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election Criteria and Formation of a Surfactant Slug for gh-Temperature, Moderate Salinity Reservoir Conditions

A.K. Sharma,* Inst. of Reservoir Studies, and Y.K. Pithapurwala and D.O. Shah,* of Florida

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ABSTRACT

The main objective of this investigation was to formulate a surfactant system for a water-flooded reservoir at 80°C and having a salinity in the range of 20-30 gms/liter. The equivalent alkane carbon number (EACN) of the crude oil at 80°C was found to be 9.3 as determined by a comparison of its optimal salinity with those of pure hydrocarbon oils. Isopropyl alcohol, isobutyl alcohol, secondary butyl alcohol and tertiary amyl alcohol (TAA) were employed as cosolvents in this study. The optimal salinity at 80°C of a petroleum sulfonate (TRS10-80), crude oil and any of the above alcohol containing system was found to be less than 1.3%. A phosphated ester (KF AA-270) was used as a cosurfactant with TRS10-80 in the weight ratio of 2/5 which increased the optimal salinity in the range of 25-35 gms/liter. However, the addition of this co-surfactant decreased the solubilization parameters drastically. In order to improve the solubilization of brine and oil in the middle phase microemulsion, inorganic salts such as Na_2CO_3 and sodium tripoly-phosphate were added to the formulation. The partitioning of alcohol in various phases was determined by gas chromatography. It was found that only TAA partitioned in the excess oil phase and middle phase whereas other alcohols partitioned in the middle and excess brine phase. Displacement tests were carried out at 80°C in sandpacks and Berea cores. The tertiary oil recovery efficiency was 92% when 0.2 PV of TAA containing surfactant slug was injected while the ter-tiary oil recovery efficiency was poor in systems con-taining other alcohols. It is concluded that the choice of alcohol and its partitioning behavior are important criteria for designing formulations for high temperature reservoir conditions. In the present study, the par-titioning of alcohol in the oil phase seems to correlate with greater oil displacement efficiency for the surf-actant system studied. It is proposed that the mass transfer of alcohol (TAA) from the aqueous surfactant slug to the oil phase in porous media promotes the oil displacement presumably due to the ultra-low IFT asso-ciated with this mass transfer process.

The tertiary oil recovery for surfactant slugs having different alcohols correlated with surfactant

breakthrough in the produced fluids. It was observed that the higher surfactant recovery in the produced fluids and a delayed surfactant breakthrough cor-responded to a greater oil recovery.

INTRODUCTION

After primary and secondary recovery, a great deal of residual oil remains in most reservoirs. Presently, a number of tertiary recovery methods aimed at recovering this residual are being investigated.[1] These processes involve the sequential injection of a number of fluids which are designed to either in-crease the portion of the reservoir being contacted or to do a better job of mobilizing oil than waterflood-ing. In many cases, the residual oil is trapped in the rock pores as blobs or ganglia. In order to mobi-lize a ganglion, the capillary forces holding it in the pore must be reduced. This effect can be accom-plished by lowering interfacial tension (IFT). One method of lowering IFT involves injecting a surfactant solution into a water flooded reservoir. These solu-tions have been shown both in the laboratory as well as in the field to reduce the oil saturation far below the values obtained with a waterflood. Polymer solu-tions are injected following the surfactant slug to propagate the micellar system efficiently through the reservoir. The polymer solutions also provide mobility control in the reservoir. Considerable research has been directed towards developing the technology of surfactant flooding.[2-8] Essentially two different concepts have developed for using surfactants. One concept uses a large pore volume of a low-concentration surfactant solution. The use of low-concentration surfactant solution has given rise to the so-called low-tension flood processes. The other concept uses a small pore volume of a high-concentration surfactant dispersion. These dispersions are called micellar solutions, microemulsions, swollen micelles, fine emulsions or soluble oils.

A surfactant slug upon injection into an oil reservoir undergoes complex changes as it traverses the reservoir. Dilution of surfactant slug occurs by mixing with reservoir oil and brine. This places stringent requirements on the design of the micellar flood. Initially, the micellar fluid is miscible with

the crude oil and reservoir brine. However, due to dilution, surfactant adsorption to the rock, precipitation of surfactants by reservoir brine of high salinity and divalent cations or penetration of the slug by drive water or polymer solution due to adverse mobility, the flood can degenerate to an immiscible displacement.[9] The retention of surfactant[10,11] in reservoir rock is a major factor limiting the effectiveness of oil recovery using micellar flooding.

The main criteria[12,13] for achieving high oil recovery are (1) ultra-low IFT between chemical bank and residual oil and between the chemical bank and drive fluid, (2) small surfactant losses to reservoir rock. If retention is excessive, IFT will eventually become high enough to retrap residual oil in the remainder of the reservoir; (3) brine compatibility and temperature stability, (4) mobility control and (5) economy of the process. Other screening criteria for chemical flooding discussed in literature[14] are the understanding of the reservoir and fluid characteristics such as the nature of oil and water content, relative permeability, mobility ratios, formation fractures and variation in permeability. Other important factors[15] for the success of micellar flood are rock stratification and heterogeneity, reservoir mineralogy, rock wettability and rock capillary properties.

Extensive work has been carried out to formulate surfactant systems for less complicated reservoir conditions (low reservoir temperature, low salinity). The main aim of this study is to find a suitable surfactant formulation for application in Ankleshwar reservoir, located in western India with reservoir temperature 80°C and brine salinity 20-30 gms/liter. Toward this goal, the dead crude oil from the reservoir was characterized as a first step. Surfactant formulations using petroleum sulfonates with suitable cosurfactant and inorganic salts were formulated such that ultra-low IFT and high salt tolerance was achieved. Phase volume behavior at 80°C was studied using crude oil as well as pure alkanes with EACN of the crude. Various alcohols, IPA, SBA, IBA and TAA were employed for the phase behavior and their concentrations in different equilibrated phases were determined. The effect of salinity and alcohols on oil displacement is explained in terms of partitioning of alcohol, on the residence time of surfactant slug in the porous media and surfactant recovery.

MATERIALS AND METHODS

A commercial petroleum sulfonate, TRS10-80 (Witco Chemical Company) was used as received. This surfactant has an average molecular weight of 418 and is 80% active. KF AA-270, a nonionic phosphated ester (BASF Wyandotte Company) was used as received. Alcohols and hydrocarbons used in this study were purchased from Chemical Samples Company with purity 99% or better. Sodium carbonate was purchased from Mallinckrodt Company and sodium tripolyphosphate from Fisher Chemical Company. Pusher-1000[TM] (Dow Chemicals) was used to prepare the polymer solutions. Deionized, distilled water was used to prepare the brine. Sandpacks with a dimension of 30 cm length and 2.5 cm diameter was used as the porous medium for the most part of this study. The sandpacks had a porosity of 38% and permeability of 3-4 Darcy. Rectangular Berea cores with a dimension of 30.5 cm by 2.5 cm by 2.5 cm were also employed in the oil displacement test which

had a porosity of 22% and permeability of 0.415 Darcy.

Interfacial tensions were measured by a spinning-drop tensiometer after phase equilibration at 25°C. The viscosity was measured by a Brookfield cone and plate viscometer at 80°C. For the phase volume behavior studies, the petroleum sulfonate-cosurfactant blend was mixed with equal volumes of brine (of the desired salinity) and oil. Surfactant and cosurfactants were added in oil while inorganic salts in brine. (Concentration of these species will be mentioned in the text. The solutions were vigorously shaken and equilibrated at 80°C in sealed glass tubes until no further change in respective phase volumes was observed. The equilibration time for this study was about two weeks to a month. Surfactant concentration of effluent was measured by a two-phase, two-dye titration method.[16] Alcohol concentration was measured using Perkin Elmer 900 gas chromatograph with SE30 column having 3% chromosorb support.

