☘ Microemulsions with Excellent Water Solubilizing Capacity at High Hydrocarbon Levels with Quaternary Ammonium Salts as Surfactants

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ABSTRACT

In W/O microemulsions prepared by adding dry surfactant to a mixture of 85% heptane or toluene and 15% pentanol, then titrating with water, systems using quaternary ammonium salts have been shown to be capable of solubilizing much larger amounts of water than systems using the anionic sodium dodecyl sulfate. In homologous series in the range C_{12} to C_{16} it would appear that, with one exception, longer chain length quaternary salts are more effective at solubilizing water than are shorter chain length compounds. With quaternary salts of equal chain length, pyridinium salts are more effective at solubilizing water at high surfactant concentrations than are corresponding trimethyl salts.

INTRODUCTION

Microemulsion systems were introduced to the scientific literature by Hoar and Schulman (1). This was followed by a series of papers by Schulman and coworkers (2-7) investigating various aspects of these systems. Strong impetus has been given to the study of microemulsions in more recent years by the need for systems with very low interfacial tensions in tertiary oil recovery and the presence of such low interfacial tensions in microemulsion systems (8-12). The thermodynamic and surfactant structural aspects of microemulsions have been addressed by Israelachvili, Mitchell and Ninham (13), Oakenfull (14), and Mitchell and Ninham (15).

Studies of microemulsion formation using anionic and nonionic surfactants are numerous, and good reviews are available (16-18). However, research involving the cationic quaternary ammonium salts appears to be very limited. Ekwall (19) published a few ternary phase diagrams involving quaternary ammonium salts, water and alcohols, and Hermansky and Mackay (20) have done some phase diagrams involving quaternary ammonium salts. Recently Friberg, Hakala and Downing (21) used cationic surfactants in their investigation of the effects of shielding of the ionic groups by hydrophobic groups on the extent of the microemulsion region. In addition the first publications dealing with catalysis in the W/O microemulsion region were concerned with cationic surfactants (22,23).

In microemulsion systems prepared using common anionic surfactants, it has been well established (24) that solubilizing capacity for water decreases drastically when hydrocarbon levels exceed 50%. This low solubilizing capacity for water in W/O microemulsions with high hydrocarbon content is a major limitation on the application of microemulsion technology, because it virtually eliminates the possibility of diluting such W/O microemulsions with hydrocarbons.

In the light of these observations, the paucity of published work dealing with microemulsions prepared with cationic surfactants is perhaps unfortunate, because as Venable and Weingaertner (25) pointed out in a recent paper, the quaternary ammonium salts with pentanol as cosurfactant give far greater solubilizing capacity for water at high hydrocarbon levels than can be attained with the much more widely studied sodium dodecyl sulfate with the same cosurfactant.

The investigations of Venable and Weingaertner (25) are extended in this present paper to include additional quaternary ammonium salts with a variety of chain lengths and utilizing different hydrocarbons. Results with sodium dodecyl sulfate are included for comparison.

EXPERIMENTAL

Materials

Of the cationic surfactants used in this work, dodecylpyridinium bromide (DPB) and tetradecylpyridinium bromide (TPB) were synthesized by refluxing the appropriate alkyl bromide with 30 mole per cent excess of freshly distilled pyridine in methanol solution. The methanol was removed by evaporation and diethyl ether added until precipitation of the surfactant was initiated. This mixture was chilled in an ice bath to complete precipitation and filtered cold. Recrystallizations were carried out by dissolving in a minimal amount of methanol and repeating the above procedure. Since quaternary ammonium salts decompose upon heating, it is not possible to determine the melting points of these products. Cetylpyridinium bromide (CPB) was purchased from BDH, while tetradecyltrimethylammonium bromide (TTMAB) and hexadecyltrimethylammonium bromide (HTMAB) were purchased from Sigma Chemical Company. The CPB and TTMAB obviously contained impurities and were recrystallized as described above. Sodium dodecyl sulfate (SDS) was BDH specially pure and was recrystallized twice from hot ethanol before using.

