

THE EFFECT OF DISSOLVED OILS AND ALCOHOLS ON THE CMC OF SYNTHETIC
AND PETROLEUM SULFONATES

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The CMC of sodium dodecyl benzene sulfonate was determined using surface tension, light scattering and electrical conductivity measurements. It is shown that the presence of alcohol or oil decreases the CMC. The decrease in CMC depends on the chain length of dissolved alcohol or oil. For oils of different chain length, it was observed that the higher the chain length of oil, the greater is the decrease in CMC.

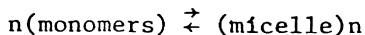
Using light scattering and osmotic pressure measurements, the CMC of a petroleum sulfonate (TRS 10-80) in 1% NaCl solution was found to be 0.005%. However, upon equilibration with n-octane, the CMC in the equilibrated aqueous phase was found to be 0.05% using light scattering and osmotic pressure measurements. The interfacial tension in TRS 10-80 solution/n-octane was found to be minimum (≈ 1 millidynes/cm) at 0.05% surfactant concentration. The electrophoretic mobility of oil droplets was also found to be maximum at 0.05% TRS 10-80. It is proposed that upon equilibration with oil, the higher equivalent weight species partition preferentially in the oil phase whereas lower equivalent weight species remain preferentially in the brine phase. Thus, after equilibration with oil, the average weight of the surfactant remaining in the aqueous phase is considerably less than the average equivalent weight of the original surfactant. This interpretation explains why the CMC increases ten-fold for TRS 10-80 upon equilibration with n-octane. A unified theory is presented to account for the observed effects

of several variables on partition coefficient and the effective CMC of a surfactant, which in turn, influence the surface concentration of surfactant, surface charge density and solubilization of oil or brine in each other. These parameters influence the magnitude of interfacial tension at the oil/brine interface.

INTRODUCTION

Various techniques have been used to determine the critical micelle concentration (CMC) of surfactants.¹ The most commonly used methods are surface tension, dye absorbance, light scattering and electrical conductivity measurements. It is well recognized that the CMC value obtained by one method may be slightly different from that determined by other techniques.¹

For a pure surfactant, the concentration of monomers increases with the increase of surfactant concentration until CMC is reached. Above the CMC, it is assumed that monomer concentration remains constant in pure surfactant solutions, if micellization process is,



where the right hand side showing a micelle with aggregation number n . If the aggregation number changes with concentration of surfactant, then monomer concentration will change above the CMC.

In the case of petroleum sulfonates, with broad equivalent weight distribution, the surface concentration of surfactant depends greatly on the micellization process in the bulk phase. Surfactants of longer chain length may be adsorbed first at the surface and then be solubilized into the micelles formed by surfactant of shorter chain length. By this process, the long chain molecules at the surface can be gradually replaced by molecules of shorter chain length. The effectiveness of surfactant molecules to decrease the surface tension depends on their chain length.² Hence, the surface tension of petroleum sulfonate solutions may increase after a minimum is reached. The CMC determined using this minimum in surface tension is actually the concentration at which the concentration of monomer is maximum. By the same reasoning, we can say that the structure and composition of the micelles in such a broad distribution surfactant system should undergo a constant change in composition as the surfactant concentration increases. Since petroleum sulfonates consist of a broad distribution of equivalent weights, we used light scattering and membrane osmometry techniques to determine the CMC. Both these techniques would mea-

sure the number of particles (presumably monomers) in the bulk aqueous phase.

It has been shown that the presence of alcohol decreases the CMC of potassium myristate.³ Short chain alcohols are commonly used in surfactant formulations for tertiary oil recovery and hence are expected to influence the micellization process or CMC of the surfactant. Studies⁴ with low concentration petroleum sulfonate solutions have shown that a crude oil may be assigned an equivalent alkane carbon number. Important parameters examined for their influence on interfacial tension include surfactant molecular structure^{5,6} as well as electrolyte concentration, surfactant concentration, surfactant molecular weight and temperature.⁷⁻⁹

MATERIALS AND METHODS

Sodium dodecyl benzene sulfonate (SDBS), originally 85% active containing about 15% salt, was first desalted by dissolving the surfactant in pure isopropanol. The clear supernatant was separated and dried to yield the semi-solid surfactant estimated to be 99.5% pure by elemental analysis. A solution of 1% SDBS in doubly distilled water was prepared and then successively diluted to any desired concentration by water of the same quality. TRS-10-80 (80% active) was supplied by Witco Chemical Company and was used without any further purification. Samples of various surfactant concentrations were prepared by successive dilution.

Surface tension measurements were made by Wilhelmy plate method using a platinum blade balanced by an extremely sensitive strain gauge. The response from this strain gauge was plotted on a strip chart recorder. Osmotic pressure was measured using a membrane osmometer (Model 502, Mechrolab Inc.) and an aqueous membrane B19 (Hewlett-Packard Company). Temperature was controlled at 25°C and the solvent was 1% NaCl. Experimental error was found to be less than ± 0.04 cm. The surfactant solutions of TRS 10-80 at various concentrations were equilibrated with n-octane and the aqueous phase was separated and osmotic pressure was also measured. Surfactant concentrations (w/v %) mentioned in the text and diagrams are always the initial surfactant concentrations before contacting oil.

