The Effect of Ethoxylated Sulfonates on Salt Tolerance and Optimal Salinity of Surfactant Formulations for Tertiary Oil Recovery

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ABSTRACT

The addition of an ethoxylated sulfonate (EOR-200) and its effect on the salt tolerance and optimal salinity of formulations containing a petroleum sulfonate (TRS 10-410 or Petrostep-465) and an alcohol was investigated. When salt concentration increases, the mixed surfactant formulations undergo the following changes: isotropic → birefringent → phase separation. The salt concentration required for phase separation increased with the fraction of the ethoxylated sulfonate in the formulation.

When mixed surfactant formulations were equilibrated with an equal volume of oil (decane or hexadecane), a middle-phase microemulsion formed in a specific salinity range. The optimal salinity increased with the fraction of the ethoxylated sulfonate in the mixed surfactant formulations. At optimal salinity as high as 32-percent NaCl, these surfactant formulations exhibited ultra-low interfacial tension (10^{-2} to 10^{-3} dynes/cm). These formulations also showed that an increase in the solubilization parameter decreases the interfacial tension.

INTRODUCTION

The potential use of petroleum sulfonates for tertiary oil recovery has been discussed and several patents[1-4] have been issued during the past two decades. The solubilization, phase behavior, and interfacial tension of petroleum sulfonates have been studied.[5-10] Petroleum sulfonates are known to exhibit relatively low salt tolerance and a low value of optimal salinity (1- to 2-percent NaCl). Dauben and Froning[11] studied the effect of Amoco Wellaid 320 (ethoxylated alcohol) on a surfactant formulation that was primarily a petroleum sulfonate. They observed that surfactant formulations prepared using ethoxylated alcohols as cosurfactants exhibited improved temperature stability and were less sensitive to salts, compared with formulations prepared with isopropanol as a cosurfactant. Several patents were issured on the possible use of ethoxylated alcohols and ethoxylated sulfonates in oil recovery formulations.[12-17]

This study reports the effect of blending an ethoxylated sulfonate (EOR-200) with a petroleum sulfonate (TRS 10-410 or Petrostep-465) on various properties of the mixed surfactant formulations (for examples, salt tolerance, optimal salinity, interfacial tension, and solubilization).

MATERIALS AND METHODS

Petroleum sulfonates TRS 10-410 and Petrostep-465 were supplied by Witco Chemicals and Stepan Chemicals, respectively. Ethoxylated sulfonate EOR-200 was supplied by Ethyl Corp. Paraffinic oils (n-hexadecane and n-decane) as well as 99-percent pure isobutanol and n-pentanol were purchased from Chemicals Samples Co. All surfactants were used as received. The average equivalent weight of TRS 10-410 and Petrostep-465 was 420 and 465, respectively, and the activity of surfactants was approximately 60 percent (as reported by the manufacturers). The molecular weight of EOR-200 was given as 523 by Ethyl and the sample contained 25.3 weight percent active solid surfactant.

Aqueous solutions composed of Petrostep-465 (5 percent) and n-pentanol (2 percent) were prepared on the basis of weight. Aqueous surfactant solutions were equilibrated with the same volume of n-decane. Optimal salinity values were obtained using the approach described by Healy and Reed.[7] The effect of EOR-200 on the properties of mixed surfactant formulations was studied by gradually replacing Petrostep-465 with EOR-200 and keeping the total surfactant concentration constant at 5 weight percent.

