

Generation of Ultralow Tensions Over a Wide EACN Range Using Pennsylvania State U. Surfactants

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Abstract

Saturated paraffinic and naphthenic hydrocarbons without aromatics have been vapor-phase oxidized to produce cyclic ethers and lesser amounts of olefins. These cyclic ethers appear to be effective cosurfactants for the preparation of slugs containing petroleum sulfonate surfactants. The cyclic-ether/olefin mixture has been reacted with SO_3 from oleum or liquid SO_3 to form sulfonates comprising a mixture of mono-, di-, and polysulfonates. The reaction products consisting of the sulfonates, unreacted oxidized products, and residual hydrocarbons have been extracted with isopropanol (IPA) to give two sulfonate fractions. The first fraction is predominantly monosulfonate with lesser quantities of disulfonates. The second fraction consists primarily of di-, tri-, and polysulfonates.

The monosulfonate fraction in a low-concentration slug exhibits ultralow interfacial tension (IFT) against hydrocarbons of low equivalent alkane carbon number (EACN). The behavior of this fraction is similar to that of the commercial sulfonates in that its ability to generate low IFT is confined to a narrow range of EACN. To achieve low IFT's at higher EACN in the range of a Pennsylvania crude oil, it is necessary to raise the equivalent weight of the Pennsylvania State U. monosulfonate fraction by blending with a commercial sulfonate of higher equivalent weight.

Recent studies show that by mixing the two IPA fractions of the sulfonation products, a remarkably new surfactant behavior is obtained. In contrast to the behavior of other surfactants that yield ultralow tensions over only a narrow range of values of EACN, this mixture of

mono- and polysulfonates generates low IFT's over a wide range of EACN extending from C_5 to C_{12} . The salt tolerance of monosulfonates and polysulfonates, either alone or in mixtures, is rather high, and even at about 4 wt% NaCl, the surfactant solutions remain stable and yield low IFT's against crude oil.

Introduction

Chemical flooding processes for tertiary oil recovery based on both low-concentration surfactant solutions (typically 2 to 3 wt% or less) and high-concentration surfactant solutions (about 10 wt%) are being investigated in a number of laboratory and field studies. In both types of processes, the ability of surfactant solutions to lower the IFT against crude oil is a major factor determining the oil displacement efficiency. A variety of surfactants, primarily sulfonates synthesized from aromatics present in petroleum fractions, have been identified as those possessing the physical and chemical properties required for the flooding process. The surfactant slug formulations typically consist of the sulfonates, electrolytes, and cosurfactants such as alcohols. The slug, when contacted with oil, can generate a microemulsion phase coexisting with oil and water phases. Low IFT's are found to occur at those conditions that favor the formation of the preceding three phases. Several investigations have focused on determining the conditions for the three-phase formation and IFT lowering in terms of the molecular structure and the molecular weight of the surfactant, the characteristics of the oil (namely, its EACN), salinity, surfactant concentration, and the type and amount of cosurfactant, if used.¹⁻³ Empirical cor-

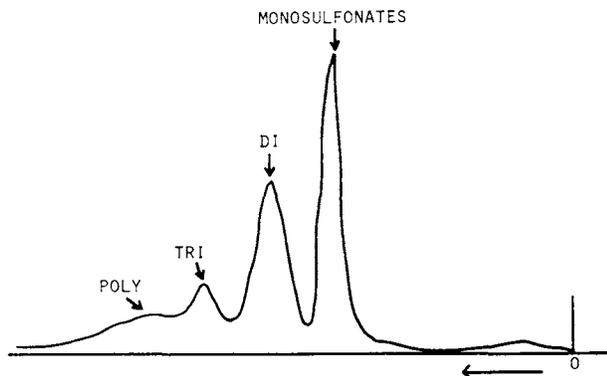


Fig. 1—HPLC separation of 85% IPA soluble sulfonates.

TABLE 1—EQUIVALENT WEIGHT OF SURFACTANTS

TRS-10B	394
TRS-16	455
TRS-10-80	422
PRL-5	414
PRL-7A	298
PRL-15	395
C-48-Mono	440
C-48-Poly	217
C-27-Mono	417
C-27-Poly	210
C-110-Mono	445
C-110-Poly	210
S-86-Mono	351
S-86-Poly	158
S-122-Mono	399
S-122-Poly	218

relations relating the value of these parameters also have been developed that lead to optimal slug properties.²

Most surfactant solutions reported in the literature give a low IFT at a given salinity and surfactant concentration over a narrow range of oil EACN. If the EACN is changed significantly, a new surfactant solution composition must be found to produce a minimal or optimal IFT. Different oil sands produce oils that differ in EACN. Even different wells in the same field may produce oil with significant differences in EACN. The purpose of this paper is to describe the preparation and use of a series of surfactants and cosurfactants that tend to produce slugs with low IFT's over a wide range of EACN values, in marked contrast to the behavior exhibited by most petroleum sulfonates.

