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THE EFFECT OF SURFACTANT PARTITIONING ON THE PHASE BEHAVIOR AND PHASE INVERSION OF THE MIDDLE PHASE MICROEMULSIONS

by K. S. Chan, Standard Oil Co.,
Ohio; and D. O. Shah, Univ. of
Florida, Members SPE-AIME

ABSTRACT

For multiphase surfactant–oil–brine systems, it was observed that the phase transition of microemulsion phase from lower to middle to upper phase can be achieved by varying any one of the seven variables: (1) emulsifier or surfactant concentration, (2) oil/brine ratio, (3) surfactant formulation/oil ratio, (4) brine salinity, (5) alcohol concentration, (6) oil chain length, and (7) temperature. The first three variables show a transition from the middle–phase to upper–phase microemulsion in which the middle–phase microemulsion grows and incorporates the excess oil into the middle phase. The resulting upper–phase microemulsion was found to be water–external. However, for the last four variables, there is a true phase inversion where a middle–phase microemulsion inverts into an oil–external microemulsion.

It has been established in low surfactant concentration systems that the transition of surfactant–rich phase from lower to upper phase is characterized by a partition coefficient of unity for the surfactant. Similarly for high surfactant concentration systems, we have observed that the phase inversion (i.e., the disappearance of the middle–phase microemulsion and formation of oil–external upper–phase microemulsion) occurs at the partition coefficient unity defined as the concentration in the oil phase divided by the concentration of surfactant in the middle and lower phases. This similarity between the effects of salt concentration on low and high surfactant concentration systems supports the view that the middle phase is an integral part of the aqueous phase. Furthermore, a careful examination of the phase–inversion region revealed that as the middle–phase volume decreases, the surfactant concentration in the oil phase increases.

We have found also that at the optimal parameters

*Now with Standard Oil Co., Ohio (SOHIO), Cleveland.
**Presently Visiting Professor of Chemical Engineering, Petroleum Engineering and Institute for Energy Studies, Stanford U., Stanford, CA.
References and illustrations at end of paper.

(e.g., salinity, oil chain length, etc.) the surfactant concentration in the excess oil phase approaches that in the excess brine phase. However, the phase inversion occurs when the surfactant concentration in the excess oil phase approaches the concentration in the combined middle and lower brine phase. The results show the similarity between the interfacial tension behavior of low concentration systems and those of high concentration systems.

INTRODUCTION

Systems containing 2 to 10% petroleum sulfonate with or without the addition of alcohol as cosolvent usually exhibit a complicated phase behavior. The surfactant can be predominantly soluble in brine and form a water–external microemulsion in equilibrium with an excess oil phase. On the other hand, if the surfactant has a greater solubility in oil, it can form an oil–external microemulsion in equilibrium with an excess brine phase. The transition of surfactant–rich phase from lower phase (brine phase) to upper (oil phase) generally goes through a region in which a middle phase, which virtually contains most of the surfactant, and remains in equilibrium with an excess oil phase and an excess brine phase. It has been well established[1,2] that the formation of this middle phase correlates with increased oil displacement efficiency of the process.

The development of the multiphase behavior from two–phase with surfactant in the brine phase through three–phase having most of the surfactant in the middle phase to two–phase with the surfactant in the oil phase can be achieved by changing one of the seven parameters in the direction described as follows: (1) increasing the total surfactant concentration in the system, (2) increasing the brine/oil ratio, (3) increasing the surfactant solution/oil ratio, (4) increasing the salinity of the brine, (5) decreasing the hydrocarbon chain length of the oil, (6) increasing the alcohol concentration, and (7) decreasing the temperature.

The first three parameters are controlling the phase behavior in quite the same manner. The third parameter is in fact the superposition of the first

two. The effects of salinity and oil chain length were studied intensively by Hsieh[3] and reported very extensively in the literature by various research groups.[4,5] Very little information has been reported about the effect of alcohol concentration on the phase behavior of the surfactant-oil-brine system.[6]

Reed and Healy[7] studied the effect of temperature on phase behavior of a synthetic petroleum-sulfonate system. They found that as the temperature increased, the surfactant molecules migrated from upper to middle phase and then to lower phase. But for a nonionic surfactant system, Shinoda and Friberg[8] observed that surfactant-rich phase shift follows the reverse trend. No attempt has been made to explain this different trend for systems using nonionic and anionic surfactants.

The middle-phase microemulsion gradually changes its composition as the parameter that is controlling the upshift of the surfactant-rich phase changes. Generally, the volume of oil solubilized in the middle phase (V_o) increases, whereas the volume of water in the middle phase (V_w) decreases. At a specific value of the parameter in control, V_o and V_w could be equal numerically. This specific value is defined as optimal parameter (e.g., optimal salinity, optimal surfactant concentration, etc.) by phase behavior.

When the surfactant-rich phase is the aqueous phase, the system is a two-phase system and there is an interface only between excess oil and microemulsion phase. The interfacial tension for this interface is termed γ_{om}. On the contrary, when the surfactant-rich phase is the upper phase, the interfacial tension is denoted as γ_{mw} for the interface between microemulsion and excess water (brine) phase. In three-phase region, both γ_{om} and γ_{mw} exist. The specific parameter value at which γ_{om} equals γ_{mw} is defined as optimal parameter by interfacial tension. In most cases, the optimal parameter defined from phase behavior coincides with the one defined from interfacial tension within experimental error. For this three-phase region, the higher interfacial tension between γ_{om} and γ_{mw} is defined by Reed and Healy[7] as the controlling interfacial tension. Healy and Reed also found that the lower the controlling interfacial tension minimum, the better the oil displacement efficiency of the surfactant formulation.

For the middle-phase microemulsion, the interfacial tensions γ_{om} and γ_{mw} are always in the ultra-low range. The mechanism of producing the ultra-low interfacial tensions by the middle-phase microemulsion still is unknown. But there is now a general consensus that the microstructure of the middle-phase microemulsion should influence greatly the nature and characteristics of the two interfaces and, hence, play an important role in the development of the ultra-low interfacial tension. By this token, the study of the microstructure assumes practical importance in the tertiary oil recovery research. Before elucidating the microstructure of the middle-phase microemulsion, it is necessary to explore the actual mechanism of the middle-phase formation and phase transition. The correct understanding of the physics of the middle-phase formation and phase transition would provide reliable clues for solving the mystery of the microstructure of the middle-phase microemulsion.

THE FORMATION AND MICROSTRUCTURE OF MIDDLE-PHASE MICROEMULSIONS

The formation of middle-phase microemulsion by adding electrolyte to the water-external microemulsion of the two-phase system has not been well understood. In a study of 5/3 TRS 10-410/IBA system, Hsieh[9] described the middle-phase formation phenomenon as the coacervation[10] of micelles swollen with solubilized oil from the equilibrated aqueous phase. He concluded that the electrical repulsion between the swollen micelles decreases due to the neutralization of surface charge by counter-ions and that the decrease in electrical repulsion enhances the aggregation of micelles, as the Van der Waals attractive force between the micelles becomes predominant. To investigate the validity of this theory, Chan[11] measured the surface charge density of the equilibrated oil droplets in the middle phase and found that the surface charge density increases to a maximum at the salinity at which the middle phase starts to form. Beyond this salinity the surface charge density decreases in the three-phase range. Based on numerous observations of various surfactant-oil-brine systems, Hsieh[9] proposed the mechanism of middle-phase microemulsion as shown in Fig. 1.

If the proposed coacervation theory for the formation of middle-phase microemulsion is valid, one could easily conclude that the middle phase should be composed of spherical oil droplets separated from the aqueous phase such that water is the external phase. But it is possible that these coacervated spherical oil droplets may be deformed and compressed due to the balance of three major forces: the buoyancy force, electrical double-layer repulsion, and Van der Waals attractive forces. Based on numerous careful observations and experimental results obtained by using various physicochemical techniques such as high resolution NMR and electrical resistivity measurements, Hsieh[9] proposed a model for the middle-phase microemulsion in three-phase systems encountered in surfactant formulations at and near optimal salinity, as the water-external microemulsion of spherical particles of oil.

In the study of a two-phase nonionic system, Shinoda and Friberg[8] observed a phase inversion from water-external microemulsion to oil-external microemulsion through a three-phase region as the temperature gradually was increased. The physical properties of their middle phase were not reported by these workers. But they concluded that their middle phase was surfactant-continuous and that oil and water in this phase were continuous also. They described the middle-phase structure as sandwich-like, with oil and water swollen between the molecular leaflets of the nonionic surfactant. From their description of the middle-phase structure, one can infer that their middle phase should be showing some degree of birefringence. For the petroleum sulfonate systems, all the middle phases observed are isotropic, clear, or translucent. A birefringent middle phase has never been observed.

