The Effect of Chain Length of Oil and Alcohol As Well as Surfactant to Alcohol Ratio on the Solubilization, Phase Behavior and Interfacial Tension of Oil/Brine/Surfactant/Alcohol Systems

by

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ABSTRACT

Economical microemulsion flooding process can be achieved by optimizing the surfactant formulation for an oil reservoir. This optimization involves the tailoring of a surfactant formulation to fit the conditions for a reservoir, namely, the temperature, the salinity and composition of formation water, and the nature of the crude oil. The general method of optimization of surfactant formulations is to investigate the phase behavior and interfacial tension of surfactant systems containing brine, oil, surfactant and co-surfactant.[1,2]

Solubilization of oil and brine by microemulsion phase containing petroleum sulfonate TRS 10-410 and alcohol was determined at room temperature. Interfacial tension between phases was correlated with solubilization behavior of surfactant formulations. The effect of the chain length of hydrocarbon oil on the solubilization and interfacial tension behavior of surfactant formulations was investigated at a surfactant concentration of 5 wt.% and isobutanol concentration of 3 wt.%. Effect of chain length and isomeric structure of alcohols on the solubilization and interfacial tension behavior of dodecane vs. surfactant solution containing 5 wt.% TRS 10-410 and 3 wt.% alcohol was investigated and correlated with the solubility of alcohol in brine. Effect of alcohol and surfactant concentrations on the formation and volume of the middle phase was determined. Surfactant to alcohol ratio was changed in the formulation in order to determine the molecular ratio of surfactant to alcohol in the middle phase. The surfactant to alcohol ratio in the middle phase microemulsion was determined using high resolution NMR spectroscopy. Interfacial tension was measured as a function of surfactant concentration to find the interfacial tension-concentration minima. The minimum interfacial tensions at low and high surfactant concentrations were correlated by changing salinity and hydrocarbon oil chain length in the surfactant formulation.

INTRODUCTION

Microemulsion flooding process has been widely tested in laboratory and has been applied in field tests in recent years for tertiary oil recovery. In this process, a microemulsion containing petroleum sulfonate, alcohol, oil and brine was used as an injection fluid. The interfacial tension between the microemulsion and reservoir oil or brine is as low as 10^{-2} dynes/cm or less. Under adequate conditions, the microemulsion slug is miscible with both oil and brine. However, beyond its solubilization limit, the microemulsion slug partitions into three phases, namely, a surf-

actant rich middle phase microemulsion as well as surfactant lean brine and oil phases.[1,2] Alternatively, an aqueous surfactant formulation containing petroleum sulfonate, alcohol and brine can be injected into oil reservoir.[3] The partitioning of this aqueous surfactant solution into three phases is allowed to take place in situ as it moves in the oil reservoir.

The maximum oil recovery efficiency is found at a salinity at which the middle phase microemulsion exhibits equal interfacial tension of the order of 10^{-3} dynes/cm or less with oil and brine phases.[4] At this optimal salinity, the middle phase microemulsion contains equal amount of oil and brine. Therefore, it is desirable to optimize a surfactant formulation so that a maximum recovery of oil can be achieved. The optimization of a surfactant formulation for a given crude oil can be achieved by : (1) the proper selection of surfactant and alcohol and (2) the proper selection of alcohol to surfactant ratio.

The optimization of a surfactant formulation for an oil reservoir is a non-trivial procedure since the choice of petroleum sulfonate, alcohol and alcohol to surfactant ratio can vary over a wide range. Therefore, a method for predicting the optimal salinity in the presence of various alcohols must be established. We believe that the surfactant formulation should be designed such that the reservoir brine becomes the optimal salinity for the formulation.

MATERIALS AND EXPERIMENTS

Petroleum sulfonate TRS 10-410 (60% active) was obtained from Witco Chemical Company. Alcohols of chain length from C_3 to C_5 were purchased from Chemical Sample Company and were 99% pure. Even number normal alkanes from C_6 to C_{16} were purchased from Chemical Sample Company and were 97% pure. Sodium chloride (analytical grade) was purchased from Fisher Scientific Company. Water was double distilled.

Surfactant solutions were made by mixing 5% (w/w) of TRS 10-410, 3% (w/w) alcohol and desirable amount of sodium chloride in distilled water. The surfactant solutions were allowed to equilibrate with equal volume of normal alkanes at $25 \pm 1°C$ in 50 ml graduated cylinders. Volume of each equilibrated phase was then recorded when the volume of each phase did not change with time. The time for the stabilization of phase volume ranged from 3 days to more than 6 weeks, with the shorter the chain length of oil, the longer the time required for phase stabilization.

After equilibration, phases were separated and the interfacial tensions between phases were measured in the spinning drop tensiometer at 25°C. Density of each phase was measured by 5 ml pycnometer. Concentration of alcohol (isobutanol) in aqueous phase, middle phase and oil phase was determined by high resolution NMR measurements using the procedure reported elsewhere.[5]

EFFECT OF CHAIN LENGTH OF OIL ON OPTIMAL SALINITY

Surfactant solution containing 5% (w/w) TRS 10-410 and 3% (w/w) isobutanol in brine was allowed to equilibrate with equal volume of n-alkane. It was observed that a surfactant rich lower brine phase remains in equilibrium with upper oil phase at low salinity. A surfactant rich upper oil phase remains in equilibrium with lower brine phase at high salinity. At medium salinity, a surfactant rich middle phase containing oil and brine remains in equilibrium with upper oil phase and lower brine phase. Nearly all the surfactant is concentrated in the surfactant rich phase. The amount of surfactant in the oil phase or brine phase is less than 0.05% (w/w). All isobutanol was assumed to be present in the surfactant rich phase. It will be shown in the latter part of this report that this is not a valid assumption. However, it is convenient and does not affect significantly the determination of the solubilization behavior.

The solubilized (or dissolved) volume of brine and/or oil was plotted as functions of salinity as shown in Figures 1 and 2. As salinity increases, the solubilized volume of brine decreases, while the solubilized volume of oil increases. The intersection of these two curves is defined as the optimal salinity for phase behavior S_ϕ. The interfacial tension of brine-surfactant phase, γ_{mw} and oil-surfactant phase, γ_{om} were plotted as functions of salinity as shown in Figures 3 and 4. As salinity increases, γ_{mw} increases and γ_{om} decreases. The intersection of these two curves is defined as the optimal salinity for interfacial tension S_γ.