Another surfactant formulation studied was composed of TRS 10-410 (5 percent) and IBA (3 percent). Optimal salinity was determined using n-hexadecane. TRS 10-410 was replaced gradually by EOR-200, keeping the total surfactant concentration constant at 5 weight percent. The systems studied are tabulated in Table 1. Systems A to E

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TABLE 1 — THE COMPOSITION OF VARIOUS FORMULATIONS STUDIED FOR SOLUBILIZATION AND INTERFACIAL TENSION DATA

Formulation	Surfactant Formulation	Oil
A	Petrostep 465 (5 percent) + n-pentanol (2 percent)	Decane
B	Petrostep 465 (4 percent) + EOR-200 (1 percent) + n-pentanol (2 percent)	Decane
C	Petrostep 465 (3 percent) + EOR-200 (2 percent) + n-pentanol (2 percent)	Decane
D	Petrostep 465 (2 percent) + EOR-200 (3 percent) + n-pentanol (2 percent)	Decane
E	Petrostep 465 (1 percent) + EOR-200 (4 percent) + n-pentanol (2 percent)	Decane
F	EOR-200 (5 percent) + n-pentanol (2 percent)	Decane
G	TRS-10-410 (4 percent) + EOR-200 (1 percent) + IBA (3 percent)	Hexadecane
H	TRS-10-410 (3 percent) + EOR-200 (2 percent) + IBA (3 percent)	Hexadecane
I	TRS-10-410 (2 percent) + EOR-200 (3 percent) + IBA (3 percent)	Hexadecane
J	TRS-10-410 (1 percent) + EOR-200 (4 percent) + IBA (3 percent)	Hexadecane

were prepared with Petrostep-465, EOR-200, and n-pentanol and G to J were prepared with TRS 10-410, EOR-200, and isobutanol.

The density of the different phases after equilibration was measured using a 5-ml density bottle. Interfacial tension was measured using the spinning drop tensiometer developed by Cayias *et al.*[18] Phase volume and interfacial tension data were obtained at toom temperature (25°C ± 1°C).

RESULTS AND DISCUSSION

SALT TOLERANCE STUDIES

Fig. 1 illustrates the effect of salt concentration on a system with Petrostep-465 + EOR-200 + n-pentanol. Fig. 2 represents the results of similar studies on surfactant formulations composed of TRS 10-410 + EOR-200 + IBA. Increasing salt concentration causes unusual changes in these surfactant formulations. Each surfactant formulation passes through different regions — stable, precipitation, birefringent to phase separation — upon increasing the salt concentration. At low salt concentrations, surfactant solutions are isotropic and clear. With increased salt concentration, the surfactant precipitates. However, on further increasing salt concentration, the precipitate redissolves in the solution and a stable birefringent phase forms. With still further increases 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 that does not cause any precipitation or phase separation as a salt tolerance limit for the surfactant formulation. Evidently, 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-percent salt when EOR-200 is 4 percent in the surfactant formulation.

Note that the salt tolerance of Petrostep-465 is smaller than that of TRS 10-410. The mixed system of Petrostep-465 + EOR-200 in a 1:4 ratio has almost the same tolerance (24 percent) as the mixed system of TRS 10-410 + EOR-200 of the same ratio. Note also that there is no precipitation region in Fig. 1 for Petrostep-465/EOR-200 ratios of 4:1 and 3:2 as compared with Fig. 2. It is evident from the Figs. 1 and 2 that as the amount of

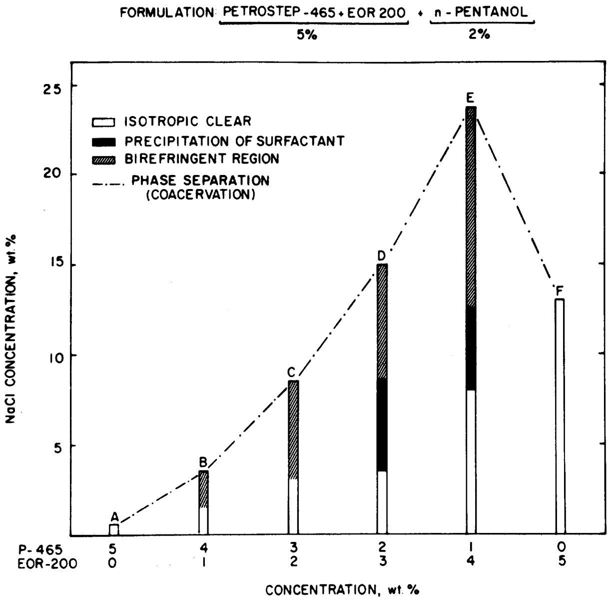

FIG. 1 — EFFECT OF NaCl CONCENTRATION ON OPTICAL APPEARANCE OF SURFACTANT FORMULATIONS (PETROSTEP-465 + EOR-200 + n-PENTANOL).