Scriven[12] proposed an equilibrium bicontinuous structure for the middle-phase microemulsion. His idea is that the minimization of area would produce a periodic bicontinuous structure of fused polyhedra from a simple cubic array of spheres. The conditions for the existence of a bicontinuous structure are

extremely sensitive to thermal fluctuations. Scriven also pointed out that this structure of minimal surface has no mean curvature and is more appropriate in the range of phase inversion.

To determine the actual structure of the middle-phase microemulsion, it is necessary to collect evidence from various observations and experiments. For this purpose, high resolution NMR half band-width, pulse NMR relaxation time T_1 (spin-lattice) and T_2 (spin-spin) measurements were used, together with dye migration tests, viscosity (η) and electrical resistivity measurements to characterize the middle-phase microemulsions.[11] The freeze-etching electronmicrographs for some of the important samples were obtained by D. W. Deamer, of the U. of California, Davis. Figs. 2 to 5 show successively the microstructure of the middle-phase microemulsions as the salinity of the system increases. The fine surface structure of aggregates shown in Fig. 2 appears to be a collection of smaller subunits (e.g., micelles). The structure seen in Fig. 2, if it indeed exists in the middle-phase microemulsions, can be referred to as "supra-micelles" consisting of smaller micellar subunits. The work is in progress to measure the dimensions of these aggregates using low-angle x-ray scattering. In this technique fast-freezing is not required. The diameter of each aggregate is about 1500 to 1700Å in Fig. 2. The particle size in the middle-phase microemulsion at 1.2% NaCl is about 800 to 900Å diameter (Fig. 3). They appear to be distributed fairly uniformly within the aqueous environment. The difference in the size of particles is presumably due to the different depth of their location. Figs. 4 and 5 are the corresponding electronmicrographs of the middle-phase microemulsion at 1.4% and 1.6% NaCl concentration. The particle size in Fig. 4 is about 400 to 500Å diameter and that in Fig. 5 is about 150 to 200Å size. We used D_2O for making these microemulsions because we also carried out extensive NMR studies[6] on these samples. Wasan et al.[18] have reported the presence of large aggregates of 1 to 4 microns in petroleum sulfonate solutions. The experimental results and observations can be summarized as follows.

1. All the surfactant-rich phases are clear and isotropic (i.e., nonbirefringent).

2. Preliminary dye-migration tests show that the middle-phase microemulsions are water-external.

3. The NMR line width for every surfactant-rich phase is narrow, comparable to those of micro-emulsions.

4. T_1 and T_2 measurements imply that the surfactant molecules have more freedom of motion in the middle-phase microemulsions than in the liquid crystalline structure (e.g., cylindrical or lamellar micelles).

5. Diffusion effect observed in T_2 measurement at 1.4% NaCl and higher salinity indicates that the particles in these systems are relatively small and exhibit a diffusion effect on NMR time scale.

6. The decrease in the size of particles with an increase in salinity is predicted by the plot $1/T_1\eta$ vs salinity.

7. Electronmicrographs confirm Conclusions 5 and 6 and strikingly reveal the structure of the middle-phase microemulsion as the water-external microemulsion and further show that the particle size in the middle-phase microemulsion decreases as the salinity increases.

The above studies were concentrated in the region of middle-phase formation, which is in most cases near the optimal salinity. The micro-structure of the middle-phase microemulsion at this end is very likely water-external, but the micro-structure of the middle-phase microemulsion at the other end where phase transition from three-phase to two-phase with surfactant predominantly in oil phase is yet to be explored. Flemming et al.[13] showed that the structure could be of "mixed external" or bicontinuous. If the continuous phase in the middle-phase microemulsion is water, the only possible region in which the microemulsion changes its structure from water-external, oil-swollen micelles to oil-external reversed micelles is the transition region where middle phase becomes the upper phase. For this transition, three possible cases can occur.

1. The transition of surfactant-rich phase from middle phase to upper phase is smooth and continuous, with no change in microstructure. The middle phase apparently becomes upper phase simply because the surfactant-rich middle phase solubilizes all the oil in the system so that no excess oil phase exists.

2. The transition from water-external micro-emulsion in the middle phase to oil-external microemulsion in the upper phase is discontinuous. When the solubility of surfactant molecules in the oil phase increases due to a change in brine salinity, oil chain length and temperature, or a change in the hydrophile-lipophile balance (HLB) of the surfactant molecules induced by the addition of alcohol, the concentration of surfactant molecules increases and reversed micelles are formed in the oil phase. For this case, the surfactant partitioning is the cause of phase inversion.

3. The transition goes through an extremely narrow region of bicontinuous structure similar to the one suggested by Scriven,[12] which may be highly unstable to thermal fluctuation.

Therefore, it is necessary to investigate the existence and to determine the actual mechanism of the phase inversion.

PHASE TRANSITION IN LOW SURFACTANT CONCENTRATION SYSTEMS

Two ultra-low interfacial tension minima can be observed in the oil-brine equilibrium systems when the surfactant concentration is the variable. A typical system such as 5/3 TRS 10-410/IBA with equal volume of dodecane and 1.5% NaCl solution as brine, the interfacial tension goes through two regions of ultra-low interfacial tension minima. Fig. 6 shows that the first minimum occurs at a lower surfactant concentration of 0.1% and the second minimum at a higher surfactant concentration of 4.5%. The mechanism of achieving the first ultra-low interfacial tension minimum in the low surfactant concentration region has been proposed

for the petroleum sulfonate systems[14] and verified by the study on a pure surfactant system.[11,15] For this low concentration region, the systems are basically two-phase. No evidence of an intermediate phase was found and a model described as an adsorbed surfactant monolayer separating the two equilibrium phases (oil and aqueous phase) has been used successfully to account for all the interfacial tension minimum phenomena.

When the petroleum sulfonates are used, the ultra-low interfacial tension in the low surfactant concentration systems always pass through a minimum where the surfactant partition coefficient is unity.[14] For the effect of brine salinity, the surfactant partition coefficient unity signifies the inversion from normal micelles to inverse micelles. In other words, partition coefficient unity reflects a true phase inversion or migration of surfactant from water to oil phase.

SURFACTANT PARTITION COEFFICIENTS FOR THE DETERMINATION OF PHASE INVERSION AND OPTIMAL PARAMETERS

When the surfactant and alcohol are mixed with equal volumes of oil and brine, one can visualize that the surfactant first will partition between oil and brine according to the relative solubilities of the surfactant molecules in each phase. If most of the surfactant molecules stay in the brine phase, the equilibrated aqueous phase will become a micellar solution phase or microemulsion phase, depending on the amount of oil solubilized in the aqueous phase and the system becomes two-phase. But if the conditions for coacervation are attained, the microemulsion particles then would separate and float from the aqueous phase to form a third phase. Hence, in addition to an oil phase, there will be a middle phase as well as an excess-brine phase. Thus, a three-phase system will be observed. On the other hand, if most of the surfactant molecules partition to the oil phase due to some effects such as salting-out by increasing salinity, the surfactant would form reverse micelles in the oil phase. And again, a two-phase system, in which an oil-external microemulsion is in equilibrium with a brine phase, will be observed.

In addition to the partitioning of the surfactant molecules, the oil solubilization ability of the mixed micelles formed by surfactant and alcohol molecules also will affect the phase behavior of the multiphase surfactant-oil-brine system. Therefore, it is desired to design an experimental method to distinguish whether the phase transition is due to the partitioning of the surfactant molecules in the oil and brine phase, or is due to the solubilization of the oil by micelles in the equilibrated aqueous phase that coacervate to achieve a phase separation.

If the formation of middle-phase microemulsion is due to the coacervation of the swollen micelles from the aqueous phase, then the middle-phase microemulsion can be regarded as part of the equilibrated aqueous phase. This viewpoint seems to be valid based on the behavior of the middle-phase microemulsions. Therefore, the whole system can be viewed as a two-phase system similar to the low-surfactant concentration systems.

In low-surfactant concentration systems, the surfactant concentration in oil changes drastically near the phase inversion point. The partition coefficient, defined as the ratio of the surfactant concentration in oil to the surfactant concentration in brine, is unity at the phase inversion point.[11] These two behaviors should be observed also in the multiphase high-surfactant concentration system, in which the true phase inversion occurs.

