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MECHANISM OF FORMATION OF OIL-IN-WATER MICROEMULSIONS

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MECHANISM OF FORMATION OF OIL-IN-WATER MICROEMULSIONS

by

ANNA WEISS-COHEN

A dissertation submitted to the Graduate
Faculty in Chemistry in partial fulfillment
of the requirements for the degree of Doctor
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1979

This manuscript has been read and accepted for the Graduate faculty in Chemistry in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

Dec-20-1979 Henri L. Rosano
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28 December 1979 David C. Locke
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The City University of New York

Abstract

MECHANISM OF FORMATION OF OIL-IN-WATER MICROEMULSIONS

by

Anna Weiss-Cohen

Adviser: Professor Henri L. Rosano

This study was undertaken to help elucidate the nature of transparent, stable mixtures of oil and water plus two surfactants. The objective was to determine whether these transparent dispersions are thermodynamically stable or metastable systems and how to differentiate between the two types of dispersions. Two series of microemulsions were prepared and studied by various techniques. Although thermodynamically stable micellar dispersions may exist, it was concluded that most of the dispersions prepared were metastable transparent emulsions which could be stable and transparent for long periods of time. This conclusion was based on the differences in transmission of 520 nm radiation in dispersions of the same composition in which only the order of combination of the components was changed. This was the main criterion used in this study to distinguish between the two types of systems. A mechanism for the formation of oil-in-water microemulsions containing oil/water/soap/short chain alcohol for the metastable systems was proposed.

A series of low viscosity, transparent oil-in-water dispersions were prepared using a titration technique. A lipophilic nonyl-phenol ethylene oxide condensate (LS) was dissolved in the oil phase, mixed with water; the resulting fine emulsion was titrated to clarity with a

more hydrophilic nonyl-phenol ethylene oxide condensate (HS). This is called the "point" method. On the other hand, adding more water to the microemulsion to produce a cloudy dispersion and then titrating to clarity again with the HS is called the "dilution" method. Since the amount of HS required to produce transparent dispersions in systems containing the same total volume of water was greater for the "dilution" method, it was concluded that these were not thermodynamic systems.

A second series of low viscosity, transparent oil-in-water and water-in-oil dispersions containing soap/oil/water/short chain alcohol were prepared by the "point" method. The nature of the short chain alcohol (cosurfactant) was investigated for the formation of o/w and w/o transparent dispersions with three different oils. All of the titration results demonstrated the extreme structural specificity of the components. Again, changing the order and method of addition of the components, at constant temperature, affected the formation of transparent dispersions. The observed results were due to the transfer of the surfactants through the oil/aqueous interphase and the interfacial structure.

Analysis of the properties of duplex film compression isotherms and surface potentials versus molecular areas of lauric acid and stearic acid films showed that the oil/surfactant aqueous interfacial film must be expandable and able to withstand interfacial pressures larger than that of the original oil/aqueous interfacial tension (negative interfacial tension).

The measurements of interfacial tension (γ_i) as a function of time showed that when a fatty acid transfers from an oil to an aqueous phase, transitory low interfacial tensions are produced. This leads to initial emulsification. When a short chain alcohol is injected into the aqueous phase of an oil/aqueous systems, the interfacial tension will be reduced below its equilibrium value for a short period of time. In the presence of an adsorbed surfactant film, γ_i can be reduced to a value very close to zero (10^{-4} or 10^{-5} dynes/cm) depending on the retarding effect of the film on the transfer and desorption of the alcohol. It is during these transitory very low interfacial tensions that transparent dispersions are produced. From these measurements it was shown that the microemulsions represent a metastable state formed by the redistribution of the two amphipathic components. The resulting surfactant/cosurfactant film must be able to stabilize the droplets against coalescence after the cosurfactant has lowered γ_i sufficiently to cause dispersions.

This is a path-dependent mechanism which depends on the method of preparation. The redistribution of a surfactant has previously been cited as necessary for spontaneous emulsification. The conclusion is that these transparent dispersions should be considered as metastable transparent emulsions, rather than thermodynamically stable swollen micellar systems.

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With sincere appreciation and respect, I would like to thank my mentor Professor Henri L. Rosano. His guidance, faith in my abilities and constant encouragement made this work possible. I would like to thank the members of my committee for their cooperation and helpful suggestions. My thanks also goes to the faculty members, students, secretaries, technicians and fellow graduate students in the Chemistry Department at CCNY who made my education a more meaningful and enjoyable experience. I would also like to thank Dr. Michael Aronson at Lever Bros. for allowing me to use the spinning drop apparatus there and for his helpful comments.

My thanks also goes to my parents-in-law for their patience and support. I would like to thank my brothers, sister and parents for putting up with me, for their constant encouragement, and for always being there when I needed them. Last, but not least, I would like to thank my husband, Kenneth, for his help in typing parts of the original manuscript, his patience, love, and constant support.

I would like to dedicate this thesis to my parents and Kenneth.

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LIST OF SYMBOLS AND ABBREVIATIONS

LS	lipophilic surfactant
HS	hydrophilic surfactant
Eto	ethylene oxide number
HLB	hydrophile-lipophile balance
PIT	phase inversion temperature
γ	surface tension
$(\gamma_{o/w})a$	tension between oil and water due to partitioning of alcohol
n_d	total number of droplets
r	radius
V	volume
A	surface area
n	number of molecules
$\gamma_{m/o}$	interfacial tension between mixed monolayer and oil phase
$\gamma_{m/w}$	interfacial tension between mixed monolayer and water phase
γ_i	interfacial tension
$\gamma_{o/w}$	tension between an oil and water phase
Π	film pressure
dA	surface area difference
$\gamma_{a/w}$	tension between air and water
Π_m	measured film pressure
AMP	2-amino-2-methyl-1-propanol
$\gamma_{a/o}$	tension between air and oil
σ	cross-sectional area of the molecules at the interface

Π_G	film pressure at a flat interface
Π'_w	film pressure of flat duplex film at water side
Π'_o	film pressure of flat duplex film at oil side
Π_w	film pressure of curved duplex film at water side
Π_o	film pressure of curved duplex film at oil side
γ_0	interfacial tension before curvature
ΔP	pressure difference
R	gas constant
T	temperature
$\bar{V}_w$	molar volume of water
X_w	mole fraction of water
n_w	number of moles of water
n_b	number of moles of ions from adsorbed surfactant in micelles
K	Boltzmann's constant
N	Avogardro's number
$\Delta\Pi_{os}$	difference in osmotic pressure across the interface
Π'_m	osmotic pressure of micellar phase
Π_b	osmotic pressure of water phase
n_{st}	number of moles of surfactant in micellar phase
σ'	cross-sectional area per mole of surfactant
ΔG_m	free energy change due to mixing
ΔG_T	total interaction free energy (energy barrier to coalescence)
ΔG_W	van der Waals interaction energy
$\Delta\rho$	density difference
d	diameter
n	refractive index of aqueous phase
P	period

Γ	osmotic coefficient
dG	increase in free energy
$\Pi_{o/w}$	interfacial pressure
Π_D	duplex film pressure
Π_c	collapse pressure
ΔV	e.m.f. difference
V_o	initial e.m.f.
dW	work done on the surface
ΔS	increase in surface
F	force
W	work done on the liquid
d	length
l	length

CHAPTER I

INTRODUCTION

Mixtures of an oil and water in the presence of a surface active agent usually form coarse emulsions which are optically opaque and usually separate on standing. In some cases, transparent mixtures of oil-in-water or water-in-oil can be prepared with the proper combination of surface active materials (1).

These systems, which have been labelled microemulsions (2), micellar emulsions (3) or swollen micellar solutions (4), are considered to be thermodynamically stable (3-7). The mixtures are transparent due to the small particle size of the dispersed components, which is usually less than 140 nm. Several investigators of the shape of the droplets have concluded that the droplets are spherical (8-10).

Recently, evidence has been presented that some transparent mixtures of this type may not be thermodynamically stable (11). This conclusion was based on whether a transparent dispersion resulted in mixtures of the same composition in which only the order of mixing of the components was changed. It was thus proposed that there may be two inherently different classes of transparent oil and water mixtures (12). One class consists of thermodynamically stable micellar systems which form spontaneously, and the other consists of metastable dispersions which can be stable and transparent for long periods of time. Gerbacia et al. (13) attributed the stability of these microemulsions to the presence of a surfactant-cosurfactant solvent film surrounding the dispersed droplets. There is an energy barrier to coalescence of the dispersed droplets. The barrier originates because of the interfacial film surrounding the dispersed phase.

Therefore, a difference of interpretation still exists as to the nature of these transparent systems, since both systems may have long term stability. Are these transparent dispersions thermodynamically stable or metastable systems? How can we differentiate between these two types of dispersions? What is their mechanism of formation? In order to answer these questions, the following approach was taken.

First, oil-in-water, low viscosity, transparent dispersions were prepared. In the first series of experiments, n-hexadecane containing an appropriate amount of a nonyl-phenol ethylene oxide condensate (4.0 Eto) with water, produced an initial emulsion. The system was then titrated to clarity with another nonyl-phenol ethylene oxide condensate (9.5 Eto). The systems prepared were studied with respect to the method of addition of the components, the temperature stability, and the effect of the concentration of the primary surfactant.

In the second series of experiments, an appropriate amount of fatty acid was dissolved in an oil, mixed with an aqueous KOH solution, and the resulting coarse emulsion was titrated to clarity with a short chain alcohol. The nature of the alcohol was investigated for the formation of oil-in-water and water-in-oil systems, with three different oils. The percent transmittance of the system as a function of the amount of alcohol added and also as a function of the volume of dispersed phase (oil) while the amount of surfactant was held constant were the other variables studied. The order of addition of the components was also studied for specific oil-in-water systems.

In this study, the major criterion used to distinguish thermodynamically stable from metastable systems was whether, for systems of identical composition, changing only the order of addition of the components affected the formation of the transparent dispersion, rather than its long term stability. If it is found at constant temperature that changing the order of addition of the components has no effect on the formation of the transparent dispersion, it can be concluded that the system is thermodynamically stable. However, for most of the systems prepared in this study, it was found at constant temperature, that the order of addition of the components affected the formation of the transparent dispersion. Therefore, although the two types of transparent systems may both exist, it was concluded that most of the dispersions prepared in this study were not thermodynamically stable.

Since the formation of the transparent dispersions depended on the order of addition of the components and in particular on the initial locations of the surfactant and cosurfactant and also since the systems were prepared by titrating the cosurfactant, it appeared that the transfer through the oil/aqueous interface and redistribution of the surfactants, played a major role in the formation of these transparent dispersions.

Therefore, the first logical problem which had to be studied was the interfacial transfer and reactions of the surfactant and cosurfactant, separately and in the presence of each other.

The interfacial transfer of the surfactant and cosurfactant independently and in the presence of each other were studied by measuring the interfacial tension of an oil/aqueous system with time, by Wilhelmy's wettable plate and the spinning drop interfacial tensiometer techniques.

In the Wilhelmy wettable plate method a sand blasted teflon blade was suspended through the intermediary of a hooked platinum wire to a microforce transducer recorder device (11). Eighty ml of an aqueous KOH solution, which had been cleaned by foaming into a sintered glass funnel, was placed into a 200 ml beaker with a water jacket. The thermostat was set at 30 °C during the interfacial tension measurements. Gentle stirring was maintained in the aqueous phase. Five ml of oil was placed gently on top of the aqueous solution. Interfacial tension (γ_i) was recorded instantaneously upon initial contact of the two phases, then continuously recorded with time as transfer of the adsorbing solute occurred. Measurements were continued until the system reached equilibrium. Experiments were done with surfactant dissolved in the oil phase and the aqueous phase. Other experiments were done with cosurfactant dissolved in the aqueous phase and with small volumes of cosurfactant injected with a micrometer syringe, into the aqueous phase in the absence and presence of adsorbed surfactant.

The spinning drop interfacial tensiometer (14) was used to measure the interfacial tension with time of an n-decane droplet injected into an aqueous KOH solution. The oil droplet and more dense phase were contained in a precision ground 0.245" O.D. pyrex glass tube. The tube was rounded on one end and sealed with a teflon stopper at the other. The tube was placed in a shaft and secured by screwing the cap onto the shaft. The capillary tube was then rotated at speeds controlled by a frequency generator. As the oil droplet was rotated its diameter changed according to the value of the interfacial tension of the oil and aqueous phase. The droplet was observed using a Gaertner travelling microscope with a filar eyepiece used to measure the width of the drop.

An equation has been presented to calculate γ_i (14). The value of γ_i depends on the difference in densities of the two phases, the diameter of the oil droplet, the refractive index of the aqueous phase and the speed of rotation. Experiments were done with the surfactant and cosurfactant dissolved in the aqueous phase and with the surfactant dissolved in the oil droplet while the cosurfactant was dissolved in the aqueous phase.

It was also found at constant temperature that the nature of the components influences transparent dispersion formation. Therefore the next logical problem to be studied was the interfacial structure and how the nature of the surfactants influences the type of interfacial structure that is conducive to transparent dispersion formation. The duplex film technique was used to study interfacial structure.

The compression isotherms and surface potentials versus molecular areas (Π-A and ΔV-A) of lauric and stearic acid films spread on an aqueous KOH solution at 30 °C were determined. An automated Langmuir trough was used with a teflon boom attached to a motor driven shaft (15). A given amount of the fatty acid solution was deposited onto the aqueous surface with an "Agla" micrometer syringe. The substrate and film were retained in a fused silica trough of 1 liter capacity filled to the brim. All experiments were conducted within a Faraday box.

Surface pressures were determined from surface tension measurements made using a sand blasted platinum blade suspended from a transducer amplifier. The transducer output was recorded continuously on a recorder. The surface tension was measured immediately after cleaning the surface of the aqueous substrate (γ_0) and compared to the surface tension obtained after spreading the film on the surface (γ_i). The difference between the two (γ_0-γ_i) gives Π, the surface pressure. The surface potentials were measured with an air ionizing electrode (16, 17) connected to a precision potentiometer, a high input resistance electrometer and the trough electrode (Ag°/AgCl) dipped into the bulk of the aqueous substrate. The emf of the cell composed of the radioactive electrode, trough electrode, potentiometer and electrometer, all connected in series, was measured immediately after cleaning the surface of the aqueous substrate (V_0) and compared with the emf obtained after spreading the film on the surface (V). The difference between the two ($V-V_0$) gives ΔV, the surface potential.

An automated barrier drive with variable speed control permitted determination of an optimum compression rate and reproducible Π-A and ΔV-A isotherms.

The experimental results obtained from these techniques provided a model for the curved interface of a transparent dispersion, since the interactions of all four of the components were directly studied. From the interpretation of the results a mechanism for the formation of transparent oil-in-water dispersions containing oil/water/soap/short chain alcohol for the metastable systems was proposed.

Chapter Two covers the concepts that are fundamental to the surface chemistry of liquid-liquid interfaces. In Chapter Three the various theories of formation and stability of transparent dispersions that have been proposed by other investigators in the field are discussed. In the following chapters, the experimental results of this study are presented. Chapter Four presents the preparation and characterization of the transparent dispersions. In Chapter Five the results of the measurements of interfacial tension vs. time are summarized. Chapter Six deals with the duplex film results and the proposed mechanism of formation of oil-in-water microemulsions. Chapter Seven summarizes the conclusions of the experimental results of this study.

CHAPTER II

THE SURFACE CHEMISTRY OF LIQUID-LIQUID INTERFACES

A. Surface Tension

As is well known, short range attractive (van der Waals') forces exist between molecules. If the surface of a liquid in contact with its vapor is considered, it is seen that in the bulk of the liquid the molecules are sufficiently close so that the effect of attractive forces are considerable. The attractive forces are sufficiently large to keep all but a small number of molecules from escaping into the vapor state. Although these forces are relatively large in magnitude, they tend to balance out in the bulk of the liquid. On the other hand, the molecules in the surface region, not being completely surrounded by other (liquid) molecules, are subjected to an unbalanced attraction, which has the net effect of an attractive force directed inward, normal to the surface. (See Figure 1.) The smaller the surface, the lower this net force. Thus, a condition of minimum surface leads to a lower energy and therefore the surface of a liquid has a tendency to contract. For example, freely suspended volumes of liquid assume a spherical shape, since a sphere has the minimum surface-to-volume ratio.

In order to bring molecules from the interior of the bulk phase, into the surface, work must be done against the cohesive forces in the liquid surface region. From the above description it is seen that the surface molecules of the liquid have a higher free energy than the bulk liquid molecules. This extra surface free energy is described by the term, surface tension. This tension acts parallel to the surface and opposes any attempts to extend the interfacial area. If the surface tension is γ, the work done on the surface in extending its area by an amount dA, is

$$dW = \gamma dA \tag{1-1}$$

This is reversible work, at constant pressure and temperature and thus gives the increase in free energy of the system

$$dG = \gamma dA \tag{1-2}$$

For a physical definition of surface tension, a small rectangular wire frame, ABCD, with one side moveable (Figure 2) is considered. If the length AD (or BC) is d, and the length AB (or CD) is l, the surface area of a film of liquid contained in the frame will be 2ld (since there are two sides to the film).

If the moveable side CD is moved through the distance Δd to a new position C'D' by the exertion of a force F, the work done on the liquid is

$$W = F\Delta d \tag{1-3}$$

The force F is balanced by a counter force operating along the length CD. If γ is defined as the force in dynes per centimeter acting along this length, then the force opposing the expansion of the film is $2\gamma l$ and equation (1-3) reduces to

$$W = 2\gamma l\Delta d = \gamma\Delta S \tag{1-4}$$

where $\Delta S = 2l\Delta d$ is the increase in surface. Thus, $\gamma = W/\Delta S$. In other words, γ may be defined as the work in ergs necessary to generate one square centimeter of surface. This is the physical definition of surface tension.

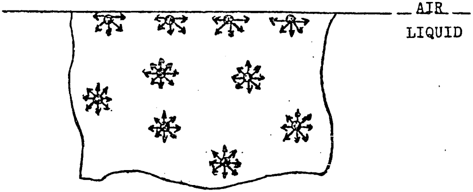


Figure 1. The Forces Acting on Molecules on the Surface and in the Interior of a Liquid

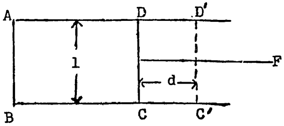


Figure 2. The Physical Definition of Surface Tension

The physical definition of surface tension given above suggests that the appropriate units for the surface tension should be ergs per square centimeter. However, since the surface tension can also be defined in terms of a force acting along a 1 cm length of surface, it is appropriate to use dynes per centimeter. Since an erg is equal to a dyne-cm, the unit usually used is dynes/cm.

B. Interfacial Tension

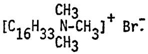
The previous discussion dealt with the properties of a surface existing between a liquid and a gas, the gas being either air or the saturated vapor of the liquid. The boundary tension existing between two liquids is referred to as an interfacial tension (surface tension is actually an interfacial tension between a liquid and a gas).

When two immiscible liquids are placed in contact, an interface results. The net attractive forces operating on a molecule in the interface will be somewhat different than in the case of a simple surface, since there will be some van der Waals' interaction with the surface molecules of the second liquid. However, this attraction will be of a different order of magnitude than that of the bulk molecules and an imbalance of forces will exist, with all the consequent physical effects. What is true of one liquid is equally true of the other. Hence, it is to be expected that the value of interfacial tension will usually lie between the individual surface tensions of the two liquids.

C. Surface Active Agents and Surface Activity

A surfactant, or surface active agent, may be defined as a solute which, when present in relatively low concentrations, lowers the surface tension of the solvent to an unusual extent. The key to surface activity lies in the highly asymmetric structure of the surfactant molecules. Molecules of surfactant are typically elongated, having one end which is nonpolar and hydrophobic, the other end being polar and hydrophilic. The term "amphipathic" has been applied to this type of structure.

An immense variety of amphipathic compounds are known. The usual classification of anionic, cationic, non-ionic or amphoteric, depends upon the nature of the head groups. Typical examples of anionic surfactants are the salts of long chain fatty acids [anionic part is COO^-] usually referred to as soaps. Sodium lauryl (dodecyl) sulfate is another typical anionic surfactant [$-OSO_3^-$ is the anionic portion]. Cationic surfactants are usually amines or quaternary ammonium salts, such as, for example, cetyl trimethyl ammonium bromide



$$[C_{16}H_{33}\overset{CH_3}{\underset{CH_3}{N}}\text{-}CH_3]^+\ Br^-$$

Typical examples of non-ionics are the polyoxyethylenated nonyl phenols formed by the reactions of phenols with ethylene oxide. The general formula of these compounds is C_9H_{19}-⟨O⟩-$(OCH_2CH_2)_nOH$, where n gives the number of ethylene oxide groups. Amphoteric agents contain both anionic and cationic groups. Typical examples of these are long chain amino acids having the general formula, $RNH_2^+CH_2COO^-$.

One of the most characteristic properties of surface active agents is their strong tendency to become adsorbed at most phase boundaries of the solution, regardless of the chemical nature of the bordering phase. Adsorption at the air interface is responsible for low surface tension. Adsorption from solution is governed by the Gibbs adsorption isotherm,

$$\Gamma_2 = -(a/RT)\ (d\gamma/da) \qquad (1\text{-}5),$$

where Γ_2 denotes the surface excess per unit area of the solute, a is the activity of the solute, R is the gas constant, T is the temperature and $d\gamma/da$ is the slope of the plot of surface tension vs. activity. Thus, any solute that lowers the interfacial free energy is accordingly adsorbed positively (Γ_2 is positive). The amphipathic characteristics of the surfactant molecules enables them to be adsorbed from aqueous solutions on to a wide variety of liquid/liquid interfaces. The molecules tend to become oriented in the adsorbed layer with the polar end toward the polar phase and their nonpolar end toward the nonpolar phase. The nonpolar and polar molecules of the phases are likewise attracted to the corresponding ends of the surface active agent molecules, and the interfacial tension is thereby greatly reduced.

D. Micelles

Modern investigations into the bulk properties of solutions of surface active solutes were begun with the publications of McBain and coworkers (18). It had long been known that dilute aqueous solutions of soaps behaved like normal solutions of these electrolytes, however anomolous behavior occurred at higher concentrations. For example, the conductivity of such solutions was found to increase to a point equivalent to that shown by strong electrolytes; whereas the colligative properties (i.e., osmotic pressure, freezing point depressions, vapor pressure lowering, etc.) fell far below those calculated from the ideal laws, even when allowances were made for ionization effect. McBain (18) introduced the concept of colloidal electrolytes. He assumed that these phenomena occur as a result of the spontaneous formation of particles of colloidal dimensions (e.g., 10^{-4} to 10^{-7} cm); that the colloidal particles are in true reversible equilibrium with the ions and therefore, the colloidal electrolytes are truly stable in the strictest thermodynamic sense. These colloidal aggregates of amphipathic electrolytes in aqueous solution were called micelles.

Micelle formation by amphipathic molecules is the result of the same dual tendencies of the molecules mentioned above. These cause them to undergo self-association in solution to produce aggregates in which the organic moieties are in close contact so that the total contact area of the hydrophobic groups of the solute molecules with water is reduced (19). For detergents and other flexible chain surfactants, the process leads to the formation of micelles; the hydrocarbon chains form a liquid-like core with the polar groups remaining exposed to the water at the surface (20).

1. Critical Micellization Concentration

Numerous investigations have shown that micelle formation begins or becomes appreciable over a narrow range of concentrations. For such systems the IUPAC Manual of Symbols and Terminology (21) makes the following statements:

> Surfactants in solution are often association colloids, that is, they tend to form micelles, meaning aggregates of colloidal dimensions existing in equilibrium with the molecules or ions from which they are formed.
>
> There is relatively small range of concentrations separating the limit below which virtually no micelles are detected and the limit above which virtually all additional surfactant forms micelles. Many properties of surfactant solutions, if plotted against the concentration, appear to change at a different rate above and below this range. By extrapolating the loci of such a property above and below this range until they intersect, a value may be obtained known as the critical micellization concentration (critical micelle concentration), symbol c_m, abbreviation c.m.c.

The "relatively small range of concentration" mentioned above which includes the c.m.c. is narrow enough, however, to allow c.m.c. values to be determined quite precisely in many cases (22).

The c.m.c. is one of the most easily obtainable and useful quantitative results about aqueous flexible chain surfactant systems (22). It has numerous applications for the thermodynamics of micelle formation and for characterizing micellar solutions (22, 23). Indeed the c.m.c. is sharp enough to form the basis of a two-phase model of micellar solutions, which seems to overemphasize the critical nature of the c.m.c. (24).

2. Structure of Micelles

The basic features of the roughly spherical micelle in aqueous solutions were worked out by G. S. Hartley in his pioneering work in the 1930s and 1940s (20). The basic features of an ionic micelle are the following: The micelle is a compact roughly spherical body with a liquid-like hydrocarbon core. The polar head groups are at the surface which is rough (25). A large fraction of the counterions is bound to the surface and forms part of the kinetic micelle. The remaining ions form the diffuse double layer. The equilibrium between micelles and monomers is generally rapid. One or more of the methylene groups attached to the polar groups may be wet (19).

In concentrated solutions of surfactants, a wide variety of structures and mesophases have been identified.

3. Micelle Formation in Nonaqueous Media

Compared to aqueous solutions, solvophobic interactions of surfactants in nonaqueous media of even relatively high polarity tend to be much weaker (26). In highly nonpolar solvents (27, 28) the polar groups of the amphipathic molecules become solvophobic and in such media, aggregates form in which the polar groups form the core. Such species are often referred to as inverse, reverse, or reverted micelles. Theories and models for aggregation in nonpolar media were based largely on models derived from aqueous micelles until recently in terms of a monomer-micelle equilibrium and a c.m.c. However, the recognition of the low degree of aggregation observed in many cases and the application of step-wise self-association models of various kinds have now raised serious questions about the usefulness of a micellar model for such systems (28). The aggregation properties of surfactants in nonpolar media are often altered markedly by the presence of traces of water or other additives.

E. Emulsions

If one surfactant is added to two immiscible liquids, which are then shaken, one liquid will become dispersed in the other. Given sufficient time, two continuous phases separated by a single interface will result. Depending on the system, however, sufficient time may mean anything from seconds to years.

An emulsion is a system consisting of one or more immiscible liquids dispersed in another. Generally there are only two immiscible liquids. Practically all emulsions are thermodynamically unstable. The interfacial free energy always has a positive value. Since coalescence results in a decrease in interfacial area and consequently in a decrease in interfacial free energy of the system, emulsion droplets will tend to coalesce. Therefore, emulsification is an irreversible process.

Practically all of the emulsions that have been studied contain water. If water constitutes the continuous phase, the emulsion is called an oil-in-water emulsion or o/w. Conversely, if the aqueous phase is the internal or disperesed phase, the system is called a water-in-oil emulsion or w/o.

