In "Surface Phenomena in Enhanced Oil Recovery", editor, D.O. Shah, Plenum Press, New York, NY, pp. 53-72, 1981.

THE PHYSICO-CHEMICAL CONDITIONS NECESSARY TO PRODUCE ULTRALOW INTERFACIAL TENSION AT THE OIL/BRINE INTERFACE

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In a petroleum sulfonate/isobutanol/dodecane/brine system, there are two regions of ultralow interfacial tension (IFT), one at low surfactant concentrations (0.1-0.2%) and the other at higher surfactant concentrations (4 to 10%). In the low concentration range, the oil/brine/surfactant/alcohol system is a two-phase system, whereas at high surfactant concentrations, it becomes a three-phase system in which a middle phase microemulsion is in equilibrium with excess brine and oil. For low surfactant concentration systems, we have shown that the ultralow IFT minimum corresponds to the onset of micellization and partition coefficient of surfactant near unity. This correlation was observed for the effect of surfactant concentration, salt concentration and oil chain length on the interfacial tension. The minimum in interfacial tension corresponds to a maximum electrophoretic mobility of oil droplets. This correlation was also observed for the effect of caustic on several crude oils.

In high surfactant concentration systems, a middle phase microemulsion forms in equilibrium with excess oil and brine in a given salinity range. The middle phase microemulsion contains equal volumes of oil and brine and practically all of the surfactant at a specific salinity defined as the optimal salinity of the given system. The interfacial tension of the two interfaces, middle phase/brine and middle phase/oil, depends on the extent of solubilization of oil and brine in the middle phase microemulsion. The higher the solubilization of oil and brine in the middle phase, the lower is the interfacial tension at both these interfaces. We have shown that the optimal salinity increases with the oil chain length for a given surfactant system. The optimal salinity decreases with an increase in the alcohol chain length. As the oil chain length increases the solubilization of oil and brine in the middle phase microemulsion at the optimal salinity decreases. The formation of middle phase microemulsions appears to be similar to coacervation phenomenon and quite different from the solubilization of brine in oil external microemulsions. The $\ell \rightarrow m \rightarrow u$ transition can be achieved by changing one of the following variables: Salinity, Temperature, Alcohol Chain Length, Oil Chain Length, Oil/Brine Ratio, Surfactant Concentration, Surfactant Solution/Oil Ratio, and the Molecular Weight of Surfactant.

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INTRODUCTION

It is well recognized that the two major forces acting on an entrapped oil ganglion in the reservoir pore structure are viscous forces and capillary forces. Melrose and Brandner (1) have shown that the capillary number must be increased from 10^{-6} to 10^{-2} for mobilization of entrapped oil ganglia in order to improve the microscopic displacement efficiency. Under practical reservoir conditions, this change can be brought about by decreasing the interfacial tension from about 20 dynes to 10^{-3} dynes/cm. It has been shown by several investigators (2-7) that using a suitable surfactant system, an ultralow interfacial tension can be achieved at the oil/brine interface. At low surfactant concentrations, the oil/brine/surfactant/alcohol systems form two phases whereas often at high surfactant concentrations, middle phase microemulsions form in equilibrium with excess oil and brine (8,9). The interfacial tension of the middle phase microemulsion with excess oil or excess brine depends upon the magnitude of solubilization of oil and brine in the middle phase. The higher the solubilization of oil and brine in the middle phase, the lower is the interfacial tension. The salinity at which the middle phase microemulsion contains equal volumes of oil and brine is defined as the optimal salinity. The oil recovery is found to be maximum at or near the optimal salinity (8,10). At optimal salinity, the phase separation time or coalescence time of emulsions and the apparent viscosity of these emulsions in porous media are found to be minimum (11,12). Therefore, it appears that upon increasing the salinity, the surfactant migrates from the lower phase to middle phase to upper phase in an oil/brine/surfactant/alcohol system. The $\ell \rightarrow m \rightarrow u$ transition can be achieved by also changing any of the following variables: Temperature, Alcohol Chain Length, Oil/Brine Ratio, Surfactant Solution/Oil Ratio, Surfactant Concentration and Molecular Weight of Surfactant. The present paper summarizes our extensive studies on the low and high surfactant concentration systems and related phenomena necessary to achieve ultralow interfacial tension in oil/brine/surfactant/alcohol systems.

EXPERIMENTAL

The petroleum sulfonates TRS 10-80 (≈ 80% active) and TRS 10-410 (≈ 60% active) were supplied by Witco Chemicals Company. The average equivalent weight of these surfactants was 420. Alkyl nonophosphate ester, Klearfac AA-270 (≈ 90% active) was supplied by BASF-Wyandotte Corporation. Paraffinic oils and short chain alcohols of > 99% purity were purchased from Chemical Samples Company. All chemicals were used as received. Aqueous solutions of surfactants were prepared on weight basis.

Low surfactant concentration systems: The systems were equilibrated by taking two-thirds aqueous solution and one-third oil by volume in 250 ml separatory funnels maintained at 25°C. After shaking vigorously for about 30 minutes using a mechanical shaker, the solutions were allowed to stand for about 3 to 6 weeks until clear interfaces were obtained. The equilibrated oil and aqueous phases were then separated from the top and bottom of the funnel respectively for various physico-chemical measurements.

For mixed surfactant systems, the effect of Klearfac AA-270 on the interfacial tension was studied by gradually replacing TRS 10-410 with Klearfac AA-270 and keeping the total surfactant concentration at 0.2%.

Interfacial tensions between the equilibrated oil and aqueous phases were measured by a spinning drop tensiometer using the method described by Schechter and co-workers (2,3,5). Each drop of oil was spun until a constant interfacial tension was reached. The temperature was maintained at 25 ± 1°C.

High surfactant concentration systems: The petroleum sulfonate and alcohol of given quantities were dissolved in equal volumes of oil and brine. The system was shaken vigorously and was rotated on a slow rotor for several days and was then allowed to stand until the phase volumes did not show any change with time. The surfactant concentration was determined by two-phase dye-titration or UV-absorbance measurements.

