Surfactants for Producing Low Interfacial Tensions: III. Di and Tri n-Alkylbenzenesulfonates

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ABSTRACT

The synthesis of several di and tri n-alkylbenzenesulfonates is described. Low interfacial tensions can be obtained against alkanes by using these materials as surfactants. The low interfacial tension properties of these surfactants are shown to be profoundly influenced by the presence or absence of an alkyl group in the ortho position relative to the sulfonate group and also to depend on the length of this alkyl chain relative to other chains in the molecule. Surfactants where this chain is relatively long tend to give their lowest interfacial tensions against the lowest molecular weight alkanes and also to be effective at lower surfactant molecular weight.

INTRODUCTION

Several publications have dealt empirically with the low interfacial tension behavior of surfactants produced by sulfonating a monoisomeric hydrocarbon (1-3). Their properties are similar in most respects to those of complex commercial sulfonates (4-11).

Measuring the interfacial tensions of a standard surfactant solution (usually 0.7 g/liter surfactant, 10 g/liter NaCl) against a homologous series of alkanes has proven to be a useful tool for examining low tension behavior and will be continued in this paper. An alkane scan of this kind allows two important variables to be defined (Fig. 1). These are the minimum interfacial tension (γ_{min}) and the alkane carbon number for minimum tension (n_{min}).

Provided that the sodium chloride concentration is within a certain range of optimum values, which varies depending on the surfactant under test but which usually includes the standard 10 g/liter concentration, γ_{min} represents the lowest interfacial tension which can be obtained for that particular surfactant against an alkane of carbon number n_{min}. (We cannot exclude the possibility that variables other than the salinity may have optimal ranges but, at our present state of knowledge, salinity appears to be the most important.)

We have demonstrated (2,3) that surfactants of similar structure and not-too-far-different molecular weight tend to give the same value of γ_{min} for a given value of n_{min}, subject always to the optimized salinity condition. This allows a graph of n_{min} vs. γ_{min} to be used as a means of characterizing the optimum low tension performance of a group of surfactants across the alkane [or other (2)] series. These n_{min}/γ_{min} plots have been called "alkane preference curves," since they show which alkanes are most preferred for giving very low interfacial tensions.

In previous work, three types of preference curve were observed (2,3). These are sketched in Figure 2 and can usefully be distinguished by the value of n_0, the alkane carbon number at the minimum in the preference curve. n_0 is the *optimum alkane carbon number* for that particular surfactant group. The three classes of surfactants are:

Group I, $n_0 \simeq 10$. Modified linear alkylbenzenesulfonates (LABS) having a short (C_3 or less) alkyl group ortho to the SO_3 group, plus one or two other alkyl groups, the major one of which is meta to the sulfonate and has at least 12 carbon atoms.

Group II $n_0 < 5$. Modified LABSs where the group ortho to the sulfonate is C_4 and/or the major chain meta to the SO_3 is C_{10} or less.

Group III $n_0 \simeq 12.5$. LABSs in the molecular weight range from a C_{11} alkylbenzenesulfonate up to a C_{18} alkylbenzenesulfonate.

Group I surfactants were identified as being the most

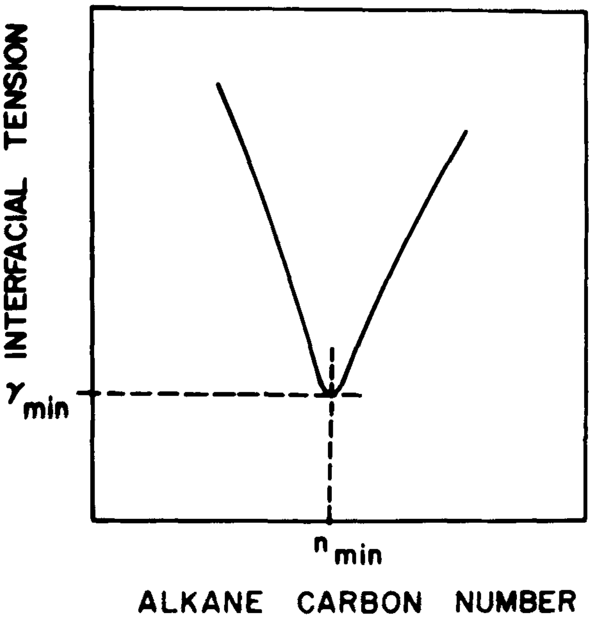

FIG. 1. The definition of n_{min} and γ_{min}.

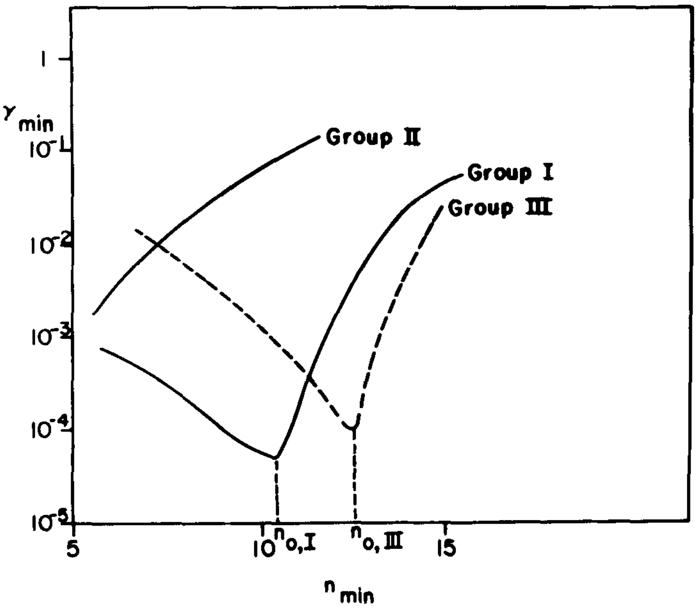

FIG. 2. The three types of alkane preference curve. The interfacial tensions are only approximate. n_0 is the carbon number for lowest γ_{min}.

