

THE MOLECULAR MECHANISM FOR ACHIEVING ULTRA LOW INTERFACIAL
TENSION MINIMUM IN A PETROLEUM SULFONATE/OIL/BRINE SYSTEM

K.S. Chan and D.O. Shah

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

ABSTRACT

A unified theory is proposed to explain the ultra-low interfacial tension minimum observed in dilute petroleum sulfonate solution/oil systems encountered in tertiary oil recovery process. The relative distribution of the surfactant in oil and aqueous phase was determined using UV spectrophotometry as well as the monolayer technique. The critical micelle concentration (CMC) of the aqueous phase equilibrated with oil was measured using surface tension, osmotic pressure and light scattering measurements. For three major variables namely, the surfactant concentration, the chain length of oil and the salinity of brine, the interfacial tension minimum was found to occur whenever the equilibrated aqueous phase was at CMC. This minimum in interfacial tension also coincided with partition coefficient of unity for surfactant distribution in oil and brine. The increase of the interfacial tension after reaching a minimum was attributed to the decrease in the monomer concentration in the aqueous phase. Three possible causes of the decrease in monomer concentration are (1) the incorporation of oil soluble fraction into mixed micelles in the aqueous phase, or (2) the decrease of the effective CMC in the equilibrated aqueous phase due to solubilization of oil or (3) the transfer of surfactant from aqueous to oil phase upon increasing the salinity. The decrease in surface concentration of surfactant at the oil-brine interface after the interfacial tension minimum is reached was confirmed by the electrophoretic mobility measurements.

The six major experimental findings related to the behavior of dilute petroleum sulfonate solutions are as follows: 1) the ultra-low interfacial tension minimum occurs at the CMC of the equilibrated aqueous phase; 2) the partition coefficient is near unity at CMC; 3) the effective CMC for concentrations above the IFT minimum decreases with an increase in petroleum sulfonate

concentration due to mixed micelle formation in the aqueous phase; 4) the effective CMC decreases as the chain-length of dissolved oil increases; 5) the partitioning of the surfactant in the oil phase increases as the salinity increases and 6) the partitioning of the surfactant in the oil phase decreases as the chain-length of oil increases. It was established experimentally that the necessary condition for achieving an ultra-low interfacial tension minimum in dilute petroleum sulfonate solution/oil systems is that the CMC of the surfactant in the aqueous phase must coincide with partition coefficient of near unity. Under this condition, the concentration of surfactant monomers is maximum in brine and oil leading to maximum surfactant concentration at the interface.

INTRODUCTION

It has been pointed out by Taber and other investigators (1-3) that capillary forces are responsible for entrapping a large amount of oil, as oil ganglia, within the porous rock during waterflooding of petroleum reservoirs. They also concluded that interfacial tension at the crude oil/brine interface, which plays a dominant role in governing capillary forces should be reduced in order to achieve an efficient displacement of the crude oil. Foster (4) evaluated various parameters for oil displacement efficiency and found that an ultra-low interfacial tension ($\approx 10^{-3}$ to 10^{-4} dynes/cm) was necessary for oil mobilization. Wilson and Brandner (5) showed that this ultra-low interfacial tension could be achieved by using a dilute solution of petroleum sulfonates. Cayias et al. (6) have also reported low interfacial tensions between homologous series of hydrocarbon oils and petroleum sulfonate solutions having surfactant concentrations less than 1 wt. %. Recently, Doe et al. (7) showed that low interfacial tensions can also be attained by using highly pure monomeric alkyl benzene sulfonates. The effect of the structure of surfactant molecules on their ability to reduce surface and interfacial tension has been reported by Rosen (8,9).

The results obtained from the studies mentioned above can be summarized as follows: (i) Interfacial tension between oil and

brine decreases with an increase in surfactant concentration. For mixed surfactants, such as petroleum sulfonates, the interfacial tension reaches a minimum value at a critical concentration. Beyond this critical concentration, the interfacial tension increases with increasing surfactant concentration. This sharp minimum (as a function of surfactant concentration), however, does not occur when pure surfactant is used; (ii) the concentration at which the minimum interfacial tension occurs shifts to a higher value if a shorter chain length oil is substituted for a longer chain length oil; (iii) at fixed surfactant and salt concentrations, interfacial tension is a function of oil chain length. The minimum interfacial tension occurs at a particular oil chain length which depends upon the surfactant structure and (iv) when all the variables, except salt concentration, are kept constant, the interfacial tension exhibits a minimum at a particular salt concentration. A great deal of effort has been spent in collecting data to evaluate the parameters governing the attainment of ultra-low interfacial tensions, but no unified theory has been proposed to account for all these experimental observations.

Miller and Scriven (10) have pointed out that when the interfacial tension is low, factors such as electrical double layer interaction at the interface might play an important role in determining the interfacial free energy at the oil-water interface. Experimentally, Chan et al. (11) demonstrated a direct correlation between interfacial tension and interfacial charge in various oil-water systems. They conclude that the interfacial charge density plays an important role in lowering the interfacial tension. Using the Gibbs adsorption isotherm equation for the interface and Gibbs-Duhem equations for each of the two contacting liquid phases, Defay et al. (12) derived an expression relating the interfacial tension with the surface excesses contributed by components of the micellar system.

Starting with this expression, Franses et al. (13) analyzed for the occurrence of interfacial tension minima in single and mixed nonionic surfactant systems. They concluded that an interfacial tension minimum can occur either when the chemical potential of the surfactant is a maximum or the interfacial excess inventory of the surfactant changes its sign. They also concluded that the conditions at which these two causes of interfacial tension minima occur depend on partition and association behaviors of surfactant molecules as well as on the interfacial adsorption mechanism.

For petroleum sulfonates which are multicomponent mixture of anionic surfactants, having a wide distribution of equivalent weights, we undertook the experimental studies on the following two factors in relation to interfacial tension:

- (1) The distribution of surfactant molecules between the oil and water phases in relation to the interfacial tension and
- (2) the properties of surfactant molecules such as CMC in relation to monomer concentration as well as interfacial tension.

This paper reports the results of a series of experiments regarding the two aspects mentioned above to explain the minimum in interfacial tension. The effect of three major variables, namely surfactant concentration, salinity and oil chain length on interfacial tension have been investigated and a unified theory is proposed to account for the observed effects of these variables on interfacial tension.

MATERIALS AND METHODS

For all the systems studied, the surfactant used was TRS 10-80 (80% active) obtained from Witco Chemicals. This surfactant is a mixture of petroleum sulfonates with wide molecular weight distribution. The average equivalent weight was reported to be 420. The water content of this surfactant was 8% as deter-

mined by the NMR spectroscopic technique using a 60 MHz high resolution NMR spectrometer (JEOL Model C-60HL). The remaining 12% was free oil and salt, the salt content being less than 0.4%. The surfactant was used as received from the manufacturer to prepare the solutions, without further purification to remove either the free oil or water. The oils used in this study were a homologous series of alkanes with chain lengths from C_6 to C_{16} . All the oils were at least 97% pure and were obtained from Chemical Samples Company.

The systems were equilibrated by taking two-thirds aqueous solution and one-third oil by volume in 250 ml separatory funnels maintained at 25°C. After shaking vigorously for about 30 minutes using a mechanical shaker, the solutions were allowed to stand for about three weeks until clear mirror-like interfaces were obtained and the oil and aqueous phases became optically clear. The equilibrated oil and aqueous phases were then separated from the top and bottom of the funnel respectively for various physicochemical measurements.

Interfacial tensions between the equilibrated oil and aqueous phases were measured by a spinning drop tensiometer using the method described by Princen *et al.* (14) and also by Cayias *et al.* (15). Each drop of oil was spun until a constant interfacial tension was reached. This usually took from fifteen minutes to three hours. The temperature was maintained at $25 \pm 1^\circ\text{C}$. A few samples were double checked by the micro-sessile drop technique (16) using the apparatus designed and constructed by the authors.

Surface tensions of the equilibrated aqueous phases were measured using a modified Wilhelmy plate method. This technique was recently re-evaluated by Orr *et al.* (17). The platinum blade used was sandblasted to produce a rough surface so that it was completely wettable by the salt solution. Double-distilled deionized water was used as the standard for calibration. The surface tension was recorded on a strip chart recorder and the

equilibrium value was taken. The temperature was controlled at 25°C by using a water jacket for the petridish (containing about 30 ml of sample). The tension measurements were accurate within ± 1 dynes/cm.

For low surfactant concentration (0 to 0.1%) solutions, both interfacial tensions and partition coefficients were measured. It was difficult to determine the trace quantity of surfactant partitioning into the oil phase using either conventional dye-titration or spectrophotometric methods. Therefore, we developed a novel monolayer technique to determine this trace quantity of surfactant partitioning into the oil phase. This method is schematically illustrated in Figure 1. First, 30 ml oil and 70 ml surfactant solution were equilibrated in a separatory funnel. Then 10 ml of equilibrated oil was pipetted

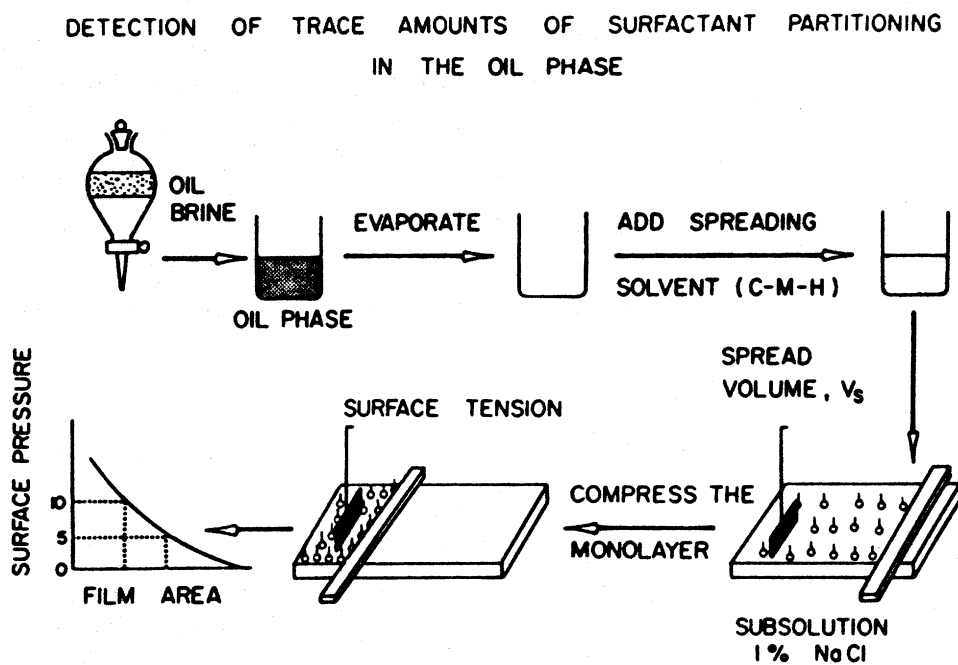


Figure 1 Detection of Trace Amounts of Surfactant Partitioning in the Oil Phase by a Monolayer Technique.

into petridishes contained in a heated vacuum dessicator. After all the oil had evaporated an equal amount of spreading agent (1:1:3 methanol-chloroform-hexane, volume ratio) was added to each petridish to dissolve the surfactant. Next, 0.25 ml of each of these solutions was spread, using a microsyringe, on a monolayer trough (surface area 240.75 cm^2) containing 600 ml brine of the same salinity (1.0% NaCl) for each system. A time of 20 to 30 minutes was allowed to ensure complete evaporation of the spreading agent. Then a slow moving Teflon bar was used to compress the film formed by the surfactant molecules present at the solution surface. Surface pressure vs. surface area was monitored. From the area of monolayers at a given surface pressure, relative amounts of surfactant partitioned into the oil phase were obtained. Precautions were taken during the monolayer experiments to prevent dissolution of surfactant from the monolayer into the subsolution. The surfactant concentration of spreading solution and the volume spread on the subsolution were adjusted to obtain a smooth surface pressure-area curve within a comparatively low surface pressure range ($< 10 \text{ dynes/cm}$; see Figure 3). The area of monolayers for each system was compared at 5 and 10 dynes/cm surface pressure. In this surface pressure range no significant dissolution of monolayer was observed.

Partition Coefficient Measurements:

At high salt concentrations, almost all the surfactant can be found in the oil phase. For such systems, the surfactant concentration in the oil phase is too large to measure by the monolayer technique. Quantitative determination of surfactant concentration in the oil phase was hence carried out by UV absorbance measurements using Beckman Model DK-2-UV Visible range spectrophotometer. This technique was recently discussed by Sandvik *et al.* (20).

Surfactant concentration in the aqueous phase was measured by spectrophotometry of methylene blue-surfactant complexes

reported elsewhere in the literature (18,19). All the measurements were done at 25°C. Partition coefficient, defined as the ratio of the concentration of surfactant in the oil phase to the concentration of surfactant in the aqueous phase, was then determined.

Osmotic Pressure Measurements:

Osmotic pressure was measured with a high speed membrane osmometer, model 502 from Mechrolab Inc., using an aqueous membrane No. B19 available from Hewlett-Packard Company. Temperature was controlled at 25°C and the solvent was 1% NaCl solution. Experimental error was found to be less than ± 0.14 cm of solvent.

