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MICELLAR SOLUTIONS FOR IMPROVED OIL RECOVERY

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Micellar solutions of various surfactants have been employed as injection fluids to improve oil recovery during the tertiary oil recovery process. These solutions produce ultra low interfacial tensions (10^{-2} to 10^{-4} dynes/cm) at the oil/micellar solution interface.

Petroleum sulfonates have been used as surfactants in improved oil recovery studies. Various physico-chemical techniques, such as electrical conductivity, light-scattering, surface tension, viscometry, and high resolution NMR have been employed to elucidate the structure of such micellar solutions. It was observed that the minimum in interfacial tension and the maximum in electrophoretic mobility of oil droplets occur at the same surfactant concentration. The micellar size increased with an increase in salt concentration. The association between surfactant and polymer molecules strikingly alters the rheology and interfacial properties of micellar solutions. Several aspects of the micellar solutions, such as adsorption, the influence of electrolytes and cosolvents, phase equilibrium with oil and brine, rheology, and polymer-surfactant interaction have been discussed.

INTRODUCTION

The recovery of oil from a reservoir can be divided into three stages. In the primary oil recovery process, oil is recovered due to the pressure of natural gases which force the oil out through production wells. When this pressure is reduced to a point where it is no longer capable of pushing the oil out, water is injected to build up the necessary pressure to force the oil out. This is generally called the secondary oil recovery or water flooding process. The average oil recovery during the primary and secondary stages is about 30% of oil-in-place. The purpose of the tertiary oil recovery process is to recover at least part of the remaining 70% oil-in-place. Various techniques proposed for this stage are carbon dioxide injection, steam flooding, or surfactant flooding by either micellar or microemulsion solutions. The use of surfactants for improved oil recovery is not a recent development in Petroleum technology. In 1930 De Groot^{1,2} filed a patent describing the use of water-soluble surfactants as an aid to improve oil recovery. In 1958, Holbrook³ filed for a patent which the use of surfactant (organic perfluoro compounds, fatty acids, soaps, poly-glycol ethers, salts of sulfonic acids) dissolved in water was proposed as an aid to improve the oil recovery process. The other patents issued to Holm and Bernard⁴, Gogarty and Olson⁵ and Jones^{6,7} essentially described the use of high concentration of surfactant in the form of microemulsion for improved oil recovery.

The process of using surfactants for improved oil recovery can be divided into two groups. In the first, a solution containing a low concentration of a surfactant in the form of micellar solution is injected. In the second, the surfactant concentration is relatively high and the injected slug is formulated with three or more components and is known as microemulsion. The basic components of the microemulsion are hydrocarbon, surfactant, water, alcohol and salt. In the second process a relatively small pore volume (about 3 to 20%) as compared to the first (15-60%) is injected. This paper deals basically with the first process i.e., using a low concentration of a surfactant in the form of micellar solution as an aid to improve oil recovery.

The micellar solution flooding process is an immiscible-type displacement process. Two basic well configurations- the "five spot" pattern or the "line drive" pattern are used for the micellar flooding process. In the "five spot" pattern (Figure 1) four production wells are drilled at the corners of a square, and the injection well through which micellar solution is pumped, is at the

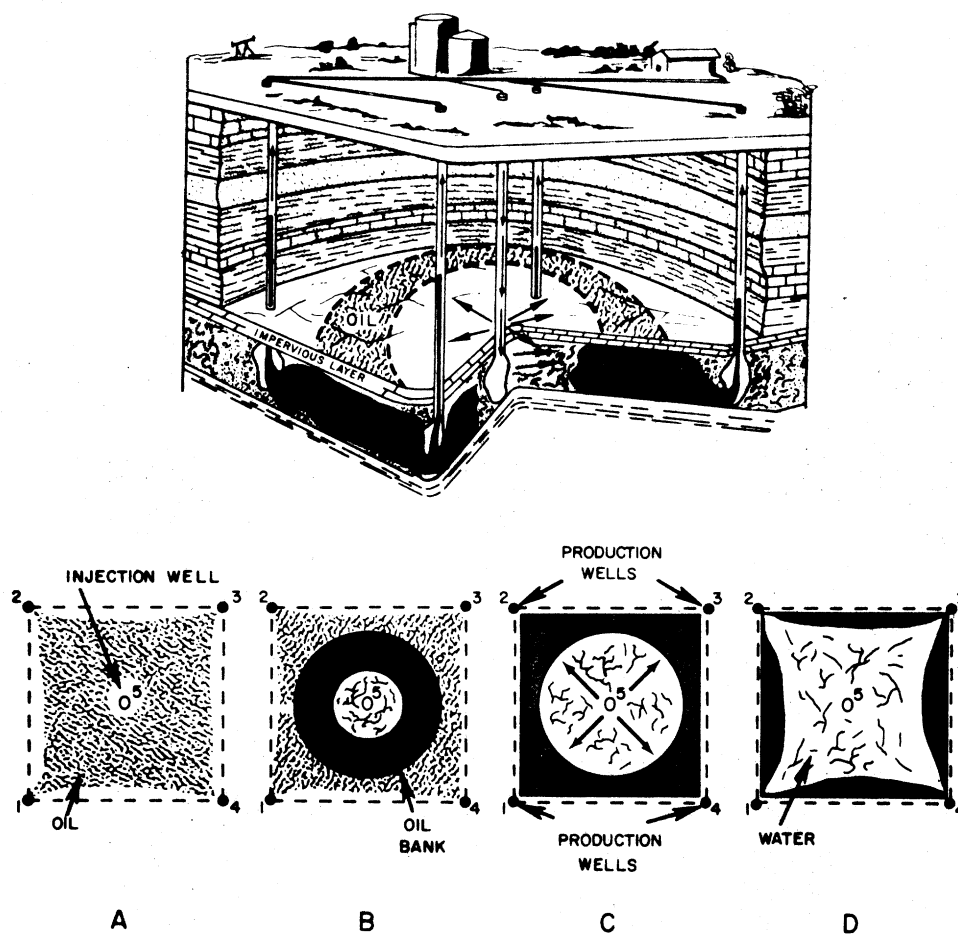


Figure 1. Five spot pattern for displacement of oil.

center of this square. In the "line drive" pattern, production and injection wells are drilled in alternate rows. In both cases, the injected micellar solution tends to displace the oil towards the producing wells. Although considerable work has been done on the oil recovery process under both laboratory and field conditions, our basic understanding of the process and mechanism of oil displacement is far from clear.

MOLECULAR AGGREGATES IN SURFACTANT SOLUTIONS

When a surfactant is dissolved in water, it tends to adsorb at the gas-liquid interface. The adsorption of surfactant at the interface results in a greater concentration at the interface as compared to that in bulk solution. Above a critical concentration depending upon the structure of surfactant molecules as well as physicochemical conditions, the surfactant molecules form aggregates called micelles (Figure 2). This characteristic concentration is called

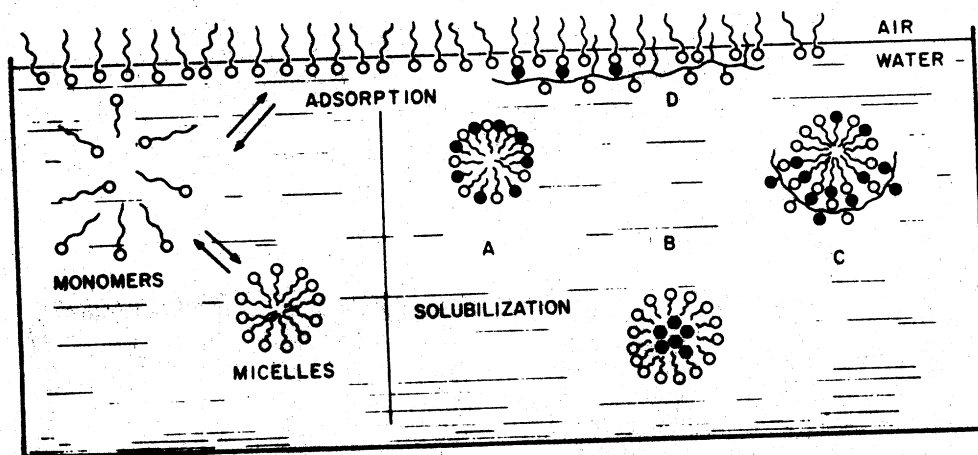


Figure 2. Adsorption, micelle formation, solubilization and interaction at the micelle surface.

the critical micelle concentration (CMC). Micelles are spherical aggregates of surfactant-molecules containing 20 to 100 molecules. The formation of micelles in aqueous solution creates local nonpolar environments within the aqueous phase. Any oil soluble materials such as dyes, pigments or nonpolar oils can dissolve within the micelles (Figure 2B). Using ionic and nonionic surfactants, one can produce mixed micelles which are often larger in size and in the number of molecules within a micelle (Figure 2A). If a surfactant solution contains a surface active polymer, then a mixed adsorbed film of polymer and surfactant occurs at the interface. The polymer surfactant interaction can also occur at the micellar surface (Figure 2C and 2D). The solubilization of oil within micelles can also occur when such micellar solutions are injected into the oil fields.