TABLE I

Properties of Alkylbenzenes

Hydrocarbon sulfonated	Abbreviation for sulfonate	Distillation		Refractive index (24 C)	Mass of molecular ion
		Boiling point (°C)	Pressure (mm Hg)		
1,4-Dibutylbenzene[a]	p di bu φS	88-90	0.05	1.4870	190
1,4-Dipentylbenzene[a]	p di pent φS	113-115	0.05	1.4851	218
1,4-Dihexylbenzene[a]	p di hex φS	142-145	0.50	1.5845	246
1-Pentyl-4-hexylbenzene	p pent hex φS	118-120	0.05	1.4852	232
1-Hexyl-4-heptylbenzene	p hex hept φS	111-113	0.02	1.4835	260
1,2-Dihexylbenzene[a]	o di hex φS	128-130	0.10	1.4857	246
1,2-Diheptylbenzene[a]	o di hept φS	140-141	0.10	1.4845	274
1,2-Dioctylbenzene[a]	o di oct φS	150-152	0.10	1.4837	302
1,4-Dibutyl-2-ethylbenzene	di bu et φS	110-112	0.05	1.4915	218
1,4-Dibutyl-2-propylbenzene	di bu prop φS	115-117	0.05	1.5895	232
1,2,4-Tributylbenzene[b]	tri bu φS	118-119	0.05	1.5890	246
1,2-Diethyl-4-butylbenzene	di et bu φS	77-78	0.02	1.4947	190
1,2-Diethyl-4-pentylbenzene	di et pent φS	80-82	0.02	1.4942	204
1,2-Diethyl-4-hexylbenzene	di et hex φS	88-90	0.02	1.4925	218
1,2-Diethyl-4-heptylbenzene	di et hept φS	114-116	0.01	1.4910	232
1,2-Dibutyl-4-hexylbenzene	di bu hex φS	130-132	0.10	1.4870	274

[a] Isomerically pure hydrocarbon and sulfonate.

[b] Isomerically pure hydrocarbon.

promising for tertiary oil recovery, since their n_0 ranges coincide most closely with the measured equivalent alkane carbon numbers (9) of crude oils. It has since been shown (Doe, P.H., unpublished work) that these surfactants usually do give lower interfacial tensions against crude oils than do Group II or Group III surfactants.

It will be useful for subsequent discussion to introduce the idea of *molecular weight efficiency*. One surfactant is said to be more molecular weight efficient than another if, at the same sodium chloride concentration and surfactant molecular weight, it has a higher n_{min} value. Group I and Group II modified LABSs are more molecular weight efficient than Group III LABSs.

All else being equal, surfactants with optimal structure would produce a desired low tension at a lower molecular weight. It is possible that this would be of some practical interest, since lower molecular weight surfactants might well be cheaper to manufacture. They might also be more salt tolerant and more soluble. However, the fact that changing a surfactant's structure also changes its n_0 value means that all else is not equal. It appeared from earlier trends (3) that the most molecular weight efficient surfactants had the lowest n_0 values, which can quickly shift them outside the range of useful low tension surfactants.

Previously, the most efficient surfactants which had been identified were those which had n-alkyl chains as minor substituents on the benzene ring. In the present study we follow up this trend by breaking away from LABS-based structures and considering surfactants which are sulfonated di and tri n-alkylbenzenes. These materials are examined from the points of view of hydrocarbon preference, molecular weight efficiency and salt tolerance, and relationships between the three properties are considered.

MATERIALS AND EXPERIMENTAL

The hydrocarbons sulfonated during this study were synthesized as follows.

I. p Di n-alkylbenzenes

An additional alkyl group was introduced into an n-alkylbenzene by performing a Friedel-Crafts acylation and reducing the resulting ketone. The reactions involved and the experimental conditions required have been given in detail elsewhere (3). Because of steric hindrance to ortho substitution, an essentially monoisomeric 1,4 dialkyl product is expected. IR and proton and ^{13}C nuclear magnetic resonance (NMR) spectra are in agreement with this conclusion.

II. Tri n-alkylbenzenes

These materials were made by carrying out two acylation/reduction cycles instead of one, beginning again with an n-alkylbenzene. The resulting substitution pattern is 1,2,4. Where the third substituent enters the molecule will once again depend upon steric hindrance, and it is expected to go predominantly ortho to the shortest of the first two substituents. However, this will not be as clear-cut a distinction as for the first acylation and a mixture of two isomers will undoubtedly be present in the finished hydrocarbon. The compounds listed in Table I are the isomers which are probably present in the highest percentage.

III. o Di n-alkylbenzenes

The preparation of these materials is outlined in Figure 3.

o-Xylene (2 moles) was placed in a 3-liter, 3-neck flask and heated to 130 C. Eight moles of bromine was added slowly through a pressure equalizing dropping funnel that extended below the liquid surface of the hydrocarbon. The rate of addition of bromine was regulated so that no visible amount persisted in the flask for more than few seconds. The reaction temperature was slowly raised during the addition to a maximum of 170-175 C. A 300 watt UV lamp was used to photolytically catalyse the reaction.

