LAN, YUH SHONG THOMAS

INTERFACIAL STOICHIOMETRY AND FORMATION OF OIL-IN-WATER MICROEMULSIONS

City University of New York

PH.D. 1981

INTERFACIAL STOICHIOMETRY AND FORMATION OF OIL-IN-WATER MICROEMULSIONS

by

YUH SHONG THOMAS LAN

A dissertation submitted to the Graduate Faculty in Chemistry in partial fulfillment of the requirements for the degree of Doctor of Philosophy, The City University of New York

1981

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

July 7, 1981
date

Steven L. Regen
Chairman of Examining Committe

24 August 1981
date

David C. Locke
Executive Officer

Steven L. Regen
Joseph Rennert
David C. Locke
Supervisory Committee

The City University of New York

Abstract

INTERFACIAL STOICHIOMETRY AND FORMATION OF OIL-IN-WATER MICROEMULSIONS

by

Yuh Shong Thomas Lan

Advisor: Professor Henri L. Rosano

Transparent colloidal mixtures of oil, water and surfactants have been described by the synonyms' "microemulsions", "swollen micellar solutions", and "micellar solutions". This dissertation has addressed itself to the question: Are microemulsions thermodynamically stable systems or are they meta-stable (i.e. kinetically stable) systems? This question was answered by examining the formation pathway of microemulsion systems, the nature of the components involved and the properties existing at the interfaces of the various components.

Microemulsions of soap/oil/water/alcohol were prepared by one of two methods. In the first method, the "titration method", a mixture of fatty acid and oil was added to a caustic solution to produce a macroemulsion, which was then titrated with a cosurfactant, an alcohol, until the system turned clear.

The second method used to prepare microemulsions, the "predistribution method", was to add the alcohol to the caustic aqueous phase and to the oil phase, before the two phases were combined. The greater the percentage of the

system's total fatty acid concentration, initially, predistributed to the oil phase, the more repid the formation of the clear microemulsion. In additional, the formation of transparent systems could be accelerated by predistributing the alcohol only to the caustic aqueour phase.

Using the "titration method" it was found that as the chain length of the surfactants increased, microemulsions with significant transmittances by visible spectrum could be formed with oils of longer chain lengths. It was also found that different alcohols affected the formation of microemulsions in different ways . The best results, in terms of the greatest percent transmittance coupled with widest range of oil (dispersed in water) concentration, were obtained from short or branched alcohols.

The properties of the transparent system, n-hexadecane/potassium-stearate (i.e. K-stearate)/4-methyl-cyclohexanol/water was investigated by photon correlation spectroscopy. Droplet sizes varied from 80 Å to 350 Å in diameter, and the surfactant cross sectional area was calculated to be approximately 56 $Å^2$ to 95$Å^2$ per molecule. This implied the surfactant molecules at the interface were incorporated by the cosurfactant molecules. For a given amount of oil and water, the particle size of a microemulsion was inversely proportional to the concentration of surfactant and cosurfactant.

Sedimentation measurements indicated that the total interfacial area of the droplets was constant regardless of the volume of the dispersed phase.

The molar ratio of cosurfactant/surfactant at the oil-in-water (O/W) interface of the microemulsion, n-hexadecane/K-stearate/1-pentanol/water system, was calculated. It ranged from 2:1 to 5:1 as the amount of oil was varied from 0.5 ml to 4.5 ml. Below or above these molar ratio ranges, microemulsions could not be formed.

In order to explain the mechanism of formation of microemulsion, the diffusion rate of a cosurfactant 1-pentanol, from a caustic solution into n-hexadecane phase was measured by gas chromatography. It was found to be severely hindered by the presence of a K-stearate film at the O/W interface. The amphiphathic 1-pentanol molecule has difficulty penetrating the wall of highly structured amphiphathic soap molecules present at the O/W interface, due to the mutual attraction between the alcohol molecules and the soap molecules.

The attraction is the consequence of the polar interactions between the charged head groups of the molecules and the van der Waals forces operative between the hydrocarbon moieties of the alcohol and soap molecules. The net accumulation of oriented 1-pentanol at the O/W interface in the presence of adsorbed surfactant results in an increase in the surface pressure. This is accoumpanied by a simultaneous decrease in the interfacial tension at the O/W interface, which in turn causes the breakdown of the initial coarse emulsion into the more energetically-

favored spherical microdroplets.

The formation of microemulsion systems (oil/soap/alcohol/water) was dependent on the order of mixing of the components. Many of these "stable" systems separate with the passage of time, such microemulsion systems are designated "Meta-stable".

ACKNOWLEDGEMENTS

I would like to thank Professor Henri L. Rosano for the support and guidance he has given me throughout the course of my garduate education at CUNY. In addition to extending to me his scientific skills, he has always shown me friendship and hospitality, which has always been greatly appreciated.

I would like to acknowledge Professors D. C. Locke, R. Birke, A. Turk, D. Sloan, and T. Haines, who opened their laboratories to me and our discussions were always a combination of delight and enlightenment.

I would also like to acknowledge Professor H. Z. Cummins and Dr. T. S. Hwang of the Department of Physics, CCNY, for performing photon correlation spectroscopy experiments and calculations.

I wish to thank Professor H. Salzberg, Dr. M. Strassfeld and Mr. R. Fisher for proof reading this manuscript. With sincere appreciation, I would like to thank Dr. M. Strassfeld again for all his help and encouragement.

My thanks also goes to my parents, my sister, my brother, and my love, Angela, for their patience, encouragement and constant support.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS AND ABBREVIATIONS

a:	total number of droplets of the dispersed phase, also, a subscript indicating alcohol
A:	total interfacial area
$A_2, A_{0.5}$:	total interfacial areas of droplets at 2ml and 0.5 ml of oil in oil-in-water system
dA:	change of total interfacial area
AMP:	2-amino-2-methyl-1-propanol
C_1, C_2, C_i:	concentration of 1-pentanol in aqueous phase(1), oil phase(2), and in the interface(i) (mM/l)
C^*:	initial concentration of 1-pentanol in aqueous phase
ΔC_{soap}:	change in soap concentration from one system to another
$\overline{C}$:	mean concentration
D:	diffusion coefficient
d:	density of continuous phase
E:	activation energy
f:	fractional coefficient
dG:	change of interfacial free energy
grad C:	concentration gradient, equals $\Delta C/h$, which is the concentration difference of a specie in two thin layers of a solution seperated by a distance h
HLB:	hydrophilic-lypophilic balance
i:	superscript indicating the interfacial region between O/W
K:	Boltzman constant, or rate transfer constant
M:	average droplet molecular weight
n:	number of surfactant molecules

N:	Avogadro's number
O:	oil phase
P_{ow}:	partition coefficient between oil phase and water phase
r:	radius of spherical droplet
R:	gas constant (1.987 Kcal/mole), or particle hydrodynamic radius
S:	sedimentation constant
T:	absolute temperature
t:	time
V_1, V_2, V_i:	volumes of aqueous phase, oil phase and interface
$\bar{V}$:	droplet partial specific volume (sedimentation experiment)
V:	droplet volume
W:	water phase
γ_i:	interfacial tension between two immisible liquids when emulsifying agent is present in the system
$\gamma_{o/w}$:	interfacial tension between oil and water in the absence of an interfacial monolayer
$(\gamma_{o/w})_a$:	interfacial tension between oil and water in the presence of an alcohol monolayer
π:	film pressure due to a monolayer
σ:	cross sectional area occupied by surfactant molecule at the o/w interface
η:	viscosity of the continuous phase
ϕ:	flux of 1-pentanol across the O/W interface

INTRODUCTION

If a mixture of two immiscible, (or partially miscible), liquids in the presence of surface active agents (i.e. emulsifiers, such as soap, detergent, etc.) results in the dispersion of one liquid into the other the new system is categorized as an "emulsion". That liquid which is broken up into droplets is termed the internal phase or dispersed phase, while the liquid surrounding the droplets is known as the external phase, dispersing medium, or continuous phase. If one of the immiscible liquids is water and the other is water-insoluble or "oil", two types of emulsions may be formed. If water is the continuous phase and oil is the dispersed phase, the system is called an "oil-in-water" (O/W) emulsion, or vice versa for "water-in-oil" (W/O) emulsion. Mixed (or double) emulsions are also possible, in which both O/W and W/O emulsions are present in the same system (e.g., the oils may be different).

W/O and O/W emulsions can be inverted from one type to the other by adding more of one phase or by changing the type of emulsifier; this process is called "inversion".

Emulsions can be classified into two groups, "Macroemulsions" and "Microemulsions". Macroemulsions consist of oil, water, and surfactants. They are opaque and have particle sizes generally larger than 2000 Å in diameter. Microemulsions differ, component wise, from

macroemulsions in that there is an additional ingredient, a cosurfactant e.g. an alcohol. Microemulsions are isotropically transparent (i.e. being transparent regardless of the direction of measurement), generally stable, and have particle sizes less than 1000 Å in diameter (1-5). The particle sizes are deduced from the fact that, the particles do not scatter visible light, and microemulsions are transparent systems (23).

The term "microemulsion" was first introduced by Schulman et al. (57), who studied microemulsion systems with a wide variety of techniques. Numerous explanations of their stability have been offered but, as yet, no complete theory explaining their formation and stability has proved completely satisfactory(15,22,36-38,40-43,70,78, 83). Some scientists believe microemulsions, like swollen micelles, are thermodynamically stable systems(4,15,25,57, 94-97). Others believe that microemulsions are thermodynamically unstable emulsions(21,31,62,69,70). If microemulsions are thermodynamically stable systems, they are independent of the order of mixing, and can be formed using different methods. If microemulsions are unstable, the order of mixing of the components will affect the formation of the microemuslion systems. The formation of these systems will also depend on factors such as pH, temperature, specie concentration, chain length of the oil and the surfactant, diffusion rate of consurfactant, and

the geometric configuration of the reaction molecules in the formation pathway. An unstable microemulsion will eventually break down into two separate layers.

As there is no theory which explains all the characteristics of microemulsions satisfactorily, it has been the objective of this work described here to study these transparent systems in order to understand better their mechanism of formation, physical-chemical properties and stablility, and finally to propose a unifying theory to explain the phenomena associated with microemulsions.

CHAPTER 1

DISPERSED SYSTEMS - A HISTORICAL PERSPECTIVE

1-1. Spontaneous Emulsification

When two immisible phases, for example, oil and water, are mixed together to form a homogeneous mixture with the assistance of a surfactant (e.g. soap), the process is called emulsification. If this homogeneous system can be made without the introduction of any external work (e.g., electrical, mechanical and chemical work) the process is called "spontaneous emulsification".

Much research has been done on spontaneous emulification by various surface scientists in the past hundred years (6-13), and numerous theories have been proposed to explain this type of emulsification. In 1878, Gad (6) and Brucke (7) observed that when a solution of fatty acid in oil was poured very gently into a sodium hydroxide solution, an emulsion was formed in the aqueous phase. Quincke (8) suggested that the non-uniform diffusion of soap across the interface (O/W) which resulted in the lowering of interfacial tension, was responsible for the spontaneous emulsification.

Davies and Haydon (9) investigated the systems studied by the previous researchers and reached the conclusion that spontaneous emulsification is the result of one or more of three conditions: (1) interfacial turbulence, (2) a high diffusion rate for a solute across the interface, and/or

(3) negative interfacial tension. It has been concluded from these conditions that the interfacial tension must be very low (9).

Davies and Rideal (10) modified the proposed mechanism by stating "the requisite energy for spontaneous emulsification comes from the free energy release as the additive is redistributed to its equilibrium state in the two phases".

In 1953, Mansfield (11) investigated the system of oleic acid, paraffin oil and aqueous solutions at different pH's without the addition of cosurfactants. He found that spontaneous emulsification occurred when the fatty acid was dissolved in oil and the mixture was put on top of the aqueous solution at pH 9 to 12. He proposed that a decrease in interfacial tension was essential for spontaneous emulsification, but did not specify the absolute value of γ_i required. Diffusion, migration and ionization were considered the main factors involved in the emulsification.

Six years later, Linde (12) and Sterling, et al. (13) proposed that spontaneous emulsification occurred by the redistribution of surfactant molecules by diffusion and convection. When two liquid phases are in contact under static conditions and one of them contains a surfactant, the interface seeks a state of lower free energy at the expense of the adjacent regions of high surface tension and results in spontaneous emulsification.

1-2 Microemulsions

1-2-1. History of Microemulsions

The term microemulsion introduced by Schulman and co-workers (57) may be one of those unfortunate words, all too common in science, which arise from the necessity to name a phenomenon before it is completely understood and remain as a source of semantic confusion. The spontaneously formed, transparent water-in-oil (w/o) systems studied by Schulman and his collaborators (4, 15, 24, 25, 50) contained spherical particles with diameters in the range of 100 Å to 1000 Å, and were thought to be in a state of thermodynamic equilibrium. Since emulsions are normally considered to be a heterogeneous mixture of phases kinetically but not thermodynamically stable, there has been a prevalent notion that microemulsions are emulsions with unique properties (e.g. small particle sizes transparent to light) (62, 67, 70). Winsor (91,92) studied similar systems and together with Palit et al. (93) characterized the clear phases obtained as solubilized systems consisting of swollen micellar units. Adamson (94) prefers the term micellar emulsions to microemulsions to emphasize the micellar nature of these systems as well as their emulsion-like properties, i.e., light scattering, similar composition, and method of formulation. On the other hand, Fowkes (95) regards

Schulman's original definition appropriate. But, Ekwall et al. (95) recommend that Schulman's microemulsions be considered as solubilized micellar solutions (96,97). Nevertheless, the opinion (36,98) persists that microemulsions are true dispersions of one liquid within another and that their formation is not the same process as the solubilization of the oil phase be the interior of the micelles. Extensive investigations of the phase equilibria and structures in ternary systems of amphiphiles (40,99,100) reveal that the phenomena of micelle formation and solubilization may have a common mechanism.

Interest in microemulsions has intensified because of their practical applications. Many reviews of microemulsions have appeared. Among the earliest, Osipow (101), pointed out the difficulty of distinguishing between microemulsions and solubilized systems. Reviews by Prince (102) and Rosano (103) expound the theories of the Schulman school while a recent review by Shinoda and Friberg (104) contrasts some of the differences in opinions with reference to their work on solubilized phases.

The details of the various theories of microemulsions discussed above are amplified in the section below.

1-2-2. Theories of Microemulsions

1-2-2-1 Schulman's Work

In 1955 the paper entitled "Emulsions, Control of Droplet Size and Phase Continuity in Transparent Oil-Water

Dispersions Stabilized with Soap and Alcohol," Bowcott and Schulman (14) made an important contribution to the theory of microemulsions. Schulman attributed the formation of these emulsions to the molecular interactions taking place in the interface. This mixed monolayer he considered as a third phase or interphase in equilibrium with the oil and water phases. Thus, the alcohol was distributed between the three phases and the whole of the potassium oleate was in the interphase. The last assumption was limited. It was not valid when there was insufficient water present to provide a large enough interfacial area for the whole of the oleate soap to be in the interphase. 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 he now included the size of the cation in anionic systems, and temperature.

A calculation of the ratio of oil:soap in these W/O systems was made in an ingenious way. First, the original W/O emulsions were made by titrating coarse emulsions of hydrocarbon and water stabilized with soap, to transparency with an alcohol. Then additional oil was added and the systems were titrated to transparency again with more alcohol, repeating this process determined the alcohol

volume per hydrocarbon volume to produce a transparent system. Extrapolation of the curve to zero hydrocarbon determined the amount of alcohol in the interface.

Previous results of monolayer penetration experiments at the air/water interface (123) 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 and one between the polar heads of the monolayer and the water. The side of the monolayer with the higher tension would be the inner surface.

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 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. This prompted him to propose that the phases were in equilibrium with each other, inferring that the interfacial tension was zero.