Surfactant molecules can be considered as building blocks. One can make various types of structures of surfactant molecules by simply increasing the concentration of surfactant in water. Figure 3 schematically shows various structures that are formed in the sur-

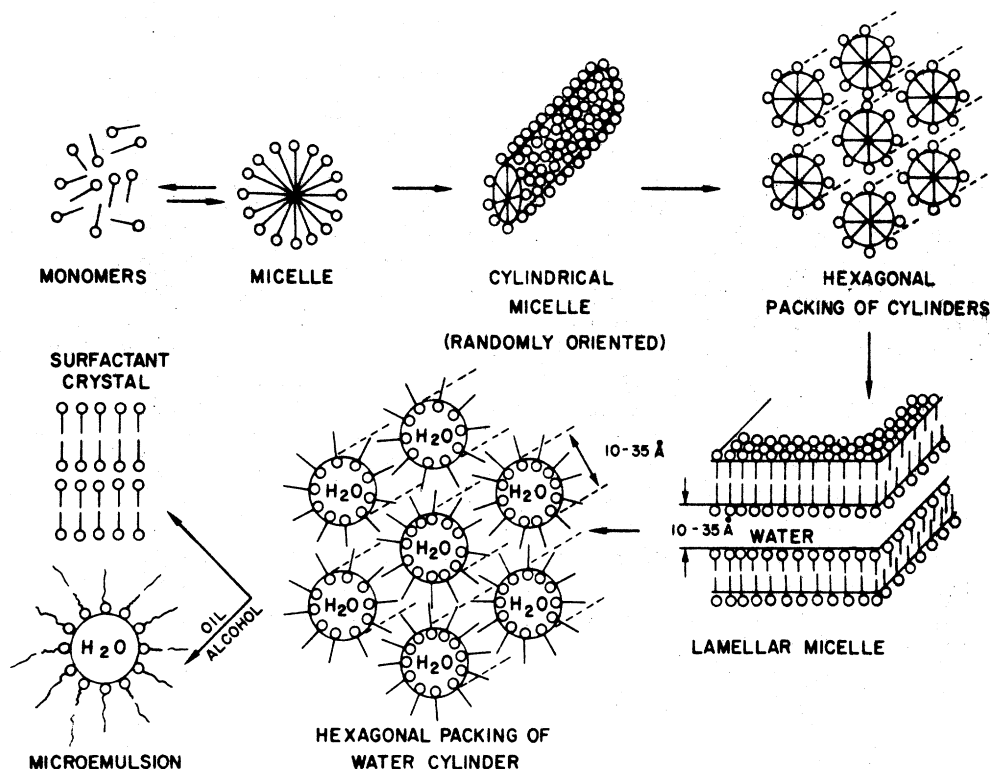


Figure 3. Structure formation in surfactant solution.

factant solution upon increasing the concentration of surfactant. The spherical micelles become cylindrical ones. Upon further increasing the concentration, there is a hexagonal packing of surfactant cylinders. If the concentration is still increased the lamellar structures are formed. Upon further addition of surfactant, the lamellar structures are converted to a hexagonal packing of water cylinders. Upon addition of oil and a short-chain alcohol, one can convert such water cylinders into water-in-oil microemulsions. It is possible to induce a transition from one structure to another by changing the physicochemical conditions such as temperature, pH, addition of mono- or divalent cations in the surfactant solution. It should be emphasized that the scheme shown in Figure 3 is a general scheme and a surfactant may skip several phases depending upon its structure and the physicochemical conditions. The flow behavior of surfactant formulations containing such structures through porous media is not explored in detail and a careful study on the effect of such structure on the oil displacement efficiency is desirable.

THE ROLE OF VARIOUS INTERFACIAL PARAMETERS IN A CONCEPTUAL OIL DISPLACEMENT MECHANISM

As we visualize, four interfacial parameters are responsible for enhanced oil recovery by micellar flooding. These parameters are: (1) interfacial tension, (2) interfacial viscosity, (3) interfacial charge, (4) contact angle. It has been established⁸⁻¹⁰ that for the success of a tertiary oil recovery process interfacial tension should be in the order of 10^{-3} dynes/cm. Foster¹¹ explained on the basis of capillary number (N_{ca}) that interfacial tension should be reduced 10,000 times to recover a larger amount of oil. Such low interfacial tensions reduce the work of deformation necessary for oil droplets to emerge from the narrow neck of pores (Figure 4). It is then necessary for these displaced oil droplets usually referred to as oil ganglia, to coalesce and thereby form an oil bank (Figure 5). For this coalescence to occur, a very low interfacial viscosity is desirable. The moving bank coalesces with more oil ganglia (Figure 6) and causes further displacement of residual oil toward the producing wells. For a hydrodynamically stable system (for mobility control) it is necessary that the micellar solution be followed by a mobility control polymer solution (Figure 7).

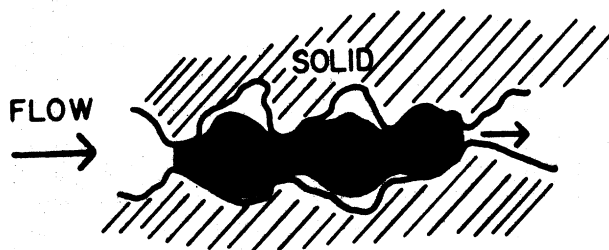


Figure 4. Movement of oil ganglia through a narrow neck of pores; a very low interfacial tension is desirable.

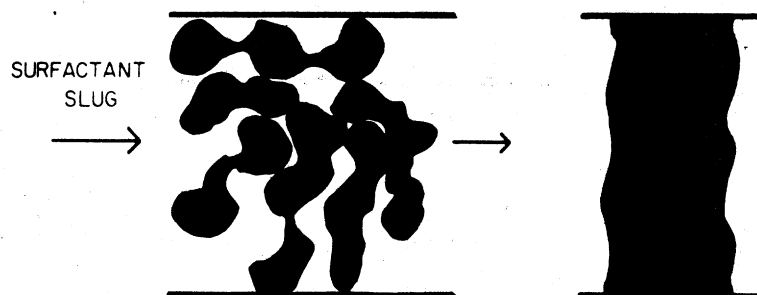


Figure 5. Formation of continuous oil bank through coalescence of displaced oil ganglia: For this a very low interfacial viscosity is desirable.

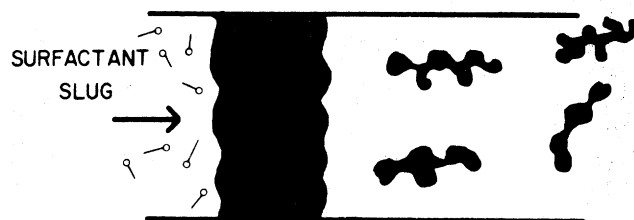


Figure 6. Coalescence of oil ganglia with oil bank.

