

The Effect of Addition of Ethoxylated Sulfonate on Salt Tolerance, Optimal Salinity, and Impedence Characteristics of Petroleum Sulfonate Solutions

V. K. BANSAL AND D. O. SHAH

Departments of Chemical Engineering and Anesthesiology, University of Florida, Gainesville, Florida 32611

Received August 18, 1977; accepted December 26, 1977

The increase in salt concentration causes very unusual changes in the optical appearance of the surfactant formulations reported in this paper. At low salt concentration, the surfactant (TRS 10-410) solutions are isotropic and clear. With an increase in salt concentration, precipitation of surfactant occurs. However, upon further increase in salt concentration, the precipitate redissolves in the solution and a stable birefringent phase forms. Upon further increase in salt concentration the birefringent phase is destroyed and phase separation occurs. The petroleum sulfonate solutions have very poor salt tolerance (about 2.5% NaCl). However, upon addition of an ethoxylated sulfonate (EOR-200) into petroleum sulfonate, the salt tolerance of the mixed surfactant formulation markedly increases. By itself, the salt tolerance for the phase separation of the petroleum sulfonate or the ethoxylated sulfonate (EOR-200) is respectively 2.5 and 18% NaCl. However; upon blending these two surfactants in a 1:4 weight ratio, the salt tolerance for phase separation is found to be 24% NaCl, suggesting a synergistic effect of blending these two sulfonates for salt tolerance. When the mixed surfactant solutions are brought in contact with an equal volume of oil, at a specific salinity a middle phase containing equal volumes of oil and brine is formed. This salinity is defined as the optimal salinity. It is observed that the optimal salinity increases with the fraction of ethoxylated sulfonate in the solution. The mixed surfactant solutions in distilled water, without added oil, were investigated using radio frequency impedence measurements. The capacitance of such solutions was interpreted in terms of surface charge density around micelles. It was shown that the micellar charge density increases with the fraction of ethoxylated sulfonate in the solution. The relevance of these findings for designing optimum surfactant formulations for oil recovery has been discussed.

INTRODUCTION

After water flooding of petroleum reservoirs (secondary oil recovery), about 70% of the oil remains trapped in the reservoirs in the form of microdroplets between sand particles (1, 2). The entrapment of these droplets in a narrow channel is due to high interfacial tension at the oil-brine interface (3, 4). It has been suggested that an injection of a surfactant solution which can lower the interfacial tension at the oil-brine interface can mobilize these droplets (4-9). The petroleum sulfonate solutions have been found to produce such low interfacial tension under appropriate conditions of surfactant and salt concentration (4, 10, 11).

However, the limitation of petroleum sulfonate is that the surfactant solutions become unstable and phase separation occurs when salt concentration is increased beyond 2 or 2.5% NaCl. In the present paper, we have added ethoxylated sulfonate (EOR-200) into the petroleum sulfonate to improve the salt tolerance of petroleum sulfonate solution. There have been several patents on the possible use of ethoxylated alcohols and ethoxylated sulfonates for the use in oil recovery application (12-18).

In general, the salt tolerance of a surfactant formulation is an important requirement for oil recovery process. When the

surfactant solution is injected into the reservoir, it is going to come in contact with the reservoir brine, and, hence, one would like to know the salt tolerance of the surfactant formulation.

When the surfactant formulation is equilibrated with the oil, the surfactant-rich middle phase is formed within a particular salinity range. This middle phase was termed as the middle phase microemulsion by Healy and Reed (21). If the volume of solubilized oil in the middle phase is V_o , the volume of solubilized water V_w , and the volume of surfactant V_s , then the solubilization parameter V_o/V_s or V_w/V_s indicates the solubilized volume of either oil or water per unit volume of surfactant in the microemulsion phase. The solubilization parameter V_o/V_s increases as salinity increases, while V_w/V_s decreases upon increasing salinity. The intersection point of V_o/V_s and V_w/V_s is defined as the *optimal salinity for phase behavior* (S_ϕ). The oil-microemulsion phase interfacial tension γ_{mo} decreases as the salinity increases, while brine-microemulsion phase interfacial tension γ_{mw} increases with salinity. The intersection point of γ_{mo} and γ_{mw} is defined as the *optimal salinity for interfacial tension behavior* (S_γ). The optimal salinity of various petroleum sulfonates has been studied by various workers and reported in the literature (22–26). It appears from the literature that the petroleum sulfonates exhibit a relatively low value of optimal salinity (1–2% NaCl). It has been reported by Reed and Healy (19) and Boneau and Clampitt (20) that oil recovery is maximum at optimal salinity value. Therefore, it is important to determine the optimal salinity of these mixed surfactant solutions and how it changes with the addition of the ethoxylated sulfonate.