The measurement of droplet size continued to be a problem. The most reliable scheme was the calculation

of droplet radius r by means of the formula

$$r = 3V/A$$

where V is the total volume of the dispersed phase and A is the total interfacial area. This presupposed a knowledge of the value of the area of the oleate molecule in the interphase and also assumed that all of it was there. In this case, A equalled 6×10^{23} x the weight of the oleic acid divided by its molecular weight and multiplied by its area in the film . Now the area of an oleate molecule at the O/W interface had been determined at 30 $\mathring{A}^2$ and that of aliphatic alcohol at 20 $\mathring{A}^2$. A 1:1 ratio in the interface should account for an oleate area of about 50 $\mathring{A}^2$. Experience, however, led Schulman to assign a value of 70 $\mathring{A}^2$ to the area of an oleate molecule at the O/W interface. This could be accounted for by an alcohol:soap ratio of 2:1 or, as proposed later, by penetration of molecules derived from the oil phase. Using this value of 70 $\mathring{A}^2$ for the area of the oleate molecule, droplet diameters ranging from 140 to 240 $\mathring{A}$ were obtained for the Bowcott and Schulman W/O emulsions. By taking the volume of the dispersed phase to include the core plus the interphase, it was not necessary to make any assumptions about chain lengths nor their orientation other than that the mixed film be in a completely liquid state.

In late 1941, Zisman (124) suggested that an alcohol monolayer at an O/W interface could be penetrated by molecules of the oil phase. Schulman noted from Zisman's

work that an alcohol layer at the O/W interface could be penetrated by long chain mineral oil molecules to form a 1:1 association and that surface pressure as high as 30 dynes/cm failed to squeeze at the nonpolar hydrocarbons. At the same time he observed that benzene could easily be ejected from a monolayer of fatty acids at the benzene/water interface. Moreover, he knew from the work of Robbins and LaMer (125) that the solvent hydrocarbons used to spread monolayers at the air/water interface could remain in the film but also could at moderate pressures be squeezed out and not form associations even at low surface pressures. From this he deduced that if there was a possibliity 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.

It was evident that a vapor, 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 the penetration of a mixed film of soap and alcohol (or their equivalents) by hydrocarbons derived from the oil phase. The second was to use large cations (i.e. 2-amino-2-methyl-1-propanol (AMP)) 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 associating alcohol) providing the film were penetrated by oil molecules which associated with the soap species but were sufficiently asymmetric therewith to produce the required disorder. Emphasis was placed on the size of the cation in effecting disorder.

Following closely on the heels of the foregoing came the concept of a transient negative interfacial tension as the factor being responsible for the formation of microemulsions (126), Schulman proposed this on two bits of information. In the monolayer studies with Goddard (123) two dimensional surface pressures of over 50 dynes/cm had been recorded. In addition, Bowcott (127) 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 the mole fraction of hexanol in benzene (32).

The negative interfacial concept was based on the thermodynamic equation that at the O/W interface,

$$\gamma_i = \gamma_{o/w} - \pi$$

where γ_i is the total interfacial tension, $\gamma_{o/w}$ is the O/W interfacial tension without the addition of amphipathic agents, and π is the two dimensional spreading pressure of the amphipathic agents. According to this equation, if as a result of the 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 the formation of a microemulsion. When $\gamma_{o/w} > \pi$, only a **macroemulsion** could form. In this view the temporary existence of a film pressure greater than $\gamma_{o/w}$ would be the driving force which reduced the droplet size of the fixed volume of dispersed phase until no more energy was available to increase the interfacial area (i.e., to decrease droplet size). Equilibrium would be attained when the negative interfacial tension returned to zero by virtue of the uncrowding of the molecules and the loss of pressure in the interface. When $\gamma_{o/w} > \pi$, droplet diameters of the order of magnitude of 10,000 Å (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 value of π or $\gamma_{o/w}$.

Schulman summed it up nicely when he said that negative interfacial tension produced by the mixing of the components would, at equilibrium, become zero and dispersion, and not separation, would be the equilibrium condition. 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 (123), would easily account for the experimental results obtained.

1-2-2-2 Prince's Modifications:

When Cooke and Schulman (32) determined experimentally that hydrocarbons would be ejected from mixed monolayers of soap and alcohol at the high pressures necessary for negative interfacial tensions. They used different hydrocarbons in their experiments and found that the distribution of hexyl alcohol between the bulk phase and the interphase varied with the hydrocarbon used. This prompted Prince (33) to propose that negative interfacial tension 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 upon 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.

The term $(\gamma_{o/w})_a$ introduced a new dimension into behavior at the O/W interface. It was soon recognized that it could approach a value of 15 dynes/cm at relatively low concentrations of alcohol in the oil phase. Essentially, the distribution or partitioning of alcohol between the interphase and the bulk oil phase, changed the composition of the oil phase and its tension with water.

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

$$\gamma_i = (\gamma_{o/w})_a - \pi$$

As a corollary to this concept, it became apparent that in any given system, zero interfacial tension may occur only at an intermediate concentration of alcohol, amphiphile, or cosurfactant (70). 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 depend upon the structure of the molecules involved, 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 the strong attraction among the heads and tails of the tenants.

Another corollary of the negative tension hypothesis offers an explanation for the stability of microemulsions systems (24,32,128). This is due to zero surface free energy. When two microdroplets coalesence to form a droplet of larger size, the interfacial tension of the new droplet becomes negative. The larger droplet now spontaneously increases its interfacial area to effect zero surface free energy and two droplets of the original size form once

again. Brownian Movement no doubt aids and abets this equilibrium. It is this thermodynamic (if not kinetic) equilibrium that keeps the emulsion stable.

1-2-2-3 Rosano's Work:

Rosano, Peiser, and Eydt (16) extended the work of Bowcott and Schulman (29) and Cooke and Schulman (32), employing both soap and lauryl sulfates as the surfactants. Microemulsion formation was insensitive to the nature of the cation with the sulfate but quite cation-dependent in the case of the soaps. They also observed that the addition of water does not increase the total interfacial area of W/O microemulsions. Utilizing Adamson's proposal (94), they suggested that the counterbalancing of the Laplace and osmotic pressures in these systems accounted for the experimental observation that W/O microemulsions are easier to form than O/W types.

Gerbacia and Rosano (31) 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 vs. alkyl sulfate). Hexadecane and benzene were used as oil phases. The cosurfactant was pentanol. Based upon the distribution of pentanol between the dispersed phase and the interphase, calculations of ΔG were made.

In a review paper Rosano (103) plotted a ternary phase equilibria diagram of 0.3M aqueous potassium oleate,

n-hexadecane, and 1-hexanol in which he found two microemulsion systems, O/W and W/O, separated by a clear birefringent gel system. Rosano presented a theory for the development of temporary zero interfacial tension based on the interfacial diffusion of the surfactant and cosurfactant. However, he did not exclude the factors of film penetration, "complexing", and zero interfacial tension which Schulman had proposed.

1-2-2-4 Shah's Work:

Shah and Hamlin (75) 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 low ratios of water to oil below 0.1, molecular solubilization of water in the system was presumed to take place. Between a ratio of water to oil of 0.1 to 0.6, the system was considered to be a W/O microemulsion. The existence of these two types of aggregates was supported by the 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 ratio of water to oil of about 1.3, the system again became clear and fluid, indicating that it had completely inverted to an O/W microemulsions. 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 (48) had demonstrated the existence of cylinders and lamellae in translucent nonionic 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.

Subsequently, Shah et al. (36) 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 (37). On the basis of the electrical measurements, it was also proposed that these microemulsions were true dispersions of one liquid in another and were not cosolubilized systems.

1-2-2-5 Robbins' Work:

A theory for the phase behavior of microemulsions has been developed by Robbins (22) which is consistent with the concept that interactions in a mixed film are responsible for the direction and extent of curvature and, thus of the type and size of the droplets of microemulsions. In his most recent model for microemulsions stabilized with nonionics, 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.

Robbins used a model (22) and predicted quantitatively the 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 measurable quantities: surfactant molecular volume, interfacial tension, and interfacial compressibility (defined as the fractional change in molecular area with interfacial pressure).

In his earlier work, the stress gradient was viewed as being responsible for the direction of film curvature and the "Laplace" pressure difference across the curved interface. Relating the pressure difference to the fugacity of water in a W/O microemulsion, Robbins established thermodynamic criteria for spontaneous water uptake without postulating a negative interfacial tension.

As a basis for this theory, he has utilized equations generated by the geometry of two concentric spherical shells surrounding the droplet and by the force balance across these shells. Equations are developed for both O/W and W/O droplets which relate phase behavior to interfacial

tension, the volume of the surfactant heads and tails, and interfacial compressibility.

Robbins' theory correlates water and oil uptake with the idealized ternary diagram and Winsor's transitions in micellar types (91, 92). Where water and oil uptake are known, interfacial tension can be predicated and vice versa. The theory also perdicts droplet size and interfacial concentration of adsorbed surfactants in terms of the number of molecules per droplet.

1-2-2-6 Other Works:

Ruckenstein (38) took a different approach to explain the spontaneous microemulsification. He took into consideration the "dilution effect", that is, the concentrations of surfactant and cosurfactant in the bulk are decreased (i.e., diluted) due to the adsorption of surfactant and cosurfactant molecules on the surface of the droplets. This has a two fold result, first, it reduces the chemical potential in the bulk and second, the presence of the extra molecules in the interface lowered the interfacial tension at the O/W interface. The net result is the lowering of the free energy of the system (78-80). If the free energy change due to the dilution effect is sufficiently negative to overcome the positive free energy change, and spontaneous dispersion occurs. When reaching the microdroplet form, the microemulsion is able to take advantage of the repulsive forces generated by

the presence of a charged double layer on each of the microdroplets to prevent the coalesence of the fine droplets into the larger ones of the macroemulsion.

Admad (17), Shinoda (39, 83) and Friberg (32,40,81) accepted the concept of association of soap and alcohol at the O/W interface proposed by Schulman, but suggested that the γ_i can only be reduced to a very low positive value, which doesn't guarantee the formation of micro-emulsion.

Davies and Rideal (41) believed the fluidity at the water layer of the interface is responsible for the formation of microemulsions. The presented evidence that several layers of water adjacent to a mixed film may be oriented to form a rather rigid layer of "soft ice". When this rigid structure is broken down by something (e.g., oil molecules) in order for water molecules to readily flow onto the water side of the interface, then microemulsification takes place.

Fowkes (42) supported Rideal and Davies' idea. He suggested that film pressure is a function of the chemical potential of water molecules, that water molecules must be area-determining and be present in film rich in alcohol and that $\gamma_i = 0$ when the ratio of alcohol to soap at the interface is equal to or greater than 1.

Pink (43) considered the effects of temperature on the disorder of the molecules at the interface of the mixed

film. He found that the formation of microemulsions could be triggered by raising the temperature of macroemulsion systems.

1-3. Summary

Even though many theories were proposed to explain the mechanism of formation of microemulsions, the negative interfacial tension proposed by Schulman is the most widely accepted hypothesis at present. Many scientists have been trying to modify Schulman's theory by changing the negative interfacial tension to a very low, positive one, or by incorporating a cosurfactant (such as alcohol) in the equation ($\gamma_i = (\gamma_{o/w})_a - \pi$), but still accept the idea of negative interfacial tension, Rosano's proposal of positive γ_i at equilibrium would then appear to be an appropriate assumption for the formation of droplets, because the interfacial tension for a droplet is always positive.

The focus of the following work is an investigation into the underlying mechanism(s) responsible for the phenomena called microemulsion.

CHAPTER 2

THE VARIABLES AFFECTING THE FORMATION OF MICROEMULSIONS

Transparent dispersions of one immiscible liquid in another have received much scientific interest in the past thirty years. They are useful in many industrial applications, such as cleaning formulations and cosmetics. The formation and stabilization of these dispersions involve the interaction of many parameters, such as pH, droplet size, interfacial geometry, the concentrations and structures of oil, surfactant and cosurfactant. As a result, these clear dispersions are usually developed empirically since no adequate theory exists on the components which will form them. HLB values (Hydrophilic-Lypophilic Balance) of surfactants and solubility parameters of surfactants and cosurfactants in oil or water have not been as helpful as when formulating coarse emulsions.

In this work, the parameters affecting the formation of dispersions were studied. Oil-in-water (O/W) systems were emphasised, but some water-in-oil (W/O) systems were also investigated. The stabilities of these systems were not investigated. For the sake of clarity the term microemulsion or transparent dispersion will be used as a label for the clear systems since some of the mixtures were not transparent.

2-1. Experimental

A. Microemulsion Preparation

The surfactants used in this investigation were potassium soaps of straight-chain primary fatty acids (C_{12}-C_{18}). The fatty acids and n-hexadecane were purchased from Eastman Kodak Company, (Rochester, New York.) The KOH pellets were from Mallinckrodt Chemical Company (St. Louis, MO). Alcohols were obtained from Aldrich Chemical Company, Inc. (Craftsman in Chemistry, Milwaukee, Wis. 53233).

The effect of pH on the type of initial coarse emulsion was determined in the following manner. A solution of 2.0×10^{-3} mole of the 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 in water while the pH was monitored. A "good" coarse emulsion was obtained above pH 12.0. This high pH was necessary to insure the complete ionization of the fatty acid (111). 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.

Microemulsions were prepared at 30°C by a titration method (i.e., the "point method") (69). As prepared above, the fatty acid was dissolved in the oil phase and then the aqueous KOH solution was mixed with it. The resulting coarse emulsion was then titrated with the cosurfactant to form the microemulsion.

B. Transmittance Measurements

A Bausch and Lomb Spectronic 20 spectrometer was used to monitor the transmittance of the emulsions at 520 nm (as chosen), during the titration with cosurfactants. Distilled water was employed as the reference solution with a transmittance of 100%. The deviations of the transmittance measurements were within $\pm$ 8%.

C. Photon Correlation Spectroscopy

Particle size measurements were performed using a photon correlation spectrometer (84,85). The instrument designed by Cummins, et al. used a single-mode, intensity-stabilized, argon ion laser (Spectra Physics Model 165) operating at 4880 Å. A 60-channel controlled digital correlator was used to receive and count the photons. Samples were loaded into 1-cm^3 cuvettes and placed in a thermostated scattering chamber which was maintained at 30°C.

When the light beam traverses a path containing scattering centers which are undergoing Brownian motion, the intensity of light scattered at an angle from the forward direction fluctuates due to the motion of the particles. If the scattered light strikes the cathode of a photomultiplier, the rate of photoelectric pulses produced also fluctuates in time. The pulses are then counted electronically. This fluctuation is used to find the translational diffusion constant (D). In turn, the particle hydrodynamic radius (R)

can be determined from D and use of the Stokes-Einstein equation,

$$R = \frac{KT}{6\pi\eta D} \qquad (1)$$

where K is the Boltzmann constant, η is the viscosity of the continuous phase (0.78 cP was used), and T is the absolute temperature. The measured dissymmetry was less than 10%, indicating that the droplets were essentially spherical.

D. Ultracentrifugation

Sedimentation measurements were made using a Beckman Model E analytical ultracentrifuge (Spinco Division, Palo Alto, Calif.). Each sample of the microemulsion was placed in a sector-shaped cell and centrifuged at an angular velocity in excess of 50,000 rpm at 25°C. The movement of the Schlieren peak with time was photographed.

2-2. Results

A. Formation of Transparent Dispersions

Two basic formulations were used:

(a) O/W (x mole of stearic acid and 2.0 ml of oil)/(16.0 ml of 0.375 N KOH)

(b) W/O (2.0 ml of 1.8 N KOH)/(10.0 ml of an oil solution containing y mole of stearic acid)

A high 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.

For emulsions prepared using n-hexadecane as the oil phase, transmittance is a function of the volume of cosurfactant added. As shown in Figures 1 and 2 each system shows a maximum. At low soap concentrations the width of the curve is narrow. At higher concentrations it becomes much broader, but more alcohol is needed to achieve maximum transmittance.

Dispersed phase volume also affects the optical properties of these systems (Figure 3 and 4). Solutions were prepared with 2.0×10^{-3} and 4.0×10^{-3} mole of stearic acid in n-hexadecane. These were dispersed in aqueous KOH and titrated with the alcohols indicated. The maximum transmittance and the volume of alcohol required are a function of the volume of oil used. The 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. The addition of cosurfactant, increases the transmittance to a maximum of 60-70%. Nevertheless, when the experiment is repeated in the presence of a small amount of oil, almost 100% transmittance is obtained.