Porous media were conditioned by saturating them with CO_2 to displace air then flooded with brine which was filtered through 0.22μ filter. The porous medium was then saturated with oil at a high flow rate to irreducible brine content and then flooded with the resident brine to residual oil saturation. A 0.2 PV surfactant slug was then injected which was displaced by polymer solution (about 1.0 PV) and subsequently by drive water. The linear displacement velocity in the water flooding and the subsequent surfactant slug and polymer solution flooding was 1 ft/day. Oil displacement experiments were performed at 80°C under a back pressure of 30-40 psi to avoid development of any gas saturation at 80°C.

EACN DETERMINATION

The EACN concept, which allows the substitution of a crude oil by an alkane or an alkane mixture for phase volume or interfacial tension studies, has been generally accepted. This concept arises from the observation that the interfacial properties of any oil with a surfactant can be modeled by the behavior of alkanes. In addition, the EACN of a mixture of hydrocarbons follows the simple mixing rule

$$(EACN)_{mixture} = \sum_i x_i (EACN)_i$$

where x_i is the mole fraction of component i. Cayias[17] found that the EACN of an oil (crude, pseudocrude or hydrocarbons) is independent of the surfactant formulation, cosurfactants used in the formulation and that this equivalence always holds. Crude oil being dark in color and usually quite viscous can make equilibrium attainment very slow and phase observation difficult. Replacing crude oil facilitates screening of surfactant formulation and therefore EACN concept is a valuable one.

Glinsman[18] defined the EACN of a crude oil by comparing its optimal salinity based on the equality of microemulsion-oil vs. brine-microemulsion interfacial tensions with those of a pure n-paraffin. Tham and Lorenz[19] used the same approach except that the optimal salinity was based on equal solubilization of brine and oil. Recently, Puerto and Reed[20] used a three parameter representation to describe equivalent carbon number. The three parameters used were, the optimal salinity, solubilization parameter and oil

olar volume. They concluded that this three parameter representation provided a more nearly unique description of microemulsion phase behavior than available in the past.

The characteristics of Ankleshwar light crude oil are shown in Table 1. The EACN of this crude was determined by comparing optimal salinity based on equal brine and oil solubilization. Figure 1 shows the solubilization parameters as a function of salinity for TRS10-80/IBA/Crude Oil/Brine formulation. The ratio of surfactant to alcohol used in this section was 1. The optimal salinity for this system was found to be 0.73% NaCl. The optimal salinities of this formulation with nonane, decane, dodecane, tridecane were found and plotted as a function of alkane carbon number (ACN) in Figure 2. It is seen that optimal salinity increased linearly with ACN. This is in agreement with earlier studies.[19,21] It was observed that as the alkane number increased, the solubilization of brine and oil in the middle phase decreased. By comparing the optimal salinity of crude oil system with the pure hydrocarbons, the EACN of the crude was found to be 9.3. Since the optimal salinity with petroleum sulfonate and IBA was found to be (7.3 gms/liter) much lower than the salinity of Ankleshwar reservoir brine (20 to 30 gms/liter), and the value of solubilization parameters was small, it was necessary to design a formulation with high salt tolerance and capacity to solubilize more oil and brine.

SALT-TOLERANCE OF MIXED SURFACTANT SYSTEMS

Petroleum sulfonates have been found to exhibit low salinity tolerance. A variety of chemical compounds have been patented for use as cosurfactants with the goal of making petroleum sulfonates more compatible with reservoir fluids.[22] Nonionic surfactants tolerate higher level of hardness and salinity, although they have lower surface activity[23] per unit weight and are more expensive than petroleum sulfonates. In this investigation, Klearfac AA-270, a phosphated ester was used as a cosurfactant in different weight ratios to increase the salt-tolerance of petroleum sulfonate. The total surfactant concentration (petroleum sulfonate, TRS10-410 and KF AA-270) used in this section was 0.2% (w/w). Surfactant to alcohol (IBA) ratio was kept at 5/3. For interfacial tension measurements, octane was used as oil (WOR=1.0). The equilibrated system was a two-phase system at various salt concentrations. Interfacial tension was measured at room temperature (25±1°C). Figure 3 shows the effect of salinity on IFT for a mixed surfactant system. It is seen that when no Klearfac was present in the system, the salt tolerance of the system was only 2% NaCl and the minimum in IFT at 1% NaCl. Beyond this salinity, surfactant precipitated. As the concentration of Klearfac was increased, the salt tolerance of the mixed surfactant system increased to as high as 15% NaCl. It is interesting to note that besides increasing the salt tolerance, the addition of KF AA-270 decreased the IFT and broadened the IFT minimum. However, KF AA-270 alone (without blending it with petroleum sulfonate) did not reduce the IFT. Similar results have been reported by Hayes et al.[24] for mixed surfactant system containing alkyl (C_{18}) xylene sulfonates and KF AA-270. One possible explanation of this synergistic behavior could be that upon adding the cosurfactant, mixed micelles are formed. The surface charge density in aqueous as well as at the interface is increased thus decreasing the IFT.

PHASE VOLUME BEHAVIOR STUDIES

It has been shown in the literature[25-27] that the phase behavior of surfactant/brine/oil systems is a key factor in interpreting the performance of oil recovery by microemulsion flooding. By systematically varying salinity, higher solubilization of brine as well as oil in the middle phase and ultra-low interfacial tensions can be achieved in or near the salinity ranges giving three phases. Optimal salinity concept has been developed as a tool for designing microemulsions. It is the salinity at which the solubilization of brine and oil in the middle phase is equal. Figures 4 through 7 show the effect of salinity on solubilization parameters and volume fraction of phases at 80°C for TRS10-80 (5% w/v), KF AA-270 (2% w/v), alcohol (3% w/v) system for different alcohols, namely IPA, IBA, SBA and TAA. The solid lines in these figures refer to the phase behavior with pure alkanes (EACN=9.3) whereas the dotted lines refer to that with the Ankleshwar crude oil. Experiments were also carried out to determine the optimal salinity of this system in the absence of KF AA-270. Table 2 summarizes these results. The optimal salinity was found to be less than 1.3% for formulations containing TRS10-80/alcohol/oil/brine for all the alcohols studied. The addition of KF AA-270 increased the optimal salinity above 2% NaCl except for IBA formulation. However, the solubilization parameter decreased significantly. The optimal salinity of KF AA-270 containing system was found to be slightly lower for crude oil than for a mixture of pure alkanes. However, the solubilization parameter at optimal salinity remained about the same except for the system containing IBA.

When 1% Na_2CO_3 was added in brine, the optimal salinity increased [case (c) in Table 2] and it was in the range of 25 to 35 gms/liter. Moreover, the solubilization parameter almost doubled for all the alcohols used in the study. It is known that[28] the effect of sodium tripolyphosphate, a common detergent builder, is to minimize adsorption loss of anionic surfactant to the rock. The addition of 0.3% sodium tripolyphosphate reduced the optimal salinity of the system slightly. Comparing case (d) and (f) in Table 2, it is seen that in the presence of these additives, the optimal salinity of crude oil containing system was somewhat lower than that with pure alkanes having the same EACN. However, the phase volume behavior of crude oil was well represented by a mixture of pure alkanes.