The heptane, toluene and pentanol were Fisher Certified and used as received. The water was triple distilled with the second distillation being from acidic permanganate solution in an all glass system and the third a simple distillation from an all glass system.

Methods

In each case the hydrocarbon and pentanol were mixed and stored at 25 ± 1 C in ground glass stoppered bottles until needed. All titration experiments were carried out at 25 ± 1 C by weighing dry surfactant into a screw cap culture vial, adding the desired amount of hydrocarbon-cosurfactant mixture, then adding water dropwise with vigorous stirring after each addition. The endpoint of the titration was taken as the appearance of permanent turbidity or of optical birefringence.

RESULTS

In all cases the hydrocarbon-cosurfactant mixture was 85% hydrocarbon-15% cosurfactant by weight. The plane is shown by the heavy lines in the total 4-component system in Figure 1. Figure 2 shows a comparison between the W/O microemulsion areas for SDS, DPB, TPB and CPB with heptane as the hydrocarbon, in the plane marked in Figure 1. There is a pronounced difference between SDS and the cationic surfactants as far as water solubilizing capacity is concerned. The maximum percentages of solubilized water of 7% (SDS), 12% (DPB), 28% (TPB) and 31% (CPB) reveal

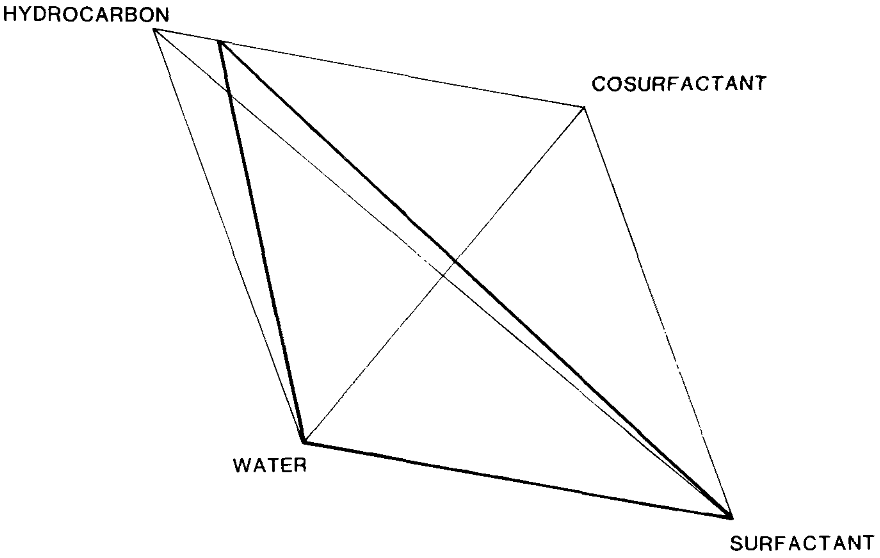

FIG. 1. Construct for a 4-component phase diagram showing the water, surfactant, 85% hydrocarbon-15% cosurfactant plane.