The lower size limit of emulsion droplets is placed at the smallest size that can be seen in an ordinary light microscope, about 0.1 μm. The largest size of an emulsion droplet is sometimes placed at the limit of visibility of the naked eye, about 50 μm (29). Emulsions are ordinarily not homodispersed.

1. Preparation

The ease of formation of an emulsion increases as the interfacial tension is reduced. Since emulsions present a large interfacial area, any reduction in interfacial tension allows for easier emulsification. Many surfactants lower the interfacial tension substantially and are useful emulsifying agents. Frequently, two or more surfactants are combined to improve emulsification.

In practice, most emulsions are made by vigorous mixing. The order of addition of the components influences the resulting emulsion type. There are four different methods of addition of the emulsifying agents. These are:

a. Agent-in-water method. The emulsifying agent is dissolved directly in the water and the oil is added, with considerable agitation. This procedure makes oil-in-water emulsions directly. For water-in-oil emulsions, the oil addition is continued until inversions takes place.

b. Agent-in-oil method. The emulsifying agent is dissolved in the oil phase. The emulation may then be formed in two ways: (1) by adding the mixture directly to the water. In this case an o/w emulsion forms spontaneously; (2) by adding water directly to the mixture. In the latter case a w/o emulsion forms. In order to produce an o/w emulsion by this method, it is necessary to invert the emulsion by the further addition of water.

c. Nascent soap (in situ) method. This method is suitable for those emulsions which are stabilized by soaps, and may be used to prepare either o/w or w/o types. The fatty acid parts of the emulsifying agent is dissolved in the oil and the alkaline part in the water. The formation of the soap (at the interface) as the two phases are brought together results in stable emulsions.

d. Alternate addition method. In this method, the water and oil are added alternately in small portions, to the emulsifying agent.

2. Emulsifier Selection System

Various methods have been proposed for choosing the proper emulsifying agent(s) for a given system. Probably the most successful approach to this problem, due to Griffin (30),has been designated the HLB method. The letters HLB stand for hydrophile-lipophile balance.

In this method, an HLB number is assigned to each surface active agent, and is related by a scale to the suitable applications. For example, only those HLB numbers in the range of 4 to 6 are suitable as emulsifiers for w/o emulsions, while those with HLB numbers in the range 8 to 18 are suitable for the preparation of o/w emulsions. Agents with HLB numbers in different ranges, while possessing important surface active properties, cannot (according to this classification) be employed as emulsifying agents.

The great merit of the HLB numbers resides in the fact that they are algebraically additive; thus the HLB of a blend of emulsifiers may be predicted.

In formulating a given emulsion, one may take any pair of emulsifying agents and vary their net HLB over the range in which they would be expected to be effective. Having found the most effective HLB, one would then try various pairs of agents until the most effective pair was found.

3. Spontaneous Emulsification

When oil and water with certain additives are brought gently into contact, spontaneous emulsification can take place on one or both sides of the interface without any mechanical agitation whatever, and even against the direction of gravity, e.g., a light oil emulsifying in the heavier water.

Spontaneous emulsification is an irreversible process. It usually occurs because of the necessary free energy provided from the free energy release as the surfactant is redistributed to its equilibrium state in the two phases. This idea was expressed in terms of the "diffusion and stranding" mechanism. This mechanism was first suggested by Gurwitsch (31) and since has been expanded upon by others (32-41). From his studies he proposed that as the surfactant diffused across the interface, solvent molecules were carried along and left stranded in the aqueous phase.

Later, McBain and Woo (34) found that spontaneous emulsification did not occur with clean Nujol (oil) placed upon sodium palmitate solution. These results indicated to the authors that preformed soap was not an emulsifiant,but merely a stabilizing or protective agent for the droplets that have been formed by some other means. To be active, the surfactant must be forming or diffusing.

Stackelberg, Klockner and Mohrhauer (36) obtained evidence using the drop-volume method which suggested that spontaneous emulsification of oleic acid-paraffin oil mixtures in dilute alkali, results from the existence of a negative interfacial tension at the oil/water interface. This condition was found to be brought about between pH9 and 12 by the transfer of the oleic acid from the oil to the aqueous phase.

A study by Mansfield (37) indicated that recourse to negative interfacial tension was not necessary. He studied changes of interfacial tension accompanying the transfer of oleic acid from paraffin oil drops to surrounding alkaline solutions (pH 9.7 - 13) by the sessile drop method. The interfacial tensions observed varied between 0.03 and 0.10 dynes/cm during transfer of the acid, but rose to equilibrium values of approximately 2-3 dynes/cm when little acid remained in the oil. The transfer of the oleic acid which produced transitory low values of the interfacial tension, was the cause of spontaneous emulsification in this system.

Most recently, analytic solutions have been proposed (40, 41) for the transfer of an adsorbing solute across a liquid-liquid interface. The time change of the interfacial tension during this mass transfer was studied by the laminar contracting liquid jet and spinning drop interfacial tensiometer techniques, respectively. The results indicated that if during the transfer of the solute there is an energy barrier to desorption into one of the phases, a minimum in the value of the dynamic interfacial tension will result due to the accumulation of solute at the interface. It is conceived that during this time of transitory very low γ_i values, the system may spontaneously emulsify.

4. Stability

Although many emulsions appear to be stable for an indefinite time, they are not stable in the strict thermodynamic sense of the word. Emulsion stability was seen to be governed by factors other than overall free energy minimization. The system consists of a network of interfaces that are prevented from coalescing by virtue of the adsorbed film or electrical repulsions. The inner phase of an emuslion constitutes a sizable fraction of the total volume.

There appears to be two stages in the collapse of emulsions; flocculation, in which some clustering of emulsion droplets takes place and coalescence, in which the number of distinct droplets decreases. Coalescence rates very likely depend primarily on the film-film surface chemical repulsion and on the rate of desorption (which provides an energy barrier to coalescence). Flocculation, on the other hand, should be sensitive to long-range forces as it involves the first stage of approach of droplets.

Three types of long-range forces between particles have been distinguished (42):

a. van der Waals forces. These are always attractive between particles of the same nature.

b. Electrostatic forces. These forces, due to the interaction of the electrical double layers surrounding the particles, always lead to a repulsion between particles if they are of the same chemical nature and have surface charges and surface potentials of the same sign and magnitude.

c. Forces connected with adsorbed macromolecules. This group of forces between particles is due to the interactions of long chain molecules adsorbed on the particles. When two particles, each carrying an adsorbed layer of dangling chains (or loops) approach one another closely, two effects lead to repulsion. In the first place each chain, if its extended length is larger than the distance between the surfaces, loses some of its otherwise available conformations (configurational entropy), and thus its contribution to the free energy of the system is increased, resulting in a repulsive force ("volume restriction" effect). Moreover, when the chains belonging to the two particles start to overlap, this amounts to a local increase of the concentration and to a local "osmotic pressure" in most cases counteracting the approach ("osmotic" effect). Generally the quantitative influence of the osmotic effect is the more important of the two. The repulsion increases with the chain length, with the quality of the solvent for the chains and with the number of chains per unit area. The repulsion as a rule is quite steep and due to these two mechanisms, the adsorbed macromolecules can keep the particles dispersed in solution by counteracting the attraction due to van der Waals forces (42). These effects can be considered as the major factor contributing to the stability of water-in-oil emulsions.

d. Combination of forces. The combination of the van der Waals attraction and electrostatic repulsion, to explain the stability of lyophobic colloids, was made. It is called the DLVO theory (43). The simple pairwise addition of the potential energy and electrical repulsion and van der Waals attraction, was assumed. According to the theory, plots of the energy vs. the distance have characteristic shapes. At short distances, a deep potential energy minimum occurs, the position of which decides the distance of closest approach. At intermediate distances, the electrostatic repulsion makes the largest contribution and hence a maximum occurs in the potential energy curve. At larger distances, a second minimum appears in the curve. The effect is that the emulsion droplets may flocculate to the distance apart of the second minimum, without any further tendency to approach each other. The DLVO theory is most useful for describing the stability of o/w emulsions because the electrostatic repulsion contributions can be easily calculated. The charges of the emulsified oil droplets can be determined from the emulsifier type used to stabilize the system (e.g., anionic surfactants give negatively charged droplets).

For describing the stability of w/o emulsions, the combination of van der Waals forces with "steric" repulsion (interaction of adsorbed chains) again leads to a minimum in the energy at large separations.

It is essential to realize that the stability of a particular dispersion does not necessarily parallel the ease of formation. The ease of formation is essentially related to the lowering of the interfacial tension, while the stability of the resulting emulsion, is a function of the structure and properties of the interfacial film. However, for the emulsions stabilized by water soluble surfactants, the two factors may occur concomittantly. In other cases, long chain polar compounds, polymers, finely divided solids, certain gums and other additives, must be added in addition to the original emulsifying agent to improve emulsion stability.

F. Transparent Emulsions

If the preparation of a transparent emulsion were undertaken, the first requirement would be to make the particle size small enough and the second would be to provide enough surfactant to cover the interfacial area created. The following calculation may be used to determine the droplet size of the transparent emulsion.

Let us consider one milliliter of the dispersed phase of the emulsion to be composed of small spherical droplets, all of radius r. Their total surface area is

$$A = n_d \times 4\Pi r^2 \qquad (1\text{-}6),$$

where n_d is the total number of droplets, and their total volume is

$$V = n_d \times 4/3\Pi r^3 \qquad (1\text{-}7);$$

therefore,

$$r = \frac{3V}{A} \qquad (1\text{-}8).$$

If $A = n\sigma$, where n is the total number of surfactant molecules covering the emulsified droplets and σ is the cross-sectional area of the surfactant molecules at the interface, then

$$r = \frac{3V}{n\sigma} \qquad (1\text{-}9).$$

For a sample calculation, if n is in the range of 6.02×10^{20} molecules and σ is approximated to be equal to 50 A^2/molecule, r has a value of 10^{-6} cm. This value is much less than one-fourth the wavelength of visible light ($4\text{-}7 \times 10^{-5}$ cm). Therefore, the resulting dispersion would be visually transparent.

1. Preparation

Transparent emulsions are not, however, experimentally simply prepared by providing enough of one surfactant to cover all of the interfacial area created. Usually a second surfactant, called the cosurfactant, is added to improve emulsification and to match the HLB. Even when the four components--oil, water, surfactant and cosurfactant--are combined, there exists the possibility for many different system types to form (i.e., sol, gel, isotropic o/w and w/o dispersions, and anisotropic liquid crystalline solutions). This is due to the fact that the requirements of the transparent emulsion are critical because of the great number of parameters which must simultaneously be met. For example, there is a much higher ratio of emulsifier to disperse phase which differentiates the transparent emulsion from the emulsion. One must match emulsifiers to oil in such a way as to produce oil-in-water and water-in-oil emulsions of small droplet sizes. The role of water in the matching process is still incompletely understood, and only a few oils seem to be chemically constituted to form these systems with water. Most oils do not form transparent emulsions, regardless of how much excess emulsifier is used.

Overall, it is difficult to find surfactants and cosurfactants which will combine with the oil at the interface to produce the state of film conducive to transparent emulsion formation, since these systems are dependent for their formation upon specific interactions among the molecules of oil, emulsifiers and water. If the specific interactions are not realizable, no amount of work input nor excess emulsifier will produce the desired product.

Nevertheless, transparent, low viscosity, stable systems, consisting essentially of monodisperse oil-in-water (o/w) or water-in-oil (w/o) droplets, with diameters generally in the range of 10 to 60 nm, have been prepared. These types of systems, which are now frequently called microemulsions, were first brought to the attention of the scientific community in the 1940s by the late J. H. Schulman and a series of collaborators (1). They prepared these systems by making a crude macroemulsion of the oil and one of the emulsifiers (e.g., a soap). This macroemulsion was then changed into a clear dispersion by titration with a second surface active agent (e.g., an alcohol).

CHAPTER III

THEORIES OF TRANSPARENT DISPERSION FORMATION AND STABILITY

A. Theories of Formation

1. Mixed Film Theory

Transparent oil, water and surfactant systems were first identified by Hoar and Schulman in 1943 (1) as a special kind of colloidal dispersion. The term "oleopathic hydromicelle" was used to describe these systems. (See Figure 3.) The essential conditions for their formation were: (a) high soap/water ratio, (b) the presence of an alcohol, fatty acid, amine or other non-ionized amphipathic substance approximately equal in mole fraction to that of the soap. They further indicated that the disperse phase consisted of submicroscopic micelles surrounded by a mixed monolayer of soap and amphipath.

They calculated the amount of surfactant needed to disperse a given volume of water by assuming all of the surfactant to be located at and completely covering the interface and all the water to be in the dispersed phase. By using a reasonable value for the surfactant-cosurfactant complex (assuming a 1:1 surfactant-to-cosurfactant ratio at the interface), the amount of soap required to give droplets of a certain size could be computed from the relationship between the surfactant area of a sphere and its volume, equation (1-8), $r = 3V/A$, where r is the radius of the droplets, V the total volume of all the droplets and A the total surface area. When $n\sigma$ is substituted for A, the result is

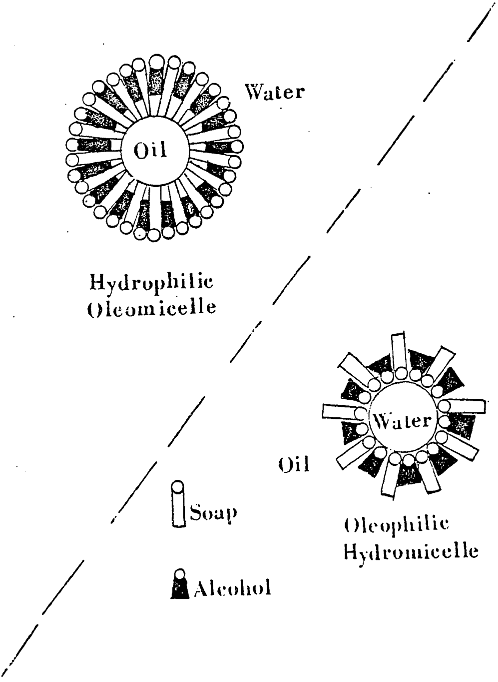


Figure 3. Hydrophilic Oleomicelle and Oleophilic Hydromicelle

equation (1-9), $r = 3V/n\sigma$, where n is the total number of soap molecules of cross-sectional area σ, required to disperse a volume of water into droplets of radius r. σ was usually obtained from the sum of the closest packing area for the surfactant and cosurfactant as measured by monolayer experiments. In their calculations the authors assumed the densities of all of the components were one.

Their calculations of the size of water droplets in w/o systems displaying a slight Tyndall effect was in the 120Å-200Å range and the vertical depth of the soap monolayer, 18Å.

It was observed that addition of water to the transparent oil continuous systems turned them into opaque and viscous systems which inverted to stable o/w dispersions. They attributed the spontaneous emulsification to very low interfacial tension.

In order to study the role that alcohol played in enabling the aqueous soap systems to absorb large quantities of oil or water and how it controlled oil or water phase continuity, Schulman and McRoberts (5) titrated benzene, paraffin, mineral oil and potassium oleate systems, with a group of aliphatic and cyclic alcohols. It was found that the number and arrangements of the carbon atoms, both in the alcohol and oil, determined whether the system was w/o or o/w. The results suggested to them that phase continuity was dependent on the wettability of the mixed interfacial monolayer. The phase that had the smaller contact angle against the interfacial monolayer would be the continuous phase.

Low angle X-ray scattering analyses were begun on these systems. With these data and on the basis of monolayer penetration experiments it was deduced that the area per pair of soap-alcohol molecules in the mixed film was 60Å and that the thickness of the interfacial film was 24Å. The area per soap molecule in the film was estimated at 30-40Å, depending upon its degree of dissociation in contact with water. The paper also discussed order and disorder in the interfacial monolayer and the bearing of this on the kind of emulsion that was formed. The penetration of the original soap film was considered in terms of the configuration and length of the alcohol molecules and strength of their adhesion to soap molecules. It was essential that the state of the mixed film be liquid in order for disperse droplets to form.

In the next two papers (44, 10), the size of the dispersed aggregates was studied by low angle X-ray measurements. Droplet sizes in the range of 100-600Å were found. The 600Å diameter droplets gave strong Tyndall scattering.

In reference (44) an alcohol was equated to a polar oil, suggesting the possibility of ternary systems.

Much of the work utilizing light scattering was done by Schulman and Friend (45). They pointed out that these fluid, isotropic dispersions were the result of a mixed monolayer of discrete molecules adsorbed at the interface between the oil and water phases. The formation of the dispersion was visualized as commencing with a lamellar micelle in strong soap solution. This micelle could be partially swollen with oil without breakdown of the crystal lattice. This lattice, however, could be further penetrated by small amphipathic molecules like an alcohol, causing the mixed film to become liquid and allowing surface tension forces to form spherical droplets of water or oil. On decreasing the soap concentration, the droplets would swell, creating a lesser total surface area and a larger droplet size. Lack of optical streaming birefringence established that the aggregates were spherical.

In view of these properties it was concluded that the structure of the fluid, isotropic dispersions was different from that of concentrated solutions of soap and of so-called "solubilized oils" which could swell only within certain definable limits (10%). Schulman believed that the disorder introduced into the interfacial film by the alcohol enabled the shell to enclose a larger volume of dispersed phase.

In 1951, Schulman, Matalon and Cohen (46) developed evidence for the existence of lamellar, cylindrical and spherical micelles in their systems. Solutions of long chain non-ionics (polyoxyethylinated alcohol) dissolved in petroleum ether were titrated with small quantities of water and the structure of the systems were investigated by X-ray, optical and rheological means. In the absence of water, the systems exhibited no structure. Upon addition of water and depending on the HLB as well as the number of different species of non-ionics (mixed emulsifiers), lamellar, cylindrical and spherical aggregates were observed; the several forms were differentiated by means of X-rays.

An isotropic system with a typical diffuse X-ray pattern was observed which was interpreted to indicate the presence of a w/o emulsion, the interfacial species of which were in a considerable state of disarray. It was proposed that as disorder among the non-ionic aggregates increased, the lamellae changed into cylinders and then into spheres.

It appears that it was not until 1955 that Schulman saw his dispersions in the perspective of emulsions (47). The formation of these emulsions was attributed to the molecular interactions taking place in the interface. The mixed monolayer was regarded as a third phase or interphase, in equilibrium with the oil and water phases. Thus, the alcohol distributed between the three phases and all of the surfactant were in the interphase. This last assumption was limited. It was not valid when there was insufficient water present to provide a large enough interfacial area for all of the potassium oleate to be in the interphase. Their sedimentation experiments agreed with their calculations using equation (1-9) for the size of the dispersed droplets, 100-500Å.

A liquid condensed film was considered essential to give the kind of flexibility to the interphase that would allow a tension gradient across it to produce curvature. The state of the film was considered to be controlled by the kind of adlineation among the film tenants. Among these factors was now included the size of the cation in anionic systems and the temperature.

Previous results of monolayer penetration experiments at the air/water interface (48) made it evident that alcohol molecules penetrated the adsorbed soap molecules and disordered the regular condensed two-dimensional packing in the micelles to produce a liquid interphase at the oil/water interface. This enabled Bowcott and Schulman to state that the interphase had two interfacial tensions, one between the monolayer and the oil ($\gamma_{m/o}$) and one between the polar heads of the monolayer and the water ($\gamma_{m/w}$). They restated the rules governing phase continuity, i.e., the phase with the higher tension with respect to the interfacial monolayer, would be the inner surface. These parameters were not amenable to direct measurement, however.

Schulman recognized that the effect of forming a complex between a water soluble soap and an oil soluble amphipath reduced the interfacial tension between oil and water to a fraction of a dyne, and it was believed that it was for this reason that the systems formed spontaneously. In the Bowcott and Schulman experiments he noted that the same transparent emulsions were obtained irrespective of the order in which the components were added. Therefore, he proposed that the phases were in equilibrium with each other, inferring interfacial tension was zero. Thus, these dispersions were treated as a three-phase thermodynamically stable system.

Electron micrographs (8) obtained by staining the double bonds of unsaturated aliphatic oils with osmium tetroxide revealed discrete spherical droplets for the water continuous systems stabilized with potassium oleate. The authors maintained that the OsO_4 caused the oil and surfactant to polymerize, producing solid spherules which could be separated and washed. These globules were then imbedded in a polymethacrylate matrix and photographed directly on the electron microscope. Since a discrete phase was observed the authors chose to call the transparent dispersions, microemulsions. Schulman et al. (8) also stated that an association between the oil and surfactant molecules was critical in forming microemulsions.

2. The Concept of Negative Interfacial Tension

The concept of a transient negative interfacial tension as the factor responsible for the formation of microemulsions was proposed (2). Essentially this was based on two pieces of information. In the monolayer studies with Goddard (46), two-dimensional surface pressures of over 50 dynes/cm had been recorded. In addition, Bowcott (49) had shown experimentally that microemulsions formed at concentrations of surface active agents in excess of those necessary to produce zero interfacial tension against $\log_{10}$ of mole fraction of hexanol in benzene (9).

The negative interfacial tension concept was based on the thermodynamic equation that at an oil-water interface

$$\gamma_i = \gamma_{o/w} - \Pi \qquad (3\text{-}1)$$

where γ_i is the total interfacial tension, $\gamma_{o/w}$ is the oil-water interfacial tension without amphipathic agents and Π is the two-dimensional spreading pressure of the amphipathic agents. According to this equation, if as a result of adsorption of soap and alcohol at the interface and its penetration by oil phase molecules, Π becomes greater than $\gamma_{o/w}$, then energy, $-\gamma_i dA$ (A = surface area), would be available to increase the total interfacial area. This was considered to be the condition for formation of microemulsions. When $\gamma_{o/w}$ was greater than Π only a macroemulsion would form. In this view the temporary existence of a film pressure greater than $\gamma_{o/w}$ would be the driving force which reduced droplet size of a fixed volume of the dispersed phase until no more energy was available to increase the interfacial area (i.e., decrease droplet size). Equilibrium would be attained when the negative interfacial tension returned to zero by virtue of uncrowding of molecules and loss of pressure in the interface. When $\gamma_{o/w}$ was greater than Π, droplet diameters of the order of magnitude of 10,000Å (1 µm) were usually observed and the systems which now appeared milky white achieved equilibrium by separating into two phases. Energy in the form of mechanical work (agitation or homogenization) may temporarily increase the interfacial area but is not capable of changing the values of Π or $\gamma_{O/W}$. With $\gamma_{O/W}$ for n-paraffin being about 50 dynes/cm and that for benzene 35 dynes/cm a Π of greater than 55 dynes/cm as measured in reference (46) would easily account for the exerpimental results obtained.

Until 1958 Schulman considered the interactions among the molecules at the oil/water interface as closely resembling those at an air/water interface. As it turned out, there were important differences that have special significance to microemulsion formation.

In 1941 Zisman (50) suggested that an alcohol monolayer at an oil/water interface could be penetrated by molecules of the oil phase. Schulman noted from Zisman's work that an alcohol layer at the oil/water interface could be penetrated by long chain mineral oil molecules to form a 1:1 association, and that surface pressures as high as 30 dynes/cm failed to squeeze the nonpolar hydrocarbon out. At the same time he observed that benzene could easily be ejected from a monolayer of fatty acid at the benzene/water interface (9). Moreover, he knew from the work of Robbins and LaMer (51) that the solvent hydrocarbons used to spread monolayers at the air/water interface could remain in the film but could also at moderate pressures be squeezed out and not form associations even at low surface pressures. From this he deduced that if there was a possibility for the oil molecules to associate with the tenants of the interfacial film, a microemulsion would form. The association could take place with either the alcohol or soap tail but the microemulsions were better if the association was with both.

Oil molecules were shown by monolayer expansion to be capable of penetrating a monolayer of AMP (2-amino-2-methyl-1-propanol) stearate at pH 10.4 at a hexadecane/water interface (52). A duplex film technique using a Langmuir trough and film balance were employed. A duplex film is a film in which the two interfaces (e.g., oil/water and oil/air) behave independently and maintain their own characteristic tension (53). To form a duplex film on the trough, the oil was spread with the monolayer (52, 54).

The uniqueness of the duplex film method is that it measures directly the force-area per molecule isotherm at the liquid/liquid interface. This permits the direct study of the interaction between the different "oil" molecules and the monolayer. This interaction is the measurement of the penetration of the "oil" molecules into the monolayer even under conditions of theoretical negative interfacial tension (when $\Pi > \gamma_{o/w}$, equation 3-1).

In the case of a duplex film,

$$\gamma_i = \gamma_{a/w} - \gamma_{o/a} - \Pi_m = \gamma_{o/w} - \Pi_{o/w} \qquad (3\text{-}2)$$

Where $\gamma_{a/w}$ is the surface tension of the air/water interface, $\gamma_{o/a}$ is the oil/air surface tension, Π_m is the measured spreading pressure of the duplex film and $\Pi_{o/w}$ is the interfacial pressure in presence of an adsorbed surfactant film. Oil layers from 100 to 350Å thick were found convenient. Under these conditions all the amphipathic molecules are present at the liquid/liquid interface.

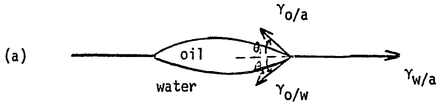
The case of an insoluble liquid monolayer of a liquid compound at its collapse pressure (Π_c) can be considered as a duplex film one molecule thick. If equation 3-2 is applied for different compounds, it is found that Π_c is identical to Π_m at the collapse pressure. The measured oil/water interfacial tension (γ_i) is equal to $\gamma_{a/w} - \gamma_{o/a} - \Pi_c$.

All are measurable terms for different compounds and duplex film mixtures. So it can be concluded that the liquid monolayer at the collapse pressure is equivalent to a duplex film where the "oil phase" corresponds to the hydrocarbon portion of the molecules, with an "independent" oil/air tension and a water/oil interfacial pressure due to the polar groups of the molecules. This was indicated theoretically long ago by Langmuir.

At the collapse pressure, lenses will form if the sum of the interfacial tension and the oil/air surface tension of the liquid compound is equal to or greater than the surface tension of the hydrocarbon portion of the liquid compound considered to be a separate oil phase. By addition of a suitable oil with a lower surface tension than this "oil phase," spreading will proceed, according to Figure 4 (b). This results in the formation of a duplex film.

To illustrate the concept of the duplex film method, several examples of substituting Π_c for Π_m according to equation 3-2 are given (52, 54). For the case of n-octyl alcohol monolayer and drop: γ_i = 7.7 dynes/cm measured between octyl alcohol and water by a platinum plate method; $\gamma_{o/w}$ = 50 dynes/cm, a literature value (by considering the hydrocarbon portion of the molecule as the oil phase similar to an n-octane hydrocarbon); $\gamma_{a/w}$ = 71.2 dynes/cm; $\gamma_{o/a}$ = 27.5 dynes/cm (surface tension of an n-C_8 hydrocarbon); $\Pi_{o/w}$ interfacial pressure; and Π_c = 36 dynes/cm, collapse pressure of the n-octyl alcohol monolayer measured at 30 °C.

