MICROEMULSION FORMATION

by

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ABSTRACT

Microemulsions, which are transparent, fluid systems of high stability, were previously thought to be thermodynamically stable systems, requiring negative interfacial tensions for their formation.

To determine if this was a correct hypothesis, microemulsions were prepared and studied by various techniques. Measurement of interfacial tension (γ_i) as a function of time showed that when a short chain alcohol is injected into one phase of an oil/water system, the γ_i will be reduced below its equilibrium value for a short period of time. If an interfacial film of surfactant is present, γ_i can be reduced to zero for a period of time depending on the rate of transport of the alcohol away from the oil/water interface. Redistribution of the cosurfactant was shown to be a necessary process for the formation of microemulsions.

The effects of the surfactant and solvent type were studied to determine the effect of these factors on microemulsion formation. Increasing the chain length of the surfactant was seen to decrease the requirement for a particular cosurfactant up to a given number of carbon atoms. Beyond that point, no microemulsions could be formed.

Previous investigators have on occasion postulated that hydrogen bonding between the cosurfactant and the surfactant was a necessary condition for microemulsion formation. NMR studies showed that this type of complex formation did not play a significant role in the formation of microemulsion. It was

also shown by light scattering that the interfacial film was not a rigid structure, but could swell within limits to accommodate the dispersed phase. The droplet diameter was found to be about 200-300A in systems stabilized by sodium dodecyl sulfate, depending on the amount of surfactant and cosurfactant.

In comparing the UV absorption spectrum of benzene-in-water microemulsions with the solution spectra of benzene in hydrocarbons, it was concluded that the environment of the benzene in the microemulsion droplets was similar to that of benaene in a hydrocarbon at a mole fraction of benzene equal to about 0.4. The benzene was shown, however to penetrate between the tails of the surfactant to some degree.

The UV absorption spectrum of I_2 dissolved in microemulsions of n-hexadecane showed that the cosurfactant actually entered the oil phase droplets increasing the polar character of the micelle interior. The distribution of the cosurfactant could then be determined.

It was concluded therefore, that the major difference between macro- and microemulsions is the degree of curvature of the interfacial film.

PREFACE

The work included in this dissertation was carried out in the Department of Chemistry at the City College of the City University of New York beginning about June, 1971 to January, 1974. Except where noted, this work is original and has not previously been submitted for a degree in any other university.

I wish to express my deep gratitude to Professor Henri L. Rosano, my research advisor, for his consistent confidence in my abilities, even though I "was too slow". His expert guidance and advise have made this work a more educational experience than it otherwise would have been.

I am also grateful to J. Whittam and E. LaGamma for their support, help and stimulating discussions.

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ILLUSTRATIONS

LIST OF SYMBOLS AND ABBREVIATIONS

a	used as a subscript to indicate alcohol
AB	2-amino-1-butanol
AMP	2-amino-2-methyl-1-propanol
AMPD	2-amino-2-methyl-1, 3-propanediol
b	fraction of hydroxyl protons in a particular environment
c	used as a superscript to indicate the continuous phase of a microemulsion
C_n	represents the hydrocarbon chain length of a surfactant, n being the number of carbon atoms
CMC	critical micelle concentration
d	used as a superscript to indicate the dispersed phase of a microemulsion
DTAB	decyltrimethylamonium
e	used as a subscript to indicate the emulsifier (surfactant)
E.P.A.	a solvent; five parts ether, five parts isopenthane and two parts ethanol by volume
HLB	hydrophilic-lipophilic balance
I	intercept of titration curves
i	used as a superscript to indicate the interfacial region between an oil and aqueous phase
$I(\nu)$	NMR absorption intensity
k	slope of titration curves; also Boltzman's constant
KDS	potassium dodecyl sulfate
l	used as a subscript to indicate the solvent
n_{ϕ}	number of moles of benzene
RbDS	rubidium dodecyl sulfate
s	used as a subscript to indicate an inorganic salt
S	initial spreading coefficient
S'	final spreading coefficient
SDS	sodium dodecyl sulfate
SDeS	sodium decyl sulfate

STS	sodium tetradecyl sulfate
T	temperature; also turbidity (eq. 3-8, page 79)
TCE	tetrachlorethylene
TMS	tetramethylsilane
$\bar{V}$	molar volume
w	used as a subscript to indicate water
X	mole fraction
γ_i	interfacial tension between oil and water
$\gamma_{o/w}$	interfacial tension between oil and water in the absence of an interfacial monolayer
Γ	osmotic coefficient
$\Delta\nu_I$	average frequency interval of progression for the benzene UV absorption
$\Delta\nu_{\frac{1}{2}}$	half-band width of the benzene UV resonance
δ	NMR chemical shift in ppm
λ	wavelength
ν	NMR resonance frequency
ν_s	NMR chemical shift in hertz
π	film pressure due to a monolayer; also osmotic pressure (eq. 1-15, page 24)
π_m	measured film pressure
$\pi_{o/w}$	monolayer pressure at the oil-water interface
π'_o	film pressure due to a monolayer on the oil side of an oil-water interface
π'_w	film pressure due to a monolayer on the water side of an oil-water interface
σ	cross-sectional area of a surfactant molecule at an interface

CHAPTER ONE

1.1 INTRODUCTION

Emulsions are of two types, oil-in-water and water-in-oil. They generally are lactescent in appearance and unstable towards phase separation. The particle size of the dispersed phase is usually 1μ or larger, which causes the milky appearance. The industrial applications of emulsions are well known (1) and more uses are likely to be found in the future.

If the particle size is made smaller to the point where the dispersion becomes transparent, the term microemulsion is applicable. These colloidal systems have also been called micellar emulsions (2) or micellar solutions (3). It is felt, however, that these appellatives offer no advantage and, therefore, microemulsions will be the preferred term, although free use will be made of all three.

The investigation of these systems has been undertaken by many scientists and their main conclusions and the methods by which they are derived will be discussed in the following section. It will become apparent that there are some discrepancies and inconsistences and that the theories are not complete. It is hoped that the present work will help to elucidate the processes of the formation of microemulsions. The various theories will now be reviewed.

1.2 THEORIES

1.2.1 Schulman's Theory of Microemulsions

In 1945, J. M. Schulman and T. P. Hoar (4) described what they termed an oleopathic hydromicelle. They maintained that these transparent oil continuous systems contained an aqueous phase dispersed in reversed spherical micelles. The essential conditions proposed for their formation were:

(1) A high soap to water ratio.

(2) The presence of a non-ionized amphipathic substance (e.g., alcohol, fatty acid, amine) in a concentration approximately equal to that of the soap.

Their contention was that the undissociated soap molecules were:

(1) Oriented at the oil-water interface with the non-ionized amphipathic substance between the soap molecules.

(2) The surfactant and cosurfactant (the non-ionized material) formed a complex to produce a net attraction among the molecules at the interface.

They calculated the amount of surfactant needed to disperse a given volume of water by assuming all of the surfactant to be located at and completely covering the interface and

all the water to be in the dispersed phase. By using a reasonable value for the surfactant-cosurfactant complex (assuming a 1:1 surfactant to cosurfactant ratio at the interface), the amount of soap required to give droplets of a certain size could be computed from the relationship between the surface area of a sphere and its volume.

$$r = \frac{3V}{A} \quad , \qquad 1\text{-}1$$

where r is the radius of the droplets, V the total volume of all droplets and A the total surface area. By substituting $n\sigma$ for A, one obtains

$$r = \frac{3V}{n\sigma} \quad , \qquad 1\text{-}2$$

where n is the total number of soap molecules of cross-sectional area σ, required to disperse a volume V of water into droplets of radius r. σ was usually obtained from the sum of the closest packing area for the surfactant and co-surfactant as measured by monolayer experiments. In their calculations, the authors assumed that the densities of all of the components were one. The radius calculated for a system which gave a slight Tyndall effect was 100A and for a completely transparent system, 60A. These values agree with those subsequently determined by empirical methods (5) for other systems. They may not, however, be reasonable values for the dispersions used at that time. The authors did not reveal the components used.

Schulman and McRoberts (6) investigated the role of the

cosurfactant in forming these transparent systems. They used potassium oleate as the soap and straight chain and cyclic alcohols of varying chain lengths as the cosurfactants. Both oil-in-water and water-in-oil transparent systems were prepared. They discovered that the composition of the continuous phase (oil or water) was dependent on the combination of oil and alcohol used. As the chain length of the alcohol was increased from C_2 - C_{10}, there was an abrupt transition from water continuous to oil continuous phases. The chain length of the alcohol at which the transition took place was dependent on the oil used. These results suggested to them that phase continuity was dependent on the wettability of the mixed interfacial monolayer. The phase that had the smaller contact angle against the interfacial monolayer would be the continuous phase.

They also found that formation of the transparent systems was dependent on the alcohol-oil combination used. For example, no transparent dispersion could be obtained when propyl alcohol was used with paraffin, but if butyl alcohol was used, a water continous system was obtained. On this basis, they concluded that the soap existed as a lamellar film which had to be penetrated by an amphipathic molecule to enable spherical micelles to form. They believed that the soap had a crystal lattice structure in the coarse dispersions which could swell only to a limited extent. It

was envisioned that the penetrating amphipathic molecules created disorder in this solid soap structure, forming a viscous liquid interfacial film which could swell or contract to accommodate the dispersed phase. NMR spectra, which will be discussed below, did not support this point (7).

X-ray studies of these systems were carried out by Schulman and Riley (8). They obtained two bands for an aqueous solution of potassium oleate. The structure of the soap in these solutions was considered to be that of a bimolecular leaflet or lamellar micelles. The long X-ray spacing was considered to be related to the distance between polar groups of layers of oriented soap molecules, and the short spacing related to the distance between adjacent molecules in the soap monolayers. They observed the change in the spacings with soap concentration for the transparent systems. On adding oil to these solutions, only a small degree of swelling was observed in the lamellar structure, as determined by the variance in the long spacings. Addition of alcohols to these mixtures caused the lamellar structure to shrink. These data seemed to fit calculations for spherical micelles when the soap concentration was less than 27.5%, and cylindrical micelles for higher concentrations.

The X-ray work of Schulman, Matalon and Cohen (9) appeared to support the existence of spherical micelles when appropriate mixtures of non-ionic polyethylene oxides were

used as the emulsifiers. Transparent systems were obtained, only when the hydrophobic and hydrophillic portions of the emulsifiers were of different length. If only one type of polyethylene oxide was used, gel structures were obtained. This again indicated to the authors that some kind of disorder had to be introduced into the interfacial film to enable the surfactant film to swell and form spherical micelles containing the oil or water.

Bowcott and Schulman (10) treated these dispersions as a three-phase thermodynamically stable system. Their sedimentation experiments agreed with their calculations (using equation 1-2)for the size of the droplets in the dispersed phase, 100-500A. They restated the conditions which determine phase continuity for the transparent systems as being the same as those that apply for course emulsions (11), and emulsions stablished by powders (12). That is, the phase that wets the interfacial monolayer more readily will be the continuous phase. Thus, for a given soap, the longer the chain length of the alcohol, the greater the paraffinic nature of the mixed film, and the more readily water-in-oil emulsions should form.

This idea was also expressed in terms of two hypothetical interfacial tensions, $\gamma_{m/o}$, the interfacial tension between the mixed monolayer and the oil phase, and $\gamma_{m/w}$, the tension between the monolayer and the aqueous phase. The side with the higher tension or interfacial

free energy with respect to the interfacial monolayer would contract to maintain the smaller surface of contact with the monolayer, thus forming the inner surface of the micelle. These parameters were not amenable to direct measurement, however.

Electron micrographs (13) obtained by staining the double bonds of unsaturated aliphatic oil with osmium tetroxide, revealed discrete spherical droplets for the water continuous systems stabilized with potassium oleate. The authors maintained that the OsO_4 caused the oil and surfactant to polymerize, producing solid spherules which could be separated and washed. These globules were then imbedded in a polymethacrylate matrix and photographed directly on the electron microscope.

Since a discrete phase was observed, the authors chose to call the transparent dispersions microemulsion, a term with which Shinoda (3) has taken issue. Schulman, et. al. (13) also stated that an association between the oil and surfactant molecules was critical in forming microemulsions.

1.2.2 The Concept of Negative Interfacial Tension

The condition was proposed (14) that it was necessary for the interfacial tension (γ_i) between the aqueous and non-aqueous phases to initially be less than zero for spontaneous microemulsification to occur. This was deduced from the relation between interfacial tension and film pressure.

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

γ_i would be negative if the film pressure (π) due to the surfactant film became greater than $\gamma_{o/w}$, the oil-water interfacial tension in the absence of an interfacial monolayer. Emulsification would then be spontaneous as there was then $-\gamma_i dA$ free energy available to subdivide the phase in question (15) (A is the interfacial area). At equilibrium γ_i was assumed to be zero and therefore, the dispersions were thermodynamically stable since there would be no concomitant decrease in free energy on coalescences of the droplets. γ_i was envisaged as becoming negative when the oil penetrated the mixed film of surfactants or by penetration of the surfactant film by an asymetric alcohol and the use of a surface active agent with a large ionic polar group or by the presence of large sized counter ions.

Oil molecules were shown by monolayer expansion to be capable of penetrating a monolayer of AMP (2-amino-2-methyl-1-propanol) stearate at pH 10.5 at a hexadecane-water interface (15). A duplex film technique using a Langmuir trough and film balance was employed. A duplex film is a film in which the two interfaces (e.g., oil-water and oil-air interfaces) behave independently and maintain their own characteristic tension (16). To form a duplex film on the trough, the oil was spread with the monolayer (15,17). If the oil did not spread, droplets of oil were seen to form (15). In order for γ_i to be negative π would

have to have been approximately 50 dyne/cm or greater when hexadecane was used as the oil phase ($\gamma_{o/w} \approx 50$ dyne/cm; see e.g. 3). The measured pressure (π_m) would only have to be about 43 dyne/cm since

$$\gamma_i = \gamma_{o/w} - \pi = \gamma_{a/w} - \gamma_{a/o} - \pi_m \ , \qquad 1\text{-}4$$

where $\gamma_{a/w}$ is the surface tension of water against air and $\gamma_{a/o}$ is the surface tension of the oil against air ($\approx$ 29 dyne/cm for n-hexadecane). Pressures higher than this were obtained using steric acid and hexadecane spread on aqueous AMP at pH 10.4. When hexadecanol was injected into the monolayer, the film became more expanded but collapsed at a lower pressure.

The authors claim that these results support their view of the role of negative γ_i in forming microemulsions. Yet none of the previous work on which they based their conclusions (13, 14) was done using their conditions.

For example, all of the reported microemulsions were prepared using oleate soaps (4, 6, 8-10, 13, 14) at pH 8.8 or 10.5 (1[illegible], none were previously reported using hexadecane as the oil phase and none were prepared using hexadecanol). Also, since pressures > 50 dynes/cm were obtained using just AMP stearate as the surfactant at pH 10.4, it should have been possible to form microemulsions with n-hexadecane using just the surfactant at this pH. It will be shown below that this is not the case. This method has another flaw in that it does not discriminate between o/w and w/o

microemulsions. To do this, the authors maintained that phase continuity would be controlled by surface charge. An unionized monolayer would produce a water-in-oil microemulsion while a charged monolayer would produce an oil-in-water microemulsion. On this basis, it would be assumed that the previous work (18) with non-ionic emulsifiers delt exclusively with w/o microemulsions and that o/w microemulsions could not be prepared using non-ionic emulsifiers. The latter deduction will be seen to be false (3).

Cook and Schulman (7) investigated surface pressure area curves for organic vapors absorbed into monolayers of oleic acid spread on boric acid and AMP at pH 8.7 (13).

From these π_m versus area curves, isotherms for the oil-water interface were calculated from the relation

$$\pi_{o/w} = (S' - S) + \pi_m \ , \qquad 1\text{-}5$$

where $\pi_{o/w}$ is the monolayer pressure at the oil-water interface, S' and S are the final and initial spreading coefficients, respectively, of the oil on water. S' is given by

$$S' = \gamma_m - (\gamma_{a/o} + \gamma'_{o/w}) \qquad 1\text{-}6$$

and S is given by

$$S = \gamma_{a/w} - (\gamma_{a/o} + \gamma_{o/w}) \qquad 1\text{-}7$$

γ_m is the surface tension of the monolayer covered water, $\gamma'_{o/w}$ is the oil-water tension in the presence of monolayer

and $\gamma_{a/o}$, $\gamma_{a/w}$ and $\gamma_{o/w}$ have been defined previously (eq. 1-4).

It was assumed that the areas per molecule were the same in the monolayer saturated with vapor as at the oil-water interface. This method was used because it was reported (7) that the hexadecane evaporated within a short period of time from the duplex films studied earlier (15). The applicability of this monolayer approach was also briefly discussed, but no definite conclusions were drawn.

In this investigation, several aliphatic hydrocarbons and benzene were used. They concluded that " ... none of the hydrocarbons increased the area per molecule at high film pressures, such as exist at the oil-water interface in the solubilized systems" (microemulsions). The data, however, show that an expansion does occur in the duplex film for the aliphatic hydrocarbons, but the extent of expansion is approximately the same for the different types of oils, with n-hexadecane giving the most expanded films. Though the difference is small, it is the reverse of what would be expected on the basis of previous conjectures, since hexadecane requires a larger amount of alcohol to form the transparent systems then the other oils. If the present theory were entirely correct, hexane would give the most expanded film since it requires the least alcohol (7). Benzene was observed not to give an expanded film. This result agrees with the theory under discussion, since benzene does not form a microemulsion under these

conditions (13).

The authors implied that the duplex film isotherms approached those for the monolayer at areas less than 30A^2/molecule, but the data was not presented. If this were true, it would mean that the oil molecules were squeezed out of the monolayer at high film pressures. This would reverse the previously held view (13, 14, 15) that the droplet size depended on the hydrocarbon used in w/o microemulsions.

They also presented the NMR spectra of the methyl and methylene protons in a solution of hexanol in benzene and a water in benzene microemulsion stabilized by potassium oleate and hexanol. The spectrum for oleic acid in benzene and potassium oleate in water were also shown.

The observed line widths indicated that the oleate chains were in a liquid-like state (<0.1 to 10 Mz in width (19)). The line shape for the methylene signal was observed to be the same before and after clearing in the dispersions. This ran contrary to the assumption that the formation of a microemulsion was a result of a solid to liquid phase transition (6) in the surfactant film, which was induced by the disrupting influence of the cosurfactant.

Proton nuclear magnetic resonance was also used in an investigation of microemulsions of chloroform, water and decyltrimethylammonium (DTAB) and benzene, water, AMP oleate or 2-amino-1-butanol (AB) oleate (18). When $CHCl_3$ was titrated into an aqueous solution of DTAB, the resonance due to the chloroform proton was observed to shift to the low field side

of the resonance in pure $CHCl_3$ by a maximum shift of -1.04 ppm. This was a very large downfield shift and from it the authors concluded the chloroform was bound to the ionic protions of the DTAB micelles.

The line width of the H_2O resonance was invariant over the concentration range studied (mole ratio of water to oleate from 1 to 10) for the system stabilized by 2-amino-1-butanol (AB) oleate, while that for the 2-amino-2-methyl-1-propanol (AMP) oleate system decreased with increasing water content. The larger bulk of the ethyl group in AB as compared to the methyl group in AMP and the constant, narrow band width for H_2O in AB lead them to believe that the interfacial monolayer in AB was more expanded leaving the water contained in the interfacial monolayer more labile in the AB oleate system. The chain methylene groups were again seen to be in a non-rigid state in all three microemulsion systems.

1.2.3 Summary

Schulman's interpretation of microemulsion formation was - as he left it - that a microemulsion would form when the interfacial tension between an oil-and-water phase was reduced below zero ($\gamma_i < 0$). This was accomplished when enough disorder was produced in the interfacial monolayer to permit it to swell and assume the curvature of a microemulsion. The interface would subdivide until γ_i rose to zero at equilibrium. The continuous phase would be the phase that had the lower tension against the inter-

facial monolayer ($\gamma_{m/o}$ or $\gamma_{m/w}$), i.e., the phase that wet the monolayer most efficiently.

1.2.4 Modification by Prince

Prince (20) accepted fully the concept of negative interfacial tensions. However, since $\gamma_{o/w}$ was in general quite high ($\approx$ 50 dyne/cm for aliphatic hydrocarbons and 35 dyne/cm for benzene), large monolayer film pressures were required to reproduce negative interfacial tensions according to equation 1-3. This was the question to which Prince addressed himself. His attention may have been unnecessary since duplex film isotherms have been shown to reach quite high pressures (7 , 15).