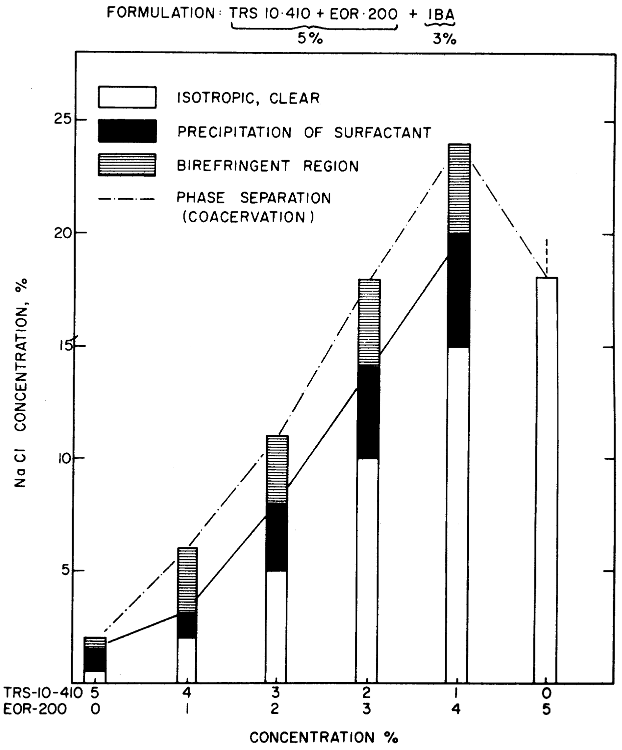

FIG. 2 — EFFECT OF NaCl CONCENTRATION ON OPTICAL APPEARANCE OF SURFACTANT FORMULATIONS (TRS 10-410 + EOR-200 + IBA).

EOR-200 in the surfactant formulation increases, the salt tolerance limit for every region increases. Also, the mixed surfactant system exhibits a much higher salt tolerance for phase separation after birefringence than that of the two individual surfactants (petroleum sulfonates or ethoxylated sulfonate), suggesting a *synergistic* effect when blending these surfactants. Note that a 5-percent EOR-200 system is isotropic and clear only up to 18-percent NaCl concentration, separating into two phases at more than 18-percent NaCl.

INTERFACIAL TENSION AND PHASE BEHAVIOR OPTIMAL SALINITY

When the surfactant formulation is equilibrated with oil, the surfactant-rich middle phase is formed in a specific salinity range. Healy and Reed[7] call this the middle-phase microemulsion. If the volume of solubilized oil in the middle phase is V_o, the volume of solubilized water is V_w, and the volume of surfactant is 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. Solubilization parameter V_o/V_s increases as salinity increases, while V_w/V_s decreases with increasing salinity. The intersection point of V_o/V_s with V_w/V_s is defined as the optimal salinity for phase behavior (S_ϕ). The oil-microemulsion phase/interfacial tension, γ_{om}, decreases as the salinity increases, while brine-microemulsion phase/interfacial tension, γ_{mw}, increases with salinity. The intersection point of γ_{om} and γ_{mw} is defined as the optimal salinity for interfacial tension behavior (S_γ).