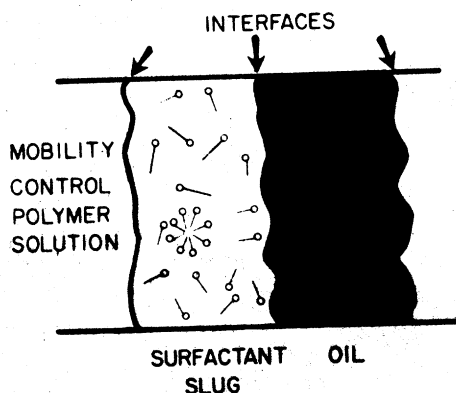


Figure 7. Formation of three interfaces in porous media during tertiary oil recovery by surfactant and polymer flooding.

The relationship between interfacial charge and interfacial tension has been established²² for the brine/oil system and it has been found that the electrophoretic mobility and interfacial tension curves are inverse images of each other. The importance of interfacial charge at crude oil/aqueous phase system suggests that the nature and magnitude of the charges on solid surfaces are also important variables in determining the efficiency of the oil displacement process. Wagner and Leach¹² and Leach *et al.*¹³ suggested that reversing wettability of a porous material (from oil-wet to water-wet) during a water flood will result in an increase in oil recovery. With a proper choice of surfactant, one can selectively alter the contact angle (wettability) of oil on solid surfaces (Figure 8) thus creating more favorable conditions for oil displacement. Melrose and Brandner⁸ and Morrow¹⁴ concluded that for optimal recovery of residual oil by a low interfacial tension flood the rock structure should be water wet. Slatery and Oh¹⁵ suggested that for the most efficient displacement of residual oil, the porous structure should be water-wet. Intermediate wettability may be less desirable than either oil wet or water-wet behavior.

The success of the above approach for improved oil recovery will depend on the proper choice of chemicals in formulating the optimum micellar slug. The composition of the micellar slug is dependent upon the properties of the micellar solution itself (e.g. viscosity, salt tolerance, temperature stability, etc.) as well as on the conditions prevalent in the reservoir.

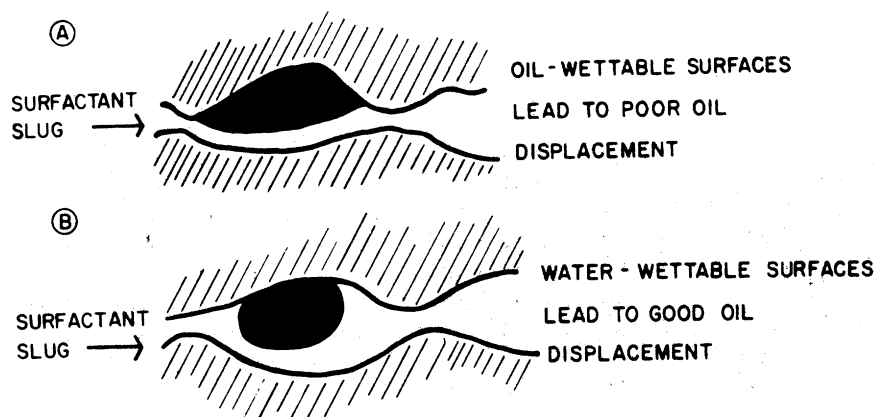


Figure 8. Effect of wettability on oil displacement.

INTERFACIAL PROPERTIES OF MICELLAR SOLUTIONS

It has been established¹¹ that for the success of a tertiary oil recovery process the capillary number (ratio of viscous to interfacial forces) should be in the region of 10^{-2} . During an ordinary water flooding process, the capillary number is of the order 10^{-6} and the residual oil at this capillary number is about 50% pore volume. To recover a larger amount of oil, i.e., to minimize the residual oil to near zero, requires a capillary number of four orders of magnitude larger than this. In practice, this can be accomplished only by reducing the interfacial tension at the oil/brine interface which has values of the order of 10 dynes/cm. Reducing this interfacial tension to a value of 10^{-3} dynes/cm will produce a capillary number in the desired range. Recently, studies have been conducted on aqueous solutions of petroleum sulfonate that demonstrate that such low tensions can be obtained with the use of relatively small concentrations of surfactants^{11,16,17,18}.

It has been shown¹⁹ that a petroleum sulfonate with an equivalent weight distribution that is relatively narrow and/or symmetrical about the median is the most effective in lowering interfacial tension. A minimum in interfacial tension can also be obtained through an adjustment of the electrolyte content of the aqueous phase. Sodium chloride was shown to be more effective than sodium sulfate, carbonate or tripolyphosphate in increasing the interfacial

activity of a petroleum sulfonate. It was pointed out that the production of low interfacial tensions for different types of oils might require different optimum electrolyte concentrations and a different equivalent weight of petroleum sulfonates.

Much of the work done on interfacial tension does not have a systematic approach for evaluating the effect of different variables on the interfacial tension at a micellar solution-oil interface. Recently, however, a systematic study has been performed^{20,21} to evaluate the effects of several variables on the interfacial tensions of a homologous series of hydrocarbons. The variables examined were: (1) salt concentration, (2) surfactant concentration, (3) average equivalent weight of petroleum sulfonate, (4) surfactant concentration and (5) aging.

It has been found^{20,21} that, for a given concentration of salt and surfactant, there is a definite affinity for a particular hydrocarbon and a pronounced minimum in interfacial tension at a particular value of R (number of carbon atoms in the oil). In some cases the interfacial tension of the two adjacent alkanes is one or two orders of magnitude larger than the minimum value. The preferred value of R varies inversely with the surfactant concentration and directly with the salt concentration. It has also been established²¹ that production of a low interfacial tension requires an optimal electrolyte concentration for a given surfactant concentration, and an optimal surfactant concentration for a given electrolyte concentration. At a given salinity and surfactant concentration, the value of R corresponding to the minimum tension is the same for alkylbenzenes and alkane. However, the absolute value of the interfacial tension at the minimum is lower for alkylbenzenes as compared to alkanes. The correlations for surfactant and electrolyte concentrations are basically the same for both the alkylbenzenes and alkanes. However, the minimum tension achieved with the alkanes seems to occur at higher surfactant and salt concentrations than with the alkylbenzenes.

The effect of the equivalent weight of petroleum sulfonate on the position of the minimum has also been studied. The main conclusion reached was that as the equivalent weight of the surfactant increases, the preferred value of R (corresponding to the interfacial tension minimum) also increases. The actual factors responsible for this shift have not been identified, but prediction of the direction of the shift of the minimum by a mixture of two surfactants is possible if the general trends of each surfactant on a homologous series is established. It has also been found that the ammonium ion shifts the minimum to higher values of R for alkanes. As the molecular weight of the cation is increased, the minimum tension is again shifted to larger R values. As has been discussed, such a shift is also characteristic of an increase in the surfactant

equivalent weight. This suggests a strong association and formation of ion pairs between the cation and surfactant.²¹

The effect of different alcohols on the value of R at the tension minimum has also been investigated²¹. It was found that an increase in the molecular weight of the alcohol shifted the tension minimum to larger values of R. Changes in interfacial tension with time has also been investigated²⁰ and the "aging" effect has been observed both in the presence and absence of co-surfactants (alcohols). The interfacial tension measured against a variety of hydrocarbons tends to change with time. The direction of change is most often toward higher interfacial tension, the magnitude of these changes being dependent on the surfactant concentration and the alcohols used as cosolvents.