In any case, the problem was attacked by modifying equation 1-3. For $\gamma_{o/w}$ he substituted $(\gamma_{o/w})_a$, the oil-water interfacial tension with the oil containing its fraction of alcohol. That is, when a microemulsion is formed, the alcohol is distributed between the interphase and the continuous phase. It was the interfacial tension between water and the alcohol-oil mixture of continuous phase which Prince felt should be used in place of $\gamma_{o/w}$. Essentially, he separated the alcohol in the oil phase from that in the monolayer. This formulation would not require such high film pressures in order to reach negative interfacial tensions since $(\gamma_{o/w})_a$ would be lower than $\gamma_{o/w}$.

What he did was to transfer the effect of the alcohol from the π term in equation 1-3 to the term containing the oil-water tension. In other words, since alcohols are surface active, their effect on the oil-water interfacial

tension can be ascribed to the generation of a film pressure (π_a) and $(\gamma_{o/w})_a$ can then be written

$$(\gamma_{o/w})_a = \gamma_{o/w} - \pi_a \qquad 1\text{-}8$$

1.2.5 The Concept of π_G

Prince assumed that the pressures necessary to develop a negative interfacial tension arose from penetration of the alcohol molecules into the surfactant film with subsequent hydrogen bond complex formation between the alcohol and the surfactant. He presented his theory in terms of o/w microemulsions with oleate as the surfactant. It was proposed that the alcohol penetrated the oleate monolayer, shielding the charged carboxyl groups, allowing the oleate monolayer to contract and bond with the alcohol. This would allow closer adlineation of the hydrocarbon tails increasing the force of attraction among them. As the alcohol content was increased, the electrostatic repulsion on the water side of the interface would decrease further and hydrogen bonding between the alcohol and carboxyl groups would increase.

Three stages were envisioned in the development of these pressures. With zero or low alcohol content in the film, the film would be expanded and the pressure low. Next, at a high enough alcohol concentration, the electrostatic repulsions in the oleate monolayer would be reduced and a liquid condensed film of high pressure would develop. Maximum pressures are attained in this stage. Finally,

with alcohol molecules in excess, "the strong electrostatic repulsive forces will be diluted so that the pressure will be lower than in the second stage "even though the film will remain condensed". It appears that the author is attributing low spreading pressures to both high and low electrostatic repulsions. In the first stage, low pressures result due to high electrostatic repulsions, while in the last stage low pressures result due to the dilution of these pressures.

In this formulation curvature of the interface arises due to the existence of a pressure gradient across the flat film. This pressure gradient develops due to the different interactions among the hydrophobic and hydrophillic portions of the oleate molecules.

The film pressure generated at a flat interface due to this pressure gradient was termed π_G. γ_ϕ was the "total potential (minimum) interfacial tension" corresponding to π_G. In other words, γ_ϕ was the interfacial tension before curvature and should reach minimum values since curvature was assumed to develop to relieve the excess pressure. γ_i was considered to be the interfacial tension after curvature and corresponded to a lower film pressure, π. Equation 1-3 was then written

$$\gamma_\phi = (\gamma_{o/w})_a - \pi_G \qquad 1\text{-}9$$

Essentially, what the author did was to remove the effect of the alcohol from the π term and put it in the $\gamma_{o/w}$ term

of equation 1-3; he made a distinction between the flat and curved interfacial film pressures and tensions.

Purely hypotetical curves of π_G and $(\gamma_{o/w})_a$ versus concentration of alcohol were then constructed. π_G was pictured as a parabola (concave down) reaching a maximum at some alcohol concentration. $(\gamma_{o/w})_a$ was represented as a monotomically decreasing function of alcohol concentration. If the two curves intersected, a microemulsion resulted. If they did not, a macroemulsion resulted. This was another way of stating that if γ_{ϕ} became negative ($\pi_G > (\gamma_{o/w})_a$) a microemulsion would form.

1.2.6 Mechanism of Film Curvature According to Prince

Prince postulated (21, 22) that a curvature of an interfacial film was the result of a difference in the film pressures on either side of the oil-water interface. π_o' was the pressure on the oil side before curvature and π_w' the pressure on the water side. This difference in tensions (pressure gradient) was relieved by curvature of the film. In the equilibrium condition, the pressure gradient was zero. This was similar to the argument presented by Schulman in terms of $\gamma_{m/w}$ and $\gamma_{m/o}$ (10). In Prince's terms $\gamma_{m/w}$ would be given by

$$\gamma_{m/w} = (\gamma_{o/w})_a - \pi_w'$$

and $\gamma_{m/o}$ would be given by

$$\gamma_{m/o} = (\gamma_{o/w})_a - \pi'_o$$

He went on further to stipulate that the total pressure was the sum of the pressures on both sides of the interface. The driving force for curvature was the difference between the initial pressure π_G and the final equilibrium value of $\pi = (\gamma_{o/w})_a$. The requirement for the formation of microemulsions was that $\pi_G > (\gamma_{o/w})_a$, if not, a macroemulsion would result. In order to illustrate his point, pressure-area curves were plotted for the oil and water sides of the interfacial film. These graphs were purely conjectural and could only be used to facilitate the authors explanation.

At equilibrium $\pi'_o = \pi'_w$, the areas per molecule were seen to be different on the two sides of the interface. He proposed that it was the ratio of the areas per molecule on both sides of the interface (σ_o/σ_w or σ_w/σ_o) that determined the droplet size.

This theory is interesting in that it elaborates further on the idea that it is an assymetry in the interactions across the interface that determines whether or not a microemulsion will form. However, the range of σ_o/σ_w for which microemulsions are postulated to form is rather large and that for macroemulsion, small. This gives the impression that microemulsions are the more common species, which is not the case. The theory is also of little value in

prognostication, for there is no way of measuring any of the parameters involved other than $(\gamma_{o/w})_a$.

1.2.7 Thermodynamic Treatments

A. Isolated Microemulsions

Rosano et. al (23) made use of a procedure developed earlier by Schulman and co-workers (10) of titrating a coarse emulsion of surfactant, water and oil as the continuous phase with an alcohol to induce clarity or water-in-oil microemulsion formation. After the first clearing point was reached, more oil was added (breaking the microemulsion and reforming a coarse emulsion). The system was then titrated back to clarity with alcohol. This procedure was repeated several times to give several points of transparency at different volumes of oil. This method was purported to give the distribution of alcohol in the microemulsion (7, 10, 23). The explanation was based on the reasonable assumption that the alcohol was distributed among three phases in the microemulsion: the dispersed phase, continuous phase and interphase (figure 1.1). If this were the case, the total number of moles of alcohol (n_a) would equal the sum of the various amounts in each phase, i.e.,

$$n_a = n_a^i + n_a^c + n_a^d \qquad 1\text{-}10$$

The i, c and d stand for the interphase, continuous phase and dispersed phase respectively. Assuming that the ratio of alcohol to oil remains constant in the continuous phase,

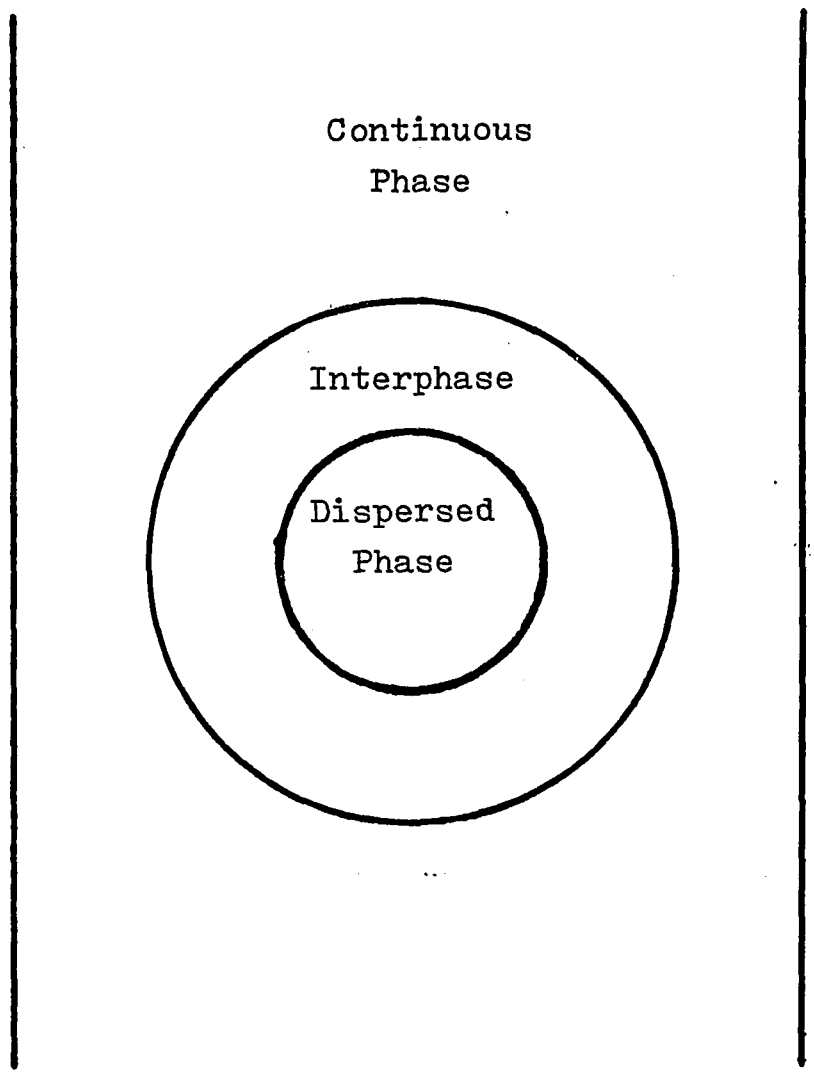


Figure 1.1

$k = n_a^c/n_1$ (n_1 is the number of moles of solvent, $k\,n_1$ may be substituted for n_a^c in 1-10. The resultant equation was then divided by n_e, the number of moles of surfactant, giving

$$n_a/n_e = \frac{n_a^d + n_a^i}{n_e} + k\,n_1/n_e \qquad 1\text{-}11$$

If n_a/n_e is plotted against n_1/n_e, a straight line should result with the slope equal to the number of moles of the alcohol per mole of solvent in the continuous phase. In the cases studied, an aliphatic oil or benzene was used as the solvent. This treatment has not been shown to hold for oil-in-water microemulsions. Since the solubility of the alcohol in water is usually small 1-11 was approximated by

$$n_a/n_e = n_a^i/n_e + k\,n_1/n_e \qquad 1\text{-}12$$

$$n_a^d \ll n_a^i$$

Bowcott and Schulman (10) reported that the error in making this assumption was no more than 1.5% when n-hexanol was used - if the alcohol saturated the aqueous phase. For pentanol, the error would be slightly higher (1.8%, see below).

With this assumption, the intercept then gives the number of moles of alcohol per mole of surfactant in the interfacial region. It was assumed in this treatment, as was done in previous models, that all of the surfactant resided at the interface. With this information and the assumption

of ideality, the free energy of absorption of the alcohol (n-pentanol was used exclusively in these calculations) from the continuous to the interphase was calculated from

$$\Delta G = -RT \ln (X_a^i / X_a^l) \qquad 1\text{-}13$$

$$X_a^i = \frac{n_a^i}{n_a^i + n_e}$$

$$X_a^l = \frac{n_a^l}{n_a^l + n_e}$$

n_l was the number of moles of solvent (oil). The values calculated on this basis were all less than 2.5 kcal/mole. This indicated to the authors that n-pentanol probably did not form a strong association with the surfactant.

This was in marked contrast to the assumption of strong surfactant or cosurfactant complexing made in the previous theories (10, 11, 21). They were of the opinion that the n-pentanol was necessary, simply to lower the oil/water interfacial tension. It was inherently assumed in this treatment that there was no water or surfactant dissolved in the continuous phase. However, the slopes of the graphs plotted according to 1-12 decreased slightly as the system became more dilute in the dispersed phase. This was interpreted to mean that some water was being abstracted into the continuous phase, but no estimate of the amount was made and it was not considered in the development.

From measurements of sedimentation constants, it was con-

cluded that increasing the volume of the dispersed phase did not increase the total interfacial area whether the alcohol content was changed or not. This would occur if the radii of the droplets increased when the total volume increased. Total surface area was also found to be the same at the clearing point for different volumes of the dispersed phase. Increasing the alcohol content at a constant volume of the dispersed phase, however, resulted in an increase in the interfacial area indicating a decrease in the radii of the droplets and/or an increase in the number of droplets.

The Laplace Pressure

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

$$\Delta P = \frac{2 \gamma_i}{r} \qquad 1\text{-}14$$

In a heterogenous dispersion, therefore, large spheres would grow larger at the expense of small spheres due to the transport of material to the region of lower chemical potential. Rosano, et. al considered the stability of water-in-oil microemulsions to be due to the balancing of the Laplace pressure against an osmotic pressure difference. For this treatment, it is necessary

to admit the existence of water with a high activity coefficient in the continuous phase. The osmotic pressure was written as

$$\pi = \Gamma \frac{RT}{\bar{V}_w} \ln X_w \approx \Gamma \frac{RT}{\bar{V}_w} \frac{n_b}{n_w} \qquad 1\text{-}15$$

Γ is an osmotic coefficient, $\bar{V}_w$ is the molar volume of water, X_w is the mole fraction of water, n_w and n_b are the number of moles of water and ions from the absorbed surfactant in the micelles. This equation applies for a non-ideal solution in equilibrium with pure solvent and is therefore an approximation to the actual situation. It is interesting to note that this type of treatment - balancing the Laplace against the osmotic pressure - was later used by Adamson (2) (see below) and Pagano (24), although the latter was concerned with calculating interfacial tensions at curved lipid membranes. Since all the surfactant was assumed to reside at the interface (following Schulman), the radius of the droplets was then

$$r = \frac{3V}{Nn_b\sigma} \qquad \text{(see equation 1-2)}$$

Substituting this into 1-14 and setting $\Delta P = \pi$ gave

$$\gamma_i\sigma = 1.5 \Gamma \frac{kTV}{V_w n_w} \qquad 1\text{-}16$$

At a constant water volume, the right hand side is a constant, C.

This relationship was used to explain the fact that many more surfactant cosurfactant combinations are able to form

water-in-oil microemulsions then are able to form oil-in-water microemulsions. This followed since in oil-in-water microemulsions, π and ΔP are in the same direction and therefore, γ_i would have to be negative at equilibrium -- in other words, γ_i would become an interfacial pressure. Using this argument, the authors were abandoning the $\gamma_i = 0$ concept of Schulman discussed previously.

With this relation and assuming $\Gamma = 0.30$, a value considered by the authors to be representative for the long chain fatty acids, it was shown that for oil-in-water microemulsions, surfactants with larger cross-sectional areas required γ_i's that were less negative than surfactants with smaller cross-sectional areas. They maintained that this was why it was "easier" to form water-in-oil microemulsions as opposed to oil-in-water microemulsions.

This treatment represents the first attempt to explain the stability and the asymmetry in formation of oil-in-water and water-in-oil microemulsions in terms of experimentally measureable parameters.

B. Micellar Emulsions In Equilibrium With An External Aqueous Electrolyte

Adamson (2) formulated a thermodynamic model of transparent water-in-oil dispersions which were in equilibrium with an external phase of aqueous electrolyte. He chose to call the dispersed phase a micellar emulsion, since he felt that these systems embodied the properties of both emulsified

and micellar type systems. Equilibrium systems of this type had been described earlier by Winsor (25, 26) and Palit and co-workers (27).

Adamson considered only systems stabilized by ionic surfactants and non-ionic cosurfactants. All the surfactant was assumed to be in the micellar phase. The interfacial film was assumed to be largely dissociated and the resultant electrical double layer in the aqueous interior of the micelles was deemed responsible for a large part of the interfacial free energy. A Donnan type equilibrium was used to describe the charged film.

The Laplace Pressure

It was also assumed in this treatment that stability occurred when the osmotic pressure was balanced by the Laplace pressure. If the interfacial film was charged and most of the surfactant was in the micellar phase, the ionic concentration would be greater in the micellar phase due to the Donnan effect. For example, if a sodium salt were used in the aqueous phase in conjunction with a long chain sodium salt, there would be an excess of Na^+ in the aqueous portion of the micellar phase. As before, this difference in aqueous concentrations would give rise to a difference in osmotic pressure across the interface $\Delta \pi_{os} = \pi_m - \pi_b$, where π_m is the osmotic pressure of the micellar phase and π_b is the osmotic pressure of the water phase. Equating this to the Laplace pressure gives

$$\Delta \pi_{os} = \frac{2 \cdot \gamma_i}{r} \qquad 1\text{-}17$$

Substituting equation 1-2 for r gives

$$\Delta \pi_{os} = (n_{st} \gamma_i \sigma')/(1.5\ V)$$

where n_{st} is the number of moles of surfactant in the micellar phase and σ' is the cross-sectional area per mole of surfactant.

It can be seen that this treatment also does not require the admission of a negative or zero interfacial tension for oil continuous systems, the only ones treated.

This model was used (28) to analyze "micellar solutions" of aqueous Na_2SO_4 in a refinery hydrocarbon liquid (crude column overhead) stabilized by isopropyl alcohol and a "monosulfonated product of the alkyl-naphthaline type". These solutions were maintained in equilibrium with an aqueous Na_2SO_4 phase. The phases were separated after equilibrating, and the components assayed.

It was determined that the water content of the micellar phase increased asymptotically, approaching infinity, as the salt content was decreased. They concluded from this that these micellar solutions would not coexist in equilibrium with pure water (28). In their analysis, they assumed that the concentration of alcohol was the same in the micellar and bulk water.

They compared their distribution data to the values calculated from

$$(2C_{sm} + C_{em})^2 C_{sm} q^3 = 4C_s^3$$
$$\approx (2 C_s' + C_e')^2 C_s q^3 = 4C_s^3$$

Which is an approximation to the Donnan relationship for this system. C_s is the concentration of Na_2SO_4 in the bottom aqueous phase and C_e is the concentration of surfactant C_{sm} and C_{em} are the moles of Na_2SO_4 and surfactant per liter of micelles, respectively. The primes represent the corresponding terms per liter of water for the top phase; q is the ratio of mean activity coefficients of Na_2SO_4 in the micellar to the bulk aqueous phase. Plots of calculated and experimental values of C_s' versus C_s showed good agreement in the range of concentrations used as did plots of C_s versus ratio of moles of water to moles of surfactant in top phase (n_w'/n_e'). At high n_w'/n_e' ratios (> 50) the calculated values were slightly higher than the experimental values.

Values for γ_i were calculated assuming a constant surfactant cross-sectional area of $70A^2$. The range of γ_i was found to be 5-7 erg/cm^2, all positive. Average micellar radii were calculated using equation 1-17. $\Delta\pi_{os}$ was obtained using several approximations, namely

$$\pi_m = -(RT/V_w) \ln f_{wm} X_{wm}$$

$$\approx -(RT/V_w) \ln (1 - X_{sm})$$

$$\approx (RT/V_w) \left((3C_s'' + C_e'')/(3C_s'' + C_e'' + C_w'' + \frac{C_w'' C_a}{C_w})\right)$$

and

$$\pi_b = -(RT/V_w) \ln f_w X_w \approx -(RT/V_w) \ln (1 - X_s)$$

$$\approx (RT/V_w) \left((3C_s/3C_s + C_w + C_a)\right)$$

Where f represents the activity coefficient, x mole fraction, c molarity; the subscripts s, w, e and a represent Na_2SO_4, water, surfactant and alcohol respectively. Double primes represent quantities per liter of the top phase and unprimed quantities are on a per liter of bottom phase basis. m has the same significance as previously noted. These equations are strictly applicable only for ideal dilute solutions.

Using an average value of γ_i of 6.3 erg/cm^2 and the approximations mentioned, the calculated radii were from 30 to 200A. These values were within the range reported by Schulman (5, 8, 14).

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

Summary

These treatments de-emphasize the importance of the co-surfactant (alcohol) given it in the treatments of Schulman and Prince. There is also an incongruity in the treatments of the interfacial monolayer. The previous theories of water-in-oil microemulsions considered the interfacial

film to be unionized due to the high surfactant to water ratio, while the present models consider a completely ionized (2) or partially ionized (23) monolayer, even in the presence of neutral salt. The discrepancies have not yet been resolved. It is likely that the treatment of Adamson is not compatible with Schulman's since it is concerned with a different type of system. This is underscored in an extension of Adamson's (29) model using the Gouy-Chapman theory to treat the diffuse double layer of the microemulsion droplets. The authors came to the conclusion several times in their presentation that microemulsion formation was impossible in the absence of added electrolyte.