Light scattering (I_{90}) measurements were done by using a Wood dual photometer, Model 5200. Monochromatic light of wavelength 436m μ was used and the intensity of light scattered at 90° (I_{90}) angle was measured for samples of various concentrations. At very low surfactant concentrations, the I_{90} value is independent of the concentration. This limiting value was taken as that of

the solvent. The I_{90} ratios of the solution and this limiting value as concentration reaches zero were plotted against the concentration of surfactant.

RESULTS AND DISCUSSION

Figure 1 shows the surface tension vs. concentration plot for the SDBS in distilled water. The CMC occurs at a concentration of 0.07%. Figure 2 shows I_{90} ratio of SDBS solutions of various concentrations. The data shown in Figure 2 can be replotted on a log-log plot as illustrated in Figure 3. It is evident that near CMC, the change in light scattering occurs gradually. This is consistent with the view that micelles do not form

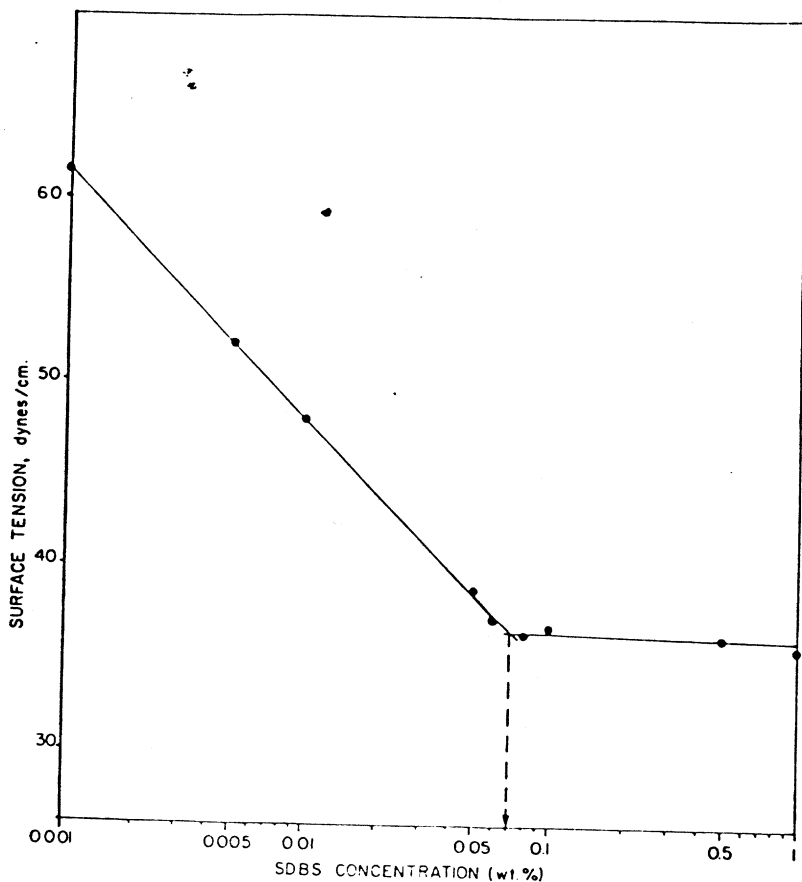


Figure 1. Surface tension of purified sodium dodecyl benzene sulfonate in distilled water at 25°C.