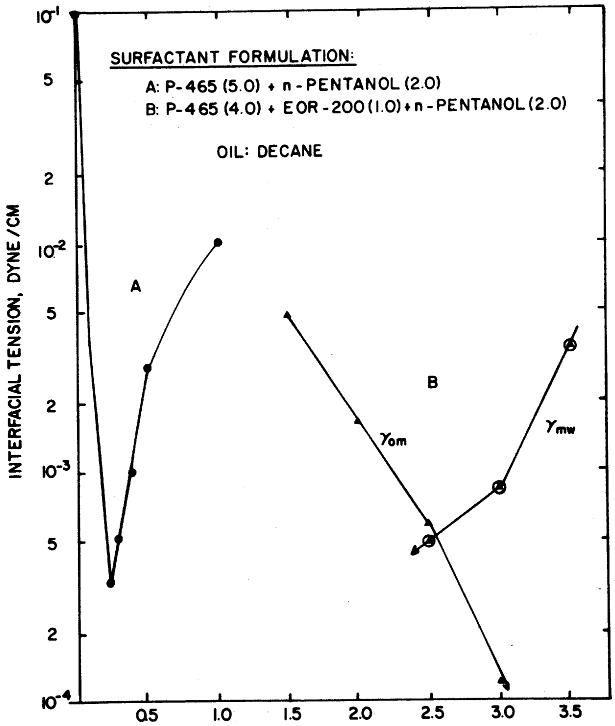

FIG. 3 — EFFECT OF NaCl CONCENTRATION ON INTERFACIAL TENSION FOR SYSTEMS A AND B.

Healy and Reed[7,10] studies the effect of $CaCl_2$ and temperature on the solubilization parameter, phase-behavior optimal salinity ($S\phi$) and interfacial tension behavior optimal salinity (S_γ). They also observed that at optimal salinity, oil recovery was maximum.[8] The inverse relationship between solubilization parameters and interfacial tension also was observed. Recently, Robbins[5] has developed a theory to correlate the solubilization parameters, V_o/V_s and V_w/V_s, with interfacial tension, γ_{om} and γ_{mw}, of systems containing nonionic surfactants. Hsieh and Shah[19] studied the effect of chain length and isomeric structure of alcohol on optimal salinity of 5-percent TRS 10-410 + 3-percent alcohol formulation with dodecane. They showed that as the chain length of alcohol increases, the optimal salinity of the formulation decreases. However, the optimal salinity increases with an increase in the chain-length of oil.

This study reports the optimal salinity values obtained by phase behavior and interfacial tension for the systems given in Table 1. Fig. 3 represents the interfacial tension for Systems A and B. System A does not form a middle phase, but it shows a minimum interfacial tension at 0.25-percent NaCl. This may result from significant partitioning of the surfactant in the oil and brine phases at this salinity.

The optimal salinity (S_γ) for System B (which formed the middle phase) is 2.5 percent. Fig. 4 shows interfacial tension data for Systems C, D, E, and F. System F (like System A) does not form a middle phase in the given salinity range. Note that the two sulfonates (Petrostep-465 and EOR-200) do not form the middle phase individually, but their mixtures do. The interfacial tension for System F is of the order of 10^{-1} dynes/cm for the salt concentration up to its salt tolerance limit. The interfacial-tension behavior/optimal salinity (S_γ) for Systems C, D, and E is 8.3, 16.5, and 25 percent, respectively. Fig. 5 shows the solubilization parameter V_o/V_s or V_w/V_s and phase-behavior optimal salinity (S_ϕ) for Systems B, C, D, and E.

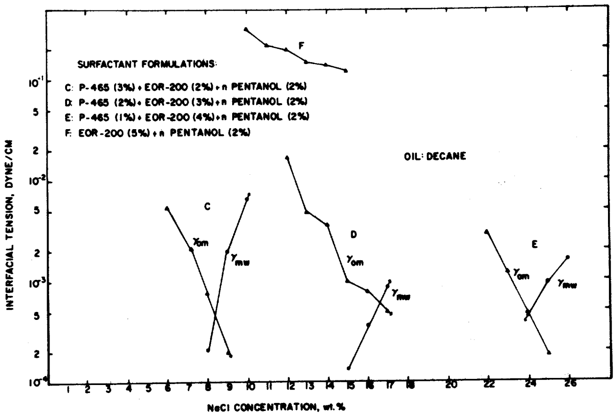

FIG. 4 — EFFECT OF NaCl CONCENTRATION ON INTERFACIAL TENSION FOR SYSTEMS C, D, E, AND F.

