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Surfactants for Producing Low Interfacial Tensions: II. Linear Alkylbenzenesulfonates with Additional Alkyl Substituents

PETER H. DOE, MAHMOUD EL-EMARY, WILLIAM H. WADE, Department of Chemistry, and
ROBERT S. SCHECHTER, Department of Petroleum Engineering, University of Texas
at Austin, Austin, Texas 78712

ABSTRACT

The synthesis and low interfacial tension behavior of a variety of di- and trialkylbenzenesulfonates are described. The benzene ring carries one major alkyl substituent, consisting of a linear chain eight to sixteen carbon atoms long, and one or two additional methyl, ethyl, propyl, i-propyl, butyl, or t-butyl groups. The addition of these extra groups causes the low interfacial tensions to shift to higher molecular weight alkanes when compared to the parent linear alkylbenzenesulfonate. Surfactants in these structural classes can give very low interfacial tensions against those alkanes which best model the behavior of crude oils, but this is influenced by the number and type of the short alkyl substituents. These surfactant structures are more attractive from the point of view of tertiary oil recovery than linear alkylbenzenesulfonates.

INTRODUCTION

Surfactants which will, in the presence of electrolyte, give very low oil-water interfacial tensions have recently been attracting much attention because they may be of great usefulness for enhanced oil recovery. The materials which have been most studied are various commercial sulfonates (1-5). These can give the desired low tensions, but progress towards a true understanding of the processes involved is hampered by the fact that their structures are invariably not well defined. They are without exception a mixture of molecular species and molecular weights.

In two earlier publications (10,11), we have shown that a monoisomeric sulfonate of high purity can give interfacial tensions as low as these commercial mixtures. This demonstrates that they are not the result of any synergistic effect between competing surfactant species and almost certainly are unrelated to phenomena seen only in impure surfactant systems, such as minima in surface tension-concentration plots.

It has long been known that the low interfacial tension for a given oil-surfactant pair is a very sensitive function of such variables as salt concentration and cosurfactant concentration. The use of the alkane scan, where interfacial tensions are measured against the homologous series of alkanes (5-7), revealed that the low tension, rather than being lost, actually shifts to different alkanes in a systematic way. The alkane carbon number giving minimum tension has been given the symbol n_{min} (8,9). Oils other than n-alkanes can be included in the discussion by employing their equivalent alkane carbon numbers, or EACNs (6,7).

The previous paper in this series (10) described the low interfacial tension behavior of *linear* alkylbenzenesulfonates (LABS). The reason for starting with these materials was an accidental one — simply that a few monoisomeric sulfonates of that type were made available to us at the beginning of our study. The results which we obtained had some interesting implications which may be summarized briefly.

First, although, under a given set of conditions, n_{min} generally increases with increasing surfactant molecular weight, it is possible to substantially increase n_{min} at a fixed molecular weight simply by shifting the benzene ring of the LABS towards the middle of the alkyl chain (10,11). This opens up the possibility that even higher values of n_{min} can be obtained by altering the molecular structure more dramatically. Thus a given n_{min} value might be achieved with a surfactant of significantly lower molecular weight. This could be of some practical importance since, *for a fixed structure,* the adsorption of a surfactant on oil reservoir rock appears to decrease significantly with decreasing molecular weight (12). The effect of structure on adsorption is unknown but, all else being equal, the lowest molecular weight surfactant which will give the desired low tension performance seems like the best one to try first.

Second, we developed the idea of the hydrocarbon preference curve. The *alkane* preference curve, for instance, is a plot of n_{min} vs. γ_{min}, the interfacial tension value at each minimum, where each pair of n_{min} and γ_{min} values is interpolated from the smooth lines joining experimental interfacial tension measurements on a single *alkane* scan such as one of those in Figure 3. Remember that n_{min} is not a fixed quantity for a given surfactant, but is rather a property of the whole formulation. It can be changed, for instance, by altering the salinity.

When a series of alkane scans for LABSs were studied in this way, we discovered that the value of γ_{min} was dependent only on the value of n_{min} and not on the particular LABS used. Within certain limits of salinity (2.5 to 15 g/liter NaCl) and cosurfactant (alcohol) concentration (up to 2 vol % isopentanol), the n_{min}/γ_{min} plot was very little changed. Outside these limits, the usual tendency was for γ_{min} to increase. Mixtures of LABSs containing up to four surfactant species acted in the same way and gave the same n_{min}/γ_{min} relationship as single surfactants (10).

Now, the best low tension performance obtainable with a given oil/surfactant pair occurs when the minimum in the surfactant's alkane scan (n_{min}) is adjusted, by changing salinity or some other variable, to match the EACN of the oil. If the oil is an alkane, as in the present paper, this rule for optimum performance becomes simply "Adjust n_{min} to match the oil's alkane carbon number." Our investigations to date indicate that this rule does indeed produce the lowest tension, or at least very close to it.

