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

Progress Report
for Period December 1, 1975-November 30, 1976

Clarence A. Miller and Tomlinson Fort, Jr.
Department of Chemical Engineering
Carnegie-Mellon University
Pittsburgh, Pennsylvania 15213

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ABSTRACT

The objective of the research reported herein was to begin developing a basic understanding of the very low interfacial tensions between oil and water which must be achieved if tertiary oil recovery processes involving surfactants are to be successful. The basic approach has been to study the relationship between interfacial structure and interfacial tension. Observations with the polarizing microscope have shown that the lowest tensions occur when rather fluid intermediate phases of low birefringence form at the interface between the aqueous surfactant solution and the oil. To explain these observations, a theory of low interfacial tension has been developed based on consideration of phase separation in micellar solutions. Predictions of the theory are generally in agreement with experimental results.

Background and Objective

Conventional primary recovery techniques and waterflooding can recover only about half the crude oil initially present in a reservoir, even under rather favorable conditions. The nation's need for oil dictates that methods be developed to recover substantial amounts of the remaining oil. One type of enhanced recovery process which is receiving considerable attention is chemical flooding with surfactant solutions. It has been estimated that a successful process of this type could recover about 30 billion barrels of oil from existing reservoirs, about five times the total annual U.S. consumption (Geffen, 1975).

Much of the oil which remains after waterflooding is present as discrete drops or globules. Trapped by capillary forces in the small pores of the reservoir rock, these drops do not move through the reservoir when ordinary water flows past. But they will move if their interfacial tension with the surrounding fluid can be reduced to extremely low values -- about 0.001 dyne/cm or less. Such ultralow tensions are orders of magnitude less than the usual reservoir oil-water tensions of about 30 dynes/cm. Even so, they can sometimes be attained by contacting the oil with aqueous solutions of certain complex surfactant mixtures, especially mixtures of petroleum sulfonates. In many cases, a short-chain alcohol is also added as a "cosurfactant."

While the ultralow interfacial tensions necessary for oil recovery have been achieved in some cases, there is no basic understanding of why they occur for some surfactant mixtures but not for others. This lack of basic understanding leads to situations such as the following:

1. For a given crude oil a suitable surfactant mixture can be found only by empirical testing of a large number of different mixtures. Were the cause of ultralow tension understood, the type of mixture needed for each oil would be known and the number of tests could be greatly reduced.

2. The processes developed independently by the various oil companies differ in such features as the size and surfactant concentration of the slug to be injected, whether the slug should contain a cosurfactant, and even whether the slug should be an oil-continuous or a water-continuous phase. At present there is no fundamental way to determine whether one of the processes is inherently superior to the others or whether some modified process might be even better. A basic understanding of why ultralow tensions occur would shed some light on these matters.

3. Process effectiveness requires not only that ultralow tensions be achieved near the injection well where the surfactant slug initially contacts trapped oil globules, but also that such tensions be maintained as the slug advances through the reservoir. But slug composition changes with time due to adsorption of surfactant on the pore surfaces, mixing with reservoir fluids, etc. Without knowledge of the cause of ultralow tensions, no way exists to predict which surfactant mixtures can best maintain low tension in spite of adsorption and mixing in the reservoir.

In view of the above considerations, the present research program was initiated to develop an improved understanding of ultralow interfacial tensions and related aspects of the surfactant processes for tertiary recovery. Work began with ERDA support on December 1, 1974. This report describes progress during the period December 1, 1975, through August 31, 1976.

Observations of Surfactant Solutions and Interfacial Structure

Our early observations with the polarizing microscope showed that when an aqueous surfactant solution of the type proposed for tertiary recovery contacts oil, the interface is not simply a surface where oil and water meet with a monomolecular layer of surfactant between them, the conventional picture of surface chemistry. Instead, one or more intermediate phases form between the oil and water, often assuming curious and fascinating forms. Thus, the "interfaces" of interest for oil recovery are special not only because they have ultralow tensions, but also because they have a macroscopic structure consisting of intermediate phases. The major portion of our effort has been directed toward investigating the relationship between macroscopic structure and interfacial tension.

Information on structure has been obtained with the polarizing microscope both for interfaces and for the surfactant solutions themselves. An experimental technique employing rectangular capillary cells has been developed especially for this work (see Figure 1a). For observation of a surfactant solution alone, the solution is allowed to fill the cell by capillary action, then the ends of the cell are sealed with paraffin wax. This technique represents an improvement over the usual one employing a microscope slide and a coverslip not only because structure changes due to evaporation are precluded, but also because the greater fluid thickness facilitates detection and observation of the rather weak birefringence often exhibited by the solutions. In fact, weak birefringence was detected by the present technique but not by the usual technique in several cases. The rectangular cells, obtained from Vitro-Dynamics, Inc., are available in several thicknesses. Most of our work has been with cells 0.2 mm thick.