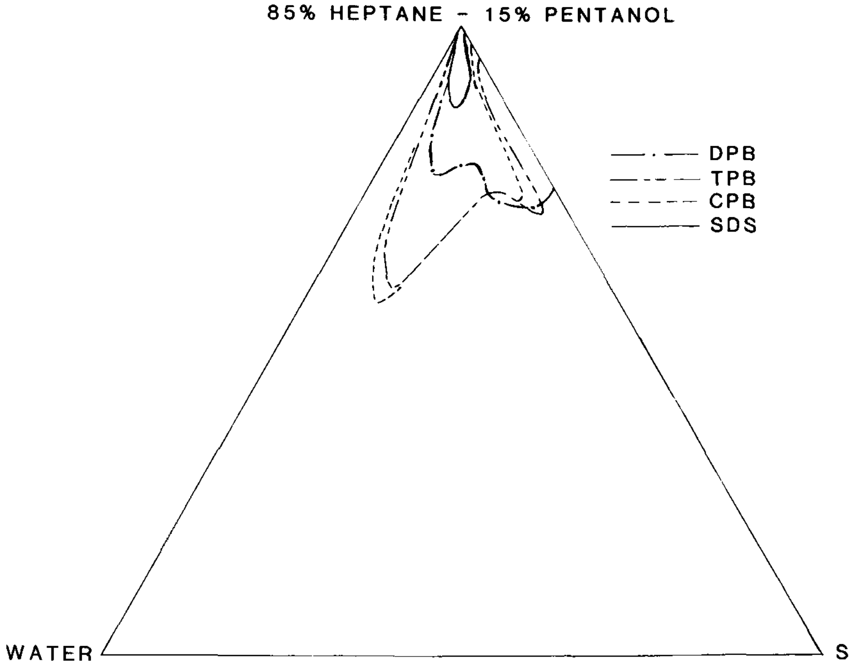

FIG. 2. Microemulsion region in the system water, surfactant, 85% heptane-15% pentanol at 25 ± 1 C. —.— = DPB; — — — — — = TPB; — — — = CPB, and —— = SDS.

the magnitude of the differences encountered. DPB obviously was less effective at solubilizing water than either TPB or CPB, and the shape of the microemulsion region is somewhat different. CPB was slightly more effective than TPB at solubilizing water as measured by total percentage water solubilized, although the difference is hardly noticeable except in the 10-15% surfactant range.

The importance of the structure of the hydrocarbon is revealed by Figure 3, where the same 4 surfactants are used, but now with toluene as the hydrocarbon. The water solubilized with all the quaternary salts was greatly enhanced over corresponding systems with heptane as the hydrocarbon. Also the situation was reversed relative to DPB, as it was here the most effective of the quaternary salts at solubilizing water. The relative maximum water solubilizing capacity remained the same for TPB and CPB, with CPB having the greater maximum capacity at high surfactant levels. At lower surfactant concentrations DPB and TPB followed the same water solubilization limit line up to surfactant concentrations between 10 and 15%, where TPB becomes less effective. However, CPB was much less effective at these lower surfactant concentrations with toluene as the hydrocarbon, then surpassed TPB in the 10-15% range.

The possibility exists that there is some impurity left in the CPB which causes the performance in toluene to be different from the performance in heptane. Solutions of CPB containing high concentrations of surfactant are slight-

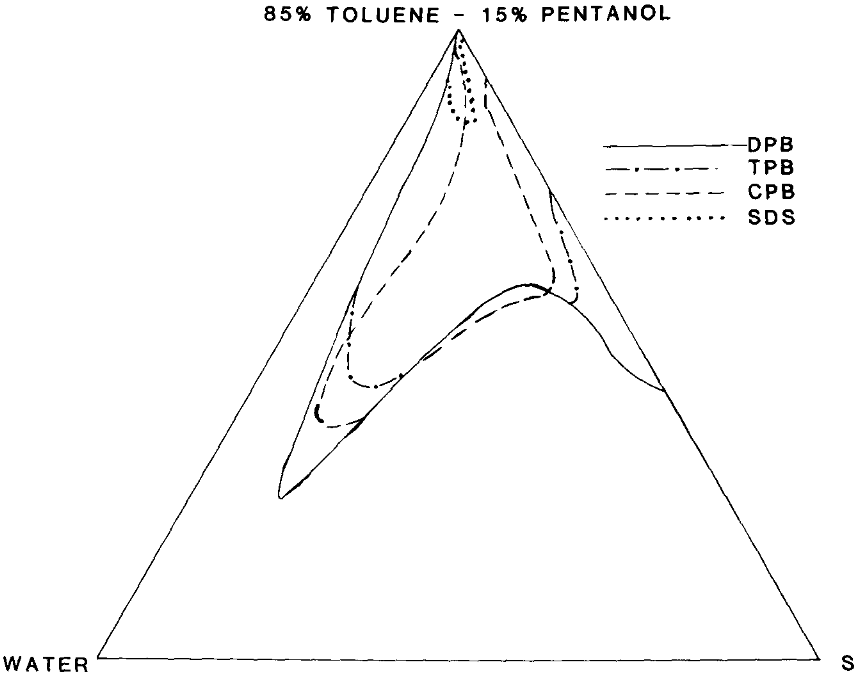

FIG. 3. Microemulsion region in the system water, surfactant, 85% toluene-15% pentanol at 25 ± 1 C: ——DPB, – . – . – TPB, – – – – CPB, ... SDS.

