

**LOW INTERFACIAL TENSION AND MISCIBILITY STUDIES FOR
SURFACTANT TERTIARY OIL RECOVERY PROCESSES**

Annual Report, December 1, 1978 – November 30, 1979
Revised July 1980

Work Performed for the Department of Energy
Under Contract No. DE-AS19-79BC10007

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Carnegie-Mellon University
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U. S. DEPARTMENT OF ENERGY

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for the Period
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SECTION I. OBJECTIVE

The main purpose of this project is to develop an improved basic understanding of how ultralow interfacial tensions arise in oil-brine-surfactant systems. Such tensions must be achieved and maintained during enhanced oil recovery processes employing surfactants if these processes are to be successful.

ABSTRACT

Two model surfactant systems, one based on Texas 1 and the other on sodium dodecyl sulfate, were developed to give ultralow interfacial tensions and middle phase microemulsions when equilibrated with oil. Examination of their aqueous and microemulsion phase behavior, and comparison of the results with results of similar studies made on a system based on WITCO TRS 10-410, led to the conclusion that it is possible to generalize the phase behavior. The liquid crystalline spherulitic and lamellar textures observed in all these systems are the only homogeneous, non-phase separating fluids which can produce ultralow tensions on contact with oil. Mapping of the phase behavior of the two model surfactant systems showed that existence of the middle phase is relatively insensitive to surfactant concentration but quite dependent on cosurfactant concentration. Preliminary study of polymer-surfactant interactions confirmed the previously reported phase separation effect. A new temperature controlled polarized light screening device was built and has already been put to use for discrimination of isotropy, birefringence, scattering and interfacial phenomena in systems of interest for enhanced oil recovery.

Two model surfactant systems, one based on Texas 1 and the other on sodium dodecyl sulfate, were developed to give ultralow interfacial tensions and middle phase microemulsions when equilibrated with oil. Detailed study was first made of the structure of the aqueous systems alone. Liquid crystal phases found were identified as spherulitic and lamellar textures very similar to those already reported for commercial petroleum sulfonates. It is therefore concluded that this is general behavior for anionic surfactant, cosurfactant, brine, water systems. This result is significant in terms of enhanced oil recovery since the liquid crystal is the only homogeneous, non-phase separating fluid yet found which can produce ultra-low tensions on contact with oil.

Viscosity measurements were used as a means of obtaining information about structure, and especially about structural changes, in the aqueous systems. Viscosity was shown to vary with system composition. If viscosity is plotted as a function of composition, maxima and minima observed correspond to structural discontinuities in the liquid crystal. For the systems studied, these maxima and minima also correspond to compositions where the lower-to-middle, and middle-to-upper, transitions occur when the system is equilibrated with a given oil.

Studies were made of the phase behavior of both the Texas 1 and SDS systems when these were equilibrated with oil. Both show continuous middle phase regions from above 10 wt % surfactant to below 0.005 wt % surfactant. The middle phase region is found over only a narrow range of cosurfactant concentrations. This range is only weakly dependent on surfactant concentration. Therefore, concentrations of cosurfactant must be optimized more than concentrations of surfactant, to achieve the middle phase and

resulting ultralow interfacial tensions necessary for efficient oil recovery processes. Understanding why cosurfactant concentrations are critical really requires knowledge of how the cosurfactant partitions between phases. The necessary analyses are planned.

Similar studies were made of a system based on WITCO TRS 10-410 (60% active) surfactant. For the aqueous solution the general trend was similar to that reported for other sulfonate surfactants. The textures changed, as salinity was increased, from a system of two-phase coexistence consisting of spherulitic and lamellar phases, to two separate phases, the upper of lamellar and the lower of isotropic character.

The aqueous TRS 10-410 systems were equilibrated with oil. At low salinities a microemulsion existed in equilibrium with excess oil. The middle phase microemulsion existed at intermediate salinities. At high salinities the system became an upper phase microemulsion in equilibrium with excess brine. Observation of the movement of schlieren peaks obtained from ultracentrifuge studies clearly indicated that the lower microemulsion phase was an oil-in-water type and that the upper microemulsion phase was a water-in-oil type. From this same method of analysis the middle phase microemulsion was determined to be water continuous at its lower salt concentration end and oil continuous at its high salt concentration end. This conclusion was supported by visual observation (not in the ultracentrifuge) of diffuse interfaces at salinities corresponding to transitions from lower-to-middle and middle-to-upper phase microemulsions.

The ultracentrifuge data showed two peaks, one moving inward and one moving outward, near the region of optimum salinity. Such behavior can be explained by a mixture of oil continuous and water continuous microemulsions, or possibly by other models such as a bicontinuous structure.

However, it is clear that the middle phase over all of its range is not bicontinuous.

Preliminary experiments showed that Shell's Neodol 25-3S, an ethoxylated sulfate, was able to increase and broaden the salt concentration range over which the TRS 10-410 system exhibits liquid crystal formation. The same influence on middle phase microemulsion behavior was noted when these systems were equilibrated with oil. Such behavior is important for efficient enhanced recovery processes in high salinity reservoirs.

Studies were begun on the phase behavior of aqueous surfactant/brine solutions containing a polymer. The polymer selected for first studies was Xanthan gum. Results of preliminary experiments to show the influence of polymer concentration on the TRS 10-410 system indicate reduced birefringence and increased viscosity as compared with the polymer-free system. Given sufficient time, phase separation may be induced by the gum in the normally single phase region of the polymer free system. Experiments are continuing.

Contacting experiments between aqueous surfactant solutions and hydrocarbon oils were continued. A manuscript titled, "Spontaneous Emulsification in Oil-Water-Surfactant Systems", is in preparation.

The development of the polarized light screening (PLS) technique for the macroscopic discrimination of birefringence, scattering, phase behavior, and interfacial phenomena such as critical end points was continued. A new instrument (PLS II) which enables isothermal operation with improved optical performance was designed and constructed.

The purification procedure for Texas 1 was extended and improved to achieve a final surfactant purity exceeding 99 percent.

A. Texas 1Introduction

Texas 1 (8-phenylhexadecane sodium sulfonate)⁽¹⁾, an isomerically pure dialkylaryl sulfonate surfactant, was purified (see Section VIII) and then developed as the basis of a model surfactant system for studies of microemulsion phase behavior giving ultralow interfacial tensions. The components of the system were Texas 1, n-propanol as cosurfactant, NaCl, water, and n-decane. The phase behavior of the aqueous solutions as well as the phase behavior of oil-equilibrated systems were mapped up to 10 wt % Texas 1, 15 wt % cosurfactant and 2.0 wt % NaCl. Additionally, studies were extended to include some preliminary results on the rheological properties of aqueous solutions of selected surfactant, cosurfactant and salinity scans of the Texas 1 system.

Aqueous Phase Behavior

One goal of this work was to extend the surfactant concentration range over which middle phase microemulsions would be observed. An earlier report⁽²⁾ showed the effect of different members of an homologous series of short chain n-alcohols on middle phase formation in systems where Texas 1 and NaCl were held constant at 2.5 wt % and 1.0 wt % respectively, and the aqueous phase was equilibrated with an equal volume of n-decane. Refer to Figure 1. The region of middle phase formation decreased in width as the chain length of the alcohol increased and the system became less polar. With butanol the system was too hydrophobic and as a result a very narrow three-phase region was formed. Methanol and ethanol were too hydrophilic and

the middle phase region was very broad. Propanol formed a middle phase with distinct lower and upper phases where hydrophilic-lipophilic balance was optimized for this composition and hence was chosen for further investigation.

Aqueous solutions were formulated in the following manner. The surfactant was first weighed into a test tube. Cosurfactant was added, and the components were then heated and mixed to form homogeneous isotropic solutions. To these solutions was added a concentrated NaCl solution. All components were mixed thoroughly and finally triple-distilled water was added to bring the solutions to the desired volume. They were then heated to 60°C and mixed, first with a vortex mixer and then by ultrasound. Finally, they were equilibrated for twenty-four hours and screened in the polarized light screen (PLS). Selected systems were studied with the polarizing microscope. The phase diagram for Texas 1 vs. n-propanol at constant 1.0 wt % NaCl ($T \approx 22^\circ \pm 1^\circ\text{C}$) is shown in Figure 2. Since these results were deduced from the PLS and polarizing microscopy, they are tentative with respect to exact positions of the phase boundaries.

When the concentrations of both surfactant and the cosurfactant are low there exists an unstable region which upon standing separates into unstable layers of liquid crystalline (l.c.) aggregates and myelins. Similar behavior has been described by the University of Minnesota group⁽³⁾ when no cosurfactant is present. This region is designated unstable l.c. in Figure 2. As the concentration of surfactant is increased from about .005 wt %, with between 6 and 10 wt % cosurfactant, the appearance is initially isotropic but with increasing surfactant concentration the samples show a bluish coloration that with further increase in surfactant exhibits flow birefringence. This is designated region S in Figure 2. Microscopy reveals an increasing concentration of aggregates (spherulites) with increasing

concentration of surfactant. The S + L and L + S regions of the phase diagram showed a two-phase coexistence region of spherulites and lamellar phase which transforms into a predominantly lamellar texture. With yet further increase of surfactant a homogeneous lamellar phase appears. To the right of the liquid crystalline phase in Figure 2 there exists an isotropic region, the structure of which is yet to be determined.

Remembering that the phase diagram represented in Figure 2 was obtained under constant salinity conditions, it is noteworthy that these are the same liquid crystalline structures that have been observed in the commercial petroleum sulfonate systems including Exxon's PDM-337, Witco's TRS 10-410 and Amoco's Mahogany AA. Various salinity scans have been conducted where a more complex phase behavior has been observed, but the basic trend is that the structure is spherulitic at low salinity, and as salinity increases passes through a two-phase coexistence region to a lamellar or isotropic phase depending upon the surfactant concentration.

Viscosity Measurements

Some preliminary studies into the rheological properties of the aqueous solutions of the Texas 1 model system were conducted. These studies are a part of our continuing investigation into the nature of smectic lyotropic liquid crystalline solutions. Rheological properties are important for several reasons. They provide further insight into the complex structural behavior of the liquid crystalline textures. Micellar solutions for enhanced oil recovery are formulated with specific, optimized properties for injectability as well as for their underground microemulsion phase behavior. The aqueous solutions will remain in their original structural form as liquid crystals long after they have been injected into the porous media under-

ground, at least in the region behind the initial microemulsion front, and hence behave as mobility control agents where viscosity is of specific relevance.

In an earlier report⁽⁴⁾, a sharp maximum in viscosity vs. salinity for the PDM-337/TAA system was shown. This maximum corresponded to the two-phase coexistence region of spherulitic and lamellar phases. The viscosity of Texas 1 solutions of selected surfactant, cosurfactant and salt concentrations has now been determined. The measurements were conducted on a Brookfield-Wells cone-and-plate microviscometer. The temperature was controlled from a water bath to $\pm .05^{\circ}\text{C}$. The results are shown in Figures 3, 4 and 5 in which surfactant, cosurfactant and salt concentrations are varied. The scans reveal a complex pattern of rheological behavior. With the surfactant scan a nearly monotonic increase in the viscosity is measured with increasing surfactant concentration, with breaks at 3.5 and 5% surfactant. With the cosurfactant scan a maximum is measured at 9% cosurfactant, but the shape of the curve is essentially hyperbolic. The salinity scan shows a more complex pattern with two distinct minima at 0.9 and 1.3 wt % NaCl, and a maximum at 1.1 wt % NaCl. This behavior is typical of non-Newtonian fluids and from the birefringent texture studies of these same solutions it is clear that the discontinuities observed in the structures correspond to maxima and minima in the viscosities. Investigations of this complex behavior are continuing. Present measurements are being conducted on a Brookfield-Wells cone and plate "Rheolog" which gives continuous shear stress measurements at varying shear rates where a pressure-transduced signal is converted to an electrical response and recorded continuously on a chart recorder. With this instrument we are now able to measure time-dependet behavior.

Behavior on Equilibration with Oil

The aqueous phases of the Texas 1 system were contacted with an equal volume of n-decane. The mixing procedure was as follows: 5 ml of the aqueous phase was mixed with 5 ml of n-decane in Teflon sealed test tubes. The mixtures were heated to 60°C and thoroughly mixed for 15 seconds with a vortex mixer. After 24 hours the mixing was repeated, without further heating, and the samples were allowed to equilibrate at room temperature, $T \sim 22^\circ\text{C} \pm 1^\circ\text{C}$. When the volumes of the phases showed no further change these volumes were measured and the discernible characteristics noted. This was accomplished by the previously described PLS technique which can easily discriminate isotropy, scattering and birefringence of samples.

The microemulsion phase behavior at constant salinity is shown in Figure 6 as a function of surfactant and cosurfactant concentrations. It can be seen that Texas 1 is a hydrophobic surfactant. With increasing cosurfactant concentration the system showed a change in microemulsion position from upper phase (u ϕ ME) to middle phase (m ϕ ME) to lower phase (l ϕ ME). At compositions below the dashed line equilibration is not easily achieved. The microemulsion middle phase formed from below .005 wt % surfactant to > 10 wt % surfactant in the cosurfactant range of 7 wt % to 10 wt %. A typical scan is shown for increasing surfactant concentrations at constant cosurfactant concentration of 8.5 wt %, in Figure 7.

These results show that a critical cosurfactant concentration is necessary for middle-phase formation. The slope of the middle-phase region indicates a critical surfactant/cosurfactant ratio is necessary for optimization. The solubilization of both oil and water into the middle phase is essentially independent of surfactant concentration if plotted as a function of

critical cosurfactant concentration. This critical concentration of cosurfactant is related to the mutual solubility of the cosurfactant in the brine and oil phases exclusive of surfactant. Diffuse, critical interfaces were observed at the upper to middle and middle to lower microemulsion phases both cosurfactant and salinity scans. Preliminary measurements using a spinning drop apparatus indicated that interfacial tensions were very low ($\sim 1.5 \times 10^{-3}$ dyne/cm).

Several salinity scans were made at various surfactant and cosurfactant concentrations. Results were the same as observed in other systems. There is first a lower phase microemulsion which proceeds into a middle phase microemulsion and, finally, an upper phase microemulsion is formed.

Preliminary ultracentrifuge studies have been conducted with microemulsions from this system at various surfactant, cosurfactant and salt concentrations. At 3.5 wt % surfactant and 8 wt % cosurfactant the effect of salinity on the middle phase region has been studied. As with commercial petroleum sulfonate systems at lower salinity, schlieren peaks of two different types (i.e., o/w and w/o) have been observed. At 12 wt % cosurfactant concentration, 1 wt % NaCl, and a surfactant concentration < 4.5 wt % the system forms an o/w lower phase microemulsion. On increasing the surfactant concentration a middle phase is formed which shows a water-continuous microemulsion. Similar results were obtained for systems containing 1 wt % NaCl, 8 wt % Texas 1 and various amounts of cosurfactant. In all the cases studied, near its upper and lower ends (in the parameter space) the middle phase always has the phase structure of the upper or the lower microemulsion phase. These studies are continuing.

Another preliminary result on the Texas 1 system is shown in Figure 8, a plot of the phase inversion temperature (PIT) vs. salinity. The surfactant and cosurfactant concentrations were held constant at 3.5 wt % and

9 wt % respectively. These data were obtained with our recently constructed PLS II, described below. The plot shows an essentially linear increase in the shift of optimal salinity with increasing temperature over the range of 20 - 45°C, which is consistent with results found for commercial petroleum sulfonates⁽⁵⁾. The effect of temperature will be explored and reported in detail in subsequent reports.