Figures 3 and 4 also show the sensitivity of the dispersions to the amount of surfactant, and the type of cosurfactant added. The volume of oil that can be

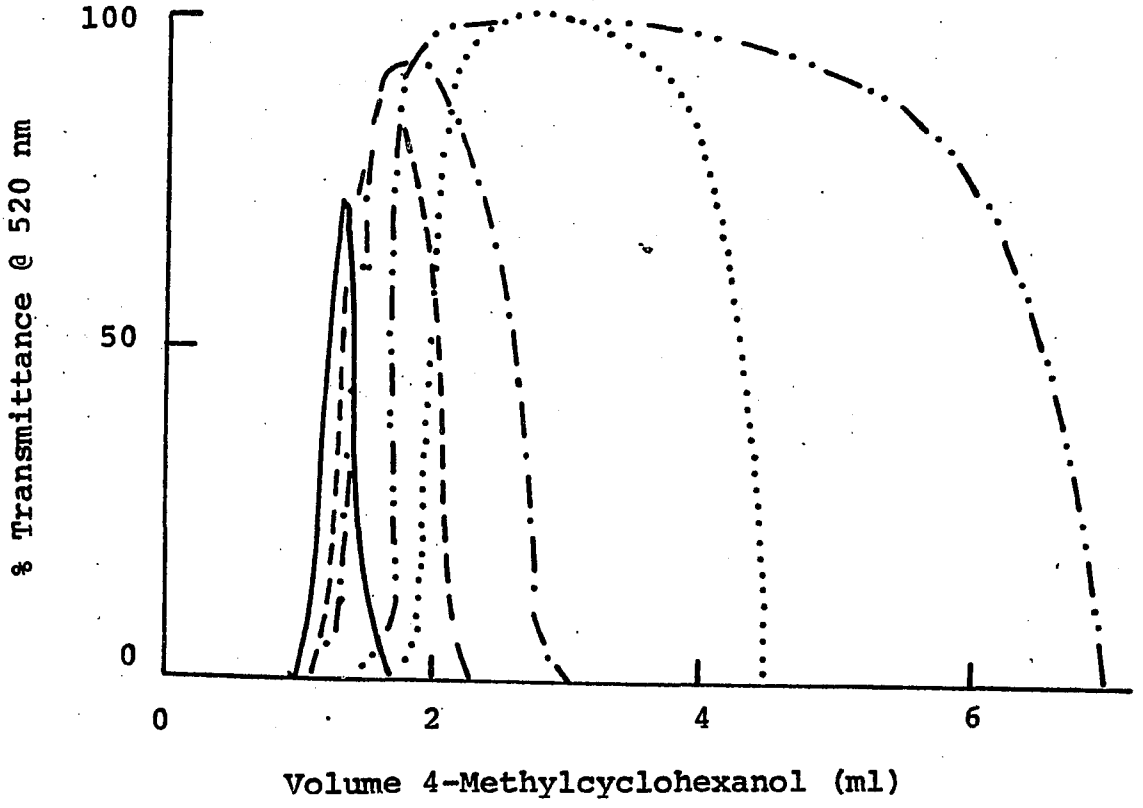

Figure 1. Transmittance Curves for O/W Systems at 30°C as a Function of Alcohol and Soap Content. 2.0 ml N-hexadecane, 16 ml of 0.375 N KOH. Millimoles of Stearic Acid: 1.5 (———), 2.0 (– – –), 2.5 (—·—), 3.0 (···), 4.0 (—··—).

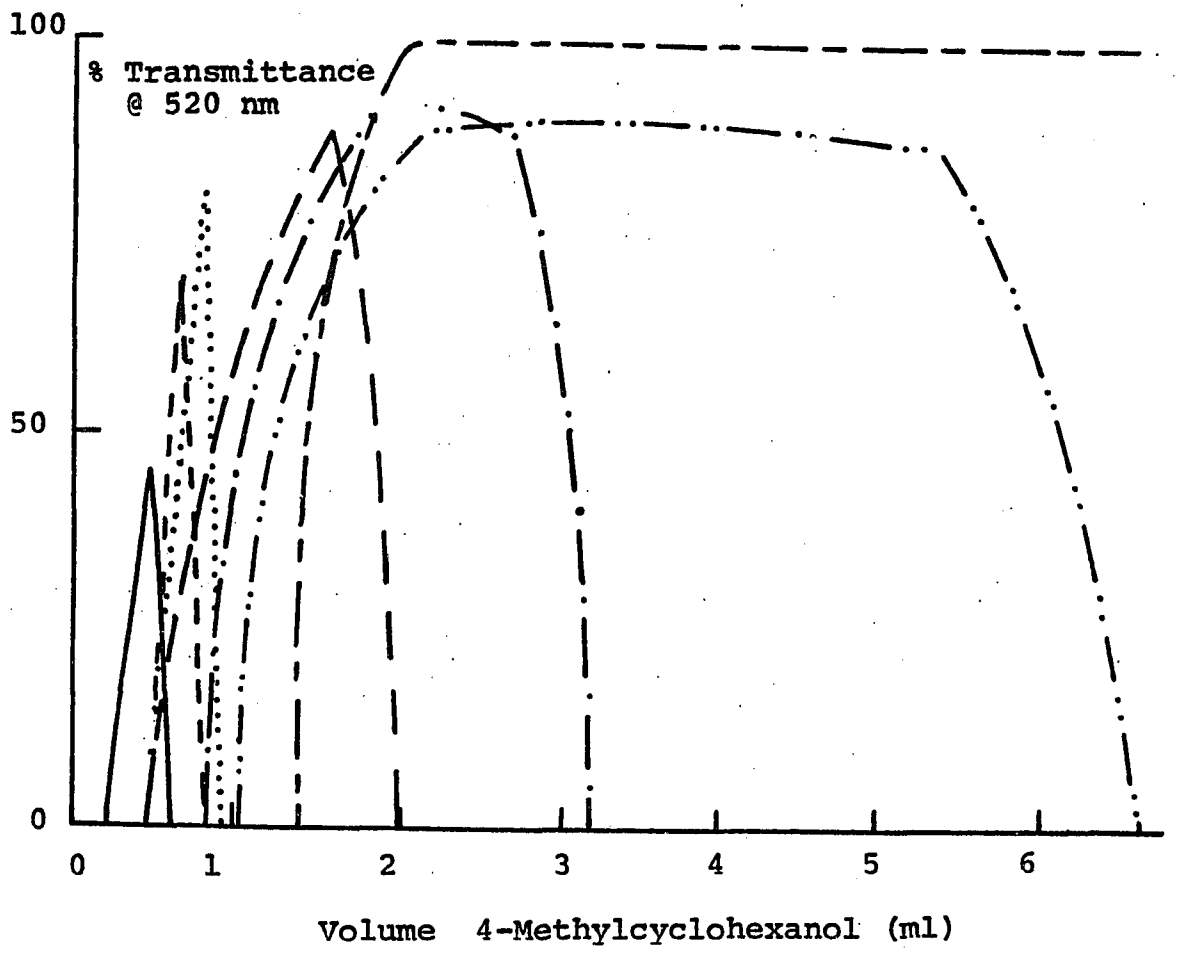

Figure 2. Transmittance Curves for W/O Systems at 30°C as a Function of Alcohol and Soap Content. 2.0 ml of 1.8 N KOH, 10.0 ml of N-hexadecane. Millimoles of Stearic Acid: 1.0 (———), 1.5 (— — —), 2.0 (· · · ·), 2.5 (— — —), 3.0 (— · —), 3.5 (— · · —), 4.0 (— ——— —).

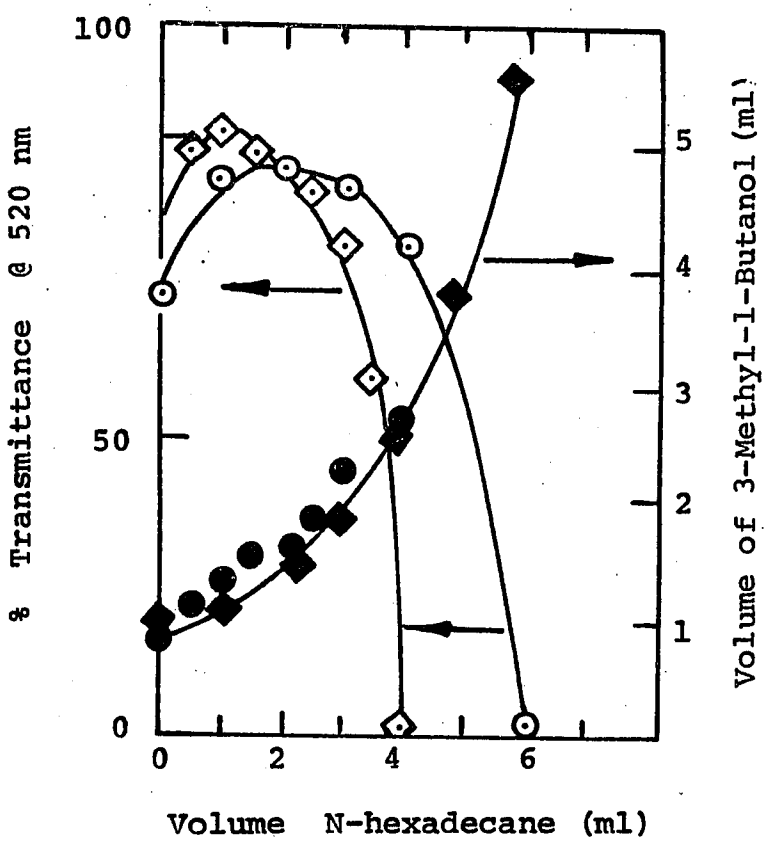

Figure 3. Transmittance Curves for Hexadecane-in-Water Systems with 3-Methy-1-butanol as cosurfactant as a function of Oil Content.
16 ml of 0.375 N KOH,pH 12.4 @ 30°C.
The Right Abscissa is for the Solid Figures.
Millimoles of Stearic Acid:
2.0 (⊙ , ●), 4.0 (◈ , ◆).

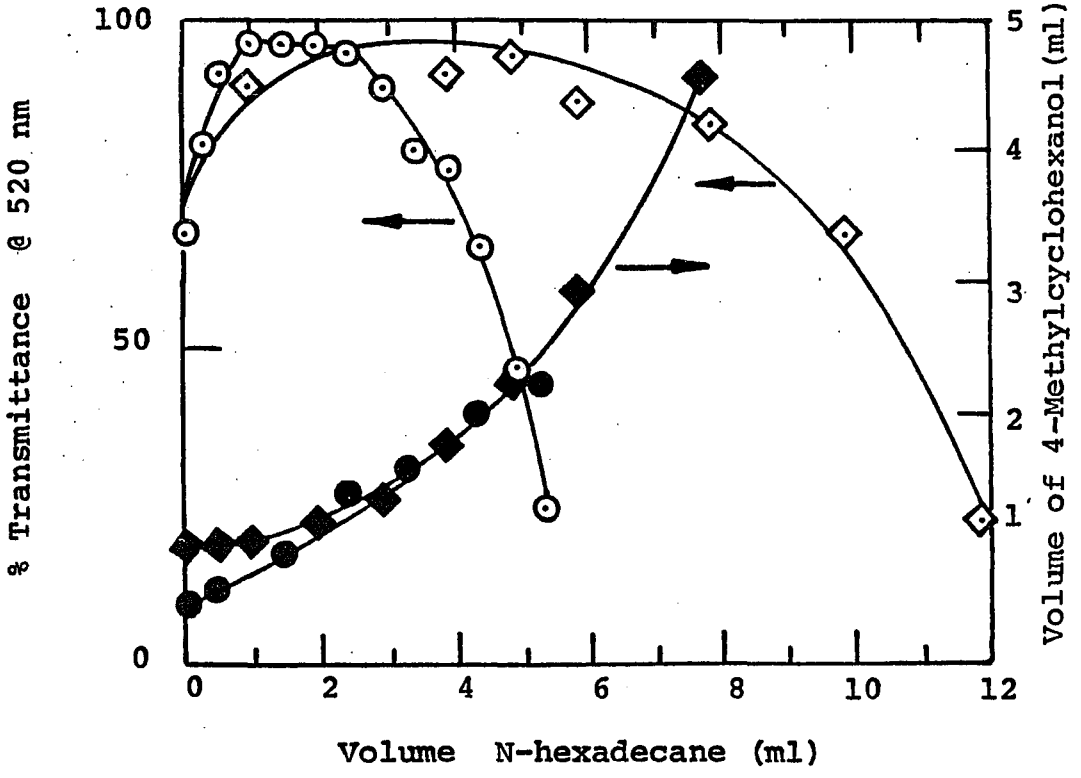

Figure 4. Transmittance Curves for Hexadecane-in-Water Systems at 30°C with 4-Methylcyclohexanol as Cosurfactant as a Function of Oil Content. 16 ml of 0.375 N KOH. pH 12.4. The Right Abscissa is for the Solid Figures. Millimoles of Stearic Acid: 2.0 (⊙ , ●), 4.0 (◇ , ◆).

dispersed at a given maximum transmittance is much higher with 4-methylcyclohexanol than with 3-methyl-1-butanol.

The marginal efficiency of the surfactant is defined here as

$$\frac{\Delta V_{oil}/\bar{V}}{\Delta C_{soap}/\bar{C}}$$

where ΔV_{oil} and ΔC_{soap} are the changes in oil volume and soap concentration from one system to another and $\bar{V}$ and $\bar{C}$ are the mean concentrations. It is found that 4-methylcyclohexanol yields a much higher marginal efficiency.

For example, at 90% transmittance, the maximum amount of n-hexadecane that can be dispersed with 2.0×10^{-3} mole of stearic acid and 4-methylcyclohexanol is about 2.6 ml. When the concentration of stearic acid is doubled about 5.6 ml of oil can be dispersed. The marginal efficiency with 4-methylcyclohexanol is $(5.6-2.6) \times 3.0 \times 10^{-3} / (4.0 \times 10^{-3} - 2.0 \times 10^{-3}) \times 4.1 = 1.1$, where 3.0×10^{-3} is the average for the two concentrations of stearic acid and 4.1 is the average oil volume. With 3-methyl-1-butanol the marginal efficiency is 0.53.

B. The Nature of the Oil Phase

A large number of other oils and surfactants were also studied using 4-methylcyclohexanol or 3-methyl-1-butanol as a cosurfactant. Table 1A and 1B show that maximum transmittance for each dispersion and the volume of alcohol

TABLE 1A

O/W Formulation---- Relation of Oil and Soap

Chain Length for 3-Methyl-1-Butanol at Maximum Transmittance

	K-Decanoate		K-Laurate		K-Myristate		K-Palmitate		K-Stearate	
	Vol.		Vol.		Vol.		Vol.		Vol.	
Oil	(ml)	% T	(ml)	% T	(ml)	% T	(ml)	% T	(ml)	% T
$-C_5$	0.6	98	0.8	99	0.6	96	0.9	90	1.8	85
$-C_6$	0.8	97	0.6	100	0.6	98	1.2	87	0.7	72
$-C_8$			1.3	87	1.0	94	0.8	92	1.3	86
$-C_{10}$			2.0	84	1.3	95	0.9	90	1.0	93
$-C_{12}$			2.2	30	1.4	97	1.2	87	1.15	95
$-C_{14}$					1.6	70	1.3	81	1.25	93
$-C_{16}$							1.6	76	1.11	93
CCl_4			1.2	88	1.2	38	0.9	97	1.1	100
$CHCl_3$			2.1	65	0.9	100	0.4	90	1.0	95
CH_2Cl_2			0.9	98	1.8	60				
C_6H_6			1.5	94	1.2	81				

TABLE IB

O/W Formulations - Relation of Oil and Soap

Chain Length for 4-Methylcyclohexanol at Maximum Transmittance

	K-Decanoate		K-Laurate		K-Myristate		K-Palmitate		K-Stearate	
	Vol.		Vol.		Vol.		Vol.		Vol.	
Oil	(ml)	% T	(ml)	% T	(ml)	% T	(ml)	% T	(ml)	% T
$-C_5$	0.5	70	0.6	85	0.4	94				
$-C_6$	1.1	94	0.4	99	1.0	80	0.9	88	0.9	62
$-C_8$	1.3	80	0.8	92	0.8	90	0.9	68	1.2	66
$-C_{10}$	1.8	56	1.0	90	0.9	93	1.0	50	1.1	54
$-C_{12}$			1.3	83	1.0	88	0.9	88	0.9	66
$-C_{14}$			1.5	80	1.1	89	0.9	85	0.8	89
$-C_{16}$					1.4	80	0.9	83	1.3	95
CCl_4										
$CHCl_3$										
CH_2Cl_2										
C_6H_6										
$C_6H_5CH_3$										

required to produce it. Arachidic and behenic acids were not used since they are not soluble at 30°C.

Photon correlation spectroscopy was used to measure particle size. This information was then related to transmittance measurements, and the amount of surfactant. Figure 5 plots measured particle size, maximum transmittance, and the volume of alcohol required to produce the maximum transmittance against the amount of surfactant used.