Since surfactant formulations used for tertiary oil recovery are opaque or turbid and consist of high surfactant concentration, conventional techniques such as light scattering cannot be used to elucidate the

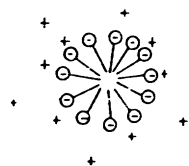
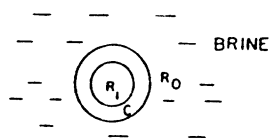
micellar structure of such formulations. Impedance or dielectric behavior over a wide range of frequency can provide useful information about the structural aspect of surfactant formulation.

Impedance measurements of biological tissues and cell dispersions have been studied extensively in the past (27, 28). Recently, dielectric measurements over a wide frequency range have been employed to study the dispersion characteristics of microemulsions (29–31) and micelles (32). In the present study, the mixed surfactant solutions in distilled water, without added oil, were investigated using radio frequency impedance measurements. The capacitance of such solutions was interpreted in terms of surface charge around micelles. The impedance measurement can also be used to determine the relative salt tolerance of the surfactant formulations.

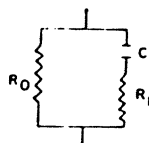
MATERIALS AND METHODS

Petroleum sulfonate (TRS 10-410) and ethoxylated sulfonate (EOR-200) were supplied by Witco Chemicals and Ethyl Corporation, respectively, and were used as received. Paraffinic oil (*n*-hexadecane) as well as isobutanol of 99% purity were purchased from Chemical Samples Company.

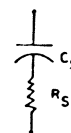
Aqueous solutions consisting of TRS 10-410 (5%) and isobutanol (3%) were prepared at various NaCl concentrations. All surfactant solutions were prepared on the weight basis. The aqueous surfactant solutions were equilibrated with the same volume of *n*-hexadecane. Interfacial tension between various phases was measured using the spinning drop tensiometer developed by Cayias *et al.* of the University of Texas at Austin (33). The density of different phases was measured using a 5-ml density bottle. The optimal salinity values were obtained using the approach described by Healy and Reed (23). Interfacial tension measurements were carried out at $25 \pm 1^\circ\text{C}$ and the

MICELLAR SOLUTIONEQUIVALENT CIRCUITS

PARALLEL



SERIES



$$Z^* = R + jX_c$$

Z^* = EXPERIMENTALLY MEASURED IMPEDENCE

R = REAL PART OF $Z^* = R_s$

X_c = IMAGINARY PART OF $Z^* = \frac{1}{2\pi f C_s}$

WHERE f IS THE FREQUENCY VALUE AT WHICH

Z^* IS MEASURED

R_o = RESISTANCE OF DISPERSING MEDIA

R_i = RESISTANCE OF DISPERSED PHASE (MICELLE)

COLE PLOT: X_c vs R

FIG. 1. Equivalent parallel and series circuits for a micellar solution.

solubilization parameters were obtained at room temperature ($25 \pm 1^\circ\text{C}$) and at least after 1 month equilibration time. The volume of different phases did not change after this equilibration time.

Impedance characteristics were measured by an HP 4815ARF vector impedance meter. The probe of the meter was connected directly to the cell. The cell used for the impedance measurement was made up of a hollow Plexiglas cylinder of $\frac{1}{4}$ in. inner diameter and 2 in. length. The electrodes were made up of stainless steel and were fixed at the two ends of the cylinder. The cell was filled with the formulation by a hypodermic syringe through a small hole in the cell. A series of measurements of the impedance of surfactant solution was carried out within the frequency range of 0.5 to 100 MHz. The value of complex impedance (Z^*) and phase angle θ were obtained directly from the meter. The complex impedance (Z^*) is given by the equation

$$Z^* = R + jX_c$$

where R is the real part of Z^* and X_c is the imaginary part of Z^* . The values of R and X_c at different frequency were separated out

from the complex impedance value with the aid of a computer program.

Figure 1 schematically presents the equivalent parallel and series circuits of a micellar solution and the relationship between the different components of the circuit. The values of X_c and R obtained at different frequencies were used to plot a Cole plot (34) for the micellar solution. The surfactant formulations used for impedance measurements were made in distilled water.

The effect of EOR-200 on the various properties (e.g., salt tolerance, optimal salinity, impedance characteristics) of mixed surfactant formulations was studied by gradually replacing TRS 10-410 with EOR-200, keeping the total surfactant concentration constant at 5%.