The increase in the optimal salinity upon the addition of nonionic surfactant, KF AA-270, does not seem to be due to the lowering of pH of the aqueous phase. The phase behavior of the system TRS10-80/IPA/brine/alkanes with the pH of aqueous phase at 2, 7 and 11 was investigated. The pH was adjusted by adding appropriate amounts of H_2SO_4 or Na_2CO_3. Figure 8 shows the effect of pH on the phase behavior of this formulation at different salinities. It is seen that the optimal salinity as well as the solubilization parameter did not change considerably at pH=2 or pH=11. Same results were obtained at pH=7.

From this section, it can be concluded that the blending of petroleum sulfonate with phosphate ester allowed the optimal salinity in the range of 20-35 gms/liter. The addition of Na_2CO_3 increased the solubilization parameters. Both these observations

are true for all four alcohols employed in the phase
behavior but the choice of alcohol was not possible
from this study.

ALCOHOL PARTITIONING

The partitioning of chemicals into different
phases has an important bearing on the transport of
these chemicals in the reservoir. In general, it is
known that most of the surfactant partitions into
microemulsion phase, regardless of whether it is
lower, middle or upper phase. The concentration of
surfactant in excess water generally tends to decrease
and that in excess oil to increase as the salinity in-
creases.[29] The partitioning of a petroleum sulfonate
also depends on its average equivalent weight, crude
oil EACN, temperature, nature of alcohol, water-oil
ratio, etc. The partitioning of alcohol, on the other
hand, determines the optimal salinity of formulation
to a certain extent. The alcohol chainlength, struc-
ture and its solubility in brine[30,31] affects the
partitioning of alcohol in different phases. High
water soluble alcohols generally give higher optimal
salinity formulation.

The alcohol concentration in the equilibrated
phases at 80°C in the three phase region is plotted
as a function of salinity in Figures 9 through 11 for
the system TRS10-80(5%)/KF AA-270(3%)/alcohol(2%)/
alkanes. It is seen that IPA partitioned mainly in
the excess brine phase and in the middle phase whereas
TAA partitioned in the excess oil and in the middle
phase. SBA and IBA partitioned significantly in all
phases. The alcohol concentration in excess brine did
not change appreciably as the salinity was increased
except for TAA which decreased slightly at a higher
salinity. The partitioning of alcohols in excess oil
phase increased as the salinity increased for all al-
cohols except for IPA which remained unchanged. In
the middle phase, however, significant amount of each
alcohol partitioned in the entire three phase region.
TAA and IPA again showed opposite effect in terms of
their partitioning dependence of salinity. TAA con-
centration increased while IPA concentration decreased
in the middle phase upon increasing the salinity.
This is expected because as the salinity was increased,
brine solubilization in the middle phase decreased and
oil solubilization increased. Now since IPA parti-
tioned mainly in the excess brine phase, its concen-
tration in the middle phase decreased upon increasing
the salinity. However, TAA partitioned mainly in oil,
upon increasing salinity, its concentration in the
middle phase increased. Partitioning of various al-
cohols in the excess brine phase correlated with their
solubility in water. IPA being infinitely soluble in
water partitioned the most in the excess brine.

VISCOSITY OF MICROEMULSIONS

When the injected surfactant forms a microemulsion
in situ, one important property is to investigate the
viscosity of the microemulsion. In Figure 12, the
viscosity at shear rate 23 sec^{-1} of the surfactant-rich
phase is plotted as a function of salinity both for for-
mulations containing pure alkanes as well as crude oil.
The viscosity of crude oil containing surfactant-rich
phase at each salinity was found to be generally higher
than that of alkane containing microemulsions. The
viscosity of these microemulsions did not depend
significantly on the shear rate. In the absence of
1% Na_2CO_3 and 0.3% sodium tripolyphosphate, the

viscosities of the surfactant-rich phase were lower
(not shown in the figure). The viscosity of the
microemulsions with TAA showed a maximum with crude
oil. This type of behavior has been reported in the
literature.[29] The increase in the viscosity could
be attributed to the increase in surfactant parti-
tioning in the middle phase. At higher salinities
(above 3% NaCl), the viscosity of crude oil contain-
ing microemulsions varied in the same way as the
alkane containing microemulsions.

OIL DISPLACEMENT STUDIES

In this section, results of oil displacement tests
are discussed wherein aqueous surfactant formulations
were injected into sandpacks to displace a mixture of
nonane and decane (EACN=9.3) and into Berea cores to
displace crude oil at 80°C. In all of the oil dis-
placement studies reported here, 90% PV of aqueous
surfactant solution containing 5% TRS10-80, 2%
KF AA-270, 3% Alcohol and electrolytes were used.
All surfactant compositions also contained sacrificial
agents, 1% Na_2CO_3 and 0.3% sodium tripolyphosphate.
Use of these agents in reducing surfactant adsorption
in porous media is well established.[32] Four dif-
ferent alcohols were selected to determine the effect
of structure of the alcohol on the phase and parti-
tioning behavior as well as oil recovery. These in-
cluded IPA, IBA, SBA and TAA. Table 3 is the summary
of flooding results. The surfactant solutions were
prepared in the respective optimal salinity brines.
It can be seen that the tertiary oil recovery effi-
ciency in sandpacks to displace a mixture of nonane and
decane was 92% when the formulation contained TAA
whereas it was poor with the other three alcohols.
The tertiary oil recovery efficiency in Berea core to
displace Ankleshwar crude was about 80% with the same
surfactant system at the optimal salinity.

All phases in the produced effluent samples from
the oil displacement tests were collected at less than
0.05 PV interval and they were analyzed for petroleum
sulfonate using a two-phase titration technique.[16]
The titration technique has significantly less accurate
in systems containing crude oils since the dark-color
crude oil interfered with the visual observations of
the endpoint. Figure 13 shows the surfactant concen-
tration in produced fluids as a function of PV inject.
The area under each curve gives the amount of surfac
ant recovered in the effluent. Table 3 summarizes th
surfactant recovery for these flooding experiments.
The amount of surfactant retention was the least for
TAA containing surfactant formulation which gave
highest tertiary oil recovery efficiency. However,
significant amount of surfactant was also recovered
for the other floods. This suggests that better-
performing slugs usually are accompanied by lower
surfactant retention even though less retention doe
not necessarily mean higher oil recovery.[10,11,33]
The effective mechanisms which are viewed as respon
sible for the mobilization of residual oil[34] dur
surfactant flooding have been discussed by Chou an
Shah[35] and by Wilhite et al.[36] The principal
mechanism is the solubilization of oil droplets i
water-external, stable, homogeneous middle-phase
microemulsion, whose volume depends on the surfac
concentration. A further mechanism which can con
ute to the mobilization of residual oil is the i
sion of water into originally immobile residual
phase, resulting from the transfer of surfactan
the oil phase. The volume increase of the oil p

SPE 11772

...ich is designated as swelling, gives rise to an increase of the relative permeability to oil and thus a mobilization of residual oil.[37]

The higher oil recovery efficiency by TAA containing surfactant formulation suggests that the choice of alcohol is a main criterion for designing formulations for high temperature reservoir conditions. In the present study, the partitioning of TAA in the oil phase (as discussed in the earlier section) seems to correlate with greater oil displacement efficiency. It is proposed that the mass transfer of TAA from the aqueous surfactant slug to the oil phase in porous media promotes the oil displacement presumably due to ultra-low IFT associated with this mass transfer process.