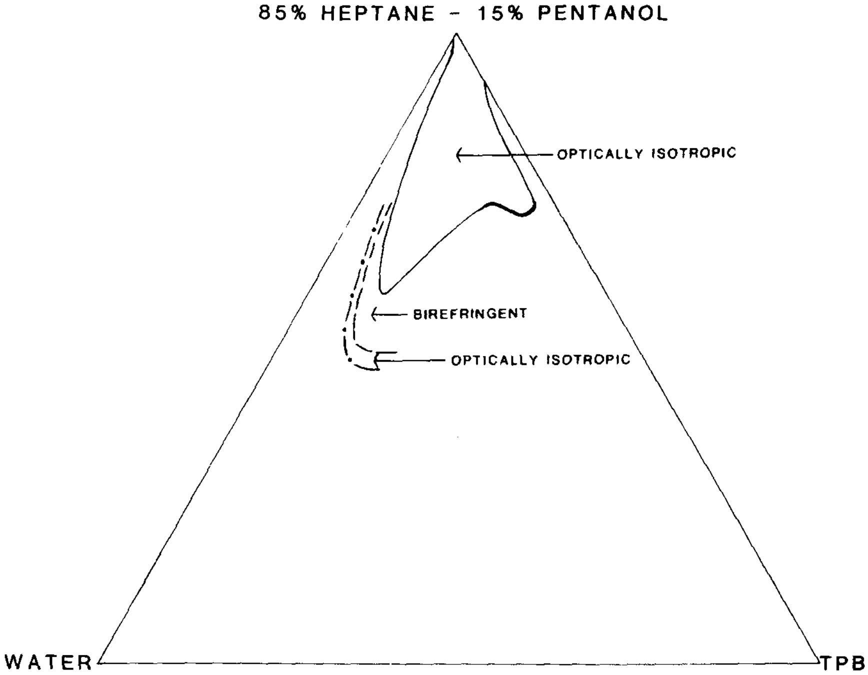

FIG. 4. Microemulsion region in the system water, surfactant, 85% heptane-15% pentanol showing optically isotropic and birefringent areas at 25 ± 1 C.

ly colored. Therefore, the presence of an impurity cannot be denied and repeated recrystallizations failed to remove the color. Phase diagrams determined before and after a recrystallization were the same with heptane. It is not at all obvious to us why an impurity would affect performance in one hydrocarbon differently, but the possibility exists.

In contrast to the behavior of the quaternary salts, changing the hydrocarbon to toluene had an adverse effect on water solubilization with SDS. The maximum water solubilization is reduced from 8.4% to 4.6%, a 45% reduction. This rather pronounced reduction in water solubilization may not be apparent from the phase diagrams.

It also is evident that the surfactants were much more soluble in the toluene-pentanol mixture than in the heptane-pentanol mixture. The quaternary salts are, in turn, much more soluble in either mixture than is SDS. The solubility of the surfactant in the hydrocarbon-cosurfactant mixture correlates with chain length for the quaternary