It is evident from Figs. 3 through 5 that optimal salinity (S_γ or S_ϕ) increases as the amount of EOR-200 in the surfactant formulation increases.

The influence of the relative amounts of ethoxylated and petroleum sulfonates on optimal salinity of the formulations is shown in Fig. 6. As the amount of ethoxylated sulfonate increases (up to 1:4 ratio), optimal salinity increases. From the interfacial tension data for the EOR-200 system (System F in Fig. 4), it is clear that EOR-200 by itself cannot produce an ultra-low interfacial tension in the salinity range studied, but adding 1-percent Petrostep-465 to the system drastically reduces the interfacial tension (Fig. 4). Fig. 7 represents the relationship between solubilization parameter V_o/V_s or V_w/V_s and interfacial tension. The inverse relationship obtained between V_o/V_s and γ_{om} and between V_w/V_s and γ_{mw} is similar to that obtained by Healy and Reed[10] for their surfactant system.

Fig. 8 shows the interfacial tension data for TRS

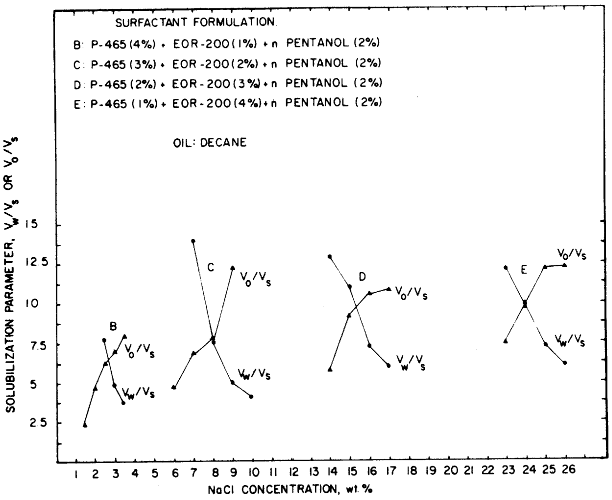

FIG. 5 — EFFECT OF NaCl CONCENTRATION ON SOLUBILIZATION OF OIL OR BRINE IN SYSTEMS B, C, D, OR E.

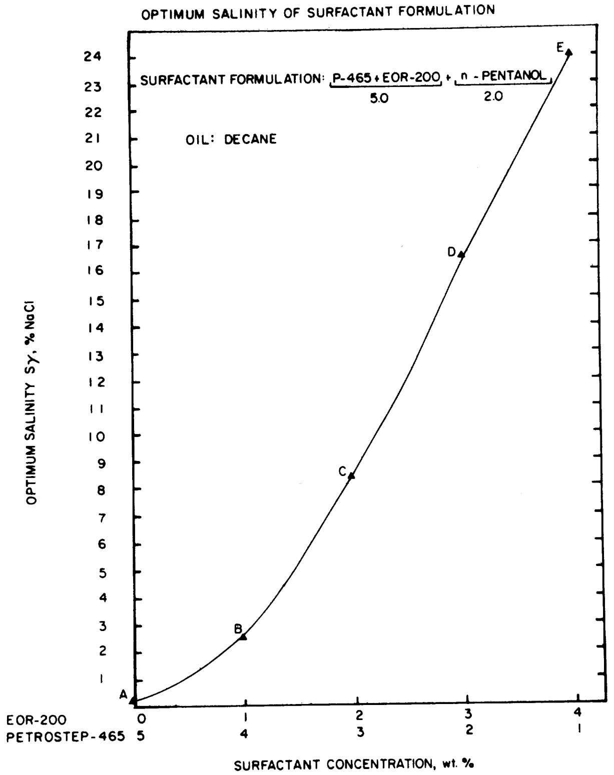

FIG. 6 — OPTIMAL SALINITY VALUES FOR VARIOUS AMOUNTS OF PETROSTEP-465 AND EOR-200 IN THE SURFACTANT FORMULATIONS.