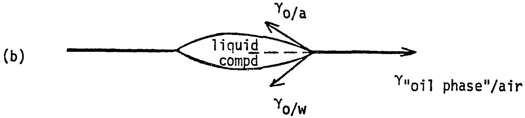
By substituting Π_c for Π_m in equation 3-1, all the terms balance --$7.7 = 50 - \gamma_{o/w} = 71.2 - 27.5 - 36$, justifying the assumption that at the collapse pressure, the monolayer is a separate two-dimensional



$S = \gamma_{w/a} - (\gamma_{o/a} + \gamma_{o/w})$

$S < 0$; no spreading if $(\gamma_{o/a} + \gamma_{o/w}) > \gamma_{w/a}$

$S > 0$; spreading of oil on water



$S = \gamma_{\text{"oil phase"/air}} - \underset{\text{Liquid compound}}{(\gamma_{o/a} + \gamma_{o/w})}$

$S < 0$; no spreading if: (lenses) $\underset{\text{Liquid compound}}{(\gamma_{o/a} + \gamma_{o/w})} \geqq \gamma_{\text{"oil phase"/air}}$

$S \geqq 0$; spreading of suitable oil on liquid monolayer of liquid compd. if: $\underset{\text{suitable oil}}{\gamma_{o/a}} < \gamma_{\text{"oil phase"/air}}$

Figure 4. Spreading of One Liquid on Another

liquid phase.

For surface potential measurements, the following theory is applicable (55). If a monolayer is spread or adsorbed on a clean water surface, the water dipoles will generally be re-oriented about the film-forming molecules because of the new dipoles introduced into the surface. This charge for each molecule in the monolayer will be denoted u_1. The dipoles of the film-forming molecules (e.g., COOH in a long chain carboxylic acid) will also contribute to ΔV by an amount depending on the group dipole moment u_2. A third component of ΔV for such electrically neutral films is u_3, the amount of the bond (e.g., $\geqslant$C-H) at the upper limit of the monolayer.

If the Helmholtz formula is applied for an array of n dipoles per cm^2, and if they are vectorially additive in the vertical direction,

$$\Delta V = 4\pi n u_1 + 4\pi n u_2 + 4\pi n u_3 \qquad (3\text{-}3).$$

Unfortunately, u_1 cannot be measured, so it is usual to combine this term with u_2; this allows for the fact that the re-orientation of the water dipoles, as expressed by u_1, may well depend on u_2.

The term u_3 is normally constant since paraffinic chains are usual in surface-active molecules, so then (3-3) simplies to

$$\Delta V = 12\pi n u_D \qquad (3\text{-}4),$$

where $u_D = u_1 + u_2 + u_3$, characteristic of the dipole moment of the head group of the molecules of the monolayer. This is true for any electrically neutral film, comprising only dipoles.

Charged monolayers contribute an electrostatic term as well as the ordinary dipole terms to ΔV. This electrostatic potential arises from the unequal distribution of ions in the vicinity of the adsorbed monolayer, and though it is therefore strictly a ψ potential, it is convenient to include this in the ΔV term because it arises directly from the presence of the monolayer. To distinguish this monolayer electrostatic potential from $\Delta\psi$, however, it is generally termed ψ_0; it represents the electrostatic potential in the interface (at zero distance from it--hence the subscript zero) relative to the subjacent aqueous phase. With these conventions, equation 3-4 may be generalized to apply to such charged monolayers,

$$\Delta V = 12\Pi n u_D + \psi_0 \qquad (3\text{-}5)$$

$$\Delta V = 4\Pi n u_{ov}$$

where u_{ov} is the overall dipole contribution from the dipoles on the surface and from the counterions in the water below. The contribution to the dipoles is large, if the ionic strength of the subsurface solution is low. In monolayers carrying no net electrical charge (e.g., long chain alcohols) ψ_0 is always zero.

Using equation 3-1, in order for γ_i to be negative, $\Pi_{o/w}$ would have to be approximately 50 dynes/cm or greater, when n-hexadecane was used as the oil phase. For the duplex film experiments the measured pressure, Π_m, would only have to be greater than about 43 dynes/cm according to equation 3-2. Pressures higher than this were obtained using stearic acid and n-hexadecane spread on aqueous AMP at pH 10.4. When hexadecanol was injected into the monolayer the film became expanded, but collapsed at a lower pressure.

The authors claimed that these results supported their view of the role of negative γ_i in forming microemulsions. Yet none of previous work on which they based their conclusions (8, 2) was done using their conditions. For example, all of the reported microemulsions were prepared using oleate soaps (1, 5, 10, 46, 47, 8, 2) at pH 8.8 or or 10.5 (none were prepared using hexadecane as the oil phase and hexadecanol as the alcohol). Also, since pressures greater than 50 dynes/cm were obtained using just AMP stearate as the surfactant at pH 10.4, it should have been possible to form microemulsions with n-hexadecane using just the surfactant at this pH. It has since been shown that this is not the case (11). Another flaw in the method is that it does not discriminate between o/w and w/o microemulsions. To do this, the authors maintained that phase continuity would be controlled by surface charge. An un-ionized monolayer would produce a water-in-oil microemulsion while a charged monolayer would produce an oil-in-water microemulsion. On this basis, it would be assumed that the previous work (56) with non-ionic emulsifiers dealt exclusively with w/o microemulsions and that o/w microemulsions could not be prepared using non-ionic emulsifiers. The latter deduction was also seen to be false (4).

In any case, it was now evident to Schulman that a looser, more expanded, rather than a liquid condensed film, was essential to the development of microemulsions and that this state could be brought about in a number of ways. The first was by the penetration of a mixed film of soap and alcohol by hydrocarbon derived from the oil phase. The second was to use large cations to make the soap molecules asymmetric and thereby produce disorder in the mixed film. Finally, a microemulsion could be produced with asymmetric soap molecules (without associated alcohol) providing the film were penetrated by oil molecules which associated with the soap species but were sufficiently asymmetric to produce the required disorder. Emphasis was placed on the size of the cation in effecting disorder (57).

3. Summary

Schulman's interpretation of microemulsion formation was that a microemulsion would form when the interfacial tension between an oil and water phase was reduced below zero ($\gamma_i < 0$). This was accomplished when enough disorder was produced in the interfacial monolayer to permit it to swell and assume the curvature of a microemulsion. The interface would subdivide until γ_i rose to zero at equilibrium. The continuous phase would be the phase that had the lower tension against the interfacial monolayer ($\gamma_{m/o}$ or $\gamma_{m/w}$), i.e., the phase that wet the monolayer most efficiently.

4. Prince's Modification

Prince (58) agreed with the concept of negative interfacial tensions. However, since $\gamma_{o/w}$ was in general quite high ($\approx$ 50 dynes/cm for aliphatic hydrocarbons and 35 dynes/cm for benzene), large monolayer film pressures were required to reproduce negative interfacial tensions according to equation 3-1. This was the factor to which Prince addressed himself, but his attention may have been unnecessary since duplex film isotherms had been shown to reach quite high presures (9, 52).

In any case, Prince claimed that equation 3-1 required modification when Cooke and Schulman (9) determined experimentally that hydrocarbons would be ejected from mixed monolayers of soap and alcohol, at high pressures necessary for negative γ_i. These authors, by using different hydrocarbons instead of different alcohols or amounts of water, as was done in the Bowcott and Schulman experiments, found that the distribution of hexyl alcohol between the bulk phase and interphase varied with the hydrocarbon used. This prompted Prince (58) to propose that negative γ_i in mixed films of soap and alcohol is the result not so much of a high value of Π, as of a large depression of $\gamma_{o/w}$. The new and much lower value of the o/w interfacial tension, $(\gamma_{o/w})a$, is dependent on the amount of alcohol left in the bulk oil phase after the chemical potential of the alcohol in each phase has been equalized by partitioning.

Essentially the distribution or partitioning of alcohol between the interphase and bulk oil phase changed the composition of the oil phase and, therefore, its tension with water.

By reason of this, the film pressures needed to reduce the net γ_i to negative values were much lower and more easily attained. The new equation became

$$\gamma_i = (\gamma_{o/w})a - \Pi \qquad (3\text{-}6).$$

As a corollary to this concept, it became apparent that in any given system, zero γ_i may occur only at an intermediate concentration of alcohol, amphipath, or cosurfactant (59). The explanation is that below this intermediate range, Π may be high but $(\gamma_{o/w})a$ has not yet been sufficiently depressed to result in a negative tension. Above the intermediate range, the predominantly alcoholic interphase, may, depending on the structure of the molecules, either squeeze the oil molecules out of the interphase making $\Pi < (\gamma_{o/w})a$, or even with oil molecules still present, become too rigid to develop curvature because of strong attraction among heads and tails of tenants.

5. Concept of Π_G

Prince assumed that the pressure necessary to develop a negative interfacial tension arose from the penetration of alcohol molecules into the surfactant film with subsequent hydrogen bond complex formation between the alcohol and surfactant. He presented his theory in terms of an o/w microemulsion with oleate as surfactant. It was proposed that the alcohol penetrated the oleate monolayer, shielding the charged carboxyl groups, allowing the oleate monolayer to contract and bond with the alcohol. This would allow closer adlineation of the hydrocarbon tails increasing the force of attraction among them. In this formulation, curvature of the interface arises due to the existence of a pressure gradient across the flat film. This pressure gradient develops due to the different interactions among the hydrophobic and hydrophilic portions of the oleate molecules. The film pressure generated at a flat interface due to this pressure gradient was termed Π_G.

The film/oil surface and the film/water surface of an o/w emulsion were characterized by their own hypothetical (Π-A) curves (60). Under these circumstances, Π_O' and Π_O' are the film pressures of the flat duplex film at the water and oil sides respectively, and Π_W and Π_O are the corresponding pressures at the sides of the curved film. The initial pressure gradient, Π_G, across the flat film derives from the relative magnitudes of Π'_W and Π'_O.

γ_ϕ was the "total potential (minimum) interfacial tension" corresponding to Π_G. In other words, γ_ϕ was the interfacial tension before curavture and should reach minimum values since curvature was assumed to develop to relieve the excess pressure. γ_i was considered to be the interfacial tension after curvature and corresponded to a lower film pressure, Π. Equation 3-6 was then rewritten

$$\gamma_\emptyset = (\gamma_{O/W})a - \Pi_G \qquad (3\text{-}7)$$

Purely hypothetical curves of Π_G and $(\gamma_{O/W})a$ versus concentration of alcohol were constructed. Π_G was pictured as a parabola (concave down), reaching a maximum at some alcohol concentration. $(\gamma_{O/W})a$ was shown as a monotomically decreasing function of alcohol concentration. If there was an intersection of the two curves, a microemulsion resulted, i.e., if $\gamma_\emptyset$ became negative ($\Pi_G > (\gamma_{O/W})a$) a microemulsion resulted.

6. Mechanism of Film Curvature

According to Prince, under the stress of these pressures, plus that due to penetration of oil molecules, expansion at both sides of the interface would occur spontaneously. This expansion would continue to different degrees at each side of the interface, until these pressures (Π_W and Π_O) became equal and the total pressure, Π, in the film dropped to $(\gamma_{O/W})a$ at equilibrium. Since $\Pi = \Pi_O + \Pi_W$, expansion would occur until at equilibrium, $\Pi_O = \Pi_W = \frac{1}{2}(\gamma_{O/W})a$. By the terms of equation 3-7, the driving force for this curvature is the difference between the initial pressure, Π_G, and the final equilibrium value of $\Pi = (\gamma_{O/W})a$. The requirement for the formation of microemulsions was that $\Pi_G > (\gamma_{O/W})a$; if not, a macroemulsion would result. In order to illustrate his point, pressure-area curves were plotted for the oil and water sides of the interfacial film. These graphs were purely conjectural and were used to facilitate the author's explanation. It is not possible to test this model directly since none of the parameters involved except for $(\gamma_{O/W})a$ are amenable to direct measurement.

7. Shah's Work

Shah and Hamlin (61) made a series of dispersions of hexadecane, hexanol and potassium oleate with increasing amounts of water. At low ratios of water to hexadecane, the system was fluid, clear and transparent. At a ratio of water-to-oil less than 0.1, molecular solubilization of water in the system was presumed to occur. Between the ratio of water/oil of 0.1 and 0.6, the system was considered a w/o microemulsion. The existence of these two types of aggregates was supported by resistance measurements as well as by an upfield shift in NMR spectra. Further addition of water caused the system to become turbid and birefringent, corresponding to cylinders of water and then lamellae. At a ratio of water/oil approximately equal to 1.3, the system again became clear and fluid, indicating that it had completely inverted to an o/w microemulsion. (See Figure 5.) The transitions from clear to turbid to clear were again supported by NMR data. This was the first time that this sequence had been demonstrated experimentally, although Schulman, Matalon and Cohen (46) had demonstrated the existence of cylinders and lamellae in translucent, non-ionic dispersions. It is noteworthy that the lamellae converted into o/w microemulsions without passing through a stage consisting of cylinders of oil, a situation which would have made the phase inversion symmetrical and would have been more in line with Winsor's proposals (62).

Subsequently, Shah et al. (63) suggested that the formation of microemulsions resulted from interfacial stability which in turn was caused by spontaneous, transient, negative interfacial tension resulting from interactions between surfactant and cosurfactant. It was assumed that the original interfacial tension was reduced by the soap and not the alcohol, as suggested by Prince (58). On the basis of the electrical measurements, it was also proposed that these micro-

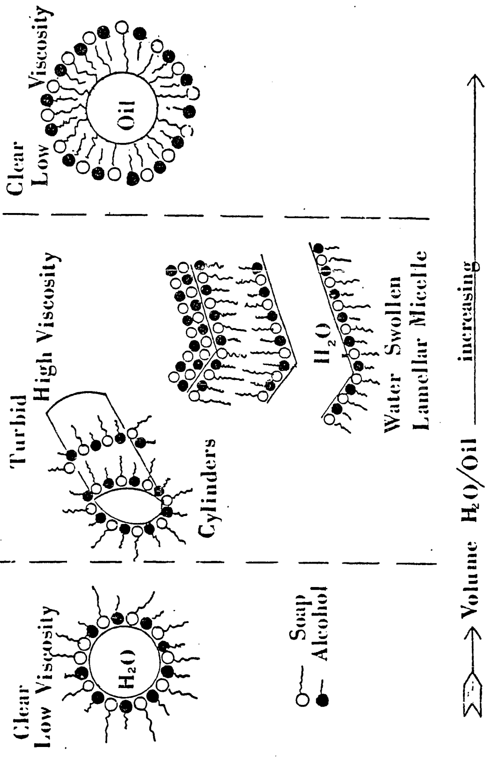


Figure 5. Inversion of a W/O Microemulsion

emulsions were true dispersions of one liquid in another and were not cosolubilized systems.

Falco, Walker, and Shah (64) extended the study of n-hexadecane, hexanol, potassium oleate and water systems by measuring their rheological properties. Striking increases in viscosity were found to correspond to the viscoelastic stages in which cylinders and lamellae existed. It was also found that the viscosity in the lamellae, liquid crystalline region increased initially and then levelled off with an increase in shearing time. This was presumed to result from disordering and entanglement of lamellar aggregates. Further work in this area utilizing X-ray scattering and freeze etching electron microscopy (65) indicated that before agitation, the lamellae were oriented parallel to one another. On shaking, the arrangement of the lamellae became disordered and a significant breakdown of lamellae took place. Careful review of the work done on a variety of mixed surfactant systems led Shah to conclude that the striking changes in the properties of these systems at the 1:3 ratio of surfactant to cosurfactant were due to the two-dimensional hexagonal packing of these species (66). This resulted in a closer molecular packing and a higher degree of stability of the mixed films at the interface. In this hexagonal packing arrangement, molecules of one type occupy the corners and those of the other type occupy the centers of hexagons in adjacent planes.

8. A Thermodynamic Treatment

The Laplace Pressure. Due to the surface tensional forces, a difference in pressure always exists on either side of a curved liquid or gas interface, such that the pressure is higher on the concave side. For a sphere, the pressure difference is also inversely proportional to the radius. This is given by the Laplace equation,

$$\Delta P = \frac{2\gamma_i}{r} \qquad (3\text{-}8).$$

Rosano et al. considered (67) the stability of a w/o microemulsion to be due to balancing of Laplace pressure against an osmotic pressure difference. For this treatment, it is necessary to admit the existence of water with a high activity coefficient in the continuous phase. The osmotic pressure was written as

$$\Pi = \frac{\Gamma RT}{\overline{V}_w} \ln X_w = \frac{\Gamma RT n_b}{\overline{V}_w n_w} \qquad (3\text{-}9).$$

Γ is an osmotic coefficient, $\overline{V}_w$ is the molar volume of water, X_w is the mole fraction of water, n_w and n_b are the number of moles of water and ions from the absorbed surfactant in the micelles, respectively. This equation applies to a non-ideal solution in equilibrium with pure solvent and is therefore an approximation to the actual situation. This type of treatment was later used by Adamson (3) and Pagano (68), although the latter was concerned with calculating interfacial tensions at curved lipid membranes. Since all of the surfactant was assumed to reside at the interface, the radius of the droplets was then

$$r = \frac{3V}{Nn_b\sigma} \qquad (3\text{-}10).$$

Substituting this into equation 1-9 and setting $\Delta P = \Pi$ gave

$$\gamma_i\sigma = 1.5\frac{\Gamma KTV}{\overline{V}_w n_w} \qquad (3\text{-}11).$$

At a constant water volume, the right hand side is a constant C. This relationship was used to explain the fact that many more surfactant and cosurfactant combinations are able to form w/o microemulsions than are able to form o/w microemulsions.

9. Micellar Emulsions in Equilibrium with an External Electrolyte

Adamson (3) formulated a thermodynamic model of transparent w/o dispersions which were in equilibrium with an external phase of aqueous electrolyte. He called the dispersed phase a micellar emulsion, since he felt that these systems embodied properties of both emulsified and micellar type systems. Equilibrium systems of this type had been described earlier by Winsor (69, 70), and Palit and coworkers (71). Adamson considered only systems stabilized by ionic surfactants and non-ionic cosurfactants. All of the surfactant was assumed to be in the micellar phase. The interfacial film was assumed to be largely dissociated and the resulting electrical double layer in the aqueous interior of the micelles, was responsible for a large part of the interfacial free energy. A Donnan type equilibrium was used to describe the charged film.

The Laplace Pressure. It was also assumed in this treatment that stability occurred when osmotic pressure was balanced by the Laplace pressure. If the interfacial film was charged and most of the surfactant was in the micellar phase, the ionic concentration would be greater in the micellar phase due to the Donnan effect. This difference in the aqueous concentration would give rise to a difference in the osmotic pressure across the interface. $\Delta\Pi_{os} = \Pi'_m - \Pi_b$, where Π'_m is the osmotic pressure of the micellar phase and Π_b is the osmotic pressure of the water phase. Equating this to the Laplace pressure gives

$$\Delta\Pi_{os} = \frac{2\gamma_i}{r} \qquad (3\text{-}12).$$

Substituting equation 1-9 for r gives

$$\Delta\Pi_{os} = \frac{(n_{st} \times \gamma_i\sigma')}{(1.5V)} \qquad (3\text{-}13),$$

where n_{st} is the number of moles of surfactant in the micellar phase and σ' is the cross-sectional area per mole of surfactant. It can be seen that this treatment does not require the admission of negative or zero interfacial tensions for oil continuous systems, which were the only ones treated. Using a value of 5 dynes/cm for γ_i, the model accounted for the general properties of micellar emulsions and specifically permitted a quantitative treatment of the effects of electrolyte concentration on the distribution of water and electrolytes between the micellar emulsion and the second aqueous phase.

This model was used (72) to analyze micellar solutions of aqueous Na_2SO_4 in a refinery hydrocarbon liquid stabilized by isopropyl alcohol and a monosulfonated alkylnaphthalene. These solutions were maintained in equilibrium with an aqueous Na_2SO_4 phase. The phases were separated after equilibrating, and the components assayed.

It was determined that the water content of the micellar phase increased asymptotically, approaching infinity, as salt content was decreased. It was concluded from this that these micellar solutions would not coexist in equilibrium with pure water (72). In this analysis, it was assumed that the concentration of alcohol was the same in the micellar and bulk water.

The theory as presented seems to be useful in predicting the concentration of electrolyte in an external phase required to maintain a given amount of water in the micellar phase, although no test has been made. As it stands, it is not applicable to the types of systems discussed by Schulman since no external phase was present in those systems and therefore this thermodynamic treatment is inapplicable. Also, the theory does not appear to be applicable to systems stabilized by non-ionic emulsifiers. It is signifcant that inversion of Adamson's micellar emulsions is not normally expected.

Summary. These treatments deemphasize the importance of the cosurfactant given it in the treatments of Schulman and Prince. There is also an incongruity in the treatment of the interfacial monolayer. The previous theories of w/o microemulsions considered the interfacial film to be un-ionized due to high surfactant to water ratio, while these models consider a completely ionized (3) or partially ionized (67) monolayer, even in the presence of neutral salt. In fact, in an extension of Adamson's (3) model, using the Gouy-Chapman theory to treat the diffuse double layer of the microemulsion droplets, the authors came several times to the erroneous conclusion in their presentation, that microemulsion formation was impossible in the absence of added electrolytes.

10. Phase Equilibria Diagrams

Micellar Solubilization. One of the most important properties of micellar systems is their ability to solubilize a variety of species. For aqueous micelles, solubilization is closely related to the hydrophobic and amphipathic properties of the solubilizate (19). Different sites of solubilization and orientations may be involved depending upon the structure of the solubilizate (73-76). It should be noted that solubilization sites are not fixed; there is a rapid equilibrium between various possible sites as also between the solubilized state and the free state in the aqueous medium of the solubilized species. In nonpolar media, polar substances tend to be solubilized by the aggregates. If the polar material is water, a hydromicelle is formed.

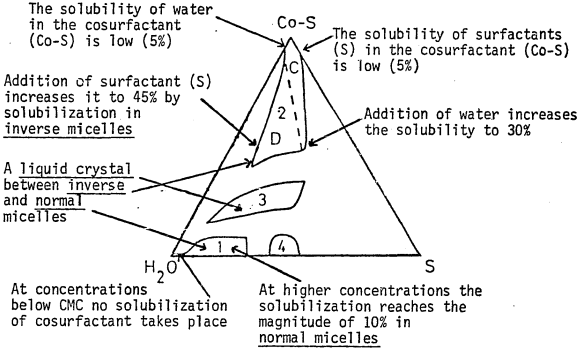
Phase equilibria diagrams have been used as another thermodynamic approach to study microemulsions. Accepting microemulsions to be colloidal dispersions, their micellar nature can be emphasized by these diagrams.

For application of the phase rule, it is always essential that the system be in true equilibrium. It is postulated that such an equilibrium may exist in any system under given conditions when parts of the system fail to undergo changes with time provided that the parts of the system have the same properties when the same conditions are arrived at by a different procedure. It is also fundamental that the phases be liquid. Since not all liquid phases are soluble in one another, phase separations can occur. Moreover, being colloidal systems, mesomorphic or liquid crystalline phases may also appear to complicate the picture.

One of the first phase equilibria diagrams to investigate the behavior of oil, water, and surfactant systems was by Per K. Ekwall (77).

Three-Component Systems. The three-component phase diagram is a practical tool for understanding the association phenomena of importance to microemulsions.

The associations between the three structure-forming components --water, surfactant and cosurfactant--form the basis of microemulsion structure. Their general behavior is illustrated (78), showing four one-phase areas, 1-4. In Figure 6, 1 and 2 are regions of isotropic solutions; 3 and 4, regions containing liquid crystals. Regions 1-3 are interesting for microemulsion study. Region 1 contains molecularly dispersed surfactant at concentrations below the CMC and normal micelles at higher concentrations.



The solubility of water in the cosurfactant (Co-S) is low (5%)

The solubility of surfactants (S) in the cosurfactant (Co-S) is low (5%)

Addition of surfactant (S) increases it to 45% by solubilization in inverse micelles

Addition of water increases the solubility to 30%

A liquid crystal between inverse and normal micelles

At concentrations below CMC no solubilization of cosurfactant takes place

At higher concentrations the solubilization reaches the magnitude of 10% in normal micelles

Figure 6. Three Component Phase Diagram. Reproduced by permission from Prince (Ref. 78), courtesy of Academic Press Inc.

Region 2 shows low solubility of water and surfactant monomer in the cosurfactant, while combinations of the two compounds dissolve to high degrees. At low water content, region 2C contains ion pairs of the surfactant, with a few associated water molecules per ion pair, serving to reduce the field strength between the two ions. Inverse micelles form first where the concentration of water extends into area D in Figure 6. These inverse micelles contain a central core of water surrounded by surfactant and cosurfactant molecules and are dispersed in the liquid cosurfactant. The water solubilizing capacity is strongly dependent on the surfactant/cosurfactant ratio. Too high a content of cosurfactant will cause a separation into two liquids while too much surfactant gives rise to a separation of a different association; a liquid crystalline phase.

This liquid crystalline phase has a lamellar structure. Its structure is characterized by long-range order organization. It is highly viscous and is a natural and expected intermediate in the transition region between normal and inverse micelles.

Four-Component Systems. In addition to the three basic components--water, surfactant and cosurfactant--microemulsions also contain hydrocarbon. To represent this, the two-dimensional, three-component phase diagram is often extended by forming a three-dimensional tetrahedron, Figure 7B (78). However, this is cumbersome and it is possible to present a great deal of information about phase equilibria by taking planes from such a tetrahedron, and presenting these on three-component phase diagrams as illustrated in (6). Such diagrams have been used by Winsor (69, 70, 79), Palit (71), Ekwall (81, 80), Gillberg (6), Adamson (3), Shinoda (4), Ahamad et al. (82) and

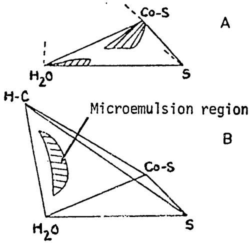


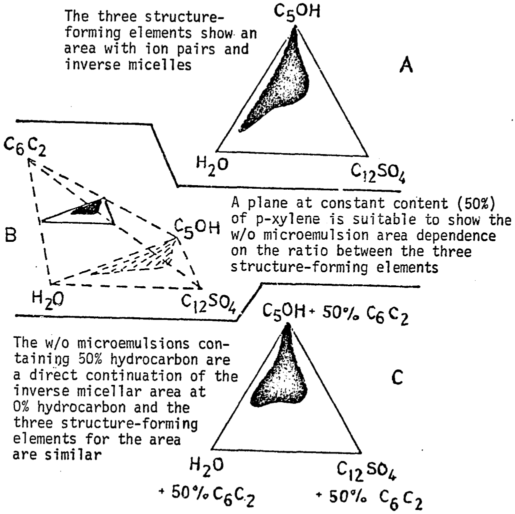
Figure 7. Four Component Phase Diagram. Reproduced by permission from Prince (Ref. 78), courtesy of Academic Press Inc.

many others.