RESULTS AND DISCUSSION

A. Salt Tolerance Study

Figure 2 illustrates the effect of salt concentration on the surfactant formulation consisting of TRS 10-410 + EOR-200 with different proportions of TRS 10-410 and EOR-200. The increasing salt concentration causes very unusual changes in these

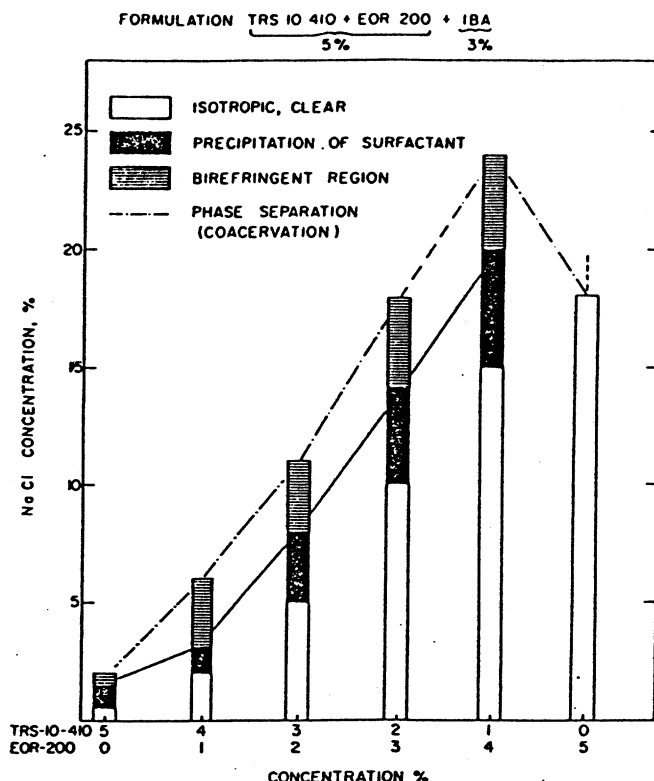


FIG. 2. Effect of NaCl concentration on optical appearance of formulations (TRS 10-410 + EOR-200 + IBA).

surfactant formulations. Mixed surfactant formulation passes through different regions, namely, isotropic, precipitation, birefringent, and phase separation upon increasing the salt concentration. At low salt concentration, the surfactant solutions are isotropic and clear. With an increase in salt concentration precipitation of surfactant occurs. However, upon further increase in salt concentration, the precipitate redissolves in the solution and a stable birefringent phase forms. Upon further increase in salt concentration, the birefringent phase is destroyed and a nonbirefringent surfactant-rich phase separates out. In this case, we take the upper limit of salt concentration which does not cause any precipitation or phase separation as a salt tolerance limit for the surfactant formulation. It is evident from Fig. 2 that as the amount of EOR-200 in the surfactant formulation increases, the salt tolerance limit for every region increases, and the

stability of surfactant formulation (phase separation limit) increases to 24% salt when EOR-200 is 4% in the surfactant formulation. The phase separation limit for ethoxylated sulfonate is 18% NaCl and that for TRS 10-410 is 2.5% NaCl. It is evident from the salt tolerance behavior that the mixed surfactant system, TRS 10-410 + EOR-200 (1:4 wt ratio), exhibits a much higher salt tolerance than that of the two individual surfactants (petroleum sulfonate or ethoxylated sulfonate), suggesting a *synergistic effect* upon blending of these surfactants. Very similar results were also obtained by us (35) for another petroleum sulfonate (Petrostep-465), and it was found that the mixed system consisting of Petrostep-465 + EOR-200 in 1:4 ratio has almost the same tolerance (24%) as the mixed system of TRS 10-410 + EOR-200 of the same ratio. It should be noted that a pure 5% EOR-200 system is isotropic and clear up to 18% NaCl concentration. It separates