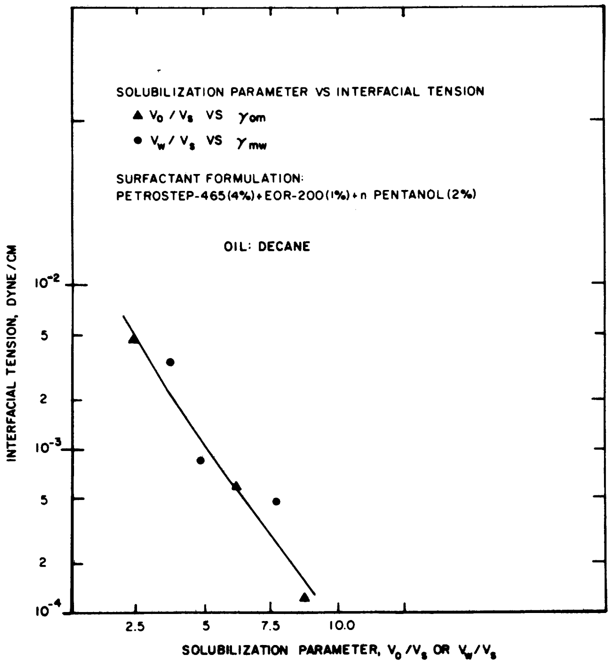

FIG. 7 — SOLUBILIZATION PARAMETER VS INTERFACIAL TENSION FOR SYSTEM PETROSTEP-465 (4 PERCENT) + EOR-200 (1 PERCENT) + n-PENTANOL (2 PERCENT) WITH n-DECANE.

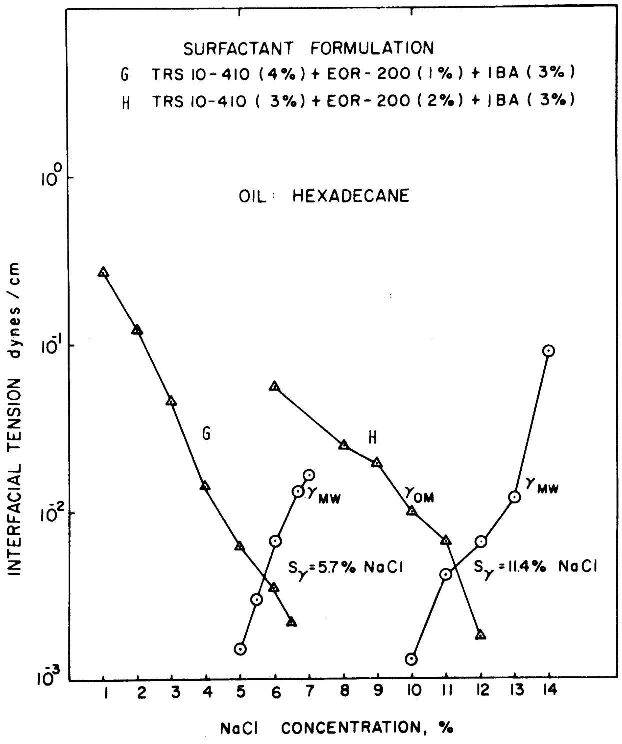

FIG. 8 — EFFECT OF NaCl CONCENTRATION ON INTERFACIAL TENSION FOR SYSTEMS G AND H.

10-410 + EOR-200 + IBA formulations (Systems G and H in Table 1). Similarly, Fig. 9 shows the interfacial tension data for Systems I and J, which have more EOR-200. The optimal salinity data obtained from Figs. 8 and 9 for Systems G, H, I, and *J* are plotted in Fig. 10. The optimal salinity obtained for these systems clearly indicates that as the amount of EOR-200 in the surfactant formulation increases, the optimal salinity value also increases.