A microemulsion region should be observed as an isotropic solution in regions containing high amounts of both water and hydrocarbon. The aim of the following was to relate microemulsion regions to normal and inverse micellar solutions with phase diagrams. The system studied was composed of water, sodium dodecylsulphate ($C_{12}H_{25}SO_4^-Na^+$) pentanol and p-xylene (C_8H_{10}).

Friberg (78) found that in these four-component systems, the w/o transparent isotropic region (Figure 8B) containing 50% hydrocarbon is a direct continuation of the ion pairs and inverse micellar solution of the three structure-forming elements--water, surfactant and cosurfactant (Figure 8A). These results show w/o systems to be inverse micelles at high water content and solutions containing water/ion pair associations, at low water content. Maximum water solubilization is obtained for a cosurfactant/surfactant ratio of 3.5 (Figure 8C), identical to the corresponding ratio for systems without hydrocarbon. The stability tolerance of ion pair solution compositions for electrolytes is extremely small. The corresponding area for higher contents of hydrocarbon are not included, but at high hydrocarbon content, water solubilizing capacity is extremely small; the solubility region is critically dependent on the ratio between ionized surfactant and water (78).

The relation between the o/w and micellar solutions is less direct (78). The solubility of cosurfactant by itself is small in normal micelles in aqueous solutions of surfactant (Figure 9A). The solubility of hydrocarbon by itself in these micelles is even smaller (Figure 9B). In the presence of each other, the combined solubilities

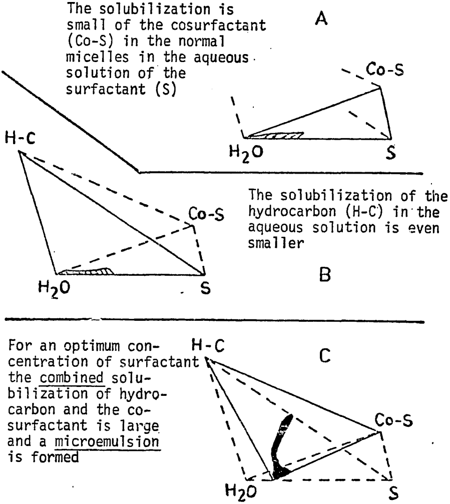


The three structure-forming elements show an area with ion pairs and inverse micelles

A plane at constant content (50%) of p-xylene is suitable to show the w/o microemulsion area dependence on the ratio between the three structure-forming elements

The w/o microemulsions containing 50% hydrocarbon are a direct continuation of the inverse micellar area at 0% hydrocarbon and the three structure-forming elements for the area are similar

Figure 8. W/O Microemulsions on Three- and Four-Component Phase Diagrams. Reproduced by permission from Prince (Ref. 78), courtesy of Academic Press Inc.



The solubilization is small of the cosurfactant (Co-S) in the normal micelles in the aqueous solution of the surfactant (S)

The solubilization of the hydrocarbon (H-C) in the aqueous solution is even smaller

For an optimum concentration of surfactant the combined solubilization of hydrocarbon and the cosurfactant is large and a microemulsion is formed

Figure 9. O/W Microemulsions on Three- and Four-Component Phase Diagrams. Reproduced by permission from Prince (Ref. 78), courtesy of Academic Press Inc.

of hydrocarbon and cosurfactant is large for an optimum concentration of surfactant and a transparent, isotropic system is formed (83) extending out from the aqueous micellar solutions (Figure 9C). The concentration of the surfactant in the aqueous solution is the critical factor. Very few systematic studies (58, 82-85), compared to those of inverse micellar systems, have been made on oil-in-water systems.

11. The Mixed Film Theory versus Micellar Aspects

Schulman never made a distinction between microemulsions and micellar solutions based on a mechanism of formation. He simply differentiated between the two systems on the basis of aggregate size when he claimed that the 75Å droplet (2) approximated the dimensions of a swollen micelle and that 100Å was about the smallest size of water droplets that can be formed in these systems (47).

This theme of differentiating microemulsions from micelles on the basis of aggregate size was recently revived by Prince (59). He claims that below a diameter of 100Å, the degree of aggregation appears to be determined by the rules governing the formation of micelles, and that above this diameter, curvature is determined by specific instructions among oil molecules and surfactant tails, as well as by the interactions between surfactant heads and water, in a well-defined interphase.

Prince went further and constructed a hypothetical phase map based on the data furnished by Shah and Hamlin (61), Bowcott and Schulman (47) and by Cooke and Schulman (9). It qualitatively defined the regions of microemulsions, micellar solutions, liquid crystalline phases (mesophases), and macroemulsions (59) (Figure 10). In this diagram the criterion used to distinguish microemulsions from micellar

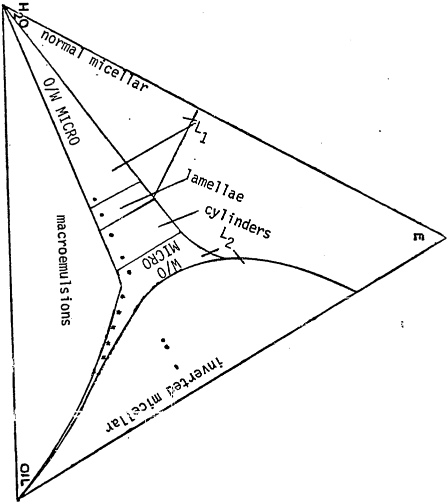


Figure 10. Prince's Phase Diagram:
• = Shah and Hamlin Points
* = Bowcott and Schulman Points

solutions, was a diameter of 100Å. The diagram differed from most "phase equilibria diagrams" of micellar solutions in that the regions of microemulsions bore a much more rigid relationship to one another.

A comparison of this phase map, which summarizes the fruits of the "mixed film theory" with the real system map was made (78).

Prince's phase map showed the combined emulsifiers to be soluble in the hydrocarbon. An ionic surfactant, such as potassium oleate, is only slightly soluble in hydrocarbon or in combination with a medium chain length alcohol (pentanol). This means that the solubility area along the emulsifier/hydrocarbon axis in this figure does not exist for soaps such as potassium oleate. The realistic diagram, as presented by Friberg (78), demonstrates the necessity of some water to obtain solubilization of emulsifier. The second point of contention was in the usage of the term "inverse micellar" to name the part to the right, in Prince's diagram. This was found by Friberg not to be correct since water and surfactant molecules exist as ion pairs in that part of the system. Inverse micelles were found first to form at higher concentrations of water.

Prince (58, 84) presents o/w microemulsions in a sectorial area emanating from the aqueous corner with a continuous transition into w/o mocroemulsions. In reality, the area for o/w microemulsions is bent, and the transition to w/o inverse micellar solutions takes place over multiphase states (82-83, 85). These latter frequently involve liquid crystals; unfortunately, that fact is sometimes not observed, and multiphase mixtures are introduced as microemulsions. The systems may appear isotropic because the liquid crystals may be dispersed in small spherical aggregates and not observed as such (82).

Friberg (86) studied the order of addition of the components in an o/w system containing water, Na dodecyl sulfate, pentanol and p-xylene. He obtained different regions depending on whether the hydrocarbon or the cosurfactant was added last. In Figure 11, region A was obtained when hydrocarbon was added last. Region D was obtained when cosurfactant was added last. Both microemulsions were transparent at preparation, but they showed different stability. Two other hydrocarbons--n-hexane and benzene--were tested for stability characteristics in this system. It was found that only those systems with low contents (less than 30% by weight) of aqueous solution in systems containing n-hexane showed no long-term changes. The conclusion reached was that these o/w systems may not be thermodynamically stable, as had been previously believed.

12. Non-Ionic Surfactant Systems

The systems presented for microemulsions with ionic surfactants were characterized by their response to surfactant/cosurfactant ratio for w/o microemulsions and by the corresponding behavior depending on water/surfactant ratio for o/w systems. The temperature effects and the influence of the nature of the hydrocarbon have little significance and have not attracted significant research interest. The conditions for microemulsions stabilized by non-ionics are entirely different; the nature of the hydrocarbon and the temperature play dominant roles in the microemulsion formulation. A good example of this is provided in (95), demonstrating the profound dependence of both temperature and the nature of the hydrocarbon. The conditions have been described in detail by Shinoda and coworkers (4, 87-98).

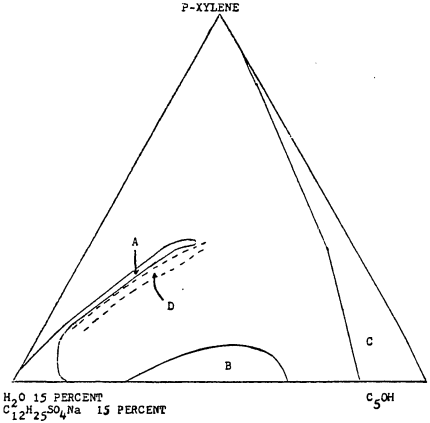


Figure 11. The Solubility Areas of O/W Microemulsions Depending on the Order of Addition of the Components. Reproduced by permission from Friberg (Ref. 86), courtesy of Marcel Dekker.

When a solution of a non-ionic surfactant in water is heated, the solution becomes visibly turbid at a temperature known as the cloud point. At this temperature the solution separates into a surfactant-rich phase and a water-rich phase (91, 95).

The important feature of a non-ionic surfactant is the notable increase in the solubility of oil in an aqueous surfactant solution at the cloud point and of water in a nonaqueous solution at the haze point (90). The solubilization curve of oil in an aqueous surfactant solution as a function of temperature is observed at a relatively low temperature. Solubilization of the oil increases as the temperature is raised and increases markedly close to the cloud point. The solubility curve of water in a nonaqueous surfactant solution is observed at relatively high temperature. The solubility of water increases as the temperature decreases, particularly near the haze point in a non-aqueous surfactant solution.

The microemulsion phenomenon with non-ionic surfactants is closely related with the PIT phenomenon (i.e., the temperature range over which a non-ionic surfactant causes the phase reversal of an o/w micellar solution to a w/o solution, also referred to as the HLB temperature). The following will describe the variation of solubilization when the temperature of a solution of a non-ionic surfactant and a hydrocarbon in water is increased through this range.

At low temperatures, far below the cloud point value, the non-ionic surfactant is soluble in water and the solubilization of hydrocarbon takes place in normal micelles (99). Figure 12-1 shows the solubilization area (A) for n-decane at 30 °C in an aqueous solution of hexaethylene glycol dodecyl ether. This solution is a

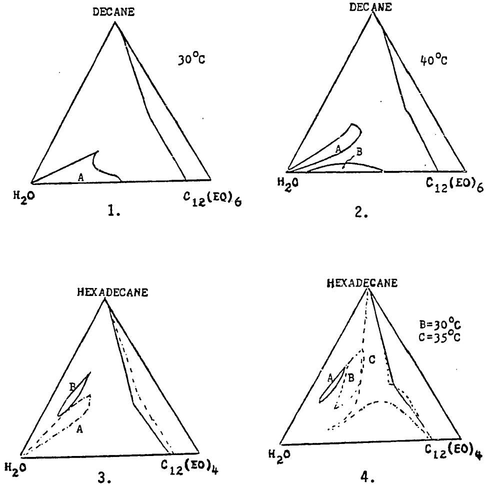


Figure 12. The Solubilization of a Solution of a Non-Ionic Surfactant and a Hydrocarbon in Water as a Function of Temperature. Reproduced by permission from Friberg (Ref. 99), courtesy of Plenum Press.

normal solution, and the term microemulsion is unwarranted. As the temperature is increased in excess of the cloud point this results in the surfactant not being soluble in the water. The solubilization area with normal micelles begins at a minimum concentration of surfactant (B in Figure 12-2) (99). In addition to normal micelles, a new solubilization phenomenon is observed, characterized by both a maximum and minimum hydrocarbon concentration for stability. This region A in Figure 12 is called a microemulsion. Although its structure has not yet been experimentally clarified, the model used by Robbins (100) appears appropriate.

The model assumes monodispersity, each oil droplet covered by an oriented monolayer of surfactant molecules. Adjacent to the oil core is a shell of hydrophobic tails. Surrounding the tails is a concentric shell of hydrophilic heads. The heads and chains act as a separate uniform liquid phase with water dissolved in the heads and oil in the chains. Curvature is imposed by the differential tendency of water to swell the heads versus oil to swell the chains. The magnitude of the interfacial stresses by this differential swelling controls the degree of curvature.

Further increase of temperature leads to a separation of the microemulsion from the aqueous phase and a three-phase area is formed. Figure 12-3 (99) shows this for the system water/tetraethylene glycol dodecyl ether and n-hexadecane. The isolated phase (B) was called the surfactant phase by Shinoda; it forms the microemulsion with minimum amount of surfactant. This kind of microemulsion cannot be diluted with water nor hydrocarbon. Its structure has not been determined with exactness. It is possible that the structure of the surfactant phase is sandwich-like with oil and water swollen between the molecular leaflet of the non-ionic surfactant. The surfactant is continuous in this phase and so also may be the water and oil (97). This type of structure has been called an equilibrium bicontinuous structure (101).

At temperatures above the HLB value, the composition of the surfactant phase (A) will be shifted towards higher surfactant concentration and will coalesce with the hydrocarbon/emulsifier solution to the right in the diagram (C) in Figure 12-4. The solubility area, after the coalescence, permits the solubilization of water, and the solutions may be defined as w/o microemulsions (99).

From Shinoda's empirical studies, the requirements for increased solubilization using a lesser amount of solubilizer may be summarized as follows:

a. Optimum Temperature for a Given Non-ionic Surfactant. The solubilization of water (or oil) in nonaqueous (or aqueous) solution of non-ionic surfactant exhibits a maximum at an optimum temperature. Thus, the optimum non-ionic surfactant, the PIT of which is close to a given temperature, exhibits large solubilizing power which means a microemulsion with less solubilizer.

b. Optimum Ratio of Surfactant. In order to increase solubilization, the HLB (or PIT) of a surfactant mixture has to be matched to the given oils. Triangular phase diagrams of water, p-xylene, octylamine and octyl ammonium chloride demonstrate the sensitivity of maximal solubilization to the ratio of the HLBs of the surfactant mixtures (102).

c. The Closer the PIT of Two Surfactants, the Wider the Solubilization Range. It became clear from recent studies (4) that the solubilization of oil (or water) is larger when the non-ionic surfactant is monodisperse than when the distribution of hydrophobic chain lengths is broad (commercial material) and when the difference in the PITs is large. The combination of dimethyl ethanol ammonium (AMP) oleate and sorbitan monododecanoate in which the HLBs of the two surfactants approach each other showed enhanced solubilization than the combination of potassium oleate and alcohol, a strongly hydrophilic and strongly lipophilic surfactant mixture.

d. The Larger the Size of the Solubilizer, the Greater the Solubilizing Power. If the size of the hydrophile and lipophile groups of the solubilizer increases, the CMC will decrease and the aggregation number will increase and the solubilizing power will be enhanced. This reasoning is confirmed by changing the size of hydrophilic and lipophilic groups while keeping the PIT (HLB-temperature) of the solubilizers constant. About 3 weight percent per system of $C_{12}H_{25}C_6H_4O(CH_2CH_2O)_{9.7}H$ seemed sufficient to yield a similar microemulsion realm as a 5 weight percent system of $C_9H_{19}C_6H_4O(CH_2CH_2O)_{8.6}H$.

e. Types of Hydrophilic Groups on Surfactants. Since the polyoxyethylene chain is not strongly lipophobic the CMC in the oil phase is not small. Substitution of a polyoxyethylene compound with a suitable mixture of sucrose monoester and sorbitan monoester in the oil phase will decrease the CMC and increase the solubilization of water because both sorbitan monoester and sucrose monoester possess efficient hydrophilic groups of different sizes (93).

f. Stability to Temperature Change. It is evident from the phase diagrams that a non-ionic surfactant is a good solubilizer at an optimum temperature but only for a limited temperature range. On the other hand, ionic surfactants are stable to temperature change but need higher concentrations. A mixture of non-ionic surfactant and ionic surfactant which is not strongly hydrophilic seems ideal (4).

13. Transient Zero Interfacial Tension

Gerbacia and Rosano (11) studied the influence on w/o microemulsions, of varying the chain length and type of cation of the surfactant as well as the nature of the surfactant (soap versus alkyl sulfate). N-hexadecane and benzene were the oil phases. Pentanol was the cosurfactant. Based upon the distribution of pentanol between the dispersed phase and interphase, calculations of ΔG were made. Small negative values were calculated. The effect of changing the chain length of the surfactant and nature of the solvent on the amount of pentanol in the microemulsion was noted. The effect of changing the size of the cation was not as clear-cut. The results did not substantiate Schulman's claim (5) that there is a sharp transition point from oil to water continuous systems as the hydrophobic-hydrophilic character of the surfactant-cosurfactant combination is varied, since the same formulations were seen to be applicable in forming o/w microemulsions in many cases, just by changing the relative concentrations of the components. Also, the claim that matching the chemical nature of the surfactant to that of the oil phase is critical (47) was seen to be unwarranted. It also seemed that Schulman's claim that alcohol remained at the interface changing its wettability, and therefore determining the nature of the continuous phase, was also unfounded.

Proton nuclear magnetic resonance (103) was used to study the microemulsion systems to determine if hydrogen bonding between the surfactant and cosurfactant played an important role in stabilizing the dispersed droplets against coalescence. Water-in-oil microemulsions were studied. The results indicated that the anionic group of the surfactant was not participating in hydrogen complexing with the cosurfactant to any appreciable extent in the systems studied.

It was claimed that the interaction does not occur with the cosurfactant except when the counterion is capable of hydrogen bonding to it. It was concluded that hydrogen bonded complexes did not play a significant role in the formation of microemulsions, contrary to what was believed by Schulman (52) and Prince (60). This did not eliminate the possibility of van der Waals interactions among the tails of the surfactants. The energy for this type of interaction would be small but could be enough to stabilize the interfacial film.

Light scattering studies were done (103) to verify the earlier results (67) and to compare the measured particle sizes with those calculated from equation 1-9. It was concluded that it was the phase volume and amount of alcohol that controlled droplet size. Adding an excess of alcohol was seen to decrease the size of the dispersed droplets. It was found that at the clearing point the configuration of the interfacial monolayer was the same for a given surfactant. This agreed with the conclusion made previously by Rosano et al. (67). They found from the measurements of sedimentation constants of w/o microemulsions stabilized by potassium oleate and hexanol and sodium dodecyl sulfate and pentanol, that at the clearing point the total interfacial area remained the same even if the volume of the dispersed phase was doubled. This led them to conclude that the configuration at the interface was the same. However, when the cross-sectional area per mole of surfactant (σ) was calculated (103), values were seen to be very low--too low to be reasonable. It was concluded, therefore, that the simple picture in which all the surfactant is located at the interface is in error, and that the interfacial configuration must indeed change to accommodate change in the amount of surfactant available. It was also seen that the size of the dispersed droplets was governed by the amount of water being dispersed as long as there was enough surfactant present to stabilize the system. If not enough soap was present, the system would not become clear until enough alcohol was added to dissolve all of the water as a solution.

The differential UV absorption spectrum of o/w microemulsions of benzene stabilized by SDS and pentanol, was compared with the solution spectra of benzene in hydrocarbons, in an attempt to determine the type of environment of the benzene in these o/w microemulsions (103). It was concluded that the environment of the benzene in the microemulsion droplets was similar to that of benzene in a hydrocarbon at a mole fraction of benzene equal to about 0.4. The benzene was shown, however, to penetrate between the tails of the surfactant to some degree.

The UV absorption spectrum of I_2 dissolved in microemulsions of n-hexadecane supported the view that the interior of the dispersed droplets in the o/w microemulsions are typically hydrocarbon in nature (103). The alcohol was observed to penetrate into the interior of the dispersed droplet and this was held responsible in part for increasing the polar character of the micelle interior.

Measurements of the interfacial tension as a function of time were made (11). The behavior of an oil/water interfacial tension as a function of time after pentanol had been injected above and below the interface was observed. Measurements were made in the absence and presence of adsorbed SDS at a concentration below the CMC to avoid any interference from micelles in the bulk of the aqueous phase. It was found that it is possible for the interfacial tension of a system to drop to zero for a certain period of time due to the redistribution of amphipathic molecules while the equilibrium γ_i remained positive.

The contention was that the reduction of γ_i to zero was a necessary condition for producing the small droplet size of the microemulsion. In the formulations discussed, it was the redistribution of the alcohol which lowered γ_i to zero. It was shown that, in a couple of w/o systems, if the alcohol was predistributed in the phases at the equilibrium concentration before combination, the system would have a positive γ_i and microemulsions would not be produced. However, in one of the o/w cases which will be discussed, predistribution of the alcohol did not adversely affect microemulsion formation. So this cannot be concluded to be a universal property of every system.

Sanfeld and Defay et al. (104, 105) have studied surface thermodynamics for nonequilibrium cases. They found that one of the causes of spontaneous emulsification may be related to the existence of a transitory state where the interfacial tension becomes negative or goes to zero due to the transfer of surface active materials. The classical equilibrium thermodynamics of interfaces may not be applied to these states where no adsorption equilibrium exists. The authors developed a multilayers model which permitted calculation of the interfacial tension for any given distribution of matter in adsorption equilibrium or not. With this model they have studied the transitory states of zero interfacial tension and they showed that a necessary condition for the existence of such a state is the presence of opposite concentration gradients of the various components in the interfacial layer.

B. Theories of Stability

Current interpretations of microemulsions either emphasize their emulsion-like properties and attempt to build molecular models of the interface (59, 63) or consider them as solubilized micellar solutions which can be systematically studied by phase diagrams (4, 6, 82). There has been insufficient experimental work to confirm the existence of stable emulsions, and thermodynamically stable or metastable disperse systems that behave like microemulsions significantly blur the current classifications. The divergence of these complementary viewpoints is not so great except over the question of the kinetic--versus the thermodynamic--stability of these disperse systems. Kinetic theories are consistent with the former point of view, while thermodynamic theories of stability are consistent with the latter point of view.

1. Thermodynamic Stability

The spontaneous formation of microemulsions has been attributed to the development of negative interfacial tension, by a number of investigators (2, 8, 63, 52, 9, 58). However, as pointed out by Miller and Scriven (106), such an explanation appears to be an oversimplification because it ignores other factors which could in principle cause the interface to become unstable, while the interfacial tension is still positive but small. Among the thermodynamic factors that have been considered are: stress gradients, solubility parameters, interfacial compressibility, chemical potentials and concentrations of all species present in the bulk phases as well as the interphase, enthalpy, entropy, the bending and tensional components of the interfacial free energy, osmotic pressure and Laplace pressure, and diffusion across curved interfaces.

One of these factors--the entropy effect--has been investigated. It has been suggested that when interfacial tension is low but positive the interface may become unstable due to a sufficiently large increase of the entropy by dispersion. The decrease of the free energy due to this entropy change may exceed the increase caused by the creation of interfacial area, thus resulting in a net negative free energy change (107). Reiss (108) investigated the possibility of entropy induced dispersion of bulk liquids and discovered that spontaneous dispersion can occur at less than 2 dynes/cm and that below tensions of 5×10^{-4} dynes/cm, small aggregates (microdroplets) are formed. He distinguished spontaneous dispersion due to entropy effects, from formation of micellar solutions due to energetics.

Taking into account the variation of the interfacial free energy with curvature in low tension systems, Murphy (109) has shown that the work necessary to deform an interface consists of work done against γ_i and the work to bend the interface. Although always present, resistance to bending is important only for low tensions of highly curved interfaces. Murphy concluded that an interface having a low but positive interfacial tension, could nevertheless be unstable with respect to bending it for some small dispersion the reduction in interfacial free energy due to bending exceeds the increase in free energy due to the γ_i contribution. He further suggested that this bending instability might be responsible for spontaneous emulsification in some water and oil systems.

Murphy's analysis led Miller and Scriven (106) to investigate the stability of interfaces with electrical double layers. Their results confirmed that the double layers may indeed affect significant interfacial stability in low surface tension systems.

Recently, Ruckenstein and Chi (110) undertook a rigorous thermodynamic treatment of microemulsions to obtain information on stability. Their model consists of monodisperse microdroplets which are randomly distributed in a continuous liquid phase.

The free energy change due to the mixing of the liquids consists of three major contributions:

$$\Delta G_m = \Delta G_1 + \Delta G_2 + \Delta G_3 \qquad (3\text{-}11).$$

The first term, ΔG_1, represents the free energy of formation of the interface and contains the surface free energy (a positive quantity) and the free energy of formation of the double layers calculated from a Debye-Huckel approximation (111) (negative, because double layers form spontaneously). The second term, ΔG_2, represents the contribution of interaction forces between globules and contains the negative term $\Delta G'_2$ due to attractive van der Waals forces (calculated using the Ninham-Parsegian approach [112]) and a positive term, $\Delta G''_2$, due to repulsion potential from the compression of the diffuse electrical double layers (calculated from Overbeek [42]). Numerical computations showed that in general the van der Waals term was negligible compared to the others. The last term, ΔG_3, represents the negative contribution of the entropy of dispersion which was estimated from geometric considerations (a reasonable average between the highest and lowest limits).

Their work indicated that when the free energy change of mixing, ΔG_m, was less than zero, spontaneous formation of microemulsions occurred, whereas, when ΔG_m was greater than zero, macroemulsions were produced, which, although thermodynamically unstable, may be kinetically stable. They found that for a specified composition it is possible to form thermodynamically stable emulsions of both o/w and w/o types, of one type, or none at all, depending on the value of the specific free energy. Moreover, they were able to account for the size of the droplets in thermodynamically stable systems and to predict the occurrence of phase inversion. The model is useful since it provides an estimate of the magnitude of different factors of importance affecting stability. It is not the final solution to the problem, however, since some interactions were not treated.

A theory for the phase behavior of microemulsions has been developed by Robbins (100), which is consistent with the concept that interactions in the mixed film are responsible for the direction and extent of curvature and thus of the type and size of droplets in the microemulsion. In his most recent model for microemulsions stabilized with non-ionics, the heads and tails of the interfacial species are seen as acting as separate uniform liquid phases, with water dissolved in the heads and oil dissolved in the tails. The kind and degree of curvature is imposed by the differential tendency of water to swell the heads and oil to swell the tails.

Robbin's model quantitatively predicted phase behavior in oil, water and surfactant systems. He proposed a lateral stress gradient resulting from differences in the swelling of the heads and tails across the interface. This stress gradient was expressed in terms of physically measureable quantities--surfactant molecular volume, interfacial tension, and interfacial compressibility (defined as the fractional change in molecular area with interfacial pressure).

As a basis for his theory, he has utilized equations generated by the geometry of two concentric spherical shells surrounding the droplet and by force balance across these shells. Equations are developed for both o/w and w/o droplets which relate phase behavior to γ_i, the volume of the surfactant heads and tails, and interfacial compressibility. Interparticle interactions are ignored.

