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I am submitting herewith a dissertation written by Craig Arlen Martin entitled "Nuclear Magnetic Resonance and Phase Behavior Studies of Aerosol OT, TR, and IB." I recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemistry.

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NUCLEAR MAGNETIC RESONANCE AND PHASE BEHAVIOR STUDIES OF
AEROSOL OT, TR, AND IB

A Dissertation
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Doctor of Philosophy
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The author dedicates this work to his mother.

ABSTRACT

^{13}C Nmr was used to study the conformational and dynamic changes which occur when water is added to Aerosol OT (AOT) inverted micelles in apolar solvents. Upon addition of water, the ^{13}C chemical shifts of AOT's carbonyls move sharply upfield in cyclohexane solution, while changes were observed in the fine structure of the carbonyl region of the dispersive ir spectra. The spin-lattice relaxation times (T_1) of all of AOT's carbons increase in this solvent up to $R = [\text{H}_2\text{O}]/[\text{AOT}] = 5 - 10$, then level off or increase slightly throughout the w/o micro-emulsion domain. The segmental mobility of AOT's alkyl chains decreases dramatically as the inverted micellar domain is transversed in cyclohexane. These results indicate an increased mobility and that gauche to trans conformational changes occur throughout the AOT molecule as water is added.

T_1 's of AOT are larger in benzene and carbon tetrachloride than in cyclohexane. The segmental mobility of AOT inverted micelles at $R = 0$ decreases in the following solvent series: cyclohexane > carbon tetrachloride > benzene. This is due to the latter two solvents intercalating AOT's alkyl chains, while in cyclohexane the voids are filled by the hydrocarbon tails. Solvent penetration decreases in the following order: benzene > carbon tetrachloride > cyclohexane.

The relaxation of carbons nearest the sulfonate head group is primarily influenced by the overall motion of the AOT molecule. At low R values, the major contribution is from overall aggregate tumbling; at high R , relaxation is due to lateral AOT diffusion along the AOT/water interface.

Frequency dependent T_1 's of AOT inverted micelles in cyclohexane indicate that a distribution of correlation times affect the relaxation of all carbons. The motion of AOT's alkyl tails in the w/o microemulsions can be described using a single correlation time.

Motional differences are observed in the AOT alkyl chains when going from the inverted micelles to the w/o microemulsions. Calculations show that the w/o microemulsions cannot be spherical at the highest water contents.

Also studied was the ternary phase behavior of AOT, Aerosol TR (ATR), and Aerosol IB (AIB) in water/oil solutions at 45°C using cyclohexane and benzene as the hydrocarbon. AOT solubilizes less water in benzene than in cyclohexane. ATR takes up a smaller amount of water in either solvent than AOT does. AIB/water solutions solubilize moderate amounts of both benzene and cyclohexane. In benzene, AIB takes up significant amounts of water, while solid AIB precipitates from cyclohexane solutions when water is added.

The effects of cosurfactants of the opposite HLB on the phase behavior of ATR and AIB were investigated. Large, isotropic, one phase regions dominated the pseudoternary phase diagrams when 2:3 (w/w) ATR/2-propanol or AIB/1-hexanol was used as the emulsifier. Attempts to characterize the aggregates in the ATR one phase solutions using ^{13}C and ^1H nmr were inconclusive, but provide the basis for further work.

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CHAPTER I

SOLUTION CHEMISTRY OF SURFACTANTS

The family of molecules known as surfactants represents an important, although incompletely understood, class of organic compounds. Included in this classification are the soaps and detergents. The word surfactant is derived from the term surface-active agent, arising from the ability of these compounds to reduce the surface tension of water. Words synonymous with surfactant are amphipath, amphiphile and tenside (Ger.).

Surfactant molecules contain a polar or hydrophilic head group and a nonpolar or hydrophobic tail. The head group can be: (1) ionic, either cationic (e.g., ammonium) or anionic (e.g., sulfate); (2) zwitterionic; or (3) nonionic (e.g., polyethylene oxide). The hydrophobic portion of the molecule may contain hydrocarbon chains of varying length and structure, more than one alkyl chain, unsaturation, or a functional group. In solution, these compounds form numerous association species, whose nature depends on the surfactant and the solvating medium. This chapter briefly reviews the solution chemistry of surfactants.

A. IMPORTANCE

Surfactants have been used by industry for a long time. Virtually any product which is required to spread, adhere or act as a solubilizing agent will contain some type of surfactant. Their solubilization and wetting properties make amphiphiles important ingredients in

paint formulations.¹ Emulsion polymerization is the preferred method when a latex is the desired product.² Surfactant solutions will displace oil from reservoirs in tertiary oil recovery.³ Other areas in which surfactants are commonly used include lubricants, dyeing of textiles, production of milk,¹ and formulation of pharmaceuticals⁴ and pesticides.⁵

Many household products contain surface-active compounds. Toothpaste, toiletries, floor waxes and polishes, perfumes and cosmetics are all surfactant concoctions,^{1,6} as are the everyday soaps and detergents.

The most important property of amphiphiles is their ability to solubilize compounds that would otherwise be insoluble in the bulk solution. The use of surfactant solutions for catalytic⁷ and photochemical⁸ studies is a practical extension of this property. Their similarity to biological systems makes micelles and microemulsions suitable candidates to mimic membrane activity.⁹ Tensides have been employed for a wide variety of analytical purposes.¹⁰ Their ability to promote light-induced charge separation and energy conversion has been studied.¹¹

B. AQUEOUS SOLUTIONS

1. Micelles

The association structures formed by surfactants in water are depicted in Figure 1. At low concentrations they behave as normal electrolytes. A monolayer is formed at the air/water interface; the surface tension decreases linearly as the amphiphile concentration

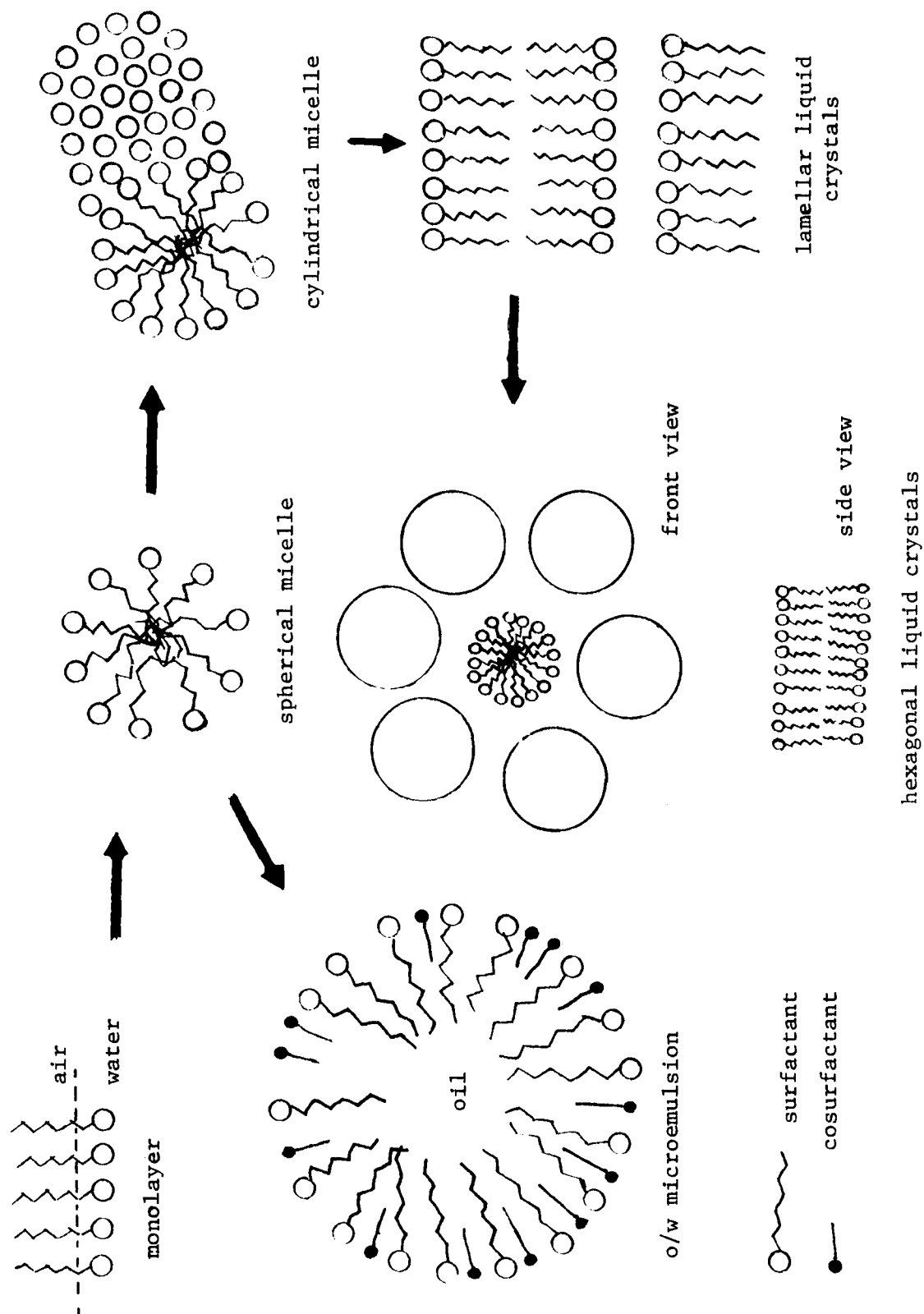


Figure 1. Schematic of surfactant association structures in water.

increases. At a well-defined concentration, called the critical micelle concentration (c.m.c.), monomers aggregate into micelles. The c.m.c. represents a narrow transition region where domination of various solution properties by the monomers changes to domination by the micelles.

Solution behavior is mostly ideal below the c.m.c.; above the c.m.c. a marked nonideality is observed.¹² McBain is usually credited with having first suggested molecular association to explain this anomalous solution behavior, but he cites conjecture by earlier workers.¹³ McBain postulated two types of association species: a neutral, lamellar micelle and a spherical, ionic micelle.¹⁴ Hartley applied the Debye-Hückel theory¹⁵ to a spherical, ionic micelle having an "ionic skin" surrounding the nonpolar core. Recently this model has been modified to include channels which allow for water and solubilize penetration.¹⁶ The concept of a spherical micelle is popularly accepted, but there exists no absolute method of determining particle shape.^{16a} Surfactants with long alkyl chains tend to form cylindrical micelles.¹⁷ Rod-like micelles can also form at high amphiphile concentrations¹⁸ and in the presence of added electrolytes.¹⁹

2. Solubilization and O/W Microemulsions

Nonpolar substances can be solubilized in the hydrocarbon interior of a micelle. Molecules having polar functionalities are often located close to the head groups, as are polarizable compounds. Solubilizates can alter the c.m.c., increase the aggregate size, or change its shape, depending on the nature of the solubilize.²⁰

Oil-in-water (o/w) microemulsion is the term used when a large amount of a nonpolar (oil) substance is dispersed into an aqueous micellar phase producing an optically transparent or translucent solution.²¹ Usually a cosurfactant is necessary for formation of this fluid dispersion. Generally, a cosurfactant is an amphiphilic substance which aids the emulsifying properties of the surfactant by lowering the interfacial tension and increasing the amount of disorder at the interface.²² Unlike macroemulsions, no work is required to prepare these systems.

There exists a controversy whether microemulsions are different from micellar systems. Some workers consider microemulsions to contain swollen micelles, while others contend they are true dispersions of one liquid within another (see discussion in reference 23). These disagreements will not be easily resolved.

Two questions are foremost; the first concerns their long-term stability. Some o/w microemulsions are thermodynamically stable, while others are only kinetically stable. In addition, the order of mixing of components will affect their stability in certain cases.^{24,25} The second point of contention is the nature of the interface. According to Prince,²⁶ oil is solubilized amongst the hydrocarbon tails in the micelles, while in the o/w microemulsions there must be a well-defined interface with a tension or pressure gradient across the interface. Other workers²⁷ maintain that since no macroscopic phase transition occurs, there is no advantage in considering microemulsions as pseudo two phase systems, and that attention should be focused on the interactions between components. Furthermore, it is difficult to

distinguish between the surfactant's hydrophobic surface and that of the solubilized oil.²³

3. Liquid Crystals

At higher surfactant concentrations in water, viscoelastic gel phases occur. These mesophases are liquid crystalline in nature. Since they exhibit a periodicity in packing, which can be analyzed by x-ray diffraction, they can be considered as crystals. Yet they retain the ability to flow; thus, liquid-like. X-Ray data show a diffuse diffraction band at $4.6 \text{ \AA}$, similar to that of liquid hydrocarbons. Lamellar and hexagonal liquid crystals are shown in Figure 1 (p 3). Isotropic cubic mesophases also exist.²⁸

C. NONAQUEOUS SOLUTIONS

Surfactants will also form aggregates in apolar solvents. The formation of inverted (reversed) micelles, Figure 2, requires a trace amount of water.²⁹ Unlike the aggregates in water, inverted micelles are built up through self-association of monomers to smaller aggregates in most cases.³⁰ There is no formal c.m.c., although often an operational c.m.c. is observed.³¹ A notable exception is Aerosol OT [AOT, sodium bis(2-ethylhexyl)sulfosuccinate], for which a c.m.c. is evinced (see Chapter II). In the case of inverted micelles, the polar portion of the molecule resides in the aggregate's core; the hydrocarbon tails form the outer mantle.

Many inverted micelles will solubilize large amounts of water, thus forming water-in-oil (w/o) microemulsions. Initially, added water binds to the surfactant's head groups. When the hydration

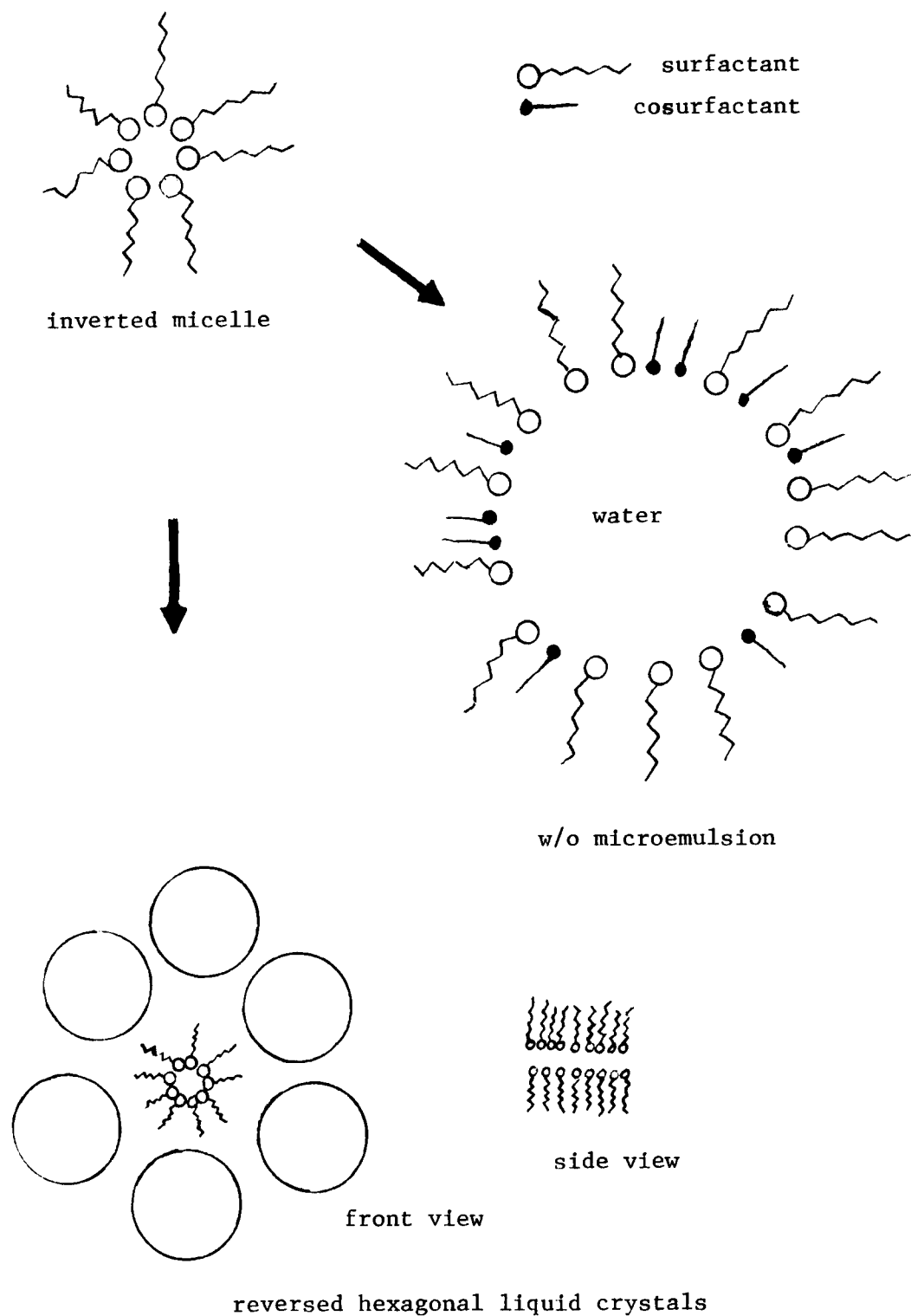


Figure 2. Schematic of surfactant association structures in nonaqueous media.

requirements of the head groups are met, additional water will be situated "free" in the core. By definition, w/o microemulsions will always contain "free" and "bound" water.⁹ As with the case for normal micelles versus o/w microemulsions, it is claimed that the distinction between inverted micelles and w/o microemulsions is merely a question of semantics.^{25,32} However, the nature of the interface is more clearly defined in the inverted case, and the two regions are governed by different thermodynamic considerations.³³ W/O microemulsions are usually thermodynamically stable, but phase separation was observed in one case after six and one-half months of storage.³⁴

Aerosol OT, the major object of study in this work, forms inverted micelles which will solubilize large amounts of water without the need for a cosurfactant. In fact, it will take up more water than there is hydrocarbon solvent! This unique behavior will be discussed fully in Chapter II, along with a more detailed analysis of a specific w/o microemulsion.

Liquid crystals may also form in nonaqueous media. Reversed hexagonal mesophases [(Figure 2 (p 7)] are most frequently observed.²⁸

D. PHASE BEHAVIOR

The relationship among the different phases in binary or ternary systems containing surfactants is useful in helping to understand why various association species occur. For example, going from a w/o to an o/w microemulsion may involve passage through one or more liquid crystalline phases. A full discussion of phase relationships and the use of phase diagrams to map out this behavior is found in Chapter V. For now, the focus is on selected types of phase behavior.

1. Emulsions

An emulsion or macroemulsion is an heterogeneous dispersion of one liquid in another. These systems are kinetically, not thermodynamically, stable. Water may be dispersed in an oil continuous phase (w/o emulsion), or vice-versa (o/w emulsion). Surface-active materials are required to maintain the stability of an emulsion. Flocculation is a process which destroys emulsions. Two or more emulsified drops stick together forming a cluster. Coalescence of flocculated droplets is irreversible.³⁵

2. Middle Phase Microemulsions

Temperature has a marked effect on the aggregation patterns of surfactants. The role of temperature is described in this section for nonionic surfactants. They become less soluble in water as the temperature is increased. Above a temperature, known as the cloud point, T_c , phase separation will occur. Just below the cloud point, solubilization of organic substances increases dramatically. T_c represents a lower consolute temperature (see I_w region in Figure 3).

As the fraction of oil in a system at certain temperatures above the cloud point is increased, a three phase system will appear (III in Figure 3). Almost all of the surfactant resides in the middle phase at this temperature (phase-inversion temperature, PIT); hence, the term middle phase microemulsion is used, since this phase contains significant amounts of water and oil. The inverted micelle-w/o microemulsion region, I_o , is reached as the temperature is further increased and more oil is added.^{27,36}

A surfactant's hydrophilic-lipophilic balance (HLB) is altered

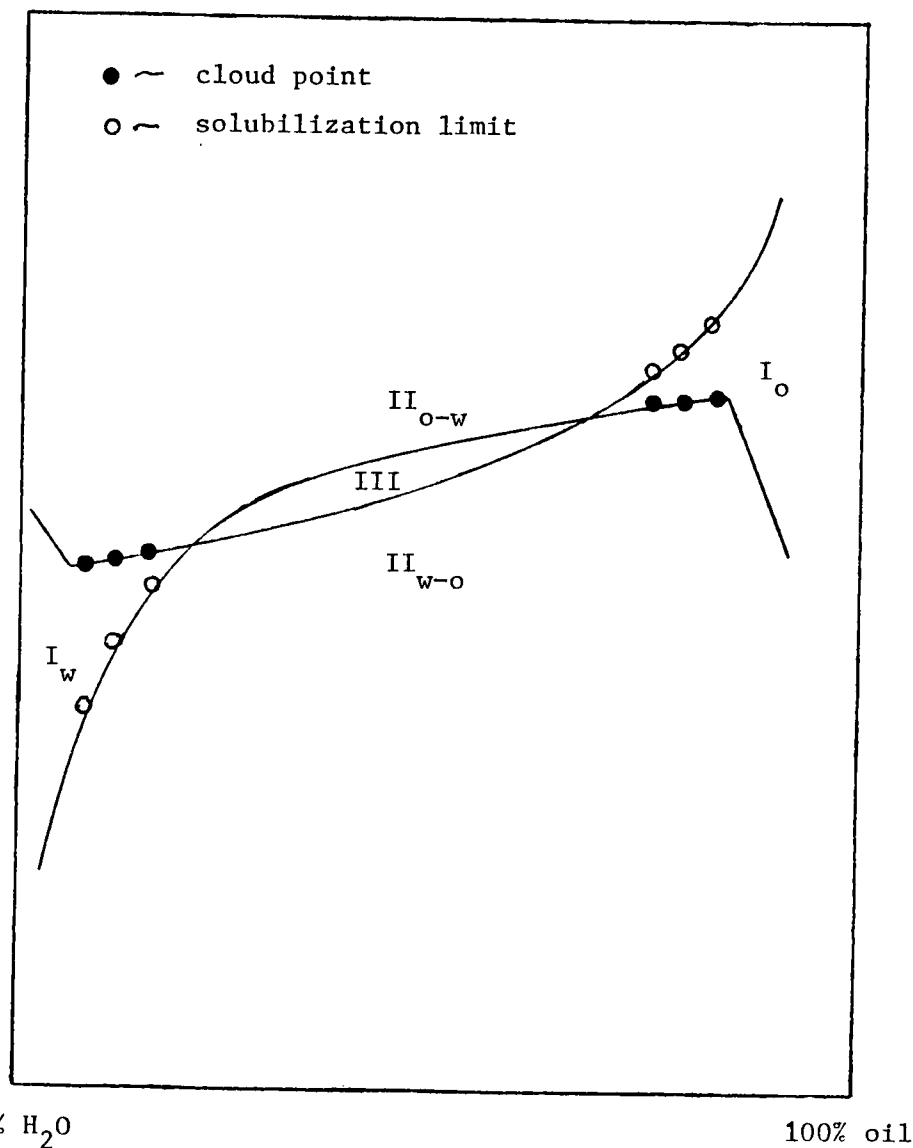


Figure 3. Temperature versus composition phase diagram.

- I_w: micelles-o/w microemulsions
- I_o: inverted micelles-w/o microemulsions
- II_{w-o}: o/w microemulsions + oil
- II_{o-w}: w/o microemulsions + water
- III: middle phase microemulsion + oil + water

by temperature. The HLB number is determined by a surfactant's partition coefficient between water and oil; the higher the HLB number, the higher an amphiphile's water solubility.³⁵ The effect of increasing the temperature is to decrease the HLB number of a nonionic surfactant. A larger HLB number is reflected in a higher PIT. The surfactant is said to be balanced at the PIT; i.e., it will behave equally well as an oil-solubilizing or a water-solubilizing emulsifier.

E. THERMODYNAMICS

Many theories have been developed to account for the self-assembly of surfactants in solution. This section gives a brief summary of the different models and should not be considered a comprehensive treatment.

The simplest model for surfactant association is based on the mass action law. A single micelle, S_n , is in equilibrium with the monomer, S_1 , (Equation 1). The most important features of this model



$$K = [S_n]/[S_1]^n \quad (1b)$$

are its prediction of a constant aggregation size above the c.m.c. and its emphasis on the cooperativity of aggregation.

The multiple self-association model assumes that micelles are formed through a stepwise aggregation process. In its simplest form,



$$K_i = [S_{i+1}]/[S_i][S_1] \quad ; \quad (2b)$$

$$K_n = \prod_{i=2}^n K_i \quad . \quad (2c)$$

This model fails because it does not predict finite aggregate sizes. A modification must be made in order to account for the cooperativity of aggregation.

A third model treats aggregation as a phase separation. Here, micelle formation is considered to be analogous to a phase transition from bulk solution to micelles plus bulk solution. This model over-emphasizes the cooperativity of micellization.

Detailed descriptions of these models and of other thermodynamic considerations are available.³⁷⁻⁴⁰ In addition, a model has been developed based on small system thermodynamics,⁴¹ as well as one which takes into account packing constraints.⁴²

The free energy of micellization, ΔG_m^0 , can be expressed as⁴³

$$\Delta G_m^0 = \Delta G_t^0 + \Delta G_h^0 \quad , \quad (3)$$

where ΔG_t^0 represents the attraction of the hydrocarbon tails and ΔG_h^0 , the repulsion between head groups. A more elaborate treatment,⁴⁴

$$\Delta G_m^0 = \Delta G_{hgi}^0 + \Delta G_{ltf}^0 + \Delta G_{lrf}^0 + \Delta G_{hb}^0 \quad , \quad (4)$$

considers contributions from head group interactions, hgi, loss of translational freedom due to aggregation, ltf, loss of rotational freedom, lrf, and hydrogen bonding, hb. An estimate of ΔG_m^0 is obtained from Equation 5.

$$\Delta G_m^0 = -RT \ln(c.m.c.) \quad (5)$$

The concept of interfacial tension, a measure of the work

required to extend the surface area between two liquids, is of fundamental importance to an understanding of microemulsions. The interfacial tension, γ_i , is lowered when surfactants adsorb at an interface. In the simplest model,⁴⁵

$$\gamma_i = \gamma_{o/w} + \pi_p, \quad (6)$$

where $\gamma_{o/w}$ is the interfacial tension between oil and water before amphiphile is added and π_p is a two-dimensional, lateral-spreading pressure across the interface. The relative surfactant/water and surfactant/oil interfacial tensions will determine whether the microemulsion is o/w or w/o.

In Robbins' model,⁴⁶ the interfacial tension is related to a lateral stress gradient across the interface which arises from the differing interactions of water and oil with the surfactant at either side of the interface. A more rigorous thermodynamic treatment has been performed by Ruckenstein,⁴⁷ who derived an expression for the interfacial tension from the Gibbs adsorption equation.

F. KINETICS

Micelles are not static species. There is constant diffusion of monomers in and out of the micelles. This is represented in Equation 7, where k_n^+ and k_n^- are the rate constants for incorporation



and dissociation of monomer, respectively. Assuming monodispersity, a relaxation time, τ_1 , for monomer dissociation is related to k_n^- by

$$1/\tau_1 = (k_n^-) [1 + n\bar{S}_{exc}/\bar{S}_1] \quad (8)$$

where $\bar{S}_1$ is the equilibrium concentration of monomers, $\bar{S}_{exc} = \bar{S}_n -$ c.m.c., $\bar{S}_n$ is the equilibrium concentration of molecules within the micelles, and n is the aggregation number. If the micelles are polydisperse, a variance factor, σ^2 , needs to be included in Equation 8.⁴⁸ This model has been extended to include the effect of monomers diffusing partway out of the aggregates.⁴⁹

Micellar formation and dissolution is a slower process than monomer diffusion.⁵⁰ The relaxation time, τ_2 , for this process is given by

$$1/\tau_2 = \{k_D + [k_F/(1/\tau_1)]\} f(\bar{S}_n, \text{c.m.c.}) \quad , \quad (9)$$

where k_F and k_D are the rate constants for formation and dissolution, respectively, and $f(\bar{S}_n, \text{c.m.c.})$ is a concentration dependent function not defined further by the authors.

Techniques used to measure these relaxation times have been covered in a comprehensive monograph.⁵¹ A large number of studies have found τ_1 to be $10^3 - 10^5$ times faster than τ_2 .^{50,52} A recent study measured the rate of cosurfactant dissociation from an o/w microemulsion; the monomer dissociation process could not be identified.⁵³ It was found that addition of alcohol decreased the rate of monomer diffusion.⁵⁴ The rotational mobility of water is slowed by the presence of micelles.⁵⁵

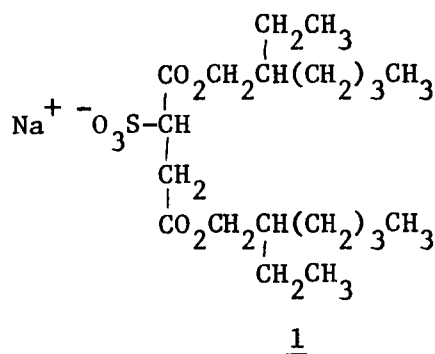
It is possible to calculate translational diffusion coefficients from τ_1 's using statistical mechanics.^{52a} Experimentally, overall aggregate diffusion coefficients can be determined by dynamic light scattering.⁵⁶ Amphiphile self-diffusion coefficients are obtained

from nmr pulsed-gradient spin-echo⁵⁷ techniques. The relationship between rotational diffusion and nmr spin-lattice relaxation is given in Chapter III.

CHAPTER II

AEROSOL OT

Aerosol OT, 1, is a double-tailed anionic surfactant. AOT has a low solubility in water, tending to form liquid crystals at low amphiphile concentrations. This surfactant is very soluble in hydrocarbons and will solubilize large amounts of water in its inverted micelles. The aggregation behavior of Aerosol OT is reviewed in this chapter, with emphasis on hydrocarbon solutions.



A. AQUEOUS SOLUTIONS

AOT forms micelles in water; its c.m.c. falls within the range $2.3 - 5.1 \times 10^{-3} \text{ M}$.^{30,58} The one-phase isotropic region extends up to 1.3 wt.% AOT.⁵⁹ Between this concentration and 12 wt.% AOT, a liquid crystalline phase is in equilibrium with the micellar solution.⁶⁰ At higher concentrations, a series of liquid crystalline mesophases are found; lamellar, cubic, and hexagonal mesophases have been identified.

The lamellar region dominates the AOT/water phase diagram; its domain exists from 12 - 75 wt.% AOT.⁶⁰ The water resides between the surfactant bilayers; two-dimensional swelling of the lattice occurs as

the wt.% water increases.⁶¹ This phase is anisotropic; birefringence is observed when the sample is held between crossed polars. Conductivity increases with increasing Aerosol OT concentration until the thickness of the water layer decreases sufficiently to cause restriction of the sodium ions' mobility.⁶² Raman spectroscopy shows that the percent of gauche conformers in the alkyl chains increases with increasing wt.% AOT.⁶³

Certain anomalies occur in the region between 35 - 40% wt.% AOT. Here the birefringence changes sign,⁶⁰ the slope of the conductivity curve changes,⁶² x-ray analysis gives low repeat distances,⁶⁴ and Raman spectra suggest more trans conformers.^{63a} The abnormal behavior in this "gap region" has been ascribed to a splaying out of Aerosol OT's hydrocarbon chains.^{60,63a}

The cubic mesophase exists over a very narrow concentration range (75 - 82 wt.% AOT). These solutions are isotropic and give sharp ¹H nmr signals.⁶⁵ Results of nmr self-diffusion studies imply that the structure of this mesophase consists of tetrahedrally arranged rods.⁶⁶

Hexagonal liquid crystals are formed at the highest AOT concentrations. This mesophase is anisotropic. 100% AOT exists in this mesomorphic structure.^{60,65}

B. NONAQUEOUS SOLUTIONS

1. Micelles

a. Formation. Unlike many surfactants, Aerosol OT exhibits a critical micelle concentration in apolar media. Two breaks are

observed in a plot of conductivity versus concentration in benzene.⁶⁷ The first break at 10^{-5} M is due to a nucleation process in which monomers form micellar subunits (premicellar aggregates). These nuclei are made up of three AOT molecules associated with a water molecule.^{29,68} Monomers bind to trimers at the c.m.c. resulting in inverted micelles. This accounts for the second break in the conductivity curve at 5×10^{-3} M. Positron annihilation studies support the existence of a c.m.c.⁶⁹

Micelle formation is accompanied by conformation changes in the AOT molecule. After micelles are formed, these structural changes make further monomer binding difficult; the micelle's aggregation number remains constant as the surfactant concentration increases. Neither the solvents nor surfactant can be rid completely of water, without which inverted micelles will not form.⁷⁰

Tamura and Schelly⁷¹ have proposed a bimodal model for AOT's aggregation in benzene. They interpreted the vapor pressure and spectrophotometric data using a model in which a discrete equilibrium is formed between monomers and inverted micelles containing 6 and 14 monomers (6-mer and 14-mer). As the AOT concentration increases, the concentrations of all three species increase. In this model, the concept of a c.m.c. has no meaning.

b. Shape. Philipoff⁷² interpreted the x-ray diffraction patterns of AOT/hydrocarbons as evidence for lamellar micelles. However, the x-ray spacing could be due to a regular arrangement of spherical micelles.⁷³ The observed dependence of the viscosity of AOT solutions in dodecane on the amphiphile concentration is consistent

with spherical solute particles.⁷⁴ A slightly prolate ellipsoid was postulated for AOT micelles in *p*-xylene on the basis of viscosity measurements. A definite micellar deformation occurs at high surfactant concentrations and the micelles become cylindrical.⁷⁵ The viscosity data in isooctane are consistent with either a prolate ellipsoid of dimensions $23 \text{ \AA}$ by $60 \text{ \AA}$, or with a sphere having a diameter of $36 \text{ \AA}$.⁷⁶ Since the length of an AOT molecule is $11 \text{ \AA}$, the ellipsoid was preferred. However, the larger radius could be due to the presence of water within the spherical micelles.

Most data support the concept of a spherical inverted micelle. Any deviation from sphericity, if real, should be small at moderate AOT concentrations. Thus, spherical micelles will be assumed for the purpose of this work.

c. Size. Two parameters are most often used to characterize micellar size: the radius of a spherical micelle, r_0 , and the aggregation number, n . Both the size and extent of aggregation are solvent dependent.

Static light scattering gives a weight-average molecular weight, M_w , while vapor pressure osmometry yields a number-average molecular weight, M_n . The ratio, M_w/M_n , is a measure of the aggregates' polydispersity. This ratio was found to be nearly unity (i.e., the aggregates are monodisperse) in carbon tetrachloride and isooctane. A significant polydispersity was observed in benzene ($M_w/M_n = 1.7$) and cyclohexane ($M_w/M_n = 3.0!$).⁷⁷ The polydispersity decreases with time in toluene.^{58d} The aggregation number increases in the order: methanol < dioxane < benzene < carbon tetrachloride < aliphatic

hydrocarbons.³⁰ Generally, n decreases as the solvent solubility parameter increases.⁷⁷ In addition, the aggregation number is affected by the method used to purify AOT.^{76b}

Micellar radii may be obtained from dynamic light scattering (photon correlation spectroscopy), fluorescence polarization measurements, and small-angle x-ray and neutron scattering. The aggregate size remains constant over a wide range of AOT concentrations.^{78,79} Small-angle x-ray scattering gives the radius of gyration, r_g ; two of the earliest studies found r_g 's of $9 \text{ \AA}$ ⁸⁰ and $11 \text{ \AA}$ ⁸¹ in dodecane. Dynamic light scattering yields the hydrodynamic radius, r_h . In isooctane³³ and heptane,⁷⁸ an r_h of $15 \text{ \AA}$ was determined by this method. The isooctane results were confirmed by fluorescence measurements.⁷⁹

2. Solubilization of Water

a. Properties of Solubilized Water. The enthalpy of solubilization of water decreases as water is added to AOT inverted micelles.⁸² The first five or six moles of added water hydrate the sodium ions; they are more energetically bound than further added water.⁷⁵ This is supported by positron annihilation investigations.⁸³ Using this technique, w/o microemulsions, as defined in Chapter I, are found at molar ratios of added water to Aerosol OT ($R = [\text{H}_2\text{O}]/[\text{AOT}]$) of 8 in isooctane and 5 in benzene.⁸⁴ Fluorescence probe studies indicate that all the water is bound up to $R = 20$.^{85,86}

Zinsli⁸⁷ discovered that the aqueous interior of AOT w/o microemulsions has a radially inhomogeneous microviscosity. There exists a viscous boundary layer, 5 to $8 \text{ \AA}$ thick, comprised of water bound to the head groups. This aqueous sheath surrounds the free water in a

less viscous core. Only one water peak is observed in the ^1H nmr spectrum, indicating that fast exchange occurs between free and bound sites.⁸⁸

How does solubilized water differ from bulk water? The activity coefficient of solubilized water approaches unity with increasing R .⁸⁹ The polarity of the largest water pool is still less than that of bulk water.⁸⁵ Addition of water causes the water protons' chemical shift to move downfield, approaching that of bulk water.⁸⁸ The correlation time, τ_c , (see Chapter III), of the water protons decreases with increasing R to $R = 6$, and then levels off, remaining larger than τ_c in pure water. These studies suggest that the nature of the water solubilized in the microemulsions is slightly different from that of bulk water, even at very high R values.

b. Overall Properties. Aerosol OT inverted micelles swell upon solubilization of water.³³ Concomitant with this increase in aggregate size is an increase in the aggregation number.⁹⁰ The size of the aggregates remains constant with increasing surfactant concentration at constant R .^{91,92} The capacity of the inverted micelles to solubilize water is solvent dependent,⁹³ as is the aggregate size.⁷⁹ The maximum amount of water solubilized by AOT in isooctane is increased by the addition of small amounts of other organic compounds, such as benzene.^{22a}

Zulauf and Eicke³³ found that the size of AOT inverted micelles is temperature-independent. These micelles are stabilized by hydrogen-bonding interactions, and behave as rigid macromolecules. When free water is present (i.e., w/o microemulsions), r_h increases with

increasing temperature. The interfacial tension of the surfactant film is the predominant contribution to the free energy of the w/o microemulsions. This study by Zulauf and Eicke emphasizes that the distinction between inverted micelles and w/o microemulsions is more than just a question of semantics, at least for the AOT case.