Light Scattering (I_{90}) Measurements:

Light scattering by the solutions at a 90° angle to the path of the incident ray was measured with a Wood dual photometer, model 5200. In this light scattering (I_{90}) measurement, monochromatic light of wavelength 436 nm was used. The turbidity (I_{90}/I_0) was found to be relatively insensitive to micellization especially around CMC because of a high value of I_0 as compared to I_{90} . However, if one normalizes I_{90} with respect to I_{90} value at infinite dilution (i.e., surfactant concentration approaching zero), the CMC can be detected as the local maximum in the normalized value of $[(I_{90})_c/(I_{90})_{c \rightarrow 0}]$ for oil-brine-surfactant systems (27). $(I_{90})_{c \rightarrow 0}$ was the extrapolated value of I_{90} when further dilution does not significantly change the value of I_{90} .

Electrophoretic Mobility Measurements:

The microelectrophoretic mobility of equilibrated oil droplets in the equilibrated aqueous phase was measured using a Zeta meter. The standard procedure for making these measurements

surfactant solution was transferred to a beaker and a few drops of equilibrated oil (0.5 ml) was dispersed in this solution using an ultrasonic probe to give a dilute oil-brine emulsion suitable for electrophoretic mobility measurements. The maximum error in these electrophoretic mobility measurements was found to be less than 4%.

All surfactant concentrations reported on the x-axis of the diagrams are the initial concentrations of the surfactant in the brine phase before equilibration with the oil.

RESULTS AND DISCUSSION

1. Effect of Surfactant Concentration on Interfacial Tension and Partition Coefficient

It has been reported by Cayias et al. (21) that the minimum interfacial tension in TRS 10-80 + n-octane + 1% brine occurs at 0.05% surfactant concentration. Our results are in agreement with their findings. Upon equilibration, it is likely that a fraction of surfactant will dissolve in the oil and the rest in brine. If a surfactant has a broad molecular weight or equivalent weight distribution, then high equivalent weight fraction would preferentially dissolve in the oil phase. We wanted to determine the separate contributions of surfactant dissolved in oil and brine phase to the interfacial tension. Therefore, after equilibration, we took equilibrated n-octane and measured the interfacial tension against 1% NaCl brine. The interfacial tension in this case is essentially determined by the surfactant dissolved in the n-octane phase. In the second experiment, interfacial tension was measured for pure n-octane against equilibrated aqueous phase. The interfacial tension in this case is primarily determined by the surfactant present in the aqueous phase. In the third experiment, interfacial tension was measured for both equilibrated n-octane and aqueous phases. Figure 2 shows three interfacial tension curves. The upper one is for equilibrated oil with 1% NaCl solution; the middle one is

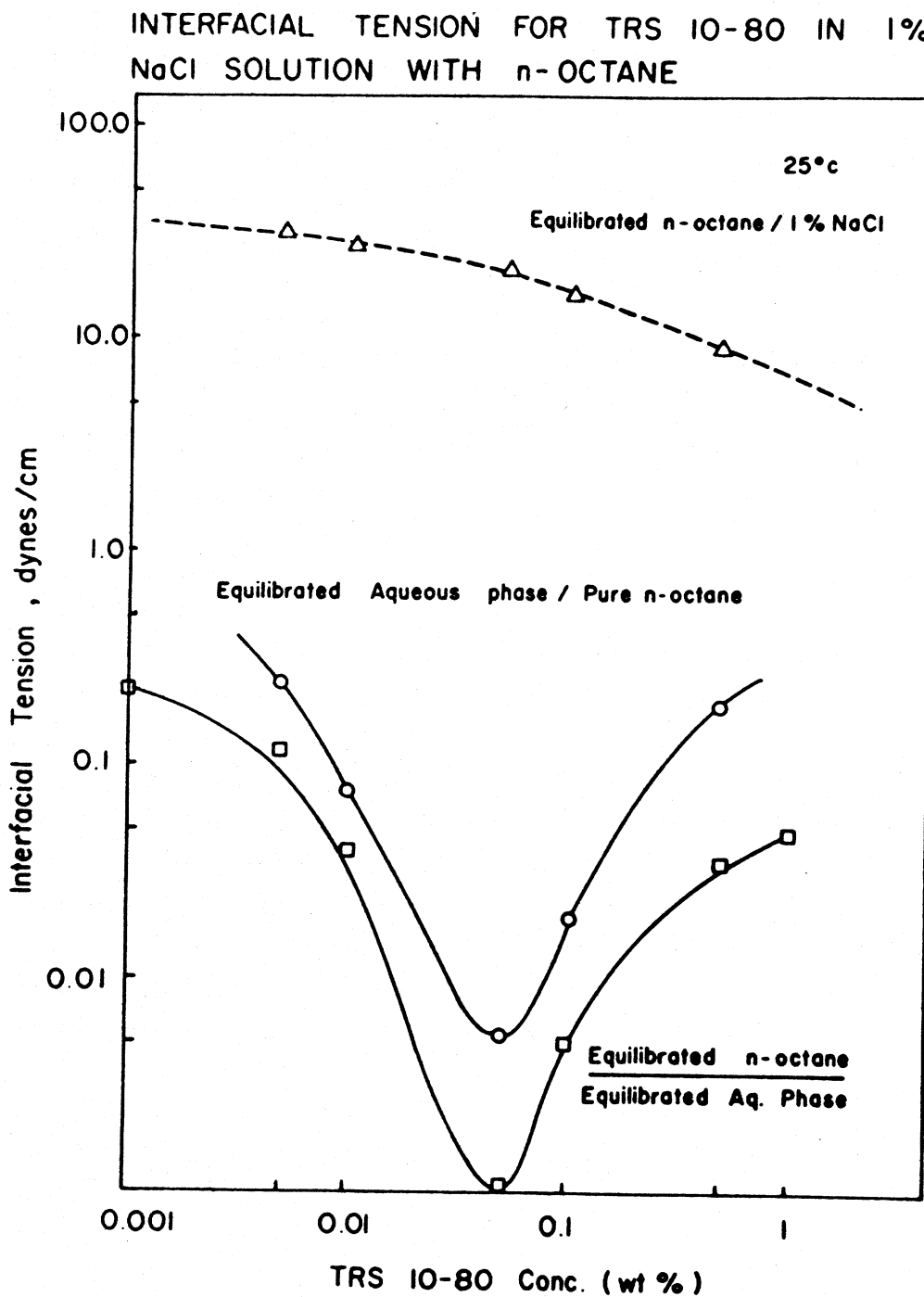


Figure 2 Interfacial Tension for TRS 10-80 in 1% NaCl Solution with n-Octane.

for the pure oil with equilibrated aqueous phase, and the lower one is for the equilibrated system. The results suggest that the aqueous phase is predominantly responsible for the ultra-low interfacial tension attainment.

Figure 3 shows the surface pressure vs. surface area curves obtained, using the method shown in Figure 1, for the surfactant partitioned into n-octane at 0.005%, and 0.05% and 0.5% TRS 10-80 concentrations. At all surface pressures, the surfactant in oil for 0.05% covered the largest area. A comparison of this area at a surface pressure of 5 or 10 dynes/cm for each concentration is shown in Figure 4. The amount of surfactant partitioning into the oil phase is maximum where the minimum

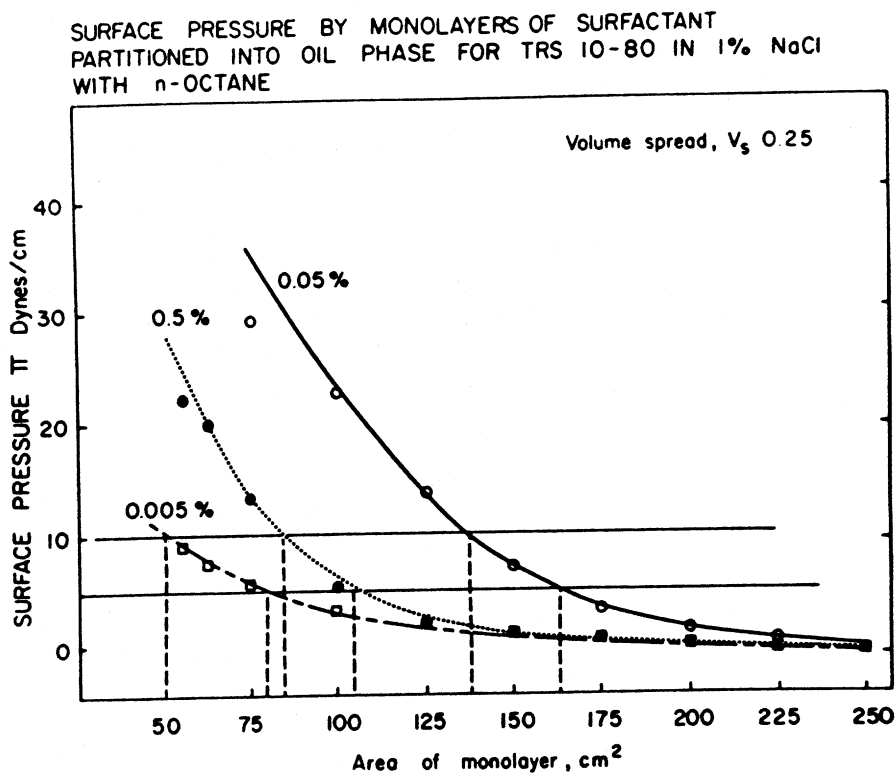


Figure 3 Surface Pressure-Area Curves of Monolayers of Surfactant Partitioned Into Oil Phase for TRS 10-80 in 1% NaCl Solution with n-Octane.

AREA OCCUPIED BY MONOLAYER OF SURFACTANT
PARTITIONED INTO OIL PHASE FOR TRS 10-80 IN
1% NaCl WITH n-OCTANE

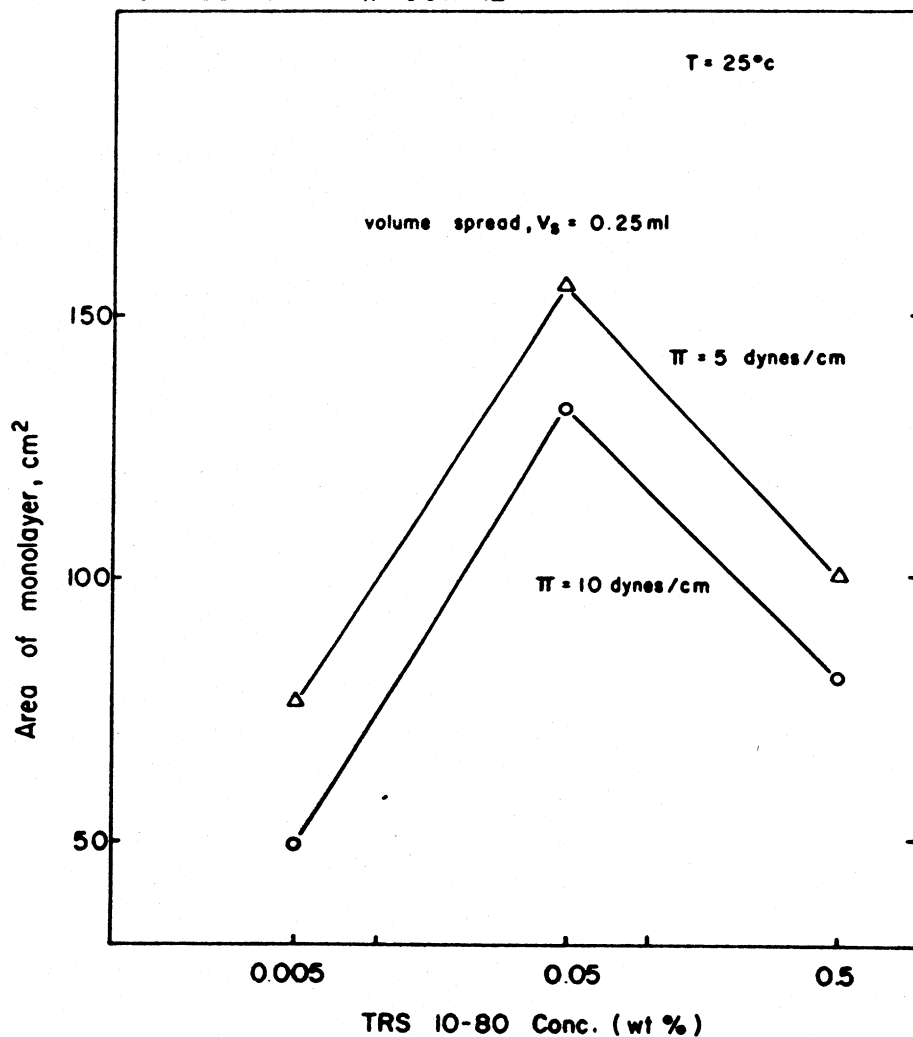


Figure 4 Area Occupied by Monolayers at a Constant Surface Pressure, of Surfactant Partitioned Into Oil Phase for TRS 10-80 in 1% NaCl with n-Octane.

interfacial tension occurs (0.05% TRS 10-80 concentration in Figure 2).