Robbin's theory correlates water and oil uptake with the idealized ternary diagram and Winsor's transitions in micellar type systems (69, 70, 62). When water and oil uptake are known, γ_i can be predicted and vice versa. The theory also predicts droplet size and interfacial concentration of adsorbed surfactants in terms of number of molecules per droplet. Robbins established thermodynamic criteria for spontaneous water or oil uptake without postulating a negative interfacial tension.

2. <u>[Meta]Kinetic Stability</u>

Gerbacia and Rosano (11, 12) experimentally found some w/o microemulsions not to be stable on a long-term basis and composed a theory to describe the kinetic stability (13). The theory was essentially limited to the energy changes occurring in the layers of surfactant and cosurfactant lining the microemulsified water droplet during coalescence. The free energy changes in the film were calculated using regular solution theory (113), both for the enthalpic and entropic components. In addition, the van der Waals attractive potential was added, using the Hamaker approach modified by Vold for droplets with surface layers (114). The total interaction free energy (energy barrier to coalescence) was then given by

$$\Delta G_T = \Delta G_M + \Delta G_W \qquad (3\text{-}12),$$

where ΔG_M is the change in free energy upon mixing ($\Delta G_M = \Delta E_M - T\Delta S_M$ is a positive term) and ΔG_W represents the van der Waals interaction energy (is a negative term). Calculations of ΔG_T were seen to be high enough to explain the long-term stability of these systems.

C. Statement of the Problem

It is apparent that there are some discrepancies and inconsistencies in the theories presented and that the theories are not complete. Moreover, even with the great amount of information that has been gathered from all of these studies there still seems to be a divergence of interpretation as to the mechanisms of formation and stability, i.e., the precise nature of these particular transparent systems. The general characteristics of the two systems will now be reviewed and the basis for the present controversy stated.

Many of the micellar solutions are ternary systems, although systems of four components have been studied extensively by phase equilibria diagrams. In this case, the surfactant or surfactants are viewed as spontaneously organizing themselves into colloidal aggregates which can bind oil and water under the appropriate conditions. Such systems are considered to be thermodynamically stable and reversible. The systems are considered to be in equilibrium since the method of preparation has no effect on the resulting dispersions. The components are simply combined in any order. The systems are then left standing and later centrifuged and analyzed for the different phases which have developed with time.

On the other hand, microemulsions usually contain oil, water, surfactant and a cosurfactant. The stabilizing monolayer consists of the two components, a mixed film, which is probably penetrated to some extent by molecules of the oil phase. Here, the surfactants are considered to be adsorbed between the two mutually insoluble liquids, causing one liquid to be dispersed as microdroplets in the other. This is the definition of an emulsion, i.e., a two-phase system. Therefore, microemulsions may be considered to be irreversible, thermodynamically unstable dispersions. The ease of formation of the microemulsions therefore depends on the method of preparation and the stability depends on the structure of the interfacial film formed.

Although the characteristics of the two types of systems appear to be clearly delineated above, there is much difficulty in practice in deciding which type one is dealing with. The confusion arises from the observation that the fluid, isotropic, transparent, stable systems formed by either method exhibit the same physical properties of light scattering, etc. As a consequence, neither of these systems has been characterized well enough in the literature, at the time of writing, to allow a clear-cut differentiation between them.

The work that will be presented was undertaken to help elucidate a mechanism of formation of an oil-in-water microemulsion containing oil/water/soap/short-chain alcohol. The experimental objectives of this study were to obtain answers to the questions posed in the introduction and to help clear up the existing confusion about the nature of these transparent dispersions.

The experimental approach to the questions raised was to first prepare transparent dispersions. Methods of preparation of two different series of transparent o/w and some w/o dispersions were developed. The systems were then studied and characterized with respect to several parameters. From the results of these studies, two additional problems evolved which needed further investigation. These were: (a) the transfer of the surfactant and cosurfactant through an oil/aqueous interace, independently and in the presence of each other, and (b) the interfacial structure that is conducive to microemulsion formation. The interfacial transfer of the surfactants was studied by measuring the interfacial tension between an oil and aqueous phase with time, as an adsorbing solute transferred between the two phases. Wilhelmy's wettable plate (11) and the spinning drop interfacial tensiometer (14) were the techniques used. The interfacial structure was studied by a comparison of the compression isotherms and surface potentials versus molecular areas of various fatty acid films spread on an aqueous KOH substrate. The duplex film technique (15) was used.

From the interpretation of all of the experimental results, a mechanism of formation of transparent oil-in-water dispersions was proposed.

CHAPTER IV

THE PREPARATION AND CHARACTERIZATION OF TRANSPARENT DISPERSIONS

A. Transparent Dispersion Formation

Transparent dispersions of one immiscible liquid in another have received much scientific interest in the past thirty years (1, 3-6, 7-11, 47, 91, 61, 110, 115, 116). The formation and stabilization of transparent dispersions involve the interaction of many parameters. As a result, these clear dispersions are usually developed empirically since no adequate theory exists on the components which will form them. HLB and solubility parameters have not been as helpful as when formulating coarse emulsions.

There has been discussion in the literature about the nomenclature for such dispersions (e.g., 6, 4, 13, 117, 81, 110). The arguments are not purely semantic. The discussions relate to the fundamental stability of the systems (81, 110), i.e., whether a given system is thermodynamically stable or not. In the former case the system has properties typical of a solution of an association colloid (4, 110). Here the final formulation is independent of the order of mixing the components. On the other hand, it has been found that the resulting system depends on the method of preparation (11, 13). The latter system is called a microemulsion, while the former system a swollen micelle. The systems discussed are the microemulsion variety.

First, transparent o/w and w/o dispersions were prepared, then some of the parameters affecting their formation and different mixing procedures were studied. Oil-in-water (o/w) systems were emphasized, but some water-in-oil (w/o) systems were also investigated. The long-term stabilities of the systems were not systematically investigated. For the sake of clarity, the terms "microemulsion" or "transparent dispersion" will be used as a label for the clear systems since some of the mixtures were not transparent.

Microemulsions were prepared using a titration technique: oil/lipophilic surfactant solution was added to the water phase; the system was then titrated to clarity with an hydrosoluble surfactant. The rationale behind this method of preparation was to obtain the optimum interfacial film combination that would produce a transitory condition of zero interfacial tension during which time the system was being dispersed.

1. Systems Containing Oil/Water/Mixture of Nonyl-Phenol Ethylene Oxide Condensates.

2. Materials

One hundred ml beakers with water jackets placed on electromagnetic stirrers were used. The thermostat was set at 30 °C. The chemicals were commercial samples of Igepal Nonylphenoxypoly (ethyleneoxy) ethanol, provided by the GAF Corporation (New York, NY 10020). The hexadecane was purchased from the Eastman Kodak Company (Rochester, NY). Freshly distilled water was used in all experiments.

3. Procedures

a. Titration Technique to Prepare w/o Microemulsions

A calculated amount of hydrosoluble or dispersible surfactant

(HS) with a high HLB value (e.g., long chain sodium sulfate), using equation 1-9 and assuming a radius of 500Å and a molecular area (σ) of 50Å , was dissolved in a small volume of water (dispersed phase). This solution was mixed with a larger volume of oil (continuous phase) to form a coarse emulsion and then titrated with a fourth component with a very low HLB value (e.g., five or six carbon chain alcohol) until the mixture became clear. If more oil was added, the system became milky again, but addition of more cosurfactant cleared the dispersion.

b. Preparation of o/w Microemulsions

Previous results dealt primarily with w/o microemulsions (103). Starting with a mixture of oil and an aqueous solution of surfactant, initial emulsification was observed. Generally, the cosurfactant used was a short chain alcohol, mostly 1-pentanol. Therefore, when the preparation of oil-in-water microemulsions were attempted, the logical approach was to first try to use an analogous procedure to the one used in the preparation of w/o microemulsions described above. An oil-in-water microemulsion was attempted using the w/o formulation presented in (103). A solution of 2-ml n-hexadecane with 0.5 ml of various short chain alcohols (such as 1-pentanol) was made, then added to 10 or 5 ml of H_2O thermostated at 30 °C. To this, various amounts of 0.2M (or 0.4M) sodium lauryl sulfate (SDS) solution were added. None of the systems cleared. Just as in the case of the w/o microemulsions that were prepared (103), it was seen that the first three components together must form an initial fine emulsion.

Short chain alcohols were not good cosurfactants with SDS for this purpose and were replaced with nonyl-phenol or long chain alcohol-ethylene oxide condensates. The following procedure was used: A given amount of water was placed into a 100-ml thermostated water jacketed (30 °C) beaker. Volumes ranging from 3 to 40 ml were used. Separately a solution of oil and lipophilic surfactant (LS) was prepared. The oil solution was added to the water. The system was continuously stirred. The LS selected was the one which appeared to form the best initial coarse emulsion, as determined by visual observation. Next, the systems were titrated to clarity with a more hydrosoluble surfactant. It was observed that once the right lipophilic surfactant was found within a narrow HLB range, a suitable cosurfactant (HS) for the system could be found within a slightly larger HLB range.

In the case of n-hexadecane at 30 °C, the combination of nonyl-phenol-4-Eto (HLB = 8.9) and nonyl-phenol-9.5-Eto (HLB = 13.4), using the above described procedure, produced a microemulsion.

4. Results

a. Influence of the Method of Preparation

i. Dilution Method

A microemulsion of n-hexadecane was prepared using the following: 5 ml of water, 2 ml n-hexadecane, 0.5 ml nonyl-phenol-4-Eto and 1.3 ml nonyl-phenol-9.5-Eto. More water was added to the transparent dispersion, the system became turbid again and addition of more nonyl-phenol-9.5-Eto cleared the dispersion. This procedure was repeated until the transparent dispersion contained a total of 40 ml of water. (See Figure 13, Curve 1.) When the initial volume of water was 20 ml using the same procedure, Figure 13, Curve 2 was obtained.

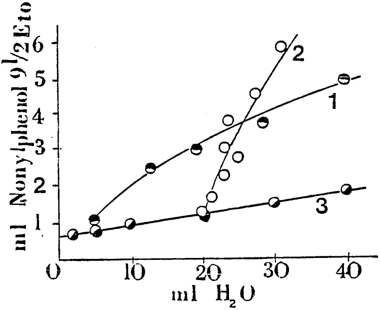


Figure 13. Dilution and Point Methods of an O/W Microemulsion at 30 °C: Curves 1 and 2, Dilution Method; Curve 3, Point Method.

ii. Point Method

While stirring, a solution containing 2 ml n-hexadecane and 0.5 ml nonyl-phenol-4-Eto was added to 3 ml of water at 30 °C. The fine emulsion was titrated to visual clarity with nonyl-phenol-9.5-Eto, which was added slowly and dropwise. A new microemulsion was then prepared in which the amount of water was increased to 5 ml; everything else was kept the same. The minimum amount of nonyl-phenol-9.5-Eto to reach the same transparency was recorded for dispersions containing up to 40 ml H_2O (Figure 13, Curve 3). In this method, each new dispersion with its volume of water required a little more hydrosoluble surfactant (HS) to reach transparency. In the "dilution" method, when more water was added to the transparent dispersion to cause turbidity, the hydrosoluble surfactant redistributed. More of it dissolved in the aqueous phase instead of at the interface. Therefore, more total HS was required for clearing these dispersions than those prepared by the "point" method.

This difference in the requirements for the hydrosoluble surfactant depending on the method and order of addition of water to the dispersions indicated that the dispersions were not thermodynamic systems.

b. Effect of the Temperature on the Stability of a Microemulsion

A microemulsion (2 ml n-hexadecane + 0.5 ml nonyl-phenol-4-Eto + 1.5 ml nonyl-phenol-91/2-Eto + 20 ml H_2O, Point Method) was found to remain clear for at least 15 hours between 4 and 50 °C. When the temperature exceeded these limits, the system became cloudy due to the cloud point, but returned to clarity when brought back around to the 30-40 °C range. Since the melting point of n-hexadecane is 18 °C these results indicate a large supercooling of the oil when it is microemulsified. However, since the surfactant acts as an impurity in the oil phase, the melting point is expected to be lowered. These results therefore cannot be concluded to be due exclusively to microemulsification. These systems were examined by broad line NMR technique over the same temperature range.* The results indicated that the n-hexadecane remains in the liquid state below its freezing point when microemulsified.

c. Effect of the Concentration of the Lipophilic Surfactant

Two ml of n-hexadecane containing varying amounts of nonyl-phenol-5-Eto as LS were added to 10, 20, or 30 ml of water, then titrated to clarity with nonyl-phenol-91/2-Eto. Table 1 summarizes the results. N.C. stands for no clearing, following the addition of a maximum of 2 ml of nonyl-phenol-91/2-Eto.

It is concluded that at least 25% of the total emulsified volume must be surfactants in order to cover the large interfacial area created during the microemulsification process. Moreover, when more water is added, more surfactant is required due to phase redistribution of the surfactant.

From these experiments it was seen that the structural requirements of the surfactants to form these transparent dispersions are very critical and specific. Often differences of just 0.5 Eto unit resulted in differences in whether the transparent dispersions formed. In fact,

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*The experiment was done by other researchers at General Foods Corporation, Tarrytown, NY.

Table 1

Ml NP*-9.5 Eto Needed to Clear System (up to 2 ml)

	NP*-9.5 Eto		
NP*-5 Eto	10**	20	30
0.1	NC	NC	NC
0.2	0.3	NC	NC
0.25	0.3	NC	NC
0.3	0.3	NC	NC
0.4	0.4	0.35	NC
0.5	0.35	0.35	0.6
0.75	0.4	0.2	0.5
1.00	0.5	0.2	0.25

*Nonylphenol ethylene oxide condensates

**ml of H_2O

out of the numerous combinations tried, only two were found to produce good dispersions of n-hexadecane in water. There are disadvantages of the non-ionics of the ethylene oxide class. They have a wide distribution of polyoxyethylene homologues. This is superimposed on the natural wide distribution of fatty acid species in any given hydrophobic moiety. Also, changes in temperature have large effects on the efficiency and stability of the systems prepared. Therefore, in order to study the influence of the structure of the surfactants on transparent dispersion formation the nonyl-phenol ethylene oxide condensates were replaced with structurally pure fatty acids and alcohols as surfactants.

5. Systems Containing Oil/Water/Soap/Alcohol

6. Materials

The surfactants used were potassium soaps of straight chain primary fatty acids (C_{12}-C_{18}). The fatty acids, n-hexadecane, and 4-methylcyclohexanol (a mixture of cis and trans isomers) were purchased from Eastman Kokak Company (Rochester, NY). The rest of the alcohols were 99% pure purchased from Aldrich Chemical Company (Milwaukee, WI). The toluene and 1-pentanol were reagent grade purchased from Fisher Scientific Company (Fairlawn, NJ). The CCl_4 was reagent grade purchased from Amend Drug and Chemical Company (Irvington, NJ). The KOH pellets were from Mallinckrodt Chemical Company (St. Louis, MO). The surface tension measurements were made with a Rosano tensiometer from Biolar Corporation (North Grafton, MA). All experiments were conducted at 30 °C unless otherwise stated. Distilled water was used in all experiements.

7. Procedures

The effect of pH on the type of initial coarse emulsion was determined in the following manner. A solution of 2×10^{-3} moles of fatty acid in n-hexadecane was added to 10.0 ml of distilled water with continuous stirring. This mixture was then titrated with 1.0 N KOH solution while the pH was monitored. NaOH, LiOH and RbOH solutions were also tested. The sodium and lithium soaps formed with stearic acid have higher Krafft point temperatures than the potassium soaps formed, and therefore precipitated at 30 °C. The rubidium soaps formed are soluble at this temperature and emulsification was achieved. A "good" emulsion was obtained above pH 12.0 with KOH. This high pH was necessary to insure the complete ionization of the fatty acid (118). From these preliminary experiments it was concluded that 0.375 N KOH produced a sufficiently high pH to insure complete ionization of the acid and formation of suitable emulsions. (See Figure 14). Curves 1, 2, 3 and 4 correspond to the lauric, palmitic, myristic and stearic acid titrations, respectively.

Microemulsions were prepared at 30 °C using the "point" method. As above, the stearic acid was dissolved in the oil phase and the aqueous KOH solution was mixed with it. The resulting coarse emulsion was then titrated with the cosurfactant to form the microemulsions. Arachidic and behenic acids were not completely soluble at 30 °C and were not used.

Transmittance measurements. A Bausch and Lomb Spectronic 20 spectrometer was used to monitor the transmittance of the emulsions at 520 nm during the titration with cosurfactants. This method defines

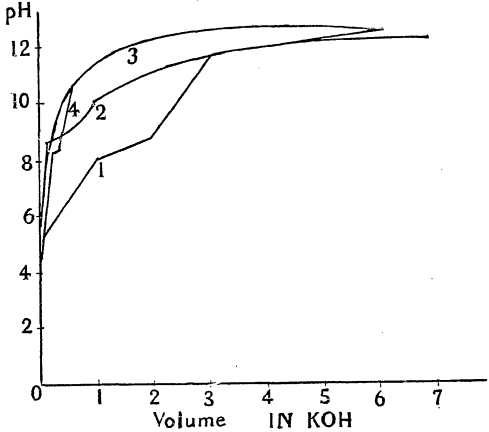

Figure 14. pH vs. Volume of 1 N KOH for Four Fatty Acids (C_{12}-C_{18}) at 30 °C:
Curve 1, Lauric Acid; 2, Palmitic Acid; 3, Myristic Acid; 4, Stearic Acid

quantitatively the extent of the clear microemulsion region. The precision for the titrations was about ±8% when measured by transmittance.

8. Results

a. The Nature of the Cosurfactant

The nature of the cosurfactant for producing transparent systems was investigated. Several hundred preparations were attempted using 52 alcohols and 3 oils. The oils were an alkane, n-hexadecane, an aromatic, toluene, and a chlorinated hydrocarbon, carbontetrachloride. Two basic formulations were used:

o/w - (2.0×10^{-3} moles of stearic acid and 2.0 ml of oil) / (16.0 ml of 0.375 N KOH);

w/o - (2.0 ml of 1.8 N KOH) / (10.0 ml of an oil solution containing 2.0×10^{-3} moles of stearic acid).

A higher concentration of KOH was used in the w/o system to provide a stoichiometric excess of KOH which assured the complete ionization of the fatty acid in all cases. The results for those systems which had a 60% or greater maximum transmittance are presented in Tables 2-5.

Oil-in-water dispersions are more preponderant with carbon tetrachloride and toluene than with n-hexadecane. CCl_4 is skewed towards o/w dispersions, while n-hexadecane is skewed towards w/o and toluene is more evenly distributed. The number of systems which had a maximum transmittance of 60% or greater, at 520 nm, are summarized in Table 4 for each oil used.

From these results it was seen that the structural requirements of the cosurfactant to produce these transparent dispersions were very

Table 2

Cosurfactant Selectivity for Producing Microemulsions with N-hexadecane and Potassium Stearate at 30 °C

Alcohol	Alcohol Volume (ml)		Maximum %T	
	w/o	o/w	w/o	o/w
2-methyl-1-butanol	1.20		100	
3-methyl-1-butanol	0.80	1.50	99	99
2-ethyl-1-butanol	1.40		95	
3,3-dimethyl-1-butanol	0.80	0.65	60	79
4-phenyl-2-butanol	1.1		100	
1-pentanol	0.90	1.20	100	89
4-methyl-1-pentanol	0.90	0.70	100	88
3-methyl-2-pentanol	1.50		84	
4-methyl-2-pentanol	1.90		98	
4,4-dimethyl-2-pentanol	3.50		100	
2,4-dimethyl-3-pentanol	8.20		84	
2-hexanol	1.70		100	
2-methyl-2-hexanol	2.60		84	
5-methyl-2-hexanol	1.50		84	
4-methylcyclohexanol	1.20	1.20	100	91
2,3-dimethylcyclohexanol	1.40		89	

Table 3

Cosurfactant Selectivity for Producing Microemulsions with Carbon Tetrachloride and Potassium Stearate at 30 °C

Alcohol	Alcohol Volume (ml)		Maximum %T	
	w/o	o/w	w/o	o/w
1-propanol	1.00	1.90	100	91
2-methyl-1-propanol	0.70		93	
2-methyl-2-propanol	1.00	3.00	100	80
1-butanol		1.30		80
3-methyl-1-butanol	0.60	0.9	100	89
2-butanol	1.00	2.20	100	80
2-methyl-2-butanol	1.00	1.70	100	93
3-methyl-2-butanol	1.00	0.80	100	88
3,3-dimethyl-2-butanol		2.10		85
2-pentanol		2.00		65
2-methyl-2-pentanol		1.60		85
3-methyl-2-pentanol		2.40		73
3-pentanol		1.00		88
3-methyl-3-pentanol		1.10		89
2,3-dimethyl-3-pentanol		1.90		74
cyclopentanol	0.60	0.90		89
1-methylcyclopentanol		1.00		87
2-methyl-2-hexanol		2.30		74
2,6-dimethylcyclohexanol		1.70		61

Table 4

Cosurfactant Selectivity for Producing Microemulsions with Toluene and Potassium Stearate at 30 °C

Alcohol	Alcohol Volume (ml)		Maximum %T	
	w/o	o/w	w/o	o/w
1-propanol	1.10		88	
2-methyl-2-propanol		1.00		72
1-butanol	1.55	1.10	94	93
2-methyl-1-butanol	1.40		95	
3-methyl-1-butanol	0.85		95	
2-ethyl-1-butanol	1.75		89	
2-methyl-2-butanol		1.15		90
3-methyl-2-butanol		2.10		97
1-pentanol	0.8		100	
2-pentanol		0.85		96
3-methyl-2-pentanol		1.20		83
4-methyl-2-pentanol	1.50	1.50	100	80
4,4-dimehtyl-2-pentanol	1.95		100	
cyclopentanol	1.50	1.75	93	94
1-hexanol	1.10		61	
2-hexanol	1.10		100	
4-methyl-2-hexanol	1.80		79	
4-methylcyclohexanol	1.00		76	

Table 5

Numbers of Systems which Had a 60% or Greater Maximum Transmittance at 520 nm when Titrated with 52 short chain alcohols

	w/o	o/w
CCl_4	8	18
N-Hexadecane	16	5
Toluene	13	8

critical and specific. Even among these alcohols, which are structurally very similar, very dissimilar resulting dispersions were obtained. Some specific illustrations of this for each oil are the following: In the case of n-hexadecane with potassium stearate, 1.70 ml of 2-hexanol was required to produce a w/o dispersions with 100% transmittance. However, 1-hexanol was not an efficient cosurfactant with these components for either type of dispersion and was not included in Table 2. In the case of toluene, 1.55 ml and 1.10 ml of 1-butanol were required to produce a w/o dispersion with 94% transmittance and an o/w dispersion with 93% transmittance, respectively. However, 2-butanol was not an efficient cosurfactant for these components and was not included in Table 3. In the case of CCl_4, 0.6 ml and 0.9 ml of 3-methyl 1-butanol was required to produce a w/o dispersion with 100% T and an o/w dispersion with 89% T, respectively. However, 2-methyl 1-butanol was not an efficient cosurfactant for either type of dispersion with these components and was not included in Table 4.

The results with n-hexadecane and the longer chain alcohols in Table 2 seem to agree with the conditions which Schulman established for phase continuity in a microemulsion, i.e., for a hydrophobic mixed monolayer, w/o diepersions form. However, the reasons for the general trends in the results found with CCl_4 and toluene are not obvious at the present time. Nevertheless, besides the structural considerations mentioned, it was thought that the distribution coefficients (the way in which a particular alcohol distributes itself between an oil and aqueous phase) would provide insights into why an alcohol was an efficient cosurfactant in a particular dispersion.

i. Procedures: Solubilities

The solubilities of 4-methylcyclohexanol and 1-pentanol in 0.375 KOH solution were determined by surface tension measurements of solutions of various concentrations at room temperature (25 °C).

A 0.375 N KOH solution was prepared by dissolving 21g KOH pellets in 1000 ml distilled water. The KOH solution was foamed in a 600 ml sintered glass funnel to remove any surface active impurities (15). Ninety ml of the KOH solution and 10 ml alcohol was placed into a 100 ml stoppered graduated cylinder. The 10 ml of alcohol was above the solubility limit and did not dissolve in the KOH to form a homogeneous solution. However, the mixture was shaken vigorously by hand to insure as homogeneous a dispersion as possible. Ten ml of this well dispersed mixture was removed and placed into another 100 ml cylinder. The remainder of the cylinder was filled with the KOH solution. Successive dilutions were made in this way until regular homogeneous solutions were obtained. All these solutions were then placed into freshly cleaned and dried crystallizing dishes and allowed to equilibrate at room temperature. After thirty minutes surface tension measurements of the various solutions were made with a platinum blade attached to a tensiometer. Surface tension (γ_s) versus log C curves were drawn to get rough estimates of the saturation concentrations. Alcohol in KOH solutions were then prepared within very small concentration ranges on both sides of this roughly estimated value of log C. The surface tensions of these solutions were measured. In this way a value as close to the saturation concentration as possible was determined.

ii. Results: Solubilities

The plots (Figure 15) of γ_s versus log C show that the solubility of 4-methylcyclohexanol in 0.375 N KOH is equal to 1 ml/100 ml solution (Curve 1), and the solubility of 1-pentanol is 2.5 ml/100 ml solution (Curve 2).

iii. Procedures: Distribution Coefficients of 1-pentanol

The distribution coefficients of 1-pentanol between carbontetrachloride and water were determined by surface tension measurements.

At 25 °C, 100 ml of aqueous solutions of 1-pentanol of various concentrations were prepared in freshly cleaned glassware. The surface tension was determined with a Rosano Tensiometer. The values were recorded after the adsorbed film had reached equilibrium (approimxately 20 minutes).

Eighty ml of each 1-pentanol aqueous solution was mixed and vigorously shaken with various volumes of CCl_4. Each system was allowed to separate until the top aqueous layer was completely clear (approximately 30 minutes). Finally, the surface tension of the top aqueous layer was determined.

iv. Results: Distribution Coefficients of 1-pentanol

It was found that the surface tension increases because of the decrease in concentration of 1-pentanol in the aqueous phase due to transfer into CCl_4.