Experimental evidence suggests that the aggregates in AOT w/o microemulsions are spherical, even at the highest R values.⁹⁴ These results contradict calculations which show that the spherical shape is geometrically unattainable at very large water concentrations.^{75,95} Perhaps lamellae are present within the isotropic phase before a macroscopic phase transition occurs.⁹⁶

Initial solubilization of water effects a conformational change within the AOT molecule.⁹⁷⁻⁹⁹ The surface area per head group at the surfactant/water interface increases with increasing R until a maximum value of $55 \text{ \AA}^2$ is reached at $R = 20$.^{90,100} Water is rapidly exchanged between aggregates.^{101,102} Utilization of a probe molecule discerned no water penetration into the surfactant film.¹⁰³

The intrinsic viscosity of AOT/water/isooctane solutions decreases with increasing R until $R = 10 - 20$ because the number of aggregates per unit volume decreases. The specific conductivity exhibits a concurrent increase. Between $R = 20$ and 40, the conductivity decreases, while the viscosity increases slightly. Aggregate swelling causes an abrupt increase in viscosity and a levelling off of the conductivity at the highest R values.¹⁰⁴ The increase in conductivity at low R values is due to monomer dissociation from the aggregates.¹⁰⁵

3. Effects of Salts

The presence of salts will decrease the solubilization capacity of AOT inverted micelles. Electrolytes, in general, break up the hydrogen-bonding network formed by water in the core.¹⁰⁶ The solubility of sodium chloride is dependent on the relative concentrations of Aerosol OT and water.¹⁰⁷ A small-angle neutron scattering (SANS) study indicated that the radius of the water core increases and the surface area at the surfactant/water interface decreases upon addition of sodium chloride at constant R.¹⁰⁸ Opposite results were obtained by dynamic light scattering.⁷⁸ The SANS conclusions are supported by ¹H nmr studies.¹⁰⁹

Commercially-obtained Aerosol OT usually contains electrolytic impurities from the synthesis of this compound. Kunieda and Shinoda¹¹⁰ demonstrated that its solubilization capacity in cyclohexane increased dramatically when salts are removed. The influence of salts on phase behavior becomes apparent when analyzing the observations of Frank and Zografi on 2 wt.% impure AOT solutions in octane.¹¹¹ The following series of phase transitions was noted upon addition of water at 25°C: isotropic, one phase → two phases, turbid → one phase, blue translucent → two phases, turbid. Later work by the same authors showed that the first turbid region disappears at 35°C, and that the maximum amount of water solubilized increases with increasing temperature.¹¹² Recently it has been found that addition of a solution of 0.6 wt.% sodium chloride in water to AOT in cyclohexane produces a middle-phase microemulsion at 43°C, using highly purified surfactant.¹¹³ There exists a striking resemblance between Frank and Zografi's blue

translucent region and the middle phase microemulsions, which bears further study.

4. Related Surfactants

Compared to the voluminous literature on Aerosol OT, little work has been performed on related dialkylsulfosuccinate surfactants. Aggregation numbers have been determined for Aerosol AY (AAY, sodium bis-1-pentylsulfosuccinate) in benzene⁹⁷ and Aerosol TR (ATR, sodium bistridecylsulfosuccinate) in dodecane.^{76b} Aggregation numbers tend to decrease with the size and amount of branching within the alkyl chains.⁷⁷ However, increasing alkyl chain bulkiness will enhance the amphiphile's ability to solubilize water.⁸² The 1-octyl- and 1-hexyl- analogs of AOT take up less than 1 mole of water per mole of surfactant.¹¹²

Kitahara, et al., determined that when the sodium ion of AOT is replaced by other cations, the surfactant's water solubilizing capacity decreases as the cation becomes larger.¹¹⁴ A similar study replaced sodium with tetraalkylammonium cations. The aggregation number decreases as the size of the alkyl group increases.²⁹

C. APPLICATIONS

1. Catalytic Studies

Aerosol OT w/o microemulsions offer an ideal medium for catalytic studies. Catalysis may arise from the amphiphile interacting with either the reactants or the catalyst, or through concentrating effects.¹¹⁵ The most extensive studies have dealt with the acid-catalyzed aminolysis of *p*-nitrophenylcarboxylates by imidazoles; the

latter resides in AOT's H_2O pools.¹¹⁶ Increasing the length of the carboxylate alkyl chain decreases the rate of reaction, while addition of water increases the rate.¹¹⁷ The rate of this reaction is proportional to the imidazole concentration, $[Im]$, at constant R , and to the water concentration at constant $[Im]$. In addition, the hydration of 1,3-dichloroacetone¹¹⁸ and the acid-catalyzed decarboxylation of benzylchloroformate¹¹⁹ have been studied.

AOT water pools have served also as a medium for studying enzyme catalysis.¹²⁰ The conformation and enzymatic activity of RNase is maintained in AOT/water/isooctane.¹²¹ AOT dispersions are stable down to $-45^\circ C$, making them suitable for cryoenzymological studies.¹²²

2. Solubilization of Species Other Than Water

Solubilization of picric acid into AOT/benzene has been studied by Tamura and Schelly.^{71,123,124} The results were interpreted on the basis of the monomer - 6-mer - 14-mer model discussed in section B. The picric acid probe forms a charge-transfer complex with either the carboxylate or sulfonate functional groups of AOT. Since the probe is colorless in benzene but turns yellow when it reaches the polar core of AOT inverted micelles, the dynamics of solubilize penetration can be studied spectrophotometrically. Four rate processes were identified: (1) penetration of the probe to the carboxyl moiety, a very fast process accompanied by the color change; (2) penetration of the solubilize to the sulfonate head group in the 14-mer; (3) penetration of picric acid to the head group in the 6-mer, only found at AOT concentrations $< 4 \times 10^{-3}$ M; (4) penetration of the probe to the carboxylates in the 6-mer, present only at AOT concentration $> 4 \times 10^{-3}$ M. The relative rates

decreased in the order: $1 > 4 > 2 > 3$. These solutions contained only residual water from the benzene used. Tamura and Schelly stated that the fourth process results from dehydration of the carboxylates in the 6-mer at the higher concentrations of AOT, and that the rate of this process is dependent on exchange of water between micelles. Two criticisms may be made. First, it is hard to envision water diffusion between aggregates occurring faster than water penetration into an aggregate. Second, the 14-mer should be dehydrated more easily than the 6-mer.

p-Nitrophenol adsorbs at the AOT/water interface.¹²⁵ The binding constants of *p*-substituted phenols to AOT inverted micelles have been determined using absorption spectroscopy.¹²⁶ Methanol association with AOT was studied by gas chromatography.¹²⁷ Hydrated electrons can be formed in AOT water pools;¹²⁸ the photochemistry of singlet and triplet biphenyl in the water pools has been investigated.¹²⁹ Copper(II) complexes have been solubilized in AOT/chloroform;¹³⁰ nickel(II) was extracted from water by AOT/heptane.¹³¹ AOT w/o microemulsions have been applied as the mobile phase for TLC separation of polynuclear aromatic hydrocarbons.¹³²

4. Commercial Applications

Aerosol OT w/o microemulsions have been employed in dry-cleaning.¹⁰⁷ AOT is found also in laxatives,¹³³ as a stabilizer in polyacrylamide emulsions,¹³⁴ in formulations for enhanced oil recovery,¹³⁵ and in vaginal suppositories.¹³⁶

CHAPTER III

NUCLEAR MAGNETIC RESONANCE

A. THEORY

1. General

Nuclear magnetic resonance (nmr) is the study of nuclear paramagnetism.¹³⁷⁻¹³⁹ A nucleus contains an intrinsic nuclear spin, $\vec{I}$, which behaves as a miniature magnet possessing a magnetic moment, $\vec{\mu}_N$. The magnetic moment is related to the spin angular momentum vector, $\vec{I}$, by Equation 10, where γ_N is the gyromagnetic ratio, h is Planck's constant divided by 2π , g_N is the nuclear g-factor and β_N is the

$$\vec{\mu}_N = \gamma_N \hbar \vec{I} = g_N \beta_N \vec{I} \quad (10)$$

nuclear magneton (5.0493×10^{-27} J/T).

For spin-1/2 systems (such as ^{13}C and ^1H) there exist two discrete spin states corresponding to spin quantum numbers of +1/2 and -1/2. Equation 11 gives the energy of separation, ΔE , between these spin states in the presence of a magnetic field, $\vec{H}_0$.

$$\Delta E = \gamma_N \hbar H_0 \quad (11)$$

The equilibrium ratio of the number of spins in each energy level is governed by a Boltzmann distribution, Equation 12, where k is Boltzmann's constant, T is the absolute temperature and $N_{+1/2}$, $N_{-1/2}$

$$N_{+1/2}/N_{-1/2} = \exp(\gamma_N \hbar H_0 / kT) \quad (12)$$

are the number of spins in the upper and lower energy levels, respectively.

Magnetic moments do not align parallel to $\vec{H}_0$, but rather precess about it with respect to a constant angle, θ , Figure 4. The Larmor (precession) frequency, ω_N , is given by Equation 13. At equilibrium,

$$\omega_N = 2\pi\Delta E/h = \gamma_N H_0 \quad (13)$$

there exists a net magnetization, M_z , along the z-axis, while the net magnetizations along the x- and y-axes, M_x and M_y , are zero.

When a radiofrequency field, $\vec{H}_1$, is applied perpendicular to $\vec{H}_0$ (conventionally along the x-axis), the magnitude of θ changes. A spin flip (i.e., a transition between energy levels) occurs when H_1 corresponds to ω_N . The result is an exponential decay in the population difference between the energy levels, Equation 14, where n_t and

$$n_t = n_0 \exp(-2Pt) \quad (14)$$

n_0 are the population differences at times t and 0 , respectively, and P is the transition probability. Eventually, n_t would equal zero, i.e., saturation would result, if this process were allowed to proceed unchecked. In order to preserve a population difference, excess magnetic energy is converted to another form of energy; a nonradiative transition takes place via interaction with other nuclei or with fluctuating local magnetic fields produced by molecular motions. The process is called spin-lattice relaxation and is characterized by a time constant, T_1 , the spin-lattice relaxation time. The change in M_z after the perturbation is applied is expressed by Equation 15, where

$$dM_z/dt = -(M_z - M_0)/T_1 \quad (15)$$

M_0 is the equilibrium value of M_z .

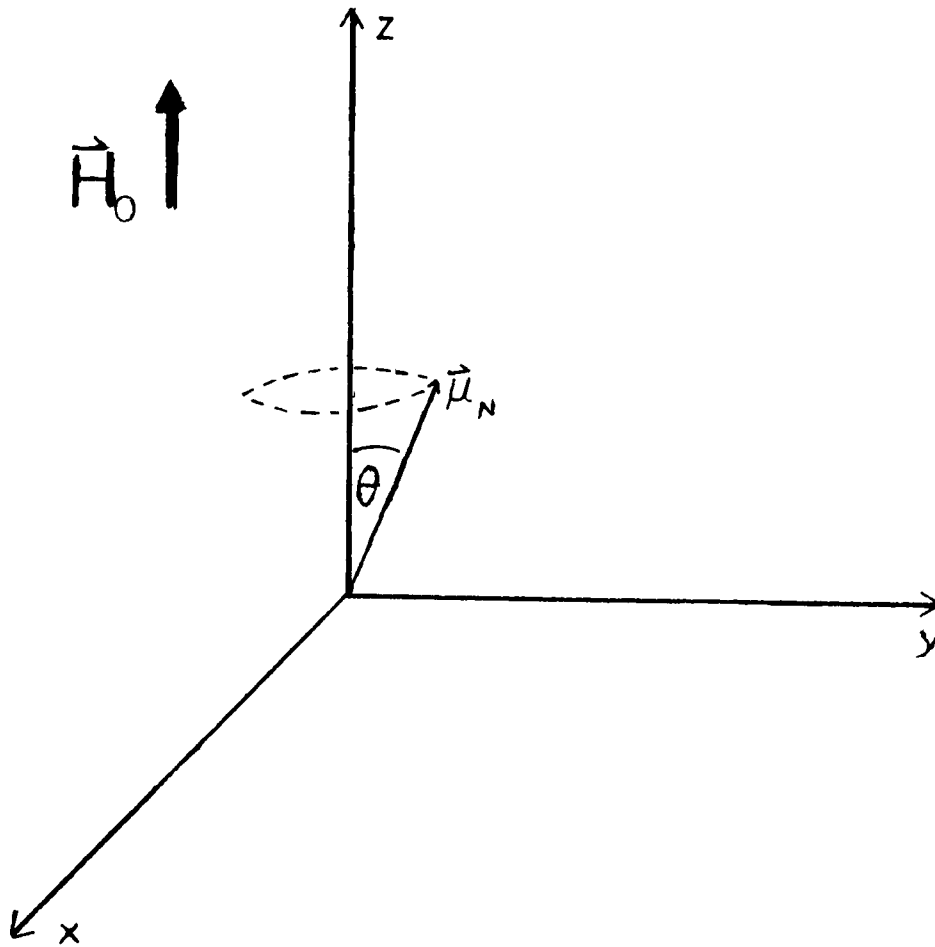


Figure 4. Magnetic moment precessing in a magnetic field.

The magnetization in the xy plane, M_{xy} , does not always average out to zero. It can be supposed that, at a certain instant in time, the nuclei precess in phase. Field inhomogeneities, spin flips, or the T_1 process may result in loss of phase coherence. Energy is exchanged between spins in this case. This process is called spin-spin relaxation and is characterized by a time constant, T_2 . The T_2 process contributes to line broadening. Equation 16 describes the

$$dM_x/dt = -M_x/T_2 \quad (16a)$$

$$dM_y/dt = -M_y/T_2 \quad (16b)$$

spin-spin decay.

Relaxation results from local time-dependent magnetic fluctuations; these variations are measured by a function, $f(t)$. These random fluctuations average out to zero. The autocorrelation function, $G(\tau)$, Equation 17, is the statistical average of the time-dependent

$$G(\tau) = \overline{f^*(t)f(t+\tau)} \quad (17)$$

vacillations. The asterisk in Equation 17 denotes a complex conjugate. For exponential decay with a characteristic correlation time, τ_c ,

$$G(\tau) = \overline{f^*(t)f(t+\tau)} \exp(-\tau/\tau_c) \quad (18)$$

Equation 18 contains the information of the time-domain spectrum. Its Fourier transform, Equation 19, is the frequency-domain spectrum. The

$$J(\omega_N) = \int G(\tau) \exp(-i\omega_N \tau) d\tau \quad (19)$$

spectral density, $J(\omega_N)$, gives the energy available at a frequency,

ω_N , due to $f(t)$. Substituting Equation 18 into Equation 19 and integrating yields

$$J(\omega_N) = \overline{f^*(t)f(t+\tau)} [2\tau_c / (1 + \omega_N^2 \tau_c^2)] \quad (20)$$

2. Relaxation Mechanisms

a. Dipole-Dipole (DD) Relaxation. The major relaxation mechanism in organic molecules is caused by interaction of a ^{13}C nucleus with its adjacent protons. Molecular motions effect the relaxation by producing local fluctuating magnetic fields, $\vec{H}_{\text{loc}}$. Quantum mechanics treats this relaxation mechanism using time-dependent perturbation theory.¹³⁹⁻¹⁴² The energy levels for a two-spin CH system are shown in Figure 5, where the first sign (+,-) refers to the ^{13}C spin. The subscript numbers of the transition probabilities indicate the total change in the spin quantum numbers. It has been shown that T_1 may be expressed in terms of the transition probabilities,¹⁴² Equation 21, where N is the number of directly bound

$$1/NT_1 = P_0 + 2P_{1C} + P_2 \quad (21)$$

hydrogens. Assuming that the reorientational motions of the CH vector are isotropic, the transition probabilities are:

$$P_0 = (K/20r^6)J(\omega_H - \omega_C); \quad (22a)$$

$$P_{1C} = (3K/40r^6)J(\omega_C); \quad (22b)$$

$$P_2 = (3K/10r^6)J(\omega_H + \omega_C); \quad (22c)$$

where $K = \frac{2}{\gamma_H} \frac{2}{\gamma_C} \hbar^2$; ω_H , ω_C and γ_H , γ_C are the Larmor frequencies and

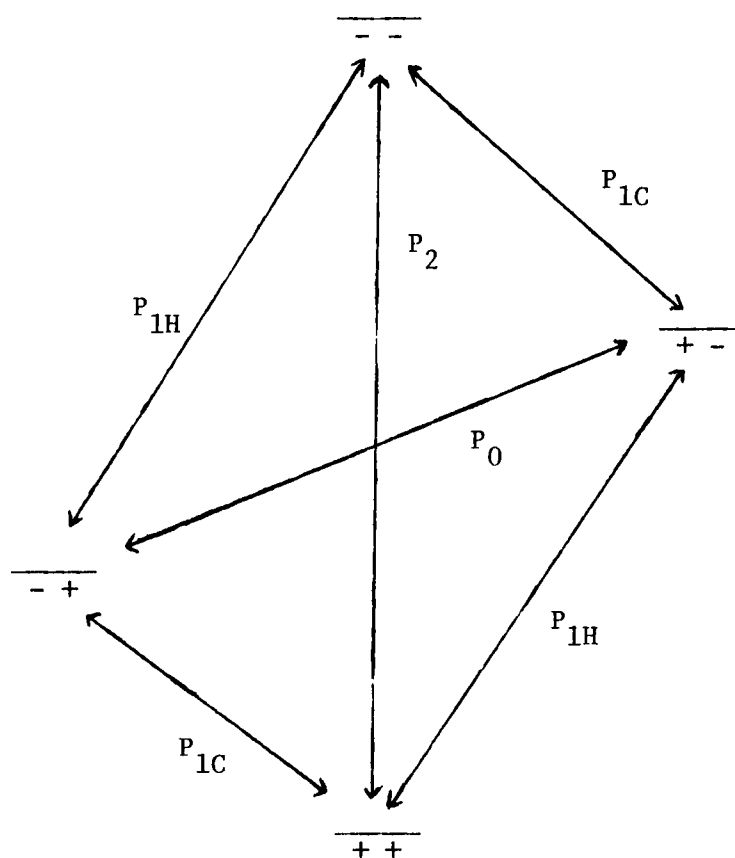


Figure 5. Energy levels of a CH 2-spin system and the transition probabilities between energy levels.

gyromagnetic ratios of hydrogen and carbon, respectively; and r is the carbon-hydrogen bond distance. Substituting Equations 22 and 20 in Equation 21 yields¹⁴³

$$1/NT_1 = K/20r^6 \left[J(\omega_H - \omega_C) + 3J(\omega_C) + 6J(\omega_H + \omega_C) \right] ; \quad (23)$$

$$\frac{1}{NT_1} = \frac{\gamma_H^2 \gamma_C^2 \hbar^2}{10r^6} \left[\frac{\tau_c}{1 + (\omega_H - \omega_C)^2 \tau_c^2} + \frac{3\tau_c}{1 + \omega_C^2 \tau_c^2} + \frac{6\tau_c}{1 + (\omega_H + \omega_C)^2 \tau_c^2} \right] . \quad (24)$$

In the extreme narrowing limit (fast exchange), $\omega^2 \tau_c^2 \ll 1$ and Equation 24 reduces to

$$1/NT_1 = K\tau_c . \quad (25)$$

A plot of T_1 versus τ_c is shown in Figure 6 at 15.1 MHz and in Figure 7 at 100.6 MHz, the frequencies employed in this study.

The above analysis assumes that relaxation is caused by interaction with attached protons only. The effect of interaction with protons on other carbons or of a small degree of anisotropic motion can be accounted for by utilizing an effective correlation time, τ_{eff} , in place of τ_c . τ_{eff} is the average time for reorientation of a C-H vector through one radian.

Woessner¹⁴⁴ has considered the case of fully anisotropic molecular diffusion. In his formalism, T_1 is related to the correlation times for rotation of the C-H vectors about each of the three principal axes.

Using Equation 24, T_1 's which fall inside the extreme-narrowing region are not expected to exhibit a frequency dependence, i.e., the

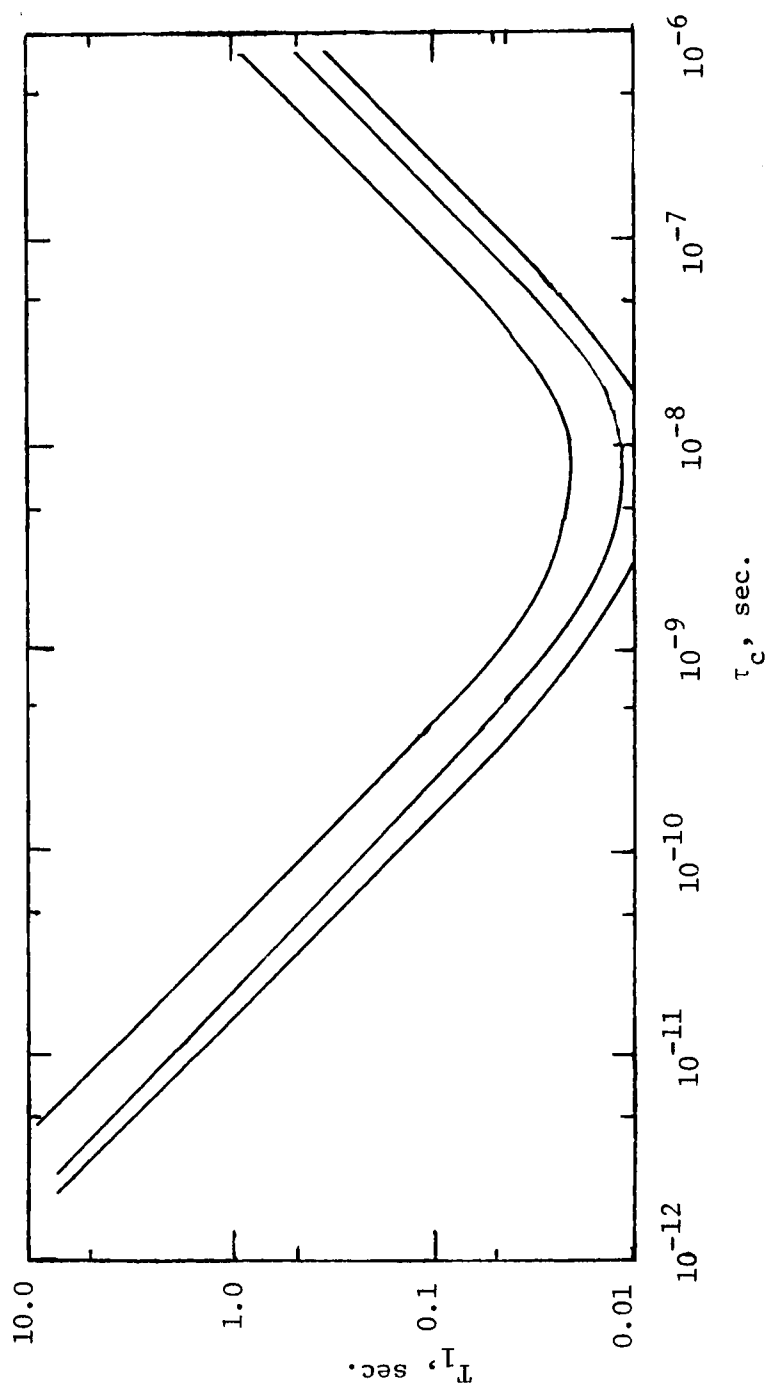


Figure 6. Plot of T_1 versus τ_c at 15.1 MHz.

Top line: CH; middle line: CH_2 ; bottom line: CH_3 .

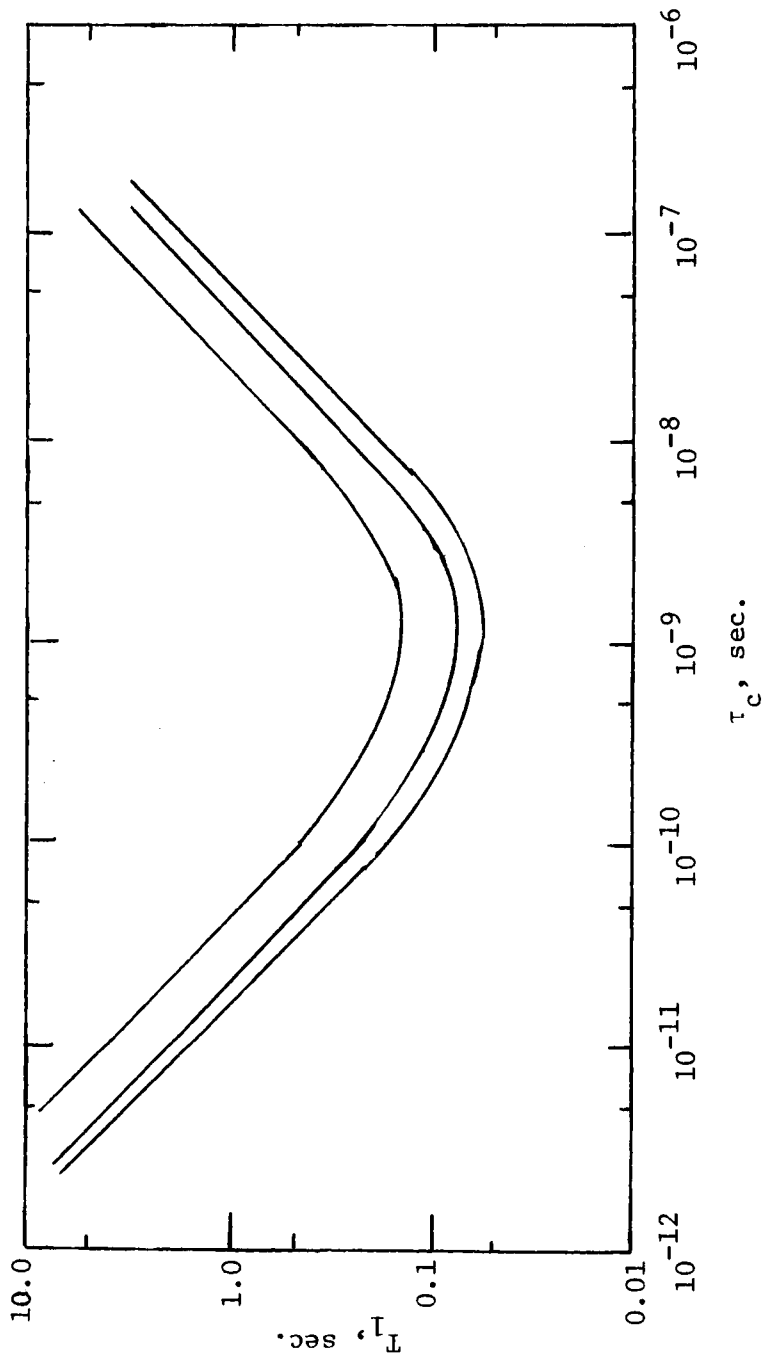


Figure 7. Plot of T_1 versus τ_c at 100.6 MHz.

Top line: CH₂; middle line: CH; bottom line: CH₃.

same value of T_1 should be obtained at all magnetic field strengths. However, T_1 in many cases will increase upon placing the sample in a higher field. It is necessary to invoke a distribution of correlation times when this happens.¹⁴⁵

b. Spin-Rotation (SR) Relaxation. Rapid rotation will affect the relaxation of small molecules and freely rotating molecular groups. This relaxation mechanism competes with dipolar relaxation. Symmetric molecules are affected the most. T_1 will decrease with increasing temperature when this mechanism dominates.¹⁴⁶

c. Chemical Shift Anisotropy (CSA) Relaxation. The local magnetic field, $\vec{H}_{loc}$, at a nucleus is given by Equation 26, where $\vec{\sigma}$

$$\vec{H}_{loc} = \vec{H}_0 - \vec{\sigma}\vec{H}_0 \quad (26)$$

is the shielding tensor. The magnitude of the shielding is dependent on the orientation of the molecule or molecular group relative to $\vec{H}_0$, and is related to the local electron density. This is the origin of chemical shifts. Normally, rapid rotational diffusion causes the directional (anisotropic) component of $\vec{\sigma}$ to average out to zero. Any anisotropy, when present, will give rise to fluctuating $\vec{H}_{loc}$, thus effecting relaxation.¹⁴⁶ The importance of CSA relaxation increases at higher magnetic fields.¹⁴⁷

d. Scalar (SC) Relaxation. This relaxation mechanism is rare, but can occur when a ^{13}C nucleus is scalar (spin-spin) coupled to a quadrupolar ($I > 1$) nucleus which is undergoing rapid spin-lattice relaxation.¹⁴⁷

e. Relaxation by Paramagnetic Species. Atoms or molecules

containing unpaired electrons may contribute to the relaxation process. The most common paramagnetic agent is oxygen. The effect of oxygen is slight when $T_1 < 10$ sec.¹⁴⁸

f. Nuclear Overhauser Enhancement. Broad band proton decoupling saturates the proton spin-energy states, increasing the number of ^{13}C spins in its lower energy state. The net result is an increase in the ^{13}C peak intensities, termed the Nuclear Overhauser Enhancement (NOE). If DD relaxation is the sole operating mechanism, the ^{13}C signal will be enhanced almost 300% (actually 2.988 times). The Nuclear Overhauser Enhancement Factor (NOEF) is the NOE minus one.

B. ACQUISITION OF DATA

1. Rotating Frame of Reference

The mathematical presentation can be simplified by defining a coordinate system which rotates at the precession frequency of the nuclei. In this frame of reference, it appears that the nuclear moments are not moving about $\vec{H}_0$. The coordinates in Figure 4 (p 29) become x' , y' , and z' . The effective magnetic field, $\vec{H}_{\text{eff}}$, in the rotating frame is¹³⁷

$$\vec{H}_{\text{eff}} = (\vec{H}_0 - \vec{\omega}_N / \gamma_N) + \vec{H}_1 \quad . \quad (27)$$

2. Pulsed NMR Experiment

Conventional (continuous wave) nmr employs a variable rf field with a spin flip taking place when H_1 corresponds to ω_N . In the pulsed nmr experiment, a short broad band pulse effects a simultaneous change in θ of all the spins. The duration of the pulse will determine the magnitude of the change in θ .

Figure 8a shows M_0 of a nuclear moment in the rotating frame of reference. An applied pulse, $\vec{H}_1$, along the x' -axis causes the magnetization to precess in the $y'z'$ plane. Important to the T_1 experiment are the 90° ($\pi/2$) pulse which flips M_0 onto the y' -axis, Figure 8b, and the 180° (π) pulse which flips M_0 onto the $-z'$ -axis, Figure 8c. Spin-lattice relaxation begins immediately following the excitation pulse, returning the magnetization to M_0 . Sensitive coils in the instrument's receiver pick up the exponential decay of nuclear induction currents in the $x'y'$ plane that are produced by relaxation. This signal is called the free induction decay, FID, Figure 8d, and represents the time-domain spectrum. Fourier transformation of the FID furnishes the frequency-domain spectrum.^{146,148}

The use of a computer is essential to this experiment. Besides carrying out the Fourier transformation itself, the low abundance (1.1%) and low sensitivity of ^{13}C requires addition of successive FID's to improve the signal-to-noise (S/N) ratio. It allows for the FID to be exponentially weighted, thus improving S/N in the transformed spectrum (sensitivity enhancement), applies phase corrections to ensure the resulting spectrum has the desired absorption mode, and aids in rapid calculation of the data.¹⁴⁶

3. Measuring T_1

There exist various methods used to collect data in order to calculate spin-lattice relaxation times. Each scheme involves a set of pulse sequences designed to generate a series of spectra differing in the time, t_d , between pulses.

a. Progressive Saturation (PSFT). This experiment involves a

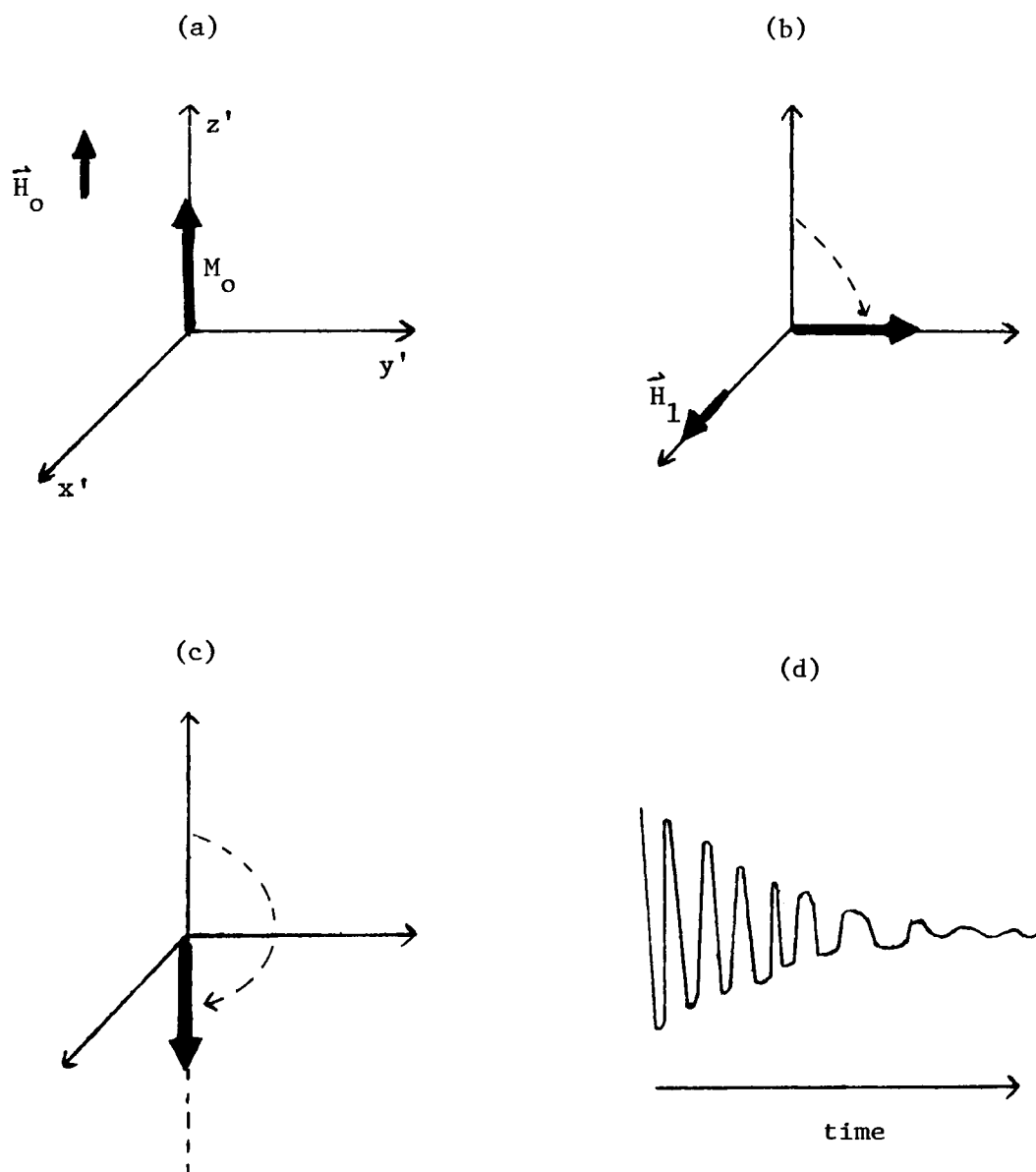


Figure 8. Net magnetization of a nuclear moment in the rotating frame of reference: (a) at equilibrium; (b) after a 90° pulse; (c) after a 180° pulse; (d) Free Induction Decay (FID).

$(\pi/2 - t_d)_{NA}$ pulse sequence,¹⁴⁹ where NA is the total number of acquisitions. After the first three or four pulses, which are not collected, the net magnetization, M_z , reaches a steady-state value. The signal intensities, A , as a function of t_d are given by Equation 28, where A_∞ is the signal intensity for the $t_d = \infty$ spectrum (considered

$$A_\infty - A_t = A_\infty \exp(-t_d/T_1) \quad (28)$$

as A when $t_d > 5T_1$), and A_t is the intensity at time t_d . T_1 is obtained from the slope of a plot of $\ln(A_\infty - A_t)$ vs t_d .

b. Inversion-Recovery (IRFT). This is the most widely used technique to generate T_1 's. Developed by Vold, et al.,¹⁵⁰ this method relies on the pulse sequence $(\pi - t_d - \pi/2 - T_d)_{NA}$, where $T_d > 5$ times the longest T_1 . The result is a series of partially relaxed spectra, as shown in Figure 9 for AOT/water/cyclohexane. For $t_d < T_1$, an inverted peak is observed. If $t_d = T_1 \ln 2$, a null signal is obtained. A positive peak is generated when $t_d > T_1$; the maximum signal occurs when $t_d > 5T_1$. For IRFT, the intensities as a function of t_d are given in Equation 29.

$$A_\infty - A_t = 2A_\infty \exp(-t_d/T_1) \quad (29)$$

The long T_d necessitates a large amount of spectrometer time in order to determine T_1 . During this time, drift may occur in the spectral resolution and/or spectrometer gain. A modified inversion-recovery method (MIRFT)¹⁴⁹ has been developed using the pulse sequence $(\pi/2_\infty - T_d - \pi - t_d - \pi/2_t - T_d)_{NA}$, thus minimizing these effects. The FID's from the $\pi/2_\infty$ pulse are added to the total accumulated FID,

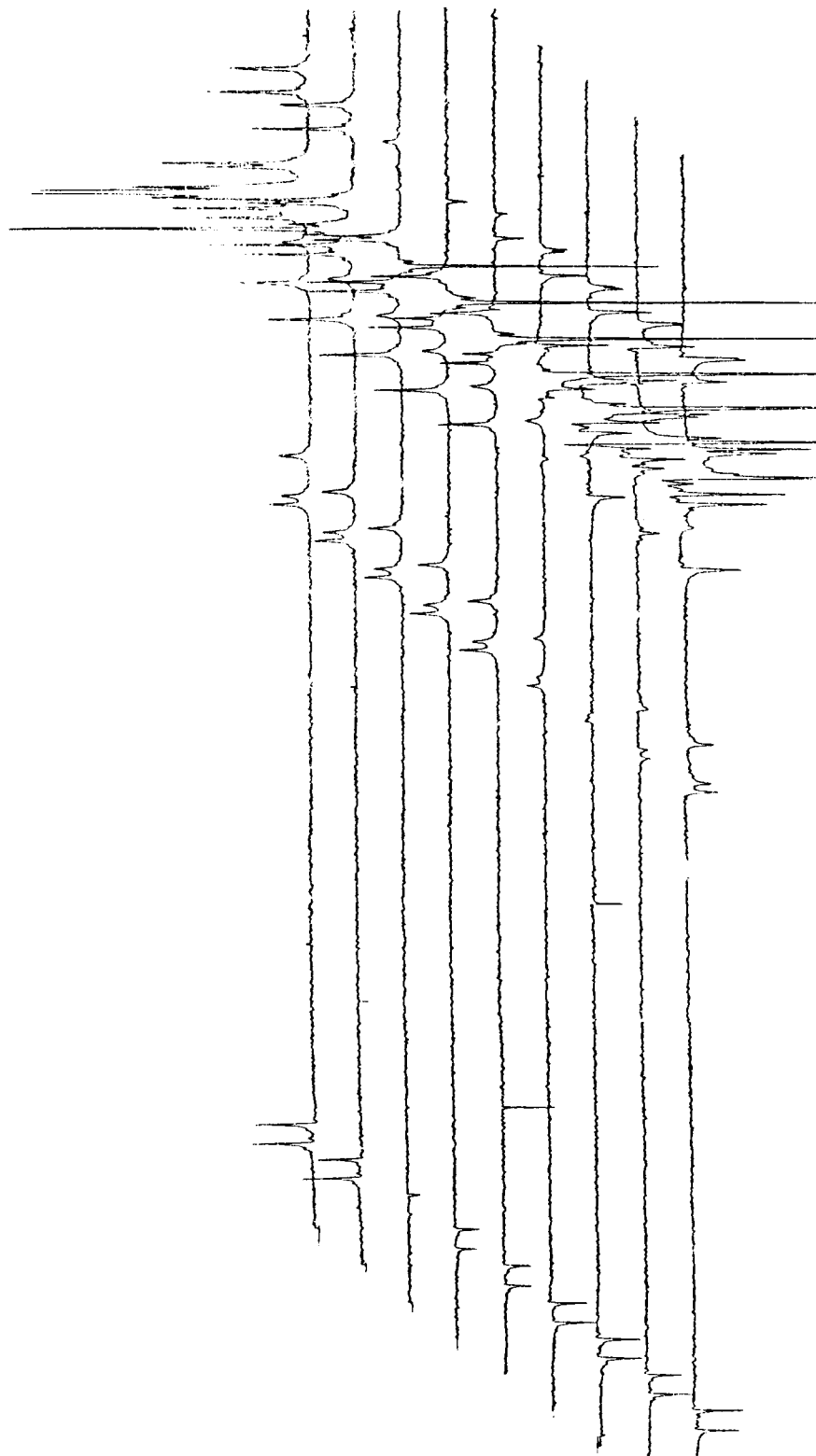


Figure 9. Set of partially-relaxed spectra of 0.5 M AOT/cyclohexane/water using the FIRFT technique at 15.1 MHz and $30 \pm 2^\circ\text{C}$.

while those from the $\pi/2_t$ pulse are subtracted. The result is a series of positive peaks with A_t decreasing with t_d .