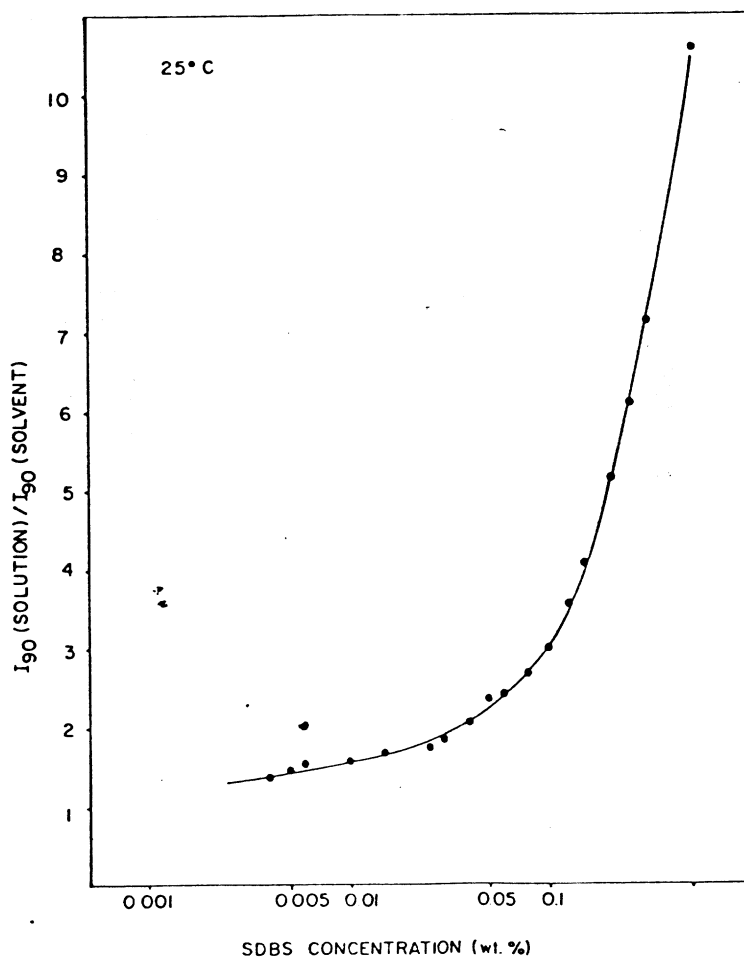


Figure 2. Light scattering measurements of sodium dodecyl benzene sulfonate solutions in distilled water at 25°C.

at a specific surfactant concentration but form over a narrow range of concentrations. The CMC as determined from light scattering measurements is around 0.06%. This value is in agreement with those reported in the literature.¹

Figure 4 shows the CMC of SDBS from electrical conductivity measurements. Here the CMC of SDBS was found to be around 0.07%. Figure 4 also shows that the presence of dissolved dodecane decreases the CMC. The lower part of Figure 4 shows the effect of increasing concentration of alcohol on the CMC. It is evident that increase in concentration of alcohol decreases the CMC. Figure 5 shows the effect of dissolved oils on the CMC of a commercial sample of pentadecyl benzene sulfonate (PDBS). It is

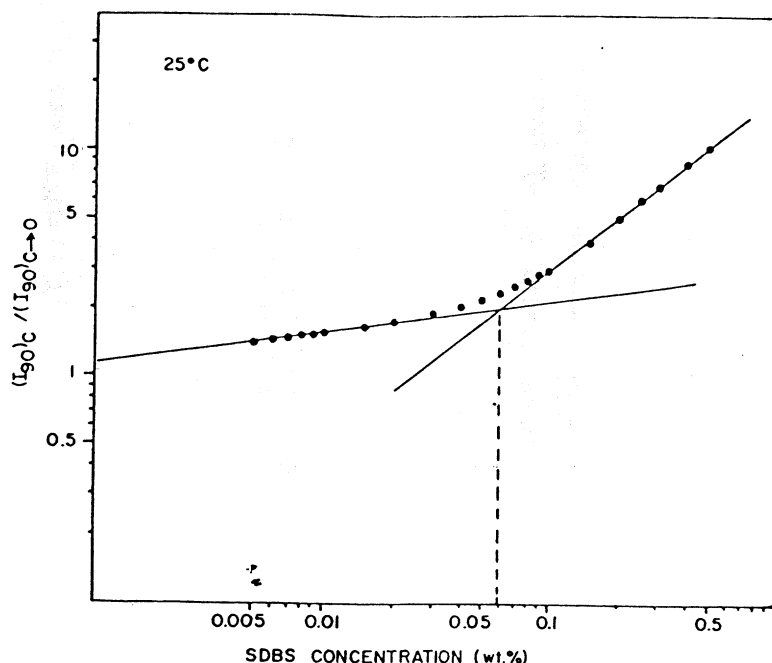


Figure 3. Light scattering data plotted on a log-log scale for sodium dodecyl benzene sulfonate solutions in distilled water at 25°C.

also evident that the greater the chain length of oil, the larger is the decrease in CMC. Unlike pure surfactants, this commercial sample of PDBS showed a non-linear change in equivalent conductance. This suggests that association of monomers must be occurring in the pre-CMC region in this system.

CMC of Petroleum Sulfonate TRS 10-80.

Figure 6 shows the light scattering measurements as a function of TRS 10-80 concentration. It is evident that the light scattering increases abruptly beyond 0.005% concentration. This suggests that the CMC of TRS 10-80 in 1% NaCl solution is 0.005%. This conclusion was also supported by the osmotic pressure measurements of these solutions (Figure 7). A maximum in osmotic pressure at 0.005% suggests that this is indeed the CMC corresponding to the maximum number of particles (i.e., monomers) in the solution.