The drastic difference in oil recovery efficiency when the formulations contained different alcohols cannot be accounted for by the small changes in the viscosity of the middle phase microemulsions containing different alcohols at their respective optimal salinities (Figure 12). The surfactant breakthrough in the effluent occurred at different pore volumes as shown in Figure 14. In surfactant formulations containing alcohols other than TAA, surfactant slug rushed through much faster than TAA containing system. Table 3 shows the PV at which the surfactant concentration reached maximum for different alcohols. The residence time available for contacting the residual oil was the highest for TAA containing system and hence it was the most effective in displacing oil.

For the TAA containing formulation, a series of displacement tests were conducted wherein the salinity of the system was varied around optimal salinity value, thereby changing the phase environment and hence the phase characteristics of the microemulsion formed in situ. Table 4 summarizes the results of these flooding tests. It is seen that the optimal salinity formulation yielded the highest oil recovery efficiency. At salinity higher than optimal salinity, oil recovery was the poorest. Figure 14 shows the surfactant concentration in effluent as a function of pore volume of fluids injected. The surfactant breakthrough was the earliest when the injected surfactant slug contained brine of higher than optimal salinity value. The surfactant recovery or the area under the curve at this salinity was the lowest. This indicates a significant surfactant retention in porous media because of the precipitation of surfactant at higher salinities. This can decrease the stability or prevent the generation of microemulsion in situ and thus can cause unstable, heterogeneous phases to occur. These changes are frequently associated with extremely pronounced differences in the mobility of the phases flowing through the porous medium[34] which results into poor oil recovery. At lower salinities than the optimal salinity, the oil recovery efficiency was higher and the surfactant loss was lower as compared to that above the optimal salinity.

CONCLUSIONS

1. The EACN of Ankleshwar crude oil was found to be 9.3. A mixture of nonane and decane with EACN 9.3 represented similar phase behavior as the crude oil.

2. The addition of KF AA-270, a phosphated ester increased the salt tolerance of the petroleum sulfonate system and broadened the IFT minimum.

3. The addition of Na_2CO_3 and sodium tripolyphosphate increased the solubilization parameters as well as the optimal salinity.

4. From the partitioning of alcohols in the equilibrated phases, it can be concluded that IPA partitioned mainly in the middle phase as well as in the excess brine phase whereas TAA partitioned in the middle phase as well as in the excess oil phase.

5. For sandpacks at 80°C, the formulations containing TAA, IBA, IPA and SBA as a cosolvent exhibited the tertiary oil recovery efficiency of 92, 27, 14 and 11 respectively.

6. For surfactant formulations containing TAA at 2.0%, 2.5%, 3.0% (optimal salinity), and 4.0% NaCl, the tertiary oil recovery efficiency was 31, 28, 92 and 10 respectively.

7. The tertiary oil recovery correlated with surfactant retention, surfactant breakthrough and alcohol partitioning in the equilibrated phases.

ACKNOWLEDGMENTS

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TABLE I

Ankleshwar Crude Characteristics

API gravity	43-51
Density (g/cc) - 15°C	0.77-0.81
Kinematic Viscosity at 50°C	1.4-2.3 c.s.
Pour Point, °C	15-24
Sulfur (% wt.)	0.01-0.04
Wax (% wt)	6.8-14.5
Asphaltenes (% wt)	0.08-0.24
Resins (% wt)	0.57-4.1
Gasoline (100-150°C), %	18.6 -42.2
Kerosene (150-200°C), %	22.9 -31.4
Gas Oil (250-350°C), %	15.0 -26.1
Residue after 350°C, %	16.5 -28.0

TABLE II

Optimal Salinity and Solubilization Parameter at Optimal Salinity of
Various Formulations

System: TRA 10-80 (5% w/v) + Alcohol (3% w/v) + Brine + Oil

Temperature: 80°C

Formulation	Type of Oil Used		Alcohol Used			
			IPA	IBA	SBA	TAA
(a) Without KF AA-270 and without Na₂CO₃ or sodium tripolyphosphate	A mixture of nonane + decane such that EACN = 9.3	o.s. s.p.	1.3% 4.0	0.7% 3.8	<1.0% 4.0	<1.0% 4.0
(b) Without sodium tripolyphosphate or Na₂CO₃	A mixture of none + decane such that EACN = 9.3	o.s. s.p.	2.6% 2.2	1.8% 2.7	2.1% 2.3	2.5% 2.5
(c) With 1% Na₂CO₃ but no sodium tripolyphosphate	A mixture of nonane + decane such that EACN = 9.3	o.s. s.p.	3.0% 4.4	2.8% 4.4	3.3% 4.0	3.4% 4.4
(d) With 1% Na₂CO₃ + 0.3% sodium tripolyphosphate	A mixture of nonane + decane such that EACN = 9.3	o.s. s.p.	2.8% 4.2	2.5% 4.0	3.1% 3.6	3.0% 4.5
(e) Same as part (b)	Ankleshwar crude oil having EACN = 9.3	o.s. s.p.	2.3% 2.4	1.3% 1.4	1.9% 2.3	1.9% 2.6
(f) Same as part (d)	Ankleshwar crude oil having EACN = 9.3	o.s. s.p.	3.2% 3.6	1.9% 4.2	2.4% 3.8	2.6% 4.2

o.s. = Optimal Salinity
s.p. = Solubilization Parameter at Optimal Salinity

TABLE III

Summary of Flooding Results[*]: Effect of Alcohol

Alcohol Used	Type of Porous Medium	Type of Oil Used	Residual Oil After Water Flooding (% PV)	Tertiary Oil Recovery Efficiency (%)	% Surfactant Recovery (%)	PV at Which Surfactant Concentration reached a maximum
SBA	Sandpacks	A mixture of nonane + decane	22	11	57.6	0.50
IPA	Sandpacks	A mixture of nonane + decane	22	14	63.8	0.71
IBA	Sandpacks	A mixture of nonane + decane	15	27	61.3	0.77
TAA	Sandpacks	A mixture of nonane + decane	10	92	78.5	1.10
TAA	Berea Core	Ankleshwar Crude Oil	43	79	NA	NA

[*] 0.2 PV of surfactant slug containing 5% (w/v) TRS 10-80, 2% (w/v) KF AA-270, 3% Alcohol in optimal salinity brine with 1% Na₂CO₃ and 0.3% sodium tripolyphosphate was injected in porous media (sandpack dimensions: 2.5 cm diameter, 30.0 cm length, permeability: 2-3 Darcy, Berea Core dimensions: 30.5 cm by 2.5 cm by 2.5 cm, permeability: 0.415 Darcy) Back pressure 40 psi, Temperature 80°C flow rate = 1 ft/day. 1500 ppm Dow pusher 1000 in optimal salinity brine when flooding was carried out with a mixture of nonane and decane 2000 ppm Dow pusher 1000 in optimal salinity brine when flooding was done with crude oil.