A drawback to MIRFT is that even larger blocks of time are needed to evaluate T_1 . A fast inversion-recovery method (FIRFT)¹⁵¹ uses an arbitrarily short T_d , producing a much quicker experiment. As in PSFT, the first three or four pulses are discarded. The calculated T_1 's are comparable to those measured by IRFT.

c. Saturation Recovery (SRFT). This technique involves a 90° pulse followed by a pulsed-field gradient (homogeneity spoiling pulse) along the z-axis which dephases the spins and reduces the net magnetization to zero.¹⁵² The spins are then allowed to relax for a time, t , after which another 90° pulse is applied. The FID is acquired, the field gradient reapplied to destroy the magnetization, and the sequence repeated.

d. Comparison of the Pulse Sequences. The saturation techniques (PSFT and SRFT) and FIRFT allow for relatively rapid measurement of T_1 's. SRFT requires extra hardware which may interfere with normal spectrometer operation. PSFT cannot be used if T_1 is short, since t_d cannot be set to a time less than the time required to acquire the FID. It is the most efficient sequence if T_1 is very long. The inversion-recovery techniques are applicable over the full numerical range of T_1 's, but a prior knowledge of the longest T_1 is needed to set the delay times. PSFT is sensitive to the accuracy of the 90° pulse, while IRFT and FIRFT are insensitive, provided that T_1 is obtained from the slope of a semilogarithmic plot.¹⁵¹

4. Accuracy in Inversion-Recovery

Errors in T_1 's can result from instrument imperfections. The use of MIRFT to compensate for the drift in spectrometer resolution is very time consuming. The use of integrated intensities instead of peak heights will compensate for this effect in IRFT and FIRFT.¹⁵³ Inhomogeneities in the magnetic field will result in all the spins not being equally excited, thus shortening the apparent T_1 's.¹⁵⁴ Volatile samples may evaporate which will also reduce T_1 's. T_1 's will be shortened by the presence of paramagnetic impurities. A three to five degree variance in the temperature can create a 16% error in T_1 .¹⁵⁵ Also of concern is the fact that the rf power falls off as the duration of the H_1 pulse increases.^{154,155}

The operator sets the pulse flip angles (pulse width), T_d and t_d in the pulsed nmr experiment. The effect of erroneous parameter settings on the calculated T_1 's is dependent on the form of the equation used for the computation.¹⁵⁶ Equation 30 represents a linear semilogarithmic plot used to obtain T_1 ; Equation 31, a 2-parameter exponential fit; and Equation 32, a 3-parameter fit. Misset pulse

$$\ln(A_\infty - A_t) = b - t_d/T_1 \quad (30)$$

$$A_t = B[1 - 2\exp(-t_d/T_1)] \quad (31)$$

$$A_t = B[1 - C\exp(-t_d/T_1)] \quad (32)$$

widths result in negligible errors when Equation 30 or 32 is used.

Equation 32 must be used when t_∞ is less than $5T_1$; otherwise the computed T_1 will be too small. Application of this equation results in

the greatest accuracy in T_1 .^{153,155-158} The use of equation 30 is satisfactory if the pulse widths have not been grossly misset. However, the semilogarithmic plot tends to skew the error analysis;^{155,157} deviations in A_t at the longer t_d values are more strongly weighted than deviations at shorter t_d 's.¹⁵⁸ Low S/N has the greatest effect on Equation 32.¹⁵⁶

T_d must be $\geq 5T_1$ in IRFT, but FIRFT circumvents this requirement.^{151,155} At least five to six t_d values are needed for a T_1 determination. Accuracy is not improved by a larger number of t_d 's, but the range of t_d 's will affect both the precision and the accuracy of the computed T_1 's.¹⁵⁷

C. APPLICATIONS

^{13}C nmr is potentially a powerful tool for obtaining structural and dynamic information on organic compounds. Its most obvious advantage over ^1H nmr is that the ^{13}C shielding range is more than 50 times larger than that of ^1H . Thus, more individual locations may be studied, and hence more data are acquired. This section presents a short review of the utilization of ^{13}C relaxation experiments. More extensive accounts are available.^{140,159-161}

1. Overall Molecular Reorientation

The rotational correlation time, τ_R , for overall isotropic tumbling in solution of a molecule behaving as a rigid rotor is estimated by the Stokes-Einstein equation, Equation 33, where r_o is

$$\tau_R = 4\pi\eta r_o^3 / 3kT \quad (33)$$

the molecule's effective spherical radius, η is the viscosity of the solvent, and f_r is the microviscosity factor. Equation 34 is used to

$$f_r = [(6r_s/r_o) + 1/(1+r_s/r_o)^3]^{-1} \quad (34)$$

calculate f_r , where r_s is the solvent's effective radius.¹⁶² For pure liquids, $f_r \approx 1/6$. τ_R is related to the overall rotational diffusion coefficient, D_o , through Equation 35.

$$\tau_R = 1/6D_o \quad (35)$$

Equation 33 predicts that τ_R , and hence T_1 , will vary as a function of the solvent's viscosity. This has been observed for the cycloalkanols,¹⁶³ 1-propanol,¹⁶⁴ and neat alkanes.¹⁶⁵

For small molecules, any anisotropy in molecular reorientation can be determined by measuring the spin-rotation contribution to T_1 . Rotation about the C_3 symmetry axis of methyl iodide is characterized by a time constant, $\tau_{||} = 0.13$ psec; rotation about an axis perpendicular to the C_3 axis by $\tau_{\perp} = 0.036$ psec. In the case of acetonitrile, $\tau_{||} = 0.09$ psec and $\tau_{\perp} = 0.032$ psec.¹⁶⁶ The degree of anisotropy in the motion of monosubstituted benzenes can be assessed from the $T_1(\text{ortho})/T_1(\text{para})$ ratio.¹⁴⁷

2. Intermolecular Association

Association of molecules through complexation and/or hydrogen-bonding will decrease the rate of rotational reorientation. This is observed experimentally as a decrease in T_1 . T_1 of 2-methyl-2-propanol increases as it is diluted with carbon tetrachloride due to the breakup of small hydrogen-bonded aggregates.¹⁶⁷ Spin-lattice

relaxation times have been used to show that urea self-associates in dimethylsulfoxide, but not in water.¹⁶⁸ The dimerization of acetic and formic acids,¹⁶⁹ and the complexation of pyridine with alcohols¹⁷⁰ have been investigated also.

3. Internal Motions

Doddrell and Allerhand¹⁷¹ noticed a T_1 gradient along the alkyl chain in 1-decanol. T_1 of the methyl group was discovered to be seven times that of carbon 1. They ascribed this gradient to restricted mobility at one end of the chain due to hydrogen-bonding. Carbons progressively further from the hydrogen-bonding center experience increased internal mobility, and this has been termed segmental motion. In liquid n-alkanes, segmental mobility is observed from the center of the chain to the ends.¹⁷² Similar results were found for methyl-substituted alkanes.¹⁷³ Segmental motion was observed also in large cycloalkanes.¹⁷⁴

The spin-lattice relaxation time is rarely, if ever, the result of only one particular motion. The effective correlation time, τ_{eff} , is used to encompass any possible motion which may effect relaxation. Equation 36¹⁷² may be employed in order to assess the contributions of

$$1/\tau_{\text{eff}} = 1/\tau_R + 1/\tau_{\text{int}} \quad (36)$$

overall molecular tumbling, τ_R , and internal motions, τ_{int} . If $\tau_R \ll \tau_{\text{int}}$, $\tau_{\text{eff}} \approx \tau_{\text{int}}$. Segmental motion is due to a decrease in τ_{int} as a carbon becomes more removed from the fixed end of the chain.

Specific internal motions include internal rotations about carbon-carbon bonds and conformational reorganization (crankshaft

motions) of two or more bonds.¹⁷⁵ The rotational diffusion coefficient, D_i , at carbon i can be calculated from Equation 37,¹⁷⁶ assuming that

$$D_i = \frac{1}{2} \left[\frac{1}{\tau_{\text{int}(i-1)}} - \frac{1}{\tau_{\text{int}(i)}} \right] \quad (37)$$

this rotation is independent of overall motions and of rotation at neighboring carbons. The multiple internal rotation model of London and Avitabile¹⁷⁷ takes into account gauche to trans conformational isomerizations, as well as rotational diffusion. T_1 of 1,2-dodecanediol increases when the magnetic field strength is increased. This suggests that segmental mobility is coupled to overall reorientation, necessitating the utilization of a distribution of correlation times.¹⁴⁵ Howarth¹⁷⁸ has considered the case of relaxation resulting from librational motions (incomplete rotations) within an alkyl chain. The anisotropy of internal reorientations in n-alkanes has been measured.¹⁶⁵

Fast methyl rotation has been of particular interest to the nmr spectroscopist. T_1 's of the methyl groups in N,N-dibutylformamide, 1-decanol, and dipalmitoyl lecithin are identical. This implies that at the free ends of a molecule the microviscosity has no relation to the macroviscosity.¹⁴⁰ The energy of activation, E_a , for methyl rotation can be calculated from an Arrhenius plot.¹⁷⁹ The barrier to rotation, V_o , is obtained from the spin-rotation contribution to T_1 ,¹⁸⁰ or from Equation 38,¹⁷² where R_o is the rate of reorientation

$$R_{\text{int}}^{\text{Me}} = R_o \exp(V_o/RT) \quad (38)$$

of a freely rotating methyl group in the gas phase ($R_o = 8.8 \times 10^{12} \text{ sec}^{-1}$), and

$$R_{\text{int}}^{\text{Me}} = \tau(\omega, \omega-1) = 1/\tau_{\text{int}}(\omega) - 1/\tau_{\text{int}}(\omega-1) \quad , \quad (39)$$

where ω represents the methyl carbon. The calculated V_0 has no real physical significance and is useful only for comparison purposes. For small molecules, V_0 increases in the order:¹⁸¹ $\text{CH}_3\text{COCH}_3 < \text{CH}_3\text{SOCH}_3 < \text{CH}_3\text{CCl}_3 < (\text{CH}_3)_3\text{CCl}$. The degree of anisotropy in methyl reorientation has been studied also.^{181,182}

4. Polymers and Biological Molecules

Large molecules will exhibit a complex, almost bewildering, series of motions; their nmr relaxation behavior will include contributions from many, if not all, of the effects described above. The discussion here will be centered on studies performed on systems which can be related to surfactant assemblies.

There have been many studies of relaxation processes for alkyl chains attached to a polymer.¹⁸³⁻¹⁸⁵ In all cases, segmental motion is observed going from the polymer backbone to the end methyl group. Levy, et al.,¹⁸⁵ have shown that a distribution of correlation times (of which no physical interpretation was given) in the backbone of poly(1-alkyl)methacrylates will result in correlated motions throughout the entire alkyl chain. The amount of rotational freedom of the alkyl chains in poly(4-vinyl-N-1-alkylpyridinium bromides) has been related to the relative rates of trans to gauche and gauche to trans conformational changes. It was noted also that the distribution of correlation times of the backbone carbons was narrower before the alkyl chains were attached.¹⁸⁴

Proteins are examples of biopolymers and exhibit an extreme

range of motional characteristics. Perly, *et al.*,¹⁸⁶ have described the various motions using different mathematical models in different areas of the molecule. A study of bovine pancreatic trypsin inhibitor identified three motions.¹⁸⁷ The two slow processes were: (1) a low amplitude wobble; and (2) anisotropic diffusion of the protein. A fast motion was identified as librational. Recently, very fast fluctuations (on a psec time scale) were observed in proteins.¹⁸⁸ The relationship between these motions and librations is unclear.

Gent and Prestegard¹⁸⁹ measured the spin-lattice relaxation times of phospholipid bilayer membranes. They found that T_1 of the lipid hydrocarbon chains is determined by β -coupled gauche isomerizations (kink formation, ttt to g^+tg^- , where t represents a trans conformer and g^+ , g^- , gauche conformers). The motion of the head group carbons was much slower than that of the phospholipid alkyl chains; the relaxation of the head group carbons was attributed to uncoupled gauche isomerizations, since the authors felt the motion was too fast to be due to overall vesicle tumbling or lateral lipid diffusion. However, lateral diffusion has been observed on the same time scale as τ_{eff} calculated for the head group carbons.¹⁹⁰ The ^1H T_1 of the methylene envelope of phosphatidylcholine (lecithin) vesicles increases as the length of the alkyl chain increases because of kink diffusion.¹⁹¹ Overall anisotropic reorientation of the lecithin vesicle is insignificant as a relaxation mechanism when $\tau_R > 10^{-9}$ sec.¹⁹² The overall rotation of chloroplast lipids varies, depending on whether they are monomeric or associated in micelles or vesicles.¹⁹³ Segmental motion of the alkyl chains was observed in phospholipid¹⁹⁴ and glycolipid¹⁹⁵ micelles. In the latter study, T_1 's were solvent dependent.

5. Surfactants

a. ^{13}C Chemical Shifts. The c.m.c. of nonylammonium bromide in D_2O was found to be 0.11 m by noting ^{13}C chemical shift changes.¹⁹⁶ It was postulated that micelle formation involves gauche to trans conformational changes in the alkyl tails. Similar results were obtained for sodium octanoate in D_2O .¹⁹⁷ Solubilization of either 1-pentanol or sodium chloride increased the trans conformer population in the latter study, while addition of 1-decanol increased the percentage of gauche conformers. It was shown also that the alkyl chains of sodium octanoate exhibit greater mobility in inverted micelles than in normal micelles. For dodecyloctaethylene oxide (C_{12}EO_8), the aliphatic chemical shifts moved downfield in the solvent series: D_2O to chloroform-d to methanol- d_4 .¹⁹⁸ The chemical shift changes of a carbonyl located in the middle of an amphiphilic chain was studied to demonstrate the extent of water penetration into a normal micelle.^{16b}

b. ^{13}C Spin-Lattice Relaxation Times. Segmental mobility is routinely observed in ^{13}C relaxation studies of micelles.¹⁹⁹⁻²⁰⁷ In a study of the alkyltrimethylammonium bromides, T_1 was found to decrease and the segmental mobility to increase in the monomer to micelle transition.¹⁹⁹ Segmental motion is observed also along the ethylene oxide chain of nonionic micelles.^{198,202} Addition of salts increased T_1 's of carbons near the head group in sodium dodecylsulfate²⁰³ and dodecylammonium chloride²⁰⁴ micelles. It was proposed that electrolytes dehydrate the Stern layer, thus increasing the mobility near the polar moiety. The c.m.c. of sodium hexanoate was determined by the change in the alkyl carbon T_1 's as a function of concentration.²⁰⁶

The alkyltrimethylammonium bromide study cited above interpreted the T_1 decrease upon micellization as due to a more restricted internal mobility of the alkyl chains in the micelle. However, other workers^{206,207} have concluded that the T_1 decrease was due to restricted overall motion of the surfactant molecule. It is likely that both effects contribute.

Wennerström, et al.,²⁰⁸ studied the frequency dependence of the T_1 's of sodium octanoate in D_2O . They interpreted the data in terms of monomer diffusion competing with slow tumbling of the micelles. They also concluded that the relative importance of aggregate tumbling will decrease as the field strength becomes larger, and as the size of the aggregates increase.

The inverted aggregates of dodecylammonium propionate in benzene have been studied as a function of solubilized water and glycine.²⁰⁰ Addition of a small amount of water affects only the carboxyl T_1 . When a small quantity of glycine was added to the above solution, none of the T_1 's changed. Further addition of water increased T_1 's of the carbons nearest the head group only.

The only T_1 study of an o/w microemulsion (1-hexadecylsulfate/1-pentanol/water/hexadecane) has appeared recently.²⁰⁹ From the ^{13}C chemical shift behavior of carbon 1 of the alcohol, it was concluded that the fraction of alcohol solubilized at the surfactant/water interface increased as the percent water in the microemulsion increased, and that significant amounts of pentanol were solubilized in the microemulsion's core. The magnitude of the T_1 increases of the resolved alcohol resonances followed the same order when the samples

were analyzed at a higher frequency. The more cosurfactant adsorbed at the interface, the more restrictions there are on its rotational mobility, and hence the broader the distribution of resulting correlation times. Interpretation of the surfactant spin-lattice relaxation times is clouded by the fact that only two of the surfactant resonances are unobscured by the solvent and/or alcohol resonances. The two resolved carbons (C-1 and C-2) also showed a field effect in their T_1 's, indicating a distribution of correlation times for the surfactant as well. For overlapping lines, T_1 was computed and the surfactant's contribution to T_1 was factored out. However, this is a questionable procedure, since it ignores the large number of factors which will affect nmr peak intensities, and hence spin-lattice relaxation times. Also studied were the sodium hexadecylsulfate micelles in D_2O . Interestingly, a T_1 minimum was observed in the middle of the surfactant chain.

CHAPTER IV

 ^{13}C NMR STUDIES OF AEROSOL OT

Previous work on AOT has centered on the overall aggregate properties such as size, shape, etc...(see Chapter II). The purpose of this study was to probe the dynamic and conformational changes which occur in the surfactant interface using ^{13}C nmr, in order to obtain a better insight on the molecular level of the nature of AOT inverted micelles and w/o microemulsions. Factors such as solvent penetration which influence the interfacial properties can then be related to overall solution properties such as the effect of solvent on the aggregates' water-solubilizing ability.

Prior to this work, some AOT micellar solutions had been investigated using ^{13}C nmr. Ueno, et al.,²¹⁰ compared the spin-lattice relaxation times of AOT normal micelles in water, monomers in methanol, and inverted micelles in chloroform and benzene at 25.2 MHz. Figure 10 shows the ^{13}C spectrum of AOT/water/cyclohexane (this work at 15.1 MHz) along with Ueno's chemical shift assignments. Ueno and coworkers found segmental motion (here an NT_1 gradient from carbons 4,4' to 8,8') in all four solvents. T_1 values decreased in the solvent series: methanol > water > chloroform > benzene except for the methyl groups, for which $T_1(\text{benzene})$ was larger than $T_1(\text{chloroform})$. Thus, the AOT molecule exhibits the greatest molecular mobility when monomeric, and the least mobility when associated in inverted micelles. Ueno calculated τ_{eff} for carbon 1, $\tau_{\text{eff}}(1)$, from the T_1 values assuming extreme narrowing conditions, Equation 25 (p 33), and compared it to τ_R ,

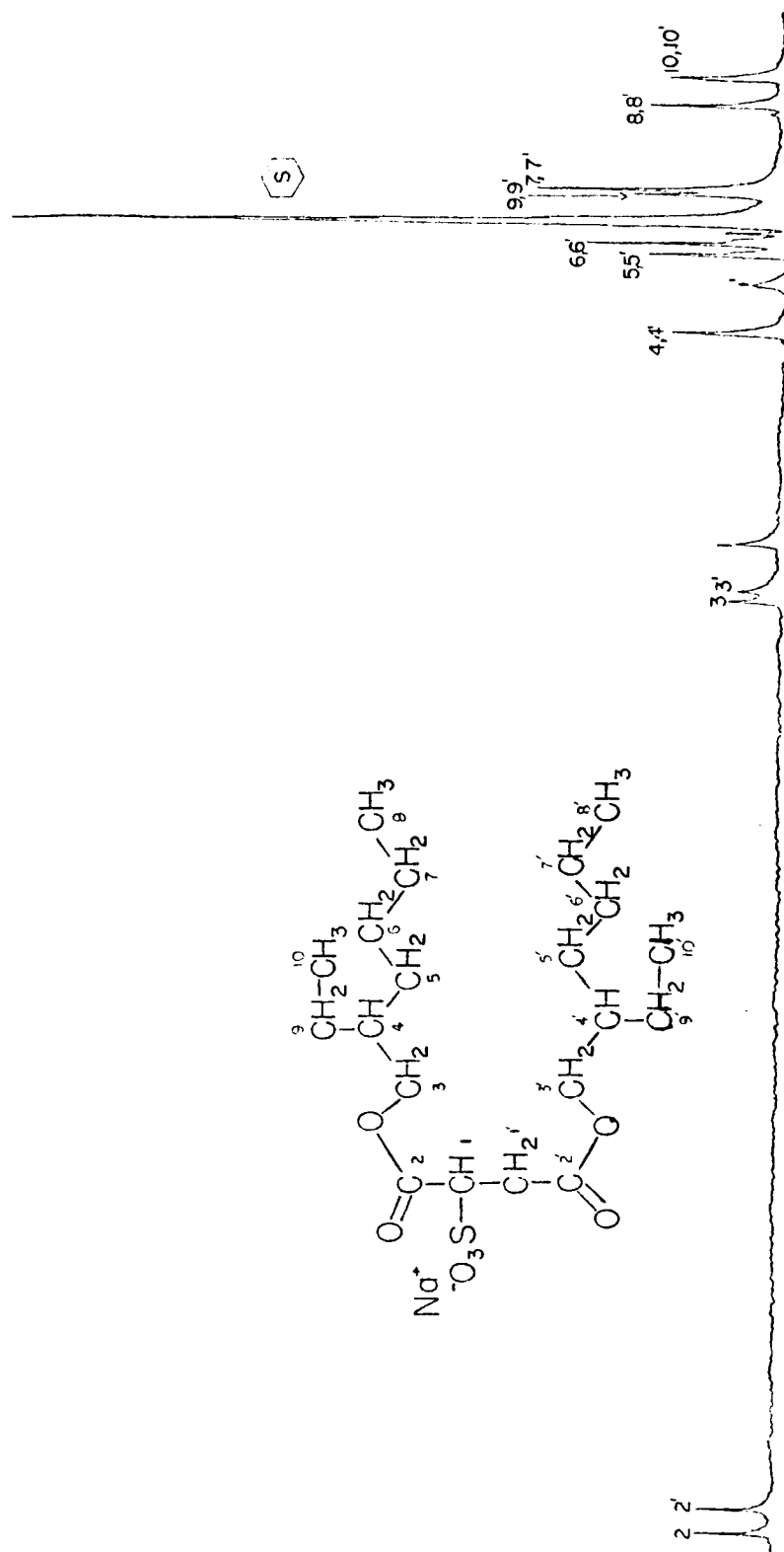


Figure 10. ^{13}C spectrum of 0.5 M AOT/cyclohexane/water at 15.1 MHz along with AOT's chemical shift assignments.

Equation 33 (p 44), assuming a micellar radius, r_o , of $11 \text{ \AA}$ (the length of an AOT molecule) and $f_r = 1$. Good agreement was observed for the aggregates in benzene and methanol ($r_o = 5.5 \text{ \AA}$), implying that the predominant contribution to the relaxation of the head group carbons is overall aggregate tumbling. In chloroform, the two τ 's were equal if r_o was taken as $10 \text{ \AA}$; this implies that the effective chain length is shortened by the occurrence of gauche conformers.

Denss^{211,212} reported τ_{eff} 's for AOT's carbons in inverted micelles in benzene as a function of added water. He found that τ_{eff} increases for all carbons as R increases, suggesting that the molecule becomes more mobile as water is added.

Denss and Ueno, et al., disagreed in their assignment of resonances. The latter authors used paramagnetic shift reagents and found that the peak attributed to carbon 2' had the largest lanthanide-induced shift. Newman projections and space-filling models support the contention that C-2' will be closer to the site of lanthanide complexation (the $-\text{SO}_3^-$ moiety) than C-2, confirming Ueno's assignments. Denss reported a 10-fold difference in τ_{eff} for carbons 1 and 1'. Apparently he misassigned the C-4,4' and C-1' resonances. That Ueno's designations for these resonances are correct can be seen in the uncoupled spectrum, Figure 11.

The present work represents the first time that the AOT w/o microemulsion region has been studied by ^{13}C nmr. The solvents chosen (cyclohexane, benzene and carbon tetrachloride) were those that allowed all of AOT's resonances to be observed. In addition, they represent three different classes of organic solvents. Since cyclohexane

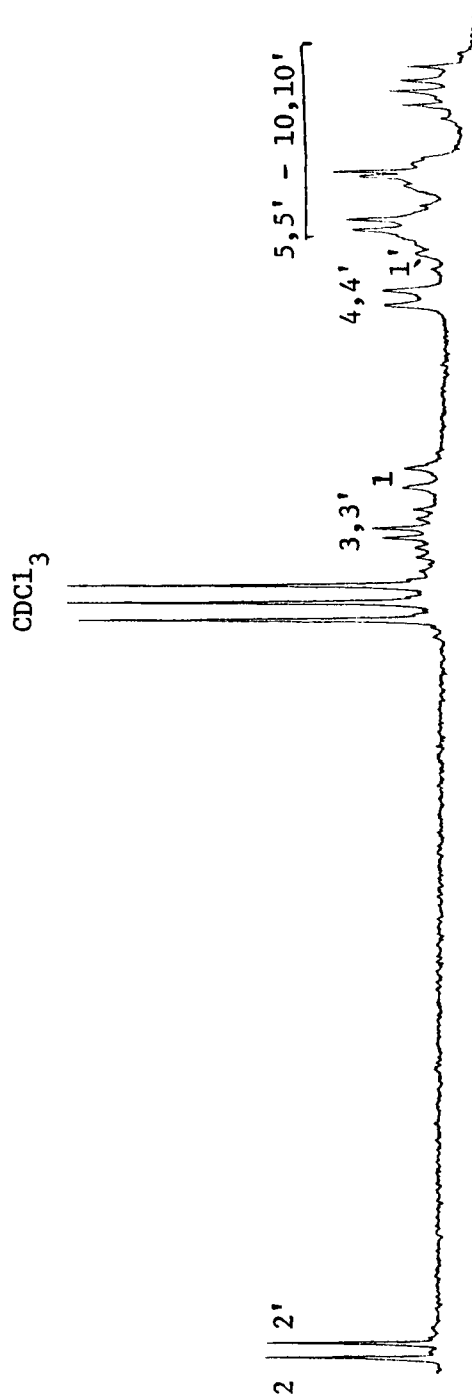


Figure 11. Undecoupled ^{13}C spectrum of 0.5 M AOT/chloroform-d at 15.1 MHz.

solubilizes the largest amount of water (see the L_2 region in the ternary phase diagram, Figure 12), these systems were studied in the most detail. The discussion of the data for the AOT/cyclohexane samples will include T_1 values at two magnetic field strengths, along with chemical shifts, line widths and Nuclear Overhauser Enhancements. Spin-lattice relaxation times and chemical shifts were measured for AOT inverted aggregates in benzene and carbon tetrachloride at 15.1 MHz.

A. RESULTS IN CYCLOHEXANE

For 0.5 M AOT in cyclohexane, T_1 's and chemical shifts, δ , were measured over the entire water-solubilizing domain. 0.25 M AOT solutions were investigated at the high R values. The sample compositions studied are given in Figure 12. Two samples, $R = 0$ and $R = 30$, were run at 100.6 MHz at the South Carolina Magnetic Resonance Laboratory in order to assess the frequency dependence of the T_1 values. In addition, attempts were made to determine ^{13}C line widths at half-height and NOE's for the 0.5 M solutions at 15.1 MHz. The inconclusive results of these latter investigations will be presented briefly. Infrared spectroscopy was performed to complement the ^{13}C δ results.

1. ^{13}C Chemical Shifts

The ^{13}C chemical shifts of 0.5 M AOT in cyclohexane are listed in Table I for $R = 0$. For C-4,4' to C-10,10' [see Figure 10 (p 54) for the assignments], the chemical shifts did not change as water was added. However, significant δ changes did occur for the carbons nearest the head group. These are shown in Figure 13.

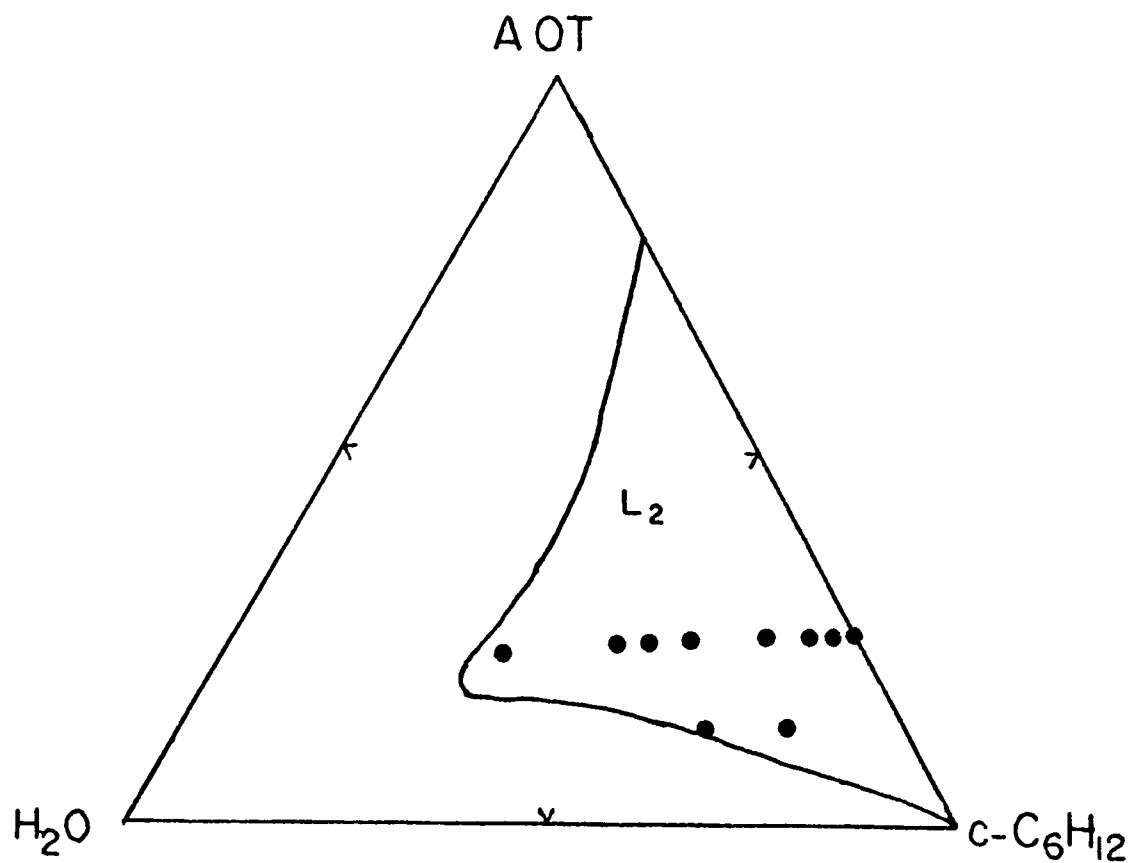


Figure 12. Ternary phase diagram of AOT/water/cyclohexane at 30±1°C. The circles represent the compositions of the solutions studied by nmr.

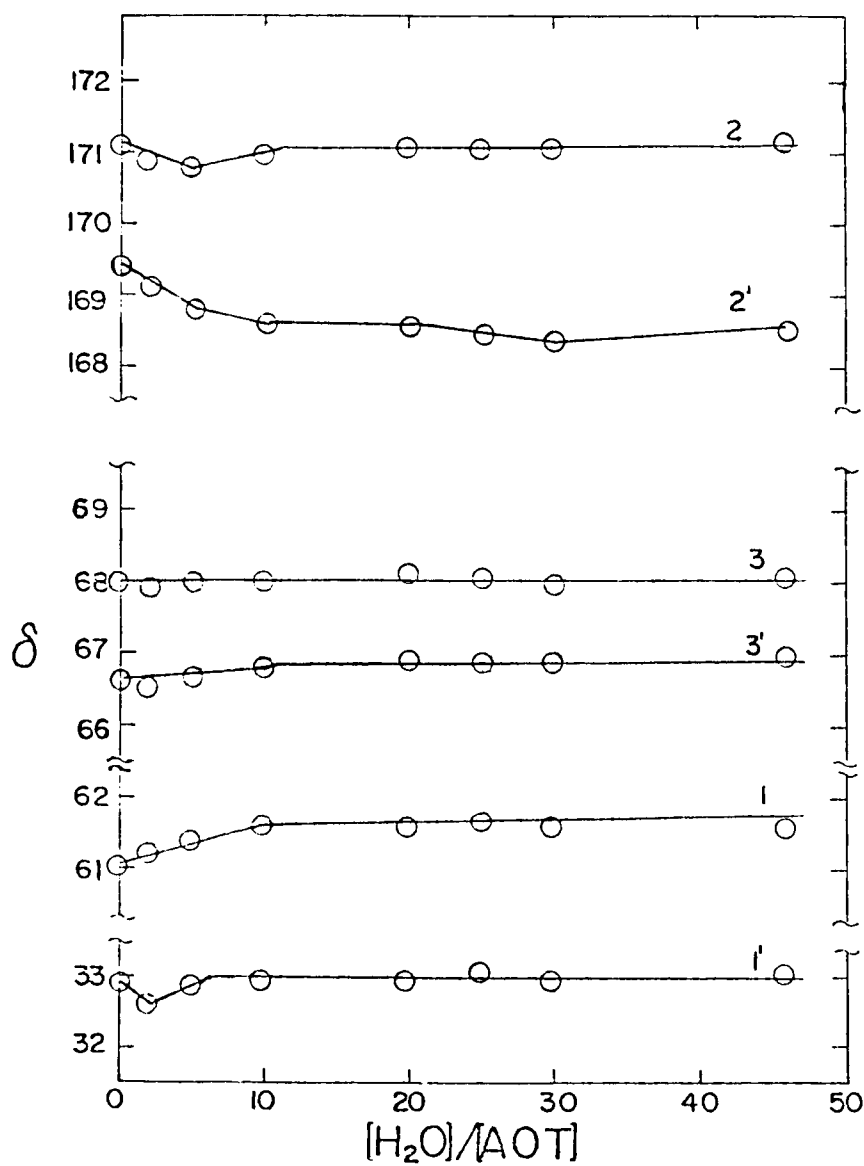


Figure 13. ^{13}C chemical shift changes of 0.5 M AOT/cyclohexane as a function of added water concentration.

TABLE I

^{13}C CHEMICAL SHIFTS (PPM FROM TMS^a) FOR 0.5 M AOT/CYCLOHEXANE, R = 0

C#	δ	C#	δ
10,10'	10.3	3	66.0
9,9'	23.3	3'	66.6
8,8'	13.4	2	171.1
7,7'	22.8	2'	169.4
6,6'	28.7	1	61.0
5,5'	29.8	1'	32.9
4,4'	38.5		

$$\text{a. } \delta_{\text{TMS}} = \delta_{\text{CDCl}_3} - 76.9$$

The chemical shift of carbon 1, $\delta(\text{C-1})$, moves downfield as water is added (up to R = 10) due to hydration of AOT's head group. After R = 10, $\delta(\text{C-1})$ levels off, signifying that the hydration requirements have been met. This indicates that R = 10 is the upper limit of the inverted micelle domain in cyclohexane. $\delta(\text{C-1}')$ and $\delta(\text{C-3}')$ show slight changes over the range of R values, while $\delta(\text{C-3})$ is invariant.

The largest changes occur in the chemical shifts of the carbonyls, 2 and 2'. δ 's of carbonyl groups are an extremely sensitive measure of their local polarity.^{16b,213} Initial addition of water causes both $\delta(\text{C-2})$ and $\delta(\text{C-2}')$ to move upfield, the opposite of the behavior expected if hydrogen-bonding occurred.²¹⁴ This result is consistent with both carbonyls moving into a more hydrophobic region of the

aggregate. The slight upfield shifts of $\delta(\text{C-2})$ at $R = 10$ and $\delta(\text{C-2}')$ at $R = 46$ imply that water begins to hydrogen-bond with the carbonyls at these respective concentrations.

2. Infrared Spectroscopy

Standard dispersive infrared spectra show two distinct micro-environments initially at each carbonyl, Figure 14. At $R = 0$, carbonyl stretches are observed at 1740 cm^{-1} and 1723 cm^{-1} . As water is added, these bands approach each other until only one peak is observed at $R = 5.5$. By analogy with the interpretation of the Raman bands of phosphatidylcholine,²¹⁵ the 1740 cm^{-1} band is assigned to a gauche conformation about the C(=O)-C bond and the 1723 cm^{-1} stretch to a trans conformation, Figure 15. The high proportion of gauche conformers at $R = 0$ is consistent with the lanthanide ^{13}C shift results²¹⁰ which showed $\text{C-2}'$ to be closer to the sulfonate head group than C-2 . Addition of water opens up the head group region (*i.e.*, the surface area at the surfactant/water interface increases^{90,100}) and the trans conformation is favored. Hydrogen-bonding could cause these spectral changes, but the ^{13}C δ 's, noted in the previous section, rule this out. A high wavenumber shoulder is seen at 1730 cm^{-1} at the high water concentrations. This is due to the two carbonyls achieving slightly different conformations.

It was hoped that Raman spectra would confirm the above conclusion. The Raman expanded carbonyl region is shown in Figure 16 for $R = 0$. The carbonyl stretches are very weak in the Raman spectrum. There appear to be two peaks at 1721 cm^{-1} and 1737 cm^{-1} . Due to their low intensity, picking out the peaks from the baseline is difficult.

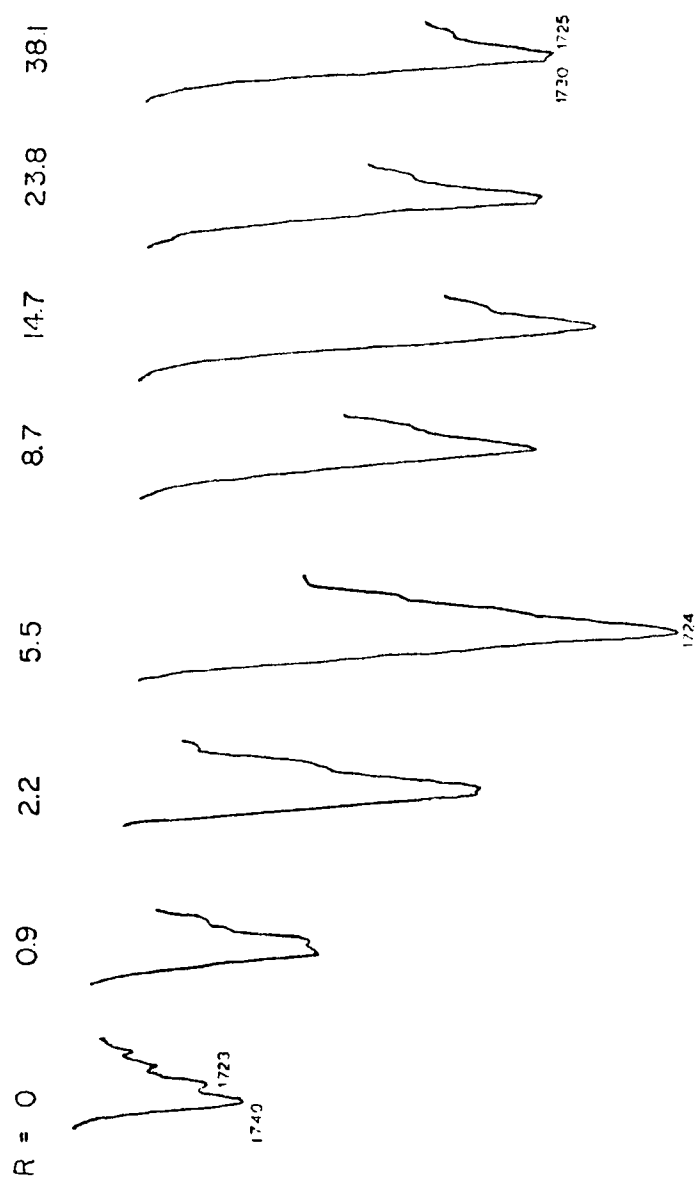
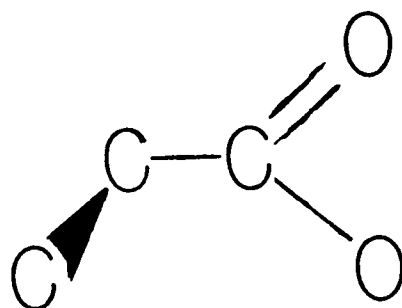


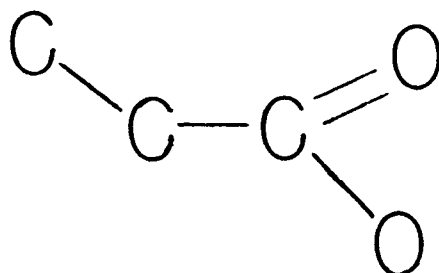
Figure 14. Changes in the dispersive ir carbonyl stretches of AOT in cyclohexane as water is added.

gauche



1740 cm^{-1}

trans



1723 cm^{-1}

Figure 15. Conformational assignments of AOT's carbonyl stretches.