In order to confirm the reliability of the monolayer data, we used a very sensitive UV-visible spectrophotometer

(Perkin-Elmer model 576) to quantitatively measure the surfactant concentration in the oil and brine phases using 225 nm wavelength. Figure 5 shows the surfactant concentration in the oil and brine phases after equilibration, determined by the

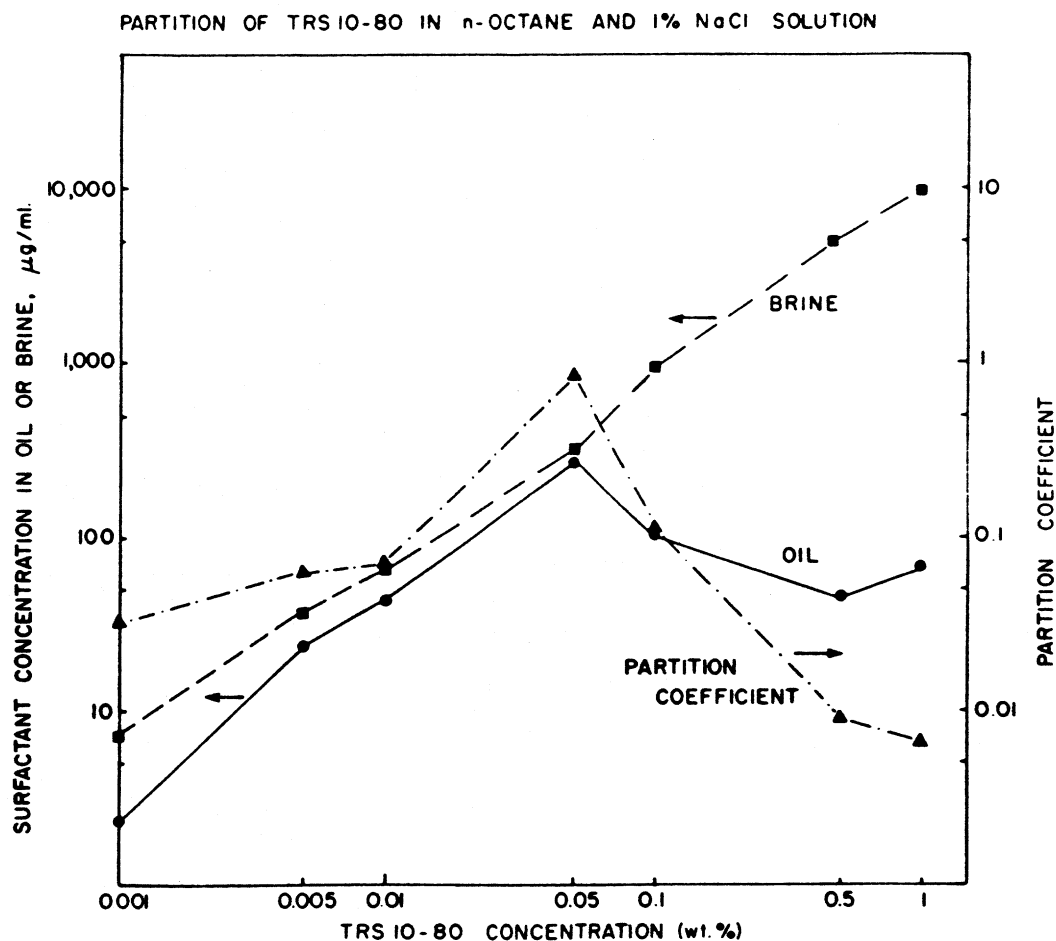


Figure 5 Concentration of Surfactant TRS 10-80 in n-Octane, Brine (1% NaCl) and the Partition Coefficient (concentration in oil/concentration in brine) as a function of the initial surfactant concentration in brine. The concentration in oil was determined by UV and that in brine by methylene blue absorption measurements.

UV measurements which essentially confirm our monolayer findings shown in Figure 4. The partition coefficients are shown also in Figure 5. The surfactant concentration in oil increases to a maximum at 0.05% initial surfactant concentration and then decreases with a further increase of surfactant concentration. The partition coefficient behaves in a similar manner. It should be emphasized that the partition coefficient is approximately unity at 0.05% initial surfactant concentration where the minimum interfacial tension occurs.

Figure 6 shows the surface tension of the equilibrated aqueous phase for various initial concentrations of TRS 10-80. The slope of the surface tension curve is seen to change at a concentration of 0.05% TRS 10-80. Figure 6 also shows the effect of aging on the surface tension. The change in the slope of the curves, however, always occur at 0.05% TRS 10-80 concentration. This suggests that 0.05% is the initial concentration for which the surfactant concentration in the aqueous phase is at the CMC after equilibration with n-octane. Further evidence was necessary to confirm this hypothesis. Figure 7 shows the osmotic pressure of the aqueous phase after equilibration with n-octane, expressed in units of height of solvent (1% NaCl solution). It is interesting to see that the osmotic pressure curve has a maximum at 0.05% TRS 10-80 concentration, and beyond this concentration the osmotic pressure decreases. This implies that the number of surfactant monomers is maximum at 0.05% TRS 10-80 concentration. This is consistent with the observed interfacial tension minimum since the maximum monomer concentration in the aqueous phase will produce the maximum surface concentration of the surfactant. The light scattering (I_{90}) measurements of the same equilibrated solutions are shown in Figure 8, which also supports the conclusion that the CMC occurs at 0.05%. The I_{90} ratio of scattered light increases to a local maximum at 0.05% TRS 10-80 concentration as the number of scattering units, i.e., monomers, reaches a maximum (22).

SURFACE TENSION OF AQUEOUS PHASE OF TRS
10-80 IN 1% NaCl SOLUTION EQUILIBRATED
WITH n-OCTANE

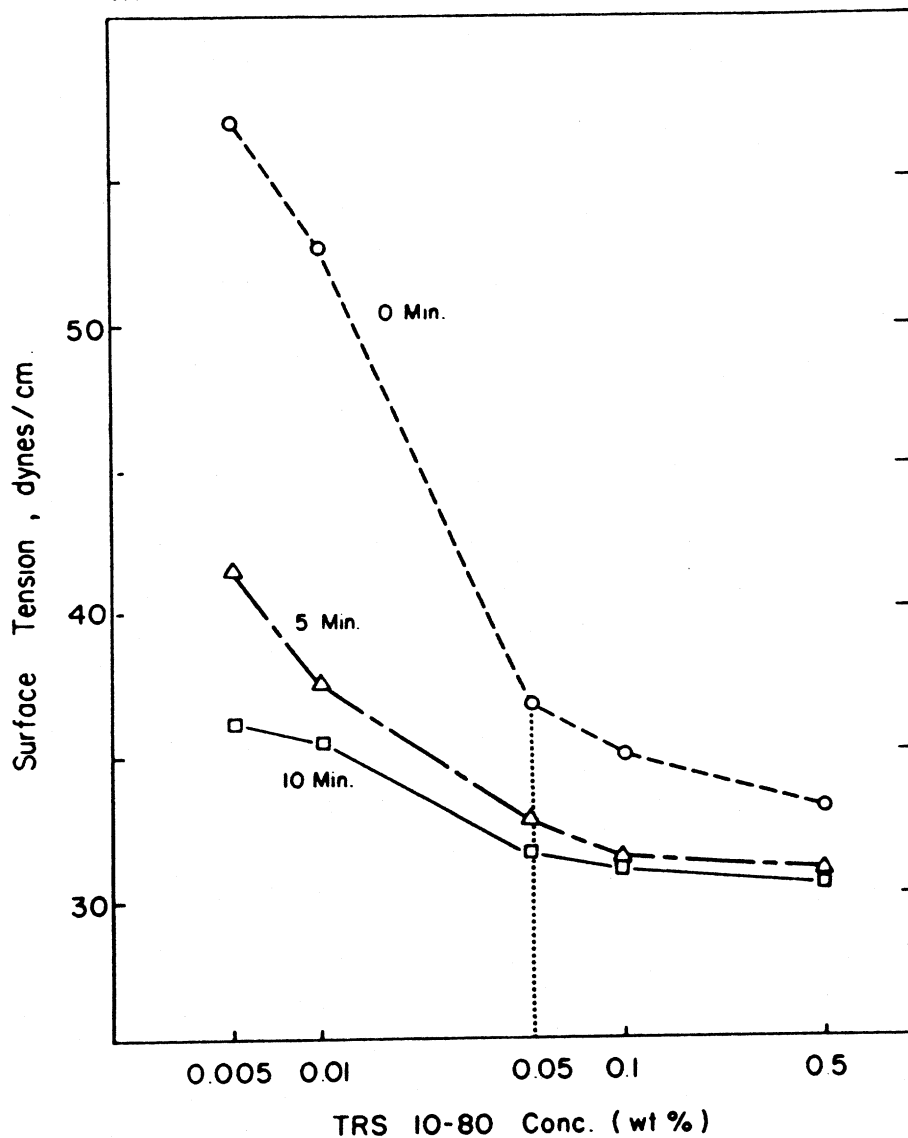


Figure 6 Surface Tension of Aqueous Phase of TRS 10-80 in 1% NaCl Solution Equilibrated with n-Octane.

Figure 9 illustrates the effect of surfactant concentration on the interfacial tension and electrophoretic mobility of oil droplets in the surfactant solution. It is obvious that the

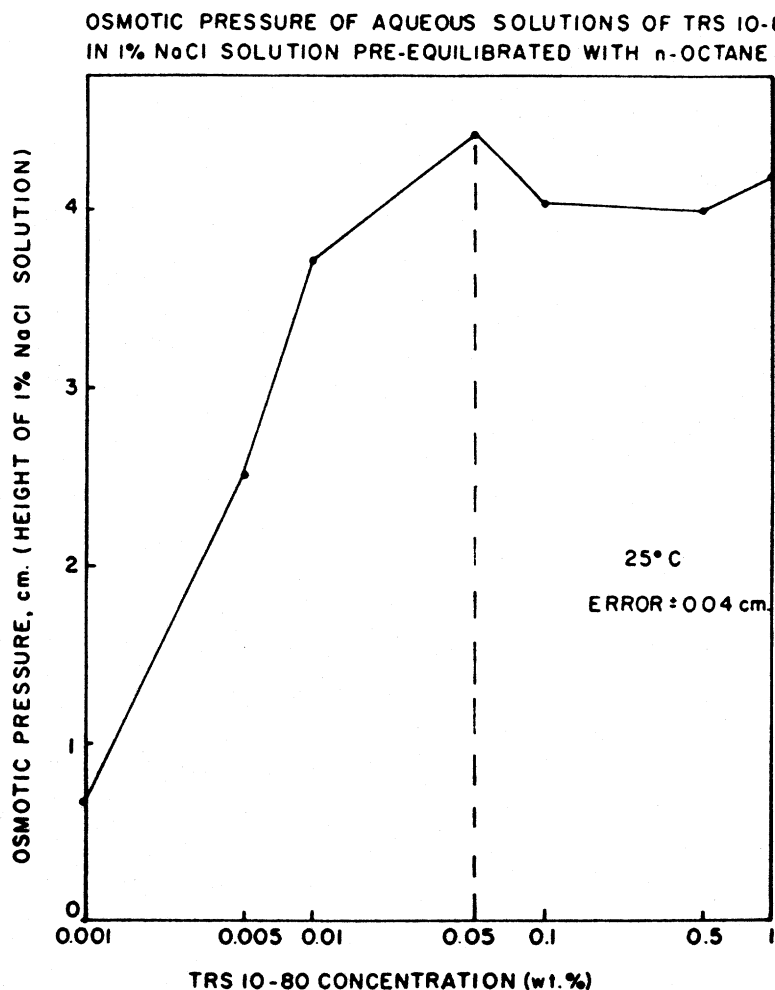


Figure 7 Osmotic Pressure of Aqueous Phase of TRS 10-80 in 1% NaCl Solution Equilibrated with n-Octane.

minimum interfacial tension coincides with the maximum electrophoretic mobility of octane droplets. The occurrence of both a minimum interfacial tension and a maximum electrophoretic mobility at 0.05% TRS 10-80 concentration suggest that the interfacial concentration of surfactant must be a maximum at this concentration. This is in agreement with our explanation that at 0.05% initial TRS 10-80 surfactant concentration, there is a maximum number of monomers in the oil as well as aqueous

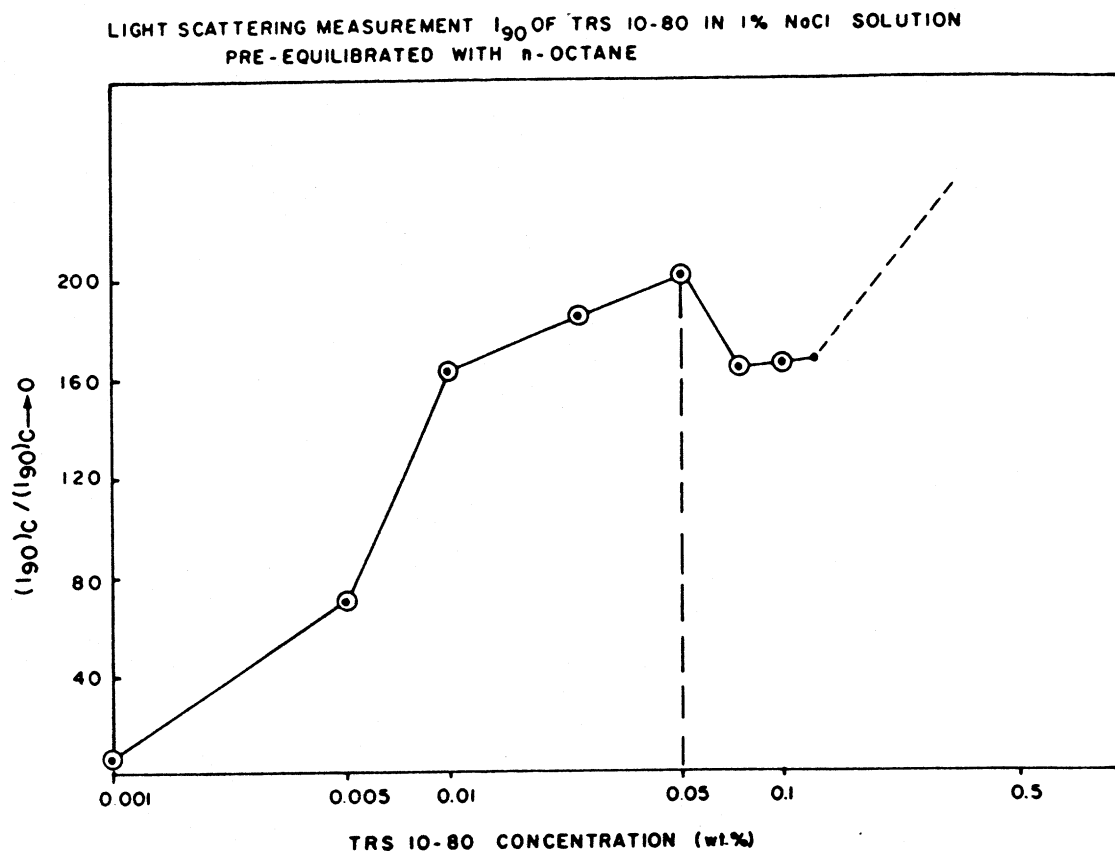


Figure 8 Light Scattering (I_{90}) Measurements of Aqueous Phase of TRS 10-80 in 1% NaCl Solution Equilibrated with n-Octane.

phase. Since surfactant molecules at the interface are in dynamic equilibrium with the surfactant in the aqueous and oil phase, it is obvious that the maximum monomer concentration in the aqueous and oil phase must lead to a maximum surfactant concentration at the interface.