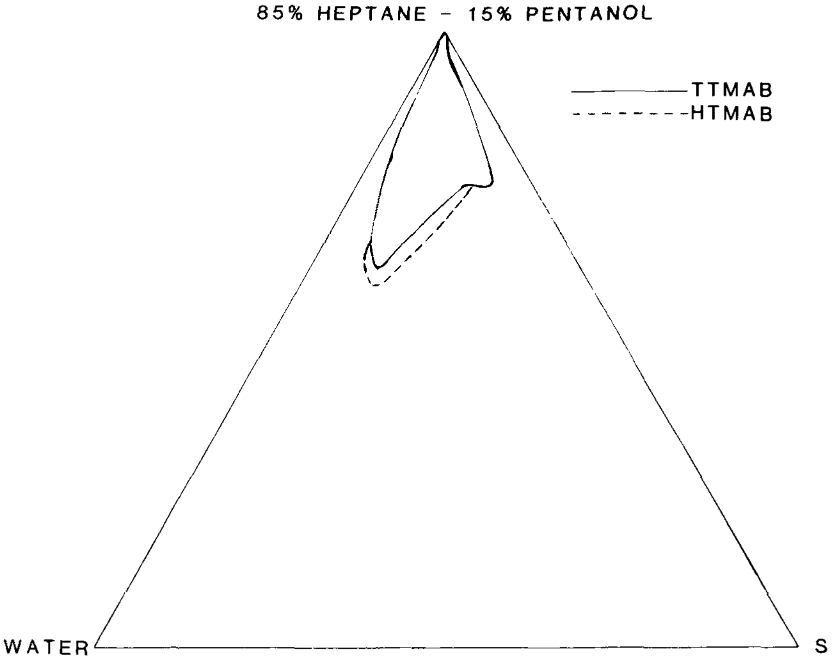

FIG. 5. Microemulsion region in the system water, surfactant, 85% heptane-15% pentanol comparing ______, TTMAB, with — — — — —, HTMAB, at 25 ± 1 C.

salts, with the shorter chain length compounds being more soluble.

TPB showed different behavior from either DPB or CPB, as shown in Figure 4. Even at initial surfactant concentrations as low as 5%, the end point of the titration with TPB was taken as the presence of optical birefringence as detected by observing the sample between crossed polarizers. Furthermore, it was possible to titrate through this region of optical birefringence to a narrow isotropic and clear region beyond. The final end point was turbidity with phase separation. As indicated above, these phase diagrams were determined by a titration procedure, and essentially no attempt has been made as of yet to check these results by long term storage of samples. Neither DPB or CPB showed the optical birefringence at initial surfactant concentrations below about 15%.

Figure 5 presents results for TTMAB and HTMAB with heptane as the hydrocarbon. It is again obvious that the longer chain compound has a greater maximum water solubilizing capacity, in parallel with the behavior of TPB and CPB. It also is apparent that both of the trialkyl compounds follow the same water solubility limit line at low surfactant concentrations, just as TPB and CPB did with heptane. When comparing results for HTMAB and CPB from Figures 2 and 5, it is found that the water solubility limit line is the same for both surfactants at lower surfactant concentrations. Also, both TTMAB and TPB give the same water solubility limit line at lower surfactant concentrations. Both pyridinium salts can solubilize more water at the maximum solubilization than can the corresponding trimethyl salt.

For TTMAB and TPB with toluene as the hydrocarbon, similar behavior to that observed with heptane is observed except much larger amounts of water can be solubilized, as shown in Figures 3 and 6. As with heptane, TPB gives a larger maximum water solubilization. When comparing results for HTMAB and CPB we again see that the pyridinium salt shows the greater maximum water solubilizing capacity in spite of the odd behavior of CPB at lower surfactant concentrations. Thus, under the conditions used in this work, pyridinium salts always show greater maximum water solubilization capacity than do the corresponding trimethyl salts.

Finally, TTMAB and HTMAB are compared directly in Figure 6 with toluene as the hydrocarbon. The similarity of solubilizing capacity at low surfactant concentrations and the greater maximum water solubilization by HTMAB are readily apparent. Therefore we see that, with the exception of DPB with toluene, the longer chain quaternary salt always gives the larger water solubilization maximum at these high hydrocarbon levels under these experimental conditions.

The results at 25 ± 1 C are summarized in Table I, where the surfactants are listed in the order of decreasing maximum percentage of water solubilized. The total composition of each system at this maximum water solubilization point is given in percentage by weight. This essentially presents in tabular form and in a quantitative way what already has been said in the text.

DISCUSSION

Venable and Nauman (26) reported head size parameters for some members of this series of compounds (DPB, TPB and TTMAB) and found them all to be about 60 square angstroms per molecule within the limits of experimental error. Therefore, to the extent that head size determines packing, we would expect no differences in the compounds studied here. Of course with the aromatic pyridinium salts there would be delocalization of charge as well as less charge shielding than with the trimethyl salts. Both of these interrelated factors undoubtedly affect interactions with water and therefore water solubilizing capacity. Both factors would tend to make the pyridinium salts more effective than the corresponding trimethyl salt, just as has been observed in this work.