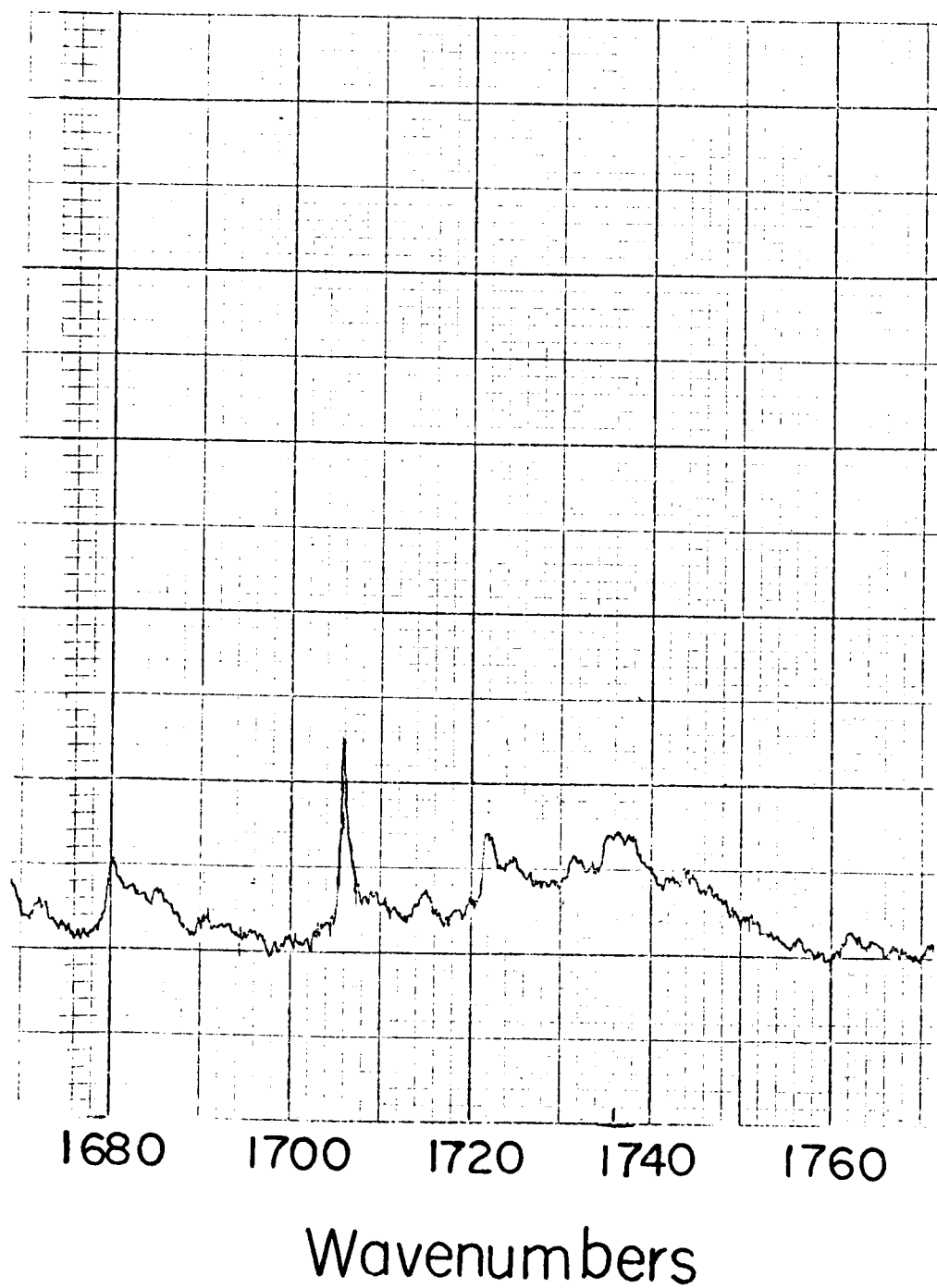


Figure 16. Expanded Raman spectrum in the expected carbonyl absorption region of 0.5 M AOT/cyclohexane, $R = 0$.

Further exploration of this region by Raman spectroscopy will not be possible until a microprocessor is attached to the spectrometer, allowing for addition of spectra, thus reducing S/N.

Next, Fourier transform infrared spectroscopy, FTIR, WAS turned to. However, the high energy of the incident radiation produced by laser excitation resulted in 0% transmittance of the carbonyl stretch for the 0.5 M AOT solutions. A representative absorption mode spectrum is shown in Figure 17 for AOT/cyclohexane, $R = 1$. A large amount of fine structure is observed in the carbonyl region. This is due to the data processor attempting to interpret zero transmitted radiation. The low transmittance is not a problem when 0.05 M AOT solutions are studied. The expanded 2000–1500 cm^{-1} region is presented in Figure 18 for AOT/cyclohexane solutions as a function of added water concentration. Curiously, no changes in the carbonyl bands are seen as R is increased. In all the spectra, three peaks are observed at 1740, 1735, and 1719 cm^{-1} . Perhaps the two carbonyls maintain their conformational inequality at low AOT concentrations throughout the water-solubilization region. However, it is more likely that a 10-fold decrease in AOT concentration will result in equivalent conformers. A preliminary FTIR study of 5.3 wt.% AOT/heptane, $R = 0$, showed only one carbonyl band at 1738 cm^{-1} .⁷⁸ The observed fine structure is probably due to noise superimposed on the carbonyl stretch. This noise could arise from the solvents being insufficiently filtered. Since high noise is prevalent also in the O-H stretching region, it is also quite likely that the sodium chloride cells were damaged in previous runs when high water concentrations were used.

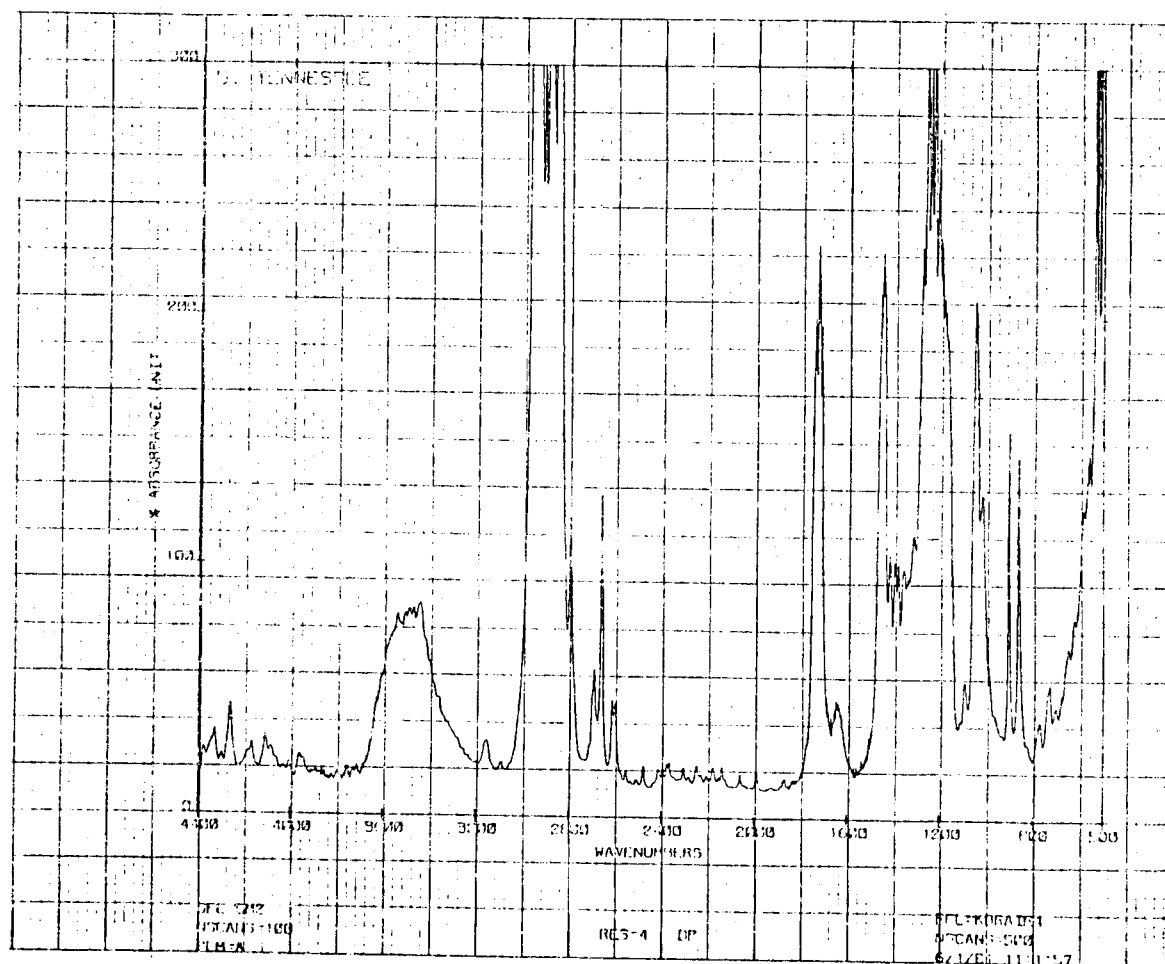


Figure 17. Absorption mode FTIR spectrum of 0.5 M AOT/cyclohexane, $R = 1$.

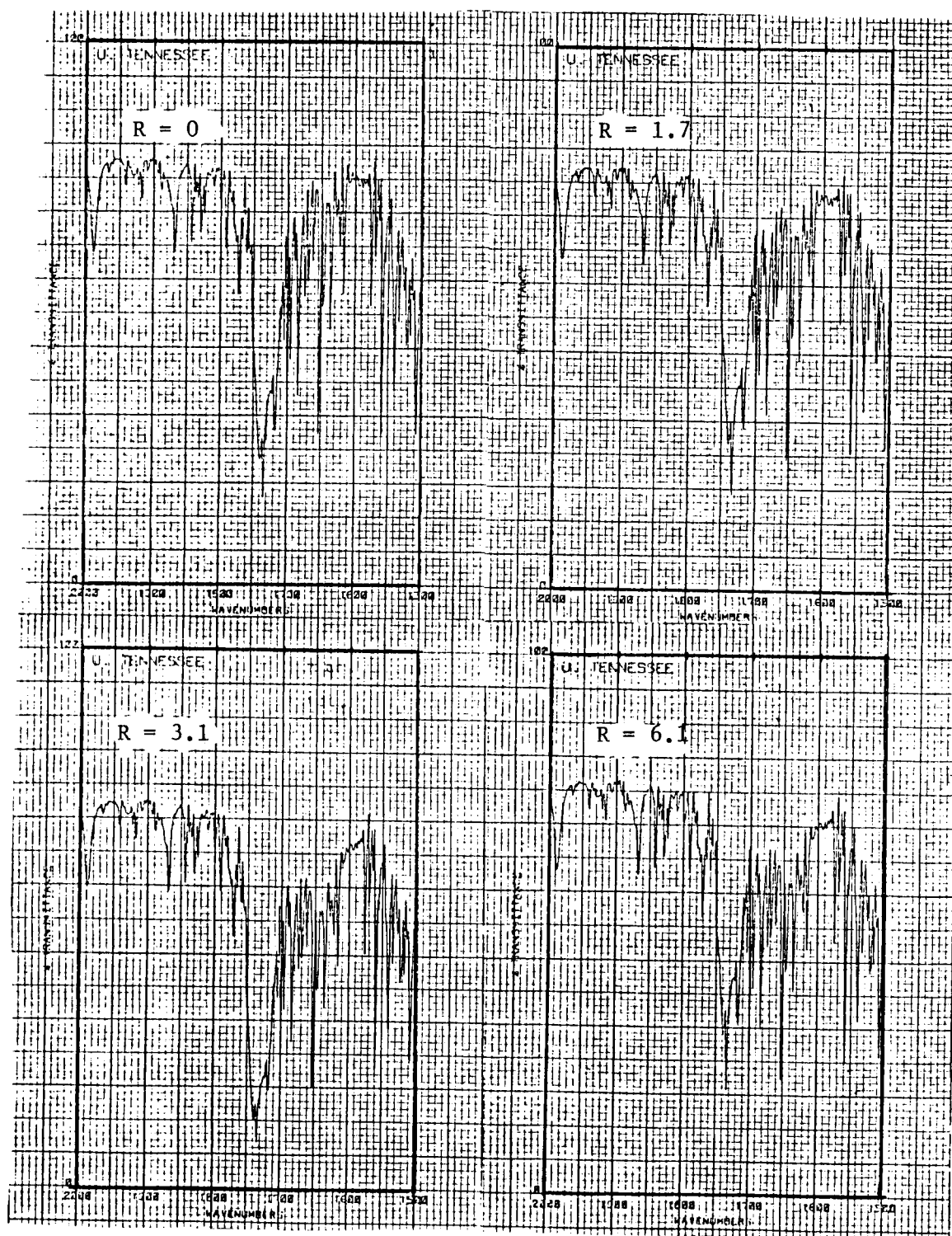


Figure 18. 2000 - 1500 cm^{-1} region of the transmittance mode FTIR spectra of 0.05 M AOT/cyclohexane as a function of added water concentration.

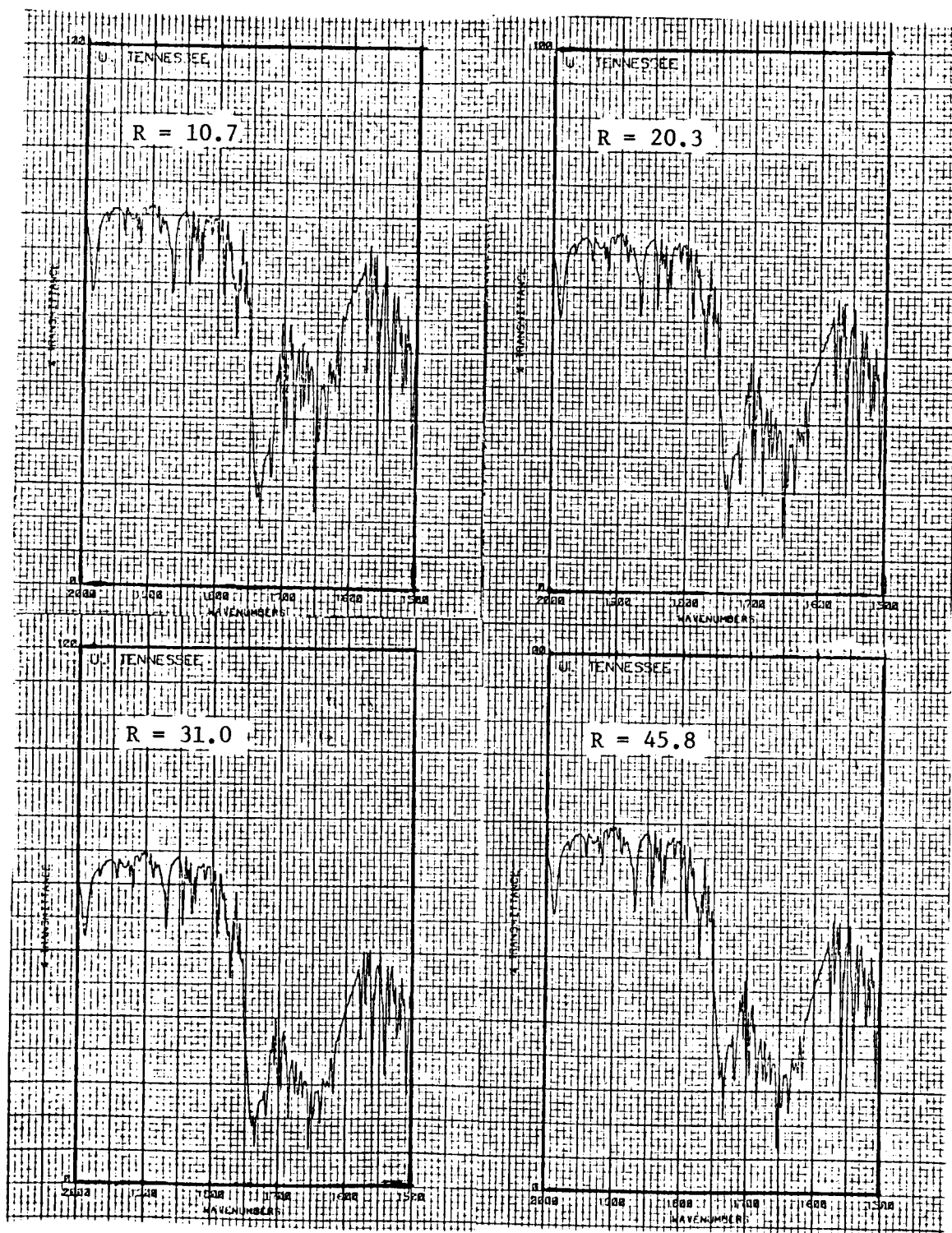


Figure 18. (Continued)

3. ^{13}C T_1 's at 15.1 MHz

a. Segmental motion. 15.1 MHz NT_1 's are tabulated in Table II for AOT/cyclohexane systems as a function of R. All NT_1 's increase rapidly as R increases up to $R = 5 - 10$ indicating that the mobility of the entire AOT molecule is increasing throughout the inverted micellar domain. Above $R = 10$, NT_1 of carbons 4,4' to 10,10' remain constant, or increase slightly. Even at the highest R values, NT_1 's in the w/o microemulsions are less than those in normal micellar solutions in water.²¹⁰ Segmental mobility is observed at all added water concentrations. Carbons 4,4' display very short T_1 's at low R; the attached ethyl group acts as an anchor and restricts the mobility of these carbons because of the tight molecular packing of the alkyl chains. This statement is supported by the fact that the NT_1 values of carbons 3 and 3' are greater than NT_1 of carbons 4,4' at the lowest water concentrations. The NT_1 gradient increases abruptly at the ends of the chains due to the increased rotational mobility of the methyl groups relative to the rest of the alkyl chains.

Effective correlation times were calculated from Equation 24 (p 33). The ratio $\tau_{\text{eff}}(4)/\tau_{\text{eff}}(8)$ can be used to represent the extent of segmental motion, see Figure 19. The addition of small amounts of water causes a sharp decrease in the segmental mobility; a slow decrease is observed over the range $R = 5 - 30$, and the segmental motion increases at the highest R. The degree of segmental motion is directly related to the amount of order within the alkyl chains.¹⁷⁷ A higher degree of disorder in the hydrocarbon chains (*i.e.*, more gauche conformers present) is evidenced in AOT inverted micelles in cyclohexane.

TABLE II

 NT_1 (SEC) OF AOT/CYCLOHEXANE/WATER SOLUTIONS AS A FUNCTION OF R AT 15.1 MHz

C [#]	R=	0.5 M AOT								0.25 M AOT		0.5 M AOT degassed
		0	2.2	5.3	10.2	19.9	25.2	29.6	46.3	26.1	46.3	
10,10'		1.50	2.10	3.24	3.51	3.57	3.42	3.96	3.75	3.12	3.30	3.33
9,9'		0.34	0.56	0.66	1.06	0.88	0.80	0.76	1.00	0.61	0.59	0.82
8,8'		3.18	4.44	5.94	6.27	5.61	5.82	6.39	6.75	5.13	4.65	5.91
7,7'		0.84	1.28	1.82	1.44	2.04	2.20	2.22	1.92	1.58	1.77	1.54
6,6'		0.50	0.68	1.00	0.96	1.14	1.00	1.46	1.26	1.27	1.32	1.28
5,5'		0.40	0.42	0.44	0.62	0.38	0.54	0.62	0.44	0.54	0.40	0.62
4,4'		0.044	0.058	0.15	0.17	0.16	0.19	0.22	0.18	0.16	0.13	0.19
3		0.044	0.090	0.12	0.16	0.17	0.15	0.22	0.13	0.12	0.14	0.17
3'		0.062	0.088	0.13	0.18	0.16	0.17	0.24	0.13	0.14	0.14	0.16
2 ^a		0.54	0.72	1.23	1.14	1.54	1.70	2.03	2.21	1.07	1.74	2.00
2' ^a		0.74	0.97	1.69	1.93	2.65	2.60	2.53	3.25	2.08	2.90	3.18
1		— ^b	0.026	0.045	0.068	0.10	0.061	0.056	0.045	0.067	0.076	0.046
1'		— ^b	— ^b	0.062	0.10	0.10	0.064	0.070	0.030	0.070	0.068	0.042

a. T_1 is reportedb. Significant line broadening resulted in insufficient S/N to measure T_1 for these resonances.

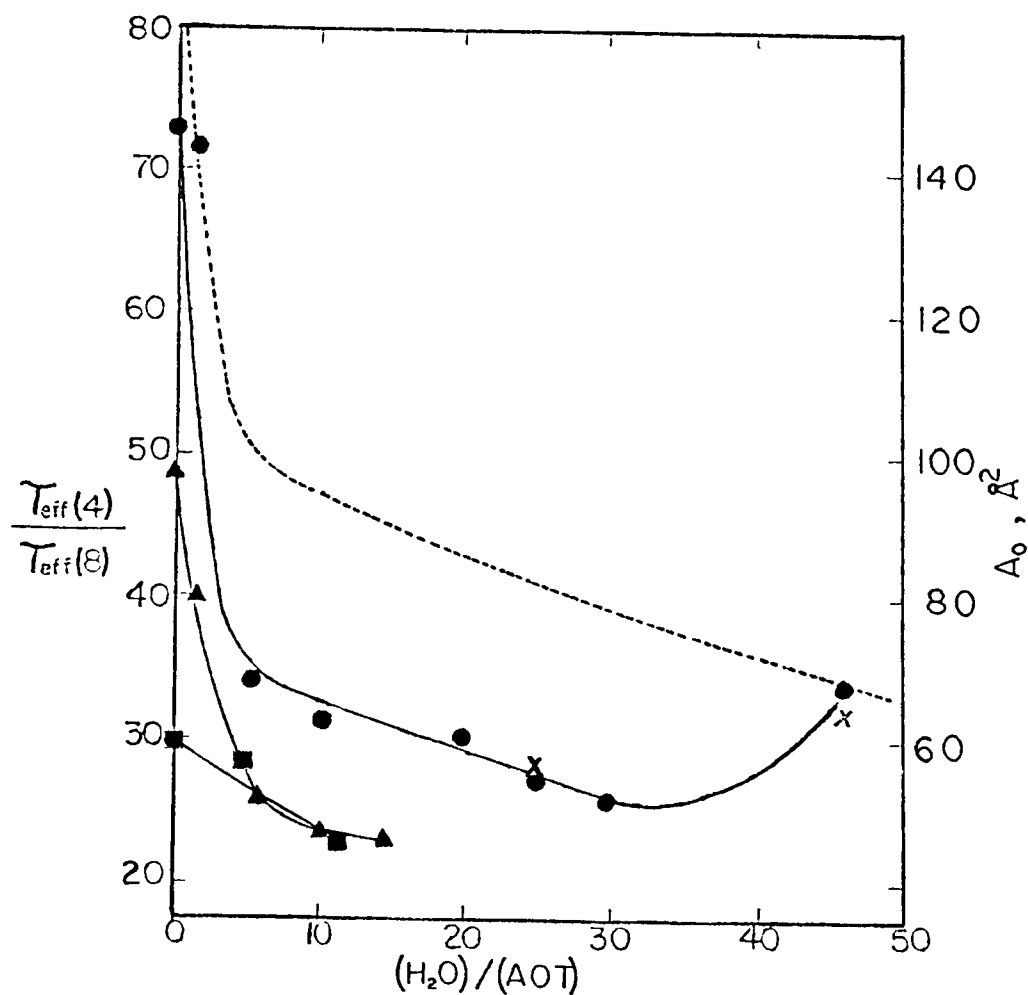


Figure 19. Changes in AOT's segmental motion (filled lines) and A_0 (dotted line) as a function of added water concentration.

Circles: 0.5 M AOT in cyclohexane.

X's: 0.25 M AOT in cyclohexane.

Triangles: 0.5 M AOT in carbon tetrachloride.

Squares: 0.5 M AOT in benzene.

The lower ratio as R increases is due to a higher probability of trans conformers along the chains as the w/o microemulsion region is reached. A more extended alkyl chain conformation is supported by a calculation of A_o , the surface area at the surfactant/oil interface using Equation 40,⁴⁵ dotted line in Figure 19 (p 71), where A_w is the

$$[r_h/(r_h - L)]^2 = A_o/A_w \quad (40)$$

surface area at the surfactant/water interface, r_h is the hydrodynamic radius of the inverted aggregates, and L is the length of the amphiphile. Both r_h ⁸⁷ and A_w ^{90,100} have been experimentally determined. The slope of this curve and the segmental motion curve are identical, except at the highest R values.

If the increase in segmental motion at R = 46 were due to crowding of the aggregates, dilution of the samples should lower this ratio. Samples were run at high water concentrations for 0.25 M AOT in order to test this hypothesis. The results, given in Table II (p 70) and Figure 19 (p 71), indicate no decrease in segmental mobility upon dilution. Segmental motion will increase if the lifetime of a trans conformer along the alkyl chains increases.¹⁷⁷ This could arise due to a tighter packing of the alkyl chains. Note that A_o is steadily decreasing as R increases, which means that the AOT hydrocarbon chains are being forced to occupy a smaller volume, thus restricting their motion.

Another explanation for the anomalous increase at high R is that the aggregates become ellipsoidal. The total surface area per aggregate, $\bar{A}_o$, can be calculated using Equation 41 for a sphere,

Equation 42 for a rod (prolate ellipsoid), and Equation 43 for a disk (oblate ellipsoid), where b is the minor axis of a prolate ellipsoid, Equation 44, Figure 20a, a is the major axis of an oblate ellipsoid, Equation 45, Figure 20b, and V_m is the total volume of the aggregate.²¹⁶ It should be emphasized here that the use of r_h is

$$\bar{A}_o^s = 4\pi r_h^2 \quad (41)$$

$$\bar{A}_o^r = 2\pi b(2r_h + b) \quad (42)$$

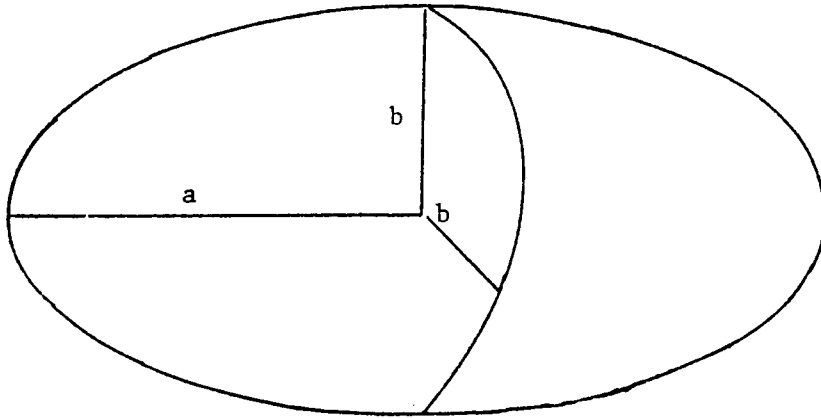
$$\bar{A}_o^d = 2\pi r_h(r_h + a) \quad (43)$$

$$b = (V_m/2\pi r_h)^{1/2} \quad (44)$$

$$a = V_m/\pi r_h^2 \quad (45)$$

strictly applicable only for spheres; the calculated values will be upper limits. In addition, r_h is actually calculated from diffusion coefficients assuming a spherical shape, thus for the present discussion V_m can be set equal to the volume of a sphere. Therefore, if r_h is taken as 120 Å and assuming an aggregation number of 2800,³³ the surface areas per molecule are: $A_o^s = 64.6 \text{ Å}^2$, $A_o^r = 74.3 \text{ Å}^2$, and $A_o^d = 75.4 \text{ Å}^2$. Similarly, A_w 's can be calculated by using r_w , the radius of the water pool. Subtracting 11 Å from r_h and computing yields: $A_w^s = 53.3 \text{ Å}^2$, $A_w^r = 69.5 \text{ Å}^2$, and $A_w^d = 65.8 \text{ Å}^2$. This long-winded, albeit simple, discussion shows that A_o is larger for ellipsoids than in spheres, thus increasing the volume that the alkyl chains must occupy, and hence increasing the probability of gauche conformers in the hydrocarbon tails.

a. Prolate ellipsoid



b. Oblate ellipsoid

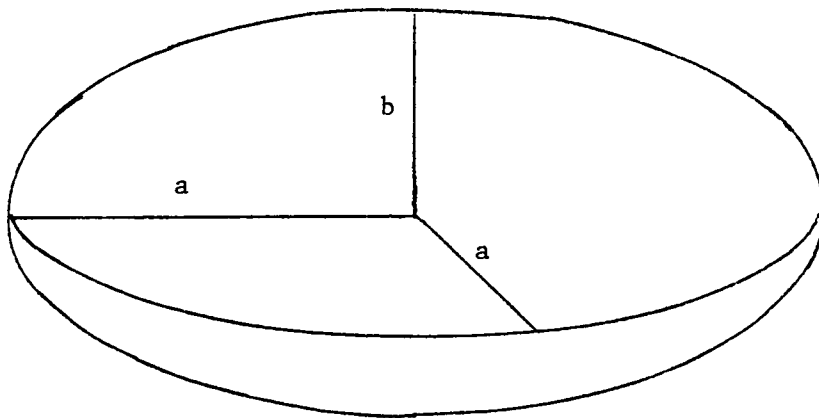


Figure 20. Prolate and oblate ellipsoids.

Yet another possible reason for the observed increase in $\tau_{\text{eff}}^{(4)}/\tau_{\text{eff}}^{(8)}$ at $R = 46$ is that lamellar aggregates are present within the isotropic one phase region in equilibrium with spherical aggregates.⁹⁶ Theoretical arguments on the nature of the AOT inverted aggregates in the presence of large amounts of solubilized water will be postponed until section C of this chapter.

b. Carbonyls. T_1 's of AOT's carbonyls, 2 and 2', show a general increase as water is solubilized. Relaxation of these carbons could be affected by intermolecular dipolar interactions, chemical shift anisotropy or dissolved oxygen. NT_1 values for a degassed sample (0.5 M AOT/cyclohexane, $R = 26$) are given in the last column of Table II (p 70). Only T_1 's of the carbonyls increased significantly.

c. Overall molecular motions. NT_1 's for the head group carbons, 1 and 1', could not be obtained for the lowest water concentrations, since line broadening appreciably reduced the S/N. From the data available, NT_1 of these carbons increases up to $R = 20$, then decreases. These carbons are not expected to exhibit any measurable amount of internal mobility; their relaxation should be due to diffusion of the aggregates and/or the AOT molecule itself. Using available size data for the aggregates, τ_R was calculated from Equation 33 (p 44), assuming $f_r = 1$, and compared with $\tau_{\text{eff}}^{(1)}$, Figure 21. It was assumed that relaxation was in the slow motion region, i.e., on the upward swing of the curve in Figure 6 (p 34), in the computation of $\tau_{\text{eff}}^{(1)}$.

Hydrodynamic radii have been determined for AOT in cyclohexane only at small water concentrations.⁹² $\tau_{\text{eff}}^{(1)}$ for $R = 10$ was obtained by extrapolation of r_h values at lower R . At all R , $\tau_{\text{eff}}^{(1)} > \tau_R$.

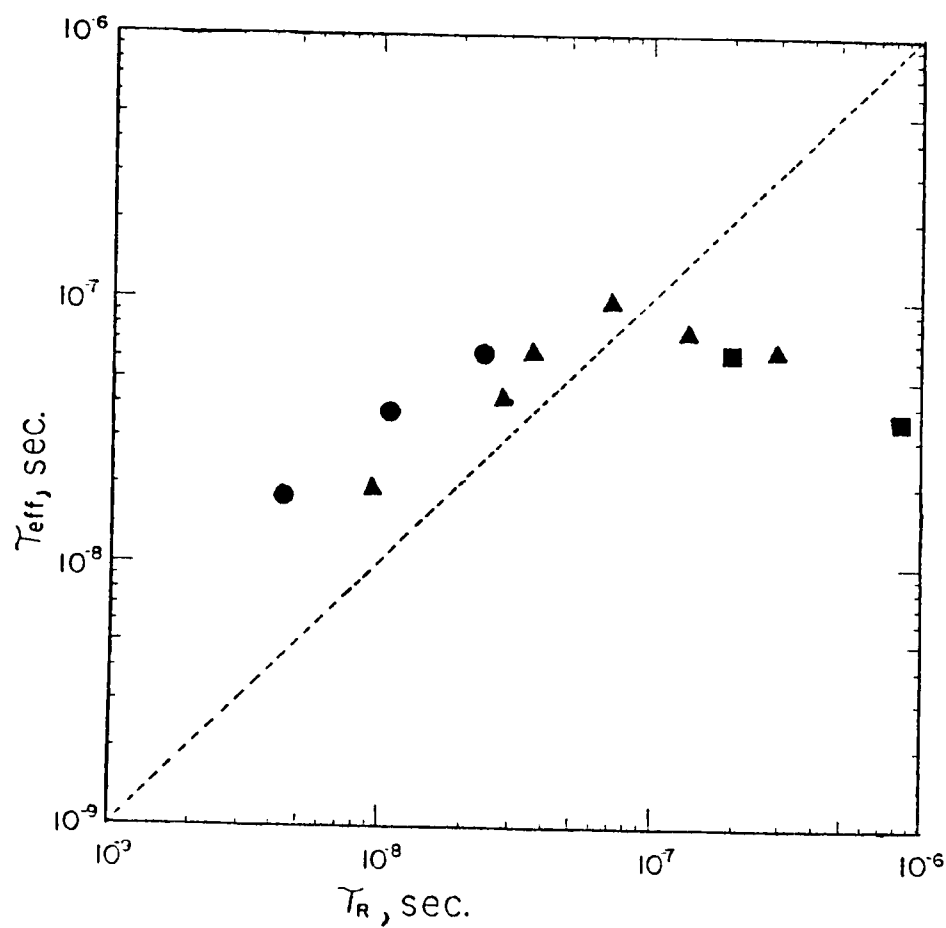


Figure 21. Comparison of $\tau_{eff}(1)$ with τ_R . τ_R calculated using r_h values in cyclohexane (circles, $R = 2, 5, 10$, left to right), isooctane (triangles, $R = 2, 5, 10, 20, 25, 30$, left to right), and heptane (squares, $30, 46$, left to right).

The poor correlation could arise from the actual solution viscosity being greater than that of the solvent. The large errors in T_1 (see Chapter VI) will also affect $\tau_{\text{eff}}(1)$; a 10% error in T_1 will produce a 50% error in τ_{eff} when relaxation is in the slow motion region.

The most extensive data on AOT aggregate size have been compiled by Zulauf and Eicke³³ using dynamic light scattering for 0.05 M AOT in isooctane. τ_R was calculated assuming that r_h for the aggregates is identical in cyclohexane and isooctane. The results in Figure 21 show good agreement between $\tau_{\text{eff}}(1)$ and τ_R up to $R = 25 - 30$. However, this may be fortuitous, since their data in isooctane consistently predict larger aggregates than the data of other workers using fluorescence polarization measurements.⁷⁹ [The latter study found $r_h(\text{cyclohexane})$ to be slightly larger than $r_h(\text{isooctane})$.] At $R \geq 25$, $\tau_{\text{eff}} < \tau_R$, suggesting that motions faster than aggregate tumbling contribute to the relaxation process.

Gulari, *et al.*,⁹⁴ have measured r_h for AOT/heptane at higher water concentrations. τ_R 's calculated from their data are shown in Figure 21; reasonable agreement occurs at $R = 30$.

d. Internal reorientations. The qualitative analysis of the previous section indicates that relaxation of the head group carbons is primarily due to the overall reorientation of the aggregates, at least up to intermediate R values. The contribution of τ_R to τ_{eff} of the alkyl chains can then be factored out employing Equation 36 (p 46); this gives the effective correlation time for internal reorientation, τ_{int} . These values are presented in Figure 22 for carbons 5,5' to 10,10'. Initially, τ_{int} of all the carbons decreases with increasing

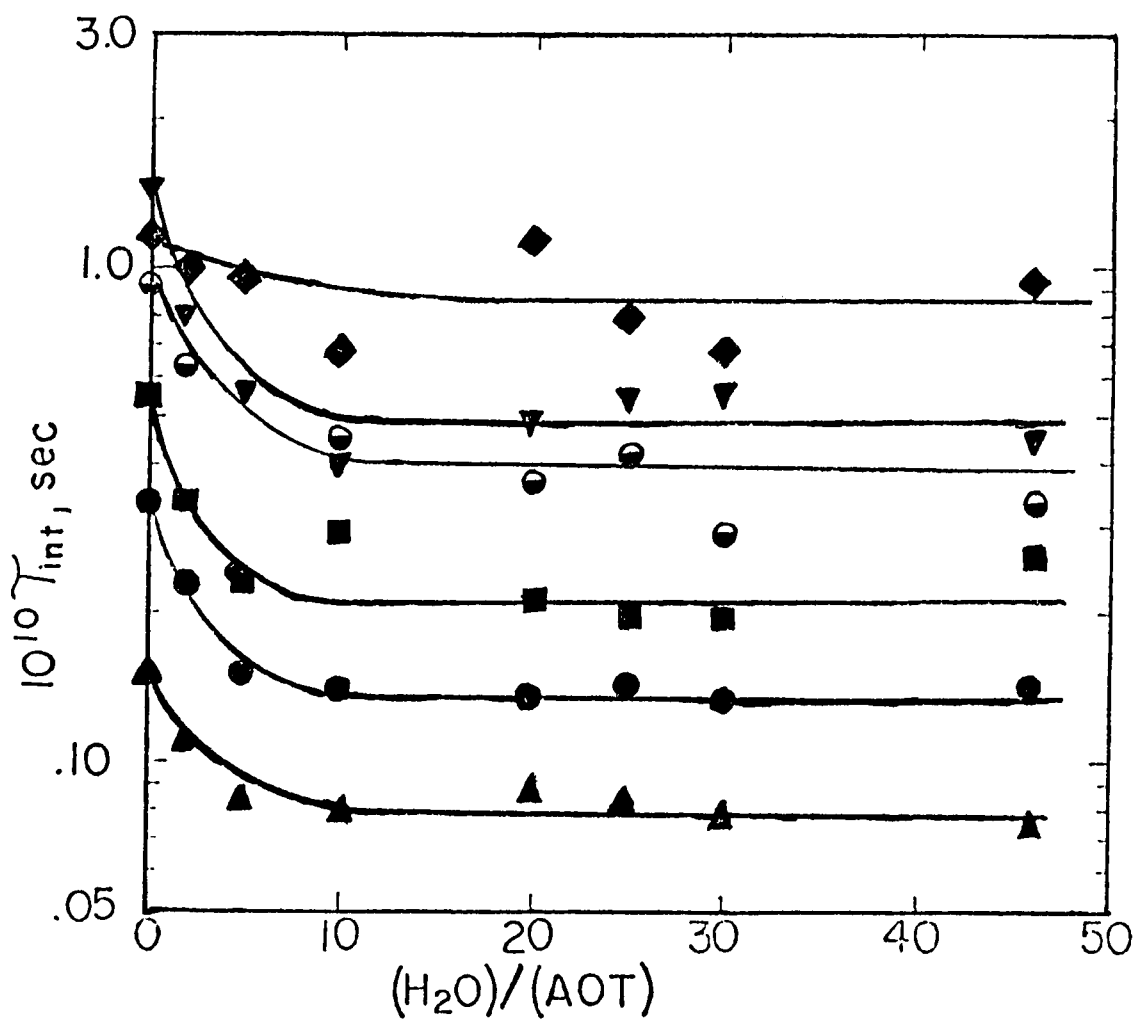


Figure 22. Change in τ_{int} of AOT's alkyl carbons as a function of added water concentration.