The optimal salinity S_ϕ or S_γ increases as the chain length of n-alkanes increases as shown in Figure 5. In contrast, the volume of the middle phase at optimal salinity decreases as the chain length of n-alkane increases as shown in Figure 6. The optimal tension ($\gamma_{om} = \gamma_{mw}$) decreases as the chain length of n-alkane decreases (Figures 3 and 4).

The optimal salinity of the microemulsion system is a linear function of the density of n-alknaes (Figure 7). This implies that for the same concentration and type of petroleum sulfonate and alcohol, the optimal salinity of the microemulsion system can be

predicted from the density of the n-alkane. Whether this kind of correlation can be applied to aromatic or unsaturated hydrocarbons is not yet explored.

EFFECT OF CHAIN LENGTH AND ISOMERIC STRUCTURE OF ALCOHOL ON OPTIMAL SALINITY

Surfactant solution containing 5% (w/w) TRS 10-410 and 3% (w/w) alcohol in brine was allowed to equilibrate with equal volume of dodecane. The phase behavior of these microemulsion systems is similar to that described above. As chain length of n-alcohol increases, the optimal salinity decreases (Figures 8 and 9). However, the solubilized volume of brine or oil and the optimal interfacial tension ($\gamma_{om} = \gamma_{mw}$) at optimal salinity are not significantly different for different alcohols.

The optimal salinity for the microemulsion systems containing isomers of butanol is in the order of $2\text{-}C_4OH > i\text{-}C_4OH \cong n\text{-}C_4OH$ as shown in Figures 10 and 11. This is parallel to the solubility of butanol isomers in brine.

The optimal salinity for the microemulsion systems containing isomers of pentanol is in the order of $tert\text{-}C_5OH > 2\text{-}C_5OH > n\text{-}C_5OH$ as shown in Figures 12 and 13. This is also parallel to the solubility of pentanol isomers in brine. Again, the solubilized volume of brine or oil at optimal salinity and the optimal interfacial tension ($\gamma_{mw} = \gamma_{om}$) are not significantly different for different alcohols. It appears that the optimal salinity of microemulsion systems containing different alcohols is a linear function of the alcohol solubility in brine.

EFFECT OF SURFACTANT TO ALCOHOL RATIO ON OPTIMAL SALINITY

The concentration of TRS 10-410 in surfactant solution was kept at 5% (w/w) while the concentration of isobutanol was varied in order to change the surfactant to alcohol ratio. At 1.0% and 1.5% salinities, the solubilized volume of brine was drastically decreased, but the solubilized volume of oil was not changed significantly (Figures 14 and 15). The interfacial tension γ_{mw} was increased about two orders of magnitude when isobutanol concentration increased from 4% to 9% at 1% NaCl and from 1% to 5% at 1.5% NaCl. The interfacial tension γ_{om} was not affected significantly as concentration of isobutanol varied.

Therefore, an optimal concentration of isobutanol can be determined at each salinity. Accordingly, optimal isobutanol concentration can be selected at 3% when salinity is 1% and at 1.5% when salinity is 1.5%. The

volume of the middle phase decreases as the concentration of isobutanol increases. This is shown in Figure 16.

In other experiments, the concentration of isobutanol was kept at 1.5% or 3% while the concentration of TRS 10-410 varied. As the concentration of TRS 10-410 increases, the volume of the middle phase increases linearly (Figure 17). Again, the volume of the middle phase is always smaller at higher isobutanol concentration, i.e. 3%. The volume of the middle phase approaches zero when the concentration of TRS 10-410 reduces to near zero. This indicates that the formation of the middle phase requires the presence of surfactant molecules.

The distribution of isobutanol in upper oil phase, lower aqueous phase and middle phase was determined by high resolution NMR measurements. Concentrations of isobutanol in the middle phase and the lower aqueous phase for microemulsions of different oils are listed in Table I. At optimal salinity or near optimal salinity, the concentration of isobutanol is 0.02258 gm/ml solution in the lower phase and 0.0176 gm/ml in the middle phase for different oils.

To calculate this isobutanol to surfactant TRS 10-410 molar ratio, the surfactant TRS 10-410 was assumed to be dissolved in the middle phase, since the concentration of TRS 10-410 in oil phase or brine phase was less than 0.05% by weight. The molecular ratio of isobutanol to surfactant TRS 10-410 in the middle phase was found to be 1.4 when oil was hexadecane and 2.85 when oil was hexane. This is shown in Table II.

ULTRA LOW INTERFACIAL TENSION BY HIGH AND LOW SURFACTANT CONCENTRATION SOLUTIONS

It has been demonstrated [6,7] that the ultra low interfacial tension also can be produced at substantially lower surfactant concentrations ($\approx 0.2\%$ w/v). However, unlike the high surfactant concentration systems, there is no middle phase present in the solution of low surfactant concentrations. The question that can be raised is whether there is any correlation between the ultra low interfacial tensions observed in high and low surfactant concentration systems. It is also desirable to investigate the dependence of the interfacial tension on the surfactant concentration, salinity and chain length of hydrocarbon oil in low surfactant concentration systems.

The interfacial tension of dilute surfactant formulations in equilibrium with dodecane and hexadecane are shown in Figure 18. The interfacial tensions have a sharp

minimum at 0.1% TRS 10-410 with 0.06% iso-butanol for dodecane and at 0.006% TRS 10-410 with 0.0036% isobutanol for hexadecane. Brine concentrations used were the same as optimal salinities (dodecane, S_γ = 1.5% NaCl and for hexadecane, S_γ = 2% NaCl).

Presence or absence of isobutanol does not shift the surfactant concentration at which the minimum interfacial tension occurs. This is shown in Figure 19. The ultra low interfacial tension only occurs at optimal salinity, i.e., 1.5% NaCl in dodecane. The interfacial tension data are shown in Figures 19 and 20.

The effect of hydrocarbon oil chain length on the interfacial tension values at 0.01, 0.1 and 5.0% surfactant concentrations are shown in Figure 21. At 0.1% TRS 10-410 with or without isobutanol the ultra low inter-facial tension appears at 12 carbon chain length of oil. At 5% TRS 10-410 with 3% isobutanol, which is 50 times more concentrated, the optimal interfacial tension also appears at 12 carbon chain length. At 0.01% TRS 10-410 with 0.0067% IBA, the interfacial tension reaches a plateau at dodecane.