Therefore, accurate measurement of surfactant concentration in the oil phase would provide means to determine the existence of phase inversion. For this purpose, the surfactant partition coefficient for multiphase systems can be defined as follows for the determination of phase inversion.

Partition coefficient =

$$\frac{\text{Concentration of surfactant in oil}}{\text{surfactant concentration in the remaining phase}}.$$

The remaining phase is considered to be a single phase combining the middle phase and brine phase in the three-phase region. The surfactant concentration of this remaining phase can be calculated from the surfactant concentration in oil by mass balance, if one knows the actual volume fraction of the phases.

If the phase transition were due to total solubilization of oil in the system, the phase inversion would never occur and the surfactant-rich phase would have the same structure whether it is a middle phase or an upper phase. For this case, one can predict that the surfactant concentration in oil would not have a drastic change and the curve of surfactant concentration in oil would never cross the curve of the surfactant concentration in the middle phase and aqueous phase combined. For this type of transition, a partition coefficient of unity (defined above) would not be achieved. It is necessary to prove this conclusion for systems in which no phase inversion occurs and hence verify the partition coefficient of unity as a criterion for phase inversion.

PHASE INVERSION BY PARTITIONING OF SURFACTANT MOLECULES BETWEEN OIL AND BRINE

For some systems, the relative solubilities of the surfactant molecules in oil are changing constantly when the factors governing their distribution behavior are continuously altered. A typical system is the surfactant-oil-brine system in which the salinity of the brine is increasing while the other factors such as oil chain length, temperature, surfactant concentration and oil/brine ratio are kept constant. At the high brine salinity, the surfactant molecules will partition preferentially in the oil phase due to the salting-out effect in the brine phase. Consequently, an oil-external microemulsion will form that is in equilibrium with the brine phase. At low brine salinity, the surfactant solubility in brine is greater and the system will be two-phase with a water-external microemulsion in equilibrium with an oil phase. If the conditions for the swollen micelles to coacervate are obtained, the micelles separate and float from the aqueous phase to form a middle phase. Therefore, apparently there is a phase inversion for the surfactant-rich phase from water-external microemulsion to oil-external microemulsion as the salinity of the brine increases. This phase inversion is confirmed usually by a

drastic increase in the electrical resistivity of the surfactant-rich phase near the phase transition point.

Besides the salinity of the brine phase, a change in the chain length of oil as well as the temperature of the system would also induce phase inversion in the multiphase systems due to the alteration of the relative surfactant solubility. It is known[16] that the addition of alcohol will affect the hydrophilic-lipophilic balance (HLB) of the surfactant. Thus, an increase in the concentration of alcohol possibly will induce a phase inversion in the multiphase surfactant-oil-brine system. In this paper, we will present the study of phase inversion mechanism for the effect of salinity and the effect of oil chain length with emphasis on the surfactant partition near phase transition point.

The phase behavior of 5% TRS 10-410, 3% IBA with equal volume of hexadecane and brine is shown in Fig. 7. For this system, the middle-phase range begins at 2% and ends at 3.8% NaCl concentrations. The optimal salinity is 2.5%, determined by the solubilization parameters and the interfacial tensions. The electrical resistivity increases drastically at around 3.8% NaCl concentration, suggesting the existence of a phase inversion. In order to determine accurately the phase inversion salinity, an extremely careful and detailed study was conducted on phase behavior around 3.8% NaCl concentration. The salinity was varied very slowly as little as 0.01%. The phase behavior in this region is shown in Fig. 8. It is very exciting to see that the middle-phase volume decreases drastically in this region and becomes zero at 3.77% NaCl concentration. To the best of our knowledge, there is no such observation reported in the literature. If no detailed phase-behavior study were conducted about the phase transition region, the upper-phase boundary curves will be plotted as the broken line curves shown in the upper parts of Figs. 7 and 8.

Hsieh and Shah[3] have shown for the same system that the middle-phase volume decreases linearly with the decrease of the total surfactant concentration and the middle-phase volume is zero at zero total surfactant concentration. Therefore, the decrease in middle-phase volume with increase of the brine salinity suggests that the surfactant concentration in oil phase should increase strikingly in this transition region. This is confirmed by the surfactant concentration measurement shown in Fig. 9. The surfactant concentration in oil remains constant from 2% to 3% NaCl concentrations. It increases strikingly from 3% to 3.77% NaCl concentration where the middle-phase volume is zero. The surfactant concentration in the remaining phase (middle-phase plus excess brine phase) decreases in the region. And the two concentrations are equal numerically at 3.77% NaCl concentration, suggesting that the partition coefficient is unity at that salinity. According to the principle discussed in the previous section, it can be concluded that the phase inversion occurs at 3.77% NaCl concentration for this system.

Light scattering turbidity measurements of the surfactant-rich phase as well as the oil phase were conducted to explore, one step further, the nature of the phase inversion point observed in this system. The results are shown in Fig. 10. It can be seen

from this figure that the turbidity of the middle phase decreases quickly from middle-phase formation salinity (2% NaCl concentration) to the optimal salinity (2.5% NaCl concentration). This turbidity remains constant with the increase of the salinity until the salinity is close to the phase inversion salinity. On the other hand, the turbidity of the oil phase increases rapidly from the optimal salinity. At 3.5% NaCl concentration, the turbidity of the middle phase increases again. The two turbidity curves approach each other and are numerically equal when the phase inversion salinity is reached. This probably suggests that the phase inversion point in this system is a thermodynamic critical point. In addition to the above findings, more evidence[13] is needed to establish the critical point as the phase inversion point for this system.

The surfactant concentrations in the excess oil and excess brine phase were measured accurately around the optimal salinity of 2.5% NaCl concentration. The results are shown in Fig. 11. It is interesting to see for this system that the two concentrations are equal at the optimal salinity. In other words, the partition coefficient of the surfactant molecules between the excess oil and excess brine phase (aqueous phase) is unity at the optimal salinity. This was observed also by Wade et al.[17] for pure alkyl benzene sulfonate systems.

In view of the fact that the partition coefficient of the surfactant molecules between oil and brine phase is unity at every optimal parameter observed for low as well as high surfactant concentration systems, we can predict that the ultra-low interfacial tension minimum will be observed at the optimal parameter if we measure the interfacial tension between the excess oil phase and the excess brine phase γ_{ow} in the three-phase region. This prediction is made as the ultra-low interfacial tension minimum correlates with the partition coefficient unity in low surfactant concentration systems. Fig. 12 confirms our prediction for the system we studied. The interfacial tension γ_{ow} has an ultra-low minimum (1.5 millidynes) at the optimal salinity (2.5% NaCl concentration).

In addition to the attainment of partition coefficient unity and the drastic increase of the surfactant concentration in oil, the most important evidence for the determination of a phase inversion is the observation that the middle-phase volume decreases with increasing salinity and is zero at phase inversion salinity. For TRS 10-410 systems studied, the dramatic decrease of the middle-phase volume occurs in a narrow salinity range from 3.55% to 3.77% NaCl concentration. In view of the fact that pure surfactant partitioning between oil and brine phase is more drastic than petroleum sulfonate partitioning, we can infer that the decrease of the middle-phase volume will be more rapid in pure surfactant system and slower if a surfactant with a broad distribution of equivalent weight is used. To demonstrate this, we used Petrostep 465, a petroleum sulfonate produced by Stepan Chemical Co. from the continuous sulfonation process, which is known to have a broad equivalent weight distribution and an average equivalent weight of 465. An emulsifier was prepared containing equal weight of Petrostep 465 and alcohol mixture which again consists of equal weight of isobutanol (IBA) and normal pentanol

(nPA). The phase behavior of 4% emulsifier with equal volume of dodecane and brine is shown in Fig. 13. There is no doubt that the middle-phase volume decreases to zero at 2.1% NaCl concentration. The surfactant concentration in oil increases gradually as the middle-phase volume slowly decreases. The optimal salinity for this system was determined by solubilization parameters at 1.32% NaCl concentration. If the partition coefficient is defined as the ratio of surfactant concentration in excess oil to that in excess brine, the partition coefficient (as shown in Fig. 14) is unity at the optimal salinity. For the determination of phase inversion, the surfactant concentration in the remaining phases (middle phase plus excess brine phase) was calculated from that in the oil phase. Fig. 15 shows that partition coefficient for phase inversion is unity at the phase inversion salinity ($\approx 2.1\%$ NaCl).