R, then remains constant as more water is added. Thus, addition of water induces an increased mobility in AOT's alkyl chains as the inverted micellar region is transversed. The average mobility of these carbons remains constant over the entire w/o microemulsion domain. The hydrocarbon membrane is quite fluid, although the calculated τ_{int} 's are an order of magnitude greater than τ_{int} 's calculated for n-alkanes.¹⁷²

Internal rotational diffusion coefficients, D_i 's, calculated from Equation 37 (p 47), are compiled in Table III. Although NT_1 's predict increased rotational diffusion along the chain away from the head group, there are five instances where $D_i > D_{i-1}$. However, the basis for this model, suggested by Levine,¹⁷⁶ is that diffusion at individual carbons is independent of rotations of other carbons in the chain. Common sense suggests that this premise is an oversimplification; the T_1 's measured at 100.6 MHz (next section) in fact predict interdependent mobilities. In order to obtain accurate D_i 's, a model incorporating multiple internal rotations²¹⁷ should be used.

Barriers to methyl group rotation, V_o , calculated using Equation 38 (p 47), have been included in Table III. Generally, V_o decreases for both methyl groups as R increases through the inverted micellar domain and then, roughly, levels off. The deviations from this trend are undoubtedly the result of the larger errors in τ_{int} (7) and τ_{int} (9), since their resonances overlap. However, V_o is still larger than the value obtained for methyl rotation in alkanes, 10.9 kJ/mol.¹⁷²

4. Frequency Dependence of T_1 's

In the previous section, analysis of T_1 's was based on the simple

TABLE III

INTERNAL ROTATIONAL DIFFUSION COEFFICIENTS, D_i , AND BARRIERS TO METHYL ROTATION, V_o ,
FOR 0.5 M AOT/CYCLOHEXANE AS A FUNCTION OF R

R	i=	$10^9 D_i \text{ (sec}^{-1}\text{)}$								$V_o \text{ (kJ/mol)}$	
		5	6	7	8	9	10	8	10		
0		4.18	1.14	3.93	23.0	3.43	11.5	13.2	15.0		
2.2		4.33	2.99	6.88	30.8	5.78	15.0	12.5	14.3		
5.3		3.40	6.35	9.59	40.5	5.81	25.7	11.8	13.0		
10.2		5.19	3.92	5.99	47.3	10.4	23.6	11.4	13.2		
19.9		2.39	8.94	23.8	33.8	8.32	26.4	12.3	12.9		
25.2		4.12	5.37	14.0	34.1	7.11	25.7	12.3	13.0		
29.6		4.66	9.99	8.71	39.7	6.31	31.8	11.9	12.4		
46.3		3.16	9.57	7.27	47.3	9.51	27.0	11.4	12.8		

model embodied by Equation 24 (p 33). Rotational diffusion was assumed to be essentially isotropic and relaxation was assumed to result solely from dipole-dipole interactions. This model is adequate in predicting general trends and average mobilities, but it gives no indication of the types of motion that the molecule is actually undergoing. Solutions of AOT inverted micelles ($R = 0$) and w/o microemulsions ($R = 30$) were studied at 100.6 MHz in order to obtain more detailed dynamic information. NT_1 's at the higher frequency are given in Table IV.

Comparing the data in Table IV with those in Table II (p 70) for $R = 0$, it is seen that NT_1 at 100.6 MHz is larger than NT_1 at 15.1 MHz for each carbon, even those carbons whose T_1 's fall within the region of extreme narrowing. This indicates the presence of correlated (interdependent) motions; a distribution of correlation times must be contributing to the relaxation of each carbon.¹⁴⁵ Correlated motions may arise from kink isomerization and diffusion,^{177,189,218} slow aggregate tumbling,^{185,208} or diffusion of monomers between⁵⁴ or within²⁰⁸ the aggregates.

The segmental mobility curve, Figure 19 (p 71), suggests that there is a large population of gauche conformers within the AOT alkyl chains in the inverted micelles. The series of motions which cause kink formation, annihilation, and diffusion are quite complex, occurring on many different time scales.²¹⁸ Conformational realignments at one bond require cooperative motions at other bonds,¹⁷⁷ thus affecting the relaxation of all the carbons in the chain. Gauche to trans

TABLE IV

 NT_1 (sec) MEASURED AT 100.6 MHz FOR 0.5 M AOT/CYCLOHEXANE- D_{12} /WATER

$C^\#$	R	
	0	30
10,10'	2.70	3.60
9,9'	0.46	0.73
8,8'	— ^a	— ^a
7,7'	1.40	1.94
6,6'	0.86	1.26
5,5'	0.50	0.82
4,4'	0.28	0.43
3	0.33	0.51
3'	0.33	0.70
1	0.24	0.31
1'	0.19	0.20

a. longest $t_d < 5 T_1$

isomerizations in liquid n-alkanes occurs within the time scale 10^{-9} to 10^{-10} sec,¹⁸³ slightly faster than the τ_{int} values, Figure 22 (p 78).

The distribution of correlation times will be further broadened if the slower overall motion of the AOT molecule affects relaxation. For $R = 0$, $\tau_{eff}^{(4)} \approx \tau_R$, indicating that the rigidity in the head group region extends into the chain. A distribution of slower correlation times could arise from polydispersity of the aggregates,⁷⁷ or through monomer translational diffusion competing with aggregate tumbling as a relaxation mechanism.²⁰⁸ Note that $T_1(100.6 \text{ MHz})/T_1(15.1 \text{ MHz})$ equals 1.3 to 1.8 for carbons 5,5' to 10,10', suggesting that the distribution of correlation times is narrower than that assumed in the sodium hexadecylsulfate o/w microemulsion study.²⁰⁹ The very large NT_1 ratios for carbons 1 to 4,4' are due to their relaxation falling outside the extreme narrowing limits.

Levy, et al.,¹⁸⁵ have analyzed the relaxation of alkyl chains attached to a polymer backbone using a model where multiple internal motions are coupled to a distribution of correlation times in the polymer backbone. A quantitative analysis of the data in this paper using Levy's model is not possible, since only two relaxation parameters are available. It has been shown that in order to describe completely M motions, $2M-1$ relaxation parameters are necessary; virtually any model can be used to fit one or two pieces of data.¹⁸⁷ Attempts were made to measure Nuclear Overhauser Enhancements (see below), but the results were irreproducible. Thus, only a qualitative description is possible using the available data.

For $R = 30$, NT_1 of carbons 6,6' to 10,10' are identical at the

two frequencies. The predominance of trans conformers in the alkyl chains of AOT w/o microemulsions produces internal correlated motions which occur on very similar time scales. The field strength-dependent increases in the T_1 for carbons 3 to 5,5' are coupled to AOT's molecular motion, possibly monomer translational diffusion.

At the highest R values, $\tau_{\text{eff}}(1) = 4 - 8 \times 10^{-7}$ sec, Figure 21 (p 76). This could represent the time constant for translational diffusion of an AOT monomer along the interior surface of a w/o microemulsion. Assuming a spherical radius of $109 \text{ \AA}^{33}$ and a path width of $\sqrt{55} \text{ \AA}^{90,100}$ gives a path area for motion of the monomer through one radian of $7.5 \times 10^{-18} \text{ m}^2$. Dividing this value by $3.4 \times 10^{-12} \text{ m}^2/\text{sec}$, the AOT self-diffusion coefficient in a cubic mesophase,⁶⁶ gives as the upper limit for monomer diffusion, $\tau_d = 2.4 \times 10^{-6}$ sec. To depict this diffusion process, it is useful to compare the AOT molecule to a feather floating in a stiff wind. The point of the feather is hard (sulfonate head group) and the vane is soft (alkyl chains). Individual carbons are the barbs. The feather floats rigidly and randomly through the air (i.e., the AOT molecule moving across the interface with its Brownian motion producing a distribution of correlation times which affect the relaxation of carbons closest to the interface). The vane follows behind, not displaying a large degree of independent motion. Very short, rapid, incomplete motions (librations¹⁷⁸) are experienced by the barbs.

With the above interpretation in mind, it may be more correct to describe the results of Figure 21 (p 76) by stating that aggregate tumbling is the predominant contribution to relaxation of carbons

nearest the head groups at low R; lateral monomer diffusion is the primary contribution at high R; at intermediate R, these two processes compete.

Wennerström, et al.,²⁰⁸ have determined τ_d to be 1.5×10^{-9} sec using Equation 46 for micellar sodium octanoate in D_2O , where D_L is

$$\tau_d = L^2/6D_L, \quad (46)$$

the amphiphile's lateral self-diffusion coefficient. Using Equation 46, τ_d for AOT is 5.9×10^{-8} sec, much faster than the τ_d derived graphically. Using Equation 46 and the τ_d value that was graphically determined, $D_L = 8.4 \times 10^{-14}$ m²/sec. Considering that Equation 46 is strictly valid for translational diffusion of a spherical molecule,¹³⁷ and that it does not appear reasonable that diffusion in a micro-emulsion should be slower than diffusion in a liquid crystal, the use of Equation 46 to predict τ_d is incorrect.

The above discussion, of course, assumes that the levelling off of τ_{eff} at higher R is due to monomer diffusion. The lateral diffusion coefficient of an AOT w/o microemulsion aggregate is 4.0×10^{-11} m²/sec for 0.05 M AOT/isooctane, $R = 44$.³³ Using a radius of $120 \text{ \AA}$ in Equation 46 gives $\tau_d^{agg} = 6.0 \times 10^{-7}$ sec. However, at the higher AOT concentrations in this study, diffusion of the aggregates should be appreciably slower.

As a final note, lateral diffusion of phosphatidylcholines across the surface of a lipid bilayer has been observed with τ_d 's on the order of 10^{-7} sec.¹⁹⁰

5. ^{13}C Line Widths

Table V lists ^{13}C line widths at half-height, $\Delta\nu_{1/2}$, for AOT/cyclohexane systems as a function of added water. The values for carbons 7,7' and 9,9' are not included because their resonances overlap. Quantitative interpretation of these data is probably not possible, since field inhomogeneities can result in significant line broadening. However, a few points will be made. Across the water-solubilizing range, there appears to be a general trend of an initial decrease of $\Delta\nu_{1/2}$ upon addition of water, a plateau region through the intermediate R values, and an increase at the highest water concentrations. This trend is most noticeable for carbons 1 to 3. The decrease at low R values is consistent with increased molecular mobility as water is added. Note that the NT_1 's of carbons 1, 1', 3, and 3' decrease at the highest R values, Table II (p 70). The obvious conclusion is that the mobility of the head group region decreases at very high water concentrations.

While conclusions that are arrived at by comparing $\Delta\nu_{1/2}$ at different water concentrations may be distrusted, comparison of line widths for various carbons at constant R is valid. For the range $R = 0 - 25$, $\Delta\nu_{1/2}(5,5') > \Delta\nu_{1/2}(4,4')$. This contradicts the concept of segmental motion which states that the relative motion increases along the alkyl chains away from the head groups. In the 100 MHz spectrum, Figure 23, two peaks are observed for both carbons 4,4' and 5,5'. It is possible that carbons 5 and 5' are less equivalent than carbons 4 and 4'.

6. Nuclear Overhauser Enhancements

Attempts were made to measure NOE's using the gated decoupling

TABLE V

 $\Delta\nu_{1/2}$ OF AOT/CYCLOHEXANE/ H_2O SOLUTIONS AT 15.1 MHz

$C^\#$	R=	$\Delta\nu_{1/2}$ (Hz)							
		0	2.2	5.3	10.2	19.9	25.2	29.6	46.3
10,10'		7.74	4.99	5.78	6.10	5.98	5.36	7.60	6.14
8,8'		6.50	4.39	4.32	4.60	4.12	4.85	4.25	4.85
6,6'		8.67	6.21	7.82	5.45	5.06	5.06	3.85	6.31
5,5'		10.55	7.34	7.31	6.97	5.62	7.58	4.15	6.88
4,4'		10.27	6.91	6.43	5.49	4.84	6.56	4.73	7.77
3		16.80	12.75	7.14	6.30	5.63	8.05	5.68	7.12
3'		13.73	9.99	7.91	7.12	6.73	7.86	7.91	14.15
2		4.58	3.40	2.66	2.97	2.84	3.60	3.75	3.97
2'		4.25	3.08	2.85	2.99	2.63	3.84	3.63	3.57
1		12.42	11.14	7.45	6.11	5.68	7.93	6.06	13.48
1'		18.55	13.98	18.92	11.23	10.90	9.10	14.68	17.69

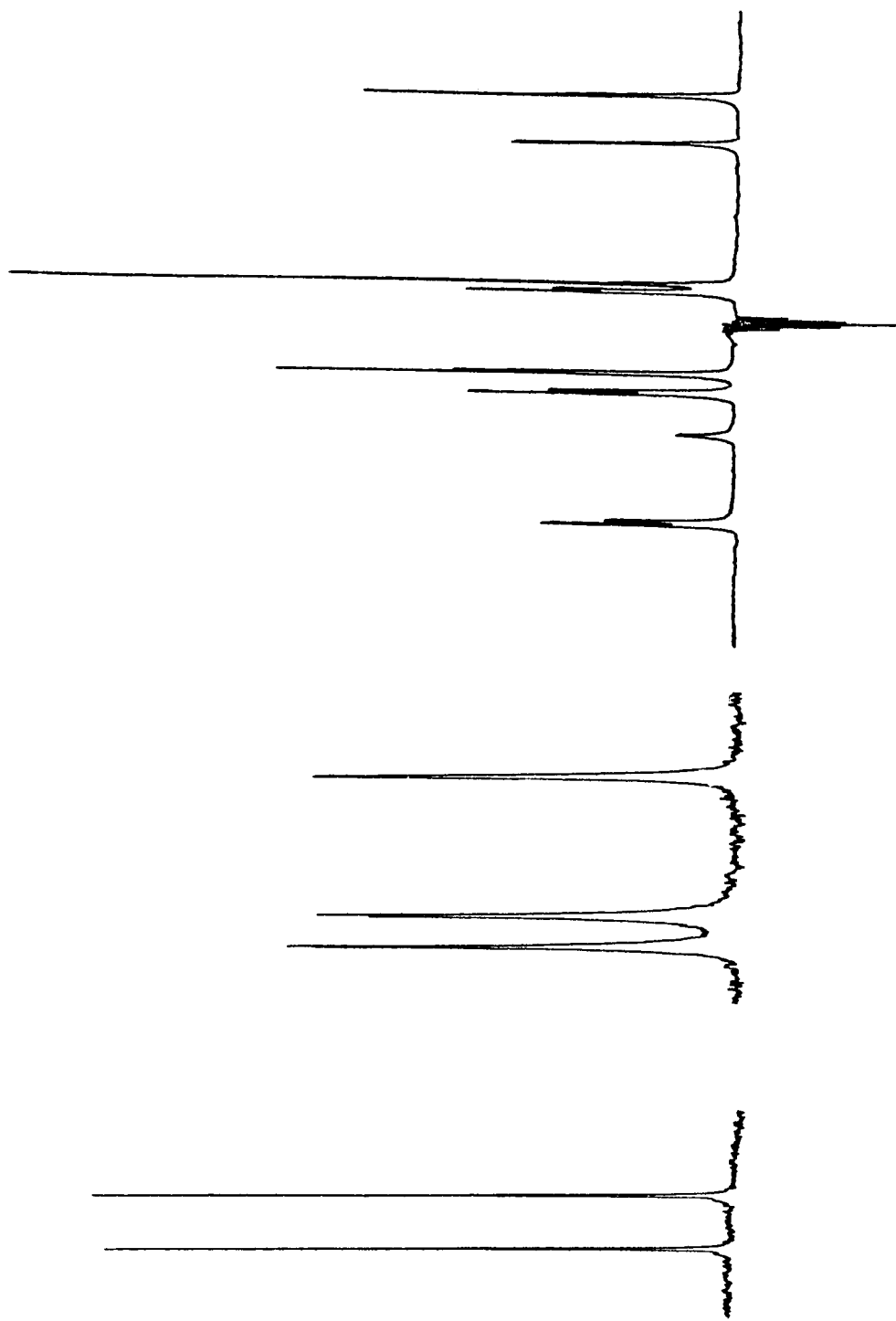


Figure 23. ^{13}C spectrum of 0.5 M AOT/cyclohexane- d_{12} /water at 100.6 MHz. (This spectrum was run in three parts which resulted in the discontinuities and differences in scaling shown.)

technique.²¹⁹ Since the values could not be reproduced, the data will not be enumerated. Generally, the NOE's were less than 3.0, the theoretical maximum for relaxation occurring only through DD interactions. Except for the carbons nearest the head group, it is unlikely that other relaxation mechanisms will contribute. There are various theoretical reasons for reduced NOE's, even with complete DD relaxation. Correlated motions may reduce NOE's.¹⁷⁷ Proton spin-diffusion will lower the NOE if $^{13}\text{C } T_1 \ll ^1\text{H } T_1$, unless extremely long delay times are used.²²⁰ $^1\text{H } T_1$'s have been measured by Wong, *et al.*,⁸⁸ and this condition is applicable only to carbons 1 and 1', for which the delay time is certainly long enough. Experimentally, reduced NOE values may arise if too long a time is needed to acquire the FID.¹⁴⁰ In this experiment, it took 0.8 sec for acquisition (the acquisition time is determined by the sweep width). Since this value is larger than most of the T_1 's, substantial relaxation occurs during acquisition while the decoupler is gated on. Thus, the NOE will not have its maximum value.

B. EFFECT OF SOLVENT

It was stressed in Chapter II that virtually all of AOT's solution properties were solvent dependent. It will be shown in this section that the choice of solvent profoundly influences the relaxation behavior of AOT molecules in inverted aggregates. T_1 's and δ 's of 0.5 M AOT in benzene and carbon tetrachloride were measured at 15.1 MHz as a function of added water concentration.

1. ^{13}C Chemical Shifts

The 15.1 MHz ^{13}C spectra of AOT/benzene and AOT/carbon tetrachloride are shown in Figures 24 and 25, respectively. As in the cyclohexane case, the ^{13}C δ 's of carbons 4,4' to 10,10' do not vary with the amount of added water. Figure 26 shows the chemical shift changes that occur in the head group region as a function of R. Note that $\delta(\text{C-1})$ levels off at $R = 5.8$ for AOT/carbon tetrachloride/water, indicating the upper limit of the inverted micellar domain in this solvent.

The largest changes occur in the carbonyl chemical shifts, as also observed for AOT/cyclohexane solutions. However, in benzene and carbon tetrachloride, $\delta(\text{C-2})$ is constant while $\delta(\text{C-2}')$ moves upfield as R increases. This suggests that only the 2' C(O)-C bond undergoes a conformational change in these solvents.

2. Fourier Transform Infrared Spectroscopy

FTIR spectra were run for AOT/benzene/water and AOT/carbon tetrachloride/water solutions. The carbonyl stretching region is identical to that observed when cyclohexane was the solvent, Figure 18 (p 67); three bands are present at 1739, 1735, and 1718 cm^{-1} .

3. ^{13}C Spin-Lattice Relaxation Times

a. Solvent penetration. NT_1 's are collected in Tables VI and VII for 0.5 M AOT solutions in benzene and carbon tetrachloride, respectively. Upon initial solubilization of water, NT_1 's increased in both of these solvents. The same behavior was observed in cyclohexane, Table II (p 70). A general trend is observed in the relaxation

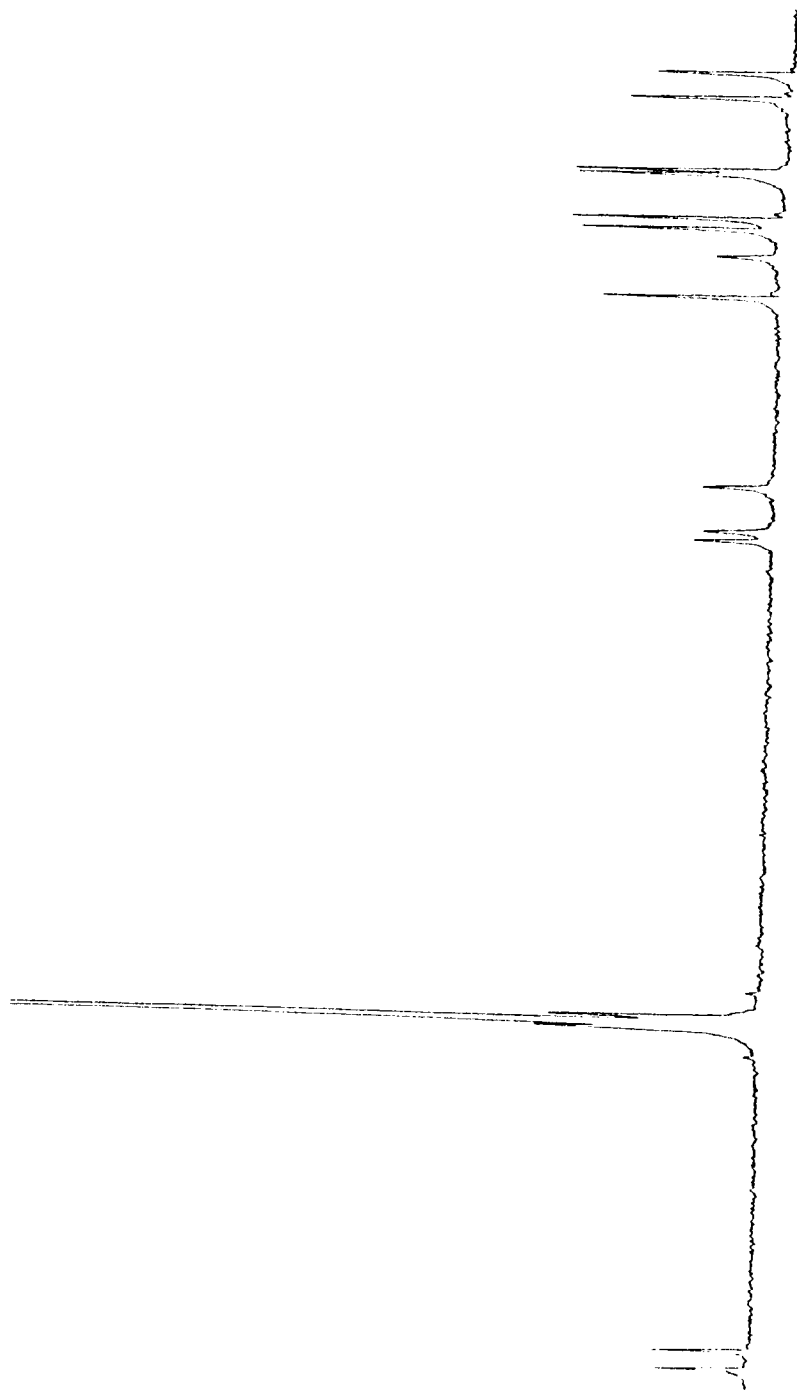


Figure 24. ^{13}C spectrum of 0.5 M AOT/benzene/water at 15.1 MHz.

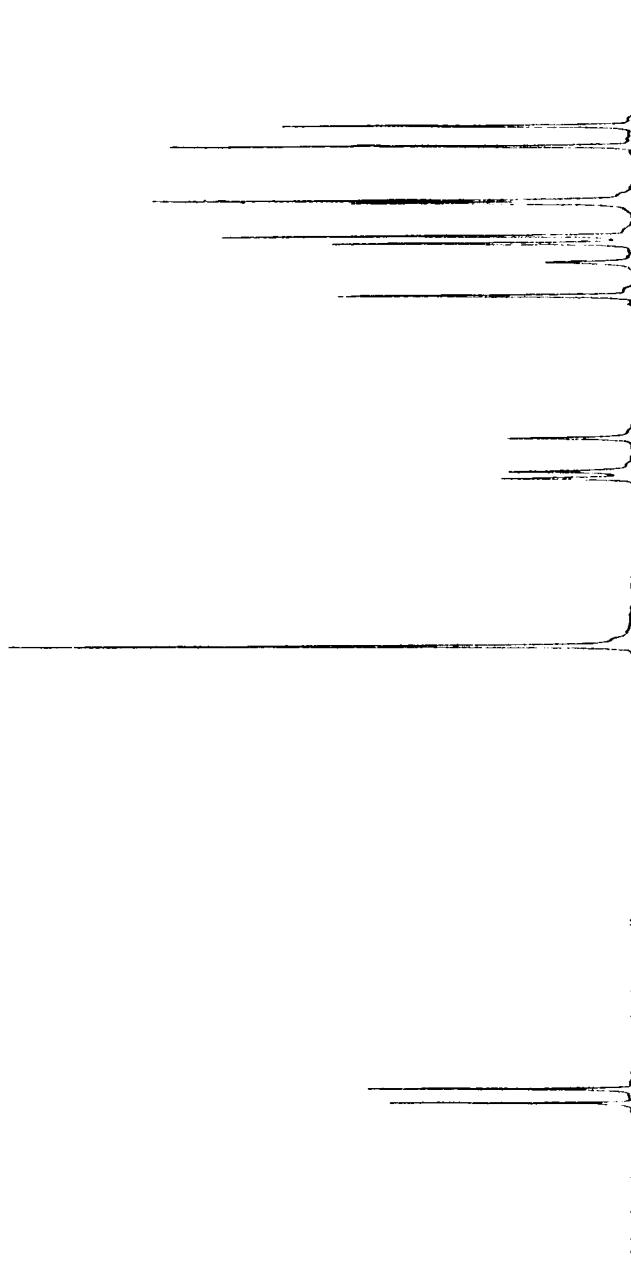


Figure 25. ^{13}C spectrum of 0.5 M AOT/carbon tetrachloride/water at 15.1 MHz.

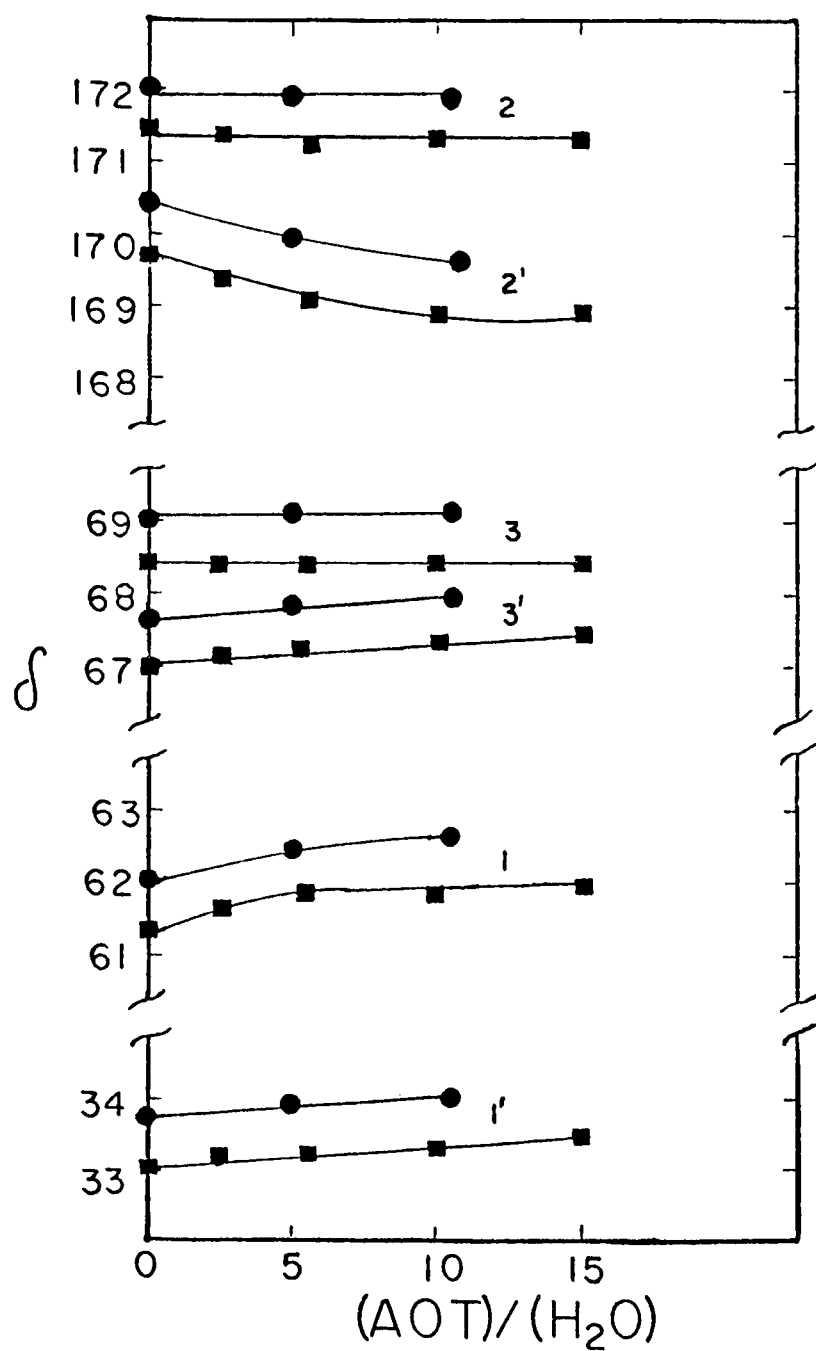


Figure 26. ^{13}C chemical shift changes of 0.5 M AOT in benzene (circles) and carbon tetrachloride (squares) as a function of added water concentration.

TABLE VI

NT₁ (SEC) OF 0.5 M AOT/BENZENE/WATER SOLUTIONS AT 15.1 MHz

C [#]	R		
	0	5.0	11.1
10,10'	2.79	4.32	4.77
9,9'	0.56	0.72	0.76
8,8'	4.89	5.85	6.93
7,7'	0.88	1.26	2.10
6,6'	0.56	0.84	1.24
5,5'	0.32	0.64	0.64
4,4'	0.14	0.18	0.26
3	0.088	0.15	0.22
3'	0.11	0.18	0.22
2 ^a	1.34	1.53	2.21
2' ^a	1.52	2.10	3.27
1	0.040	0.81	0.11
1'	0.040	0.062	0.12

a. T₁ is reported.

TABLE VII

NT₁ (SEC) OF AOT/CARBON TETRACHLORIDE/WATER SOLUTIONS AT 15.1 MHz

C [#]	R				
	0	2.5	5.8	10.3	15.3
10,10'	2.34	3.21	3.90	4.38	4.35
9,9'	0.20	0.56	0.56	0.56	0.62
8,8'	4.14	5.85	6.42	6.99	7.71
7,7'	0.84	1.18	1.86	2.26	1.86
6,6'	0.46	0.74	0.98	1.36	1.12
5,5'	0.20	0.46	0.50	0.66	0.62
4,4'	0.077	0.13	0.21	0.26	0.29
3	0.041	0.11	0.19	0.21	0.22
3'	0.083	0.17	0.18	0.25	0.25
2 ^a	0.68	1.19	1.52	2.04	2.33
2' ^a	0.87	1.42	2.39	3.09	3.52
1	0.050	0.039	0.093	0.10	0.15
1'	0.052	0.075	0.062	0.084	0.16

a. T₁ is reported.

results in the three solvents: $NT_1(\text{cyclohexane}) < NT_1(\text{carbon tetrachloride}) < NT_1(\text{benzene})$ at $R = 0$; $NT_1(\text{cyclohexane}) < NT_1(\text{carbon tetrachloride}) \approx NT_1(\text{benzene})$ at $R = 5$ and 10 . Thus, the AOT molecule displays a greater mobility in its inverted aggregates in the latter two solvents than in cyclohexane.

The segmental mobilities of the AOT alkyl chains in benzene and carbon tetrachloride are compared in Figure 19 (p 71) with those in cyclohexane. At $R = 0$, $\tau_{\text{eff}}^{(4)}/\tau_{\text{eff}}^{(8)}$ decreases in the following order: cyclohexane > carbon tetrachloride > benzene. This ratio is approximately the same in the latter two solvents at $R = 5$ and 10 . The results imply more extended alkyl chain conformations, on the average, in benzene and carbon tetrachloride at lower R values than in cyclohexane.

It can be proposed that benzene and carbon tetrachloride intercalate the AOT hydrocarbon chains, while in cyclohexane the voids are filled by the alkyl tails themselves. This explains the preference for gauche conformers in cyclohexane at lower R . Benzene solubilization at the AOT/water interface was suggested to explain its quenching efficiency on a water-soluble fluorescence probe.⁷⁹ Benzene intercalation into AOT's alkyl chains has been proposed by Atik and Thomas²²¹ in connection with a study of transport of ions between water pools in AOT w/o microemulsions. Benzene interaction with the ethylene oxide moieties of nonionic inverted micelles was used to explain the observed ^1H nmr data.²²² Evidence exists that toluene associates with the surfactant's alkyl chains in potassium oleate/1-hexanol w/o microemulsions.²²³ Chloroform interaction with the head group of decyltrimethylammonium bromide has been proposed.²²⁴

Solvent properties which may be used to rationalize the penetration abilities are collected in Table VIII. Water is included for comparison. Since these solvents are nonpolar, any interaction with the AOT head group should be due to dipole-induced dipole interactions. The polarizability parameter,²²⁵ p , decreases in the order: benzene > carbon tetrachloride > cyclohexane. Other factors also influence penetration. Benzene exhibits a surprisingly large polarity parameter,²²⁵ π^* , occupies the smallest molar volume,²²⁶ V , and has a slight hydrogen-bonding accepting ability,²²⁶ δ_h . When these factors are combined with the mutual solubilities between each solvent and water,²²⁷ a convincing argument is made for solvent penetration into AOT inverted micelles decreasing in the solvent series: benzene > carbon tetrachloride > cyclohexane.

Generally, the aggregation numbers of AOT inverted micelles decrease as the solubility parameter,²²⁶ δ_s , increases (an exception being chlorinated hydrocarbons).⁷⁷ In benzene, $n = 14$, and in cyclohexane, $n = 18$, at $R = 0$. However, r_h are almost identical in the two solvents.⁷⁹ Penetration of benzene into the inverted micelles swells the aggregates, explaining this anomaly. The highest R values studied in this work were close to the maximum amount of water, $R_{\max}$, which can be solubilized; $R_{\max}$ decreases in the order: cyclohexane > carbon tetrachloride > benzene. While a small amount of an organic compound can act as a cosurfactant,^{22a} too much of the organic species will break up the interface, resulting in a lowered water-solubilizing capacity. Much of the discussion on the nature of w/o microemulsions appears to be centered on maintaining the surfactant/water interface.²³

TABLE VIII

SOLUBILITY PARAMETERS OF THE SOLVENTS USED IN THIS WORK

Solvent	δ_s^a	δ_o^b	δ_d^c	δ_p^d	δ_h^e	π^{*f}	p^g	v^h
cyclohexane	16.8	16.8	16.8	0	0.2	0.000	0.0	108.7
carbon tetrachloride	17.6	17.8	17.8	0	0.6	0.294	0.5	97.1
benzene	18.8	18.6	18.4	0	2.0	0.588	1.0	89.4
water	47.9	47.8	15.5	16.0	42.3	1.090	---	18.0

a. Hildebrand solubility parameterⁱ; $\delta_s = (-E/V)$ where $-E$ = molecular cohesive energy.

b. total solubility parameterⁱ; $\delta_o^2 = \delta_d^2 + \delta_p^2 + \delta_h^2$.

c. solubility parameter due to dispersion interactionsⁱ.

d. solubility parameter due to polar interactionsⁱ.

e. solubility parameter due to hydrogen-bonding interactionsⁱ.

f. solvent polarity parameter^j.

g. polarizability parameter (δ in Reference 225).

h. molar volumes (ml/mole)ⁱ.

i. data from reference 226.

j. data from reference 225.

These ^{13}C nmr results point out the importance of a stable surfactant/oil interface as an additional factor in order for large amounts of water to be solubilized in w/o microemulsions. This is underscored by the fact that increasing the bulkiness of the alkyl tails in dialkylsulfosuccinates will increase their water-solubilizing capacity.⁸²

b. Overall molecular motions. The effect of overall aggregate tumbling on the relaxation process can be estimated. Table IX compares $\tau_{\text{eff}}(1)$ with τ_R in benzene and carbon tetrachloride using available size data for the aggregates.^{79,91,92} In all instances $\tau_{\text{eff}}(1) > \tau_R$. As in cyclohexane, the actual solution viscosities and the T_1 errors contribute to this discrepancy.

c. Internal reorientations. D_i and V_o for the alkyl chains of AOT in benzene and carbon tetrachloride are given in Table X for cases where available size data allowed τ_R , and hence τ_{int} , to be calculated. These results are similar to those in cyclohexane, Table III (p 80). No solvent trends can be deduced from the D_i 's. The V_o 's are larger at a given R value in cyclohexane than in benzene and carbon tetrachloride.

C. NOTE ON THE HIGH R REGION OF AOT/CYCLOHEXANE SOLUTIONS

It is interesting to speculate on the nature of the aggregates that are present in AOT/cyclohexane solutions containing large amounts of solubilized water. The segmental mobility curve, Figure 19 (p 71) and the line widths at half-height, Table V (p 87) both suggest a third distinct subregion within the isotropic L_2 region when $R > 30$.

TABLE IX

COMPARISON OF τ_R AND $\tau_{eff}(1)$ FOR AOT INVERTED AGGREGATES
IN BENZENE AND CARBON TETRACHLORIDE

	R	$r_h^{\bullet}$ (Å)	$10^9 \tau_R$ (Sec)	$10^9 \tau_{eff}(1)$ (Sec)
Benzene	0	16 ^a	2.4	32
	5	23 ^a	7.1	72
	11 ^b	28 ^a	12.7	94
	5.2	26.4 ^c	10.7	72
CCl ₄	5	28.8 ^c	20.6	83
	10	31.4 ^d	26.7	88

a. data in toluene, reference 92.

b. extrapolated from data at smaller R.

c. data from reference 79.

d. data from reference 91.