The minima in the surface and interfacial tension curves have been rigorously discussed in the literature. Alexander (23) has pointed out that the minimum occurs at or near the CMC. Reichenberg (24) clearly showed that impurities play an important role in producing this minimum in the surface or interfacial tension. In our systems it is due to the molecular

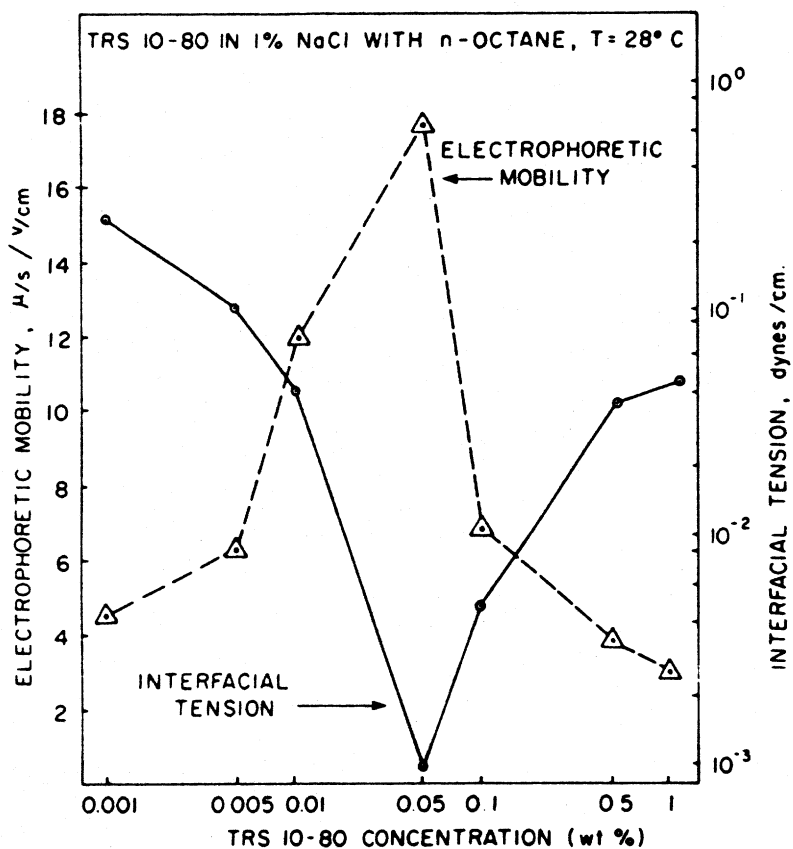


Figure 9 The Effect of TRS 10-80 Concentration on Electrophoretic Mobility of Oil Droplets and on Interfacial Tension of n-Octane/Surfactant Solution Interface.

weight distribution of the surfactant. The decrease in partitioning of the surfactant to the oil phase is due to the incorporation of oil soluble surfactant molecules with water soluble surfactant molecules to form mixed micelles in the aqueous phase beyond CMC.

We propose that the concentration at which the minimum interfacial tension and surface tension as well as the maximum amount of surfactant partitioning into the oil phase occur is the true critical micelle concentration (CMC) for the surfactant remaining in the aqueous phase after equilibration with oil.

The surfactant TRS 10-80 consists of several molecular species ranging in equivalent weights from 320 to 510. Although the average equivalent weight of TRS 10-80 is 420, upon equilibration of oil and brine, the higher equivalent weight species would be preferentially found in the oil phase, whereas the lower equivalent weight species would preferentially be found in the aqueous phase. Therefore, the average equivalent weight of the surfactant partitioning to the oil phase would be considerably greater than 420 and that in the aqueous phase would be considerably smaller than 420.

Figure 10 schematically illustrates our proposed molecular mechanism for the interfacial tension minimum observed in these

THE MOLECULAR MECHANISM FOR THE EFFECT OF SURFACTANT CONCENTRATION
ON INTERFACIAL AND SURFACE TENSIONS

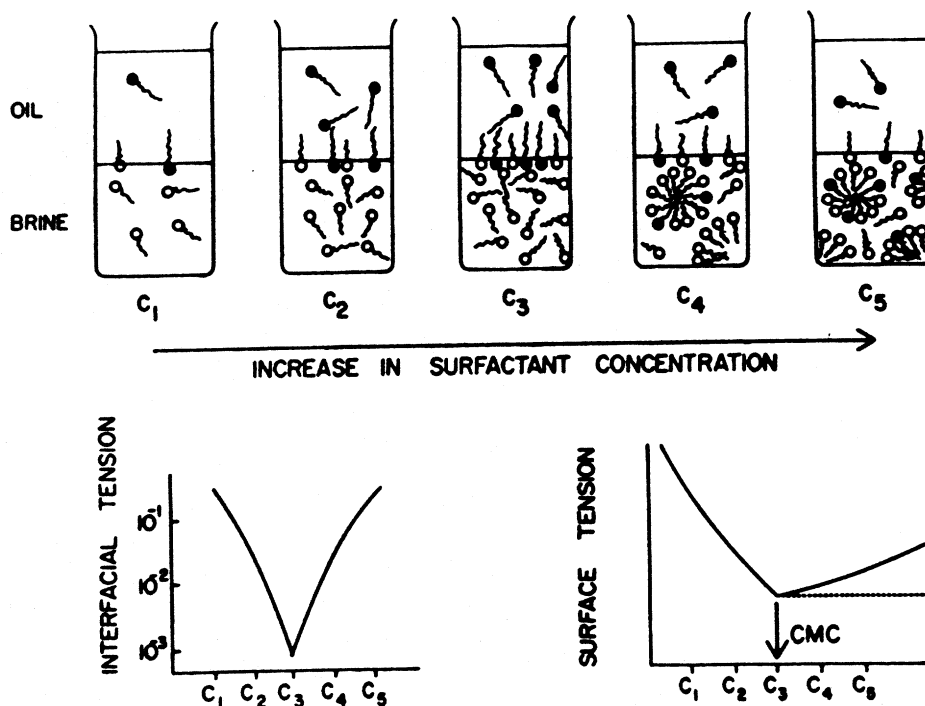


Figure 10 The Proposed Molecular Mechanism for the Effect of Surfactant Concentration on Interfacial and Surface Tensions.

systems. At very low surfactant concentrations, (e.g., C_1 , C_2 below CMC), the surfactant would partition between the oil and brine phases in such a way that the water soluble species would remain in the aqueous phase whereas the oil soluble species would partition into the oil phase. At these low concentrations, it can be assumed that the surfactant is in monomeric form. As one increases the concentration of TRS 10-80, the amount of surfactant in both the oil and brine phases will increase. However, at the critical micelle concentration for the surfactant species remaining in the brine phase, micelle formation will begin to occur in the aqueous phase. (It should be emphasized that we are here dealing with a micelle formation process in a solution containing several water soluble surfactant species.) Beyond this concentration, one would expect that the number of surfactant monomers in the aqueous phase should remain constant, and, that further addition of surfactant should result in the formation of more micelles. However, if one considers that the oil soluble species now have two possible sites, namely, they can be incorporated into the existing micelles within the aqueous phase or they can be partitioned into the oil. For surfactant concentrations above C_3 , we have mixed micelles consisting of oil soluble and water soluble molecular species. The incorporation of the oil soluble molecular species in the micelles will cause a decrease in the CMC of the original water soluble species: For example, when lauryl alcohol is added to a micellar solution of lauryl sulfate, it decreases the effective CMC of lauryl sulfate because it enhances the micellization process. Therefore, the addition of any molecular species which enhances the micellization process would decrease the effective CMC. This would also decrease the number of monomers existing in the solution. Therefore, as oil soluble molecules are incorporated into the micelles within the aqueous phase, they will decrease the effective CMC of the water soluble surfactant fraction, which in

turn will decrease the monomer concentration in the aqueous phase. If this occurs, it should decrease the amount of surfactant in the oil phase as well as decrease concentration of the surfactant at the interface because the interfacial concentration of the surfactant depends upon the monomer concentration in the oil as well as in the aqueous phase. Both these predictions were experimentally confirmed for higher surfactant concentrations; namely, the surfactant concentration in the oil phase did decrease after the CMC (0.05%) and the interfacial concentration of the surfactant also decreased as shown by electrophoretic mobility measurements (Figures 5 and 9). The predicted decrease in monomer concentration in the aqueous phase is also supported by the decrease in osmotic pressure as well as in light scattering just after 0.05% surfactant concentration (Figures 7-8). For isomerically pure surfactants one does not expect such mixed micelle formation to occur and hence a sharp minimum is not observed. On the other hand, these surfactants would produce a broad region of low interfacial tension as has been reported by various investigators (26) and has also been observed in our own laboratory. We have proposed (28) that the decrease in interfacial tension beyond CMC for an isomerically pure surfactant is related to the aggregation and solubilization phenomena in the oil phase from light scattering measurements.

Partitioning of surfactant molecules between the oil and water phase depends upon the relative solubility of the surfactant in the two phases. As the chain-length of the oil increases, the solubility of surfactant in the oil decreases (discussed in section 3, Figure 20). According to the proposed mechanism more surfactant would remain in the brine phase if oil chain length is increased. Hence the CMC would occur at a lower initial surfactant concentration. On the contrary, the CMC would appear at a higher initial surfactant concentration if the chain length of the oil is decreased.

This prediction was tested and confirmed using *n*-decane and *n*-hexane as the oil in place of *n*-octane. Minimum interfacial tension for the *n*-decane/TRS 10-80 (1% NaCl) system shifted to 0.01% surfactant concentration (Figure 11) as compared to 0.05% concentration for *n*-octane system. The monolayer area for the surfactant partitioning in the oil phase is shown in Figure 12. The surface tension of the equilibrated aqueous phase is shown

INTERFACIAL TENSION FOR TRS 10-80 IN 1% NaCl SOLUTION
WITH *n*-DECANE

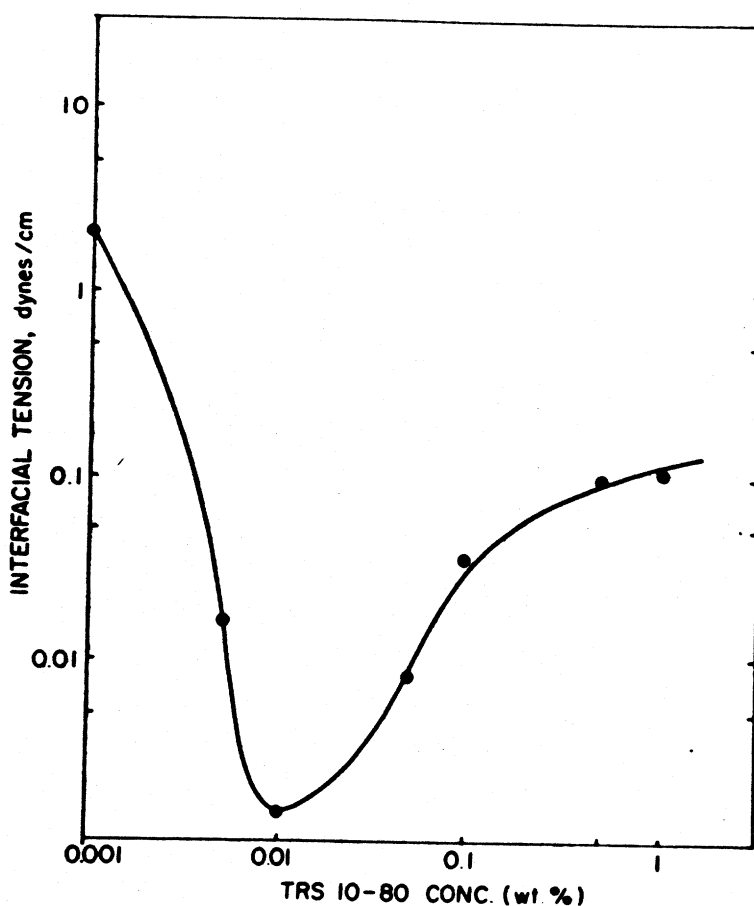


Figure 11 Interfacial Tension for TRS 10-80 in 1% NaCl Solution with *n*-Decane.

