Surfactants for Producing Low Interfacial Tensions I: Linear Alkyl Benzene Sulfonates

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ABSTRACT AND SUMMARY

The synthesis of a variety of linear alkylbenzenesulfonates is described. These materials have been examined for their ability to promote very low interfacial tensions between alkanes, alkylbenzenes, or alkylcyclohexanes and water. Each surfactant gives its lowest tension against a particular member of each of these homologous series. For these surfactant structures, the magnitude of this minimum tension is determined by the oil phase equivalent alkane carbon number (EACN) and structure and is largely independent of the particular surfactant used. The position of the minimum tension within the alkane series varies in a systematic and predictable manner. The significance of these results for tertiary oil recovery by surfactant flooding is discussed.

INTRODUCTION

The existence of surfactant systems which promote very low interfacial tensions is now a well established phenomenon. There is currently much interest in such systems because of their potential usefulness in tertiary oil recovery processes (1,2). For this reason, the earliest studies involved complex commercial surfactants and crude oils or ill-defined hydrocarbon mixtures (3-6).

In previous work at the University of Texas, surfactants have been characterized by measuring interfacial tensions against all or part of the homologous series of liquid alkanes (7-10). The behavior of both monoisomeric (10) and commercial (7-9) surfactants is similar. Either no very low tension is observed, or a curve is produced showing a minimum tension for one particular alkane carbon number. This carbon number for minimum tension, given the symbol n_{min}, is a function of many variables such as electrolyte concentration, cosurfactant concentration, and temperature (11). However, since n_{min} shifts in the same direction for all surfactants as one of these variables changes, surfactants fall into the same order of n_{min} values under one set of conditions as under another.

In many cases, those surfactants which do not show a minimum in their alkane scan can be regarded as having an n_{min} value which lies outside the liquid alkane range. Often, a minimum position can be estimated, although it is "off scale," by using an extrapolation technique involving mixtures with a commercial surfactant (12).

This concept of a carbon number for minimum interfacial tension can be extended to oils other than n-alkanes. It has been shown that an equivalent alkane carbon number (EACN) can be determined for any pure hydrocarbon (8,9), for any mixture of hydrocarbons (8,9), or even for a crude oil (9). The EACN of an oil is the carbon number of the alkane which most closely models its interfacial tension behavior. It is an invariant property of the oil and is not affected by the variables which change n_{min}, at least not by those which have been examined (11).

The lowest tension for any chosen oil-surfactant pair is obtained when n_{min} is adjusted to match the EACN of the oil. What this means is that, to obtain the lowest tension possible with a given surfactant against an oil whose EACN is known to be, say 7, the system variables should be adjusted so that the minimum in the surfactant's alkane scan occurs at heptane.

The EACN/n_{min} concept is an extremely useful way of characterizing the low tension behavior of oils and surfactants, but it is obviously not the whole answer to the problem of devising surfactant systems for tertiary oil recovery. The question here is more one of what surfactant will work best with a given oil, rather than how to get the best performance from a given surfactant.

In order to tackle this problem in a clear-cut and systematic way, it is necessary to work with surfactants whose structures are accurately defined, a criterion which even the cleanest of commercial products do not satisfy. We have therefore made our own surfactants, those reported on in this series of papers being alkylbenzenesulfonates of various structures. These are materials of the same basic structure as the sulfonates used in commercial low tension applications, but the hydrocarbons from which the sulfonates are made and, in many cases, the finished surfactants are monoisomeric.

This paper deals specifically with the low tension behavior of linear alkylbenzenesulfonates. A preliminary report on some of these surfactants has already been given (10). Here, their synthesis is described and the discussion of their properties is amplified, revealing some new phenomena which are of considerable significance for deciding whether a surfactant looks promising in oil recovery applications.

MATERIALS AND EXPERIMENTAL

The general synthesis scheme for the linear alkylbenzenesulfonates is shown in Figure 1. In a "linear" alkylbenzene, the groups R and R′ in Figure 1 are both n-alkyl chains. Alkylbenzenes containing C_{11} to C_{18} n-alkyl chains with an internally substituted phenyl group were prepared and sulfonated according to the following sequence of reactions.

Tertiary Carbinols (Phenyl Hydroxy Alkanes)

An ether solution containing 0.4 mole of the appropriate alkyl phenyl ketone, I, was added to an equimolecular amount of the appropriate alkyl magnesium bromide, II. The resulting Grignard addition complex was decomposed using ice-cooled dilute hydrocholoric acid. This produced an ether solution of the tertiary carbinol, III, which was washed with aqueous alkali and dried over anhydrous potassium carbonate. These phenyl hydroxy alkanes were distilled under reduced pressure. Some physical properties are included in Table I.

Phenylalkanes

Two techniques have been used to prepare phenylalkanes from the corresponding tertiary alcohols. For the 2, 4, 6, 7, and 8 phenylhexadecanes (10), ca. 0.2 mole (64 g) of the alcohol was dehydrated using 10 g of anhydrous cupric sulfate at 175-180 C for 2 hr. The crude olefin mixture was dissolved in n-pentane and passed through a 1 ft by 1 in. ID column containing 60-200 mesh anhydrous activated silica gel. The pentane was evaporated and the olefin mixture distilled under reduced pressure (0.1 mm Hg). Fifty g (ca. 0.2 mole) of the olefin mixture was hydrogenated for 24 hr using 40 psi pressure of H_2 and 5 g of a catalyst consisting of palladium (5%) on a charcoal support (95%) in ethanol solution. The catalyst was removed by filtration and the ethanol evaporated under reduced pressure. The hydrogenated product was purified by dissolving in n-pentane and passing through a silica gel column (see above). The pentane was evaporated, and the phenylalkane which remained (IV) was distilled under reduced pressure.

The remaining phenylalkanes were prepared by direct reduction of the tertiary carbinol (50 g) over 5 g of the Pd/C catalyst in a mixture of glacial acetic acid (150 ml) and 70% perchloric acid (2 ml). This hydrogenation was carried out for 24 hr at 60 psi H_2 pressure. The catalyst was filtered off and washed with n-pentane. The filtrate was decomposed using an ice/water mixture and the pentane extract processed as in the previous paragraph.

Some physical properties of the various phenylalkanes are included in Table I.