We have shown[14] that a surfactant is preferentially soluble in oil phase if the oils are of shorter chain length and in brine phase if the longer chain length oils are used. Therefore, the difference in the surfactant partitioning when the chain length of oil is varying also can induce a phase inversion in the system. The effect of oil chain length on phase inversion was studied using the system 5% TRS 10-410 plus 3% IBA in 1.5% NaCl brine equilibrated with oils of various chain length from C_6 to C_{16} for a volume ratio of 2:1.

Fig. 16 shows the phase behavior of the system. Below oil chain length C_{10}, the surfactant molecules stay in oil phase and form an oil-external microemulsion. The middle-phase microemulsion was observed in the range from C_{11} to C_{14}. For C_{15} and C_{16}, a water-external microemulsion was observed to be in equilibrium with the oil phase. The solubilization parameters determined the optimal oil chain at about 11.8, which was confirmed by the interfacial tension measurements as shown in Fig. 17. Here again, the interfacial tension between excess oil and excess brine phase goes through a minimum at the optimal oil chain length. Fig. 18 shows the surfactant distribution between phases as a function of oil chain length. It can be concluded from this figure that the phase inversion oil chain length is 9.5 where the partition coefficient for phase inversion is unity. For this system, it also is observed that the partition coefficient for oil and excess brine is unity at the optimal oil chain length ($C_{11.8}$).

CONCLUSION FROM THE STUDIES OF PHASE INVERSION BY SURFACTANT PARTITIONING

For the systems in which the surfactant partitioning is influenced greatly by the change in the variables such as brine salinity and oil chain length, the phase inversion occurs at a specific point where the middle-phase volume becomes zero. The transition from water-external microemulsion to oil-external microemulsion is induced by the increasing surfactant partitioning in the oil phase. At the phase inversion point, the partition coefficient, defined as the ratio of the surfactant concentrations in oil and the remaining phase, is unity for the two effects studied, namely, the effect of brine salinity and the effect of oil chain length. The partition coefficient of surfactant between oil and excess brine phase is also unity at the optimal salinity.

The nature of the phase inversion point is still unconfirmed. The light scattering turbidity data obtained from the study of the effect of brine salinity seems to be suggesting that the phase inversion point is a thermodynamic critical point. The confirmation of this possibility would provide a better approach to predict theoretically the phase inversion phenomenon of the surfactant-oil-brine system.

PSEUDO-PHASE INVERSION BY SOLUBILIZATION OF OIL

The investigation of the possibility that the solubilization of all the oil phase gives an apparent phase inversion was conducted on two major effects, namely, the effect of surfactant concentration and the effect of surfactant solution/oil ratio. The system used in this study was 5% TRS 10-410, 3% IBA, and 1.5% NaCl solution, with dodecane as oil. The phase behavior and interfacial tension of the system were studied. The electrical resistivity of the surfactant-rich phase was measured. The equilibrated phase volume fraction of the system 5/3 TRS 10-410/IBA in 1.5% NaCl solution with equal volume of dodecane as a function of surfactant concentration is shown in Fig. 19. The middle phase started to separate from the aqueous phase at 0.5% TRS 10-410 concentration and the high turbidity was observed in the excess brine phase as well as middle phase. The turbidity of both phases decreases quickly when the surfactant concentration increased from 0.5% to 2.25% TRS 10-410 concentration. At about 2.25% TRS 10-410 concentration, the middle phase became well separated and compressed from the aqueous phase. Beyond this concentration, the middle volume increased with the increase of surfactant concentration. At 15% TRS 10-410 concentration, the excess oil phase ceases to exist. Thus, the middle phase is observed between 2.25% to 15% TRS 10-410 concentration.

Electrical resistivity of the surfactant-rich phase for the entire range of surfactant concentration studied was measured. It was observed that the electrical resistivity increases with the increase of the amount of oil solubilized in the surfactant-rich phase. But the resistivity values remain low even when the surfactant-rich phase is an upper phase with all the oil solubilized. The upper-phase microemulsion range begins from 15% TRS 10-410 concentration. But the resistivity increases slightly to a low value of about 15 ohm-m. There is no drastic increase in the electrical resistivity at around 15% TRS 10-410 concentration, suggesting a lack of phase inversion. These results suggest that the commonly accepted notion that upper-phase microemulsions are always oil-external is not necessarily correct. In many instances, the upper-phase microemulsions can be identical to middle-phase microemulsions, which we believe to be water-external type.

The distribution of surfactant molecules in each phase is shown in Fig. 20. As the total surfactant concentration increases, the surfactant concentrations in oil and the remaining phases (taking middle phase and brine phase as a whole) increases proportionally. There is no drastic increase in the surfactant concentration of the oil phase near 15% TRS 10-410 concentration, where the surfactant-rich phase changes from middle phase to upper phase. The surfactant concentration

curves for oil phase and the remaining phase (middle phase plus brine phase) can never intersect at 15% TRS 10–410. According to the conclusion made in the previous section, these two surfactant partitioning behaviors suggest that there is no phase inversion taking place at the phase transition point of 15% TRS 10–410 concentration.

The surfactant concentration in excess brine phase also was determined for the entire range of middle-phase microemulsion. It can be seen from Fig. 20 that the surfactant concentrations in excess oil and brine are equal at 4.0% TRS 10–410 concentration that has been determined from phase behavior as well as interfacial tensions for the system. Therefore, if the partition coefficient is defined as the ratio of surfactant concentration in excess oil to that in excess brine, the partition coefficient is unity at the optimal surfactant concentration.

The transition of surfactant-rich phase from lower phase through middle phase to upper phase can be observed clearly in a system in which the relative volumes of surfactant solution and oil before mixing are varied. Surfactant solution containing 5% TRS 10–410 and 3% IBA in 1.5% NaCl solution was prepared first. This solution then was equilibrated with dodecane in different volume ratios ranging from 0.111 to 9. A surfactant solution/oil ratio of 0.111 means that 10 ml of surfactant solution is to be equilibrated with 90 ml of dodecane. The ratio of 9 is just the other way around, having 90 ml of surfactant solution for 10 ml of oil. Therefore, as this ratio increases, the relative volume of brine and the total surfactant concentration increase simultaneously. Thus, this effect is indeed the superposition of the two effects, namely, the effect of brine/oil ratio and the effect of surfactant concentration, which was studied in the previous section.

The volume fraction of each phase in equilibrium as a function of surfactant solution/oil ratio is shown in Fig. 21. The middle phase appears at a ratio of 0.43 (3/7) and gradually disappears at the ratio of 9.

It is interesting that beyond the ratio of unity, the volume of oil solubilized per unit volume of surfactant, V_o/V_s, remains very much the same. It is due to the decrease in the total volume of oil as well as the increase in the total amount of surfactant that the surfactant-rich phase gradually solubilized all the oil in the system. This gives the illusion of the surfactant-rich phase transition from middle phase to upper phase. Since the salinity of the brine and the oil chain length, as well as the temperature are fixed, there is driving force for phase inversion in this system. This is confirmed by the electrical resistivity data. The electrical resistivity increases from 1.8 to 2.5 ohm-m for the entire range studied. Taking the fluctuation of the experimental data into account, one can draw the conclusion that the surfactant-rich phase always maintains a low value at around 2.2 ohm-m, which suggests obviously that the microstructure of the surfactant-rich phase is unchanged. The low electrical resistivity of the microemulsion phase also suggests that the external phase is water.

The absence of the phase inversion is supported by the surfactant partition data shown in Fig. 22. The surfactant concentration in oil increases because the total surfactant concentration of the system increases. For the entire range of surfactant solution/oil ratio (upper limit at 10), the surfactant concentration in oil curve cannot intersect the curve for the remaining phases (brine and middle phase combined). This suggests that no phase inversion occurs in this system.

The solubilization parameters V_o/V_s and V_w/V_s define an optimal ratio at 1.4 where the two parameters are numerically equal. It is interesting to see from Fig. 22 that at this optimal surfactant solution/oil ratio, the surfactant concentration in oil and surfactant concentration in excess brine phase are nearly equal. Thus, if we again define the surfactant partition coefficient as the ratio of the surfactant concentration in oil to the surfactant concentration in excess brine, the partition coefficient is near unity at the optimal surfactant solution/oil ratio.