The original surface tension versus concentration curve was used to determine the amount of 1-pentanol extracted by CCl_4. The results were expressed in terms of distribution coefficient: K = weight percent in oil/weight percent in H_2O. Table 6 summarizes the results:

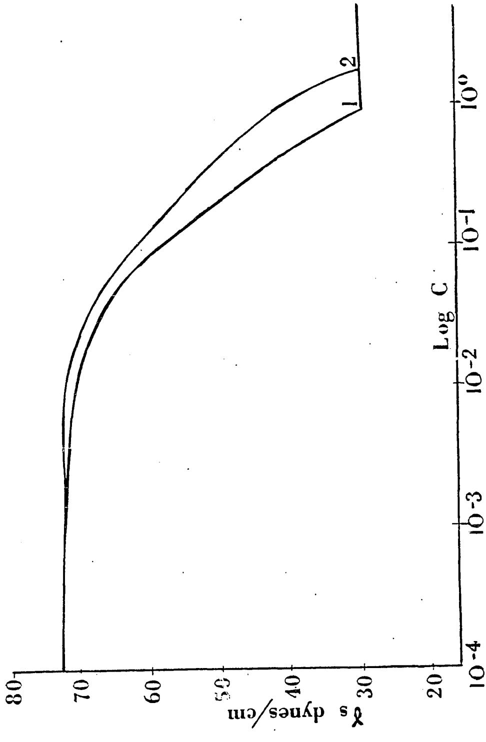

Figure 15. Surface Tension vs. Log C of 1-Pentanol and 4-Methylcyclohexanol in 0.375 N KOH Solutions at 25 °C: Curve 1, 4-Methylcyclohexanol; Curve 2, 1-Pentanol

Table 6

Distribution Coefficient of 1-Pentanol

Volume percent of aqueous alcohol solution	Weight percent of alcohol in H_2O	K*	Volume of CCl_4
.3	.258	1.3	20
1.0	.417	2.1	20
1.5	.596	3.0	20
4	1.77	8.9	20
6	2.00	10.1	20
2	.743	3.74	20
2	.59	3.68	30
2	.56	2.98	40
2	.49	2.91	50
2	.48	2.50	60

Note. The volume of aqueous alcohol solutions used was 80 ml.

$$*K = \frac{\text{Weight percent in oil}}{\text{Weight percent in } H_2O}$$

the first column represents the volume percent of 1-pentanol in the initial aqueous solution; the second, the weight percent of alcohol in water; the third, the distribution coefficient; and the last column, the volume of CCl_4 used.

As the volume percent of alcohol in the original aqueous solution is increased for a constant volume of CCl_4, the K values increase due to the amount of alcohol being extracted into the oil phase. For a constant volume percent of alcohol in the original aqueous solution, and an increased volume of CCl_4, the weight percent in the oil decreases, and therefore K decreases.

b. Titration Curves

The transmittance as a function of the volume of 4-methylcyclohexanol (a mixture of the cis and trans isomers) added to emulsions containing 2 ml n-decane, various amounts of lauric acid and 16 ml 0.375 N KOH is shown in Figure 16. Curve 1 represents the results obtained with 1.5×10^{-3} moles of lauric acid; Curve 2, 2.0×10^{-3}; Curve 3, 3.0×10^{-3}; and Curve 4, 4×10^{-3} moles. A maximum is observed for all systems. At high soap concentrations it becomes broader, but more alcohol is required to achieve maximum transmittance.

c. Effect of Oil (Dispersed Phase) Volume

Dispersed phase volume also effects the optical properties of these systems. Figure 17 depicts this effect. Solutions were prepared with 4.0×10^{-3} moles of stearic acid in various volumes of n-hexadecane. These were dispersed in 16 ml 0.375 N KOH and titrated with 4-methylcyclohexanol (Curves 2 and 2a) and 3-methyl-1-butanol (Curves 1 and 1a). The maximum transmittance (Curves 1 and 2) and the volume of alcohol

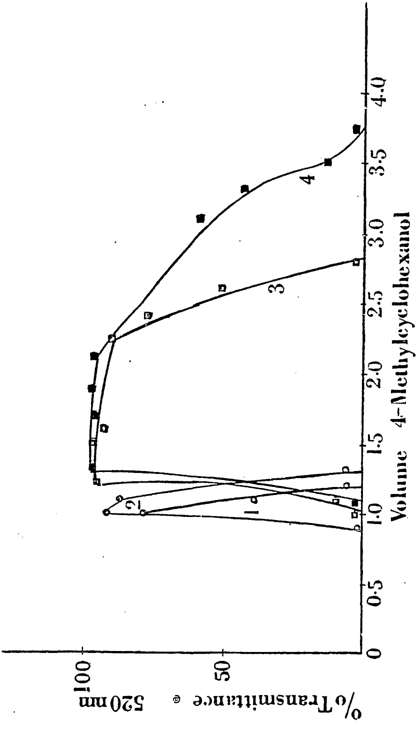

Figure 16. Percent Transmittance vs. Volume of 4-Methylcyclohexanol at 30 °C: Curve 1, 1.5 x 10^{-3} moles lauric acid; 2, 2.0 x 10^{-3} moles; 3, 3.0 x 10^{-3} moles; 4, 4.0 x 10^{-3} moles

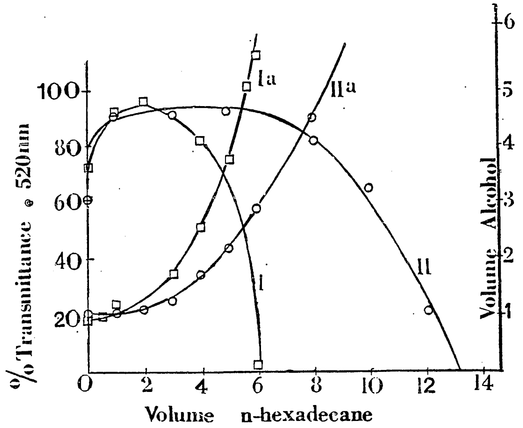

Figure 17. Percent Transmittance vs. Volume of N-hexadecane at 30 °C: Maximum Transmittance: Curve 1, 3-Methyl-1-butanol; 2, 4-Methylcyclohexanol; Volume Required: Curve 1a, 3-Methyl-1-butanol; 2a, 4-Methylcyclohexanol

required (Curves 1a and 2a) are given as a function of the volume of oil used. These results show that for a given oil, aqueous phase, surfactant and cosurfactant combination, there is an optimal amount of dispersed phase required to produce maximum clarity.

It is interesting to note that when the aqueous phase and stearic acid are mixed the system is turbid. At the addition of cosurfactant, the transmittance increases to a maximum of 60-70%. When the experiment is repeated in the presence of a small amount of oil almost 100% transmittance is obtained. Figure 17 shows the sensitivity of the dispersions to cosurfactant type. The volume of n-hexadecane that can be dispersed at a given maximum transmittance is much higher with 4-methylcyclohexanol than with 3-methyl-1-butanol.

From these titration results it was seen that transparent dispersion formation depends on many interacting variables. Among these are the types and amounts of surfactant, oil and cosurfactant used at constant aqueous phase ionic concentration. The next variable to be tested was whether the method of preparation influenced the transparent dispersion formation.

d. Influence of the Method of Preparation

The influence of the method of preparation of some transparent dispersions was investigated to determine whether they were thermodynamically stable dispersions.

i. Procedures

The cosurfactant was titrated. While stirring, a solution containing 2 ml oil and 2×10^{-3} moles was added to the aqueous phase containing 1 N KOH to produce an emulsion, at 30 °C. The emulsion was titrated slowly and dropwise with the alcohol (cosurfactant) until a dispersion with approximately 90% T at 520 nm was obtained. The method of addition of the aqueous phase to the dispersion was then investigated by the "point" and "dilution" methods.

While stirring, a solution containing 2 ml n-hexadecane and 2×10^{-3} moles stearic acid was added to 5 ml H_2O containing 6 ml 1N KOH solution, at 30 °C. The fine emulsion was then titrated to 87% transmittance at 520 nm, with 0.6 ml 4-methylcyclohexanol, which was added slowly and dropwise. A new microemulsions was then prepared in which the amount of water was increased to 10 ml, everything else kept the same. The minimum amount of alcohol needed to reach at least 80% transmittance was recorded for preparations containing up to 25 ml of water (Figure 18, Curve 1).

While stirring, a solution containing 2 ml n-hexadecane and 2×10^{-3} moles of stearic acid was added to 5 ml H_2O containing 6 ml 1N KOH solution at 30 °C. The resulting fine emulsion was titrated slowly and dropwise with 0.6 ml of the 4-methylcyclohexanol. Once 87% transmittance was obtained, the entire system was diluted by the addition of 5 ml of water. Alcohol was added to bring the transparency of the system back to at least 80%, then 5 ml of water was added to again induce turbidity. This procedure was repeated until the system contained a total of 25 ml H_2O (Figure 18, Curve 2).

While stirring, a solution containing 2 ml of n-decane and 2×10^{-3} moles lauric acid was added to 16 ml 0.375 N KOH at 30 °C. The fine emulsion was then titrated to 92% transmittance (at 520 nm), 1.0 ml of 4-methylcyclohexanol (a mixture of the cis and trans isomers) was required. 0.95 ml of the <u>trans</u> isomer produced a dispersion with

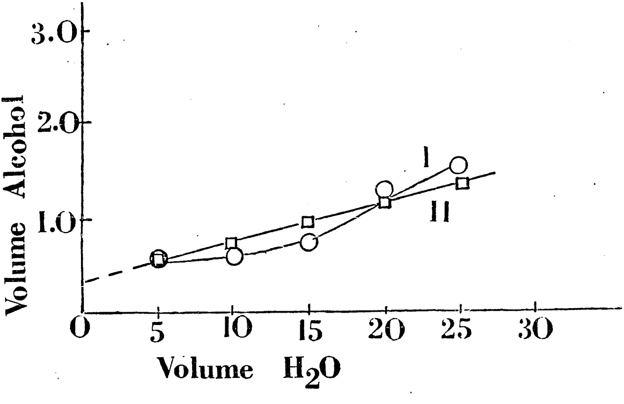

Figure 18. Dilution and Point Methods of an O/W Microemulsion at 30 °C: Curve 1, Point Method; 2, Dilution Method

95% transmittance, while the cis isomer alone did not produce a clear dispersion.

The cosurfactant was predistributed. From the above titration experiment it was determined that a total of 1 ml of 4-methylcyclohexanol was required to produce a dispersion with a transmittance of 92% at 520 nm. In order to investigate whether this dispersion could be prepared without titrating the alcohol, the 1 ml of 4-methylcyclohexanol was apportioned between the oil and aqueous phases before they were combined. For example, in one case a solution containing 2 ml n-decane, 2×10^{-3} moles lauric acid and 0.1 ml alcohol was prepared and added with stirring at 30 °C to 16 ml 0.375 N KOH which contained 0.9 ml of the alcohol.

It was found that all predistributions of 1 ml of 4-methylcyclohexanol between the aqueous and oil phase in the above experiment resulted in a clear dispersion (percent transmittance between 89 and 93) within 10 to 15 minutes of stirring.

At 30 °C, 2 ml n-decane was added to 16 ml 0.375 N KOH which contained 2×10^{-3} moles lauric acid while 1 ml of 4-methylcyclohexanol was predistributed between the aqueous and oil phases. The results are tabulated in Table 7.

2×10^{-3} moles of stearic acid in 2 ml n-hexadecane was added at 30 °C to 16 ml 0.375 N KOH while stirring. The resulting fine emulsion was titrated to clarity with 1.0 ml 1-pentanol. The 1.0 ml of 1-pentanol was predistributed between the oil and aqueous phases but clearing only occurred within 15 minutes of stirring when all of the alcohol was put into the aqueous phase. Results are shown in Table 8.

Table 7

2×10^{-3} Moles Lauric Acid in 16 ml 0.375 N KOH Added to 2 ml N-decane Titrated to 92% Transmittance with 1 ml 4-Methylcyclohexanol at 30 °C

Volume alcohol (ml)			
Aqueous phase	Oil phase	Percent transmittance @ 520 nm	Time to reach > 90%T
0	1.0	0	> 2 days
.2	.8	0	> 2 days
.5	.5	91	34 minutes
.8	.2	94	17 minutes
1.0	0	94	13 minutes

Table 8

2×10^{-3} Moles Stearic Acid in 2 ml N-hexadecane Added to 16 ml 0.375 N KOH Titrated to 85% Transmittance with 1 ml 1-Pentanol at 30 °C

Volume alcohol (ml)			
Aqueous phase	Oil phase	Percent transmittance @ 520 nm	Time to reach > 85%T
1.0	0	87	5 minutes
.8	.2	Cloudy	
.5	.5	"	
.2	.8	"	
.0	1.0	"	

ii. Results

The results of the point versus the dilution method experiments are not so divergent as in the case of the nonyl-phenols. The results are consistent with the distribution characteristics of an alcohol between an oil and aqueous phase, i.e., when more aqueous phase is added to the system more alcohol is required to initially sature it, and therefore the total volume of alcohol required to produce systems of equivalent transparency is increased.

In the last four experiments described, it is seen that 4-methylcyclohexanol (cis and trans mixture) or the trans isomer clears an n-decane/Klaurate/water emulsion (the cis isomer does not work due to its nonplanar structure) when added dropwise or predistributed between aqueous and oil phases provided that the soap is prepared in situ (by placing lauric acid in the oil phase). The same system cannot be cleared if 4-methylcyclohexanol has been initially predistributed in the oil phase (Table 7), when Klaurate was initially formed in the aqueous phase. Although Kstearate is produced in situ (stearic acid is dissolved in n-hexadecane before being added to the 0.375 N KOH solution), the system cannot be cleared if 1 ml of 1-pentanol--the volume of alcohol required to clear the system by titration--is predistributed between the oil and aqueous phases.

B. Discussion

Several investigations have shown transparent dispersions of oil and water can be either inherently thermodynamically stable (110) or kinetically stable (13). Most recently, Friberg and Miroslava (117) have characterized the two systems using a phase diagram approach. Shah et al. (119) prefer to make a distinction between micellar solutions and microemulsions on the basis of the ratio of the number of molecules of dispersed phase to surfactant. This may be an unnecessary and arbitrary division if both are thermodynamically stable.

Since the long-term stabilities of all the formulations prepared were not determined systematically, such a distinction cannot be made for all these systems. However, it is generally observed that the stability of these systems is variable. Most systems with a transmittance below 90% at preparation are unstable on a long-term basis, i.e., they are not thermodynamically stable. That is, the stability is linked to the size of the dispersed droplets, which then is determined by the free energy balance in the system.

The other aspect of this study was the formation or preparation of these dispersions. It was seen that in order to prepare a microemulsion, an initial fine emulsion is necessary. Before clearing of the system an increase in viscosity is generally observed. Clearing is associated with a decrease in viscosity. The following is concluded:

1. Fine emulsification provides the necessary interfacial area and low initial interfacial tension.
2. The cosurfactant is added into the continuous phase and will redistribute between the oil and water phases.
3. During this process of redistribution of the cosurfactant, transitory zero interfacial tension is responsible for the formation of high viscosity elongated structures.
4. Eventual distribution of the cosurfactant between the oil and water phases is followed by an increase of the interfacial tension.

5. Associated with a positive interfacial tension is the formation of the microemulsion.
6. Stability of these systems is variable.

Several points can be seen in the results of the titration experiments. It has often been observed (119, 9) that a critical amount of cosurfactant was required before these dispersions became transparent. This is reemphasized in Figure 16. Furthermore, maxima are observed in most cases. These maxima can be explained by the distribution of the cosurfactant. As the alcohol is added, it partitions among the aqueous phase, oil phase and interface (105). This dynamic process provides some of the energy to subdivide the dispersed phase. As the alcohol diffuses, the droplet size is made smaller and the transmittance increases. Once the capacity for alcohol of the aqueous phase and interface is exceeded, the excess dissolves in the oil phase. For o/w systems this means an increase in droplet size and a concomitant decrease in transmittance.

The same effect is seen when the volume of the dispersed phase is increased while the amount of surfactant is held constant. When the amount of the dispersed phase exceeds the capacity of the surfactant to stabilize it, the transmittance fails (Figure 17).

All of the titration results (Tables 2-5 and Figure 16) show the specificity of the various components. For a given oil-surfactant pair, the stearic requirements of the cosurfactant determine the volume of dispersed phase which can be stabilized (Figure 17). Whether an o/w, w/o or both types of systems can form is also cosurfactant-dependent. This factor necessarily interacts with the nature of the oil (Tables 2-5).

The surfactant type also plays a significant role in determining whether a transparent system will form (11). The hydrocarbon chain lengths of the surfactant and oil must be structurally matched for microemulsion formation. For example, in o/w systems titrated with 4-methylcyclohexanol, potassium stearate did not microemulsify 2 ml n-pentane and potassium laurate did not microemulsify 2 ml n-hexadecane (120). Potassium laurate works better with shorter chain length oils such as n-decane, as shown in Figure 16.

Surfactant type, cosurfactant type and the nature of the oil phase are three of the interacting factors that determine the size of the dispersed phase droplets. The aqueous phase was kept constant throughout this study so that such factors as a change in ionic strength would not affect the resulting dispersion (3).

When preparing microemulsions by the titration method, dramatic increases in the viscosity are sometimes noted just before clearing of the system occurs. Also, the mixture may progress from opalescent to clear quickly or slowly as drops of cosurfactant are added. These effects are probably related to the rate of diffusion of alcohol between the oil and aqueous phases.

While the alcohol does diffuse through the interface (11), some remains there (13) in weak association with the surfactant molecules. The amount that remains at the interface is specific for producing a particular microemulsion system. It has been estimated in the following way (121): (a) The percent transmittance versus volume of 1-pentanol was plotted for systems containing 2 ml n-hexadecane, various amounts of stearic acid and 16 ml 0.375 N KOH, at 30 °C. (b) The percent transmittance at the initial point of clearing was plotted against the soap concentration for this system. (c) The intercepts at zero soap concentration of this curve represent the volume of 1-pentanol distributed between the 2 ml n-hexadecane and 16 ml 0.375 N KOH when no soap is present. Similar experiments were repeated with various volumes of n-hexadecane. These estimated volumes were plotted versus ml n-hexadecane. (d) 2×10^{-3} moles of stearic acid was mixed with various volumes of n-hexadecane. Each solution was added to 16 ml 0.375 N KOH and titrated to clarity with 1-pentanol. For each emulsion, the volume of alcohol corresponding to the increase in percent transmittance was recorded. This curve corresponds to the total volume of alcohol distributed in the oil, aqueous phase and oil/aqueous interface. The volume of 1-pentanol distributed between the oil and aqueous phases when no soap is present (c) was subtracted from this curve to obtain the volume of 1-pentanol at the interface. This amount is different for each microemulsion system and also changes with the manner of preparation (11). Thus, it is path-dependent.

It is seen that these systems are not thermodynamically stable because when only the method of preparation was changed, in dispersions of identical compositions, a transparent dispersion did not always form. From all of the above experimental results, the conclusion is that the interfacial transfer and reactions of the surfactants play a major role in the mechanism of formation of these transparent dispersions. It is seen, therefore, that the mechanism of transfer of the surfactant and cosurfactant at the oil/aqueous interface and the subsequent effect on the interfacial free energy must be further studied. Also, the proper structure of the oil/aqueous interface that is conducive to microemulsion formation must be investigated.

CHAPTER V

TRANSFER OF SURFACE ACTIVE MOLECULES ACROSS LIQUID-LIQUID INTERFACES

A. Transfer of Lauric Acid through n-Decane/0.375 N KOH Interface

It has been indicated that when a solution composed of n-decane and 2×10^{-3} moles of lauric acid is added to 16 ml 0.375 N KOH, a fine emulsion is obtained at 30 °C. The system may be titrated to clarity with 1.0 ml of 4-methylcyclohexanol (Experiment 3, Section IVA-8di). It was also found that any predistribution of the 1.0 ml of 4-methylcyclohexanol resulted in a clear system (Experiment 4, Section IVA-8di). Nevertheless, if the same proportions are used but the lauric acid is saponified first in the aqueous phase (Experiment 5, Section IVA-8di), predistribution of the cosurfactant affects the resulting dispersions. (See Table 7.) The difference between these results may be explained by the following experiment.

1. Materials

The same chemicals as in Chapter Four, Section IVA-6, except for the n-decane and n-hexadecane, which were 99%+ Gold Label, purchased from the Aldrich Chemical Company (Milwaukee, WI), were used. The interfacial tension measurements were made with a Model 311A transducer amplifier from Sanborn Co. (Waltham, MA). A Model DSRG recorder, purchased from Sargent Welch (Springfield, NJ), was used to record the surface tension measurements. Two hundred ml beakers

(5.3 cm diameter) with water jackets, placed on electromagnetic stirrers were used. The thermostat was set at 30 °C during the interfacial tension measurements. Injections of alcohol into the aqueous phase were made with an Agla micrometer syringe accurate to ± 0.0005 ml, purchased from Burroughs-Wellcome & Company (Durham, NC).

2. Procedures

The interfacial tension between n-decane and 0.375 N KOH solution was determined using the Wilhelmy's wettable plate method. A 2.5 cm x 0.03 mm sand blasted teflon blade was suspended through the intermediary of a hooked platinum wire to a microforce recorder device (11). The transducer output was recorded continuously on a recorder. The surface tensions were reproducible within ±2 dynes/cm. Following sandblasting, the blade was cleaned with CCl_4 in a sonifier for 10 minutes, then placed into a soxhlet containing CH_2Cl_2 and refluxed for at least 4 hours. The blade was finally allowed to dry and then used.

The 0.375 N KOH solution used was first foamed into a sintered glass funnel to remove any possible traces of surface active substances (15). Eighty ml of that solution was placed into a clean 200 ml beaker. The glassware had been thoroughly cleaned with fresh sulfochromic solution. Gentle stirring was maintained in the aqueous phase throughout all the experiments. 1×10^{-5} moles of lauric acid was first mixed with heated KOH solution. The thermostat was raised to 45 °C to allow the complete neutralization of the fatty acid, then lowered to 30 °C during the interfacial tension measurements.

Five ml of n-decane was placed gently on top of the 80 ml containing 1×10^{-5} moles of potassium laurate solution. The interfacial tension (γ_i) was recorded with time.

3. Results

The values of the interfacial tensions with time are shown in Figure 19. For this first case (Curve 1), γ_i remains practically constant.

However, when 1×10^{-5} moles (Curve 2); 3×10^{-5} moles (Curve 3); 6×10^{-5} moles (Curve 4) or 1×10^{-4} moles (Curve 5) of lauric acid was first dissolved into 5 ml of n-decane and then placed gently above 80 ml 0.375 N KOH, γ_i is initially markedly low and eventually reaches a plateau at a much higher interfacial tension when all the lauric acid has been converted into Klaurate. The initial interfacial tension lowering may be attributed to the presence of an acid soap (118) and desorption of the produced soap into the aqueous phase (40-41).

These results explain the difference between Experiments B1 and B2 (Section IVA-8d). In situ saponification produces transitory lowering of γ_i which in turn results in a much finer initial emulsion which can then be titrated to clarity more easily with the cosurfactant (Experiment B1) than when the soap is in the aqueous phase (Experiment B2).

4. Transfer of 1-Pentanol through an n-Hexadecane/0.375 N KOH Interface in the Presence and Absence of Soap

The effect of adding 1-pentanol into a KOH solution in contact with n-hexadecane for three different cases was studied by measuring the interfacial tension between 5 ml hexadecane and 80 ml 0.375 N KOH solution versus time.

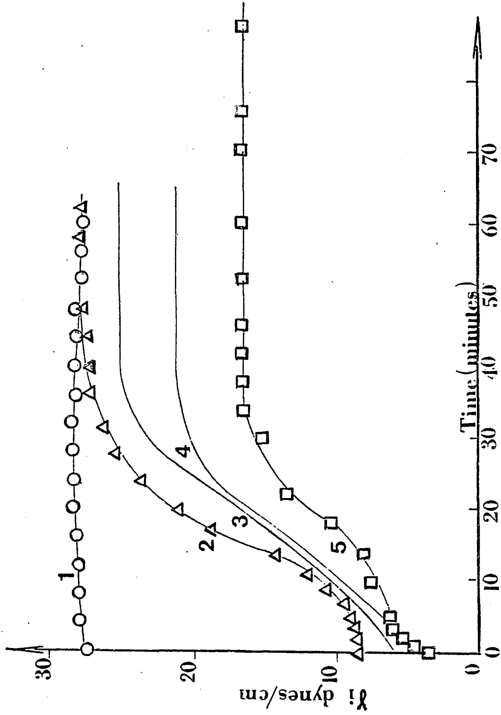

Figure 19. Interfacial Tension vs. Time. Transfer of Lauric Acid through an N-decane/0.375 N KOH Interface at 30 °C: Curve 1, 1×10^{-5} moles lauric acid in the KOH; 2, 1×10^{-5} moles in the oil; 3, 3×10^{-5} moles in the oil; 4, 6×10^{-5} moles in the oil; 5, 1×10^{-4} moles in the oil

5. Procedures

In the first case, 0.03 ml of 1-pentanol was dissolved in the 0.375 N KOH solution. The 5 ml of n-hexadecane was gently placed on top and γ_i was measured as a function of time. Next, the 0.03 ml of 1-pentanol was injected with an "Agla" micrometer syringe into the 0.375 N KOH solution, after the 5 ml of n-hexadecane had been gently placed on top. Then a similar experiment was done in the presence of 1×10^{-5} moles of lauric acid and then stearic acid.

6. Results

The results are shown in Figure 20. For the first case, Curve 1 shows that γ_i decreases only slighlty due to adsorption of the alcohol at the interface. Due to desorption of 1-pentanol into n-hexadecane, γ_i increases to an equilibrium value within 27 minutes. For the second case, Curve 2 shows γ_i decreases rapidly then increases. After 27 minutes, Experiments 1 and 2 have the same γ_i value. Droplets of 1-pentanol are in fact injected in Experiment 2. The droplets rise to the oil/aqueous interface, spread and eventually desorb. From Curves 3 and 4 it is seen that the presence of the adsorbed film at the oil/aqueous interface (especially in the case of potassium stearate) slows the diffusing alcohol molecules. Upon penetrating into the film, they interact with the film molecules and spend a much greater time at the interface before passing into the n-hexadecane phase, i.e., the film acts as a diffusion barrier.

7. Transfer of the Cis, Trans, and a Mixture of the Cis and Trans Isomers of 4-Methylcyclohexanol through an n-Decane/0.375 N KOH Interface in the Presence of Soap

The difference in the behavior of the cis, trans and a mixture

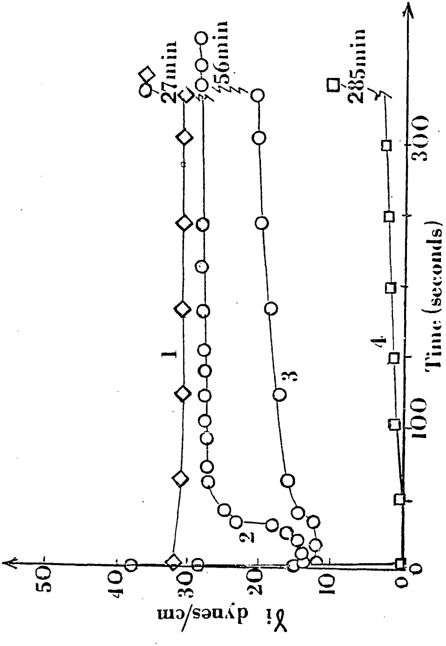

Figure 20. Interfacial Tension vs. Time. Transfer of 1-Pentanol through an N-hexadecane/0.375 N KOH Interface at 30 °C: Curve 1, 0.03 ml pentanol dissolved in the KOH; 2, 0.03 ml pentanol injected into the KOH; 3, 0.03 ml pentanol injected into the KOH in the presence of 1×10^{-5} moles lauric acid; 4, 0.03 ml pentanol injected into the KOH in the presence of 1×10^{-5} moles stearic acid.

of these isomers of 4-methylcyclohexanol at an oil/aqueous interface was studied by measuring γ_i versus time, to elucidate why a microemulsion forms with the pure trans isomer and the mixture of the cis and trans isomers, but not with the pure cis isomer.