Phenylalkane Sulfonates

The 1, 2, 3, and 4 phenylhexadecanes, which form crystalline sulfonates, were sulfonated as follows. Fifteen g (ca. 0.05 mole) of the hydrocarbon was reacted with 25 ml of fuming sulphuric acid (containing 20% SO_3) at 70-80 C for 3 hr. The crude sulfonation product was neutralized with 400 ml of 5% sodium hydroxide solution. The solid precipitate was filtered off and washed repeatedly with 25 ml portions of ice-cooled distilled water. Repeated crystallization from aqueous isopropanol yielded white needles of the pure sodium sulfonates (VI), which were dried in a vacuum oven at 80 C.

The remaining phenylalkanes, which form more water soluble and only semi-crystalline sulfonates, were sulfonated in the same way. This time, however, the sulfonation product was decomposed with an ice/water/hydrochloric acid mixture, extracted with ether, and dried over anhydrous sodium sulfate, producing the sulfonic acid, V. The acids were neutralized with 10% sodium hydroxide solution. The sodium alkylbenzenesulfonates precipitated as creamy, hygroscopic semi-solids and were deoiled and desalted by partitioning between aqueous isoproponol and n-pentane, the surfactant going almost entirely into a middle phase. The purified sodium salts, VI, were dried in a vacuum oven at 80 C.

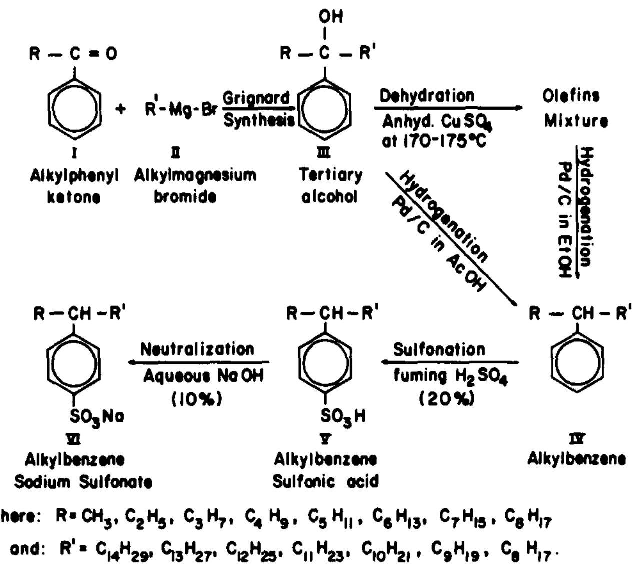

FIG. 1. Synthesis scheme for linear alkylbenzenesulfonates.

Mass spectrometry, infrared (IR), and nuclear magnetic resonance (NMR) investigations were used at each stage to check the structures of intermediates. Titrations on finished materials showed the sodium sulfonates to contain 1% or less of nonsulfonate impurities. ^{13}C NMR detected only the para isomer, structure VI, indicating that less than 5% of the sterically hindered ortho sulfonate is present.

The present materials are thus essentially monoisomeric. However, this is not true for those which we will report on in subsequent papers. In order to be consistent in our nomenclature we have named these materials as sulfonated hydrocarbons (e.g., sulfonated 6-phenylhexadecane), rather than using systematic names for the sulfonates. This has an additional advantage in that it makes more obvious the changes in molecular weight and isomer number. It is to be understood that all sulfonates were used as the sodium salts.

The measurements using these materials as surfactants were carried out at 26 C using the spinning drop interfacial tensiometer (13). Hydrocarbons used were of 96% to 99% purity. The isopentanol was reagent grade.

TABLE I

Physical Properties of Intermediates

Hydrocarbon sulfonated	Alkyl group of starting materials (see Fig. 1)		Phenylhydroxyalkane				Alkylbenzene			
				Distillation				Distillation		
	R	R′	Yield (%)	Boiling pt. (°C)	Pressure (mm Hg)	Refractive index at 24 C	Yield (%)	Boiling pt. (° C)	Pressure (mm Hg)	Refractive index at 24 C
1-phenylhexadecane[a]	–	–	--	–	–	–	–	134-135	0.1	1.4789
2-phenylhexadecane	C_1	C_{14}	90	164-165	0.04	1.4917	83	133-134	0.1	1.4770
3-phenylhexadecane	C_2	C_{13}	90	162-163	0.04	1.4884	86	132-133	0.1	1.4760
4-phenylhexadecane	C_3	C_{12}	95	161-162	0.04	1.4870	80	131-132	0.1	1.4783
5-phenylhexadecane	C_4	C_{11}	95	160-162	0.04	1.4857	85	130-132	0.1	1.4735
6-phenylhexadecane	C_5	C_{10}	92	160-161	0.04	1.4850	90	128-130	0.1	1.4778
7-phenylhexadecane	C_6	C_9	91	158-160	0.04	1.4880	85	127-129	0.1	1.4777
8-phenylhexadecane	C_7	C_8	95	156-158	0.04	1.4882	95	126-127	0.1	1.4779
6-phenylundecane	C_5	C_5	94	122-123	0.03	1.4961	90	81-82	0.04	1.4803
6-phenyldodecane	C_5	C_6	95	126-128	0.03	1.4931	90	84-85	0.03	1.4789
7-phenyltridecane	C_6	C_6	92	130-132	0.03	1.4918	88	90-91	0.03	1.4795
6-phenyltetradecane	C_8	C_5	95	143-144	0.04	1.4913	87	104-105	0.05	1.4790
7-phenylpentadecane	C_8	C_6	93	144-145	0.03	1.4895	86	111-112	0.04	1.4772
8-phenylpentadecane	C_7	C_7	91	148-150	0.04	1.4898	90	113-114	0.04	1.4784
9-phenylheptadecane	C_8	C_8	90	162-163	0.04	1.4872	87	128-129	0.04	1.4773
9-phenyloctadecane	C_8	C_9	90	167-169	0.04	1.4868	90	137-138	0.04	1.4755

[a] Purchased from Chem. Samp. Co., Columbus, OH.

