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RESEARCH ON SURFACTANT POLYMER
OIL RECOVERY SYSTEMS

Quarterly Report: June 1—August 31, 1978

Date Published—January 1979

Work Performed Under Contract No. EW-78-S-19-0008

University of Florida



U. S. DEPARTMENT OF ENERGY

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RESEARCH ON SURFACTANT POLYMER OIL RECOVERY SYSTEMS

Project Status Report
First Quarter: June 1—August 31, 1978

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CONSORTIUM OF INDUSTRIAL ASSOCIATES FOR
TERTIARY OIL RECOVERY RESEARCH
PROGRAM AT THE UNIVERSITY
OF FLORIDA

1. Amoco Production Company
2. Atlantic-Richfield Company
3. Cities Service Oil Company
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5. Ethyl Corporation
6. Getty Oil Company
7. Gulf Research & Development Company
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10. Phillips Petroleum Company*
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12. Stepan Chemical Company
13. Sun Oil Company
14. Texaco Incorporated
15. Union Carbide Corporation
16. Union Oil Company
17. WestVaco
18. Witco Chemical Corporation

*Phillips Petroleum Company has provided a graduate student fellowship for the oil recovery research program.

Milestone Schedule: DOE Contract EW-78-S-19-0008 (University of Florida)

First Quarter: June 1-August 31, 1978

I. Interfacial Phenomena

Milestones

A. Measure CMC and Partition Co-efficient of Synthetic and Petroleum Sulfonates

1. Determine CMC of SDBS in distilled water at 25°C using surface tension, electrical conductivity, and light scattering.
2. Determine CMC of SDBS in the presence of dissolved alcohols ($C_2 - C_6$).
3. Determine CMC of SDBS in distilled water in the presence of dissolved oils at 25°C.
4. Determine PC of TRS 10-80 in 1% NaCl against oils of various chain length.

B. Determine microstructure of multi-component surfactant formulation

1. Determine the microstructure related parameters in TRS-10-410 + IBA (5:3 w/w) system using spin-label probes. Calculate correlation time, order parameter, and line width as a function of NaCl concentration.
2. Using the above mentioned ESR technique, determine these parameters in lower, middle and upper phase microemulsions.

II. Polymer Rheology and Fluid Mechanics

A. Molecular Characterization of Polymers

1. Determine the effect of aging (0-45 days) on screen factor, intrinsic and shear viscosity of polyacrylamide (Calgon-815, and Calgon-835) solutions (500 ppm).
2. Determine the effect of temperature (30°C, 45°C and 65°C) on aging on the polyacrylamide solutions using the above mentioned parameters.

First Quarter (Cont'd)

II. Polymer Rheology and Fluid Mechanics (Cont'd)

Milestones

- A. Molecular Characterization of Polymers (Cont'd) 3. Determine the effect of salinity and calcium chloride concentration on the polyacrylamide solutions using the above mentioned parameters.
- B. Surfactant/Polymer Interactions
1. Determine the effect of a partially hydrolyzed polyacrylamide (Calgon 835) on the interfacial tension of TRS 10-410 (0.01-0.5%) in 1.5% brine equilibrated with equal volume of dodecane.
 2. Compare the IFT behavior of the above mentioned surfactant formulation with two types of polymer
 - (a) partially hydrolyzed Calgon 835
 - (b) unhydrolyzed Calgon 800

III. Thermodynamic Properties

A. Theory

1. General Expressions will be written to relate molecular and macroscopic quantities to all thermodynamic properties of aqueous solution of spherical nonpolar gases over the temperature range 0 - 100°C.

B. Experiment

1. The high pressure apparatus will be assembled, tested for leaks, temperature control, and spurious observations. It will be filled with the potassium oleate liquid crystal for preliminary observations.

IV. Rock/Fluid Interactions

A. Surfactant/Polymer Precipitation

1. Surfactant Salting-Out
Establish basic experimental procedures and methods of analysis for quantitative measurement of surfactant salting out by NaCl.

Milestone Schedule: DOE Contract EW-78-S-19-0008 (Cont'd)

First Quarter (Cont'd)

IV. Rock/Fluid Interactions (Cont'd)

Milestones

A. Surfactant/Polymer Precipitation (Cont'd)

1. Surfactant Salting-Out (Cont'd)
 2. Measure influence of NaCl concentration on salting-out of a commercial surfactant (SUL-FON-ATE AA10) and a pure, monoisomeric sulfonate (UT-1=8 phenyl hexadecane sodium sulfonate).
 3. Measure influence of oil (n-octane) on salting-out by NaCl and on distribution of surfactant between oil and aqueous phases.
1. Measure quantitatively the fraction of surfactant remaining in solution as a function of initial calcium ion concentration and surfactant/calcium ratio for sodium lauryl sulfate, Aerosol-OT, and SUL-FON-ATE AA10.

2. Multivalent Cation Precipitation

B. Surfactant/Polymer Adsorption

NOTE: Since interpretation of adsorption data requires a knowledge of the CMC of the surfactant at the conditions of the experiment (CMC is affected by NaCl concentration, alcohol type and concentration, and oil chain length), some measurements of CMC are required though not covered in the original proposal.

1. Surfactant CMC

1. Measure effect of NaCl concentration and of excess oil (n-dodecane) on the CMC of selected anionic surfactants.
NOTE: Semi-quantitative measurements of surfactant solubility and salting-out are also required.

Milestone Schedule: DOE Contract EW-78-S-19-0008 (Cont'd)

First Quarter (Cont'd)

IV. Rock/Fluid Interactions (Cont'd)

Milestones

B. Surfactant/Polymer Adsorption (Cont'd)

2. Surfactant Adsorption

1. Measure rate of adsorption of SUL-FON-ATE AA10 on Na-kaolin.

2. Measure equilibrium adsorption of SUL-FON-ATE AA10 on Na-kaolin.

3. Polymer Adsorption

1. Evaluate methods for polymer analysis for application to equilibrium polymer adsorption experiments.

C. State-of-the-Art survey of surfactant loss by precipitation (added to contract during August, but not officially approved until September 13, 1978).

1. Initiate literature search, and identify sources of information.

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I. Interfacial Phenomena

A 1. Determine CMC of SDBS in Distilled Water at 25°C Using Surface Tension, Electrical Conductivity and Light Scattering

The importance of micelle formation and the occurrence of the CMC has been well established in this research program. The two most common methods of measuring the CMC are surface tension and conductivity measurements. In the presence of salt however, the latter method fails. As such we have investigated the use of light scattering as a method of double checking the CMC obtained by other methods. The light scattering method is very simple and involves only the measurement of the light scattered at 90° to the incident light (I_{90}).

Materials and Methods

Sodium dodecyl benzene sulfonate (SDBS), originally 85% active containing about 15% salt, was first desalted by dissolving the surfactant in pure isopropanol. The clear supernatant was separated and dried to yield a semi-solid surfactant estimated to be 99.5% pure. Solution of 1% SDBS in doubly distilled water was prepared and then successively diluted to any desired concentration by water of same quality.

Surface tension measurements were done by Wilhelmy plate method using a platinum blade balanced by an extremely sensitive strain gauge. The response from this strain gauge was plotted by a strip chart recorder.

Light scattering I_{90} measurements were done by using a Wood dual photometer, Model 5200. Monochromatic light of wave length 436 m μ was used and the intensity of light scattered at 90° (I_{90}) angle was measured for samples of various dilutions. The cell used in the I_{90} measurements was a square optically polished quartz cell (30 x 30 mm) which requires about 30 ml of solution. The cell was first washed with acetone, both inside and out, to remove materials which are insoluble in water. It was then cleaned with a detergent solution in an ultra-sonic bath.

A stock solution of 1.0% (w/v) of SDBS in distilled water was prepared, and solutions of lower concentration were prepared by dilution. All solutions were clear and colorless. Solutions prepared were kept in a constant temperature box for about 24 hours to ensure the attainment of the equilibrium between micelles and surfactant monomers in the solutions. Before transferring the solution from vial to the cell, the surface of the surfactant solution was cleaned by removing any insoluble particle or trace of oil which can be redispersed in the cell due to the mechanical agitation generated during the transfer. Occasionally, centrifugation at high speed (3,000 rpm) was applied to some translucent solutions to check the stability of the solutions.

Results and Discussions

To demonstrate that the I_{90} ratio measurement can be used to determine the CMC accurately, the log-log plot of I_{90} (solution)/ I_{90} (solvent) for pure SDBS in distilled water against SDBS concentration is shown in Figure I-1. In the range of surfactant concentration studied, the solutions remain absolutely clear. But the I_{90} ratios increases rapidly only after a certain concentration is reached. The curve at high concentration and low concentration regions is linear. Intersection of these extrapolated parts is at 0.06% SDBS. Surface tension curve is shown in Figure I-2 which also shows a CMC at the same concentration. Below CMC, the scatterers are monomers or dimers or other sub-micellar aggregates. The value of I_{90} increases slowly with the addition of more surfactant molecules in the solution. After CMC, the scatterers are micelles, their number increases also with the increase of surfactant concentration and thus I_{90} increases rapidly. The drastical change of slope of I_{90} curve as shown in Figure I-1. clearly shows the micellization of the surfactant molecules.

For sodium dodecyl sulfate solutions at various NaCl concentrations, Kushner and Hubbard (1955) showed that the turbidity of the surfactant solution increases strikingly.

Conclusions

Light scattering I_{90} ratio for surfactant solution and solvent was shown to be proportional to the ratio of the turbidity of the micellar solution (monomers and micelles) to that of the monomer solution. The I_{90} ratio was found to be very sensitive to the structural change of the surfactant solution.

For pure sodium dodecyl benzene sulfonate in water, the I_{90} ratio accurately determined the CMC at 0.06% SDBS in excellent agreement with the value determined by surface tension and electrical conductivity measurements

LIGHT SCATTERING MEASUREMENT (I_{90}) OF SDBS IN DISTILLED WATER

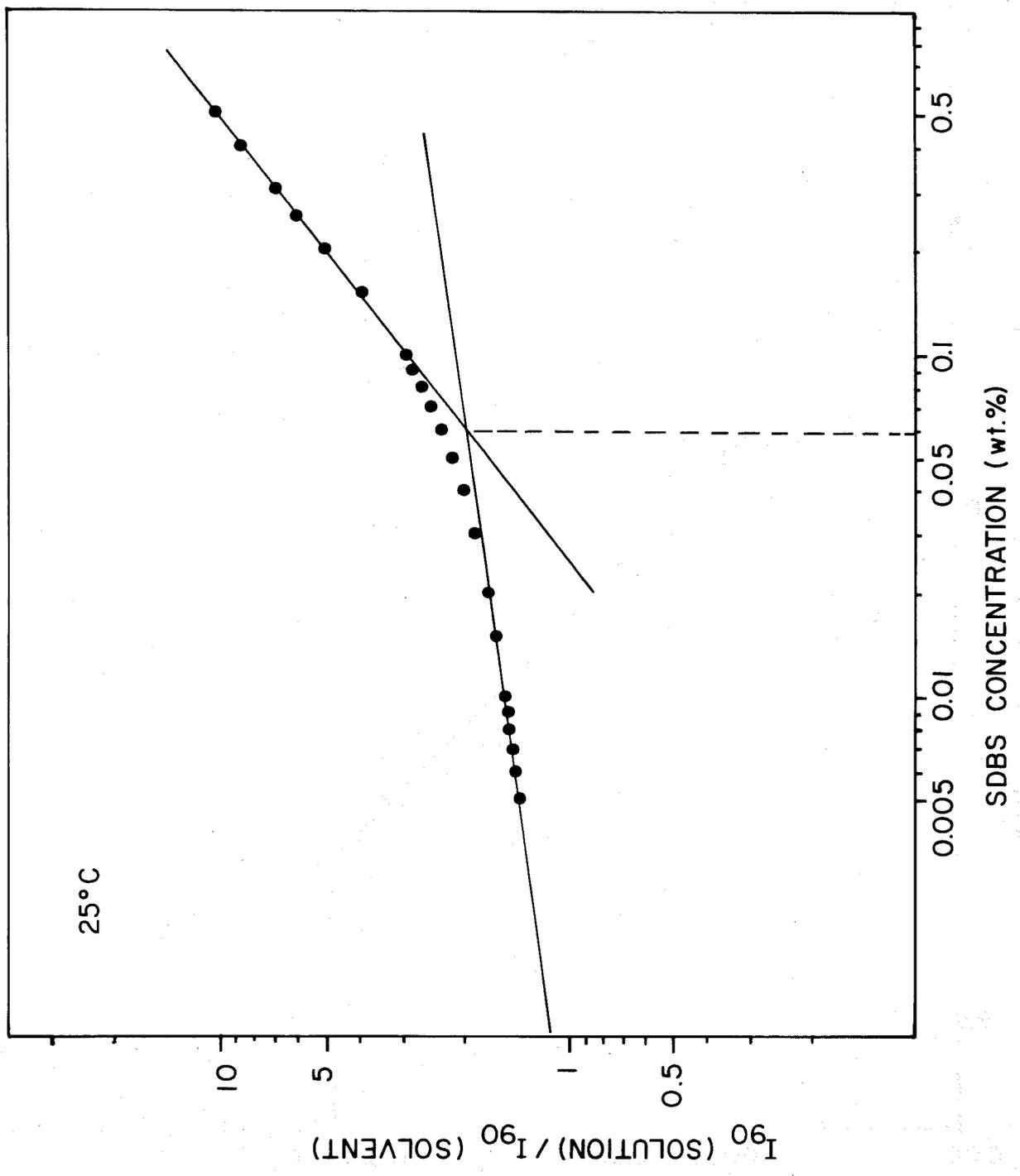


Figure I-1

SURFACE TENSION OF PURIFIED SDBS IN DISTILLED WATER

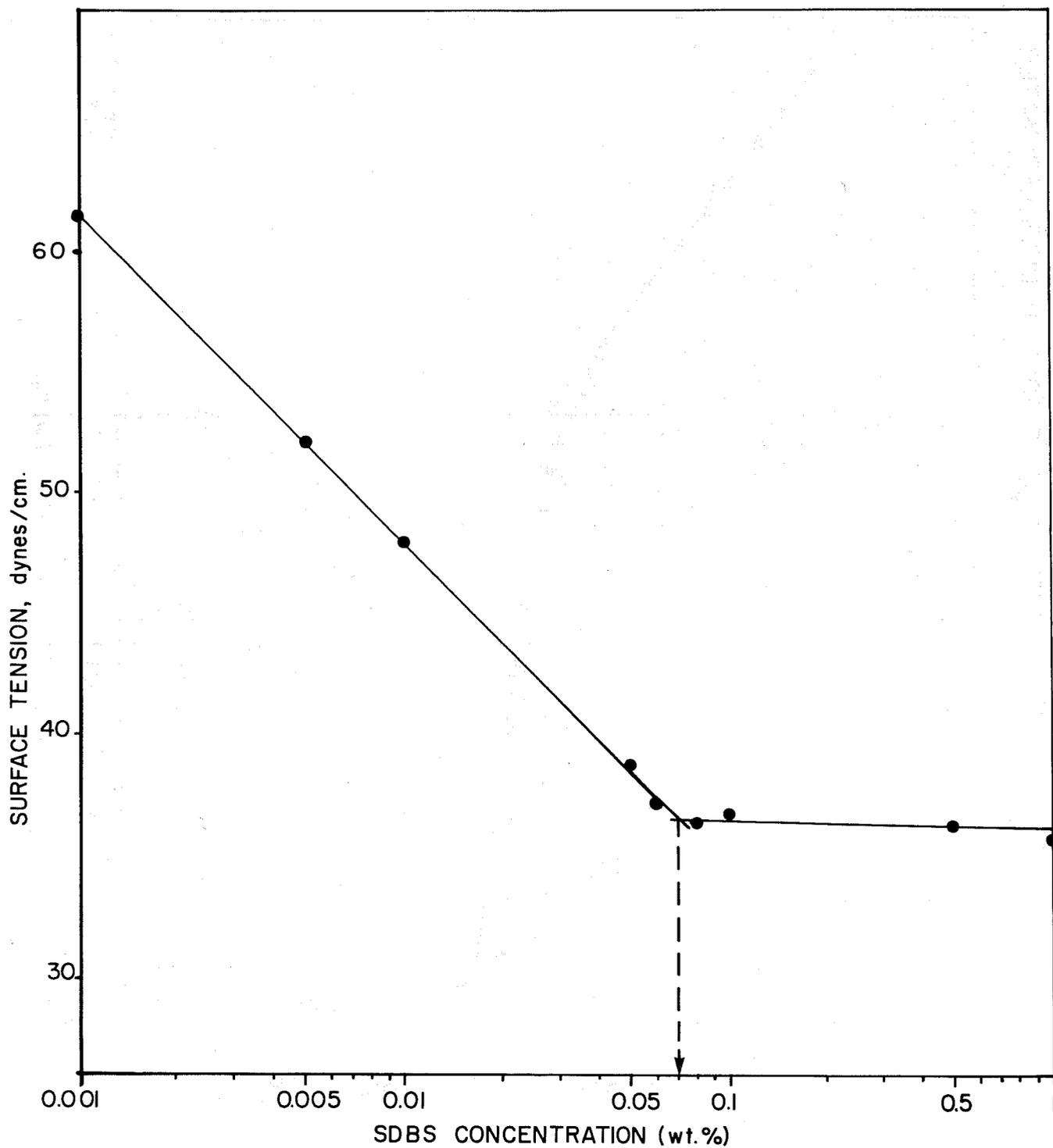


Figure I-2

A 2. Determine CMC of SDBS in The Presence of Dissolved Alcohols (C₂ - C₆)

In the previous section we have illustrated a new light scattering method of measuring the CMC, and applied it to measure the CMC of SDBS in distilled water. Surfactant formulations made up for use in tertiary oil recovery however, are not such simple 2-component (surfactant + water) solutions. Among the other components that are usually present in the formulation is the cosurfactant or alcohol. Hence, in this section, we investigate the effect of a variety of alcohols on the CMC of SDBS in distilled water.

Materials and Methods

Sodium dodecyl benzene sulfonate (SDBS) was obtained from Pfaltz and Bauer, Inc. As received, it contained about 15% salt and was free of oil. The structure of SDBS was confirmed by High Resolution NMR Spectroscopy study in our laboratory (Hsieh and Shah, 1977). The surfactant hydrocarbon chain length is linear and is composed mostly of single species such that the molecular weight distribution is narrow and the average equivalent weight was determined to be 384.8. The surfactant was desalted by dissolving the surfactant in pure isopropanol. The clear supernatant was separated and dried to yield a semi-solid surfactant estimated to be 99.5% pure.

Light scattering I_{90} measurements for the determination of CMC was used in this study. The CMC determined by this technique was cross-checked by electrical resistivity measurements. All the measurements were done at a constant temperature of 25°C. Occasionally, surface tension measured by Wilhelmy plate method was used to confirm the CMC determined by the two methods mentioned above.

Results and Discussions

Figure I-3 shows the effect of alcohol chain length on the CMC of SDBS in distilled water at various alcohol concentrations. For a fixed alcohol concentration, the decrease in the CMC is larger when the alcohol of longer chain length is used. We observed a linear decrease of CMC for SDBS over the range of ethanol concentration up to 7%. The effect of normal propanol, butanol and pentanol on the CMC of SDBS in water at 25°C is shown in Figure I-4. The CMC vs alcohol concentration for each alcohol is linear. The logarithmic relation between the rate of change of CMC with alcohol concentration, $d(\text{CMC})/dC_A$ and number of hydrocarbon chain in alcohol is also linear. This can be seen from Figure I-5. The effect of isomers of butanol and pentanol on the CMC of SDBS are shown in Figure I-6 and Figure I-7. The CMC curves are also linear.

It is known that the alcohol molecules penetrate the surfactant association of the micelles (Ekwall, 1954). The penetration of alcohol to surfactant monolayer produces a screening effect which re-