We have shown[11,14] that partition coefficient of unity for surfactant is very important in both low as well as high surfactant concentration systems. In low concentration petroleum sulfonate systems, the minimum in interfacial tension, surface tension, and maximum in surface charge density correspond to partition coefficient unity. In high surfactant concentration systems, the optimal parameter and phase inversion parameter correspond to partition coefficient of unity for the surfactant. Our related studies on the interfacial tension, surface charge density, microstructure, high salinity formulations, and oil displacement efficiency have been reported elsewhere.[19-32] The studies on coalescence of oil drops, formation of oil bank and liquid crystalline structures,[33-34] and electron microscopy of microemulsions and equilibrium bicontinuous structures[35-36] have been reported by other investigators. Interfacial tension behavior of dilute petroleum sulfonates have been reported by Cayias et al.[37] and Cash et al.[38]

SUMMARY AND CONCLUSIONS

From the study of the surfactant-rich phase transition (from the middle phase to the upper phase) of the multiphase surfactant-oil-brine systems, the following general conclusions can be drawn.

1. For all the systems studied, the surfactant partition coefficient between oil and excess brine phase is unity at the optimal parameter value (optimal salinity, optimal surfactant concentration, etc.) defined by the equal solubilization of oil and water, as well as the equal interfacial tension at the two interfaces in the three-phase region.

2. For systems in which the parameters controlling the surfactant partitioning between oil and brine phase are changing, phase inversion occurs in a very narrow region near the transition point. In the study of the effect of brine salinity, the partition coefficient for phase inversion was unity at the phase inversion salinity. For the effect of oil chain length, this partition

coefficient was found to be near unity. The existence of phase inversion always is marked by a sudden increase of the electrical resistivity as well as the drastic increase of the surfactant concentration in oil.