A CORRELATION OF INTERFACIAL TENSION WITH ELECTROPHORETIC MOBILITY

The salt or surfactant concentration in a micellar solution is one of the most important and effective variables in manipulating the interfacial tension between the micellar solution and oil, although the molecular mechanism of this process is not elucidated. It is known that the salt concentration in a micellar solution affects both the interfacial charge and micellar size. In our laboratory, the relationship between interfacial charge and interfacial tension²² has been studied extensively by measurements of the interfacial tensions and electrophoretic mobilities of various systems. It has been established for the brine/oil system that the electrophoretic mobility and interfacial tension curves are inverse images of each other. The micellar system used for these measurements consisted of TRS-10-80 (surfactant) + 1% NaCl + n-octane (oil) and the results obtained are shown in Figure 9. The results of interfacial tension measurements obtained by K. Chan²³ are in agreement with those reported by Cash *et al.*²⁰. The above system exhibits an unusual minimum in interfacial tension at 0.05% TRS-10-80. At the same concentration, the electrophoretic mobility exhibits a striking maximum. From the results reported previously²³ it is clear that the electrophoretic mobility, which is an indirect measurement of interfacial charge density, has a strong correlation with the interfacial tension for the oil/brine or oil/surfactant system. These results also demonstrate that the electrophoretic mobility and interfacial tension curves are almost inverse images of each other. We have shown²³ a similar correlation between interfacial tension and electrophoretic mobility for various crude oils in the presence of NaOH solutions. These results indicate that perhaps a detailed study of the electrochemistry of the oil/water interface in the presence of a surfactant may provide a better insight into how the ultra-low interfacial tension is achieved, rather than attacking this problem by looking at the more structural aspects of the surfactant molecule.

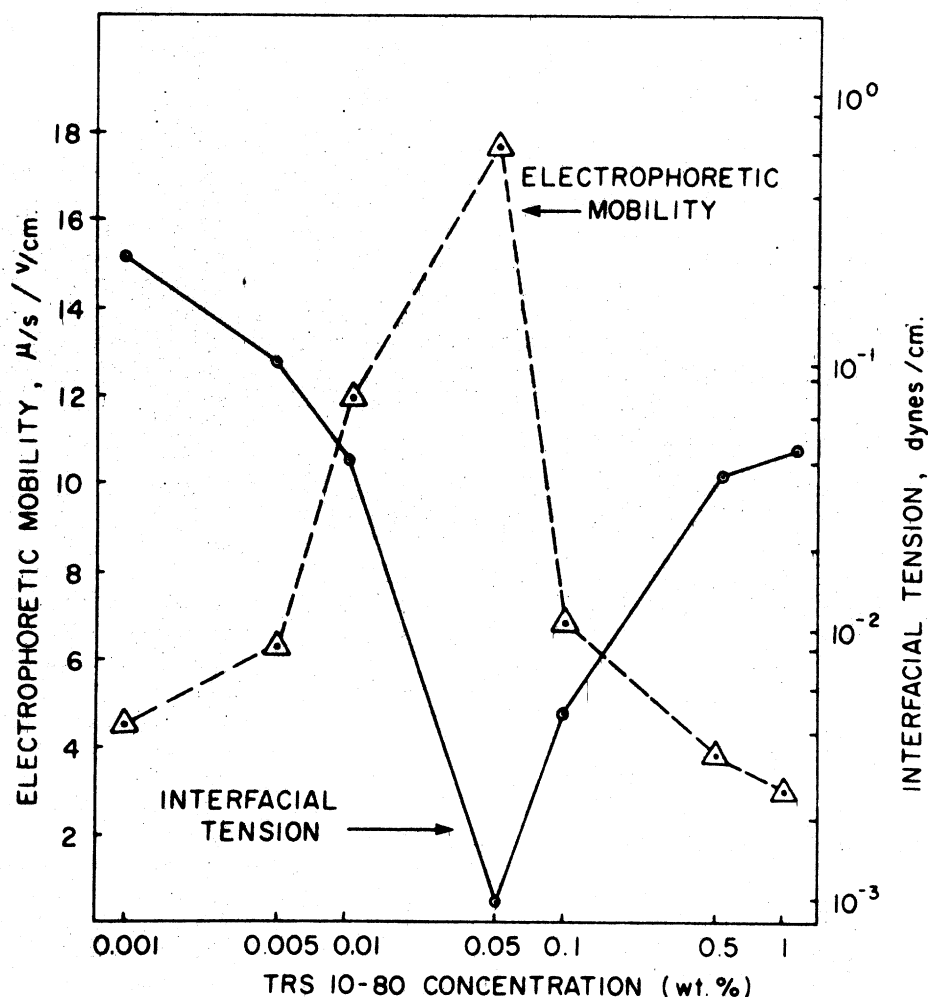


Figure 9. Effect of surfactant concentration on interfacial tension and electrophoretic mobility of oil droplets.

We believe that a greater emphasis on interfacial charge as compared to interfacial tension is highly desirable. If one considers only the ultra-low interfacial tension in the oil displacement process, then the nature of the charge on the solid surfaces (rocks, minerals and clays) is of no consequence. However, if one considers the interfacial charge at the crude oil/surfactant formulation interface, then the nature and magnitude of the charges on the solid surfaces become extremely important in determining the efficiency of the oil displacement process. A better understanding

of interfacial electrochemistry may assist us in producing a desirable broad minimum in interfacial curves as compared to the sharp minimum obtained by various workers.

LIGHT SCATTERING STUDIES ON MICELLAR SOLUTIONS OF PETROLEUM SULFONATES

Light scattering methods have been used to calculate the molecular weight of a micelle for the system TRS-10-410 + isobutanol in different salt concentrations. The surfactant (TRS-10-410) concentration was 5% by weight and the alcohol (isobutanol) concentration 3% by volume. A Wood dual photometer, model 5000 was used to measure the light scattered at 90° by these solutions. The formulation was then diluted with a salt solution, thereby keeping the salt concentration constant, and varying the concentrations of TRS-10-410 and isobutanol, the ratio of surfactant to cosolvent remaining constant. Figure 10 illustrates the effect of NaCl concentration on the light scattered at 90° by the TRS-10-410 solutions. The average molecular weight of a micelle was calculated from the position of the maximum using the approach of Debye and Bueche²⁴ for concentrated solutions. According to their analysis, the concentration at which the maximum occurs depends on the ratio of the molar volumes of the solute and solvent and is given by the equation

$$\phi_{\max} = (1 + \sqrt{n})^{-1}, \quad \phi_{\max} \approx (\sqrt{n})^{-1} \quad [1]$$

for large n (high molecular weight of solute) where n is the ratio of the molar volume of the solute to that of the solvent and ϕ_{\max} is the volume fraction calculated at the maximum in light scattering. For the system when the solvent is water and assuming the density of micelle is one, Equation 1 reduces to

$$\text{Molecular weight of micelle} = \frac{18}{\phi_{\max}^2} \quad [2]$$

From Figure 10 it can clearly be seen that as the concentration of NaCl increases, the light scattered at 90° exhibits a sharper maximum that is shifted toward the left (lower concentrations). Calculated values of the molecular weight of a micelle by Equation [2] and the number of surfactant molecules per micelle are given in Table I. Our results, as shown in Figure 10, are very similar to those obtained by Tager and Andreeva²⁵ for polymer solutions of increasing molecular weight. We would like to emphasize that the molecular weight of a micelle should be accepted as an approximate value in view of the complex nature of the surfactant. We believe that this is as far as we can go quantitatively with this "impure" but practical system.