Figure 8 shows the interfacial tension of TRS 10-80 against n-octane. It is interesting that the minimum in interfacial tension occurred at 0.05% concentration, a value about ten times higher than the CMC measured in TRS 10-80 before contacting oil. Using light scattering and osmotic pressure (Figures 9 and 10) we

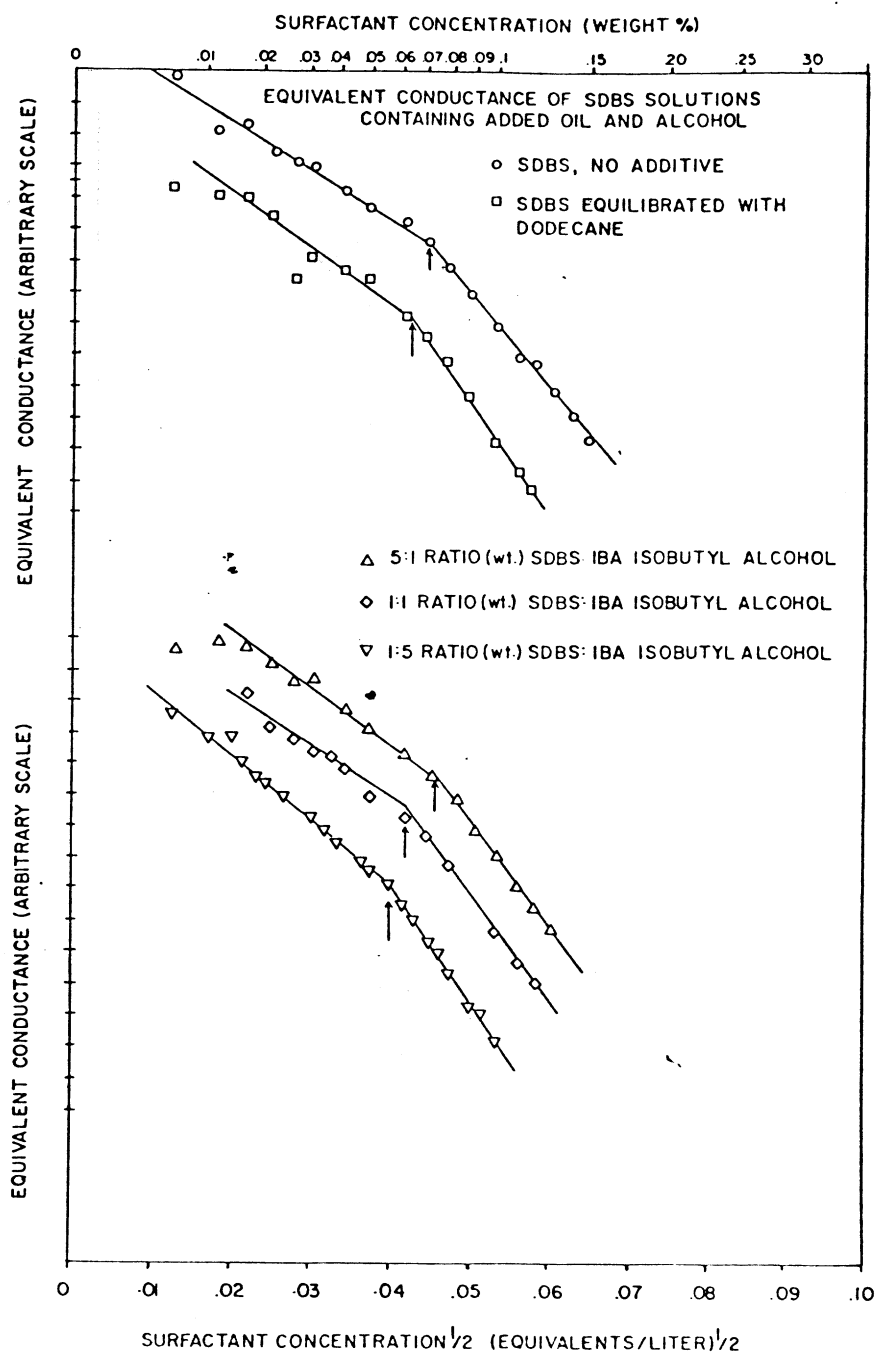


Figure 4. CMC from equivalent conductance measurements of sodium dodecyl benzene sulfonate solutions before and after equilibration with dodecane, and in the presence of various amounts of isobutanol at 25°C.