Surfactant Synthesis, Separation, and Characterization

Paraffinic and naphthenic hydrocarbons are used to produce the sulfonates by employing a two-step procedure involving vapor-phase oxidation of the hydrocarbon followed by the sulfonation of the oxidized product. The major products of the oxidation are cyclic ethers mixed with various proportions of olefins. The liquid oxygenated products are sulfonated with either a semibatch or a continuous reactor, with SO_3 from oleum or liquid SO_3 as the sulfonating agent. Detailed descriptions of the vapor-phase oxidation and the sulfonation processes are given elsewhere.⁴⁻⁶

The sulfonated products consist of two layers: an oil layer and a viscous layer consisting of the acid products. Both layers are dissolved in a 40% IPA/water solution. The acid product containing sulfonic and sulfuric acids is neutralized by the addition of aqueous NaOH solution. The neutralized product is cooled slowly and is allowed to stand overnight in an ice bath. Crystals of Na_2SO_4 that deposit are filtered out. The solution then is extracted with n-hexane four or five times. The hexane layer consists mainly of unreacted oil and small amounts of oil-soluble sulfonates. The IPA layer containing most of the sulfonates and some inorganic salt is evaporated to remove the solvent. The dry product again is extracted with an 85% IPA/water solution. The resulting system consists of a portion dissolved in 85% IPA. Both the soluble and insoluble portions are evaporated to remove

the solvent and to recover dry sulfonates denoted "monosulfonates" and "polysulfonates."

The average equivalent weight, oil content, amount of inorganic salts, and residual water content of these sulfonates are determined by procedures described in Ref. 6. The 85% IPA soluble portions of the sulfonate has a relatively high equivalent weight consistent with the presence of predominantly monosulfonates. The inclusion of some di-, tri-, and polysulfonates is responsible for the difference between the experimentally determined average equivalent weight and the expected equivalent weight. The expected equivalent weight of the sulfonate is estimated from the average molecular weight of the oxidized hydrocarbon, assuming that only monosulfonates are formed. Fig. 1 shows the compositional distribution of a typical 85% IPA soluble portion of the sulfonate, obtained from an analysis involving high-pressure liquid chromatography (HPLC). Note that in addition to the predominantly monosulfonate fraction, small quantities of di-, tri-, and polysulfonates are also present, thus confirming the origin of the less-than-anticipated average equivalent weight of the soluble sulfonate. The 85% IPA insoluble sulfonate consists predominantly of di-, tri-, and polysulfonates and also a considerable amount of inorganic salt resulting from the earlier neutralization step. Consequently, the average equivalent weights obtained for the insoluble sulfonates are substantially lower than those of the soluble sulfonates. The average equivalent weight data for the sulfonates discussed in this paper are summarized in Table 1.

In addition to mono-, di-, and polysulfonates, the products of the sulfonation reaction include some organic sulfates. From the procedure described in Ref. 7, the organic sulfate content in the reaction products was determined. The procedure involves acid hydrolysis of the sulfonates and sulfates in the presence of hydrochloric acid. Whereas the sulfates are hydrolyzed completely to form alcohols, the sulfonates undergo no change during the hydrolysis step. A two-phase titration method was used to determine the total sulfonates and sulfates before the hydrolysis step and the total sulfonates after the hydrolysis. From the difference between the preceding two titre values, the organic sulfate content in the reaction products was estimated. For the

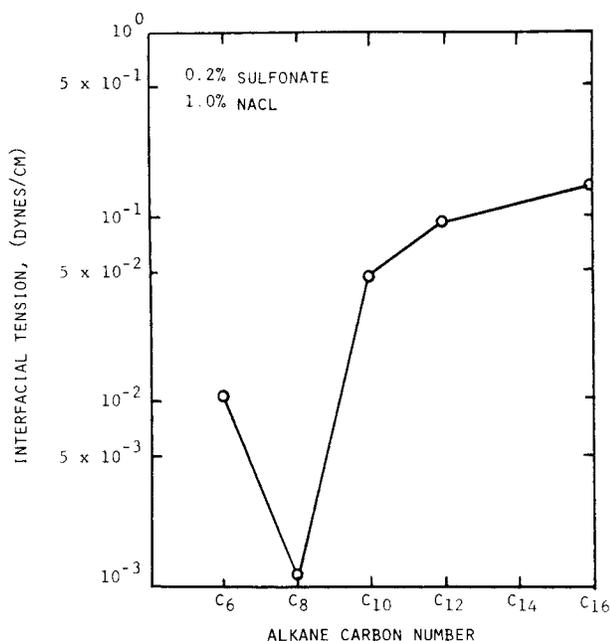


Fig. 2—Alkane scan for TRS 10-80.

different sulfonate samples discussed in this paper, the organic sulfate content was found to be relatively small, confirming that the predominant products of the sulfonation reaction were organic sulfonates and not organic sulfates.

IFT Characteristics of Surfactant Systems

The systems compared in this study include seven low-concentration surfactant solutions: (1) commercial aromatic petroleum sulfonates, (2) commercial aromatic petroleum sulfonates plus our monosulfonates, (3) commercial aromatic petroleum sulfonates plus our mono- and polysulfonates, (4) commercial aromatic petroleum sulfonates plus our mono- and polysulfonates and cyclic ethers, (5) our monosulfonates, (6) our mono- and polysulfonates, and (7) our mono- and polysulfonates with cyclic ethers.

All IFT measurements and phase behavior studies were conducted at room temperature. The procedure involved pre-equilibrating the aqueous surfactant solution and oil, with the water-to-oil ratio maintained at unity. In most cases, the IFT between excess oil and excess water phases (σ_{ow}) was measured. For a few systems, the IFT's between excess oil and microemulsion (σ_{om}), excess water and microemulsion (σ_{wm}), and excess oil and excess water (σ_{ow}) were measured. Further, the amounts of oil and water solubilized in the middle-phase microemulsion also were determined.