In conclusion, the ultra low interfacial tension can be produced at a high surfactant concentration, e.g., 5% and at a low surfac-tant concentration, e.g., 0.1%. The attain-ment of low interfacial tension strongly depends on the electrolyte as well as surfac-tant concentrations and on the chain length of oil. Both in the high and low surfactant concentration regions, the attainment of ultra low interfacial tension requires the same salinity and the same chain length of oil for the TRS 10-410 surfactant solutions. Therefore, we believe that the behavior of high and low surfactant concentration systems is interrelated.

Recently we have proposed molecular mechanisms to account for the observed effects of surfactant and salt concentrations and of oil chain-length on the ultra low interfacial tension.[5,8] We have shown that ultra low interfacial tension occurs at the critical micelle concentration (CMC) for synthetic or natural petroleum sulfonates. The oil chain length effect is attributed to parti-tioning of the surfactant and CMC phenomena.

From electrophoretic mobility, and inter-facial tension measurements we have shown[9] that for the effect of surfactant, salt, or caustic concentration, the minimum in interfacial tension corresponds to a maximum in electro-phoretic mobility of oil droplets and hence presumably to the interfacial charge at the oil/brine interface. We believe that the generation of ultra low interfacial tension in

part may be due to high surface charge density. We also observed[10] that the maximum oil recovery of a crude oil occurred in sand-packs and berea cores at a salt concentration where the oil droplets exhibited a maximum in electrophoretic mobility.

The effect of NaCl concentration on the microstructure of TRS 10-410 plus isobutanol system was investigated using freeze-fracture electron microscopy, pulse and high resolution NMR spectroscopy and optical anisotropy meas-urements. With increasing NaCl concentration, the surfactant system undergoes various phase transitions and at 2.0% NaCl, the system consists of "birefringent cellular fluids."[11] The freeze-fracture electron micrographs re-vealed a lamellar, membranous foam-like structure of the birefringent solution.

APPLICATIONS

The methods of selecting components for a surfactant formulation to exhibit its max-imum capacity to solubilize oil and brine and consequently produce an ultra low interfacial tension are desirable in the surfactant flooding process. These methods can be defined as the optimization of a surfactant formula-tion. It has been shown [1,2] that the optim-ization of a surfactant formulation can be achieved by adjusting the salinity of the brine. In this work, the relation between optimal salinity and various factors was in-vestigated. These factors include hydrocarbon oil chain length, alcohol chain length and its isomeric structure, alcohol and surfactant concentrations as well as the alcohol to surf-actant ratio. The results of this study form a framework of guide lines to optimize a surfactant formulation. This study clearly demonstrates how the nature and concentration of various components, namely, hydrocarbon oil, alcohol, electrolytes as well as the alcohol to surfactant ratio, can influence the solubilization, phase behavior and interfacial tension of a surfactant formulation.

CONCLUSIONS

(1) The surfactant migration from lower to middle to upper phase is promoted by an increase in salinity.

(2) Optimal salinity for phase behavior S_ϕ correlates well with optimal salinity of inter-facial tension behavior S_γ as demonstrated by Healy and Reed.[1]

(3) Optimal salinity S_ϕ and S_γ increase as oil chain length increases.

(4) Optimal salinity S_ϕ and S_γ for surfactant formulations containing alcohol isomers of C_4 or C_5 or C_3OH increase with increasing

alcohol solubility in brine. There is no significant difference in ultra low interfacial tension achieved and volume of oil or brine solubilized at optimal salinity by using different alcohols with chain length from C_3 to C_5. This indicates that one can select an alcohol according to reservoir salinity and still produce an ultra low interfacial tension.

(5) Studies with increasing alcohol concentration indicate that there exists an optimal alcohol concentration which can produce ultra low interfacial tension and solubilize maximum amount of oil and brine. The optimal alcohol concentration depends on brine salinity.

(6) The optimal salinity of an oil/brine/surfactant/alcohol system depends upon the solubility of alcohol in brine. The higher the solubility of alcohol in brine, the higher the optimal salinity.

(7) Middle phase volume is proportional to the concentration of surfactant. However, the middle phase volume decreases as concentration of isobutanol increases in the surfactant formulations.

(8) A molar ratio of alcohol to surfactant in the middle phase was found to be 1.5 when oil was hexadecane and about 3 when oil was hexane.

(9) For a given oil, ultra low interfacial tension occurs at the optimal salinity and at a specific surfactant concentration.

(10) At low surfactant concentrations, the ultra low interfacial tension occurs at a specific chain length of oil. At high surfactant concentrations, the middle phase microemulsion forms with the same chain length of oil resulting in the ultra low interfacial tension. This suggests that ultra low interfacial tensions observed at the low and high surfactant concentrations are interrelated. Perhaps, the middle phase does form at low surfactant concentrations but remain invisible because of extremely small volume. However, its effect on interfacial tension is evident and measurable.

ACKNOWLEDGEMENTS

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TABLE I

Distribution of Isobutanol in Middle and Lower Phases
after Equilibration of Various Hydrocarbon Oils
with 5% TRS 10-410 plus 3% Isobutanol Formulation

Oil Chain Length	Salinity wt.%	Concentration of Isobutanol middle phase (grams/ml solution)	lower phase	K*
C_6	0.50	0.01648	0.02015	0.818
C_8	0.75	0.01690	0.02340	0.722
C_8	0.875	0.01813	0.02371	0.765
C_{10}	1.125	0.01524	0.02285	0.667
C_{10}	1.25	0.01688	0.02392	0.706
C_{12}	1.50	0.01785	0.02143	0.833
C_{12}	1.50	0.01761	0.02241	0.785
C_{14}	1.75	0.01999	0.02235	0.895
C_{16}	2.00	0.01935	0.02303	0.840
Average value		0.01760	0.02258	0.7795

$$* \ K = \frac{\text{conc of IBA in the middle phase}}{\text{conc of IBA in the aqueous phase}}$$

TABLE II

Composition of the Middle Phase after Equilibration
of 5% TRS 10-410 plus 3% Isobutanol Formulation
with Equal Volume of Various Hydrocarbon Oils