For observation of an interface between oil and a surfactant solution, the latter is allowed to fill about half the cell by capillary action, and the end of the cell adjacent to the liquid is sealed. Then enough oil is injected with a hypodermic needle to fill the rest of the cell and the other end is sealed. When the cell is placed in a horizontal position for observation, the interface assumes an S-shaped configuration as shown in Figure 1b with the oil occupying much of the upper part of the cell. The actual interfacial shape reflects a balance between gravitational and capillary effects, so that the S-curve is more pronounced, i.e., the oil occupies more of the upper part of the cell, in cases where interfacial tension is lowest. Thus, with the present technique interfacial tension can be estimated to an order of magnitude at the same time as observations of interfacial structures are made. Actual measurements of interfacial tension are made with the pendant drop and the spinning drop techniques. The spinning drop device has been built during the current period of support.

Numerous observations of structure in petroleum sulfonate solutions have been made using the microscopic technique just described. The solutions contained various surfactants and cosurfactants. Surfactant concentrations were between 1% and 8% by volume, which covers the range of surfactant concentrations which have been proposed for injection. Both salinity and cosurfactant concentration varied as well. The solutions were turbid in appearance and, in almost all cases, exhibited some weak birefringence. Sometimes the solution appeared uniformly birefringent; in other cases a dispersion of small particles or drops of one phase in another could be seen. In the latter situation sometimes only one of the phases was birefringent, sometimes both were birefringent.

Plate 1 shows structures seen in solutions which contain a petroleum sulfonate made by Stepan, isopropyl alcohol, and salt. In Plate 1a, at 1% salt, drops or particles of a lamellar liquid crystal are dispersed in another weakly birefringent phase. In Plate 1b, at 2% salt, only a single phase is seen, and it is birefringent. The texture is similar to that seen in nematic liquid crystals formed by some organic compounds (Hartshorne, 1974), but the structure in this solution is not presently known. In general, the textures observed in these studies were suggestive of a lamellar structure or some variant thereof.

From the above observations it seems fair to conclude that some liquid crystalline material is present in most petroleum sulfonate solutions in the concentration ranges being considered for tertiary recovery. This point is significant because it indicates the futility of trying to avoid liquid crystals altogether in tertiary recovery processes. Instead, it is necessary to develop enough information about when the various types of liquid crystalline phases form to avoid the highly viscous types of liquid crystals which may cause undesirable plugging of the reservoir. At the same time efforts should be made to use the existence of liquid crystals to control the viscosity of the surfactant solutions and to facilitate the achievement of ultralow interfacial tensions between the solutions and oil.

Observations were also made with the polarizing microscope of behavior exhibited by various petroleum sulfonate solutions when contacted by oil. In some experiments the oil was a pure hydrocarbon such as n-hexadecane; in other cases a crude oil was used. In all cases at least one intermediate phase developed between the oil and the aqueous surfactant solution. When the interfacial tension was relatively high -- around 0.1 dyne/cm -- some of the intermediate phases were highly birefringent and had textures characteristic of lamellar liquid crystals. On the oil side of the interface the liquid crystal appeared as individual drops or particles (Plate 2b), while on the aqueous side it appeared as filaments which grew toward the bulk of the surfactant solution (Plate 2a).

In contrast, when interfacial tensions were very low -- between 10^{-4} and 10^{-3} dyne/cm -- the intermediate phases were much less birefringent than in the higher tension situations. They were also more fluid as shown by the ease of deformation and coalescence of the drops of a new phase which were ejected into the oil (Plate 3). Of particular interest is that the drops were not formed uniformly over the entire area of contact but at specific locations where dark lines or curves appeared at the interface and, in some cases, extending some distance toward the aqueous phase (Plates 3 and 4). These lines or curves are apparently defects in an intermediate phase which has some structure even though it is but weakly birefringent. The formation of drops of an intermediate phase at the defect sites suggests that the defects promote enhanced transport of various species between the aqueous and oil phases. Similar defects which are somewhat analogous to dislocations in crystalline phases have been observed previously in certain types of liquid crystalline phases (Kleman, 1975).

From these observations it appears that ultralow interfacial tensions are associated with the presence of intermediate phases which are rather fluid and weakly birefringent but which do have some structure. That the intermediate phases are structured to some extent and that at least certain features of the structure can be detected by optical microscopy give hope that continuing work will be able to clarify how the structure is related to ultralow tensions.

Experiments with Well Defined Surfactants

Most of our experiments to date have used petroleum sulfonates as surfactants, both because they are currently the prime candidates for use in tertiary recovery processes and because particular combinations of surfactant and oil compositions which would produce ultralow tensions were known. Since the composition of conventional petroleum sulfonates is not well defined and even the synthetic sulfonates are mixtures of several components, it is desirable in developing an understanding of ultralow tensions to perform some experiments with a minimum number of well characterized materials.