B. Sodium Dodecyl Sulfate

Introduction

A second model system for studies of microemulsion phase behavior was developed.⁽⁶⁾ This second system was built around the surfactant sodium dodecyl sulfate (SDS). Other components were hexanol as cosurfactant, NaCl, water and n-decane. SDS was selected because it can be obtained as a very pure (99.9%) crystalline reagent from Gallard-Schlesinger Corporation and because it is probably the classical model surfactant for scientific studies. Comparison of results obtained with Texas 1 with results obtained with SDS provides most useful information about microemulsion phase behavior, and ultralow interfacial tension in systems of interest for enhanced oil recovery.

Two related sets of SDS based systems were studied. The first were aqueous solutions containing varying quantities of SDS, hexanol and NaCl. The second were some of the solutions from the first set which had been equilibrated with an equal volume of n-decane. Examination consisted of observations with PLS, measurement of phase volumes, some polarizing microscopy, and measurement of interfacial tensions by both the sessile and spinning drop techniques. The middle phase microemulsion region was easy to identify with the PLS. This region was observed at low SDS concentrations

(.0005 molar or .0144 wt %). Measured interfacial tensions for these systems were as low as 3.4×10^{-4} dynes/cm.

Aqueous Phase Behavior

There were no long lasting order of mixing effects observed with the SDS solutions. All such effects were limited to the formation of a transient liquid crystal phase that dissolved in about twelve hours. The formation of metastable liquid crystal was only noticed at the high salt and the high n-hexanol concentrations.

Stock solutions of SDS (.5 molar) and NaCl (2.0 molar) were prepared and the serial dilutions reported below were made from them. The usual procedure was to blend SDS, NaCl and n-hexanol, then dilute to the desired volume with water. An alternate order of mixing was to blend SDS and NaCl (or hexanol), dilute to the desired volume, and then add the hexanol (or salt).

Figure 9 shows the phase behavior of structures observed for the SDS system at varying surfactant and n-hexanol concentrations. Results are similar to those found for Texas 1 (Figure 2). As the cosurfactant concentration is increased the S to S+L to L liquid crystalline regions are observed. But Figure 9 shows that the SDS system deviates from the Texas 1 system in that a three-phase coexistence region also exists. Both the liquid crystalline and three-phase coexistence regions extend towards low surfactant concentration. The lower phase of the three coexisting phases is isotropic, the middle phase scatters light and the upper phase is isotropic. The hydrophobic cosurfactant, n-hexanol, appears to be behaving like an oil and it is possible that the middle scattering phase is a microemulsion.

Unlike Texas 1 and other petroleum sulfonates, the S to L transition in the initial aqueous solution of SDS does not indicate where the middle phase microemulsions in the oil-equilibrated solutions will be found. For SDS it is

a two-phase to three-phase transition in the initial aqueous solutions that is tied to the middle microemulsion phase in the oil-equilibrated solutions. The difference is probably due to the fact that SDS is much more hydrophilic than Texas 1 or commercial petroleum sulfonate surfactants. The fact that a phase transition in the initial aqueous solutions of both types of surfactants is linked to a phase transition in the oil-equilibrated solution is felt to be significant.

Behavior on Equilibration with Oil

Screening of oil-equilibrated SDS solutions to find the middle-phase microemulsion region was conducted with the aid of the PLS. The critical region involves relatively narrow hexanol and NaCl concentration bands. The necessary concentrations of hexanol and NaCl are a small region of phase space and were found empirically. The NaCl concentration range was from a little less than .3 molar to a little more than .4 molar. The hexanol concentration range was from about 8 vol % to 10 vol %.

The phase diagram for the SDS:hexanol plane at a constant salt concentration of .4 molar NaCl is shown in Figure 10. The middle-phase microemulsion region is outlined. It has a two-phase region on all sides. An upper phase microemulsion coexists with a lower brine phase on the more hydrophobic (more hexanol and/or less SDS) sides. A lower phase microemulsion coexists with an upper oil phase on the more hydrophilic (less hexanol and/or more SDS) sides. It can be seen that the middle-phase microemulsion region extends to very low (.001 molar) SDS concentrations. This fact is significant. The behavior of Texas 1 systems is similar and suggests this as general rather than unique behavior.

Interfacial tensions were measured at many points in Figure 10. The lowest IFTs (3.8×10^{-4} dynes/cm) were found for a four-phase sample. This

four-phase sample is thought to contain a tricritical phase. The second lowest IFT (3.6×10^{-3} dynes/cm) was found for a two-phase sample with a lower-phase microemulsion. This sample was very close to the three-phase envelope.

SDS, as can be seen from Figure 10, is nearly identical in its phase behavior to Texas 1 and commercial petroleum sulfonates around the middle-phase microemulsion region. This fact shows that SDS is an excellent model surfactant for studies of microemulsion phase behavior, analogous in most ways to the petroleum sulfonates.

If SDS is analogous to the petroleum sulfonate, then phenomena seen in SDS should be found in petroleum sulfonates. Studies of both SDS and Texas 1 indicate that the ultralow IFTs needed for good enhanced oil recovery may be related to higher order critical points. These studies also indicate that the middle-phase microemulsion region can be produced with very low ionic surfactant concentration if the critical cosurfactant and salt conditions are met. Further characterizations of SDS and Texas 1 solutions are proceeding and will be reported subsequently.

A. Introduction

The phase behavior of Witco TRS 10-410 (60% active) surfactant when contacted with isobutylalcohol and n-dodecane has been studied in order to extend understanding of the structures and their relationship to ultralow interfacial tension. This section includes several experimental results on these systems. Part B describes the results obtained from studies of 5 wt % TRS 10-410, 3% IBA and x% brine where the aqueous structures have been observed by polarizing microscopy and by the PLS technique. Part C describes phase volume and ultracentrifugal measurements of the TRS 10-410 system equilibrated with n-dodecane. Part D gives the results of increasing the salinity tolerance of the aqueous phases of TRS 10-410 by addition of Neodol 25-3S, an ethoxylated surface. Part E describes the phase behavior of the TRS 10-410/Neodol 25-3S system equilibrated with n-dodecane.

B. Aqueous Phase Behavior

The TRS 10-410 surfactant is a 60% active petroleum sulfonate with an average molecular weight of 424. Aqueous solutions of TRS 10-410 were formulated with cosurfactant and brine. The surfactant/cosurfactant (IBA) solutions were mixed thoroughly by magnetic stirrer for twenty-four hours. To the surfactant/cosurfactant solutions were added concentrated brine solutions until the systems were homogeneous. To these homogeneous solutions were added triple-distilled water to make 10 ml aliquots. The final formulations were 5 wt % TRS 10-410 and 3 wt % IBA. The salinity was varied from 0.5 wt % to 3 wt %. Each solution was thoroughly mixed with a vortex mixer followed by ultrasound and heated to 60°C for two hours. Then the solutions were cooled to room temperature, remixed, and allowed to equilibrate. They were then studied with the PLS and in sealed rectangular optical capillaries by microscopy.

Figure 11 demonstrates the birefringent textures of a salinity scan of TRS 10-410/IBA by the PLS technique. The salinity is varied from 0.8 wt % to 2.2 wt % NaCl in 0.2 wt % increments. The general trend is similar to the variance in texture reported for other model and commercial petroleum sulfonate solutions⁽⁷⁾. At 0.8 wt % NaCl an aggregated phase of spherulites in brine exists. As the salinity increases to about 1.4 wt % NaCl the textures show a two-phase coexistence region consisting of spherulites and lamellar phases, with the spherulites predominating. At 1.6 wt % NaCl the two phases coexist in equal proportions and at 1.8 wt % NaCl the aqueous solution is a homogeneous lamellar phase. At 2.0 wt % NaCl the solution separates into two phases, the upper of which is a lamellar phase and the lower a yellowish isotropic phase. If the lower phase is disturbed it exhibits "streaming" or "flow" birefringence which is indicative of a close-packed cubic structure of aggregates, generally known as the 'viscous' or 'cubic' isotropic phase. At 2.2 wt % NaCl phase separation also occurs but the upper phase being the 'viscous' isotropic phase and the lower being a clear isotropic phase with a high viscosity. All the solutions in the one-phase region are light yellow in color when first formulated, but the coloration darkens over time, even though the structures generally show little change on aging.

C. Behavior on Equilibration with Oil

The aqueous solutions of TRS 10-410, IBA and brine described in the previous section were equilibrated with an equal volume of n-dodecane. The procedure for forming the microemulsions was as follows: 5 ml of n-dodecane was added to 5 ml of the aqueous solution, then mixed with a vortex mixer and temperature cycled. The samples were then allowed to equilibrate in a constant temperature environment. Equilibrium was assumed to have been established when no further changes in phase volumes occurred. In general, one month was adequate.

Solubilization data are presented in Table 1. At low salinity a microemulsion phase exists in equilibrium with excess oil. The middle phase appears at 1.2 wt % NaCl. At 2.2 wt % and higher salinities the system becomes an upper phase microemulsion in equilibrium with excess brine. As shown in Figure 12 the oil solubilization increases with increasing salt concentration. The reverse is the general trend for water solubilization.

Ultracentrifuge studies were undertaken on the microemulsion phases using a Beckman Model E Analytical Ultracentrifuge. The ultracentrifuge studies were conducted at various speeds and for different periods of time. The results are shown in Table 2 and plotted in Figure 13.

The following equation (8) is used to calculate the radius, a , of the drop.

$$a = \left[\frac{9 \mu s}{2(\rho_D - \rho_m)} \times \frac{(1 + \phi^{1/3}) \exp\left(\frac{5\phi}{3(1-\phi)}\right)}{(1 - \phi)^2} \right]^{1/2}$$

where

a = radius of the drop in cm

μ = viscosity of the continuous phase in poise

s = sedimentation coefficient in sec^{-1}

ρ_D = density of the dispersed system in gms/cc

ρ_m = density of the continuous medium in gms/cc

ϕ = $\frac{\text{volume of the dispersed phase}}{\text{total volume of the phase}}$

It is assumed that all of the surfactants and cosurfactants are at the interface. For mixtures of oil-in-water and water-in-oil microemulsions it is assumed that the surfactants and cosurfactants are distributed between the microemulsions in the same ratio as oil and water in the total phase.

The lower microemulsion phase was an oil-in-water type. This designation was indicated by a schlieren peak moving inwards. The drop size increased with increasing salt concentration (Figure 13). The upper

microemulsion phase is a water-in-oil type as indicated by a schlieren peak moving outwards. The results indicate a decrease in drop size with increasing salt concentration. The results are not as consistent as were found in the lower phase microemulsion.

The middle phase has been studied rather extensively in the ultracentrifuge. The results indicate that at the lower end (≤ 1.3 wt % NaCl) it was water-continuous. This behavior was indicated by the appearance of a single inward-moving schlieren peak. This result is in agreement with that of Chan and Shah⁽⁹⁾. But at higher salinity (≈ 1.8 wt % NaCl), contrary to their findings, the middle phase was distinctly a water-in-oil type microemulsion. The appearance of a single well-characterized outward-moving schlieren peak confirms this fact. These results are in agreement with Hwan et al's hypothesis of middle phase structure near the end points⁽¹⁰⁾.

Between 1.4% and 1.8% salt concentration we observe two peaks, one moving inwards and the other outwards. This has been explained previously by Miller et al⁽¹¹⁾ as indicating the existence of a mixture of o/w and w/o microemulsions. The calculated values of drop diameters are less reproducible. It is possible that the actual structure in the optimum region may be approximated by other models such as a bicontinuous structure⁽¹²⁾. But it is obvious that the middle phase over all of its range is not bicontinuous. The drop diameters, assuming it to be a mixture of o/w and w/o microemulsions, are shown in Table 2.

In all of these experiments, diffuse interfaces near the transition (lower to middle or middle to upper) region have been observed. The interfacial tensions for this system have already been obtained by other workers^(9,14). A few data obtained by our group confirm the low IFT values obtained by other groups.

Some preliminary results on the effect of increasing the salinity tolerance of the TRS 10-410 system described in the previous section are reported here. Conventional commercial petroleum sulfonate systems will generally form microemulsions and give ultralow interfacial tensions at relatively low salinities (≤ 4 wt %). Yet many underground reservoirs have latent brine concentrations which are much higher; as a result it is necessary to formulate micellar solutions that will tolerate these high salinities. Several methods of increasing the salinity tolerance of petroleum sulfonate systems have been reported including the addition of ethoxylated alcohols, ethoxylated sulfates and ethoxylated sulfonates^(13,14,15). In this study Shell's Neodol 25-3S, an ethoxylated sulfate, has been used in order to understand the effect of salt tolerance on the phase behavior of both the aqueous solutions and the oil equilibrated microemulsion phases.

The procedure for formulating the aqueous solutions for this series of experiments was the same as outlined in the previous section. Six TRS 10-410/Neodol 25-3S blends were formulated such that the surfactant blend was held constant at 5 wt % and the cosurfactant at 3 wt %. However, the surfactant ratio was varied starting with 4.5 wt % TRS 10-410 and 0.5 wt % Neodol 25-3S to 2 wt % TRS 10-410 and 3 wt % Neodol 25-3S. The salt concentration was varied from 0.5 wt % to 10.5 wt % for each of the six surfactant blends.

The phase behavior of the aqueous solutions is plotted in Figure 14 with salinity along the x-axis vs. weight percent Neodol 25-3S in TRS 10-410. The basic trend of the liquid crystal (S&L) formation observed in the TRS 10-410 system in the absence of Neodol 25-3S is also seen with the addition of increasing Neodol 25-3S. But as the concentration of Neodol 25-3S increases the liquid crystal region broadens and shifts to higher

salinities. The PLS and polarizing microscopy techniques showed that the general appearance of liquid crystal textures was the same as found for the TRS 10-410, and other petroleum sulfonate systems; i.e., a spherulitic phase at low salinity, passing through a two-phase coexistence region of spherulite and lamellar phases, to an homogeneous lamellar phase at higher salinities. Below the liquid crystal region at lower salinities a transparent isotropic phase (Iso) is present. As the liquid crystal region is approached with increasing salinity an opaque precipitate exists at the bottom of the isotropic phase samples (Iso + precip). With further increase in salinity the solutions become stable liquid crystalline structures. At salinities above the liquid crystal region the solutions separate into two phases. The upper phase is a lamellar liquid crystal and the lower an isotropic phase that exhibits 'streaming' or 'flow' birefringence. At even higher salinities yet another two-phase region exists. The upper phase exhibits 'streaming' birefringence, contains most of the surfactant, and is designated V.Iso. The lower phase is a viscous clear isotropic phase and is designated Iso.

E. High Salt-Tolerant Systems Equilibrated with Oil

As with the previous oil-equilibrated systems, equal volumes of the aqueous solutions and n-dodecane were thoroughly mixed, temperature cycled, and then allowed to equilibrate until no further change in the phase volumes was apparent. Figure 15 is a plot of the microemulsion phase behavior for x wt % salinity versus y wt % Neodol 25-3S in TRS 10-410. With increasing Neodol 25-3S the middle phase microemulsion region broadens and shifts to higher salinities. For the range of Neodol 25-3S studied the shift is from 1.6 wt % NaCl at 0 wt % Neodol 25-3S to around 9 wt % for 3 wt % Neodol 25-3S and 2 wt % TRS 10-410. Also, an essentially one-to-one correspondence exists between the formation of the liquid crystalline region of the aqueous solutions

and the formation of the middle phase microemulsion when the systems are oil equilibrated. As is to be expected the volume of water solubilized (V_w) in the microemulsion decreases with increasing salinity and conversely, the volume of oil solubilized (V_o) increases with increasing salinity. The behavior of the V_o/V_s and V_w/V_s curves for this series indicate that the solubilization at optimum salinity is not a linear function of the Neodol concentration. These results along with further studies of high salt-tolerant systems will be the subjects of a subsequent report.