EFFECT OF CHAIN LENGTH OF NORMAL ALCOHOL ON
CRITICAL MICELLE CONCENTRATION OF SDBS IN
DISTILLED WATER

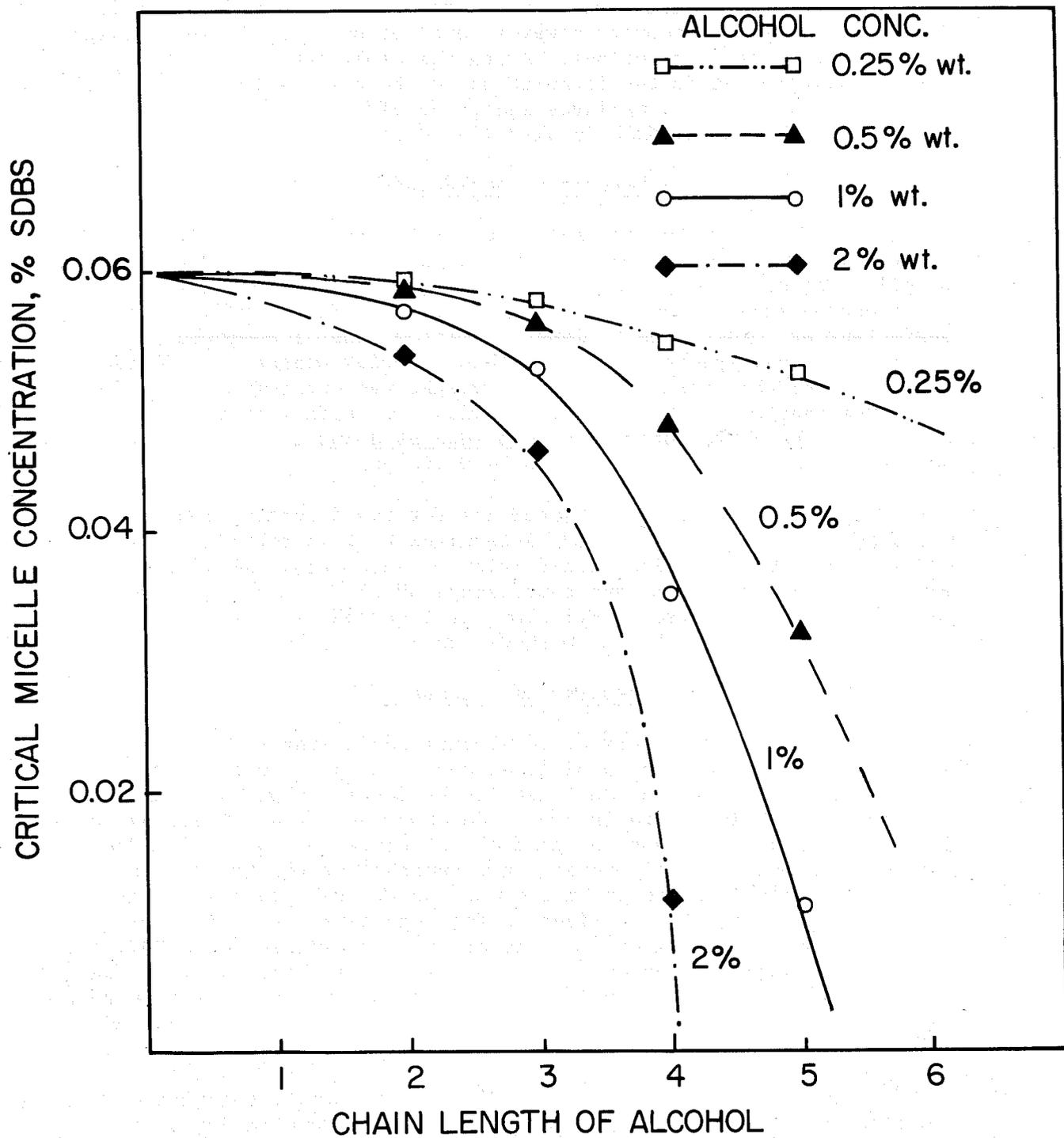


Figure I-3

EFFECT OF STRAIGHT CHAIN ALCOHOL ON CRITICAL MICELLE CONCENTRATION OF SDBS IN DISTILLED WATER

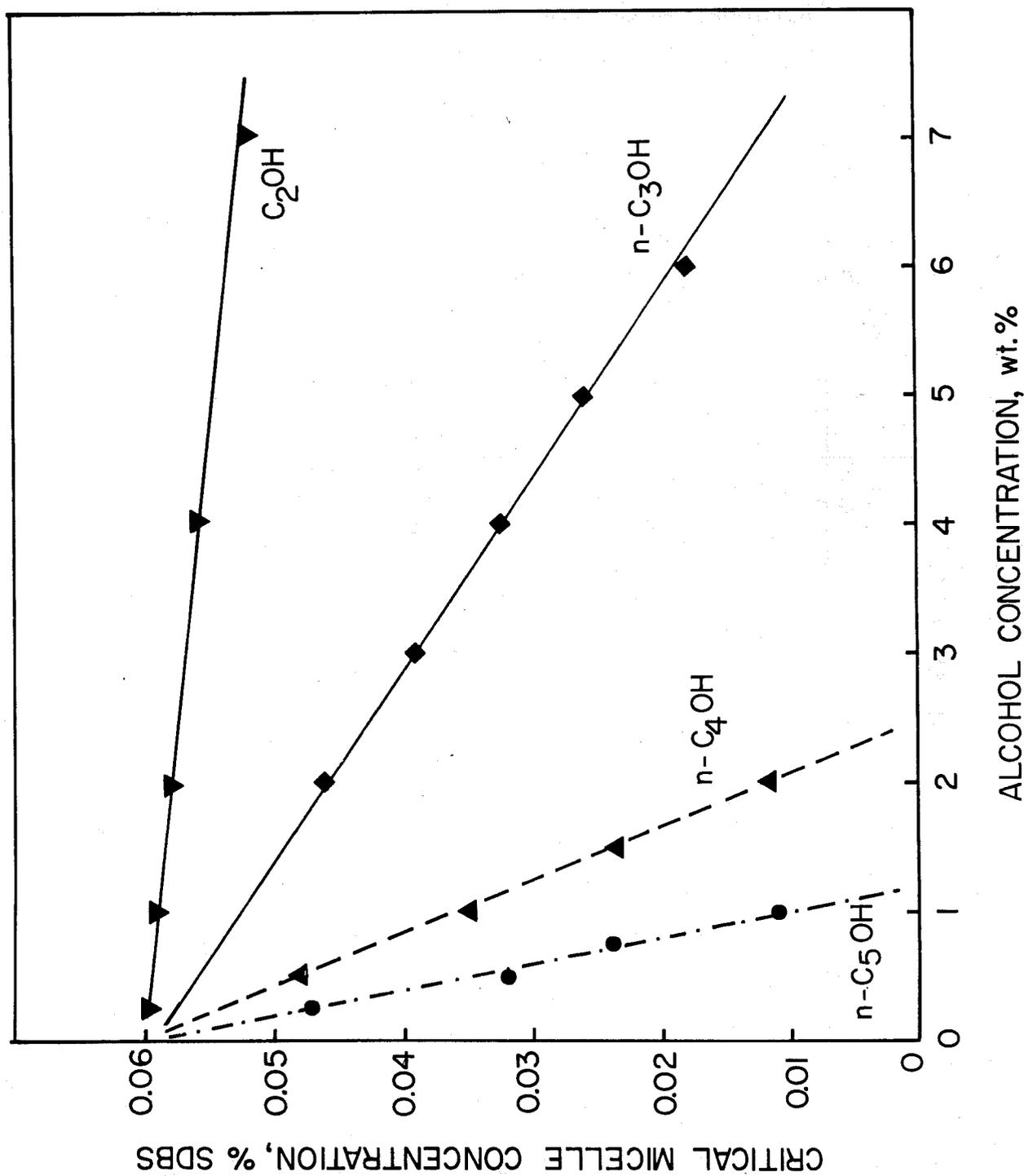


Figure I-4

THE LOGARITHM OF RATE OF CHANGE OF CMC WITH ALCOHOL CONCENTRATION VS. CHAIN LENGTH OF NORMAL ALCOHOLS

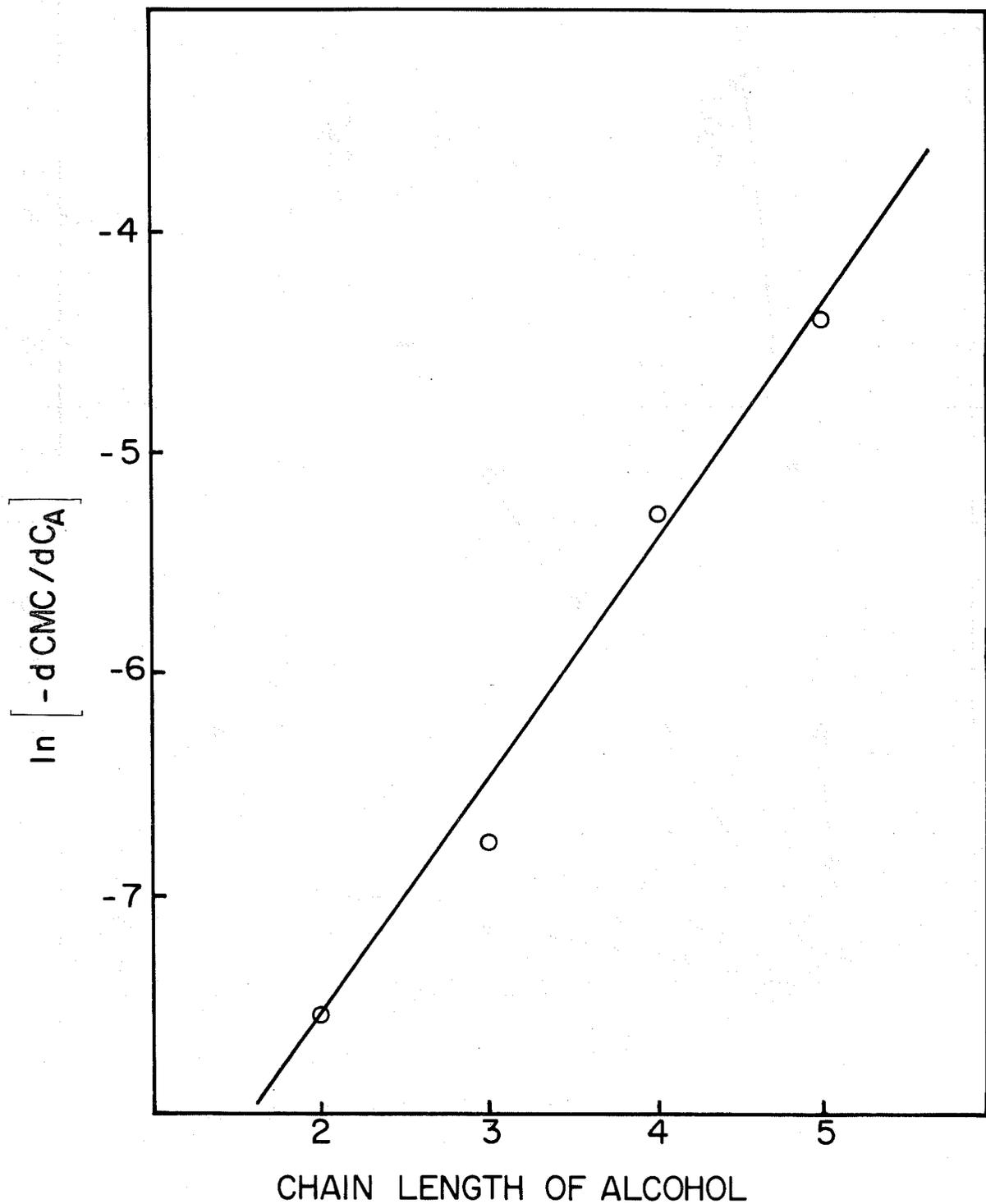


Figure I-5

EFFECT OF ISOMERS OF BUTANOL ON CRITICAL MICELLE CONCENTRATION OF SDBS IN DISTILLED WATER

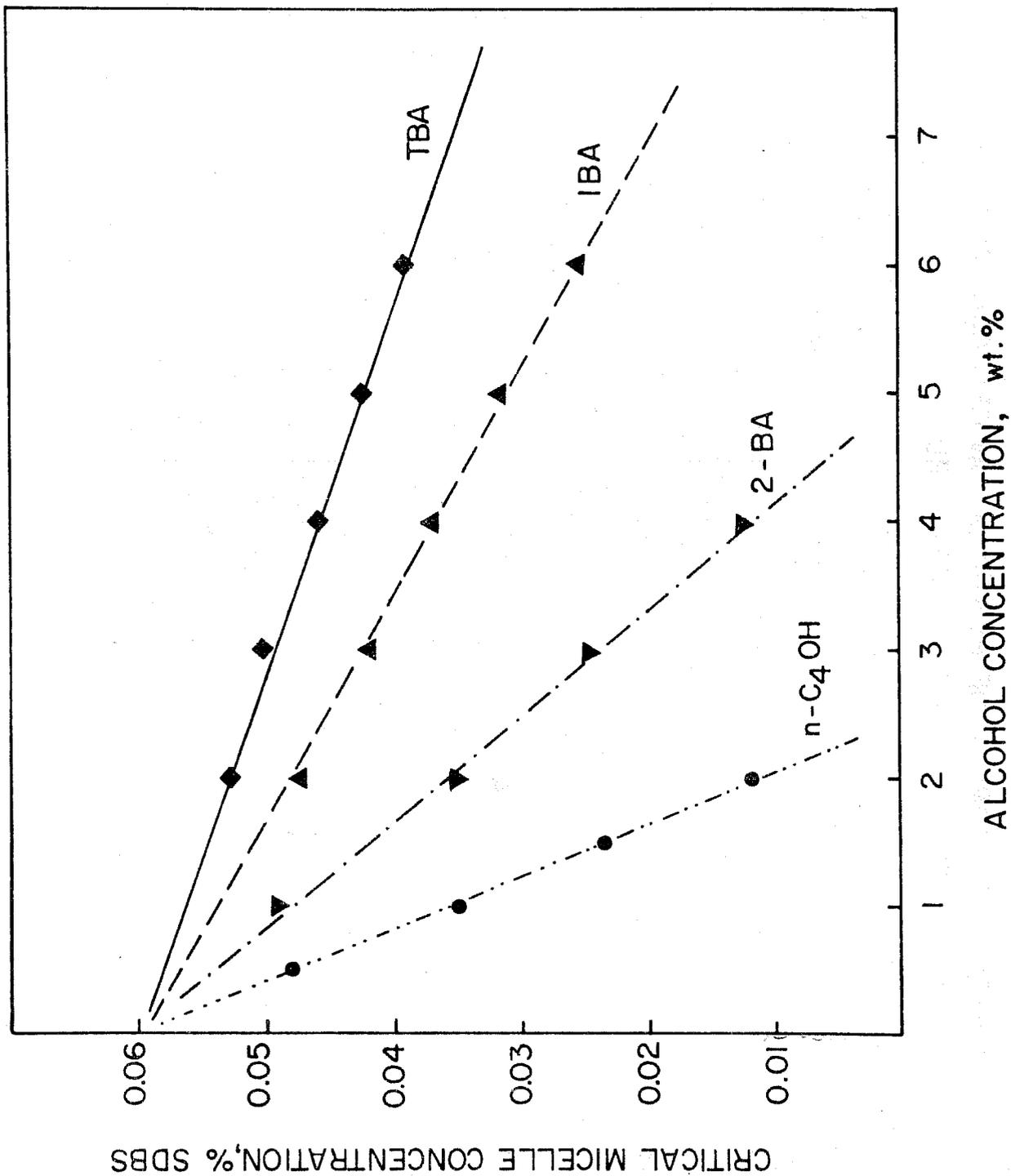


Figure I-6

EFFECT OF ISOMERS OF PENTANOL ON CRITICAL MICELLE CONCENTRATION OF SDBS IN DISTILLED WATER

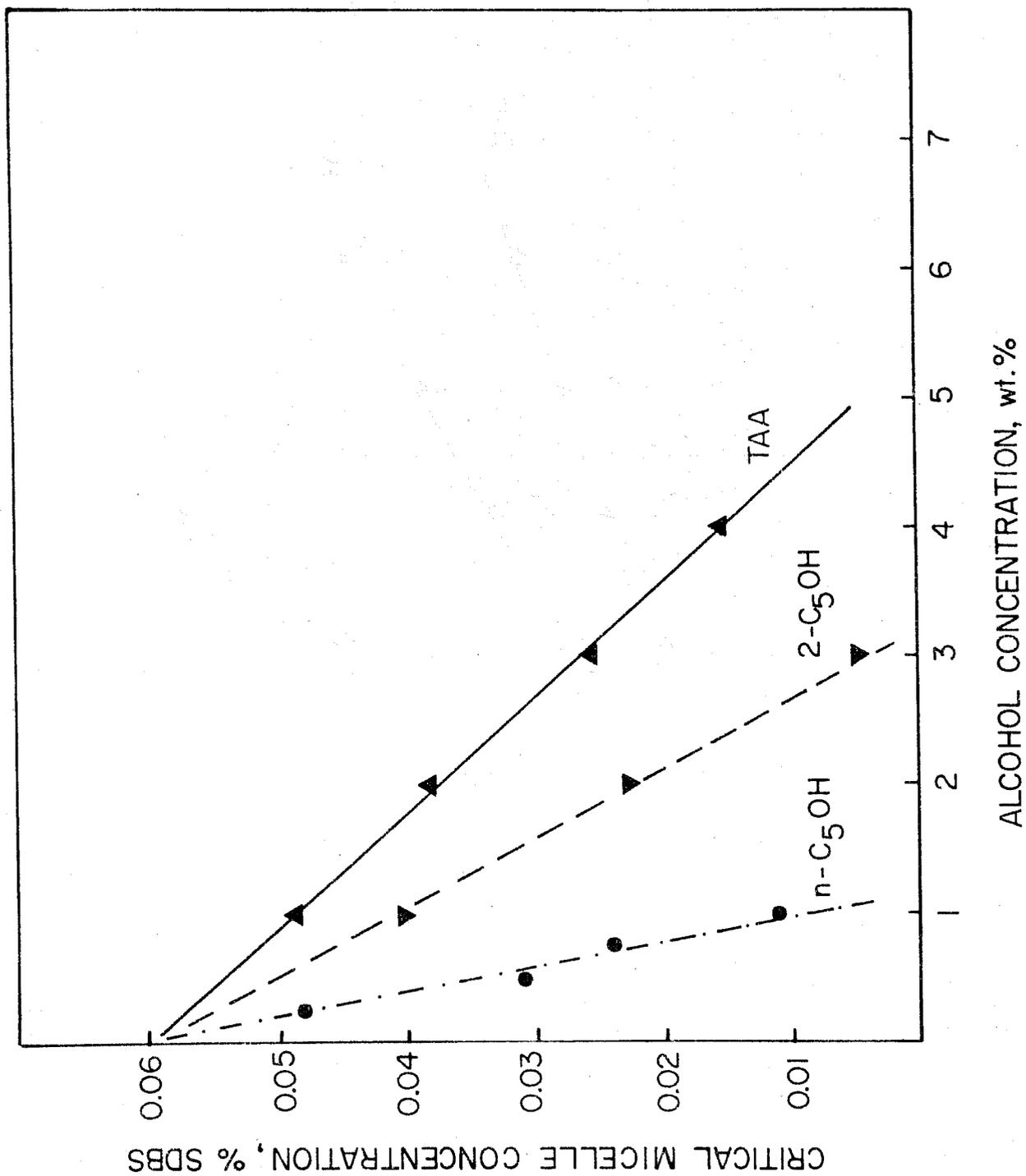


Figure I-7

duces the surface charge density of the micelles (Shinoda, 1954). Besides this, the increase of entropy of mixing due to the penetration of alcohol molecules into the micelle would also contribute to the decrease of the CMC.

Conclusions

- (1) The CMC of SDBS varies linearly with alcohol concentration for normal alcohols as well as isomers of butanol and pentanol.
- (2) For normal alcohols, the logarithm of the rate of decrease of CMC with respect to alcohol concentration

$$\ln \left(\frac{d\text{CMC}}{dC_A} \right)$$

is a linear function of alcohol chain length.

- (3) The decrease in the CMC of SDBS depends on the alcohol chain length and hence its solubility in water. The lower is the solubility, the more effective is the decrease in CMC.

A 3. Determine CMC of SDBS in Distilled Water in The Presence of Dissolved Oils at 25°C

In the preceding sections we have measured the CMC of one surfactant (SDBS) in distilled water and in the presence of added alcohol. There is yet another parameter that can effect the CMC of this surfactant in distilled water, namely, the addition of oil. Once the surfactant formulation contacts oil in the porous medium through which it is being pumped, the solubilization of oil within the formulation can shift the CMC of the surfactant. In this section we examine the effect of a homologous series of oils upon the CMC of SDBS in distilled water.

Materials and Methods

Sodium dodecyl benzene sulfonate (SDBS), originally 85% active containing about 15% salt, was first desalted by dissolving the surfactant in pure isopropanol. The clear supernatant was separated and dried to yield a semi-solid surfactant estimated to be 99.5% pure. Solution of 1% SDBS in doubly distilled water was prepared and then successively diluted to any desired concentration by water of same quality.

Surface tension measurements were done by Wilhelmy plate method using a platinum blade balanced by an extremely sensitive strain gauge. The response from this strain gauge was plotted by a strip chart recorder.

Light scattering I_{90} measurements were done by using a Wood dual photometer, Model 5200. Monochromatic light of wave length 436 m μ was used and the intensity of light scattered at 90° (I_{90}) angle I_{90} measurements was a square optically polished quartz cell (30 x 30 mm) which requires about 30 ml of solution. The cell was first washed with acetone, both inside and out, to remove materials which are insoluble in water. It was then cleaned with a detergent solution in an ultra-sonic bath.

A stock solution of 1.0% (w/v) of SDBS in distilled water was prepared and solutions of lower concentration were prepared by dilution. All solutions were clear and colorless. Solutions prepared were kept in a constant temperature box for about 24 hours to ensure the attainment of the equilibrium between micelles and surfactant monomers in the solutions. Before transferring the solution from vial to the cell, the surface of the surfactant solution was cleaned by removing any insoluble particle or trace of oil which can be redispersed in the cell due to the mechanical agitation generated during the transfer. Occasionally, centrifugation at high speed (3,000 rpm) was applied to some translucent solutions to check the stability of the solutions.

Results and Discussion

There are two methods by which the equilibration with oil can be carried out. In the first, the distilled water is pre-saturated with the oil and that saturated water is then used to make the solutions. In the second method, the surfactant solutions are first made up to the right concentrations in pure distilled water. These solutions are then equilibrated with oil. It should be noted that measured of the light scattered at 90° (I_{90}) for the latter case always showed a local maxima at the CMC. This was absent for the solutions made by the former method. The characteristic maxima in the latter set of experiments was attributed to the stabilization of micro-droplets of oil due to a maximum monomer concentration at CMC.

The CMC of SDBS solutions determined for the two sets of experiments as a function of hydrocarbon chain length of oils is shown in Figure I-8. For the first set of experiments, the distilled water was presaturated with oil and then used to prepare surfactant solution. Thus, for a certain hydrocarbon oil under study, the amount of oil dissolved in each surfactant solution was the same, regardless of the surfactant concentration. Under this condition, the CMC of SDBS increases with the increase of chain length of the oil used. For the second set of experiments, surfactant solutions were first prepared and then equilibrated with oil. Under this condition, the amount of oil dissolved in the surfactant solutions at different concentrations cannot be the same. Generally, the amount of dissolved oil is insignificant below the CMC and is larger beyond the CMC. The exact amount would be governed by the solubilization capacity of micelles and other interactions concerning the formation of the micelles. For this set of experiments, the effective CMC decreases linearly with the increase of the chain length of oils. The extrapolation of this linear curve to zero carbon chain length gives 0.04% as the CMC for SDBS in distilled water without any dissolved oil, which is slightly lower than 0.06% determined experimentally as the CMC of SDBS in distilled water.

For the first set of experiments, the solutions were prepared using the water pre-saturated with oil. As the solubility of alkanes in water decreases as the chain length increases, the amount of oil dissolved in water will not be the same for each oil due to the difference in chain length. Thus n-hexane dissolves seven to eight orders of magnitude more than n-hexadecane does in water. Therefore, the higher chain length oil (e.g., C_{12} , C_{14} , C_{16}) have negligibly small effect on the CMC as compared to the CMC without the dissolved oil.

In the second set of experiments, excess oil was provided for solutions of different surfactant concentrations during the equilibration. In this case, the oil chain length is the predominant factor in the decrease of the CMC. Therefore, the CMC decreases as the chain length of dissolved oil increases.

THE EFFECT OF OIL CHAIN-LENGTH ON THE CMC OF SDBS IN DISTILLED WATER

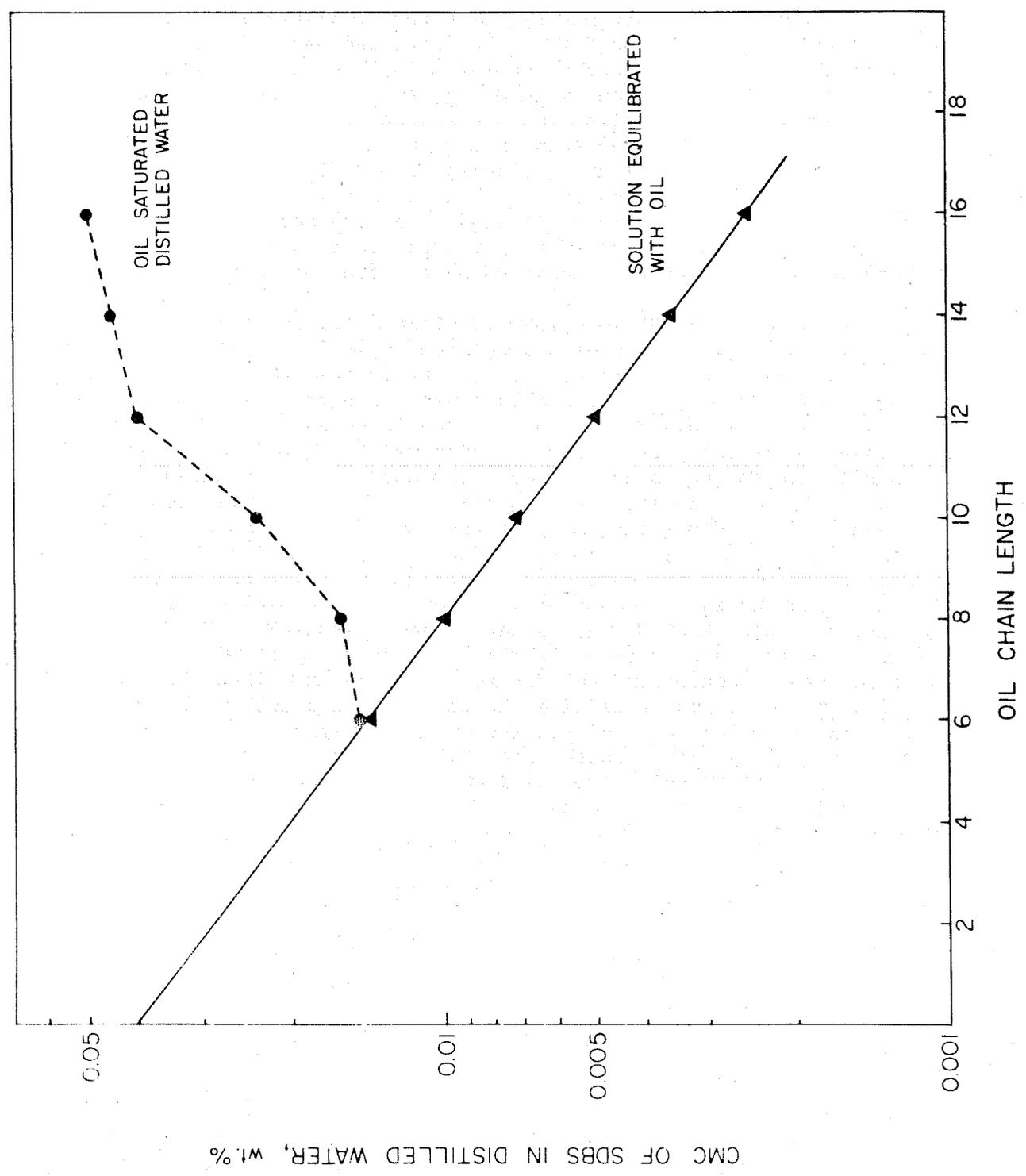


Figure I-8

Conclusions

- (1) For the surfactant solutions prepared using water presaturated with oil, the decrease in CMC is larger with shorter chain length of oil.
- (2) For the surfactant solution equilibrated with oil, the CMC decreases as the oil chain length increases. The logarithm of CMC in the presence of dissolved oils varies linearly with the chain length of oil.
- (3) The determination of CMC from solubilization of oil technique can introduce error as the CMC is strongly affected by the nature of the oil solubilized.