3. For the effect of salinity, the middle-phase volume decreases with the increase of salinity in the phase inversion region. The phase inversion salinity can be determined as the salinity at which the middle-phase volume is zero. This decrease of the middle-phase volume should be observed in the study of the effect of oil chain length, if the chain length of oil can be increased in decimal fraction near the phase transition region. The rate of the decrease of the middle-phase volume is extremely fast for the pure surfactant (or surfactant with narrow equivalent weight distribution) systems and is slow if the surfactant of a broad equivalent weight distribution is used.

4. For the studies on the effect of surfactant concentration and the effect of surfactant solution/oil ratio on the phase transition of surfactant-rich phase, no actual phase inversion (water-external to oil-external, or vice versa, of the surfactant-rich phase microemulsion) was observed. The complete solubilization of oil in the aqueous phase that separates into a surfactant-rich phase in equilibrium with an excess brine phase gives an apparent phase inversion behavior. The partition coefficient defined for the determination of phase inversion cannot be unity in these systems.

5. For the four effects studied in this paper (namely, the effect of surfactant concentration, the effect of surfactant solution/oil ratio, the effect of salinity, the effect of oil chain length) the phase transition mechanisms were identified as either due to the complete solubilization of oil and the coacervation of oil-swollen micelles or due to the partitioning of surfactant molecules in the oil phase.

ACKNOWLEDGMENT

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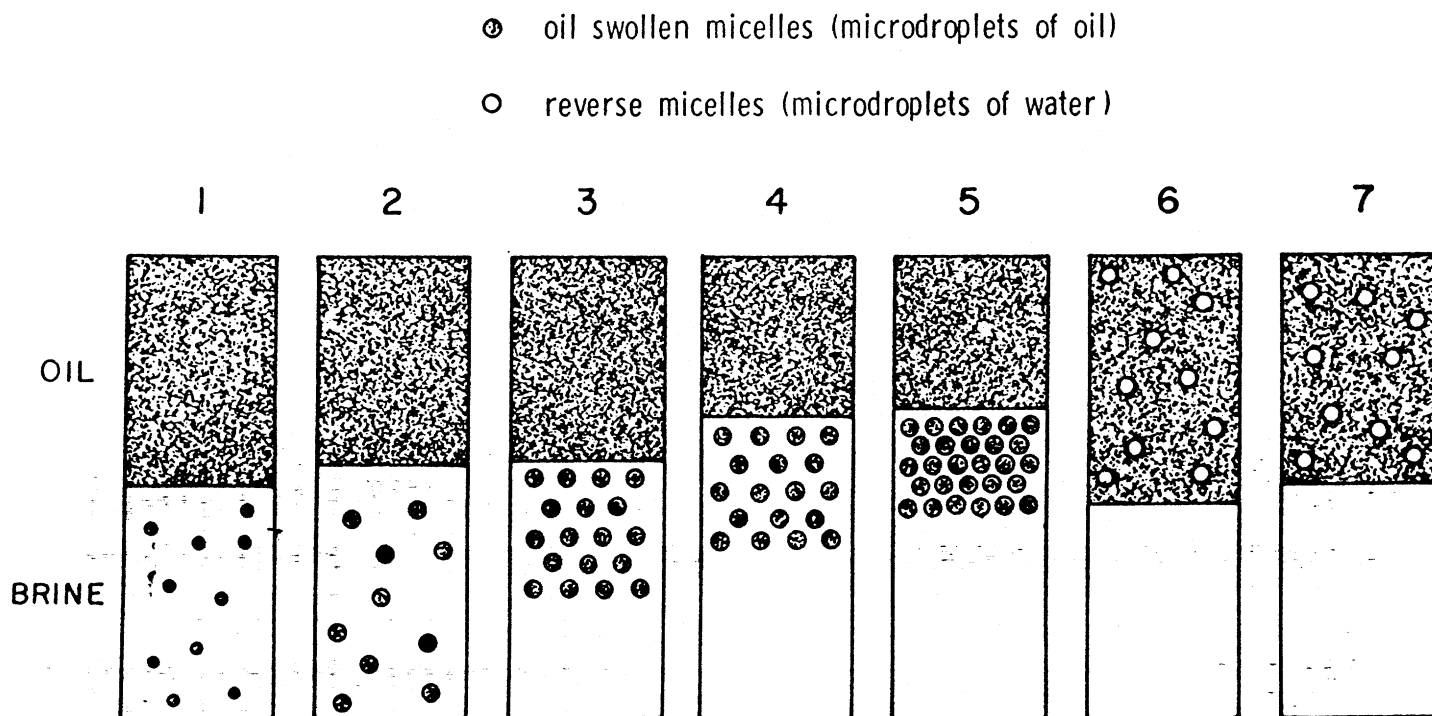
Fig. 1 - Schematic representation of the effect of salinity on the behavior of TRS 10-410 + isobutanol + oil + brine system. Cylinders 3, 4 and 5 show that water in the middle phase microemulsion is structurally continuous with excess brine whereas the oil in the middle phase is discontinuous from the excess oil.
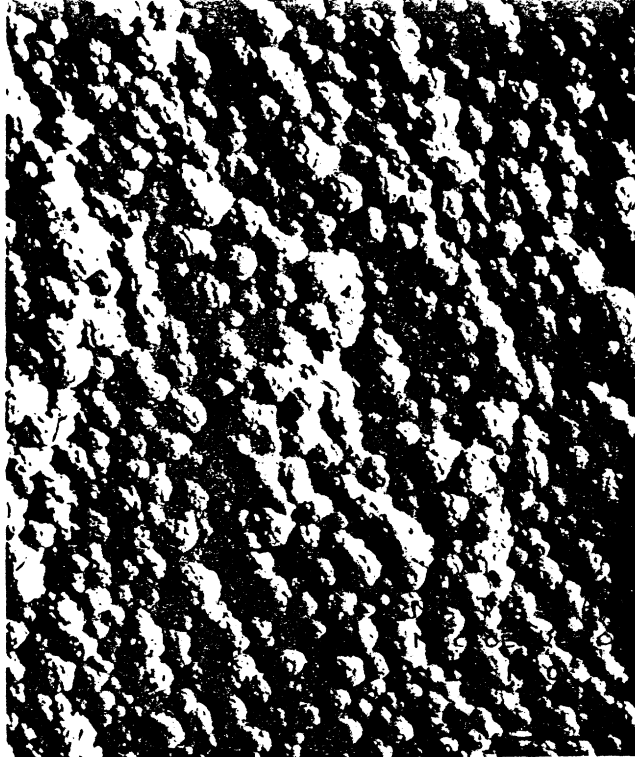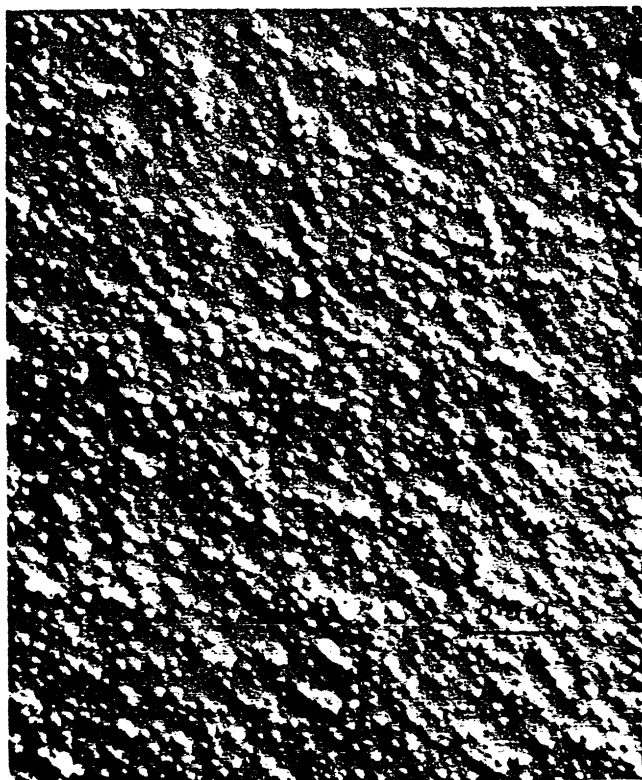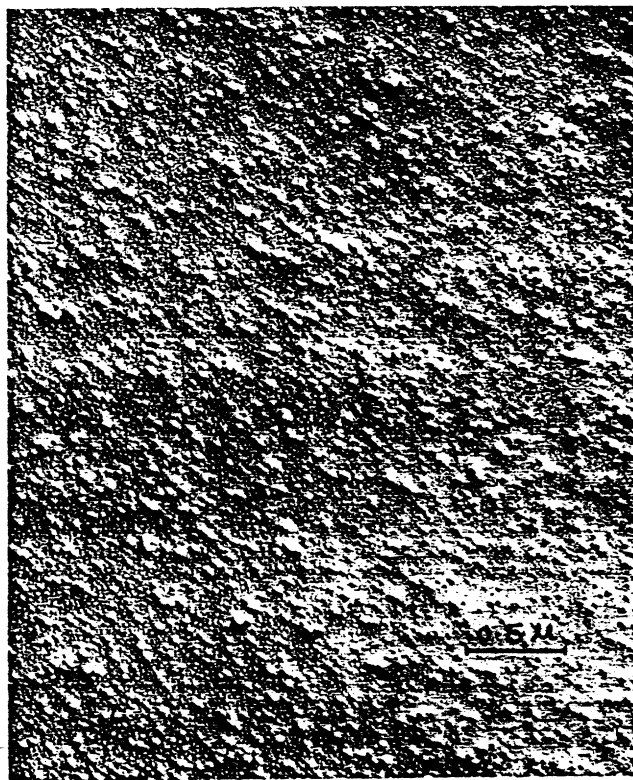
Fig. 2 - Freeze-fracture electronmicrograph of a middle phase micro-emulsion in the Exxon system [4% emulsifier (MEAC120XS/TAA::63/37) + 48% oil (ISOPAR M/HAN::90/10) + 48% brine (1% NaCl) in D_2O]. The bar represents 0.5.
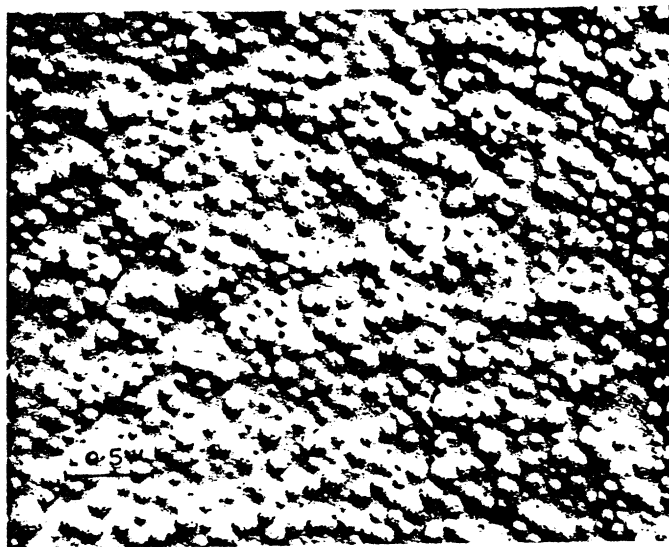