Studies have begun on the phase behavior of an aqueous surfactant/brine solution containing a polymer. Determination of the effect of polymer on the aqueous/oil phase behavior has also been initiated as part of a program to investigate the interactions between polymer and surfactant systems as relevant to enhanced oil recovery.

Interactions in the polymer-surfactant mixing zone have received attention from some investigators⁽¹⁵⁻¹⁸⁾. Trushenski⁽¹⁶⁾ reported that high mobility and phase separation can occur due to polymer-surfactant incompatibility leading to excessive sulfonate retention through "phase entrapment." Szabo⁽¹⁷⁾ studied a number of polymer-surfactant systems and found that mixtures of sulfonate and polymer solutions form a two-phase system. One phase contains most of the polymer complexed with the sulfonate, while the other is rich in sulfonate and low in polymer. More recently Hesselink and Faber⁽¹⁵⁾ investigated the effect of polymer and found that the polymer is usually present in an aqueous phase which can be highly concentrated. They pointed out that the polymer may extract water from a microemulsion phase and hence increase the microemulsion/brine interfacial tension.

Water-soluble polymers have been the most commonly used mobility control agents. Practical application has been restricted to two types: (i) a polysaccharide biopolymer, Xanthan gum and (ii) partially hydrolyzed polyacrylamides. Both polymers suffer limitations that cause process inefficiencies or loss of cost-effectiveness. Martin⁽¹⁹⁾ recently reviewed the potential inadequacies of existing mobility control agents. An evaluation of water-soluble polymers for secondary oil recovery has also been presented by Szabo^(20,21).

Xanthan gum is the polymer so far investigated in this laboratory. The polymer content of the Xanthan broth supplied by Abbott Laboratories is 2.91%⁽²²⁾. Xanthan gum has advantages in terms of good shear stability and brine compatibility. But it also suffers from a number of inadequacies such as high cost, microbial and thermal degradation, filtration requirements, and hydrolysis. Hence, other water-soluble polymers, particularly polyacrylamides, will also be investigated. Our initial experiments have been with TRS 10-410 (Witco), a commercial petroleum sulfonate that has been studied extensively in this laboratory and by several other groups^(9,14). But a model surfactant, Texas-1, will also be investigated. The phase behavior of the Texas-1 system without polymer has been reported in Section III and will be used as a standard for evaluating the effect of polymer.

The viscosity of the aqueous polymer solution was measured as a function of salt concentration using a Wells-Brookfield microviscometer (Model RVT-C/P). Addition of 0.4% (w/w) NaCl decreased the viscosity of the polymer solution significantly. Further increases in salt concentration had negligible effect. The relative change in viscosity on addition of NaCl was found to depend on the polymer concentration as well as the shear rate. The viscosity change varied from about 14% for 1500 ppm to about 27% for 750 ppm Xanthan gum at a shear rate of 150 sec^{-1} . The change was higher for decreasing shear rate (increasing RPM). Hence, the general trends observed in the viscosity behavior of Xanthan gum solutions are consistent with those reported by other investigators^(22,23).

Several TRS 10-410 aqueous systems have been prepared as a function of Xanthan gum concentration. The surfactant concentration is fixed at 5% (w/w). The brine (NaCl) concentration is varied in each system from 0.8 to 2.4% at an

interval of 0.2% (w/w). The surfactant-polymer systems are made by diluting concentrated polymer and surfactant solutions to the desired composition.

The aqueous phase behavior of the polymer-free TRS 10-410 (Witco) system as a function of brine concentration is described in Section IV of this report. A spherulitic liquid crystalline phase exists at 0.8% (w/w) NaCl and transforms into a lamellar phase at about 1.8% NaCl with an intermediate two-phase coexistence region of spherulites-plus-lamellar textures. Above 2.0% salt there exists a surfactant-rich upper phase in equilibrium with a lower brine phase, the volume of the latter increasing with increasing electrolyte concentration. The addition of the polymer to the surfactant solution results in a reduced birefringence and increased viscosity as compared to the polymer-free system. However, no macroscopic phase separation was observed immediately on contacting the polymer with the surfactant solution. But given enough time (weeks to months, depending on the brine and polymer concentration) a phase separation may be induced by the Xanthan macromolecules in the otherwise one-phase region of the polymer-free system.

The phase behavior of the aqueous surfactant solutions with 750 ppm Xanthan polymer is shown in Figure 16, and may be compared with Figure 11 for the polymer-free system. The first sample on the left in Figure 16 is at 0.8% NaCl and shows phase separation into an upper aqueous phase (weakly birefringent) and a lower liquid crystalline phase. Although the next sample (1.0% NaCl) appears to be one phase, it did separate into two phases (an aqueous upper in equilibrium with a lower liquid crystalline phase). Thus, two phases exist over the whole salinity range examined. Between 1.0 and 2.0 wt % NaCl (samples no. 3 to 7 from the left in Figure 16), the upper phase is liquid crystalline and the lower phase aqueous with some streaming birefringence. It should be noted that the interface between the two phases is

not very sharp, an indication that the interfacial tension is low. Indeed, low interfacial tensions between such separated phases have been reported by Szabo⁽¹⁸⁾. At 2.2 and 2.4 wt % salt, two phases exist as in the polymer-free system. The interface is sharp although not very distinct in Figures 16 and 11. However, the viscosity of the lower phase is much higher as expected due to the presence of the added polymer.

Samples of the aqueous surfactant-plus-polymer solutions with varying salt concentration were contacted with an equal volume of dodecane and allowed to equilibrate. The objective was to evaluate the effect of the polymer by comparison with the results of the polymer-free system described in Section IV. of this report. The addition of the polymer tends to slow down the equilibration process. The basic pattern of phase behavior is the same as in the polymer-free system except in the lower phase microemulsion region. A middle phase microemulsion is observed at intermediate salt concentrations and at higher salinity an upper phase microemulsion exists in equilibrium with an excess brine phase. With 750 ppm Xanthan gum it was observed that at low salinities (0.8-1.0% (w/w)) the aqueous phase microemulsion in equilibrium with excess oil separates out into two phases. A small but highly viscous polymer phase (apparently a gel) separates out at the bottom of the sample. Such a phase separation will significantly affect the performance of a micellar-polymer flooding process. The details of the phase behavior on contacting with oil will be reported later.

SECTION VI. CONTACTING EXPERIMENTS WITH AQUEOUS SOLUTIONS AND HYDROCARBONS

Contacting experiments between aqueous surfactant solutions and hydrocarbons were continued. Studies of the contacting of both commercial petroleum sulfonates and model surfactants with various hydrocarbons were made. The experiments were conducted in sealed rectangular capillaries and observed under the microscope, and in test tubes with a polarized light screen. Some of these results have been reported^(2,6). A manuscript entitled "Spontaneous Emulsification in Oil, Water and Surfactant Systems" is in preparation.

SECTION VII. POLARIZED LIGHT SCREEN II. (PLS II.)

In past reports⁽⁶⁾, the useful development of the polarized light screening (PLS) technique for the macroscopic discrimination of birefringence, scattering, and interfacial phenomena, in aqueous solutions and in oil-equilibrated microemulsion systems has been demonstrated. The use of the PLS technique has now been extended to enable studying solution samples under isothermal conditions. The PLS II as described here also provides better optical properties than the PLS I. Through its use phase volumes can be measured, birefringence and scattering discriminated, and interfacial phenomena such as critical end points and probable tricritical points studied and photographically recorded.

The PLS II is designed to operate between 10 and 80°C holding temperatures to within $\pm 0.05^\circ\text{C}$. The body of the system consists of a rectangular Pyrex tank with inside dimensions of 22"x6"x12" filled with water to a depth of 10" (approximately 20 liters). The Pyrex glass sheets were cut to size and then assembled using a silicone glass sealant. Figure 17 is a photograph of the instrument.

Temperature fluctuations are regulated using a YSI Thermistemp Model 71A on/off controller connected to a 500-watt submersible heating coil through a Powerstat 3PN116B variable transformer to allow variance of the heating rate, thus minimizing temperature overshoots. The tank is constantly cooled by a copper refrigeration coil which is suspended along the bottom of the tank. This coil is attached to a common Freon-12 refrigeration unit which was salvaged from an old refrigerator. A 1/35 HP centrifugal circulation pump is sufficient to keep spatial temperature variations to $\pm .05^\circ\text{C}$.

Tank temperature is monitored via an Omega Model 2170A-T digital thermometer attached to two copper-constantan thermocouples (one placed at

each end of the tank) along with one mercury thermometer (accurate to within 0.1°C). The controller itself has its own YSI Model 403 temperature probe which means that four temperatures are monitored at all times in the PLS II. As with the probes for the digital thermometer, the other probes are placed throughout the tank so as to allow uniform sampling of the tank temperature. A voltage regulator is used along with the digital thermometer to eliminate voltage fluctuations which could lead to uncertainties in the temperature readings.

A bank of 12 8-inch fluorescent bulbs aligned vertically behind the tank at one-inch intervals is used as the light source. This bank allows viewing up to twelve test tubes at one time while allowing room for up to twelve more tubes to be kept in isothermal storage. The light is diffused, polarized, and then passed through the tank and samples. An analyzer viewing screen in front of the tank allows for viewing the samples. The polarizing filters were cut from HN 22 Neutral Linear sheets 0.137" thick, supplied by Polaroid Corp., Cambridge, Mass. Figure 18 shows a cross-sectional view of the optics of the system.

The water is kept free of dust and dirt particles which would reflect light by a standard charcoal aquarium filter. This arrangement proved to be more than sufficient to keep the water free from dust and dirt.

An auxiliary heating coil, identical to the first, is included in the tank. It is wired directly to a toggle switch on the control panel and used to cut down transient times while raising the PLS II up to a desired temperature. It is switched off after the desired temperature is reached.

A ventilation system, consisting of three fans, is used to keep the bank of lights, the refrigerator's compressor, and the refrigerator's heat

exchanger from overheating since the PLS II is designed for continuous duty. Figure 19 shows a front and top schematic view of the PLS II.

A rack was designed to fit on top of the tank in order to suspend 13 mm diameter test tubes. The actual design of the rack is quite arbitrary as long as it holds the samples securely and spaces them apart from each other in a uniform manner.

All of these systems were wired together into three electrical circuits in a manner that distributes the load equally. See Figure 20. Each piece of equipment is fused, along with the main power cord for each circuit.

To equilibrate samples, the PLS II is first set at the desired temperature with the sample tubes in place. Once the system has reached the desired temperature the samples are thoroughly mixed with a vortex mixer and replaced in the tank. They are then equilibrated until no further change in the volumes or behavior is observed, at which time measurements and data are recorded. Transient liquid crystalline phases and other transient effects may occur if this procedure is not followed. On reequilibration by the above-mentioned procedure, results are reproducible at least with the pure surfactant systems studied to date. Some preliminary results for studies of the shift in the optimum salinity with increasing temperature for the Texas 1 model system are reported in Section III of this report.

SECTION VIII. PURIFICATION OF 8-PHENYLHEXADECANE
SODIUM SULFONATE (TEXAS 1)

Texas 1 was obtained from the University of Texas group in two lots, each from a different batch. The University of Minnesota group reported various impurities in Texas 1 samples and a procedure for separating some of these impurities⁽²⁵⁾. This procedure has been extended in our laboratory, by passing the surfactant through a liquid chromatographic column^(2,24). This extension has markedly improved the purity of Texas 1 to better than 99%. The results of elemental analysis on five separate column runs and both lots of Texas 1 are shown and compared to theoretical in Table 3. Highest purity was obtained with sample #5, which was from lot #2 and was passed through the column twice. This result indicates that the column loading of 10 wt % solution was slightly overloaded and that a more dilute solution would produce a better yield and purity.

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Presentations by Group

Presentation by Enhanced Oil Recovery Group, Department of Chemical Engineering, Carnegie-Mellon University at CMU for industrial representatives, February 1979.

Presentations by C. A. Miller

- a. "Interfacial Phenomena in Enhanced Oil Recovery Processes"
Mobil Research and Development, Princeton, N.J., May 1979.
- b. "Liquid Crystals in Systems for Enhanced Oil Recovery"
53rd Colloid and Surface Science Symposium, Rolla, Mo., June 1979.
- c. "Interfacial Phenomena in Enhanced Oil Recovery Processes"
New Mexico Petroleum Recovery Research Center, N.M., June 1979.
- d. "Aqueous Surfactant Solutions and Microemulsions of Petroleum Sulfonates and Well-Characterized Surfactants"
Fifth Annual DOE Symposium, Tulsa, Oklahoma, August 1979.
- e. "Research at Carnegie-Mellon University on Chemical Flooding Processes"
British Petroleum Research Center, Sunbury-on-Thames, England, October 1979.
- f. "Interfacial Phenomena in Enhanced Oil Recovery Processes"
Loughborough University of Technology, England, October 1979.

Presentations by W. J. Benton

- a. "Phase Behavior and Structure of Surfactant Solutions and their Relation to the Micellar Flooding Technique for Enhanced Oil Recovery"
Institute of Offshore Engineering, Herriot-Watt University, Edinburgh, May 1979.
- b. "Interfacial Behavior Accompanying Contact of Oil with Aqueous Solutions of Petroleum Sulfonates"
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SECTION XI. TABLESTable 1Ultracentrifuge Results for Witco TRS 10-410

<u>% NaCl</u>	<u>Microemulsion</u>	<u>Drop Dia (Å)</u> ^o	
		<u>o/w</u>	<u>w/o</u>
0.8	lower	230	-
0.9	l	270	-
1.0	l	315	-
1.1	l	410	-
1.2	middle	455	-
1.3	m	575	-
1.4	m	495	1430
1.5	m	770	1020
1.6	m	1200	550
1.7	m	500	740
1.8	m	-	650
1.85	m	-	480
1.9	m	-	470
1.95	m	-	400
2.0	m	-	400
2.1	m	-	510
2.15	upper	-	440
2.2	u	-	480
2.3	u	-	380
2.4	u	-	340

Table 2

Solubilization Data for Witco TRS 10-410-IBA-
n-Dodecane System

<u>% NaCl</u>	<u>V_o (o=oil)</u>	<u>V_o/V_s</u>	<u>V_w/(w=brine)</u>	<u>V_w/V_s</u>
0.8	0.4	0.93	-	-
0.9	0.5	1.14	-	-
1.0	0.6	1.36	-	-
1.1	0.75	1.70	-	-
1.2	0.95	2.16	3.26	7.41
1.3	1.15	2.61	2.16	4.91
1.4	1.1	2.50	1.31	2.98
1.5	1.1	2.50	1.15	2.61
1.6	1.15	2.61	0.81	1.84
1.7	1.1	2.50	0.76	1.73
1.8	1.3*	2.95	0.61	1.39
1.9	1.3*	2.95	0.56	1.27
1.95	1.9*	4.32	0.56	1.27
2.0	1.85*	4.20	0.46	1.05
2.1	2.3**	5.23	0.41	0.93
2.15	-	-	0.46	1.05
2.2	-	-	0.26	0.59
2.3	-	-	0.26	0.59
2.4	-	-	0.26	0.59

* Interface between middle and upper phase is diffuse

** Interface between middle and upper phase is very diffuse. Very close to critical point.

V_s = volume of surfactant + cosurfactant.