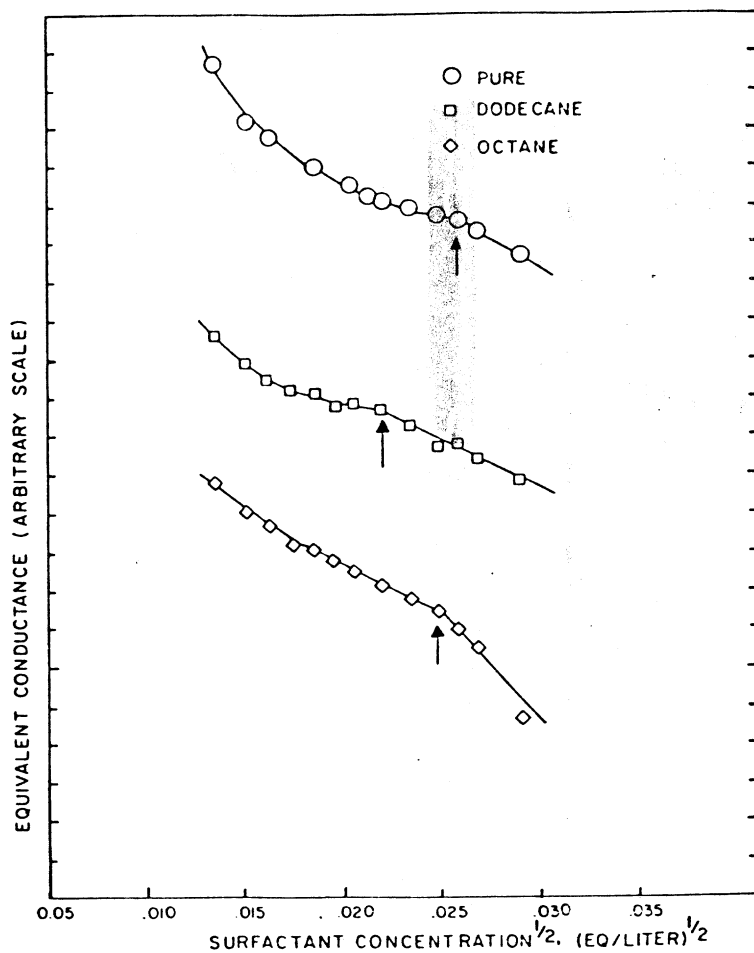


Figure 5. CMC from equivalent conductance measurements of Pentadecyl benzene sulfonate solutions before and after equilibration with octane and dodecane.

have shown that the CMC in the equilibrated aqueous phase occurs at 0.05% TRS 10-80 concentration. Therefore, we have proposed that the maximum monomer concentration in the aqueous phase at 0.05% TRS 10-80 concentration causes maximum adsorption at the oil/water interface resulting in the ultra-low interfacial tension. The maximum electrophoretic mobility of oil droplets in TRS 10-80 solutions (Figure 8) support the conclusion that the interfacial concentration of the surfactant is maximum at 0.05%. We have further shown ^{10,11} that at 0.05% TRS 10-80, the maximum amount of surfactant also partitions in the oil phase. The

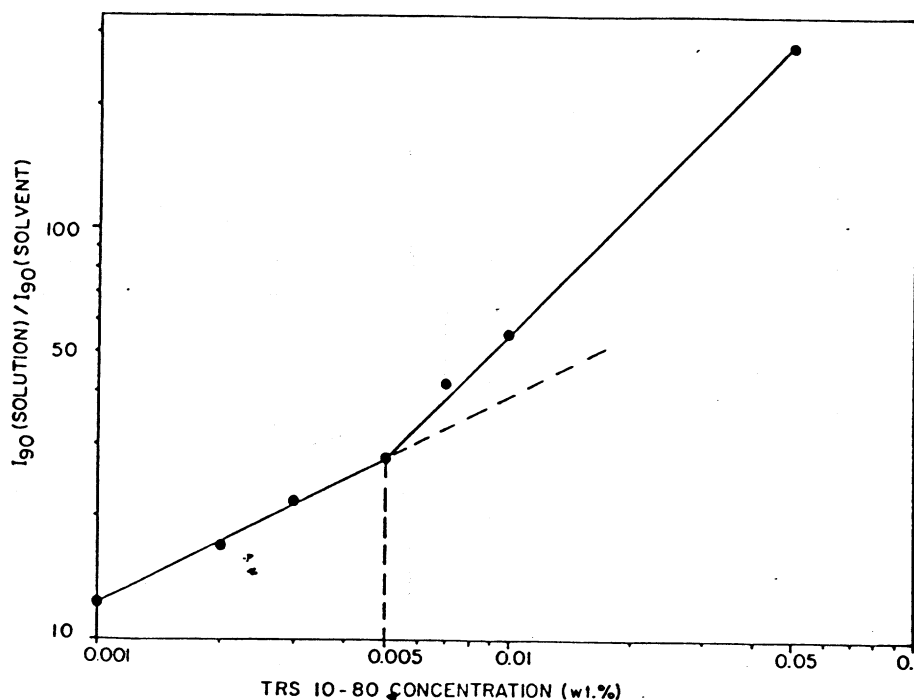


Figure 6. CMC from light scattering measurements of TRS 10-80 in 1% NaCl solutions, 25°C.

minimum in interfacial tension coincides with the CMC of the aqueous phase and the partition coefficient unity of the surfactant in oil and brine.¹²