Because of this rule, the preference curve, or n_{min} vs. γ_{min} plot, is a representation of what the *lowest obtainable* interfacial tensions are against each of the alkanes. The remarkable thing about the results for the LABSs was that the preference curve showed a pronounced minimum in γ_{min} for alkane carbon numbers around 12. Interfacial

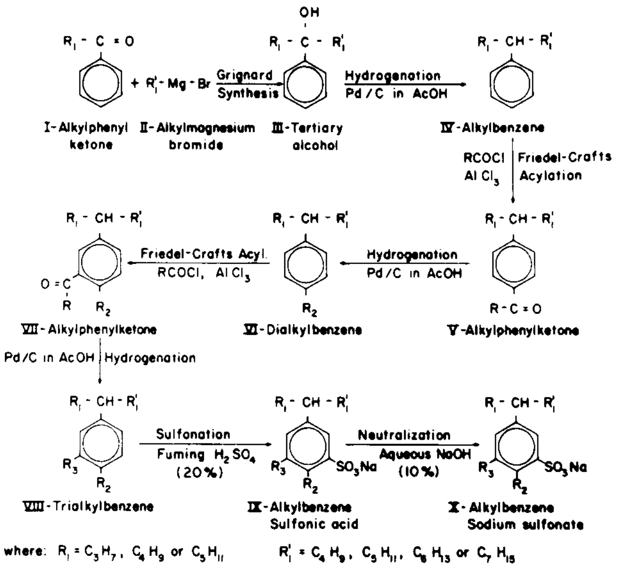

FIG. 1. Synthesis scheme I for di- and trialkylbenzenesulfonates.

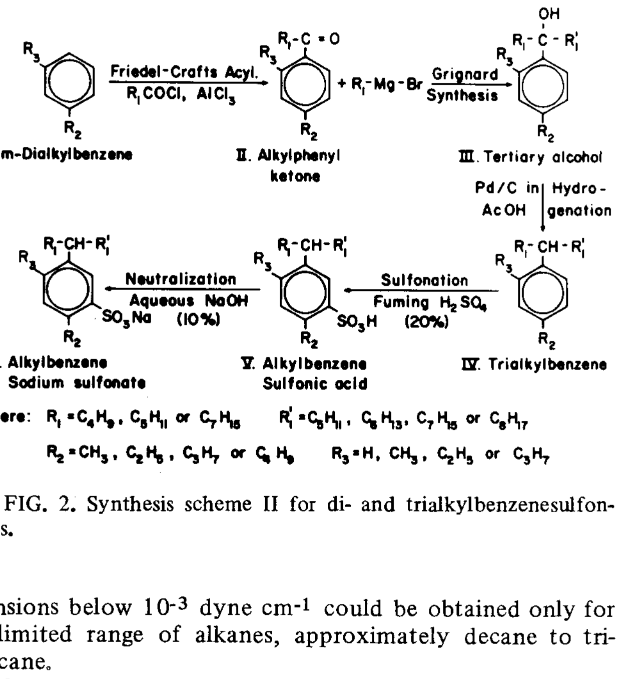

FIG. 2. Synthesis scheme II for di- and trialkylbenzenesulfonates.

tensions below 10^{-3} dyne cm^{-1} could be obtained only for a limited range of alkanes, approximately decane to tridecane.

We take this as indicating that the LABSs *prefer* those alkanes for giving low tension, hence the name "preference curve." The most important thing about the curve is that it represents the minimum low tension behavior of a whole group of surfactants against a whole homologous series of oils. The preference curve thus becomes an extremely compact way of summarizing a good deal of important information about the low tension properties of a group of surfactants.

Since the LABSs preferred EACNs in the range 10 to 13 and since the EACN range of crude oils is generally lower, at 6 to 9 (6), we deduced that LABSs were unlikely to be the best possible type of surfactant for use in surfactant flooding for tertiary oil recovery. The optimum surfactant structures for this purpose would show a minimum in their preference curve at EACNs which corresponded to those of crude oils.

Therefore, in this paper and subsequent ones we are looking for surfactants having properties which differ in two important ways from those of the linear alkylbenzenesulfonates. (a) For a given molecular weight, they will have a higher n_{min}; and (b) their preferred EACN ranges will include the alkanes hexane to nonane, meaning they will give very low tensions against these alkanes.

We start this survey with materials which are very close to LABSs. They are, in fact, linear alkylbenzenesulfaontes having one or two additional short alkyl substituents on the benzene ring. These have similar structures to some petroleum (4,5) and alkyl xylene sulfonates (1-3) used in much oil recovery research, but they contain only two or three molecular species. This allows firm conclusions to be drawn about the effects of specific changes in surfactant structure. We will show that the present structures have promise for oil recovery purposes.

MATERIALS AND EXPERIMENTAL

The surfactants used in this study are linear alkylbenzenesulfonates having from eight to sixteen carbon atoms in the linear chain. One or two additional alkyl substituents of the groups methyl, ethyl, propyl, i-propyl, butyl, or t-butyl have been added to the benzene ring. Two different synthesis schemes have been used and are represented by Figures 1 and 2. The first two steps in Figure 1 produce a linear alkylbenzene, or phenylalkane (structure IV). The details of these stages have been given (10).