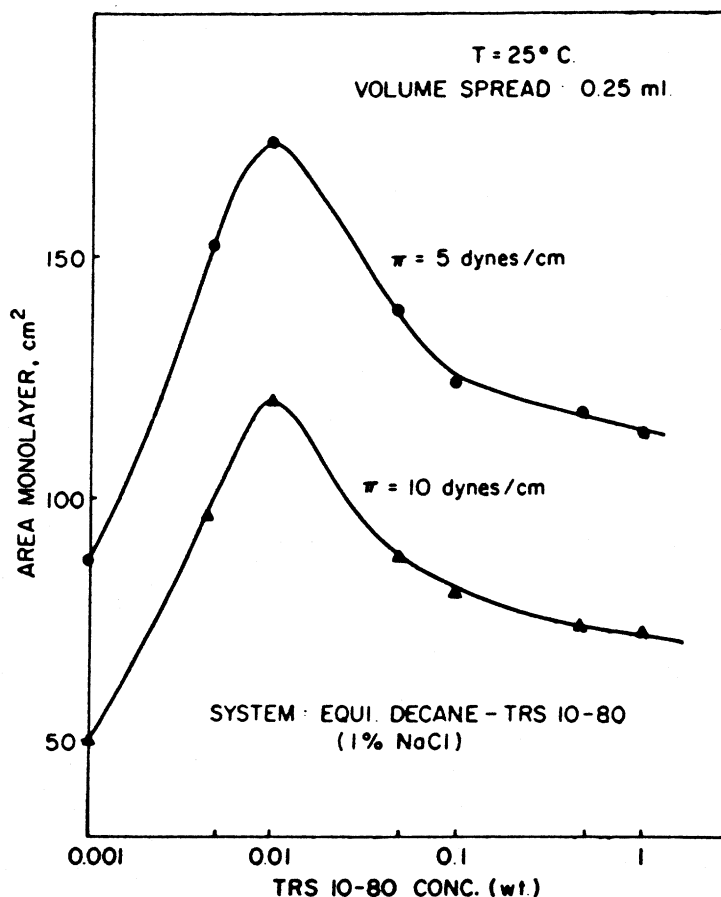


Figure 12 Area Occupied by Monolayers of Surfactant Partitioned into Oil Phase for TRS 10-80 in 1% NaCl with n-Decane.

in Figure 13. The minimum in interfacial tension and surface tension and maximum concentration of surfactant in the oil phase occurred at an initial surfactant concentration of 0.01%. The surface tension and interfacial tension increase for concentrations higher than 0.01% (Figs. 11 and 13), suggesting a decrease in the concentration of monomers of surfactant as more micelles are formed. For the n-hexane/TRS 10-80 (1% NaCl) system, Figures 14 and 15 show the same correlation between interfacial tension, concentration of surfactant in oil phase and surface tension. The

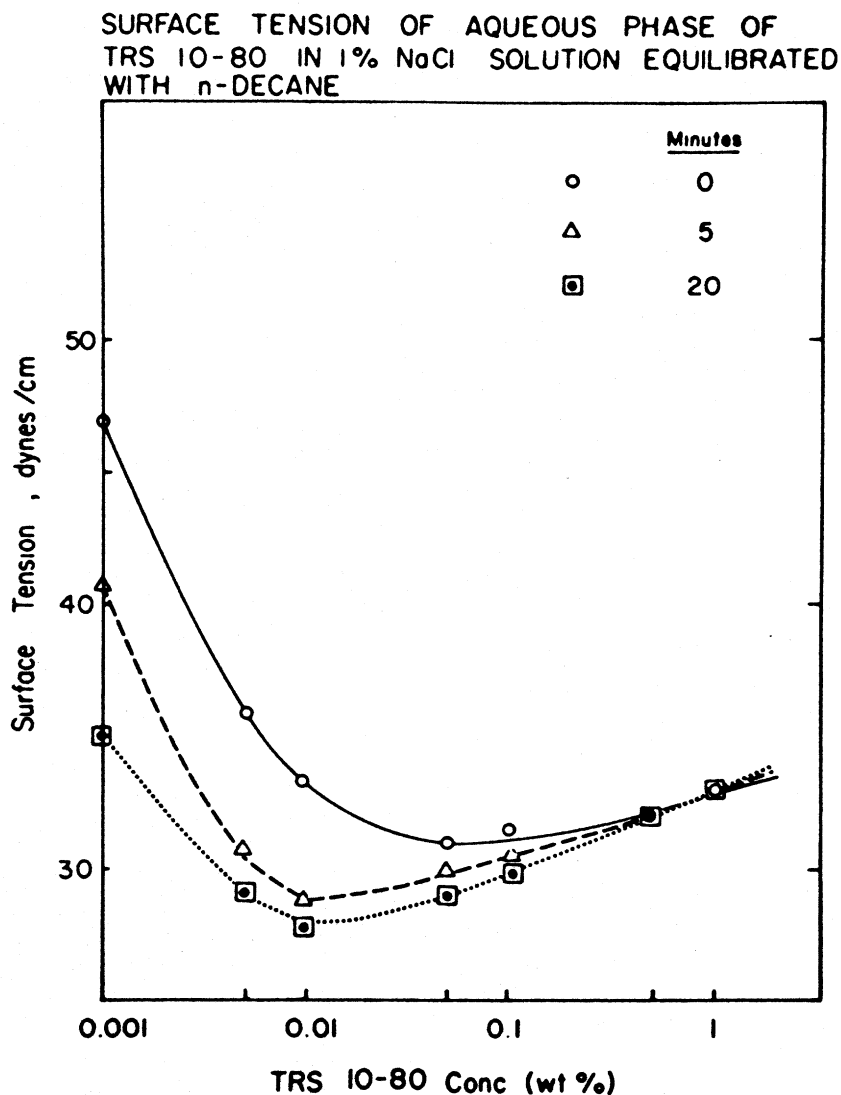


Figure 13 Surface Tension of Aqueous Phase of TRS 10-80 in 1% NaCl Solution Equilibrated with n-Decane.

minimum interfacial tension for the n-hexane system was about 1% initial surfactant concentration as compared to 0.05% for the n-octane system in agreement with the proposed mechanism.

In summary, the surface tension, electrophoretic mobility, partition coefficient, osmotic pressure and light scattering (I_{90}) measurements support the view that the minimum in

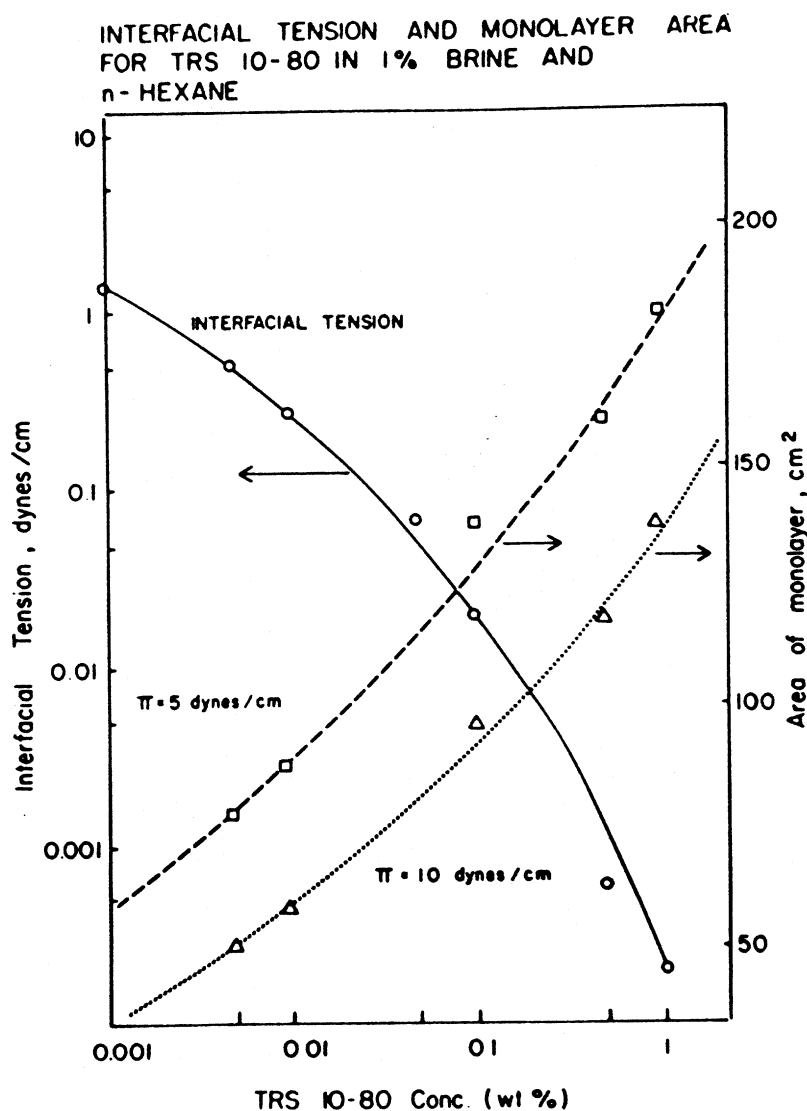


Figure 14 Interfacial Tension and Monolayer Area of Surfactant Partitioned in Oil for TRS 10-80 in 1% Brine and n-Hexane.

interfacial tension occurs at that surfactant concentration for which the surfactant concentration in the equilibrated aqueous phase is the CMC and the partition coefficient near unity. Beyond the CMC, the number of monomers in the oil and aqueous phase as well as at the interface decreases, possibly due to the

SURFACE TENSION OF AQUEOUS PHASE OF
TRS 10-80 IN 1% NaCl EQUILIBRATED WITH
n-HEXANE

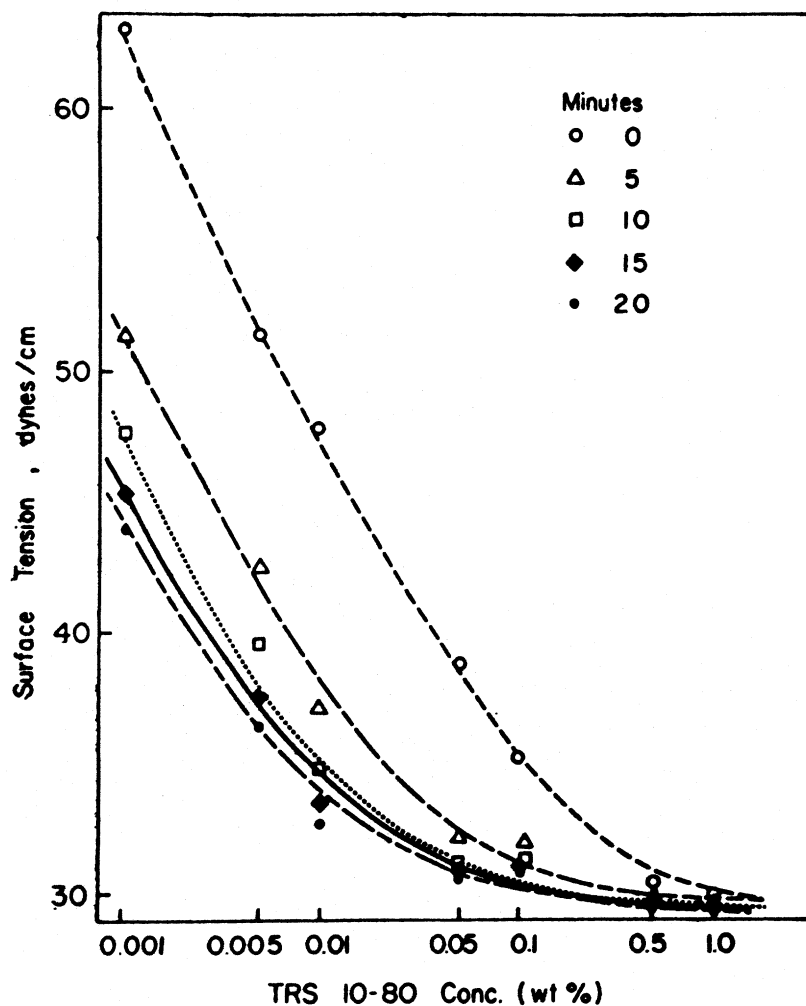


Figure 15 Surface Tension of Aqueous Phase of TRS 10-80 in 1% NaCl Equilibrated with n-Hexane.

incorporation of oil soluble surfactant molecules into the micelles predominantly formed by water soluble surfactant molecules in the aqueous phase.

2. Effect of Salinity on Interfacial Tension and Partition Coefficient

Surfactant partitioning is extremely sensitive to salt concentration. By adding salt to the aqueous phase, we are changing the solubility of surfactant in this phase. When the solubilities of the surfactant in oil and aqueous phases become the same, a maximum number of surfactant molecules can be expected to be present at the interface, and thus the interfacial tension should have a minimum at this salt concentration. The system studied to elucidate this point of view was 0.2% TRS 10-80 equilibrated with 30% (v/v) of n-octane at 25°C.

Figure 16 shows the interfacial tension and partition coefficient (measured by UV-absorption) at various NaCl concentrations. The minimum interfacial tension occurs at the same salt concentration where the partition coefficient is unity. Surface tensions of the aqueous phase for various salt concentrations is shown in Figure 17. It is interesting to note that both the interfacial tension and surface tension are minimum at the same NaCl concentration (2%). The same correlation between interfacial tension and partition coefficient was also obtained by Baviere (25) using a paraffin oil and sodium alkylbenzene sulfonates of average molecular weight 380 with isopropyl alcohol. The minimum interfacial tension in his study was only about 0.18 dynes/cm. Furthermore, the surface tension minimum also suggests that the equilibrated aqueous phase may be at CMC. This was confirmed by the light scattering (I_{90}) measurements as shown in Figure 18. The light scattering (I_{90}) curve changes its slope at 2% NaCl concentration which implies that below 2% NaCl concentration, the surfactant molecules are associated in micelles and that above 2% NaCl concentration, the degree of molecular association is much less in the aqueous phase because surfactant molecules are driven into the oil phase by "salting out" process.