TABLE IV

Summary of Flooding Results: Effect of Salinity[*]

Salinity of surfactant slug, % NaCl	Type of Porous Medium	Type of Oil Used	Residual Oil After Water Flooding % PV	Tertiary Oil recovery efficiency,%	Surfactant recovery (%)	PV at which surfactant concentration reached a maximum
2.0	Sandpacks	A mixture of nonane + decane	18	31	68.7	0.86
2.5	Sandpacks	A mixture of nonane + decane	16	28	0.59	0.86
3.0 (optimum salinity)	Sandpacks	A mixture of nonane + decane	10	92	0.64	1.10
4.0	Sandpacks	A mixture of nonane + decane	18	10	0.23	0.65
2.8 (optimum salinity)	Berea Core	Ankleshwar Crude Oil	43	79	NA	NA

[*] 0.2 PV of surfactant slug containing 5% (w/v) TRS 10-80, 2% (w/v) KF AA-270, 3% TAA in resident brine with 1% Na₂CO₃ and 0.3% sodium tripolyphosphate was injected in porous media (sandpack dimensions: 2.5 cm diameter, 30.0 cm length, permeability 2-3 Darcy, Berea core dimensions: 30.5 cm by 2.5 cm by 2.5 cm, permeability 0.415 Darcy) Back pressure 40 psi, Temperature 80°C, Flow 1 ft/day, 1500 ppm Dow pusher 1000 in resident brine when flooding was carried out with a mixture of nonane and decane, 2000 ppm Dow Pusher 1000 in resident brine when flooding was carried out with Ankleshwar crude oil.
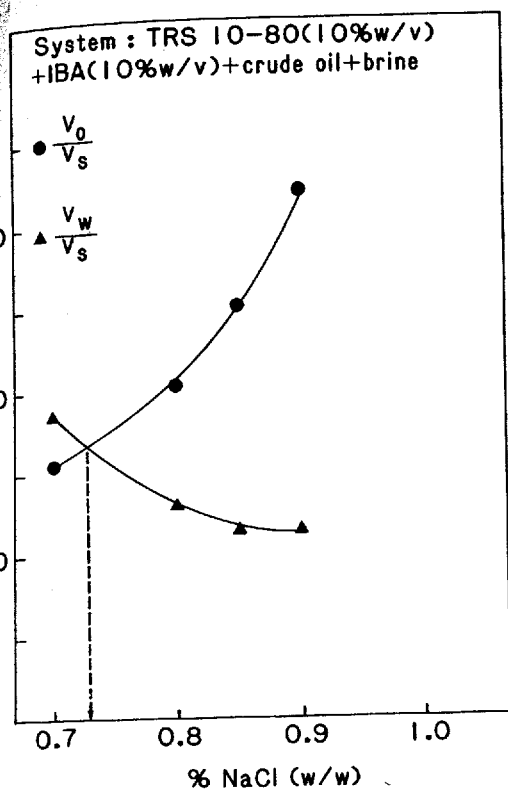
Fig. 1—Effect of salinity on solubilization parameters of TRS 10-80/IBA/crude oil/brine system.
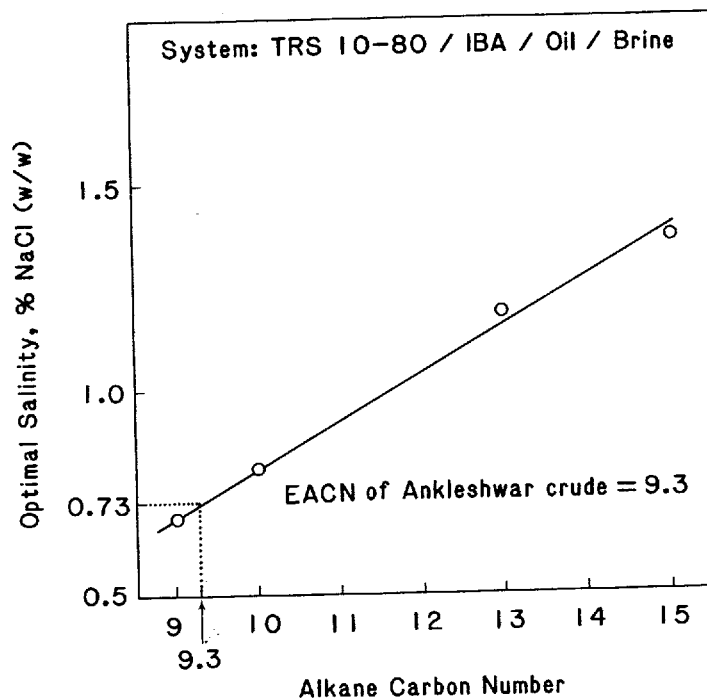

Fig. 2—Effect of alkane carbon number on optimal salinity of TRS 10-80/IBA/alkane/brine system.
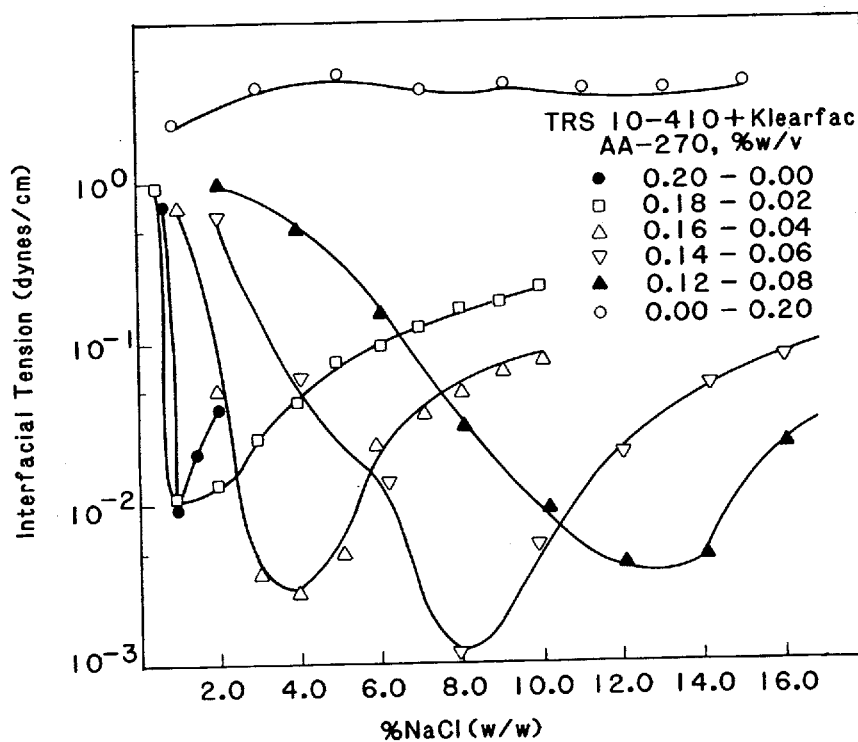

Fig. 3—Effect of addition of KF AA-270 on salt tolerance and broadening of IFT minimum of TRS 10-410/IBA/octane/brine system.

Effect of salinity on solubilization parameters and volume fraction of phases for TRS 10-80(5% w/w)+Klearfac AA 270 (2% w/w) +Isopropyl Alcohol (3% w/w) with and without the addition of 1% Na_2CO_3 and 0.3% Sodium Tripolyphosphate. Oils used were a mixture of nonane + decane (2.14:1.0 v/v; (EACN=9.3), and Ankleswar crude. Temperature 80 °C.