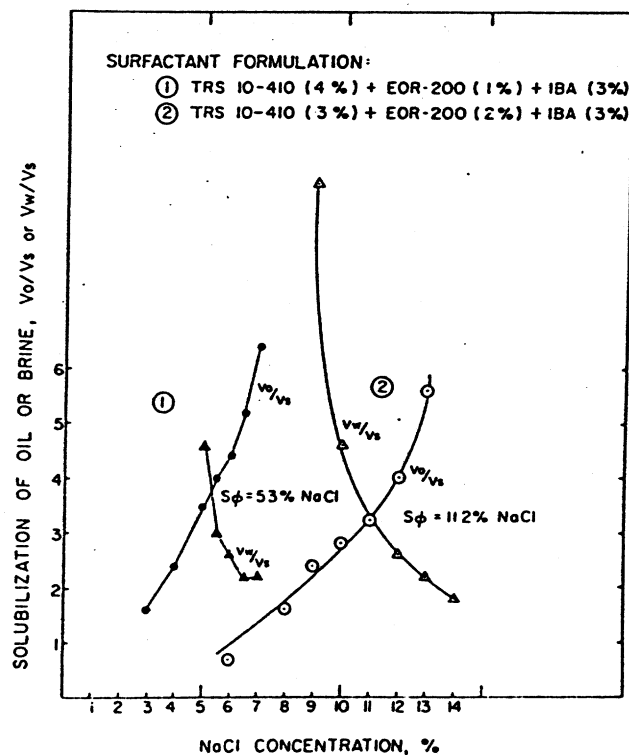


FIG. 3. Effect of NaCl concentration on the solubilization parameter of surfactant formulations (TRS 10-410 + EOR-200 + IBA).

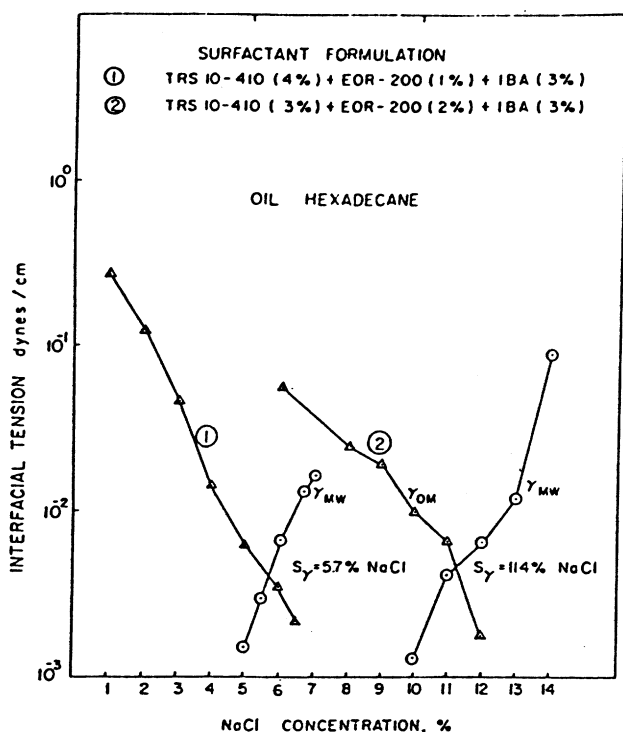


FIG. 4. Effect of NaCl concentration on interfacial tension of surfactant formulations (TRS 10-410 + EOR-200 + IBA).

into two phases above 18% NaCl concentration without going through a birefringent region.

When the surfactant solution is injected into reservoirs, it comes in contact with reservoir brine. The salt concentration in various reservoir brines varies from 649 ppm of Na^+ to 76200 ppm of Na^+ (36). The results presented here suggest an approach to improving salt tolerance by incorporation of appropriate amounts of ethoxylated sulfonate into petroleum sulfonate formulation.

B. Interfacial Tension and Phase Behavior Optimal Salinity

Figures 3 and 4 show the solubilization and interfacial tension data for TRS 10-410 + EOR-200 + IBA formulations containing TRS 10-410 and EOR-200 in ratios 4:1 and 3:2. The optimal salinity values (S_ϕ or S_γ) obtained from the intersection point of