A 4. Determine PC of TRS 10-80 in 1.5% NaCl Against Oils of Various Chain Lengths

Thus far, we have been investigating the micellar properties of single phase solutions. When such a solution is contacted with oil (as in an oil field), local mixing will partition the available surfactant between the aqueous and oil phases. The amount of surfactant in each phase will control the bulk and interfacial properties of that phase. In this section, we have taken a commercial petroleum sulfonate (TRS 10-80) in a medium (1.5% NaCl) that is close to many real situations. This solution has been contacted with half its volume of oil (homologous alkane series) and the partitioning of the surfactant determined.

Materials and Methods

The surfactant used was TRS 10-80 (80% active) obtained from Witco Chemicals. This surfactant is a mixture of petroleum sulfonates with wide molecular weight distribution. The average equivalent weight was reported to be 420. The water content of this surfactant was 8% as determined by the NMR spectroscopic technique using a 60 MHz high resolution NMR spectrometer (JEOL Model C-60HL). The remaining 12% was free oil and salt, the salt content being less than 0.4%. The surfactant was used as received from the manufacturer to prepare the solutions, without further purification to remove either the free oil or water. The oils used in this study were a homologous series of alkanes with chain lengths from C_6 to C_{16} . All the oils were at least 97% pure and were obtained from Chemical Samples Company.

The systems were equilibrated by taking two-thirds aqueous solution and one-third oil by volume in 250 ml separatory funnels maintained at 25°C. After shaking vigorously for about 30 minutes using a mechanical shaker, the solutions were allowed to stand for about three weeks until clear mirror-like interfaces were obtained and the oil and aqueous phases became optically clear. The equilibrated oil and aqueous phases were then separated from the top and bottom of the funnel respectively for various physicochemical measurements.

Interfacial tensions between the equilibrated oil and aqueous phases were measured by a spinning drop tensiometer using the method described by Princen et al., (1967) and also by Cayias, et al., (1975). Each drop of oil was spun until a constant interfacial tension was reached. This usually took from fifteen minutes to three hours. The temperature was maintained at $25 \pm 1^\circ\text{C}$. A few samples were double checked by the micro-sessile drop technique (Healy and Reed, 1974) using the apparatus designed and constructed by the authors.

Surface tensions of the equilibrated aqueous phases were measured using a modified Wilhelmy plate method. This technique was recently re-evaluated by Orr et al., (1977). The platinum blade used was sand-

blasted to produce a rough surface so that it was completely wettable by the salt solution. Double-distilled deionized water was used as the standard for calibration. The surface tension was recorded on a strip chart recorder and the equilibrium value was taken. The temperature was controlled at 25°C by using a water jacket for the petridish (containing about 30 ml of sample). The tension measurements were accurate within ± 1 dyne/cm.

For low surfactant concentration (0 to 0.1%) solutions, both interfacial tensions and partition coefficients were measured. It was difficult to determine the trace quantity of surfactant partitioning into the oil phase using either conventional dye-titration or spectrophotometric methods. Therefore, we developed a novel monolayer technique to determine this trace quantity of surfactant partitioning into the oil phase. In this method, the surfactant in the oil phase was recovered by evaporating the solvent. Subsequently, this surfactant was dissolved in a spreading agent (1:1:3 methanol: chloroform: hexane, volume ratio) and spread as a monolayer in a Langmuir trough. Comparison of the surface pressure-area per molecule curves with a standard allowed determination of the concentration of the surfactant.

Surfactant concentration in the aqueous phase was measured by spectrophotometry of methylene blue-surfactant complexes reported elsewhere in the literature (Smith et al., 1975; Shah et al., 1975). All the measurements were done at 25°C. Partition coefficient, defined as the ratio of the concentration of surfactant in the oil phase to the concentration of surfactant in the aqueous phase, was then determined.

All surfactant and salt concentrations, unless otherwise specified, refer to the initial surfactant concentration in the aqueous phase before equilibration with the oil.

Results and Discussion

Figure 1-9 shows the partition coefficient and interfacial tension for 0.1% TRS 10-80 in 1.5% NaCl as a function of chain length of the oil. It should be noted that the minima in interfacial tension and surface tension occur at the same chain length of oil. The partition coefficient decreases logarithmically. The partition coefficient unity once again corresponds to the minimum in interfacial tension. It is evident from the partition coefficient data that as the chain length of oil increases, the partitioning of the surfactant in the oil phase decreases. Consequently, the concentration of surfactant in the brine phase must increase as the oil chain length is increased from C_6 to C_{16} . It would appear from the interfacial tension and surface tension results that the concentration of surfactant in the aqueous phase equilibrated with C_6 and C_8 oils is below the CMC. The surfactant concentration in the aqueous phase equilibrated with decane is the CMC, and with higher chain lengths of oil, the surfactant concentration in the aqueous phase is higher than the CMC. The question is why the monomer concentration decreases above CMC? We believe that even though the aqueous phase in equilibrium with C_{12} , C_{14} or C_{16} oil is above CMC, the monomer concen-

INTERFACIAL TENSION AND PARTITION COEFFICIENT FOR 0.1% TRS 10-80 IN 1.5% NaCl SOLUTION WITH OILS OF VARIOUS CHAIN LENGTH

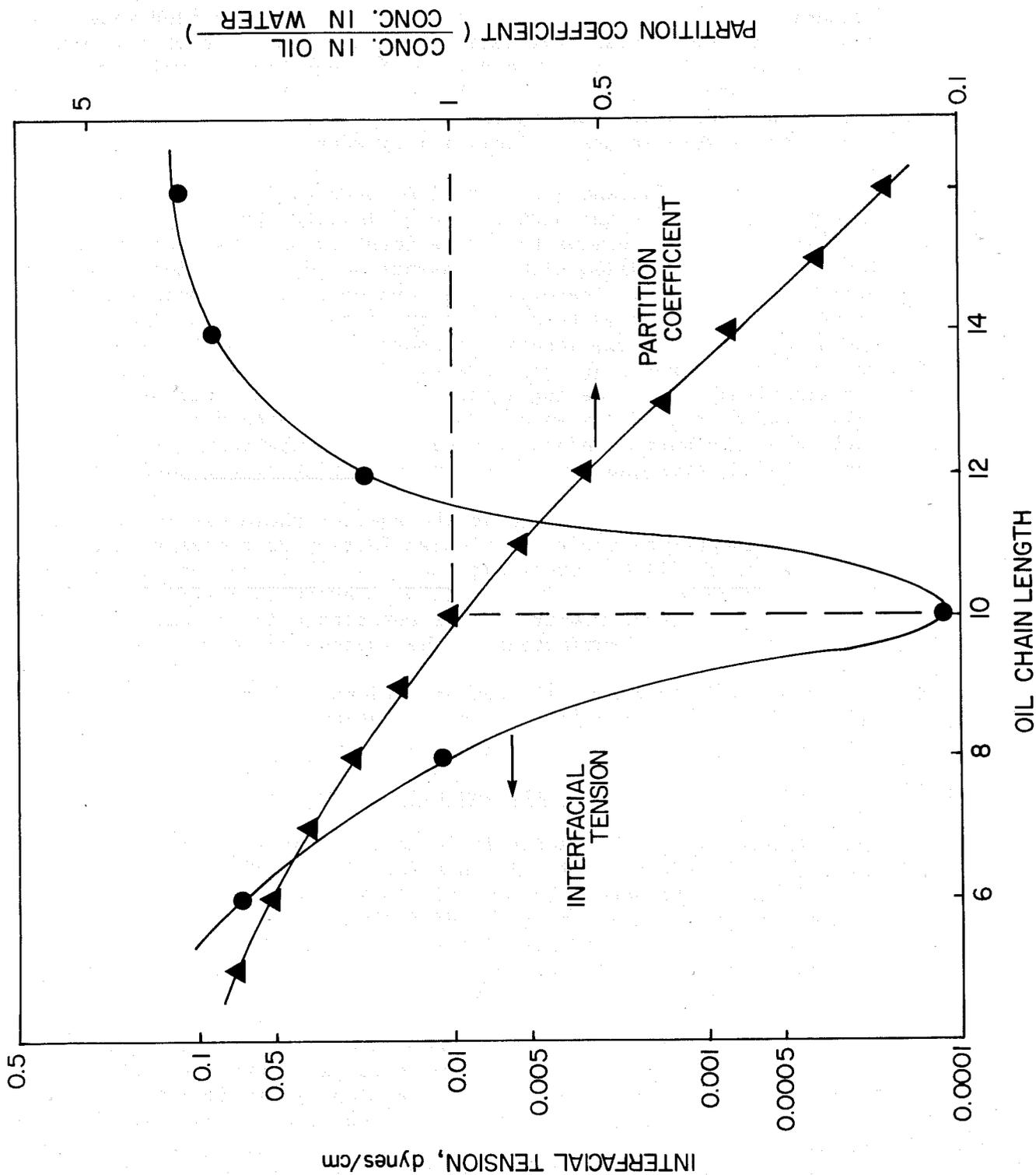


Figure I-9

tration must decrease with increased chain length of dissolved oil as inferred from surface tension and interfacial tension data. We indeed, confirmed this by measuring the CMC of sodium dodecyl benzene sulfonate in the presence of various dissolved oils (Sections A 2. and A 3.)

Summary and Conclusion

This section reports the occurrence of a minimum in ultra-low interfacial tension curve as a function of the chain length of oil. The minimum interfacial tension occurs at that concentration which is the critical micelle concentration for the aqueous phase after equilibration with the oil. The minimum interfacial tension is always observed when the partition coefficient is unity. This implies that the interaction of surfactant molecules at the interface will experience equal affinity for oil and brine and consequently will produce a very high concentration at the interface. The observed effect of the oil chain length on the interfacial tension was explained based on the partitioning of the surfactant in the oil phase and the micellization phenomenon in the brine phase. The minimum interfacial tension is observed with that oil for which the surfactant remaining in the aqueous phase is at the CMC.

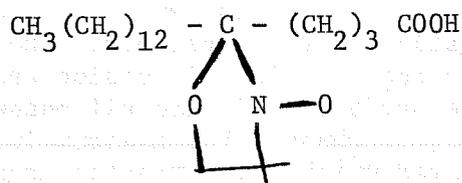
B 1. Spin Label Studies of Microstructure of Surfactant Formulations

It was felt that the use of spin-labelling techniques can lead to a better understanding of the structures involved in surfactant formulations and in emulsions. Two different spin labels, one partly water-soluble and partly oil-soluble and other water insoluble were employed.

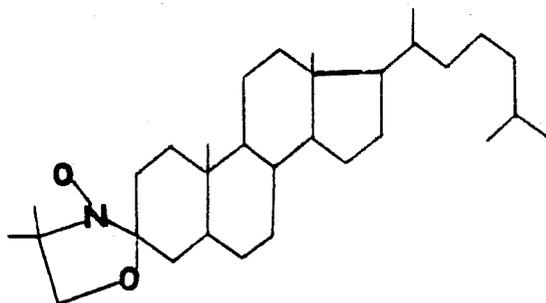
Experimental

The spin labels used were

(1) 5-Ketostearic Acid Label



(2) Cholestane Label



Both labels were obtained from Syva Company, California and were used as such. The concentrations used were 1×10^{-4} for Probe II. Probe I was first dissolved in a 5:3 mixture of TRS 10-410/IBA and then appropriate amounts of saline and oil were added and sonicated. Probe II was dissolved in dodecane and this was then added to the desired aqueous solution of 5:3 TRS 10-410/IBA followed by sonication. Higher concentrations of Probe I were necessitated by the low solubility of the label in water.

Samples for ESR were gently withdrawn using a syringe to avoid foaming and transferred to Pyrex capillary tubes of uniform inner diameter of 1mm and sealed. Deoxygenation of solutions was not attempted

due to the adverse effect concomitant with foaming. Water used in these solutions was deionized distilled water obtained by passing doubly distilled water through a Barnstead mixed-bed ion-exchange resin column and had a specific conductivity of less than 2 $\mu\text{S}/\text{cm}$. All other chemicals were Analar grade or better through recrystallizations except for the surfactant TRS 10-410 which was supplied by Witco and was used as such. All spectra were recorded using a Varian E-9 spectrometer, operating at a frequency of 9.5 GHz. Ambient temperature was $23 \pm 1^\circ\text{C}$. The modulation frequency used while recording the spectra was 100 KHz, while the time required to scan the peak-to-peak width was about a minute. At least two sets were run for a single sample. Reproducible spectra were obtained under these conditions and the reproducibility of line widths was within 10-14 mG. The microwave power used was 32mW for all the spectra. The order parameter ΔT from spectra of Probe I in samples was calculated according to the method of Hubbell and McConnell (1971), where $\Delta T = \frac{T_{11} - T_{\perp}}{2T_{11}}$, $2T_{11}$ being the outer peaks separation and T_{\perp} that of the inner ones. The other order parameter, S_3 , S_3 is given by

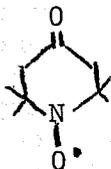
$$\frac{T_{11} - T_{\perp}}{T_{zz} - T_{xx}} \quad \text{where } T_{zz} \text{ and } T_{xx} \text{ are the splitting in gauss for oriented}$$

layers. The hyperfine splitting constant A_N is given by $1/2[T_{11} + 2T_{\perp}]/3$. The maximum error in determination of ΔT was $\pm 0.5\text{G}$.

The correlation time for rotational tumbling motion of the spin-label, τ_θ , roughly the time the probe molecule as a whole takes to define an angle of 2π radians, is calculated using the method of Stone et al., (1965) wherever isotropic spectra are obtained. Although the theory strictly applies to dilute solutions and isotropic motion of the probe, the correlation times obtained justifies the use of the method. Essentially, τ_θ is given by

$$\tau_\theta = 6.5 \times 10^{-10} \times W_0 \times \left[\left(\frac{h_0}{h_{-1}} \right)^{1/2} + \left(\frac{h_0}{h_{+1}} \right)^{1/2} - 2 \right] \text{ seconds}$$

where W_0 = linewidth of central line, h_{-1} , h_0 , h_{+1} are the peak heights of lowfield, zero or central and high-field lines. The maximum uncertainty was $\pm 15\%$ but in most cases the error limit was within $\pm 5\%$. Spin-probe studies of aqueous solutions of 5:3 TRS 10-410: isobutanol and the emulsions obtained with addition of equal volume of dodecane were carried out using yet another label, the 2,2,6,6-tetramethyl piperid-4-one-N-oxide/ (TEMPO).



All experimental factors are similar to those described for the other labels. Three lines due to the spin on the nitrogen nucleus are obtained. The separation between the lines is the isotropic hyperfine splitting constant, A_N . Correlation time for rotational tumbling motion is calculated as described earlier.

Results and Discussions

Spin probe studies of fresh aqueous solutions of 5:3 TRS 10-410 and isobutanol indicates that as the salinity increases the correlation time shows an initial increase at 0.5% followed by a gradual decrease up to 1.8%. Beyond this salinity the correlation time is essentially constant. Aged solutions of the same system behaves in a different fashion. The correlation time in these solutions shows an initial increase up to 1% followed by a steep drop at 1.5%. The trend beyond 1.5% salinity is also different from those of fresh solutions in that instead of a levelling effect we observe a significant increase at 1.8% followed by a decrease at 2% (Figure I-10.) We studied fresh solutions of this surfactant system using a stearate label in addition to the above studies using TEMPO. Our results for the stearate label indicates that the order parameter which is a direct reflection of the packing (and the rigidity as seen in the separation of the outermost peaks) increases as the salinity increases; This is a maximum at around 1.5% and then shows a slight decrease (Figure I-11.) The polarity of the label does not vary significantly reflecting an environment that does not change with salinity. The linewidth on the other hand remains constant up to 1.25% NaCl, increasing enormously at 1.5 to 1.9%. The linewidth drops as abruptly beyond these salinities to those obtained below 1.25% NaCl (Figure I-12).

It is known from literature that fresh solutions of these systems are birefringent beyond 1.5% NaCl. Liquid crystalline lamellar structures might be involved. The maximum order parameter obtained around 1.5% might be the region where the tightest packing of surfactant molecules are possible. Viscosity, screen factor, linewidth all support this possibility. Our previous studies on similar systems using the stearate label and NMR also supports the view that birefringence is maximum where packing is tightest. In our opinion the decrease in order parameter above this salinity could be the result of a more fluid structure. A close packed cylindrical structure is indicated at 1.5 to 1.6% whereas beyond this gradual breakdown or at the most an almost constant, similar, but less rigid structure exists.