1.2.8 Micellar Solutions

Shinoda has done a large amount of work on solubilization in aqueous and non-aqueous solutions by non-ionic surfactants (3, 30-39). Recently, he has regarded the term "microemulsion" as applied by Schulman (10), Prince (20-22), and Rosano (23), to be a misnomer. In this criticism, he has had some company (2, 16, 25, 27, 28). He argued that that according to that IUPAC definition of solubilization (40), these systems should be termed micellar solutions since they are thermodynamically stable and of one phase, while an emulsion is defined as a heterogeneous system (1, 41). However, the question is moot, since it is not immediately obvious whether these systems are thermodynamically stable, one phase system (as will be discussed

below). Ultracentrifugal stability is not necessarily a criteria for thermodynamic stability and the question of whether the micelle is a separate phase reduces to whether it has a definite boundary and is itself a homogenous entity (42). McBain and Hutchinson (43) include emulsification as partof a continuous sepectrum of solution phenomenon. In any case, previous theories treating the micelle as a separate phase in microemulsions have met with some success in considering stability to be induced by mechanical means (2, 28). Shinoda and Hutchinson (30) and Shinoda (38) considered the micelle as a "psuedo-phase".

Shinoda treats micellar solutions (or microemulsions) of oil-in-water or water-in-oil on an empirical basis as did the previous workers. He maintains that the phase inversion temperature (PIT) is a totally acceptable parameter in characterizing the solubilizing power of solutions of non-ionic surfactants. The PIT is the temperature at which the solubility curve of water (oil) in a non-aqueous (aqueous) solution of surfactant meets the curve of the cloud point and at which a given solution of surfactant has the greatest solubilizing power. He considers it to be equivalent to an optimum HLB mixture of the surfactant. He concludes from his studies that for efficient solubilization one must have

1. Optimum HLB or PIT of a surfactant
2. Optimum temperature for a given non-ionic solubilizer

He also concludes that for mixtures of surfactants

1. There is an optimum mixing ratio of surfactants which will increase solubilization
2. The closer the PIT of the surfactants, the lower will be the amount of surfactant needed to solubilize a given amount of oil or water.

He further states that as the size of the hydrophile and lipophile groups of the non-ionic surfactant increases, the CMC will decrease, the aggregation number of the surfactant will increase and the solubilizing power of the surfactant will increase. This was similar to the findings of Rosano, et. al (23) with regard to increasing the size of the polar group of an ionic surfactant in oil-in-water microemulsions, but as will be dicussed below, is not strictly applicable to the lipophile of ionic surfactants in water-in-oil microemulsions.

In brief, the rules which the author has derived are not applicable to systems stabilized by ionic surfactants (34). The rules are useful, however, in choosing a non-ionic surfactant to solubilize water in a given oil or the reverse, if the PIT for a number of surfactants are known. Unfortunately, the rules give no insight into the solubilization (or microemulsification) phenomenon itself.

Gillberg, et. al. attempted to determine the types of interactions occurring in micellar solutions of benzene(44),

water, hexanol and potassium oleate by studying these systems by NMR. These compositions differed from those presented by Shinoda in that the surfactant was ionic in nature, but they were similar to those studied by Schulman. They concluded from measurements of chemical shifts and half band widths for the various species, that it was the distribution of hexanol between micelles and the continuous phase which determined the amount of water that could be solubilized in a water-in-oil microemulsion. This is similar to the conclusions drawn by Schulman and co-workers (10).

1.2.9 Inversion

It has been proposed that the inversion of one type of microemulsion into another occurs through the mediation of an intermediate phase in which the surfactant/co-surfactant monolayer forms layered structures of oil alternating with water (45) (figure 1.2).

This was based on measurements of viscosity, conductance and NMR chemical shifts. The intermediate phase was seen to be a highly viscous, transparent, birefringement gel. Shinoda calls this phase, when it is observed, a surfactant phase (I_{III}) (3). He noted that when the non-ionics used to make the micellar solutions were highly purified, this phase was reduced in area or eliminated completely. Moreover, this phase does not always appear even when ionic surfactants are used.

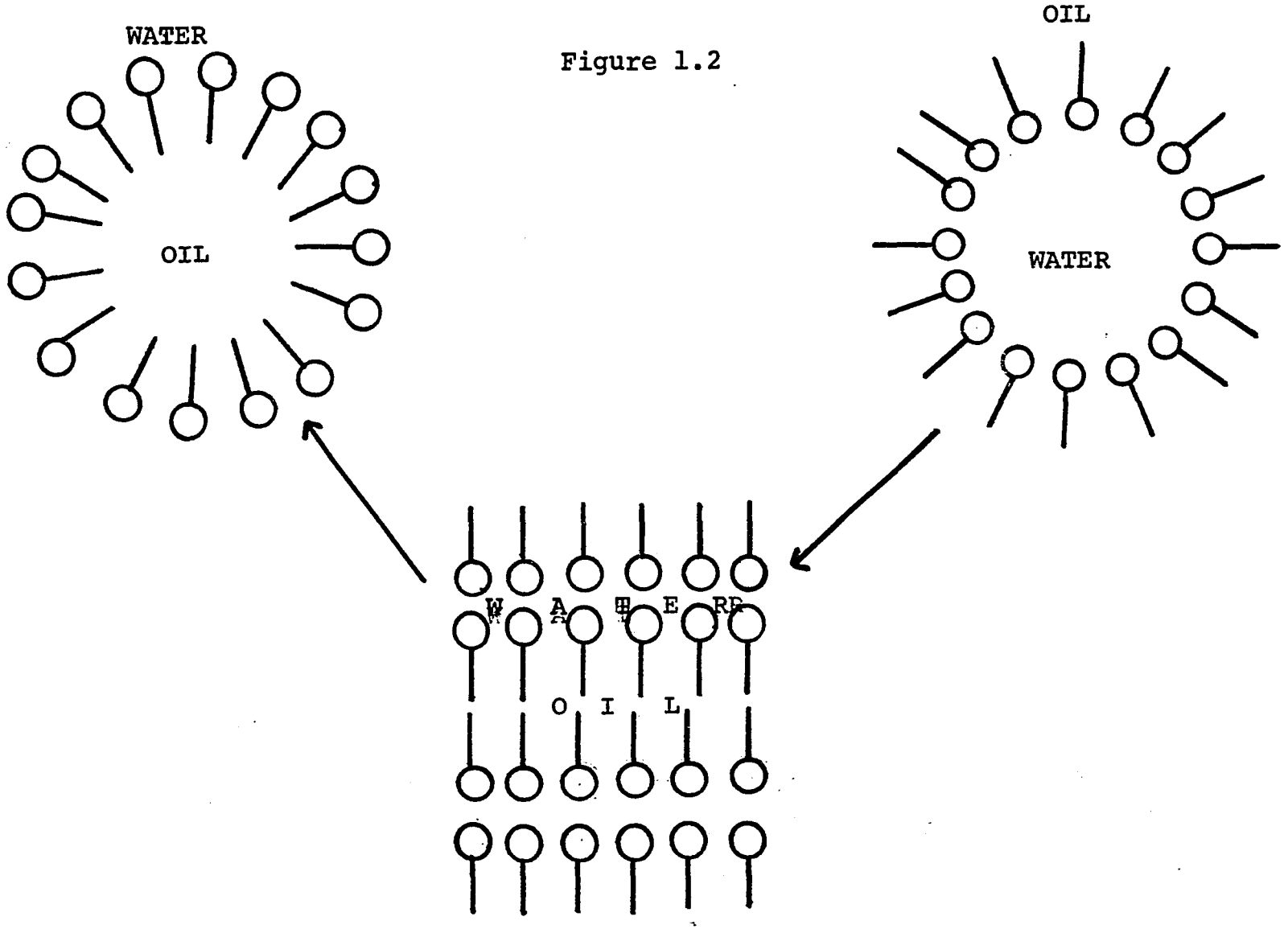


Figure 1.2

CHAPTER TWO

2.1 THE FORMATION OF MICROEMULSIONS

Microemulsions have hitherto been considered (10, 14) to be thermodynamically stable systems. That is, the dispersed micellar phase was considered to be in thermodynamic equilibrium with the continuous phase (20, 21). This was stated in the condition $\gamma_i = 0$.

The systems we are concerned with here consist of oil, water and two amphiphatic components. The condition of $\gamma_i = 0$ was thought to be brought about by the addition of the second amphiphatic component to the mixture of the other three substances. At a certain composition of the fourth component γ_i was thought to become negative, the interface would expand spontaneously until γ_i returned to zero (15). This model implies that since $\gamma_i = 0$ at equilibrium, the order of combining the materials should be unimportant.

If this model were correct, it would be important to understand how γ_i becomesnegative; for supposedly this is the origin of the driving force responsible for forming the microemulsion. To produce a $\gamma_i < 0$, π in equation 1-3 must become larger than $\gamma_{o/w}$. Schulman (4) postulated that this was accomplished by penetration of the cosurfactant into the interfacial film of the surfactant and complexing with the surfactant. Although it is possible to produce film pressures of sufficient magnitude to imply a negative γ_i in equation 1-3 (15), the relevance of the methods used to accomplish this ($\pi > \gamma_{o/w}$) to emulsion systems can be questioned.

In any case, if γ_i approaches zero, emulsions will form spontaneously (7, 46, 47). If the droplet size is small enough, the stability can be explained by means other than postulating $\gamma_i < 0$.

2.2 MEASUREMENT OF INTERFACIAL TENSION AS A FUNCTION OF TIME

The following experiments were undertaken in order to determine an alternate criteria to the negative interfacial tension requirement postulated by Schulman for the formation of microemulsions. This was done by observing the behavior of the oil/water interfacial tension as a function of time, after 1-pentanol had been injected above or below the interface. Measurements were made at the plain interface and in the presence of adsorbed SDS at a concentration below the CMC to avoid any interference from micelles in the bulk of the aqueous phase. It was hoped that this would provide an analogy to the curved interface of an emulsion.

2.2.1 Procedures

The interfacial tension of water against oil as a function of time was monitored by using an automated Wilhelmy slide method. A sandblasted Pt blade prewet with water was attached by a thread to a microforce transducer. The signal from the transducer was amplified by a transducer amplifier (transducer and amplifier were manufactured by Hewlett-Packard Corporation).

The signal was then plotted as a function of time on a

calibrated strip-chart recorder (Sargent-Welch Corporation). If the blade was drawn through an aqueous-oil interface, the signal was proportional to γ_i. No hysteresis was observed on drawing the blade through the interface from either side, therefore it was assumed that the contact angle was zero (48) for water.

1-pentanol was injected into one of the phases by using an agla micrometer syringe accurate to $\pm$.0005 ml (Burroughs-Welcome and Co., Durham, North Carolina). Gentle stirring was maintained in the phase in which the alcohol was being injected by using a magnetic stirrer (aqueous phase) or a motorized glass stirrer (oil phase). Several injections were made into each phase so that the systems in Fig. 2.1 contain varying amounts of alcohol. Fifty ml each of the oil and aqueous phase were used. Sodium dodecyl sulfate (SDS) solution was introduced into the aqueous phase by injecting an appropriate amount of an SDS solution. Sufficient time was allowed for the interface to reach equilibrium before any alcohol was injected. This was judged by the stability of γ_i as a function of time.

All systems were maintained at 30°C in a thermostated beaker 4.90 cm in diameter. The interface was cleaned initially before any injections were made by using suction from an aspirator through a narrow pipet.

2.2.2 Materials

The n-hexadecane and benzene were reagent grade (Eastman Organic Chemicals, Rochester, New York) and were used with-

out further purification. Sodium dodecyl sulfate (SDS) was a high purity grade (99%), purchased from A&S Corporation, Verona, New York. Fresh distilled water was used in all experiments.

2.3 RESULTS

The effect of diffusion of pentanol was measured for different volumes of 1-pentanol injected into the aqueous or oil phase. Measurements were also made with SDS in the aqueous phase. An SDS solution was injected into the water phase to give a concentration of 1.37×10^{-3}M. The CMC for SDS in the presence of the hexadecane water interface was observed to be 2×10^{-3}M. The volume of pentanol was increased until a transient $\gamma_i = 0$ was obtained (Fig. 2.1). The upper curve represents the variation of γ_i after 0.03 ml of 1-pentanol was injected into the oil phase with water as the aqueous phase; the two lower curves were measured with the SDS solution as the aqueous phase. The middle curve was determined after 0.04 ml of 1-pentanol was injected into the aqueous phase, while the bottom curve was the result after 0.03 ml of 1-pentanol was injected into the oil phase. It was observed that it took less alcohol to reduce γ_i to zero when injecting into the oil phase than when injecting into the water phase. After injection of the pentanol, the interfacial tension returned to approximately the same value as prior to injection. It is to be noted that the rate of diffusion (as determined by the time required for γ_i to reach a stable value) was greatly decreased in the presence

of the adsorbed monolayer of surfactant.

Microemulsions are usually prepared either by titrating with one of the components (as was described previously) or by mixing the pure components together. Either method permits transport of the amphiphatic components through the interface to occur. To avoid this and determine if transport is a necessary condition for microemulsification, an aqueous solution of surfactant and pentanol was prepared. The solution contained the amount of pentanol that would be present in the final microemulsion, as determined by the distribution data reported in chapter three. For example, 1.44 ml of water, 0.0032 moles of SDS and 0.024 moles of pentanol were used in one of the solutions. Another solution of oil and its ratio of pentanol was prepared. For example, 0.042 moles of pentanol and 40.0 ml of n-hexadecane was used in conjunction with the aqueous solution. The two solutions were then mixed together for approximately twenty minutes at 30°C but no microemulsion resulted. It is to be emphasized that these components, when combined in the usual way (i.e., by titrating the alcohol) in the amounts described, would have resulted in the formation of a microemulsion. Microemulsions generally form almost immediately when the proper conditions are provided. These systems prepared in this way were not even stable with regard to phase separation. Upon standing for a few minutes, the system separated into a lower clear aqueous phase and an upper hazy water in oil emulsion phase.

The solutions actually used were:

A. 0.92 gm SDS
1.44 ml water
3.61 ml pentanol

Mixed with:

40.0 ml n-hexadecane
4.57 ml pentanol

B. 0.92 gm SDS
1.44 ml water
3.16 ml pentanol

Mixed with:

60.0 ml benzene
7.95 ml bentanol

2.4 DISCUSSION

It is apparent from the above experiments that it is possible for the interfacial tension of a system to drop to zero for a certain period of time due to redistribution of amphiphatic molecules while the equilibrium γ_i remains positive.

The requirement of diffusion across the interface in these systems was demonstrated in the experiments last described. The transport process has been mentioned before as a necessary condition for spontaneous emulsification (49, 50), but it is not a sufficient condition for microemulsification in these systems since pentanol does not produce microemulsions in all of the dodecyl sulfate systems. It is reasonable that the surfactant must be able to stabilize the system against coagulation and coalescence after the cosurfactant has lowered the interfacial tension sufficiently to cause dispersion. The ability of the surfactant to accomplish this would depend upon the type of interfacial film it forms

and its solubility in the phases present.

While there is no way to simulate, on a macroscopic level, an interface with the degree of curvature exhibited by microemulsions, many studies have been performed at planar oil/water interfaces (15, 50) with the assumption that the results obtained will hold, at least in a qualitative manner, at the curved interface. However, in the case of pure substances the interfacial tension would, theoretically, decrease with increasing curvature. With the multi-component mixtures discussed here the situation is not as straight forward (51).

In any case, if the general type of curve observed in Fig. 2.1 is indicative of the processes occurring in the emulsion systems, then an explanation of experiments A and B reported above is immediately apparent. To rationalize this result the processes which led to the formation of a microemulsion, i.e., a small droplet size, must be considered.

If pentanol is added to a mixture of soap, water and oil (for a w/o microemulsion), the pentanol will diffuse through the continuous phase until it reaches an interface. When it contacts the interface between the oil and water, three possibilities are available to it:

A. The alcohol can adsorb at the interface and remain there;

B. It can adsorb at the interface for a certain length of time and then desorb into the continuous or dispersed phase;

C. It can remain in the continuous phase without adsorption.

Adsorption of the cosurfactant at the interface would cause the interfacial tension between the oil and water phases to drop to a lower value, as would adsorption of any surface active substance. If this were followed by desorption of some or all of the cosurfactant and/or expansion of the interfacial film, the interfacial tension would then rise again. If enough cosurfactant was added, at some point, the interfacial tension would reach a very low value ($\approx$ 0 dyne/cm). When this occurred, the amount of work required to subdivide the phase and disperse it would be very low.

This scheme describes qualitatively the data reported in Fig. 2.1. It can be seen that this model does not require a negative γ_i or a $\gamma_i = 0$ at equilibrium.

The previously described experiments, A and B, can be seen to support this view. The contention is that the reduction of the interfacial tension to zero is a necessary condition for producing the small droplet size of the microemulsions. In the formulations discussed here, it is the redistribution of the alcohol which lowers γ_i to zero. If the alcohol were predistributed in the phases at the equilibrium concentration before combination, the system would have a positive interfacial tension and the microemulsion would not be produced. This was the case in experiments A and B. For this reason, no microemulsions were formed.

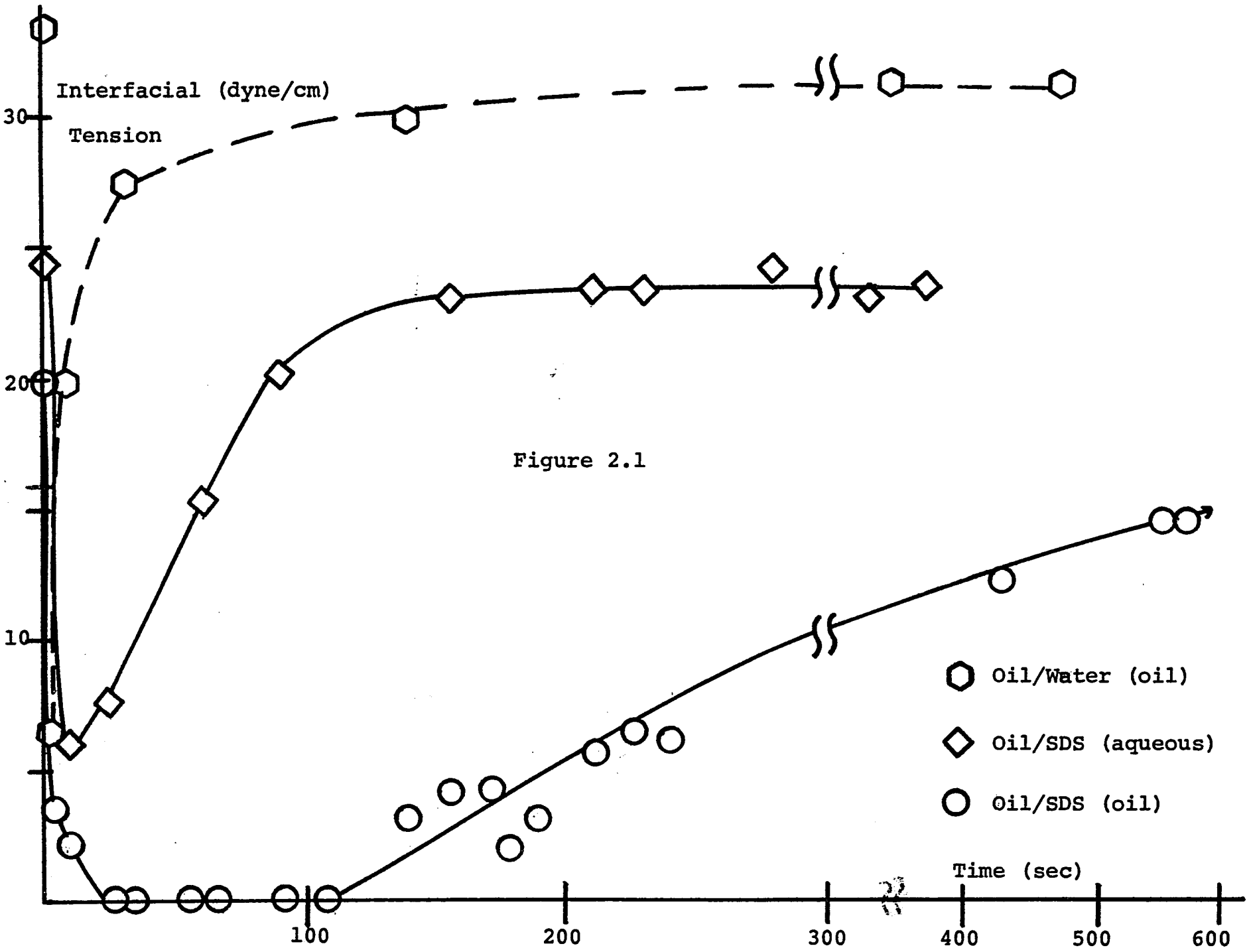

Interfacial (dyne/cm)
Tension
30
20
10
100
200
300
400
500
600
Time (sec)
Oil/Water (oil)
Oil/SDS (aqueous)
Oil/SDS (oil)

Figure 2.1

CHAPTER THREE

3.1 THE STABLIZATION OF MICROEMULSIONS

In the previous chapter, the mechanism by which microemulsions are formed was discussed. It was concluded that after the microemulsion was formed the droplets had to be stabilized against coalescence in order to prevent phase separation. A low γ_i does not guarantee stability (52).