Oil Chain Length	Salinity wt.%	Volume fraction of Middle Phase, %	Composition (moles) TRS 10-410:Isobutanol:Oil:Water
C_6	0.50	46	1 : 2.85 : 43.9 : 336
C_8	0.75	41.3	1 : 2.63 : 40 : 224
C_8	0.875	34.7	1 : 2.36 : 38.8 : 131
C_{10}	1.125	36	1 : 2.06 : 31.4 : 159
C_{10}	1.25	32	1 : 2.03 : 30.5 : 110
C_{12}	1.50	28	1 : 1.88 : 19.6 : 130
C_{12}	1.50	28	1 : 1.85 : 17 : 156
C_{14}	1.75	21.3	1 : 1.60 : 7.9 : 154
C_{16}	2.00	19	1 : 1.40 : 7.4 : 154
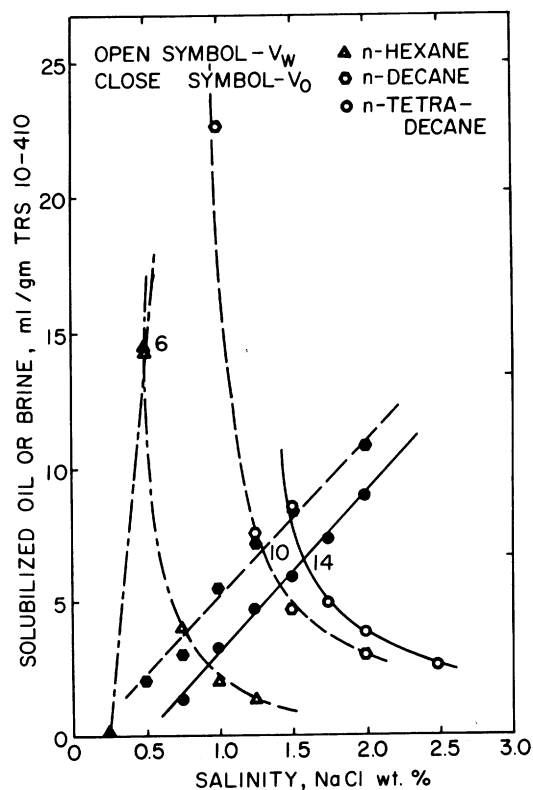
Fig. 1 — Effect of oil chain length on the solubilization behavior of 5% TRS 10–410 + 3% isobutanol.
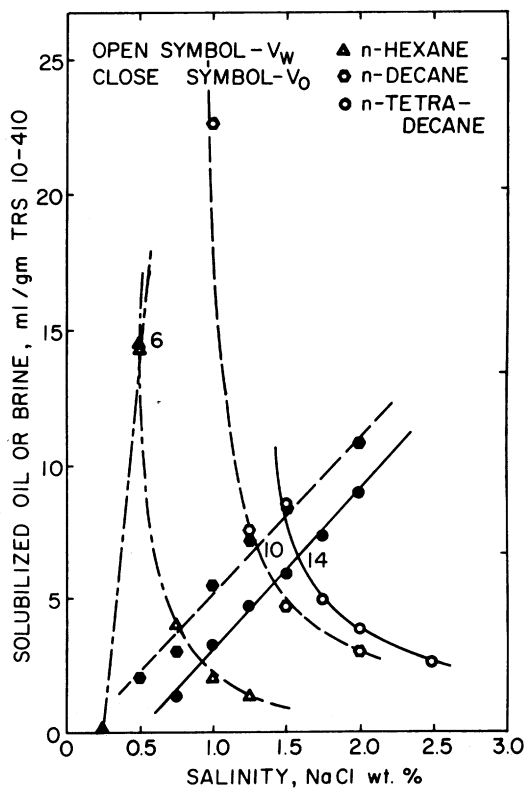
Fig. 2 — Effect of oil chain length on the solubilization behavior of 5% TRS 10–410 + 3% isobutanol.
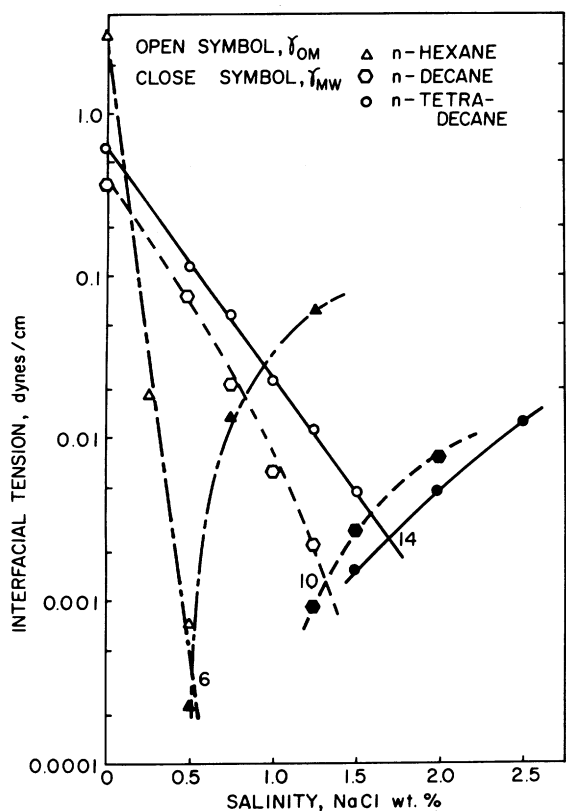
Fig. 3 — Effect of oil chain length on the interfacial tension behavior of 5% TRS 10–410 + 3% isobutanol.
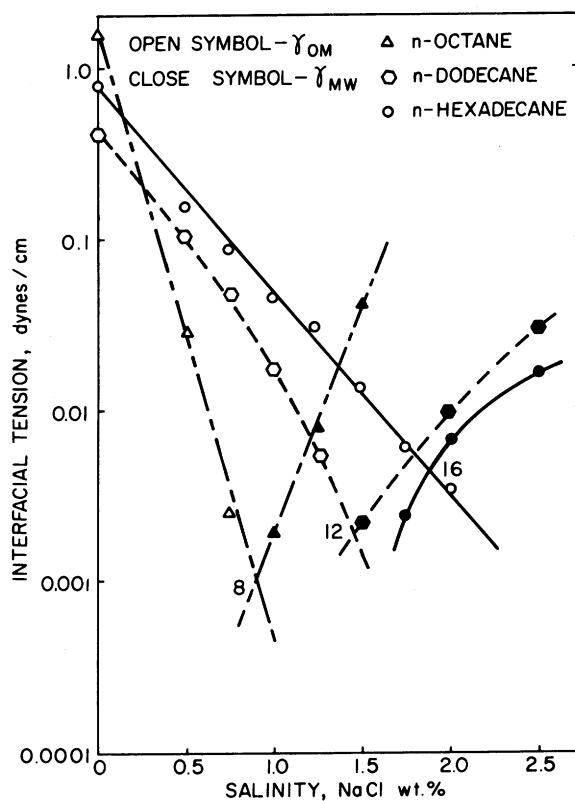