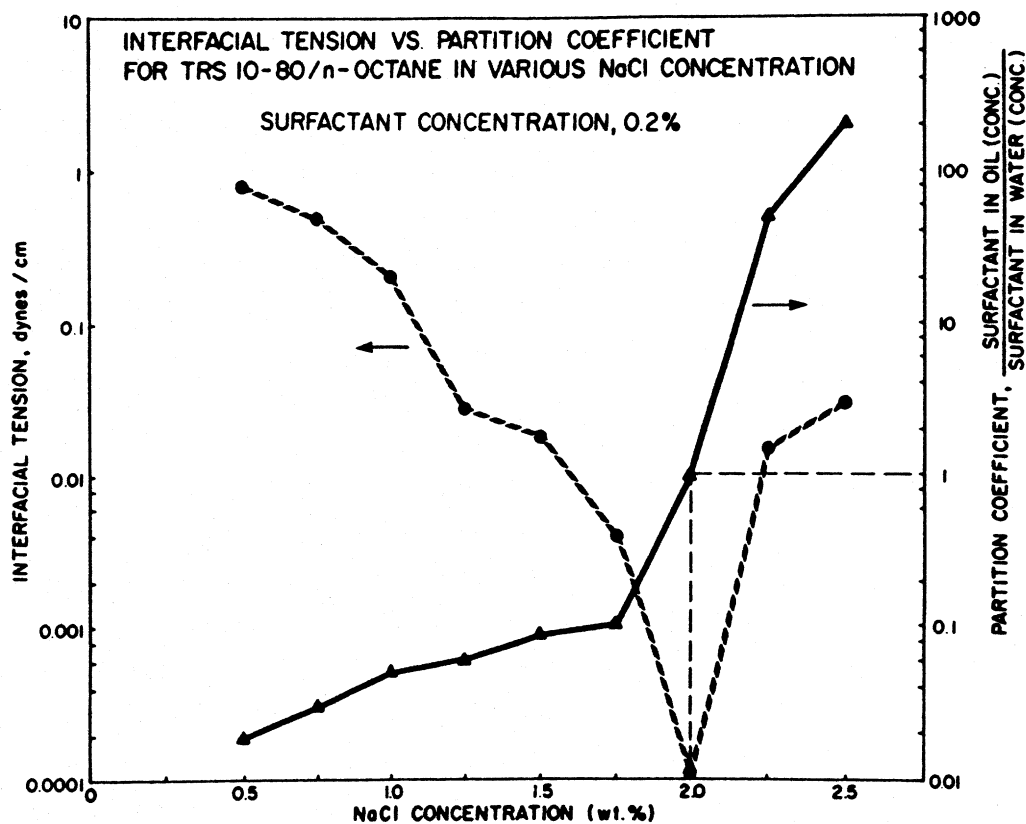


Figure 16 Interfacial Tension and Partition Coefficient (Concentration in Oil/Concentration in Brine) for TRS 10-80/n-Octane for Various NaCl Concentrations. The concentration in oil was determined by UV and that in brine by Methylene blue absorption measurements.

Our proposed molecular mechanism for the effect of salt concentration on interfacial tension and partition coefficient is schematically illustrated in Figure 19. At zero salt concentration, most of the surfactant remain in the aqueous phase, and hence a very little amount of it partitions into the interface or oil phase. As the salt concentration increases, the surfactant preferentially dissolves in the oil phase due to the "salting out" process. At the optimal salinity, the surfactant concentration is equal in the oil and brine phases. This

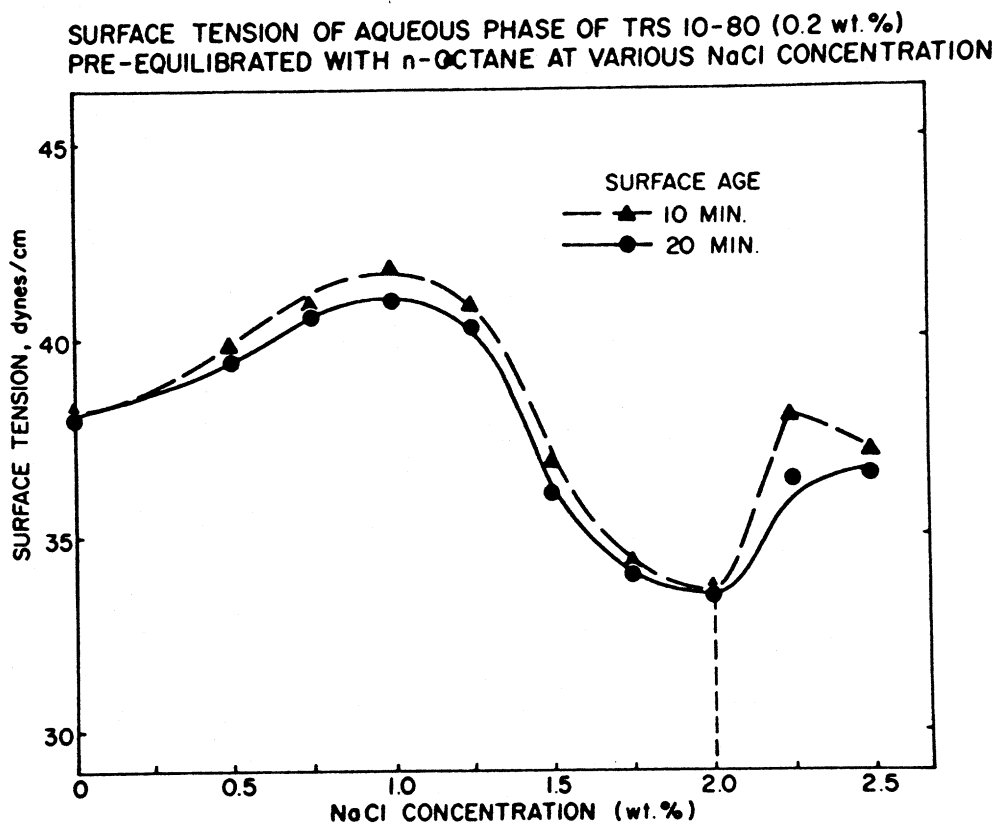


Figure 17 Surface Tension of Aqueous Phase of TRS 10-80 (0.2 wt.%) Equilibrated with n-Octane at Various NaCl Concentrations.

implies that the surfactant molecules have the same affinity for oil and brine. This presumably results in the highest interfacial concentration of surfactant, and hence the lowest interfacial tension. At high salt concentrations, the surfactant is predominantly dissolved in the oil phase and the monomer concentration in the aqueous phase decreases. This would cause an increase in interfacial tension (Figure 16). It is interesting to note that similar to surfactant concentration effect, the CMC, partition coefficient unity and interfacial

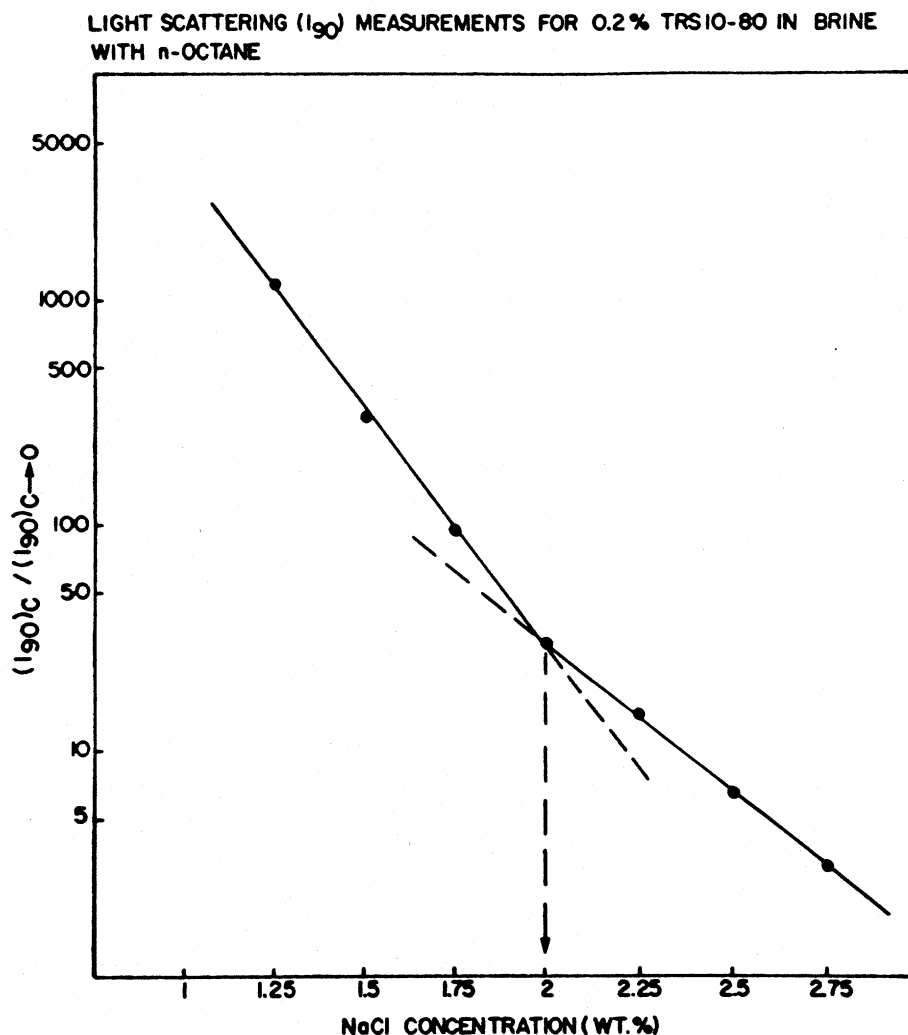


Figure 18 Light Scattering (I_{90}) Measurements of the Aqueous Phase of 0.2% TRS 10-80 in Brine with n-Octane at Various NaCl Concentrations.

tension and surface tension minimum occurred at the same salt concentration.¹

¹This correlation of partition coefficient unity with CMC will not be observed for all surfactants. For example, we have found that sodium dodecyl benzene sulfonate does not exhibit this correlation; however, 8-phenyl-hexadecane sulfonate does show this correlation. It appears that this correlation is observed only for those surfactants which produce ultra-low (less than 0.1 dyne/cm) interfacial tension.

THE EFFECT OF SALT CONCENTRATION ON INTERFACIAL AND SURFACE TENSIONS

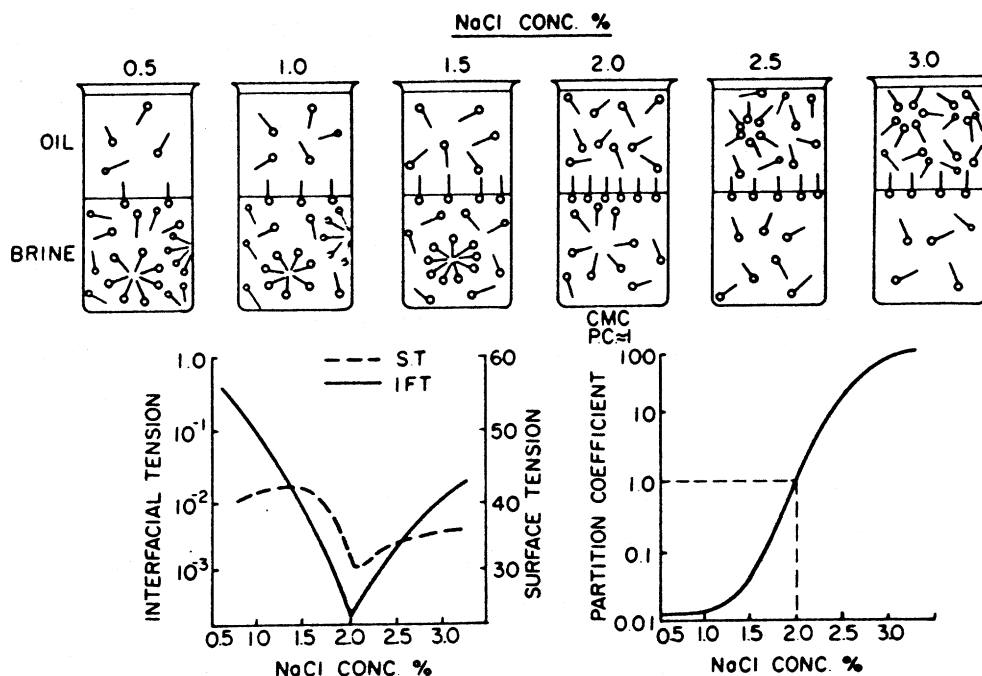


Figure 19 The Molecular Mechanism for the Effect of Salt Concentration on Interfacial and Surface Tensions.

3. Effect of Oil Chain Length on Interfacial Tension and Partition Coefficient of Surfactant

Figure 20 shows the partition coefficient and interfacial tension for 0.1% TRS 10-80 in 1.5% NaCl as a function of chain-length of the oil. The surface tension of the equilibrated aqueous phase is shown in Figure 21. It is interesting to note that the minima in interfacial tension and surface tension occur at the same chain length of oil. The partition coefficient decreases logarithmically. The partition coefficient unity once again corresponds to the minimum in interfacial tension. The minimum in surface tension (Figure 21) suggests that the surfactant concentration in the aqueous phase equilibrated with decane must be at the CMC.