Part of our program has been to conduct experiments with the system water, n-hexadecane, sodium dodecyl sulfate, and various pure alcohols. Figure 2 shows the results of experiments in which aqueous solutions of sodium dodecyl sulfate were contacted with n-hexadecane containing some n-dodecanol. The interfacial tensions were measured shortly after contact using the pendant drop technique. The break in the two lowest curves at 1.6 volume percent dodecanol indicates that the interfacial tensions at this composition were too low to be measured with the pendant drop, i.e., they were less than about 0.008 dyne/cm. Of importance here are that (a) ultralow tensions were achieved with this system though they were probably of a transient nature, (b) the ultralow tensions were associated with the presence of an intermediate phase as indicated by a texture observable at the surface of the pendant drop, and (c) the intermediate phase formed even though the surfactant concentration in the aqueous phase was only a factor of three or four above the critical micelle concentration. This last point is significant because while the work described in the preceding section and that of Healy et al (1976) have demonstrated that ultralow tensions are associated with the presence of intermediate phases in systems where the surfactant concentration is relatively high (at least 1%), it is not clear whether the same is true for lower surfactant concentrations. The present work shows that, in at least some cases, intermediate phases are, in fact, associated with ultralow tensions in dilute systems.

Preliminary observations with the polarizing microscope indicate that the intermediate phase in this system associated with the very low tensions is rather fluid and only weakly birefringent, as was found in the petroleum sulfonate systems.

It should be mentioned that the existence of intermediate phases whenever ultralow tensions occurred in these systems has prevented us from applying radioactive tracer techniques to determine interfacial composition, as we had originally proposed. The radioactive tracer method is suitable for an oil-water interface with a monolayer of surfactant, but it is not suitable for thick interfacial regions of the type we have encountered. If subsequent work shows that ultralow tensions can also occur under conditions when there is a monolayer, the use of radioactive tracers will be reconsidered.

Some other aspects of this work are noteworthy. One is that intermediate phases did not always form in these dilute systems. They were not seen at all when the alcohol used was hexanol. For dodecanol they formed only when (a) initial surfactant concentration in the aqueous phase exceeded the critical micelle concentration and (b) initial alcohol content of the oil phase was sufficiently large (see Figure 2). Their occurrence seemed rather sensitive to temperature variations as well, although this matter has not yet been thoroughly explored.

Theory of Low Interfacial Tensions

Our observation that rather fluid intermediate phases are associated with ultralow interfacial tensions seems consistent with the work of others, e.g., that of Healy et al (1976). Recently we have developed a simple theory which indicates that low interfacial tensions do exist between phases formed as a result of phase separation in micellar solutions.

Consider, for example, what happens in an aqueous micellar solution of an ionic surfactant as salinity increases with temperature, micelle size, and the number of micelles per unit volume held constant. The increased concentration of ions in solution reduces the thickness of the "electrical double layer" region around each micelle in which the micelle's surface charge can induce an electric field. The result is a decreased electrical repulsion between micelles. If the micelles have solubilized enough oil to be sufficiently large -- greater than about 100 Å in diameter, according to our calculations -- a salt concentration is eventually reached where attraction between micelles due to London-van der Waals forces outweighs the electrical repulsion and the random thermal motion of the micelles and produces a phase separation. Our calculations, which are described in detail in the attached manuscript, show that interfacial tension between the micelle-rich and micelle-lean phases so formed is very low, even when the system is far from any type of consolute point.

The reason that low tensions occur in such situations can be understood by recalling that interfacial tension is basically the excess free energy per unit area of an interfacial region having a finite thickness. Thus, interfacial tension depends strongly on the free energy per unit volume in the interfacial region, which, in turn, is an increasing function of the total interaction energy among all the micelles in the unit volume. The larger the micelles, the fewer of them can be accommodated in a unit volume, and the lower the total interaction energy and free energy per unit volume. Thus, interfacial tensions should be much lower when phase separation occurs in solutions containing micelles a few hundred Angstrom units in diameter than when it occurs in an ordinary binary mixture of molecules a few Angstrom units in diameter. This expectation is confirmed by calculations described in the attached manuscript, which adapt to the present case of micellar solutions, a theory developed by Cahn and Hilliard (1958) for calculating interfacial tension in ordinary binary mixtures of small molecules.

We have compared predictions of our model with the data of Healy et al (1976) for a system whose predominant surfactant was the monoethananolamine salt of dodecylorthoxylene sulfonic acid. While our very simple model is not intended to provide precise quantitative predictions of interfacial tension, its success in predicting the salinity at initial phase separation as well as the order of magnitude and variation with salinity of interfacial tension strongly suggests that the proposed mechanism of low interfacial tensions is correct, at least in systems such as this one where low tensions are associated with formation of an intermediate phase.