The results given in Figures 9 and 10 support the conclusion that the CMC after equilibration with n-octane occurs at 0.05%. The question that arises is that how can we reconcile the observations that before equilibration with oil, the CMC of TRS 10-80 is 0.005% whereas after equilibration with oil it becomes 0.05%? Figure 11 shows our explanation of the increase in CMC upon equilibration with oil. It is recognized that the petroleum sulfonate TRS 10-80 consists of a distribution of equivalent weights shown by the upper curve in Figure 11. However, when oil is brought in contact with the surfactant solution, each species of the surfactant will distribute itself between oil and brine. Low equivalent weight species will remain in water, whereas high equivalent weight species will partition in oil. However, the species having intermediate equivalent weights may partition in oil and brine depending upon their HLB value. Therefore, as shown in Figure 11, the amount of surfactant in oil is proportional to the

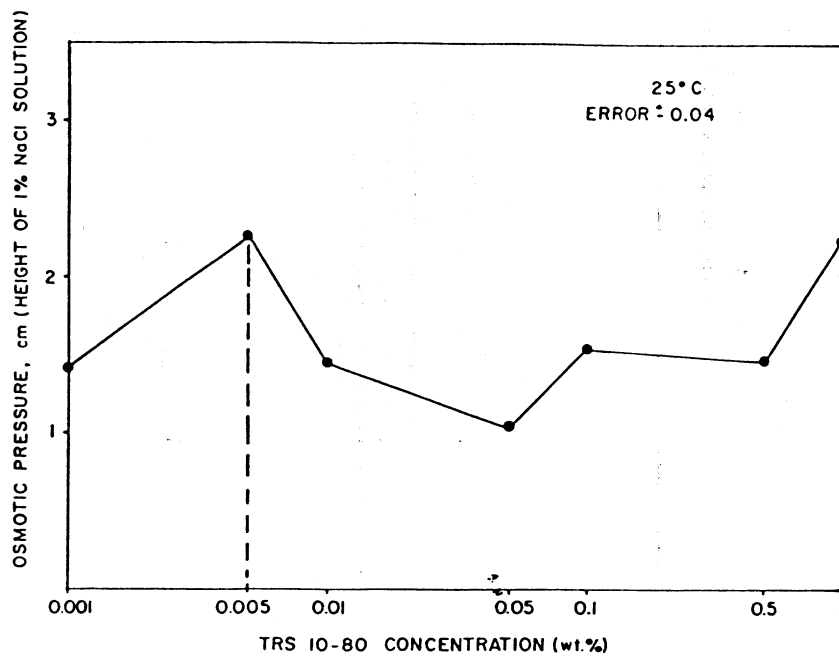


Figure 7. CMC from osmotic pressure measurements for TRS 10-80 in 1% NaCl solutions, 25°C.

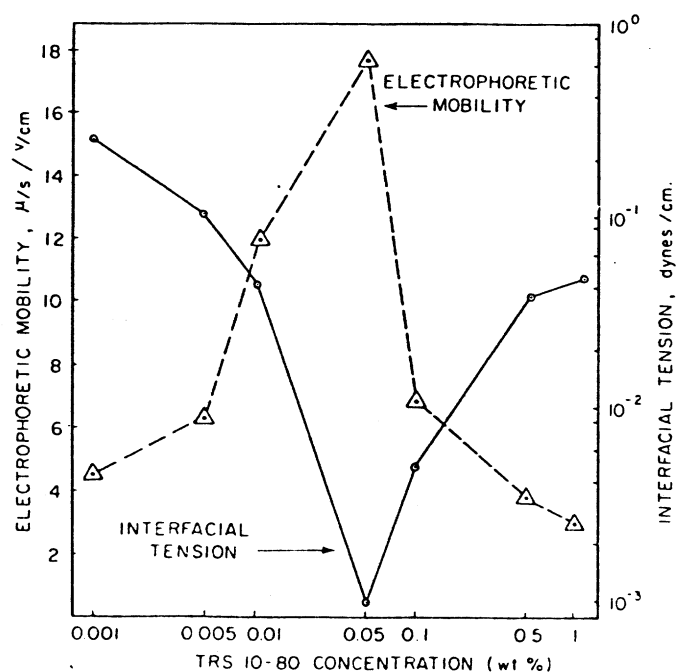


Figure 8. Interfacial tension and electrophoretic mobility of equilibrated n-octane/TRS 10-80 in 1% NaCl system, 28°C.