RESULTS AND DISCUSSION

The effect of surfactant concentration on interfacial tension in the TRS 10-410/IBA/Dodecane/Brine system is shown in Figure 1. It is evident that there are two regions in which ultralow interfacial tension is observed, i.e., in the low concentration region around 0.1% and the other around 4% surfactant concentration. In the low concentration region, the system forms two phases, namely, oil and brine whereas in the high concentration region the middle phase microemulsion is in equilibrium with excess oil and brine

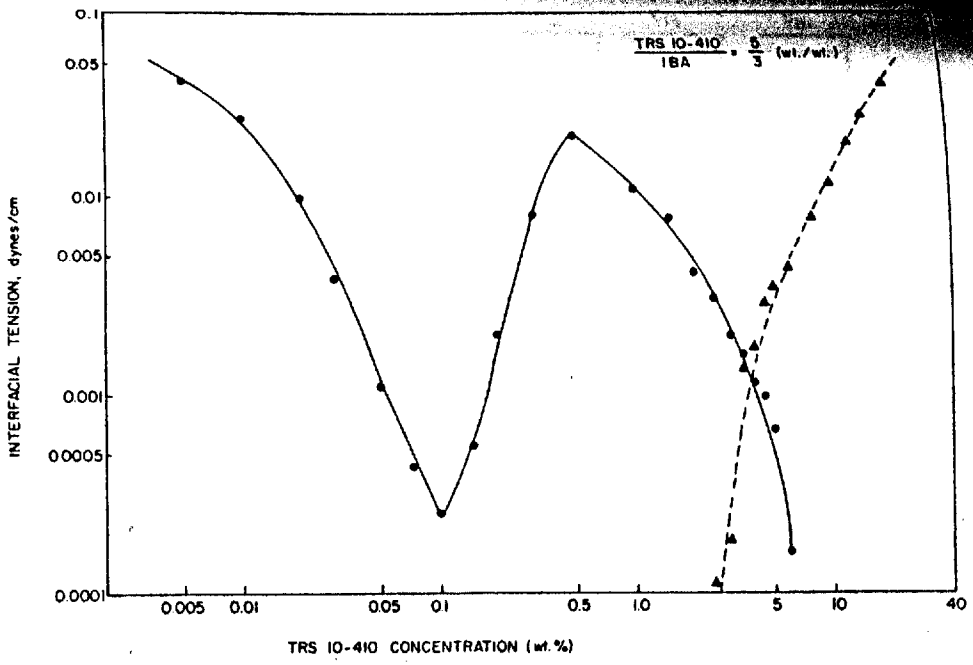

Fig. 1. Effect of surfactant concentration on interfacial tension of TRS 10-410 + IBA in 1.5% NaCl solution with dodecane.

(13). First, we will discuss the molecular mechanism responsible for the ultralow interfacial tension in the low concentration region and, subsequently, we shall discuss the phenomena related to the three-phase system.

Figure 2 summarizes the effect of NaCl concentration, oil chain length and surfactant concentration on the interfacial tension in this system. It is evident that ultralow interfacial tension minimum occurs at a specific salinity or specific oil chain length or specific surfactant concentration. Using light scattering, osmotic pressure, surface tension, dye solubilization and various other techniques, we have shown that the ultralow interfacial tension minimum in this system correlates with the onset of micellization in the aqueous phase and the partition coefficient of surfactant near unity (14). Baviere (15) has also shown that the partition coefficient is near unity at the salinity where minimum interfacial tension occurs.

Figure 3 schematically illustrates the effect of NaCl concentration on the partitioning of surfactant molecules in an oil/brine system. At low salinities, most of the surfactant molecules are found in the brine phase whereas at very high salinities, most of the surfactant molecules are found in the oil phase. Hence, as the

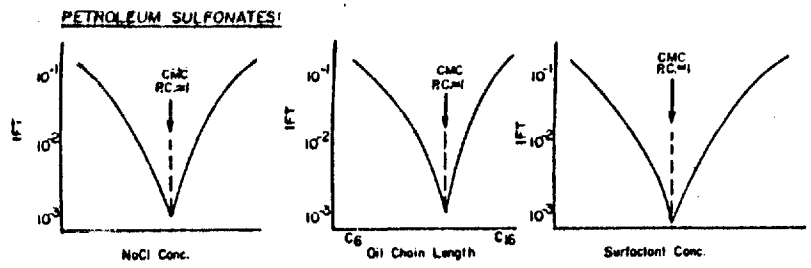

Fig. 2. The effect of salt concentration, oil chain length and surfactant concentration on interfacial tension.

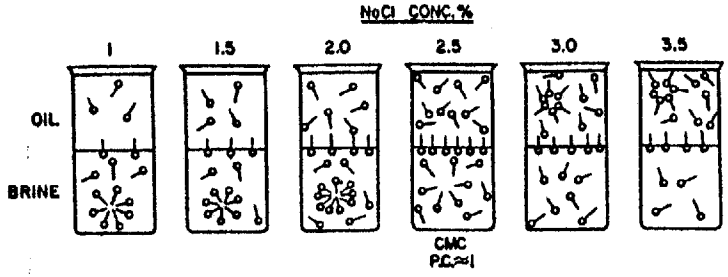

Fig. 3. The effect of salt concentration on the partitioning of surfactant and micelle formation.

salinity is increased, the surfactant molecules gradually migrate from the aqueous to the oil phase. At a specific salinity, the surfactant concentration in the oil and aqueous phase becomes equal leading to the partition coefficient of unity. Also there will be a specific salinity at which the surfactant concentration in the aqueous phase reaches the value of the 'apparent cmc'. We are using the words apparent cmc because the micellization in this case occurs in the presence of dissolved oil and salt and hence it is likely to be different from the cmc of the same surfactant in pure water without oil. In the system studied in this paper, both the apparent cmc and the partition coefficient near unity occurred at the same salinity. However, we have found (16) that in other systems, this may occur at different salinities. Thus, it appears that the minimum in ultralow IFT corresponds to the onset of micellization rather than to the partition coefficient of unity.