The solubilization parameters for Systems G and H are shown in Fig. 11. Similar studies of Systems I and J exhibited higher optimal salinity. For each system, S_{ϕ} and S_{γ} were approximately the same (Figs. 8 and 11). The relationship between V_o/V_s and γ_{om} and between V_w/V_s and γ_{mw} for Systems G and H is shown in Fig. 12. Comparing Fig. 7 with Fig. 12 reveals that a greater solubilization occurs in the Petrostep-465 + EOR-200 system compared with the TRS 10-410 + EOR-200 system. Consequently, the interfacial tension values are smaller in the Petrostep-465 system than in the TRS 10-410 system. This effect presumably results from the difference in oil chain length used for the two systems. In fact, Hsieh and Shah[19] reported that as the chain length of oil increases, the solubilization parameter decreases and interfacial tension

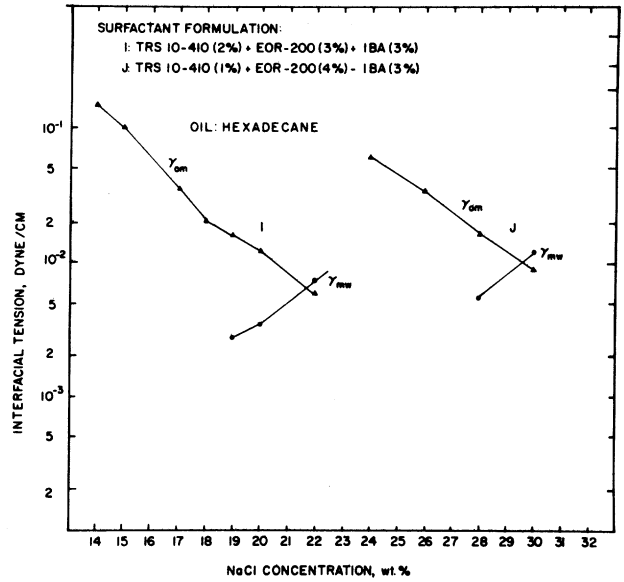

FIG. 9 — EFFECT OF NaCl CONCENTRATION ON INTERFACIAL TENSION FOR SYSTEMS I AND J.

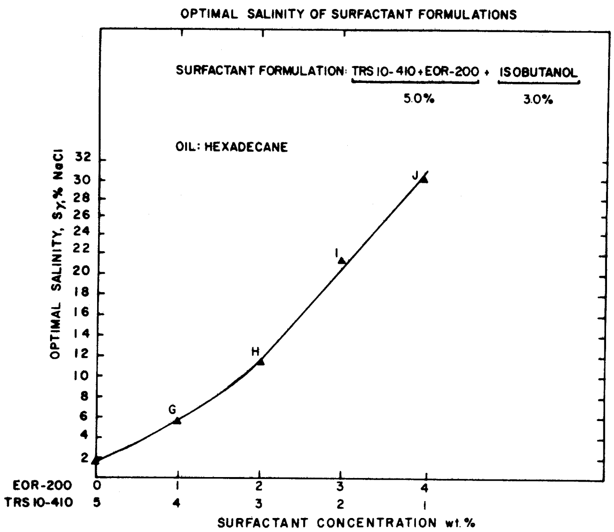

FIG. 10 — OPTIMAL SALINITY VALUES FOR VARIOUS RATIOS OF TRS 10-410 AND EOR-200 IN THE SURFACTANT FORMULATIONS.