Fig. 3 - Freeze-fracture electronmicrograph of a middle phase microemul-sion in the Exxon system [4% emulsifier (MEAC120XS/TAA::63/37) + 48% oil (ISOPAR M/HAN::90/10) + 48% brine (1.2% NaCl) in D_2O]. The bar repre-sents 0.5.

Fig. 4 - Freeze-fracture electronimicrograph of a middle phase micro-emulsion in the Exxon system [4% emulsifier (MEAC120XS/TAA::63/37) + 48% oil (ISOPAR M/HAN::90/10) + 48% brine (1.6% NaCl) in D_2O]. The bar represents 0.5.

Fig. 5 - Freeze-fracture electronmicrograph of a middle phase micro-emulsion in the Exxon system [4% emulsifier (MEAC120XS/TAA::63/37) + 48% oil (ISOPAR M/HAN::90/10) + 48% brine (1.6% NaCl) in D_2O]. The bar represents 0.5.
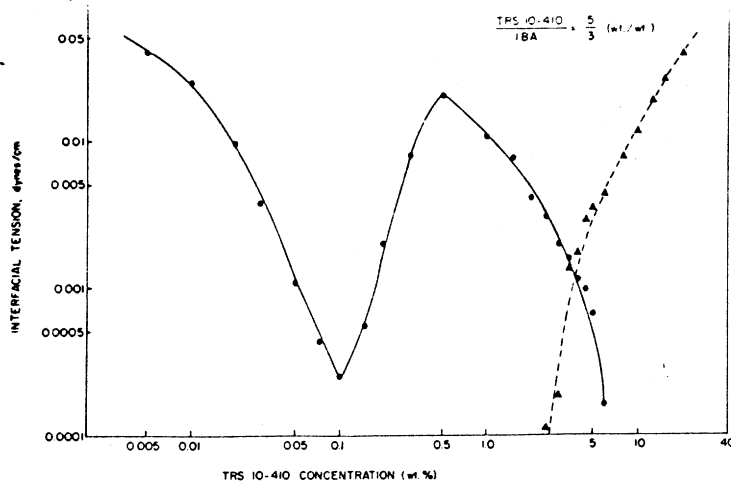
Fig. 6 - Effect of surfactant + alcohol concentration on interfacial tension of TRS 10-410 + IBA in 1.5% NaCl solution against dodecane. The first minimum at 0.1% concentration is a two-phase system whereas the second minimum at 4.5% concentration is a three-phase system.
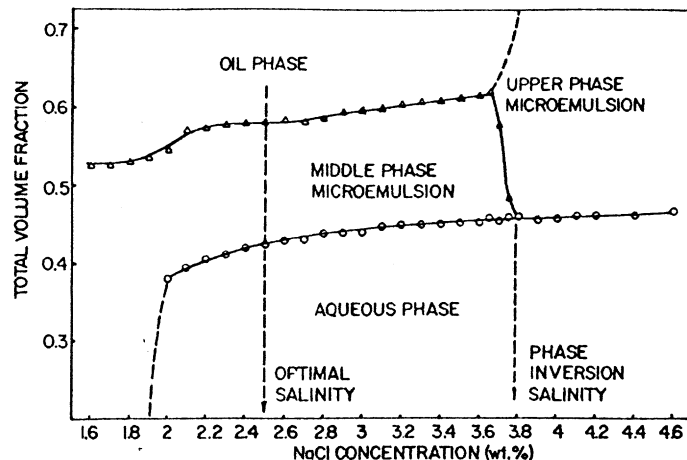
Fig. 7 - Phase behavior of 5% TRS 10-410 + 3% IBA with brine and hexadecane. The middle phase volume decreases abruptly around 3.8% NaCl.
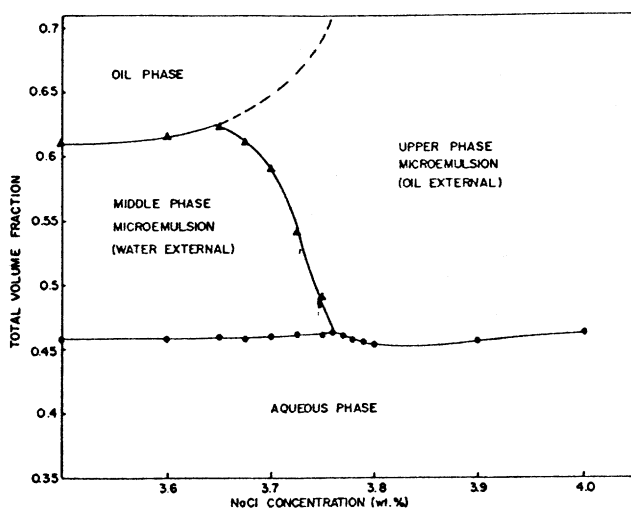
Fig. 8 - A more detailed phase behavior of 5% TRS 10-410 + 3% IBA with brine and hexadecane near the phase inversion point (i.e. the surfactant migration from the middle to upper phase). The middle phase volume decreases abruptly between 3.7% and 3.8% NaCl concentration.
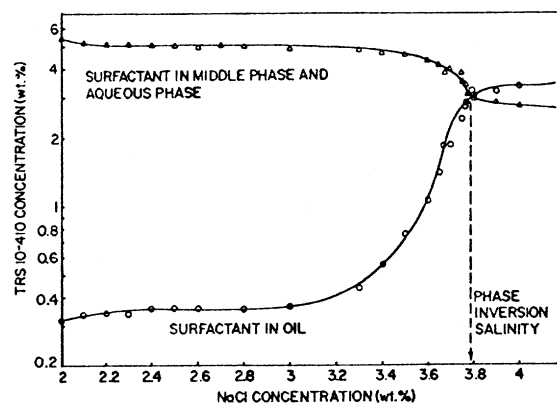
Fig. 9 - Partitioning of surfactant in oil and in the middle + excess brine phase. The partition coefficient is near unity around 3.8% NaCl.
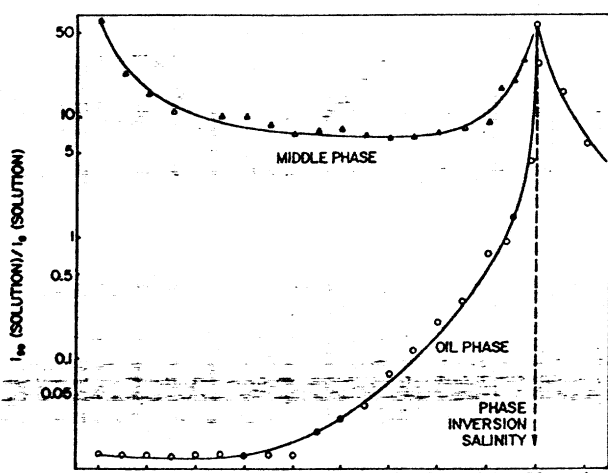
Fig. 10 - Light scattering measurements for the middle phase microemulsion and oil phase at various salinities. The scattered light intensity approach each other at phase inversion salinity.
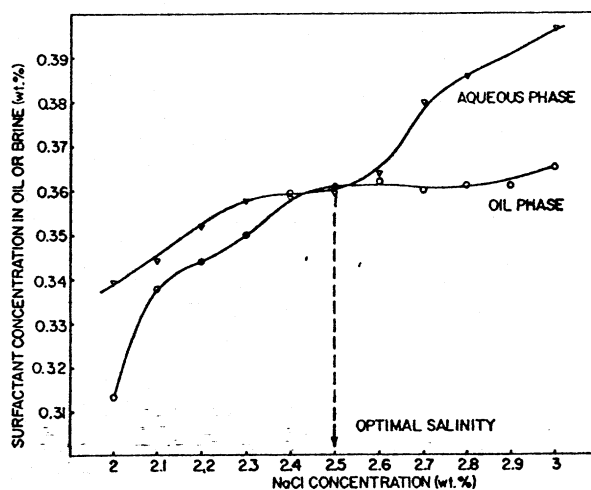
Fig. 11 - Surfactant concentration in excess oil and excess brine phase in the 5% TRS 10-410 + 3% IBA + hexadecane + brine systems. The partition coefficient is near unity at 2.5%-NaCl.
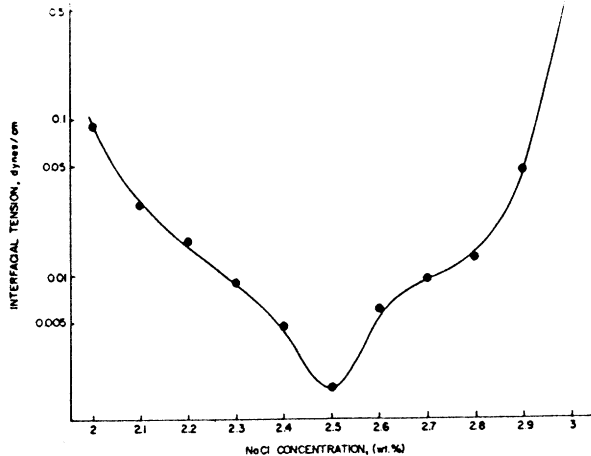
Fig. 12 - Interfacial tension between excess oil and excess brine in three-phase region in 5% TRS 10-410 + 3% IBA + hexadecane + brine systems. The minimum interfacial tension occurs at optimal salinity.
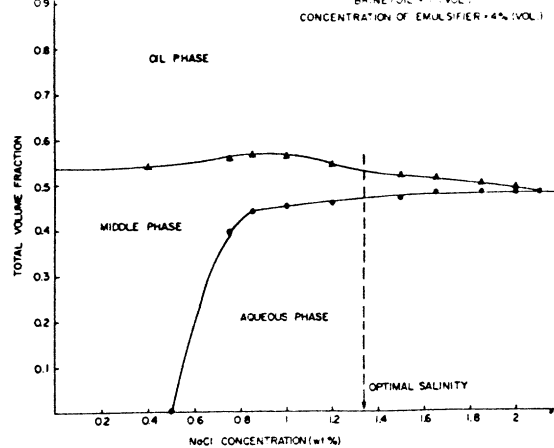

Fig. 13 - Phase behavior of 2% Petrostep 465 + 2% alcohol (IBA:n-Pa = 1:1 wt.) + dodecane + brine systems. A gradual decrease in the volume of the middle phase microemulsion is evident.
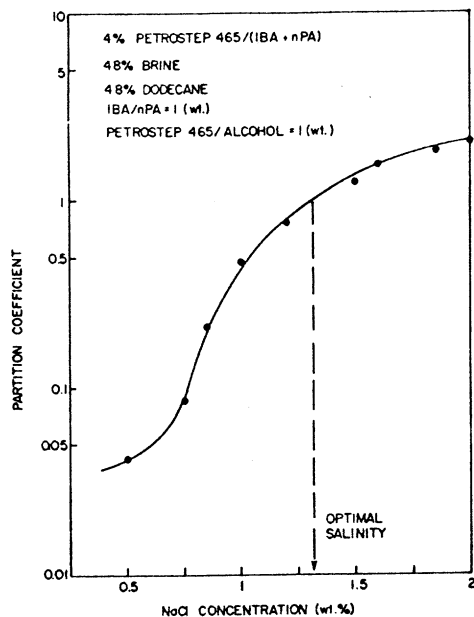

4% PETROSTEP 465/(IBA + nPA)
48% BRINE
48% DODECANE
IBA/nPA = I (wt.)
PETROSTEP 465/ALCOHOL = I (wt.)

Fig. 14 - Partition coefficient of Petrostep 465 in excess oil and excess brine phase. The partition coefficient unity occurs at the optimal salinity.