The effect of oil chain length on the partition coefficient of surfactant in the oil/brine system is explained in Figure 4. We have shown (14) that as the oil chain length is increased, the partitioning of the surfactant in the oil phase decreases and consequently the surfactant concentration in brine increases. Therefore, at a specific oil chain length, surfactant concentration becomes equal in both the oil and the brine phase. Similarly, at a specific oil chain length, the surfactant concentration in the aqueous phase reaches the value of the apparent cmc. Therefore, on the left hand side of the critical oil chain length (Figure 4), the aqueous phase has no micelles whereas on the right hand side of the critical oil chain length, the micelles are present in the aqueous phase. In the present system, both the onset of micellization and the partition coefficient near unity occur at the same oil chain length. Our light scattering results (14) also confirm that the micelles begin to form at the same chain length where the minimum IFT is observed.

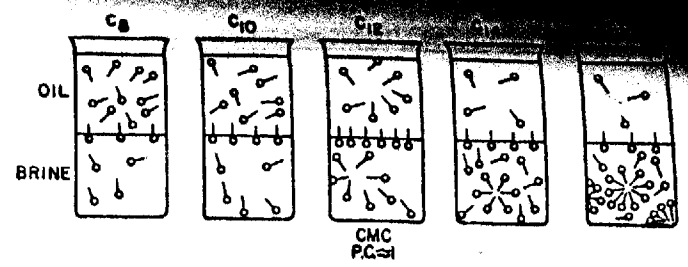

Fig. 4. The effect of oil chain length on the partitioning of surfactant and micelle formation.

Figure 5 schematically illustrates the effect of surfactant concentration on partitioning of the surfactant and micellization phenomena. One can consider that the petroleum sulfonate is having both oil soluble and water soluble species. At very low surfactant concentrations (e.g., C_1), water soluble species will remain in brine and the oil soluble species will partition into oil. At the oil/brine interface both these species can be adsorbed. However, as the surfactant concentration is increased, the concentration of oil soluble species in oil and water soluble species in brine increases. At a specific concentration (e.g., C_3), the water soluble species can reach to its cmc and begin to form micelles. Above this critical concentration, the oil soluble species can remain in the micelles. In other words, once the water soluble species begin to form micelles in the aqueous phase, the oil soluble species can either solubilize in micelles or partition into oil. The solubilization of the oil soluble species in the micelles decreases the apparent cmc and hence the surfactant monomer concentration. The reduction in monomer concentration results in the decrease of surface concentration of the water soluble species and hence the interfacial tension increases. The more oil soluble species dissolve into the micelles, the greater is the decrease in the apparent cmc and hence the corresponding decrease in the monomer concentration resulting in the increase in interfacial tension. The explanation as shown in Figure 5 explains the

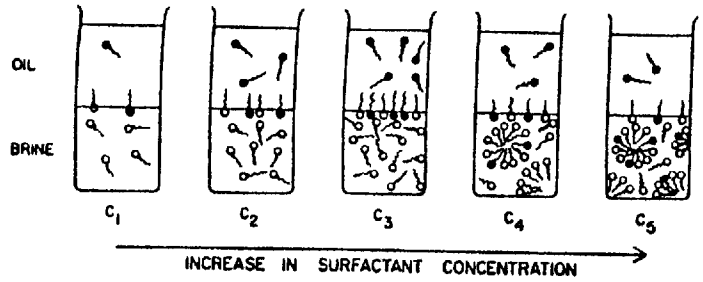

Fig. 5. The molecular mechanism for the effect of surfactant concentration on interfacial and surface tensions.

effect of surfactant concentration on interfacial tension in the systems studied in this paper.

Figure 6 shows the effect of surfactant concentration on interfacial tension and electrophoretic mobility of oil droplets (14). It is evident that the minimum in interfacial tension corresponds to a maximum in electrophoretic mobility and hence in zeta potential at the oil/brine interface. Similar to the electrocapillary effect observed in mercury/water systems, we believe that the high surface charge density at the oil/brine interface also contributes to lowering of the interfacial tension. This correlation was also observed for the effect of caustic concentration on the interfacial tension of several crude oils (Figure 7). Here also, the minimum interfacial tension and the maximum electrophoretic mobility occurred in the same range of caustic concentration (17). Similar correlation for the effect of salt concentration on the interfacial tension and electrophoretic mobility of a crude oil was also observed (18). Thus, we believe that surface charge density at the oil/brine interface is an important component of the ultralow interfacial tension.

An overview of several variables that influence the interfacial tension and the important processes that occur in oil/brine/surfactant systems, namely, the partitioning of the surfactant and the effective cmc or monomer concentration of the surfactant are shown in Figure 8. These two processes will determine the three major components of the interfacial tension, namely, surface concentration of the surfactant, surface charge density and solubilization of oil or brine in each other. Hence, as shown in Figure 9, the magnitude of interfacial tension can be adjusted by changing any of these three variables. The surface concentration is the major variable, then surface charge density and then solubilization of oil or brine. By adjusting these variables, one can push the system to ultralow interfacial tension. Using this concept, we were able to decrease the interfacial tension by increasing the surface charge density upon the addition of alkyl monophosphate esters in this system.

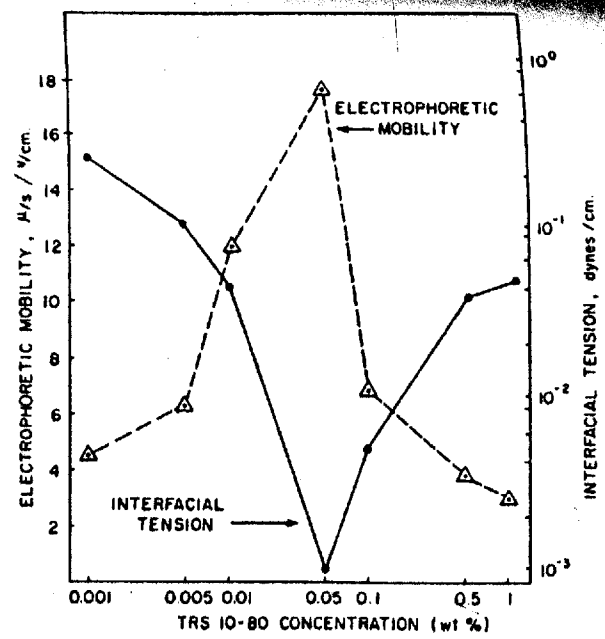

Fig. 6. The effect of TRS 10-80 concentration on interfacial tension and electrophoretic mobility of n-octane droplets in surfactant solutions, Temp. ≈ 28°C.