Table III

Results of Elemental Analysis for Texas 1.

	%C	%H	%S	%Na	%O	%Cl	Formula Weight
Theoretical	65.31	9.22	7.93	5.68	-	-	404.59
Lot #1 #1	-	-	7.93	5.55	-	0.68	-
Lot #1 #2	64.34	9.48	7.81	5.04	-	0.23	401.59
Lot #1 #3	64.47	9.09	8.18	5.39	-	1.56	397.9
Lot #1 #4	62.85	9.47	7.40	5.65	-	0.31	403.24
Lot #2 #5	65.18	9.14	7.77	5.69	-	0.13	404.6

SECTION XII. FIGURES

List of Figures

- Figure 1. Effect of n-Alcohol Chain Length on Microemulsion Phase Formation ~ 2.5 wt % Texas 1, 1.0 wt % NaCl Contacted 1:1 with n-Decane, $T \sim 22^{\circ}\text{C}$. u = upper phase, m = middle phase, l = lower phase
- Figure 2. Phase Behavior of Aqueous Solutions of y wt % Texas 1, x wt % n-Propanol, 1.0 wt % NaCl $T \sim 22^{\circ}\text{C}$. S = Spherulitic, S + L = Spherulitic + Lamellar, L + S = Lamellar + Spherulitic, L = Lamellar, Iso = Isotropic, unstable l.c. = unstable liquid crystals
- Figure 3. Viscosity of 8.5 wt % n-Propanol, 1.0 wt % NaCl, x wt % Texas 1.
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Figure 17. Polarized Light Screen II (PLS II)

Figure 18. Schematic Cross-Section of PLS II Optics.

Figure 19. Schematic Front and Top View of PLS II.

Figure 20. Schematic Circuits of PLS II.

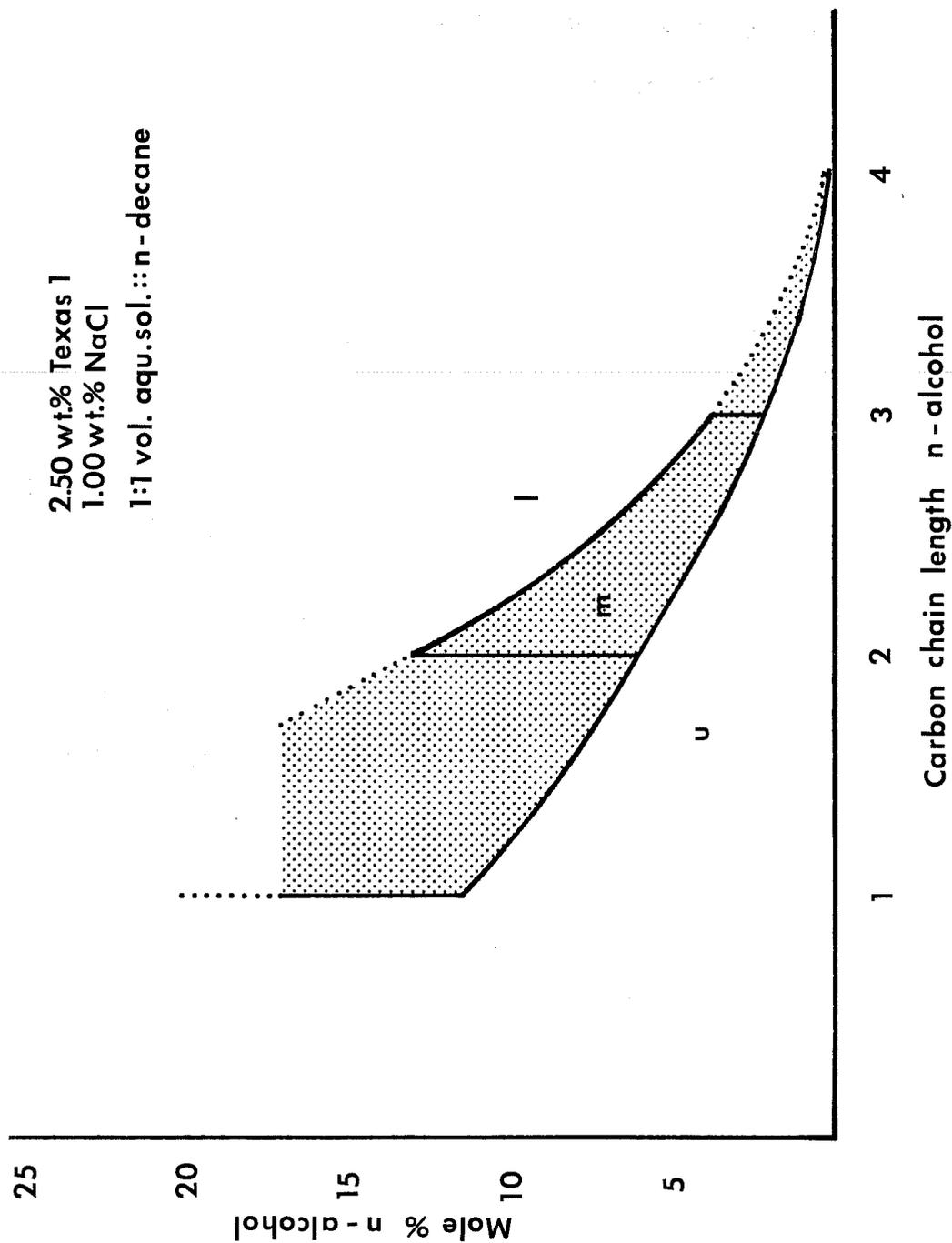


Figure 1. Effect of n-Alcohol Chain Length on Microemulsion Phase Formation - 2.5 wt % Texas 1, 1.0 wt % NaCl Contacted 1:1 with n-Decane, $T \sim 22^{\circ}\text{C}$. u = upper phase, m = middle phase, l = lower phase

Y% Texas 1 : X% n-propanol : 1.0% NaCl Aq. \emptyset . T ~ 22°C

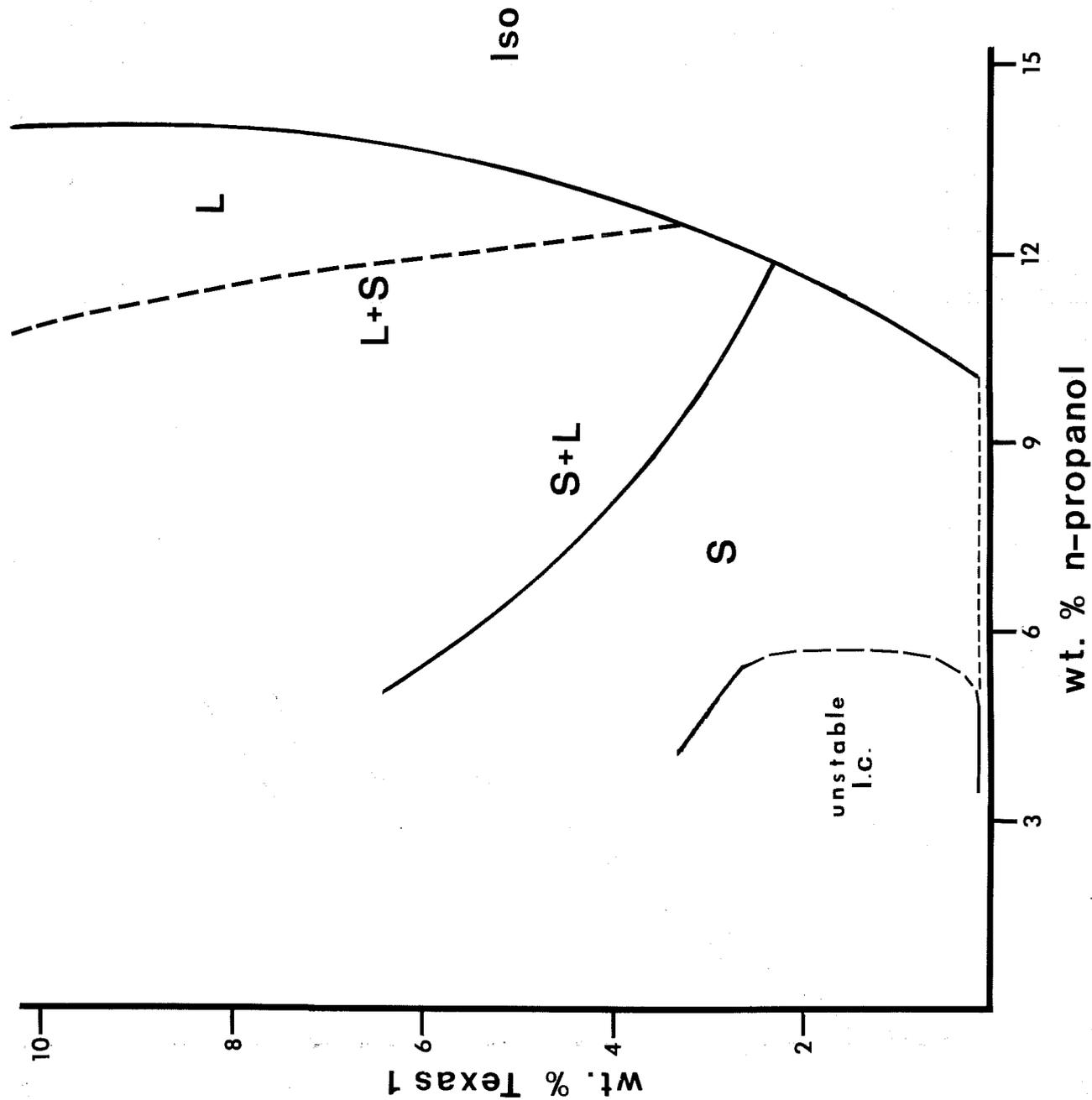


Figure 2. Phase Behavior of Aqueous Solutions of y wt % Texas 1, x wt % n-Propanol, 1.0 wt % NaCl T~22°C. S = Spherulitic, S + L = Spherulitic + Lamellar, L + S = Lamellar + Spherulitic, L = Lamellar, Iso = Isotropic, unstable l.c. = unstable liquid crystals

TG Series:
8.5 % Propanol; 1% NaCl; X% Texas-1 Aq. \emptyset

Temp. ($^{\circ}$ C): 26.0
Cone Angle: $.8^{\circ}$
Vol. of Sample (ml.): 1.1

Shear Rate
 \circ 75 sec^{-1}
 \square 150 sec^{-1}

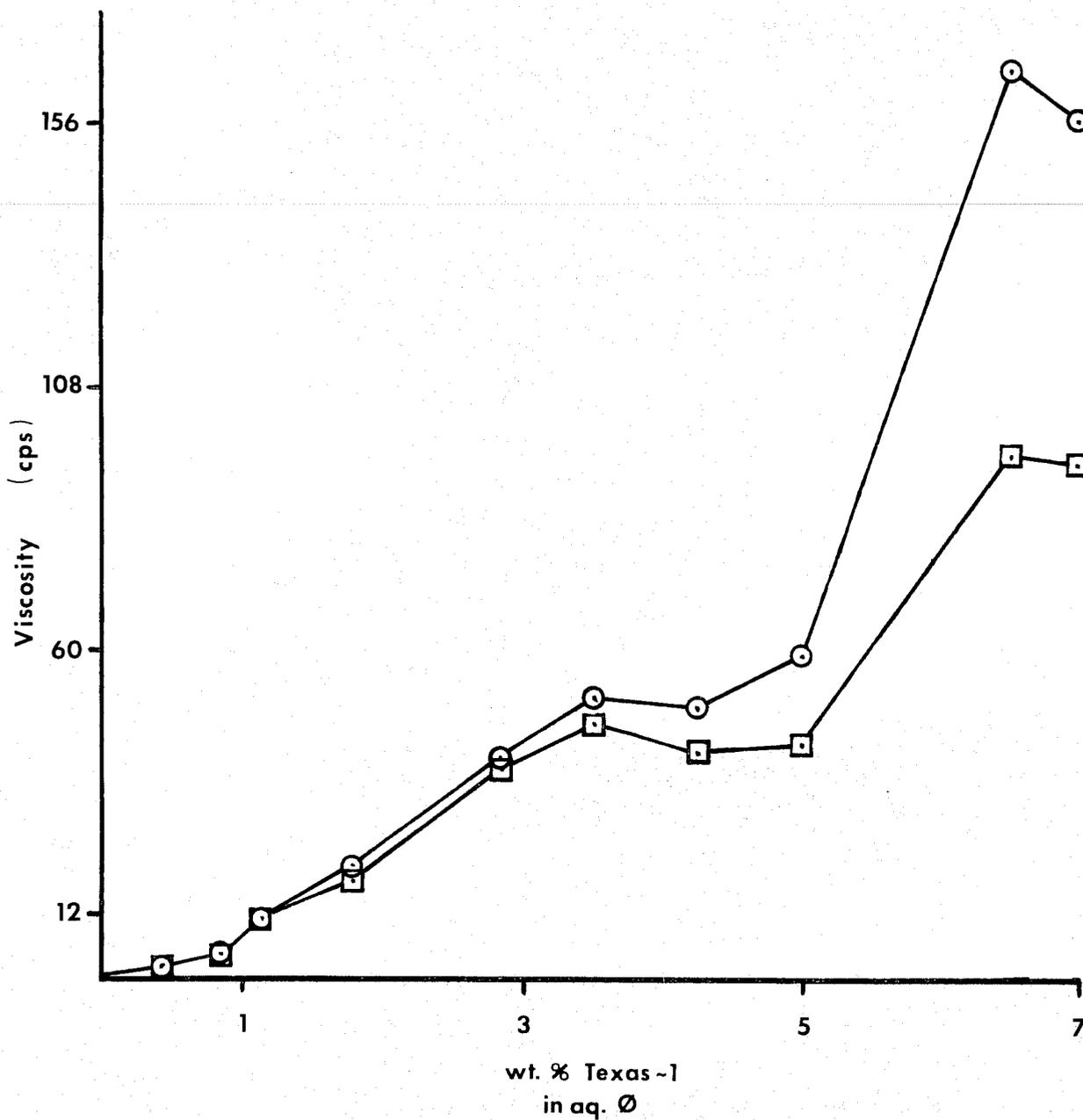


Figure 3. Viscosity of 8.5 wt % n-Propanol, 1.0 wt % NaCl, x wt % Texas 1.