Fig. 2 shows the typical IFT behavior of a commercial aromatic petroleum sulfonate against various hydrocarbons.⁸ The data are for Witco TRS-10-80 surfactant. Low IFT's (less than 10^{-2} dyne/cm) were found to occur in a relatively narrow range of alkane carbon

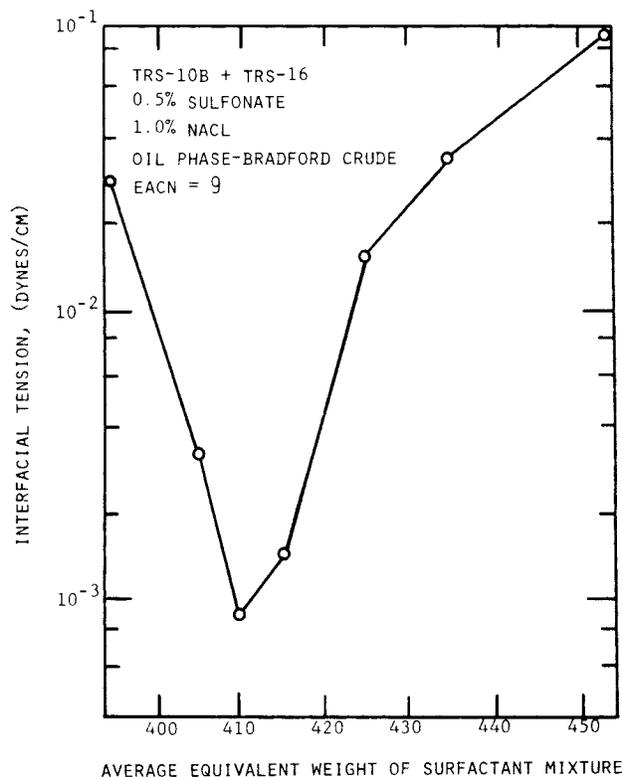


Fig. 3—IFT against oil vs. equivalent weight of the TRS-10B/TRS-16 mixture.

numbers, from C₆ to C₉. In Fig. 3, the IFT against crude oil is presented as a function of the sulfonate equivalent weight for mixtures of Witco's TRS-10B and TRS-16. The equivalent weight range over which the system exhibits low IFT's is found to be rather narrow. Fig. 4 shows the influence of salinity on the IFT's generated by the TRS-10B/TRS-16 mixture of average equivalent weight 410. The ultralow tensions occur only for a small region of salt concentrations, and the sulfonate is salted out as the concentration of salt is increased further. The data presented in Figs. 2 through 4 are typical of conventional aromatic sulfonates, commonly available.

Mixtures of our paraffinic sulfonates and conventional aromatic petroleum sulfonates have been used to obtain the data in Figs. 5 and 6. The two Pennsylvania State U. sulfonates chosen for these blends are PRL 15 and PRL 7A. Neither of these sulfonates was subjected to the isopropanol extraction step that separated the mono- from the polysulfonates. The equivalent weight of 395 determined for PRL 15 indicates that it is primarily a monosulfonate, whereas the low equivalent weight of 298 for PRL 7A suggests that it contains a significant amount of polysulfonates. Fig. 5 shows the relationship between the average equivalent weight of the sulfonate mixtures and the IFT against crude oil. The data in Fig. 6 show the dependence of IFT on oil EACN for a given surfactant mixture.

The data in Figs. 5 and 6 indicate that a mixture of our monosulfonate (PRL 15) with conventional aromatic sulfonates produces an IFT vs. equivalent weight relationship comparable to the mixture of two conventional aromatic sulfonates shown in Fig. 3. On the other hand,

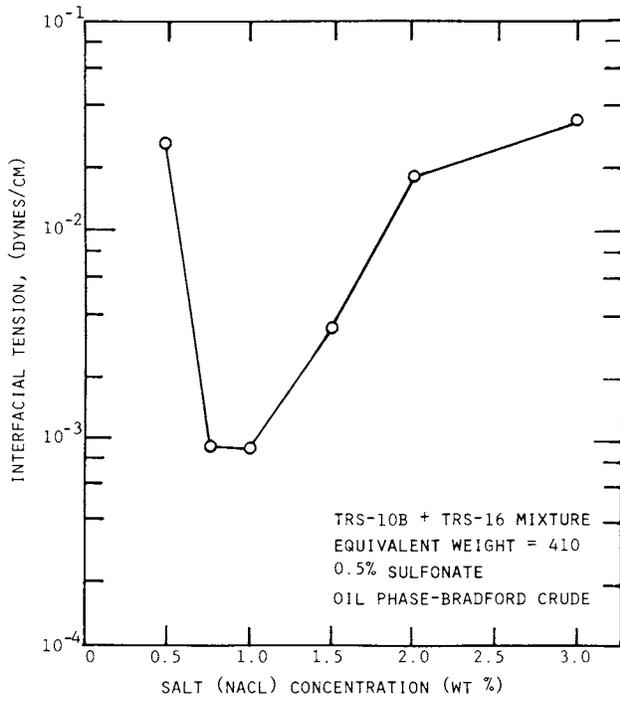


Fig. 4—IFT against oil vs. salinity for TRS-10B/TRS-16 mixture.