Figure 10 shows the interfacial tension of an oil/brine system by a mixture of petroleum sulfonate (TRS 10-410) and alkyl monophosphate ester (Klearfac AA-270). As the proportion of phosphate ester increases, the magnitude of interfacial tension decreases and there is a considerable broadening of the interfacial tension minimum. Moreover, the minimum shifts to a higher salinity. We explained this on the basis of the number of anionic atoms per polar group. In the petroleum sulfonate, there is one negatively charged oxygen per sulfonate group whereas in the phosphate group, there are two negatively charged oxygens per polar group. Therefore, as shown in Figure 11, the mixed micelles of the petroleum sulfonate and the alkyl monophosphate esters will have a greater surface charge density at the micelle surface as well as at the oil/brine interface. We believe that these results support our conclusion that the surface charge density is an important component of the ultralow interfacial tension.

The Formation of Middle Phase Microemulsions in High Surfactant Concentration Systems

The effect of salinity on the surfactant rich phase in the oil/brine/surfactant/alcohol systems is shown in Figure 12. It is

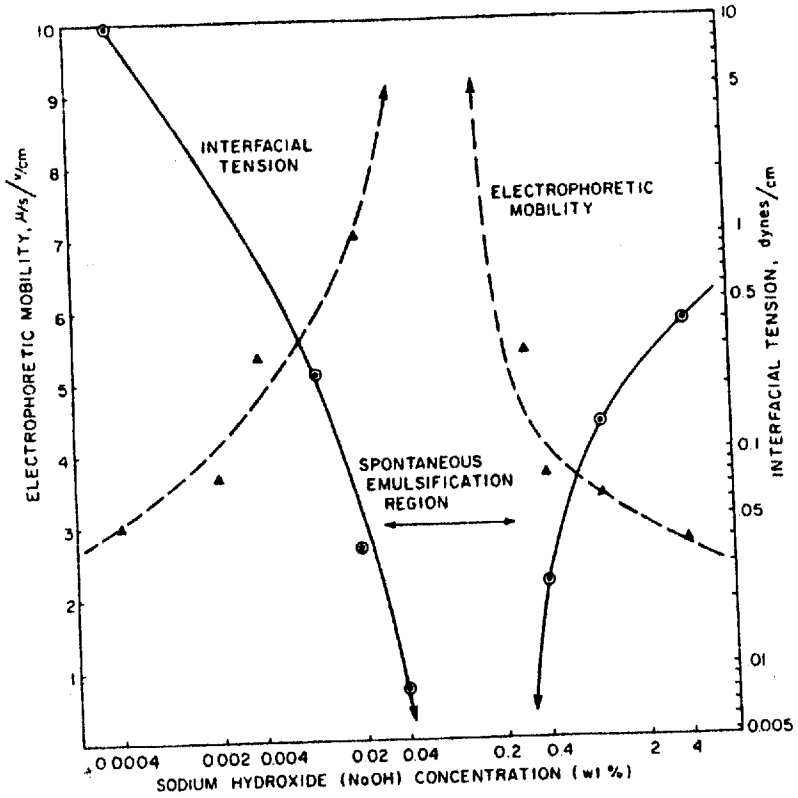

Fig. 7. Electrophoretic mobility and interfacial tension for crude oil-NaOH solutions.

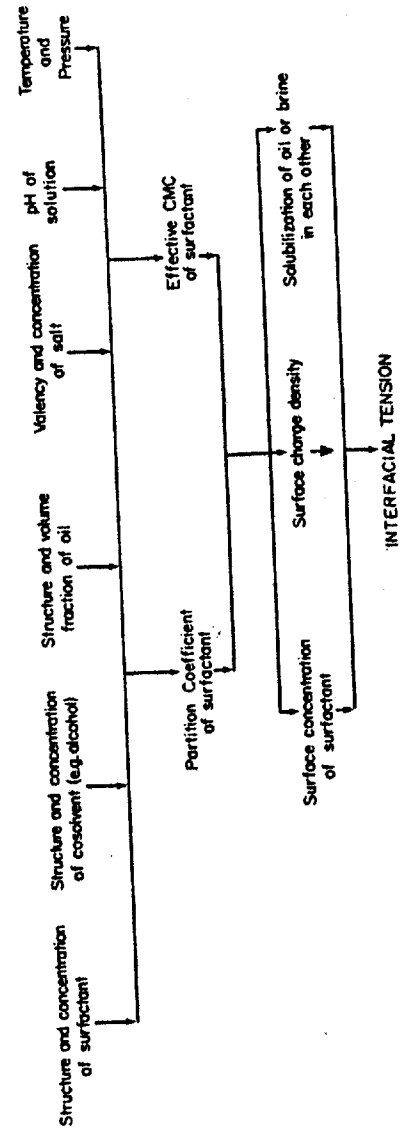

Fig. 8. An overview of the effect of several variables on processes occurring in oil/brine/surfactant/alcohol systems in relation to the three parameters influencing the magnitude of interfacial tension.

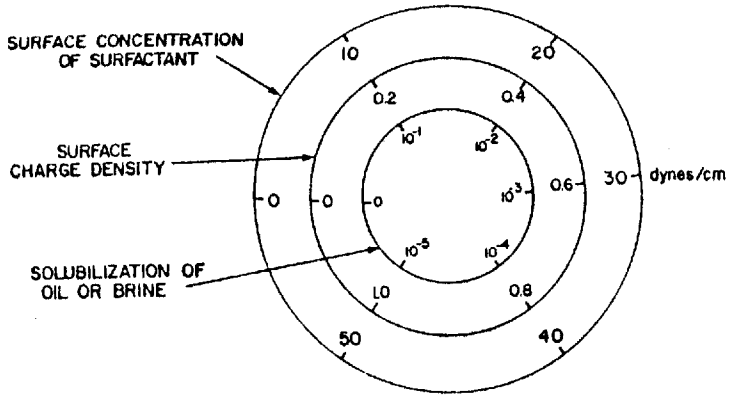

Fig. 9. A schematic presentation of three components of interfacial tension in the oil/brine/surfactant systems.