Additives : no Na_2CO_3 or Sodium Tripolyphosphate
——— mixture of nonane and decane
------ crude oil

SOLUBILIZATION PARAMETERS
VOLUME FRACTION OF PHASES

$\frac{v_o}{v_s}$
$\frac{v_w}{v_s}$

uϕ
mϕ
lϕ

Additives : 1% Na_2CO_3 + 0.3% Sodium Tripolyphosphate in brine

SOLUBILIZATION PARAMETER
VOLUME FRACTION OF PHASES

$\frac{v_o}{v_s}$
$\frac{v_w}{v_s}$

uϕ
mϕ
lϕ
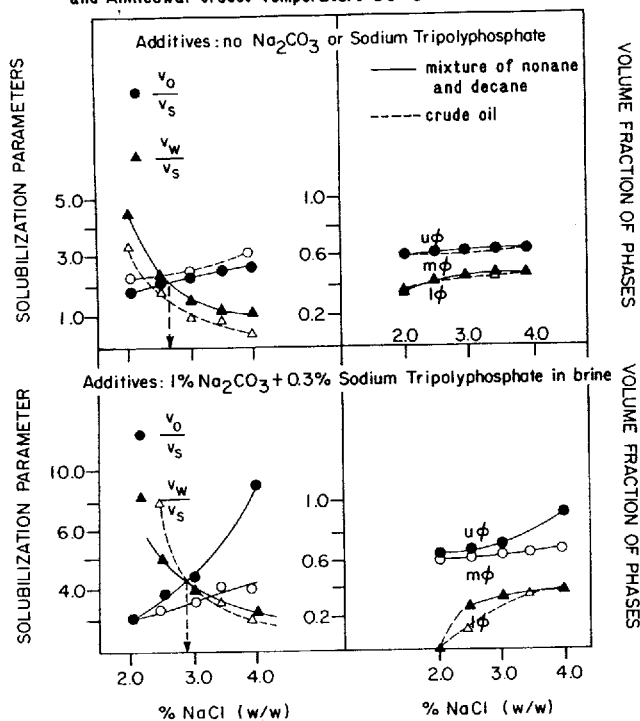
% NaCl (w/w)   % NaCl (w/w)

Fig. 4—Effect of additives on phase behavior of TRS 10-80 (5%) + KF AA-270 (2%) + IPA (3%) + oil at 80°C.

Effect of salinity on solubilization parameters and volume fraction of phases for TRS 10-80 (5% w/w)+Klearfac AA 270 (2% w/w) +Isobutyl Alcohol (3% w/w) with and without the addition of 1% Na_2CO_3 and 0.3% Sodium Tripolyphosphate in brine. Oils used were a mixture of nonane and decane (2.14:1.0 v/v; EACN=9.3), and Ankleswar crude. Temperature 80 °C.

Additives : no Na_2CO_3 or Sodium Tripolyphosphate
——— mixture of nonane and decane
------ crude oil

SOLUBILIZATION PARAMETER
VOLUME FRACTION OF PHASES

$\frac{v_o}{v_s}$
$\frac{v_w}{v_s}$

uϕ
mϕ
lϕ

Additives: 1% Na_2CO_3 + 0.3% Sodium Tripolyphosphate in brine

SOLUBILIZATION PARAMETER
VOLUME FRACTION OF PHASES

$\frac{v_o}{v_s}$
$\frac{v_w}{v_s}$

uϕ
mϕ
lϕ

% NaCl (w/w)   % NaCl (w/w)

Fig. 5—Effect of additives on phase behavior of TRS 10-80 (5%) + KF AA-270 (2%) + IBA (3%) + oil at 80°C.

Effect of salinity on solubilization parameters and volume fraction of phases for TRS 10-80(5% w/w)+ Klearfac AA 270 (2% w/w) +Secondary Butyl Alcohol (3% w/w) with and without the addition of 1% Na_2CO_3 and 0.3 % Sodium Tripolyphosphate in brine. Oils used were a mixture of nonane + decane (2.14:1.0 v/v; EACN=9.3) , and Ankleswar crude. Temperature 80°C.
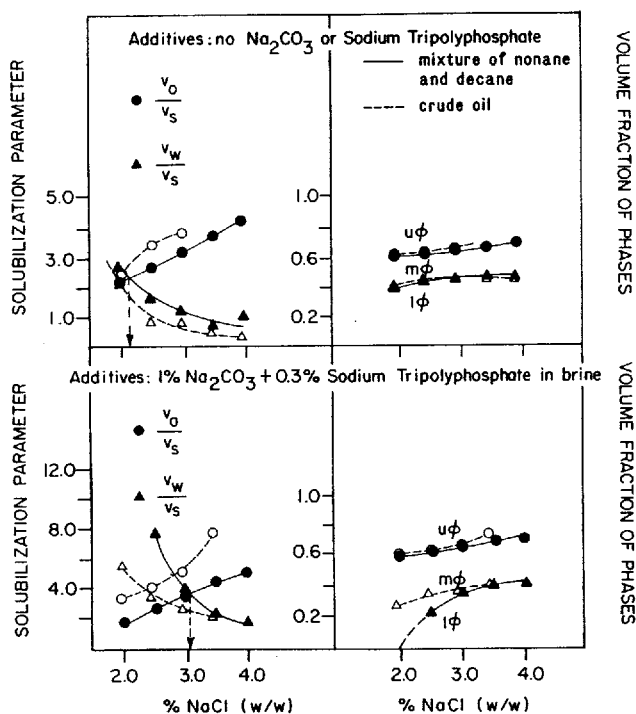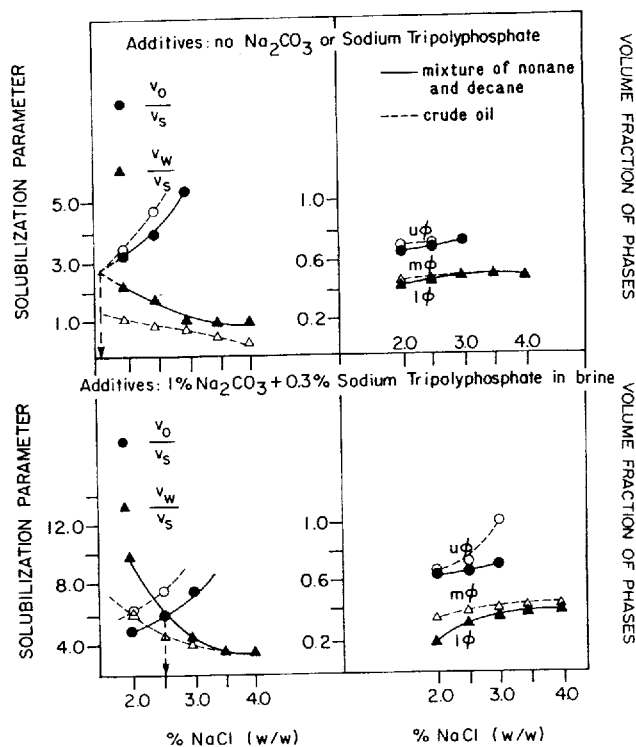
Additives : no Na_2CO_3 or Sodium Tripolyphosphate
——— mixture of nonane and decane
------ crude oil

SOLUBILIZATION PARAMETER
VOLUME FRACTION OF PHASES

$\frac{v_o}{v_s}$
$\frac{v_w}{v_s}$

uϕ
mϕ
lϕ

Additives: 1% Na_2CO_3 + 0.3% Sodium Tripolyphosphate in brine

SOLUBILIZATION PARAMETER
VOLUME FRACTION OF PHASES

$\frac{v_o}{v_s}$
$\frac{v_w}{v_s}$

uϕ
mϕ
lϕ

% NaCl (w/w)   % NaCl (w/w)

Fig. 6—Effect of additives on phase behavior of TRS 10-80 (5%) + KF AA-270 (2%) + SBA (3%) + oil at 80°C.