When the addition of bromine was complete, the mixture was held at 170-175 C for 2 hr and then left to stand overnight. The reaction product is 1,2 di(dibromomethyl) benzene, which was recrystallized from chloroform to yield colorless needles, mp 114-116 C [literature value 116 C (12)].

The brominated xylene was hydrolyzed to 1,2 benzene dicarbonal (o-phthalic aldehyde) by refluxing for about a week in 50% aqueous ethanol in the presence of potassium oxalate, until a clear solution was obtained. The alcohol was removed by distillation, and the aldehyde was steam distilled in the presence of Na_2HPO_4. The aldehyde was extracted with ether and dried over anhydrous magnesium sulfate. The ether was then evaporated, and the aldehyde was dried in a vacuum oven over anhydrous phosphorous pentoxide. The melting point of the o-phthalic aldehyde was 54-55 C [literature 55.5-56 C (12)].

The aldehyde (0.3 mole) was dissolved in dry ether and

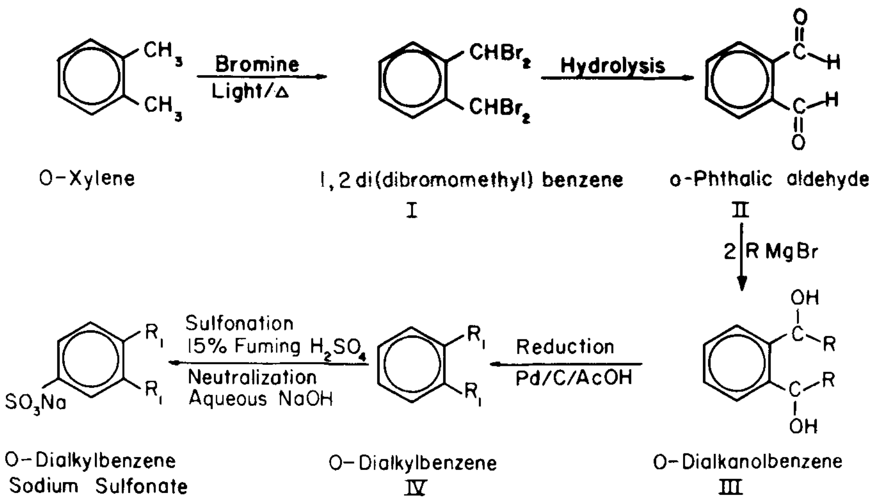

FIG. 3. Synthesis scheme for o di n-alkylbenzenesulfonates.

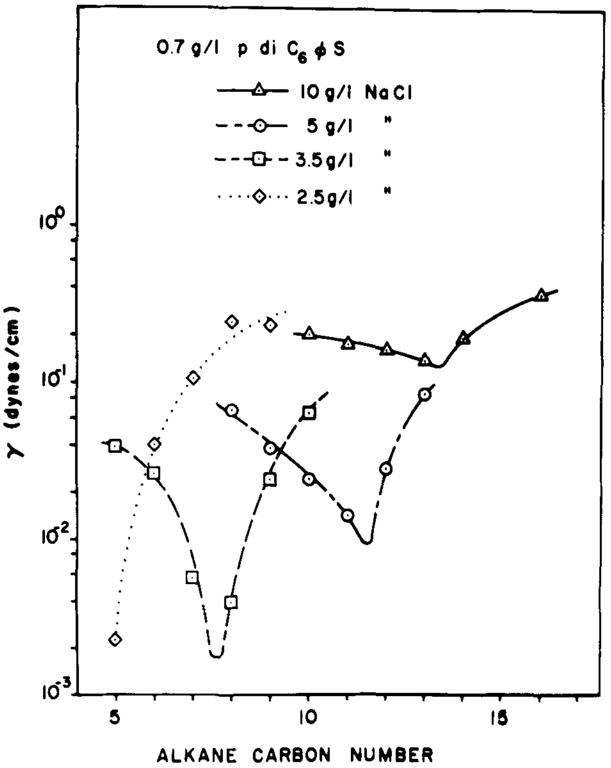

FIG. 4. Alkane scans for sulfonated p dihexylbenzene at various NaCl concentrations.

added dropwise to 1 mole of n-pentyl, n-hexyl, or n-heptyl magnesium bromide. The mixture was refluxed gently for 2 hr and then left to stand overnight. The Grignard complex was decomposed and processed in the usual manner (2,3).

The hydrogenation of the resulting alcohols and the purification of the resulting o di n-alkylbenzenes followed the usual techniques (2,3).

Purity of all samples was checked by measuring various physical properties and by spectral analysis. A list of all hydrocarbons (major isomers in some cases) and their physical properties is given in Table I.

The sulfonation and neutralization of the hydrocarbons to produce sodium sulfonates followed procedures fully described elsewhere (2,3). Purity was checked by titration with Hyamine 1622 (Rohm & Haas Co. Philadelphia, PA) (13) and indicated that the finished product was 99 +% sodium sulfonate.