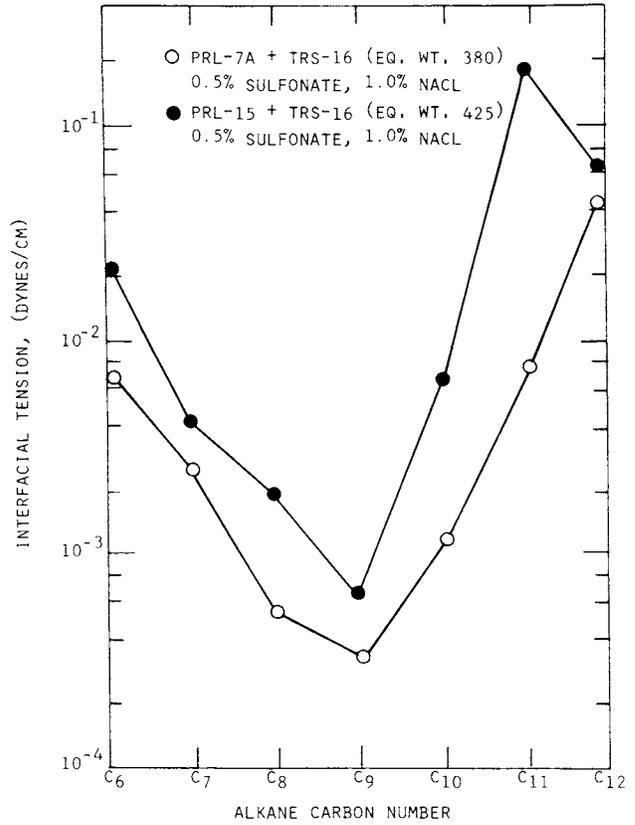


Fig. 6—Alkane scans for PRL 15/TRS-16 and PRL7A/TRS-16 mixtures at their optimal equivalent weights.

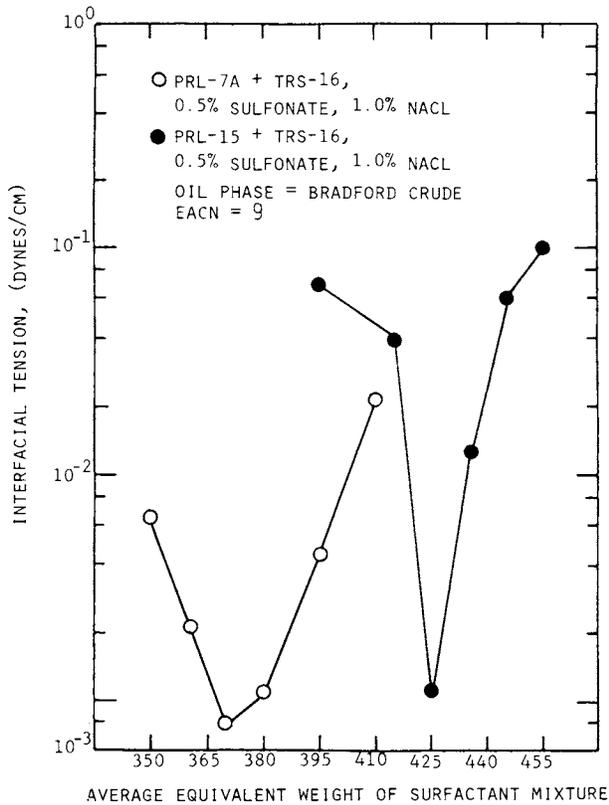


Fig. 5—IFT against oil vs. equivalent weight for PRL 7A/TRS-16 and PRL 15/TRS-16 mixtures.

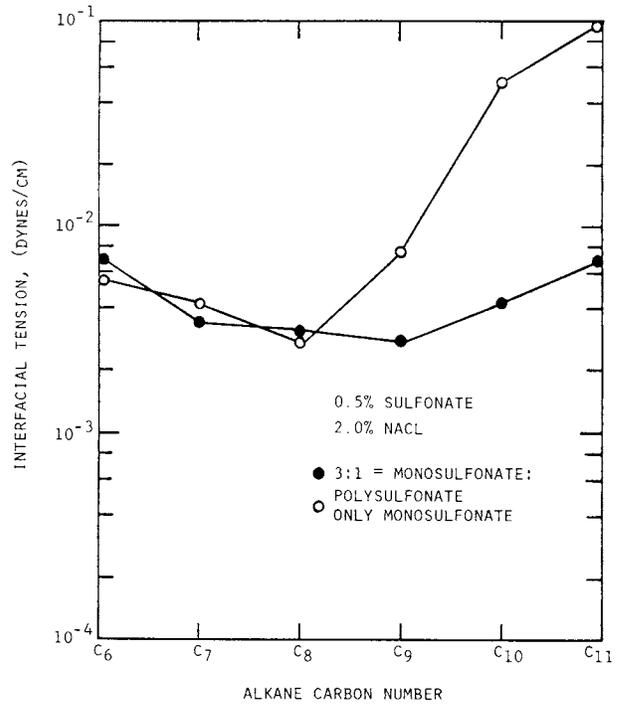


Fig. 7—Alkane scan for C-48 sulfonates.