Effect of salinity on solubilization parameters and volume fraction of phases for TRS 10-80 (5 % w/w) +Klearfac AA 270 (2% w/w) +Tertiary Amyl Alcohol (3% w/w) with and without the addition of 1% Na_2CO_3 and 0.3% Sodium Tripolyphosphate. Oils used were a mixture of nonane + decane (2.14:1.0 v/v; EACN =9.3), and Ankleswar crude. Temperature 80°C.
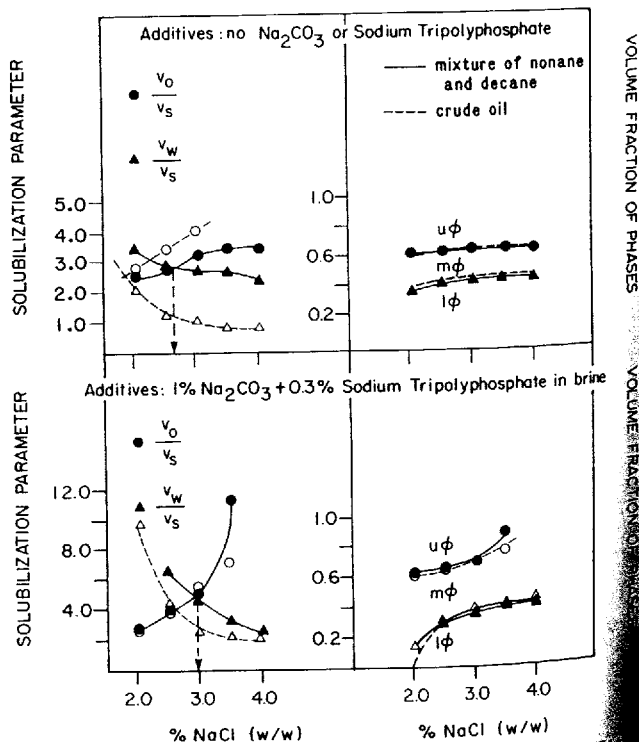
Additives : no Na_2CO_3 or Sodium Tripolyphosphate
——— mixture of nonane and decane
------ crude oil

SOLUBILIZATION PARAMETER
VOLUME FRACTION OF PHASES

$\frac{v_o}{v_s}$
$\frac{v_w}{v_s}$

uϕ
mϕ
lϕ

Additives: 1% Na_2CO_3 + 0.3% Sodium Tripolyphosphate in brine

SOLUBILIZATION PARAMETER
VOLUME FRACTION OF PHASES

$\frac{v_o}{v_s}$
$\frac{v_w}{v_s}$

uϕ
mϕ
lϕ

% NaCl (w/w)   % NaCl (w/w)

Fig. 7—Effect of additives on phase behavior of TRS 10-80 (5%) + KF AA-270 (2%) + TAA (3%) + oil at 80°C.

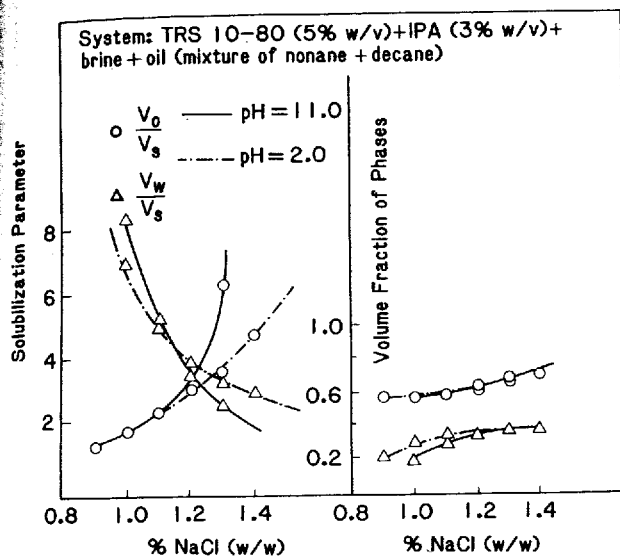Effect of pH on phase volume behavior of
petroleum sulfonate system.

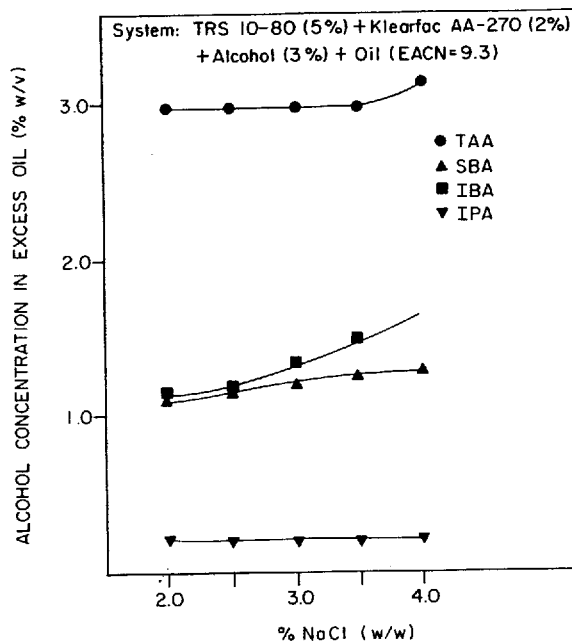Fig. 8—Effect of pH on phase behavior of petroleum sulfonate system.

Fig. 9—Effect of salinity on alcohol partioning in excess oil phase in three-phase systems containing different alcohols.

EFFECT OF SALINITY ON ALCOHOL PARTITIONING IN
EXCESS BRINE PHASE IN 3 PHASE SYSTEMS
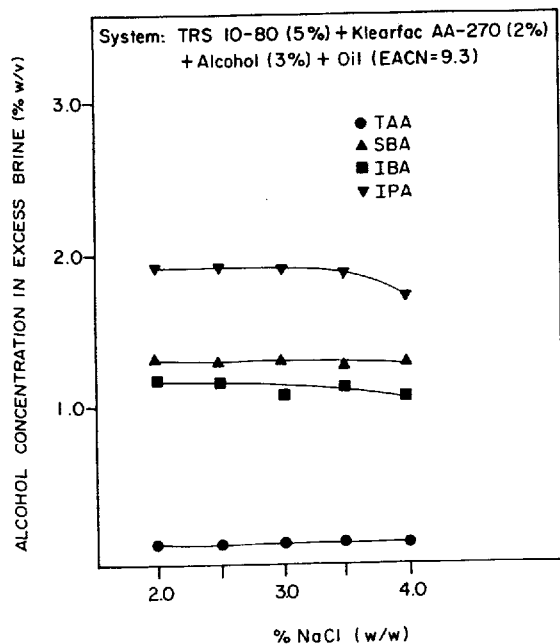CONTAINING DIFFERENT ALCOHOLS

Fig. 10—Effect of salinity on alcohol partitioning in excess brine phase in three-phase systems containing different alcohols.