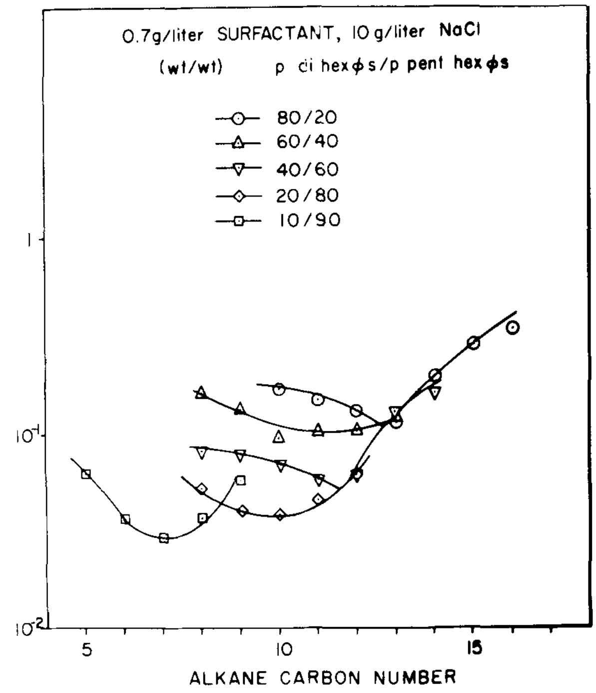

FIG. 5. Alkane scans for mixtures of p di n-alkyl surfactants at 10 g/l NaCl. Note the absence of low interfacial tensions.

All interfacial tensions were measured at 27 C using the spinning drop technique (14).

RESULTS

I. p Di n-alkyl compounds

This group consists of the first five compounds of Table I. They all have a butyl or larger n-alkyl group ortho to the sulfonate, which, we would expect from earlier work, should make them very molecular weight efficient. In all cases both alkyl groups are equal or nearly equal in length. This means that neither the group o to the SO_3 nor the group m to it can reasonably be regarded as the major alkyl chain. Modified LABSs where the two chains were closest together in total numbers of carbon atoms did not show very good low tension performance (3).

A series of alkane scans for sulfonated p dihexylbenzene are shown in Figure 4, where the salinity is varied from 2.5

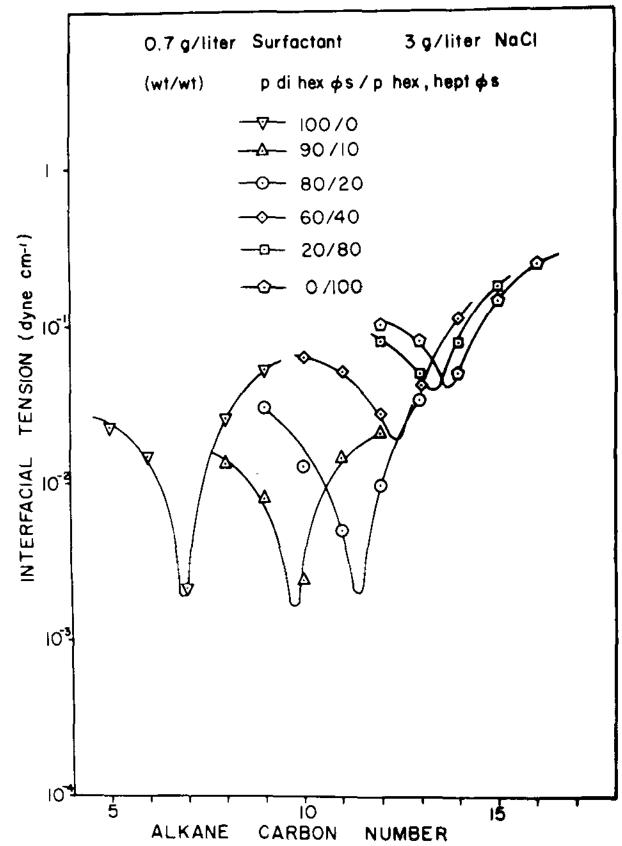

FIG. 6. Interfacial tension scans for some o di n-alkyl surfactants.

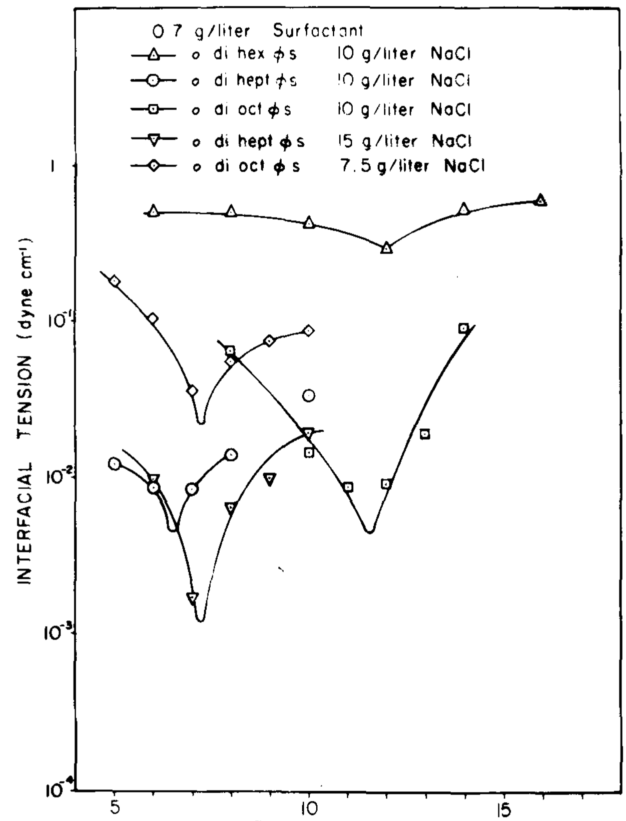

FIG. 7. Alkane scans for mixtures of p di n-alkyl surfactants near their optimum salinity.