The reader is referred to the attached manuscript for details. We emphasize here, however, that ours is the first reasonable mechanism for ultralow tensions to be proposed and that it provides a qualitative framework for thinking about low tensions which should prove valuable in further research on tertiary oil recovery.

Summary

Observations with the polarizing microscope have shown that many petroleum sulfonate solutions of the type proposed for tertiary oil recovery contain some liquid crystalline material. When these solutions contact oil, intermediate phases are formed. For the lowest values of interfacial tension these intermediate phases are quite fluid and only weakly birefringent. Intermediate phases are also associated with low tensions in a system containing well defined surfactants, even for surfactant concentrations only three or four times greater than the critical micelle concentration.

A theory has been developed showing that low interfacial tensions can arise as a result of phase separation in micellar solutions. While it is a simple theory which cannot as yet explain all aspects of the experimental observations, its predictions are in general agreement with the data of Healy et al (1976) for a system containing a synthetic sulfonate surfactant.

Thus, progress has been made in both experimental and theoretical aspects of clarifying the relationship between interfacial structure and interfacial tension, the chief objective of this research program.

References

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Hartshorne, N.H. 1974. "Optical Properties of Liquid Crystals," pp 24ff in Liquid Crystals and Plastic Crystals, Vol. 2, G.W. Gray and P.A. Winsor (ed.), Chichester, Ellis Horwood, Ltd.

Healy, R.N., Reed, R.L., and Stenmark, D.G. 1976. Soc. Pet. Eng. J., 16, 147.

Kleman, M. 1975. "Defects in Liquid Crystals," pp 267ff in Advances in Liquid Crystals, Vol. 1, G. Brown (ed.), New York, Academic Press.

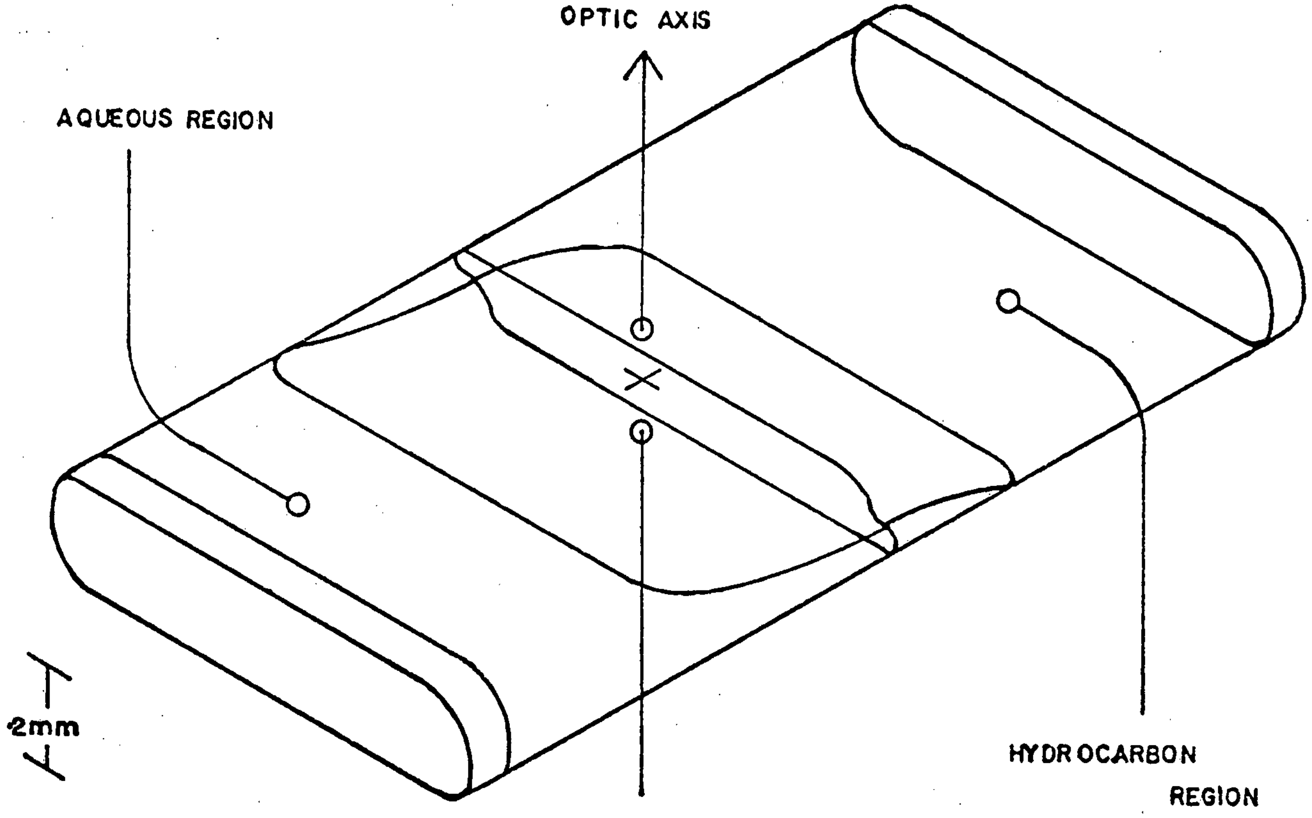
Captions for Figures

Figure 1. Rectangular capillary cell used for microscope observations.

a. Overall view of cell and the fluids within it during a contacting experiment (top).

b. Side view showing S-curve formed by the interface (bottom).