An additional point to be mentioned in comparing systems involving heptane as the hydrocarbon with systems involving toluene is interaction between the aromatic hydrocarbon and the head group of the surfactant. Sjoblom

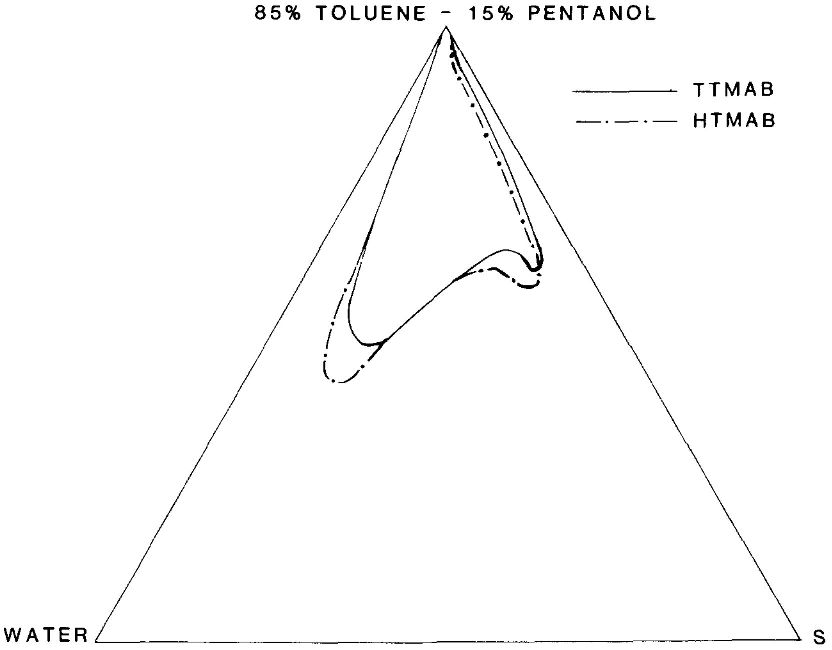

FIG. 6. Microemulsion region in the system water, surfactant, 85% toluene-15% pentanol comparing ______, TTMAB, with – . – . –, HTMAB, at 25 ± 1 C.

TABLE I

System Composition at Maximum Water Solubilization

Surfactant	Percentage Composition			
	Water	Surfactant	Heptane	Pentanol
85% Heptane-15% Pentanol				
CPB	33.2	10.0	48.3	8.5
TPB	30.6	10.5	50.1	8.8
HTMAB	30.4	10.4	50.3	8.9
TTMAB	28.3	8.5	53.7	9.5
DPB	15.2	8.4	64.9	11.5
SDS	8.4	4.6	74.0	13.0
85% Toluene-15% Pentanol				
DPB	61.4	11.6	23.0	4.0
CPB	47.3	12.0	34.6	6.1
HTMAB	45.2	11.0	37.2	6.6
TPB	42.6	12.6	38.1	6.7
TTMAB	38.6	12.2	41.8	7.4
SDS	4.6	5.7	76.3	13.4

and Friberg (27), in a very careful light scattering and electron microscopy study of microemulsion systems with an anionic surfactant, reported two transitions as water was added during a titration. The first transition was interpreted to be from a molecularly dispersed system to a system containing small aggregates. The second transition was reported to give rise to inverse micelles or microemulsion droplets. Aromatic hydrocarbons were reported to have a dramatic impact on these transitions but not on the maximum water solubilizing capacity of stable microemulsions. On the other hand, Gerbacia and Rosano (28) and Rosano (29) reported a pronounced effect of the nature of the hydrocarbon on water solubilization in unstable microemulsions. Further work will be needed to find a satisfactory explanation for the effects of different hydrocarbons.