Schulman (7, 10) stated previously that complex or mixed film formation between the surfactant and cosurfactant was essential for the formation of microemulsions, since it was believed that under these conditions γ_i would assume negative values. However, no evidence was presented for this complex formation. Moreover, Goodrich (53) evaluated surface isotherms for monolayers of long chain sulfate, sulfonate, and ammonium surfactants penetrated by long chain alcohols. He concluded that there was no hydrogen bonding between the polar groups, although such interactions would not have been inconceivable. The data were interpreted as supporting the view that 1:1 complexes had formed through association of the hydrocarbon tails. However, it has been alleged (15, 21) that hydrogen bonding between the amphiphiles at the oil-water interface is responsible for the stability of microemulsions. If Schulman's ideas were correct and hydrogen bonding were an important factor in microemulsion stability, it would be expected to be in evidence in measurements of certain properties of the system (e.g., NMR chemical shift, free energy of adsorption).

Hydrogen bonding and the factors determining the stability of microemulsions will now be discussed.

3.2 PREPARATION OF MICROEMULSIONS

3.2.1 Procedure

Microemulsions were prepared in the manner described by Schulman (6,10). That is, a given amount of oil, water and surfactant were combined in a thermostated beaker at 30°C. The mixture was titrated to clarity with pentanol or some other long chain alcohol. More oil was then added and the titration to clarity was repeated. This was done four or five times.

Specifically, the microemulsions reported on in tables 1 thru 7 were prepared using 40.0 ml of oil, 0.0032 moles of surfactant and 1.44 ml of water or 2.2 N base solution when the carboxylates were the surfactants. The mixture produced a coarse turbid emulsion which was titrated to clarity with 1-pentanol. Ten or twenty milliliters of oil was then added causing a transition from the clear microemulsion to a macro-emulsion with a concomitant increase in turbidity. Clarity was then reproduced in the sample by again titrating with pentanol. The compositions at which the system first became clear were plotted according to equation 1-11. Representative curves for water in n-tetrachloroethylene (TCE) microemulsions stabilized by long chain sodium sulfates are given in Fig. 3.1 the chain length of the surfactant was varied from C_6 to C_{14}. It can be seen that all the points are well represented by

equation 1-11 in the composition ranges studied here.

3.2.2 Materials

The n-hexadecane and benzene were reagent grade (Eastman Organic Chemicals, Rochester, New York). They were used without further purification. The o-xylene, carbon tetrachloride and tetrachloroethylene were also reagent grade (Fisher Scientific).

Dodecyl sulfates with various cations were prepared from SDS by an ion exchange process described by Rosano, et. al. (23). The remaining long chain sulfates were practical grade (Eastman Organic Chemicals). The LiOH, NaOH, KOH, NH_4OH and $(CH_3)_4NOH$, were reagent grade (J. T. Baker Co., Phillipsburg, New Jersey). The CsOH and RbOH were 99.5% pure (Amend Drug and Chemical Co., Inc., New York). The tetraethyl ammonium hydroxide was reagent grade (Matheson Coleman & Bell, Cincinnati Ohio). The 2-amino-2-methyl-1-propanol (AMP) was a commercial sample for Commercial Solvents Corporation (N.Y., N.Y.). Distilled water was used in all experiments.

3.2.3 Distribution Curves

Curves such as those shown in Fig. 3.1 can be interpreted by equation 1-11 to give the distribution of cosurfactant (pentanol) between the dispersed and continuous phases in the microemulsion system. The intercept (I) shows the number of moles of pentanol per mole of surfactant in the dispersed phase. The slope (k) of the distribution curves gives the number of moles of pentanol per mole of oil

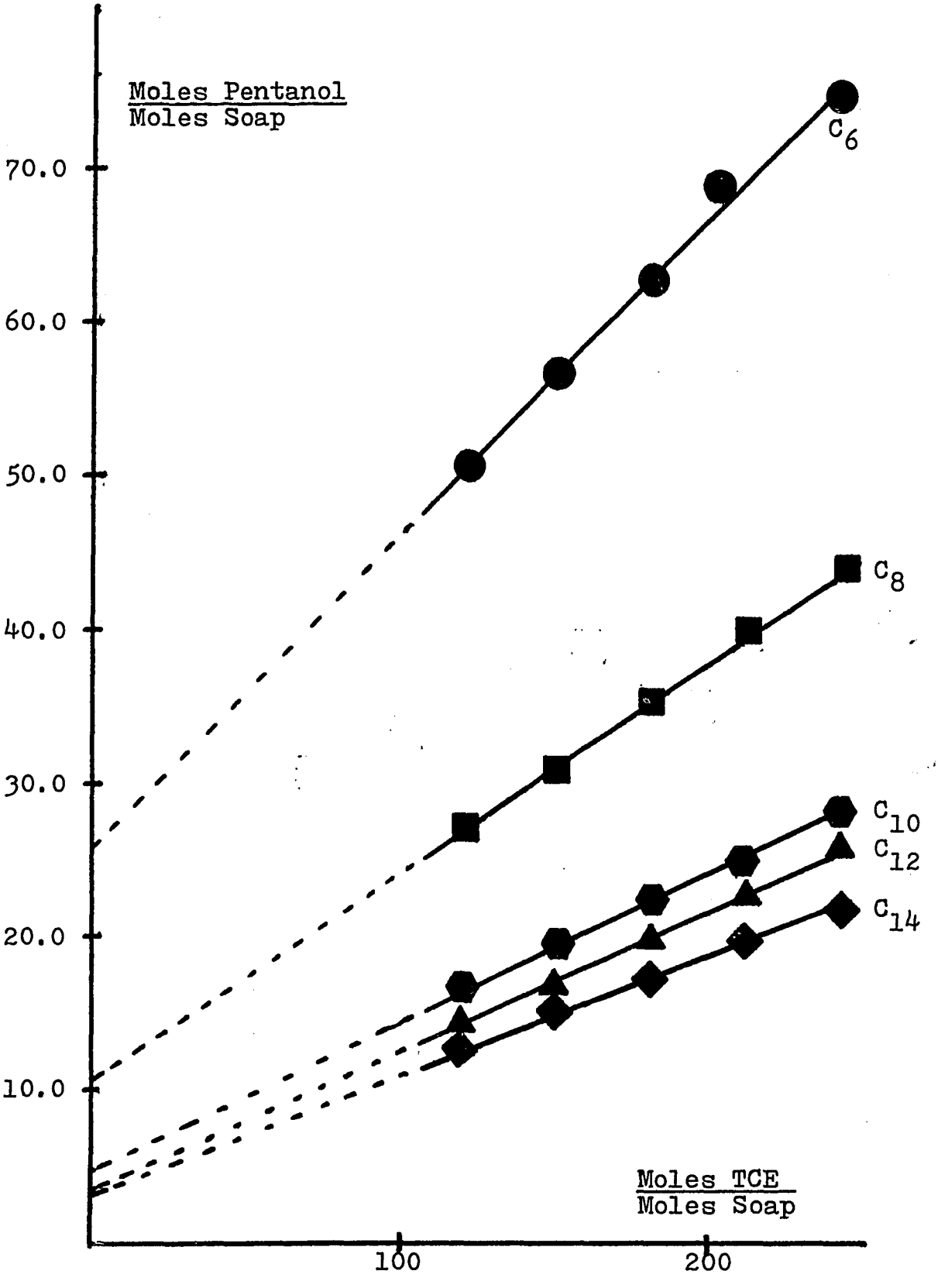


Figure 3.1
Microemulsions of Water-in-TCE Stabilized by Long Chain Sodium Sulfates (30°C).

molecules in the continuous phase. I and k were determined by a least squares fit of the data.

It can be seen from tables 1 thru 7 that I and k vary with the type of surfactant and oil. Generally, both parameters decrease with increasing chain length of the surfactant in a given oil. For a given oil, the requirement for pentanol diminished as the surfactant became more hydrophobic in character (longer chain length). The more hydrophilic oils showed a decrease in k as compared to the values in n-hexadecane and an increase in I for the same surfactant. The ability of a certain type of surfactant (e.g., sodium carboylate or sulfate) to stabilize a microemulsion reached an abrupt cut off point in many cases. For instance, when sodium carboxylates were used as the surfactants, microemulsions were produced in n-hexadecane (table 1) when the hydrocarbon chain length varied from twelve to eighteen carbon atoms, but no w/o microemulsions could be produced when sodium eicosanoate (C_{20}) was used as the surfactant. The lower limits of the hydrocarbon chain length of the emulsifier, below which no microemulsion could be formed, were, in general, not observed. An exception was seen in using AMP carboxylates to stabilize microemulsions in n-hexadecane. When AMP was used under these conditions, microemulsions were formed only with the palmitate and the stearate. AMP palmitate and laurate were also unusual in that the requirements for alcohol were extremely low. Ammonium and lithium carboxylates were also unusual in that

Table 1

WATER-N-HEXADECANE MICROEMULSIONS

Long Chain Sodium Sulfates

Chain Length	k Moles Pentanol / Mole Oil	I Mole Pentanol / Mole Soap
C_6	.57	28.0
C_8	.54	24.0
C_{10}	.41	14.0
C_{12}	.25	7.5
C_{14}	.27	6.5

Dodecyl Sulfates

Counter Ion	k	I
Li+	.29	3.5
Na^+	.28	7.5
K^+	.28	7.5
Cs+	.29	3.5
Rb^+	.31	5.0
NH_4^+	.29	5.0
$(CH_3)_4N^+$	.38	11.5
$(C_2H_5)_4N^{++}$	.45	13.5
AMP^+	.40	8.5

Table 2

WATER-BENZENE MICROEMULSIONS

Long Chain Sodium Sulfates

Chain Length	k	I
C_6	.12	23.5
C_8	.13	9.0
C_{10}	.11	7.5
C_{12}	.10	9.5
C_{14}	.04	9.5

Table 2
(Continued)

Dodecyl Sulfates

Counter Ion	k	I
Li^+	.09	6.0
Na^+	.11	9.0
K^+	.09	6.0
Cs^+	.07	5.0
Rb^+	.07	4.0
NH_4^+	.08	4.0
$(CH_3)_4N^+$	.10	5.5
AMP^+	.04	25.

Table 3

WATER-CARBON TETRACHLORIDE MICROEMULSIONS

Long Chain Sodium Sulfates

Chain Length	k	I
C_6	.23	27.6
C_8	.02	7.0
C_{10}	.08	7.5
C_{12}	.10	4.2
C_{14}	.07	4.5

Table 4

WATER-TETRACHLOROETHYLENE MICROEMULSIONS

Long Chain Sodium Sulfates

Chain Length	k	I
C_6	.30	27.5
C_8	.14	10.0
C_{10}	.09	6.0
C_{12}	.09	3.5
C_{14}	.08	3.5

Table 5

WATER-O-XYLENE MICROEMULSIONS

Long Chain Sodium Sulfates

Chain Length	k	I
C_6	.21	26.0
C_8	.18	11.0
C_{10}	.14	6.7
C_{12}	.13	6.7
C_{14}	.12	5.0

Table 6

WATER-N-HEXADECANE MICROEMULSIONS

Long Chain Carboxylates

Sodium Carboxylate

Chain Length	k	I
C_{12}	.36	7.5
C_{14}	.25	5.0
C_{16}	.20	3.0
C_{18}	.16	2.5
C_{20}	No Microemulsion	

Potassium Carboxylate

Chain Length	k	I
C_{12}	.38	10.0
C_{14}	.27	5.0
C_{16}	.23	5.0
C_{18}	.17	5.5

Rubidium Carboxylate

Chain Length	k	I
C_{12}	.44	7.0
C_{14}	.30	2.5
C_{16}	.26	2.5
C_{18}	.22	2.5

Table 6
(Continued)

AMP Carboxylate

Chain Length	k	I
C_{12}	No Microemulsion	
C_{14}	No Microemulsion	
C_{16}	.16	0.5
C_{18}	.13	0.5
C_{20}	No Microemulsion	

Table 7
WATER-BENZENE MICROEMULSIONS
Long Chain Carboxylates

Sodium Carboxylate

Chain Length	k	I
C_{12}	.14	10.0
C_{14}	.12	9.0
C_{16}	.11	5.5
C_{18}	No Microemulsions	
C_{20}	No Microemulsions	

Potassium Carboxylate

Chain Length	k	I
C_{12}	.13	18.5
C_{14}	.12	15.5
C_{16}	.11	12.0
C_{18}	.11	9.0

Rubidium Carboxylate

Chain Length	k	I
C_{12}	.13	15.0
C_{14}	.14	10.5
C_{16}	.13	8.0
C_{18}	.12	7.0
C_{20}	.10	7.0

no microemulsions were successfully prepared using these surfactants. In fact, the longer chain carboxylates (C_{16} to C_{20}) precipitated as pentanol was added to the initial dispersions, indicating a decrease in solubility of these longer chain ammonium and lithium carboxylates.

The temperature of the system was seen to have little effect upon the distribution curve for microemulsions in n-hexadecane stabilized by SDS (Fig. 3.2). The slight decrease in I with increasing temperature, however, indicates that the equilibrium between pentanol in the continuous phase (A_c) and pentanol in the dispersed phase (A_d).

$$A_d \rightleftharpoons A_c$$

is shifted to the right and that the equilibrium is exothermic on going to the left.

The effect of changing the counterion is not clear cut. The stericly larger counterions such as tetramethyl and tetraethylammonium ion required the largest amount of pentanol in the interface in n-hexadecane but these cations do not show any significant difference from Cs^+, K^+, Li^+, Rb^+ and NH_4^+ in benzene when the dodecyl sulfate was the anion. Varying the cation of the surfactant had no apparent effect on k as would be expected if the surfactant counterions were isolated from the continous medium, except when tetramethyl, tetraethylammonium or AMP was the cation. This might be accounted for by an increased solubility of these particular species in the continuous medium which then might effect the alcohol content of the oil phase.

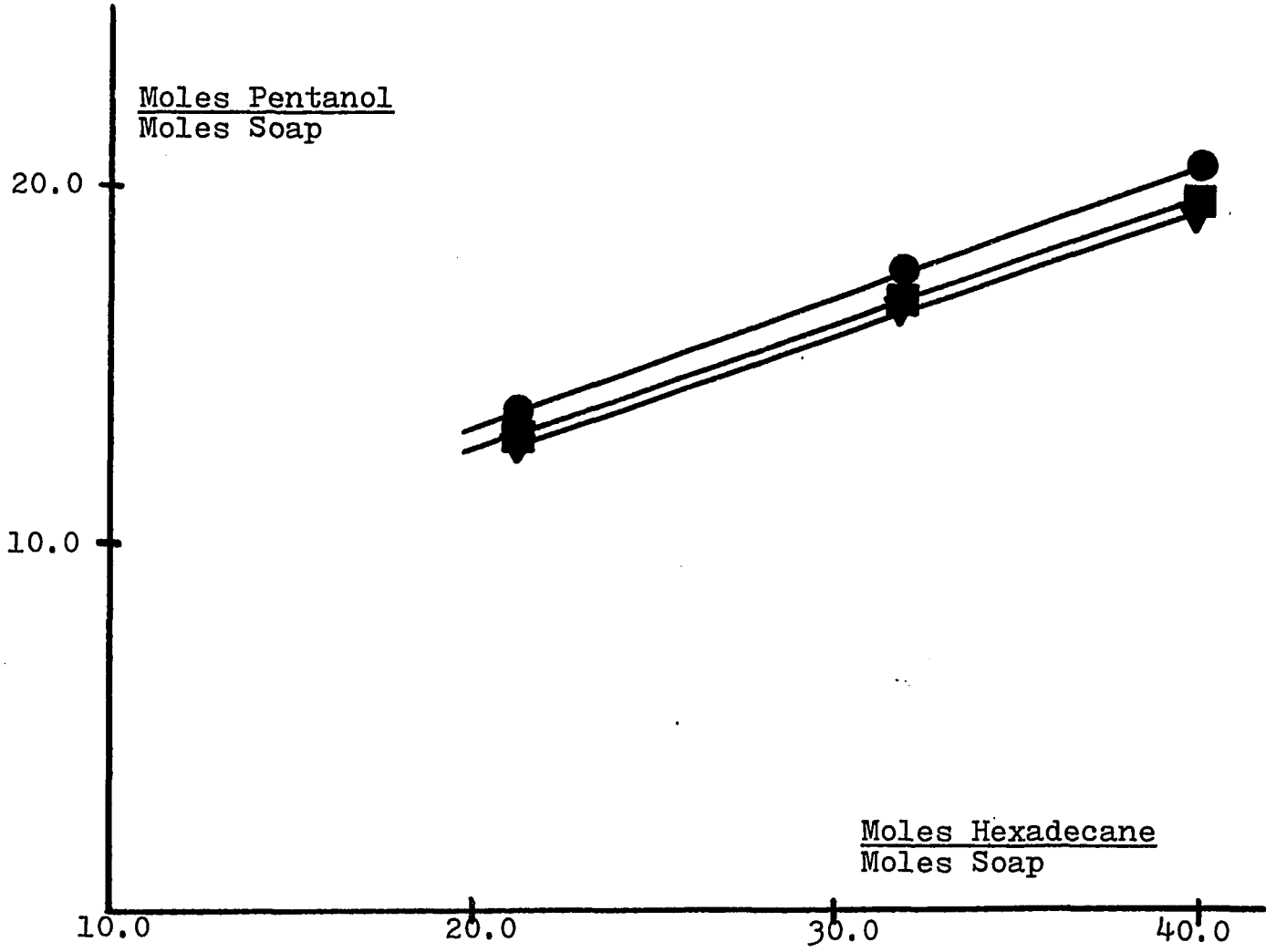


Figure 3.2

Effect of Temperature on the Formation of Water-in-n-Hexadecane Microemulsions
(● 20°C; ■ 30°C; ▼ 40°C)

Changing the counterion, however, did have an effect on the magnitude of I, although it did not correlate with the order of the size of the ion (54). Instead of a continual decrease or increase, the intercept reached a maximum at potassium or sodium. No explanation can be offered for this effect at this time except to say that it could possibly be caused by differences in the extent of solvation of the cations at the oil-water interface. The results do not substantiate Schulman's claim (6) that there is a sharp transition point from oil to water continuous systems as the hydrophobic - hydrophillic character of the surfactant cosurfactant combination is varied, since the same formulations will be seen to be applicable in forming o/w microemulsions, in many cases, just by changing the relative concentrations of the components. Also, the claim that matching the chemical nature of the surfactant to that of the oil phase is critical (10), is unwarranted. It would seem also that Schulman's claim that the alcohol remained at the interface changing its wettability, and therefore determining the nature of the continuous phase, is also unfounded, since it was observed that the slope did not vary in the same manner as I.

3.3 SOLUBILITIES OF SURFACTANTS, ALCOHOLS AND WATER IN THE VARIOUS PHASES OF A MICROEMULSION

It was necessary to know the solubility or at least an order of magnitude of the solubility of the surfactants in the continuous phase (pentanol and oil) of the micro-

emulsion. Any significant solubilization of surfactant would effect the various measured and calculated parameters (e.g., hydroxyl chemical shift, particle size). The solubility of pentanol in water and of water in pentanol-n-hexadecane solutions were also measured for the same reason. The values were determined experimentally as none were found in the literature.