Figure 2. Interfacial tensions measured when aqueous solutions of pure sodium dodecyl sulfate contact solutions of n-dodecanol in n-hexadecane. The dark points are those where an intermediate phase formed, as indicated by texture at the interface of the pendant drop.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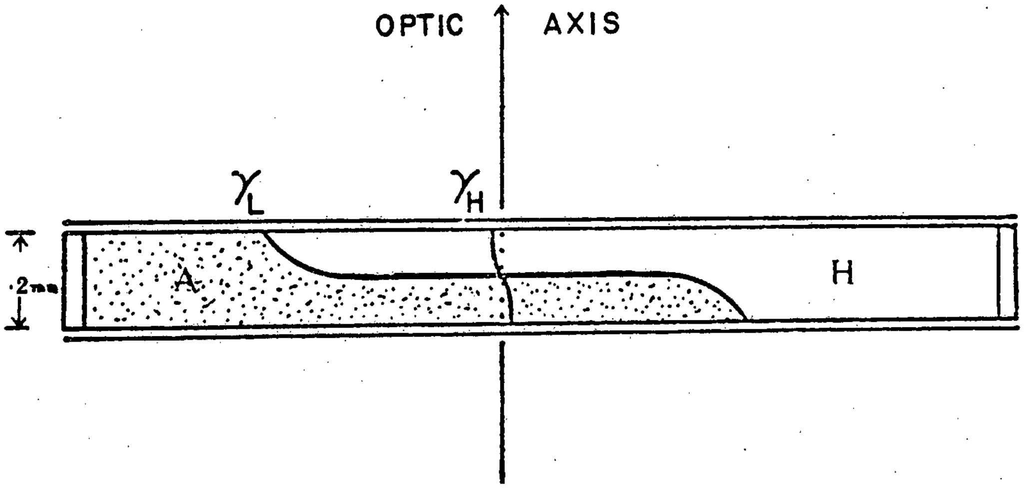
HYDROCARBON REGION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γ_L
γ_H
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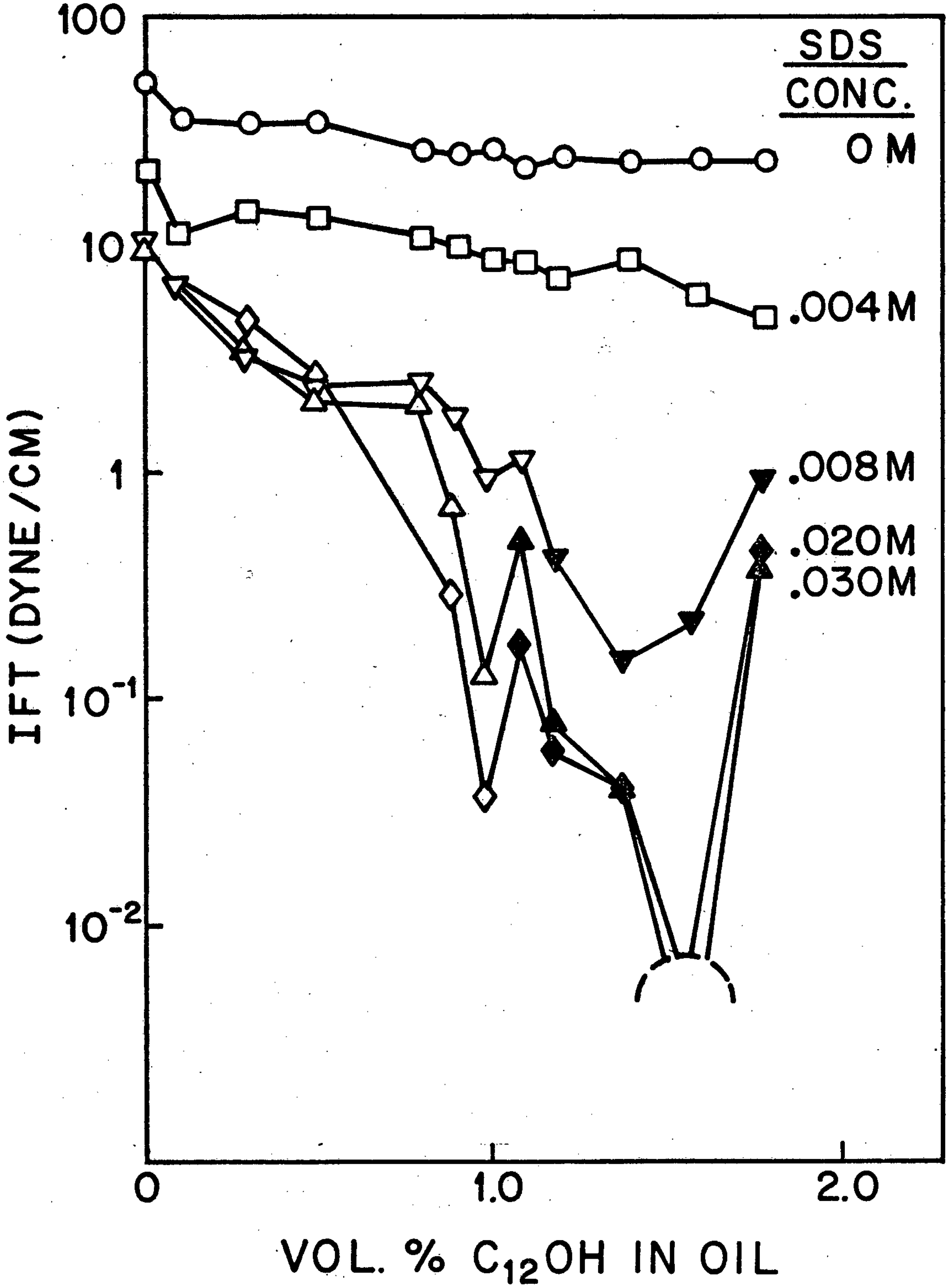
A
H