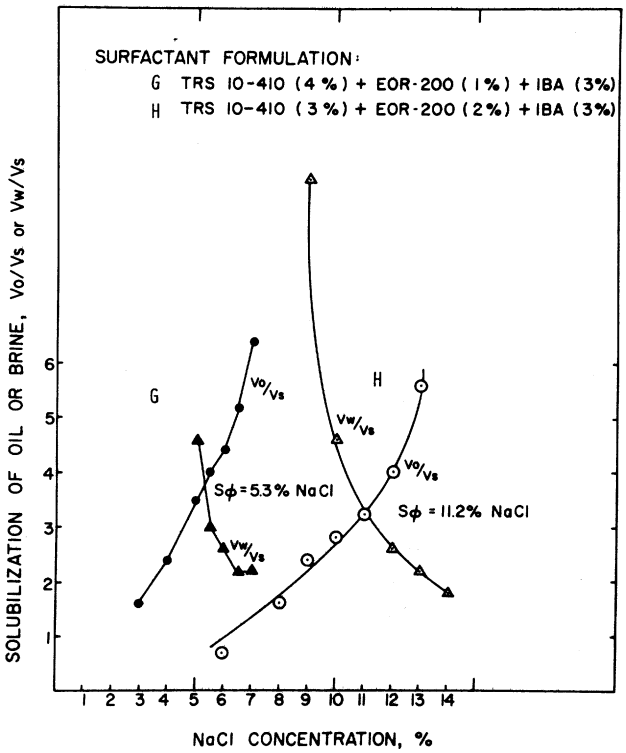

FIG. 11 — EFFECT OF SALT CONCENTRATION ON PHASE BEHAVIOR FOR SYSTEMS G AND H.

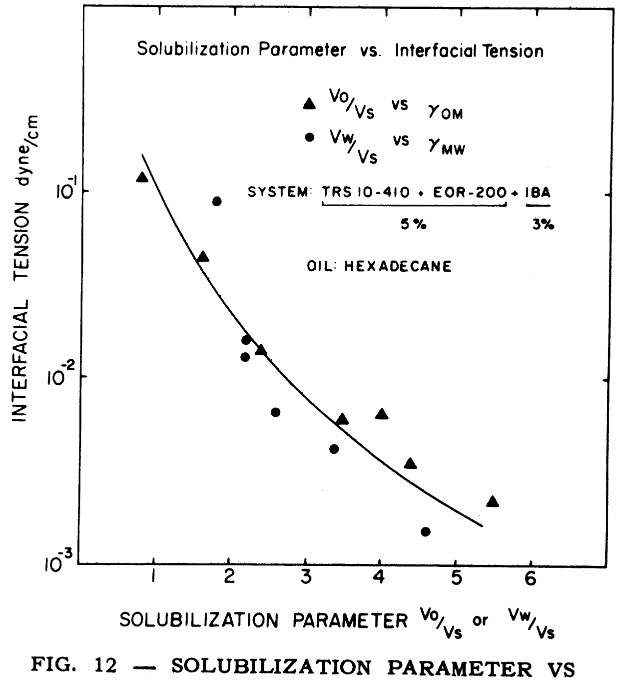

FIG. 12 — SOLUBILIZATION PARAMETER VS INTERFACIAL TENSION FOR SYSTEMS G AND H.

increases at corresponding optimal salinity values.

The interfacial tension data and optimal salinity values reported for these systems suggest that one can improve the salt tolerance and increase the optimal salinity of petroleum sulfonate formulations by adding an appropriate amount of an ethoxylated sulfonate. Interestingly, the minimum interfacial tension at optimal salinity is relatively unchanged by adding the ethoxylated sulfonate in these formulations. Our results suggest an approach for designing suitable surfactant systems for oil reservoirs with high salinities.

SUMMARY AND CONCLUSIONS

We observed for the surfactant formulations studied that surfactant formulations pass through different regions (stable, precipitation, birefringent to phase separation) when increasing the salt concentration. Also, we observed that as the amount of ethoxylated sulfonate (EOR-200) in the surfactant formulation increased, the salt concentration limit of every region increased. The increase in salt tolerance by blending an ethoxylated sulfonate with a petroleum sulfonate suggests an approach for designing surfactant formulations for high salinity conditions. From phase behavior and interfacial tension data, we concluded that optimal salinity increases when EOR-200 is added to the surfactant formulation. The interfacial tension at optimal salinity remains relatively unchanged for these mixed surfactant formulations.

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