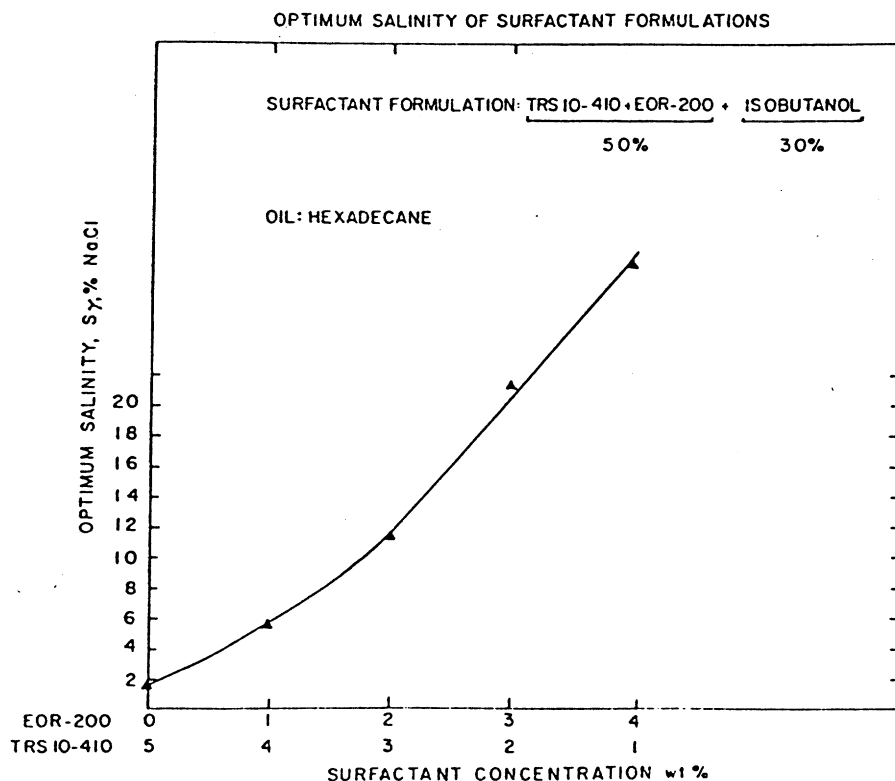


FIG. 5. Optimal salinity values for various ratios of TRS 10-410 and EOR-200 in the surfactant formulations.

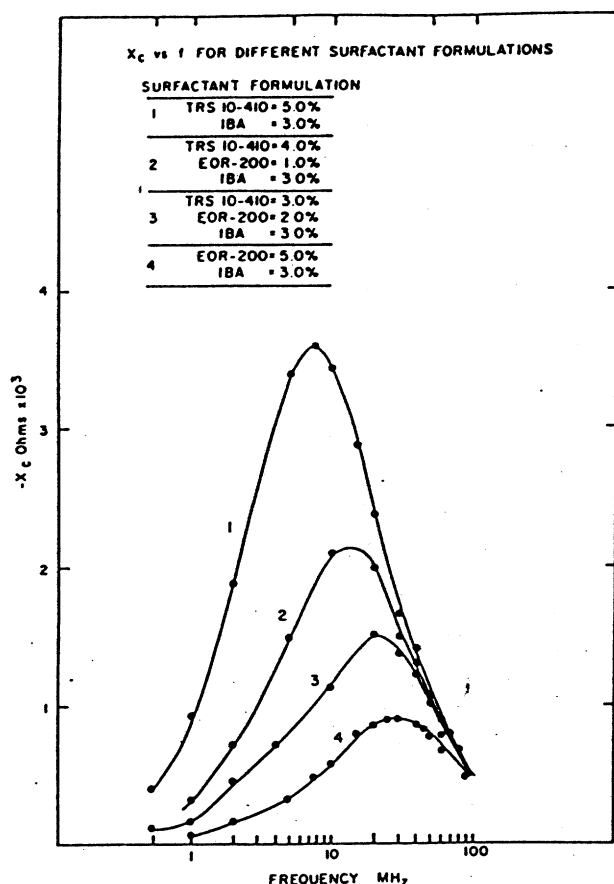


FIG. 6. Reactance values (X_c) at different frequencies for various ratios of TRS 10-410 and EOR-200 in the surfactant formulations.

V_0/V_s and V_w/V_s or γ_{mo} and γ_{mw} clearly indicate that as the amount of EOR-200 in the surfactant formulation increases, the optimal salinity value also increases. The optimal salinity values for other TRS 10-410 and EOR-200 ratios were also obtained in the similar way and are shown in Fig. 5. It is evident from this figure that as the amount of ethoxylated sulfonate increases (up to 1:4 ratio), the optimal salinity value also increases (up to 32% NaCl). We have also observed that EOR-200 (5%) + IBA (3%) is not able to produce ultra-low interfacial tension with Decane as oil, but the addition of 1% petroleum sulfonate in the system drastically reduces the interfacial tension (35).

The interfacial tension data and optimal salinity values reported for the above sys-

tems suggest that one can increase the optimal salinity of petroleum sulfonate formulation by the addition of an appropriate amount of an ethoxylated sulfonate. The results presented here suggest an approach for designing suitable surfactant systems for reservoirs with high salinities.

It was also observed (Fig. 4) that the minimum interfacial tension at optimal salinity is not significantly influenced by the addition of the ethoxylated sulfonate (EOR-200). This insensitivity of interfacial tension at optimal salinity by the addition of EOR-200 could result in a constant capillary number (3, 4), which in turn would not effect the oil displacement efficiency by the addition of EOR-200 in the surfactant formulation but would provide a greater salt tolerance to the formulation.