3.3.1 Solubility of Surfactants in Oleophillic Solutions

The solubility of long chain sulfate surfactants in solutions of n-pentanol and n-hexadecane were measured at 30°C by flame emission photometry. A Jarrell Ash Atomic Absorption Flame Emission Spectrophotometer (Model JA 82-500, Fisher Scientific, Waltham, Mass.) was used for the measurements. The amount of sodium present was taken as an indication of the amount of long chain surfactant that had been solubilized. The 586 mμ emission line of sodium was used in the determinations. Solutions of n-pentanol and n-hexadecane were saturated with the surfactant to be measured at 30°C. The supernatant was then decanted and the sodium emission measured immediately. The instrument was adjusted to zero with the pentanol and hexadecane solution. Standards were prepared using sodium hexyl or octylsulfate. Sodium octylsulfate showed the highest solubility in the mixed solvents and, therefore, its solubility could not be determined by this procedure. The solubility of the sodium sulfates from C_{10} to C_{20} are shown in Fig. 3.3 as a function of the volume ratio of n-pentanol to n-hexadecane. The maximum relative

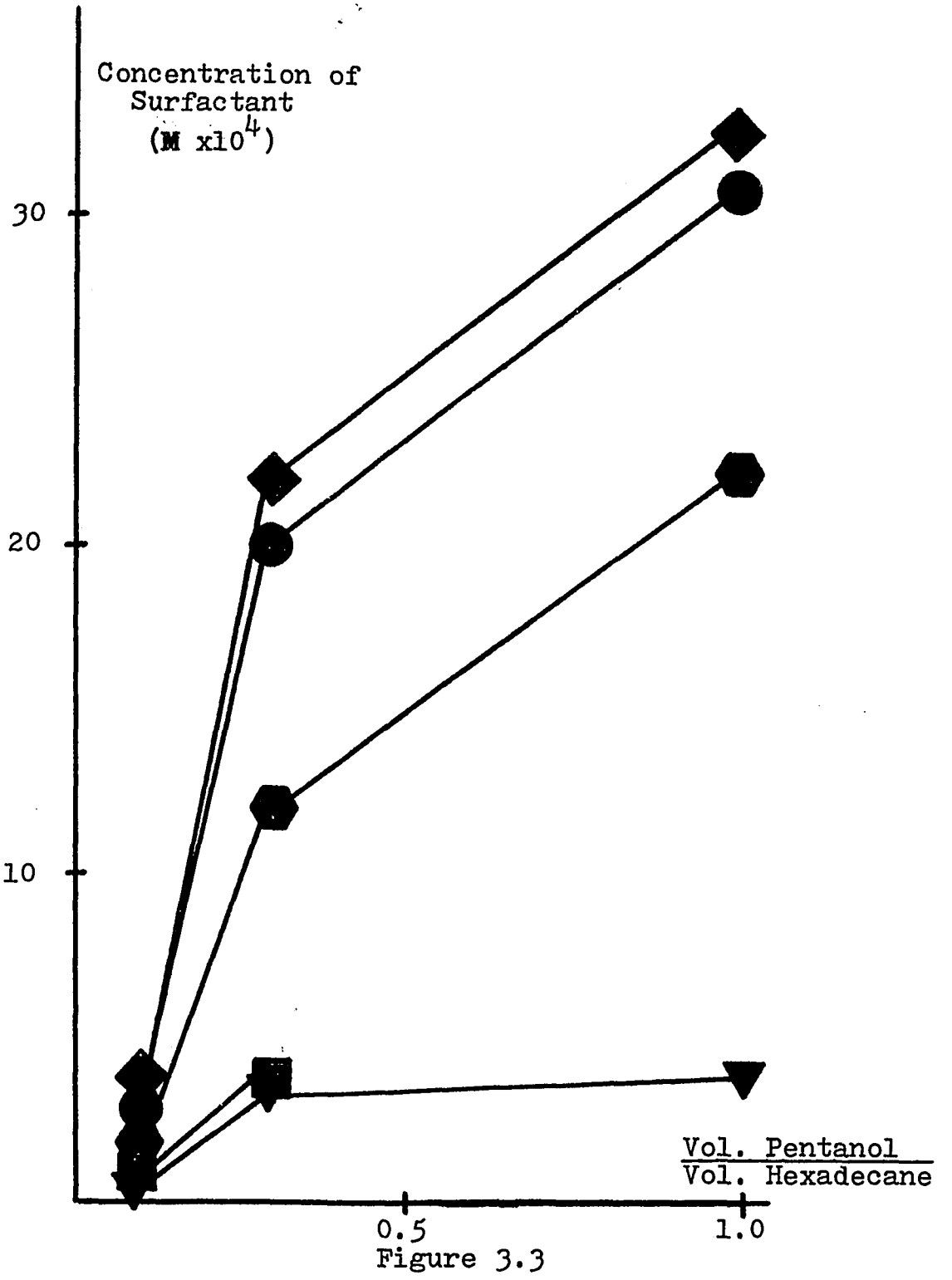


Figure 3.3

Solubility of Sodium Sulfates in n-Pentanol/ n-Hexadecane (30°C).
(◆ C_{10}; ● C_{12}; ● C_{14}; ■ C_{16}; ▼ C_{20})

average deviation was 7% and was usually less. The solubilities were found to be very low, on the order of 10^{-4}M.

The relative order of solubilities of the surfactants follows that seen in the titration experiments. That is, the lower the solubility of the surfactant in the solvent mixture, the lower was the requirement for alcohol in the microemulsions.

The values reported in Fig. 3.3 are not expected to be the actual amounts of surfactant dissolved in the continuous phase of a microemulsion system, but only an upper limit. The actual amount would be less due to the presence of the oil-water interface, which the surfactant should favor. In any case, the amounts of surfactant dissolved in the continuous phase in a microemulsion would be negligible for the purposes of the discussion here. For example, in a microemulsion consisting of 80 ml of n-hexadecane and pentanol, only about 8 X 10^{-6} moles of surfactant would be expected to dissolve in the continuous phase as an upper limit. The rest would be in the dispersed droplet. It is therefore assumed in the discussion to follow that any solubility of surfactant does not affect the parameter being discussed.

3.3.2 Solubility of Alcohols In Water

The solubilities of alcohol in water and of water in the various alcohols were measured by a procedure reported by Hill (55) using 100 ml ground glass graduated cylinders in

place of the volumetric apparatus constructed by Hill. Different weights of the alcohol and water were placed in two cylinders. The volume ratios of the upper and lower phases were 1:9 and 9:1, respectively, in the two cylinders. The cylinders were shaken vigorously, sealed with parafilm to prevent evaporation, and placed in water bath (Hot Pack Corporation, Philadelphia, Pa., Model 334) at 30 $\pm$ .5^{0}C for 24 hours. The procedure was also repeated at 25^{0}C.

The volume of the upper phase (alcoholic) and the lower phase were then measured. The solubilities were calculated from

$$m = v_1 x + v_2 y \qquad (3\text{-}1)$$

$$m' = v_1' x + v_2' y \qquad (3\text{-}2)$$

where m and m' are the weights of alcohol used, v_1, v_1' and v_2, v_2' are the volumes of the upper and lower phases, respectively in each cylinder; x and y are the concentration of alcohol (gm/ml of solution) in the upper and lower phases, respectively. Equivalent equations can be written for the concentration of water. The two equations (3-1 and 3-2) can then be solved for x and y once the volumes in the two cylinders are known.

Hill obtained excellent precision ($\pm$.09%) and agreement with previous work done by Klobbie (within .06%) on the measurement of the solubility of water in ether. Klobbie (56), using a different procedure, evaporated the solutions through calcium chloride tubes designed to retain water. Hill's

apparatus was specially designed, for these measurements, although he does state that accuracy within a few percent can be obtained using ordinary 100 ml graduated cylinders, as was done here.

The method was also used by Hill (57) to determine the mutual solubility of phenol and water, and butyl alcohol and water. Kablukov and Malischeva (58) used the same method for ethyl ether - water and iso-amyl alcohol - water systems, good agreement was found with previous work done by Hill (55). The results of the measurements done here for n-pentanol and isoamyl alcohol were 1.8 and 2.0 gm n-pentanol/ml at 25°C and 30°C, respectively, and 2.2 gm of isoamyl alcohol/ml at 30°C. The solubility of n-octanol could not be measured by this procedure as it was too small.

3.3.3 The Solubility Of Water In Pentanol And n-Hexadecane Solutions

The volume of water solubilized by mixtures of n-hexadecane and n-pentanol at 25 and 30°C was determined by using the apparatus diagramed in Fig. 3.4. The reservoir (A) was a 500 ml glass stoppered flask. The volumetric section (B) was constructed from a 10 ml buret, calibrated in 0.02 ml intervals.

The apparatus was calibrated by delivering known amounts of water into the volumetric section by means of an agla micrometer syringe. Hexadecane was then added to the reservoir. The whole apparatus was inverted and shaken and placed in a water bath at a given temperature and allowed to equilibrate.

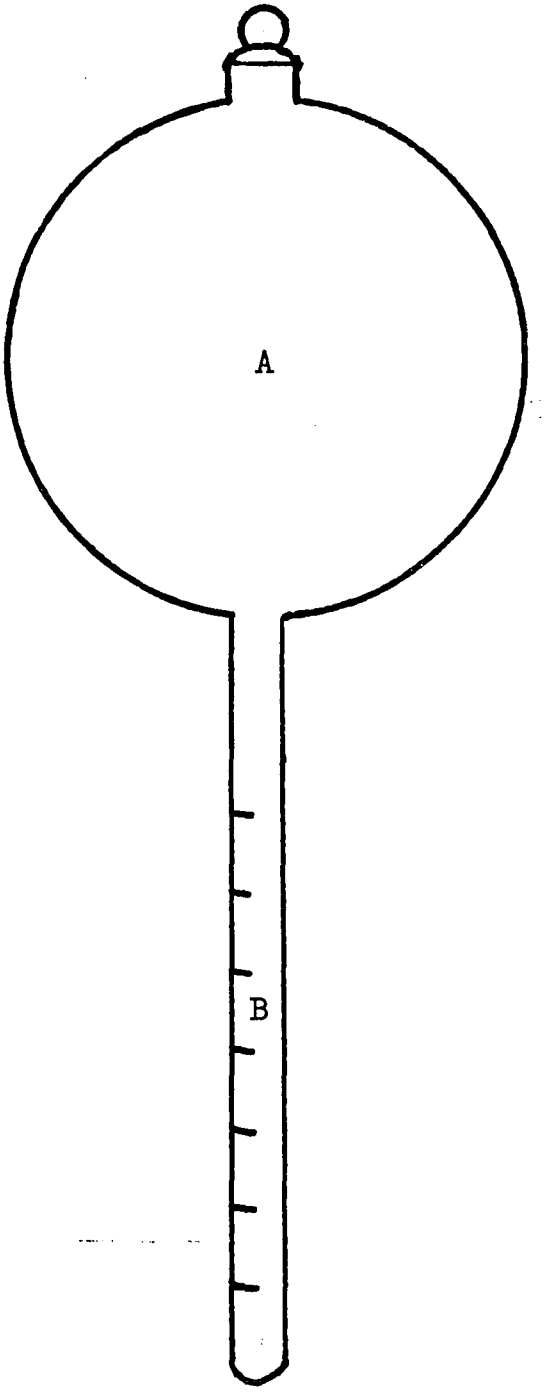


Figure 3.4

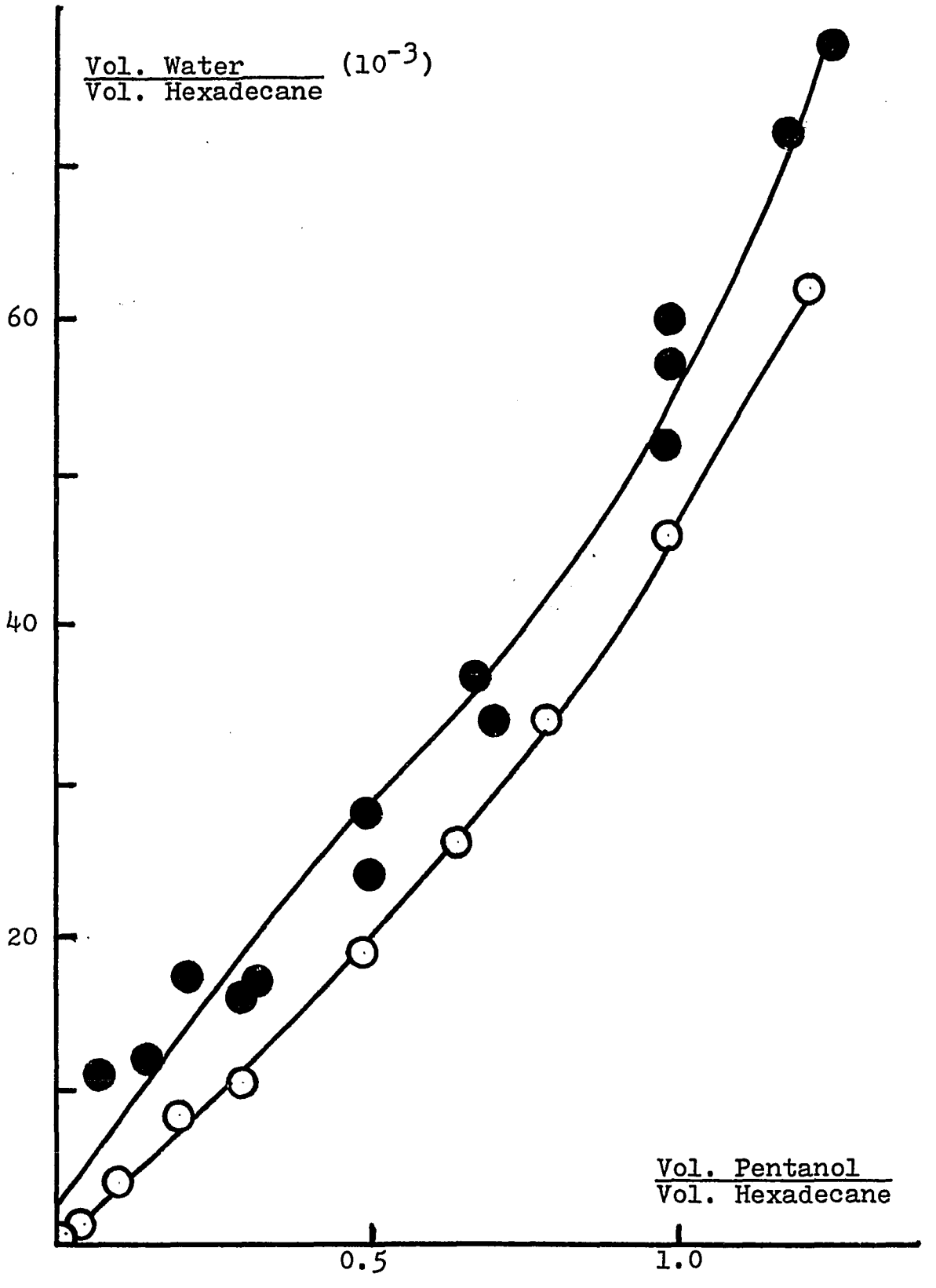


Figure 3.5

Volume of Water Solubilized by Pentanol in n-Hexadecane
(● 30°C; ○ 25°C)

The interface position was read and n-pentanol was added from a buret. The apparatus was again inverted, shaken and returned to the water bath to equilibrate. This process was repeated until all of the water had been solubilized.

The major source of error in this procedure was due to the adhesion of water to the sides of the reservoir. This could not be completely eliminated even though the apparatus was washed several times with hot chromic acid cleaning solution. This necessitated removing the apparatus from the bath occasionally to shake down the drops of water. Due to this circumstance, the volume readings were lower by approximately 0.05 ml; causing an increase in the apparent volume of water solubilized.

The results are reported in Fig. 3.5 at 25 and 30°C. The solubility of water was found to be dependent only on the amount of pentanol present, indicating a specific interaction between the pentanol and water.

3.4 INVESTIGATION OF SURFACTANT -COSURFACTANT COMPLEXING BY NMR

Proton nuclear magnetic resonance was used to study the microemulsion systems to determine if hydrogen bonding between the surfactant and cosurfactant played an important role in stabilizing the dispersed droplets against coalescence.

Nuclear magnetic resonance techniques involve the application of a magnetic and radio frequency field to the nuclei under

study. A NMR absorption occurs when the nuclei in question oriented in the applied magnetic field (H_o) absorbed enough energy from the radio frequency field to attain a higher nuclear spin state.

The great usefulness of NMR spectrometry arises from the fact that the resonance of a nucleus is affected by the electron density around it and the magnetic environment created by neighboring nuclei.

Historically, proton NMR has proven the most useful up to this time, but other nuclei, particularly ^{13}C, are being used more and more frequently (59-61). Since the NMR spectrum of a hydrogen nucleus is affected by the surrounding nuclei, proton NMR has served as a useful tool in elucidating molecular interactions that affect protons (62-73). Specifically, emulsions (63), and microemulsions (18, 45), surfactant solutions (64-66), and micellarization (67-70), micellar solubilization (71), gels and liquid crystals (72-74), mixed surfactant interactions (75-77), and hydrogen bonding (78, 79) have all been investigated by NMR techniques.

Three empirical parameters are most often used in NMR studies: chemical shift, spin-lattice relaxation time, and half-band width.

A. The chemical shift arises from the magnetic screening of the nuclei produced by surrounding electrons. Due to these electrons, the nuclei do not experience the applied magnetic field, but the field perturbed by the shielding

electrons. Any influence that affects the electron density around the nucleus, therefore, will affect the magnetic field at the nucleus and consequently the nuclei will resonate at an applied field different from that of the unshielded nuclei.

B. The spin-lattice relaxation time is the time that the particular nuclear spins require to equilibrate with the environment through non-radiative decay processes. Spin-lattice relaxation arises because the Boltzman distribution of nuclear spins is not established instantaneously when a system of nuclei are put in a magnetic field. Initially, the population of spins in the upper and lower spin states are equal. The spin population is redistributed by interaction of the nuclei with the surrounding "lattice". This decay process is characterized by a time T_1, the spin-lattice relaxation time, which is the life time of the decay process. The existence of spin-lattice relaxation implies that the NMR resonance line must be broadened at least of the order of $1/T_1$. This would produce, for liquids, line widths at half-maximum of the order of 10^{-2} to 10^{2} Hz (80). If the line width is larger than that predicted from T_1, the additional broadening is attributed to spin-spin relaxation characterized by T_2. It results from the interaction of the magnetic moments of the various nuclei present with the resonating nuclei. T_2, the spin-spin relaxation time, is defined as $T_2 \approx 1/\nu_{\frac{1}{2}}$, where $\nu_{\frac{1}{2}}$ is the half-band width.

In most liquids broadening due to spin-spin relaxation is

negligible, but becomes important with increasing viscosity.

C. The half-band width is related to the freedom of motion of a particular nucleus. If the nucleus is in rapid motion $\nu_{\frac{1}{2}}$ is small, but if the nuclear motions are slow, dipole-dipole interactions become important and the line width increases.

All three parameters can give valuable information about the environment of the nucleus.

3.4.1 Procedures And Results

NMR spectra were recorded using a Varian A-60 (Varian Associates, Palo Alto, California) and a Jeolco C-60 (Japan Electron Optics Labs, Tokyo, Japan) 60 MHz nuclear magnetic resonance spectrometers. Water in oil microemulsions were studied by first preparing emulsions containing 4.0 ml of n-hexadecane, 0.5 ml of n-pentanol, 3.2×10^{-4} moles of long chain sulfate surfactant, and 0.14 ml of water. These materials were described in section 3.2.2. This emulsion was thoroughly mixed and pipetted into an NMR tube. The NMR spectrum was then recorded as 1-pentanol was added using a micrometer syringe. Spectra were recorded throughout the titration with pentanol, but due to separation of the initial coarse emulsion in the NMR tube, much scattering in the initial data points occurred before the microemulsions were formed. Measurements were performed using an expanded scale to increase the precision of the measurements, as suggested by Schulman (18). Tokiwa and Tsujii (75) have stated that to obtain quantitative data, the average chemical

shifts should be evaluated by equation 3-3. That suggestion was followed here.

$$\nu_s = \frac{\int_{\nu_1}^{\nu_2} \nu I(\nu)\, d\nu}{\int_{\nu_1}^{\nu_2} I(\nu)\, d\nu} \qquad (3\text{-}3)$$

where $I(\nu)$ was the absorption intensity at frequency ν, ν_1 and ν_2 are the frequencies at the limits of the resonance signal, and ν_s was the calculated average chemical shift. Equation 3-3 was evaluated using the parabolic approximation, employing a $\Delta\nu$ of 0.5 Hz. Frequencies were measured relative to the methyl resonance as an internal standard and then converted to δ (ppm) values. Previous work showed that the position of the methyl peak did not vary as a function of the cation type, surfactant chain length or pentanol concentration when tetramethylsilane (TMS) was used as an internal standard. The position of the methyl resonance has also been seen by other investigators to be insensitive to its environment (60, 78). Moreover, if the hydrocarbon chain was long enough, the chemical shift of the chain methylene groups was also seen to be invariant on going from a hydrocarbon to an aqueous environment (61). Using an internal standard eliminated the necessity of making bulk magnetic susceptibility corrections. While using a standard contained in the component molecules eliminated uncorrected dilution errors made by adding another substance (e.g., TMS) as an internal standard.