Fig. 4 — Effect of oil chain length on the interfacial tension behavior of 5% TRS 10–410 + 3% isobutanol.
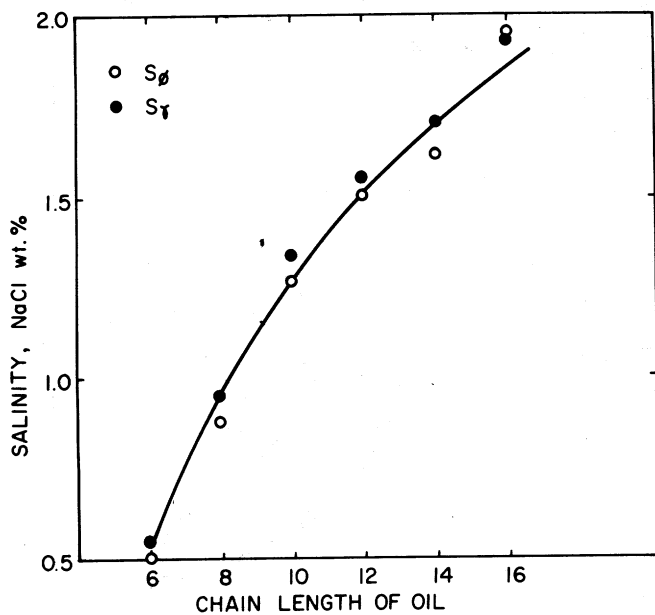
Fig. 5 - Optimal salinities S_γ and S_ϕ of 5% TRS 10-410 + 3% iso-butanol vs. chain length of oil.
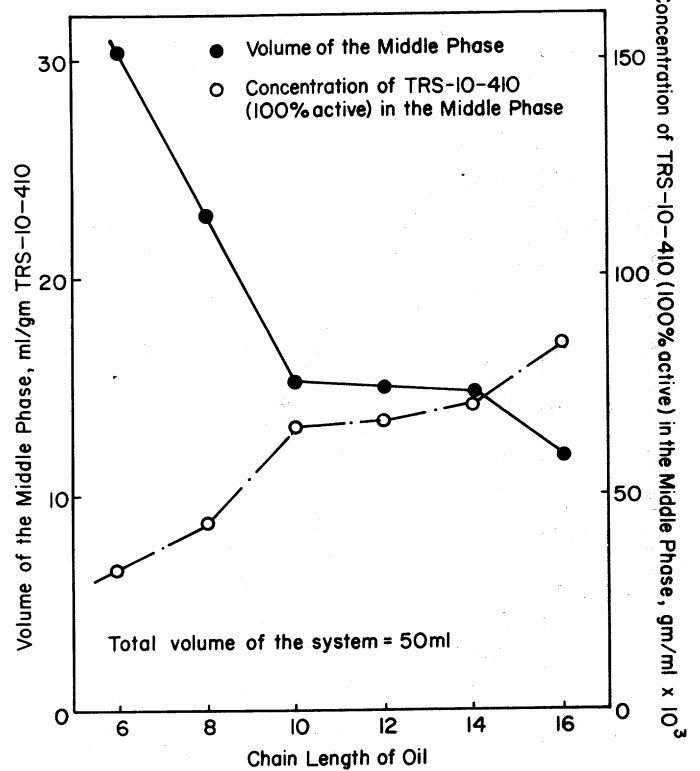
Fig. 6 - Volume of the middle phase and concentration of TRS 10-410 (100% active) in the middle phase at optimal salinity for different chain length of oils.
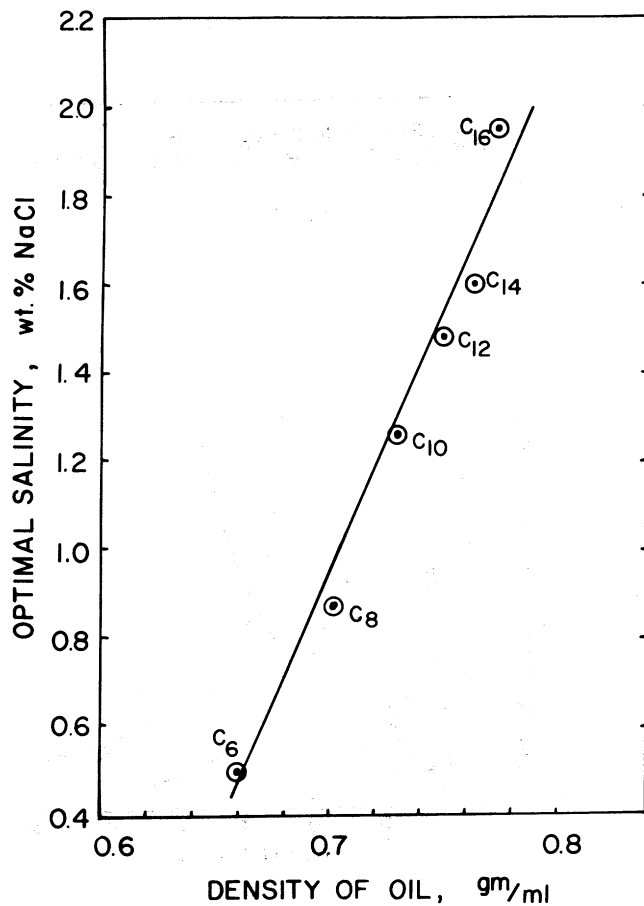
Fig. 7 - Optimal salinity as a function of density of hydrocarbon oils.
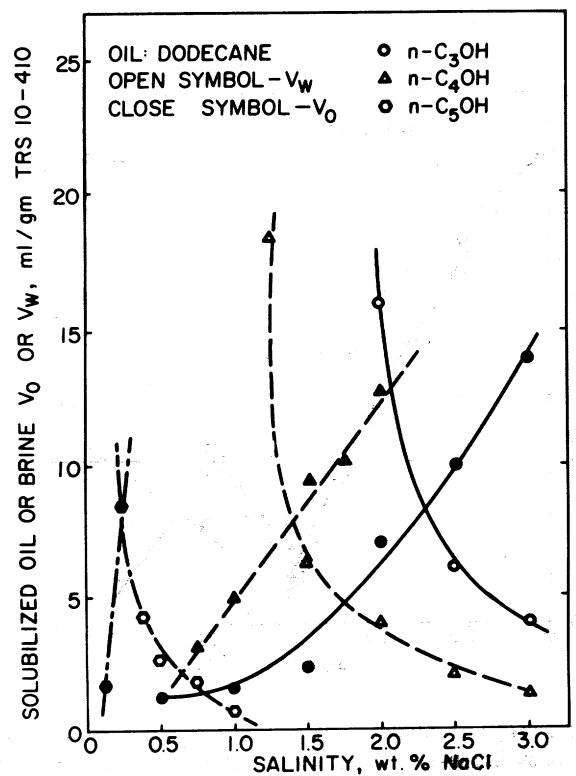
Fig. 8 - Effect of alcohol chain length on the solubilization behavior of 5% TRS 10-410 + 3% alcohol at various salt concentrations.
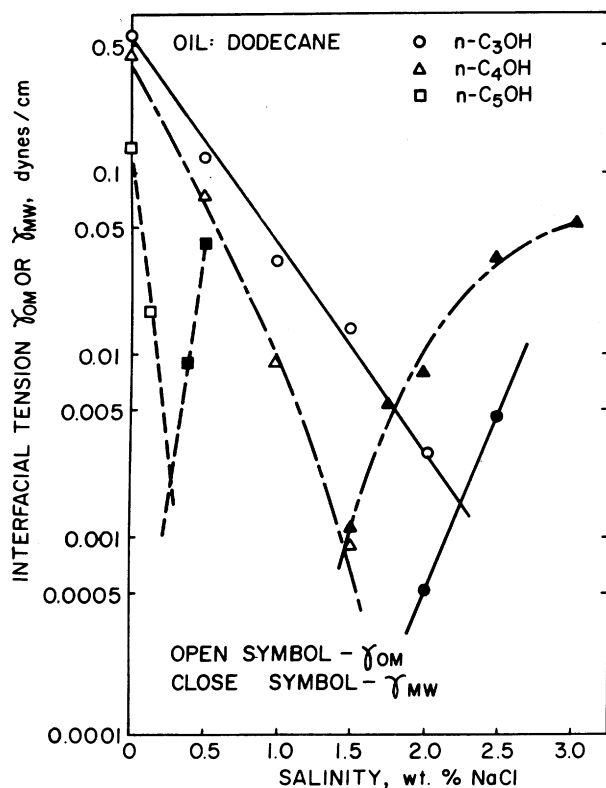
Fig. 9 – Effect of alcohol chain length on the interfacial tension behavior of 5% TRS 10–410 + 3% alcohol at various salt concentrations.