The results confirm the hypothesis, that the transmittance increases as the particle size decreases. That is, increased transmittance represents physical diminution of the dispersed phase droplets.

Three other points are also evident. First, increasing the amount of surfactant in the system decreases the particle size. Second, a larger amount of cosurfactant is required to produce maximum transparency. Third, a significant amount of surfactant must be added before the transmittance increases appreciably.

Sedimentation rate measurements of O/W systems provided insight into how the dispersed phase droplet changed size with changes in the system variables. Sedimentation constants were measured from the movement of the observed Schlieren peak with time. Table 2 presents the calculated sedimentation constants for a number of systems, calculated from (16,106,107)

$$S = \frac{M(1-\bar{V}d)}{Nf} \qquad (2)$$

TABLE 2

Sedimentation Constants of N-Hexadecane in Water

Experiment Number	Oil Volume (ml)	KOH Volume (ml)	Alcohol Volume (ml)	% T	S (sved.)
1	0.5	64	0.75	90	2.5
2	1.0	64	0.90	90	[illegible].1
3	2.0	64	1.10	91	18.7
4	3.0	64	1.20	78	32.5
5	1.0	32	0.75	92	3.1
6	1.0	48	0.85	96	5.0
7	1.0	64	0.90	94	7.8
8	1.0	80	1.10	94	8.1

Alcohol: 4-methylcyclohexanol

Surfactant: 2.0×10^{-3} moles K-stearate

Temperature: 25°C

where M is the average droplet molecular weight, $\bar{V}$ is the droplet partial specific volume, d is the continuous phase density, N is Avogadro's number, and f is the frictional coefficient. It was assumed that the particles were approximately spherical, and, therefore, the frictional coefficient(106, 107) is

$$f = 6\eta nr$$

where η is the viscosity coefficient of the medium and r is the droplet radius. The precision of these constants estimated from experiments 2 and 7 were about $\pm$ 8%.

2-3. Discussion

Several points can be seen in the results of the titration experiments. It has often been observed (e.g., (52, 126)) that a critical amount of cosurfactant is required before these dispersions become transparent. This is reemphasized in Figures 1 and 2.

Furthermore, transmittance maxima are observed in most cases. These transmittance mixima can be explained by the distribution of the cosurfactant. As the alcohol is added it partitions among the aqueous phase, oil phase, and interface (127). This dynamic process provides some of the energy to subdivide the dispersed phase. The distribution data (114) show that the aqueous phase is very quickly saturated with alcohols of five carbon atoms or greater. As the alcohol diffuses through the interphase and lowers the γ_i, 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. For W/O systems the excess of alcohol in the continuous phase will extract the soap from the interface. With less surfactant at the interface to stabilize the droplets, they will grow in size and the transmittance will fall.

The same effect is seen when the volume of the dispersed phase is increased and 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 falls (Figures 3 and 4). A given dispersed phase volume requires a critical amount of surfactant to form a transparent dispersion (Figure 5c).

All of the titration results (Table 1A, 1B and Figs. 1-5) show the specificity of the various components. For a given oil-surfactant pair, the steric requirements of the cosurfactant determine the volume of dispersed phase that can be stabilized (Figs. 3 and 4).

The surfactant type also plays a significant role in determining whether a transparent system will form (52). As shown in Tables 1A and 1B, as the chain length of the surfactant increases, dispersions with significant transmittance can be formed with oils of longer chain length.

Surfactant type, cosurfactant type, and the nature of the oil phase are three of the interacting variables that

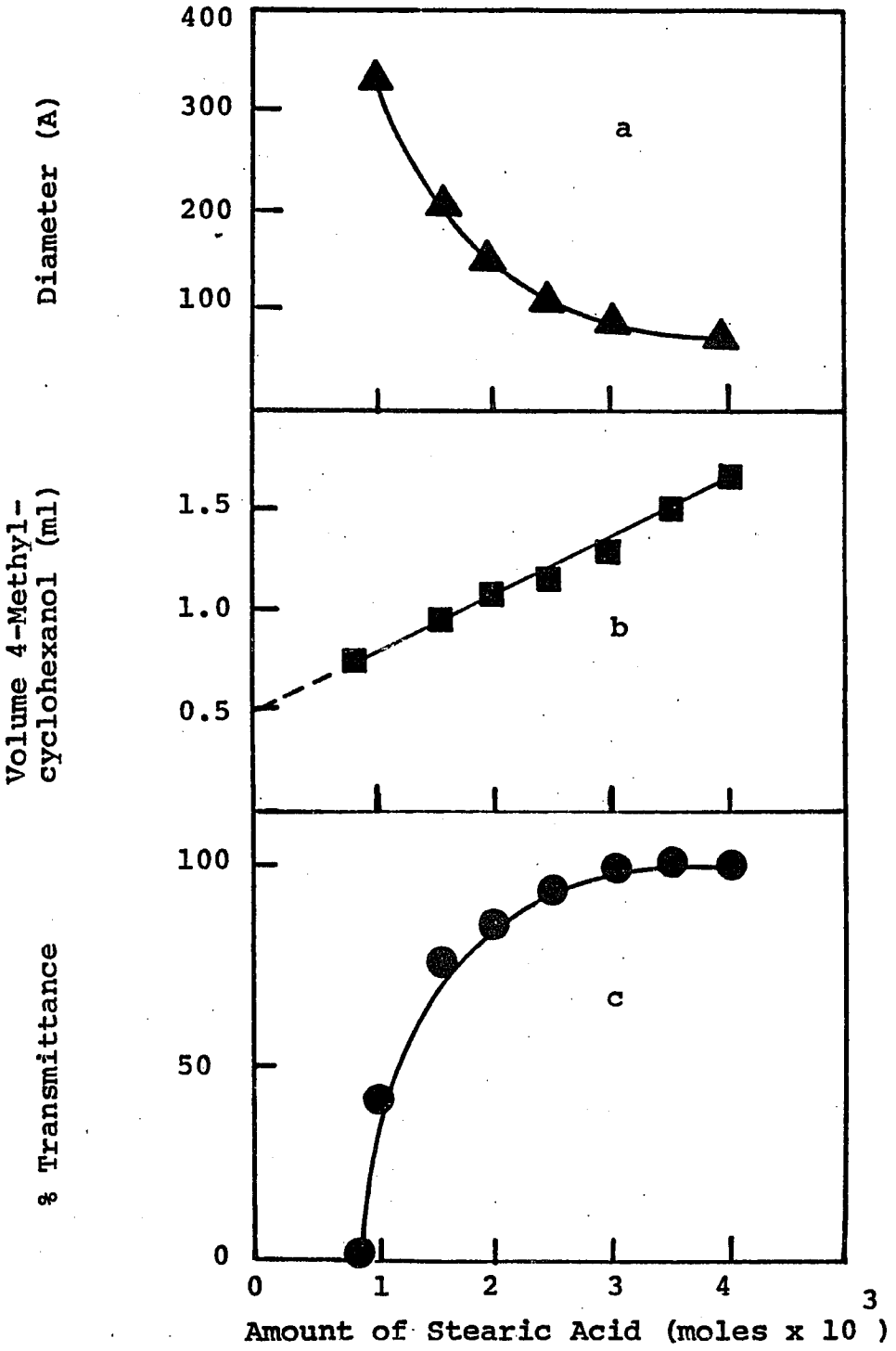

Figure 5. Three of the Variables Dependent on the Amount of Surfactant.

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 resultant dispersion (94).

When preparing microemulsions by the titration method, various physical changes are often noted. Sometimes, there are dramatic increases in viscosity just before the mixture becomes transparent. Also, the mixture may progress from lactescent to clear rapidly or slowly as drops of cosurfactant are added. These effects are probably related to the rate of alcohol diffusion between phases.

While the alcohol does diffuse through the interface (62), some remains there (68) in weak association with the surfactant molecules. The amount that remains at the interface can be estimated. It is different for each system and also changes with the manner of preparation (69). Thus, it is path dependent. For the system depicted in Fig. 5b, it was determined from the slope that about two molecules of 4-methylcyclohexanol remain at the interface for every molecule of surfactant. To calculate this, the assumption is made that all of the surfactant is at the interface. In addition, the incremental amount of alcohol required for each additional increment of surfactant (slope of 5b) is also at the interface.

Surfactant and cosurfactant maintain a definite configuration at the interface with a given cross-sectional

area. This area can be calculated from the measured droplet size if it is assumed that all of the surfactant resides at the interface and the droplets are spherical. With these assumptions the cross-sectional area per surfactant molecule (σ) is calculated by $\sigma = 3V/nr$ (103), where V is the droplet volume, n is the number of surfactant molecules, and r is the radius of the droplet. The results are shown in Fig. 6.

More explicitly, parameter V was taken as the sum of the volume of oil, surfactant, and alcohol in the dispersed phase. The amount of alcohol in the dispersed phase was calculated from the titration curve in Fig. 5b. That is, the intercept gives the amount in the continuous phase. The difference from the total alcohol gives the amount in the dispersed phase.

Figure 6 shows that the apparent interfacial molecular area increases as the droplet diameter of the dispersed phase decreases. The area per molecule changes considerably at small diameters. As the droplet sizes varied from 80 Å to 350 Å in diameter, the surfactant cross-sectional area was calculated to be approximately 56 Å^2 to 95 Å^2 per molecule. This could imply that the cosurfactant molecules were incorporated with surfactant molecules at the O/W interface.

Further insight into the molecule configuration at the interface can be deduced from the sedimentation data, Table 2. For a spherical droplet S in Equation (2) is proportional to M (16,105), since M is proportional to r^3. The ratio

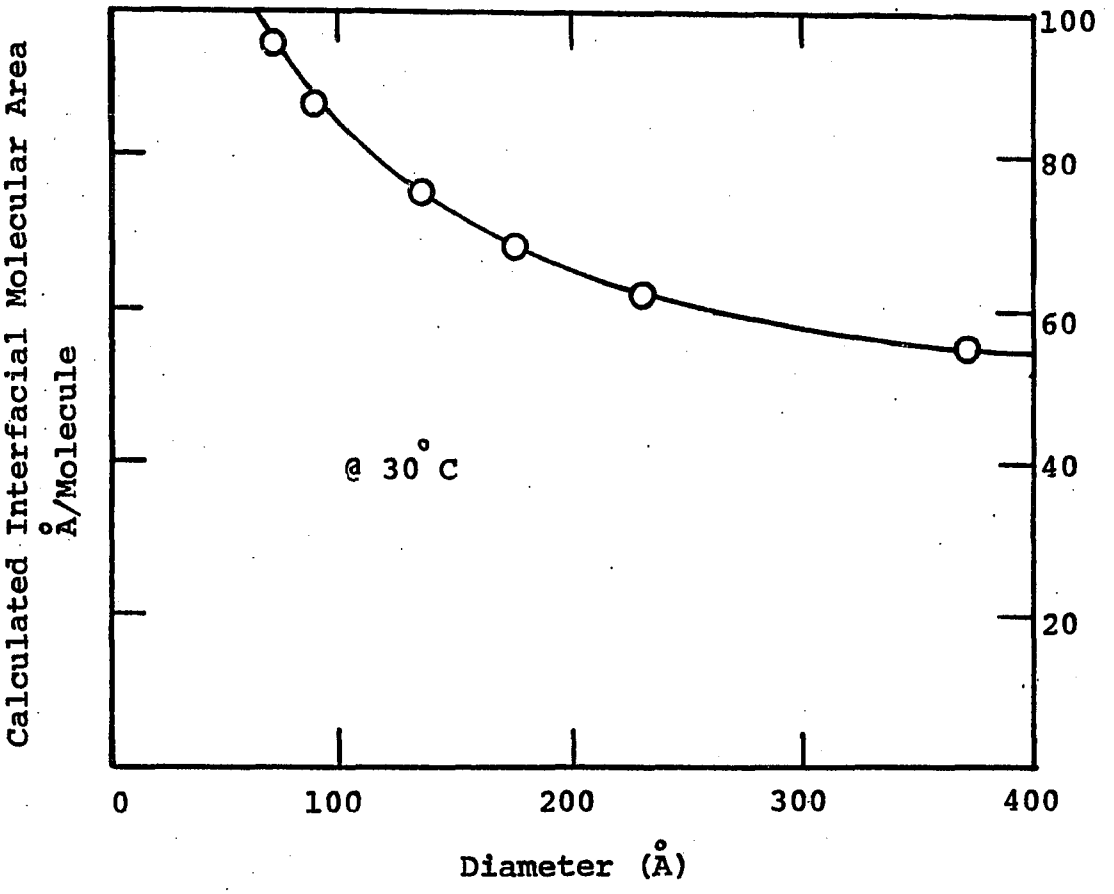

Figure 6. Calculated Interfacial Molecular Area as a Function of the Dispersed Phase Droplet Diameter for the System in Figure 5.

of the total interfacial areas is then given by (16,105)

$$\frac{A_1}{A_2} = \frac{V_1}{V_2} \cdot \frac{S_2}{S_1} \cdot \left(\frac{1-\bar{V}_1 d}{1-\bar{V}_2 d} \right)^{1/2} \qquad (4)$$

where V includes the volume of n-hexadecane, surfactant, and alcohol. The volume of alcohol in the dispersed is estimated from the extrapolated volumes in experiments 1,2,3, and 4. The difference between the total amount of alcohol and the amount in the dispersed phase gave the amount in the continuous phase. The average of the ratios was found to be 1.0 ± 0.3. This indicates that a fixed amount of surfactant will cover only a constant total interfacial area. Within this constraint, a change in dispersed phase volume will cause the droplets to swell, shrink, or change in number. A similar result had been found previously for W/O micro-emulsions (16).

CHAPTER 3

THE INTERFACIAL STOICHIOMETRY AND THE STABILITY OF MICROEMULSIONS

There has been discussion in the literature about nomenclature for transparent dispersions (e.g., (68,83,96, 111)). The arguments are not purely semantic. The discussions relate to the fundamental stability of the system (78,112), i.e., whether a given system is thermodynamically stable or not. In one case the system has properties typical of a solution of an association colloid (78,83), and the order of mixing the components is dependent of the final formulation, this system is considered as thermodynamically stable "swollen micelle". In another type, the resultant system depends on the method of preparation (68,69), this system is regarded as kinetically stable (or meta-stable) "microemulsions".

Several investigations (68,78) have shown that transparent dispersions of oil and water can be inherently thermodynamically or kinetically stable. Most recently Friberg and Miroslava (111) have characterized the two types of stability using a phase diagram approach. Shah et al. (13) on the other hand 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 that of the surfactant. This may be unnecessary and an arbitrary division if both are thermodynamically stable.

Since the long-term stabilities of the formulations studies here were not determined, such a distinction can't be made for these systems. It is assumed in this work that most systems with transmittance below 90% are thermodynamically unstable. This is, stability is linked to the size of the dispersed droplets, which is determined by the free energy balance in the system.

In this chapter, the effect of method of preparation (e.g., order of mixing of components) on the formation of microemulsions, the surfactant/cosurfactant interfacial stoichiometry, and the structure of the O/W interface are discussed. Finally, the stability of the transparent system, oil/soap/alcohol/water, is proposed.

3-1. Experimental

Microemulsion Preparation

The same "titration method" (as in Chapter 2) was used to prepare microemulsions (66,69,105). An oil/surfactant mixture is added to the water phase to form a coarse macroemulsion. This system is then titrated to clarity with a second surfactant. The rationale behind this method or preparation is to obtain the optimum interfacial condition that will produce a transitory condition of low interfacial tension during which the system is further dispersed. Titrations were done in a 100 ml thermostated (water Jacketed) flask with a magnetic stirrer. When possible, the cosurfactant is titrated using a buret.

The second method used to prepare microemulsions was to predistribute the cosurfactant between the oil and aqueous phases. That is, a portion of the cosurfactant was dissolved in the aqueous phase and a portion was dissolved in the oil phase before the oil and aqueous phases were mixed together.

At constant temperature, surfactant type and the nature of the oil and water phases are all interacting variables which determine the size of the dispersed phase droplets and ultimately the stabilty of the system. The general formulation used in this study was: 2.0×10^{-3} moles of a long chain fatty acid, 2 ml of oil and 16.0 ml of 0.375 N KOH at 30°C.

Note that the KOH concentration is based on the amount required to neutralize the fatty acid.