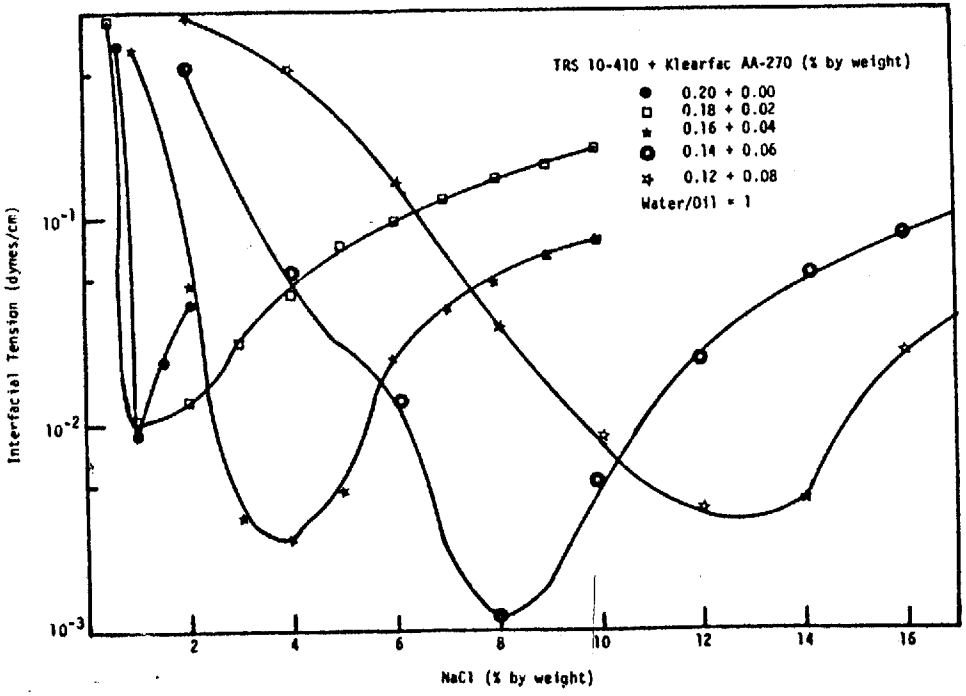

Fig. 10. Effect of salinity on the magnitude and broadening of the interfacial tension by the addition of Klearfac AA-270 in 0.2% surfactants + 0.12% IBA/n-octane system.

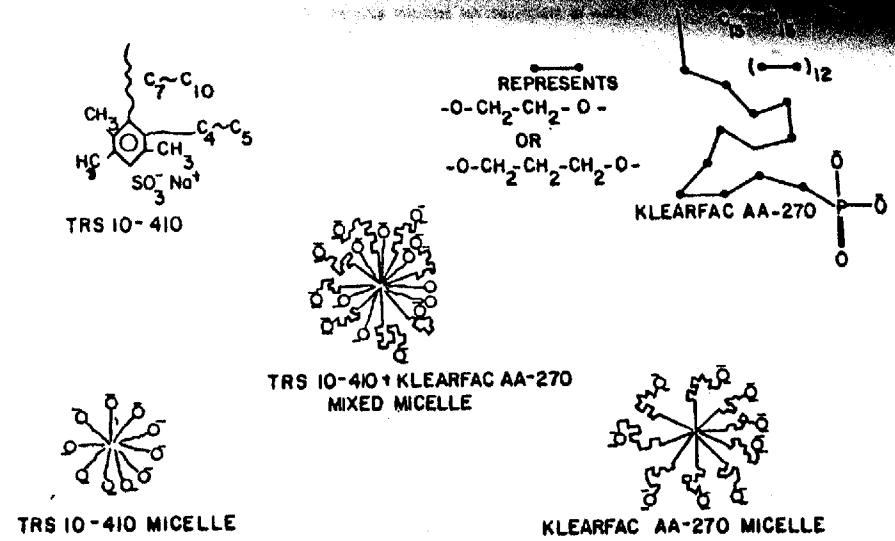

Fig. 11. The schematic presentation of the increase in the surface charge density at the micellar surface and oil/water interface due to mixing of Klearfac AA-270 with petroleum sulfonate TRS 10-410.

evident that as the salinity increases the surfactant migrates from the lower phase to middle phase to upper phase microemulsions. The salinity at which equal volumes of oil and brine are solubilized in the middle phase microemulsion is defined as the optimal salinity (8). It has been further shown that the higher the magnitude of solubilization, the greater is the reduction in interfacial tension at the oil/microemulsion or brine/microemulsion interface (8,19-21). The optimal salinity can be shifted to a higher value by incorporation of ethoxylated sulfonates or alcohols in the surfactant formulation (19-21).

Figure 13 schematically illustrates our proposed mechanism for the formation of middle phase microemulsions (13). At low salinities, micelles are formed in the aqueous phase in equilibrium with oil. As the salinity increases, the solubilization of oil within the micelles increases and the thickness of electrical double layer around the micelles decreases. The reduction in repulsive forces allows micelles to approach each other closely and subsequently a micelle-rich phase separates out due to the density difference from the aqueous phase forming the middle phase microemulsion. Hence, the middle phase microemulsion is similar to coacervation process in micellar solution where a micelle-rich phase separates out upon addition of salts. The presence of oil only contributes towards the solubilization of oil within the micelles. Ultimately, at higher salinities, surfactant preferen-