TABLE X
INTERNAL ROTATIONAL DIFFUSION COEFFICIENTS AND BARRIERS TO METHYL ROTATION FOR AOT
SOLUTIONS IN BENZENE AND CARBON TETRACHLORIDE

	R	i=	$10^9 D_i$ (Sec)							V_o (kJ/mol)
			5	6	7	8	9	10	8	10
Benzene	0		2.04	2.78	3.66	40.0	4.84	22.1	11.9	13.3
	5.0		5.32	2.24	5.01	45.4	6.21	36.2	11.5	12.1
	11.1		4.46	6.88	16.9	46.7	5.79	40.0	11.5	11.9
CCl ₄ ^a	5.9		3.39	5.51	10.3	44.3	3.99	33.8	11.4	12.3
	10.3		7.68	8.10	11.3	45.4	3.51	38.5	11.5	11.9

a. Size data not available, hence τ_R at other R values cannot be calculated.

Viscometric measurements show a sharp increase in the viscosity of AOT/isooctane solutions for $R > 40$.¹⁰⁴ The hydrodynamic radii of AOT/isooctane systems increase almost linearly with increasing R until $R = 30$, then break sharply upward.³³ Are these observations consistent with the AOT w/o microemulsions maintaining a spherical shape, even as the liquid crystalline region (see Chapter V) is approached?

For 0.5 M AOT/cyclohexane, $R = 46.3$, the weight percents of the solution are approximately: 23% AOT, 33% cyclohexane, and 43% water. For the present purposes, it is more important to consider the volume percents of each component. Taking the partial specific volume, $\bar{V}$, of AOT as 0.81 ml/g,⁷⁵ the density of cyclohexane as 0.77 g/ml, and the density of water as 1.00 g/ml, the approximate volume percents are: 18% AOT, 41% cyclohexane, and 41% water. This suggests that it is equally likely for the aggregates to be w/o, o/w, or lamellar. A structural inversion to o/w can be ruled out since the microviscosity of a water-soluble probe molecule in AOT/isooctane is 7 cP at the highest R ,⁸⁷ while the macroviscosity is 1 P.¹⁰⁴ Lamellar structures can be discarded, since the solution did not show any birefringence when viewed through crossed polars. The possibilities that remain are: (1) a spherical w/o aggregate; (2) an ellipsoidal w/o aggregate; (3) a cubic mesophase-like structure; and (4) a bicontinuous microemulsion.²²⁸

Both the spherical and ellipsoidal structures were found suitable in explaining the segmental mobility at high R . According to Biais, et al.,⁹⁵ aggregates can be spherical only if A_w is greater than an optimum value, A_w^{opt} , defined by Equation 47, where MW is the

$$A_w^{\text{opt}} = \frac{(r_h - L)^2}{r_h^3 - (r_h - L)^3} \frac{3\bar{V}MW}{N_A}$$

surfactant's molecular weight and N_A is Avogadro's number. A_w^{opt} is compared with the experimentally determined A_w for AOT in Table XI. The conclusion from this model is that AOT inverted aggregates are always spherical.

TABLE XI
COMPARISON OF A_w^{opt} WITH A_w EXPERIMENTALLY DETERMINED

R	A_w (Å ²) ^a	r_h (Å) ^b	A_w^{opt} (Å ²)
3.5	27	23	25
11	46	36	36
22	55	50	42
33	<u>>55</u> ^c	86	47
44	<u>>55</u> ^c	120	49

- a. data from reference 90.
- b. data from reference 33.
- c. highest R studied = 25.

Mitchell and Ninham²²⁹ have found that the packing ratio, $v/A_w L_c$, rather than just A_w , is an important criterion in determining surfactant aggregation patterns. In the packing ratio, v is the partial molecular volume of the amphiphile, A_w is the optimum head group area, and L_c is the length of the alkyl chain(s). Equation 48 must hold

$$v/A_w L_c > 1 \quad (48)$$

in order for spherical w/o microemulsions to be present. With $\bar{V} = 0.81$ cm³/g for AOT, v is computed to be 5.98×10^{-28} m³. If $L_c = 9$ Å, ²³⁰ and $A_w = 55$ Å², $v/A_w L_c = 1.21$. The volume fraction of water, ϕ_w , within the drop can be calculated from Equation 49. For $R = 45$,

$$\phi_w = [r_h/(r_h - L)]^{-3} \quad (49)$$

$r_h = 120$ Å, and $\phi_w = 0.75$. The optimal parameter for the existence of spherical w/o microemulsions with $\phi_w = 0.75$ is $v/A_w L_c = 1.1$, smaller than the value calculated above. For spherical inverted aggregates to be allowed, the packing ratio must be reduced. Since an increase in L_c or a decrease in v are physically unreasonable, A_w must be increased; computation gives $A_w = 60.4$ Å². Note that $A_w = 65 - 77$ Å² in AOT lamellar liquid crystals,^{64a} so that an increase in A_w is not unreasonable. Also compare the values for $R = 30$: $r_h = 80$ Å, $\phi_w = 0.64$, optimum $v/A_w L_c = 1.2$. So far the curvature at the surfactant/water interface has been ignored. The domain of spherical aggregates is further constrained by the condition in Equation 50, where d is

$$v/A_w L_c < \sqrt{1 + d/L_c} \quad (50)$$

the distance of closest approach between head groups. For the optimum parameters determined above, $d = 6$ Å (see Table 6 in reference 229), and $\sqrt{1 + d/L_c} = 1.29$. Since Equation 50 is not fulfilled, inverted spherical w/o microemulsions cannot be present at the highest water concentrations.

A bicontinuous microemulsion would be associated with an opening

up of the aggregates.²²⁸ This should be accompanied by an increase in the solution's conductivity. In the region $R = 40 - 60$, the conductivity of 0.28 M AOT/isooctane systems remains constant.¹⁰⁴ Thus, a bicontinuous system can be excluded from consideration.

Two possible structures remain: an ellipsoidal aggregate and a mesophase-like packing for AOT w/o microemulsions at high R values. Both types of aggregates are consistent with the observed high viscosities.¹⁰⁴ The packing criteria for inverted ellipsoids is absent from the Mitchell and Ninham model. Although theory can be used to determine what structures are disallowed, at this time the exact nature of the aggregates remains a matter of conjecture and needs to be determined experimentally. In addition, it is possible that more than one aggregation pattern is present within the isotropic one phase region, e.g., lamellar aggregates in equilibrium with spherical aggregates.⁹⁶

D. CONCLUSIONS

For AOT inverted micelles in cyclohexane at $R = 0$, the molecules' head group regions are arranged into a compact structure, while the alkyl chains are arrayed so that solvent cannot penetrate into the micelle. Addition of water induces conformational changes throughout the molecule, resulting in a more open, extended structure. This extended conformation is observed at lower R in benzene and carbon tetrachloride because of solvent penetration. The water-solubilizing capacity of AOT in the latter solvents is reduced because of more favorable AOT-solvent interactions.

Addition of water increases the fluidity of the alkyl chains of AOT in all three solvents. However, their mobilities remain more restricted than that of neat alkanes.

In cyclohexane, motional differences in the AOT alkyl chains exist between the inverted micelles and the w/o microemulsions. The frequency dependence of T_1 's indicate a complex series of motions in the inverted micelles; motion at each carbon-carbon bond cannot be considered independent of other motional contributions. The higher predominance of trans conformers along the AOT alkyl chains in w/o microemulsions simplifies the set of motions which affect relaxation. While nmr offers the promise of a complete dynamic description, in practice this may be impossible.

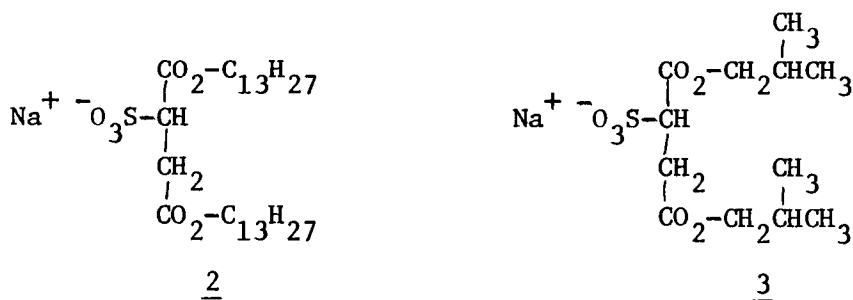
The motion of the AOT molecule as a whole dominates the relaxation of carbons 1 and 1'. At low R, relaxation is primarily due to overall aggregate tumbling. At high R, other motions, perhaps monomer diffusion, contribute to the relaxation process.

Calculations show that the AOT inverted aggregates cannot be spherical at the highest water concentrations in cyclohexane. This work has further emphasized the distinction between Aerosol OT inverted micelles and w/o microemulsions.

CHAPTER V

PHASE BEHAVIOR OF SODIUM DIALKYLSULFOSUCCINATES

Aerosol OT is the most widely studied of this class of surfactants. The dearth of information on related compounds is surprising in light of the many systematic studies which have been performed on other types of amphiphiles (see below). Aerosol TR (ATR, sodium bistridecylsulfosuccinate, 2) is more hydrophobic than AOT, while Aerosol IB [AIB, sodium bis(2-methylpropyl)sulfosuccinate, 3] is more hydrophilic. This chapter compares the phase behavior of these three amphiphiles, with emphasis on the one phase regions. The purpose of this study was to determine whether the HLB's of ATR and AIB could be altered by the addition of a suitable cosurfactant in order to mimic AOT's solubilization ability in apolar media. The results will show that these surfactants can indeed take up large amounts of water in the hydrocarbon solvents, benzene and cyclohexane, in the presence of alcohols. In fact, one phase regions are discovered which extend to the surfactant/water axis of the phase diagram.



A. GENERAL BACKGROUND

1. Phase diagrams

Phase diagrams map out the number and type of phase relationships in temperature, pressure and composition space. Surfactant phase behavior is quite complex and has been investigated by many workers; some of these studies will be mentioned in this section. The phase designations used depend on the author. Table XII lists the designations which will be employed in this study; the author has chosen these labels for ease of understanding.

The phase behavior of a ternary mixture at constant temperature and pressure can be easily conveyed in a triangular representation; each apex represents 100% pure component. However, many surfactant solutions of interest contain four or more substances. Pseudoternary phase diagrams illustrate the phase behavior within one triangular plane of the full tetrahedral representation of the quaternary system. The most common ways to construct pseudoternary phase diagrams are for one axis to represent a constant ratio of two components, or for one component to be distributed equally along all three axes.

This work is primarily concerned with identifying one phase, isotropic solutions which may be found in the phase diagram of the Aerosol surfactants. The regions tentatively identified as containing liquid crystals will be indicated with dotted lines. There are two paths by which L_2 solutions can be converted to L_1 . The first is $L_2 \rightarrow LC \text{ (or E)} \rightarrow L_1$. This type of transition was initially reported in the pioneering work of Winsor,²³¹ who studied how composition and temperature affect the phase behavior of a large variety of surfactant

TABLE XII
PHASE DESIGNATIONS USED IN THIS STUDY

Designation	Type of phase(s)
L_1	one phase, isotropic solution adjacent to the water apex normal micelles-o/w microemulsions
L_2	one phase, isotropic solution adjacent to the oil apex ion pairs-inverted micelles-w/o microemulsions
1ϕ	one phase, isotropic solution covering too large an area of the phase diagram to be called L_1 or L_2
LC	birefringent solution; liquid crystalline in most cases structural types not determined
E	emulsion; contains two or more phases
2L	two separated liquid phases
S	solid

systems. The second is $L_2 \rightarrow 1\phi \rightarrow L_1$. Here, a one phase region dominates the phase diagram. The structural inversion may be abrupt or continuous. These contrasting patterns will be considered separately in this section.

2. $L_2 \rightarrow L_1$ Transitions Via Liquid Crystals

Ekwall, et al.,²³² have studied the phase behavior of the sodium octanoate/water/1-decanol system. The phase diagram is dominated by a large array of liquid crystalline phases whose structures were determined by x-ray diffraction. The L_2 region extends from the alcohol corner and increases in size as the temperature is raised. Both the L_1 and L_2 regions of this system have been studied by ^1H nmr.¹⁹⁷ The effect of addition of octane on the L_2 region has been investigated.²³³

Commercial nonionic surfactants exhibit a complex phase behavior because of inhomogeneities in the ethylene oxide chain. For p-t-nonylphenol polyethylene oxide/water/hydrocarbon solutions, as the length of the ethylene oxide chain decreases, the size of the L_2 region becomes larger, while the LC domain decreases. Changing the oil from p-xylene to hexadecane decreases the extent of both regions.²³⁴ In general, the amount of water solubilized in the L_2 region becomes smaller as the dielectric constant of the solvent increases, or as the HLB of the surfactant decreases. In addition, the uptake of oil in the lamellar liquid crystals decreases as the oil's dielectric constant increases.²³⁵ A larger amount of aliphatic hydrocarbon than aromatic hydrocarbon will be solubilized in the liquid crystals.²³⁶ Nonionic emulsions are often multiphasic.²³⁷

Mixtures of homogeneous nonionics have been investigated. Even though the mixtures may contain the same average number of ethylene oxide units, their phase diagrams show distinct differences.^{238,239} Differential scanning calorimetric analysis of monodisperse dodecanol pentaethylene oxide/dodecane/water systems indicated that the phase transitions are exothermic.²⁴⁰

The phase behavior of potassium oleate/alcohol/water/hydrocarbon systems has been investigated by many workers. This system is characterized by a small L_1 region in the water corner and a large L_2 region along the oil/emulsifier axis.²⁴¹ Friberg and coworkers,^{242,243} using ternary and pseudoternary representations of the 1-pentanol/benzene systems, have shown the L_2 region in the presence of hydrocarbon to be an extension of the inverted micelle (L_2) domain in the absence of hydrocarbon. At low water concentrations, only small aggregates (ion pairs) are found when hydrocarbon is present; a large amount of water is necessary for the formation of inverted micelles. This view is supported by positron annihilation studies^{83,244} and nmr self-diffusion measurements.²⁴⁵ Different behavior is noted when the alcohol is 1-hexanol and the oil is hexadecane. Water is not necessary to produce inverted micelles in this system.²⁴⁶ The latter case has been studied by ^1H nmr.²⁴⁷ At both the $L_2 \rightarrow L_1$ and $\text{LC} \rightarrow L_1$ phase boundaries, the chemical shift of the water protons moves upfield, and the resonance's line width increases, returning to its original value in the new phase. Note that the birefringent region in this system is much more fluid than AOT's lamellar liquid crystals.⁶⁵

The phase behavior of sodium dodecylsulfate (SDS)/alcohol/water/

oil systems has been extensively studied also. When the solutions are comprised of 1-dodecanol/p-xylene²⁴⁸ or 1-decanol/hexadecane,²⁴⁹ ion pairs are present at low water contents. The L_1 region of 1-pentanol/hexadecane systems shows both kinetically and thermodynamically stable domains. In this case, the L_1 region was found to be skewed in the direction of the last component added.²⁵ Tondre and Zana²⁵⁰ have studied the rate of dissolution of solubilizates in the L_1 and L_2 domains of the 1-pentanol/dodecane system. Solubilization of water in the L_2 solution is more rapid than solubilization of n-alkanes in L_1 .

The $L_2 \rightarrow L_1$ transition in AOT ternary solutions occurs through liquid crystalline phases. AOT's phase behavior will be discussed later in this chapter.

3. $L_2 \rightarrow L_1$ Transitions Via Isotropic Solutions

At fixed alcohol/surfactant molar ratios (usually high), the pseudoternary phase diagrams of certain amphiphile-containing systems show that the L_1 and L_2 solutions are connected by an isotropic one phase region, 1ϕ . The structural inversion may occur abruptly, or it may take place gradually, perhaps through a bicontinuous micro-emulsion.²⁵¹

Ultrasonic absorption studies of the 1:2.5 (w/w) SDS:water/1-pentanol/cyclohexane system showed that the structural inversion occurred in a narrow concentration range.⁵³ However, this technique is insensitive to any structural changes which may take place in the 1:2 (w/w) SDS:1-butanol/toluene/water system. Bellocq, et al.,²⁵² identified w/o aggregates on the oil-rich side of the one phase region

and o/w aggregates on the water-rich side in the latter system. A viscosity maximum in the intermediate zone was identified with a structural inversion. Lamellar aggregates were proposed for the subregion of the $l\phi$ area at high emulsifier concentrations. However, the presence of lamellar structures is not supported by nmr self-diffusion studies.²⁴⁵ These results indicate that small aggregates are present. Unfortunately, self-diffusion studies were not performed near the proposed structural inversion region.

Conductivity and SANS measurements suggest that the structural inversion of SDS/1-pentanol/cyclohexane/water microemulsions occurs when the volume fraction of the w/o aggregates exceeds 0.64.²⁵³ Conductivity and diffusion data have been interpreted as evidence for a bicontinuous zone in the sodium *p*-octylbenzenesulfonate/1-pentanol/water/sodium chloride/decane $l\phi$ region.²²⁸ Boned, *et al.*,²⁵⁴ used conductivity studies to show that three subregions exist within the $l\phi$ region of the 3:5 (w/w) potassium oleate:1-hexanol/water/hexadecane system. They are: (1) hydrated detergent aggregates; (2) w/o microemulsions; and (3) clusters of nonspherical aggregates. Subregions (1) and (2) were identified for a 1:5 (w/w) surfactant/alcohol ratio of the same components using the positron annihilation technique.²⁴⁴ Large, one phase regions have also been observed in ternary solutions of 2-propanol, water, and oil containing no surfactant,²⁵⁵ and for an amphiphilic polymer/2-propanol/water/toluene system.²⁵⁶

In closing this section, it is clear from the above discussion that the types of aggregates, if any, which may exist in a $l\phi$ region vary widely, depending on the components present. Virtually every

possible type of association behavior and mode of structural inversion have been proposed in one system or another.

B. RATIONALE FOR THE EXPERIMENTAL PROCEDURE

Aerosol TR is a hydrophobic surfactant. In apolar media, it solubilizes only very small amounts of water. Its solubilization capacity was studied as a function of temperature in cyclohexane; the largest amount of water incorporation occurred at 45°C. Thus, this temperature was used for all the phase studies.

Next, the effects of twenty alcohols (twelve primary straight chain alcohols ranging from propanol to octadecanol, three primary branched alcohols, four secondary alcohols including cyclohexanol and, 2-methyl-2-propanol) on the water-solubilizing capacity of ATR in cyclohexane were compared at 45°C using a constant molar ratio of alcohol to ATR of 4.0. Three alcohols, 1-propanol, 2-propanol, and 1-butanol, gave the largest enhancement of water solubilization. The final choice of alcohol was made by a Bowcott-Schulman analysis.²⁵⁷ An emulsion of ATR, cyclohexane, and water was titrated to clarity with each of the alcohols. The resulting one phase solution was then titrated back to turbidity with cyclohexane. Repetition of these steps generated the plots shown in Figure 27. Since 2-propanol allowed ATR to solubilize the most water with the least amount of alcohol, it was chosen for the ATR experiments.

Cyclohexane was used as a solvent because of the AOT nmr work described in Chapter IV. Since aliphatic and aromatic solvents often give contrasting phase behavior, phase diagrams were constructed using benzene as the hydrocarbon also.

Figure 27. Bowcott-Schulman plots of ATR/alcohol/water/cyclohexane solutions.

The axes are in molar ratios.

1-Propanol: circles. Open: $R = (\text{H}_2\text{O})/(\text{ATR}) = 13.4$; half-filled: $R = 19.5$; filled: $R = 30.9$.

2-Propanol: squares. Open: $R = 22.8$; filled: $R = 33.2$.

1-Butanol: triangles, $R = 25.2$.

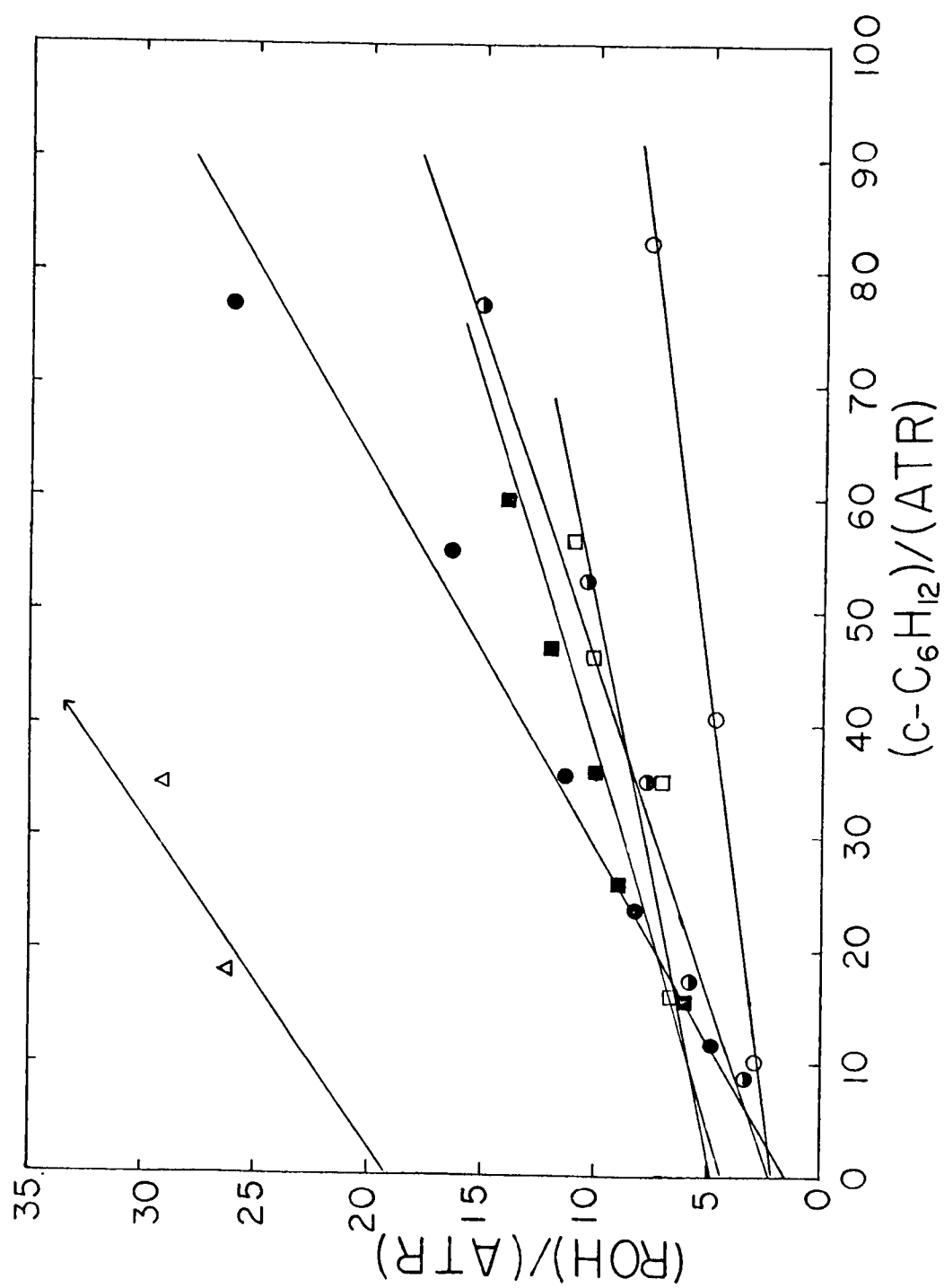


Figure 27.

Aerosol IB is a hydrophilic surfactant. Since a hydrophilic alcohol was used in the ATR work, the hydrophobic alcohol, 1-hexanol, was arbitrarily chosen for the AIB studies.

C. AEROSOL OT PHASE BEHAVIOR

Ekwall, et al.,⁷⁵ have presented the ternary phase diagrams for AOT/water/oil systems at 20°C using p-xylene, octanoic acid and 1-decanol as the oils. A large L_2 region extends from the AOT/oil axis; the L_2 phase bulges toward the water corner at high AOT concentrations. Liquid crystalline phases along the AOT/water axis were identified by x-ray diffraction. The complete ternary phase diagrams of AOT/water/isooctane at 25°C¹⁰⁴ and AOT/water/benzene at 25 and 50°C²⁵⁸ have been published. The AOT L_2 regions in decane and heptane have also been studied.²⁵⁹ The L_2 region extends up to 60 wt.% water in the last four cases mentioned. The effects of temperature and surfactant purity on AOT's phase behavior in cyclohexane and isooctane have been investigated.^{110,113}

1. AOT/Water/Cyclohexane at $45.0 \pm 1.0^\circ\text{C}$

The ternary phase diagram of this system is presented in Figure 28. The inverted micelle-w/o microemulsion region, L_2 , occupies a large space adjacent to the AOT/cyclohexane axis. Note that AOT solubilizes less water at 45°C than at 30°C [c.f. Figure 12 (p 58)]. This behavior has been described previously.¹¹⁰ Dominating the AOT/water axis are liquid crystalline phases, LC. These phases are anisotropic; observation between crossed polars revealed birefringence. The LC region is expected to consist of lamellar, hexagonal and cubic

mesophases.⁷⁵ The exact phase boundaries of these mesomorphic structures are not readily apparent from visual examination, but it is safe to assume that lamellar liquid crystals are present at low to intermediate AOT concentrations, and that the hexagonal mesophase exists at the highest. In the middle of the phase diagram, two phases coexist, one anisotropic and one isotropic. This area is designated $LC + L_2$, since it is adjacent to those two regions. The normal micellar domain, L_1 , is observed at very low AOT concentrations in water. A two phase region, $LC + L_1$, exists along the AOT/water axis, marking the transition from micelles to lamellar liquid crystals. At the lowest AOT concentrations (<5 wt.%), relatively stable emulsions are present, region E; partial phase separation occurred after 24 hours. The region $LC + E$ represents an emulsified solution in which birefringence was noted.

2. AOT/Water/Benzene at $45.0 \pm 0.2^\circ\text{C}$

Figure 29 shows the observed phase behavior of AOT/water/benzene. The same phase regions as observed in the cyclohexane case are apparent, but the extent of the regions changes. The smaller L_2 region in benzene is evidence that AOT solubilizes less water in this solvent. However, previous work has suggested that the L_2 domain should be much larger in benzene.²⁵⁸ It is seen that the AOT concentration which solubilizes the highest wt.% water is larger in benzene than in cyclohexane. At the lower AOT concentrations (17 - 46 wt.%), the LC region solubilizes less benzene than cyclohexane. This suggests that solvent penetration is detrimental to the growth of stable AOT lamellar liquid crystals, as was postulated in the previous chapter for AOT w/o microemulsions.

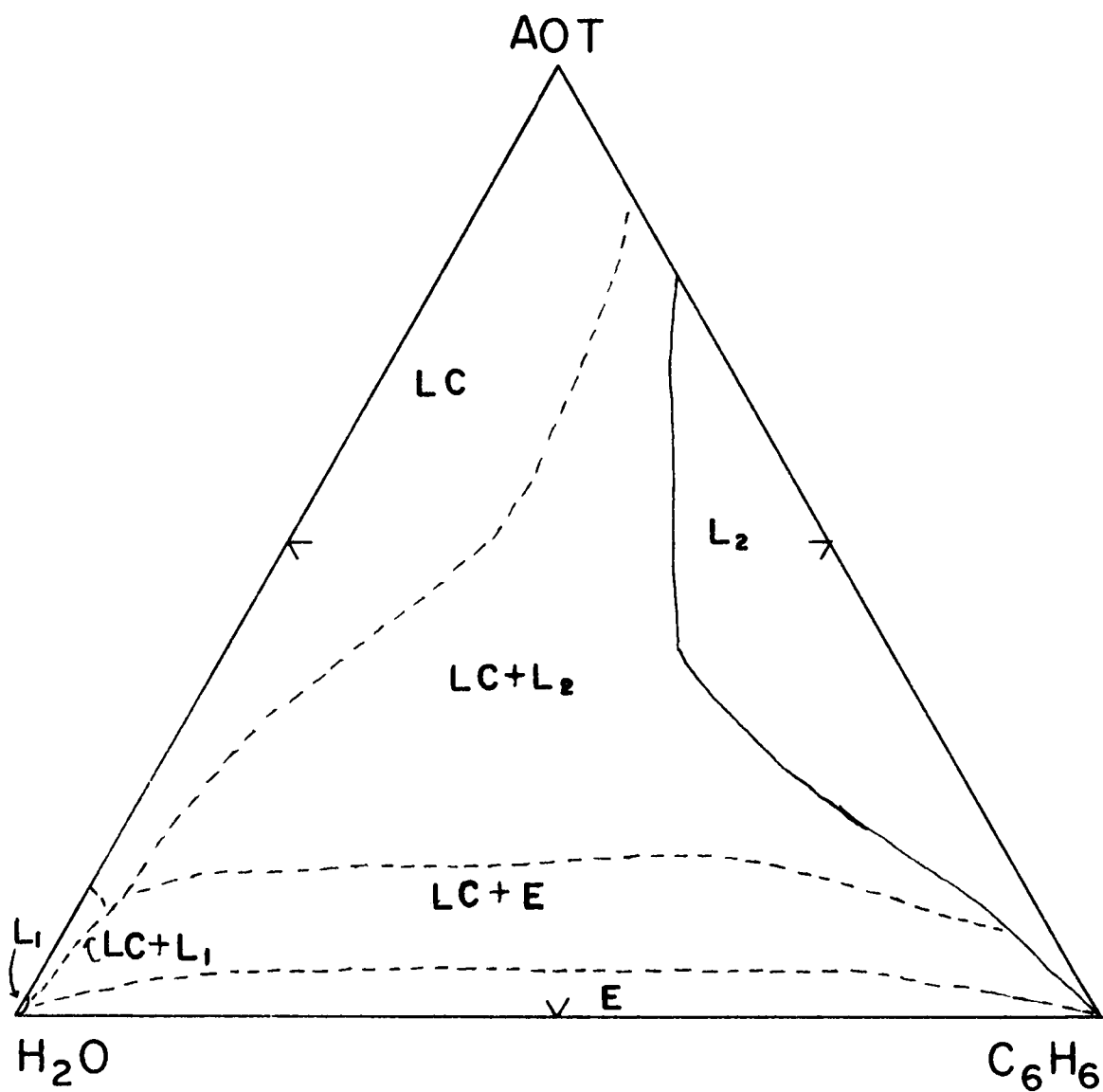


Figure 29. Ternary phase diagram of AOT/water/benzene at $45.0 \pm 0.2^\circ\text{C}$.

D. AEROSOL TR PHASE BEHAVIOR

1. ATR/Water/Cyclohexane at $45.0 \pm 0.2^\circ\text{C}$

The water-solubilizing capacity of ATR in cyclohexane is much less than that observed for AOT (see L_2 region in Figure 30). At 25 wt.% ATR, 7 wt.% water is solubilized. This corresponds to an R of 9.1. Thus, no w/o microemulsions are present, only inverted micelles. The most dominant region of this phase diagram is the emulsion region, E. These emulsions are more stable than AOT emulsions; very little, if any, phase separation occurs after 24 hours. No L_1 region was directly observed; the lowest ATR concentration studied was 0.5 wt.%. A large liquid crystalline domain is apparent along the ATR/water axis. Although this region is designated LC, in much of this domain and in the LC + E region, there is a white amorphous solid present. Since solid AOT has an hexagonal mesomorphic structure, it is likely that the same is true for solid ATR. Thus, this solid mass is probably ATR hexagonal liquid crystals.

2. ATR/Water/Benzene at $45.0 \pm 0.2^\circ\text{C}$

ATR is less soluble in benzene than in cyclohexane (see Figure 31). At the highest ATR concentrations, water is necessary for the L_2 solution to be present. The rest of the ternary phase diagram is essentially the same as in the cyclohexane case.

3. ATR/2-Propanol/Water/Cyclohexane at $45.0 \pm 0.2^\circ\text{C}$

The phase behavior of ATR changes dramatically in the pseudo-ternary representation, Figure 32, when 2:3 (w/w) ATR/2-propanol is used as the emulsifier. The main feature in this phase diagram is an

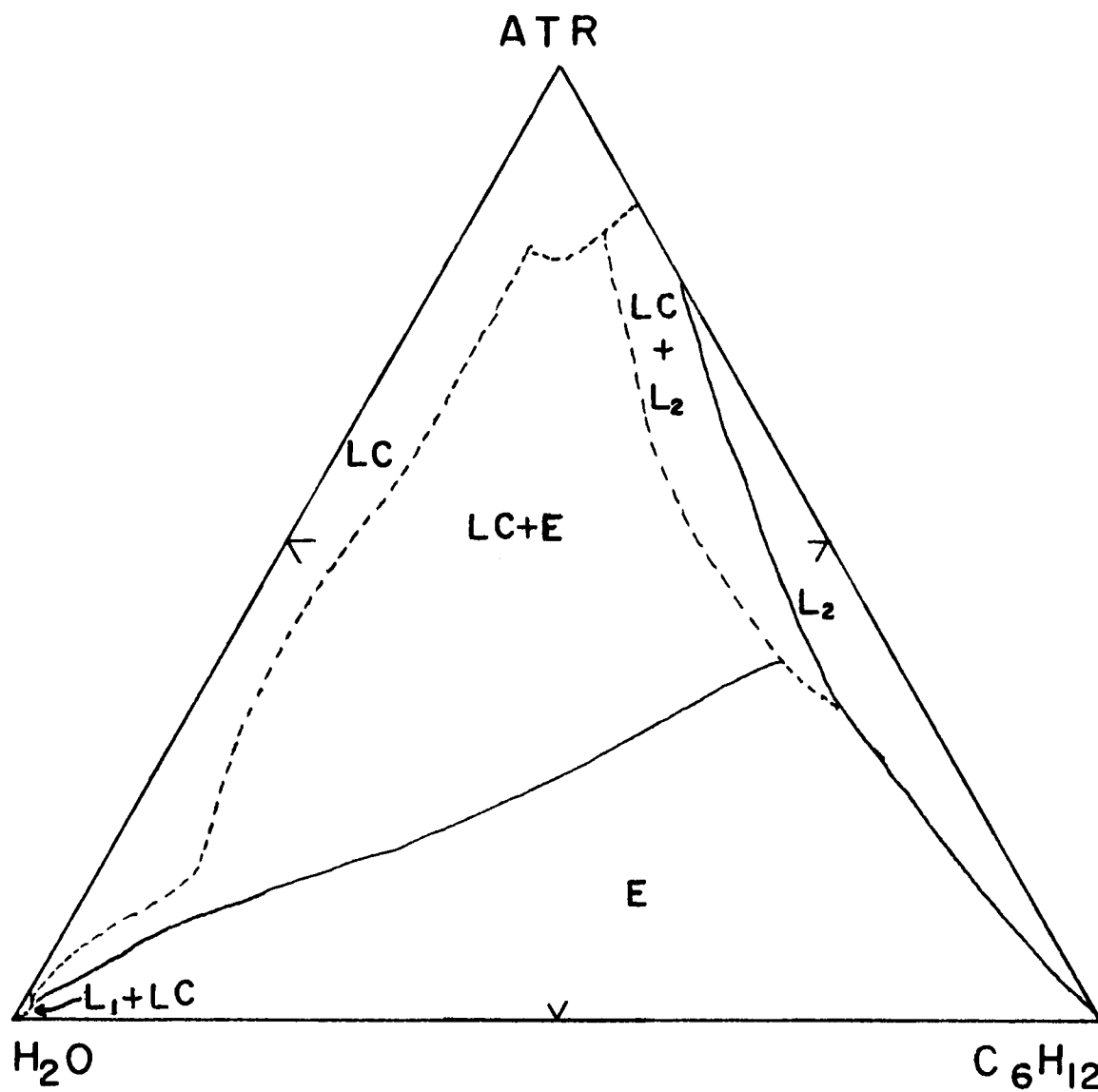


Figure 30. Ternary phase diagram of ATR/water/cyclohexane at $45.0 \pm 0.2^\circ\text{C}$.

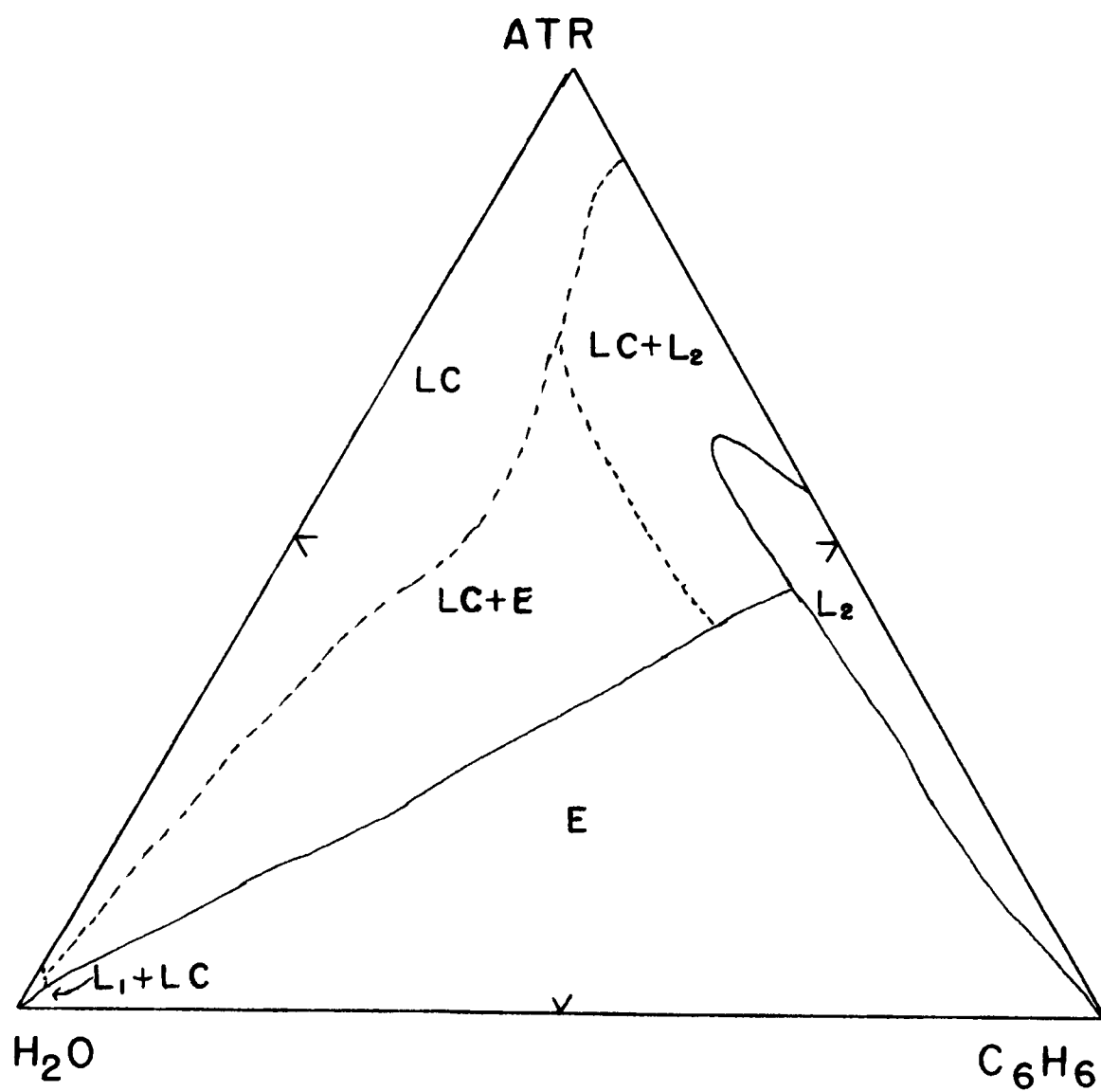


Figure 31. Ternary phase diagram of ATR/water/benzene at $45.0 \pm 0.2^\circ\text{C}$.