Fig. 10 – Effect of isomeric structure of butanol on the solubilization behavior of 5% TRS 10–410 + 3% alcohol at various salt concentrations.
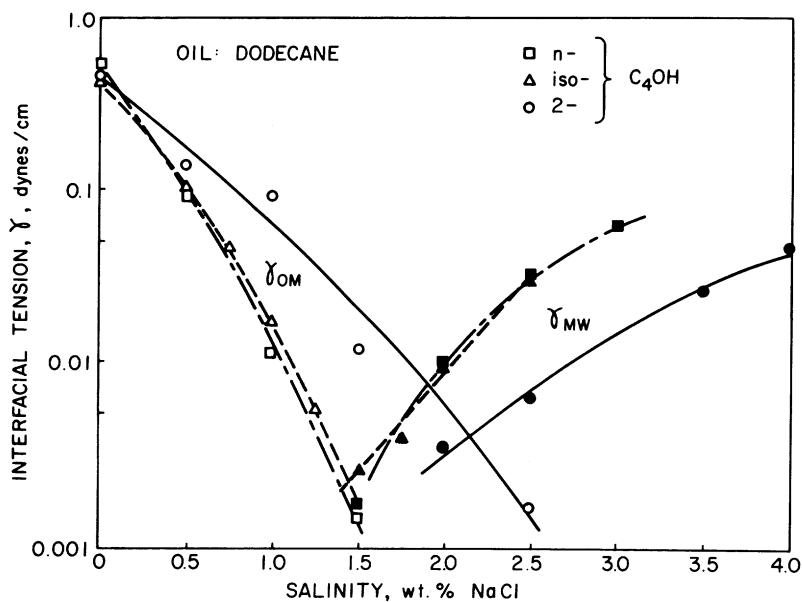
Fig. 11 – Effect of isomeric structure of butanol on the interfacial tension behavior of 5% TRS 10–410 + 3% alcohol at various salt concentrations.
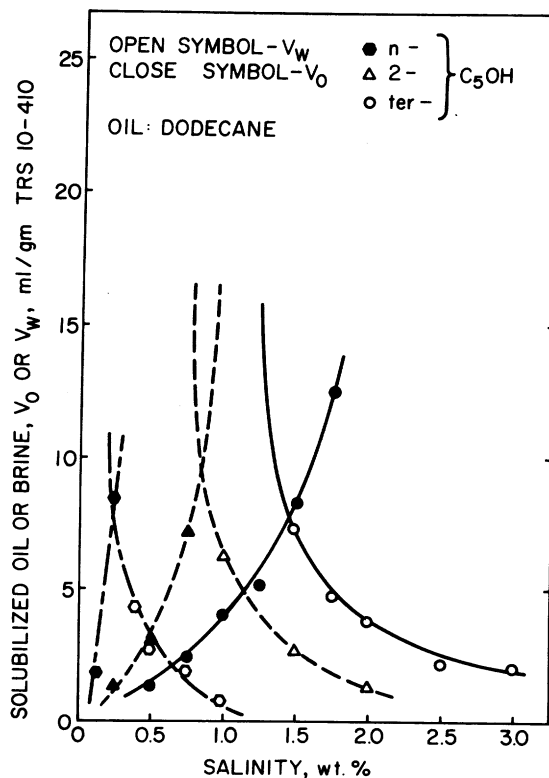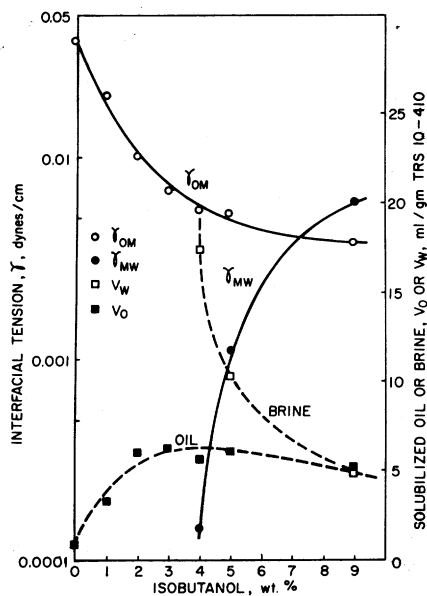