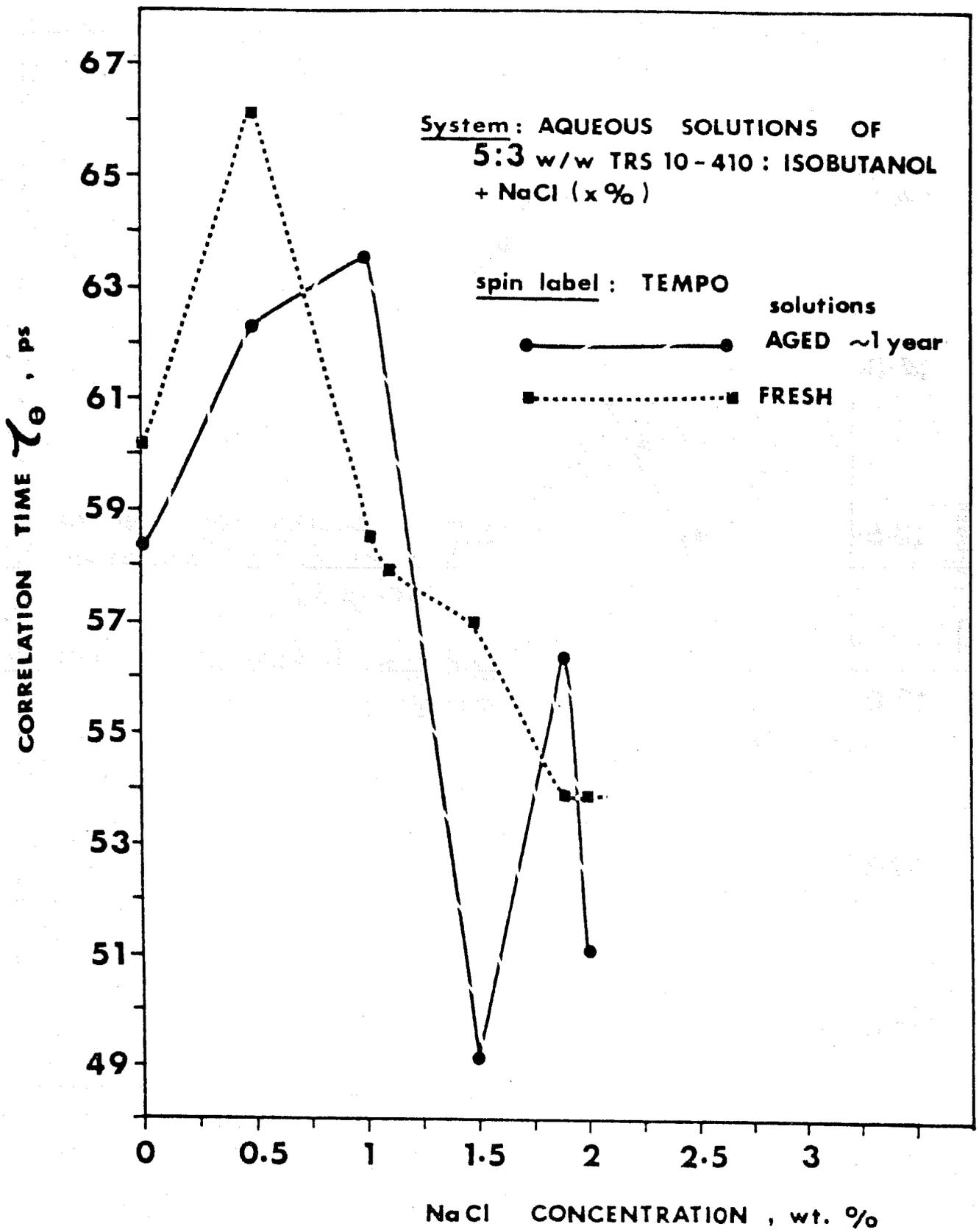


Figure I-10 - CORRELATION TIME OF TEMPO IN AQUEOUS SOLUTIONS OF 5:3 TRS 10-410: ISOBUTANOL

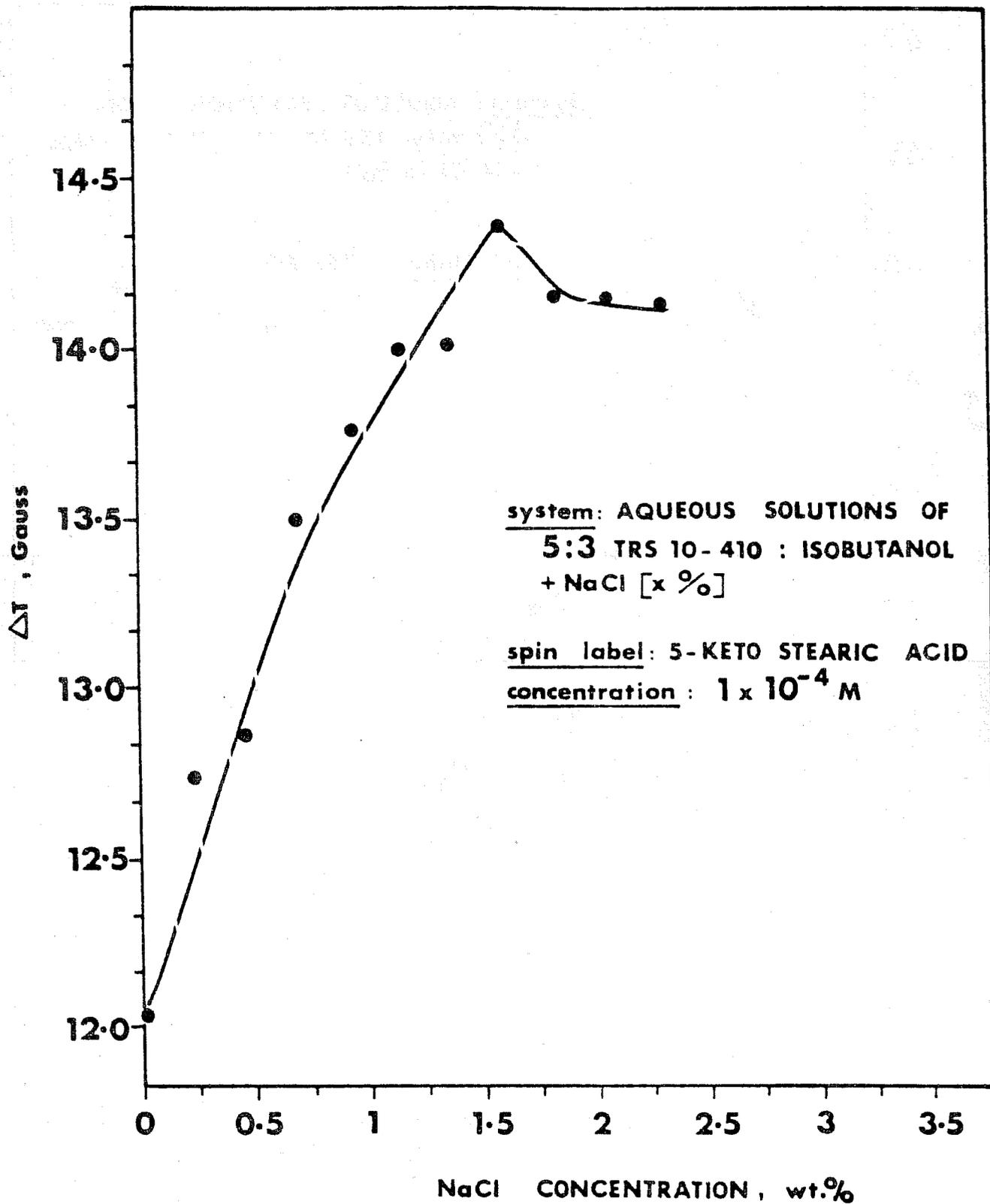


Figure I-11 - ORDER PARAMETER FOR 5-KETOSTEARIC ACID IN AQUEOUS SOLUTIONS OF 5:3 TRS 10-410: ISOBUTANOL

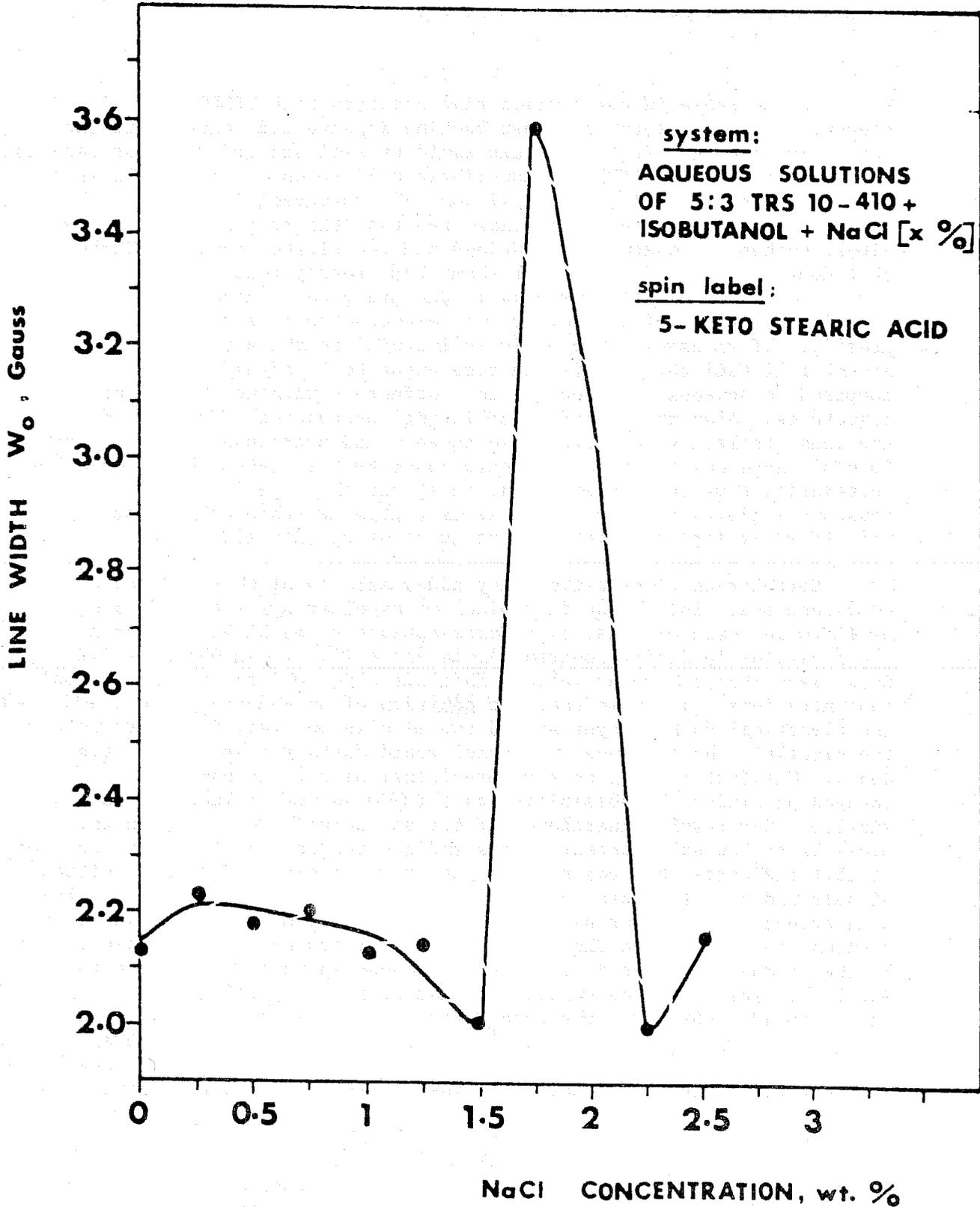


Figure I-12 - LINewidth OF CENTRAL LINE, $m_N = 0$, OF 5-KETOSTEARIC ACID LABEL IN AQUEOUS SOLUTIONS OF 5:3 TRS 10-410: ISOBUTANOL

The decrease in correlation time obtained with TEMPO label at concentrations where the tightest packing is expected leads us to the conclusion that the TEMPO molecule would be excluded from such structures. Partition studies of TEMPO in equilibrated mixtures of equal volumes of water and dodecane oil with and without 3% isobutanol in the total absence of surfactant and salt indicates that the correlation time is almost unchanged in aqueous solutions but the slight amount of TEMPO that does partition into the oil phase has greatly reduced correlation times and is drastically affected in the presence of alcohol. Therefore, low concentrations of alcohol are not expected to alter correlation times greatly. If we assume that TEMPO is included in the structures formed around 1.5% NaCl the correlation time ought to be significantly high compared to aqueous solutions of the surfactant without these special structures. Also the hyperfine splitting constant of TEMPO should at the least reflect an average of an aqueous and hydrocarbon environment. Both of these observations are conspicuous by their absence. Indeed the correlation time shows a marked decrease and the hyperfine splitting constant exhibits water values. It is highly improbable therefore that TEMPO is included either as it is or along with alcohol molecules.

Correlation times without any added salt is of the order of about 60 picosecond. This value is typical of micellar systems. The inclusion of TEMPO in these micellar structures appears to be highly probable since the hyperfine splitting constant A_N is about 14.9 Gauss which is 0.2 Gauss less than the water value. This situation exists even at low salt concentrations. It known that the addition of an electrolyte would decrease the electrical double layer around the micelle and facilitate growth of the micelle. The presence of alcohol would further enhance this tendency. The fact that A_N in a water-alcohol mixture is only slightly changed precludes the possibility that TEMPO is not included in the micelle. Our results therefore reflect an inclusion of TEMPO in the micelles at low salt concentrations and the increase of τ_θ with addition of salt indicates that the micelle has grown in size. Further addition of salt induces structural changes and also the exclusion of TEMPO from such structures. Closer packing of the spherical micelles leading to the eventual formation of a close packed cylinder around 1.5% is indicated by the gradual decrease in τ_θ and the gradual increase in order parameter ΔT . The hyperfine splitting constant is identical to the water value around 1.65% NaCl, the concentration where ΔT is a maximum indicating the complete and total exclusion of TEMPO at this concentration. The decrease in hyperfine splitting constant A_N of TEMPO beyond these concentrations also gives weight to the supposition that the structures are less rigid.

In summary, fresh aqueous solutions of 5:3 (%w/w) TRS 10-410: Iso-butanol exhibit structural changes upon the addition of Sodium Chloride. Starting from a micellar system, we have initial growth of the micelle which gradually pack themselves more and more tightly as salt is added, finally transforming into close packed structures. Birefringence begins around 1.5% and continues up to 2.25%, this region also being the region of maximum order and linewidth. There is a possibility that these structures are completely destroyed prior to phase separation as indicated by the return to normal linewidths. However the order parameter is only slightly changed inviting the possibility of bi-layer structures.

The continuance of birefringence even at 2.5% at least does not exclude this possibility while effectively negating the notion of complete disorder. The water sheet contains TEMPO and the correlation time could decrease significantly.

B 2. Microstructure of Mutually Saturated Oil, Middle and Aqueous Phases Using Spin Labels

Experimental

A stearic acid spin label and a cholestane label were used separately in an attempt to understand the structural aspects in the different phases obtained when the sonicated emulsion was allowed to equilibrate upon standing. The experimental details have already been discussed in Section B-1

Cholestane Label:

This label is insoluble in water and can be assumed to be always present in the oil phase of the micro or macroemulsion. The spectra obtained from all solutions were isotropic indicating the absence of a significant degree of "anchoring" at the oil/water interface. The axis of rotational averaging assumes all possible orientations that are allowed and averages any axial symmetry that could be present. The correlation time for rotational tumbling motion, τ_{θ} was calculated for all the different phases studied and are shown in Figure I-13.

For aqueous phases, at 0% salinity there was a negligible amount of the label and a high receiver gain was needed. At 0.5% the label concentration was high enough to be detected with comparative ease. The high correlation times in 0% and 0.5% \approx 1100 and 800-900 ps respectively were interesting in terms of solubilized oil in the aqueous phase. At 1% the correlation time is still large but the value indicates that the freedom for rotational motion is considerably higher than in 0% and 0.5% aqueous phases. This indicates that the micellar core volume available to the oil has increased considerably compared to 0.5%. The absence of a detectable signal in aqueous phases from a three phase system indicates the absence of solubilized oil.

For the middle phases, both 1.5%, and 1.8% show correlation times that are lower than the 1.0% aqueous phase result. At 1.5% τ_{θ} is 270 ps and at 1.8% it is about 215 ps. It is conceivable that a water external microemulsion is the major component in these middle phases. Calculations based on Schulman's model have indicated that the core diameter is about 350 Å, which is 10 times the length of the probe used. In the light of our τ_{θ} studies this appears reasonable.

Spectra from oil phases at lower salinities gave rise to correlation times that were close to the value in pure oil. Increasing salinity in the three phase region increased correlation time and indicates an increase in surfactant concentration in the oil phase. The system at 2% NaCl is interesting. At 2% a two phase system is obtained. The oil phase correlation time is high compared to the lower salinity oil phases (.177 ps). However upon standing for extended periods of time, the 2%

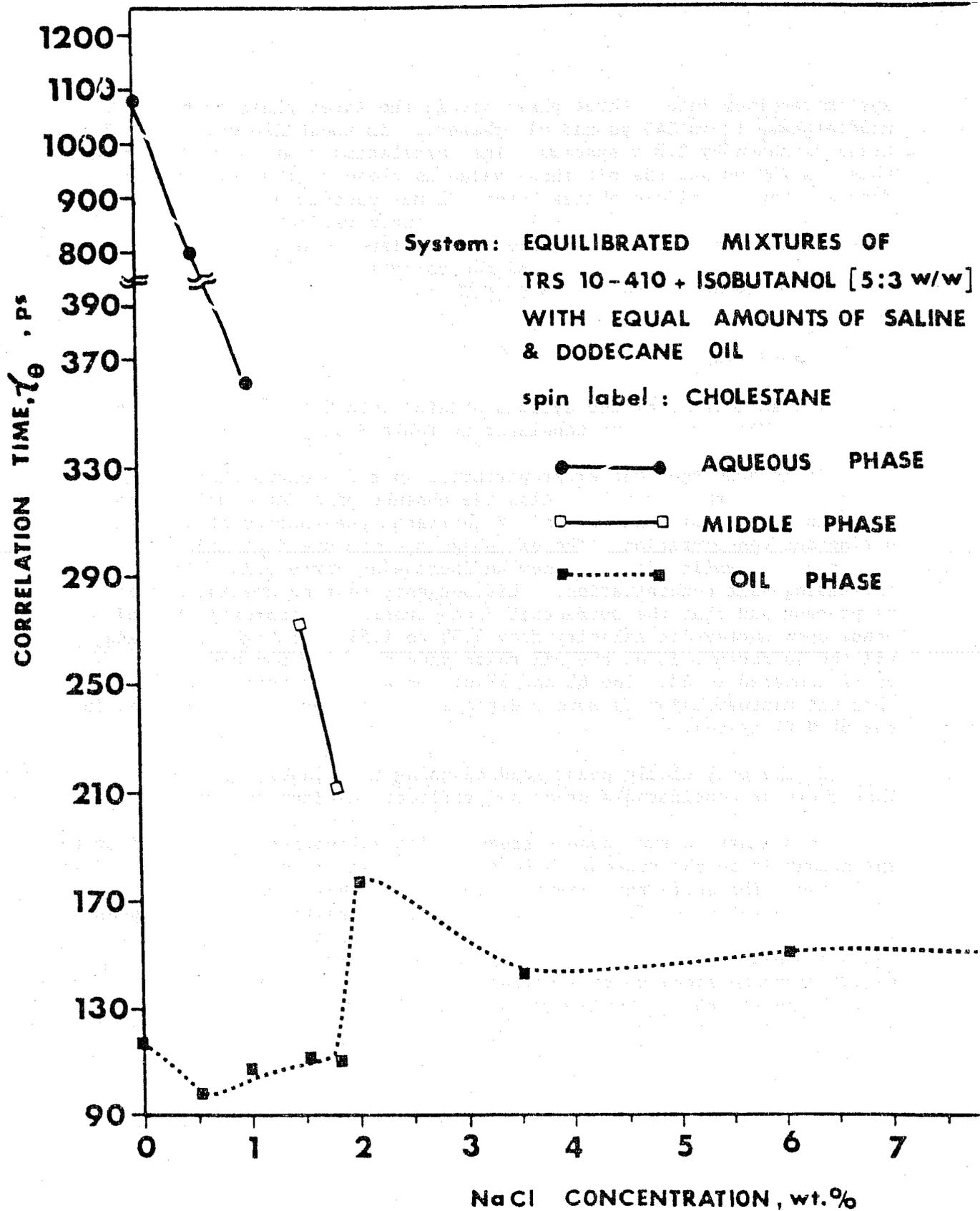


Figure I-13 - CORRELATION TIME, τ_c , OF CHOLESTANE LABEL IN DIFFERENT PHASES OF EQUILIBRATED MIXTURES OF TRS 10-410/ISOBUTANOL (5:3 w/w) WITH EQUAL AMOUNTS OF SALINE AND DODECANE OIL.

system resolves into a three phase one in the three phase system. The middle phase τ_{θ} is 240 ps and oil phase τ_{θ} is about 120 ps. A similar trend is shown by 2.5 x systems. The correlation time for a 2.5% middle phase is 250 ps and the oil phase value is close to 120 ps. This indicates that the middle phases beyond 2% may contain oil external microemulsions as well. The high surfactant concentration in the bulk would offer greater restriction to motion of the label compared to the water-external case. At 3.5% and beyond the correlation time is about 140-150 ps and remains unaffected up to 8% NaCl indicating the total absence of water-external microemulsions.

Stearic acid label:

The salinities of the systems studied were 0.5%, 1.0%, 1.5%, 6.0% and 8.0%. The results are tabulated in Table I-1.

It is seen that the order parameter in the aqueous phase of 1% is higher than that of 0.5%. Also the absence of a detectable signal in aqueous phase of 1.5%, 6% and 8% indicates the absence of a significant surfactant concentration. The oil phase spectra are isotropic for 0.5%, 1.0% and 1.5% salinities and show an increasing correlation time upon increasing salt concentration. This suggests that no special structure is present and that the surfactant concentration increases in the oil phase upon increasing salinity from 0.5% to 1.5%. At high salinities all the surfactant is on the oil phase and the order parameter is lower at 8% compared to 6%. The 6% and 8% oil phase order parameters indicate that the microemulsion is more ordered and hence more tightly packed in the 6% NaCl system.

In the only middle phase studied using this label, it was found that there is considerable order and reflected a tight packing.

In summary in two-phase systems at low salinities; almost all of the surfactant is in the aqueous phase and is present as water-external microemulsions. The surfactant migrates to the oil phase upon increasing salt concentration until a three phase system results. The three phase systems are characterized by the total absence of surfactant and oil in the aqueous phase. The middle phase appears to consist mainly of water-external microemulsions up to a salinity of 2% NaCl. Beyond this whenever a middle phase can be obtained we believe that the major constituent is an oil-external microemulsion. Almost all of the surfactant resides in the middle phase for all three phase systems. When the three phase system reverts to a two phase system at higher salinities, the surfactant is now mainly confined to the oil phase and is present at oil-external microemulsions. No water-external microemulsions were formed in these phases.

Table I-1

Spin Label Studies on The Different Aqueous, Middle and Oil Phases of Equilibrated Mixtures of 1:1 Aqueous Solutions of 5:3 (%w/w) TRS 10-410: Isobutanol with Dodecane Oil Using 5-Ketostearic Acid Label

Salinity %	0.5	1.0	1.5	6.0	8.0
Aqueous Phase	$\Delta T = 12.00$ Gauss	$\Delta T = 12.375$ Gauss	Negligible Concentration of Label	Negligible Concentration of Label	Negligible Concentration of Label
Middle Phase	-	-	$\Delta T = 12.5$ gauss	-	-
Oil Phase	$\tau_{\theta} = 88$ ps	$\tau_{\theta} = 132$ ps	$\tau_{\theta} = 150$ ps	$\Delta T = 12.375$ Gauss	$\Delta T = 11.625$ Gauss

II. Polymer Rheology and Fluid Mechanics

A. Effect of Aging, Salt Concentration and Temperature on Polymer Rheology

It has long been recognized that the stability of polymer solutions used in the tertiary oil recovery process is of major importance since the polymer must function for a long period of time and frequently at elevated temperatures. Mechanical and chemical stability of the polymer could present further practical problems in the field operations. Though a considerable number of publications have appeared in the recent literature dealing with some of these aspects, the main objective of our effort in this area has been to correlate the molecular properties of these polymers with their rheological properties. The first phase of the study has been mainly on the chemical or physical stability of polyacrylamides at different temperatures and in different ionic environments. The second phase of the study, that we have just initiated, will deal with similar correlations for flow through porous media studies.

Materials and Methods

For our study we selected two partially hydrolyzed polyacrylamides (supplied by Calgon), P815 and P835. In order to evaluate the effect of Na^+ and Ca^{++} ion concentration on these polymers, solutions of 500 ppm concentrations of the polymers with different levels of Na^+ and Ca^{++} were made and placed in incubators at 30° , 45° and 65°C . The temperature of each incubator was maintained within 0.5°C . Distilled water was used for making the solutions and no attempts were made to remove dissolved oxygen. Samples were collected at different lengths of time and the respective properties were measured for these samples as well as the fresh samples. Viscosity was measured using a Cannon Fenske viscometer (no. 100) at 30°C , intrinsic viscosity was obtained by interpolating the reduced viscosity vs concentration plots to zero concentration. Screen factor was measured using an ordinary screen viscometer for solutions at room temperature of 100 ppm concentration. Since the polymer degrades when it passes through a set of screens, the time required for the solution to go through the same set of screens, keeps decreasing with the number of the passes. The polymer solution is also liable to degrade when it is being sucked into the viscometer. The time taken by the solution to go through the set of screens was measured for the first four runs. Time taken vs no. of times the solution went through the screen was interpolated to zero and this value was used for obtaining the screen factor. The slope of the time taken vs number of passes through the screens was also measured and hereafter it is called as Screen Factor Slope (SFS) (Figure II-1)

Results and Discussion

Screen factor, screen factor slope, intrinsic viscosity and shear viscosity for these polymer solutions are reported in Table II-1 - II-10 as a function of time. Table II-11 shows the SF, SFS and the

intrinsic viscosity for these two polymers in solutions of different ionic environments. It must be remembered that polymer P815 and P835 originate from the same basic polymer but the only difference is that P835 is hydrolysed to larger extent than P815. This is why P815 and P835 give rise to the same intrinsic viscosity in solutions of high ionic strength. Due to the electrostatic repulsion between the carboxyl group, P835 has a higher intrinsic viscosity in H₂O than P815 (intrinsic viscosity in effect is a measure of the hydrodynamic volume of the macromolecules). But on the other hand, the screen factor for P835 polymer is lower than that of P815 which indicates that P835 polymer molecules can pass through the holes more easily than the P815 molecules. The higher magnitude of screen factor for P815 could be due to adsorption of the molecules on the screen. The magnitude of SFS is higher for P815 than for P835 which signifies that P815 is more degradable than P835. Comparison of SF, SFS and η for one polymer in different solvents (Table II-11) indicates that as the effective hydrodynamic volume of the molecules decreases, the screen factor also decreases with a few exceptions for example, the magnitude of SF for P815 in 3% NaCl is slightly higher than that of P815 in 1% NaCl. This discrepancy probably is due to the aging of 1% NaCl solution. However, the magnitude of SFS increases as the ionic strength of the medium increases, which indicates that polymer is more degradable in solutions in higher ionic strengths.

Being aware of the fact that one cannot describe the polydispersed systems adequately enough just by measuring one moment of the distribution (Mv in this case), due to the experimental difficulties and with the limited manpower available, it was not possible to obtain the other moments of the distribution. In spite of this restraint, one can obtain valuable information with a bit of caution. Since the appropriate Mark Houwink constants for these polymers were not available in the appropriate solvents, we have tabulated the intrinsic viscosity itself. Since the magnitude of screen factor was fairly low, we have plotted $\frac{SF-1}{SF_0}$ instead of $\frac{SF}{SF_0}$, which would be more appropriate. Some

of the data tabulated in Tables II-1 to 10 are plotted in Figures II-2 to II-5. The following conclusions can be drawn from this data.

(1) The higher the salt concentration of the medium, the higher is the loss in SF, SFS, η and shear viscosity.

(2) The loss in SF, SFS, η and shear viscosity also increases with age and temperature.

(3) Comparison of two polymers with different degree of hydrolysis but with the same molecular weight indicated that the one with higher degree of hydrolysis leads to lower screen factors and is less degradable as well.

(4) In almost every case it was found that in the first ten days the intrinsic viscosity decreased by about 30% to 40% of its original value whereas the loss in screen factor was about 2-3% (for solutions stored at 30°C). Decrease in the magnitude of intrinsic viscosity means that some of the large molecules which were present originally are no longer there. This could occur due to thermal decomposition, chemical action, adsorption or precipitation, etc. However, the deduction from this information is that a few macromolecules can give rise to large screen factor and further addition of macromolecules does not seem to increase the screen factor significantly. It is observed that a large decrease in the magnitude of intrinsic viscosity is accompanied by a small change in the screen factor for most of the solutions in the first ten days. Furthermore, reasonably large changes in the screen factor slope seem to indicate the presence of fewer larger degradable molecules.

COMMENTS

Some of the abnormalities in the data could be explained in the following manner:

(1) Slight increase in SF, e.g., in case of P815 (in 3% NaCl, 0.3% CaCl₂ at 30°, (Table II-7) from fresh to 10 day-old solution) could be due to slight change in the mesh, or bubbles in the mesh.

(2) Slight increase in viscosity for P815 in 1% NaCl (Table II-1, solution stored at 65°C) could be due to evaporation of water from the solution, hence leading to a more concentrated solution.

Having studied the stability of polyacrylamides in different ionic environments and at different temperatures, we now have started the flow through porous media studies using these polymers, where the polymer undergoes degradation due to the shearing also. In order to study the effect of shearing on SF, SFS, $\frac{\Delta P}{L}$, η and n , the following experiment was carried out.