Equation 3-3 was originally proposed to obtain the average

chemical shift of peaks broadened due to intermolecular interactions. In the microemulsions studied here the resonance lines were found to be narrow enough in most cases to give results equal to those obtained from equation 3-3. This procedure was found useful, however, in helping to minimize errors due to inconsistent tuning of the NMR spectrometer.

The observed chemical shift for the hydroxyl protons in a water in oil microemulsion is an average of the effects of several environments. The shift can be attributed to that of the water protons in the disperse phase (d) and the continous phase (c), and to the alcohol protons in the disperse phase (d), interphase (i), and the continuous phase (c). The total observed chemical shift (δ, in ppm) in the case of rapid exchange is the sum of the contributions from the individual environments, weighted according to the probabilities of the nuclei being at each site (81), thus

$$\delta = p_a^d\delta_a^d + p_a^c\delta_a^c + p_a^i\delta_a^i + p_w^d\delta_w^d + p_w^c\delta_w^c \qquad 3\text{-}4$$

where p is the probability of a particular proton being in a certain environment (i, c, or d) and δ_k^m is the chemical shift in that particular environment (m); a and w refer to alcoholic and water protons respectively. Since the probability of a proton being at a particular site is equal to the fraction of protons at that site, equation 3-4 becomes

$$\delta = b_a^d\delta_a^d + b_a^c\delta_a^c + b_a^i\delta_a^i + b_w^d\delta_w^d + b_w^c\delta_w^c \qquad 3\text{-}5$$

where b is the fraction of the total hydroxylic protons (water and alcohol) in each phase

$$\sum_{\substack{\text{All}\\\text{Phases}}} b_i = 1$$

For example b_w^d would be given by

$$b_w^d = \frac{2n_w^d}{2n_w + n_a} \qquad 3\text{-}6$$

where n_w and n_a are the total number of moles of water and of alcohol in the system, and n_w^d is the number of moles of water in the dispersed phase.

To determine if there is any hydrogen bonding between the alcohol and surfactant at the interface, it is necessary to determine δ_a^i as a function of the surfactant type. Since strong hydrogen bonding gives shifts as much as 10 ppm (82) over those of the unbonded species; hydrogen bonding at the interface should be evident in δ_a^i, if the alcohol is involved in this type of interaction.

To evaluate δ_a^i, each term in equation 3-5 must be evaluated.

The b_a terms were evaluated from the distribution data given in the previous section. The k values were used to determine b_c. The intercept, I, cannot be used to give both b_a^d and b_a^i. It was assumed therefore, that the amount of alcohol in the dispersed phase was governed by the solubility in water and on this basis, b_a^d was found to be negligible (≤ 0.002) and, therefore, it was neglected. The first term in equation 3-5 was therefore, eliminated.

The chemical shifts appropriate to a given phase were taken from Figures 3.6 and 3.7, which give the chemical shift of

n-pentanol (δ_a^o) in n-hexadecane at various ratios of alcohol to oil (Fig. 3.6) and the chemical shift of water (δ_w^o) in n-hexadecane at various ratios of water to oil (Fig. 3.7). Figure 3.7 was constructed by measuring the chemical shift of the hydroxyl protons in solutions of 1-pentanol and n-hexadecane saturated with water. The amount of water solubilized was determined from Figure 3.5. The chemical shift of water was separated from that of the pentanol by an equation analogous to 3-5:

$$\delta_{wa} = f_w^o \delta_w^o + f_a^o \delta_a^o$$

Where δ_{wa} is the total chemical shift due to water and pentanol hydroxyl protons, δ_w^o is the chemical shift due to the water protons in the hydrophobic environment, δ_a^o is the chemical shift of the hydroxyl protons of pentanol at the appropriate ratio of pentanol to n-hexadecane taken from Figure 3.6, f_w^o and f_a^o are the fraction of the hydroxyl protons due to the water and pentanol dissolved in the oil. Therefore,

$$\delta_w^o = \frac{\delta_{wa} - f_a^o \delta_a^o}{f_w^o}$$

δ_w^d was measured in water saturated with 1-pentanol as 3.88 ppm. This agrees well with the value reported for the chemical shift of water reported by Hindman (83) using cyclopentane as a reference. His value was 3.54 ppm. Since the methylene resonance appears 0.37 ppm down field of the methyl resonance, the hydroxyl shift for water on this basis would be 3.91 ppm.

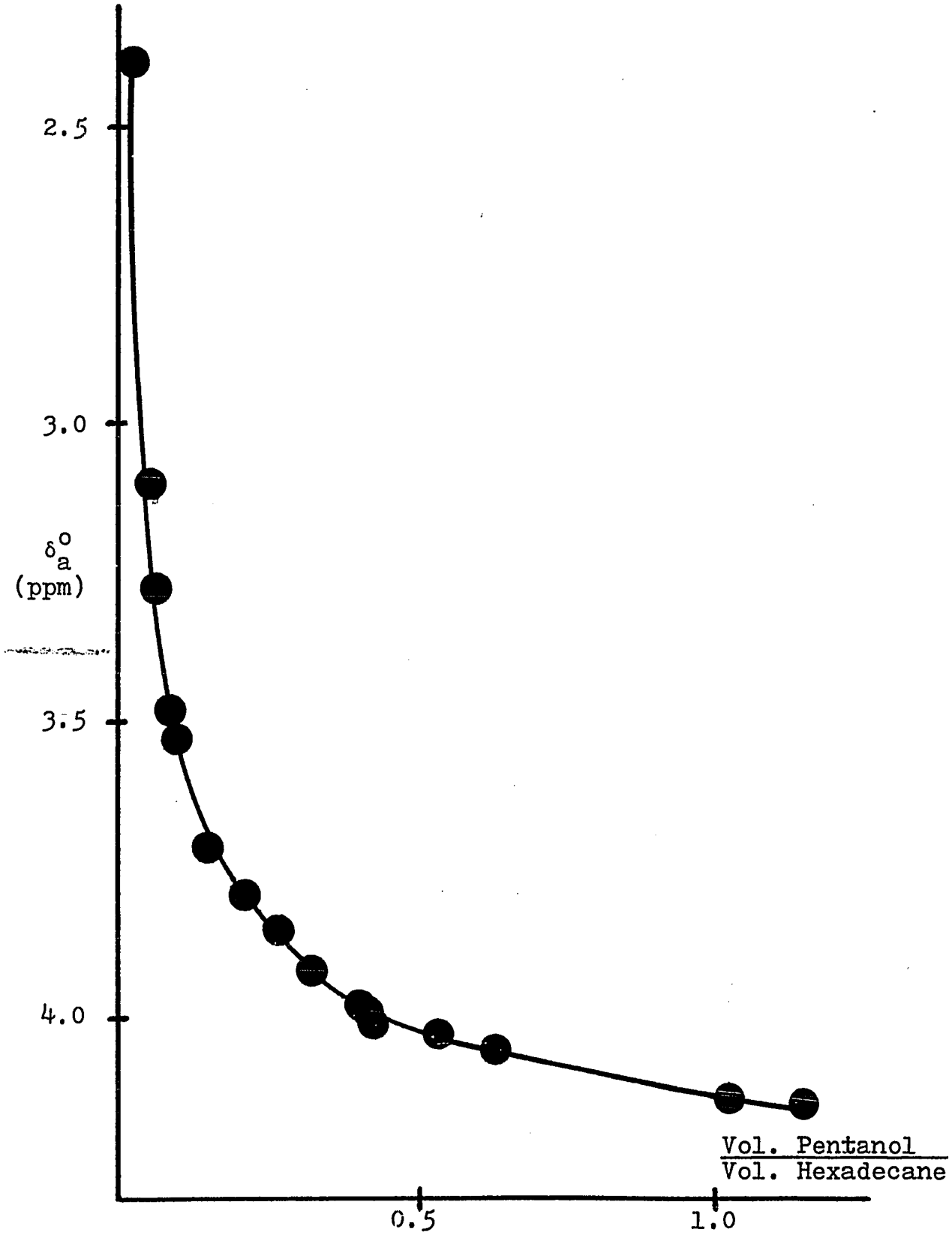


Figure 3.6

Chemical Shift of Alcoholic Hydroxyl Protons in n-Hexadecane

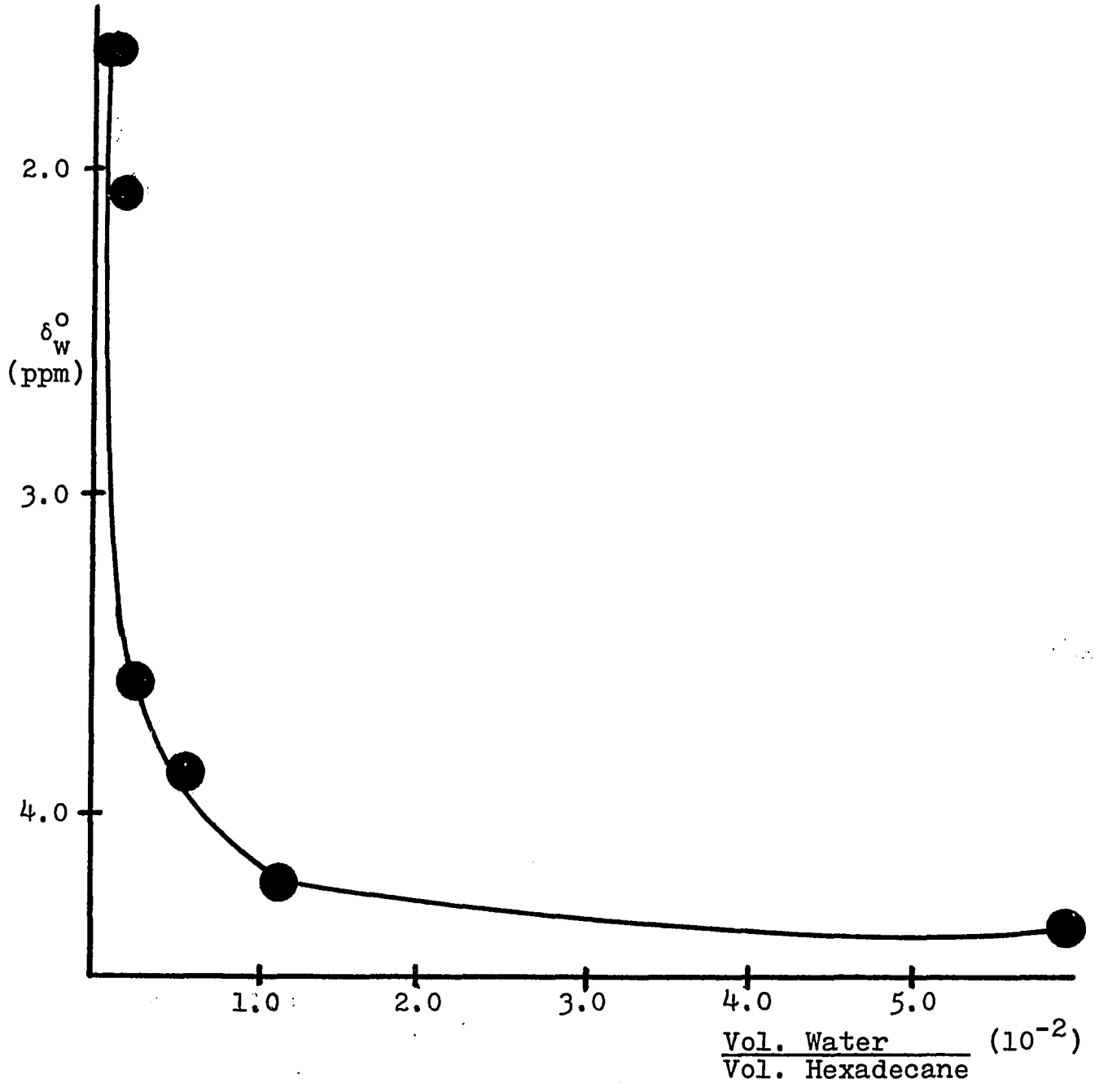


Figure 3.7

Chemical Shift of Water Hydroxyl Protons in n-Pentanol/ n-Hexadecane

No account was taken of the effect of the surfactant counter ions on the hydroxyl resonance. In any case, this effect was not large for the alkali cations or the ammonium group, as judged by the results of Hindman (83) for measurements of the chemical shift of water as a function of the cation concentration.

After all of these terms have been evaluated, the chemical shift due to the pentanol at the interface can be evaluated, from 3-5

$$\delta_a^i = \frac{\delta - b_a^c\delta_a^c - b_w^c\delta_w^c - b_w^d\delta_w^d}{b_a^i} \qquad 3\text{-}7$$

Values calculated in this manner are reported in table 8, along with the ratio of pentanol to surfactant (n_a/n_e), and the total chemical shift (δ) observed in the microemulsion. All of these values were determined above the clearing point for each microemulsion. The values are seen to be comparable to the shift observed in very dilute solutions of pentanol in n-hexadecane (Fig. 3.6) in which hydrogen bonding is not prevalent.

The values are well below the point at which the slope of the δ_a^o versus the ratio of alcohol to oil changes, where species higher than the monomer predominate. As the amount of alcohol at the interface increases, the resonance moves progressively downfield, as one would expect if hydrogen complexing were becoming important. The results indicate then that the anionic group of the surfactant is not participating in hydrogen complexing with the cosurfactant to

Table 8
Chemical Shift of the Hydroxyl Resonance
in w/o Microemulsions

Surfactant	n_a/n_e	δ	δ_a^i
SDeS	32.5	3.68	3.0
(Sodium Decyl-	35.3	3.72	3.2
sulfate)	43.0	3.78	3.5
	47.7	3.81	3.6
SDS	23.6	3.67	2.8
	28.1	3.70	2.9
	32.7	3.71	3.1
STS	20.3	3.67	2.6
	24.8	3.68	2.7
	29.4	3.70	2.7
KDS	21.5	3.67	2.6
	26.0	3.68	2.8
	30.6	3.69	2.8
	33.7	3.70	3.0
RbDS	21.0	3.65	1.8
	25.7	3.68	2.5
	30.4	3.70	2.4
	35.2	3.71	2.5
(AMP)DS	31.0	3.87	4.2
	36.3	3.86	3.9
	39.8	3.86	3.7
	45.0	3.86	3.6
(AMPD)DS	39.5	3.91	4.1
	42.8	3.91	4.0
	46.0	3.92	4.0
NH_4DS	23.0	3.72	2.3
	28.0	3.75	2.6
	33.0	3.74	2.2

any appreciable extent in the systems studied here as seen by the relatively low values of δ_a^i. Hydrogen bonding does become effective when the counterion can participate in such bonding, as shown by the results of the AMP and AMPD (a-amino-2-methyl-1, 3-propanediol) dodecyl sulfate microemulsions. The interaction then does not occur with the cosurfactant except when the counterion is capable of hydrogen bonding to it.

It therefore seems doubtful that hydrogen bonded complexes play a significant role in the formation of microemulsions, contrary to what was believed by Schulman (15) and Prince (21). This does not eliminate the possibility of Van der Waals interactions among the tails of the surfactants. The energy for this type of interaction would be small but could be enough to stabilize the interfacial film.

3.5 PARTICLE SIZE DETERMINATION

Rosano, et. al. (23) concluded from measurements of sedimentation constants of w/o microemulsions stabilized by potassium oleate and hexanol, and sodium dodecyl sulfate and pentanol that at the clearing point, the total interfacial area was the same even if the volume of the dispersed phase was doubled. This led them to conclude that the configuration at the interface was the same. This contention was also supported by titration curves which had approximately the same intercept for different volumes of the dispersed phase, indicating the same ratio of cosurfactant to surfactant in the dispersed

droplets. It should be pointed out, however, that some systems deviate from this result more than others (see Fig. 2.8 and reference 23). Furthermore, Figure 3.9 shows that when the ratio of water to surfactant is varied by changing the amount of soap present, the results are different from the results obtained when the ratio is changed by varying the amount of water present.

Light scattering studies of some of the systems in Fig. 3.9 were undertaken to verify these earlier results and to compare the measured particle sizes with those calculated from equation 1-2.

3.5.1 Procedures And Results

Microemulsions were prepared from components filtered by pressure filtration through a medium porosity scintered glass filter. The initial emulsion was prepared with 1.00 ml water, 4.0 ml n-hexadecane, and the appropriate amount of SDS; this was titrated to clarity with pentanol, as described earlier (Sect. 3.2.1). Microemulsions were prepared with 3.20×10^{-3} and 1.73×10^{-3} moles of SDS. The components were combined directly into an octaganol light scattering cell (Brice Phoenix, D101). A Brice Phoenix light scattering photometer (Model 1000) was used for all measurements. Indices of refraction were measured on an Abbe refractometer at the temperature of the microemulsion as the values obtained on that instrument were found to agree up to the third decimal place with those measured at 546 nm (the wave length used in the light scattering measurements) by the more tedious proce-

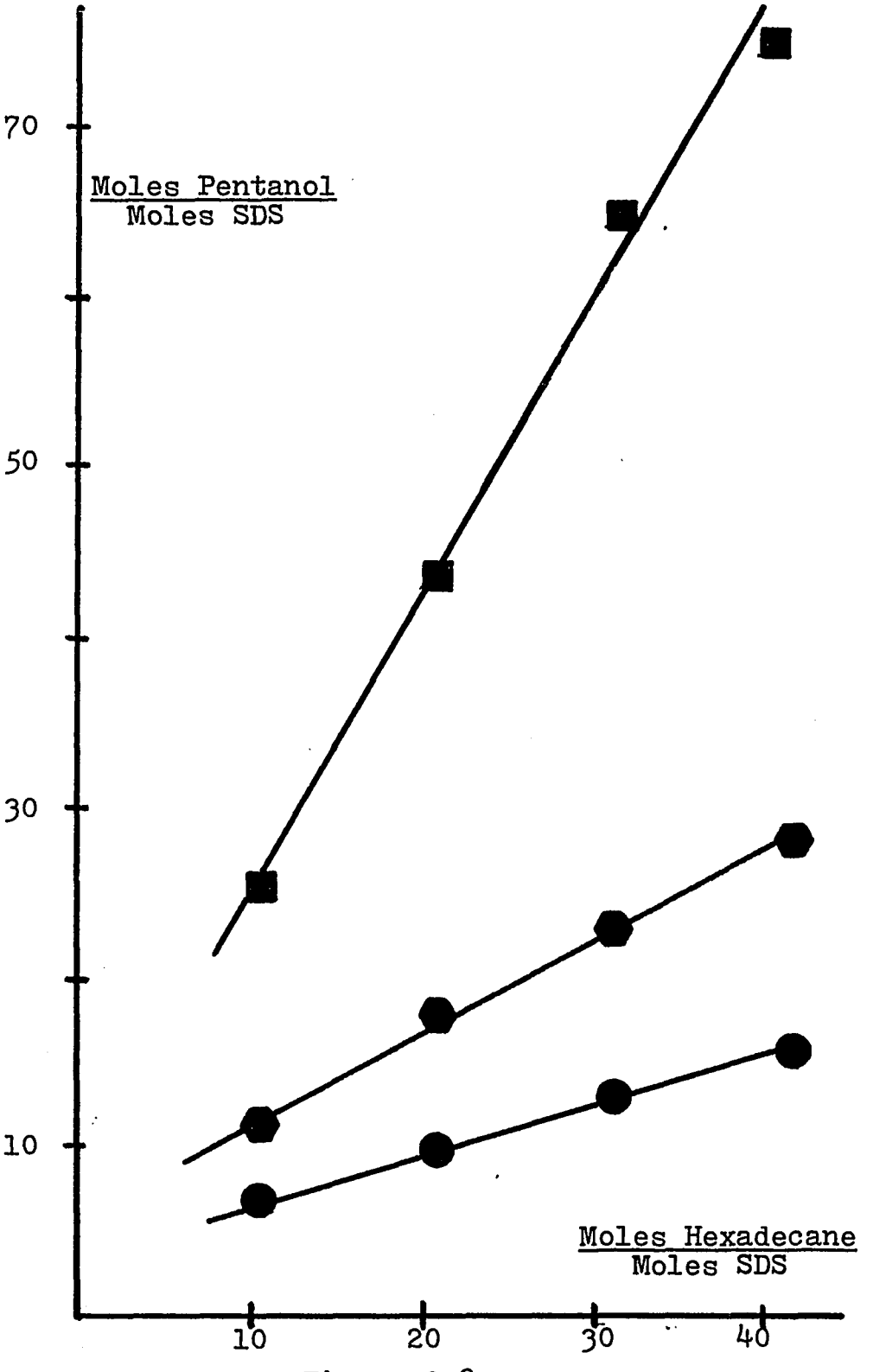


Figure 3.8

Variation of the Volume of the Dispersed Phase in Water-in-n-Hexadecane Microemulsions (30°C). (■ 4.0ml; ● 2.0ml; ● 1.0ml of Water)