Fig. 12 – Effect of isomeric structure of pentanol on solubilization behavior of 5% TRS 10–410 + 3% alcohol at various salt concentrations.
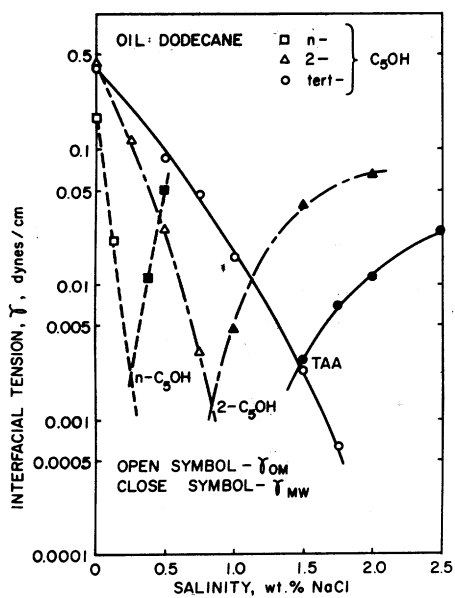
Fig. 13 – Effect of isomeric structure of pentanol on the interfacial tension behavior of 5% TRS 10–410 + 3% alcohol at various salt concentrations.

Fig. 14 – Effect of amount of isobutanol on the solubilization and interfacial tension of 5% TRS 10–410 + isobutanol with dodecane at 1% NaCl.
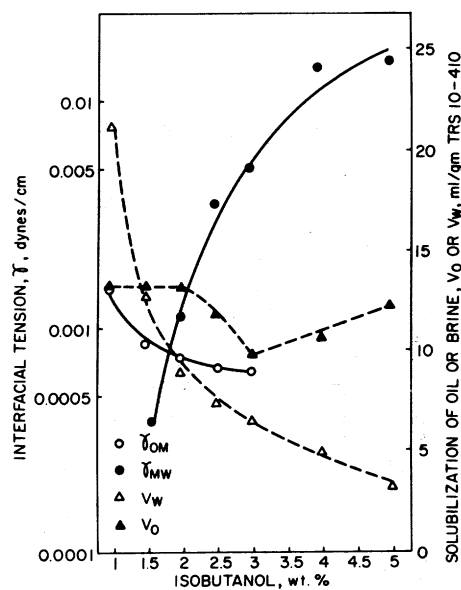
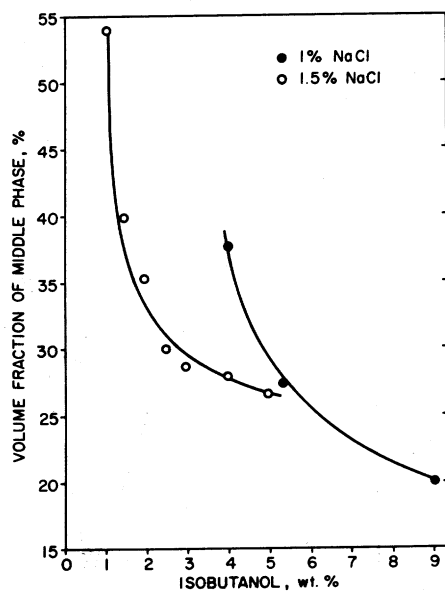Fig. 15 – Effect of amount of isobutanol on the solubilization and interfacial tension behavior of 5% TRS 10–410 + isobutanol with dodecane at 1.5% NaCl.