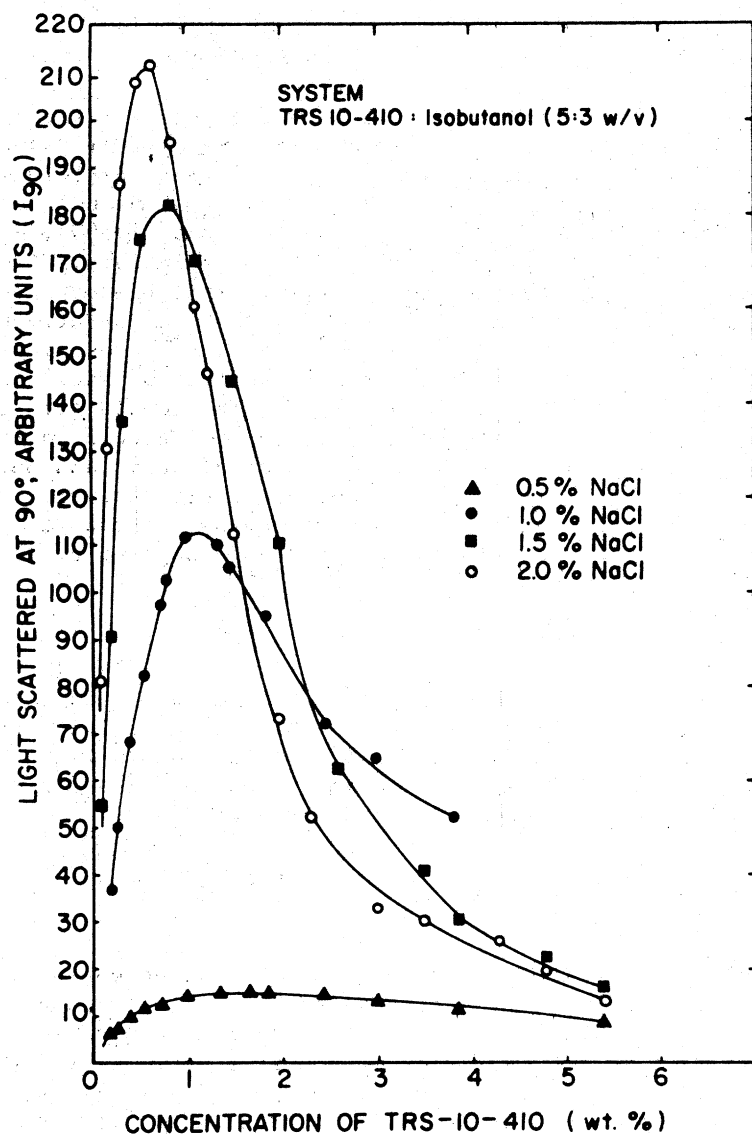


Figure 10. Effect of NaCl and surfactant concentration on light-scattered at 90° by a surfactant formulation.

Table I. The Effect of NaCl Concentration on Micellar Weight of a Surfactant Formulation

System	Surfactant Formulation			Number of Molecules in a Micelle	
	NaCl Conc. %	Position of Maxima wt. %	Mol. Weight of micelle	TRS-10-410 ¹	Isobutanol ²
TRS-10-410 + IBA	0.5	1.6	7.0×10^4	121	121
TRS-10-410 + IBA	1.0	1.0	1.8×10^5	364	364
TRS-10-410 + IBA	1.5	0.8	2.8×10^5	566	566
TRS-10-410 + IBA	2.0	0.6	4.9×10^5	992	992

1. The equivalent weight of 420 for TRS-10-410 has been assumed to be its molecular weight. The weight of surfactant is not corrected for its oil content (i.e., it is assumed that TRS-10-410 is 100% active surfactant).

2. It is assumed that the surfactant and Isobutanol molar ratio in a micelle is 1:1.

Interfacial tensions of the above systems, used for light scattering, were measured with a spinning drop interfacial tensiometer against hexadecane oil. Interfacial tensions at two different TRS-10-410 concentrations (0.5% and 1.0%) and various salt concentrations are shown in Figure 11. It is evident from this figure that there is a decrease in the interfacial tension with increasing salt concentration. This decrease in interfacial tension with increasing salt concentration is associated with an increase in the micellar size as shown by the light scattering results (Table I).

PHASE EQUILIBRIUM AND SOLUBILIZATION PHENOMENA

In general, the oil displacement process involves the interaction of three components, namely, oil, surfactant and brine. It is therefore both convenient and instructive to employ a ternary representation for a phase equilibrium study. A simple ternary diagram for the three component system is shown in Figure 12.²⁶ In this Figure, the multiphase region is bounded by a continuous binodal curve. Everywhere above this binodal curve there exists a single phase that undergoes transitions among various structural states as the compositional point moves about the diagram.

In the multiphase region, the most simple three-component system involves only two phases throughout the region; an oil-external phase and a water-external phase. The actual micellar solutions used in tertiary oil recovery are more complex than this, always involving more than three components and three or more phases in equilibrium. Despite these complexities, the ternary diagram representing the system can be used to trace the possible events that can occur in a micellar solution that is injected into a porous medium.

It is evident that a large variety of phases can exist in equilibrium with each other. Each phase might involve a different micellar structure, and in equilibrium with each other. This intermicellar equilibrium concept was put forth by Winsor²⁷ and is illustrated in Figure 13. Spherical micelles consisting of oil cores in a water continuous medium are called an S_1 or water-external phase. The inverse of this is the S_2 or oil-external phase. An intermediate lamellar structure, which may be a gel or liquid crystal, is called the G phase. It has been proposed¹⁸ that for the oil recovery process, the structural state of the single phase region is unimportant as long as its viscosity is not large. This requirement rules out the use of highly viscous lamellar structures and microgels for the tertiary oil recovery process.

The effect of important variables such as salt, surfactant and cosolvents concentrations have been studied on the phase behavior²⁸⁻³⁰ and on other properties such as viscosity, electrical conductance and birefringence. It has been observed that the use of alcohols as cosolvents modifies the phase behavior of brine/oil/

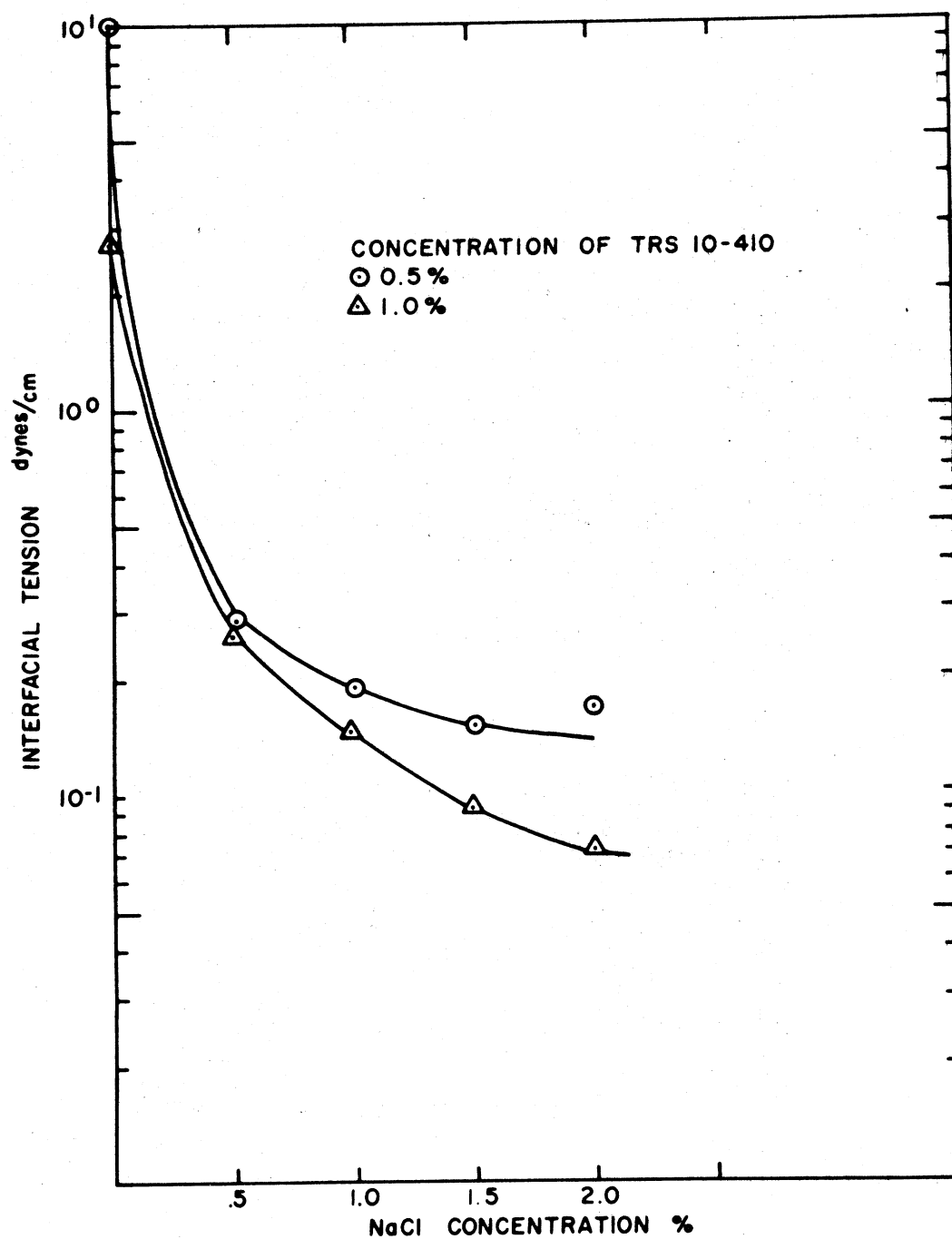


Figure 11. Effect of NaCl concentration on interfacial tension of hexadecane/micellar solution.