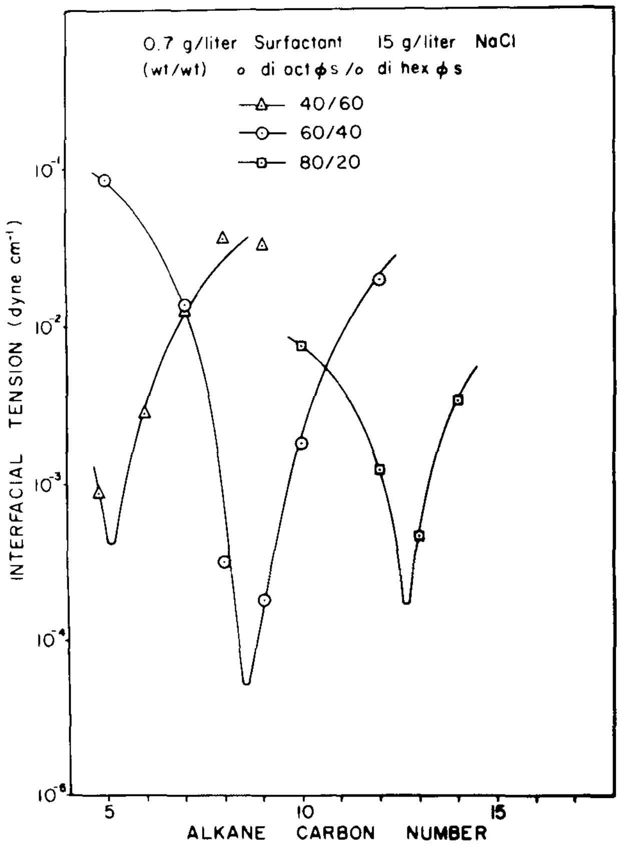

FIG. 8. Scans for o di n-alkyl surfactants at 15 g/liter NaCl. These surfactants give low tensions under these conditions, but also precipitate.

to 10 g/liter NaCl. Taking first the results for our standard 10 g/liter salinity, we see a high minimum tension at an n_{min} of 13.4. This value is an estimated (15) 17 carbon numbers higher than that for the most molecular weight efficient of the C_{12} LABSs and at least 9 carbon numbers higher than a modified LABS of the same molecular weight (3). Hence, our expectation of a high molecular weight efficiency is borne out. No other C_{12}-alkyl compound has approached the p dihexyl material in this respect.

Now, the γ_{min} values in Figure 4 get lower as n_{min} is decreased. This is the result one would expect from a type II preference curve. However, these p di n-alkyl surfactants are not very salt tolerant and in fact tend to precipitate in 10 g/liter NaCl. Hence it is possible that some of the observed decrease in γ_{min} in Figure 4 is caused by moving into the optimal salinity range rather than towards optimal alkanes.

These two effects can be separated by employing surfactant mixtures, which, as has been shown, act like a single surfactant of the same group in terms of their alkane preference (2,3). Figure 5 shows results for a series of mixtures of the p dihexyl with the p pentylhexyl surfactant. At a salinity of 10 g/liter, no low tensions are observed anywhere, but there is still some tendency for γ_{min} to decrease as n_{min} decreases. When comparing a different series of mixtures, this time of the sulfonated p dihexyl and p hexylheptylbenzenes at 3 g/liter NaCl, we see very different behavior. (Fig. 5) This time, moderately low γ_{min} values are observed until n_{min} reaches about 12, and then the interfacial tensions increase sharply. The conclusion from all this is that the optimal salinity range for these surfactants has a lower upper limit than any other group of surfactants we have examined. It certainly does not extend as far as 5 g/liter NaCl. No lower limit was established, but for most materials this is around 2 g/liter NaCl. The shape

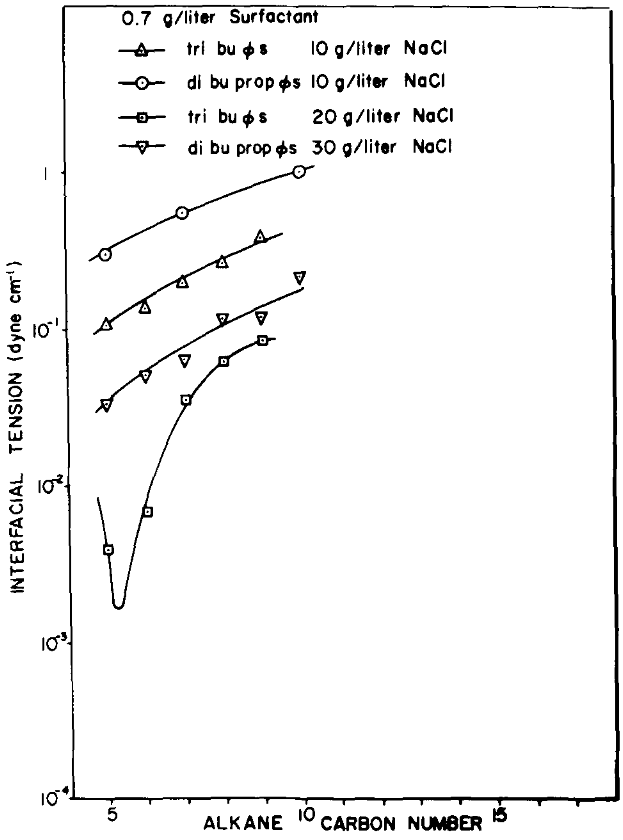

FIG. 9. Alkane scans for the di bu prop and tri bu surfactants.

of the preference curve is basically group II, but there is a wider range of moderately low (lower 10^{-3}s) tensions than is the case with other group II surfactants.