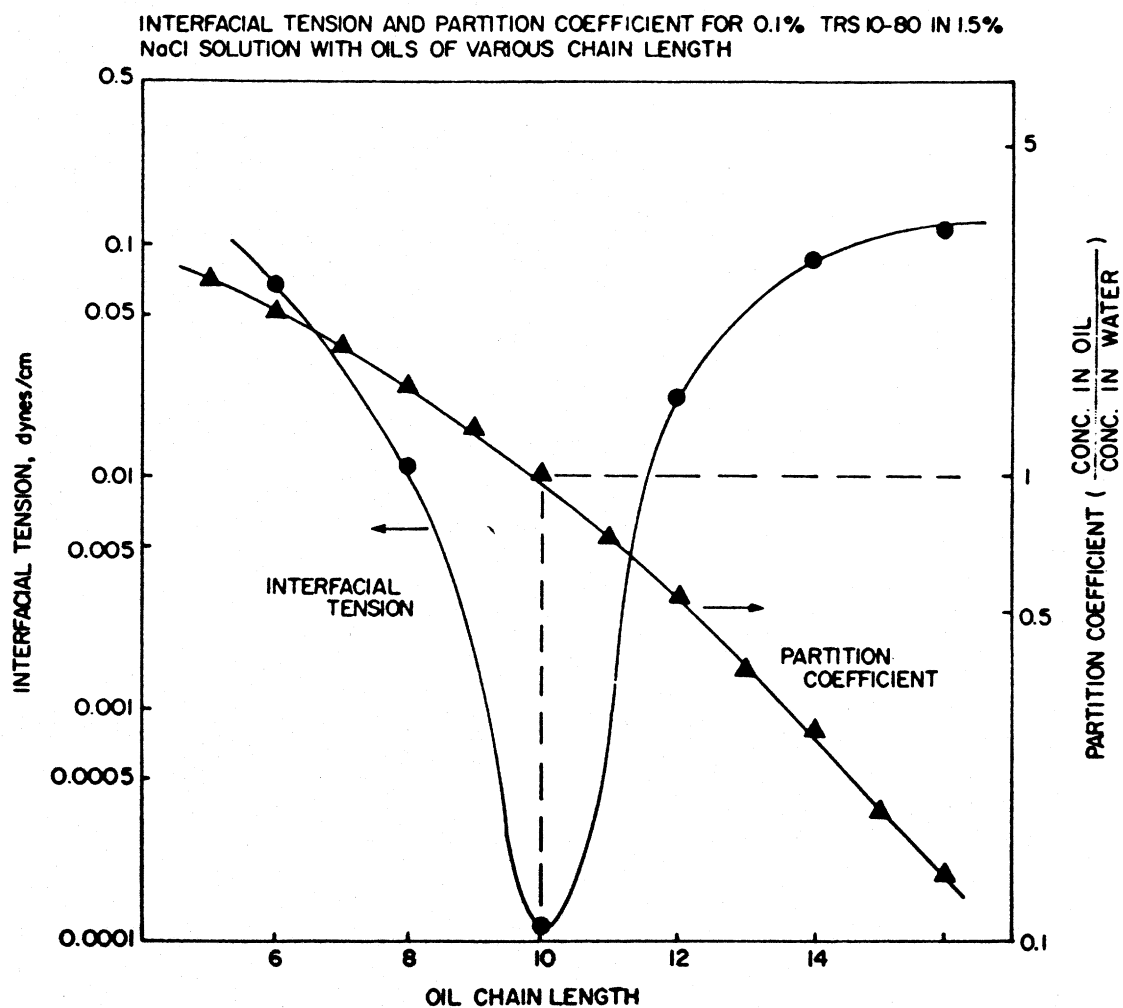


Figure 20 Interfacial Tension and Partition Coefficient for 0.1% TRS 10-80 in 1.5% NaCl with Oils of Various Chain Length. The concentration in oil was determined by UV and that in brine by methylene blue absorption measurements.

Our proposed molecular mechanism for the effect of oil chain-length on interfacial tension is illustrated schematically in Figure 22. It is evident from the partition coefficient data that as the chain-length of oil increases, the partitioning of the surfactant in the oil phase decreases. Therefore, as shown in the upper part of Figure 22, the concentration of surfactant

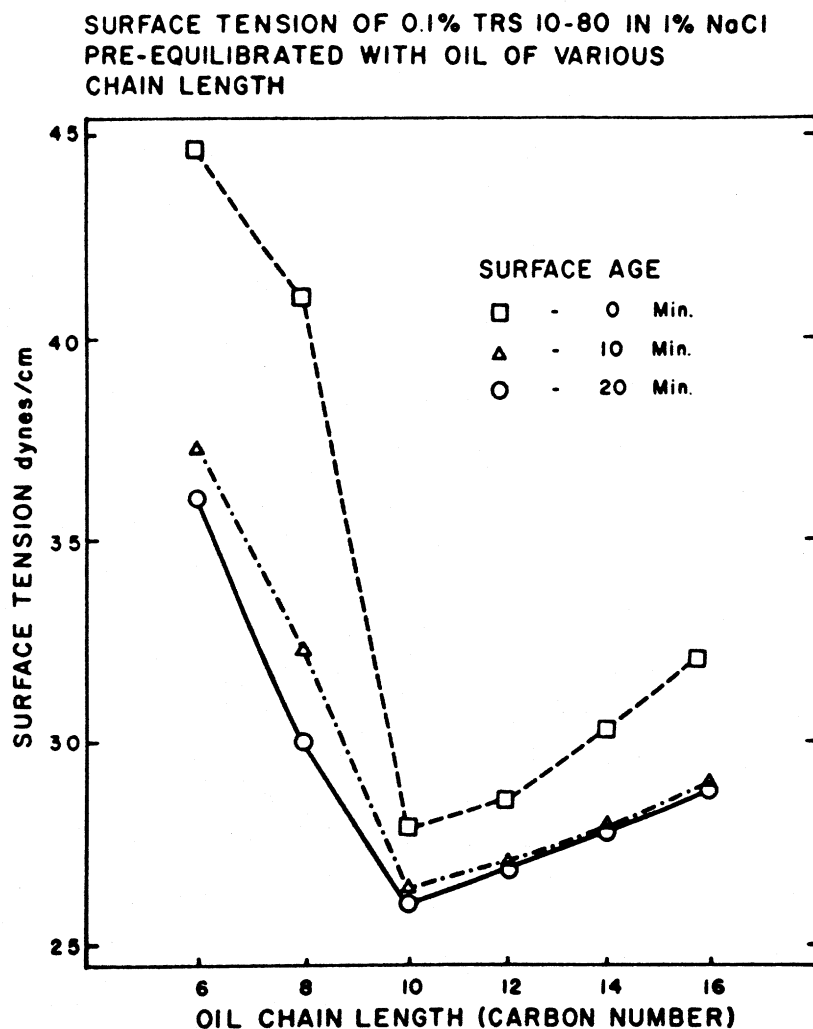


Figure 21 Surface Tension of Aqueous Phase of 0.1% TRS 10-80 in 1.5% NaCl Equilibrated with Oils of Various Chain Length.

in the oil decreases as the oil chain length increases from C_6 to C_{16} . Consequently, the concentration of surfactant in the brine phase must increase as the oil chain length is increased from C_6 to C_{16} because the total amount of surfactant is constant in each cylinder. It would appear from the interfacial tension and surface tension results that the concentration of surfactant in the aqueous phase equilibrated

THE EFFECT OF CHAIN-LENGTH OF OIL ON INTERFACIAL AND SURFACE TENSIONS

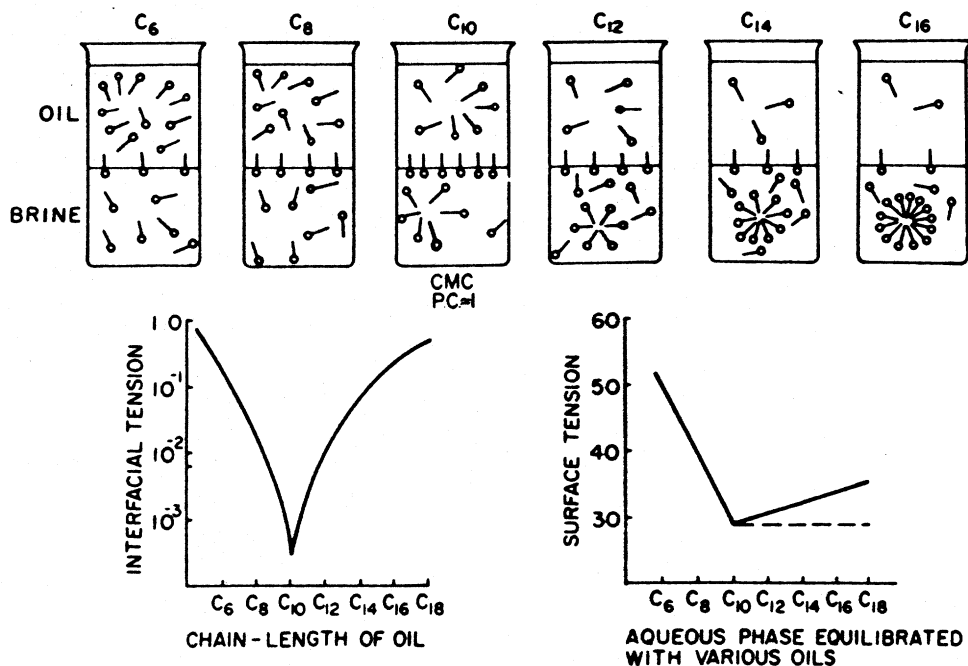


Figure 22 The Molecular Mechanism for the Effect of Chain-Length of Oil on Interfacial and Surface Tensions.

with C_6 and C_8 oils is below the CMC. The surfactant concentration in the aqueous phase equilibrated with decane is the CMC, and with higher chain-lengths of oil, the surfactant concentration in the aqueous phase is higher than the CMC. The question is why the monomer concentration decreases above CMC? We believe that even though the aqueous phase in equilibrium with C_{12} , C_{14} or C_{16} oil is above CMC, the monomer concentration must decrease with increased chain length of dissolved oil as inferred from surface tension and interfacial tension data (Figures 20,21). We, indeed, confirmed this by measuring the CMC of sodium dodecyl benzene sulfonate in the presence of various dissolved oils (27). Figure 23 shows that as the

THE EFFECT OF OIL CHAIN-LENGTH ON THE CMC OF SDBS IN DISTILLED WATER

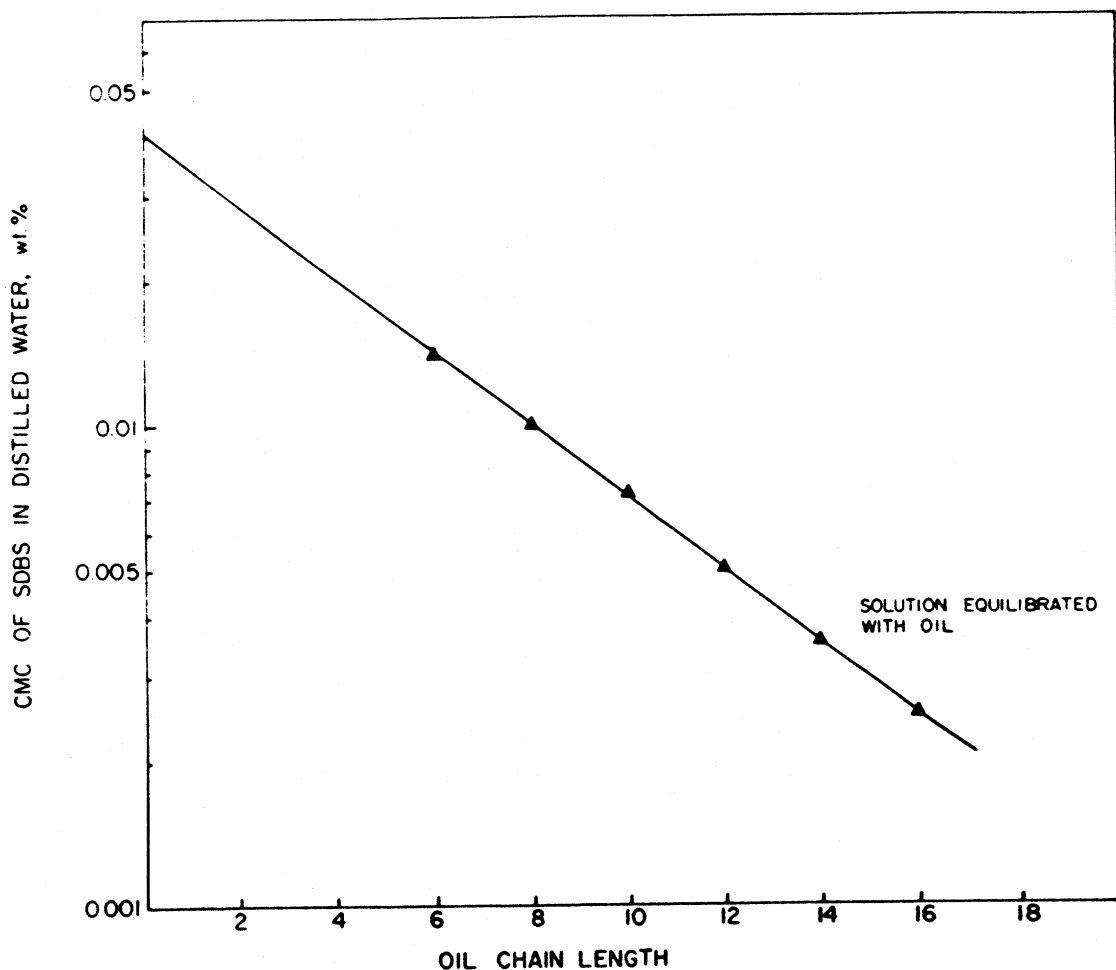


Figure 23 The Effect of Oil Chain-Length on the CMC of SDBS in Distilled Water.

chain-length of dissolved oil increases, the CMC decreases linearly on a semilog plot of CMC vs. chain length of dissolved oil. Therefore, this observation leads to the conclusion that the surfactant remaining in the aqueous phase will have a different effective CMC because of the different chain-length of dissolved oil. In the study of the effect of surfactant concentration on interfacial tension (Figure 10), the increase in

the interfacial tension beyond the CMC was attributed to the decrease in the monomer concentration in the oil phase as well as in the aqueous phase due to the incorporation of the oil soluble species into the mixed micelles in the aqueous phase. In the case of the effect of oil chain length on the interfacial tension, the decrease in monomer concentration in the aqueous phase is attributed to the decrease in the effective CMC as the oil chain length increases from C_{10} to C_{16} . This decrease in the monomer concentration is reflected in a decrease in interfacial concentration which, in turn, causes an increase in interfacial tension as a function of oil chain-length so that for C_{12} , C_{14} and C_{16} oils, the interfacial tension is higher than that for C_{10} oil.