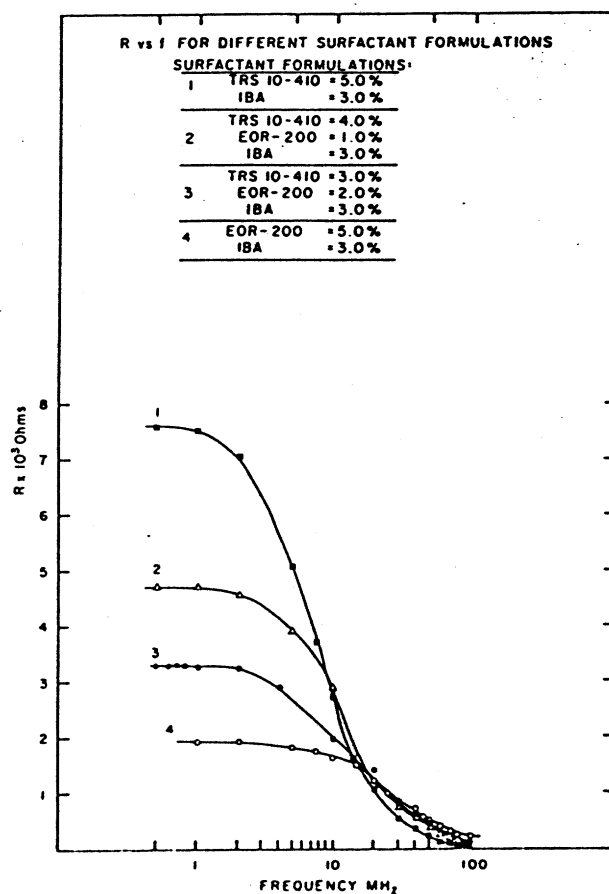


FIG. 7. Resistance values (R) at different frequencies for various ratios of TRS 10-410 and EOR-200 in the surfactant formulations.

TABLE I

The Characteristic Frequency (f_c) and Reactance X_c of Surfactant Formulations in Distilled Water at $T = 22^\circ\text{C}$

Sample number	Surfactant formulation	Critical frequency (f_c) (MHz)	X_c value at f_c (ohms)
1	TRS 10-410 (5%) + IBA (3%)	7.5	3600
2	TRS 10-410 (4%) + EOR-200 (1%) + IBA (3%)	15	2140
3	TRS 10-410 (3%) + EOR-200 (2%) + IBA (3%)	20	1500
4	EOR-200 (5%) + IBA (3%)	30	990

C. Impedance Characteristics of Surfactant Formulations

Figures 6 and 7 show respectively reactance (X_c) and resistance (R) values at different frequency for the surfactant

formulations in distilled water without added oil. The characteristic frequency f_c obtained from Fig. 6 (frequency at which maximum value of X_c is observed) or from Fig. 7 (inflection point for R vs f behavior) is tabulated with the value of X_c at the critical frequency in Table I.

It is evident from the values of f_c for different surfactant formulations that as the amount of EOR-200 in the surfactant formulation increases, the value of f_c increases and simultaneously the value of X_c at critical frequency decreases. Qualitatively the increase in the value of f_c can be interpreted as the decrease in the thickness of ionic atmosphere around the micelles. A very similar conclusion was made by Sachs *et al.* (37) for polyelectrolyte systems. Figure 8 is the plot of X_c vs R which is known as the Cole plot (34). For all the systems the Cole plot indicates that there is no leakage current across the electrical double layer (the plot is a semicircle). The surfactant formulation [TRS 10-410 (3%) + EOR-200 (2%) + IBA (3%)] exhibits a