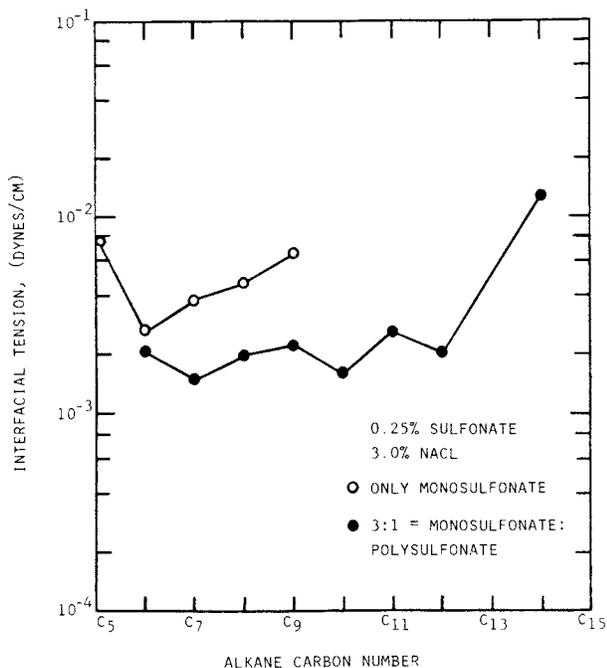


Fig. 8—Alkane scan for C-110 sulfonates.

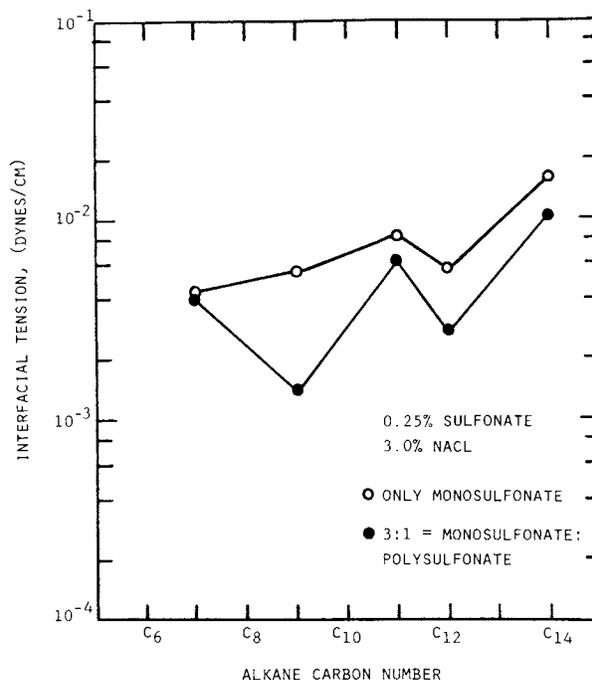


Fig. 9—Alkane scan for C-27 sulfonates.

the mixed sulfonates containing PRL 7A exhibit ultralow IFT at a much lower average equivalent weight (Fig. 5) and over a broader range of average equivalent weights. Fig. 6 shows that the PRL 7A/TRS-16 mixture (equivalent weight 380) generates tensions of less than 10^{-2} dyne/cm over a somewhat wider range of EACN, from C_6 to C_{11} , compared with the PRL 15/TRS-16 mixture. Note that the principal difference between PRL 15 and PRL 7A is a higher concentration of polysulfonates in the PRL 7A sulfonate.

Previously published data⁹⁻¹¹ for mixtures of our sulfonates with Witco's aromatic sulfonates have shown good blending characteristics. The relatively low optimal equivalent weight (required to achieve a minimum IFT against a given EACN oil for one of our sulfonates) compared with a typical aromatic sulfonate appears to be directly related to the beneficial role of the presence of some polysulfonates in our sulfonate.

The earlier data on our sulfonates were obtained on reaction products that had not been separated into component fractions. The ability to separate the sulfonation reaction products into monosulfonates, polysulfonates, oxygenated compounds, and unreacted hydrocarbons makes it possible to evaluate the various component fractions either alone or in predetermined mixtures. A comparison of the monosulfonates alone and a 3:1 by weight blend of mono- and polysulfonates from three of our sulfonates is shown in Figs. 7, 8, and 9. In all three cases, the PRL monosulfonates show a low IFT over a wider EACN range ($\Delta EACN=3$ to 4) than that shown by conventional aromatic sulfonates ($\Delta EACN=1$ to 2). More interestingly, in all cases the addition of polysulfonates to the monosulfonates results in a lower-equivalent-weight surfactant that generates ultralow IFT over a wider range of oil EACN ($\Delta EACN=4$ to 6). The monosulfonates show a decrease in IFT with the addition

of polysulfonates (Fig. 10), and a 3:1 ratio of mono- to polysulfonates yields the lowest tension. The preparation of the sulfonates is versatile enough to allow for product mixtures approximating the 3:1 ratio of monosulfonates/polysulfonates. This can be done by controlling the reaction temperatures and SO_3 input rates. Another interesting property for the PRL sulfonates is shown in Fig. 11. These data show that, for the monosulfonates and the blend of 3:1 mono- to polysulfonates, the IFT continues to decrease with salt concentrations up to at least 4% NaCl. Even at this high salt concentration, the surfactant solutions are found to remain stable. One may observe that to achieve low values of IFT upon the addition of electrolytes, a larger concentration of Na_2CO_3 is required compared with that of NaCl.