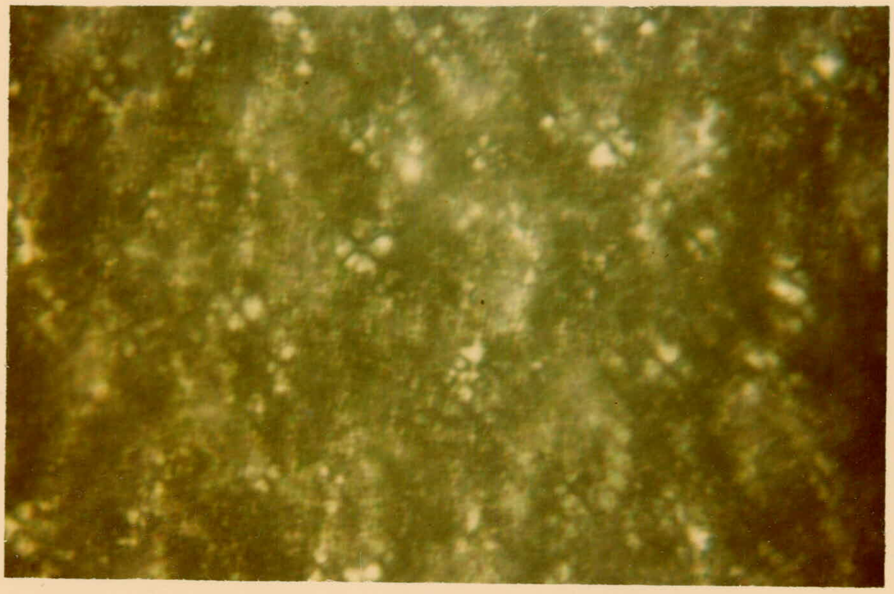


SDS
CONC.
0 M
.004 M
.008 M
.020 M
.030 M
100
10
1
10^{-1}
10^{-2}
IFT (DYNE/CM)
0
1.0
2.0
VOL. % $C_{12}OH$ IN OIL

<u>Plate 1</u>

<u>a</u>. Two-phase structure seen in aqueous solution containing 8% of a Stepan petroleum sulfonate, 0.8% isopropyl alcohol, and 1% NaCl. Crossed polarizers, magnification 130 X.

<u>b</u>. Single phase structure seen in aqueous solution with the same surfactant and alcohol concentrations but with 2% NaCl. Crossed polarizers, magnification 130 X.