EFFECT OF SALINITY ON ALCOHOL PARTITIONING IN THE
MIDDLE PHASE MICROEMULSIONS FOR SYSTEMS
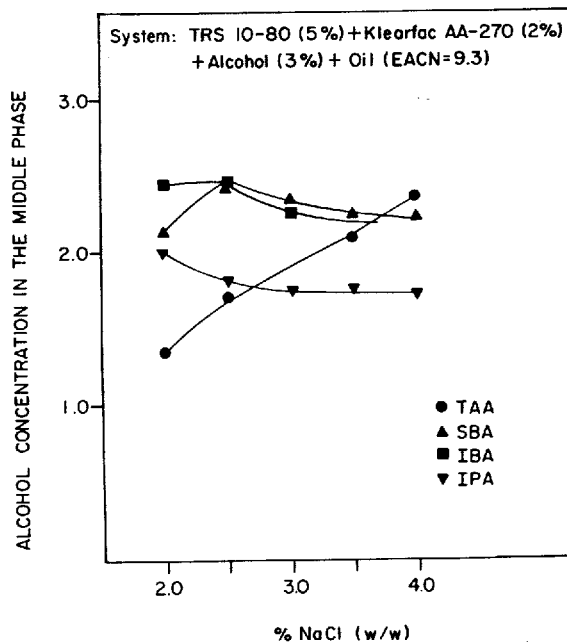CONTAINING VARIOUS ALCOHOLS

Fig. 11—Effect of salinity on alcohol partitioning in the middle phase microemulsions for systems containing different alcohols.

Viscosity of surfactant—rich phase at 80°C for crude oil and pure alkane systems at various salinities for different alcohols for TRS 10-80 (5%w/v)+KF AA-270(2%w/v)+Alcohol(3%w/v) +Na$_2$CO$_3$(1%w/v)+Sodium tripolyphosphate (0.3%w/v)

Mixture of Nonane+Decane (EACN 9.3)

○TAA
△SBA
□IBA
▲IPA

Ankleshwar Crude Oil
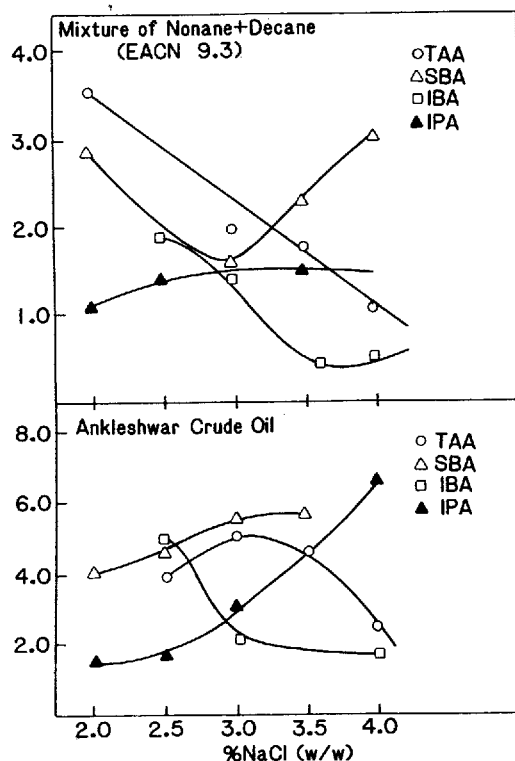
○ TAA
△ SBA
□ IBA
▲ IPA

%NaCl (w/w)

Fig. 12—Viscosity of surfactant-rich phase at 80°C for TRS 10-80 (5%) + KF AA-270 (2%) + alcohol + oil + brine containing 1% Na$_2$CO$_3$ + 0.3% sodium tripolyphosphate at 23 sec^{-1}.

EFFECT OF ALCOHOL ON EFFLUENT SURFACTANT CONCENTRATION AT OPTIMAL SALINITY OF VARIOUS FORMULATIONS

System: TRS 10-80 (5%)+ Klearfac AA-270 (2%) +Na$_2$CO$_3$(1%)+ Sodium Tripolyphosphate (0.3%) at optimal salinities with:

(11%)*
(14%)*
(27%)*
(92%)*

▲ SBA
■ IPA
● IBA
● TAA
* Tertiary Oil Recovery Efficiency
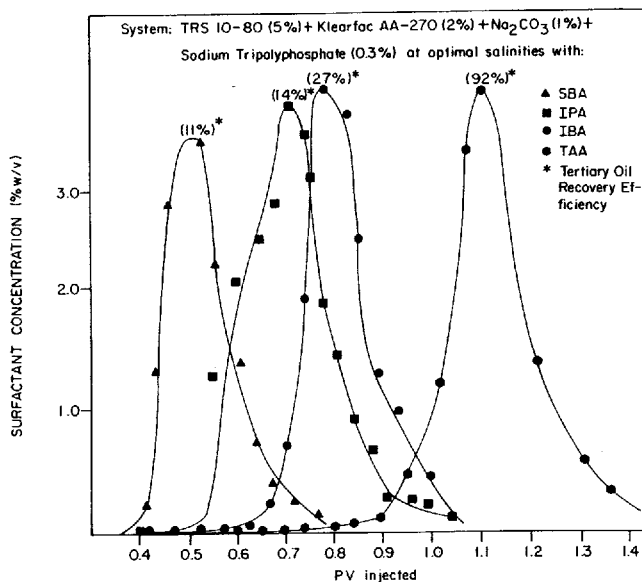
SURFACTANT CONCENTRATION (%w/v)

PV injected

Fig. 13—Effect of alcohol on surfactant concentration in the produced fluids at optimal salinity of various formulations.

EFFECT OF SALINITY ON SURFACTANT CONCENTRATION IN THE EFFLUENT FLUIDS

System: TRS 10-80 (5%)+ Klearfac AA-270 (2%)+TAA(3%) + Na$_2$CO$_3$ (1%)+Sodium Tripolyphosphate (0.3%)

(92%)*

● 2.0%
▲ 2.5%
● 3.0%(Optimal salinity)
■ 4.0%
* Tertiary Oil Recovery Efficiency

(28%)*
(31%)*
(10%)*

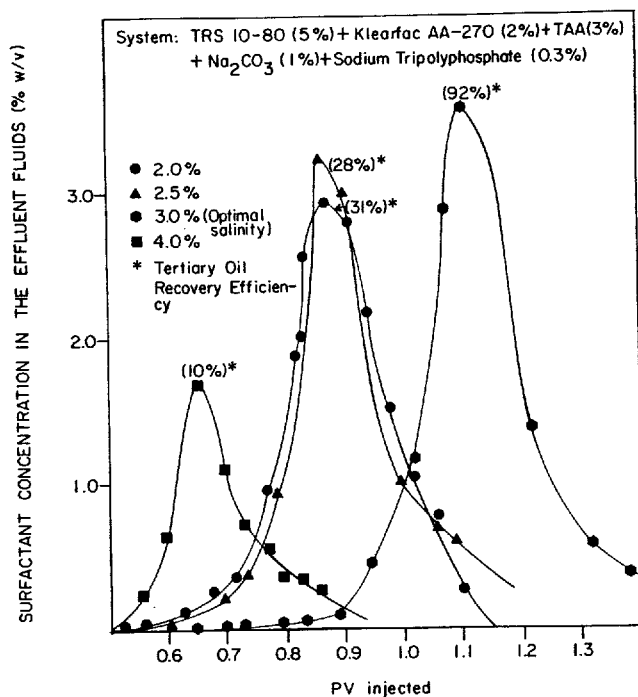SURFACTANT CONCENTRATION IN THE EFFLUENT FLUIDS (% w/v)

PV injected

Fig. 14—Effect of salinity on surfactant concentration in the produced fluids.