500 ppm of P815 in 1% NaCl was sheared in a blender for different lengths of time. Samples were collected at different intervals and these parameters were evaluated the same way as described earlier. Figure II-6 shows the effect of time shearing on these parameters. It is quite clear from the plot that about 20% decrease in intrinsic viscosity causes about 75% decrease in the screen factor and about 97% decrease in SFS. $\Delta P/L$ agrees quite well with screen factor data. The similar decrease in intrinsic viscosity of about 20% causes only a small decrease in screen factors (especially for samples stored at 30°). This is an agreement with the conclusion made earlier and one can explain this on the basis of the fact the shearing will break the larger molecules preferentially and hence lead to lower SF and SFS, whereas in age experiments even though intrinsic viscosity does decrease we still have a few large molecules which give rise to higher values of SF and SFS.

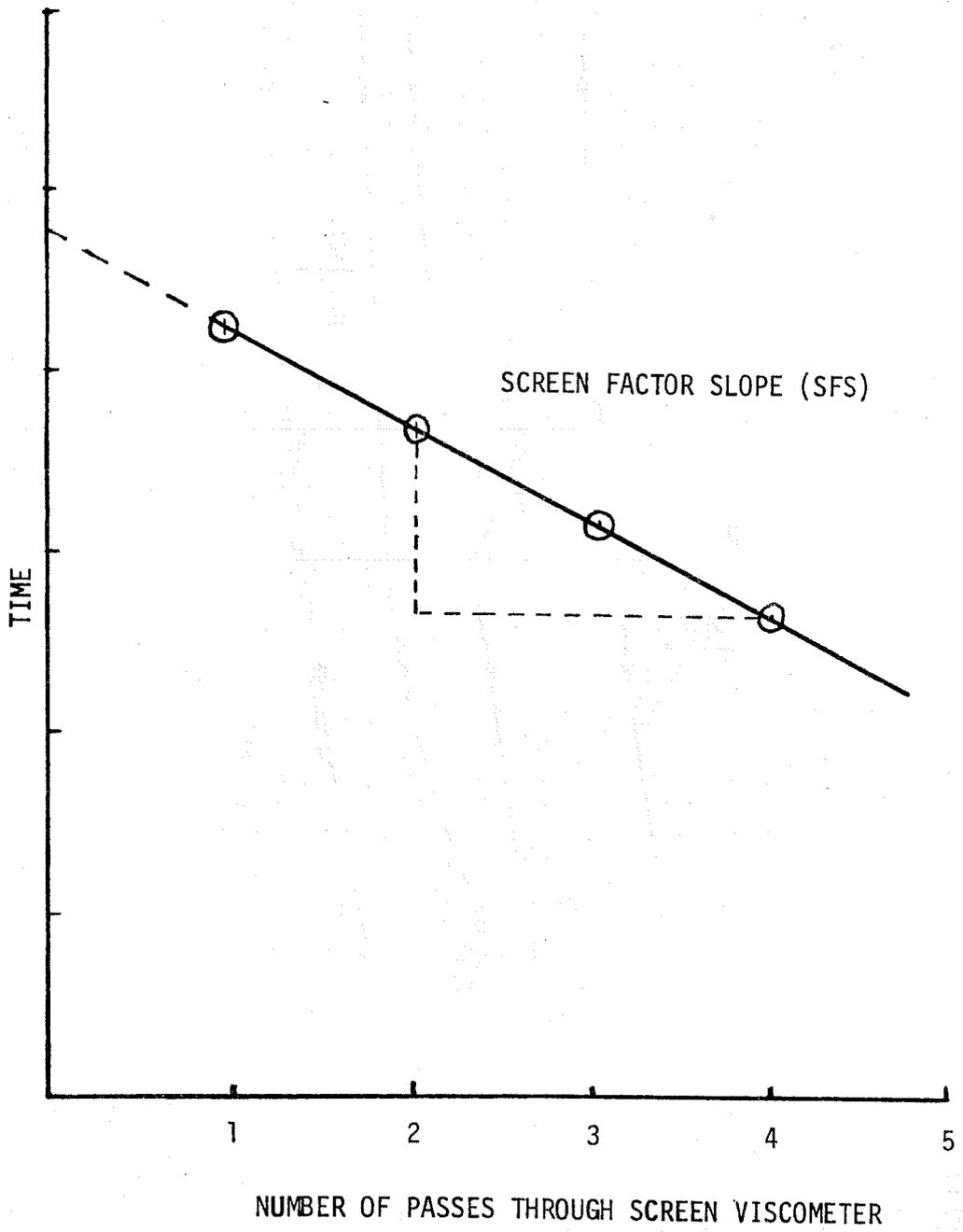


Figure II-1

EFFECT OF TEMPERATURE AND AGE ON SF AND SFS FOR P815 IN 3% NaCl SOLUTION

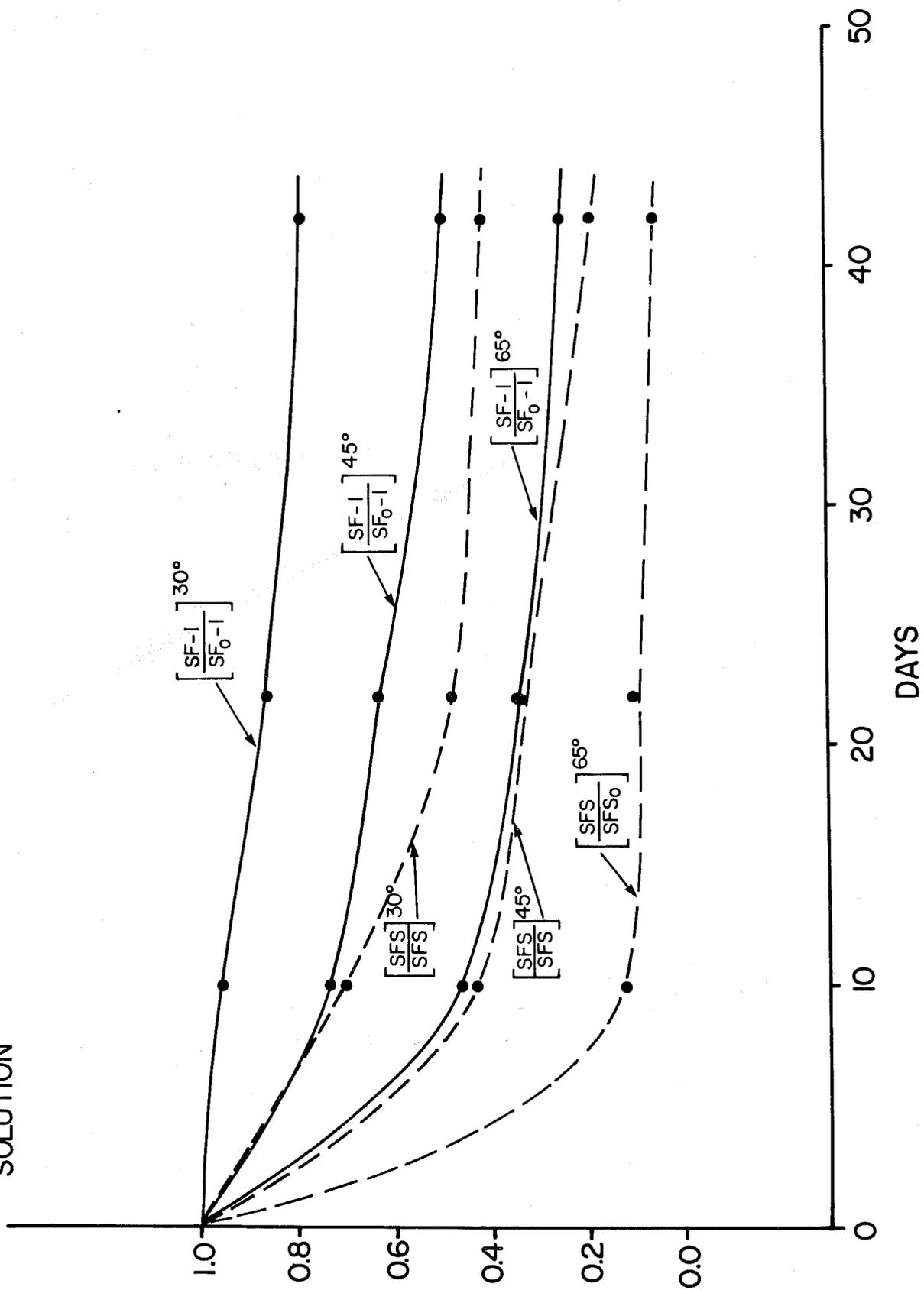


Figure II-2

EFFECT OF TEMPERATURE AND AGE ON INTRINSIC VISCOSITY FOR P815 IN 3% NaCl SOLUTION

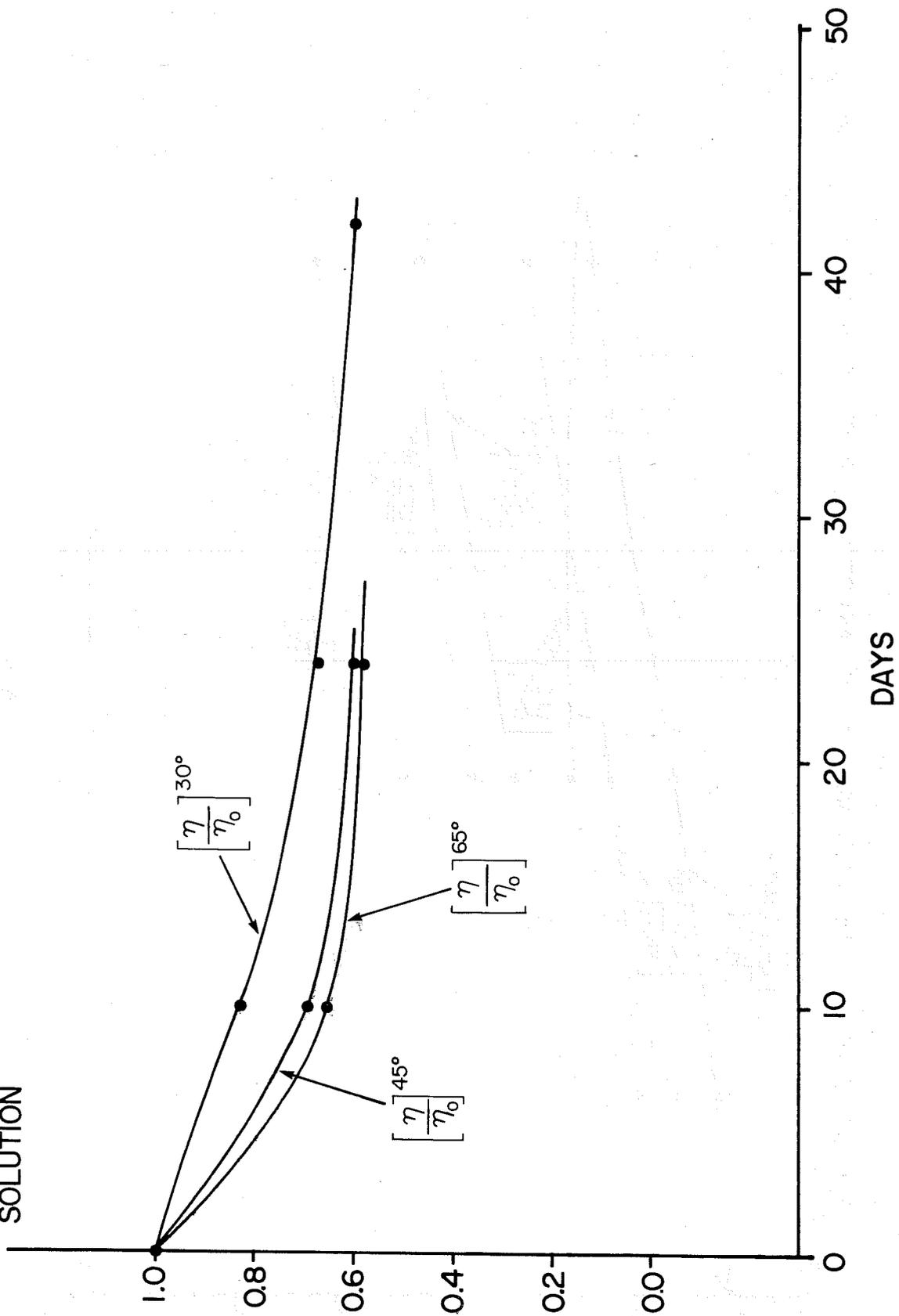


Figure II-3

EFFECT OF TEMPERATURE AND AGE ON SF AND SFS ON P815 IN 3% NaCl+0.1% CaCl₂ SOLUTION

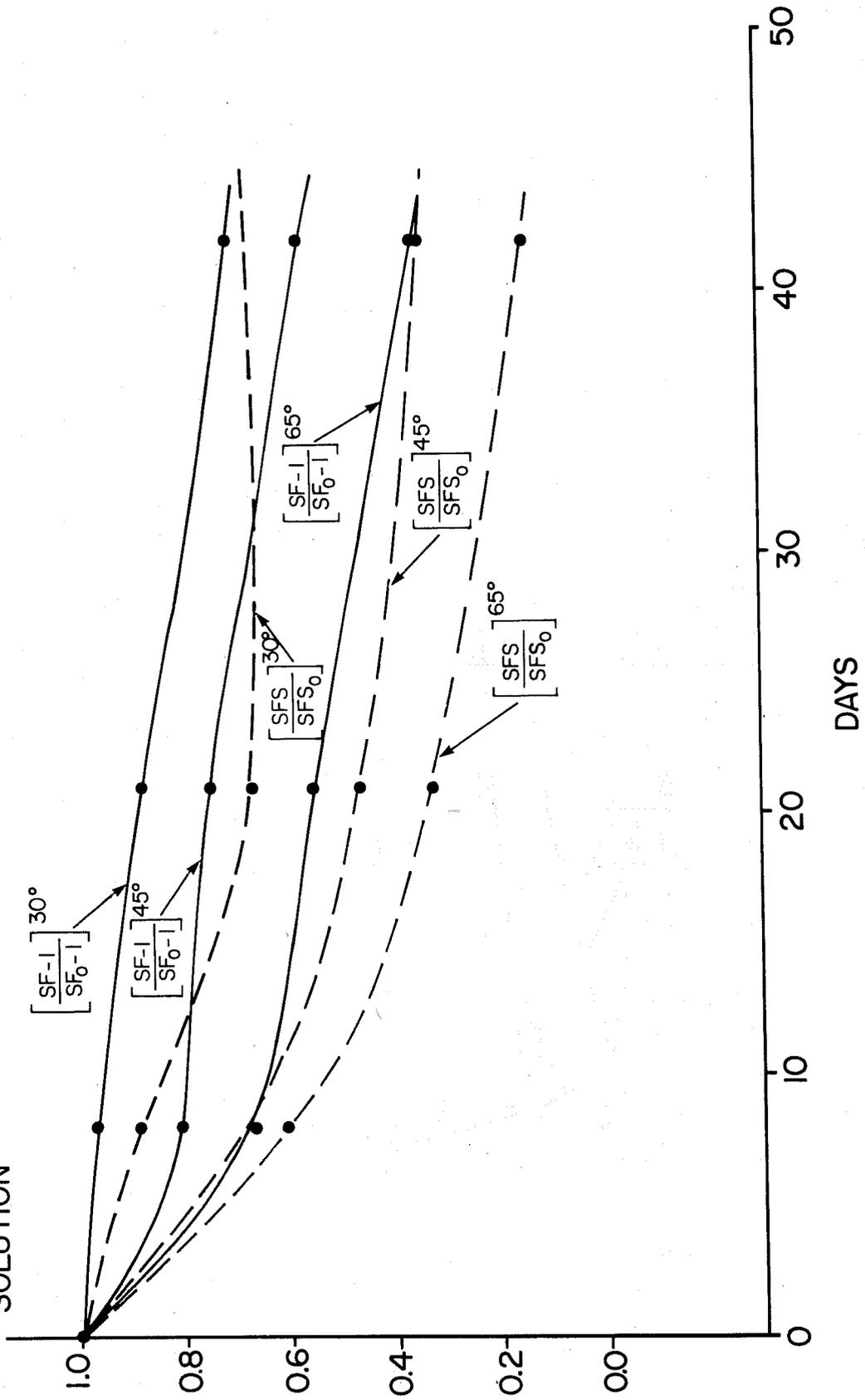


Figure II-4

EFFECT OF TEMPERATURE AND AGE ON SF AND SFS FOR P815 IN 3% NaCl+0.3% CaCl₂ SOLUTION

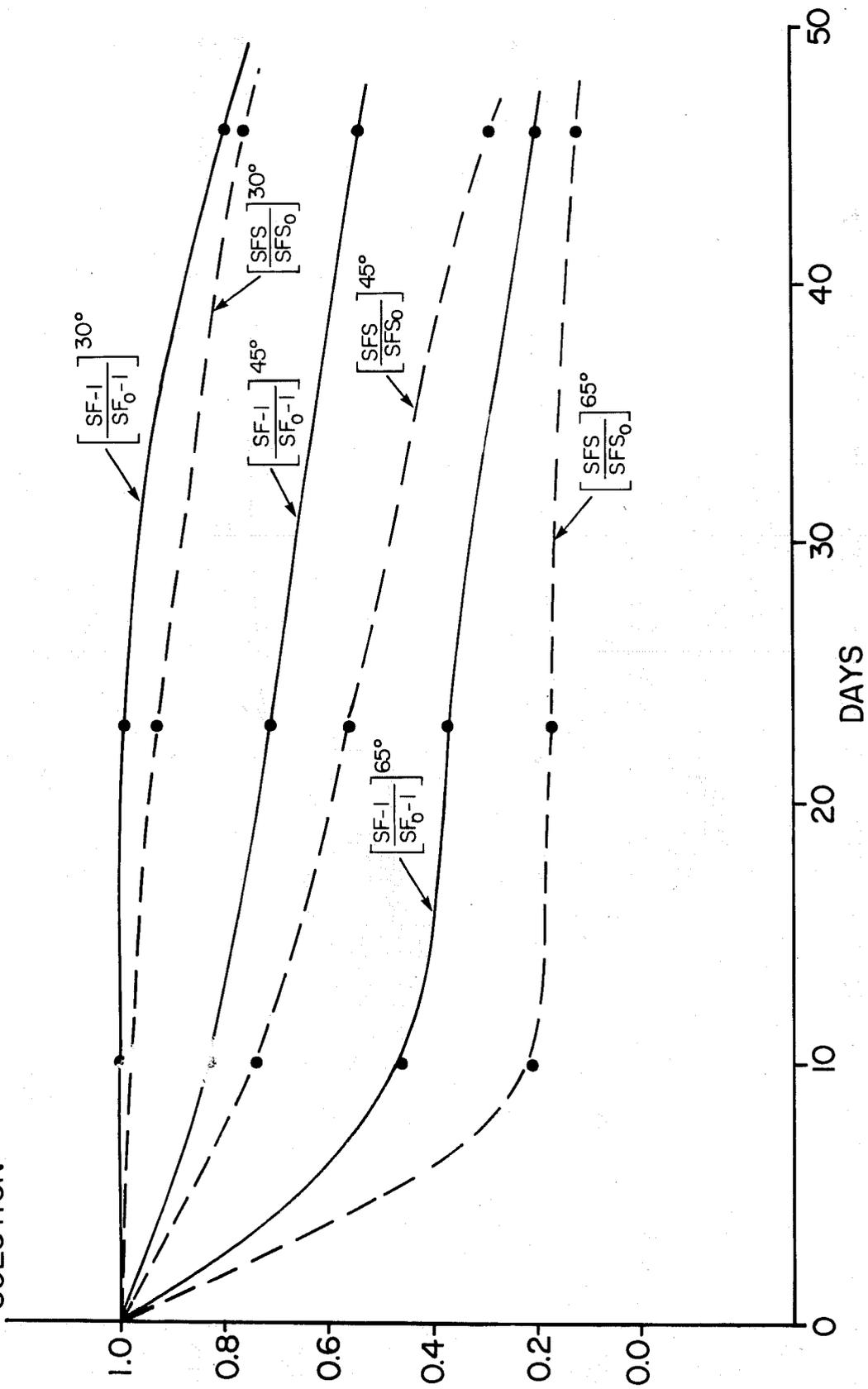


Figure II-5

EFFECT OF CONSTANT SHEARING ON SCREEN FACTOR, SCREEN FACTOR SLOPE, $\frac{\Delta P}{L}$,
 INTRINSIC AND SHEAR VISCOSITY FOR 500ppm P815 IN 1% NaCl SOLUTION

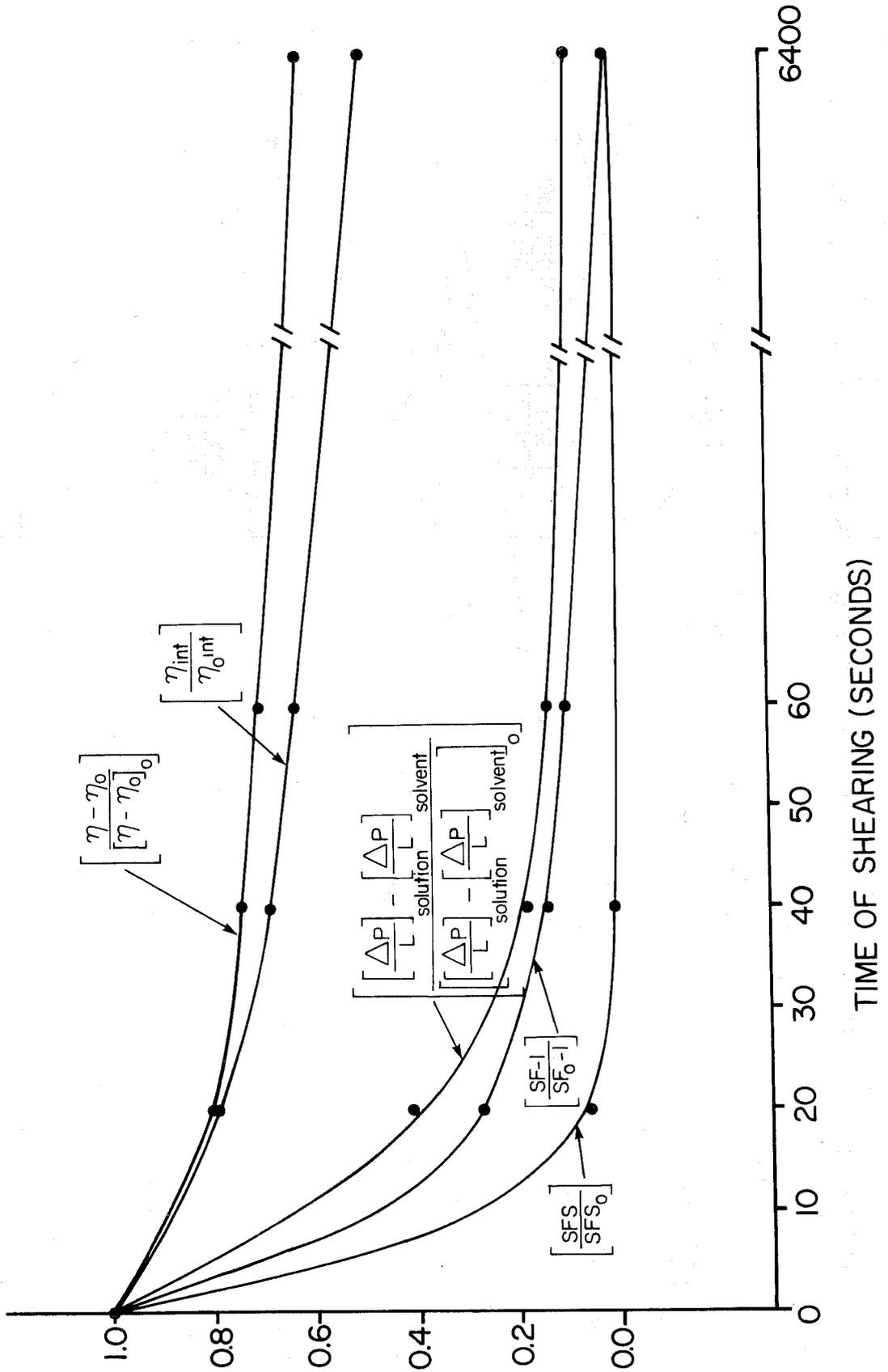


Figure II-6

Table II-1 Effect of Temperature and Age in Screen Factor, Screen Factor Slope, Intrinsic, and Shear Viscosity for P815 in 1% NaCl

Time (days)	Solution Stored At		
	30°C	75°C	65°C
0	4.30(0.50)	4.30(0.50)	4.30(0.50)
	1.46(1.05)	1.46(1.05)	1.46(1.05)
10	4.25(0.16)	4.10(0.19)	3.72(0.09)
	0.90(1.02)	0.87(1.013)	1.04(1.02)
22	4.03(0.22)	3.83(0.14)	3.32(0.10)
	0.87(1.015)	0.87(1.014)	1.06(1.048)
42	3.88	3.67	2.47(0.09)
	0.85(1.010)	0.89(1.019)	(1.036)

Intrinsic Viscosity in l/g
Shear Viscosity in CP

In the above and succeeding tables, in order to save space, the following convention was used.