8. Procedures

0.03 ml of each of the alcohols were injected with an "Agla" micrometer syringe into the 80 ml 0.375 N KOH solution in the presence of 1×10^{-5} moles of lauric acid, after the 5 ml of n-decane had been placed on top. γ_i was measured for the three different alcohols as a function of time.

9. Results

The results of the measurements of γ_i versus time are shown in Figure 21. Curve 1 corresponds to the trans isomer, Curve 2 to the mixture of the cis and trans isomers, and Curve 3 to the cis isomer. It is seen that the degree of lowering of γ_i is comparably equivalent for all three alcohols. The pure trans isomer has the greatest lowering ability. However, the rates of desorption between the pure cis isomer and the other two are markedly different. A much more rapid desorption rate is evidenced for the pure cis isomer. This is seen by the more rapid return of the interfacial tension to a higher equilibrium value.

B. Transfer of 4-Methylcyclohexanol through an n-Decane/0.375 N KOH Interface

The spinning drop interfacial tensiometer was used to measure the interfacial tension versus time of an oil droplet in a more dense medium. It was hoped to visualize the microemulsification of an oil droplet in the spinning tube.

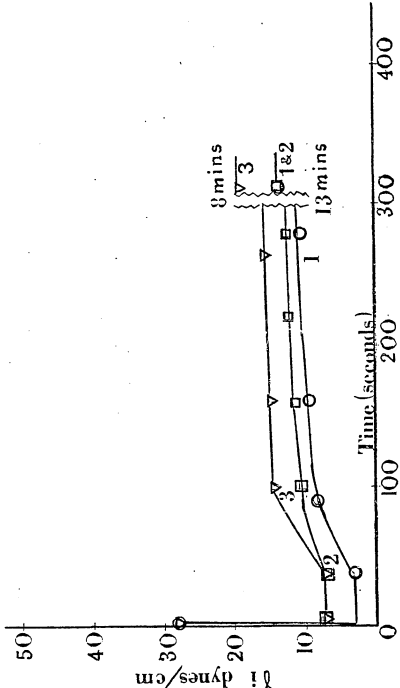

Figure 21. Interfacial Tension vs. Time. Transfer of Cis, Trans, and a Mixture of the Cis and Trans Isomers of 4-Methylcyclohexanol through an N-decane/0.375 N KOH Interface in the Presence of Soap at 30 °C: Curve 1, Trans Isomer; 2, Mixture of Cis and Trans Isomers; 3, Cis Isomer.

1. Materials

The spinning drop interfacial tensiometer was a Control Unit Model 300 from Austin, Texas. The n-decane was purchased from Fluka, A. G., Buchs, S. G. free of olefins = 99% G. C. Switzerland. The Gaertner travelling microscope was purchased from the Scientific Corporation (Chicago, IL). A hysteresis synchronous motor was purchased from Electro-Crafts Corporation (Hopkins, MN). All other materials as had previously been used were used here. Doubly distilled water was used in all experiments. All experiments were conducted at room temperature, 25 °C.

2. Preparation of the Microemulsion

While stirring at room temperature, 2.5 ul of a solution containing 2 ml n-decane and 2×10^{-3} moles lauric acid was added to 1 ml 0.375 N KOH in a small vial. A fine emulsion was produced and titrated to visual clarity with exactly 0.008 ml of 4-methylcyclohexanol (a mixture of cis and trans isomers). The same quantities were used in a spinning drop interfacial tensiometer.

3. Procedures

The spinning drop interfacial tensiometer was used to measure the interfacial tension of an n-decane droplet in a 0.375 N KOH solution containing alcohol and lauric acid. The apparatus has been previously described by Schecter et al. (14).

A precision ground .245" O.D. pyrex glass tube rounded on one end and sealed with a teflon stopped at the other was filled completely with 1 ml of a solution containing 16 ml 0.375 N KOH, 6.67 mg lauric acid, and .128 ml 4-methylcyclohexanol. Holding the tube upside down (capillary pressure retains the more dense phase in the tube), 2.08 ul of n-decane was then injected into the tube with a microliter syringe. The tube was placed in the cap and the whole assembly placed in the shaft and secured by screwing the cap onto the shaft.

The droplet was observed using a Gaertner travelling microscope with a filar eyepiece used to measure the width of the drop and to calibrate the glass tube for the magnification of the drop diameter. A hysteresis synchronous motor was used. Its speed was controlled by varying the frequency from a frequency generator. The range of speeds used was from 1200 to 24,000 RPM. All experiments were conducted at room temperature.

The equation used to determine the interfacial tension is:

$$\gamma_i = 1.234 \times 10^6 \; \frac{\Delta\rho \, d^3}{n^3 \, P^2} \qquad (5\text{-}1),$$

where $\Delta\rho$ is the difference in densities of the two phases determined at room temperature with a pyconometer in g/cc, d is the measured diameter in cm, n is the refractive index of the aqueous phase determined with an Abbe refractometer at room temperature, P is the period in msec/rev, taken from the counter. This equation applies when the cylinder with hemispherical ends approximation to the shape is assumed, and the length to diameter ratio of the drop is greater than 3.5 (14).

4. Results

In a test of the equipment using the n-decane/water system with a literature value* for the interfacial tension of 50 dynes/cm

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*Handbook of Chemistry and Physics, p. 2016.

at 20 °C, a value of 43.91 ±.05 dynes/cm was obtained at room temperature (25 °C). The lower value could possibly be due to impurities in the system or the higher temperature or both. For ultra low tensions in the range of 10^{-4} to 10^{-6} dynes/cm, there is a 10% relative error in the measurements. Using the 10% error limit, tensions of 10^{-6} dynes/cm could be measured with the Gaertner filar eyepiece (accurate to 5×10^{-5} cm) with some difficulty. This is not a lower limit of the method--only of the optical equipment used.

The main difficulty encountered was to deliver small volumes of 10^{-3} cc or less. The discharge of a single drop of such small volumes from a syringe was found to be very difficult. A complication was that as the needle was retracted from the liquid, some small drops of the less dense phase would be left behind and after starting the rotation these small drops could coalesce with the large drop changing its volume. Therefore, the method used to calculate the tension was to measure the diameter of the final large drop formed, instead of the volume (14).

The purpose of this experiment was to reproduce the microemulsion in the spinning tube as it had been prepared in the vial (Section VB-2). Therefore, the volume proportions of all of the components were adjusted to be equal in both experiments. 2.08 ul of n-decane was injected into 1 ml of an aqueous solution (made up of 16 ml 0.375 N KOH, 0.128 ml 4-methylcyclohexanol and 6.667 mg lauric acid). A stream of tiny droplets came out of the syringe tip. Within a few seconds of spinning, they coalesced and a large droplet formed. It was suspended in the center of the tube and equation 5-1 was used to calculate γ_i.

The plot of interfacial tension versus time is shown in Figure 22 (Curve 1). There is a dramatic decrease in the value of the dynamic interfacial tension, then an increase to its original value. This decrease is due to the interfacial transfer and adsorption of 4-methylcyclohexanol. The potassium laurate present in the aqueous phase is adsorbed at the interface and is not diffusing. The transferring 4-methylcyclohexanol remains adsorbed at the interface, interacting with the potassium laurate for approximately 5 minutes, then transfers into the oil droplet increasing γ_i to its original value.

When lauric acid is placed into the oil droplet, saponification occurs instantaneously upon injection of the droplet into the aqueous alcohol phase. This transfer of the lauric acid from the oil droplet to the aqueous phase produces very low γ_i values and distortion of the droplet. Now, as the alcohol transfers through the interface, γ_i goes down to very low values (10^{-4} or 10^{-5} dynes/cm), there is a great distortion at the ends of the droplet and violent shattering of pieces of the droplet can be seen to occur in the spinning tube. (Figure 22, Curve 2a.) This "microemulsification" does not occur uniformally to the entire oil droplet and requires at least one hour of spinning. While this violent shattering occurs at one end of the droplet at these very low values of γ_i at the other end, very slow dissolution of the droplet occurs at fairly high γ_i values (.02 dynes/cm) (Curve 2b). It was found that the overall microemulsion process is greatly aided by tilting the apparatus.

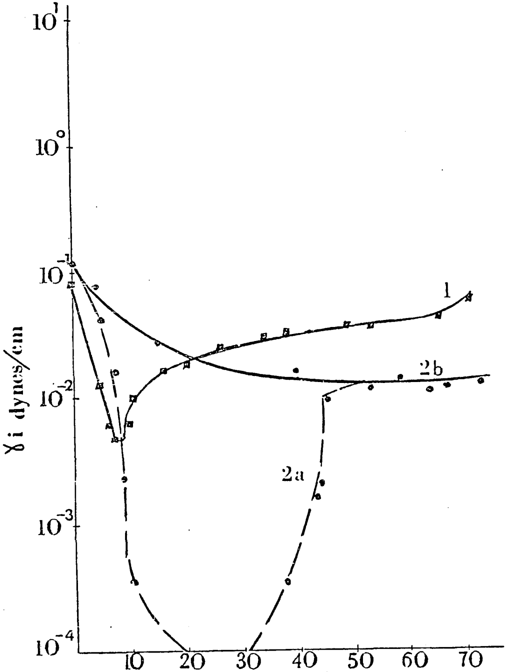

Figure 22. Interfacial Tension vs. Time. Transfer of 4-Methylcyclohexanol through an N-decane/0.375 N KOH Interface at 25 °C: Curve 1, 2.08 ul C_{10} in 1 ml (16 ml 0.375 N KOH, 0.128 ml 4-methylcyclohexanol and 6.67 mg lauric acid); Curve 2a, 2b, 2.5 ul (2 ml n-C_{10} + 2×10^{-3} moles lauric acid) in 1 ml (20 ml 0.375 N KOH + 0.160 ml 4-methylcyclohexanol).

C. Discussion

The chemical literature contains several studies on the transfer of surface active agents across a liquid-liquid interface (40-41, 122-142).

In 1971 D. C. England and J. C. Berg (40) determined the dynamic interfacial tensions for oil-water systems using a laminar contracting jet. Their data indicate the presence of a small net desorption barrier to the transfer of normal and isobutyric acids from oil to water and large barriers to both adsorption and desorption of 1-5 pentanediol. For the transfer of an adsorbing solute across a liquid-liquid interace they took into account: (1) the effect of molecular diffusion in both bulk phases, (2) adsorptive accumulation at the interface, and (3) energy barriers to adsorption and/or desorption.

They found that while the adsorptive accumulation alone affects the transfer rate very little, the presence of an adsorption or desorption barrier can significantly affect the bulk concentration profiles and decrease the mass transfer rate. They observed that the presence of a desorption barrier may cause the dynamic interfacial tension to pass through a minimum below the steady state value. They even predicted that the interfacial tension minimum would be sufficiently low that a slight agitation would result in spontaneous emulsification. Their conclusions are in accord with this interpretation. It was shown above that the presence of an adsorbed monolayer may greatly reduce the rate of transfer of 1-pentanol into n-hexadecane when injected into the aqueous phase, during which time the value of the dynamic interfacial tension passes through a minimum.

England and Berg proposed analytical solutions for the transfer of one adsorbing solute across a liquid-liquid interface.* Unfortunately, the difficulty in correlating interfacial free energy variation to actual experimental solute concentration involved in the transfer limits their mathematical model. Recently, Rubin and Radke (41) studied the dynamic interfacial tension minima for acidic organic phases contacting an alkaline aqueous phase using the spinning drop interfacial tensiometer. Again, the difficulty in correlating interfacial tension to actual amount of solute involved in the transfer limits their mathematical analysis. Also, for the case of two adsorbing solutes, application of the Gibbs adsorption equilibrium--as both these authors have done in their analyses--is not possible because the concentrations of both of the adsorbing species cannot be determined. Although the analytical solutions obtained by both these authors cannot predict the exact interfacial tension versus time plots that were experimentally obtained in this study, their models do nevertheless predict the general characteristics of γ_i versus time, when an adsorbing solute transfers through an oil/aqueous interface in the presence of a desorption barrier.

A study was done by E. Hutchinson (142) on the diffusion of various alcohols from water to benzene across the benzene/water interface. The retarding effect of films of surface active materials on the diffusion was noted. Measurement of interfacial tensions of the various systems led Hutchinson to the hypothesis that interaction in the film is responsible for the retardation of the transfer of the alcohol.

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*See Appendix I.

As of now, the results found in the literature may be considered as semiquantitative. The interfacial free energy of the surface measures an overall property of the surface. It is a complex function which depends on the temperature, concentrations and compositions of the bulk phases and transferring species. In the preceding experiments, the individual effects of each of these variables on the rate of transfer of the solute has not been studied. These overall effects were measured in terms of an all-inclusive variable--namely, interfacial tension. A more direct method of studying an energy barrier to desorption would be to analyze the actual solute concentrations involved in the transfer. Presently, the amounts of short chain alcohol crossing an oil/water interface in the absence and presence of an adsorbed film at different temperatures are being determined. The amount transferred will then be related to an overall energy barrier to transfer.

CHAPTER VI

STUDY OF THE INTERFACIAL STRUCTURE

A. Duplex Film Experiments

The duplex film technique was used to characterize the structure of an n-hexadecane, 0.375 N KOH interface in the presence of an adsorbed soap monolayer.

In the experiments plotted in Figure 20 (Curves 3 and 4), it is apparent that there is a distinct difference between the role played by potassium stearate and potassium laurate on the rate of transfer of 1-pentanol at the oil/aqueous interface. The experiments were run in identical fashions with the same molar soap concentrations. However, the lowering of interfacial tension and time of transfer of the 1-pentanol from the aqueous to the oil phase was much more pronounced in the presence of potassium stearate. In this case an interfacial tension very close to zero was obtained compared to 11 dynes/cm, obtained in the presence of potassium laurate. Also, the rate of desorption of the 1-pentanol from the oil/aqueous interface was much slower in the presence of potassium stearate (285 minutes) compared to 56 minutes in the presence of potassium laurate. It is reasonable to assume that the structure of the two fatty acid soap films at an n-hexadecane/0.375 N KOH interface must be markedly different. This is the object of the study of duplex films of soap/n-hexadecane/0.375 N KOH at 30 °C, with a Langmuir trough.

1. Materials

The surface pressure measurements were made with a Model 311A transducer amplifier from Sanborn Co. (Waltham, MA). The same recorder as used in Chapter Five was used here. The surface potential measurements were made with an air-ionizing electrode which was a radium-226 source from the U. S. Radium Corp. (Morristown, NJ). The potentiometer was a Model 2704-G from Rubicon Instruments (Southampton, PA). The high input resistance electrometer was a Model 610B from Keithley Instruments (Cleveland, OH).

The aqueous substrate used was 0.375 N KOH with 0.2 g KCl (reagent grade, Baker Chemical Co., Phillipsburg, NJ) added per 3 liters of solution plus 10^{-3} M versene tetrasodium EDTA from Dow Chemicals (Saddle Brook, NJ) added as a complexing agent to sequester any polyvalent ions present. The aqueous solution was first foamed in a 600 ml sintered glass funnel before use, to remove any surface active impurities (15). The pH of the substrate was measured to be 13.2.

The spreading solutions contained about 25 mg of fatty acid (Eastman Kodak Co., Rochester, NY) and 0.32 ml n-hexadecane (99+% Gold Label, Aldrich Chemical Co., Milwaukee, WI) added to n-hexane (Fisher Scientific Co., Fairlawn, NJ) into a 25 ml volumetric flask. The volume of n-hexadecane was calculated to produce a duplex film about 300-400Å thick. In one experiment, 0.019 ml of 1-pentanol (99+% Gold Label, Aldrich Chemical Co., Milwaukee, WI) was added into the spreading solution. This volume of alcohol was calculated to obtain a two pentanol/one stearic acid molar ratio. The "Agla" micrometer syringe was purchased from Burroughs Wellcome & Co. (Durham, NC).

2. Procedures

The compression surface isotherms (Π - A and ΔV - A) of stearic acid, stearic acid and n-hexadecane duplex film, stearic acid plus 1-pentanol and n-hexadecane duplex films and lauric acid and lauric acid-n-hexadecane duplex films, spread over a 0.375 N KOH solution at 30 °C were determined. An automated Langmuir trough was used with a teflon boom attached to the motor driven shaft.

The experimental apparatus for measuring surface pressures has been previously described (15). All experiments were conducted within a Faraday Box.

A given volume of the fatty acid solution was deposited onto the aqueous surface with an "Agla" micrometer syringe. The substrate and (duplex) film were retained in a fused silica trough (31.2 x 14.2 x 2.5 cm) of 1 liter capacity filled to the brim. The upper edges of the trough were coated with solid paraffin. The temperature of the substrate was regulated by circulating water from a contant temperature (30 ± 0.2 °C) bath through a glass coil submerged in the substrate.

Surface pressures were determined from surface tension measurements which were made using a sandblasted platinum blade suspended from a transducer amplifier. The transducer output was recorded continuously on a recorder. The surface tensions were reproducible within ±0.2 dynes/cm.

Surface potentials were measured with an air-ionizing electrode (16, 17) placed 1 to 2 mm above the surface of the liquid substrate and connected to a precision potentiometer a high input resistance electrometer and the trough electrode (Ag°/AgCl) dipped into the bulk of the aqueous substrate. The radioactive electrode was connected to the input terminal of the electrometer with low noise graphitized shielded cable and connectors. The entire circuit was grounded. The e.m.f. of the cell composed of the radioactive electrode, trough electrode, potentiometer and electrometer, all connected in series, was measured immediately after cleaning the surface of the aqueous substrate (V_0) and compared with the e.m.f. obtained after spreading the Duplex film on the surface (V). The difference between the two e.m.f.s ($V-V_0$) is the surface potential (ΔV). The potentiometer opposed a convenient fraction of the cell e.m.f. and the electrometer output was recorded continuously. Sensitivity of the surface potential measurements was about ±1 mV, and reproducible within about ±5 mV.

An automated barrier drive with variable speed control permitted determination of an optimum compression rate and reproducible Π-A and ΔV-A isotherms. Before depositing the spreading solution, the surface of the substrate was cleaned several times by dusting calcinated talcum powder onto it and removing it with a hollow glass tip connected to a vacuum aspirator. V_0 and γ_0 were then measured. Compression of the film was started within 30 seconds of its deposition onto the surface. Compression rates between 0.067 cm/sec and 0.31 cm/sec were tested. Collapse pressures of the stearic acid and stearic acid/n-hexadecane duplex films were found to be reproducible for compression rates between 0.13 and 0.31 cm/sec. For rates below 0.13 cm/sec there was a decrease in the value of Π_d for the duplex film isotherms due to desorption of the films. Therefore, a compression rate of 0.31 cm/sec was used to minimize desorption of the films.

3. Results

In Figure 23 the compression isotherms and surface potentials versus molecular area of a lauric acid film (Curve 1a); lauric acid-n-hexadecane duplex film (Curve 1); stearic acid film (Curve 2); stearic acid and 1-pentanol (1:2 mole ratio) (Curve 2a); stearic acid-n-hexadecane duplex film (Curve 3); and with 1-pentanol (Curve 4) spread on 0.375 N KOH at 30 °C are shown.

Upon compression of the lauric acid films, it was seen that because the potassium laurate formed is very soluble in the strongly alkaline aqueous subphase solution the resulting films are very unstable. The "isotherms" plotted (Curves 1 and 1a in Figure 23) represent the amount of potassium laurate that remained at the interface as the potassium laurate formed and then dissolved very rapidly into the aqueous subphase (143). The surface potential reaches a value of -60 mv, which confirms that the film is completely ionized since the pH of the substrate is 13.2.

On the other hand, since stearic acid is a longer chain fatty acid (C_{18}), more stable films were obtained. Curve 2 is the compression surface isotherm and surface potential versus molecular area of stearic acid. Curve 2a corresponds to stearic acid and 1-pentanol (1:2 mole ratio) film. The collapse pressure of this film is practically identical to the value obtained for Curve 2, but a slightly more condensed film is obtained. Curve 3 corresponds to the case of stearic acid-n-hexadecane duplex film and Curve 4 refers to the stearic acid (1 mole)/1-pentanol (2 moles)-n-hexadecane duplex film.

Upon comparison of Curves 2 and 3 in Figure 23, it is seen

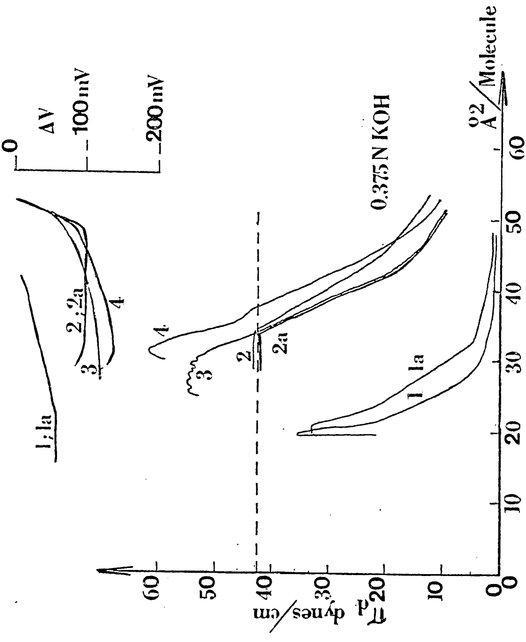


Figure 23. Π_d - A and ΔV - A Isotherms at 30 °C: Curve 1a, Lauric Acid Film; 1, Lauric Acid-N-hexadecane Duplex Film; 2, Stearic Acid Film; 2a, Stearic Acid-1-Pentanol (1:2 mole ratio) Film; 3, Stearic Acid-N-hexadecane Duplex Film; 4, Stearic Acid-N-hexadecane Duplex Film + 1-Pentanol

that n-hexadecane has a slight condensing effect on the expanded potassium stearate film. The duplex film has a distinctively higher collapse pressure. The presence of 1-pentanol in the duplex film produces film expansion and an even higher collapse pressure (Curve 4). The surface potential curves all have negative values. The most negative surface potential is produced when 1-pentanol is oriented in the duplex film.

B. Discussion

On the 0.375 N KOH subsolution, the lauric acid-n-hexadecane duplex film, Π-A compression isotherm, shows the same instability as the lauric acid film. The n-hexadecane does not increase the ability of the potassium laurate formed to remain anchored at the interface, as evidenced by the low collapse pressure of the film. Therefore, it is seen that the n-hexadecane is squeezed out of the potassium laurate monolayer upon compression. This is probably because chain-chain interactions between the oil and the hydrocarbon chain of the fatty acid are minimal due to lack of improper chain length matching.

The Π-A compression isotherm of the stearic acid monolayer is typical at this high pH value (15, 144). The highly expanded isotherm has been attributed to ionization of the carboxyl groups and their instability at this high pH value due to solubility in the subphase. The collapse pressure (approximately 43 dynes/cm) occurs at a molecular area of $35A^2$. This is in agreement with the results of Sears and Schulman.

Condensation of the Π-A compression isotherm in the presence of n-hexadecane illustrates that the oil is taking part in chain-chain interactions with the hydrocarbon chain of the stearic acid molecules. Thus, it is as if a longer chain length fatty acid is being compressed (15, 145). In this case the chain length is such that a more stable film is obtained and the potassium stearate molecules are anchored at the interface. This leads to a higher collapse pressure (56 dynes/cm) at an area of $31A^2$/molecule.

The Π-A compression isotherm of stearic acid and 1-pentanol (1:2 mole ratio) is slightly more condensed than the one obtained for potassium stearate. This indicates interactions between the hydrocarbon chains of the 1-pentanol and stearic acid molecules. However, the collapse pressure of the film is at approximately the same value (43 dynes/cm at 35A /molecule) as for stearate alone. This indicates that without the n-hexadecane the hydroxyl groups are not anchored at the interface and the 1-pentanol is squeezed out of the potassium stearate monolayer upon compression.

The Π-A compression (duplex) isotherm in the presence of 1-pentanol is expanded. This is due to the hydrophobic portions of the alcohol and stearic acid molecules being randomly intertwined, as in a liquid phase, rather than in a regular orientation. The ionized polar functional groups are anchored in the interface. There is an increased stability of the film evidenced by its high collapse pressure. The hydroxyl groups of the alcohol (some of which may be ionized forming alkoxide RO^- ions) increase the stability of the film by buffering the repulsions between the negatively charged carboxylate groups of the fatty acid molecules (143).

The presence of 1-pentanol molecules at the interface results in a collapse pressure of 61 dynes/cm at an area of $31A^2$ per stearate molecule. The cross-sectional area of a soap molecule oriented at an o/w interface has been taken to be between 30 and 40Å^2/molecule, depending on its degree of dissociation. The cross-sectional area of an alcohol molecule has been estimated as 20Å^2/molecule (57, 5). If the compression of this mixed monolayer resulted in the formation of a 1:1 or 2:1 stoichiometric complex, and the simple additivity rule was followed for the molecular areas, it would be expected that the collapse pressure would occur at an area per potassium stearate molecule of approximately 55Å^2 or 75Å^2, respectively (48). However, since this is not the case, it is seen that complex formation between the Kstearate and 1-pentanol does not occur under these conditions.

Surface potential area curves versus pH can be treated as a first approximation only by the Helmholtz formula for a partially charged weak acid monolayer (equation 3-5):

$$\Delta V = 12\Pi[n_1u_1 + n_2u_2]$$

where ΔV is the surface potential in millivolts; n_1 and n_2 are the number of dipoles per square centimeter in the monolayer of fatty acid and soap, respectively; and u_1 and u_2 are the vertical components of the surface dipole moments (in milli-D) for the uncharged fatty acid and charged soap forms of the molecules, respectively.

The electrical contribution of the diffuse layer (ψ_0) is effectively incorporated in the u_2 term (it will be only a small contribution at the high ionic concentration used in this study) and u_1 and u_2 are assumed constant with pH at a given molecular area. The contribution of only one term in equation 3-5 remains since this work was done at very high pH (n_1 and u_1 are negligible) and the equation may be rewritten

$$\Delta V = 12\Pi n_2 u_2 \qquad (6\text{-}1),$$

where u_2 is the surface moment of the carboxylate ion.