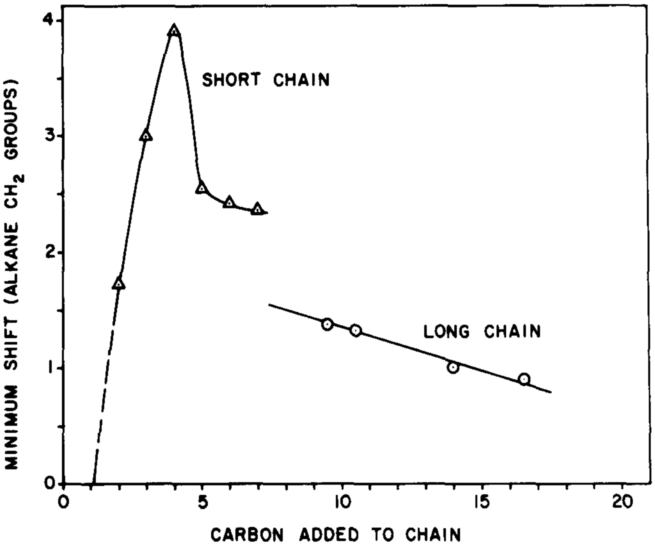

FIG. 2. The observed shifts in n_{min} caused by addition of extra carbon atoms to the linear alkyl chain, for solutions containing 2% isopentanol and 3 g/liter NaCl. The dotted extrapolation allows integration of these curves via equations II and III.

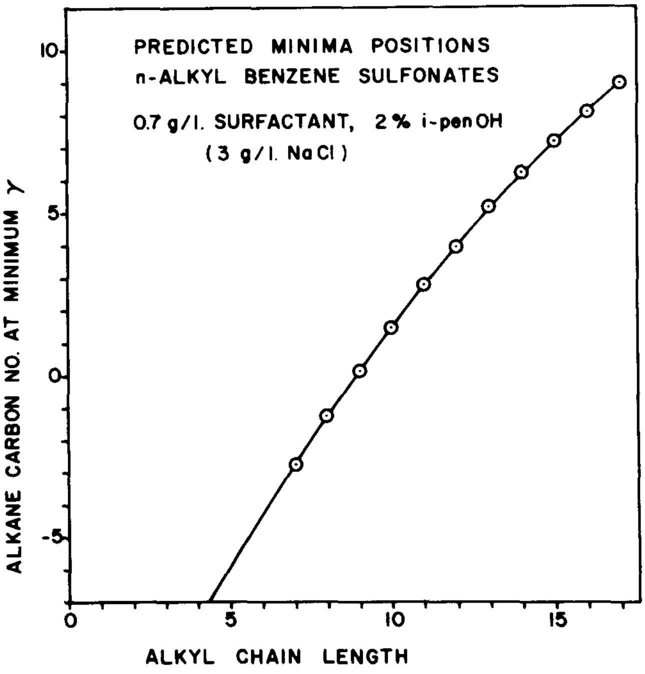

FIG. 3. Predicted minimum positions for n-alkylbenzene sulfonates. (2% isopentanol, 3 g/liter NaCl).

RESULTS AND DISCUSSION

The Effects of Surfactant Molecular Weight and Isomerization on the Value of n_{min}

In the first report on these linear alkylbenzenesulfonates (10), it was shown that the alkane carbon number for minimum tension is a function not only of alkyl chain length, but also of the position of the ring on the chain.

For both pure and commercial surfactants, it is necessary to have electrolyte present in the solution before an ultra low interfacial tension is developed. Sodium chloride is usually employed for this purpose and for most of the low surfactant concentration work reported on previously, a concentration of 10 g/liter was used. In all cases examined, the value of n_{min} increases with increasing sodium chloride concentration. This means that surfactant n_{min} values must be compared at a fixed electrolyte concentration. For solutions of the present surfactants which do not contain an alcohol cosurfactant, the 10 g/liter NaCl concentration is appropriate, being high enough to develop the low tension but not so high that the surfactant precipitates, as well as being above the low end of the range of salinities which are of interest for oil recovery.

Often, however, 2 vol % of isopentanol has been added in order to dissolve some of the more insoluble compounds (10). Since the addition of such a high molecular weight alcohol increases n_{min} substantially (11), the sodium chloride concentration must be lowered, relative to that for the nonalcohol-containing solutions, in order to keep n_{min} in the liquid alkane range. A sodium chloride concentration of 3 g/liter was found to be suitable.

A standard surfactant concentration of 0.7 g/liter was adopted for our previous report on pure sulfonates (10). It has since emerged (J.C. Morgan, unpublished work) that surfactant concentration can sometimes have a significant effect on the interfacial tension for these materials, even at concentrations above their critical micelle concentration (CMC). However, the 0.7 g/liter concentration is at least ten times the highest measured CMC in 10 g/liter NaCl (J.C. Morgan, unpublished work), and in this concentration range all tested surfactants gave close to their optimum low tension performance. We have, therefore, once again used a standard concentration of 0.7 g/liter.

When discussing the variation of n_{min} from surfactant to surfactant it is convenient to regard each linear alkylbenzenesulfonate (LABS) as a normal C_n alkylbenzenesulfonate (having n-1 carbons in group R of Fig. 1) with a substituent m-carbon chain (R$'$ in Fig. 1), where m<n. The alkane carbon number giving minimum tension can be regarded as a sum of contributions from these two parts of the molecules. Thus

$$n_{min} = L_n + S_m \tag{I}$$

where L_n is the alkane carbon number giving minimum tension with the normal C_n-alkylbenzenesulfonate, and S_m is the shift in carbon number for minimum tension produced by adding the substituent C_m chain.

Each of the L or S quantities if taken as a sum of contributions from the individual carbon atoms in the chain. Hence,

$$L_n = \ell_1 + \ell_2 + \dots\dots + \ell_n \tag{II}$$

$$S_m = s_1 + s_2 + \dots\dots + s_m \tag{III}$$

Neither L_n nor S_m is directly observable; only n_{min} can be measured. However, by comparing n_{min} values for a pair of surfactants having the same value of m (and hence, by assumption, the same value of S_m), it is possible to derive the ℓ_i quantities (10). An analogous procedure can be used to obtain s_i values.

As previously mentioned (11), n_{min} varies with most system parameters. The initial derivation of some of the ℓ_i and s_i for a limited range of values of the subscript i was for 2% isopentanol 3 g/liter NaCl solutions. The short chain (s_i vs. i) and long chain (ℓ_i vs. i) curves obtained are reproduced in Figure 2.