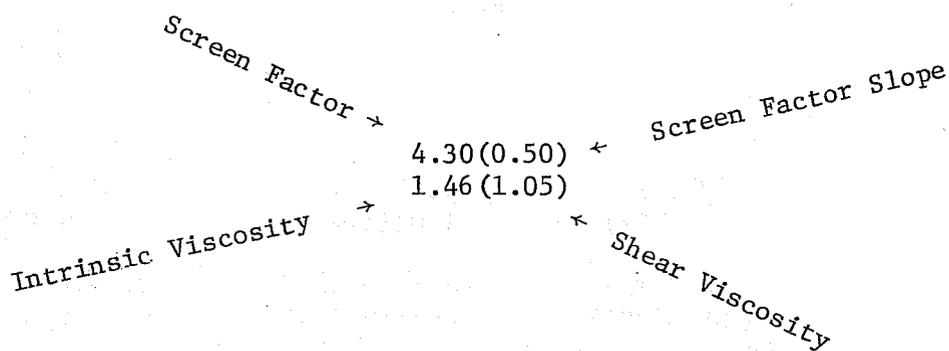


Table II-2 Effect of Temperature and Age on Screen Factor, Screen Factor Slope, Intrinsic and Shear Viscosity for P835 in 1% NaCl

Time (days)	Solution Stored At		
	30°C	45°C	65°C
0	3.85 (0.26)	3.85 (0.26)	3.85 (0.26)
	1.58 (1.134)	1.58 (1.134)	1.58 (1.134)
20	3.86 (-)	2.61 (0.08)	2.15 (0.06)
	1.18 (1.084)	1.10 (1.02)	1.26 (1.024)
50	3.57 (0.21)	2.36 (0.10)	1.67 (0.05)
	1.14 (1.072)	1.03 (1.038)	1.25 (0.997)

Table II-3 Effect of Temperature and Age on Screen Factor, Screen Factor Slope, Intrinsic and Shear Viscosity for P815 in 3% NaCl

Time (days)	Solution Stored At		
	0°C	45°C	65°C
0	4.47 (1.17)	4.47 (1.17)	4.47 (1.17)
	1.02 (1.05)	1.02 (1.05)	1.02 (1.05)
10	4.30 (0.82)	3.55 (0.50)	2.59 (0.14)
	0.85 (0.986)	0.71 (0.954)	0.67 (0.946)
22	3.99 (0.56)	3.19 (0.39)	2.18 (0.12)
	0.69 (0.965)	0.64 (0.948)	0.60 (0.952)
42	3.76 (0.49)	2.72 (0.22)	1.87 (0.07)
	0.62 (0.960)	(-) (-)	(-) (-)

Table II-4 Effect of Temperature and Age in Screen Factor, Screen Factor Slope, Intrinsic and Shear Viscosity for P835 In 3% NaCl

Time (Days)	Solution Stored At		
	30°C	45°C	65°C
0	4.50(0.25)	4.50(0.25)	4.50(0.25)
	1.27(1.05)	1.27(1.05)	1.27(1.05)
7	4.33(-)	3.77(0.24)	3.04(0.10)
	0.88(1.007)	0.84(0.999)	0.75(0.996)
35	3.19(0.16)	2.96(0.14)	2.11(0.0)
	0.82(0.998)	0.76(0.994)	0.69(0.974)

Table II-5 Effect of Temperature and Age on Screen Factor, Screen Factor Slope, Intrinsic and Shear Viscosity for P815 in 3% NaCl, 0.1% CaCl₂

Time (days)	Solution Stored At		
	30°C	45°C	65°C
0	4.51(1.30)	4.51(1.30)	4.51(1.30)
	0.97(0.985)	0.97(0.98)	0.97(0.98)
8	4.42(1.16)	3.85(-)	3.35(0.80)
	0.64(0.96)	0.65(0.96)	0.59(0.94)
21	4.09(0.87)	3.65(0.61)	2.97(0.43)
	0.60(0.95)	0.60(0.95)	0.50(0.95)
42	3.49(0.89)	3.04(0.45)	2.26(0.20)
	- (-)	- (-)	- (-)

Table II-6 Effect of Temperature and Age on Screen Factor, Screen Factor Slope, Intrinsic and Shear Viscosity for P835 In 3% NaCl, 0.1% CaCl₂

Time (days)	Solution Stored At		
	30°C	45°C	65°C
0	3.70(0.23) 1.09(1.05)	3.70(0.23) 1.09(1.05)	3.70(0.23) 1.09(1.05)
9	3.63(-) 0.67(0.98)	3.33(0.69) 0.58(0.98)	2.87(0.30) 0.54(0.97)
21	3.27(0.33) 0.60(0.98)	3.06(0.20) - (-)	2.56(0.21) - (-)
42	2.82(0.29) - (-)	2.62(0.27) - (-)	2.14(0.21) - (-)

Table II-7 Effect of Temperature and Age on Screen Factor, Screen Factor Slope, Intrinsic and Shear Viscosity For P815 in 3% NaCl, 0.3% CaCl₂

Time (days)	Solution Stored At		
	30°C	45°C	65°C
0	3.85(1.14) 0.83(0.97)	3.85(1.14) 0.83(0.97)	3.85(1.14) 0.83(0.97)
10	3.94(-) 0.59(0.94)	3.38(0.84) 0.56(0.93)	2.32(0.24) 0.52(0.92)
23	3.82(1.06) 0.59(0.94)	3.04(0.64) 0.56(0.93)	2.06(0.19) 0.42(0.92)
46	3.29(0.87) 0.56(0.94)	2.55(0.33) 0.53(0.94)	1.59(0.14) 0.40(0.91)

Table II-8 Effect of Temperature and Age on Screen Factor, Screen Factor Slope, Intrinsic and Shear Viscosity for P835 in 3% NaCl, 0.3% CaCl₂

Time (days)	Solution Stored At		
	30°C	45°C	65°C
0	3.36 (0.55) 0.90 (0.98)	3.36 (0.55) 0.90 (0.98)	3.36 (0.55) 0.90 (0.98)
10	3.41 (0.86) 0.55 (0.96)	3.44 (1.16) 0.55 (0.96)	3.07 (0.76) 0.55 (0.95)
23	2.99 (0.38) 0.52 (0.94)	3.10 (0.65) 0.50 (0.95)	2.72 (0.53) 0.47 (0.93)
46	2.24 (0.53) 0.50 (0.94)	2.62 (0.62) - (0.95)	2.11 (0.70) 0.44 (0.92)

Table II-9 Effect of Temperature and Age on Screen Factor, Screen Factor Slope, Intrinsic and Shear Viscosity for P815 in 3% NaCl, 0.5% CaCl₂

Time (days)	Solution Stored At		
	30°C	45°C	65°C
0	3.96 (1.51) 0.81 (0.96)	3.96 (1.51) 0.81 (0.96)	3.96 (1.51) 0.81 (0.96)
9	3.88 (2.06) 0.46 (0.93)	3.49 (1.52) 0.42 (0.93)	2.72 (0.75) 0.38 (0.91)
37	3.12 (0.98) 0.40 (0.93)	2.61 (0.59) 0.41 (0.92)	2.02 (0.23) 0.36 (0.91)

Table II-10 Effect of Temperature and Age on Screen Factor, Screen Factor Slope, Intrinsic and Shear Viscosity for P835 In 3% NaCl, 0.5% CaCl₂

Time (days)	Solution Stored At		
	30°C	45°C	65°C
0	3.03(0.85)	3.03(0.85)	3.03(0.85)
	0.81(0.96)	0.81(0.96)	0.81(0.96)
9	2.69(0.98)	2.72(1.96)	2.41(0.67)
	0.49(0.93)	0.46(0.93)	0.40(0.92)
37	2.52(0.50)	2.22(0.27)	1.96(0.27)
	0.48(0.93)	0.41(0.92)	0.31(0.90)

Table II-11 Effect of Solvent on Screen Factor and Screen Factor Slope for Polymers With Different Degree of Hydrolysis

SOLVENT	POLYMER 815			POLYMER 835		
	SF	SFS	η	SF	SFS	η
Distilled Water	5.48	0.47	3.8	4.88	0.11	11.0
1% NaCl	4.30*	0.50	1.46	3.85*	0.26	1.58
3% NaCl	4.47	1.17	1.02	4.50	0.25	1.27
3%NaCl, 0.1% CaCl ₂	4.51	1.30	0.97	3.70	0.23	1.09
3%NaCl, 0.3% CaCl ₂	3.85**	1.14	0.83	3.36	0.55	0.90
3%NaCl, 0.5% CaCl ₂	3.96	1.51	0.81	3.03	0.85	0.81

* 16 days old solution

** 9 days old solution

η in 1/g

B. Surfactant-Polymer Interactions

It has been demonstrated that surfactant-polymer interactions could have significant effect on the oil recovery efficiency. (Szabo, 1976; Trushenski, 1977) It certainly would be detrimental to the process, if mixing with the polymer caused an increase in the interfacial tension, between the surfactant formulations and oil. The interfacial behavior of surfactant alone has been reported in our earlier reports. Here we are focused on the effect, the presence of the polymer has on the interfacial tension of the surfactant system.

Materials and Methods

The surfactant and polymers used were TRS 10-410 and Calgon polyacrylamides. The samples for IFT measurements were made as follows:

The aqueous solution of 1.5% brine containing the appropriate amounts of the surfactant and polymer were equilibrated with an equal volume of dodecane (99% pure, Chemical Samples Co.). The equilibration was done over a period of 18 hours by means of a mechanical rotator at a low speed, followed by centrifugation for 20 minutes. The interfacial tension was then measured using the spinning drop tensiometer, at room temperature. The results are plotted in Figures II-1 and II-2.

Figure II-7 plots the effect of added Calgon 835 polymer (35% hydrolyzed) on the interfacial tension of TRS 10-410. The surfactant-along shows a minimum interfacial tension at 0.1% TRS 10-410 concentration. The salient points are that the minimum is observed even when the polymer is present; moreover the polymer does not cause a shift in the TRS 10-410 concentrations at minimum interfacial tension. But, all three concentrations of polymer, viz. 50, 250, 500 ppm cause a drop in the minimum interfacial tension value, and the interfacial tension decreases as the polymer concentration is increased from 50 to 500 ppm. Another point of note is that, at 0.5% TRS 10-410 which is beyond the minimum point, all the interfacial tension values are nearly the same.

We studied two polyacrylamides, a partially hydrolyzed one (C-835) and an unhydrolyzed one (C-800). The main difference being the presence of charged groups on the polymer molecule. The objective was to study the nature of the interactions. Our initial results are shown in Figure II-8. Again, the minimum is observed at the same TRS 10-410 concentration. At the minimum, i.e. 0.1% TRS 10-410, the IFT is decreased more by C-835 than by C-800; and, again the interfacial tension values seem to coincide at higher TRS 10-410 concentration viz. at 0.5%. The above observations serve as a precursor to studies on the interfacial behavior of surfactant-polymer systems; we also plan to correlate these with their oil-displacement behavior porous media.

Effect of the Concentration of a Partially Hydrolyzed Polyacrylamide (Calgon 835) on the Interfacial Tension of TRS10-410/1.5% brine/dodecane System

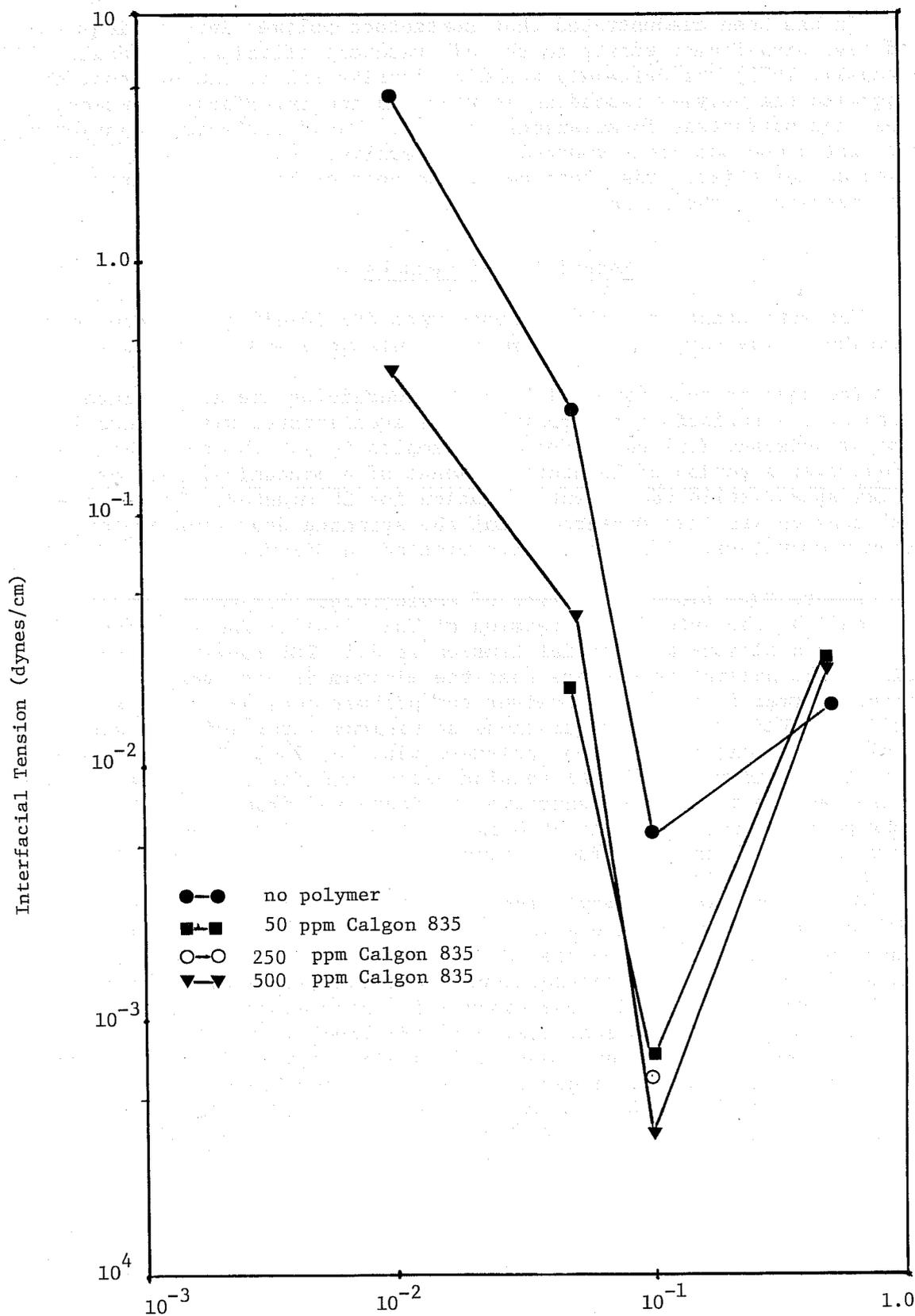


Figure II-7

TRS10-410 Concentration (gm/100 ml)

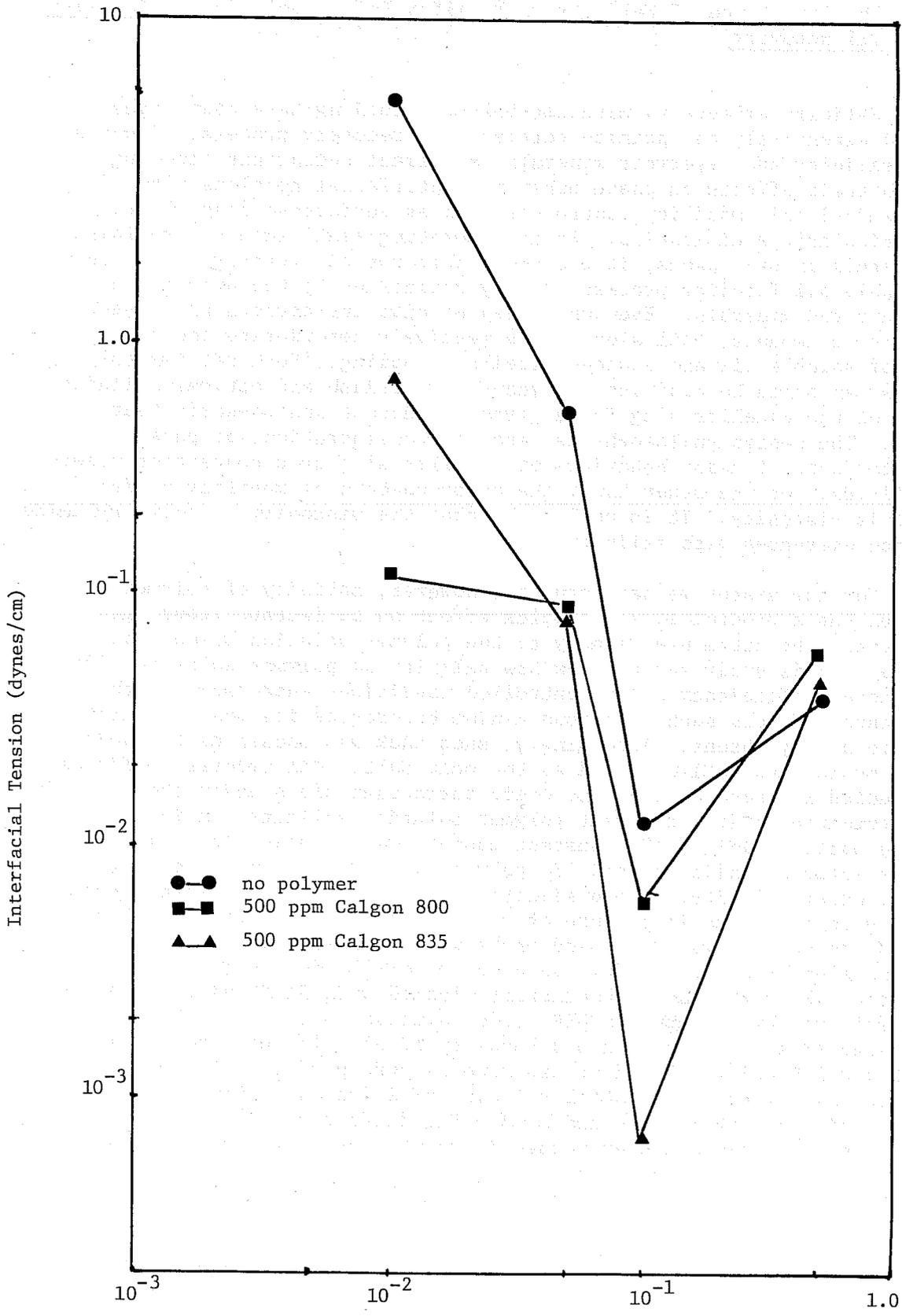


Figure II-8

TRS10-410 Concentration (gm/100 ml)

C. The Importance of Salinity of Mobility Buffer Solution In Tertiary Oil Recovery

Salinity effects in micellar-polymer flooding have been investigated extensively to optimize tertiary oil recovery process. Connate water salinity and reservoir minerals can affect surfactant flooding through their effects on phase behavior, interfacial tensions with slug and residual oil, mobility control as well as surfactant loss due to adsorption and precipitation. By incorporating small amounts of clays or minerals in sand packs, it was shown that the oil recovery efficiency by soluble oil flooding process greatly diminishes by the presence of the clays and minerals. Even when clay or divalent cations are absent or in trace amounts, NaCl alone can effectively deteriorate the performance of soluble oil and aqueous micellar flooding. Such detrimental effects can often be minimized by means of preflush and optimal salinity design of the micellar slug for a given surfactant and co-surfactant system. The design philosophy is based on considerations of phase and interfacial tension behaviors of micellar slug upon contacting reservoir fluids. On the other hand, the major concern of mobility buffer design is viscosity. It is well-known that the viscosity of polyacrylamide solution decreases with salinity.

For the system we have studied, however, salinity of polymer solution has a pronounced and complex effect on surfactant flooding, which cannot be attributed simply to the polymer solution viscosity. The purpose of this study was to show how salinity of polymer solution affects oil recovery efficiency under controlled conditions where some of the detrimental effects such as porous medium heterogeneities and surfactant loss are nearly absent. Accordingly, sand pack was chosen as the model porous medium and NaCl was used as the only salt. Oil recovery efficiency was studied for both aqueous and oleic surfactant slugs under the following three conditions: (1) constant polymer solution salinity, variable connate water salinity, (2) constant connate water salinity, variable polymer solution salinity, and (3) polymer solution salinity equal to connate water salinity, varied simultaneously. Such experimental design should give a systematic picture on salinity effects. Experimental procedures are as follows. The sand packs were saturated with water, driven to connate water saturation by dodecane, water-flooded to residual oil saturation ($24 \pm 2\%$), and subsequently flooded with 5% PV micellar slugs which followed by 1000 ppm PUSHER - 700 solution to provide mobility control. The 13"x1" sand pack had a porosity of $37 \pm 1\%$ and a permeability of 4.2 ± 0.2 Darcies. Flooding experiments were performed at room temperature ($24 \pm 1^\circ\text{C}$) at a frontal velocity of 2.8ft/day. Slug formulations are specified in Figure II-9 and II-10. The difference in concentration of aqueous and oleic slugs expressed in wt/wt, was to account for their density difference. In this way, the amount of surfactant and alcohol injected was the same. Several experiments were repeated and the reproducibility was established to be within $\pm 2\%$ in tertiary oil recovery.

THE EFFECT OF RESIDENT BRINE AND POLYMER DRIVE SALINITY ON THE OIL-DISPLACEMENT EFFICIENCY OF AQUEOUS SURFACTANT SLUG IN SAND PACKS.