Fig. 16 – Effect of amount of isobutanol on the volume of middle phase of 5% TRS 10–410 + isobutanol with dodecane.
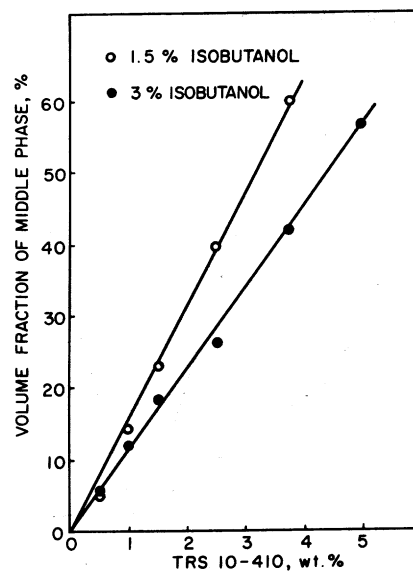
Fig. 17 – Effect of surfactant concentration on the volume of middle phase of TRS 10–410 + isobutanol with dodecane at 1.5% NaCl.
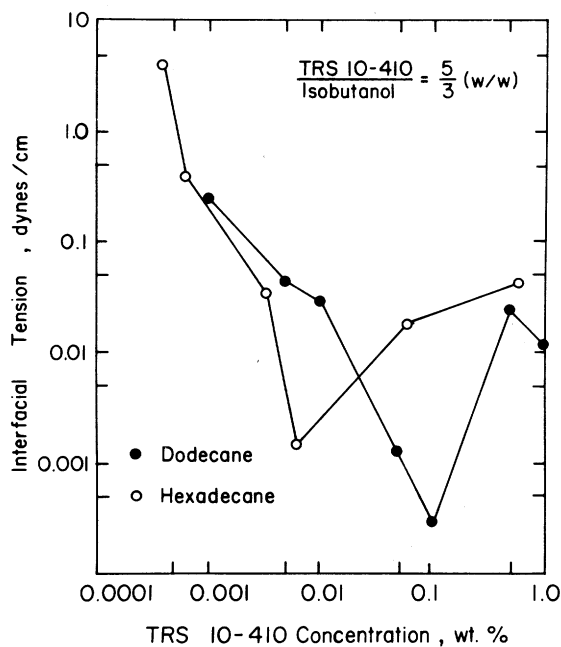
Fig. 18 – Effect of surfactant concentration on the interfacial tension of TRS 10–410 + isobutanol with dodecane at 1.5% NaCl and with hexadecane at 2% NaCl.
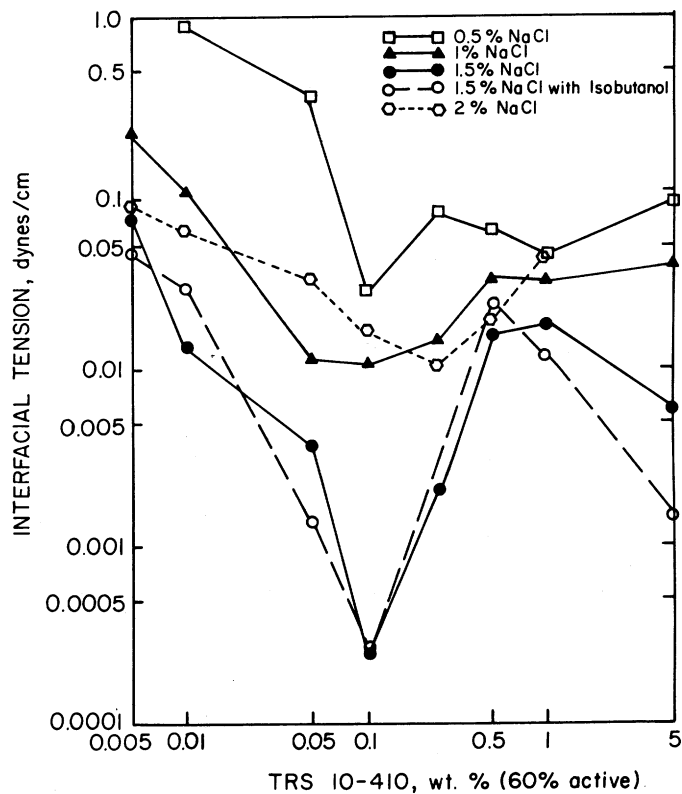
Fig. 19 – Effect of salinity and surfactant concentration on the interfacial tension between surfactant solution and dodecane.
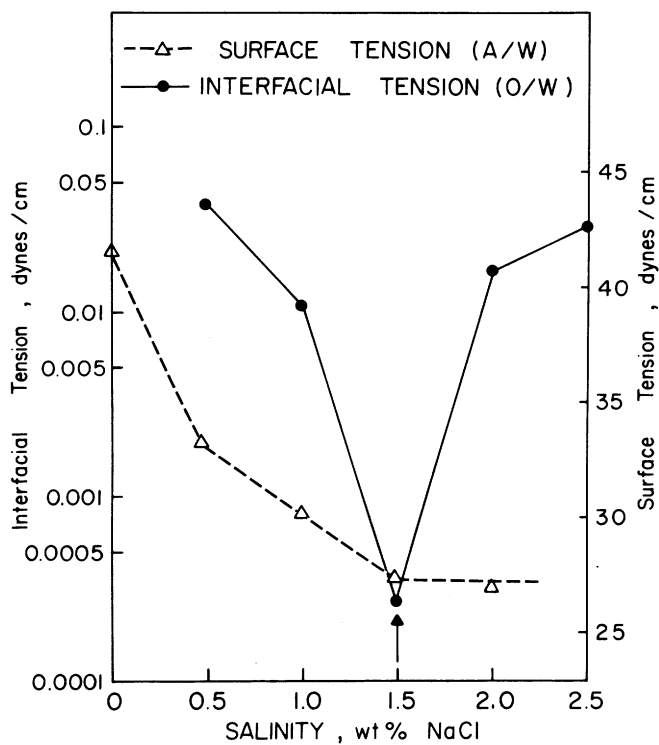
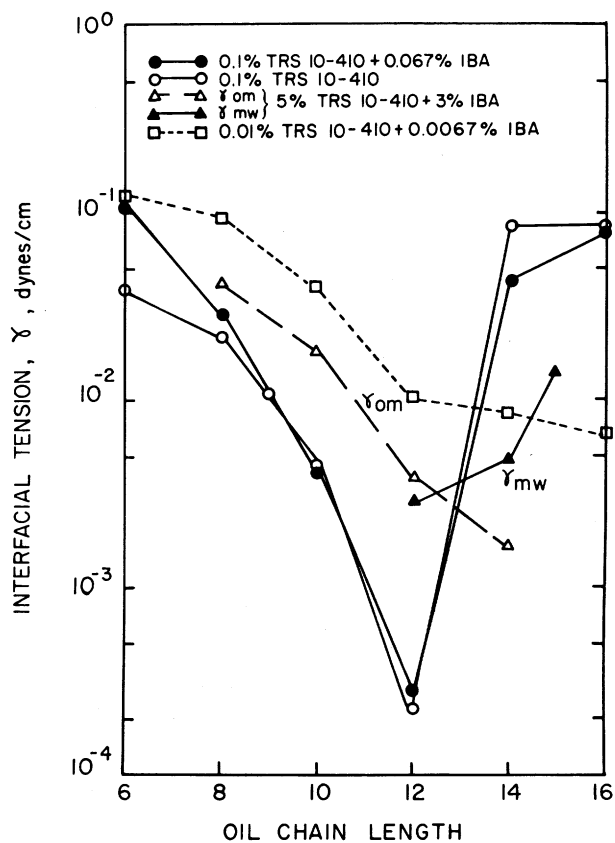Fig. 20 – Effect of salinity on the interfacial tension between 0.1% TRS 10–410 and dodecane.

Fig. 21 – Effect of oil chain length on the interfacial tension between surfactant solution of TRS 10–410 and oil.