No experimental measure of s_1, the shift for the substituent methyl group, has been made. To do this requires obtaining a minimum position for a normal alkylbenzenesulfonate, which is difficult because of its low solubility. Both the n-C_{15} and n-C_{16} compounds have been made and tested, but are effectively insoluble in 2% isopentanol in the presence of 3 g/liter NaCl. We can, however, estimate s_1 by extrapolating the short chain curve of Figure 2 (dotted line). This suggests that its value is close to zero. By taking it as exactly zero, we can 'integrate' the short chain curve using Equation III and generate a plot of S_m vs. m, Figure 4. Values of L_n vs. n can then be obtained by making use of

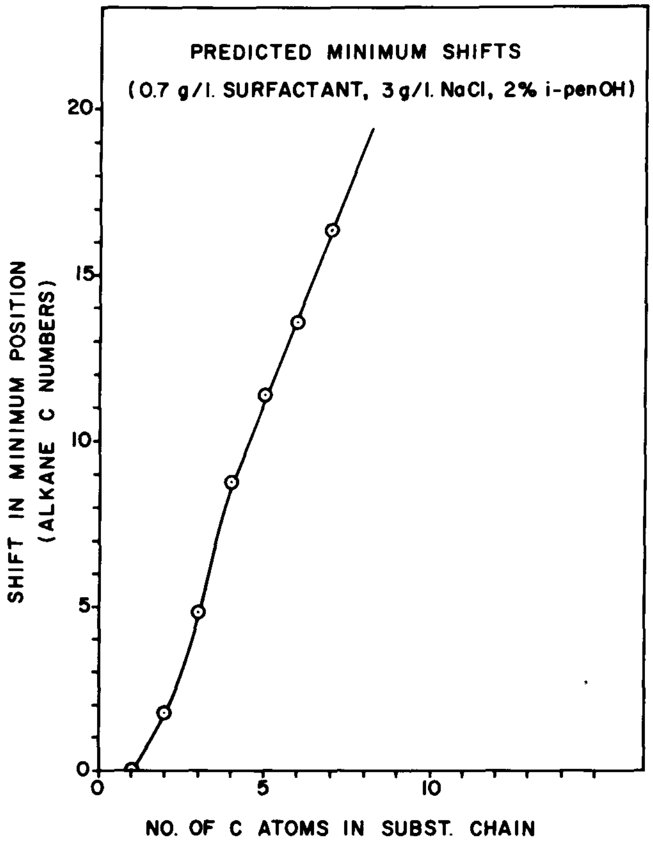

FIG. 4. The shift in minimum position caused by adding a substituent n-alkyl group to the first carbon of a n-alkylbenzenesulfoante. (2% isopentanol, 3 g/liter NaCl).

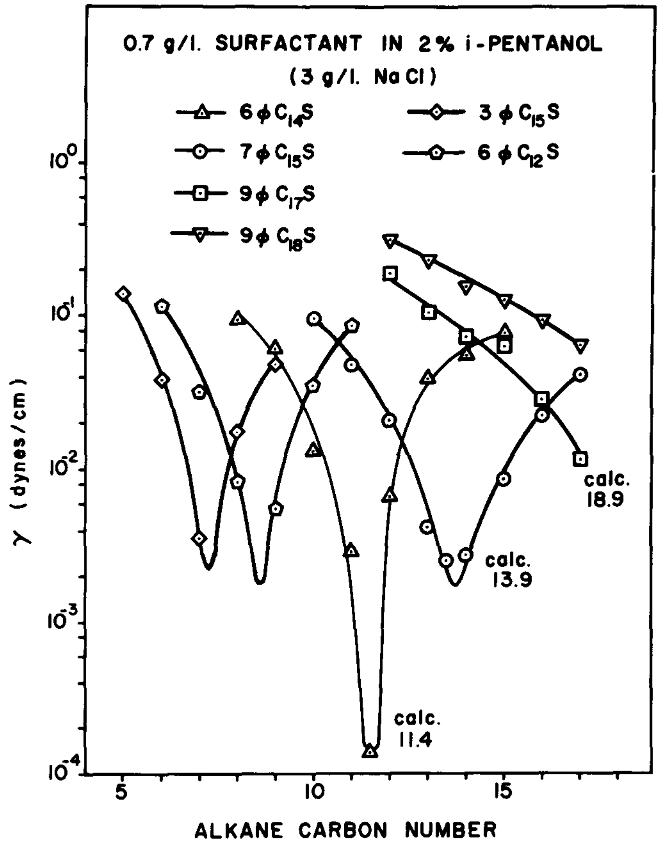

FIG. 5. Experimental alkane scans for several surfactants, comparing observed minimum position with calcualted n_{min} values.

Equation I and the calculated S_m terms, (Fig. 3). The significance of Figure 3, then, is that is shows the alkane carbon numbers (or EACNs) which we would expect to given minimum (not necessarily ultra low) interfacial tensions against solutions of the n-alkylbenzenesulfonates in 2% isopentanol, 3 g/liter NaCl. Figure 4 shows the predicted shifts in these minimum positions produced by adding a substituent n-alkyl chain to the first carbon of the long chain.

Implicit in the above discussion is the idea tha the shift values for specific carbon atoms (s_i or ℓ_i) are independent of the particular molecule of which they form a part. If this is so, then Figures 3 and 4 are useful in that they allow a very simple prediction of the minimum position for untested surfactants, under the same conditions of 26 C, 2% isopentanol and 3 g/liter NaCl. The prediction is made by looking up the appropriate values of L_n and S_m from the graphs and adding them together. Thus, for the sodium salt of sulfonated 6-phenyltetradecane ($6\phi C_{14}S, R=C_8\ R'=C_5$) we have $n = 9$, $m = 5$. The graphs give $L_9 = 0.2$ and $S_5 = 11.2$. Hence, the predicted minimum position is at an alkane carbon number of 11.4. Of course, there may be errors in the L and S values because of the approximate value used for s_1, but these are of opposite sign and cancel, so the minimum position should still be accurately predicted.

Figure 5 shows alkane scans for four new surfactants and includes calculated minimum positions for three of them. The position is correctly predicted for the sulfonated 6-phenyltetradecane and 7 phenylpentadecane and is clearly off scale for the sulfonated 9-phenylheptadecane and more so for the sulfonated 9-phenyloctadecane as it should be. (Earlier results for $6\phi C_{12}S$ and $3\phi C_{15}S$ are included for a reason which will become apparent a little later.)

This predictive power breaks down when the two groups R and R′ are the same. The benzene ring is then placed symmetrically in the molecule and there are no distinguishable long and short chains, so perhaps this breakdown is not surprising. Interfacial tension results for three such surfactants are shown in Figure 6, indicating that the error in the prediction is substantial only for $8\phi C_{15}S$, being less at higher ($9\phi C_{17}S$, Figure 5) and lower molecular weights.