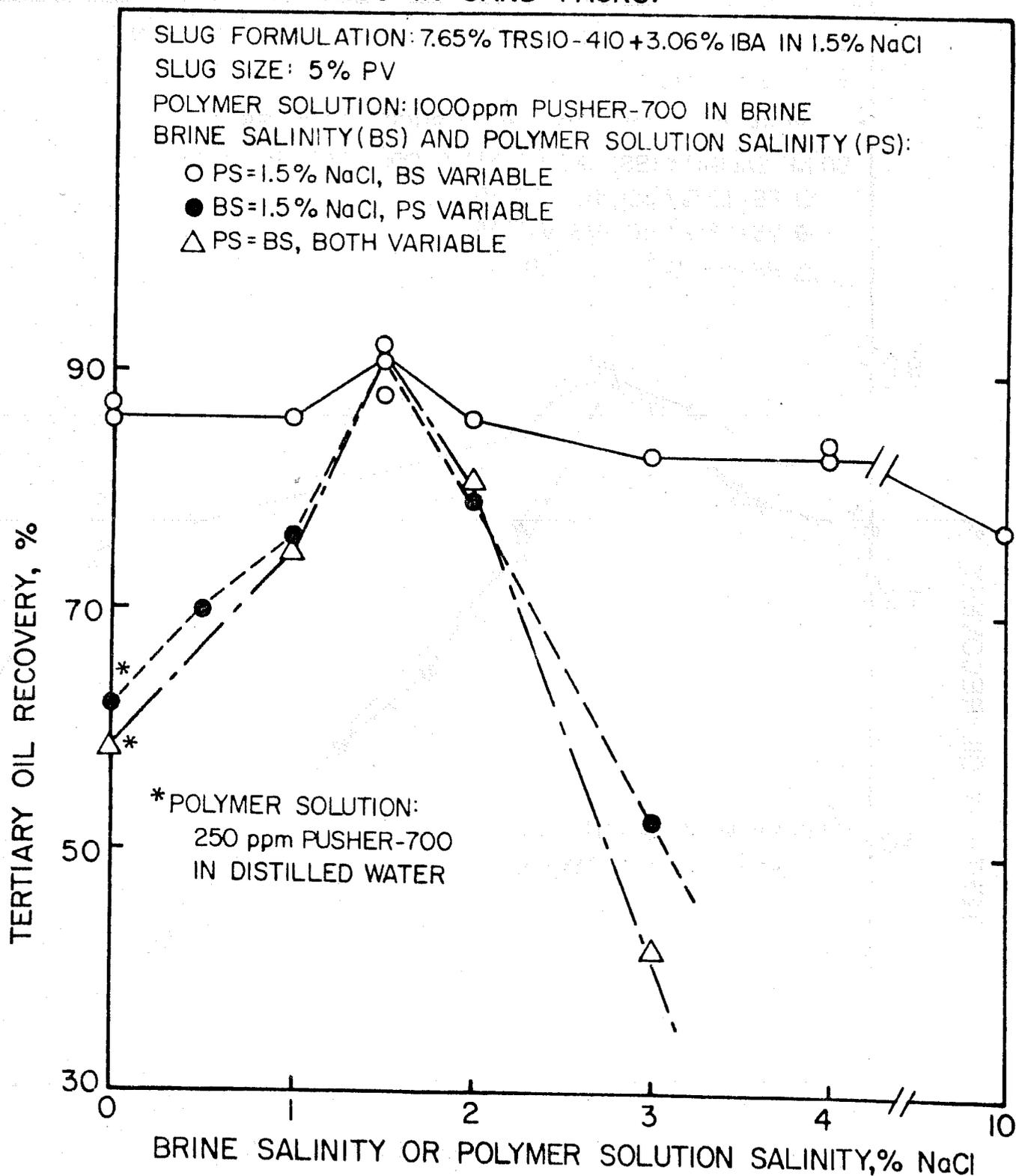


Figure II-9

THE EFFECT OF RESIDENT BRINE AND POLYMER DRIVE SALINITY ON THE OIL-DISPLACEMENT EFFICIENCY OF SOLUBLE OIL IN SAND PACKS.

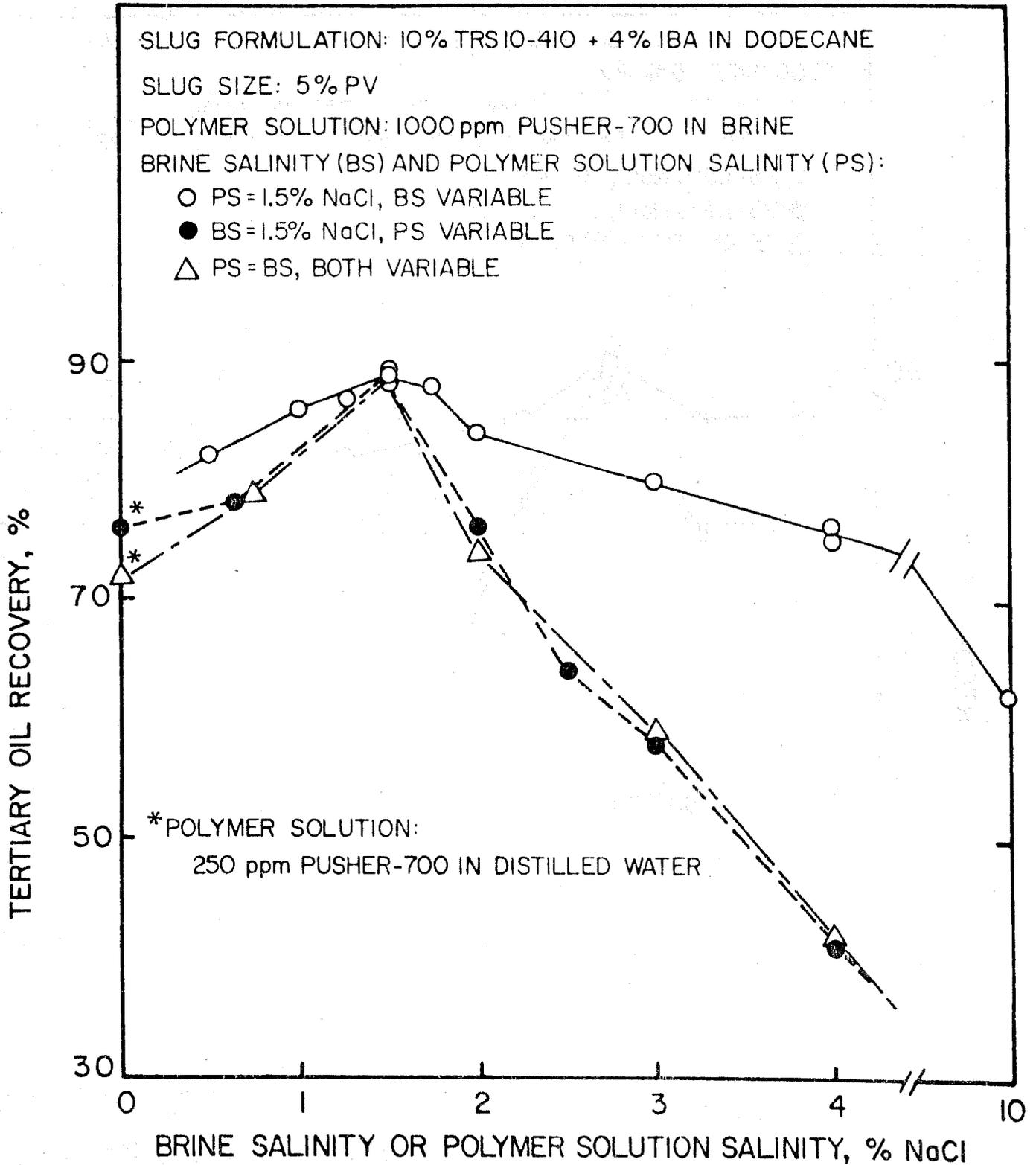


Figure II-10

Contrary to some literature data^{3,4} it is clearly evident that there exists an optimal salinity (1.5% NaCl in this case) for polymer solution which is the same as the optimal connate water salinity, as illustrated in Figure II-9 and II-10. Maximal oil recovery of 89% or 90% was obtained at the optimal salinity for either slug formulation. On the other hand, oil recovery was only 75% or 62%, respectively, for soluble oil and aqueous formulation, using fresh polymer solution (250 ppm PUSHER-700 in distilled water) and optimal connate water. Viscosities of the fresh and saline polymer solutions, as measured by a Brookfield viscometer at a shear rate of 6.6 sec.⁻¹, were 31 cp and 6.8 cp. The total apparent viscosities in porous media were 250 cp and 12 cp, respectively. However, the much higher viscous driving force in oil-displacement resulted from using fresh polymer solution only corresponded to a considerably lower recovery efficiency. It is clear, then, some other properties of polymer solution in addition to its viscosity must be taken into considerations for optimal design of oil recovery process.

The study also revealed other important information. When polymer solution was at the optimal salinity, the minimum oil recovery was 75% (Figure II-9) for soluble oil slug and a minimum of 83% for aqueous surfactant slug (Figure II-10), for the entire range of connate water salinity (0 to 4% NaCl). Shown in Figures II-9 and II-10 the oil recovery was found to be 62% for soluble oil and 77% for aqueous formulation for connate water salinity as high as 10% NaCl. This means a deviation of connate water salinity from its optimal value by a factor of more than 6 only resulted in a decrease in oil recovery by less than 30% in one case (soluble oil) and 15% in another (aqueous micellar solution). While a deviation of polymer solution salinity from its optimal value by a factor of 2 can cause the oil recovery to decrease as much as 40%, irrespective of whether connate water salinity was optimal or not. In conclusion, for the system we have studied and using sand pack as the model porous medium, it is the polymer solution salinity rather than connate water salinity that controls the oil recovery efficiency. These results also suggest that it is the interfacial tension of surfactant slug (soluble oil or aqueous formulation) - polymer solution interface that dominates the final oil saturation and oil recovery efficiency in the systems reported here. The polymer solution having optimal salinity of the surfactant slug assures that the surfactant-polymer interface will maintain a low interfacial tension.

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III. Thermodynamic Properties

The two milestones of the Thermodynamic Properties area have been met. In addition, some extra theoretical considerations and experimental results have been found.

A. Theory

The June 1978 semi-annual report (USDOE Contract EW-77-S-05-5341) described some details of the theory for micellization which we are developing in order to decide the properties of low concentration surfactant solutions. During the present quarter, we have focused on two aspects of development: the question of the temperature dependence of aqueous solubility and micelle formation, and the appropriate "macroscopic" expression for cavity formation. We have been asserting that the driving force for micelle formation is the removal of large surface area, highly curved cavities in the water. Calculation of this effect for spherical nonpolar gas solubility was in agreement with the fact that there is a significant increase in entropy when a micelle is formed at room temperature while the enthalpy change can be of either sign, but is small. At the Gordon Research Conference on Aqueous Solutions, it was pointed out that at elevated temperatures the enthalpy change becomes significantly negative and the entropy change is small. We have now determined that our model precisely describes this effect, the evidence being not only direct high temperature calculations, but also the very large heat capacity change associated with cavity creation or removal. Thus, we believe even more firmly that we are addressing the major effect observed in aqueous solutions and micellization. More details will be shown in the next quarterly report but at this point we can say that our predictions of thermodynamic properties compare quantitatively with gas solubility results as well as with chain effects on the infinite dilution properties of surfactants as obtained from calorimetric measurements at varying temperatures.¹

As discussed in the June report, we have been using the aqueous scaled-particle theory of Stillinger² to obtain the aqueous cavity properties. A crucial ingredient in this theory is matching of a molecular correlation function with the macroscopic result. One of the parameters obtained in this matching is the curvature dependence of the surface tension whose temperature dependence controlled the actual thermodynamic behavior of the system. In the search to insure that this vital quantity was proper, we determined that there were several severe approximations in Stillinger's development (which, however, have been common in scaled-particle theory) which were unrealistic, unnecessary, and could cause significant errors in cavities of the size of micelles. Returning to the fundamental work of Koenig³ in this area, we have rewritten the macroscopic expressions in terms of fewer variables and have initially observed more satisfactory variation of the molecular parameters with the more fundamental theory. Detailed discussion will be deferred until the next report when more complete comparisons are available.

Calculations were nearly completed for exploring the Reiss⁴ and Ruckenstein and Chi⁵ theories of microemulsions. The fundamental assumptions involved were that the stabilizing factor for the dispersed phase was an entropy increase due to the dispersed molecules having access

to a greater region of space. Our calculations have been based on the Reiss model with a perturbation term of electrostatic repulsion based on the Verwey-Overbeek⁶ method. It became clear that, even though the Barker-Henderson perturbation method⁷ is probably inaccurate for repulsive forces such as those due to electrostatic change, our estimates of the free energy of dispersion were too small compared to thermal energies to actually be the driving force. We now believe the proper driving force is the surfactant, which can significantly lower its free energy by adsorbing at an interface, a factor which is omitted in both of the above theories. The best method of including this factor is presently being sought.

B. Experiment

The high pressure optical cell has been installed completely (except perhaps for some temperature control equipment), leak tested, checked for spurious pressure-induced optical anisotropies (there were none), and filled which forms a lyotropic liquid crystal at room temperature. The transition to an isotropic system is complete at 351°K and two phases coexist for approximately 5 degrees below that. When the pressure is raised from atmospheric to 600 bar (~9000 psia), the anisotropic phase is stabilized. If two phases are present, say 1/4 anisotropic and 3/4 isotropic, the proportions of the phases are reversed up on pressurization. The temperature for complete transition is increased approximately 3-4°K by the above pressure. These changes appear instantaneously.

When the pressure is reduced after pressurization, the system does not immediately return to its original state, i.e., become an atmospheric fluid again. It appears as if some time (of the order of a day) is required for the anisotropic phase to rearrange to isotropic if the temperature is close to the transition temperature.

These last results are similar to some effects we have noticed with petroleum sulfonate three-phase systems with which we are studying temperature-salt relations. At room temperature, if the salt concentration of the brine is raised sufficiently high, the middle and upper phases are no longer distinguishable (whether the upper or middle phase "disappears" by some mechanism, or they both reach a critical end point is still a matter of speculation). Increasing the temperature will result in reforming the upper phase by ejection of oil from the "middle" phase. For a system in which the third phase disappears at 3.5 wt.% salt, a temperature of 350°K is enough to keep the three phases, even at 4.2 wt.% salt. If a sample of two phases with salt only slightly above the transition (0.1% salt) is heated to form three phases and then cooled, it will not return to two phases without agitation. Even with agitation, it may temporarily appear as two phases, but then reappears as three phases in a day or so. We are studying the transition and the time effects further using more carefully controlled temperature and sample concentrations to better discern the phenomena.

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IV. Rock/Fluid Interactions

During this quarter experiments which relate to surfactant salting-out, multivalent cation precipitation, surfactant and polymer adsorption were carried out. In addition, a survey of current knowledge of surfactant loss by precipitation was initiated. The paragraphs which follow will reveal that the milestones set forth in our Milestone Schedule of 10/23/78 for the first quarter of the present contract have been met with one exception: polymer adsorption has been hampered by lack of adequate analytical procedures.

A. Surfactant/Polymer Precipitation

A 1. Surfactant Salting-Out

Surfactant salting-out (by so-called indifferent electrolytes such as NaCl) is not a new phenomenon. It is, however, inadequately understood, and it appears to have been a factor in several surfactant adsorption investigations which have been described in the literature. The present study is concerned with the influence of NaCl concentration, alcohol type and concentration, and oil on the precipitation of selected commercial and monoisomeric anionic surfactants by salting-out as distinguished from multivalent cation precipitation.

Aqueous solutions of Cities Service SUL-FON-ATE AA10 (1.0 wt.%) and University of Texas 8-phenyl hexadecane sodium sulfonate (0.05 wt.%) were made with 0, 1, 2, and 5 wt.% NaCl by mixing more concentrated surfactant solutions with aqueous NaCl. Salting-out was observed immediately on mixing for SUL-FON-ATE AA10 in 2 and 5 wt.% NaCl and for all NaCl solutions of 8-phenyl hexadecane sodium sulfonate. Thus, salting-out is observed for dodecyl benzene sulfonates when the NaCl concentration exceeds about 2 wt.% and for the hexadecyl benzene sulfonate for any appreciable concentration of NaCl.

When n-octane was added ($V_{oil} = V_{aq}$) and the mixtures contacted for approximately 24 hours while being rotated at one rpm at 30°C, the precipitate disappeared from all samples containing the hexadecyl benzene sulfonate while the precipitate remained in the samples containing dodecyl benzene sulfonate (2 and 5 wt.% NaCl). The octane layer was centrifuged until clear, and the concentration of surfactant in the octane was measured by UV absorption. The final surfactant concentrations in the oil phase and the approximate fraction of surfactant in the oil are shown in Table IV-1 below.

These results, though only preliminary and semi-quantitative, make clear that the presence of oil can have a very significant effect on salting-out of surfactant, especially for the more oil-soluble, higher equivalent weight surfactants. The aqueous solutions of both of the surfactants were well above the CMC, especially for the NaCl solutions, but the salt effects noted seem to more closely related to surfactant solubility in oil and water and to the common ion effect of sodium de-

precipitation curve is shown in Figure IV-1 for a calcium ion concentration of 50 ppm (2.5×10^{-3} N). It can be seen that the minimum in the curve (corresponding to maximum precipitation) occurs at a surfactant to calcium ratio near unity, and that two plateaus in the solubilization branch occur at surfactant/calcium ratios of approximately 2 and 3. Thus, the earlier observations are completely confirmed.

The minimum in the curve implies appreciable though small solubility of calcium lauryl sulfate. The significance of the two plateaus in the solubilization branch is not clear, but may indicate the formation of intermediate complex species which are also sparingly soluble and which are solubilized by additional excess surfactant. We can also note that complete solubilization of the precipitate occurs at a surfactant to calcium ratio of about 5.

Precipitation and Solubilization of Other Calcium Surfactants

Precipitation and solubilization of the calcium salts of Aerosol-OT and a dodecyl benzene sulfonate (Cities Service SUL-FON-ATE AA10) are depicted in Figure IV-2 for a calcium concentration of 50 ppm (2.5×10^{-3} N). The data for sodium lauryl sulfate are also included. It is clear that the behavior of each of these materials is generally similar, but differences do exist. Both sodium lauryl sulfate and Aerosol-OT are pure, monoisomeric compounds, and it can be noted that distinct minima and plateaus exist for each of these in contrast to the generally smooth curve for the dodecyl benzene sulfonate which is known to be a mixture of compounds. Maximum precipitation occurs at a surfactant/calcium ratio in the vicinity of unity for each of the surfactants, but the shape of the solubilization branch of the curve appears to depend on the particular surfactant being studied.

It seems worth noting that the precipitate was completely solubilized for SUL-FON-ATE AA10 for a short range of surfactant/calcium ratios and it then reappeared at higher S/Ca ratios; for Aerosol-OT, the precipitate never completely disappeared. The significance of these observations is not clear at this time, but since the surfactants were quite pure (apparent purity > 96% based on C and S analyses), it is difficult to believe that they can be attributed to impurities. The point will require further investigation.

These results, combined with those reported earlier, support the belief that precipitation of surfactants by multivalent cations may not be significant in the main body of a micellar slug. Surfactant precipitation could occur at the leading edge of the slug, but the precipitate would tend to be dissolved as the main body of the slug reached it. At the trailing edge of the slug one would also expect precipitate and since this would reduce the inventory of surfactant in the slug, it could be a significant surfactant loss.

Extension of these experiments to other surfactants and to higher calcium concentrations is in progress, as are experiments to evaluate the influence of oil.

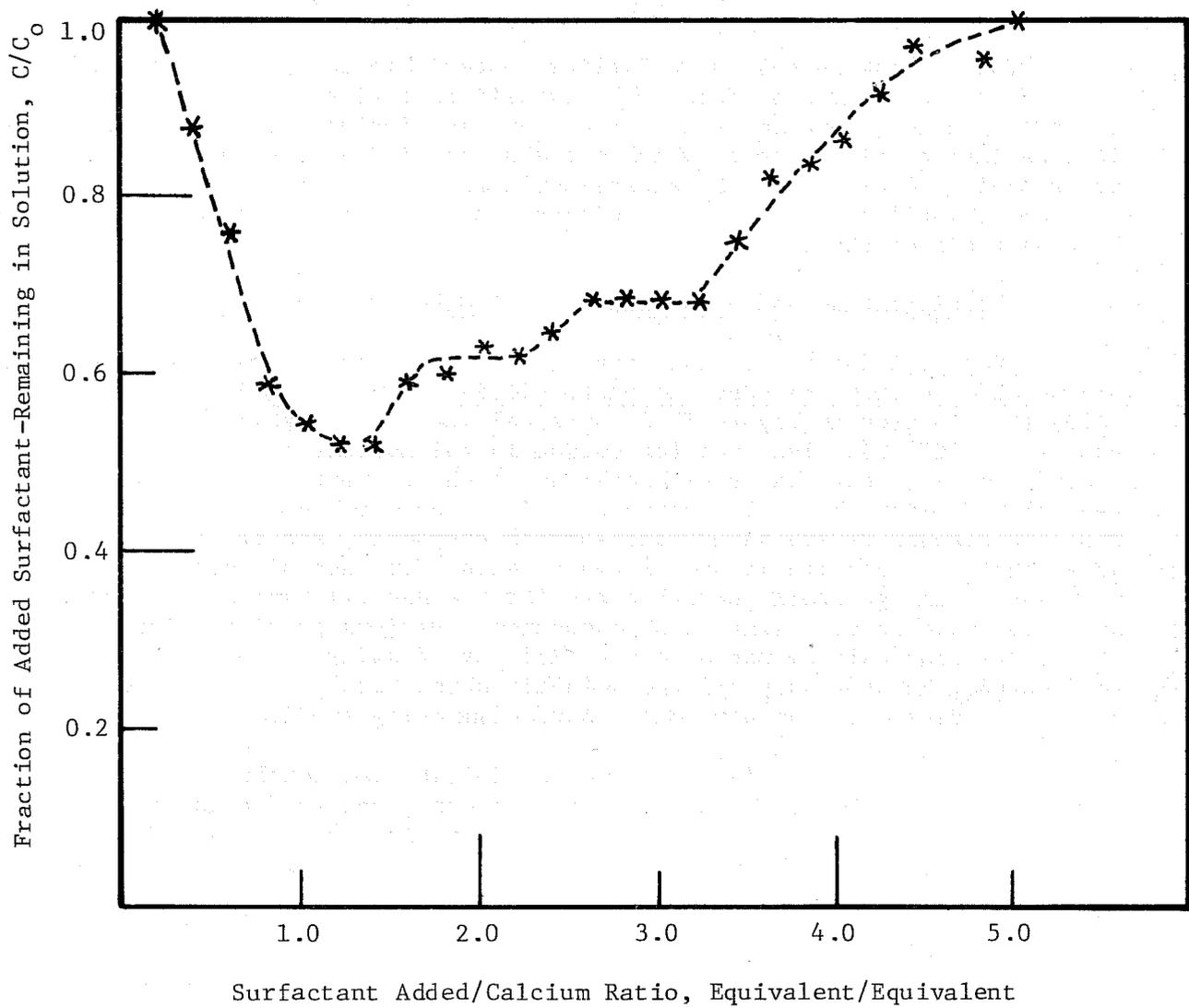


Figure IV-1. Concentration Dependence of Precipitation and Solubilization of Calcium Lauryl Sulfate. Ca^{+2} Concentration = 50 ppm = $2.5 \times 10^{-3} N$

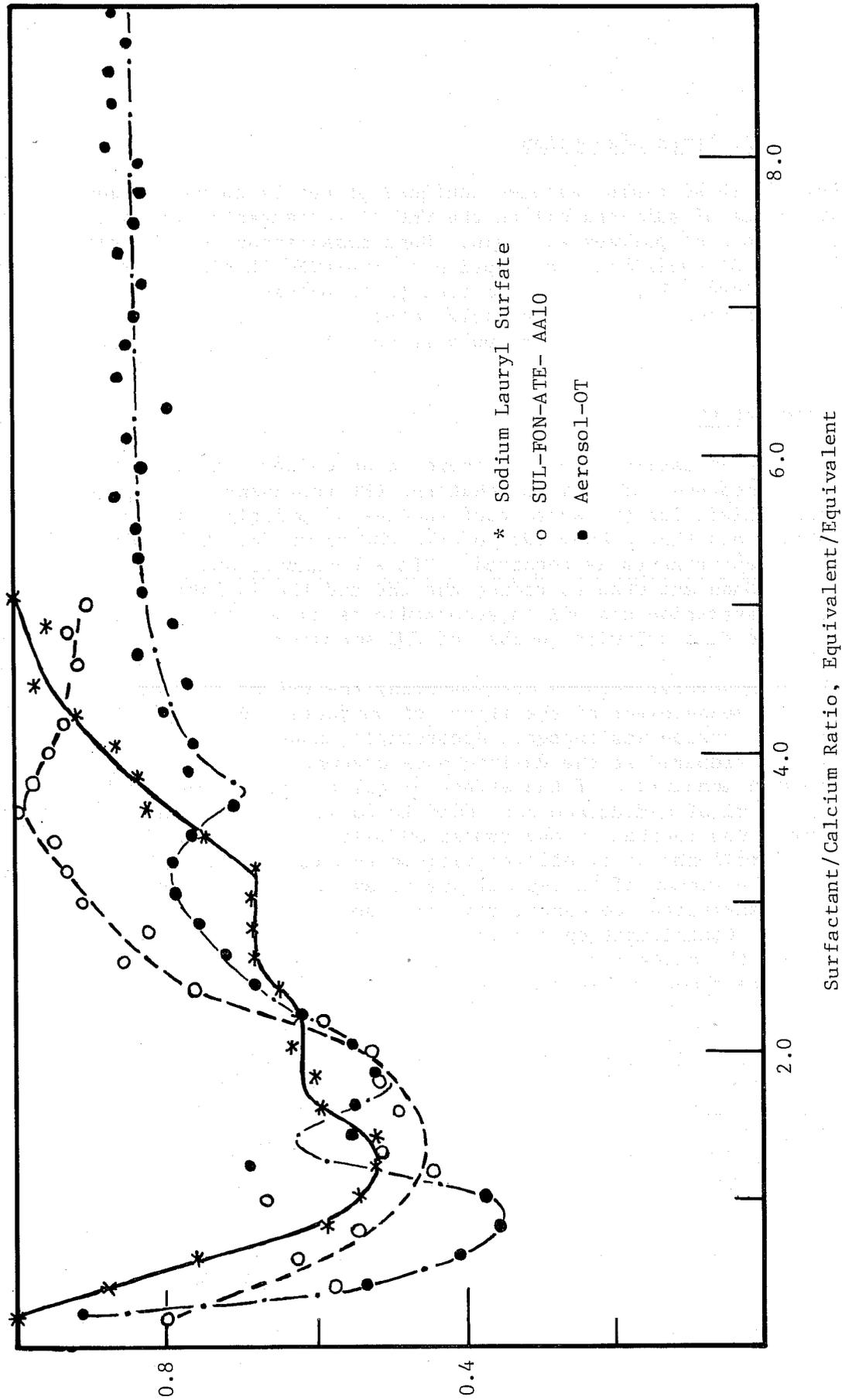


Figure IV-2. Concentration Dependence of Precipitation and Solubilization of Sulfonates with 50 ppm Calcium.

