles, where the
scattering takes place in a few inches, the size of the scat-
terers must be in the 100 A to 1000 A range for our eyes to
see the Tyndall Effect.

Accordingly, the appearance of scattered light may be
used to identify microemulsions and to roughly measure the
size of their droplets. It is therefore appropriate to tabu-
late the kind of light scattering the naked eye can see under
normal conditions. With the aid of Table 1 and a little
practice, the eye can become a very sensitive piece of light-
scattering apparatus.

TABLE 1

Visual Guide for Estimating Aggregate Size

Material Structures	Diameter (A)	Appearance to Naked Eye
Water Molecules	2.7	Transparent
Soap Micelles	35-75	Transparent
Micellar Solutions	50-150	Transparent and translucent
Microscopically Resolvable Units	1000-2000	Translucent when dispersed
Macroemulsions	2000-100,000	Opaque, milky
Visually Resolvable Units	500,000	Discrete aggregates

Where more quantitative information is required, as in
research studies or quality control, light scattering