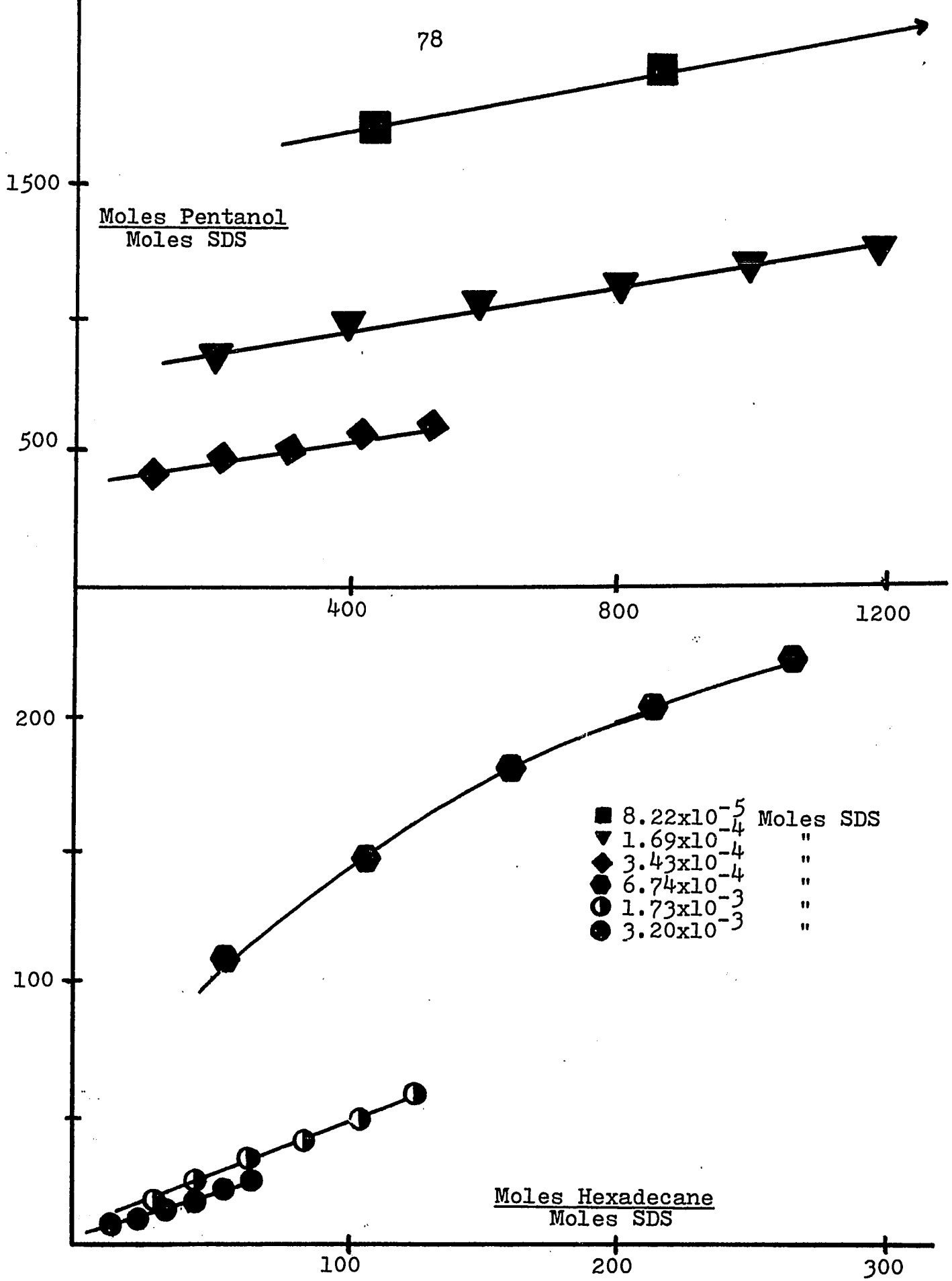


Figure 3.9

Effect of Changing the SDS Concentration on the Formation of Water-in-n-Hexadecane Microemulsions (30°C; 1.0ml water).

dure using the Becky lines (84).

The photometer was used to measure turbidities (T) from which were calculated the droplet radii by using the Rayleigh formula (85).

$$R_{90} = \frac{9\pi^2 NV^2}{2\lambda^4} \left(\frac{n^2 - 1}{n^2 + 2} \right)^2 = \frac{3T}{16}$$

giving

$$T = \frac{24\pi^3 NV^2}{\lambda^4} \left(\frac{n^2 - 1}{n^2 + 2} \right)^2 \qquad 3\text{-}8$$

where R_{90} is the Rayleigh ratio of the scattered to the incident intensity, n is the relative refractive index of the scatterer, N is the number of scattering particles per unit volume, V is the volume of the scatterer and λ is the wave length of the light in vacuum. NV is therefore, the volume fraction of the dispersed phase. V can therefore, be determined if the volume of the system and dispersed phase are known. Heller (86) discussed the theoretical validity of this equation and concluded that the error was about 2% for the particle sizes measured here.

For the systems studied here, the refractive index of the dispersed phase was assumed to be that of water, SDS and pentanol in the ratio determined by the intercept of the titration curve. The index of refraction of the dispersed phase was assumed to be that of pentanol and n-hexadecane in the proportion dictated by the slope of the titration curve. For the microemulsion prepared with 3.20×10^{-3} moles of SDS the continuous phase was determined to have a composition of .095 ml n-pentanol/ml n-hexadecane, and that for the microemulsion prepared with 1.73×10^{-3} mole of SDS, .147 ml of n-pentanol/ml n-hexadecane. The composition used for the

dispersed phase were; 1.0/ml water, 2.04 ml n-pentanol and 3.20×10^{-3} moles SDS and 1.00 ml water, 2.45 ml n-pentanol and 1.73×10^{-3} mole of SDS.

The particle radii were calculated by assuming that all of the water was in the dispersed phase (R) and also by assuming that the distribution of water between the dispersed and continuous phase was determined by Figure 3.5, (R'). The results of either method were comparable.

Dilute systems were used to avoid complications due to multiple scattering. The turbidity was corrected for the dissymetry by multiplying by the reciprocal of the particle scattering factor, $P(\theta)$, (87). The corrections were small due to the low values of the dissymetry (1.1 - 1.7). The dissymetry itself was corrected for reflections in the cell (88). Here also the corrections were small.

At the clearing point, the results reported in table 9 show that for a given volume of water, the radii of the droplets are the same when dispersed in a given volume, even though the amount of surfactant was doubled. The data for both systems, at the clearing point, was found to follow the equation for a straight line

$$\log d = bNV + a \qquad 3\text{-}9$$

where d is the diameter of the droplet in angstoms, b is the slope and a is the intercept (Fig. 3.10). Therefore, it was concluded that it was the phase volume and the amount of alcohol that controls the droplet size. Adding an excess of alcohol was seen to decrease the size of the dispersed droplets.

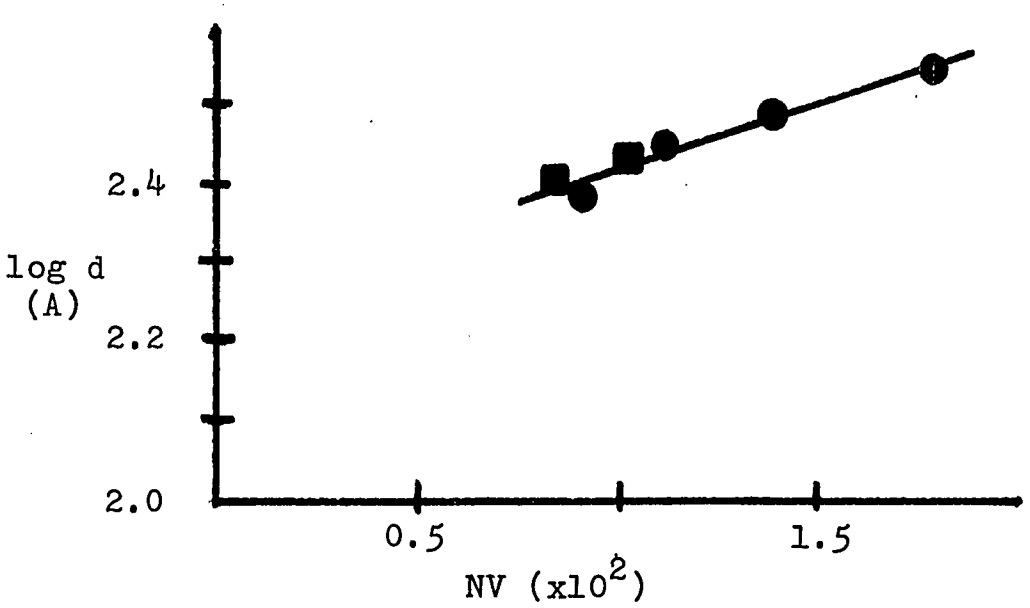


Figure 3.10

Change of the Droplet Diameter with the Phase Volume
(● 3.21×10^{-3}; ■ 1.72×10^{-3} Moles SDS)

Since the intercepts for the two titration curves (Fig. 3.9) are the same, the conclusion made previously by Rosano, et. al. (23) seems to apply. That is, that at the clearing point the configuration of the interfacial monolayer is the same, for a given surfactant.

However, if the cross-sectional area per molecule of surfactant (σ) is calculated, the values are seen to be very low; too low to be reasonable. It is concluded therefore, that the simple picture in which all of the surfactant is located at the interface is in error, and that the interfacial configuration must indeed change to accommodate the change in the amount of surfactant available. It must be assumed that there is an equilibrium between surfactant in the interior of the droplet and that in the interface, as was done by Schulman and Friend (5).

It is seen then that the size of the dispersed droplets is governed by the amount of water being dispersed, as long as there is enough surfactant present to stabilize the system. If not enough soap is present, the system will not become clear until enough alcohol is added to dissolve all of the water as a solution, as in the upper three curves of Fig. 3.9.

Table 9

Moles of Surfactant (x1000)	Vol. of Hexadecane (ml)	Vol. of Pentanol (ml)	R (A)	R' (A)	σ (A^2/molec)
3.2	40.0	5.80	157	174	7.6
	50.0	6.75	143	152	8.2
	60.0	7.63	129	141	8.5
	70.0	8.54	111	120	9.5

Table 9 (cont.)

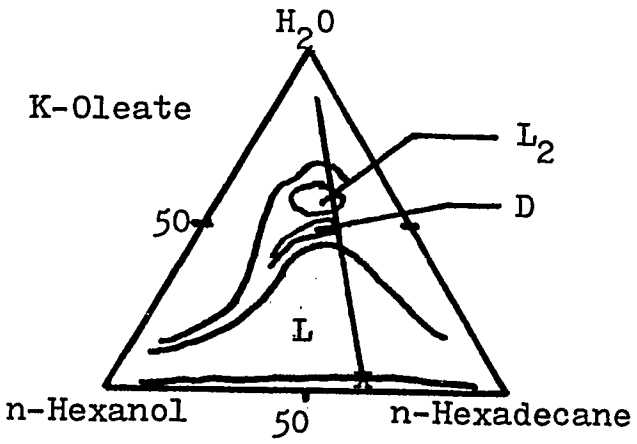
Moles of Surfactant (x1000)	Vol. of Hexadecane (ml)	Vol. of Pentanol (ml)	R (A)	R' (A)	σ (A^2/molec)
3.2	70.0	9.98*	99	110	10
1.73	60.0	11.28	124	137	16
	70.0	12.32	117	129	16
	70.0	15.30*	89	103	18

* These systems contain excess alcohol above that necessary to induce clarity.

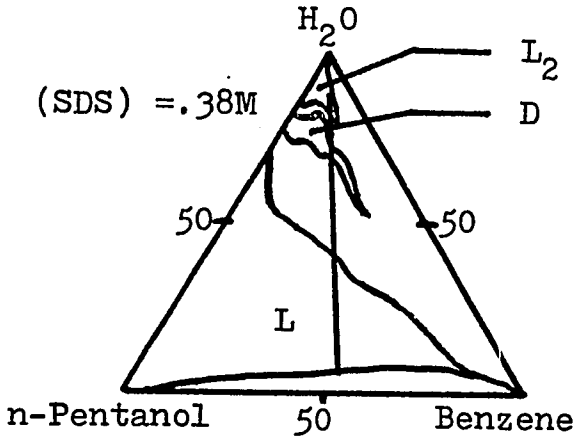
3.6 OIL-IN-WATER MICROEMULSIONS

The previous sections have dealt with water-in-oil microemulsions. It is possible to some cases, however, to form microemulsions of the reverse type. This situation is analogous to the case of coarse emulsions in which the oil or water may be the continuous phase. The microemulsions, however, are of much higher stability.

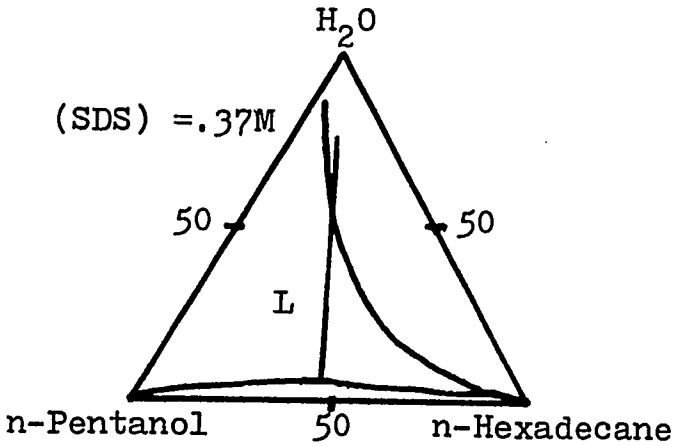
When a water-in-oil emulsion inverts to an oil-in-water emulsion by the addition of water, for example, there is usually a phase of high viscosity intervening between the two. The same holds true, in most cases, for microemulsions. This is pictured in Fig. 3.11A, in which are diagramed the phases resulting when the components are added to an initial water-in-oil microemulsion indicated by an X. The intervening gel phase (D) of high viscosity is clearly apparent. The relative viscosity changes occurring along the indicated line are depicted in Fig. 3.12. Fig. 3.11B shows another



(A)



(B)



(C)

Figure 3.11

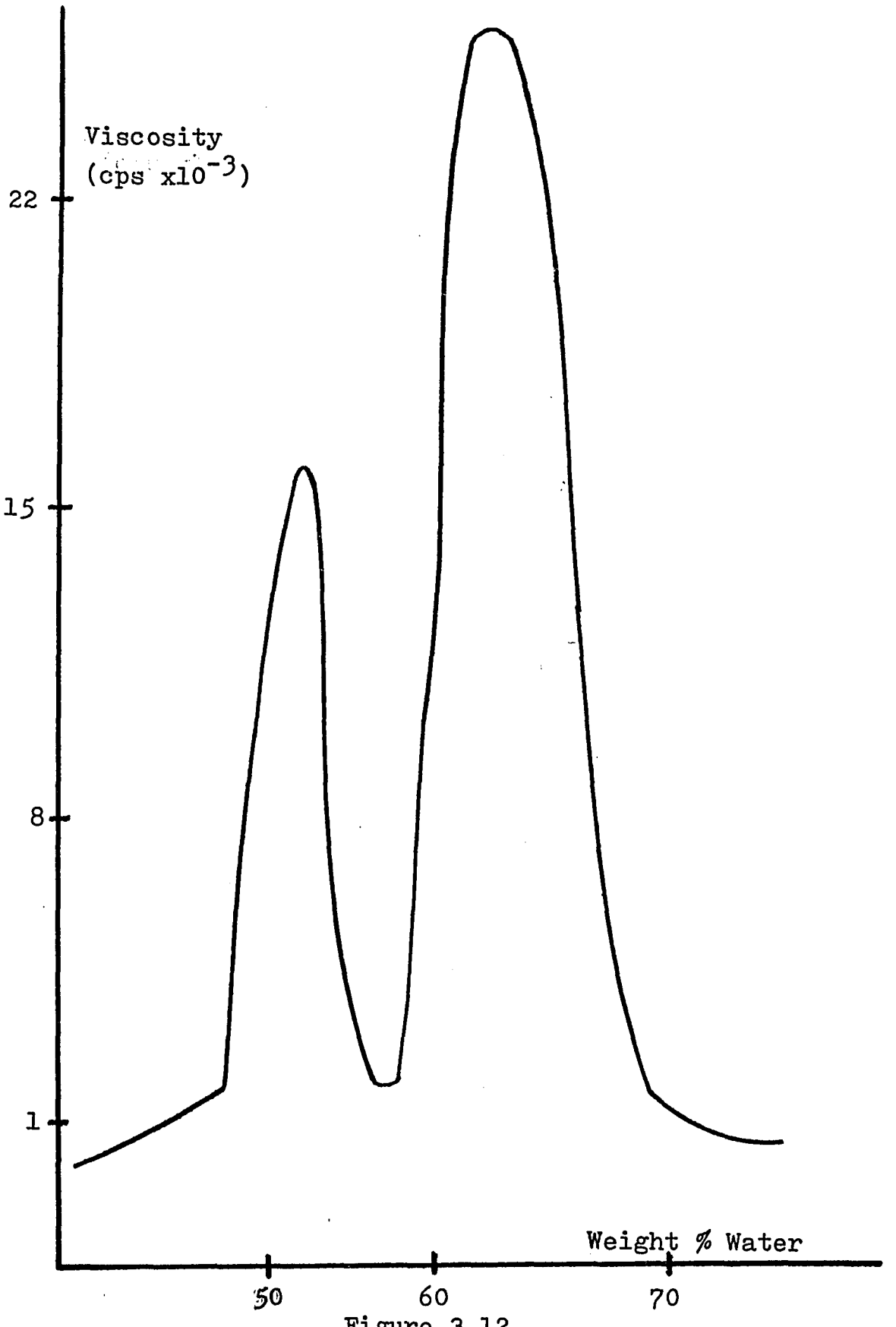


Figure 3.12

Viscosity Changes Along the Line Indicated in Fig. 3.11A

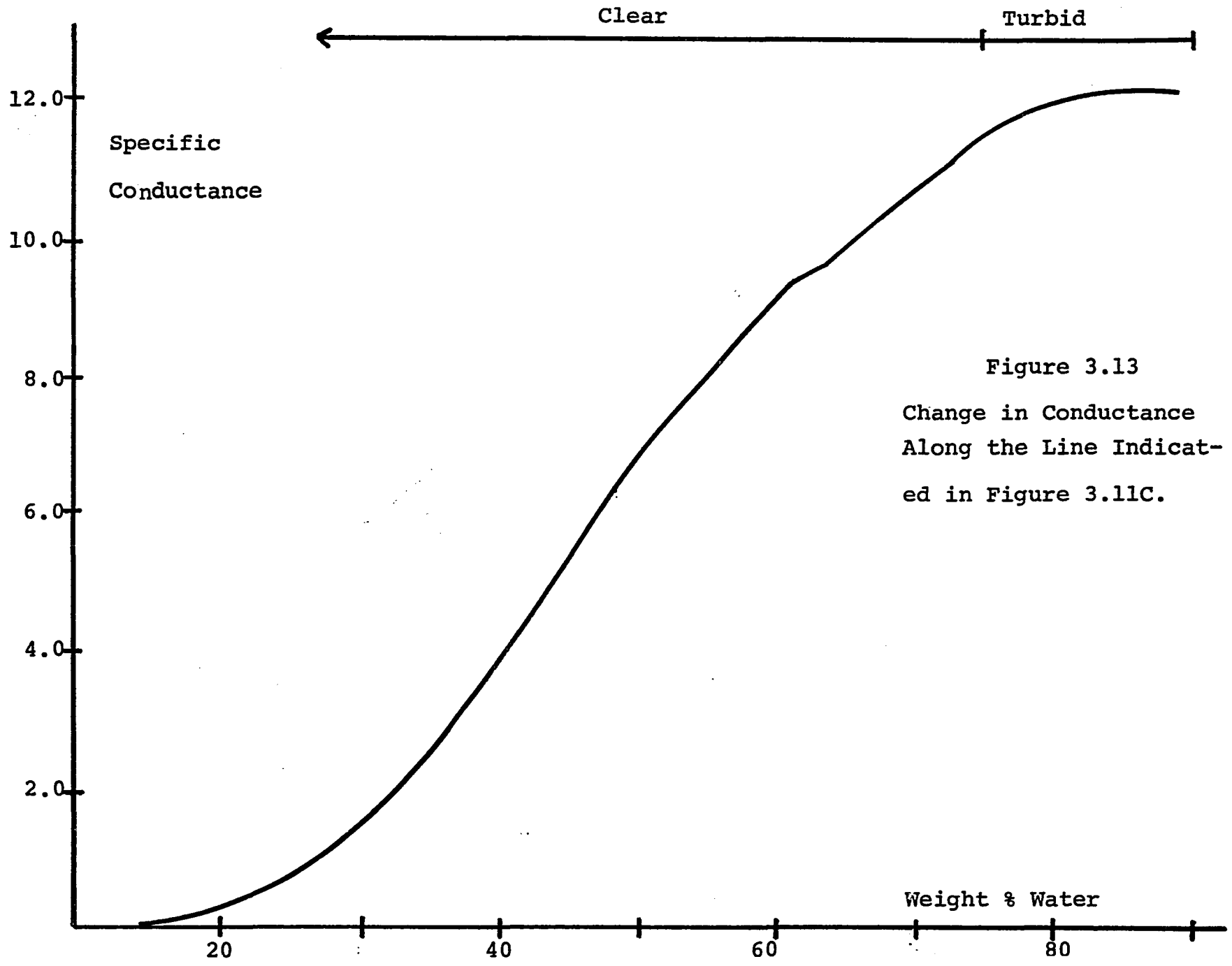


Figure 3.13

Change in Conductance Along the Line Indicated in Figure 3.11C.

typical diagram in that there is an intervening viscoelastic phase (D) between the two clear, fluid, isotropic phases (L and L_2). Fig. 3.11C, however, is atypical in that no viscoelastic phase is noted, although the system inverts from an oil continuous to a water continuous system (as seen by measurements of the specific conductance, Fig. 3.13).