B. Surfactant/Polymer Adsorption

Work on these tasks has been confined primarily to measurement of the influence of salt and oil on the CMC of surfactants and to evaluation of methods of polymer analysis. Some measurements of the rate of adsorption and of equilibrium adsorption of SUL-FON-ATE AA10 on Na-kaolin have been completed, but no reliable results of polymer adsorption have been obtained because a really suitable method of polymer analysis for the entire range of salt, oil, and polymer concentration has not yet been found.

B 1. Surfactant CMC

As noted in earlier reports, there is no evidence that surfactant micelles are adsorbed. This means that the CMC represents an upper concentration limit for the surfactant species of principal interest in adsorption, and that a knowledge of the CMC value for the conditions of adsorption experiments is required. Since both salt and oil have been shown by Shah and Chan to reduce the CMC and the influence of both salt concentration and oil on adsorption is to be investigated, it is necessary to make a limited number of CMC measurements.

Although several methods for measuring the CMC of surfactants are available, measurement of the effect of surfactant concentration on the surface tension was chosen. Accordingly, aqueous surfactant solutions were prepared at the desired NaCl concentration and the surface tension measured. If the effect of oil on the CMC was to be evaluated, 0.1 ml of n-dodecane was added to 20 ml of surfactant solution, and the sample was rotated at one rpm at 30°C for three days. In all cases a very small amount of oil was visible throughout the equilibration process, but the amount of excess oil was so small that no appreciable change in the surfactant concentration could occur by partitioning into the oil phase. Centrifugation separated the excess oil which was then withdrawn, and the surface tension was measured. The results of these measurements are shown in Figures IV-3, IV-4, and IV-5.

In Figure IV-3 the surface tension vs surfactant concentration data are shown for Cities Service SUL-FON-ATE AA10 dissolved in distilled water, with and without contact with excess n-dodecane; in 0.1 wt.% NaCl; and in 1 wt.% NaCl, with and without excess n-dodecane.

The plot for SUL-FON-ATE AA10 in distilled water is entirely normal in that the surface tension declines linearly as the log of the surfactant concentration increases until the CMC (0.05 wt.%) is reached, after which the surface tension is essentially independent of surfactant concentration. Similar results are observed when the salt concentration is 0.1 and 1.0 wt. %. If surfactant in distilled water is equilibrated with a slight excess of oil, however, different behavior is observed: The surface tension decreases until a plateau is reached at a CMC value of 0.01 wt.%; at a surfactant concentration of 0.032 wt.% a second de-

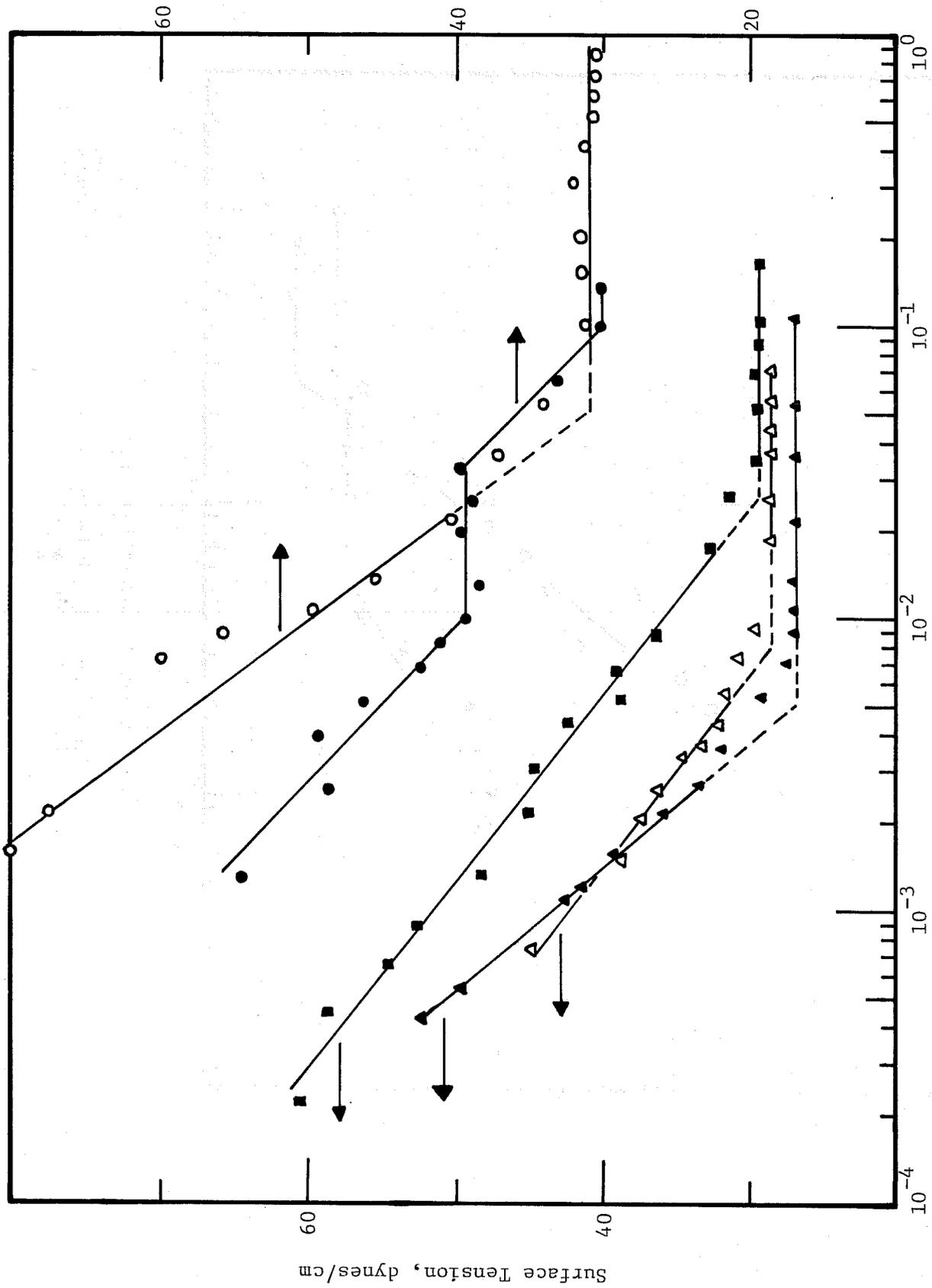
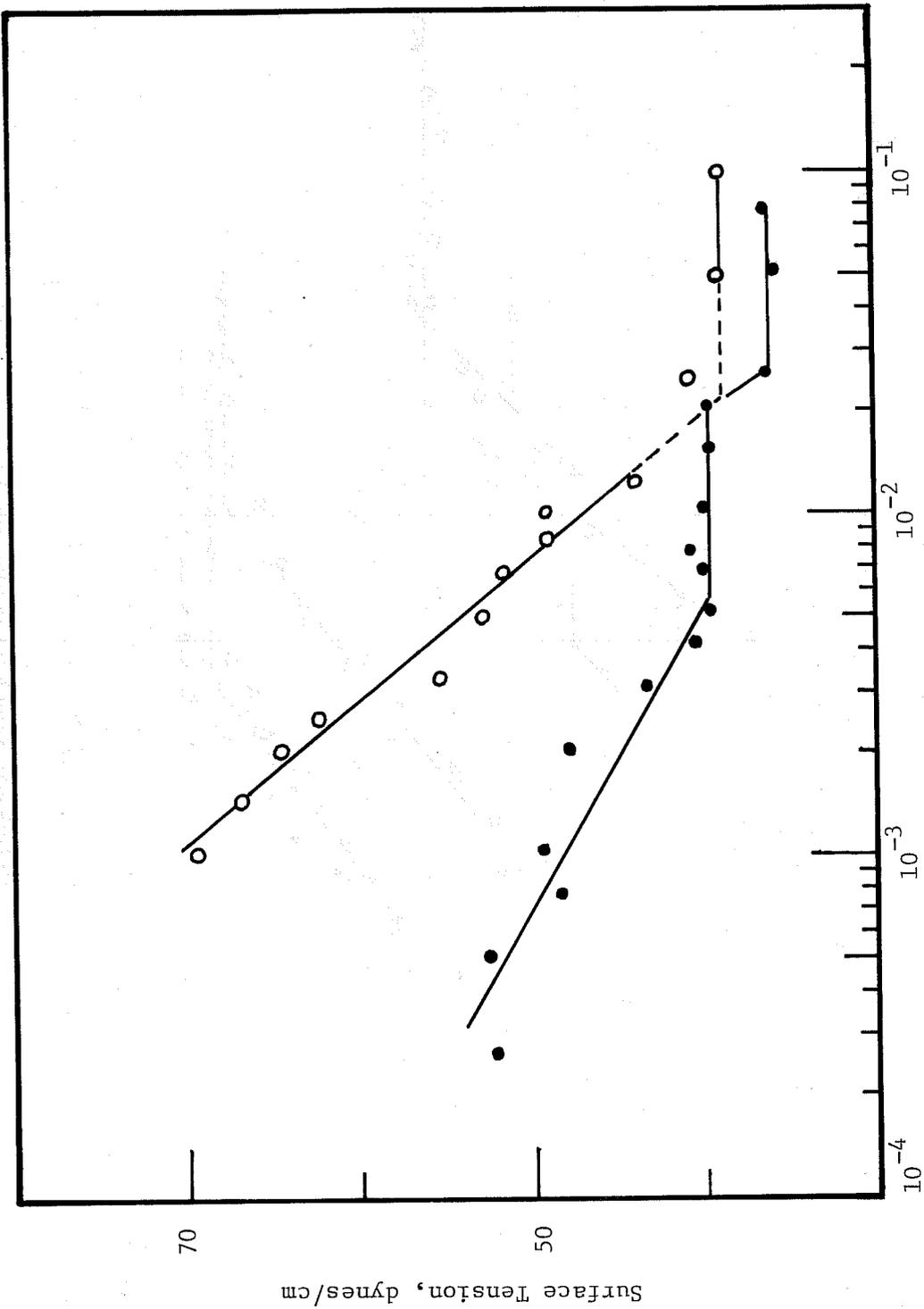


Figure IV-3. Surface Tension of SUL-FON-ATE AA10: o, in distilled water; ▲, in 1% sodium chloride; ●, after equilibration for 3 days with 0.5 vol. % of n-dodecane (Phillips, 95%) in distilled water; ■, 0.1% NaCl; Δ in 1% NaCl equilibrated with excess n-dodecane.



Surfactant Concentration, Wt. %

Figure IV-4. Surface Tension of 2-phenyl dodecane benzene sulfonate-sodium salt (CONOCO): o Distilled water; ● after equilibration for 3 days with 0.5 vol. % n-dodecane (Phillips, 95% min).

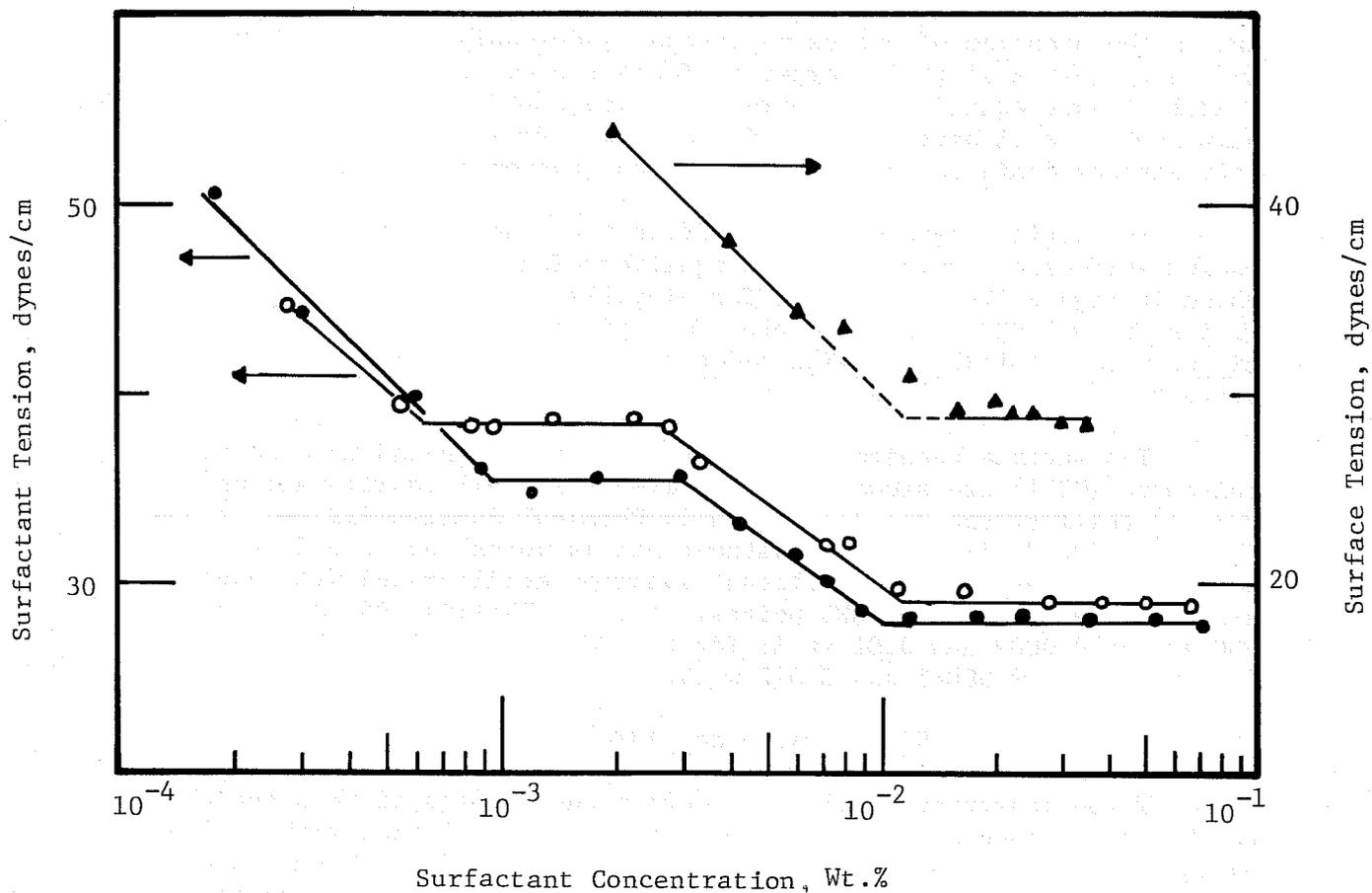


Figure IV-5. Surface Tension of $8-\phi C_{16}SO_3Na$ (UT-1)

- ▲ In Distilled Water
- Equilibrated with 0.5 vol.% of n-dodecane (Phillips 95% min.)
- Equilibrated with 0.5 vol.% of n-dodecane (Chemical Samples, 99% min.)

cline in surface tension begins, and a second CMC appears to be reached at 0.1 wt.%. It appears, therefore, that equilibration with excess oil reduces the CMC of a surfactant as reported earlier by Shah and Chan, (1) but it also appears that a second species having a CMC at or higher than the original material is present: [NOTE: electrolytic conductivity measurements completed as this report is being typed confirm that changes in electrolytic conductivity occur at each of the discontinuities in the surface tension-concentration plot.]

The surface tension-log C plot for the surfactant in 1 wt.% NaCl and in the presence of excess n-dodecane shows only one discontinuity and that is at a slightly larger surfactant concentration than for 1 wt.% NaCl without equilibration with oil, i.e., CMC (1 wt% NaCl-no oil)= 0.005 wt.%; CMC (1 wt.% NaCl - oil)= 0.008 wt.%. These curves indicate that salt effects dominate when the NaCl concentration is 1 wt.%.

The surface tension vs log C data for Conoco 2-phenyl dodecane sodium sulfonate with and without equilibration with n-dodecane are shown in Figure IV-4. The plot for distilled water is normal and yields CMC = 0.022 wt.%. The plot for this surfactant dissolved in distilled water equilibrated with n-dodecane contains a plateau and reveals two CMC's at 0.0055 wt.% and 0.025 wt.%.

The surface tension-log C data for 8-phenyl hexadecane sodium sulfonate (UT-1) are shown in Figure IV-5. Two oil equilibrations were run: 1) Phillips 95% n-dodecane and 2) Chemical Samples 99% n-dodecane. The curve for distilled water without oil is normal and yields CMC = 0.012 wt.%; the curves for the surfactant solution equilibrated with excess n-dodecane each show two CMC points. For the Phillips 95% dodecane the CMC are at 0.0009 and 0.01 wt.%; for the Chemical Samples 99% dodecane the CMC are at 0.00065 and 0.012 wt.%.

Significance for Adsorption

These measurements clearly confirm the results of Shah and Chan to the effect that equilibration of a surfactant solution with a slight excess of an oil results in a substantial reduction of the CMC. In addition, however, we observe an apparent second CMC at a surfactant concentration near the CMC in the absence of any oil. This is particularly noteworthy for the two pure monoisomeric surfactants; for SUL-FON-ATE AA10, which is a mixture, the agreement is much poorer though the two CMC are of similar magnitude.

Although the significance of the apparent second CMC is not entirely clear at the moment, it seems very likely that adsorption of surfactant will be sharply reduced when the solutions are equilibrated with a slight excess of oil as compared to adsorption from distilled water. On the other hand, it appears that salt effects dominate in NaCl solution, i.e., oil does not appear to affect the CMC in 1 wt. % NaCl. The CMC is sharply reduced by NaCl as compared to distilled water, but adsorption isotherms usually show that the addition of salt results in a substantial increase in the "apparent" adsorption. In view of recent observations on surfactant salting-out and the influence of oil on that phenomenon, it

seems likely that for NaCl concentration of one wt.% or greater, the influence of oil is principally on salting-out rather than on adsorption, especially for the higher equivalent weight surfactants. In any event, it is clear that very careful attention to the preparation of surfactant solutions and to the adsorbents is required to obtain unequivocal adsorption data.

B 2. Surfactant Adsorption

Both the rate of adsorption and the equilibrium adsorption of SUL-FON-ATE AA10 on Na-kaolin (crude Georgia kaolin which has been desanded, cation-exchanged with 1 N NaCl, and then washed free of NaCl) have been measured. However, the results are quite inconclusive and they are being checked and extended to somewhat higher surfactant concentrations. As noted in Section B 1, the CMC of this surfactant in distilled water is at 0.05 wt.% while in one wt.% NaCl the CMC is 0.005 wt.%. The adsorption data in hand suggest that adsorption of SUL-FON-ATE AA10 from distilled water onto Na-kaolin is nearly negligible (there was little or no diminution of the residual surfactant concentration for clay-surfactant contact times as long as six days). For one wt.% NaCl solutions significant adsorption was observed for contact times as short as two hours and equilibrium appeared to be reached in less than 24 hours. In any event, the low tolerance for calcium of the surfactants with which we have been working and the total absence of oil raises questions in our mind as to the possibility that enough calcium may still be dissolved from the cation-exchanged clay to cause surfactant precipitation and lead to erroneous adsorption data.

B 3. Polymer Adsorption

Polymer adsorption continues to be hampered by lack of an adequate method of polymer analysis for all of the conditions anticipated in adsorption experiments. Most of the work on this task has been concerned with evaluation of analytical procedures. These results can be summarized as follows:

- 1) Viscosity Measurements - too sensitive to pH, salt concentration, and shear degradation. Also not specific for polymer.
- 2) Turbidity of Polymer-Hyamine 1622 Solutions - investigated extensively with recording spectrophotometer. Method depends on development of turbidity by adding excess of Hyamine 1622 to polymer solution. Turbidity is a function of time, polymer concentration, amount of excess Hyamine 1622, and of salt concentration. Hyamine 1622 very sensitive to salting-out by NaCl and most of the turbidity is due to salted-out Hyamine 1622 (rather than polymer) when the NaCl concentration is one wt.% or greater.

- 3) Precipitation of Polymer With Hyamine 1622 and Measurement of Excess Hyamine - appears to be suitable for solutions which contain little or no salt. Analysis of excess Hyamine 1622 by two-phase titration using dimidium bromide and disulfine blue as indicators appears satisfactory. Salting-out of Hyamine 1622 restricts application of method to low NaCl concentrations; upper limit of NaCl not yet determined.

NOTE: Polymer precipitation by chlorox-acetic acid solutions as described by Willhite and Dominguez (2) has not been evaluated owing to potential damage to the spectrophotometer by chlorine fumes. A modification of this procedure appears to offer promise as a method of polymer analysis but the uncertainty of the nature of the reaction by which polymer is precipitated is disturbing. In any event, several modifications of the technique used by Willhite and Dominguez are being considered.

C 1. State-of-the-Art Survey of Surfactant Loss by Precipitation

This task was initiated about mid-August so very little work was done by the end of the quarter. In the time that was available several relevant papers were analyzed and potential sources of information identified. In addition recruitment of personnel was initiated.

At this point it appears that a considerable literature exists on multivalent cation precipitation, although much of it refers to detergents in dilute solutions and generally with little or no salt. The published literature on surfactant salting-out appears considerably sparser.

An information storage and retrieval system has been established to enable us to both store and retrieve relevant information. Based on past experience, it should meet the needs of the small group working on this task.

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