Some results from the phase behavior studies are presented in Figs. 12 and 13. Fig. 12 shows the phase uptake ratio (defined as the volume of oil or water solubilized per unit volume of surfactant in the microemulsion) and the IFT between excess oil and the excess water (σ_{ow}) as a function of electrolyte concentration. The optimal salt concentration obtained by use of either the minimization of IFT or the maximization of solubilization parameters as the criterion is found to be the same in conformity with similar measurements reported in the literature. One remarkable characteristic of our sulfonates is the formation of middle-phase microemulsions over a wide range of salt concentration, consistent with their IFT behavior. In Fig. 13 the IFT and the phase uptake ratio are shown for a system containing a higher concentration of surfactant. Since the volume of the middle-phase microemulsion generated is large in this case, the IFT's at the two interfaces, namely microemulsion/excess water (σ_{mw}) and microemulsion/excess oil (σ_{mo}), are measured easily in addition to σ_{ow} . The optimal salt concentration where σ_{mw} is equal

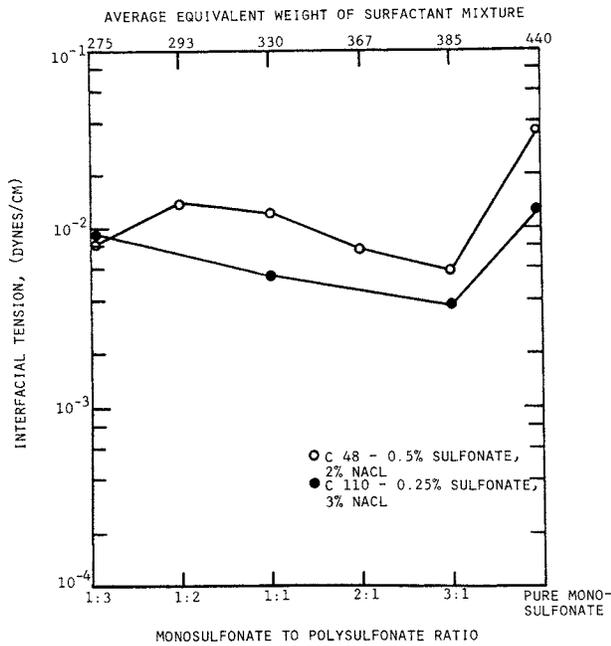


Fig. 10—IFT against oil vs. equivalent weight of mixtures of mono- and polysulfonates.

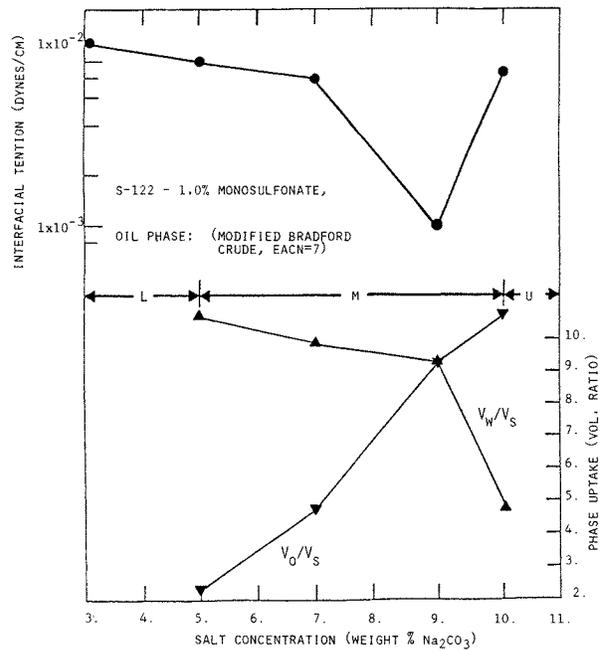


Fig. 12—IFT and solubilization parameters vs. salinity for S-122 sulfonate.

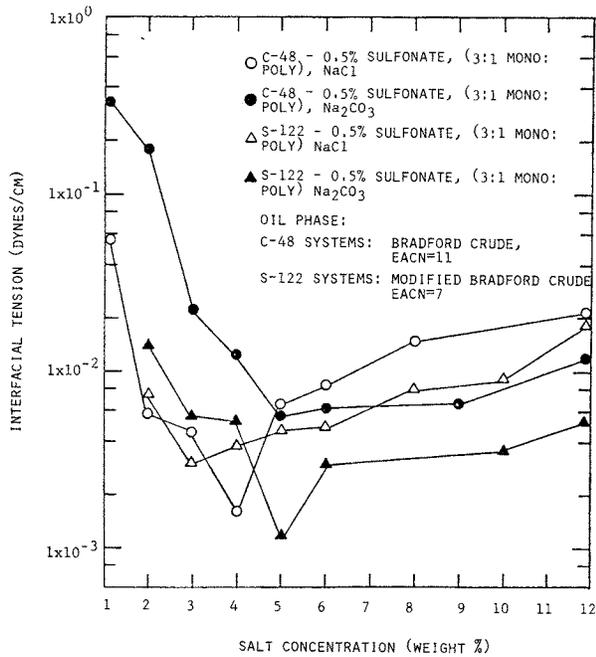


Fig. 11—IFT vs. salt concentration for C-48 and S-122 sulfonates.