Synthesis of Dialkylbenzenes – Scheme 1

A mixture of 0.5 mole of the phenylalkane (IV) and an equimolar amount of the appropriate acyl chloride (RCOCl) was added dropwise to 0.5 mole of aluminum chloride suspended in 300 ml of carbon disulfide. The temperature was maintained below 5 C throughout this addition. The mixture was stirred for 2 hr at room temperature, then allowed to stand overnight. The Friedel-Crafts acylation product was decomposed with ice-cooled dilute hydrochloric acid, extracted with ether, washed with 5% sodium hydroxide solution, and dried over anhydrous magnesium sulfate. The ether was evaporated and the n-alkyl penyl ketone (V) was distilled under reduced pressure. The structures of the ketones were verified by checks on their physical and spectroscopic properties.

The ketones were reduced to the corresponding dialkylbenzenes using a catalyst of 5% palladium over powdered charcoal in acetic acid solvent. The hydrocarbons were purified by fractional distillation under reduced pressure, passing through a silica gel column and further distillation (10).

The IR and mass spectra of these dialkylbenzenes showed the total absence of the parent ketones. Proton nuclear magnetic resonance (NMR) indicated that the second alkyl group is predominately para to the initial alkyl chain.

Scheme 2

An alternative approach was used for certain of the dialkylbenzenes (Fig. 2). This was through the Friedel-Crafts acylation of toluene, i-propylbenzene or t-butylbenzene with octanoyl chloride in the presence of aluminum chloride catalyst, as described above. The resulting n-alkyl phenyl ketones were reacted with an equimolecular amount of n-alkyl magnesium bromide. Reduction of the resulting tertiary alcohols with 5% Pd over charcoal yielded the desired dialkylbenzenes.

Some physical properties of the dialkylbenzenes are given in the first part of Table I.

Synthesis of Trialkylbenzenes – Scheme 1

Further acylation of some of the dialkylbenzenes (VI, Fig. 1), followed by reduction of the resulting alkyl phenyl

TABLE I

List of Hydrocarbons Synthesized, Giving Physical Properties

Alkylbenzene and abbreviation	Alkyl groups				Distillation		Refractive index at 22 C	Mass of molecular ion	Synthesis scheme
	R_1	R_1'	R_2	R_3	Boiling point (°C)	Pressure (mm Hg)			
5(p methyl phenyl) dodecane 5(p me ϕ) C_{12}	C_4	C_7	C_1	H	103-104	0.04	1.4825	260	II
5(p ethyl phenyl) dodecane 5(p et ϕ) C_{12}	C_4	C_7	C_2	H	114-116	0.05	1.4840	274	I
5(p i-propyl phenyl) dodecane 5(p i-prop ϕ) C_{12}	C_4	C_7	C_3	H	116-118	0.04	1.4825	288	II
6(p t-butyl phenyl) dodecane 6(p t bu ϕ) C_{12}	C_5	C_6	C_4	H	118-119	0.04	1.4811	302	II
6(p n-butyl phenyl) dodecane 6(p bu ϕ) C_{12}	C_5	C_6	C_4	H	121-122	0.04	1.4810	302	I
8(p methyl phenyl) hexadecane 8(p me ϕ) C_{16}	C_7	C_8	C_1	H	133-134	0.04	1.4800	316	II
4(p n-butyl phenyl) octane 4(p bu ϕ) C_8	C_3	C_4	C_4	H	100-102	0.05	1.4870	246	II
4(p n-butyl phenyl) nonane 4(p bu ϕ) C_9	C_3	C_5	C_4	H	123-125	0.05	1.4830	260	II
5(p n-butyl phenyl) decane 5(p bu ϕ) C_{10}	C_4	C_5	C_4	H	134-137	0.05	1.4820	274	II
5(2,4 dimethyl phenyl) dodecane 5(di me ϕ) C_{12}	C_4	C_7	C_1	C_1	110-111	0.05	1.4875	274	II
6(2,4 diethyl phenyl) dodecane 6(di et ϕ) C_{12}	C_5	C_6	C_2	C_2	111-112	0.04	1.4898	302	II
6(2,4 di isopropyl phenyl) dodecane 6(di i-prop ϕ) C_{12}	C_5	C_6	C_3	C_3	116-117	0.03	1.4820	330	II
4(3,4 diethyl phenyl) octane 4(3,4 di et ϕ) C_8	C_3	C_4	C_2	C_2	97-99	0.05	1.4905	246	I
4(3,4 di n-propyl phenyl) octane 4(di prop ϕ) C_8	C_3	C_4	C_3	C_3	107-109	0.05	1.4880	274	I
4(3,4 diethyl phenyl) nonane 4(di et ϕ) C_9	C_3	C_5	C_2	C_2	110-112	0.05	1.4890	260	I
4(3,4 di n-propyl phenyl) nonane 4(di prop ϕ) C_9	C_3	C_5	C_3	C_3	119-120	0.05	1.4865	288	I
5(3,4 diethyl phenyl) decane 5(di et ϕ) C_{10}	C_4	C_5	C_2	C_2	128-130	0.15	1.4885	274	I
5(3,4 di n-propyl phenyl) decane 5(di prop ϕ) C_{10}	C_4	C_5	C_3	C_3	135-138	0.025	1.4860	302	I

ketones (VII) yielded trialkylbenzenes (VIII). Steric hindrance by the long alkyl chain causes the third alkyl group to substitute predominately ortho to the short alkyl chain.