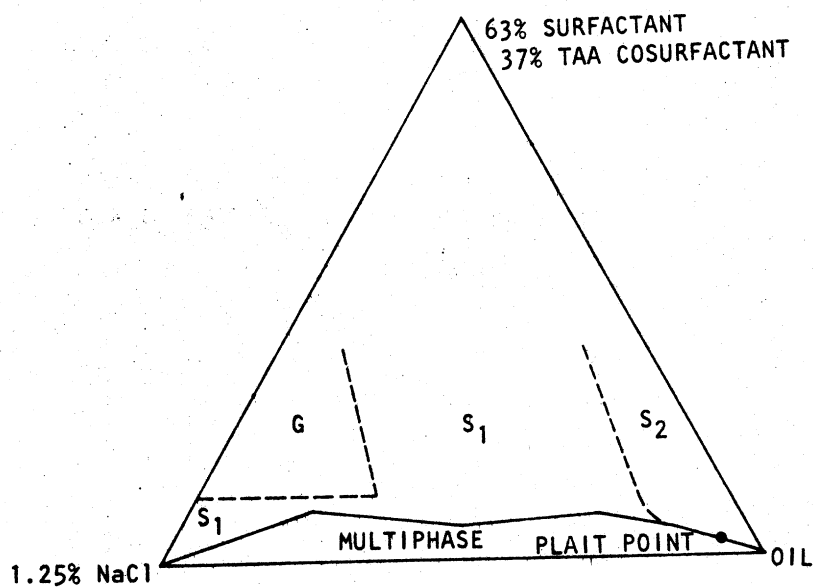


Figure 12. Phase equilibrium diagram (ref. 26).

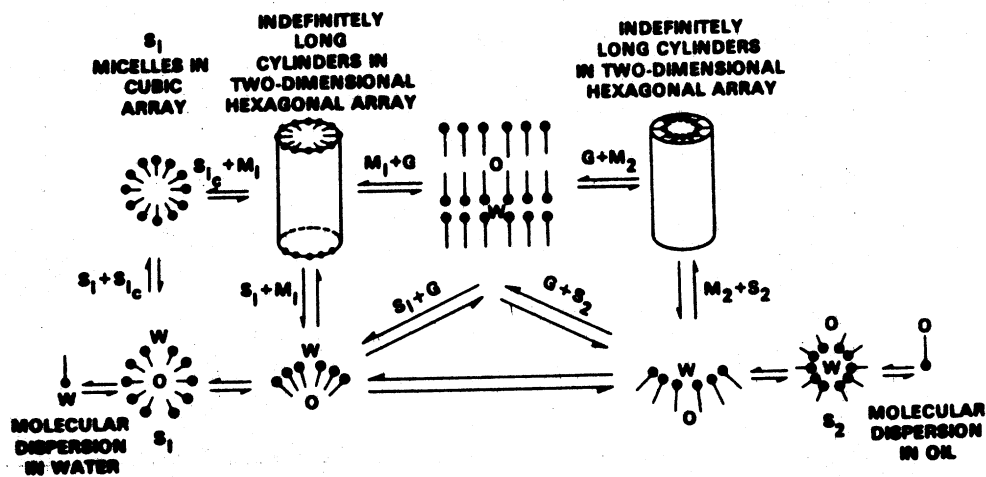


Figure 13. Winsor's concept of intermicellar equilibrium.

surfactant systems. A water soluble alcohol increases the solubility of surfactant in a brine while a water insoluble alcohol decreases the surfactant solubility. The concentration of NaCl changes the alcohol requirements. An increase in electrolyte concentration decreases the requirement of water insoluble alcohols and increases the requirement for water soluble alcohols.

Robbins^{31,32} suggested a model which predicts quantitatively the phase behavior of micellar and microemulsion systems consisting of nonionic surfactants. The model relates the volume uptake of water and oil in the microemulsion phase with HLB value of surfactant. It was also shown that water uptake in microemulsion depends on the oil type used. The inverse correlation between V_w/V_s or V_o/V_s (where V_w is volume of water, V_o of oil and V_s of surfactant in the microemulsion) with the interfacial tension was found. It was observed that for ethoxylated surfactant, the increase in temperature, salt concentration and oil aromaticity increase the oil uptake and decrease water uptake.³² Reed and Healy³³ related interfacial tension γ_{mo} and γ_{mw} (γ_{mo} interfacial tension between microemulsion phase and oil and γ_{mw} interfacial tension between microemulsion phase and water) and solubilization parameter, V_o/V_s and V_w/V_s to salt concentration. It was observed that as salt concentration increases, γ_{mo} decreases and γ_{mw} increases. The salinity, C_γ , where γ_{mo} intersects γ_{mw} was defined as the interfacial tension optimal salinity. Similarly, C_ϕ , the phase behavior optimal salinity, was defined by the intersection of V_o/V_s with V_w/V_s . It was also observed that C_γ value was very close to C_ϕ value. Puerto and Gale³⁴ developed the methods for estimation of optimal salinity and solubilization parameters for alkyl orthoxylene mixtures. It was found that as the amount of low molecular weight sulfonate ($C_n \leq 9$) in surfactant mixtures increases, C_ϕ increases, but solubilization parameter V_o/V_s or V_w/V_s decreases resulting in higher interfacial tensions. Higher molecular weight sulfonates ($C_n \geq 12$) and highly oil soluble alcohols increase the solubilization parameter at C_ϕ but the value of C_ϕ is considerably reduced. Correlation between interfacial tension and solubilization parameters suggests that phase volumes can replace the interfacial tension measurements as a preliminary measure of interfacial activity.

THE EFFECT OF DILUTION ON THE RHEOLOGICAL PROPERTIES OF SURFACTANT FORMULATIONS

The effect of surfactant concentration on the bulk properties (bulk viscosity, screen factor, NMR half band width), of the system TRS-10-410 + isobutanol in brine has been investigated. The original formulation contained 5% by weight of TRS-10-410 and 3% by volume of isobutanol in a 2% NaCl brine. This was diluted with a solution of 2% NaCl. Bulk relative viscosities were measured with a Cannon-Fenske Capillary Viscometer. A screen viscometer was used to obtain screen factors and the half band width was calculated from the NMR spectra obtained at different surfactant concentrations.