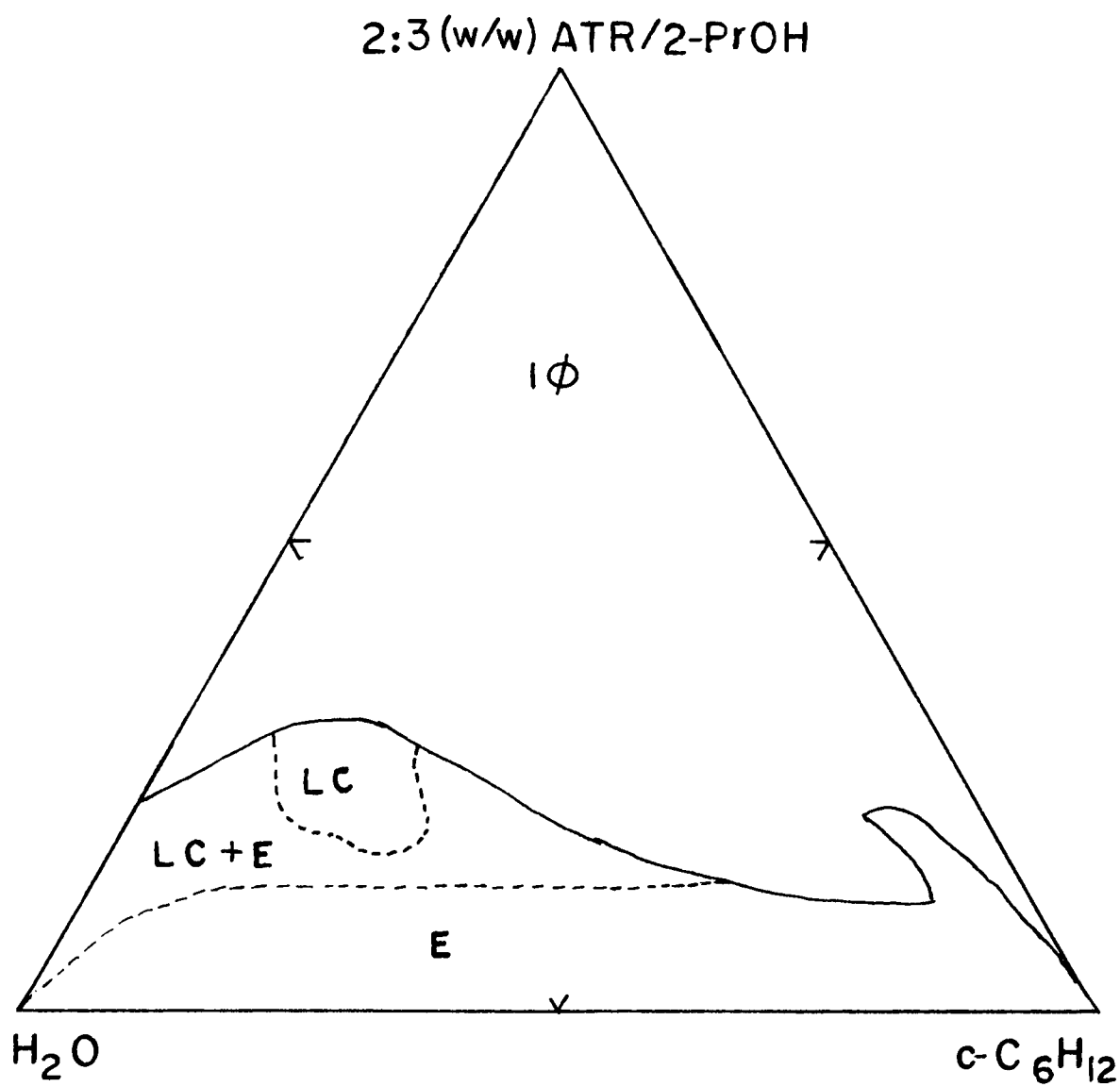


Figure 32. Pseudoternary phase diagram of ATR/2-propanol/water/cyclohexane at $45.0 \pm 0.2^\circ\text{C}$.

isotropic one phase region, 1ϕ , which extends from the water to the oil axis. The nature of this phase has been studied by ^1H and ^{13}C nmr. The results will be presented in section F of this chapter. A small birefringent region, LC, which is not adjacent to any axis, is observed. Curiously, the emulsion region, E, extends somewhat towards the ATR/alcohol apex at low water concentrations. In order for the phase rule not to be violated, different structures must be present on either side of this finger. The solutions to the left of this finger were blue translucent to the eye.

4. ATR/2-Propanol/Water/Benzene at $45.0 \pm 0.5^\circ\text{C}$

Again, the major feature of the pseudoternary phase diagram, Figure 33, using an identical emulsifier composition, is the 1ϕ region. However, this region is observed at higher emulsifier concentrations than in the cyclohexane case. At the same time, the E region increases in size. An LC region is seen which is much smaller than that noted in the cyclohexane case. A two phase region, $\text{LC} + \text{L}_1$, extends from the water apex. The L_1 designation is used because of its location in the phase diagram. This region is undoubtedly present in the cyclohexane case but was apparently mistaken for an emulsion. Alternatively, this designation is incorrect while the previous one was correct. It will suffice to say that there exists more than one phase in this region, and that there is evidence of birefringence. Another two phase domain, 2L , is observed near the ATR/alcohol corner. These systems are initially blue turbid in appearance; a small amount of a milky liquid is found at the bottom of the test tube after one week of storage.

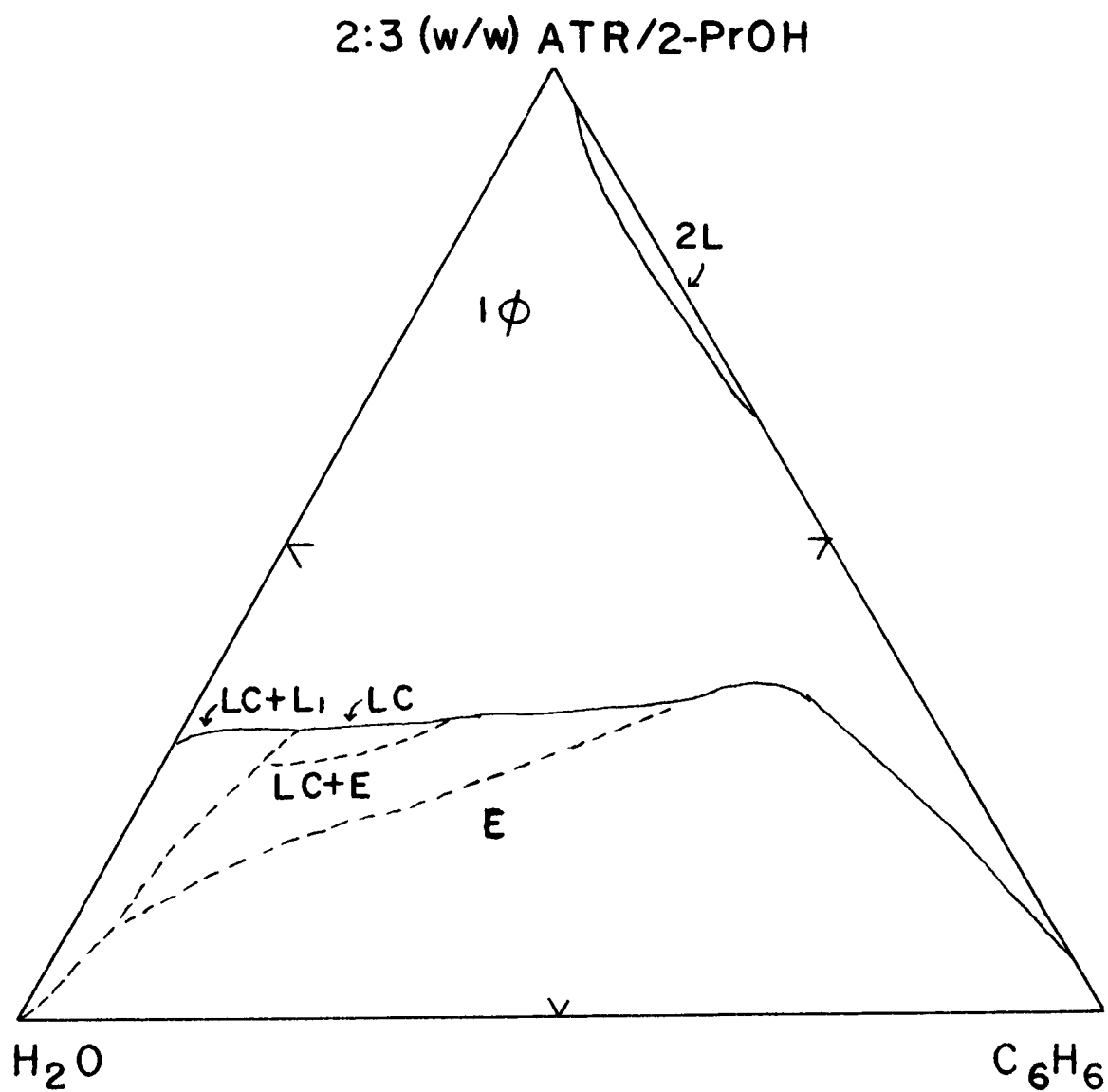


Figure 33. Pseudoternary phase diagram of ATR/2-propanol/water/benzene at $45.0 \pm 0.5^\circ C$.

E. AEROSOL IB PHASE BEHAVIOR

1. AIB/Water/Cyclohexane at $45.0 \pm 0.2^\circ\text{C}$

Since AIB is a hydrophilic surfactant, it is not surprising to see an o/w microemulsion region, L_1 , in its ternary phase diagram, Figure 34. AIB is miscible with cyclohexane up to 60 wt.% surfactant. However, addition of very small amounts of water caused needles of AIB to precipitate from solution. This phase diagram is dominated by a two phase region, $2L$. When these solutions are shaken, emulsions form, but these separated into two phases within one to two hours. Crystalline AIB is observed at the highest surfactant concentrations. A narrow birefringent region, LC , is seen extending from the AIB/water axis. The visual texture of these solutions is similar to that of AOT lamellar liquid crystals, although their exact nature needs to be determined experimentally.

2. AIB/Water/Benzene at $45.0 \pm 0.5^\circ\text{C}$

Changing the oil from cyclohexane to benzene causes a dramatic change in AIB's phase behavior (see Figure 35). AIB's solubility in benzene is about one-half what it is in cyclohexane. In addition, AIB now exhibits a large water-solubilizing capacity; a 50 wt.% AIB solution in benzene will take up almost 20 wt.% water. Since benzene is a more polar and polarizable solvent,²²⁵ the formation of small aggregates is probably favored in benzene, but not in cyclohexane. In addition, a large liquid crystalline phase is now observed in the middle of the ternary phase diagram.

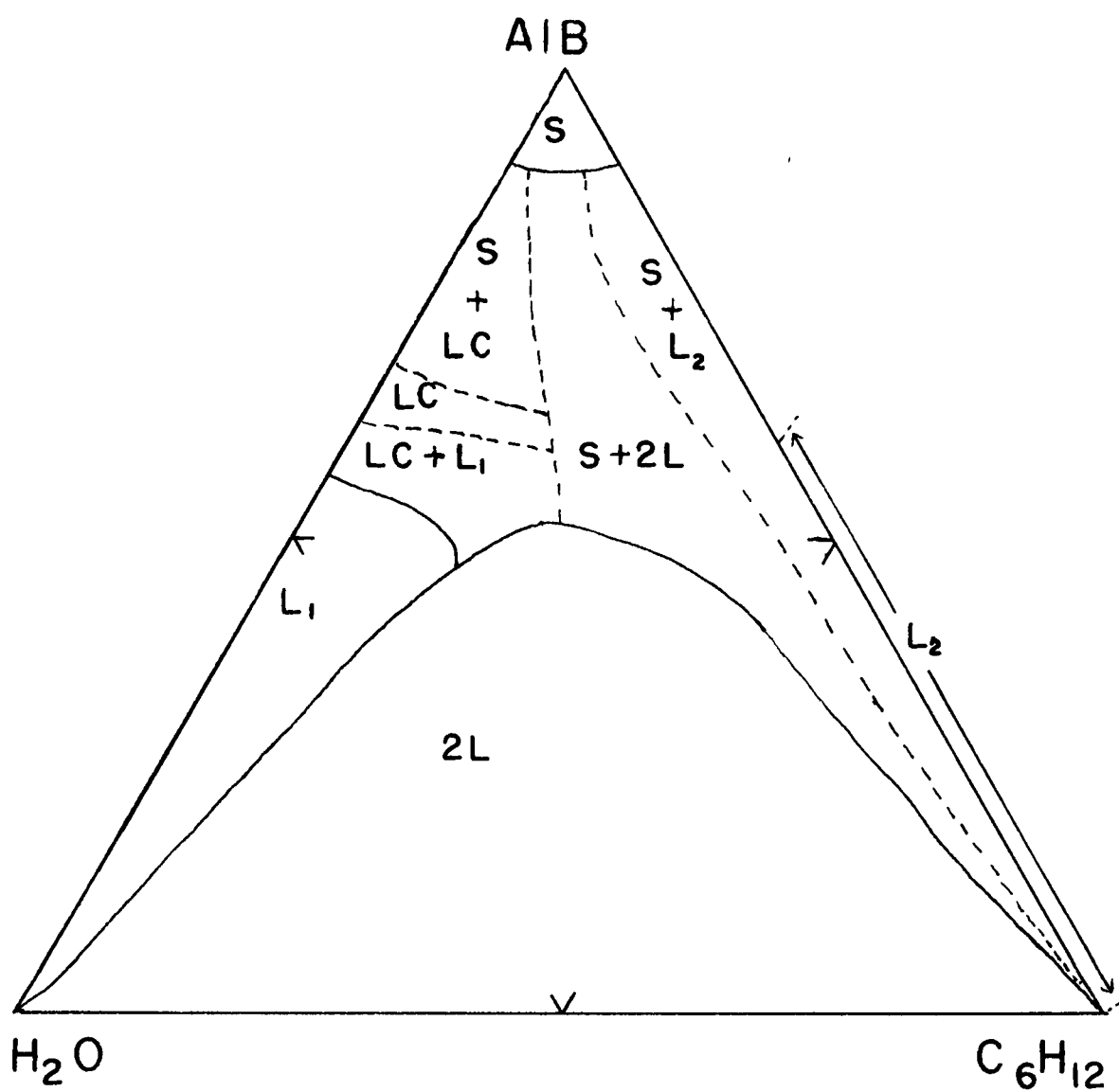


Figure 34. Ternary phase diagram of AIB/water/cyclohexane at $45.0 \pm 0.2^\circ\text{C}$.

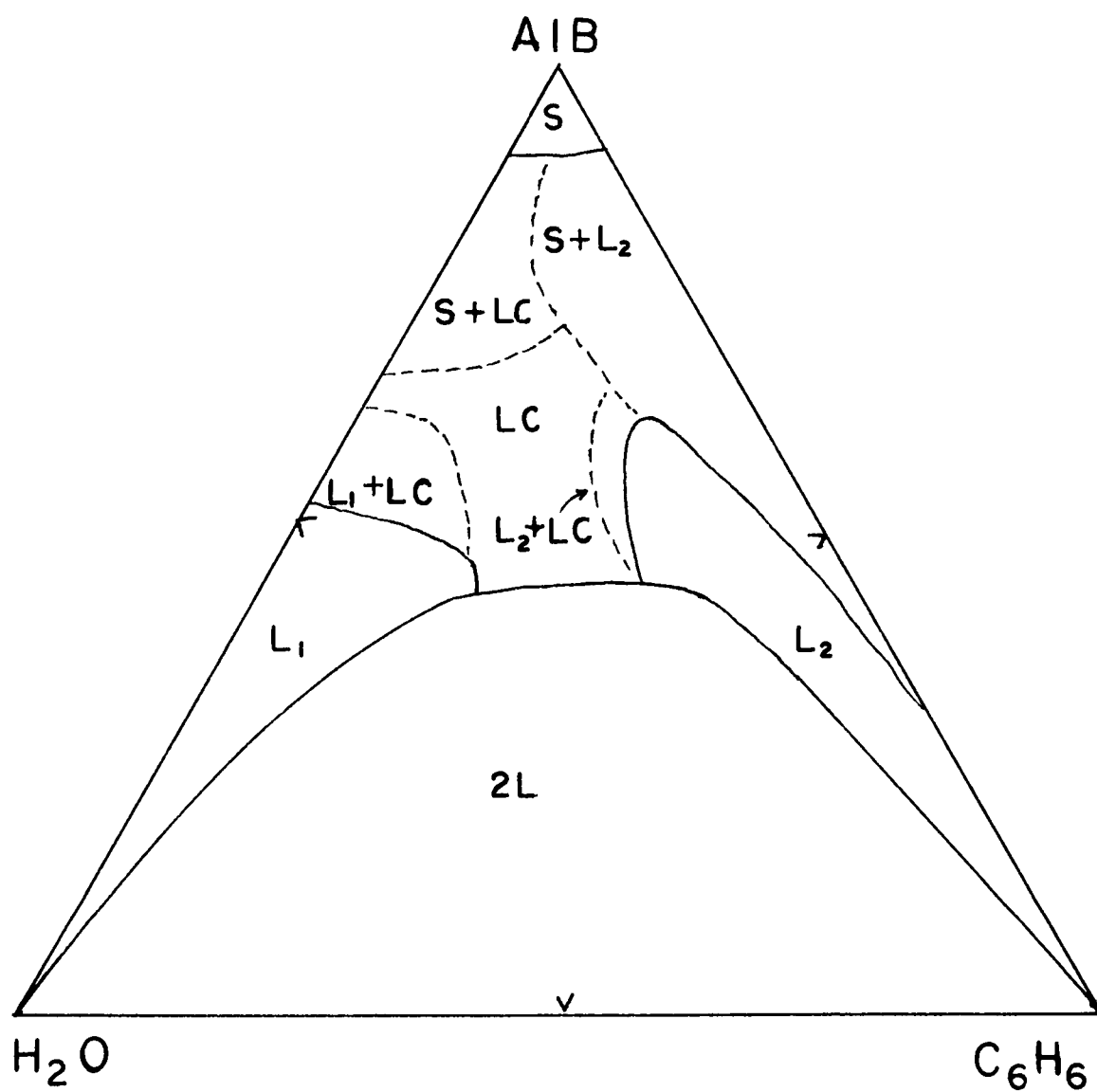


Figure 35. Ternary phase diagram of AIB/water/benzene at $45.0 \pm 0.5^\circ\text{C}$.

3. AIB/1-Hexanol/Water/Cyclohexane at $45.0 \pm 0.5^\circ\text{C}$

Figure 36 shows the pseudoternary phase diagram of this system using 2:3 (w/w) AIB/1-hexanol as the emulsifier. The phase behavior is greatly simplified over the case where no alcohol is present. Two main regions are observed: a two phase solution, 2L; and a one phase isotropic region, 1 ϕ . At the emulsifier apex, liquid crystalline phases are present.

4. AIB/1-Hexanol/Water/Benzene at $45.0 \pm 0.5^\circ\text{C}$

The features of this phase diagram, Figure 37, are virtually identical to the cyclohexane case, except that the 1 ϕ region in benzene extends to smaller water contents than it does in cyclohexane at low emulsifier concentrations.

F. NMR STUDIES OF ATR/2-PROPANOL 1 ϕ REGIONS

A study of the ATR/2-propanol/water/hydrocarbon 1 ϕ solutions using ^{13}C and ^1H nmr was undertaken in anticipation that the nature and extent of the various types of possible association species (i.e., w/o or o/w aggregates, ion pairs, bicontinuous microemulsions, etc...) could be identified. Specifically studied in the ^{13}C spectra were the chemical shifts of the methyl and methine resonances of 2-propanol, the hydrocarbon solvents, and ATR's carbonyl groups. ATR's hydrocarbon tail is a mixture of branched alkyl chains; a complex shielding pattern is observed from which no information is gained. In the ^1H nmr spectra, attention was paid to the hydroxyl chemical shift (only one peak was observed at all water concentrations), the methyl resonance, and the solvent resonances. Attempts were made to measure

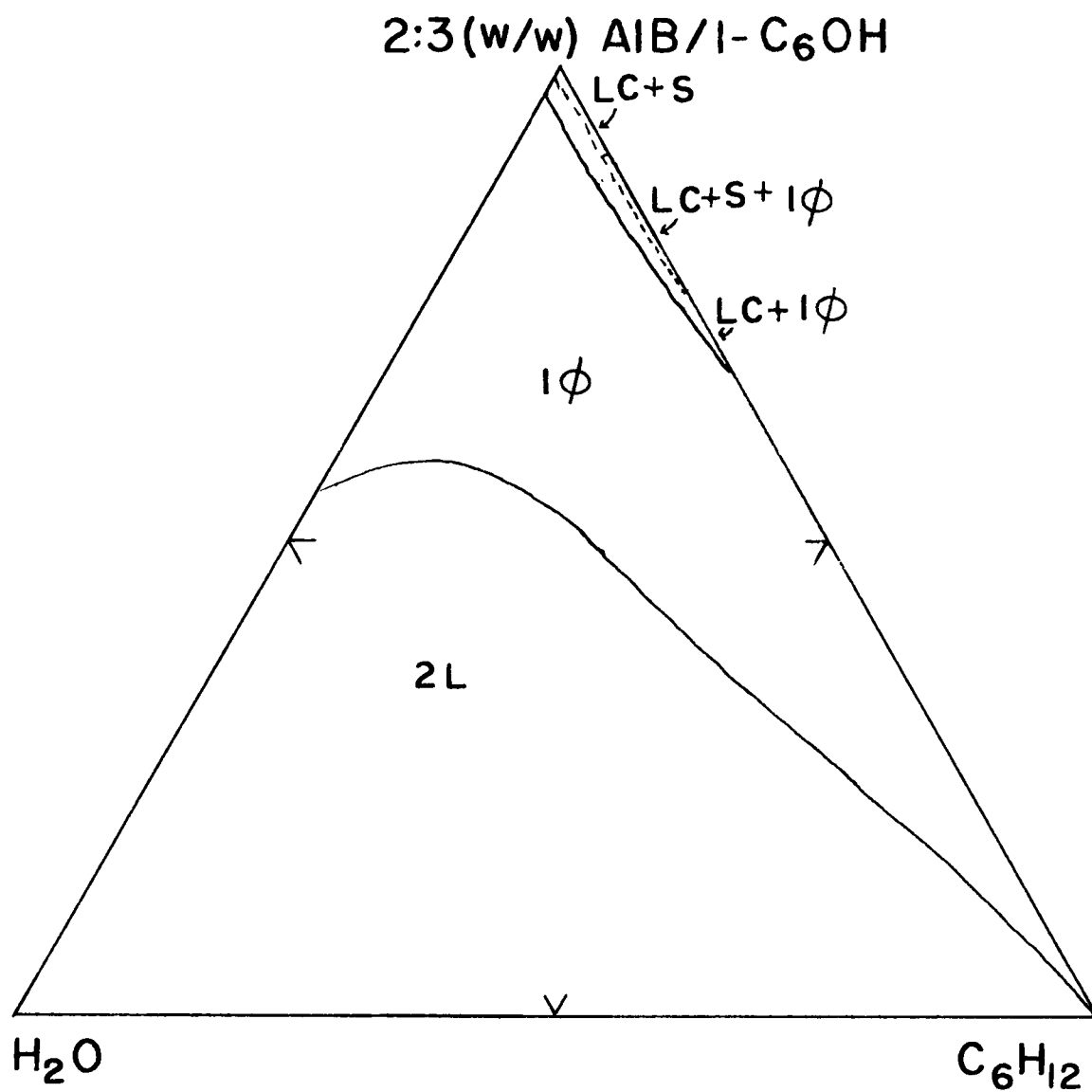


Figure 36. Pseudoternary phase diagram of AIB/1-hexanol/water/cyclohexane at $45.0 \pm 0.5^\circ\text{C}$.

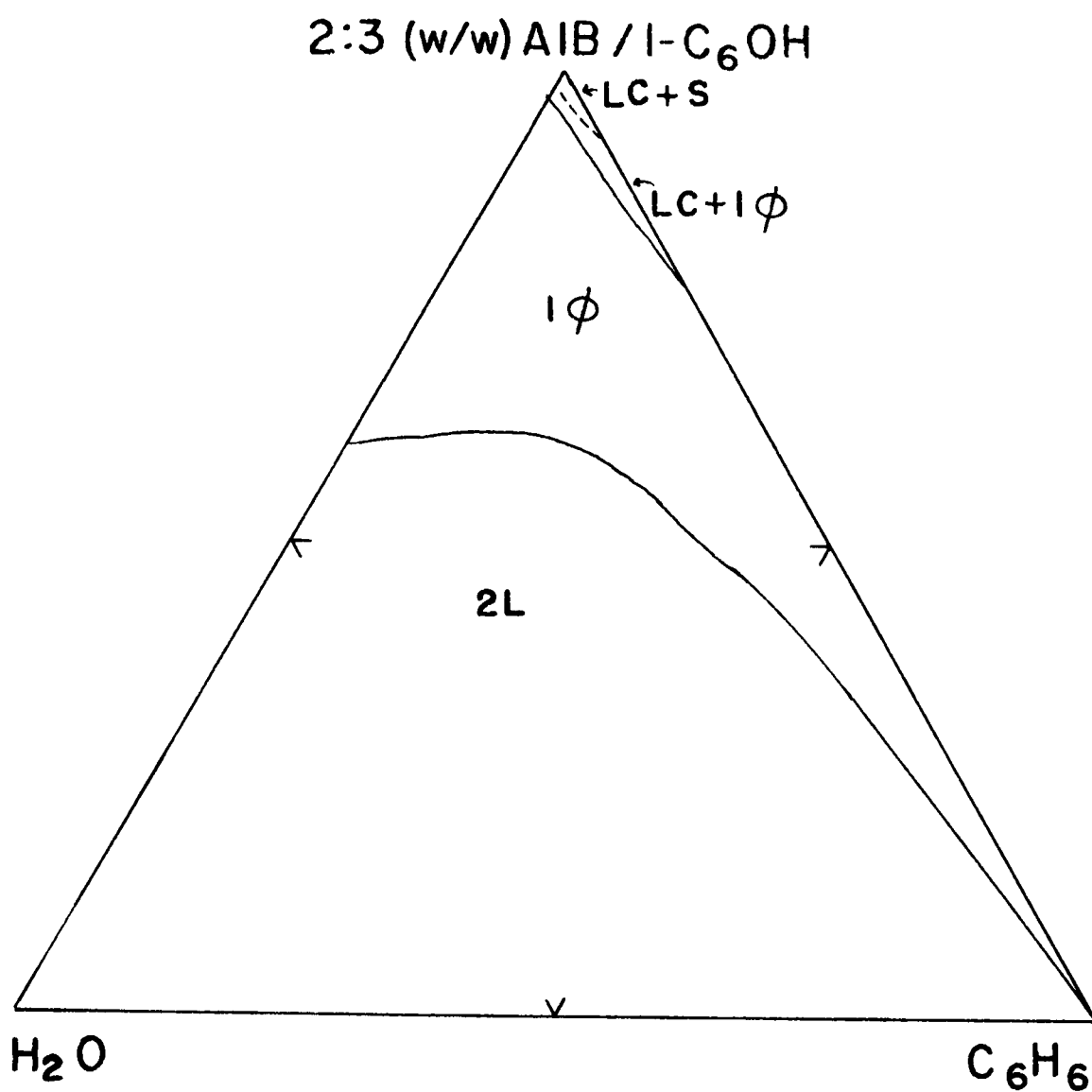


Figure 37. Pseudoternary phase diagram of AIB/1-hexanol/water/benzene at $45.0 \pm 0.5^\circ\text{C}$.

the ^{13}C $\Delta\nu_{1/2}$ of the alcohol's methine resonance. Lund and Holt²⁶⁰ have shown that this parameter decreases at the boundaries where structural transitions occur. However, the scatter in $\Delta\nu_{1/2}$ in this work was so large that no clear pattern could be discerned.

Runs were made at three constant emulsifier concentrations (40, 60, and 80 wt.%) for both the cyclohexane and benzene solutions, varying the hydrocarbon/water ratio. In this section, an attempt will be made to rationalize the chemical shift behavior in terms of recognizable association species.

1. ATR/2-Propanol/Water/Benzene

The ^1H nmr results will be discussed first. The hydroxyl resonance is found at $\delta 4.00$ in the absence of any added water. Assuming any residual water is negligible, Equation 51 can be used to calculate

$$\delta_{\text{obs}} = X_{\text{hb}} \delta_{\text{hb}} + X_{\text{nhb}} \delta_{\text{nhb}} \quad (51)$$

the mole fraction of alcohol involved in hydrogen-bonding. The subscripts in Equation 51 refer to hydrogen-bound (hb) and nonhydrogen-bound (nhb) alcohol. δ_{hb} is taken as the experimentally determined value for neat 2-propanol: 5.12 ppm (a doublet). The alcohol hydroxyl resonance for a dilute alcohol solution in benzene was found to occur at 2.80 ppm; this was used for δ_{nhb} . Calculation yields $X_{\text{hb}} = 0.52$; half of the alcohol is hydrogen-bound, either to itself or to ATR. Since 2-propanol is very soluble in benzene, the nonhydrogen-bonded half is dispersed in the oil-continuous phase, along with some of the hydrogen-bonded alcohol.

Figure 38 shows the changes which occur in the hydroxyl and

Figure 38. ^1H chemical shift changes of the ATR/2-propanol/water/benzene 1 ϕ system. a. Hydroxyl resonance. b. 2-Propanol methyl resonance.

Circles: 40 wt.% emulsifier; triangles: 60 wt.% emulsifier;
squares: 80 wt.% emulsifier.

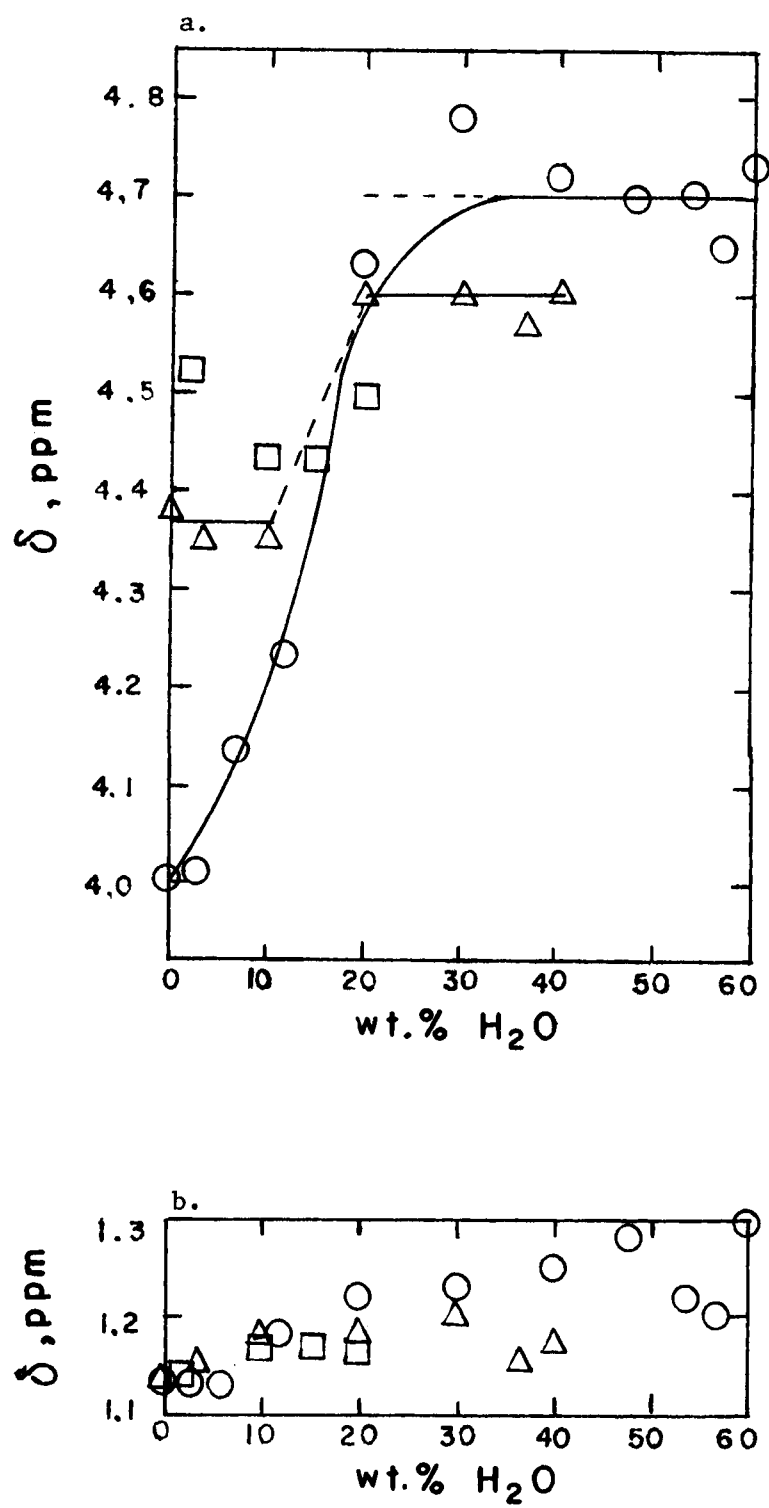


Figure 38.

methyl resonances when water is added to the system. Interpretation of the hydroxyl's chemical shifts (Figure 38a) becomes more complex because both water and alcohol contribute to this resonance. For 40 wt.% emulsifier, this resonance moves steadily downfield until the water content reaches 20 wt.%. A further increase in the water content results in little change; the chemical shift maintains a plateau value of 4.70 ± 0.05 ppm. Upon increasing the emulsifier content to 60 wt.%, the range of the chemical shift change decreases. Before any water is added, $\delta(\text{OH})$ is found at 4.38 ppm, indication that more 2-propanol is involved in hydrogen-bonding than at 40 wt.% emulsifier. $\delta(\text{OH})$ is constant in this case over the range 0 - 10 wt.% water; between 20 - 40 wt.% water, a higher value of 4.60 ppm is observed. At 80 wt.% emulsifier, $\delta(\text{OH})$ is further downfield at low water concentrations; the chemical shift moves slightly upfield when water is added, then back downfield. The methyl ^1H chemical shift changes are found in Figure 38b. For 40 wt.% emulsifier, $\delta(\text{Me}_2)$ shows a small downfield movement as water is added. This doublet's δ is practically constant at higher emulsifier ratios when water is added.

2-Propanol's ^{13}C chemical shift changes are plotted in Figure 39. Analogous to the hydroxyl resonances, the ^{13}C methine δ moves downfield as water is added (Figure 39a). This resonance is, for the most part, shifted upfield as the emulsifier content increases. In Figure 39b are presented the changes in the methyl carbons' chemical shifts. There is observed a steady, almost linear, upfield change as water is added at all three emulsifier concentrations.

Figure 40 shows the ^{13}C chemical shift changes of ATR's

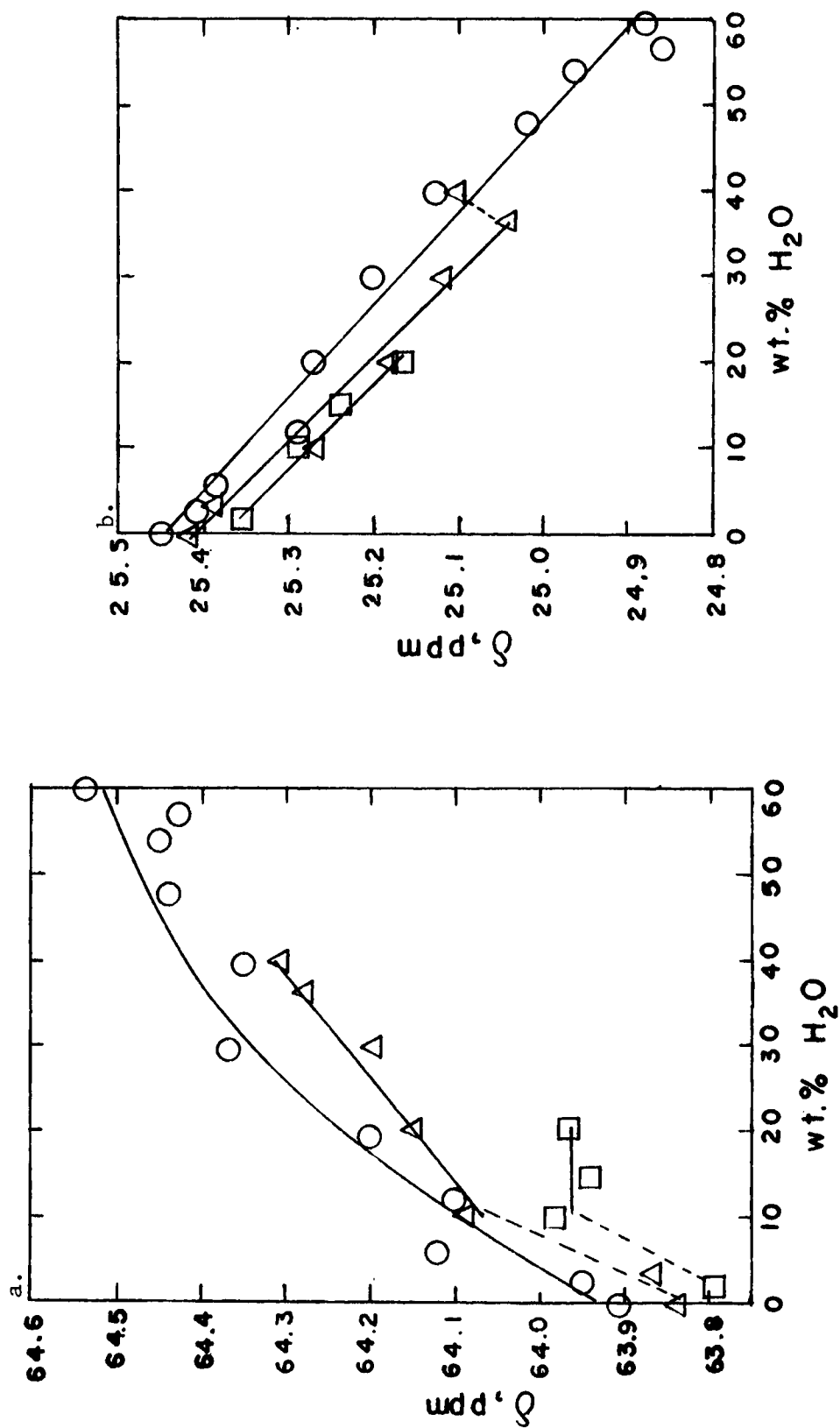


Figure 39. ^{13}C chemical shift changes of 2-propanol in the ATR/2-propanol/water/benzene 1 ϕ system. a. Methine. b. Methyl.

Circles: 40 wt.% emulsifier; triangles: 60 wt.% emulsifier; squares: 80 wt.% emulsifier.

Figure 40. ^{13}C chemical shift changes of ATR's carbonyls in the ATR/2-propanol/water/benzene 1 ϕ system. a. Carbon 2'. b. Carbon 2.

Circles: 40 wt.% emulsifier; triangles: 60 wt.% emulsifier;
squares: 80 wt.% emulsifier.