Ternary phase diagrams of this sort have been used extensively by Mandel, Ekwall and Friberg (65, 85, 89-95) to study aqueous systems of mixed surfactants.

The diagrams reported in Fig. 3.11 differ from previous studied in that four components were present somewhat in the manner of Gilberg (96).

The mechanism for the inversion of microemulsions is usually interpreted by the description given in Fig.1.2. That is, the system goes from reversed micelles (oil continuous) through a lamellar structure to normal micelles (water continuous) Since the inversion mechanism has received some attention (18, 20), it will not be discussed further. It is the second isotropic region (L_2) that will next draw attention.

3.6.1 The Hydrophobic Environment in Oil-In-Water Microemulsions

The region of solubilization of oils in aqueous solutions of surfactants has been studied by many investigators. Specifically, Rehfeld (97) studied the 2600A bands of benzene to determine the environment of the oil solubilized in aqueous solutions of sodium dodecyl sulfate (SDS). He concluded that the environment was similar to a solution of benzene in

hydrocarbon. The environment was not seen to be completely uniform, however. Waggoner and co-workers (98-100) had come to a similar conclusion of the basis of ESR studies of solubilized long chain nitroxides.

Riegelman and co-workers (101) postulated several different sites for solubilization in micellar solutions depending on the type of solute. They studied the solubilization of ethylbenzene, naphthalene, anthracene and several others in micellar solutions of potassium laurate, dodecylamine hydrochloride and polyoxyethylene ether using differential UV absorption spectroscopy. Fluorescence and differntial UV spectra of aqueous micellar solutions of 10-phenylundecanoic acid reported by Rehfeld (102) revealed that the phenyl ring of the acid was in a "liquid" state inside the micelle similar to that in the pure acid.

In the present work differential UV absorption and fluorescence spectra have been obtained for o/w (oil-in-water) microemulsions of benzene stabilized by SDS and n-pentanol in an attempt to determine the type of environment of thebenzene in these o/w microemulsions. Benzene was used as the oil phase since it has a well defined and much studied absorption spectrum.

With the same purpose in mind, microemulsions of n-hexadecane in water stabilized by SDS were studied in which the n-hexadecane contained a certain ratio of iodine. Since the iodine "tag" in the droplets interacts with donor solvents (103), it was hoped that these systems would give further information

about the role played by the alcohol in o/w microemulsions.

3.6.2 Procedures

The materials have been previously described except for the oleic acid which was a highly purified grade purchased from Hormel Institute (lot F-1A).

A solution of 0.28 M K-oleate was prepared by adding an excess of KOH to oleic acid and adding water to make the final solution. The final pH was 10.5. Benzene was then added to 25.0 ml of the K-oleate solution in a thermostated flask (30 $\pm$ .5°C). This was mixed using a magnetic stirrer to give a coarse emulsion, lactescent in appearance, which would separate rapidly on standing. The coarse emulsion was then titrated to the clearing point with the alcohol. The systems used are listed in table 10 along with the mole fraction of benzene (X_ϕ), n_ϕ/n_a the molar ratio of benzene to 1-pentanol, λ_{max} - the wavelength of the maximum absorption for the second peak in the 2600A band, $\Delta\nu_I$ - the frequency of the progression and $\Delta\nu_{\frac{1}{2}}$ - the half-band width.

The microemulsions of n-hexadecane were prepared from a stock solution of I_2 dissolved in the oil (5.940 X 10^{-4} gm I_2/gm n-hexadecane). SDS was used as the surfactant because it was found that the double bond of oleate soaps interacted strongly with I_2, defeating its purpose. The coarse emulsions initially formed with SDS were purple while those with K-oleate were lactescent in appearance. I_2 did not dissolve in solutions of SDS below the critical micelle concentration (.006M).

The microemulsions used contained approximately 0.9 ml of

oil, and 10.0 ml of 0.28M SDS solution which required 1.67 ml of n-pentanol to obtain a clear, light brown microemulsion.

UV Spectra

Differential UV spectra were measured on a Cary 14 automatic spectrometer using matched cells. The benzene microemulsions were run against the 0.28M SDS solution; both solutions contained the appropropriate amount of pentanol. The hydrocarbon solutions were measured against the solvent.

Fluorescene Spectra

A Perkin-Elmer 203 fluorescence spectrophotometer was used to measure the relative fluorescence emission spectra. The excitation wavelength was 285 nm. The solvent or K-oleate solution was used to zero the spectrophotometer.

Uncorrected spectra are reported as they were considered adequate for comparative purposes.

3.6.3 Results

The values of λ_{max}, $\Delta\nu_I$, and $\Delta\nu_{\frac{1}{2}}$ in table 10 are seen to be the same range as those reported by Rehfeld (97). The λ_{max} remained constant in the benzene microemulsified system over the concentration range studied. The solution spectra, on the other hand, showed a bathochromic (blue) shift with increasing benzene concentration. The fluorescence emission spectra Fig. 3.14 showed a broad emission band around 350 nm (2871 cm^{-1}), which shifted to longer wavelengths in more concentrated solutions (table 11).

This is the range of the emission bands reported by Gilmore, et. al. (104) for benzene dissolved in E.P.A. at 77°K (24000 -

Table 10

UV Absorption Spectrum

Solvent	X_ϕ	n_ϕ/n_a	λ_{max} (A)	$\Delta\nu_I$ (cm^{-1})	$\Delta\nu_{\frac{1}{2}}$ (cm^{-1})
			Microemulsions		
water	.00108	1.06	2546	931±10	415±10
"	.00065	0.64	2545	915±10	453±10
"	.00065	0.93	2545	926±10	462±20
"	.00022	0.21	2546	933±10	400±10
			Solutions		
n-hexane	.00123	-	2539	938±25	320±15
n-pentanol	.44	0.80	2545	885±15	410±20
"	.088	.096	2542	938±15	378±10
"	.0078	.0079	2541	934±15	365±10

Table 11

Fluorescence Emission Spectrum

Solvent	X_ϕ	n_ϕ/n_a	Fluorescent Maximum (nm)
		Microemulsion	
water	.00108	1.06	337±5
		Solutions	
n-hexane	.012	-	332±5
n-pentanol	.016	.016	328±5
"	.70	4.2	355±5

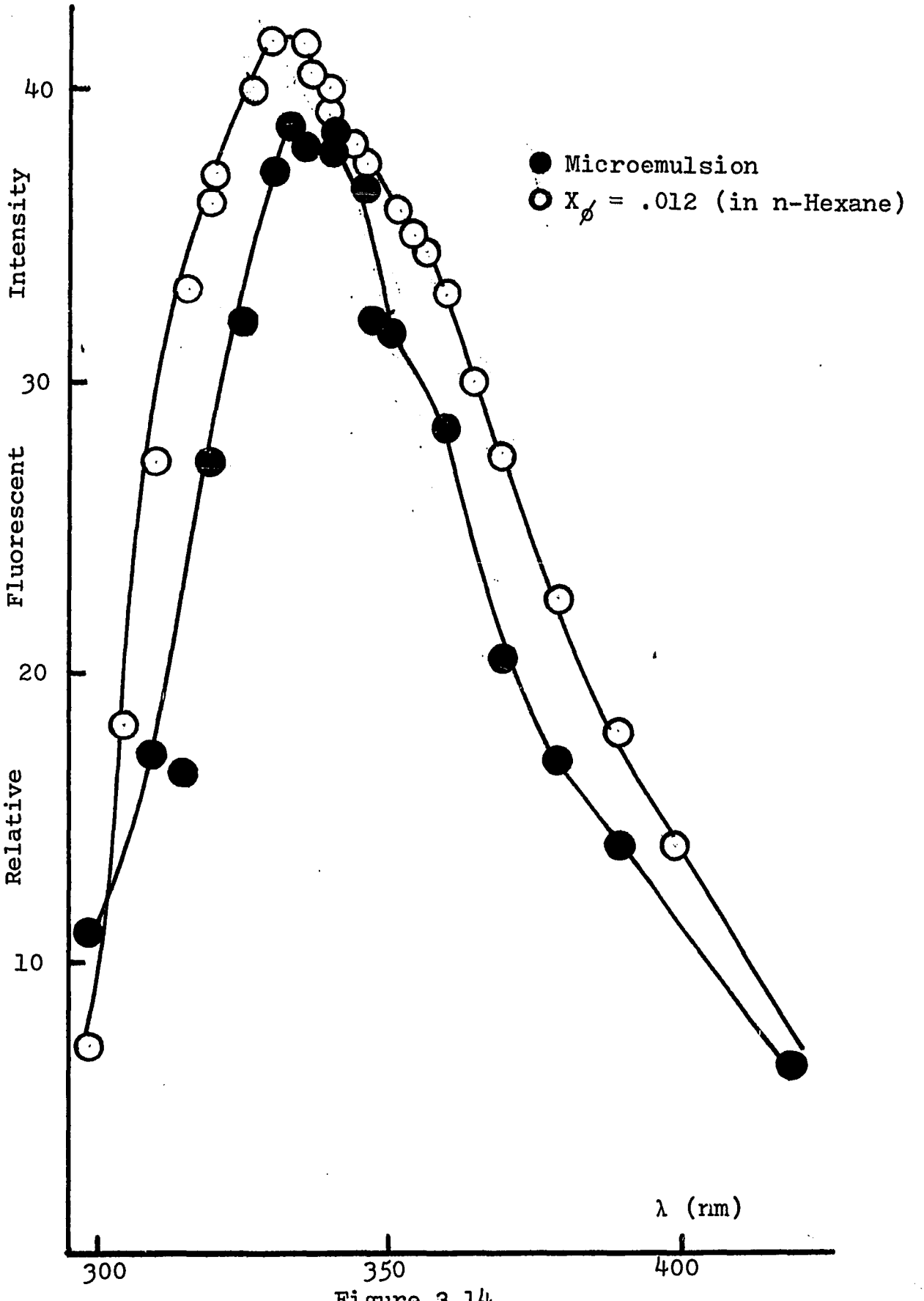


Figure 3.14

Uncorrected Emission Spectra of Benzene

29000, 34000 - 37000 cm^{-1}). However, it is red shifted with respect to the fluorescence emission at 36372 cm^{-1} reported by Kistiakowsky and Nelles (105) for benzene vapor at .01 mm pressure. This is to be expected, since at this pressure the effect of inelastic collisions would be diminished.

No significant difference was observed in the NMR chemical shift for the aromatic protons in any of the systems studied here. The benzene resonance appeared at 374 $\pm$ 1 Hz in all cases, and the half-band width was $\leq$2 Hz indicating that the aromatic protons were in a state of high mobility.

The solubility of benzene and n-pentanol was found to be the same in water and K-oleate solution just below the cmc (14 mmole/liter). This was also seen to be the case for benzene in SDS solutions below the cmc (97). Shinoda reports the cmc for K-oleate as 14 mmole/liter (106).

Since the amount of pentanol in the microemulsion seemed to have little effect, the systems with I_2 dissolved in n-hexadecane were used to help explain why. Two possible reasons were considered: either the alcohol was not penetrating into the interior of the micelle, which seemed unlikely due to the high solubility of the alcohol in the oil, or the benzene absorption was not sensitive enough to the influence of pentanol. The latter seemed to be the most likely, judging from the values of the solution spectra in table 10, which did not vary greatly with concentration.

I_2 dissolved in hydrocarbon solutions has one fairly broad absorption band and is very sensitive to the presence of

alcohols and other electron donor solvents, forming charge transfer complexes (103). Figure 3.15 shows the variation of the I_2 absorption maxima with pentanol content.

After determining the peak position in the microemulsion, the ratio of pentanol to I_2 could be determined from Fig. 3.15. From this and a knowledge of the amount of I_2 dispersed in the microemulsion, the amount of pentanol in the dispersed phase could be determined. Of the 1.67 ml of pentanol used to produce the microemulsion, 0.56 $\pm$ .07 or .0052 moles was determined to be wholly in the dispersed droplets. This corresponds to a mole fraction of n-hexadecane of 0.36, which is of the same order as that observed with benzene.

3.6.4 The Interior Of The Dispersed Phase

The absorption and fluorescence emission spectra of microemulsified benzene supports the view that the interior of the dispersed droplets in these o/w microemulsions are typically hydrocarbon in character. The work of Rehfeld (97) showed similar results for micellar solutions of benzene in SDS. The peak positions in the UV spectrum were not found to be sensitive to the dielectric constant of the medium, since the positions were practically the same in either hexane or pentanol, which has a much higher dielectric constant. This could also be seen

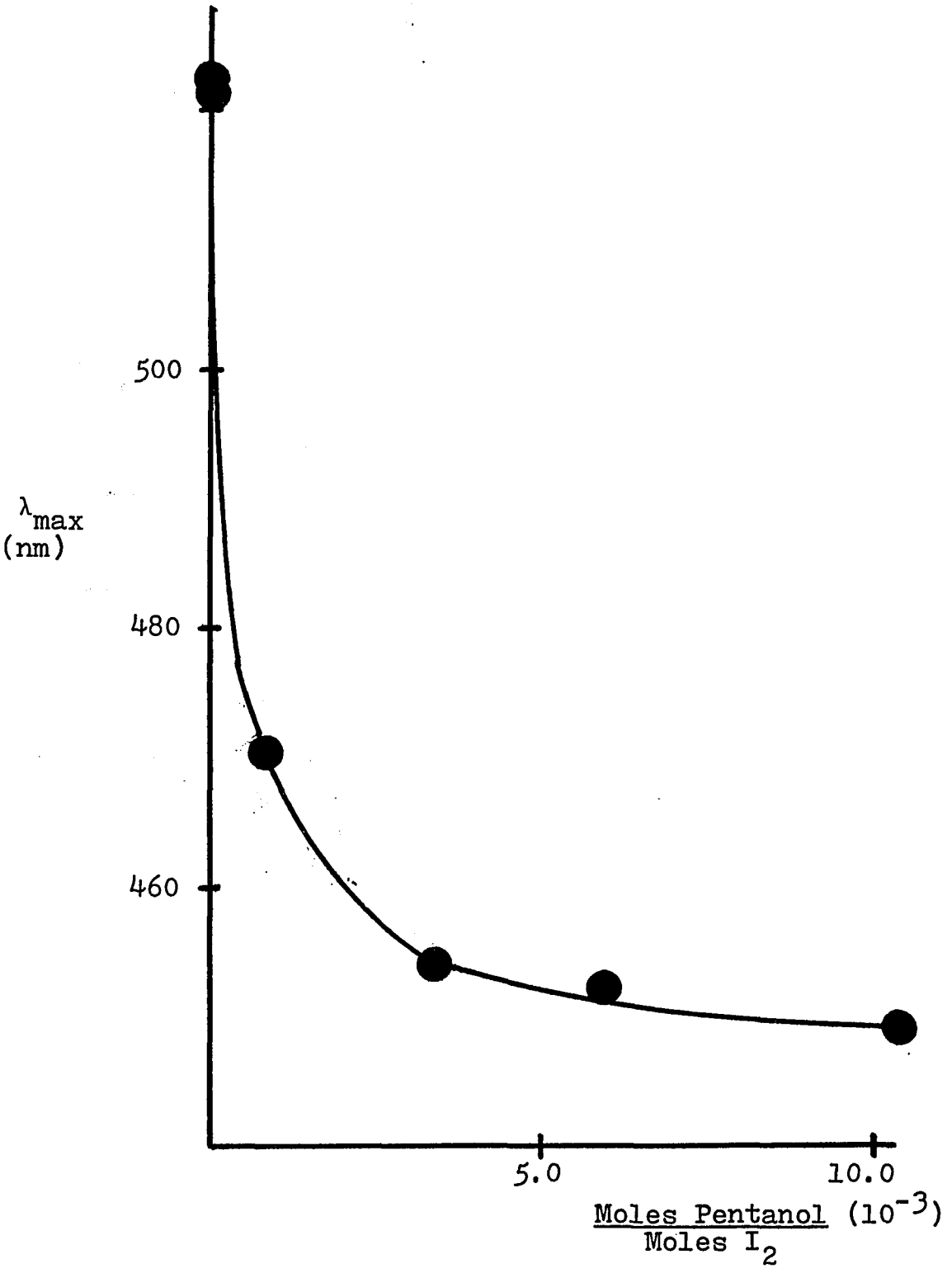


Figure 3.15

Variation of λ_{max} for I_2 in n-Hexadecane as a Function of the Pentanol Content

in the earlier results (88).

The alcohol in these microemulsified systems was observed to penetrate into the droplet interior, and this is in part responsible for the increased polar character of the micelle interior. In fact, most of the increase polar character of the droplet interior can be accounted for by this mechanism as judged by the $\Delta \nu_{\frac{1}{2}}$ values reported in table 10.

CHAPTER FOUR

4.1 CONCLUSION

In chapter one the theories concerning microemulsions were discussed. In the following chapters experimental evidence was presented which refuted many aspects of these theories, and a modified theory for the formation of microemulsions was proposed.

It can now be asserted that microemulsions are not thermodynamically stable systems, the more stable state being the separate phases. As shown in chapter two, changing the order of mixing of the components altered the results radically. The microemulsified systems represent a metastable configuration formed by the redistribution of an amphiphatic component. For a certain period of time the oil water interfacial tension is reduced to zero due to an accumulation of excess surface active material at the interface which lowers γ_i allowing the interface to expand. An accumulation of excess material above the equilibrium level has been observed previously in bulk phases in connection with spontaneous emulsification (49). This effect has been attributed to the existence of the initial concentration gradients which cause excess material to be carried along with the diffusing species and to a lowering of γ_i for the system (49).

The amount of alcohol required to form a microemulsion was seen to depend upon the type of interfacial film formed by the surfactant, depending upon the chain length, the counterion and the anionic group. The distribution of the cosurfactant was also seen to depend upon the activity of the cosurfact-

ant in the continuous phase. This was observed when changing the solvent.

Hydrogen bonding between the surfactant and c
was seen to play a nonessential role in stabilizing microemulsions. Van der Waals interactions might play a more significant role in this type of complex formation if it occurs.

The particle size was determined to be 200 to 300A for the systems studied. These values were consistent with those reported by earlier workers. The droplet size varied with the amount of alcohol present since the alcohol dissolved some of the water in the continuous phase. Over the range studied, however, the droplet size was independent of the amount of surfactant present. That is, the surfactant film could swell within certain limits to accommodate larger volumes of the dispersed phase per unit weight of surfactant.

Finally, by studying oil-in-water microemulsions, it was determined that the cosurfactant penetarted into the droplet interior, increasing its polar character. This showed that the cosurfactant was in fact redistributing as the microemulsion was formed.

Since there is no particular thermodynamic advantage to the formation of microemulsions, it must be concluded that the drpplets are stable due to their small size and the interfacial film surrounding the droplet which provides a barrier against the coalescence of the drpplets. If the particle size and the density differences between the dispersed and contin-

uous phases are small enough, the particles will be prevented from sedimenting by their own kinetic energy.

It seems, therefore, that the most distinctive feature between macro- and microemulsions is the degree of curvature and the manner in which they are formed. The concepts used in treating macroemulsions should be useful then (with some modifications to take into account the higher degree of curvature) in the treatment of microemulsions.

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