TC Series:
3.5 % Texas-1; 1% NaCl; X% Propanol ; Aq. \emptyset

Temp. ($^{\circ}$ C): 25.5
Cone Angle: $.8^{\circ}$
Vol. of Sample (ml.): 1.1

Shear Rate
 \bigcirc 75 sec^{-1}
 \square 150 sec^{-1}

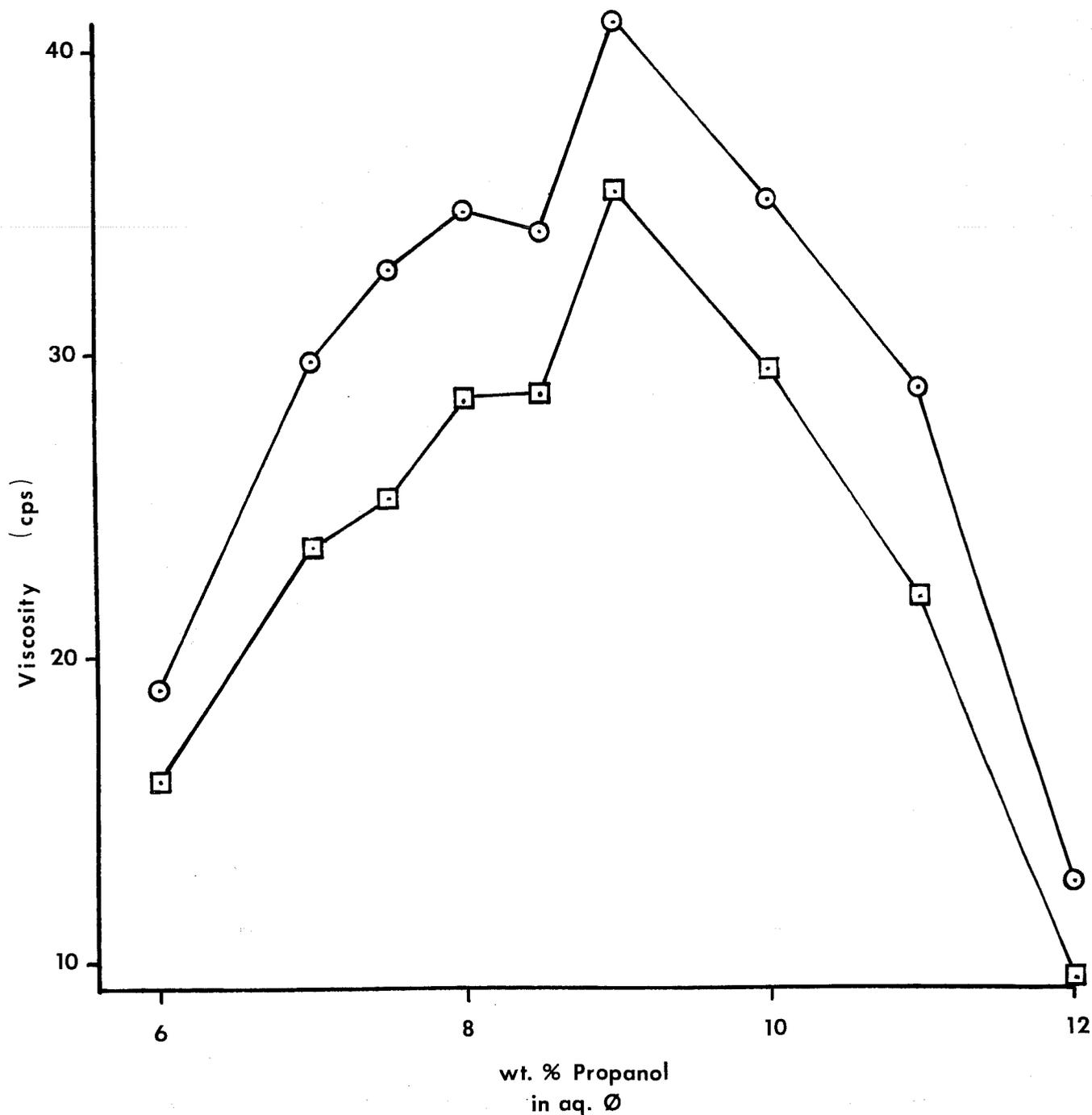


Figure 4. Viscosity of x wt % n-Propanol, 1.0 wt % NaCl, 3.5 wt % Texas 1.

TD Series:
8% Propanol; 3.5% Texas-1; X% NaCl Aq. \emptyset

Temp. ($^{\circ}\text{C}$): 23.5
Cone Angle: $.8^{\circ}$
Vol. of Sample (ml.): 1.1

Shear Rate
 \bigcirc 75 sec^{-1}
 \square 150 sec^{-1}

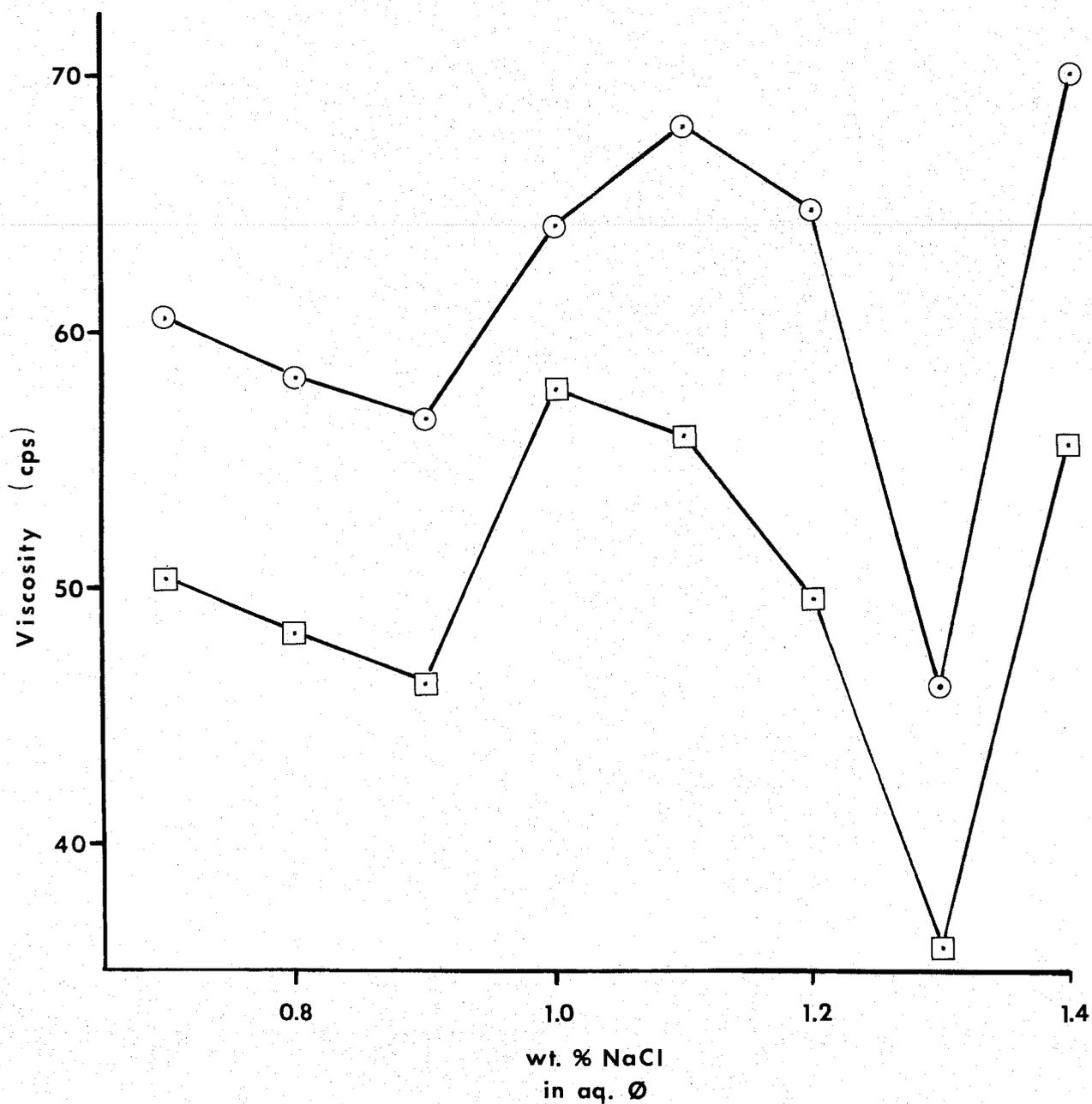


Figure 5. Viscosity of 8.0 wt % n-Propanol, x wt % NaCl, 3.5 wt % Texas 1.

Y% Texas 1 : X% n-propanol : 1.0% NaCl Aq. ϕ
 contacted 1:1 with n-decane. T = 22°C

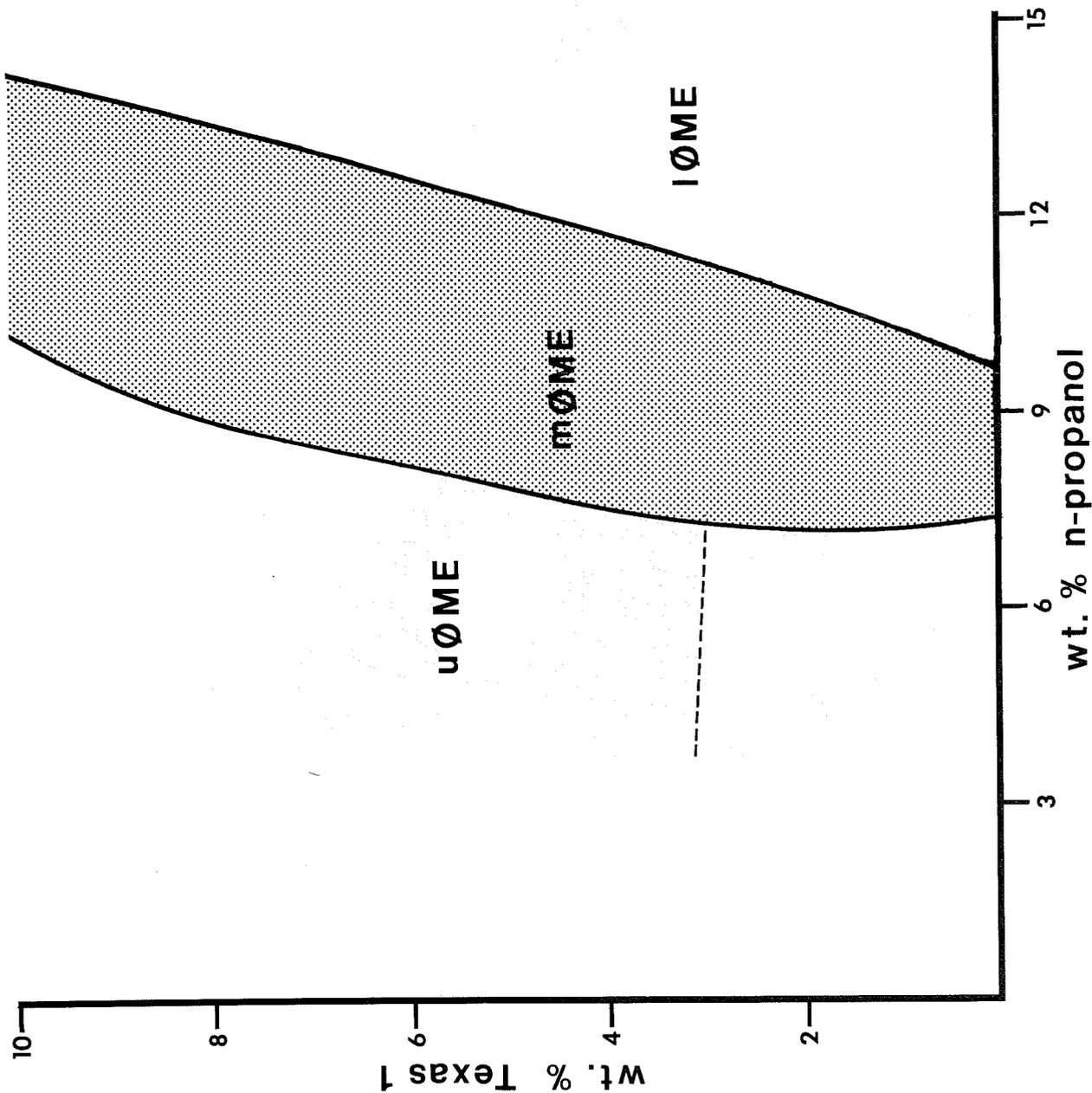


Figure 6. Effect of y wt % Texas 1, x wt % n-Propanol, 1.0 wt % NaCl on the Microemulsion Phase Behavior, T=22°C, Equilibrated 1:1 with n-Decane.

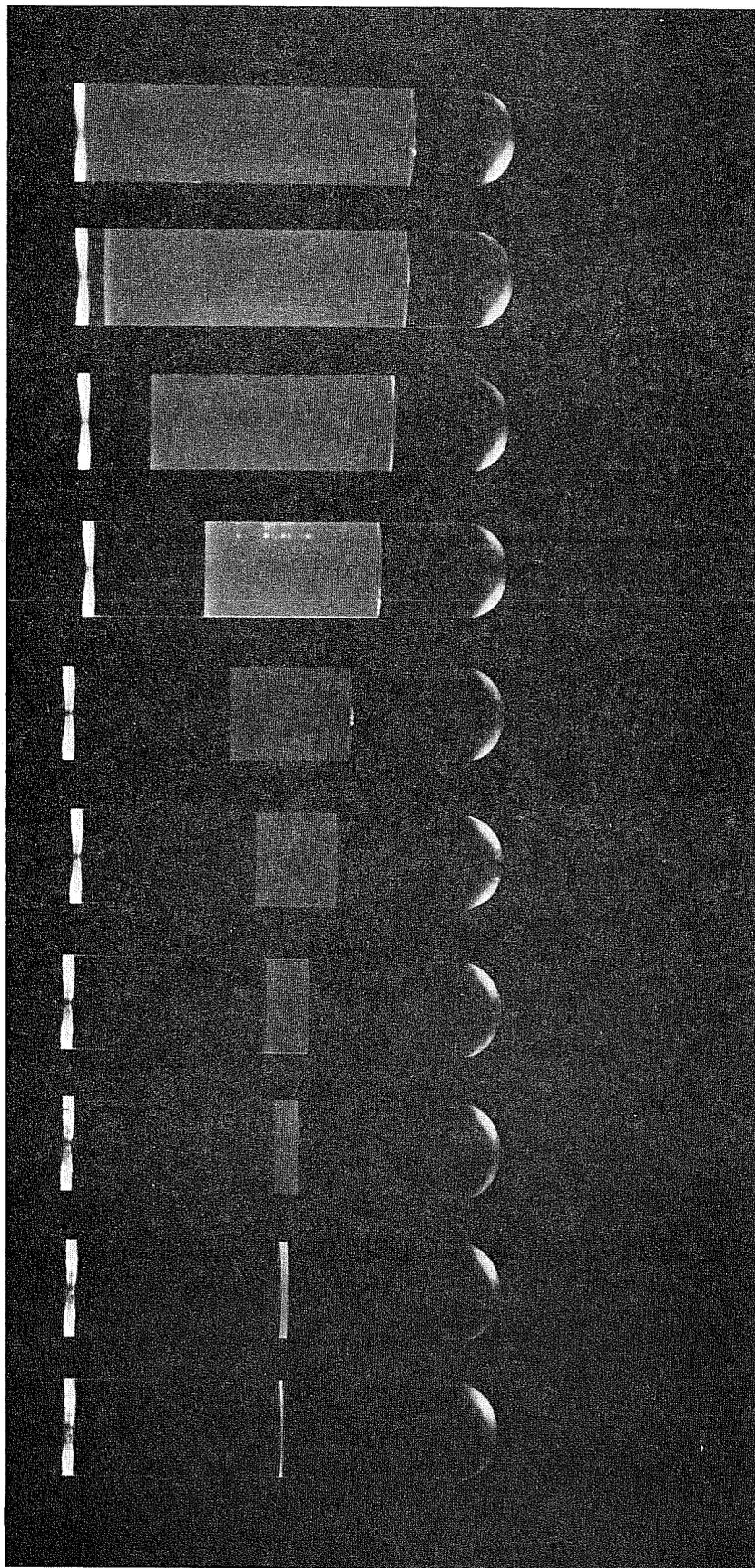
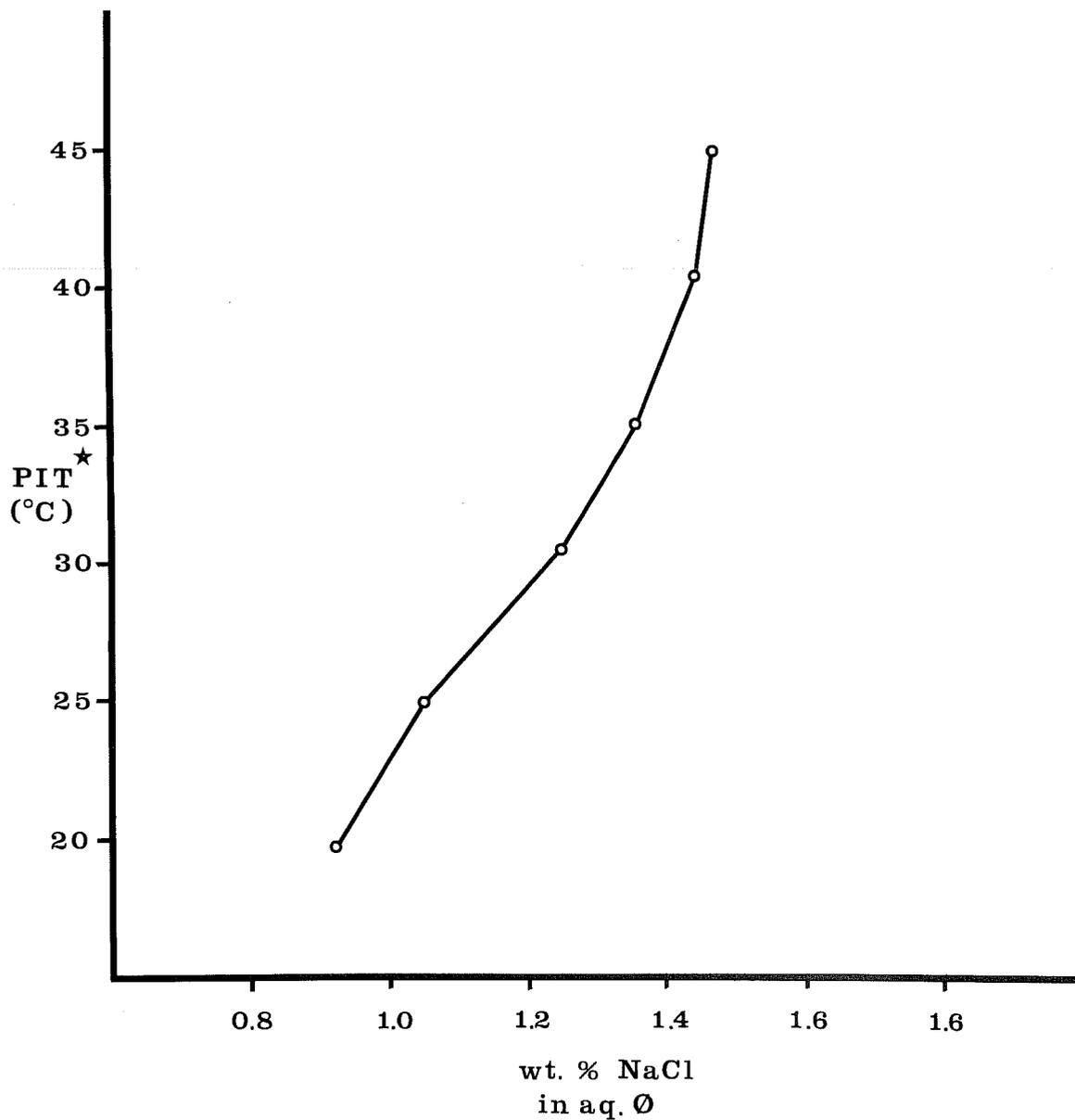