Scheme 2

The second synthetic route to trialkylbenzenes is identical to the second route to dialkylbenzenes, except that the starting material is a m-dialkylbenzene.

Properties of the trialkylbenzenes are given in Table I.

Sulfonation

Fifteen grams of the prepared alkylbenzene were sulfonated with 20% fuming sulfuric acid at 40 to 50 C for 2 hr. The sulfonation product was decomposed with ice-cooled dilute hydrochloric acid and then isolated, as previously reported (10), as the corresponding sodium sulfonate.

An alternative technique must be used for processing some of the more soluble sulfonates. The sulfonation product was decomposed with 400 ml of 10% sodium hydroxide solution. The pH was then adjusted to 7 using dilute sulfuric acid. Four hundred milliliters each of isopropyl alcohol and n-pentane were added to the mixture, which was stirred vigorously for 15 min. Three layers developed – a top layer containing unreacted hydrocarbon, a middle layer containing the sodium sulfonate in aqueous alcohol, and a bottom aqueous layer containing the inorganic salts. The sulfonate solution was diluted with 3 liters of isopropyl alcohol and was left to stand overnight. The suspended inorganic salt was filtered off and the sulfonate solution was decolorized with charcoal. The alcohol was removed by vacuum distillation and the remaining alkylbenzene sodium sulfonate was dried in a vacuum oven at 80 C over anhydrous phosphorous pentoxide. The sulfonation of alkylbenzenes has been discussed by several authors (13-15).

Sulfonation is not a stereospecific reaction and hence isomers are present in the finished surfactants. Which one predominantes is determined by the amount of steric hindrance caused by the substituent alkyl groups. We would expect this hindrance to be greater for sulfonation ortho to the linear alkyl chain and hence the product will be predominantly that shown in Figures 1 and 2, where the SO_3 group enters meta to the main chain. It is difficult to measure precisely the amount of each isomer which is present. A useful technique for getting an estimate is carbon-13 NMR, which can separately detect each aromatic carbon atom in these di- and trialkylbenzenesulfonates. If two isomers are present, there are twice as many lines in the aromatic part of the ^{13}C spectrum.

Spectra were collected for a selection of trialkylbenzenesulfonates. All contained substantial amounts of the ortho isomer, probably 15-20%, and this proportion did not vary significantly with the relative lengths of the major and

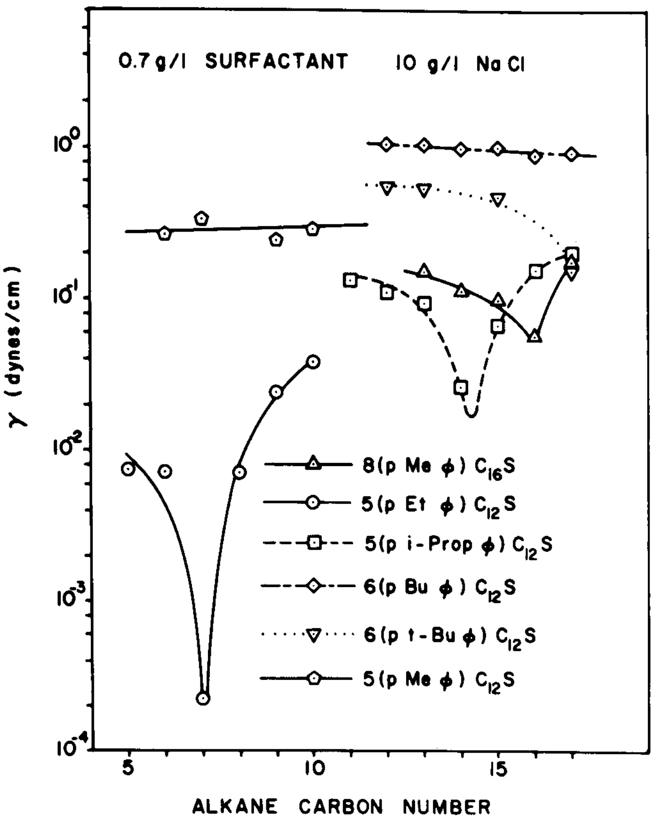

FIG. 3. Alkane scans for the dialkyl surfactants with a C_{12} or C_{16} major chain.