4% PETROSTEP 465/(IBA+nPA)
48% BRINE
48% DODECANE
IBA/nPA = I (wt.)
PETROSTEP 465/ALCOHOL = I (wt.)
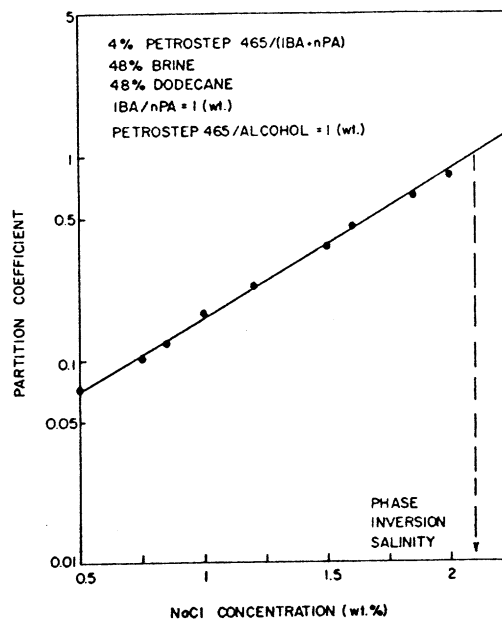
Fig. 15 - Partition coefficient of Petrostep 465 in excess oil and in the middle + Excess brine phase. The partition coefficient is near unity at phase-inversion salinity.
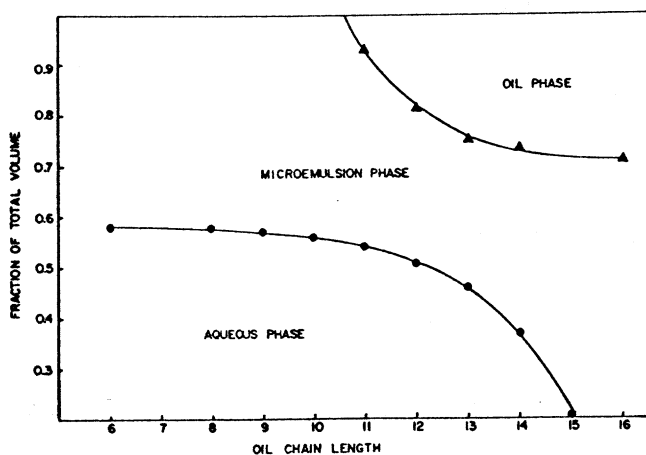
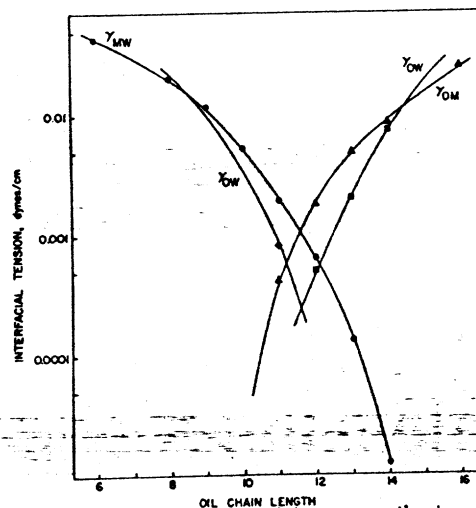Fig. 16 - Phase behavior of 5% TRS 10-410 + 3% IBA in 1.5% NaCl solution with oils of various chain length.

Fig. 17 - Interfacial tension, γ_{OW}, between excess oil and excess brine in three-phase systems and γ_{MW} and γ_{OM} for interfacial tension between microemulsion/brine and microemulsion/oil interfaces. The system is 5% TRS 10-410 + 3% IBA in 1.5% NaCl solution with oils of various chain length.
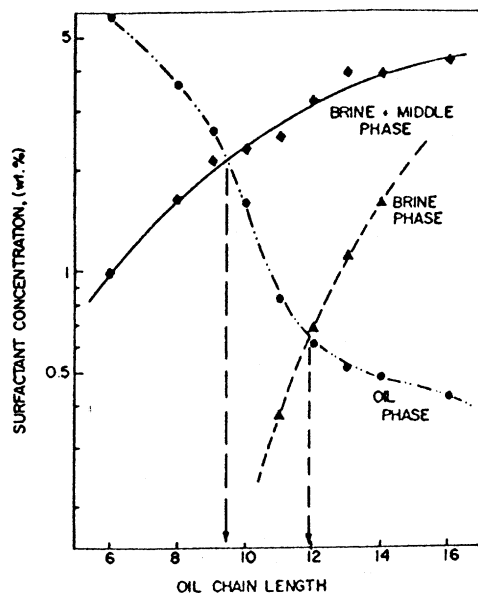
Fig. 18 - Surfactant concentration in excess oil, excess brine and the middle phase + excess brine for the system 5% TRS 10-410 + 3% IBA in 1.5% NaCl with oils of various chain length.1 The optimal chain length is around c_{12} whereas the phase inversion chain length is around $c_{9.5}$.
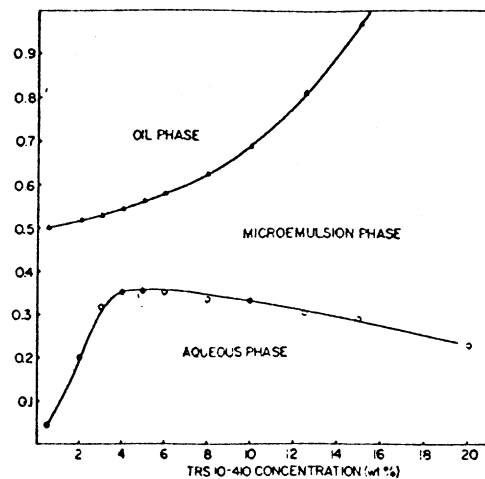

Fig. 19 - Effect of surfactant concentration on phase behavior of 5% TRS 10-410 + 3% IBA in 1.5% NaCl solution with dodecane.
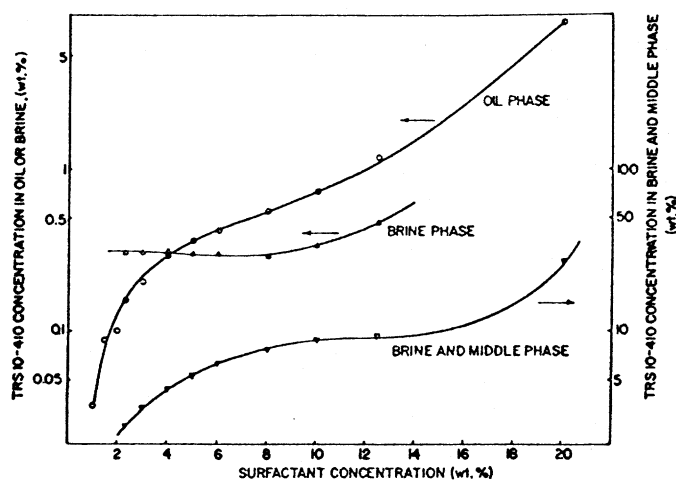

Fig. 20 - Surfactant concentration in excess oil, excess brine and the middle phase + excess brine for the system 5% TRS 10-410 + 3% IBA in 1.5% NaCl with dodecane as a function of total surfactant concentration.
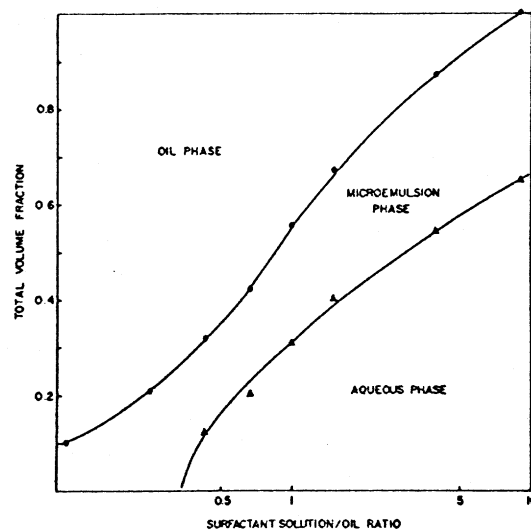

Fig. 21 - Phase behavior of 5% TRS 10-410 + 3% IBA in 1.5% NaCl solution in contact with dodecane as a function of total surfactant solution/oil ratio.
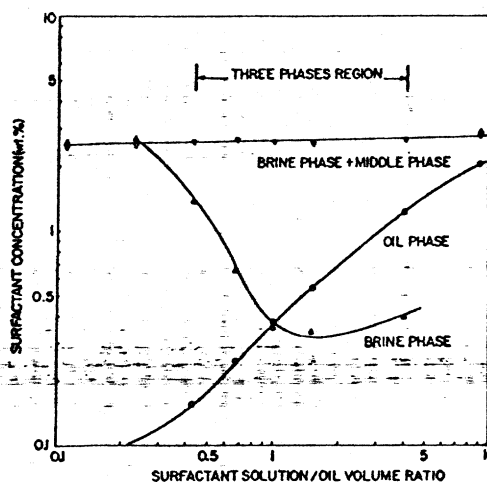

Fig. 22 - Surfactant concentration in excess oil, excess brine and the middle phase + excess brine for the system 5% TRS 10-410 + 3% IBA in 1.5% NaCl solution with dodecane as a function of surfactant solution/oil ratio.