Figure 7. Middle Microemulsion Phase Behavior in Polarized Light. 8.5 wt % n-Propanol, 1.0 wt % NaCl, .05 wt % Texas 1 to 7.5 wt % Texas 1, T-220 C.

TO Series:
9% Propanol; 3.5% Texas-1; X% NaCl Aq. Ø
contacted 1:1 with Decane



*Phase Inversion Temperature

Figure 8. Effect of Temperature on the Optimum Salinity of 9 wt % n-Propanol, 3.5 wt % Texas 1 from PLS II.

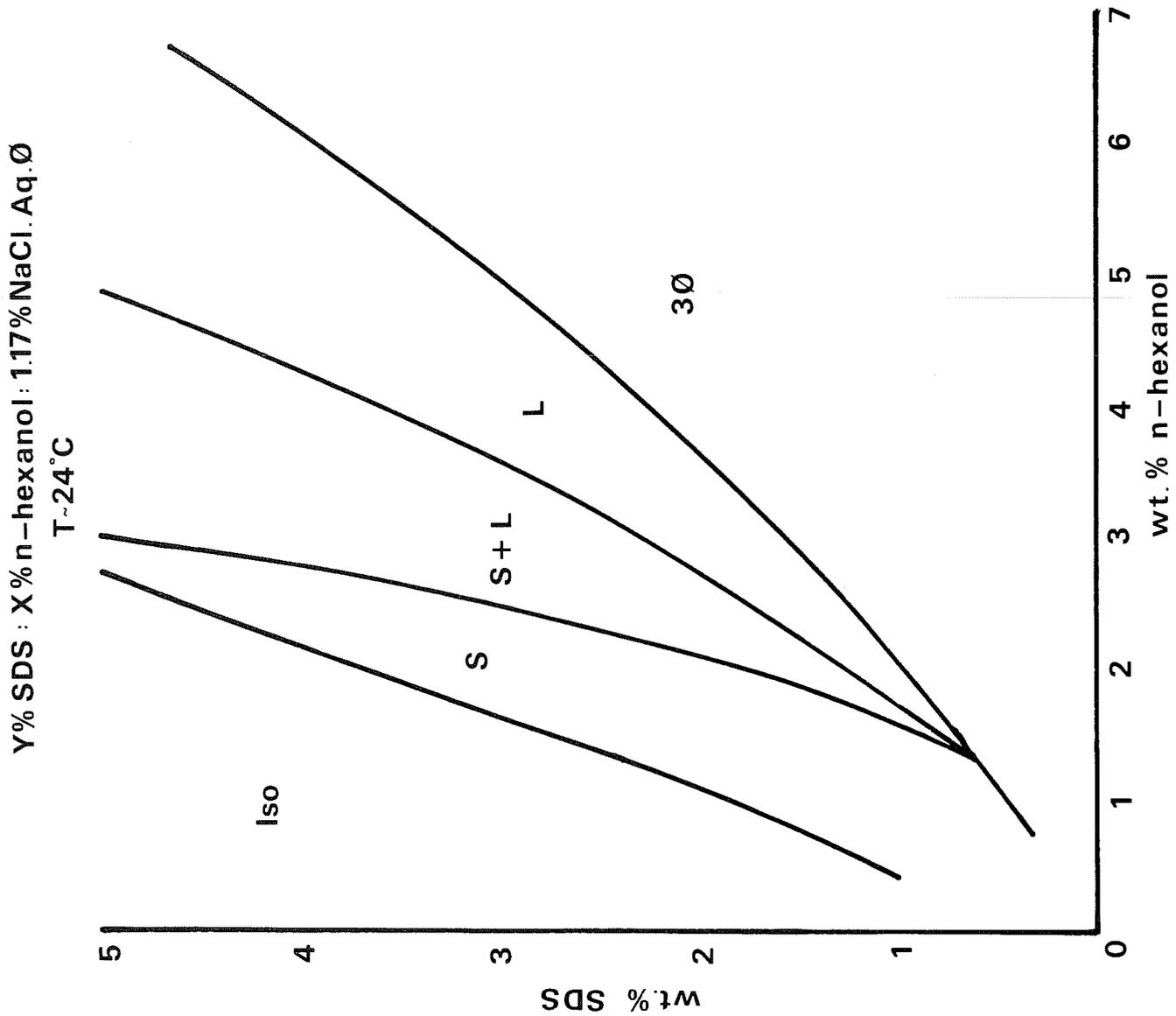


Figure 9. Phase Behavior of Aqueous Solutions of y wt % SDS, x wt % n-Hexanol, 1.17 wt % NaCl.

Y% SDS: X% n-hexanol: 2.33% NaCl. Aq. \emptyset
 contacted 1:1 with n-decane. T=24°C

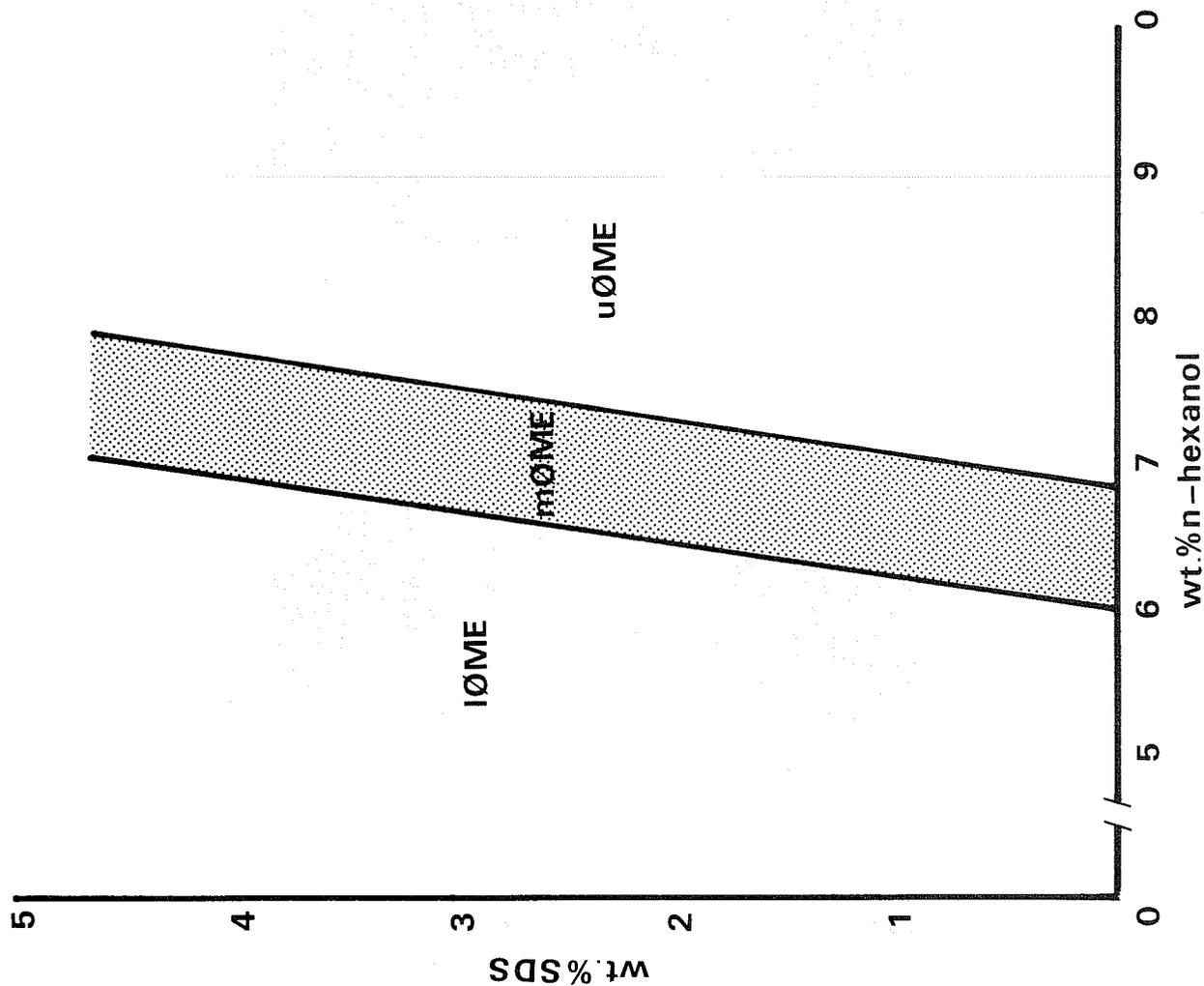


Figure 10. Effect of y wt % SDS, x wt % n-Hexanol, 2.33 wt % NaCl on the Microemulsion Phase Behavior. T=22°C, Equilibrated 1:1 with n-Decane.

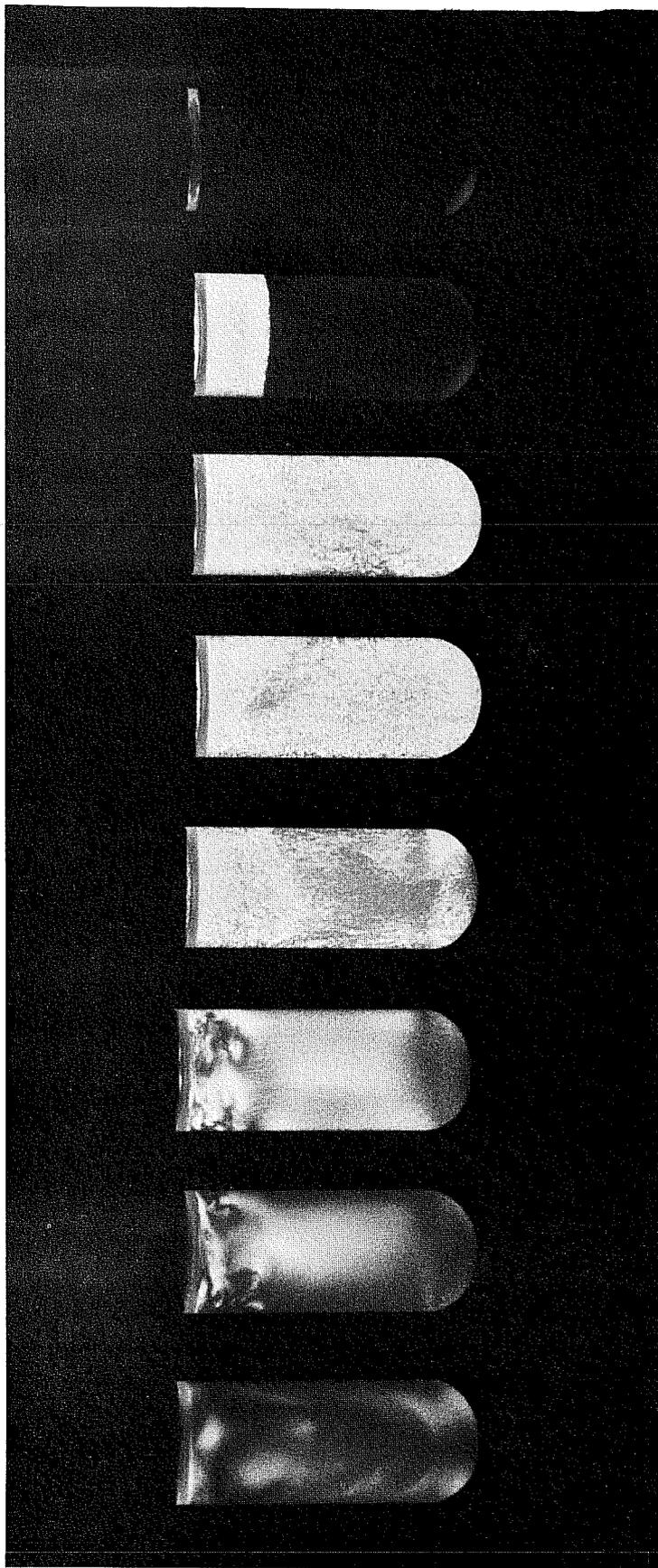


Figure 11. Aqueous Structures in Polarized Light of 5 wt % TRS 10-410, 3 wt % IBA, 0.8 \rightarrow 2.2 wt % NaCl in 0.2 wt % increments, $T \sim 22^\circ\text{C}$.