II. o Di n-alkyl compounds

The three surfactants of this structure which have been examined, sulfonated o-dihexyl, o-diheptyl, and o-dioctylbenzenes, show interesting differences in behavior from their p-dialkyl counterparts just discussed. A series of alkane scans is shown in Figure 6.

Looking first at the scans for each of the three surfactants at 10 g/liter NaCl, both the diheptyl and dioctyl surfactants give γ_{min} values in the upper 10^{-3}, while the dihexyl fails to give a low tension. The n_{min} values of these materials compare very closely with those for certain LABSs of the same molecular weight. For instance, sulfonated 7-phenylhexadecane, n_{min} = 12.2; sulfonated o-dioctylbenzene, n_{min} = 11.6. There is a similar correspondence between sulfonated 6-phenyltetradecane, n_{min} = 7.5 and sulfonated o-diheptylbenzene, n_{min} = 6.5.

The γ_{min} values for these surfactants at 10 g/liter NaCl are much lower than those for any p di n-alkyl surfactant at the same salinity. Also, if the salinity is increased, the γ_{min} values decrease (e.g., sulfonated o-diheptylbenzene at 15 g/liter NaCl, Fig. 7) and vice versa (e.g., sulfonated o-dioctylbenzene at 7.5 g/liter NaCl, Fig. 7). These compounds are thus different in that their optimum low tension performance is not developed until an unusually high salinity. Most surfactants perform well at 2.5 to 5 g/liter NaCl and above. These do not do well until 15 g/liter NaCl is reached.

Unfortunately, because of their relatively long n-alkyl chains, these surfactants are not very salt tolerant, and they all precipitate to a certain extent in 15 g/liter sodium chloride. A few alkane scans for mixed surfactant systems were collected at this salinity, however, and they are shown in Figure 8. They indicate that some very low tensions can be

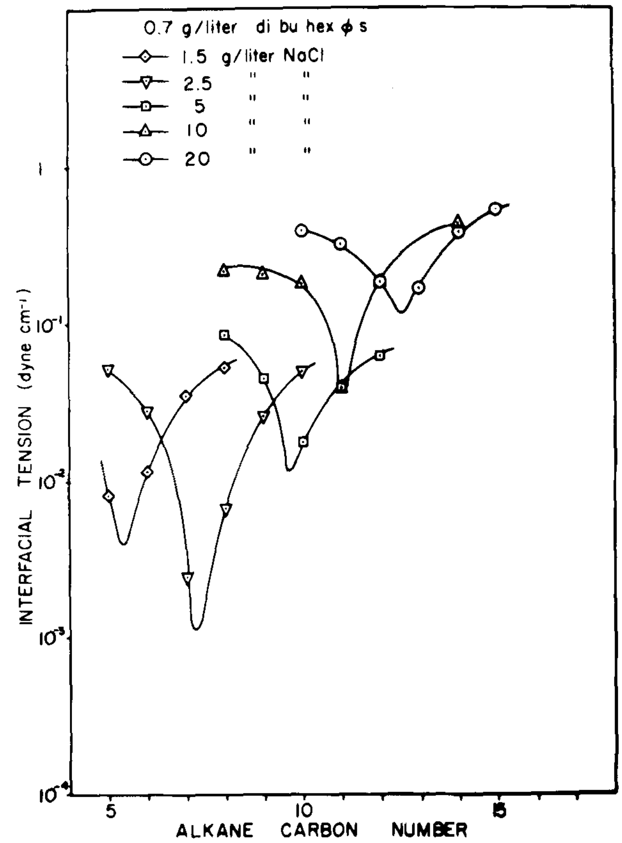

FIG. 10. Alkane scans for dibutylhexyl surfactant at various salinities. The decreasing γ_{min} as n_{min} decreases is caused by moving towards optimal alkanes. The higher minimum tension for 1.5 g/liter NaCl indicates that this is below the optimal salinity range.

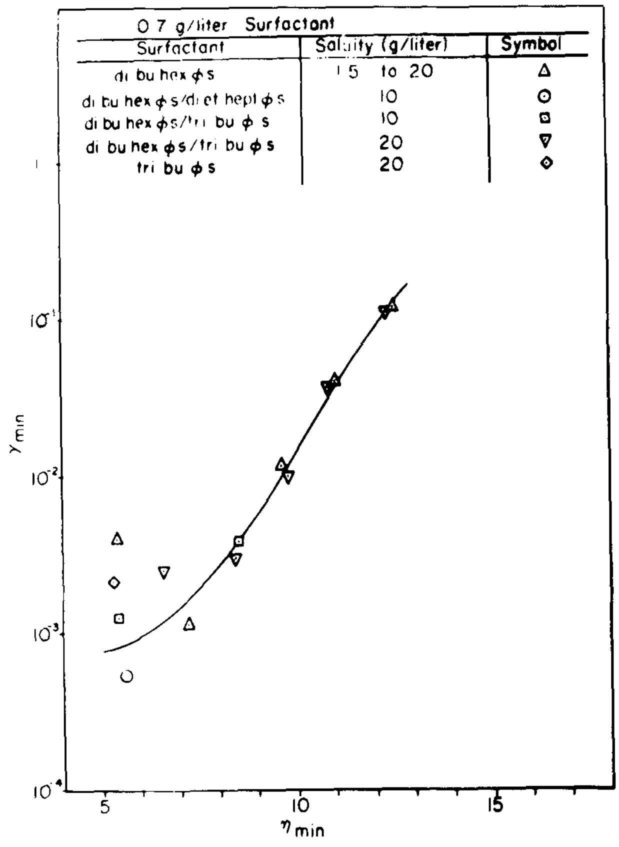

FIG. 11. Alkane preference curve for tri n-alkyl surfactants.