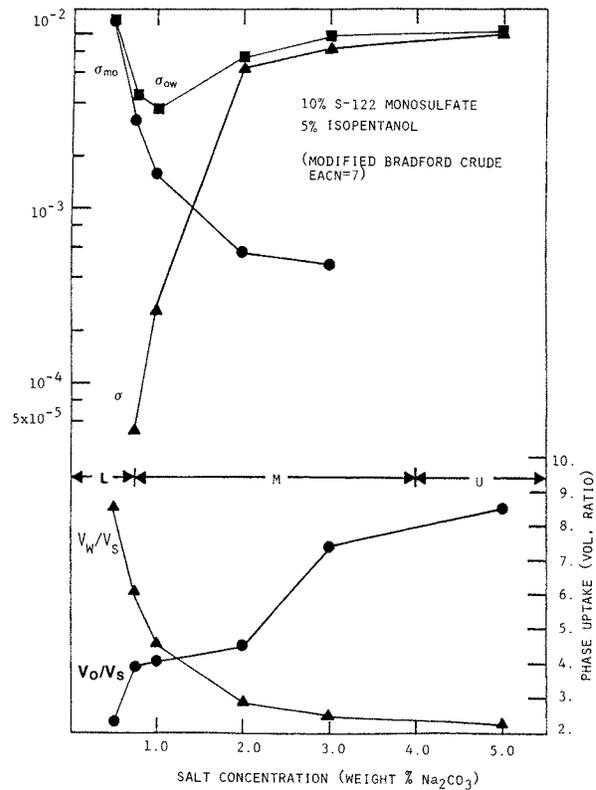


Fig. 13—IFT and solubilization parameters vs. salinity for S-122 sulfonate.

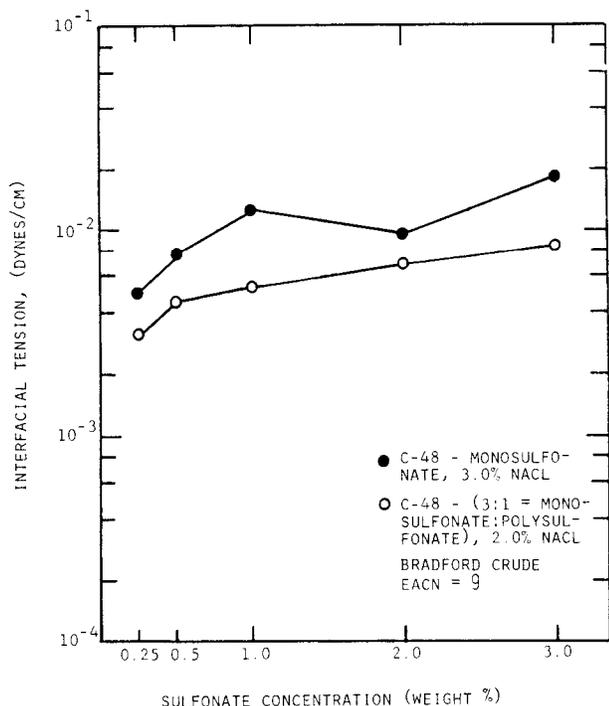


Fig. 14—IFT against oil vs. sulfonate concentration for C-48 sulfonates.

to σ_{mo} is practically the same as the optimal salt concentration where solubilization parameters of oil and water are equal. This salt concentration also corresponds to a minimum in σ_{ow} . Fig. 14 presents the IFT data as a function of the sulfonate concentration. For the range of values examined from 0.25 to 3.0 wt%, there is no essential alteration in the low IFT's generated against oil.

Data have been presented¹⁰ to show the effect of the addition of cyclic ether oxidation products as cosurfactants in PRL sulfonates. Some trends noted with these mixtures are shown in Fig. 15. These data show the effects of increasing the concentration of cyclic ethers from 10 to 25% of the PRL 15 sulfonate, which is predominantly a monosulfonate. The use of cyclic ether cosurfactants can decrease the IFT values and increase the EACN range over which IFT's of less than 10^{-2} dyne/cm are observed.

Early in the PRL surfactant preparation studies, PRL 5A sulfonate was prepared and used without being subjected to separation of any components.⁹ It has been established that PRL 5A contained a mixture of monosulfonates, polysulfonates, and cyclic ethers. The concentrations of the polysulfonates and the cyclic ethers each may represent as much as 25% of the total surfactant. For this system, the IFT data⁹ as a function of alkane carbon number are shown in Fig. 16.⁹ At concentrations of 0.08 and 0.27 wt% sulfonate, the IFT values of less than 0.01 dyne/cm are obtained over an EACN range of 6 to 15. On the basis of our current studies in which all the components of the sulfonation products have been separated and individually evaluated, the low IFT's of PRL 5A over this wide EACN range could be attributed to the presence of both polysulfonates and

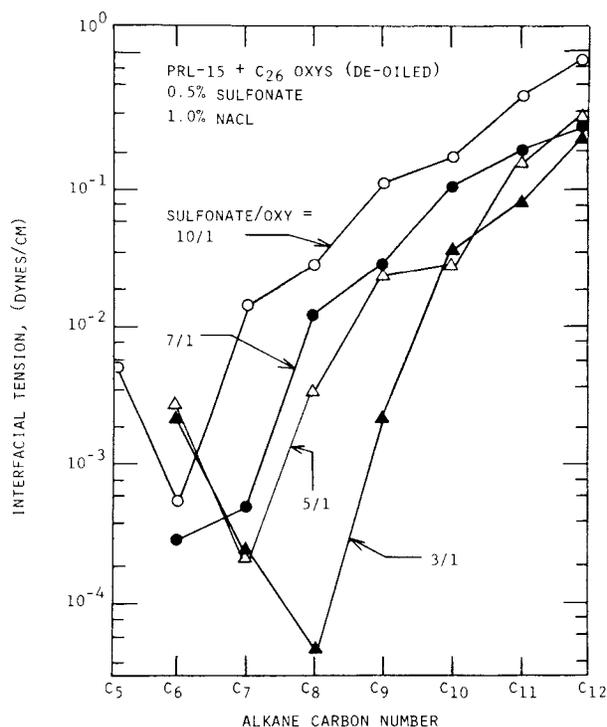


Fig. 15—Effect of sulfonate to C_{26} oxy ratio on the IFT behavior of PRL-15 sulfonates.