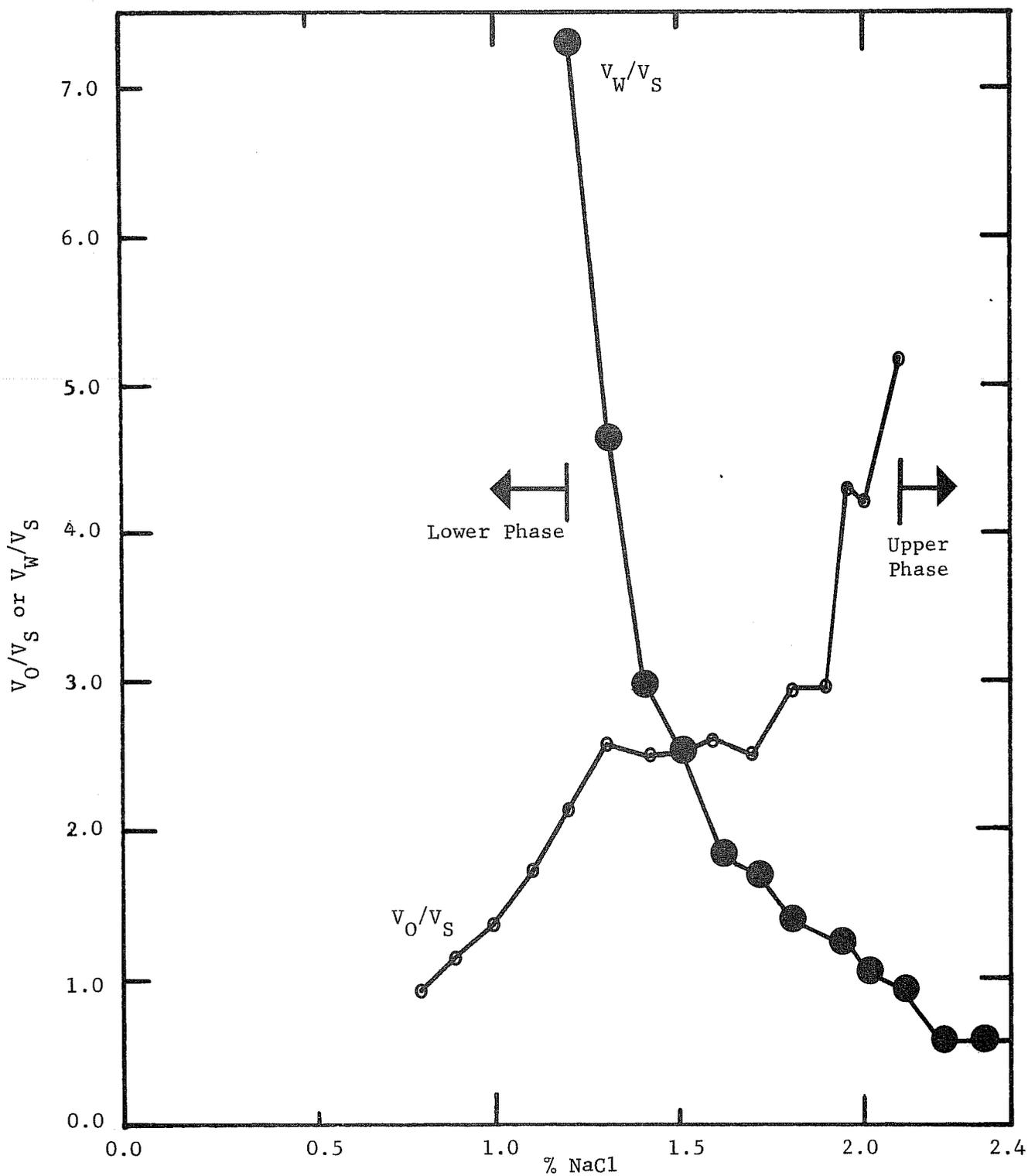


Figure 12. Solubilization Data for TRS 10-410, IBA Equilibrated 1:1 with n-Dodecane, $T \approx 22^\circ\text{C}$.

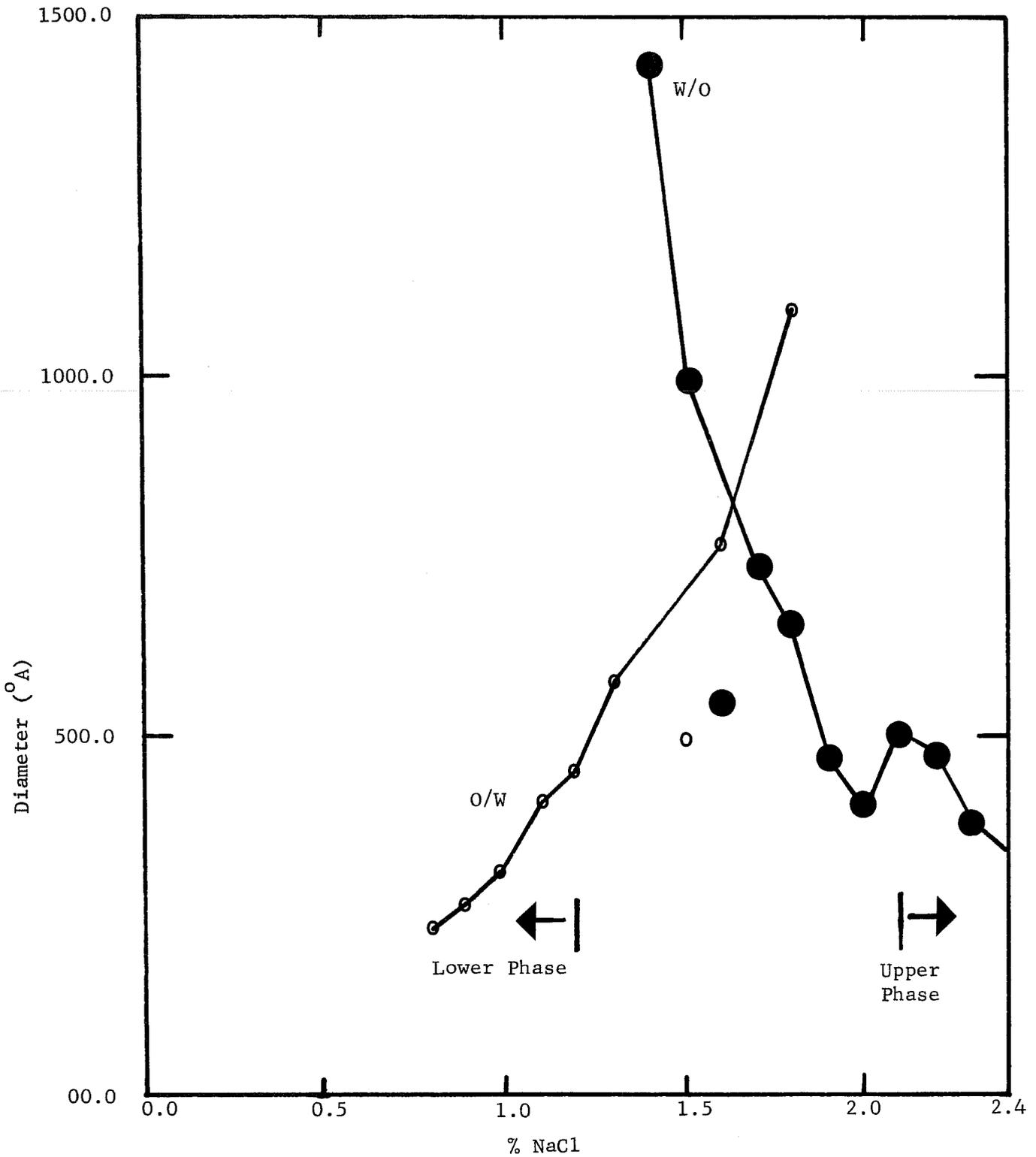


Figure 13. Drop Diameters of Microemulsion Phases of TRS 10-410, IBA Equilibrated 1:1 with n-Dodecane from Ultracentrifugal Experiments. $T \sim 22^{\circ}\text{C}$.

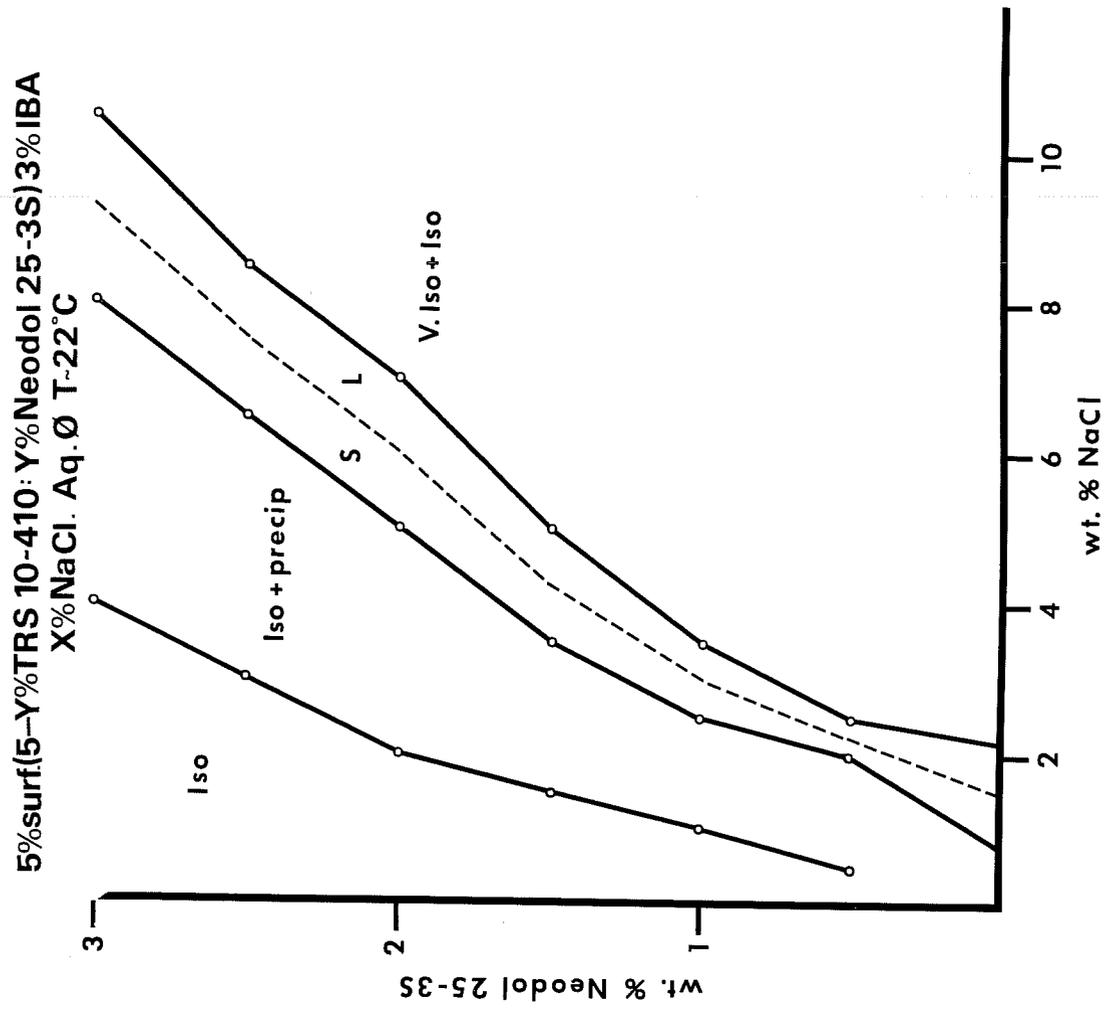


Figure 14. Effect on the Phase Behavior and Salt Tolerance of Aqueous Solutions on Addition of Neodol 25-3S. T-22°C.

5% surf (5-Y% TRS 10-410, Y% Neodol 25-3S) 3% IBA
 X% NaCl. Aq. Ø contacted 1:1 n-dodecane. T=22°C

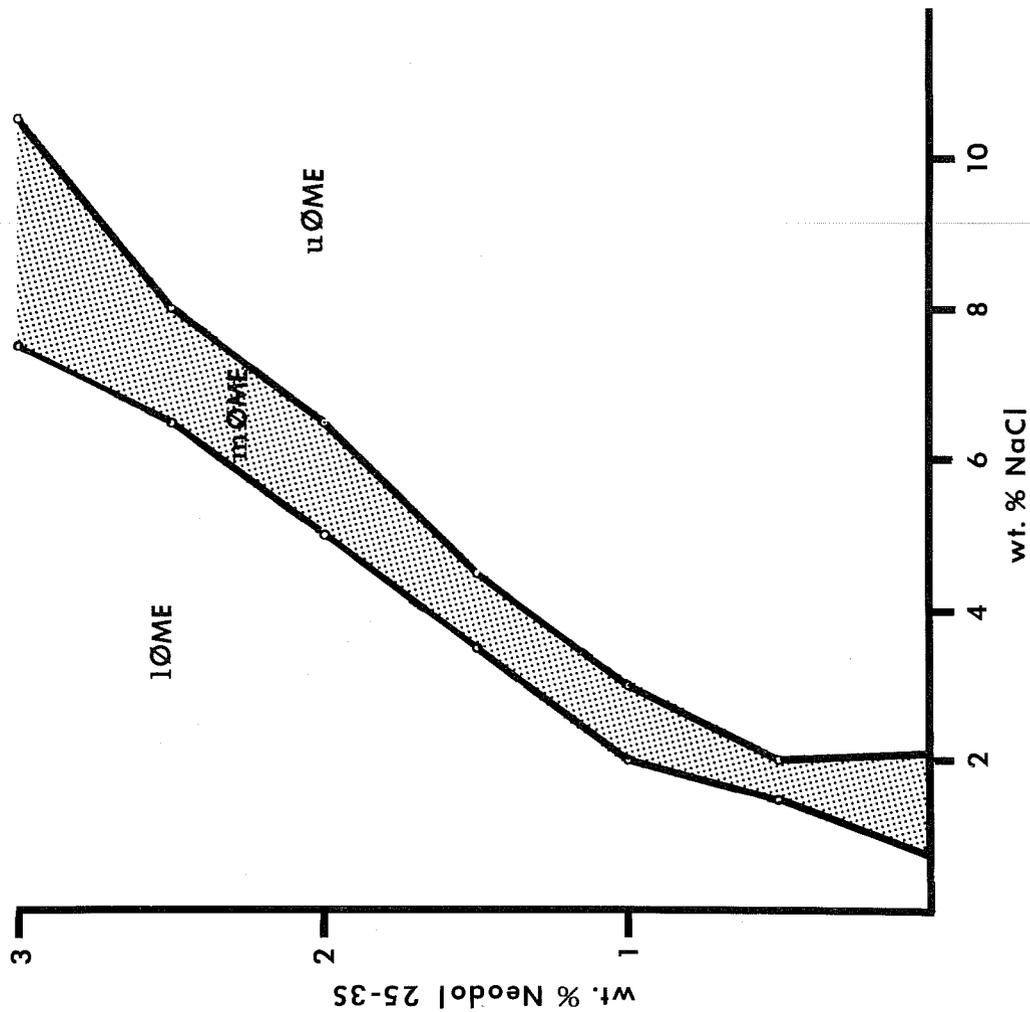


Figure 15. Effect on the Phase Behavior and Salt Tolerance of Oil Equilibrated Neodol 25-3S System. T=22°C.