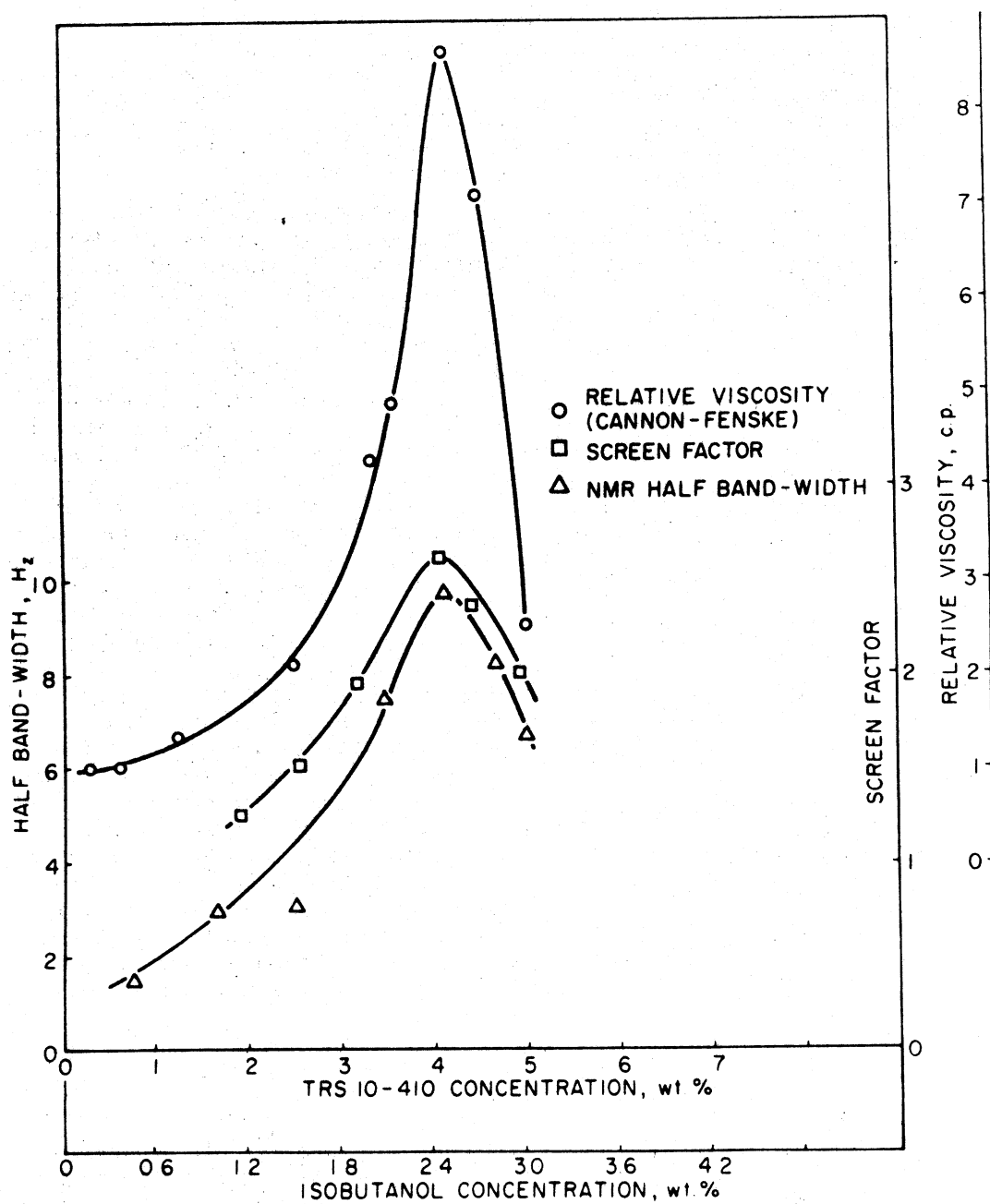


Figure 14. Effect of dilution of a surfactant formulation on relative viscosity, screen factor and NMR half band width.

The results shown in Figure 14 indicate that around a TRS-10-410 concentration of 4% there is a maximum in screen factor and relative viscosity. This indicates that the bulk viscosity is maximum at this point. The NMR half band width is related to the molecular packing in the solution. The broader the peak, i.e., the larger the half band width, the longer it takes for the excited proton to relax back to its original state, hence the closer is the packing of the surfactant and alcohol molecules. Thus the peak in the half band width at 4% TRS-10-410 indicates that the surfactant-alcohol molecular packing is closest at this concentration.

We believe that the above mentioned effect observed upon dilution is an indication of structural changes occurring in the surfactant formulation. This study has implications for injection of such a formulation in the reservoir. As the concentrated surfactant formulation is injected into the ground, there will not be any injectivity problem because of the low viscosity of the formulation. However, once into the ground, it will be diluted with the field brine and will exhibit a higher viscosity presumably more appropriate for the mobility control of the surfactant slug. Therefore, we believe that such a formulation which at the injection point exhibits a low viscosity and upon subsequent dilution increases the viscosity might have certain advantages. However, if the viscosity peak is very high or narrow then it may create a conformance problem.

ADSORPTION FROM MICELLAR SOLUTIONS

It is well known that surface-active agents tend to concentrate at interfaces. In the tertiary oil recovery process, when the micellar slug comes into contact with the reservoir rocks and clays, there would be a loss of surfactant due to adsorption at the solid-liquid interface. The adsorption loss is taken into consideration for the selection of an optimum micellar slug size and its ability to lower the oil-water interfacial tension. Adsorption of various petroleum sulfonates on reservoir cores has been studied by various investigators.^{11,16,17,35,36,37} The following factors are important in determining the adsorption loss of petroleum sulfonates:

1. Specific surface area and electrochemical characteristics of reservoir solids
2. Temperature of the reservoir
3. Composition and concentration of electrolytes in reservoir brine
4. Equivalent weight of the surfactant
5. pH of the reservoir brine and micellar solution
6. Structure and concentration of cosolvent
7. Microstructure of surfactant formulation, e.g. spherical, cylindrical, lamellar structures, or microemulsions (oil- or water-external).

It has been found that an increase in salt concentration increases the adsorption of petroleum sulfonates^{11,17,35}. The adsorption of petroleum sulfonate was also found to be a strong function of its equivalent weight; a sharp increase in adsorption being observed at a petroleum sulfonate equivalent weight of about 450.³⁵ Some inorganic salts were found to decrease the adsorption of petroleum sulfonates.^{11,16} Sodium tripolyphosphate effectively reduces the adsorption of petroleum sulfonate and apparently some inorganic salts can be used as sacrificial chemicals to reduce the adsorption of petroleum sulfonates.¹¹

The adsorption isotherm for petroleum sulfonate does not correspond to any of the Langmuir types, since the isotherm exhibits a maximum^{31,32} which is reported to occur near the critical micelle concentration. A minimum in adsorption is also observed to occur at higher surfactant concentration. At this concentration, the physical appearance of the micellar fluid changes from a turbid, caramel colored fluid to an amber, transparent solution, thus indicating a change in the micellar structure.³⁷

The adsorption isotherms of TRS-10-410 in zero and 1% NaCl for crushed Berea sandstone at 30°C are shown in Figure 15.³⁸ Both these isotherms exhibit maxima. The clay fraction of the crushed Berea sandstone was separated and it was found that most of the adsorbed petroleum sulfonate was on the clay fraction and a negligibly small amount of adsorption occurred on the sand. The maximum observed in the isotherm near the CMC was explained on the basis of competition for the calcium-surfactant anion complex (formed due to adsorption of surfactant on clay) between the clay surface and micelles.

SURFACTANT-POLYMER INTERACTION

In tertiary oil recovery, it is customary to follow the slug of micellar solutions with a mobility control polymer solution (Figure 7). Often the polymer is added also to the micellar solution to increase its viscosity for mobility control purposes. There is thus a large possibility of the polymer and micellar solutions coming in contact with each other and leading to surfactant-polymer interaction. Such interactions can affect the properties of the interface between the polymer and micellar banks, as well as the properties of the micellar solution due to mixing effects. It has been found³⁹ that there is a decrease in apparent viscosity at the micellar slug-polymer interface.