The molecular mechanism illustrated in Figure 22 suggests that the aqueous phases in equilibrium with oils C_6 , C_8 must be below CMC and those in equilibrium with C_{10} to C_{16} oils must be above CMC. This prediction indeed was confirmed by light scattering measurements on the equilibrated aqueous phases as shown in Figure 24. The light scattering results confirm that the light scattered at 90° by the aqueous phase in equilibrium with hexane and octane was much smaller than the light scattered by the aqueous phases in equilibrium with the oils of chain lengths C_{10} , C_{12} , C_{14} and C_{16} . Figure 24 suggests that micelles are present in the aqueous phases equilibrated with these oils (C_{10} to C_{16}) whereas there is no micelle formation in the aqueous phase equilibrated with C_6 and C_8 . It should be pointed out that although the surfactant concentration is above the CMC in the aqueous phases in equilibrium with C_{12} to C_{16} oils, the effective CMC would be smaller as the chain length of oil increases. Moreover, the monomer concentration in brine would be smaller as the chain length of the dissolved oil is increased. This explains why the interfacial tension should increase as the oil chain length is increased from C_{10} to C_{16} .

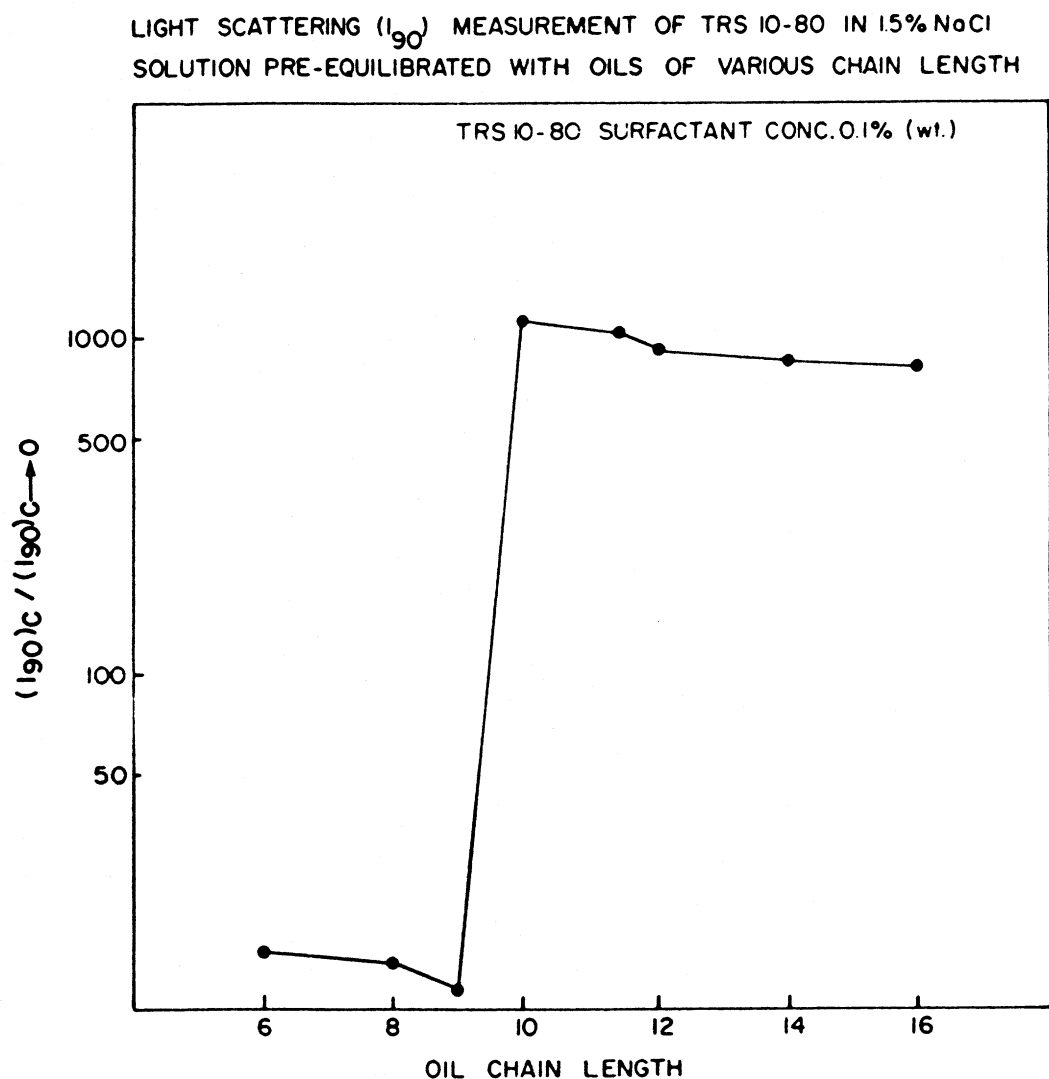


Figure 24 Light Scattering (I_{90}) Measurements of the Aqueous Phase of 0.1% TRS 10-80 in 1.5% NaCl Solution Equilibrated with Oils of Various Chain Lengths.

The molecular mechanism proposed in Figure 22 explains clearly the oil chain-length effect reported by us and other investigators (6). It appears to us that the sharp chain-length dependence is due to a partitioning of surfactant into the oil phase and the effective critical micelle concentration phenomenon

in the aqueous phase. Our results also have established that the partitioning of surfactant in oil strikingly decreases as the chain-length of oil increases. The molecular mechanism proposed in Figure 22 also suggests that if we use a higher concentration of surfactant then the CMC will occur earlier in the aqueous phase equilibrated with a shorter chain-length of oil. This, indeed, was confirmed experimentally by us as well as by Cayias et al. (6). It should be noted that similar to surfactant and salt concentration effects, the CMC, partition coefficient unity and the minimum interfacial tension occurred at the same oil chain length.

SUMMARY AND CONCLUSION

This paper reports the molecular mechanism for the occurrence of a minimum in ultra-low interfacial tension curve as a function of surfactant concentration, salinity, and the chain-length of oil for dilute petroleum sulfonate solutions. For all the three effects studied, the minimum interfacial tension occurs at that concentration which is the critical micelle concentration for the aqueous phase after equilibration with oil. The minimum interfacial tension also coincides with the partition coefficient unity. This implies that the interaction of surfactant molecules with brine and oil phase is equal and the surfactant molecules at the interface will experience equal affinity for oil and brine and consequently will produce a very high concentration at the interface. The observed effect of the oil chain-length on the interfacial tension was explained based on the partitioning of the surfactant in the oil phase and the micellization phenomenon in the brine phase. The minimum interfacial tension is observed with that oil for which the surfactant remaining in the aqueous phase is at the CMC, and the partition coefficient near unity.

From surface tension, interfacial tension, osmotic pressure, light scattering, electrophoretic mobility and partition coefficient data, it was conclusively shown that the monomer

concentration is maximum in the oil and brine phase where the minimum interfacial tension is observed. It is likely that other factors such as the mutual solubilization of oil and brine phase, the binding of counterions and the surface charge on micelles may also influence the magnitude of the ultra-low interfacial tension.

In summary, we have proposed a molecular mechanism to account for the observed minimum in the ultra-low interfacial tension curves for dilute solutions of petroleum sulfonates. It was shown that the minimum in ultra-low interfacial tension occurs when the concentration of surfactant monomers in the aqueous phase is maximum. The minimum interfacial tension coincides with the CMC of the surfactant in the equilibrated aqueous phase and with the partition coefficient unity of surfactant between the aqueous phase and the oil phase. This unified theory accounts for all observed effects of variables such as concentration of surfactant and salts as well as the chain length of oil on interfacial tension minimum reported for commercial petroleum sulfonates.

ACKNOWLEDGMENTS

The authors wish to take this opportunity to thank Department of Energy (Grant No. EY-27-S-05-3341) and the industrial 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. Taber, J.J., Soc. Petrol. Eng. J., 3-12, March 1969.
2. Melrose, J.C. and Brandner, C.F., J. Can. Pet. Tech., 54-62, Oct.-Dec., 1974.
3. Wagner, O.R. and Leach, R.O., Soc. Pet. Eng. J., 335-344, Dec. 1966.
4. Foster, W.F., J. Pet. Tech., 25, 205-210 (1973).

5. Wilson, P.M. and Brandner, C.F., "Aqueous Surfactant Solutions Which Exhibit Ultra-Low Tensions at the Oil-Water Interface," paper presented at the 165th National Meeting of the American Chemical Society, Dallas, Texas, April 8-13, 1973.
6. Cayias, J.L., Schechter, R.S., and Wade, W.H., "The Utilization of Petroleum Sulfonate for Producing Low Interfacial Tension Between Hydrocarbon and Water," *J. Colloid Interface Sci.*, in press.
7. Doe, I.H., Wade, W.H., and Schechter, R.S., *J. Colloid Interface Sci.*, 59, 525-531 (1977).
8. Rosen, M.J., *J. Amer. Oil Chemists Soc.*, 51, 461-465 (1974).
9. Rosen, M.J., *J. Colloid Interface Sci.*, 56, 320-321 (1976).
10. Miller, C.A., and Scriven, L.E., *J. Colloid Interface Sci.*, 33, 360-370 (1970).
11. Shah, D.O., Chan, K.S., and Bansal, V.K., "The Importance of Interfacial Charge vs. Interfacial Tension in Secondary and Tertiary Oil Recovery Processes," paper presented at the 83rd National Meeting of AIChE, Houston, Texas, March 20-24, 1977.
12. Defay, R., Prigogine, I., Bellemans, A., and Everett, D.H., "Surface Tension and Adsorption," Chapter VII, Wiley, N.Y. (1966).
13. Franses, E., Bidner, M.S., and Scriven, L.E., "Interfacial Tension Minima in Two-Phase Micellar Systems," in *Micellization, Solubilization, and Microemulsions*. Editor, K.L. Mittal, Vol. 2, pp. 855-876, Plenum Press, N.Y. (1977).
14. Princen, H.M., Zia, L.Y.Z., and S.G., *J. Colloid Interface Sci.*, 23, 99-107 (1967).
15. Cayias, J.L., Schechter, R.S., and Wade, W.H., pp. 234-247 in Mittal, K.L., ed.: *Adsorption at Interfaces*, ACS Symposium Series No. 8 (1975).
16. Healy, R.N. and Reed, R.L., *Soc. Petrol. Eng. J.*, 14, 49 (1974).
17. Orr, Jr., F.M. and Scriven, L.E., *J. Colloid Interface Sci.*, 60, 402-405 (1977).
18. Smith, L., Malmberg, E.W., Kelley, H.W., and Fowler, S., paper SPE 5369 presented at the 45th Annual California Regional Meeting of the Society of Petroleum Engineers of AIME, Ventura, California, April 2-4, 1975.
19. Tham, M.K., and Walker, Jr., R.D., Semi-Annual Report, Improved Oil Recovery Research Program, University of Florida, Dec. 1975.
20. Sandvik, E.L., Gale, W.W., and Denekas, M.O., paper SPE 6120 presented at 51st Annual Fall Technical Conference and Exhibition of the Society of Petroleum Engineers of AIME, New Orleans, Oct. 3-6, 1976.

21. Cash, R.L., Cayias, J.L., Hayes, M., MacAllister, D.J., Schares, T., Schechter, R.S., and Wade, W.H., paper SPE 5564 presented at 50th Annual Fall Meeting of the Society of Petroleum Engineers of AIME, Dallas, Texas, Sept. 28-October 1, 1975.
22. Chan, K.S. and Shah, D.O., Semi-Annual Report, Improved Oil Recovery Research Program, University of Florida, June 1977.
23. Alexander, A.E., Trans. Faraday Soc., 38, 248-254 (1942).
24. Reichenberg, D., Trans. Faraday Soc., 43, 467-479 (1947).
25. Baviere, M., SPE 6000, paper presented at 51st Annual Fall Technical Conference and Exhibition of the Society of Petroleum Engineers of AIME, New Orleans, Oct. 3-6, 1976.
26. Wade, W.H., Morgan, J.C., Jacobson, J.K., Salager, J.L., and Schechter, R.S., paper SPE 6844 presented at 52nd Annual Fall Technical Conference and Exhibition of the Society of Petroleum Engineers of AIME, Denver, Colorado, Oct. 9-12, 1977.
27. Chan, K.S. and Shah, D.O., "The Effect of Dissolved Oils Alcohols on CMC of Synthetic and Petroleum Sulfonates," paper presented at 52nd Colloid and Surface Science Symposium, Knoxville, TN, June 1978.
28. Chan, K.S. and Shah, D.O., Semi-Annual Report, Improved Oil Recovery Research Program, University of Florida, June 1978.