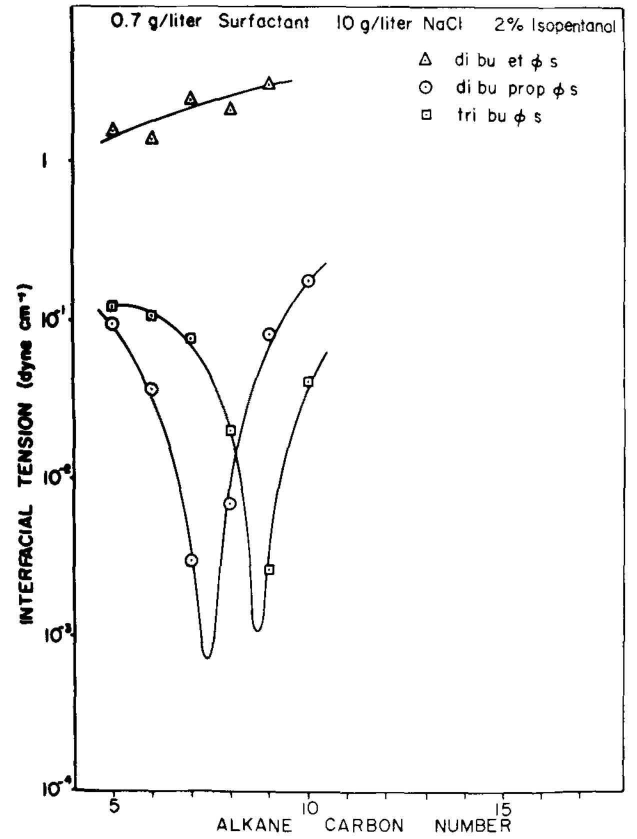

FIG. 12. Some results for surfactants based on 1,4 dibutylbenzene with an additional alkyl group. No low tensions were obtained with the C_{10} alkyl surfactant.

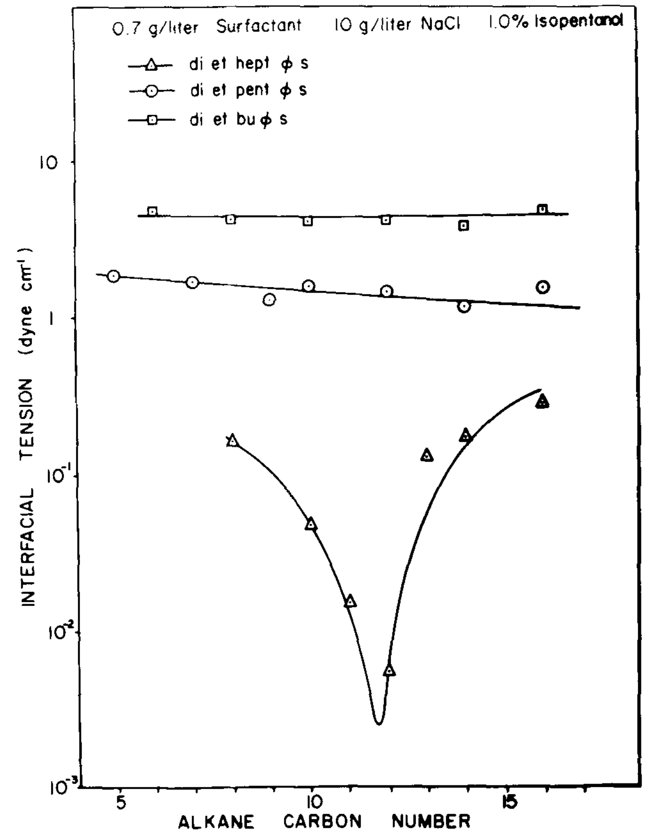

FIG. 13. Alkane scans for another surfactant series, based on diethyl benzene. Again, no low tensions were seen with a total C_{10} alkyl surfactant or below.

obtained, with the lowest ones probably showing up in the middle of the liquid alkane range. Tentatively, we place these o di n-alkyl surfactants in group I, with some obvious reservations because of the paucity of data.

III. Tri n-alkyl compounds

Eight surfactants of this class were synthesized, and they fall into two groups: those based on diethylbenzene and those based on dibutylbenzene. The first group turned out to be rather too low in molecular weight to be very interesting, but we shall say something about them a little later.

Consider first the results for sulfonated dibutylpropylbenzene and tributylbenzene shown in Figure 9. At 10 g/liter salinity both surfactants have n_{min} values below 5. The interfacial tensions can be improved by increasing the salinity, as is shown by the other curves in Figure 9, but only the tributyl surfactant can be brought to an on-scale n_{min} value before it precipitates and the low tensions begin to be lost.

More can be learned from the alkane scans for the dibutylhexyl surfactant at various salinities (Fig. 10). This family of curves looks similar to those for the p-dihexyl surfactant in Figure 4, but the causes are not the same. In the present instance, only the somewhat higher γ_{min} value for 1.5 g/liter NaCl can be attributed to an optimal salinity effect and here it is because 1.5 g/liter is too low a salinity. Indeed, 1.5 g/liter would be too low a salinity for optimum performance with most, if not all, of the surfactants examined.