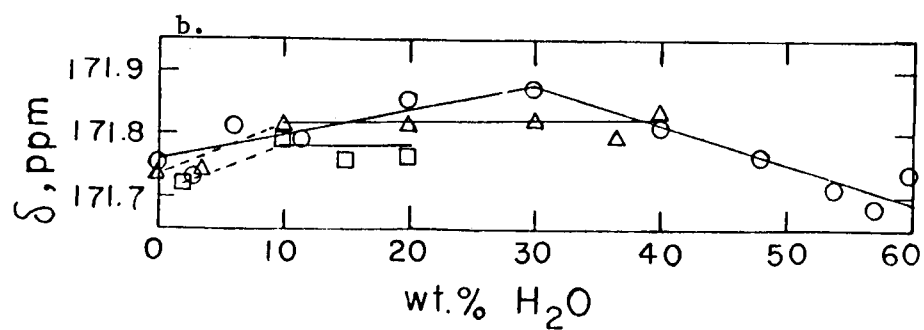
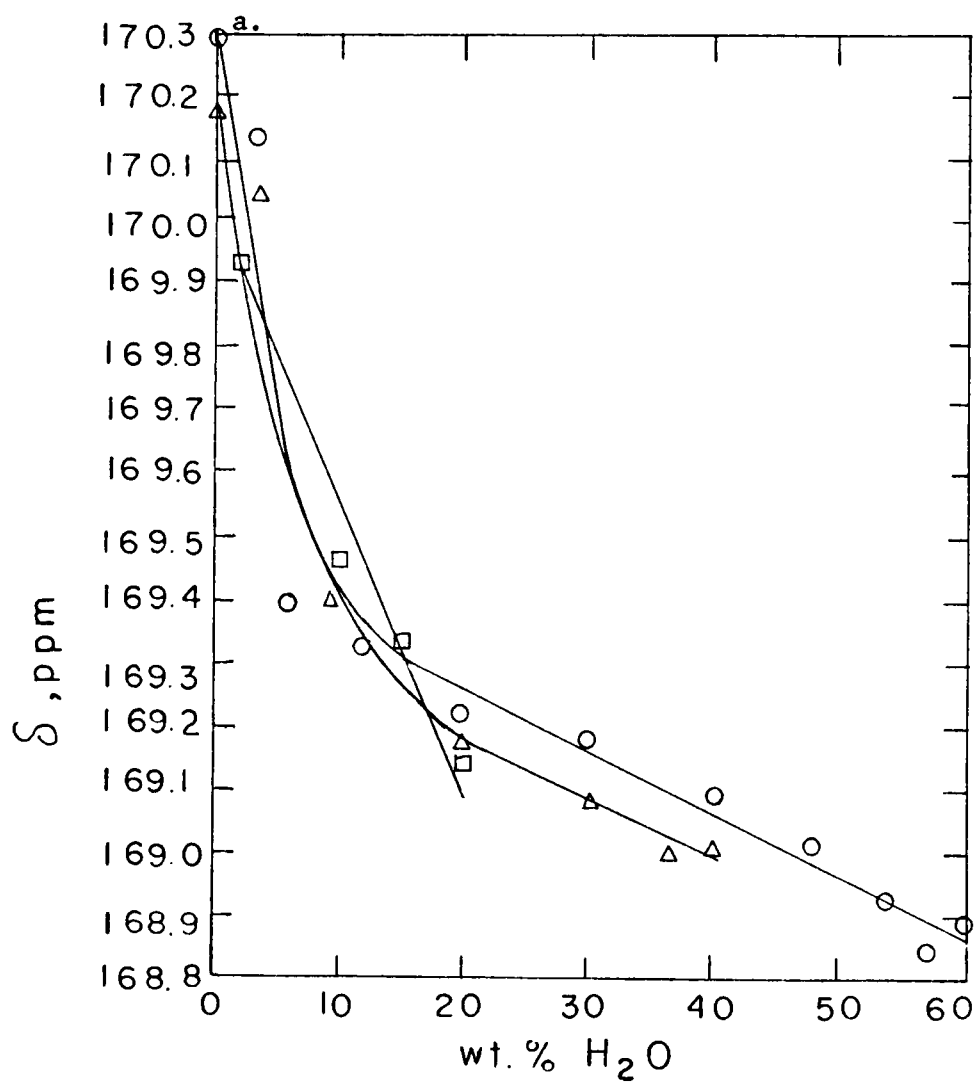


Figure 40.

carbonyls. $\delta(\text{C-2}')$, for the 40 wt.% emulsifier case, exhibits a sharp upfield shift as the wt.% water is increased to 6% [Figure 40a (p 138)]; further addition of water results in a slower increase in the shielding of this carbon. Similar behavior is observed at higher emulsifier contents, except that no break is observed in the 80 wt.% line. When water is added to the 40 wt.% emulsifier system, $\delta(\text{C-2})$ shows a slight downfield shift up to 30 wt.% water, then slowly moves upfield [Figure 40b (p 138)]. In going to a higher emulsifier content, $\delta(\text{C-2})$ remains constant over the high water regions.

The ^1H and ^{13}C chemical shifts of benzene were recorded also, but not shown here. Benzene's ^{13}C δ is virtually constant for all the runs ($\delta = 128.60$ ppm). Its proton resonance varies in value between 7.05 and 7.22 ppm, generally at lower field at the higher alcohol and water concentrations.

Analysis of these results is not straightforward. Before any water is added there could exist in solution: (1) ATR inverted micelles with alcohol solubilized in their core (alcohol-in-oil microemulsions?); (2) small aggregates of ATR/2-propanol; (3) monomeric ATR solvated by up to seven 2-propanol molecules (the molar ratio of 2-propanol to ATR is 14.6). At least half of the alcohol is dispersed in the benzene-continuous phase. The ^{13}C δ behavior of ATR's carbon 2' is very similar to that noted for AOT inverted micelles. This suggests that ATR aggregates of some size are present. As the emulsifier content is increased, the alcohol's ^1H hydroxyl and ^{13}C methine resonances both approach their values in neat alcohol solution (5.12, this work, and 63.7, ^{213} respectively). At the highest emulsifier ratio, there may also be oil-in-alcohol microemulsions.

The downfield change in the ^1H hydroxyl and ^{13}C methine chemical shifts as water is added could indicate a gradual change from an oil-continuous to a water-continuous solution; for 40 wt.% emulsifier, the region 20 to 60 wt.% water is likely water-continuous based on the ^1H hydroxyl plateau observed in Figure 38a (134). For the 60 wt.% emulsifier run, there appears to be a distinct change from an oil-continuous to a water-continuous solution. Since 2-propanol is very soluble in both benzene and water, much of the alcohol will be in the continuous phase. Thus, these results do not obviate the presence of small ATR aggregates in a ternary solution of benzene, water and 2-propanol.

The continued upfield movement of $\delta(\text{C-2}')$ as water is added is unexpected, as is the similar behavior of $\delta(\text{C-2})$ in the 40 wt.% emulsifier run between 30 and 60 wt.% water. Note also that in all of the figures, the chemical shift in the absence of benzene is more downfield than that when a small amount of benzene is present for the 40 and 60 wt.% emulsifier runs. This small region could be the realm of true ATR normal micelles in water (or o/w microemulsions). If this is true, further addition of benzene breaks down the relatively large micelles. Smaller aggregates are formed until enough benzene is present to promote formation of inverted micelles.

These results are inconclusive. ATR aggregates of some sort appear to be present, but the size and extent of these aggregates cannot be determined using nmr alone.

2. ATR/2-Propanol/Water/Cyclohexane

The chemical shift changes that were observed in this system are

shown in Figures 41 to 44. Except for the ^1H hydroxyl resonance, Figure 41a, and the oil's ^{13}C chemical shift, Figure 44, the graphs are analogous to those observed in the benzene case and will not be discussed here.

$\delta(\text{OH})$ is found at 4.53 ppm in the absence of any added water for the 40 wt.% emulsifier content. Since 2-propanol is less soluble in cyclohexane than in benzene, alcohol is more likely to be solubilized in the core of an inverted micelle (alcohol-in-oil microemulsion?) in this case. Addition of water displaces the alcohol from the core and at a concentration of 12 wt.% water, $\delta(\text{OH})$ begins to behave as it did in the benzene case.

Whereas benzene's ^{13}C resonance did not change upon addition of water, that of cyclohexane shows a general upfield shift as the wt.% water is increased, Figure 44. This behavior is surprising but could be the result of cyclohexane's environment becoming less polar, perhaps via solubilization in an o/w microemulsion formed at the highest wt.%'s of water.

G. CONCLUSIONS

The phase behavior of AOT, ATR, and AIB was studied in cyclohexane and benzene at 45°C. AOT solubilizes less water in its L_2 region in benzene than in cyclohexane. ATR's water-solubilization capacity is less than AOT's in both solvents. AIB shows a large L_1 region in cyclohexane and benzene. In the latter solvent, an L_2 region was observed in the AIB phase diagram, probably containing small aggregates. Emulsion stability appears to decrease in the following order:

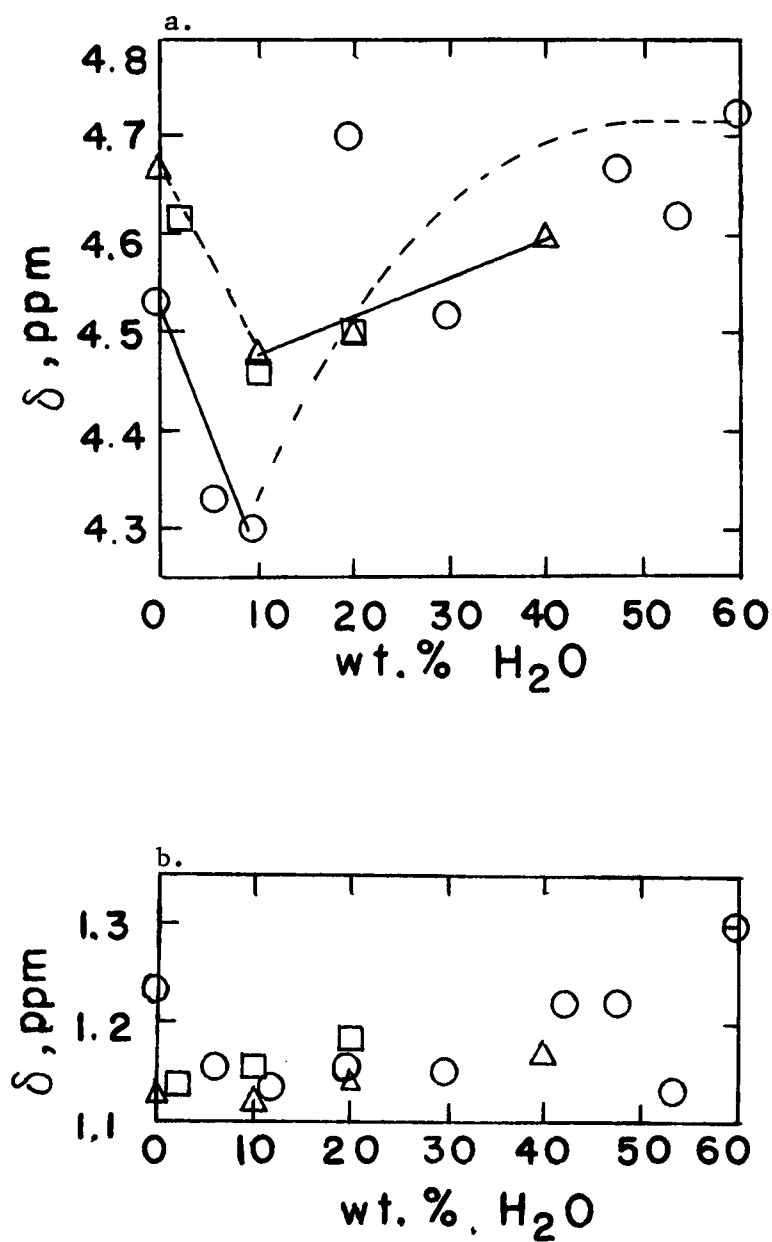


Figure 41. ^1H chemical shift changes of the ATR/2-propanol/water/cyclohexane 1ϕ system. a. Hydroxyl resonance. b. 2-Propanol methyl resonance.

Circles: 40 wt.% emulsifier; triangles: 60 wt.% emulsifier; squares: 80 wt.% emulsifier.

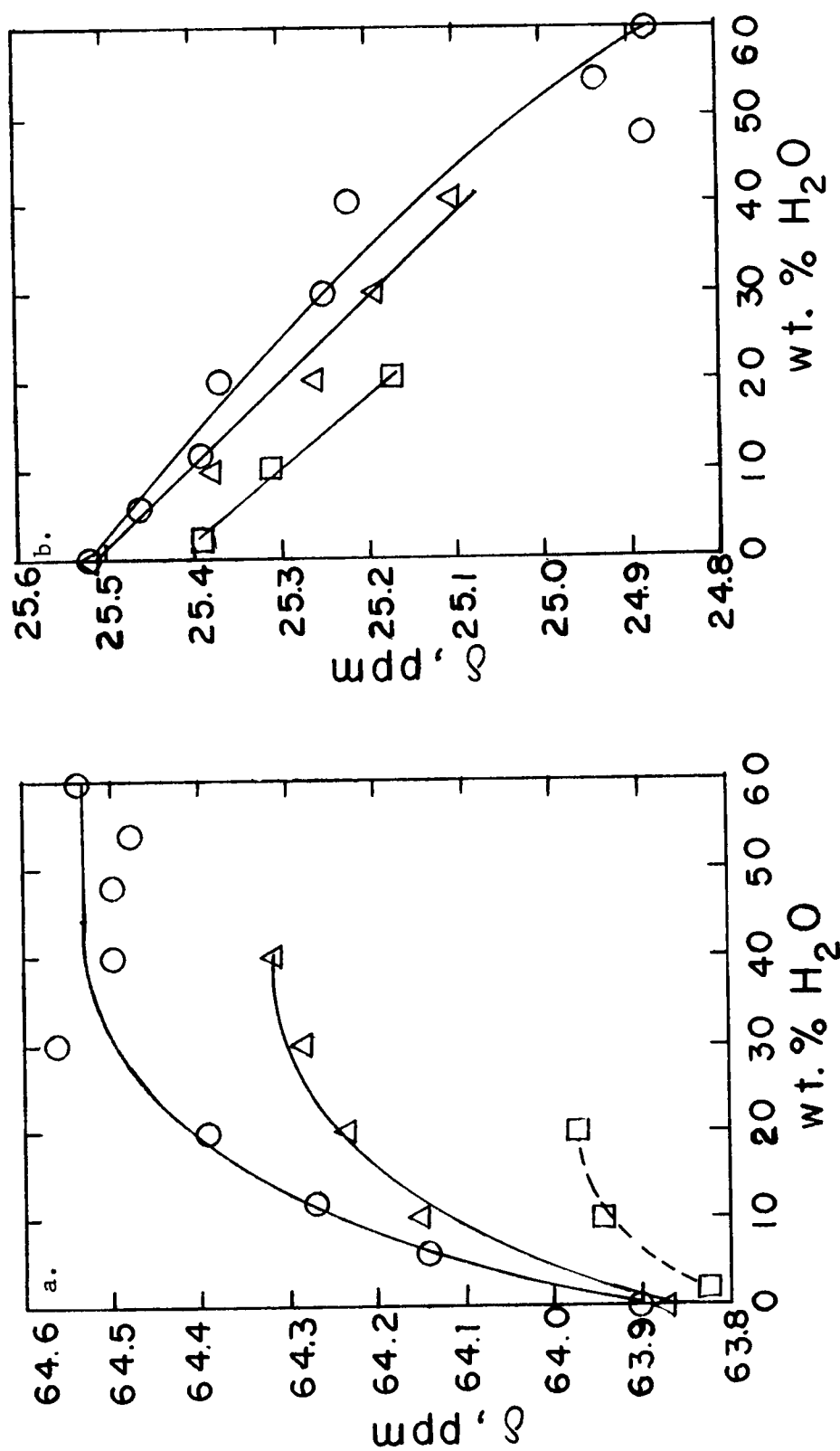


Figure 42. ^{13}C chemical shift changes of 2-propanol in the ATR/2-propanol/water/cyclohexane 1ϕ system. a. Methine. b. Methyl.

Circles: 40 wt.% emulsifier; triangles: 60 wt.% emulsifier; squares: 80 wt.% emulsifier.

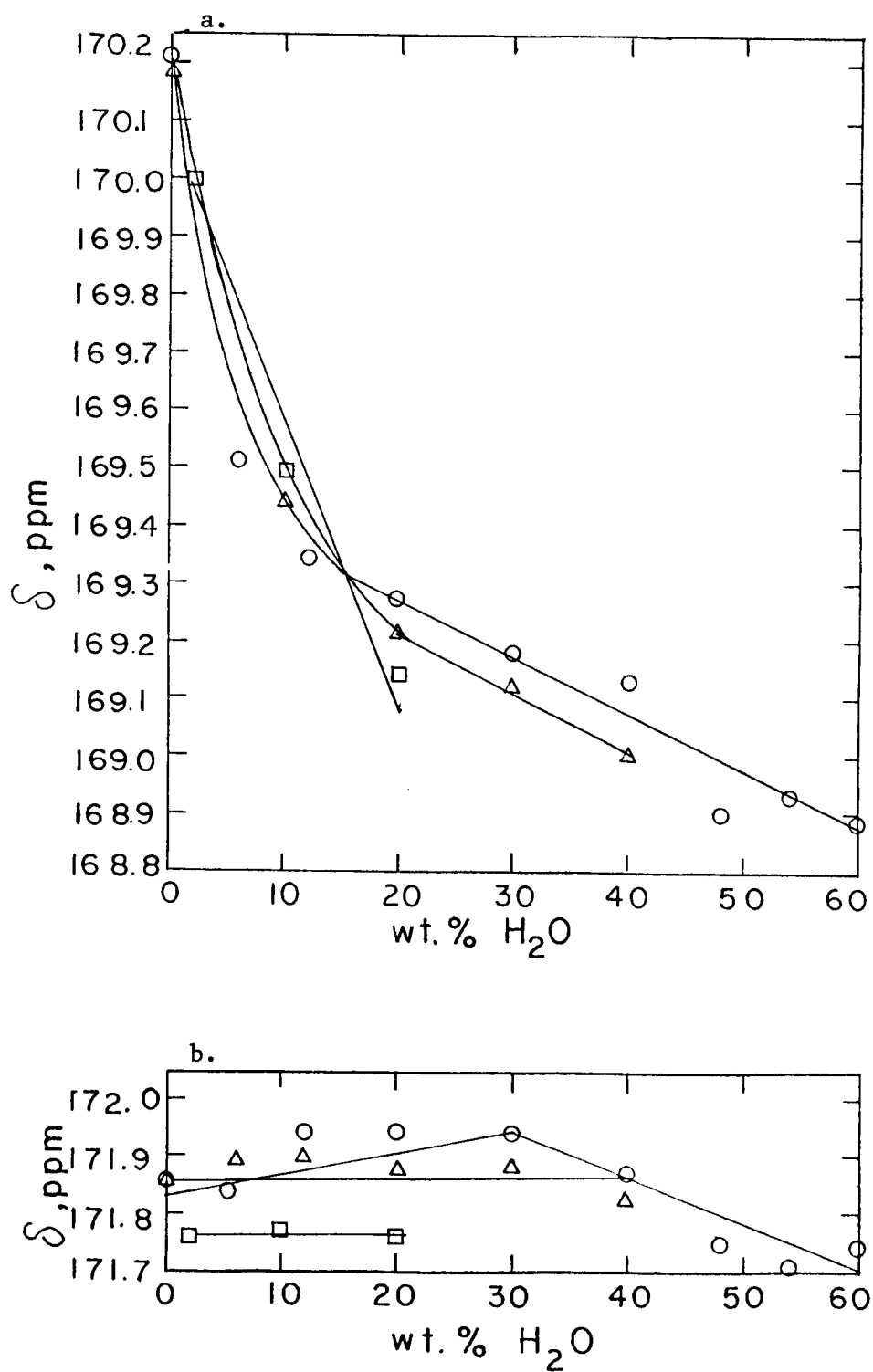


Figure 43. ^{13}C chemical shift changes of ATR's carbonyls in the ATR/2-propanol/water/cyclohexane 1:1 system. a. Carbon 2'. b. Carbon 2.

Circles: 40 wt.% emulsifier; triangles: 60 wt.% emulsifier; squares: 80 wt.% emulsifier.

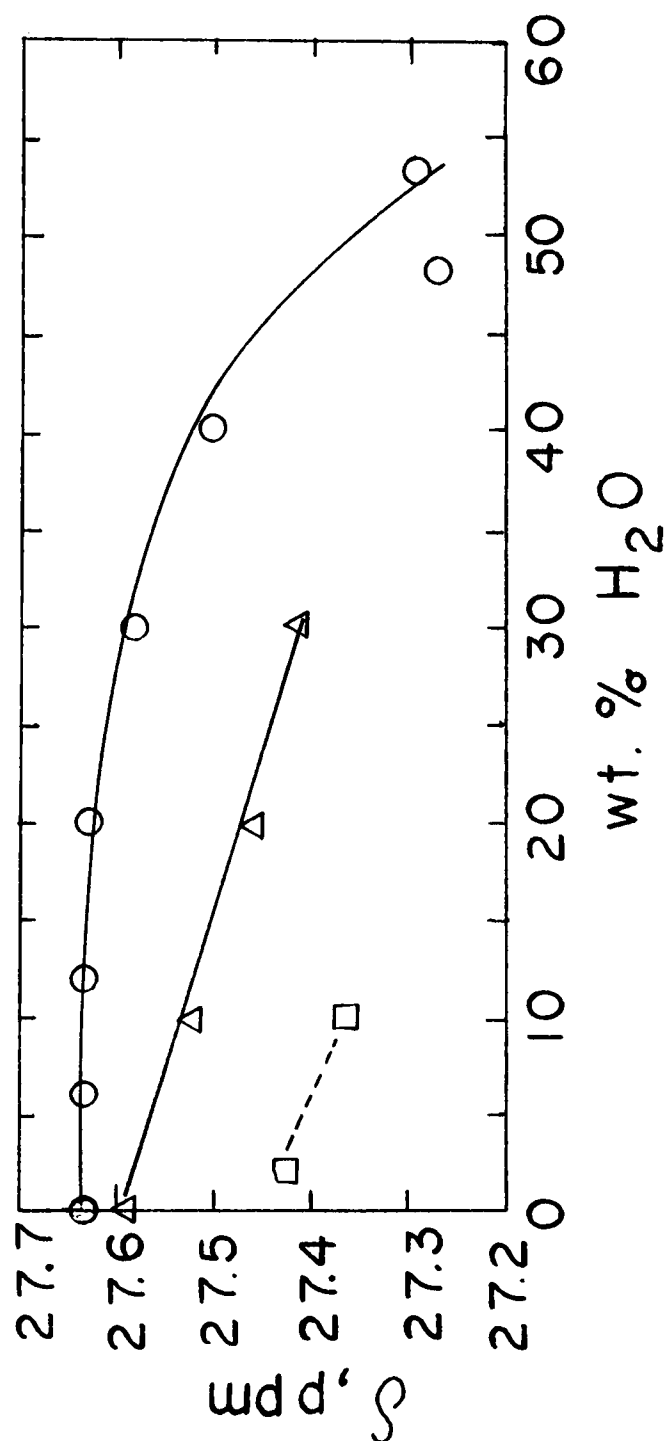


Figure 44. ^{13}C chemical shift changes of cyclohexane in the ATR/2-propanol/water/cyclohexane 1ϕ system.

Circles: 40 wt.% emulsifier; triangles: 60 wt.% emulsifier; squares: 80 wt.% emulsifier.

ATR > AOT > AIB. The minimum concentration of surfactant necessary for the formation of liquid crystals appears to increase in this order:

ATR < AOT < AIB.

The pseudoternary phase behavior of ATR and AIB in the presence of alcohols was studied. Using cosurfactants of opposite HLB, large one phase regions were observed for both surfactants in cyclohexane and benzene. The attempts to characterize the ATR $l\phi$ regions using ^1H and ^{13}C nmr were not conclusive, but provide the basis for further study. The nmr data do seem to suggest, however, a gradual change in the type and extent of aggregation upon changing the composition of the solution. Conductivity and nmr self-diffusion measurements offer the promise of unraveling this region's apparent complexity. Also, use of the positron annihilation technique may be helpful.

CHAPTER VI

EXPERIMENTAL

A. INSTRUMENTATION

1. Nuclear Magnetic Resonance

^{13}C nmr spectra were obtained at 15.1 MHz on a Nicolet TTY-14 system consisting of a Varian 14.1 kG magnet, a Bruker console and a Nicolet 1080 data processor.

Spin-lattice relaxation times were determined using the fast inversion-recovery technique.¹⁵¹ Typical parameter settings were: 3000 Hz sweep width; 90° pulse = 30-35 μsec ; 180° pulse = 80-85 μsec ; $T_d = 2$ sec; 8K data points in the time domain; and the time to acquire the FID = 1.360 sec. 13 - 15 t_d values were used in each run, ranging from 0.005 sec to $5T_1$. The number of acquisitions was 256 for the 0.5 M AOT solutions, and 512 for the 0.25 M AOT samples. Broad-band proton decoupling was used throughout. Twenty mm sample tubes were employed. Temperature was maintained at $30 \pm 2^\circ\text{C}$ with a Varian V-6040 variable temperature controller. The nitrogen flow for the controller was first passed through a Dewar flask containing 2-propanol/dry ice. The temperature was set before each run using a 5:1 methylene iodide/cyclooctane solution.²⁶¹ Samples were locked onto a capillary of D_2O within the probe.

T_1 's reported are the average of 3 - 5 runs; the values were calculated using integrated intensities and Equation 30 (p 43). The estimated error in T_1 is 5 - 10% for T_1 's > 0.1 sec, and 10-20% for $T_1 < 0.1$ sec and for overlapping resonances 7,7' and 9,9'.

Effective correlation times were calculated from Equation 24 (p 33) using a FORTRAN program based on Newton's method for determining roots. This program fails when the T_1 values fall in the slow motion region. These numbers were obtained from the plot of T_1 versus τ_c , Figures 6 and 7 (pp 34, 35). The choice of r can have a profound effect on the accuracy of T_1 .²⁶² The values of r were chosen as: $r(\text{CH}_3) = 1.096 \text{ \AA}$; $r(\text{CH}_2) = 1.073 \text{ \AA}$; $r(\text{CH}) = 1.070 \text{ \AA}$.²⁶³

T_1 's at 100.6 MHz were obtained at $28 \pm 1^\circ\text{C}$ on a Bruker WH-400 mmr at the South Carolina Magnetic Resonance Laboratory using cyclohexane- d_{12} as solvent.

One sample (0.5 M AOT/cyclohexane, $R=25$) was degassed by injecting liquid nitrogen into the solution in the mmr tube while the tube was contained in a glove bag. After four or five injections, the solution froze, and was then allowed to thaw before it was run.

^{13}C chemical shifts of the AOT microemulsions were measured relative to an external capillary of CDCl_3 . The accuracy of δ is ± 0.1 ppm. Line-widths at half-height were computed using a line fitting routine within the NTCFT program.

The measurement of NOE's was attempted by the gated-decoupling technique.²¹⁹ The decoupler was gated on during collection of the FID, then shut off during a delay time, $10T_1$. A spectrum was also obtained with full decoupling so that the NOE is allowed to build up. The ratio of integrated intensities of the second spectrum to the first gives the NOE. Typical parameter settings that differed from FIRFT were: 5000 Hz sweep width; 1000 - 1500 acquisitions; and an acquisition time of 0.819 sec.

^{13}C chemical shifts of the ATR one phase systems were obtained using 10 mm OD nmr tubes and referenced to internally added tetramethylsilane, TMS. The accuracy of these values is ± 0.05 ppm. Parameters differing from the above experiments were: 4000 Hz sweep width; 2500 acquisitions; and 1.024 sec. acquisition time. The pulse sequence was $(45^\circ - t_d)_{\text{NA}}$, where the 45° pulse width was 10 μsec . and $t_d = 1$ sec. Since the line fitting routine was "crashed" during another user's computer troubles, $\Delta\nu_{1/2}$ was hand-calculated from an expanded plot.

^1H nmr were run on a Varian T-60 spectrometer and referenced to internal TMS.

2. Infrared Spectroscopy

Dispersive ir spectra were obtained on a Perkin-Elmer 257 spectrophotometer with solvent in the reference beam. Fourier transform ir spectra were obtained on a Digilab FTS-20C spectrometer system equipped with a Data General Nova 3 data processor. One hundred acquisitions were made per spectrum.

3. Raman Spectroscopy

Raman spectra were acquired on a J-Y Optical Systems Ramanor HG.2S laser-Raman spectrometer.

4. Absorption Spectroscopy

Ultraviolet absorption spectroscopy was performed on a Cary-17 spectrophotometer.

B. METHODS AND MATERIALS

1. Purification of AOT

Aerosol OT was purchased from Aldrich (sold as sodium dioctylsulfosuccinate, 96%) and purified by the following method, which is a combination of other published procedures.^{67,110,125}

50-60 g AOT was stirred overnight with 5-10 g coconut charcoal in 500 ml benzene. After filtration through a 0.5 μ FH Millipore filter, 25 ml water was added, the solution shaken and the flocculant allowed to settle. The benzene solution was decanted and the procedure repeated with 15 and 10 ml water respectively, followed by removal of the benzene. The solid was then dissolved in 400 ml 1:3 methanol/water and washed with 3 x 100 ml 60-80 ligroine to remove any remaining organic impurities. The aqueous methanol was then carefully evaporated (to avoid foaming), after which the recovered solid AOT was dried overnight in vacuo at 75°C. Dissolution in anhydrous methanol and filtration through a 0.08 μ polycarbonate filter (Nucleopore) removed any remaining salts. Methanol was stripped off and the solid dried for 48 hours in vacuo. Percent recovery was 50 - 60%; a solution of 10% AOT in cyclohexane incorporated > 70 moles water per mole AOT. The presence of residual acidic impurities was checked by analyzing the uv absorption spectrum of CPO, 1-methyl-4-cyanoformylpyridinium oximate. This probe molecule's $\pi \rightarrow \pi^*$ transition occurs at 340 nm with an absorptivity of $24,000 \text{ M}^{-1} \text{ cm}^{-1}$ in water.²⁶⁴ In the presence of acids, a band is found at 280 nm. Figure 45 shows the AOT/CPO/water spectrum, and no 280 nm band is evident. The calculated

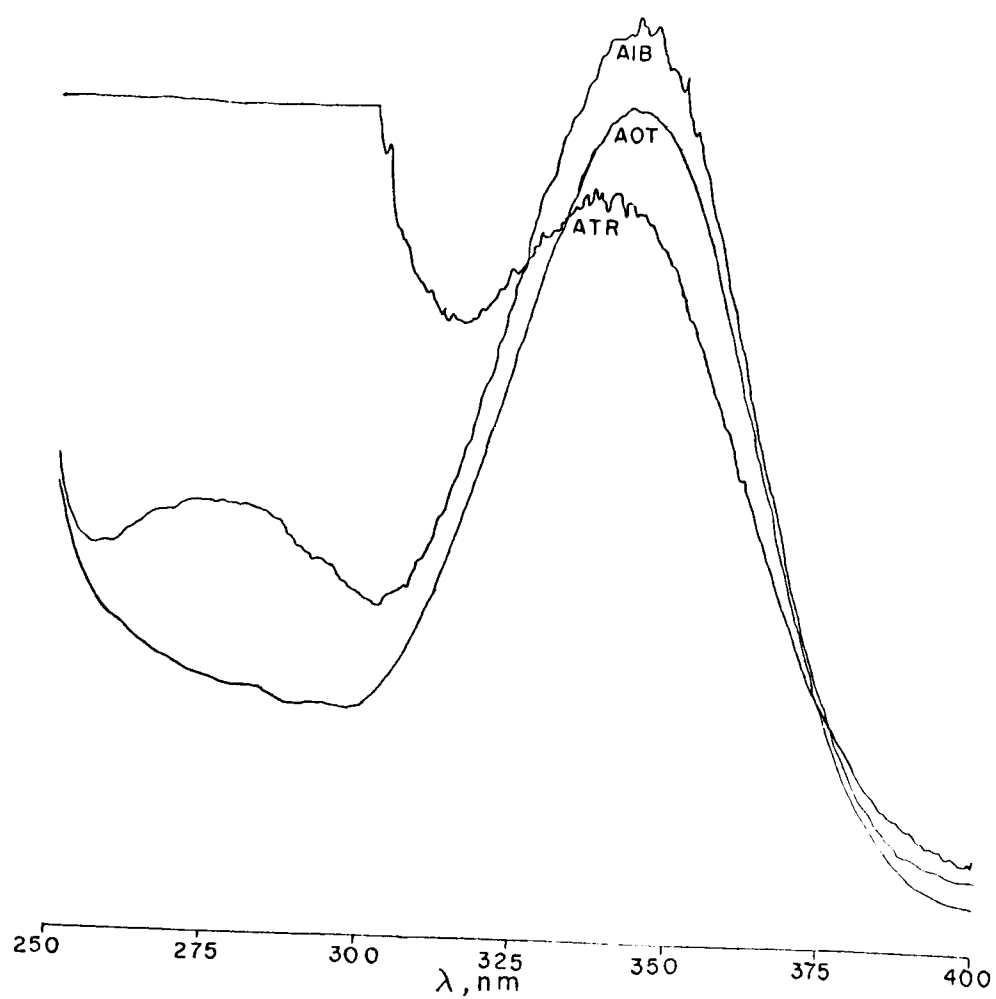


Figure 45. UV absorption spectra of CPO/water/surfactant solutions.

absorptivity was $22,000 \text{ M}^{-1} \text{ cm}^{-1}$ for the 340 band. Elemental analysis: Calc. 54.04% C, 8.39% H; Expt. 53.87% C, 8.53% H.

2. Purification of ATR

Aerosol TR-70 was a gift from American Cyanamid as a 70% solution in alcohol. After stripping off the solvent, ATR was purified by the same procedure as AOT with the following exceptions. Before charcoal treatment, 80-100 g of the dried solid was dissolved in 500 ml anhydrous methanol, the precipitates allowed to settle, and the solvent decanted. In addition, the washing step with ligroine was omitted, since an inseparable emulsion was formed. Its CPO spectrum is shown also in Figure 45 (p 152). The region at 280 nm is obscured, probably due to the liquid crystalline nature of the solution. The calculated absorptivity of the 340 nm band is $23,000 \text{ M}^{-1}$. Percent recovery was 35 - 55%. Elemental analysis: Calc. 61.62% C, 9.82% H; Expt. 61.46% C, 9.99% H.

3. Purification of AIB

Aerosol IB-45 was a gift from American Cyanamid as a 45% solution in water. Since AIB is very water soluble, the benzene/water decantation method could not be used. After removal of the water, 40-60 g AIB was dried overnight in vacuo. The dried solid was dissolved in 500 ml anhydrous methanol and the precipitates allowed to settle. Since a large amount of solid was obtained, and since AIB is a good wetting agent causing the solution to flow out the sides of the Millipore filter assembly, the solution was filtered using regular filter paper in a Büchner funnel. The methanol was removed, the solid dried overnight, then dissolved in 400 ml anhydrous methanol, followed

by filtration through Whatman 50 hardened filter paper. This step was repeated with 250 ml methanol. The recovered solid was then dissolved in 100 ml distilled water and washed with 3 x 35 ml 60-80 ligroine. After the aqueous solution was evaporated, the AIB was stirred overnight with 5 g coconut charcoal in 500 ml benzene. Final filtration was performed through a 0.5 μ filter fitted into a fine sintered glass funnel, and the solvent was removed. The solid was dried 48 hours in vacuo at 75°C. CPO analysis, Figure 45 (p 152), shows a small absorbance at 280 nm. The calculated absorptivity of the 340 nm band is 29,000 $M^{-1} \text{ cm}^{-1}$. Percent recovery was 30 - 50%.

4. Phase Diagrams

Ternary and pseudoternary phase diagrams were constructed in the following manner. Thirty solutions were prepared, with surfactant concentrations ranging from 20 to 95 wt.% in oil or water or a solvent mixture, and equilibrated 48 hours at 45°C. The phase behavior was visually observed; the presence of liquid crystalline phases was determined by examining the solution between crossed polars. A small amount of solvent (either oil or water) was added from a buret; weights were calculated assuming densities of 1.00 g/ml for water; 0.879 g/ml for benzene; and 0.774 g/ml for cyclohexane. Solutions were equilibrated for 24 hours between titrations. After the rough phase diagram was constructed, selected solutions of larger volumes were prepared, allowing 2 days to 1 week between titrations. Particular attention was paid to confirming the one phase domains.

5. Sample Preparation

Since all these surfactants are hygroscopic, they were always stored in a desiccator and handled under an inert nitrogen atmosphere in a glove bag or box.

a. AOT nmr solutions. Approximately 2.20 g AOT (for 0.5 M solutions) was weighed into a 10 ml volumetric flask, the desired amount of water added, and the flask filled to the mark with solvent. Solutions containing large water concentrations were placed overnight in a constant-temperature water bath to induce solubilization.

b. IR solutions. These solutions were prepared as above, but in 1 ml volumetric flasks using solvents filtered through a 0.5 μ filter.

c. UV solutions. 0.13 - 0.15 g surfactant was weighed into a 10 ml volumetric flask, 30 μ l 1.107×10^{-2} M CPO/water added, and the flask filled to the mark with distilled water.

d. ATR nmr solutions. Stock solutions were prepared containing 40% surfactant (2:3 ATR/2-propanol)/60% solvent (benzene, cyclohexane or water), 60% surfactant, and 80% surfactant. NMR samples were prepared by pipetting known volumes into the nmr tubes.

6. Cleaning NMR Accessories

All nmr glassware, after washing with soap and water, was soaked overnight in a caustic methanol bath, rinsed with copious amounts of laboratory-distilled water, soaked one or two days in an alkaline EDTA bath, and rinsed with glass-distilled water. All other accessories, such as vortex plungers, were soaked in the EDTA bath.

7. Chemicals

a. Methanol. Methanol was Fisher certified ACS grade, dried over 3 Å molecular sieves.

b. Benzene. Benzene was Fisher certified ACS grade, distilled, and dried over 3 Å molecular sieves.

c. Cyclohexane. Cyclohexane was Fisher certified ACS grade, distilled, and dried over 3 Å molecular sieves.

d. Water. Laboratory deionized water was distilled in a Kontes WS-2 still.

e. Carbon tetrachloride. Carbon tetrachloride was Aldrich Gold Label (99+%), dried over 3 Å molecular sieves.

f. Cyclohexane-d₁₂. Cyclohexane-d₁₂ (99 mol% D) was purchased from Merck.

g. Ligroine. Ligroine was Eastman practical reagent, b.p. 63 - 75°C.

h. 2-Propanol. 2-Propanol was Fisher certified ACS grade, distilled, and dried over 3 Å molecular sieves.

i. 1-Hexanol. 1-Hexanol was purchased from Eastman, distilled, and dried over 3 Å molecular sieves.

j. Nitrogen. For use in the glove box, nitrogen was Linde prepurified grade.

k. 1-Methyl-4-cyanoformylpyridinium oximate. A 1.107×10^{-2} M solution of CPO in water was prepared by K. Kon-no.

1. 3 Å molecular sieves. Davison 3 Å molecular sieves, grade 564, 8-12 mesh, were taken up in drum-grade methanol and collected in a fine sintered glass funnel to remove any dust. They were then cooked under a vacuum at 300°C for 3 hours to dry.

m. Charcoal. Activated cocoanut charcoal, 50-200 mesh, was obtained from Fisher. Before use it was extracted overnight in a Soxhlet extractor with benzene.

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