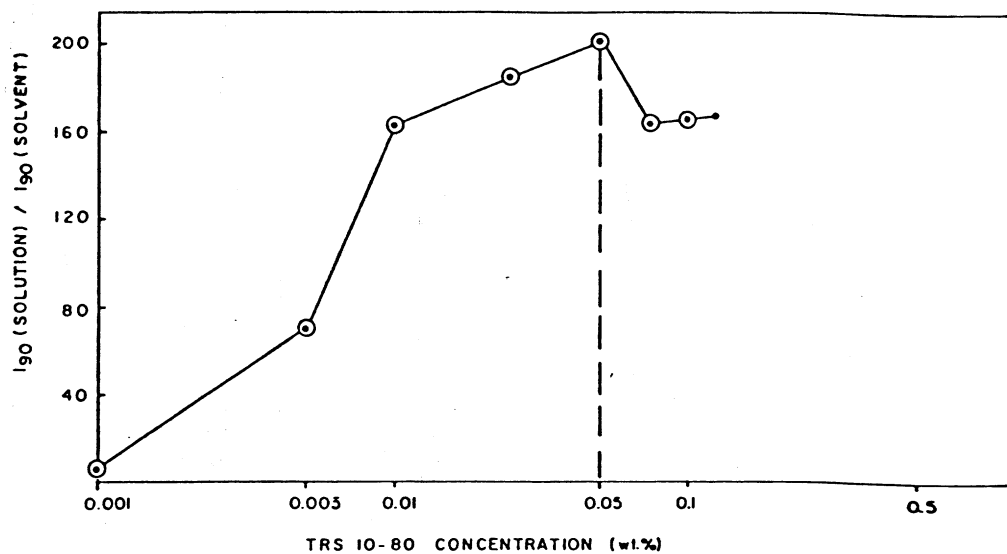


Figure 9. CMC by light scattering measurements of aqueous solutions of TRS 10-80 after equilibration with n-octane, 15°C.

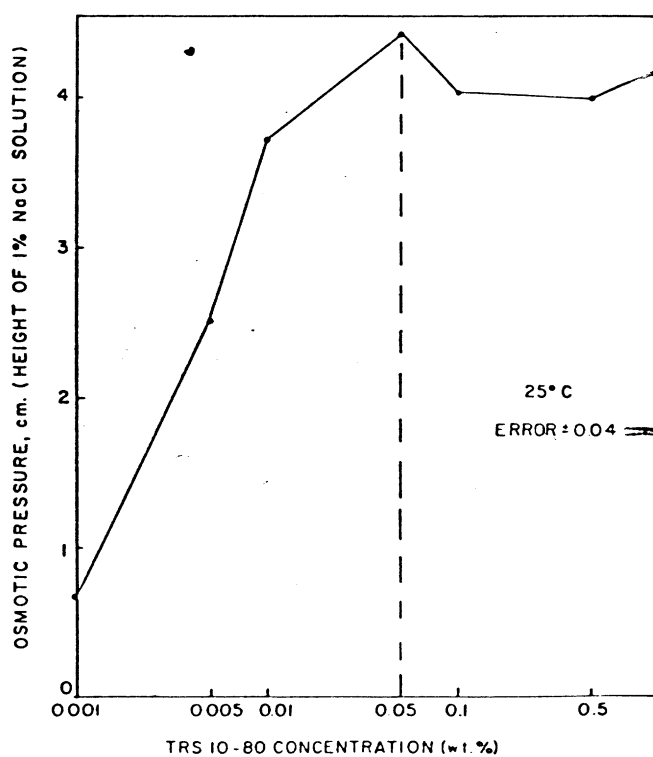


Figure 10. CMC by osmotic pressure measurements of aqueous solutions of TRS 10-80 equilibrated with n-octane, 25°C.

area of the stipled region whereas the area under the lower curve represents the amount of surfactant in the brine phase. If the two regions consist of about equal area, then the partition coefficient of the surfactant will be near unity. However, it is very clear from Figure 11 that the average equivalent weight of the species remaining in brine will be less than the average equivalent weight of the original surfactant because only preferentially water soluble species have remained in the brine phase. In other words, one cannot and should not equate the CMC of a petroleum sulfonate before and after equilibration with oil, because in both cases we are dealing with different surfactant species. Figure 11 also illustrates the phenomena of fractionation and partitioning. We consider a major separation of oil soluble and brine soluble species as fractionation (shown by vertical broken line), whereas the species partitioning into both oil and brine phase as a partitioning phenomenon as shown in region B of Figure 11.

Figure 12 shows schematically the six variables related to surfactant formulations and their interfacial tension behavior. These variables determine partition coefficient as well as the effective CMC of the surfactant. These two determine three parameters, namely, surface concentration of surfactant, surface