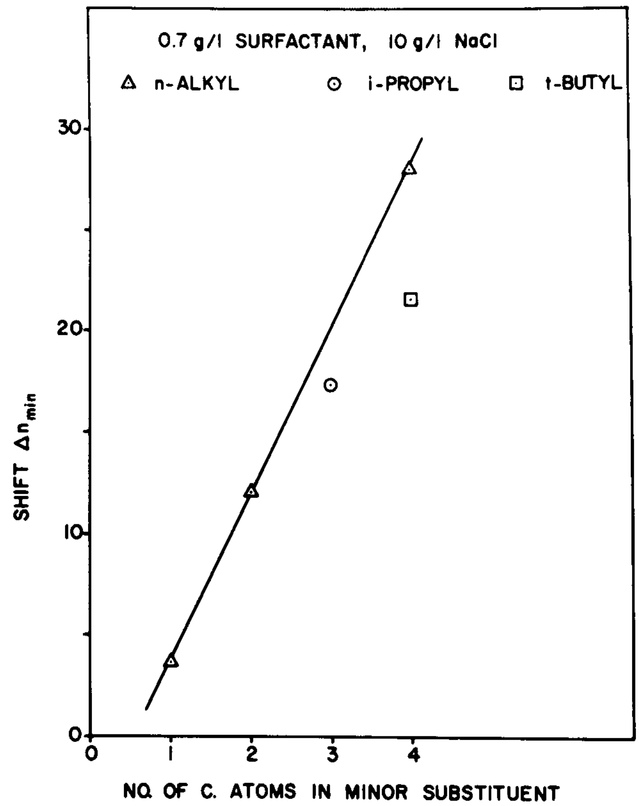

FIG. 4. The shifts in n_{min} caused by the addition of a minor alkyl group para to the major chain.

minor substituents. Apparently the sulfonate group is so large that any short substituent causes a good deal of steric hindrance during sulfonation. These results are in contrast to those for the LABSs (10), where no ortho isomer could be detected.

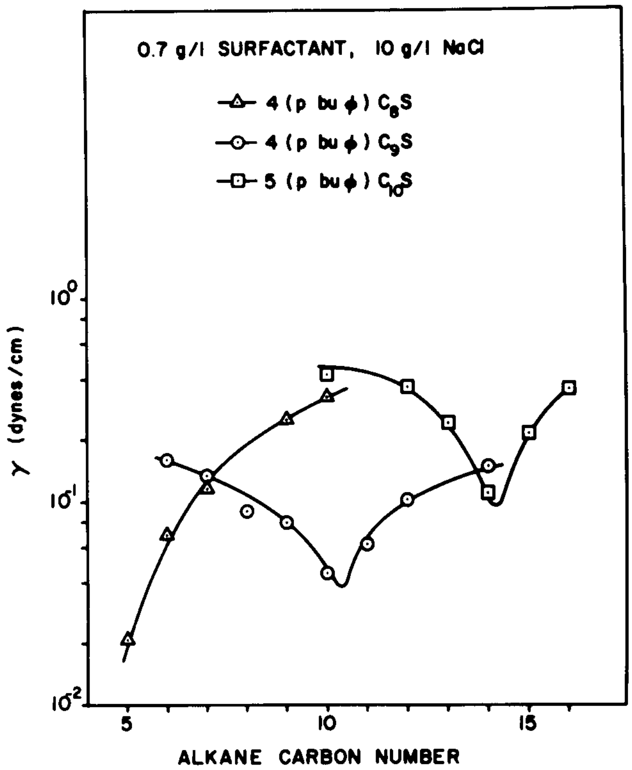

FIG. 5. Alkane scans for dialkyl surfactants with a C_8, C_9, or C_{10} main chain and a p butyl minor chain.

Our final comment on the purity of these surfactants, then, is that the dialkyl compounds contain two molecular species and the trialkyl ones will contain three. Probably the bias is 4 to 1 in favor of those isomers where the SO_3 group is meta to the major alkyl chain. The hydrocarbons from which they were made were monoisomeric by ^{13}C NMR.

Cooper and Paul (16,17) have described a technique for putting an SO_3 group on an alkylbenzene in a stereospecific position. Their method is severly limited, however, by a lack of availability of suitable starting materials.

The purity of the finished surfactants was checked by titration with Hyamine 1622 (Rohm & Haas Co., Philadelphia, PA) (18). All surfactants were ca. 99% sodium sulfonate according to this analysis. The remaining 1% is presumably unreacted hydrocarbon and sodium sulfate.

For the work which follows, interfacial tensions were measured using the spinning drop technique, which has been fully described elsewhere (19). All experiments were conducted at 26 C without prior equilibration of the oil and aqueous phases. The alkanes used were 99 mole % pure as received and were not specially treated before use. A standard surfactant concentration of 0.7 g/liter and a standard NaCl concentration of 10 g/liter were adopted for most comparisons between surfactants. The justification for this has been given earlier (10,11).

RESULTS AND DISCUSSION

Table I contains a complete list of compounds synthesized, together with the abbreviations we shall be using. Cross-reference between there and Figures 1 and 2 will help in understanding what follows.