We have thus shown that, under a fixed set of conditions, the low tension behavior, or at least the n_{min} value, of untested surfactants may be predicted from the measured behavior of related compounds. An interesting application of the method is to predict the behavior of an actual commercial surfactant. This was done for a sample of a C_{11}-C_{14} LABS provided by Universal Oil Products, which was a mixture of 26 individual LABSs. The company provided an analysis, which allowed the mole fraction of each component to be calculated. Their n_{min} values were derived by the technique described above. The minimum position for the 26 compoent mixture was then calculated using the linear averaging formula (12).

$$n_{min}(\text{mixture}) = \sum_i n_{min_i} \cdot \text{mole fraction}_i$$

The minimum position was predicted to within 0.5 of a carbon number, which is a very satisfactory achievement.

This detailed analysis of n_{min} shifts is possible only because a wide range of surfactants can be compared under the same conditions. This cannot be done with solutions which do not contain an alcohol cosurfactant, first because some surfactants are not soluble and second because the shift values turn out to be much higher, making a smaller range of surfactants useful in wholly aqueous solutions.

The alkane scans for those surfactants which will develop a minimum tension in a 10 g/liter NaCl solution in water are given in Figure 7, excluding $6\Phi C_{16}S$ which gave a minimum but also gave very irreproducible tensions. The

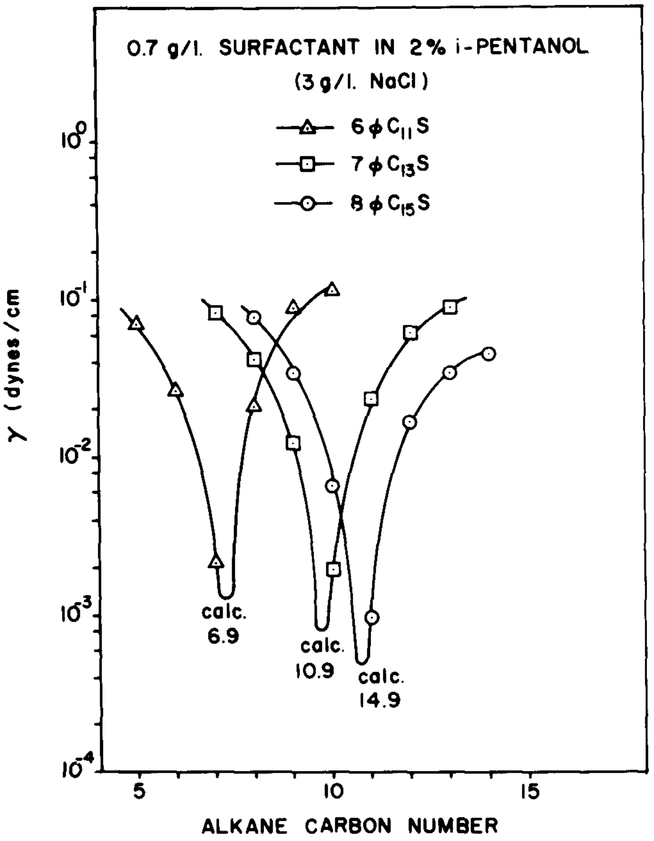

FIG. 6. Alkane scans for symmetrical surfactants, showing that measured and calculated n_{min} values differ.

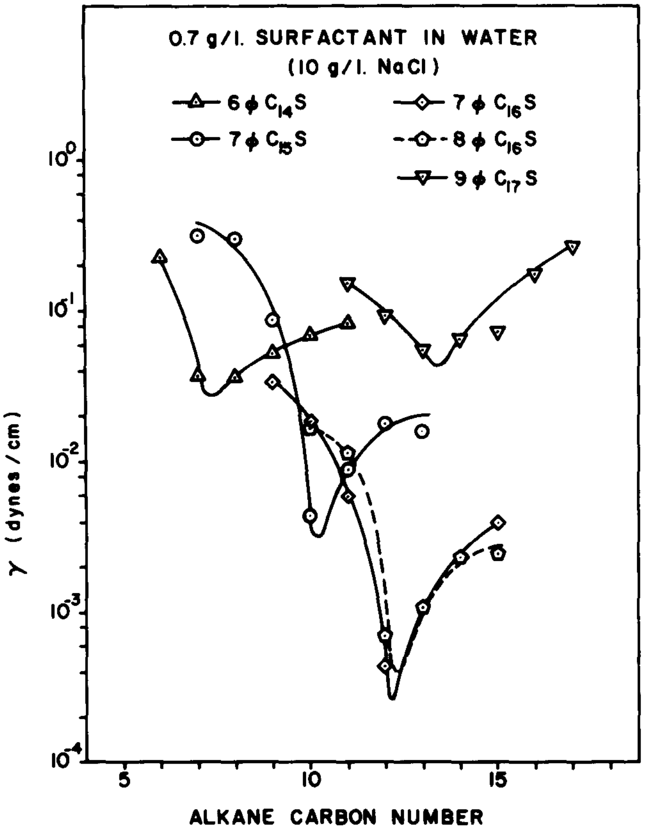

FIG. 7. Alkane scans for the group of water soluble LABSs which given on-scale minima.

shift values which can be calculated are shown in Figure 8. Qualitatively, they are similar to those in 2% isopentanol—tending to decrease as the chains get longer, but they rise to much higher values at short chain lengths. The information embodied in Figure 8 is not extensive enough to allow n_{min} to be calculated for untested surfactants.

The shift values (ℓ_i and s_i) are also dependent on the sodium chloride concentration. The effect of this variable on the n_{min} values of some of the LABSs is shown in Figure 9. The surfactants tend to fall into two groups, with the low molecular weight or low isomer number ones being less influenced by salt than the others.

On an empirical basis, it appears that those surfactants whose n_{min} value at 3 g/liter NaCl, 2% isopentanol (measured or calculated) is 10 or less belong to the small-salt-effect group. Since the salt shifts within each group are very similar, Figure 9 can be used to correct n_{min} values, calcualted at 3 g/l NaCl, to other salinities. This represents a useful extension of our predictive ability.