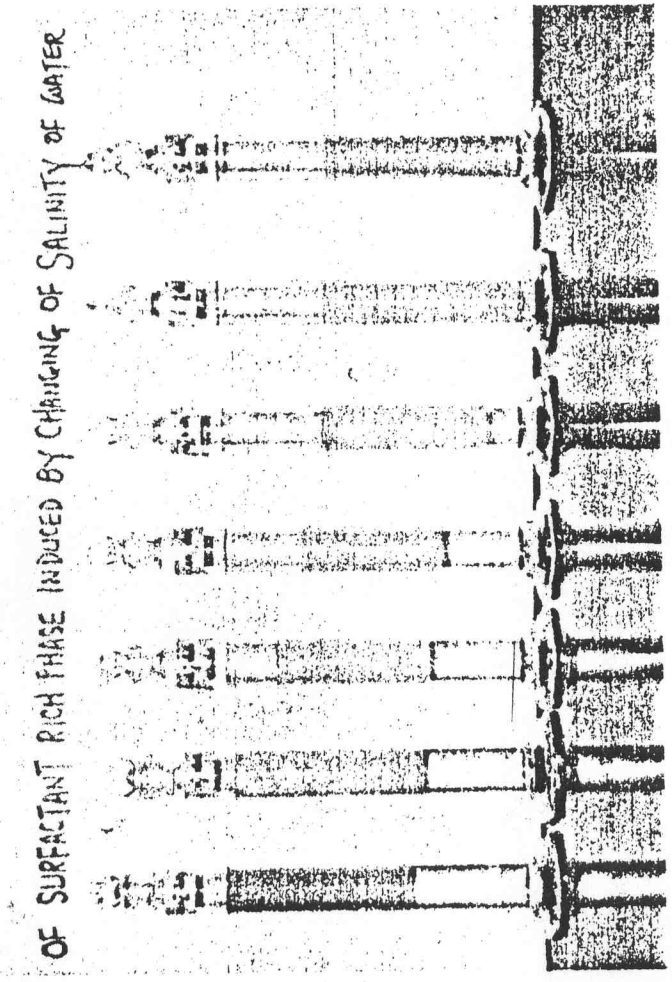

Fig. 12. The formation of lower phase, middle phase and upper phase microemulsions due to increase in salinity of oil/brine/surfactant/alcohol systems.

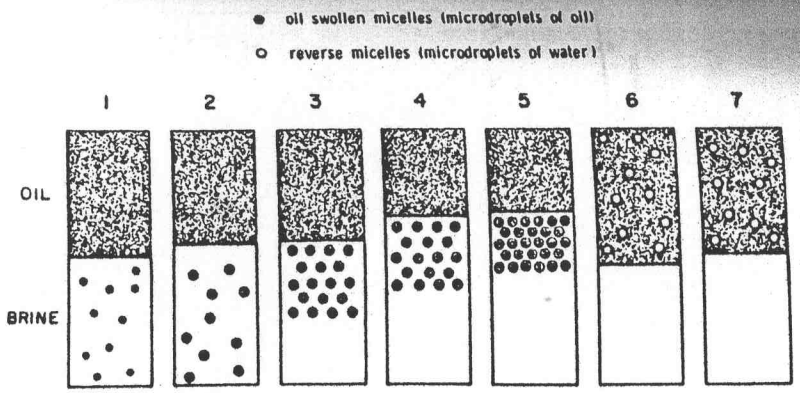

Fig. 13. A schematic presentation of the mechanism of formation of the middle phase microemulsions upon increasing salinity.

tially partitions into the oil phase forming reverse micelles or water-in-oil microemulsions. Figure 14 shows the freeze-fracture electronmicrograph of a middle phase microemulsion at optimal salinity. It clearly shows the swollen microemulsion droplets in a continuous aqueous phase. Our additional studies (22) on sodium/calcium equivalent ratio strongly support the conclusion that at the optimal salinity, the middle phase microemulsion is water-external. However, it is well recognized that the microemulsion structure changes in the salinity range over which middle phase microemulsion exists because the solubilization of oil and brine in the middle phase microemulsion changes depending upon the salinity.

Figure 15 shows the effect of oil chain length on the optimal salinity in the present system (23). It is evident that as the oil chain length increases, the optimal salinity also increases. The interfacial tension at the corresponding optimal salinity also increases with the chain length of oil. Figure 16 shows the volume of the middle phase and the surfactant concentration in the middle phase as a function of the oil chain length. It is clear that the solubilization of oil and brine in the middle phase decreases as the oil chain length increases (23).

Figure 17 schematically illustrates the $\ell \rightarrow m \rightarrow u$ transition in the oil/brine/surfactant/alcohol systems in relation to several variables. Therefore, it appears that the surfactant migration is a general phenomenon that can be brought about by changing of several variables. Figure 18 schematically illustrates the comparison of low surfactant concentration and high surfactant concentration systems. It is interesting that in low surfactant concentration systems (two phase systems) the ultralow interfacial

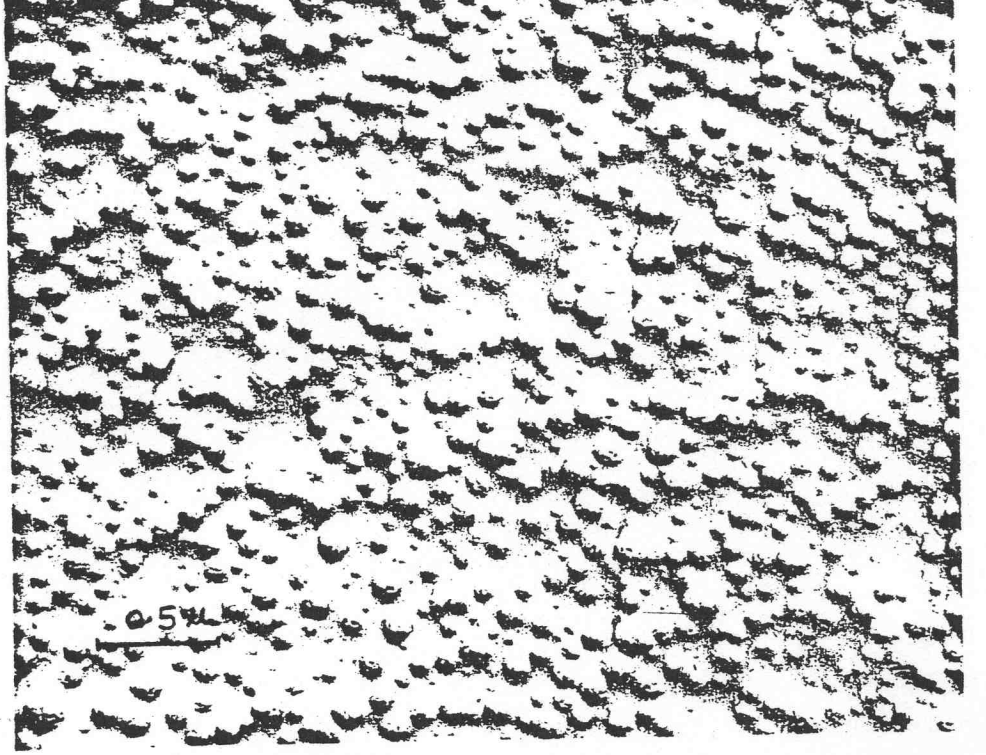

Fig. 14. Freeze-fracture electronmicrograph of a middle phase microemulsion in the Exxon system [4% emulsifier (MEAC 120 XS/TAA:: 63/37) + 48% oil (ISOPAR M/HAN::90/10) + 48% brine (1.2% NaCl) in D_2O.] The bar represents 0.5 micron.