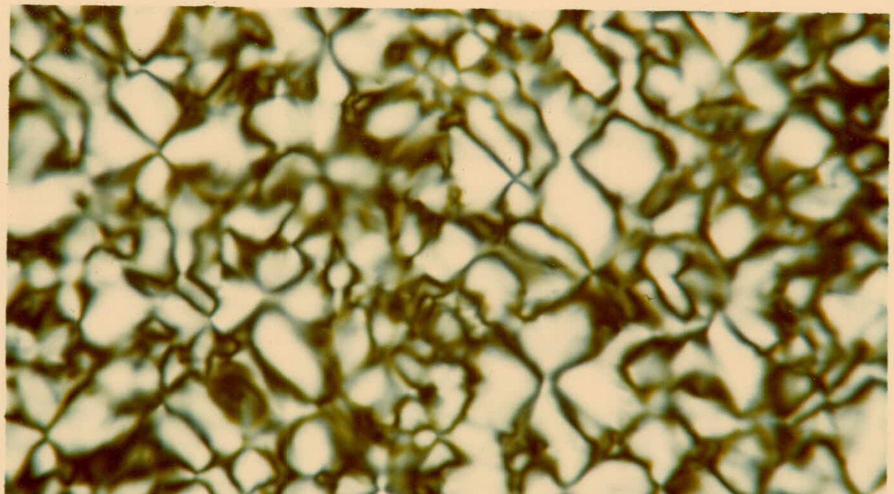
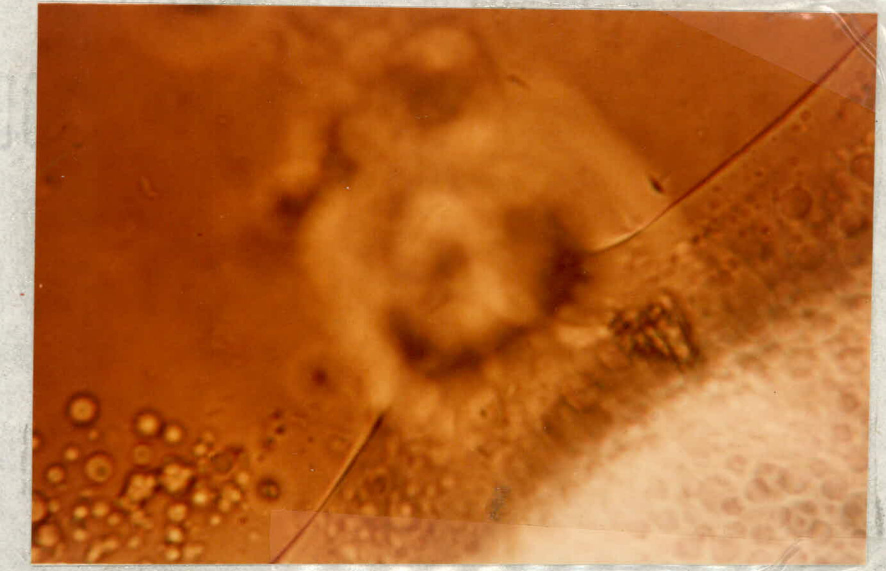


Plate 2

a. Liquid crystalline material growing toward aqueous phase following contact of petroleum sulfonate solution with n-hexadecane. The surfactant solution contained 8% Exxon FA-400 sulfonate and 0.8% butanol in 3% NaCl brine. Crossed polarizers, magnification 100 X, 18 hours after initial contact. Note filaments of birefringent material. Interfacial tension in this system is about 0.4 dyne/cm.

b. Liquid crystalline particles forming on oil side of interface in the same system. Crossed polarizers, magnification 100 X.



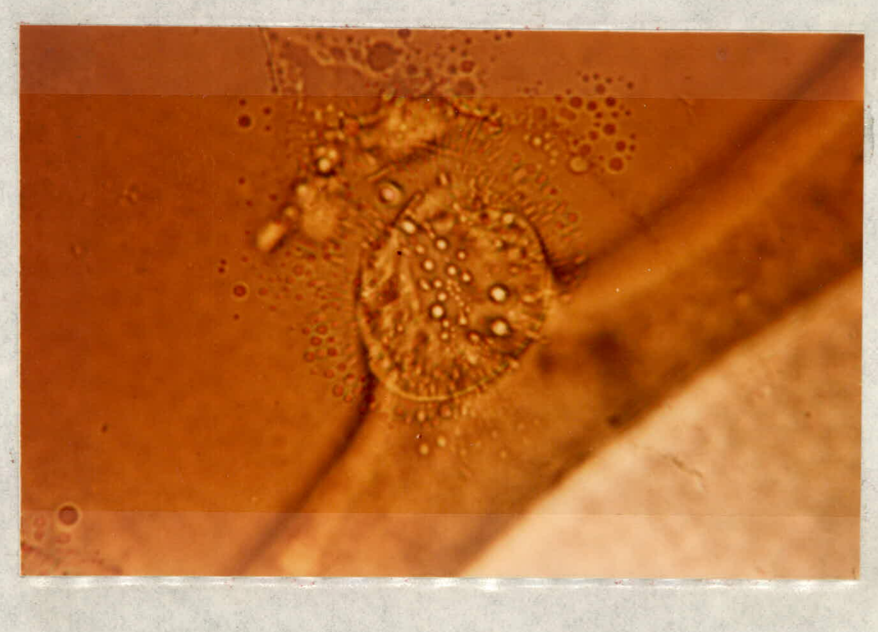


Plate 3

Drops of rather fluid intermediate phase formed after contact of an aqueous solution containing 8% of an Amoco sulfonate, 2.4% butyl alcohol and 1% NaCl, with Glenn Pool crude oil. Crossed polarizers + quarter wave plate, magnification 200 X, 30 minutes after initial contact. The dark lines are the defects discussed in the text. Interfacial tension is about 6×10^{-4} dyne/cm.