I. Dialkyl Surfactants — Effect of Structure on n_{min}.

The dialkylbenzenesulfonates fall into two groups: (a)

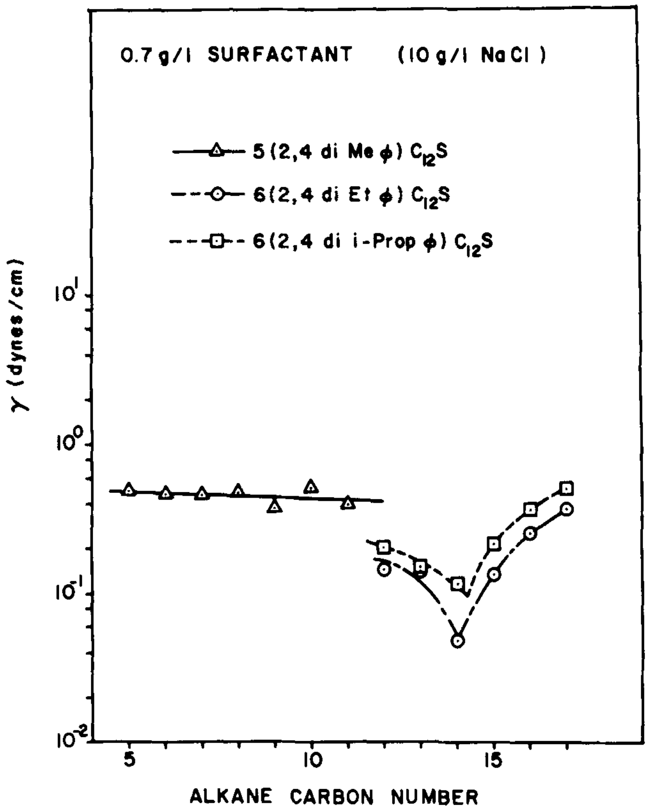

FIG. 6. Alkane scans for trialkyl surfactants with C_{12} major chains.

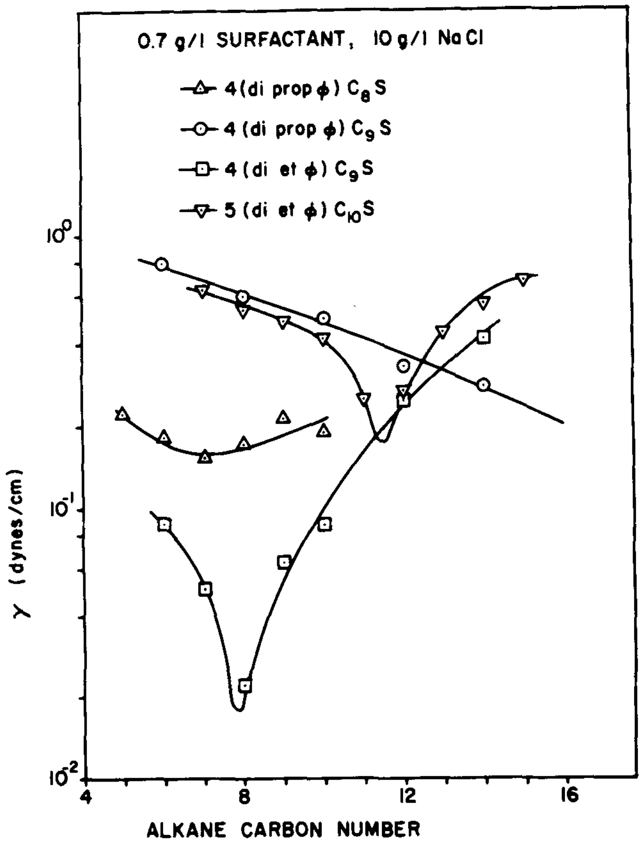

FIG. 7. Alkane scans for a selection of the trialkyl surfactants with C_8 to C_{10} major chains.

those having a C_{12} or C_{16} chain, where the properties of the parent LABS have been investigated; and (b) those based on a lower molecular weight LABS, having a C_8 to C_{10} linear chain (see Table I).

The alkane scans for the first group, under our usual standard conditions, are shown in Figure 3. The minimum position is off scale at the low carbon number end for the p methyl C_{12} surfactant, shifts on scale for the p et C_{12}, p ipropyl C_{12}, and p me C_{16} surfactants, and goes off scale at the other end for the two p bu C_{12} materials. The overall trend, as usual (4,5,8,10,11) is for n_{min} to increase with increasing surfactant molecular weight.