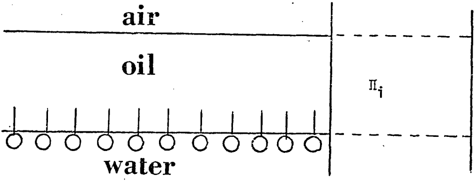
The ΔV-A curves (1-4) deal essentially with isotherms of ionized carboxyl groups and since for close-packed monolayers the electrical characteristics are determined largely by the head groups alone (142), the contribution to ΔV for all four experiments is essentially equivalent. However, there are slight differences in the ΔV values due to these factors. For the laurate-potassium-n-hexadecane duplex film, the value of n is the smallest due to the increased solubility of potassium laurate in the subphase solution. Next is the stearate value. For the stearate-n-hexadecane duplex film, n is evidently increased due to more stearate (carboxylate ion) held anchored at the interface by the oil. Finally, the presence of oriented hydroxyl groups (or RO^- ions) at the interface results in an increased value for n and therefore the largest negative ΔV value. These results indicate that the hydroxyl groups of the 1-pentanol are anchored in the interface by the oil, since without n-hexadecane (Curve 2a) the ΔV-A curve is identical to that obtained for potassium stearate (Curve 2).

The surface potential values remain quite small which seems to indicate charge penetration of the cations into the plane of the monolayers. This is a characteristic of ionized monolayers (143).

In the case of a duplex film (Figure 24), equation 3-2 may be written when $\gamma_i = 0$, as

$$\Pi_D = \gamma_{a/w} - \gamma_{o/a} \qquad (6\text{-}2).$$

In this case, $\gamma_{a/w} = 72.2$ dynes/cm and $\gamma_{o/a} = 29$ dynes/cm or $\Pi_D = 43.2$ dynes/cm. On Figure 23 a dotted line was drawn at this value



$$\Pi_D = \gamma_{wa} - \gamma_D = \gamma_{wa} - \gamma_{oa} - \gamma_{wo} + \Pi_i$$

$$\Pi_D = \gamma_{wa} - \gamma_{oa} - \gamma_{wo} + (\gamma_{wo} - \gamma_i)$$

$$\Pi_D = \gamma_{wa} - \gamma_{oa} - \gamma_i$$

$$[\Pi_D]_{\gamma_i = 0} = \gamma_{wa} - \gamma_{oa}$$

Figure 24. Duplex Film Theoretical Equations: ⫰, Surfactant Molecules

of 43.2 dynes/cm for Π_D. The fact that the collapse pressures of the compression isotherms for Curves 3 and 4, have values way above that, leads to the conclusion that an n-hexadecane/potassium stearate/0.375 N KOH interphase may be compressed to interfacial pressures corresponding to a negative interfacial tension. It is understood, however, that conditions of negative interfacial tensions are unattainable in practice during the preparation of an emulsion, since spontaneous dispersion occurs.

The process of microemulsification involves many interacting variables. The type and amount of oil, cosurfactant and surfactant all interact to determine whether a microemulsion will form.

Taking into account published results and those presented, the following mechanism of formation is proposed for an o/w microemulsion containing soap/alcohol/oil/water.

Initially, the fatty acid present in the oil phase transfers into the aqueous phase (KOH) and interacts with it. When the soap is formed initially in the aqueous phase, it will not work as well. This interfacial transfer and saponification produces low values of interfacial tension, enabling the formation of a fine initial emulsion.

The surfactant/oil/aqueous interphase thus formed must be expandable and able to withstand high transitory interfacial pressures which lead to very low values of interfacial tension. In addition, the chain lengths of the surfactant and oil must match to allow for the proper curvature needed in a microemulsion.

Next, the system is titrated with the cosurfactant (alcohol). It rapidly saturates the aqueous phase. Further addition of cosurfactant to the system results in droplets capable of spreading over the emulsified oil surface. This interfacial spreading and transfer produces even higher transitory interfacial pressures of the interfacial soap film which is also penetrated by individual alcohol molecules. The result is a very low interfacial tension which in turn allows the resolution of the coarse droplets into microdroplets. This mechanism is pictorially represented in Figure 25. The volume of each microdroplet is drawn as one-third the volume of the original emulsion droplet. The resulting surfactant-cosurfactant film must be able to stabilize the microdroplets against coalescence.

This mechanism is affected by the method of preparation of the microemulsion. It therefore is a path-dependent process. The transfer, redistribution and accumulation of excess amphipathic molecules at the oil/aqueous interface has been cited as necessary for spontaneous emulsification in terms of the transfer of a single surfactant (31-41). It is therefore concluded that these transparent dispersions are transparent emulsions (metastable dispersions) rather than swollen micelles (thermodynamic systems).

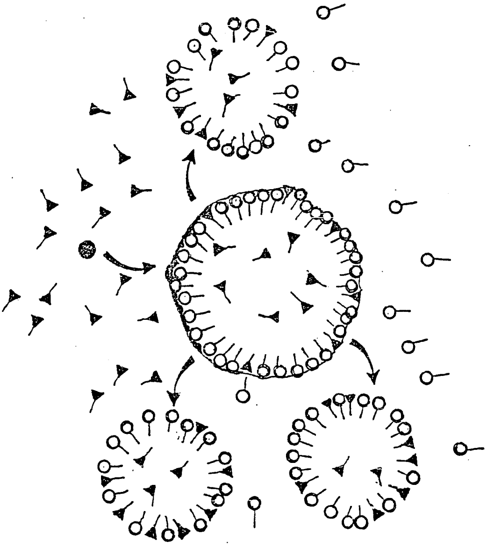


Figure 25. Mechanism of Formation of an Oil-in-Water Microemulsion: δ, Surfactant (Soap) Molecules; ▲, Cosurfactant (Alcohol) Molecules; ●, Alcohol Droplet.

CHAPTER VII

CONCLUSIONS

This study was undertaken to help elucidate the nature of stable transparent mixtures of oil and water plus two surfactants. The objective was to determine whether these transparent dispersions are thermodynamically stable or metastable systems and how to differentiate between the two types of dispersions. Although thermodynamically stable micellar dispersions may exist, it was concluded that most of the transparent dispersions prepared were metastable transparent emulsions. This conclusion was based on the differences in transmission of 520 nm radiation in dispersions of the same composition in which only the order of combination of the components was changed. This was the main criterion used in this study to distinguish between the types of systems. Two series of transparent dispersions were prepared by a titration technique and characterized with respect to certain parameters. Aspects of their formation were then studied by various techniques. Finally, a mechanism for the formation of transparent oil-in-water dispersions containing oil/water/soap/short chain alcohol for the metastable systems was proposed.

The first series of transparent oil-in-water dispersions contained n-hexadecane, water and an HLB mixture of two nonyl-phenol ethylene oxide condensates. A lipophilic nonyl-phenol ethylene oxide condensate (4.0 Eto) was dissolved in n-hexadecane, mixed with water and the resulting fine emulsion was titrated to clarity with a more hydrosoluble nonyl-phenol ethylene oxide condensate (9.5 Eto). This was the "point" method of preparation. On the other hand, adding more water to this transparent dispersion to produce a cloudy dispersion and then titrating again to clarity with the (HS) was called the "dilution" method.

It was observed that once the right surfactant was found within a narrow HLB range, a suitable cosurfactant (HS) for the system could be found within a slightly larger HLB range. However, out of the numerous combinations tested, only two pairs of nonyl-phenol ethylene oxide condensates gave good dispersions of n-hexadecane in water. Transparent dispersion formation was extremely sensitive to both the LS and HS structure. In fact, differences of only 0.5 Eto units resulted in critical differences in whether a transparent dispersion formed. It was concluded that the structural requirements for the two surfactants needed to produce these transparent dispersions were within very narrow limits.

Changing the temperature from 4 °C to 50 °C of a dispersion containing 2 ml n-hexadecane and 0.5 ml nonyl-phenol-4-Eto and 1.5 ml nonyl-phenol-9.5-Eto plus 20 ml water showed that when the temperature of the dispersion was raised above 50 °C, the dispersion became turbid. This was concluded to be due to the cloud point. Within 30-40 °C the dispersion remained clear.

From varying the concentration of nonyl-phenol-5-Eto in a dispersion containing 2 ml n-hexadecane plus 10, 20 or 30 ml water with nonyl-phenol-9.5-Eto as cosurfactant, it was concluded that at least 25% of the total emulsified volume must be surfactants in order to cover the large interfacial area created during the micro-emulsification process. Moreover, when more water was added, more surfactant was required due to the phase redistribution of the surfactant.

It was observed that fine initial emulsification was a prerequisite for transparent dispersion formation in these systems. Before clearing of the system an increase in viscosity was generally observed. Clearing was associated with a decrease in viscosity. It was concluded that fine initial emulsification provided the necessary interfacial area and low initial interfacial tension. As the second surfactant was added into the continuous phase it redistributed between the oil and aqueous phase. During this process of redistribution of the cosurfactant, transitory zero interfacial tension was responsible for the formation of high viscosity elongated structures. Eventual distribution of the cosurfactant between the oil and aqueous phase was followed by an increase of the interfacial tension. Associated with a positive interfacial tension was the formation of the transparent dispersion. The stability of these systems was variable.

The "point" and "dilution" methods were used to investigate the influence of the method of addition of water to the dispersions. In dispersions containing the same total volume of water, it was found that more HS was required to clear the dispersions prepared by the "dilution" method. Therefore, it was concluded that these transparent dispersions were not thermodynamic systems.

In the second series of dispersions, the nonyl-phenol ethylene oxide condensates were replaced by structurally pure fatty acids and alcohols. Transparent o/w and w/o dispersions containing oil/water/soap/short chain alcohol were prepared by the "point" method. A vast amount of routine experimental testing was done as the nature of the short chain alcohol was investigated for the formation of o/w and w/o dispersions with three different oils. It was found that out of the 52 alcohols tested, only 8 w/o and 18 o/w systems with CCl_4, 16 w/o and 5 o/w systems with n-hexadecane, and 13 w/o and 8 o/w systems with toluene had a maximum transmittance of 60% or greater at 520 nm. It was seen that CCl_4 was skewed towards o/w dispersions, n-hexadecane towards w/o and toluene was more evenly distributed. The results demonstrated the extreme sensitivity of the dispersion formation to the structure of the cosurfactant. Even among these alcohols, which were structurally very similar, transparent dispersions did not always form. For example, with n-hexadecane and potassium stearate as surfactant, 1.70 ml of 2-hexanol was required to produce a w/o dispersion with 100% transmittance. However, 1-hexanol did not produce any sort of dispersion with n-hexadecane and was not included in Table 2. Another example of the extreme structural specifications of the cosurfactant to produce these transparent dispersions was the case of n-decane and potassium laurate as surfactant. 0.95 ml of trans 4-methylcyclohexanol was required to produce an o/w dispersion with 95% transmittance, while the cis isomer of the same alcohol did not produce a dispersion with these components. This was concluded to be due to the flatter structure of the trans isomer which allows for closer alignment with the surfactant at the oil/aqueous interface.

The distribution coefficients of 1-pentanol between CCl_4 and water were determined to gain some insight into why an alcohol is an efficient cosurfactant in a particular system. It was found that the distribution coefficients increased as the volume percent of alcohol in the original aqueous solution was increased for a constant volume of CCl_4. It was concluded that the K value increased due to the increased amount of alcohol being extracted into the oil phase. For a constant volume percent of alcohol in the original aqueous solution and an increased volume of CCl_4, the weight percent in the oil decreased and therefore K decreased.

These results explained the titration results obtained from measuring the transmittance as a function of the volume of cosurfactant added for the system containing 2 ml n-decane, 16 ml 0.375 N KOH, 4-methylcyclohexanol and different amounts of lauric acid. It was observed that a critical amount of cosurfactant was required before these dispersions became transparent. Furthermore, maxima were observed in most cases. These maxima were explained by the distribution of the cosurfactant. As the alcohol was added, it partitioned among the aqueous, oil and inter phases. This dynamic process provided some of the energy to subdivide the dispersed phase. As the alcohol diffused, the droplet size was made smaller and the transmittance increased. Once the capacity for alcohol of the aqueous and inter phase was exceeded, the excess dissolved in the oil phase. For the o/w dispersion studied, this meant an increase in droplet size and a concomitant decrease in transmittance.

The same effect was seen when the volume of the dispersed phase was increased while the amount of surfactant was held constant in the dispersion containing n-C_{16}/4×10^{-3} mole stearic acid/ 16 ml 0.375 N KOH/ 4-methyl-cyclohexanol/ and 3-methyl-1-butanol. When the amount of dispersed phase exceeded the capacity of the surfactant to stabilize it, the transmittance fell. Also, it was found that a minimum amount of oil was needed to produce systems of high transparency, since without oil the dispersion reached only 60-70% maximum %T. There was also an optimal amount of dispersed phase required to produce maximum clarity. These results also showed the sensivitity of the dispersions to cosurfactant type. The volume of n-C_{16} that was dispersed at a given maximum %T was much higher with 4-methylcyclohexanol than with 3-methyl-1-butanol.

To summarize, all of the titration results showed the specificity of the various components. For a given oil-surfactant pair, the stearic requirements of the cosurfactant determined the volume of dispersed phase which could be stabilized. Whether o/w or w/o or both types of systems formed was also cosurfactant-dependent. This factor also interacted with the nature of the oil to determine whether a microemulsion formed. Furthermore, the hydrocarbon chain lengths of the surfactant and the oil had to be structurally matched for microemulsion formation. The structure and amounts of the surfactant, cosurfactant and oil all interacted to determine the size of the dispersed droplets at constant aqueous phase ionic concentration.

When preparing transparent dispersions by the titration method, dramatic increases in viscosity were sometimes noted just prior to clearing. Also, the emulsion progressed from opalescent to clear quickly or slowly, as drops of cosurfactant were added. These effects were concluded to be related to the rate of diffusion of the alcohol between the phases.

However, while the alcohol does diffuse through the interface, some remains there in weak association with the surfactant molecules. The amount that remains at the interface for producing a particular dispersion is specific and can be estimated. It is different for each system and also changes with the manner of preparation. Thus, it is path-dependent.

The long-term stabilities of the systems prepared were not systematically studied. However, it was generally observed that the dispersions had variable stability. Most dispersions with a transmittance below 90% at preparation were unstable on a long-term basis, i.e., they were not thermodynamically stable. Therefore, it was concluded that the stability is linked to the size of the dispersed droplets which then is determined by the free energy balance in the system.

Preparation of the surfactant in situ versus in the aqueous phase and titration versus predistribution of the cosurfactant affected transparent dispersion formation of these systems at constant temperature. Therefore, according to the criterion established to differentiate between the two types of dispersions, it was concluded that most of these dispersions were not thermodynamically stable.

From all of the above results, it was concluded that the interfacial transfer and reactions of the surfactants, as well as the proper interfacial structure, played a major role in the mechanism of formation of these transparent dispersions.

The interfacial transfer of the surfactants was studied by measuring the interfacial tension with time as an adsorbing solute transferred through an oil/aqueous interface. From these measurements, it was shown that the microemulsions represent a metastable state formed by the redistribution of the two amphipathic components.

Initially, the fatty acid present in the oil phase transferred into the aqueous phase (KOH) and interacted with it. The interfacial transfer and saponification resulted in an accumulation of excess surfactant at the interface which lowered the interfacial tension, enabling initial emulsification.

Molecular dissolution of alcohol (cosurfactant) in the aqueous phase did not result in a dramatic lowering of the interfacial tension. However, when droplets of alcohol spread over the oil phase, low values of the interfacial tension were obtained for a certain period of time. This lowering of γ_i was due to an accumulation of excess amphipathic molecules above the equilibrium value at the interface, as the alcohol transferred from the aqueous to the oil phase. The length of time that γ_i remained at this minimum value was determined by the rate of desorption of the alcohol from the oil-aqueous interface. The most efficient cosurfactant for a particular system had the slowest rate of desorption from the interface.

In the presence of an adsorbed surfactant, the interfacial spreading and transfer of the alcohol produced very high interfacial pressures of the interfacial soap film (which was also penetrated by individual alcohol molecules). This resulted in an oil/aqueous interfacial tension of very low values (10^{-4} or 10^{-5} dynes/cm) for a longer period of time depending on the retarding effect of the film on the transfer and desorption of the alcohol. During these very low γ_i values, the interface was able to expand again to produce microemulsification.

The compression isotherms and surface potentials versus molecular areas of surfactant/oil/cosurfactant films spread on an aqueous substrate allowed structural interactions to be observed and illustrated the type of interfacial film that is conducive to microemulsion formation. From the results of the duplex film experiments, it was seen that the interfacial film formed by the oil/surfactant and aqueous phase must be expandable and able to withstand interfacial pressures greater than the original oil/water interfacial tension. This leads to hypothetical "negative" γ_i values. In addition, the chain lengths of the surfactant and oil must match to allow for the proper curvature needed in a transparent dispersion.

It is therefore concluded that for these metastable systems, since there is no particular thermodynamic advantage to their formation, the more stable state is the separate oil and water phases. The stability of the dispersions can be attributed to the small droplet size and the particular surfactant-cosurfactant film surrounding the dispersed droplets. There is an energy barrier to coalescence of the dispersed droplets originating from this structurally specific interfacial film. This energy barrier may be high enough to account for the long-term stability of the dispersions.

Since it seems that the most distinctive feature between macro- and microemulsions is the degree of curvature and the manner in which they are prepared, the concepts used in treating macroemulsions can be useful in treating microemulsion formation. In fact, the interfacial transfer of a single surfactant and accumulation of excess surfactant at the interface has previously been cited as necessary for spontaneous emulsification. Therefore, the overall conclusion of this study is that the transparent dispersions which were prepared are not thermodynamically stable micellar systems, but are metastable transparent emulsions.

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APPENDIX

ENGLAND AND BERG'S (40) MATHEMATICAL MODEL

Mass Transfer with Adsorptive Accumulation

The system to be considered consists of two semi-infinite immiscible bulk phases meeting at a plane interface, across which the solute is transferred. Initially, phase 1 has uniform solute concentration x_0, while phase 2 is devoid of solute. The phases are brought together at time zero, and diffusive transfer ensues in accord with the equations (valid for dilute solutions)

$$\frac{\partial x}{\partial t} = \frac{D_1 \partial^2 x}{\partial z_1{}^2}, \text{ in phase 1} \tag{1}$$

$$\frac{\partial y}{\partial t} = \frac{D_2 \partial^2 y}{\partial z_2{}^2}, \text{ in phase 2} \tag{2}$$

where x and y are solute concentrations in phases 1 and 2 respectively, and z_1 and z_2 are distances taken as positive moving away from the interface into phases 1 and 2 respectively. The initial conditions are

$$x = x_0 \text{ (for all } z_1\text{)}, \; y = 0 \text{ (for all } z_0\text{) at } t = 0 \tag{3}$$

and the boundary conditions

$$\frac{\partial x}{\partial z_1} = 0, \quad \frac{\partial y}{\partial z_2} = 0, \quad z_1, z_2 = \infty \tag{4}$$

The two additional boundary conditions needed at the interface to specify completely the system are usually provided by a solute material balance (ignoring adsorption of solute):

$$\frac{D_1 \partial x}{\partial z_1} = \frac{-D_2 \partial y}{\partial z_2} \qquad z_1, z_2 = 0 \tag{5}$$

and an equation of solute distribution equilibrium (ignoring possible barriers to adsorption or desorption) such as

$$y = mx \qquad z_1, z_2 = 0 \tag{6}$$.

If the effect of adsorption is to be taken into account, the mass balance (5) is inadequate and must be modified to require that the rate of transfer into a unit area of interface from phase 1 be equal to the rate of transfer out of a unit area into phase 2 plus the rate of accumulation in the interface:

$$\frac{D_1 \partial x}{\partial z_1} = \frac{-D_2 \partial y}{\partial z_2} + \frac{d\Gamma}{dt} \qquad z_1, z_2 = 0 \tag{7}$$,

where the amount adsorbed, Γ, has the units of mass per unit area. The equilibrium boundary condition (6) still applies as long as barriers are assumed absent. If the solutions are very dilute the amount adsorbed varies linearly with the bulk concentration in accord with

$$\Gamma = cx \tag{8}$$,

where c is the adsorption equilibrium constant between the interface and phase 1. C may be expressed as $c = \alpha/RT$ when $\alpha = -(\partial\sigma/\partial_x)_{x=0}$ and σ is the interfacial tension. Equation 8 then becomes the classical Gibbs adsorption isotherm equation.

With the additional stipulation that the amount adsorbed at time zero is zero, the following solutions were obtained for the bulk phase concentration profiles and the amount adsorbed by the method of Laplace transforms:

$$x/x_0 = 1 - \beta \operatorname{erfc} (z_1/(2\sqrt{D_1}) - (1 - \beta)\exp (-z_1{}^2/(4D_1)\ e^{w_1{}^2} \operatorname{erfc} (w_1)) \tag{9}$$

$$y/mx_0 = (1-\beta) \operatorname{erfc} (z_2/(2\sqrt{D_2 t}) - (1-\beta) \exp (-z_2{}^2/(4D_2 t)e^{w_2{}^2} \operatorname{erfc} (w_2)) \tag{10}$$

$$\Gamma/c_{x_0} = (1-\beta)\ [1 - \exp (\omega^2 t) \operatorname{erfc} (\omega\sqrt{t})] \tag{11}$$,

where

$$\beta = m(m + \sqrt{D_1/D_2})$$
$$w_i = \frac{m}{c\beta}\sqrt{D_2 t} + \frac{z_i}{2\sqrt{D_i t}}, \quad i = 1 \text{ or } 2, \text{ and}$$
$$\omega = (m/c\beta)\sqrt{D_2}$$

The effect of adsorptive accumulation on the concentration profiles near the interface a short time after contact was analyzed in terms of dimensionless coordinates (concentration and distance). The adsorptive accumulation effect in terms of an apparent interfacial resistance to the transfer of solute across the interface for two representative samples was then analyzed. The interfacial resistance was defined as the total resistance to mass transfer in the presence of interfacial effects (in this case adsorptive accumulation) minus the total resistance to transfer in the absence of those effects, that is,

$$R_i = x_0/-D_2(\partial y/\partial z_2)_{z_2=0}^{\text{with ads}} - x_0/-D_2(\partial y/\partial z_2)_{z_2=0}^{\text{no ads}}$$

The effect of interfacial accumulation in terms of mass transfer resistance was seen to be negligible for contact times in excess of a millisecond.

Mass Transfer in the Presence of Barriers

A boundary condition alternate to (6) was developed because when there is resistance to mass transfer across the interface, the bulk concentrations adjacent to the interface may be far removed from distribution equilibrium. It was assumed that the resistance could be attributed to first order adsorption and/or desorption reactions as follows:

$$A_{\text{phase 1}} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A_{\text{adsorbed}} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} A_{\text{phase 2}} \qquad z_1 = z_2 = 0$$

The net rate of adsorption from phase 1

$$\delta k_1 x - k_{-1}\Gamma \qquad z_1 = 0$$

must be equal to the rate at which molecules enter a unit area of interface from phase 1, or

$$D_1 \frac{\partial x}{\partial z_1} = \delta k_1 x - k_{-1}\Gamma, \quad z_1 = 0 \tag{12}$$

δ is the thickness of the adsorbed layer, introduced to make the concentrations dimensionally consistent. Similarly, the rate of desorption into phase 2 must equal the flux away from the interface in phase 2, or

$$k_2\Gamma - \delta k_{-2} y = -D_2 \frac{\partial y}{\partial z_2}, \quad z_2 = 0 \tag{13}$$

Adsorption Barrier

The adsorption step is considered to be slow, but the desorption into phase 2 is essentially an equilibrium step. It may be assumed that the amount adsorbed is related to the phase 2 subsurface concentration by

$$\Gamma = y\delta/K_{11} = \frac{c}{m} y, \quad z_2 = 0 \tag{14}$$

where $K_{11} = k_2/k_{-2}$ is the equilibrium constant. Equations 12 and 14 were combined, making use of the relationship $K_1K_{11} = m$ to obtain the necessary boundary condition for the adsorption barrier case:

$$y = mx - \frac{m}{c}\,\frac{D_1}{k_{-1}}\,\frac{\partial x}{\partial z_1}\,, \qquad z_1,\ z_2 = 0 \tag{15}$$

Solutions were again obtained by the method of Laplace Transforms.

Desorption Barrier

The adsorption step is considered rapid, but the desorption into phase 2 is limited. The amount adsorbed is once again related to the phase 1 subsurface concentration by the linear relationship

$$\Gamma = K_1\,\delta\,x = cx, \qquad z_1 = 0 \tag{16}$$

Equations 13 and 16 are combined to obtain the necessary boundary condition for the desorption barrier case:

$$Y = mx + \frac{m}{c}\,\frac{D_2}{k_2}\,\frac{\partial y}{\partial z_2}\,, \qquad z_1,\ z_2 = 0 \tag{17}$$

Again, this reduces to the equilibrium boundary condition for an infinitely large rate constant. Solutions for this case were again obtained by the method of Laplace Transforms.

Adsorption and Desorption Barriers Simultaneously Present

In this case the rate of adsorption from phase 1 and the rate of desorption into phase 2 are given by equations 12 and 13, which were combined to eliminate Γ and give the boundary condition,

$$Y = mx + \frac{m}{c}\left(\frac{D_2}{k_2}\,\frac{\partial y}{\partial z_2} - \frac{D_1}{k_{-1}}\,\frac{\partial x}{\partial z_1}\right) \tag{18}$$

Equation 13 was then combined with the mass balance boundary condition (7) to eliminate Γ from that boundary condition. The concentration profiles were then obtained after application of Laplace Transforms.

The above equations were made dimensionless by the following dimensionless variables:

Rate constant: $K_1 = c^2 \frac{k_{-1}}{D_1}$, $K_2 = \frac{c^2 k_2}{D_1}$

Time: $\theta = \frac{4}{\pi} \frac{D_1 t}{c^2}$

The interface: $\zeta_1 = z_1/(c\sqrt{\pi})$, $\zeta_2 = z_2 \frac{(D_1/D_2)}{c\sqrt{\pi}}$

Concentration: $X = x/x_0$, $Y = y/mx_0(1 - \beta)$

After the appropriate substitutions the equations are found to depend only upon the parameters, K_1 and K_2 and β and ζ_1, ζ_2, and .

The effect of desorption barriers on the concentration profiles in dimensionless coordinates was shown and the effect of barriers to adsorption or desorption was shown in terms of interfacial resistance for two representative samples. Depending upon the magnitude of the rate constant for adsorption or desorption, the interfacial resistance may be large and remain large for long periods of time. The effect of adsorption or desorption barriers was shown in terms of the amount of adsorption. In the case of a desorption alone, the supply of solute to the interface from phase 1 may be much greater than desorption into phase 2, so that the amount adsorbed rises to a maximum and then falls to the steady state value. The interfacial tension, corresponding to the maximum in the amount adsorbed, depends on the magnitude of the rate constant; the smaller the rate constant the lower the minimum and the longer the time required to reach the minimum.

The proposed mechanism for adsorption and desorption are reversible; therefore, knowledge of one of the rate constants enables estimation of the other, that is,

$$K_{11} = k_2/k_{-2} = \delta m/c$$

or

$$k_{-2} = k_2\ c/\delta m$$

If c/m is known and δ can be estimated, and either rate constant can be determined from the data, then estimation of the other rate constant is possible.