The clarity of the dispersions were based on transmittance measurements using a Bausch and Lomb Spectronic 20.

3-2. Results

(1) Titration Method (66,105):

Two ml of a 1 M solution of lauric acid in n-decane (2×10^{-3} moles of lauric acid in 2 ml of n-decane) was added to 16 ml of 0.375 N KOH. The temperature was maintained at 30°C during the saponifaication reaction. This macroemulsion was then titrated with 4-methylcyclohexanol (MCH). A clear dispersion having 95% transmittance at 520 nm formed after adding 1.0 ml of trans MCH. The pure cis isomer didn't

produce a clear system.

(2) Predistribution Method (114):

In another set of experiments, 1.0 ml of MCH was predistributed between the aqueous phase and oil phase. The total amount of alcohol was kept at 1.0 ml. A clear system (transmittance between 89 and 93%) resulted for every combination tried within 10 to 15 minutes of stirring when the oil contained the lauric acid as described above. However, if the 16 ml of aqueous solution initially contained the lauric acid (2×10^{-3} moles), the results were quite different as shown in Table 3. Two of the combinations, 1.0 ml of alcohol in decane and 0.2 ml in the aqueous solution with 0.8 ml in decane, didn't produce a clear system after two days of stirring.

Similar results were also obtained when n-hexadecane was substituted for n-decane as the oil phase and 1-pentanol was the cosurfactant (instead of MCH). In this case, however, the distribution appears even more critical since the only system to clear was the one in which all the 1-pentanol was placed in the aqueous phase (Table 4).

This last system was studied (using titration method) further by monitoring the transmittance of the emulsion as 1-pentanol was added to it. Two milliliters of a hot stearic acid in n-hexadecane solution was added to 16 ml of 0.375 N KOH in a thermostated vessel at 30°C. It was necessary to heat the n-hexadecane to dissolve the stearic

TABLE 3

Transmittance of Emulsions for Predistribution Experiments with Lauric Acid in Water and N-decane as the Oil Phase

VOLUME MCH (ml)		% Trans. @ 520 nm	Time
Aqueous Phase	Oil Phase		
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

2×10^{-3} Mole Lauric Acid in 16 ml 0.375 N KOH Added to 2 ml N-decane Titrated to 90% Transmittance with 1 ml 4-Methylcyclohexanol (MCH) at 30° C.

TABLE 4

Transmittance of Emulsions for Predistribution Experiments with Stearic Acid in N-hexadecane

Volume 1-Pentanol (ml)		% Trans. @ 520 nm	Time
Aqueous Phase	Oil Phase		
1.0	0	87	5 minutes
.8	.2	cloudy	
.5	.5	"	
.2	.8	"	
.0	1.0	"	

2×10^{-3} Mole 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.

acid. Three different concentrations of stearic acid in n-hexadecane were used: 1, 1.5 and 2 M (2×10^{-3}, 3×10^{-3}, and 4×10^{-3} moles of stearic acid in 2 ml of n-hexadecane, respectively.) The transmittance of the emulsion increased abruptly after a certain amount of 1-pentanol was added to it. A maximum in the transmittance was reached. As shown in Figure 7, the width of the transmittance curve and position of the initial increase are dependent on the amount of stearic acid present.

Figure 8 shows the relationship between the volume of alcohol and the concentration of stearic acid for the first and last clear (transmittance $\geq$ 90%) points for the titration curves in Figure 7. Additional concentrations of stearic acid were used to fill out the curves. The curve for the initial clear point is linear but the curve for the final clear point is parabolic. The shape of these functions is related to ways in which the alcohol is distributed between the bulk phases and the interfacial phase.

The curve for the initial clear point can be extrapolated to zero concentration of stearic acid. The intercept indicates the value of 1-pentanol distributed between the oil and aqueous phase. These titrations were repeated for different volumes of n-hexadecane. The intercepts for the initial clear point curves are graphed in Figure 9. As expected the y-intercept (1.5% by weight) is somewhat lower

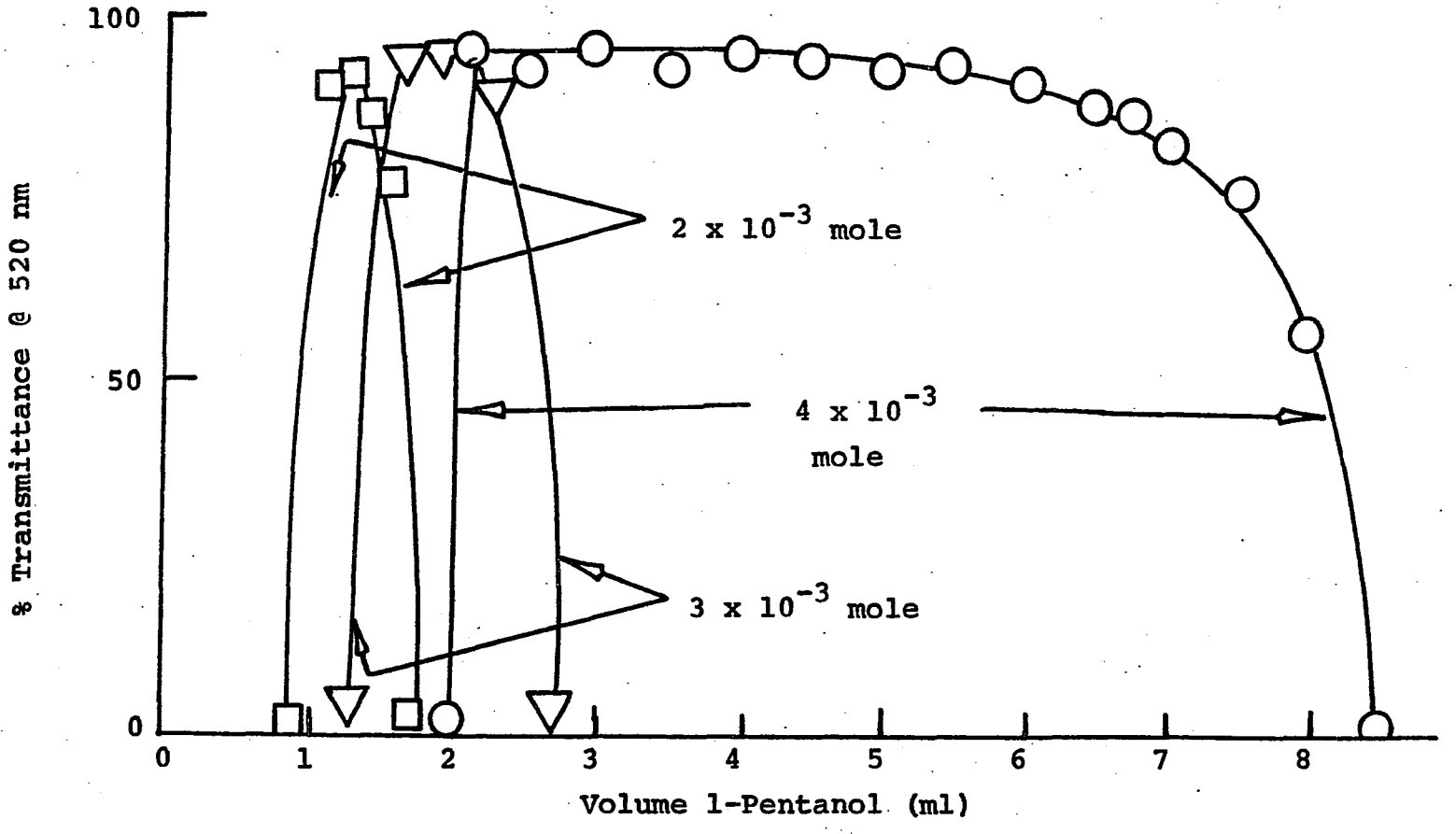

Figure 7. O/W Microemulsions: 2 ml N-hexadecane, 16 ml 0.375 N KOH, Various Amount of Stearic Acid; Titrated with 1-Pentanol at 30°C.

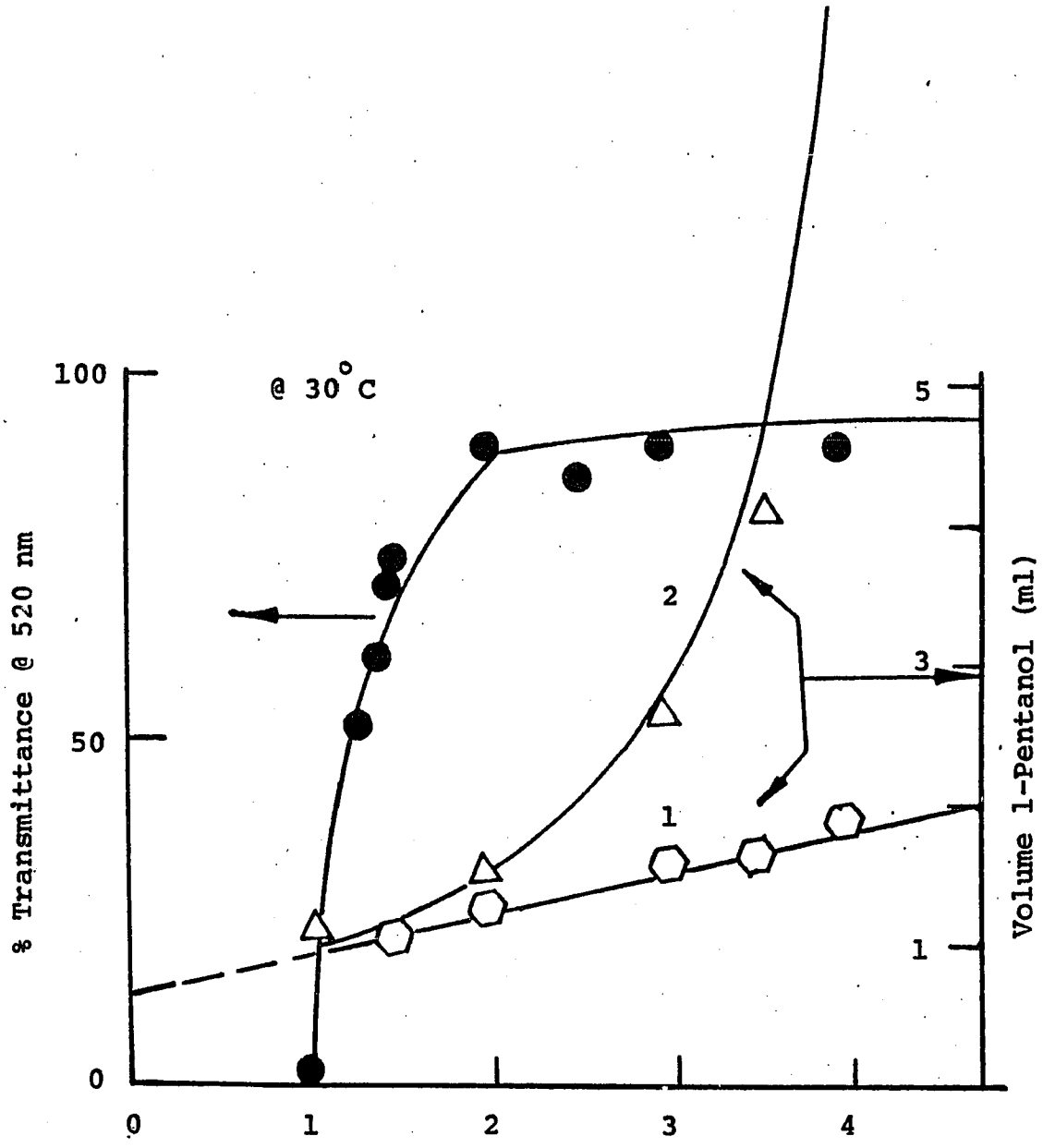

Figure 8. O/W Microemulsions:
N-hexadecane/K-stearate/1-Pentanol/Water
Curve 1: the Amount of 1-Pentanol Required at Initial Point of Clearing
Curve 2: the Amount of 1-Pentanol Required at Last Point of Clearing

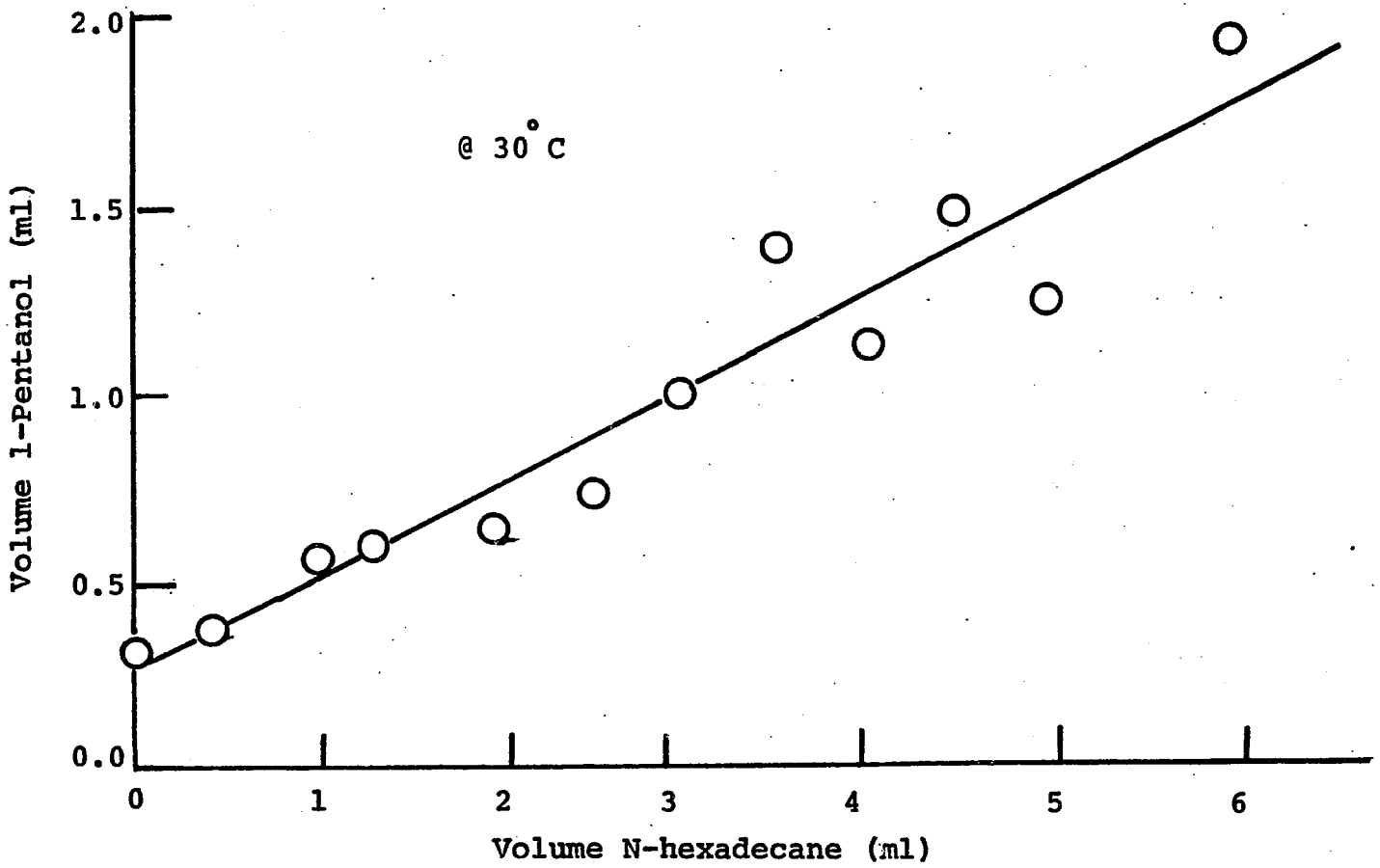

Figure 9. O/W Microemulsions: N-hexadecane/K-stearate/1-Pentanol/Water The Amount of 1-Pentanol Distributed between N-hexadecane and Water Phases in the Absence of K-stearate at the O/W Interface.

than the value for the solubility of 1-pentanol of water at 30°C (2.09% by weight). This is due to the dissolved KOH in the aqueous phase, which lowers the solubility of 1-pentanol.

Figure 10 shows the ratio of 1-pentanol of stearic acid versus the volume of n-hexadecane at the initial clear point for the titrations. The curve bends sharply upward above 4 ml of n-hexadecane. This is probably related to a change in the structure of the system.

Figure 11 indicates the distribution of alcohol at the O/W interface and the maximum percent transmittance at various oil concentrations (refer to Figure 7).