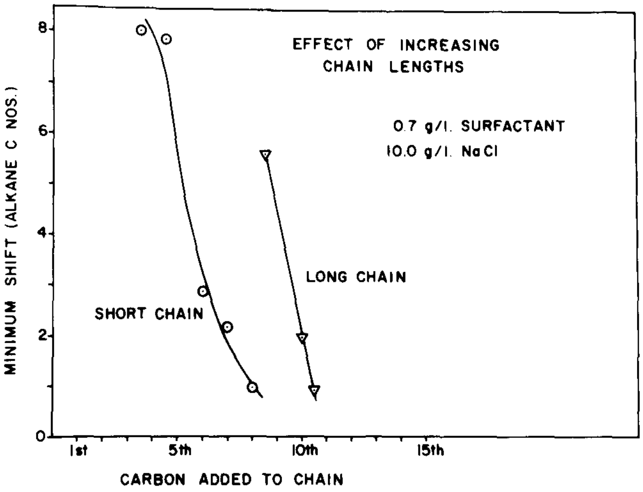

FIG. 8. The shifts in n_{min} for addition of particular carbon atoms to the linear alkyl chain. These curves refer to the data plotted in Figure 7.

Interfacial Tensions Against Oils Other than n-Alkanes

Previous publications have pointed out that there are correlations between the minimum positions when a surfactant is run against different homologous series. In particular, a cyclohexyl group was found to be equivalent to 3 to 4 alkane CH_2 groups and a benzene ring to -1 to +1 alkane CH_2 groups (8,9). This means that a surfactant formulation which gives a minimum tension at heptane should give a minimum in the alkylbenzene series near heptylbenzene and in the alkylcyclohexane series near propylcyclohexane. (Putting it another way, the EACN is an additive property, and the EACN of benzene is zero and that of cyclohexane is 3.5, on average). The six surfactants which gave alkane minima at 10 g/liter NaCl were run against these two homologous series. In Figure 10, the minimum positions obtained are compared with the corresponding n_{min} values for alkanes and with the lines corresponding to the usual EACN scaling rules. These results show that the EACN concept is still valid for monoisomeric surfactants and demonstrate once again its apparent universality and independence of surfactant type.

The Influence of EACN on the Value of the Minimum Interfacial Tension

A very important question, both from the point of view of oil recovery and from that of basic physical chemistry, is whether some surfactants are better at producing very low tensions than others.

A superficial examination of Figure 7 reveals that

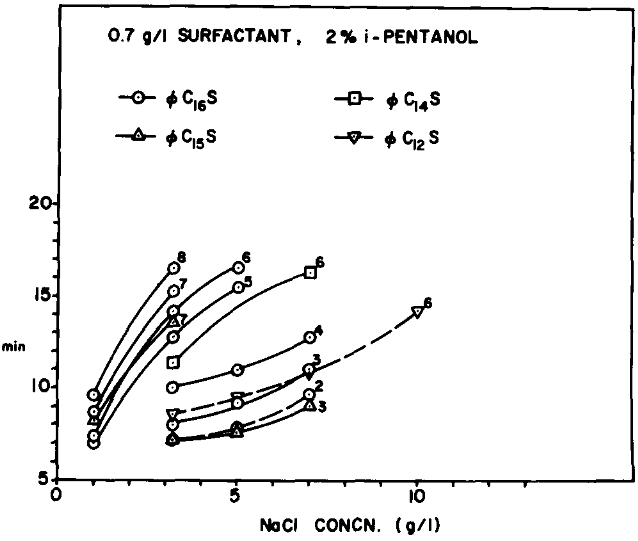

FIG. 9. The variation of n_{min} with changing salinity for several surfactants in 2% isopentanol. Symbols indicate surfactant molecular weight and numbers indicate the isomer.

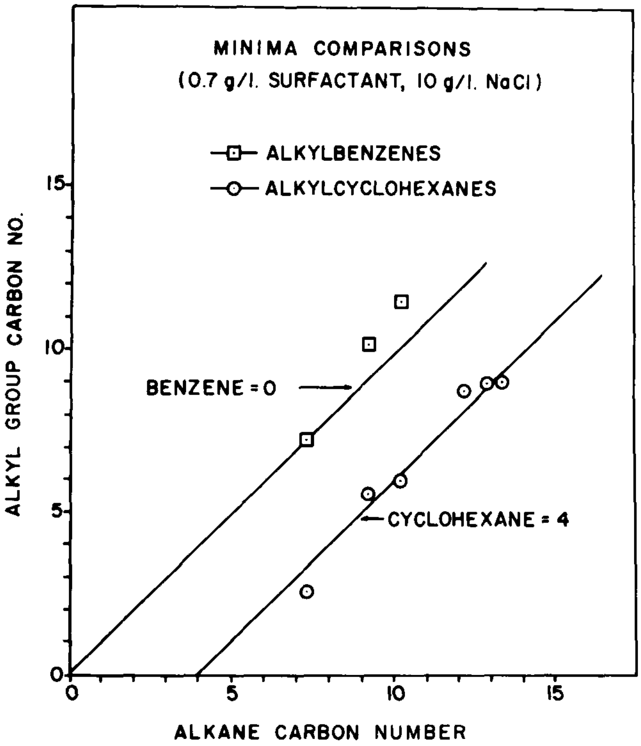

FIG. 10. A comparison of the position of minimum tension in the alkane series (alkane carbon number) with the positions in the alkylcyclohexane and alkylbenzene series (alkyl group carbon number). Each square or circle represents such a comparison for one of the surfactants of Figure 7.

the lowest interfacial tensions are given by 7 and $8\phi C_{16}S$. We might conclude that these are "better" low tension surfactants than the others represented in this diagram. That this is not correct can be demonstrated by developing the idea of the hydrocarbon preference curve.

To derive the alkane preference curve for the surfactants of Figure 7, we begin by extracting, for each surfactant, the alkane carbon number at the minimum (i.e., n_{min}) and the interfacial tension at the minimum. This is done by interpolation on the experimental tension vs. carbon number curves and hence the interfacial tension is subject to a considerable uncertainty which explains much of the scatter in the results. The information obtained is plotted in Figure 11, where the shape of the symbol indicates the surfactant molecular weight, and the numbers indicate the surfactant isomer. The data are obviously very sparse, but the trend in these results is indicated by the solid line.