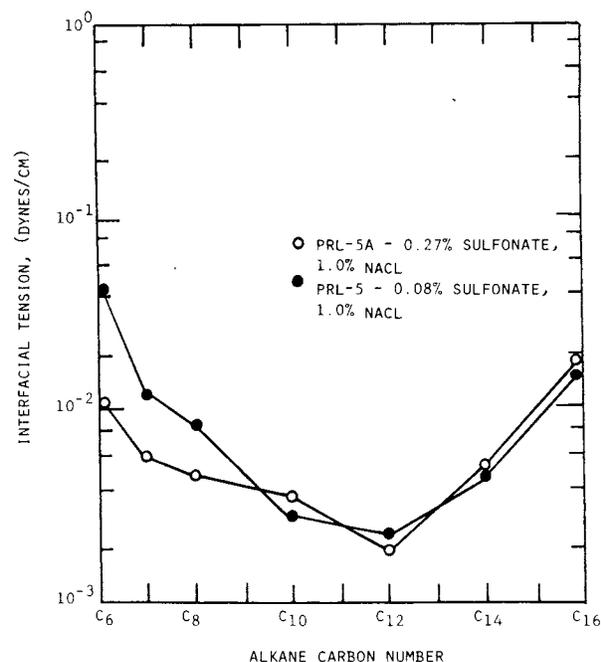


Fig. 16—Alkane scans for PRL-5 and PRL-5A sulfonates.

cyclic ethers. The presence of a significant amount of unreacted oil in this PRL 5A surfactant did not appear to play any role in the behavior of the mixture.

The data presented here tend to show a different type and level of effectiveness associated with the PRL surfactants. The surfactants reported in this study were made in vapor-phase oxidation reactions and subsequent sulfonations that were not optimized with respect to either of the reaction steps. The variations accompanying improvements in both oxidation and sulfonation reactors and the reaction products do not appear to affect the trends noted in this paper. There is no indication that using optimal oxidation conditions and then tailoring the sulfonation to an optimal product will change the unique properties of the PRL surfactants and cosurfactants.

In several cases, long core tests have been conducted with some of the types of surfactant solutions discussed here. The core test program thus far has covered only a fraction of the systems described in this paper. Where core test data are available, there appears to be a general trendwise agreement between low IFT's and effective enhanced oil recovery.⁴ These core test data continue to show encouraging results with the PRL surfactant and PRL surfactant/conventional sulfonate mixed systems.

Conclusions

Three types of ingredients for surfactant slugs have been prepared from saturated hydrocarbons by use of vapor-phase oxidation followed by sulfonation. The three ingredients include: (1) oxidized hydrocarbons in the form of cyclic ethers, (2) predominantly monosulfonates from the sulfonation of these cyclic ethers, and (3) polysulfonates from multiple sulfonation of the cyclic ethers. The cyclic ethers can be separated from the vapor-phase-oxidized product by a methanol extraction procedure, while the two sulfonate fractions can be separated from the sulfonation product by isopropyl alcohol extractions.

The PRL monosulfonates show surfactant behavior very similar to that of the conventional aromatic sulfonates. The PRL monosulfonates can be blended with or substituted for conventional aromatic sulfonates to produce low IFT's between brine and oil. The use of PRL polysulfonates with either conventional aromatic sulfonates or PRL monosulfonates appears to enhance the lowering of brine/oil IFT. More significant is the observation that the use of PRL polysulfonates gives low IFT's over a very wide range of oil EACN values. In addition, for the same or lower average equivalent weights, these mixed surfactants provide low IFT's against oils of higher EACN.

The use of cyclic ethers as a cosurfactant with conventional sulfonates, PRL monosulfonates, or mixed sulfonates appears to enhance the mixture by producing lower IFT's that generally extend to higher values of EACN. The combinations of PRL mono- and polysulfonates with cyclic ethers appear to provide a unique surfactant system that will tolerate high salt concentrations and will provide low IFT's over a wide range of EACN.

The three PRL surfactants discussed in this paper can be generated from the desired fraction of any crude oil as produced by a combination of simple energy-efficient reactors.

Nomenclature

- L = lower phase microemulsion
 M = middle phase microemulsion
 U = upper phase microemulsion
 V_o = volume of oil in middle phase microemulsion (cm^3)
 V_s = volume of surfactant in middle phase microemulsion (cm^3)
 V_w = volume of water in middle phase microemulsion (cm^3)
 σ_{mo} = IFT between microemulsion and excess oil, dyne/cm (mN/m)
 σ_{mw} = IFT between microemulsion and excess water, dyne/cm (mN/m)
 σ_{ow} = IFT between excess oil and excess water, dyne/cm (mN/m)

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SI Metric Conversion Factor

$$\text{dyne} \times 1.0^* \quad \text{E}-02 = \text{mN}$$

*Conversion factor is exact.

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