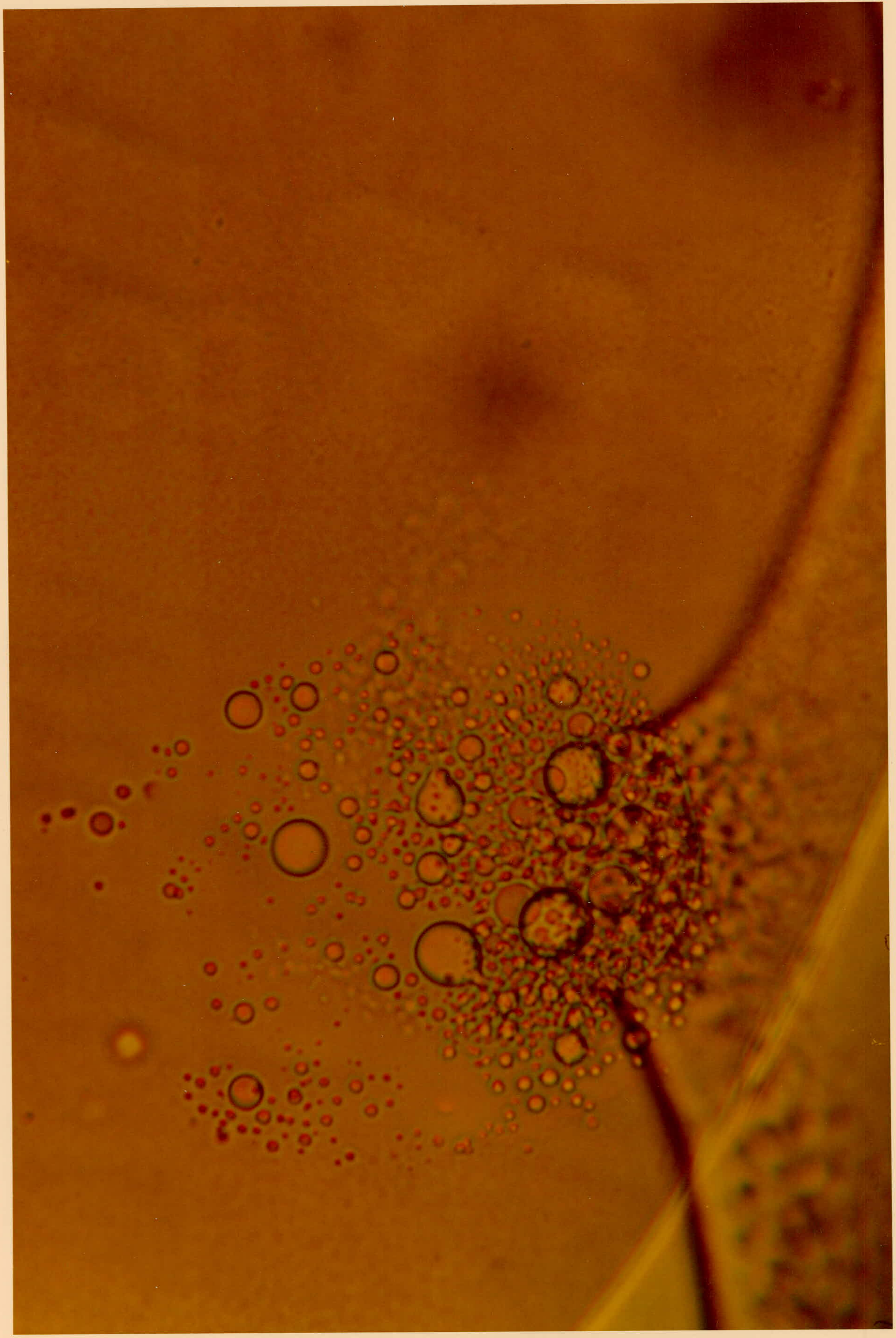


Plate 4

Interfacial behavior seen after contact of Glenn Pool crude oil with an aqueous solution containing 8% of an Amoco sulfonate, 2.4% butyl alcohol, and 1% NaCl. Crossed polarizers + quarter wave plate, magnification 200 X, 40 minutes after initial contact.

a. Focused in aqueous phase showing defects clearly.

b. Focused on drops of intermediate phase rising into the oil.