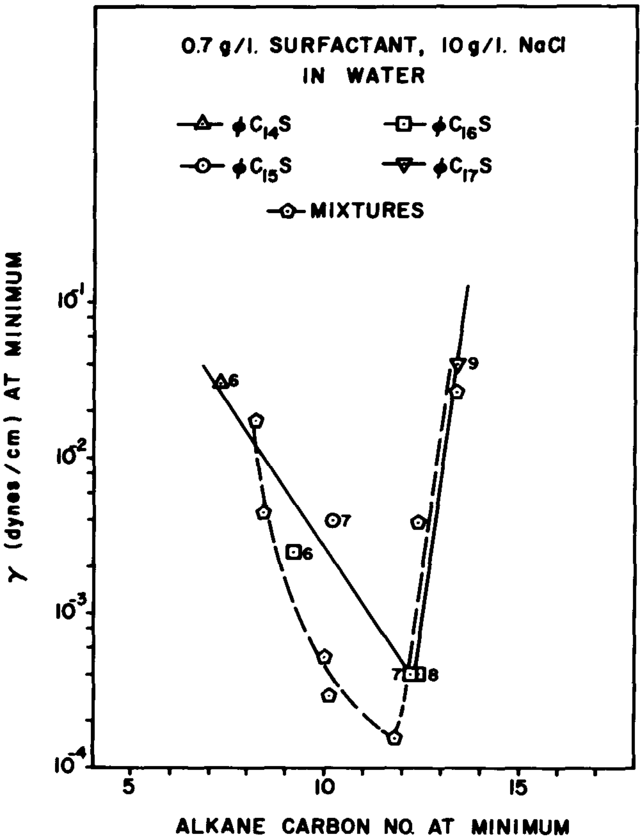

FIG. 11. The relationship between minimum position (n_{min}) and minimum interfacial tension. These results are interpolated from the alkane scans of Figure 7, plus others for mixed surfactants. The shape of the symbol indicates surfactant molecular weight, adjacent numbers indicate the isomer. This is the alkane preference curve for the stated conditions.

None of the other LABSs, used alone, gives a detectable minimum tension in its alkane scane at 10 g/liter NaCl, so, in order to collect additional information, several binary mixtures were made, each combining a different pair of LABSs. All mixtures were 50/50 by weight. To save space, the alkane scans are not given, but the minimum position-minimum tension correlations have been added to Figure 11. These are the "mixture" symbols, joined by the dotted line. Within experimental error, the dotted and solid lines correspond, with only $7\phi C_{15}S$ lying a little too high. The mixture which gave the lowest interfacial tension, of 2 x 10^{-4} dynes cm^{-1} at dodecane, was 50% sulfonated 5-phenylhexadecane and 50% sulfonated 9-phenyloctadecane, neither of which develops a minimum when used on its own.

This leads us to the remarkable conclusion that it is not the particular LABS used which determines the magnitude of the low tension, but the value of n_{min}. Putting it somewhat differently, with a LABS, ultra low tensions of the levels important for tertiary oil recovery ($<10^{-3}$ dynes cm^{-1}), can only be obtained for the alkanes decane to dodecane.

This argument receives extra support from the data given in our earlier paper (10) and in Figures 5 and 6 for 2% isopentanol 3 g/liter NaCl solutions, where the lowest tensions again occur near dodecane. The results this time are more extensive, and the alkane preference curve (Fig. 12) has a similar shape to, although it is not identical with,

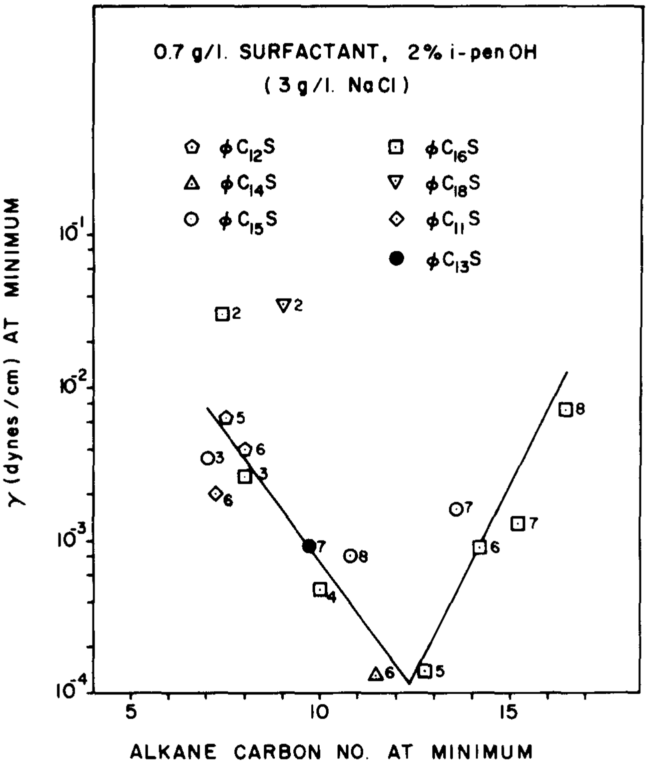

FIG. 12. A duplicate of Figure 11, but this time for formulations containing isopentanol. The general character of this curve is very similar to Figure 11. Symbols have the same meaning. Points are derived from Figures 5 and 6, plus Ref. 10.

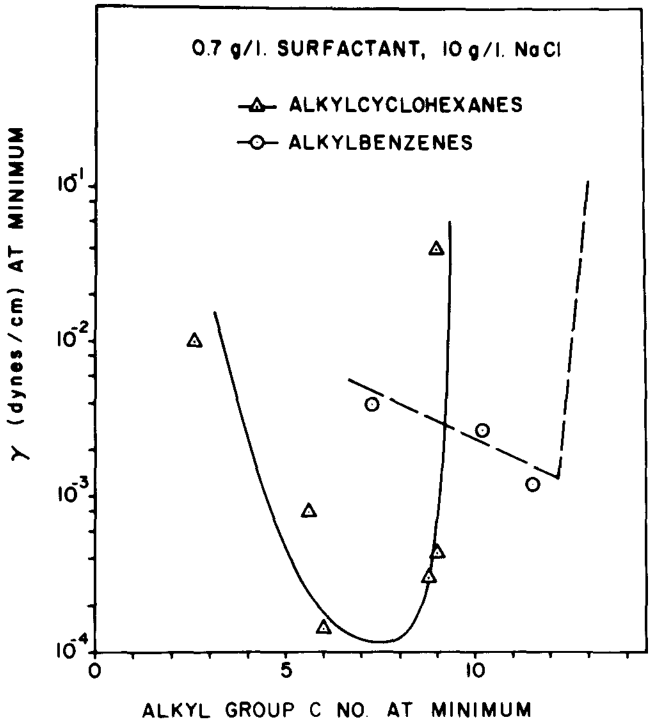

FIG. 13. Alkylcyclohexane and alkylbenzene preference curve The surfactants used are the same ones as in Figures 7 and 10.