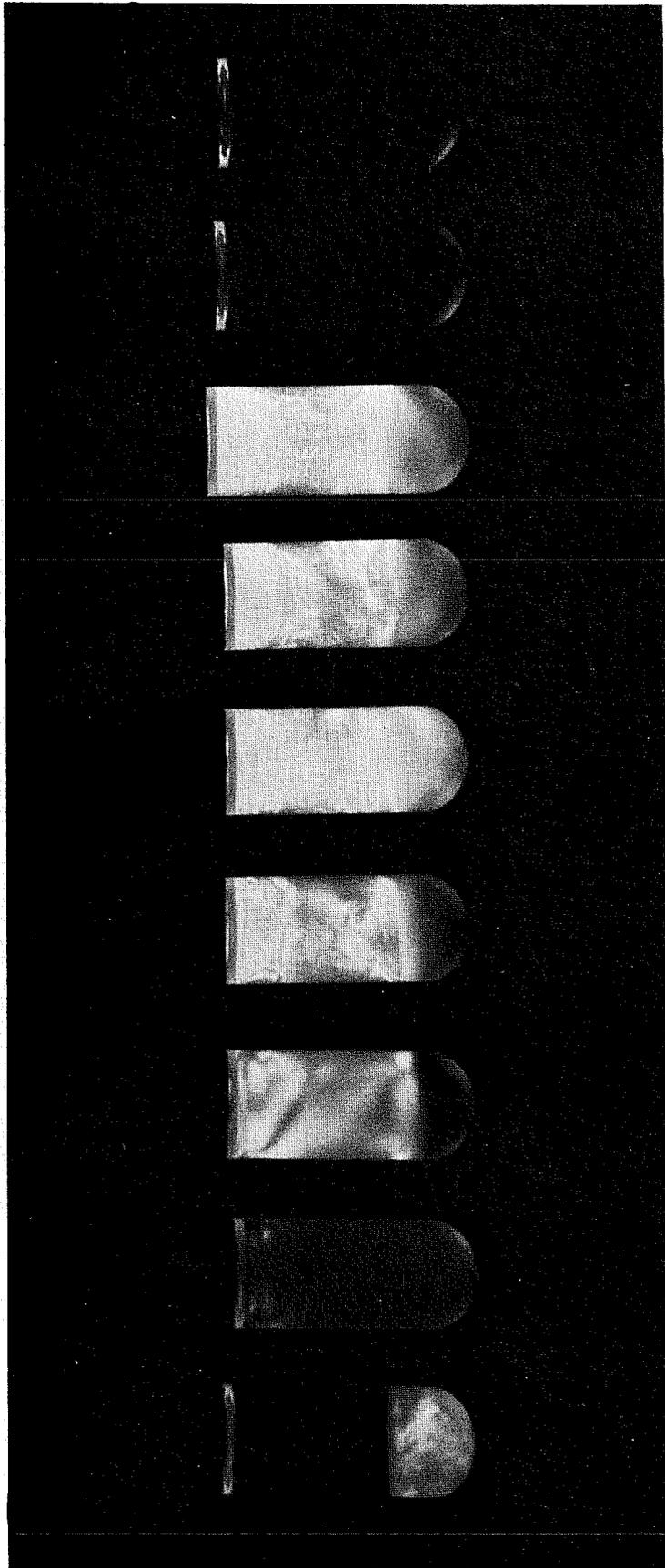


Figure 16. Aqueous Structures in Polarized Light of 5 wt % TRS 10-410, 3 wt % IBA, 0.8 - 2.2 wt % NaCl in 0.2 wt % increments, 750 ppm Xanthan Gum Biopolymer. T 22°C.

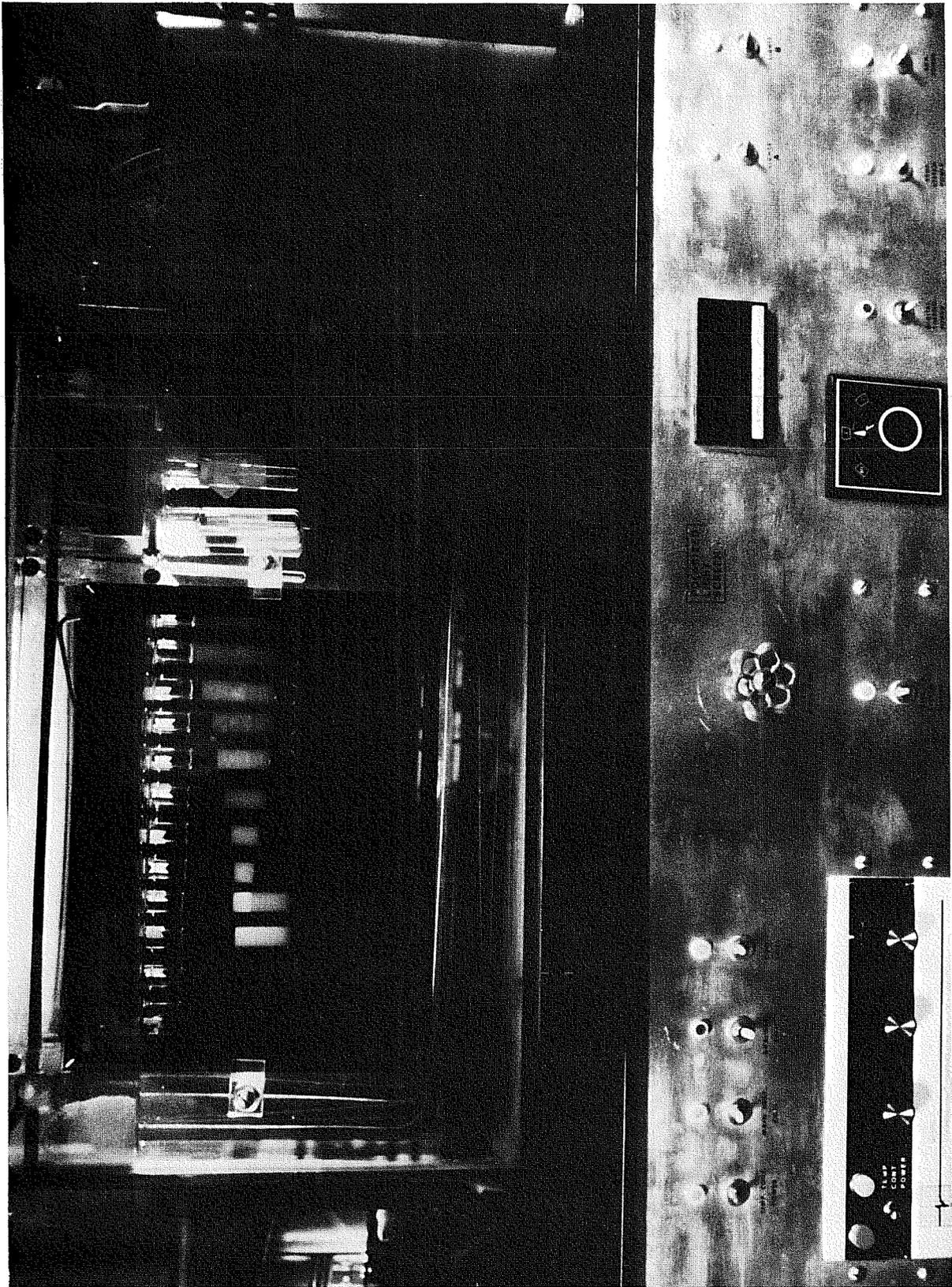


Figure 17. Polarized Light Screen II (PLS II)

CROSS-SECTION OF PLS II OPTICS

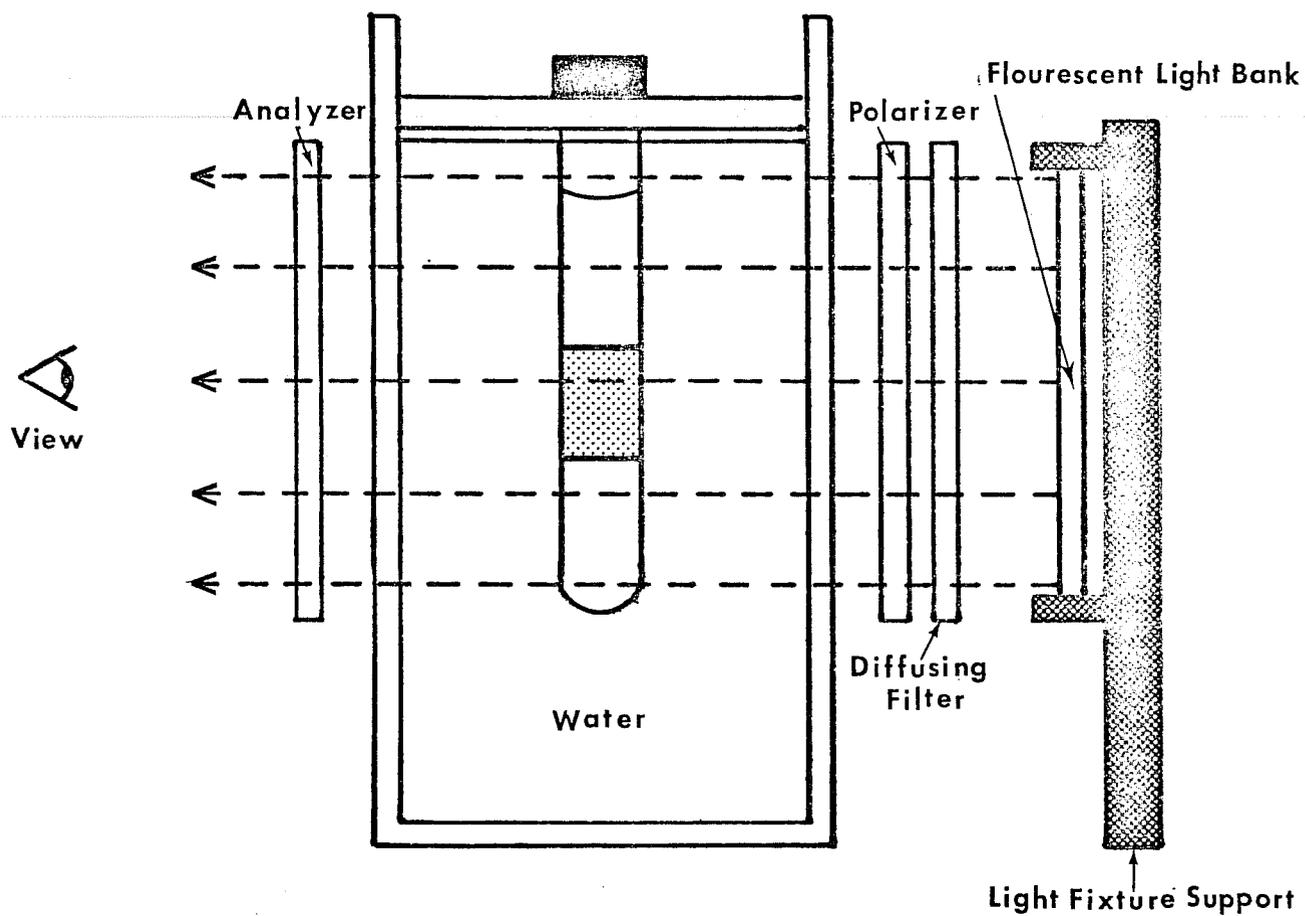


Figure 18. Schematic Cross-Section of PLS II Optics.

FRONT AND TOP VIEW OF THE PLS II

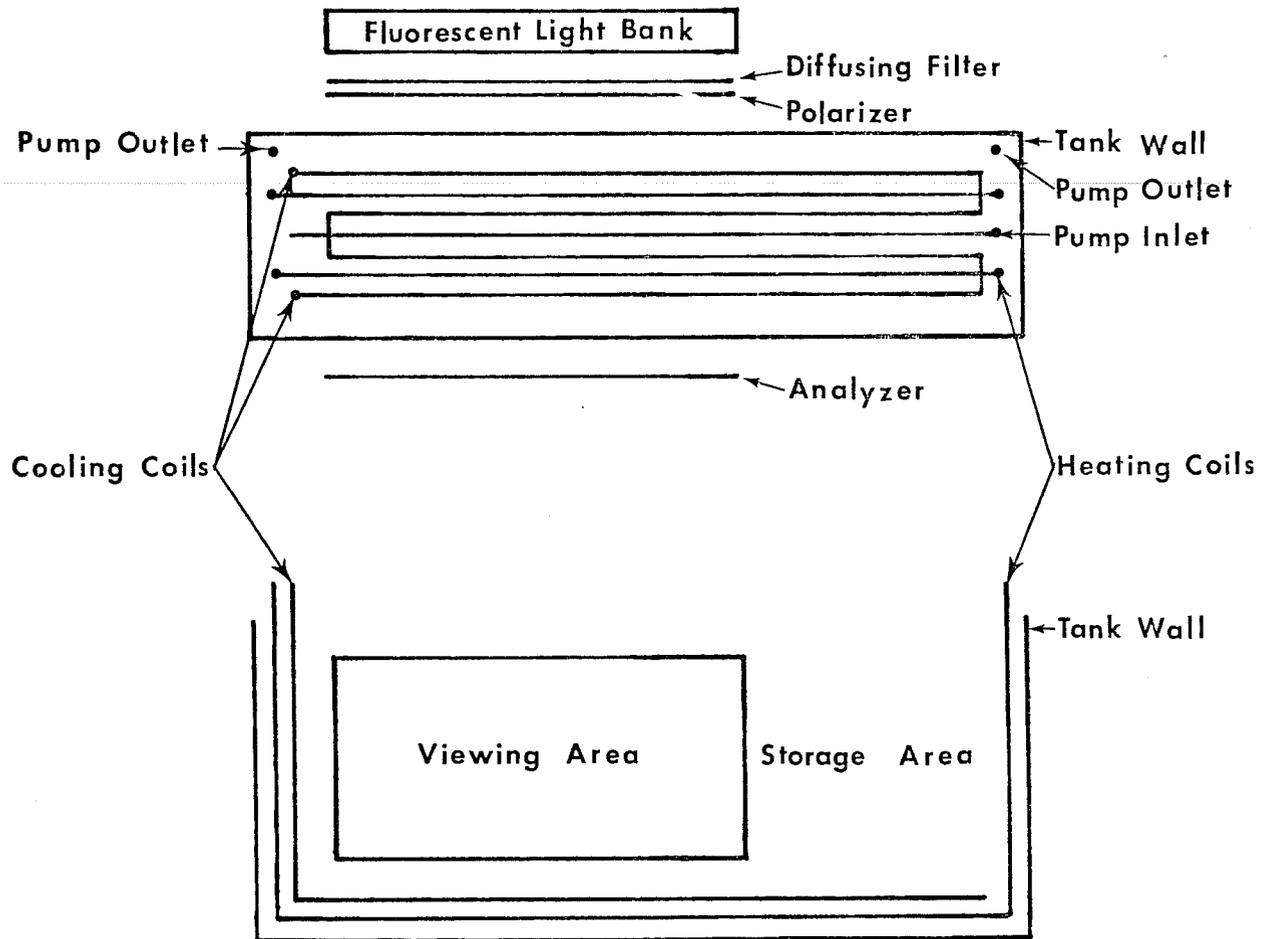


Figure 19. Schematic Front and Top View of PLS II.

Figure 20. Schematic Circuits of PLS II.

SCHEMATIC OF CIRCUIT FOR PLS II