It has been found⁴⁰ that the polymer tends to move ahead of the surfactant solution. This phenomenon was explained by the concept of the "polymer inaccessible pore volume".⁴⁰ This arises from the fact that due to their greater molecular weight, polymer

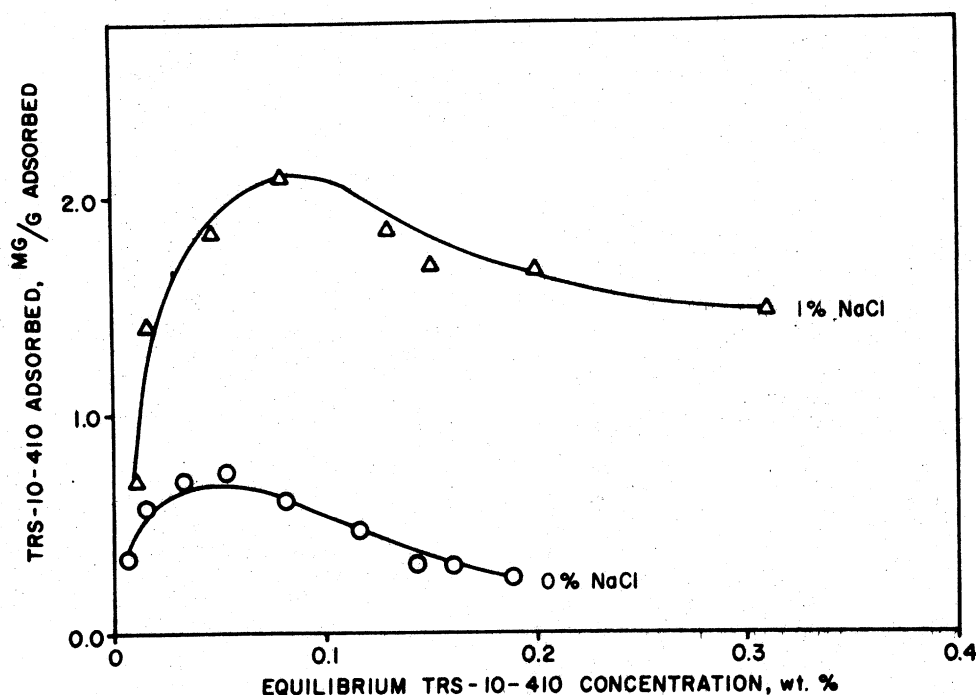


Figure 15. Adsorption of Deoiled TRS-10-410 on crushed Berea sandstone at 30°C.

molecules are excluded from the small pores and can propagate through only larger pores in the porous media. In contrast, water can travel through both the small and large pores. The pore volume available to the polymer molecules is hence less than that available to water. This phenomenon leads to polymer molecules moving faster than the carrier water, and thus can move ahead of the micellar-polymer interface leading to a surfactant-polymer interaction in the micellar fluid. It has been observed⁴¹ that such interactions cause a separation of the micellar formulation into two phases, one of which is trapped in the porous medium. These polymer-surfactant interactions can also cause flocculation to take place in the micellar slug. Both phase separation and flocculation in the micellar slug lead to a substantial loss of surfactant from the micellar slug, with consequent impairment of the efficiency of the process. This surfactant-polymer interaction can be reduced⁴¹ if the salinity of the mobility buffer bank is lower than the salinity of the micellar fluid. The phase separation can also be eliminated by the addition of cosolvents or cosurfactants to the mobility buffer or micellar solution.

In our laboratory, the effect of a surfactant (sodium pentadecyl benzene sulfonate) on the bulk and surface properties of a poly-

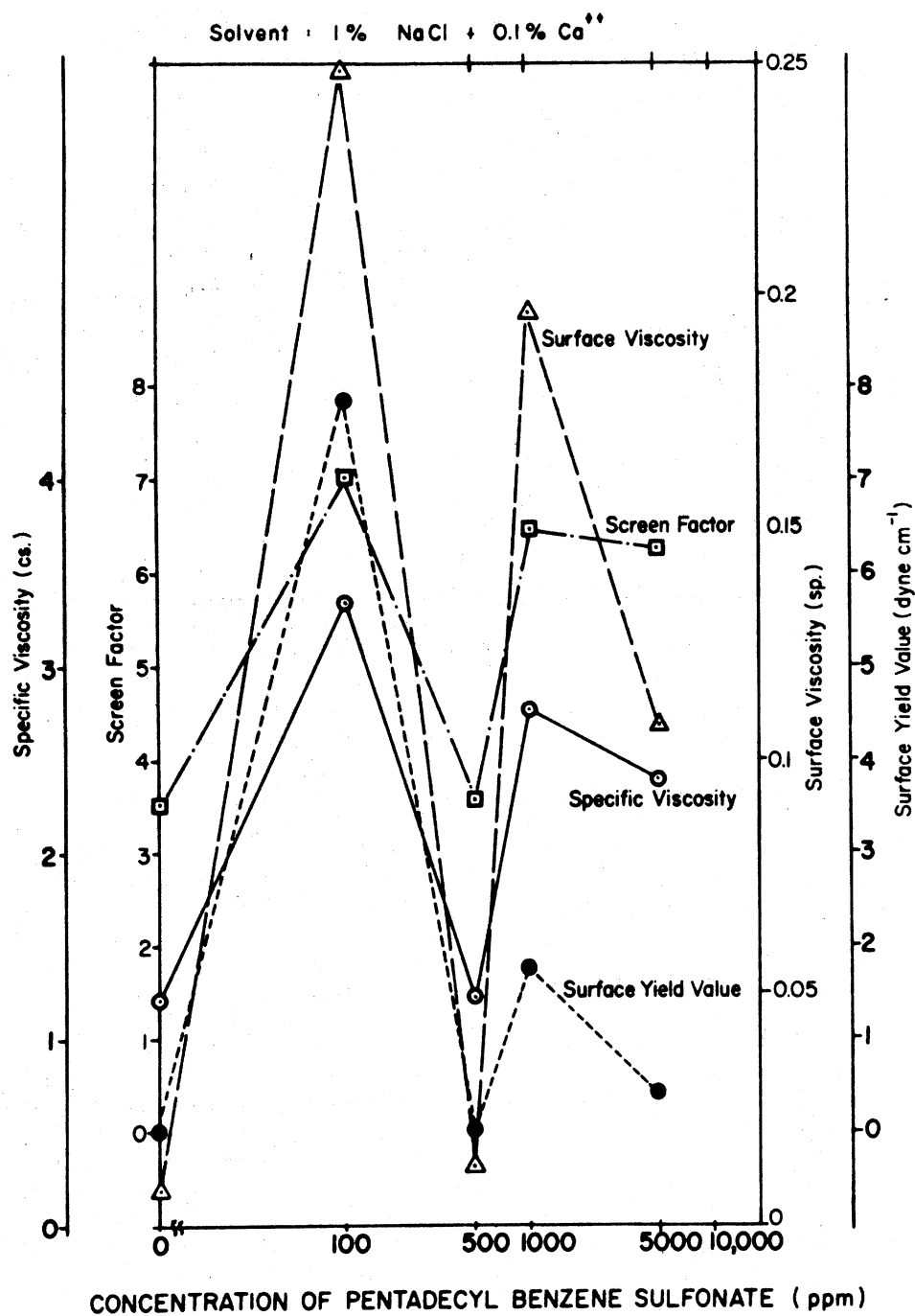


Figure 16. Effect of surfactant concentration on bulk and surface properties of a polyacrylamide solution.

acrylamide solution (Nalco VX 222) has been studied in three solvents, namely, distilled water, 1% NaCl, and 1% NaCl + 0.1% CaCl₂.⁴² The measured parameters were screen factor and relative viscosity (both bulk properties) as well as surface viscosity and surface yield value (both surface properties). With use of either of the former two solvents (water and 1% NaCl), all the measured properties, with the exception of the screen factor, exhibited a smooth decrease with increasing surfactant concentration. This indicates a greater fluidity of both the bulk and surface phases with increasing surfactant concentration. The results obtained with 1% NaCl + 0.1% CaCl₂ as the solvent (Figure 16), however, were strikingly different. Unlike the previous cases, all the measured parameters exhibited a trend of maxima and minima. The addition of the divalent calcium ion has obviously caused tremendous changes in both the surface and bulk properties of the solutions. The evidence suggests possible aggregate formation at a specific surfactant concentration of 500 ppm. In summary, the results obtained on this polymer-surfactant system illustrate the importance of investigating and understanding the polymer-surfactant interaction for the development of an efficient tertiary oil recovery process.

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