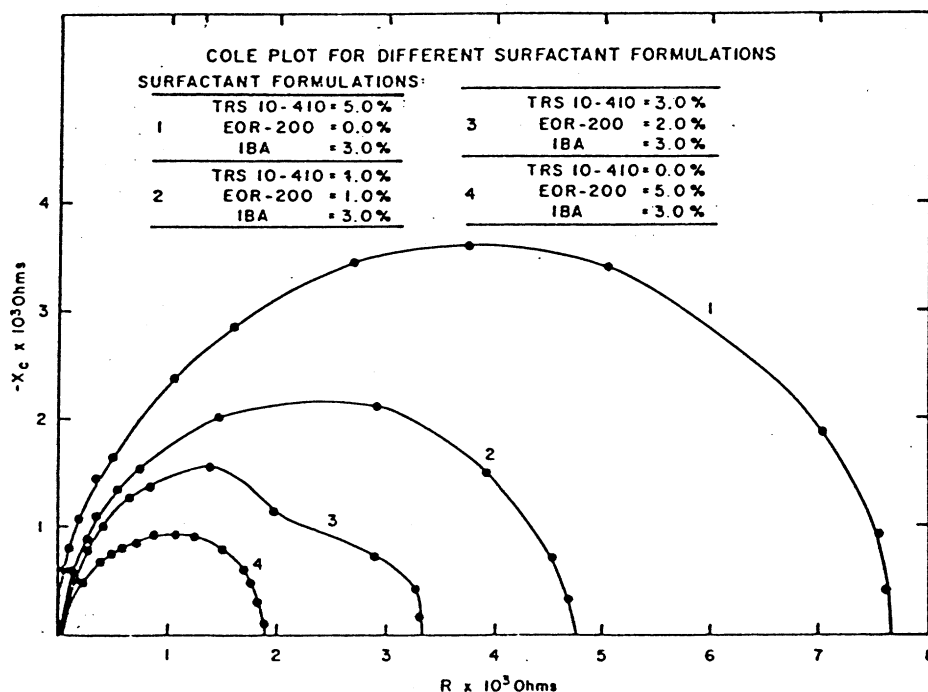


FIG. 8. Cole plot (R vs X) for various ratios of TRS 10-410 and EOR-200 in the surfactant formulations.

deviation from a smooth semicircle in the Cole plot, presumably indicating the deviation from the monodisperse state of the system. From the Cole plot (Fig. 8), it is evident that there is a drastic decrease in R_0 value (the right hand side intersection of semicircles on the R axis) upon the addition of EOR-200 in the TRS 10-410 surfactant formulation. This increase in ionic strength of the dispersing phase can be explained either by the formation of mixed micelles, i.e., EOR-200 molecules entering in the TRS 10-410 micelles, or by an increase in the number of surfactant monomers, or both.

The capacitance (C) of a micellar solution can be expressed as follows,

$$C = \frac{1}{2\pi f X_c}$$

where f is the frequency and X_c is the reactance. For micellar solutions considerably above CMC, the capacitance C reflects the magnitude of micellar charge. Therefore, the lower value of X_c at critical frequency upon the addition of EOR-200 in the surfactant formulation (Table I) indicates that upon the addition of EOR-200, the capacitance of the double layer around micelles and hence micellar charge increases.

Impedance characteristics of the middle phase microemulsions at different salt concentration has also been reported (38) and it was observed that the value of critical frequency is maximum and the value of reactance (X_c) at the critical frequency is minimum at optimal salinity value, indicating maximum charge density at optimal salinity value.

The impedance characteristics of mixed surfactant formulations reported here suggest that for a greater salt tolerance and optimal salinity, the capacitance of formulations should be increased. From the results presented in this section, it is also obvious that one can predict the order of salt

tolerance of various surfactant formulations from their impedance characteristics.

CONCLUSIONS

It was observed that as the amount of an ethoxylated sulfonate (EOR-200) in the surfactant formulation increases, the salt tolerance limit of the formulation increases. The increase in salt tolerance by blending of ethoxylated sulfonate and a petroleum sulfonate suggests that there is a *synergistic* effect of these mixtures on salt tolerance behavior. From the phase behavior and interfacial tension data it was found that the optimal salinity increases upon the addition of EOR-200 in the surfactant formulation. From the impedance measurement it was also observed that the addition of EOR-200 in the surfactant formulation increases the critical frequency and capacitance. This increase was interpreted as an increase in the micellar charge. The impedance dispersion characteristics of the surfactant formulation can be represented by the Cole plot.

ACKNOWLEDGMENTS

The authors wish to convey their sincere thanks to ERDA (Grant No. EY-77-S-05-5341) and the consortium of twenty-one oil and chemical companies for their generous support of the improved oil recovery research program at the University of Florida.

REFERENCES

1. Moor, T. F., and Slobod. R. L., *Prod. Monthly* 20, 20 (1956).
2. Stegemeier, G. L., SPE 4754 presented at SPE Symposium on Improved Oil Recovery, Tulsa, Oklahoma, 1974.
3. Taber, J. J., *Soc. Petrol. Eng. J.* 9, 3 (1969).
4. Foster, W. R., *J. Petrol. Tech.* 25, 205 (1973).
5. Poettman, F. H., "Secondary and Tertiary Oil Recovery Process," p. 82. Interstate Oil Compact Commission, Oklahoma, 1974.
6. Holm, L. W., and Bernard, G. G., U. S. Patent No. 3,082,822, 1959.
7. Gogarty, W. B., and Olsen, R. W., U. S. Patent No. 3,254,714, 1962.