3-3. Discussion

A. The Method of Preparation and the Stability of Microemulsions

The results presented above show that the methods used to combine components can control the properties of the dispersion. This path dependence is analogous to the behavior of ordinary coarse emulsions. These observations, along with the previously noted separation of a transparent dispersion over a long time period (113), these indicate that in some cases transparent dispersions are inherently metastable systems. The mixtures studied in this investigation fit this description.

Microemulsions are more readily formed if the acid is initially in the oil phase. It is speculated that the finer

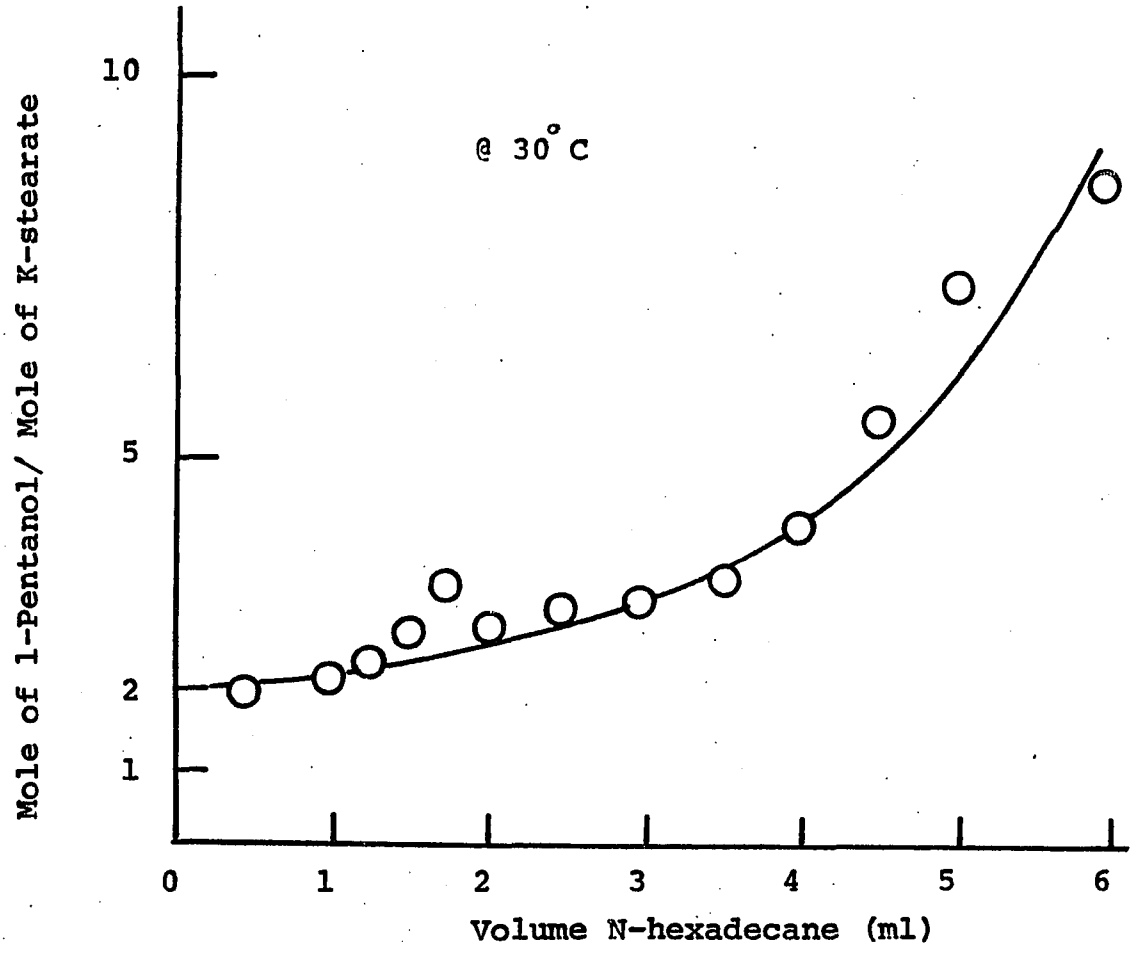

Figure 10. O/W Microemulsions:
N-hexadecane/K-stearate/1-Pentanol/Water
Molar Ratio of 1-Pentanol/K-stearate at the O/W Interface at Various Concentrations of N-hexadecane.

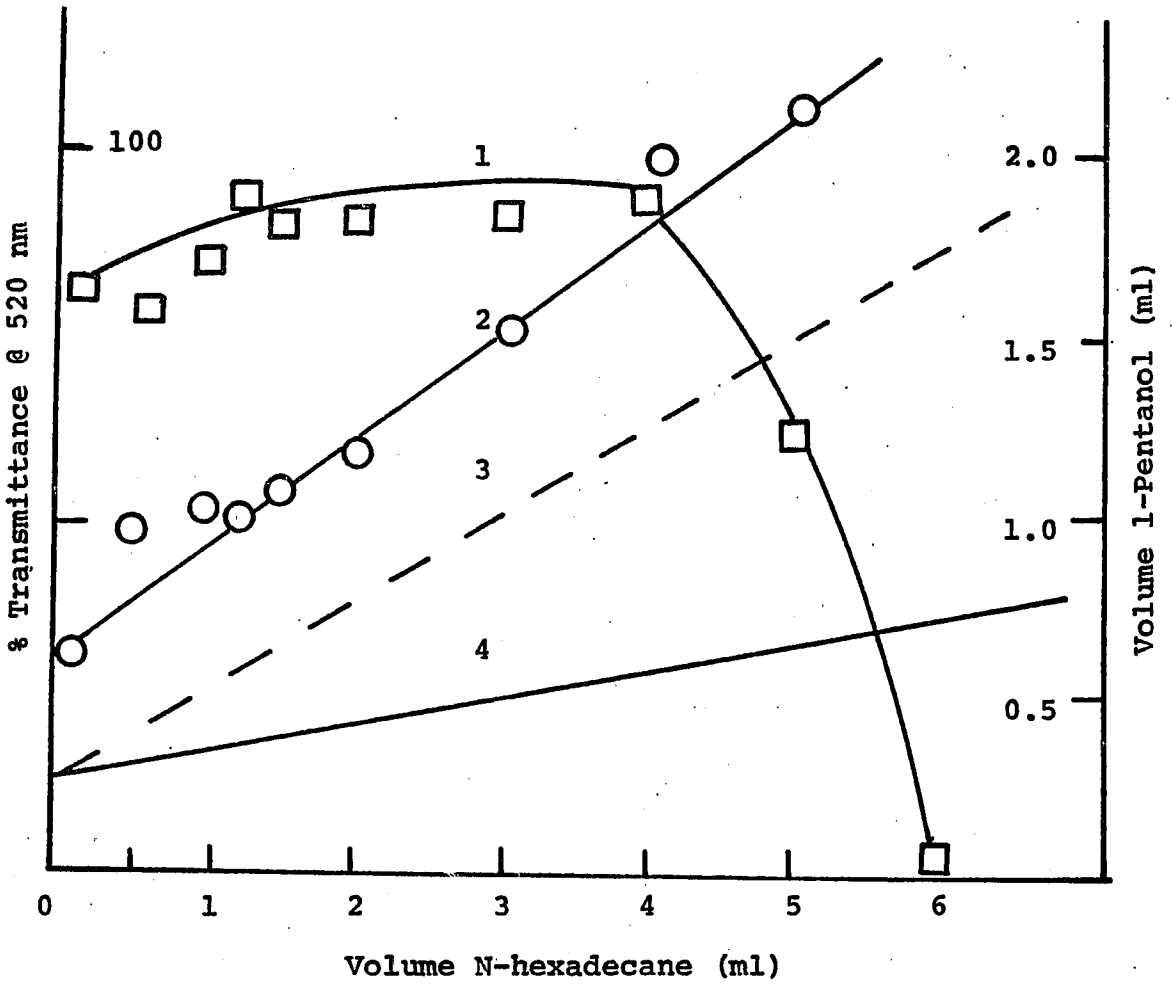

Figure 11. O/W Microemulsions:
N-hexadecane/K-stearate/1-Pentanol/Water
Curve 1: % Transmittance
Line 2: Volume of 1-Pentanol Corresponding to the Transmittance Point Plotted on Curve 1.
Line 3: Volume of 1-Pentanol Distributed between the Oil and Aqueous Phases When No Soap is Present
Line 4: Volume of 1-Pentanol at the Interface (i.e., the Difference between Curves 2 & 3).

emulsion produced by the interfacial turbulence, which in turn is caused by in-situ saponification, aids in forming the microemulsion. This is supported by the predistribution experiments. If the cosurfactant is initially in the aqueous phase, there is a potential gradient causing the alcohol to move into the interior of the oil droplet and to the interface. Interfacial tension measurements showed that this transfer can cause a temporary decrease in interfacial tension (114). Due to the lower interfacial tension and perhaps the interfacial turbulence, the droplets can break up and form the microemulsion. This process is naturally aided by small initial emulsion droplets.

B. Interfacial Configuration

The structure of the O/W interface may play a role in the formation of microemulsions. The surfactant must be able to stabilize the droplets against coagulation and coalescence after the cosurfactant has lowered the interfacial tension sufficiently to cause dispersion. The ability of a surfactant to accomplish this depends upon the type of interfacial film it forms with the cosurfactant and oil.

Figure 9 and 10, which were derived from the initial clear point titration curve in Figure 8, give some indication of what is occurring in the microemulsion droplet. The intercept (Figure 9) at a zero volume of oil is the amount of alcohol dissolved in the microemulsion droplet. The slope of this graph shows that the ratio of 1-pentanol to oil in the

microemulsion droplet is constant. If we assume the slope of the titration curve (Figure 10) at a given oil volume is related to the amount of surfactant and cosurfactant at the interface. It is seen that an abrupt change occurs at approximately 4.5 ml of n-hexadecane.

In the previous sedimentation study, the total interfacial area of oil droplets in an O/W microemulsion was shown to be relatively constant for small changes in the volume of oil dispersed.

The ratio of area on changing the volume of oil dispersed or the volume of the dispersing medium was 1.0 ± 0.3. The ratio of 1-pentanol of K-stearate, if it is all at the interface, determines the total interfacial area (A). Below 4.5 ml, the change in the ratio 1-pentanol to K-stearate, and therefore A, is small. For example, $A_2/A_{0.5}$ is 1.25. This agrees with range of values determined from the sedimentation studies. However, above 4.5 ml the dramatic changes in the interfacial area increase (Figure 10) and in the percent transmittance decrease (Figure 11) may imply the systems are no longer microemulsions.

Figure 11 provides some information of the alcohol (cosurfactant) present at the interface of the hexadecane/K-stearate/KOH dispersion, the volume of alcohol corresponding to the sudden increase in percent transmittance (curve 2).

If 80% transmittance is considered the minimum acceptable clarity for this microemulsion system (Figure 11, curve 1), then the molar ratio of cosurfactant/surfactant at the O/W interface of this microemulsion (Figure 10) ranged from 2:1 to 5:1 as the concentration of oil was varied from 0.5 ml to 4.5 ml. Below or above these molar ratio ranges microemulsions could not be formed.

Curve 2 on Figure 11 represents each volumes of 1-pentanol corresponding to the transmittance points plotted on Curve 1. Curve 2 corresponds to the total volume of alcohol distributed in the oil, aqueous phases and the oil/water interface.

Curve 3 on Figure 11 is in fact, Figure 9 and represents the volume of 1-pentanol distributed between the oil and aqueous phases when no soap is present. Curve 4 of Figure 11 is the difference between Curve 2 and 3 or, the volume of 1-pentanol at the interface.

From these experiments, it was found that the proper structure of the O/W interface is very important in the formation of this microemulsion system.

It is therefore, concluded that some microemulsion systems are "path-dependent" or "meta-stable", they can not be formulated unless the right order of mixing, the proper concentrations of all the components, and the appropriate structure at the O/W interface have been reached.

CHAPTER 4

THE MECHANISM OF MICROEMULSION FORMATION

The chemical literature contains several studies on the transfer of surface active agents across a liquid-liquid interface (11,28,115,116,118,119). In 1971, England and Berg (119) determined the dynamic interfacial tension of oil-water systems using a laminar contracting liquid jet technique. Their data indicate the presence of a small desorption barrier to the transfer of normal and isobutyric acids from oil to water and a large desorption barrier for 1,5 pentanediol. For example the desorption rate constants were estimated from the data to be on the order of 4 to 5 sec^{-1} for isobutyric acid transferring from oil to water. The adsorption rate constants for transfer in the opposite direction are apparently greater than 100 sec^{-1}. In the case of 1,5 pentanediol the variation of interfacial tension with time (> 10 sec) lasted much longer indicating a large energy barrier. This transfer of an adsorbing solute across a liquid-liquid interface must take into account: (1) the effect of molecular diffusion in both bulk phases, and (2) adsorptive accumulation at the interface, and (3) energy barriers to adsorption and/or desorption. While the adsorptive accumulation affects the transfer rate negligibly, 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. Berg's work even predicted that the interfacial tension minimum would be sufficiently low that a slight agitation would result in spontaneous emulsification. These conclusions are in accord with the interpretation (31) that the presence of an adsorbed monolayer greatly reduces the rate of transfer of 1-pentanol into n-hexadecane when injected into the aqueous phase.

England and Berg (119) proposed analytical solutions for the transfer of an adsorbing solute across a liquid-liquid interface. Unfortunately, no simple relationship between interfacial tension and actual transferring solute concentration exists, especially, in the presence of an adsorbed film at the O/W interface. So, this limits the applicability of England and Berg mathematical model. Recently, Rubin and Radke (117), studied the dynamic interfacial tension minima for acidic organic phases contacting an alkaline aqueous phase using the rotating drop method. Again, the difficulty of correlating interfacial tension with actual amount of solute involved in the transfer limits their mathematical analysis. A third study by Hutchinson (120), provids information on the diffusion of various alcohols from water into benzene across the benzene-water interface. The retarding effect of films of surface active materials on the diffusion

was suggested. Interfacial tension measurement of the various systems led Hutchinson (120) to hypothesize that interaction in the film is responsible for the retardation of the transfer of the alcohols. Up to now, the transfer of surfactant through the liquid-liquid interface has mainly been studied by determining the variation of interfacial tension vs. time following addition of the transferring agent to the system. Unfortunately, the interfacial tension only provides a measure of the overall change in interfacial free energy and doesn't give the actual amount of material transferring with time. Consequently the results found in the literature may be considered only as semiquantitative. In the present studies the amount of short chain alcohol passing through an O/W interface in the absence and presence of an adsorbed film has been determined directly.

The diffusion of cosurfactant from aqueous phase into oil phase in the presence and absence of a soap film at the O/W interface was investigated by gas chromatography. The system studied consists an oil phase on top of an aqueous phase. In these experiments,the bulk concentration remains essentially homogeneous because of stirring in both aqueous and oil phases.

Ficks' Law gives the flux density

$$F = D \Delta C$$

where D is the diffusion coefficient and ΔC is the grad of the concentration of the diffusing species. D is of the order of $10^{-5} cm^2/sec$ in most liquid systems (86). In these

experiments, because of stirring , the thickness of the water/oil interface must be very thin.

Schulman and Teorell (87) estimated the thickness of water bound under a moving monolayer to be 30 μ; moreover, the thickness of the unstirred film at the surface of a solid ion-exchange membrane increases from 1 to 30 μ as stirring is decreased. Mibashan-Sharaga (89), after studying the desorption of a lauric acid monolayer spread on a 0.01 M HCL solution, estimated a quiet zone of 800 μ just under the film. Rosano (90) studied the mechanism of water transport through nonaqueous liquid membranes separating two stirred aqueous solutions. The diffusion layer at a 1-pentanol-water interface was estimated to be of the order of 150 μ. In the present study it is suggested that the thickness of oil-water interface is probably of the order of 100 μ.

In this experiment 0.8 ml 1-pentanol are dissolved in 64 ml 0.375 N KOH and allowed to diffuse through a 23.8 cm^2 oil/water interface. Initially the 1-pentanol concentration in the water phase (64 ml) is 74 x 10^{-4} mole (or 115 mM/1) and zero in the n-hexadecane phase.