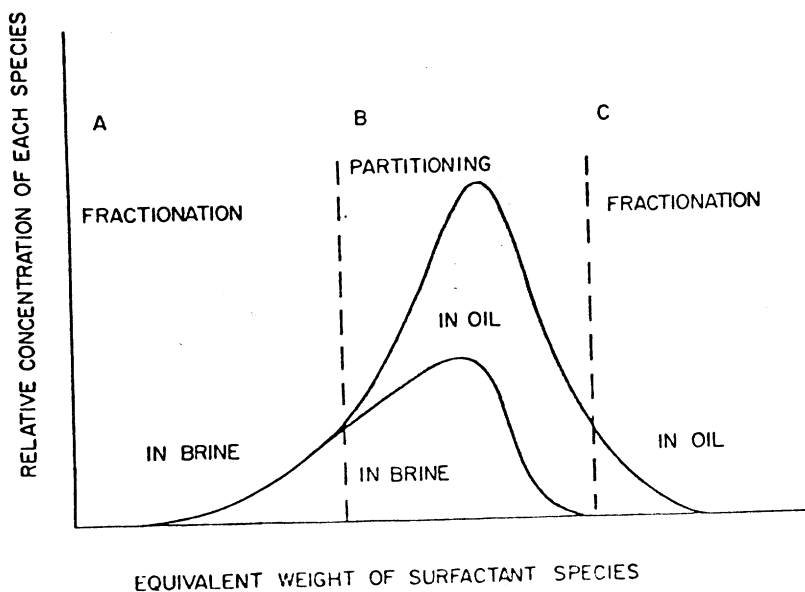


Figure 11. A schematic presentation of the distribution of surfactant species of different equivalent weights in oil and brine upon equilibration. The areas under stipled and clear regions are proportional to the relative amounts of surfactant in oil and brine.

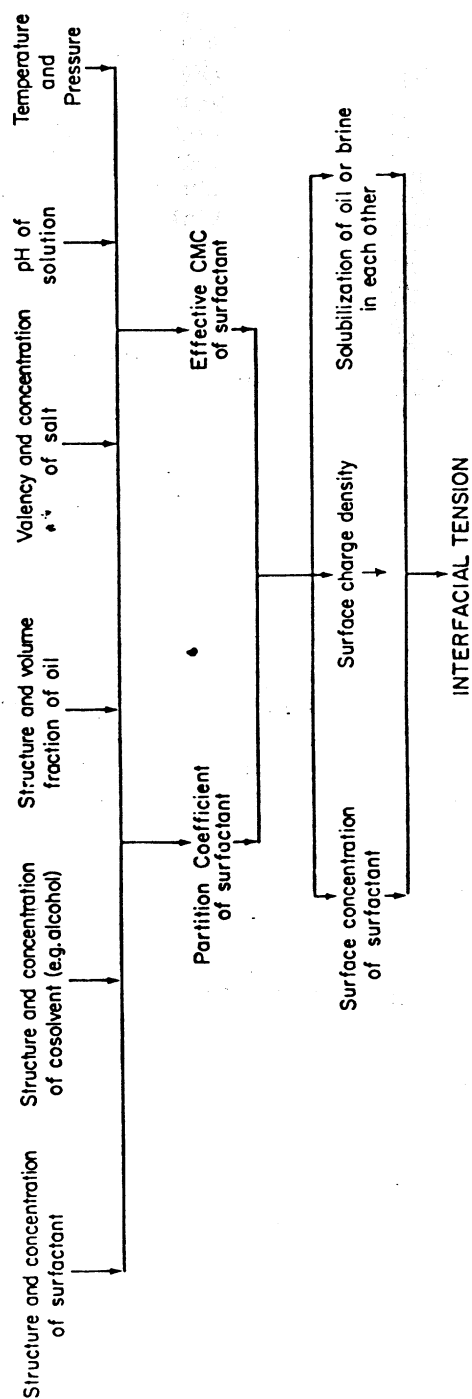


Figure 12. A schematic presentation of the effect of several variables on the interfacial tension and related phenomena and parameters.

charge density, and solubilization of oil or brine in each other. These three parameters together ultimately determine the magnitude of interfacial tension at the oil/brine interface. We have shown¹¹ that for both petroleum sulfonates and for isomerically pure synthetic sulfonates, the partition coefficient unity and CMC of the equilibrated aqueous phase coincide with the ultra-low interfacial tension.

We have also shown¹³ that a higher surface charge density leads to a lower interfacial tension. This was also observed¹⁴ for caustic solution/crude oil systems where the minimum in interfacial tension occurred in the range of NaOH concentration for which the electrophoretic mobility was very high. In other words, the maximum in electrophoretic mobility coincided with the minimum in interfacial tension. The high surface charge density also can be achieved by the maximum adsorption of sulfonate molecules (Figure 8). The interfacial charge can be influenced also by adding ethoxylated sulfonates in order to improve salt tolerance of surfactant formulations.¹⁵⁻¹⁷ Other relevant studies for micellar-polymer flooding have been reported from this laboratory previously.¹⁸⁻²⁴

In summary, the results reported in this paper lead to the following conclusions:

- 1) The addition of alcohols or oils decreases the CMC of a surfactant depending upon the chain length of alcohol or oil.
- 2) The CMC of a commercial petroleum sulfonate shifts to a higher value upon equilibration with an oil because of fractionation and partitioning phenomena.
- 3) The surface concentration of surfactant, surface charge density and the solubilization of oil or brine in each other appear to influence the magnitude of the interfacial tension.

ACKNOWLEDGMENT

This research has been supported in part by the Department of Energy Grant No. EY-27-S-05-3341 and by a consortium of twenty major oil and chemical companies at the University of Florida. The authors also wish to extend their thanks to Dr. V. K. Bansal for many helpful comments and suggestions.

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