8. Cooke, C. E., Jr., U. S. Patent No. 3,373,809, 1965.
9. Melrose, J. C., and Brandner, C. F., *J. Canad. Petrol. Tech.* **13**, 54 (1976).
10. Cayias, J. L., Schecter, R. S., and Wade, W. H., *J. Colloid Interface Sci.* **59**, 31 (1977).
11. Wilson, P. M., Murphy, C. L., and Foster, W. R., SPE 5812 presented at SPE Improved Oil Recovery Symposium, Tulsa, Oklahoma, 1976.
12. Dauben, D. L., and Froning, H. R., *J. Petrol. Tech.* **23**, 614 (1971).
13. Maddox, J., Jr., Tate, J. F., and Shupe, R. D., U. S. Patent No. 3,916,994, Nov. 4, 1975.
14. Shupe, R. D., Maddox, J., Jr., and Tate, J. F., U. S. Patent No. 3,916,995, Nov. 4, 1975.
15. Shupe, R. D., Maddox, J., Jr., and Tate, J. F., U. S. Patent No. 3,916,996, Nov. 4, 1975.
16. Shupe, R. D., Maddox, J., Jr., and Tate, J. F., U. S. Patent No. 3,945,439, March 23, 1976.
17. Tate, J. J., Maddox, J., Jr., and Shupe, R. D., U. S. Patent No. 3,946,813, March 30, 1976.
18. Gale, W. W., Saunder, R. K., and Ashcraft, T. L., Jr., U. S. Patent No. 3,977,471, Aug. 31, 1976.
19. Reed, R. L., and Healy, R. N., "Improved Oil Recovery by Surfactant and Polymer Flooding" (D. O. Shah and R. S. Schechter, Eds.), p. 383. Academic Press, New York, 1977.
20. Boneau, D. F., and Clampitt, R. L., *J. Petrol. Tech.* **29**, 501 (1977).
21. Healy, R. N., and Reed, R. L., *Soc. Petrol. Eng. J.* **14**, 451 (1974).
22. Anderson, D. R., Bidner, M. S., Davis, H. T., Manning, L. D., and Scriven, L. E., SPE 5811 presented at SPE Improved Oil Recovery Symposium, Tulsa, Oklahoma, 1976.
23. Healy, R. N., Reed, R. L., and Carpenter, C. W., *Soc. Petrol. Eng. J.* **15**, 87 (1975).
24. Healy, R. N., and Reed, R. L., SPE 5817 presented at SPE Improved Oil Recovery Symposium, Tulsa, Oklahoma, 1976.
25. Healy, R. N., Reed, R. L., and Stenmark, D. G., SPE 5565 presented at Fall SPE Meeting, Dallas, Texas, 1975.
26. Hsieh, W. C., and Shah, D. O., SPE 6594, Paper presented at SPE-AIME International Symposium on Oilfield and Geothermal Chemistry, La Jolla, California, June 27-28, 1977.
27. Schwan, M. P., "Physical Technique in Biological Research," Vol. 6, ch. 6. Academic Press, New York, 1963.
28. Grant, E. H., South, G. P., Takashima, S., and Ichimura, H., *Biochem. J.* **122**, 691 (1971).
29. Clausse, M., Sherman, D., and Sheppard, R. J., *J. Colloid Interface Sci.* **56**, 123 (1976).
30. Clausse, M., Sheppard, R. J., Boned, C., and Essex, C. G., "Colloid and Interface Science" (M. Kerker, Ed.), Vol. II, p. 233. Academic Press, New York, 1976.
31. Peyrelasse, J., Boned, C., Xans, P., and Clausse, M., Paper presented at 51st National Colloid Symposium, Grand Island, N. Y., June 19-22, 1977.
32. Beard, R. B., McMaster, T. F., and Takashima, S., *J. Colloid Interface Sci.* **48**, 92 (1974).
33. Cayias, J. L., Schecter, R. S., and Wade, W. H., "Adsorption at Interfaces" (K. L. Mittal, Ed.), ACS Symposium Series No. 8, 1975.
34. Cole, K. S., *J. Gen. Physiol.* **12**, 20 (1928).
35. Bansal, V. K., and Shah, D. O., *Soc. Petrol. Eng. J.* (1978) in press.
36. Wilson, L. A., Jr., "Improved Oil Recovery by Surfactant and Polymer Flooding" (D. O. Shah and R. S. Schecter, Eds.), p. 1. Academic Press, New York, 1977.
37. Sachs, S. B., Raziell, A., Eisenberg, H., and Katchalsky, A., *Trans. Faraday Soc.* **65**, 577 (1969).
38. Improved Oil Recovery Research Program at University of Florida, Gainesville. Semi-annual Report, June 1977.