The concentration gradient (grad C) is the driving force for diffusion. Since by Fick's Law

$$\text{(total flux)} = F \times A \text{ (interfacial area)} =$$

$$D \times (\Delta C/h) \times A \qquad (5)$$

Thus the estimated initial resulting flux = 3600 sec/hr x 10^{-5} cm^2/sec x (74 x 10^{-4} mole/64 cm^3) x (23.8 cm^2/h cm) = 9.9/h x 10^{-5} mole/hr.

The actural rate that was observed for 1-pentanol diffusion from water to n-hexadecane at 30°C is 16.6 x 10^{-4} moles/hr., and in presence of K-stearate: 6.6 x 10^{-4} mole/hr.

From the discussion above it is hypothesized that the thickness of the O/W interface is of the order of 100 μ. Using this value in equation 5, the rate of transfer would be 99 x 10^{-4} mole/hr., which is much larger than the actual observed rates, especially in the presence of an adsorbed film. Consequently, the diffusion in these concentration interface layers is not the only rate determining factor. This conclusion could be understood since 1-pentanol is a surface active molecule adsorbing preferentially at an O/W interface. The system studied consists of an oil phase (2) on top of an aqueous phase (1).

The change of number of moles of 1-pentanol leaving

phase (1) into phase (2) is

$$\phi = \frac{d(V_2C_2)}{dt} = \frac{-d(V_1C_1)}{dt} \tag{6}$$

but $V_1 = V_2 = V$, and

$$\text{the flux } (\phi) = AKP_{ow}(C_1 - C_2) \tag{7}$$

moreover the total amount of 1-pentanol is constant and

$$V(C_1 + C_2) + V_iC_i = C^* V \tag{8}$$

V_i is very small and V_iC_i is negligible, therefore, $C_1 + C_2 = C^*$, and substitute into equations 6 and 7, then

$$\frac{dC_2}{dt} = \frac{AP_{ow}K}{V} (C^* - 2C_2) \tag{9}$$

For the initial condition $t = 0$, $C_2 = 0$ then

$$C_2 = \frac{C^*}{2} [1 - \exp.(\frac{-2AP_{ow}Kt}{V})] \tag{10}$$

or

$$C^* - 2C_2 = \exp.(\frac{-2AP_{ow}K}{V})t \tag{11}$$

By plotting $\ln(C^* - 2C_2)$ vs. t, the slope equals $\frac{-2AP_{ow}K}{V}$

Where $A = 23.8$ cm^2, $V = 64$ cc.

The experimental values of K at various temperatures were plotted on a semilogarithmic graph, and the values of activation energy E were obtained by analyzing the slopes of these plots.

4-1. Experimental

A. The Cell

A 250 ml thermostated glass cell with a cross sectional area of 23.8 cm^2 was used. A glass stirrer with two sets of blades 3 cm apart was utilized. At 40 rpm the interface was not disturbed.

B. Solutions

Soultion 1: 0.8 ml 1-pentanol was dissolved in 64 ml 0.375 N KOH. Solution 2: 4×10^{-5} mole stearic acid, 7.4×10^{-3} mole 1-pentanol in 64 ml 0.375 N KOH

C. Systems

64 ml n-hexadecane were poured gently on top of the solution 1, the stirrer was set to 40 rpm and a timer started. The n-hexadecane phase was analyzed for 1-pentanol content, following procedures (D) and (E), over a 3.5 hour time span.

D. 1-Pentanol Analysis

100 µl of n-hexadecane phase was dissolved in 0.5 ml ethyl ether and 2 µ l of the ether solution were injected into a G. C.

E. Gas Chromatography Analysis

The instrument used was a Hewlett Packard Model 5721A, a single column instrument with a flame ionization detector. A 6 ft x 0.125" OD Tenax Porous Polymers with 60-80 Mesh column was operated at 150°C.

4-2. Results

The amount of 1-pentanol transferring from the aqueous phase into the n-hexadecane phase (for solution 1/n-hexadecane and solution 2/n-hexadecane systems) was monitored at various temperatures. A net retardation effect on the rate of transfer of 1-pentanol due to the presence of an adsorbed film of K-stearate at the O/W interface was noticed, as indicated in Fig. 12, the concentrations of the equilibrium distribution of 1-pentanol between n-hexadecane (64 ml) and 0.375 N KOH (64 ml) were also determined at various temperatures and the partition distirbution coefficients were calculated and tabulated in Table 5.

Also listed in Table 5 are the rate constant of transfer (K) calculated from equation

$$C_2 = \frac{C^*}{2} \left[1 - \exp. \left(\frac{-2AP_{ow}K}{V} \right) t \right]$$

Since K is a rate transfer constant, an Arrhenius plot may be applied. lnK vs. 1/T is plotted in Figure 13. Activation energies were calculated to be 2.1 Kcal/mole with no K-stearate present and 11.4 Kcal/mole in the presence of soap.

4-3. Discussion

The application of the concept of energy of activation for values less than 5 Kcal/mole probably loses its meaning. The process of transfer of 1-pentanol from aqueous phase to

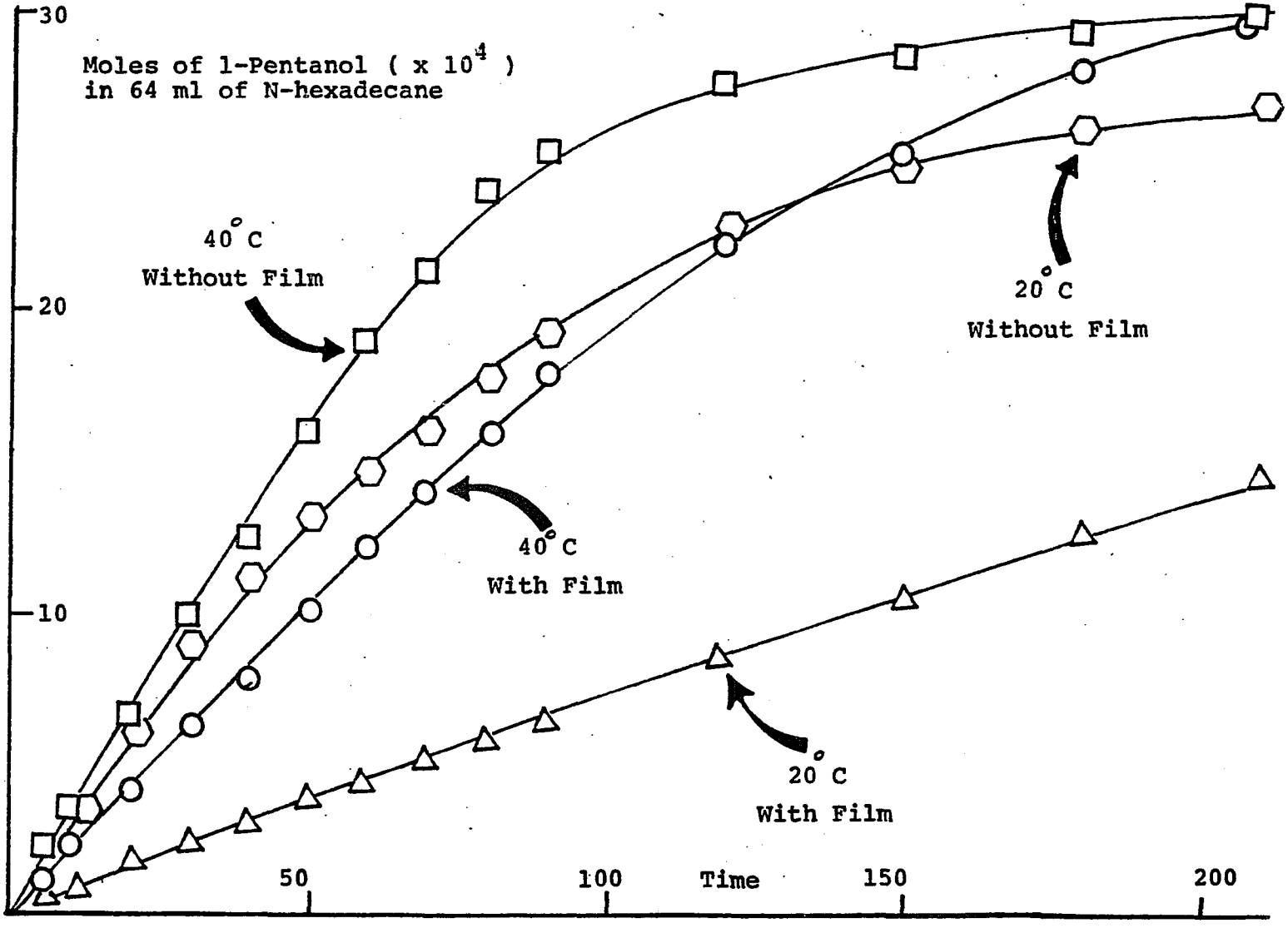

Figure 12. Concentration of 1-Pentanol in N-hexadecane versus Time (Minutes)

TABLE 5

Rate Constants of 1-pentanol Diffusing from KOH Solution into N-Hexadecane Phase in the Presence and Absence of K-Stearate Film at the O/W Interface

			WITHOUT FILM		WITH FILM	
T (C)	$1/T \times 10^3$ (K^{-1})	P_{ow}	-slope x 10^3 ÷2.303 (min^{-1})	K x 10^3 (cm. min^{-1})	-slope x 10^3 ÷2.303 (min^{-1})	K x 10^3 (cm. min^{-1})
40.00	3.195	1.040	3.744	11.145	3.487	10.382
35.00	3.247	1.028	3.376	10.166	2.441	7.351
30.00	3.300	1.020	3.092	9.385	1.903	5.775
25.00	3.336	1.000	2.964	9.177	1.264	3.912
20.00	3.413	0.976	2.789	8.846	0.974	3.089

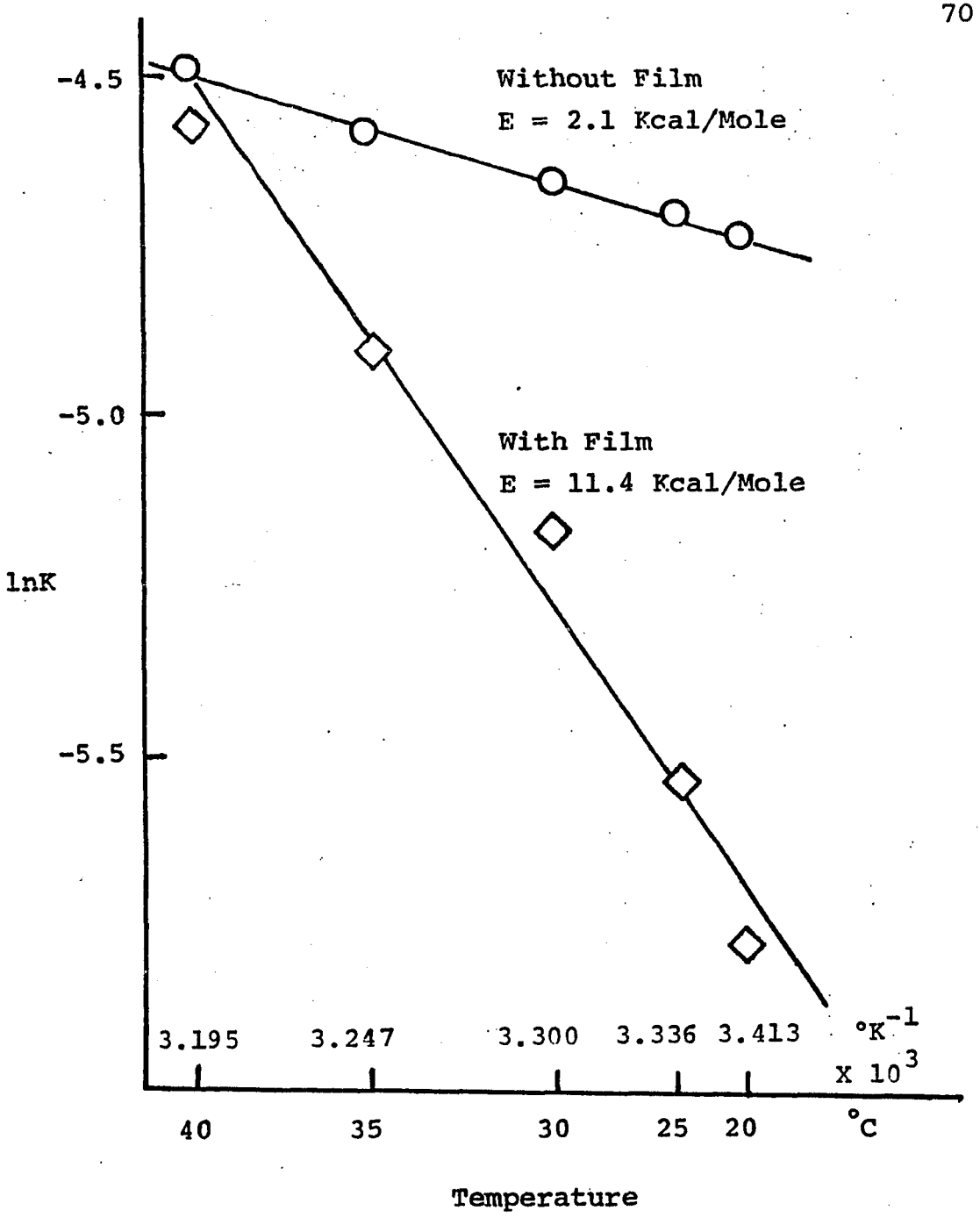

Figure 13. Temperature v.s. Diffusion Rate Constant of 1-pentanol in the Presence and Absence of K-stearate Film

oil phase in the absence of an adsorbed film may be regarded simply as an adsorption-diffusion process through a thin unstirred interfacial liquid layer. In the case of an adsorbed film at the oil/water interface, the situation may be equivalent to the retardation of water evaporation due to the presence of a monolayer of a condensed alkyl alcohol, or fatty acid film on the surface of the water. An activation energy is necessary to remove the water molecule from the interface in the presence of an array of orientated hydroxyl groups attached to the film forming molecules. In the case of pentadecylic acid this has been calculated to be of the order of 11 Kcal for the polar end of the molecule (108). In this work, the activation energy (11 Kacl/mole) may be related to the energy required by the diffusing 1-pentanol molecules to push apart the adsorbed soap molecules at the interface in addition to the energy for the diffusion through the liquid interphase.

These adsorbed soap molecules have a high permanent dipole moment. Dipole-dipole interaction and van der Waals forces are operative in the formation of soap-alcohol mixed films.These transitory retardation of oriented 1-pentanol molecule at the oil-water interface in the presence of an adsorbed soap film may explain how extremely low interfacial tensions may be achieved.

The stirring of the two phases is important in the mechanism of transfer discussed in this work. This makes

the system equivalent to a very thin membrane in which the activation energy found for the 1-pentanol migration corresponds to the energy barrier on taking a hydrated 1-pentanol molecule from the aqueous into the oil phase. It is because of this high activation energy which keeps the 1-pentanol molecules stay at the O/W interface and reduces the interfacial tension.

CHAPTER 5

CONCLUSIONS

A close analysis of the author's data has resulted in two conlusions, which leads to a proposal for the driving mechanism responsible for microemulsification.

The first conclusion, that some microemulsion systems are not thermodynamically stable, was based on the observation that the formation of these systems were path dependent (i.e,. the order of mixing of components affected the formation of microemulsions.)

The second conclusion, which suggests that the driving force for microemulsification results from an association of the surfactant and cosurfactant at the interface, is supported by the following abservations. A significant difference is observed in the energy of activation for the diffusion of 1-pentanol from 0.375 N KOH solution into n-hexadecane in the presence and absence of K-stearate film at the interface, i.e. 11.4 kcal/mole vs. 2.1 kcal/mole respectively. This indicates that soap films have a "retardation" effect on the diffusion of alcohols. The association between these two surface active agents (soap and alcohol) results in the anchoring of the cosurfactant to the interface for a time sufficient to reduce the interfacial tension to a very low value.

The formation of the microemulsions investigated was dependent on several parameters, including the type of oil, the surfactant and the cosurfactant, and the

concentration of these species; and the interfacial stoichiometry between surfactant and cosurfactant, the matching of chain lengths of oil and surfactant, and the structure of cosurfactant. These all appear to be important parameters in the formation of microemulsions. The amount of oil that can be dispersed in an O/W system is related to the amount and type of surfactant present and to the steric configuration of the cosurfactant used.

With regard to the properties of microemulsions studied, it was found that the particles of microemulsion droplets were spherical with diameters ranging from 80 Å to 350 Å, which are consistent with those reported by earlier workers (4,15,24,25,50). The total interfacial area of dispersed phase in an O/W microemulsion was controlled primarily by surfactant molecules, which is in agreement with the results obtained by Rosano et al. (16) for W/O microemulsions.