Explanation of the effects of the length of the hydrocarbon chain of the surfactants apparently will have to await further experimental results and/or further theoretical developments of the type put forth by Israelachvili, Mitchell and Ninham (13), Oakenfull (14) and by Mitchell and Ninham (15).

REFERENCES

1. Hoar, T.P., and J.H. Schulman, Nature 152:102 (1943).
2. Schulman, J.H., and D.P. Riley, J. Colloid Sci. 3:383 (1948).
3. Schulman, J.H., and J.A. Friend, Ibid. 4:497 (1949).
4. Bowcutt, J.E.L., and J.H. Schulman, Z. Electro. Chem. 59:283 (1955).
5. Schulman, J.H., W. Stoeckenius and L.M. Prince, J. Phys. Chem. 63:1977 (1959).
6. Stoeckenius, W., J.H. Schulman and L.M. Prince, Kolloid Z. 169:170 (1960).
7. Cooke, C.E. Jr., and J.H. Schulman, in Surface Chemistry, edited by P. Ekwall, K. Groth and V. Runnstrom-Relo, Munksgaard. Copenhagen, pp. 231-251, 1965.
8. Shah, D.O., V.K. Bansal, K.S. Chan and W.C. Hsieh, Improved Oil Recovery by Surfactant and Polymer Flooding, edited by D.O. Shah and R.S. Schechter, pp. 293-337, Academic Press, New York, 1977.
9. O'Connell, J.P., and R.J. Brugman, Ibid. pp. 339-382.
10. Reed, R.L., and R.N. Heely, Ibid. pp. 383-437.
11. Puig, J.E., L.E. Scriven, H.T. Davis and W.G. Miller, Interfacial Phenomena in Enhanced Oil Recovery, edited by D. Wasan and A. Payatakes, American Institute of Chemical Engineers Symposium Series 78, pp. 1-27 (1982).
12. Miller, C.A., S. Mukherjee, W.J. Benton, J. Natoli, S. Qutubuddin and T. Fort Jr., Ibid, 28-41.
13. Israelachvili, J.N., D.J. Mitchell and B.W. Ninham, J. Chem. Soc. Faraday Trans. II 72:1525 (1976).
14. Oakenfull, D., J. Chem. Soc. Faraday Trans. I 76:1875 (1980).
15. Mitchell, D.J., and B.W. Ninham, Ibid II, 77:601 (1981).
16. El-Nokaly, M., and S.E. Friberg, Cosmetics and Toiletries 97:55 (1980).
17. Friberg, S.E., Prog. Colloid Polymer Sci. 68:41 (1983).
18. Friberg, S.E., and R.L. Venable, Encyclopedia of Emulsion Technology, Vol. 1, p. 287, edited by P. Becher, Marcel Dekker Inc., New York (1983).
19. Ekwall, P., Advances in Liquid Crystal, edited by G. Brown, Vol. 1, p. 1, Academic Press, New York, 1975.
20. Hermansky, C., and R.A. MacKay, Solution Chemistry of Surfactants, edited by K.L. Mittal, pp. 723-732, Plenum Press, New York (1979).
21. Friberg, S.E., M.R. Hakala and D.M. Downey, AOSTRA J. Research, in press, 1984.
22. Friberg, S.E., and S.I. Ahmad, J. Phys. Chem. 75:2001 (1971).

23. Ahmad, S.I., and S.E. Friberg, J. Amer. Chem. Soc. 94:5196 (1972).
24. Friberg, S., and I. Burasczenska, Progr. Colloid Polymer Sci. 63:1-9 (1979).
25. Venable, R.L., and D.A. Weingaertner, J. Dispersion Sci. Techn. 4(4):425-430 (1983).
26. Venable, R.L., and R.V. Nauman, J. Phys. Chem. 68:3498 (1964).
27. Sjoblom, E., and S. Friberg, J. Colloid Interface Sci. 67:16 (1978).
28. Gerbacia, W., and H.L. Rosano, J. Colloid Interface Sci. 44:242 (1973).
29. Rosano, H.L., J. Soc. Cosmetic Chem. 25:609 (1974).

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