Since the n_{min} values for the parent LABSs have either been measured (11) or can be estimated by extrapolation (9) we can calculate how much n_{min} has been increased by the addition of the para substituents. The various shifts in n_{min} are plotted in Figure 4. The values for butyl and t-butyl substituents were obtained by comparing results at salt concentrations below 10 g/liter, when the surfactants containing those groups will give on-scale minima. Two things are revealed: (a) The shift in n_{min} for an n-alkyl group increases approximately linearly with the number of carbon atoms it contains, except that a methyl group has a disproportionately small effect. This may be because the first carbon atom is held close to the benzene ring, with its effect on interfacial tension being masked by the adjacent sulfonate group. (b) Branched alkyl groups have a smaller effect on n_{min} than n-alkyl groups containing the same number of carbon atoms. The i-propyl and t-butyl groups can be regarded as ethyl groups with dependent methyls. The results indicate that these "mid-chain" methyls have a shift value about three alkane carbon numbers less than an extra carbon atom added to the *end* of a methyl, ethyl, or propyl chain. Again, this could be because they are partly buried close to the benzene ring and cannot make their full presence felt.

The shift in n_{min} for addition of a normal butyl group

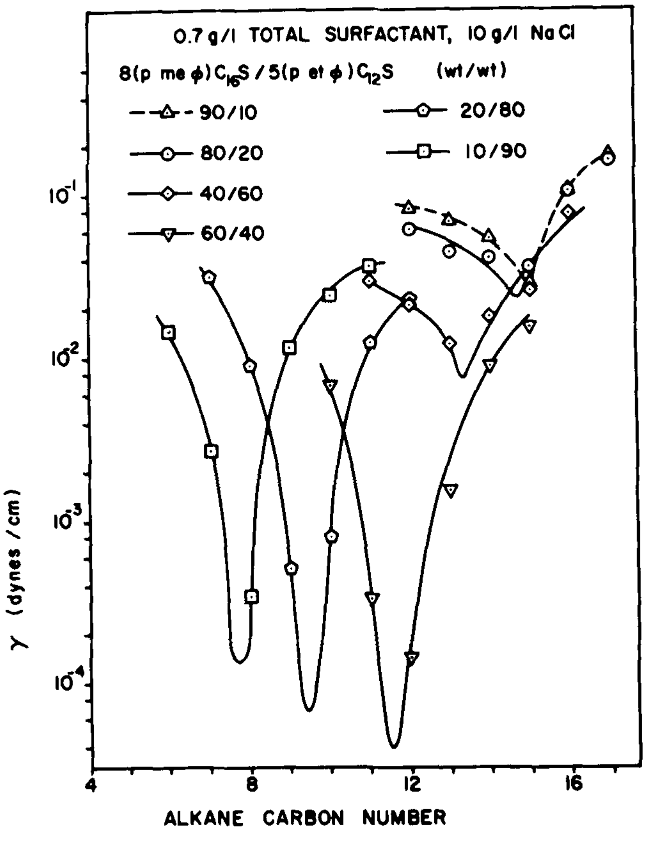

FIG. 8. Alkane scans for mixtures of 8(pmeϕ)$C_{16}S$ with 5(p et ϕ)$C_{12}S$.

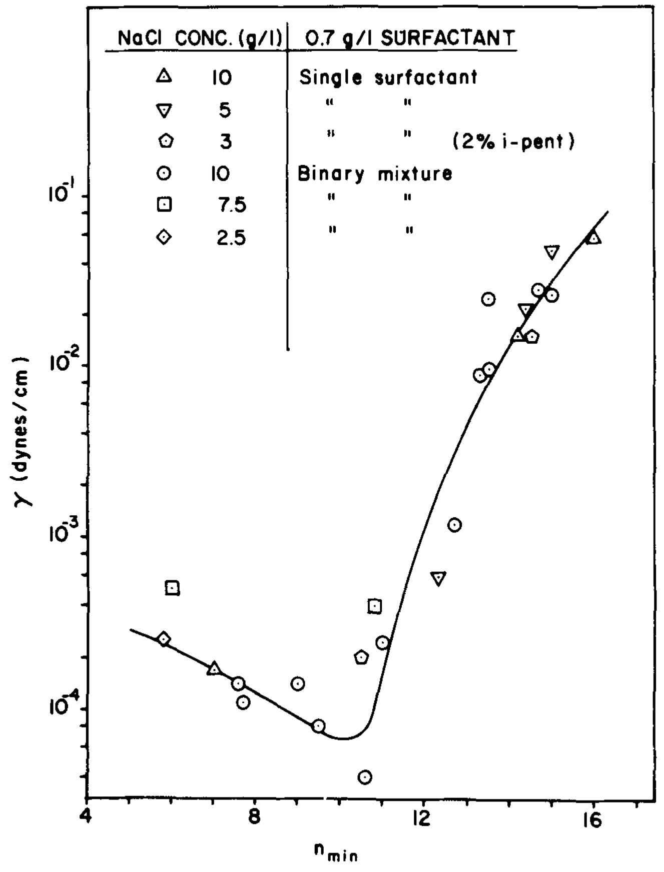

FIG. 9. Alkane preference curve; dialkylbenzenesulfonates with a p methyl, p ethyl, or p i-propyl short chain.