The above conclusions then lead to the following proposal for the mechanism responsible for microemulsification. The process starts with the surfactant producing a fine O/W emulsion (69). The cosurfactant is then titrated into the continuous phase. The role of the surfactant is to lower the interfacial tension and to retard the redistribution of the cosurfactant into the dispersed phase. This temporary accumulation of cosurfactant at the oil-water interface results in a transitory very low interfacial

tension, which lasts long enough to allow the resolution of the opaque dispersion into a transparent emulsion. The magnitude of the energy barrier offered by the adsorbed film of surfactant to the transfer of the cosurfactant is high enough to explain the retarding effect of the surfactant. Finally, gentle stirring produces the resolution of the macro-droplets into micro-droplets and the systems become transparent (kinetically stable or meta-stable) micro-emulsions (109).

REFERENCES

(1) Eicke, H. F.; Christen, H. J. Colloid Interface Sci. 1974, 46, 417.

(2) Schulman, J. H.; McRoberts, T. S. Discuss Faraday Soc. 1946, 42B, 165.

(3) Schulman, J. H.; Riley, D. P. J. Colloid Science. 1948, 3, 333.

(4) Schulman, J. H.; Friend, J. A. ibid. 1949, 4, 497.

(5) Schulman, J. H.; Friend, J. A. Kolloid-Z. 1949, 115, 67.

(6) Gad; Arch. Anat Phaysiol Lpz.1878, 181.

(7) Brucke; Akad. Wiss. Wien. 1879, 79, 267.

(8) Quincke. Wiedemans Ann., 1888, 35, 593.

(9) Davies, J. T.; Haydon, D. A. Second International Congress of Surface Chemistry, Vol. 1, p. 417, Sept., 1957.

(10) Davies, J. T.; Rideal, E. K. "Interfacial Phenomena", 2nd ed. Academic Press, N. Y. 1963, pp. 64-70, 335-336, 359-386 and 391-392.

(11) Mansfield, W. W. Aust. J. Sci. Res. 1952, Ser. A.5. 331.

(12) Linde, H.; Monatsber. Dtsch. Akad. Wiss. Berlin. 1959, 1, 586, 699.

(13) Sternling, C. V., and Scriven, L. E., Am. Inst. G.J.E., Eng. J. 1959, 5, 514.

(14) Bowcott, J. E.; Schulman, J. H. Z. Electrochem. 1955, 59, Heft 4, 283.

(15) Schulman, J. H.; McRoberts, T. S.; Riley, D. P. Proc. Physiological Soc. 1948, 107, 15.

(16) Rosano, H. L.; Peiser, R. C; Eydt, A. Revue Francaise, Des. Corp. Eras., 1969, 16, 249.

(17) Syed, T.;Ahmad, Shinoda, K.; Friberg, S. J. Colloid and Interface Sci. 1974, 47,32.

(18) Prince, L. H., "Microemulsions, Theory and Practice", Academic Press, 1977.

(19) Rance, D.; Friberg, S., to be published.

(20) Schulman, J.H.; Stoeckenius, W.; Prince, L.M. J. Phys. Chem. 1959, 63, 1677.

(21) Soderlund, G.; Friberg, S. Zeit fur physik. Chemie Neue Folge. 1970, 70, 39.

(22) Robbins, M. L. "Theory for the phase Behavior of Microemulsions", Paper No. 5839, presented at the Improved Oil Recovery Symposium of the Society of Petroleum Engineers of U.S.A.

(23) Schulman, J.H.; Cockbain, E.G. Trans. Faraday Soc. 1940, 36, 651-668

(24) Prince, L.M. in "Emulsion and Emulsion Technology"; J. Lissant. Ed. Marcel Dekker, N.Y., 1947, Part 1, pp. 164-165.

(25) Hoar, T.P.; Schulman, J.H. Nature, 1943, 152, 102.

(26) Stoeckenirs, W.; Schulman, J.H., Prince, L. M. Kolliod Zietschrift. Band 169, Heft 1-2, pp. 178-180.

(27) Schulman, J.H. Riley, D.P.J. Colloid Sci. 1948, 3, 383.

(28) Schulman, J.H.; Montagne, J.B. Ann. N. Y. Acad. Sci. 1961, 92, Art 2, 336-371.

(29) Bowcott, J.E.; Schulman, J.H.; Z. Elektro. Chem. 1955, 59, Heft 4, 283.

(30) Schulman, J.H.; Friend, J. A. J. Colloid Sci. 1953, 309, 329.

(31) Gerbacia, W.; Rosano, H. L. J. Colloid Interface Sci. 1973, 44, 242.

(32) Cooke, C. E. Jr.; Schulman, J.H. "Surface Chemistry". Munksgard Copenhagen, 1965, pp. 231-251.

(33) Prince, L. M. J. Colloid and Interface Sci. 1967, 23, 165-173.

(34) Bancroft, W. D. J. Phys. Chem. 1923, 17, 501,

(35) Monton Rosff. "The Nature of Microemulsions" Progress in Surface and Membrane Science. A & P, Vol. 12.

(36) Shah, D. O.; Tamjedi, A.; Falco, J. W.; Walder; R R. D. Jr. AICHE J. 1972, 18, 1116.

(37) Prince, L. M.; J. Colloid Interface Sci. 1967, 23, 165.

(38) Ruckenstein. Chemical Physics Letter. 1978, 5,517.

(39) Shinoda, K.Ed. "Solvent Properties of Surfactant and Solutions"; Marcel Dekker, New York, 1967,p.4.

(40) Friberg, S. J. Am. Oil Chem. Soc. 1971, 48,578.

(41) Davies, J. T.; Rideal, E. K. "Interfacial Phenomena". 2nd ed. Academic Press. New York, 1968; P.369.

(42) Fowkes, F. H.; J. Phys. Chem. 1963, 67, 1982.

(43) Pink, R. C.; Discuss Faraday Soc. 1946, 8, 170.

(44) Reiss, H. M.; J. Colloid Interface Sci. 1975, 53, 61.

(45) Schulman, J. H.; Stoeckenius; Prince, L. M. J. Phys Chem. 1959, 63, 1677.

(46) Harkins; Zollman J.Amer. Chem. Soc. 1926, 48,80.

(47) Stoeckenius, W.; Schulman, J. H.; Prince, L. M. Kolloid Z. 1960, 169, 170.

(48) Schulman, J. H.; Matalon, R.; Cohen, M. Discuss Faraday Soc. 1951, 11, 117.

(49) Sherman, P., Editor, "Emulsion Science", Academic Press. New York, 1968, p. 205.

(50) Schulman, J. H. Friend, H.A. J. Colloid Interface Sci. 1949, 4, 497.

(51) Schulman, J. H.; Riley, D. P. J. Colloid Sci. 1948, 3, 383.

(52) Cooke, C. E. Jr.; Schulman, J. H. Proc. and Scandinavian Symposium, Surface Actiivty, Stockholm, Sweden, Nov. 1964.

(53) Ruschak, K. J.; Miller, C. A. Ind. Eng. Chem.Fundam. 1972, 11, 634.

(54) Kai Li Ko Yuan. Ph. D. Dissertation, Tulane University, New Orleans, Louisiana, 1974.

(55) Bowcott, J. E.; Schulman, J. H. Z. Electrochem. 1955, 59, Heft 4, 283.

(56) Schulman, J. H.; McRoberts, T. S.; Riley D. P. J. Colloid Sci. 1949, 3, 383.

(57) Schulman, J. H. McRoberts, T. S. Discuss Faraday Soc. 1946, 8, 165.

(58) Syed; Admak; Shinoda; K; Friberg, S. Journal of Colloid and Interface Science. 1974, 47, 32.

(59) Tosch, W. C. "Technology of Micellar Solutions" paper 1847B, 42 nd Annual Fall Meeting of Petroleum Engineers, Houston, Texas., Oct. 1947.

(60) Ziochower, J.; Schulman, J. H. J. Colloid Interface Sci. 1967, 24, 115.

(61) Price, L. M. In "Emulsion and Emulsion Technology", Lissant. J. Ed. Marcell Dekker, N. Y.,1974; Part 1, 164-165.

(62) Gerbacia, W. E.; Rosano, H. L. J. Colloid Interface Sci. 1973, 44, 242.

(63) Soderlund, G.; Friberg, S. Zeitschrift fur. Physikache Chemie Neue Folge. 1970,70, 39.

(64) Prince, L. M. J. Colloid and Interface Sci. 1967, 23, 165-173.

(65) Gerbacia, W. E.; Rosano, H. L.; Zajac, M. J. Amer. Oil Chem. Soc. 1976, 53, 101.

(66) Rosano, H. L.; Peiser, R. A. ; Eydt, A. Rev. Franc Corp. Gas. 1969, 16, 29.

(67) Elbing, E.; Parts, A. G. J. Colloid Interface Sci. 1971, 37, 635.

(68) Gerbacia, W. E.; Rosano, H. L. Colloid and Interface Science. Kerker, M. Ed. Accdemic Press, N. Y., Vol. 2, p. 245.

(69) Rosano, H. L.; Weiss, A.; Gerbacia, W. E. in "Proceedings of the 12th Internation Congress on Surface Active Substances" Moscow, USSR, September, 1967, 1, 453.

(70) Prince,L. M. J. Colloid Interface Sci. 1975, 52, 182.

(71) Prince, L. M. "Micellization, Solubilization and Microemulsions", Mittal, K. L., Plenum Press, 1977, Vol. 1, p. 45.

(72) Prince, L. M. Cosmetics and Perfumery, 1947, 89, 47.

(73) Prince, L. M., 48th Nat'l . Colloid Symposium of the Amer. Chem.Soc. June 1974, p. 181.

(74) Shah, D. O. 48th Nat'l. Colloid Symposium of the Amer. Austin, Texas., 1974,p. 173.

(75) Shah, D. O.; Hamlin, R. M. Jr. Science. 1971,171, 483.

(76) Shah, D. O. J. Colloid Interface Sci. 1971, 37, 744.

(77) Hoar, T. P.; Schulman, J. H. Nature, 1943,152, 102.

(78) Ruckeinstein, E.; Chi, J.C. J. Chem. Soc. Faraday Trans 1975, 2, 71, 1690.

(79) Ruckeinstein, E.; Chi, J. C. J. Chem. Soc. Faraday Trans. 1975, 11, 1690.

(80) Ruckeinstein, E. in "Micellization, Solubilization and Microemulsions". Mittal, K. L. Ed.; Plenum Press. 1978, 67, 16.

(82) Cooke, C. E. Jr.; Schulman, J. H. "Surface Chemistry", Munksgard Copenhagen, 1965, 231-251.

(81) Sjoblom, E.; Friberg, S.,J. Colloid Interface Sci. 1978, 67, 16.

(83) Shinoda, K.; Kunieda, J. J.Colloid and Interphase Sci. 1973, 42, 381.

(84) Cummins, H. Z.; Knable, N.; Yeh, Y. Phys. Rev. Letters. 1964, 12, 150.

(85) Cummins, H. Z.; Pusey, P. N. in "Photon Correlation Spectroscopy and Velocimetry. Cummins, H. Z.; Pike, E. R. ed, Plenum Pub. Corp., New york; 1974.

(86) Glasston, S.; Laidler, K. J.; Erying, H. "The Theory of Rate Process", McGraw-Hill, New York.

(87) Schulman, J. H.; Teorell, T. Trans. Faraday Soc. 1978, 34, 1338.

(88) Peterson, P.; Gregor, H. J. Electro Chem. Soc. 1959, 106, 1051.

(89) Mibashan-Sharaga, L. Comptes Rensus J. Chimie Physique, 1950, 47, No. 5-6, 26-27.

(90) Rosano, H. L. J. Colloid and Interface Science. 1967, 23, No. 1.

(91) Winsor, P. A. Trans. Faraday Soc. 1948, 44, 376.

(92) Winsor, P. A. Trans. Faraday Soc. 1950, 46, 762.

(93) Palit, S. R.; Moghe, V. A; Biswas, B. Trans. Faraday Soc. 55, 463.

(94) Adamson, A. W. J. Colloid Inteface Sci. 1969, 29, 261.

(95) Fowkes, F. M. in "Solvent Properties of Surfactant Solutions". Shinoda, K., Ed. Dekker, M., New York, 1967, p.112.

(96) Gellberg, G.; Lehtinen, H.; Friberg, S. J. Colloid Interface Sci. 1970, 33, 40.

(97) Ahmad, S. I.; Shinoda, K.; Friberg, S. J. Colloid Interface Sci. 1974, 47, 52.

(98) Shah, D. O. Reprints 48th Nat'l. Colloid Symposium, Austin, Texas, 1974, 173.

(99) Ekwall, P.; Mandell, L.; Fontell, K. Mol. Cryst. Liq. Cryst. 1969, 8, 157.

(100) Winsor, P. A. Chem. Rev. 1968, 68, 1.

(101) Osipow, L.I. J. Soc. Cosmet. Chem. 1963, 14, 277.

(102) Prince, L. M. J. Soc. Cosmet. Chem. 1970, 21, 193.

(103) Rosano, H. L. J. Soc. Cosmet. Chem. 1974, 25, 609.

(104) Shinoda, K.; Friberg, S.; Adv. Colloid Interface Sci. 1975, 4, 281.

(105) Rosano, H. L.; Lan, T.; Weiss, A. J. colloid Interface Sci. 1979, 72, No. 2, Nov.

(106) Svedberg, T. Colloid Chemistry, 2nd ed.; American Chemical Society Mongraphy Series. The Chemical Cataolg Co. Inc., 1928.

(107) Svedberg, T. "The Ultracentrifuge". Oxford, The Clarendon Press, 1940.

(108) Archer, R. D. Ph.D. Dissertation, Columbia University, 1954.

(109) Rosano, H. L. U. S. Patent 4,146,499,1979.

(110) Rosano, H. L. Feinstein, M. E. J. Phys. Chem. 1969, 73, 601.

(111) Freiberg, S.; Miroslava, P. "Abstr. of 175th ACS Nat'l Meeting, Colloid and Surf. Chem. Div, Anaheim, Calif., March 1978; N. 28.

(112) Ekwall, P.; Mandell, L.; Fontell, K. J. Colloid Interface Sci. 1970, 33, 216.

(113) Gerbacia, W.; Rosano, H. L.; Whittam, J. H. In "Colloid and Interface Science" Kerker, M., Ed.; A & P, New York, 1976, Vol.11, p. 245.

(114) Rosano, H. L.; Lan, T., Weiss, A.; Whittam, J. H.; Gerbacia, W. "Metastable Microemulsions", J. Phys. Chem, March 1981.

(115) Mc Bain, J. W.; Woo. J. Proc. Roy. Soc. A163, 182.

(116) Stackebherg, V. M.; Klockner, E.; Möhrauer, P. Kolloid-Z., 1949, 115, 153.

(117) Rubin, E.; Radke, C.; J. Chem. Eng. Sci. in press.

(118) Berg, J. C.; 164th Acs National Meeting, New York N. Y., Aug 1972; Div. of Colloid and Surface Chemistry, Paper No. 21.

(119) England, D. C.; Berg, J. C. AICHEJ. 1971, 17, 313.

(120) Hutchinson, E. J. Phys. Coll. Chem. 1948, 897, 52.

(121) Shah,D. O.; Bansal, V. K.; Chan, K.; Hsieh, W. C. In "Enhanced Oil Recovery by Surfactant and Polymer Flooding", Shah, D. O., Schechter R. S., Ed.; A & P, New York, 1977, p. 293.

(122) Defay, R.; Sanfeld, A. J. Chem, Phys. 1973, 70, 895.

(123) Goddard, E. G.; Schulman, J. H. J. Colloid Sci. 1953, 8, 309.

(124) Zisman, W. A. J. Chem. Phys. 1941, 9, 789.

(125) Robbins, M. L.; La Mer, V. K. J. Phys. Chem. 1958, 62, 1291.

(126) Stoeckenius, W.; Schulman, J. H.; Prince, L. M. Kolloid Z. 1960, 169, 170.

(127) Bowcott, J. E. Ph.D. Dissertation, Cambridge, 1957.

(128) Prince, L.M. In "Emulsions and Emulsion Technology" Lissant, K. J., Ed.; Marcel Dekker, New York, 1974; Part 1, p. 144.