If we combine the n_{min}/γ_{min} values from Figure 10 with those from Figure 9 and for a variety of mixtures for which, to save space, the alkane scans are not shown, one can obtain the preference curve shown in Figure 11. The shape of the symbols on this curve indicates the surfactant and salinity to which they refer. Considering the approximations (via interpolation) to obtain γ_{min} and n_{min}, the scatter of points on this curve is very small. It is very definitely of group II, meaning that these surfactants are of limited usefulness for giving low tensions against alkanes.

DISCUSSION

I. Limitations on Molecular Weight

There are several surfactants listed in Table I for which the results have not been given. This is because they do not give low tensions under the conditions used. Since they are all the lower molecular weight members of their particular series, it seems reasonable to assume that no low tension was observed simply because n_{min} was not shifted up to an on-scale value.

One way of doing this is to add a relatively high molecular weight alcohol to the solution (1). Isopentanol, for instance, can give extremely large shifts in n_{min} when added in amounts up to 2 vol % (16). This can help to produce low interfacial tensions using surfactants which are superficially ineffective for that purpose. It is instructive, therefore, to examine the results in Figure 12, where isopentanol has been added to solutions containing some of the trialkyl surfactants. Compare this with Figure 13, which shows some alkane scans for surfactants based on diethylbenzene in the presence of isopentanol.

On both these figures, the C_{11}-alkyl or above surfactants show moderate to good low tension performance, whereas the C_{10}-alkyl or below do not. In each case the difference is orders of magnitude. We were never able, by verying conditions such as alcohol concentration, surfactant concentration and salinity, to achieve an interfacial tension below 10^{-1} dyne cm^{-1} with any C_{10}-alkyl surfactant regardless of the deployment of alkyl groups.

These results cannot be regarded as absolutely con-

TABLE II

Hydrocarbon sulfonated	n_{min} at 10 g/liter NaCl	K	Preference group
p Diheptylbenzene[a]	>17	1	II
5-(p Butylphenyl) decane	12	2.5	II
Dibutylhexylbenzene	11	1.5	II
5-(Diethylphenyl) decane	11	5	II
6-Phenyltetradecane	7.5	infinite	III
5-(p Ethylphenyl) dodecane	7	6	I
o Diheptylbenzene	6.5	infinite	I[b]
6-(Dimethylphenyl) dodecane	< 5	12	I

clusive. Nevertheless, one thing is clear; it is at least very difficult, and it may be impossible, to obtain a low interfacial tension with an alkylbenzenesulfonate which does not have at least 11 alkyl carbon atoms. To the present, this conclusion carries over to each structural group we have examined. If it holds up, it would place a lower molecular weight limit of 334 on useful sodium sulfonates for low interfacial tension applications.

II. Molecular Weight Efficiency and Alkane Preference

It was pointed out above that the finished surfactants are sometimes monoisomeric and sometimes not, but it is always possible to identify a most common isomer by assuming that the sulfonate group will enter preferentially in the position of minimum steric hindrance.

Thus, in a monoalkylbenzene, sulfonation is exclusively para to the alkyl chain (2). In a p-dialkylbenzene the SO_3 group goes preferentially ortho to the shorter chain and in a m-dialkylbenzene it goes ortho to the shorter chain. With a 1, 2, 4 trialkylbenzene, sulfonation will tend not to occur in the 3-position, where there is hindrance from two substituents, but ortho to the shorter of the 1 or 4 substituents. When all of the alkyl group are close together in chain length, there is little tendency for one isomer to be preferred over another. However, under these circumstances, the ratio discussed below is similar for all isomers.

Once the most common isomer is decided, we may proceed as follows. Any alkyl group ortho to the SO_3 must have an interfering effect on sulfonate-water interactions when the molecule is used as a surfactant. For this reason such a group is called the *interfering* group. The longest of the remaining alkyl group carbons is the *major* hydrophobic group. The ratio

$$K = \frac{\text{no. of major group carbons}}{\text{no. of interfering group carbons}}$$

is a quantity which varies from 1 for certain p-dialkyl surfactants (see above) to infinity for surfactants with no interfering group (2).

Table II lists the K and n_{min} values for a series of surfactants, all of the same molecular weight (14 alkyl carbons), together with the preference group to which they belong.

The first four compounds in the list are group II and they have the four lowest values of K and the four highest values of n_{min}. The remaining surfactants, with lower n_{min} and higher K values are group I or group III in preference . The same trends can be observed for surfactants of other molecular weights.

It is clear from these results that the major/interfering group balance is important in determining the overall low tension behavior of a surfactant. As K decreases, the overall trend is for molecular weight efficiency to improve and for the preference to shift towards lower molecular weight alkanes. The detailed arrangement of the alkyl groups around the benzene ring is less important, apparently, although it does have some influence. For instance, the presence of the o-dialkyl surfactants in group I suggests that a sufficiently long group meta to the SO_3 can exert some interfering effect.

The surfactants examined here and previously (1-3) most probably scan the full range of useful alkylbenzenesulfonates for low interfacial tensions, in terms of their molecular weight ranges and K values. It is striking that they can be divided into only three groups, with all surfactants of a particular group having similar preferred alkane ranges. This may in part be due to the necessity of employing surfactant mixtures when determining the alkane preferences, which probably means that an average behavior is being observed. More subtle effects of structural variations might be demonstrated if the n_o values for single surfactants were determined. This is difficult, however, and we have not attempted to do so.

It is obvious from the observed differences in alkane preference that surfactants must be chosen carefully for particular low tension applications. Group II (K < 5) surfactants are likely to work best with oils whose equivalent alkane carbon number (EACN) is less than five. For oils having EACNs in the range 5 to 11, group I surfactants look most promising and for higher EACNs, group III surfactants (no interfering group) should work best.

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