Figure 11. The same correlation has been done for the alcohol-containing solutions at higher salt concentrations, and once again the lowest tensions are given by the same alkanes, although the minimum in the preference curve is shallower. If the molecular weight of the oil can determine whether these surfactants are good or bad, it is hardly surprising that the structure of the oil is an equally important variable. Figure 13 shows the preference curves for the alkylbenzene and alkylcyclohexane series at 10 g/liter NaCl in water. The dotted alkylbenzene curve is somewhat speculative, but has been drawn to fit the experimental observation that no minima are observed in this series for substituents longer than 12 C atoms (dodecylbenzene). The preference for particular molecular weights is seen in both these series, just as it was for alkanes. Furthermore, the minima on the three preference curves are at corresponding EACN values, 10-12 in each case. Notice, however, that the alkylbenzenes never give interfacial tensions below 10^{-1} dyne cm^{-1}, whereas the alkylcyclohexanes do so over a wider range of EACNs than the alkanes. Thus linear alkylbenzenesulfonates can be very good low tension surfactants against alkanes or alkylcyclohexanes, but are rather poor performers with alkylbenzenes.

There are two related conclusions to be drawn from the existence of the hydrocarbon preference curve. First, within experimental error, all of the tested LABSs are equally good or equally bad for giving very low interfacial tensions. Second, whether they are good or bad depends on the oil against which the low tension is needed. The only exceptions to this rule are the 2 isomers of hexadecyl and octadecyl benzenesulfonate (Fig. 12) which give substantially higher tensions than any other surfactants at the same n_{min}.

The question of how deep the minimum in the preference curve can be, or rather of under what conditions it is deepest, is obviously of considerable practical significance. Now, for any chosen surfactant, there are many sets of variables which produce the same n_{min} value. Not all of these will give an equally low tension against a selected oil. There will be a certain optimum range of salinity and possibly also of temperature and cosurfactant concentration (11). This means that the derived hydrocarbon preference curves vary with the experimental conditions. Our earlier examination of the salt effect (10) suggests that 10 g/liter NaCl is in the optimum salinty range for these monoisomeric surfactants when no cosurfactant is used. This implies that the derived curves of Figures 11 and 13 represent optimal performance, and changing the salinity will not give significantly lower tensions. The effect of changing temperature is unknown in detail, although it does seem possible that lower tensions can be produced for the lower EACNs, since n_{min} is known to decrease with increasing temperature (11). It is uncertain what will happen to the minimum tension at higher EACNs.

The situation in alcohol-containing formulations is more complex. The higher salt scans used to derive Figure 9 showed that the preference curve shifts to higher interfacial tensions. However, at 1 g/liter NaCl, lower tensions can be obtained for lower molecular weight alkanes. Furthermore, some results using mixed surfactants at 3 g/liter NaCl (including those for the 26 component LABS mixture mentioned above) also show lower tensions for the lower alkanes. In the case of 2% i-pentanol solutions, then, the curve of Figure 12 does not represent the optimum low tension performance which can be obtained for each particular alkane. For those alkanes from pentane to decane this performance can be improved by using mixed surfactants or by lowering the salinity.

It seems rather inappropriate to conduct experiments with crude oils and these expensive monoisomeric surfactants, so the preference curves for crudes have not been measured. It is known, however, that crude oils have EACNs in the range 6 to 9 (9). Since LABSs in general prefer an EACN range of 10 to 12, it does not seem that they would be the best surfactants for giving low tensions with a crude oil, making them rather unpromising candidates for tertiary recovery.

CONCLUSIONS

The alkane carbon number, n_{min}, giving minimum interfacial tension is a composite result of many intermolecular interactions. It is not a property of the surfactant per se, but of the whole surfactant formulation, including temperature, electrolyte concentration, and cosurfactant type and concentration. Despite this, certain very systematic changes in its value can be demonstrated as a result of variations in surfactant structure, provided all other conditions are held constant.

Under these circumstances, n_{min} is an additive property of separate parts of the surfactant structure. For this purpose, the LABS molecule is conveniently split into two parts – an n-alkylbenzenesulfonate and a dependent, shorter n-alkyl chain. The contribution of the n-alkylbenzene portion to the observed n_{min} is independent of the chain length of the substituent alkyl group, and vice versa.

This independence makes it possible to predict n_{min} values for untested surfactants.

When the benzene ring is centrally placed on the linear alkyl chain, these predictions are less accurate. Possibly this is because the symmetrical molecules orient differently at the oil-water interface. This incidates how sensitive the n_{min} values are to surfactant structure, since even a symmetrical LABS falls into a separate class from the asymmetrical ones.

The various contributions to n_{min} alter with changing salt and cosurfactant concentration. In 2% i-pentanol, LABSs fall into two groups with respect to the effect of salt, which makes predictions of their behavior at untested sodium chloride concentrations possible.

The range of LABSs giving low tensions in wholly aqueous solutions is so limited that no predictive power can be developed.

The EACNs for alkylbenzenes and alkylcyclohexanes are the same when measured against a monoisomeric LABS as when measured using commercial surfactants.

The selectivity which is observed in an individual alkane scan is not the only level of selectivity involved in the production of low interfacial tensions. We have shown that a "hydrocarbon preference curve" may be constructed for any series of oils having the same structure but varying EACN. These curves reveal that, even when the conditions are optimized for each oil, some EACNs give lower interfacial tensions than others and that some oil structures given lower tensions than others.

We have been unable to produce much evidence that any one LABS formulation, whether it consists of a single surfactant species or a mixture, will give significantly lower interfacial tensions then another at the same value of n_{min}. An exception to this rule probably occurs with alcohol-containing formulations at low salt concentrations and low values of n_{min}, where mixtures seem to have some advantage.

The hydrocarbon preference curves, which select for the same EACNs in all oil series, plus the apparent lack of influence of the surfactant itself on the minimum tension, lead us to conclude that linear alkylbenzenesulfonates are unlikely to be the best candidates for surfactant flooding in tertiary oil recovery.

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