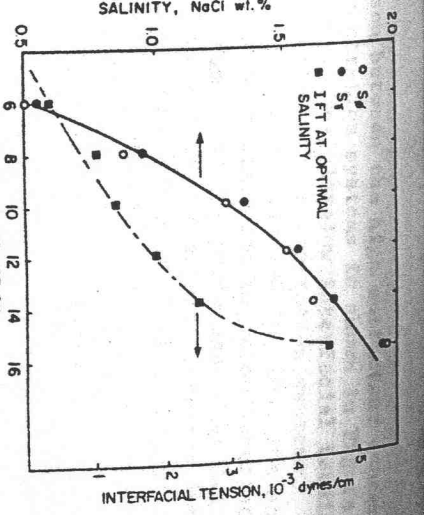

Fig. 15. The effect of oil chain length on the optimal salinity and the corresponding interfacial tension of 5% TRS 10-410 + 3% IBA system.

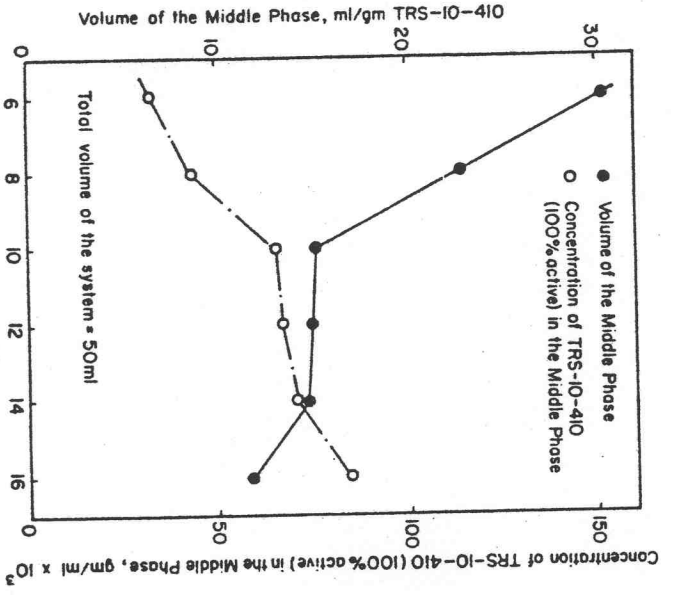

Fig. 16. Volume of the middle phase and concentration of TRS 10-410 (100% active) in the middle phase at optimal salinity for different chain length of oils.

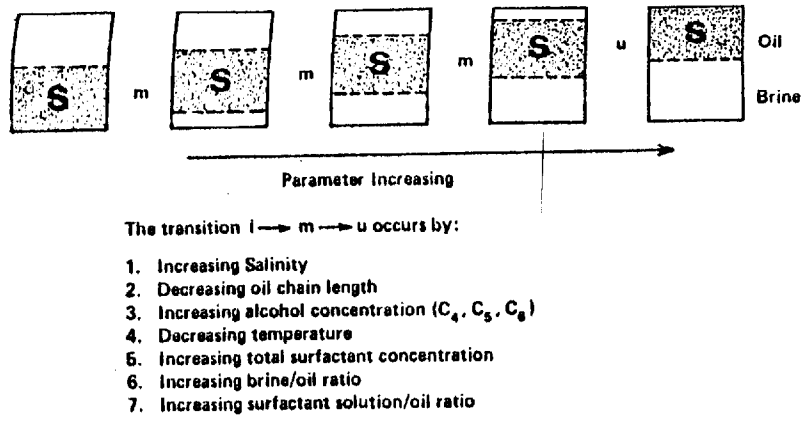

Fig. 17. Factors influencing the formation of ℓ-, m-, u- microemulsions for oil/brine/surfactant/alcohol systems.

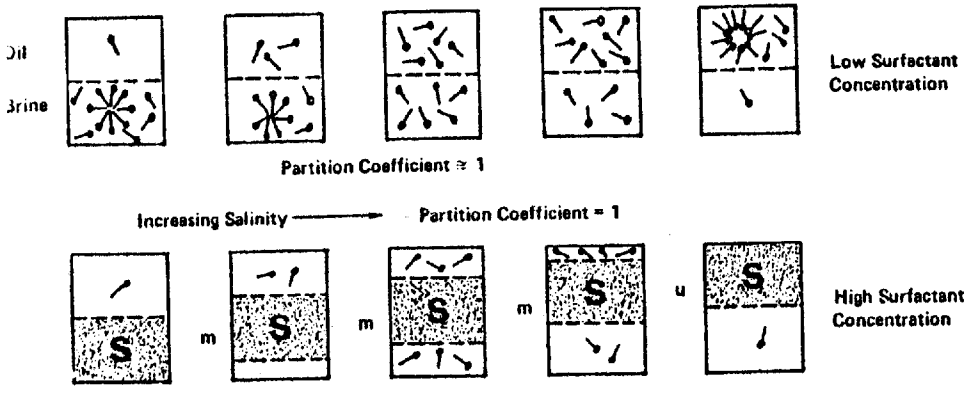

Fig. 18. A comparison of phenomena occurring in low and high surfactant concentration systems.

tension is observed near the partition coefficient unity (14). In the high surfactant concentration systems, at optimal salinity the partition coefficient of surfactant in excess oil and excess brine is also near unity (13). In other words, the middle phase microemulsion seems to be a reservoir of excess surfactant, whereas the excess oil and brine phase resemble that of low surfactant concentration systems. We have also found that at optimal salinity the interfacial tension between excess oil and excess brine is minimum due to partition coefficient near unity (13).

A comparison between the high surfactant concentration and low surfactant concentration systems is shown in Figure 19. The optimal oil chain length for ultralow interfacial tension is found to be C_{12} for high surfactant concentration systems. For low surfactant concentration systems (0.1% TRS 10-410), the same chain length (C_{12}) was found to be optimum for ultralow interfacial tension. Therefore, we propose that the phenomena occurring in low surfactant concentration and high surfactant concentration systems are similar. We have further shown (23) that the optimal salinity decreases with alcohol chain length (23). In other words, the higher the alcohol chain length, the lower is the optimal salinity of a given surfactant/alcohol/oil/brine system. The effect of alcohol on the optimal salinity is related to the brine solubility of the alcohol. The higher the solubility of the alcohol in brine, the higher is the optimal salinity (24).

In summary, the formation of middle phase microemulsion at the optimal salinity is an important phenomenon with respect to ultralow interfacial tension, solubilization, rate of coalescence and oil displacement efficiency in porous media (10,11,25). Also, the optimal salinity can be shifted to a desired value by adjusting several variables.

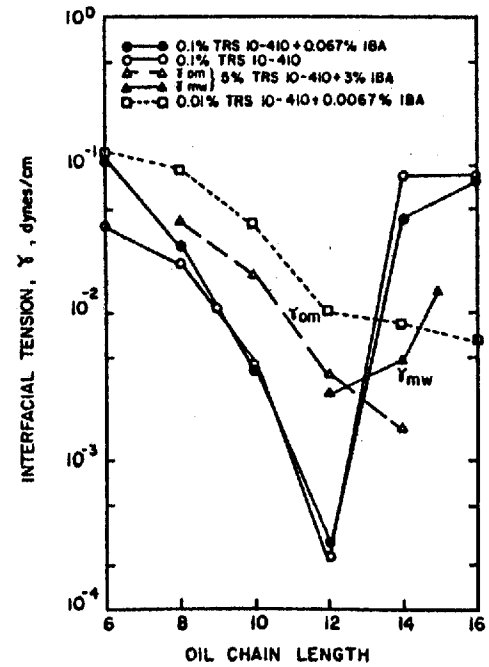

Fig. 19. Effect of oil chain length on the interfacial tension in high and low surfactant concentration systems.

ACKNOWLEDGMENTS

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REFERENCES

1. J. C. Melrose and C. F. Brandner, J. Can. Pet. Tech., 54 (Oct.-Dec., 1974).
2. I. H. Doe, W. H. Wade, and R. S. Schechter, J. Colloid Interface Sci., 59, 525 (1977).
3. J. L. Cayias, R. S. Schechter, and W. H. Wade, J. Colloid Interface Sci., 59, 31 (1977).
4. P. M. Wilson and C. F. Brandner, paper presented at the 165th National Meeting of the American Chemical Society, Dallas, Texas, April 8-13, 1973.
5. J. C. Morgan, R. S. Schechter, and W. H. Wade, in "Improved Oil Recovery by Surfactant and Polymer Flooding," D. O. Shah and R. S. Schechter, eds., Academic Press, New York, p. 101, 1977.
6. K. Shinoda and S. Friberg, Adv. Colloid Interface Sci., 4, 281 (1975).
7. D. R. Anderson, M. S. Bidner, H. T. Davis, C. D. Manning, and L. E. Scriven, SPE 5811 presented at the Improved Oil Recovery Symposium held in Tulsa, Oklahoma, March 22-24, 1976.
8. R. L. Reed and R. N. Healy, in "Improved Oil Recovery by Surfactant and Polymer Flooding," D. O. Shah and R. S. Schechte eds., Academic Press, New York, p. 383, 1977.
9. M. Y. Chiang, Ph.D. Thesis, University of Florida, 1979.
10. M. Y. Chiang and D. O. Shah, SPE 8988 presented at the 5th International Symposium on Oilfield and Geothermal Chemistry held in Stanford, California, May 28-30, 1980.
11. S. Vijayan, C. Ramachandran, H. Doshi, and D. O. Shah, in "Surface Phenomena in Enhanced Oil Recovery, D. O. Shah, ed., Plenum Press, New York (in press).
12. J. E. Vinatieri, Soc. Pet. Eng. J., 20, 402 (1980).
13. K. S. Chan and D. O. Shah, SPE 7869 presented at the International Symposium on Oilfield and Geothermal Chemistry held in Houston, Texas, January 22-24, 1979.
14. K. S. Chan and D. O. Shah, J. Disp. Sci. Tech., 1, 55 (1980).
15. M. Baviere, SPE 6000 presented at the 51st Annual Fall Technical Conference and Exhibition of the Society of Petroleum Engineers of AIME, New Orleans, Louisiana, October 3-6, 1976.
16. J. C. Noronha, Ph.D. Thesis, University of Florida, 1980.
17. V. K. Bansal, K. S. Chan, R. McCullough, and D. O. Shah, J. Canad. Pet. Tech., 17(1), Jan.-March, 1978.
18. M. Y. Chiang, K. S. Chan, and D. O. Shah, J. Canad. Pet. Tech. 17(4), Oct.-Dec., 1978.
19. V. K. Bansal and D. O. Shah, J. Colloid Interface Sci., 65, 451 (1978).
20. V. K. Bansal and D. O. Shah, Soc. Pet. Eng. J., 167 (June, 1978).
21. V. K. Bansal and D. O. Shah, J. Amer. Oil Chem. Soc., 55, 367 (1978).
22. S. I. Chou and D. O. Shah, J. Colloid Interface Sci. (in press).
23. W. C. Hsieh and D. O. Shah, SPE 6594 presented at the International Symposium on Oilfield and Geothermal Chemistry held in La Jolla, California, June 27-28, 1977.
24. W. C. Hsieh, Ph.D. Thesis, University of Florida, 1977.
25. D. O. Shah, in "Surface Phenomena in Enhanced Oil Recovery," D. O. Shah, ed., Plenum Press, New York (in press).