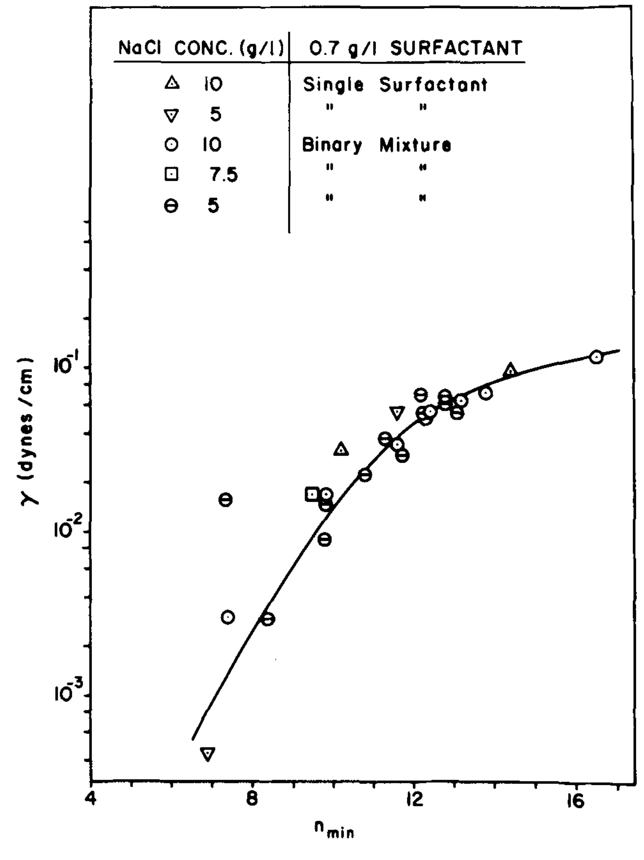

FIG. 10. Alkane preference curve for dialkyl surfactants with a p butyl or p t-butyl substituent.

is larger than the effect of adding four carbon atoms to the main alkyl group (10). Hence the p butyl C_{12} compound has an n_{min} value substantially higher than the on-scale $8\phi C_{16}S$. This suggests that the lower molecular weight group of compounds with a p n-butyl group should give on-scale minima. They are compared in Figure 5, where we can see that they do, although the C_8 compound is a little too low in molecular weight to work successfully at 10 g/liter NaCl. We have thus produced an on-scale minimum with a surfactant having only 13 alkyl carbons, as compared with the minimum of 14 required for a LABS (10) under the same conditions.

II. Trialkyl Surfactants – Effect of Structure on n_{min}

These surfactants can again be divided into two groups, based on the lengths of their main alkyl chains (Table I). It should be noted, however, that the two groups were synthesized by different routes and hence the relative positions of their alkyl groups is not the same.

Figure 6 shows the alkane scans for the high molecular weight group. Two of them give on-scale minima, and the di-methyl C_{12} surfactant is off scale at the bottom end. Comparison of these materials with the corresponding dialkyl surfactants of Figure 3 reveals that the n_{min} shift for the second ethyl group is seven carbon numbers, compared with ten for the first, while the second i-propyl group does not change n_{min}, although the interfacial tension is higher. Previous results (10) indicate that a larger shift in n_{min} may be achieved by increasing the lengths of the long chain. Hence we would expect these tri-substituted compounds to require a *higher* molecular weight than the di-substituted ones just discussed in order to produce the same n_{min} value.

When we examine some results from the lower molecular weight group (Fig. 7), we see that the diethyl C_9 surfactant is the lowest molecular weight material which gave an on-scale minimum. This again has 13 alkyl carbon atoms, making it more efficient than a LABS, but its n_{min} value is two less than the corresponding p butyl C_9 surfactant (Fig. 5). Thus, a butyl group has a bigger effect on n_{min} than two ethyl groups, and similarly an ethyl group shifts n_{min} more than two methyls.

This suggests that maximum molecular weight efficiency is obtained with dialkylbenzenesulfonates. We saw earlier that normal chains are more efficient than branched ones. The possibilities raised by these points will be pursued in a subsequent publication.

III. The Alkane Preference Curves

Most of the interfacial tensions in Figure 7 are rather high. We demonstrated in part one of this series of papers that a high minimum tension is often a result of the fact that surfactants show a preference for certain alkanes. This means that when we optimize conditions to get the lowest tension possible against each alkane in turn, these minimum interfacial tensions may vary across the alkane (or other) series by orders of magnitude (10).

To obtain a preference curve we must simply plot n_{min} vs. the minimum tension for all available alkane scans. This requires scans having minima in many positions across the alkane series, otherwise the preference curve will only be partly defined. In other words, we need to vary n_{min} at will. As pointed out in the introduction, the preference curve is the same for single surfactants and for mixtures of surfactants of similar structure. The most convenient way to obtain a preference curve is thus to make a series of mixtures of a low n_{min} surfactant with a high n_{min} surfactant. This allows n_{min} to vary between those two limits without changing any other system variables, such as NaCl concentration, which might shift the preference curve. A

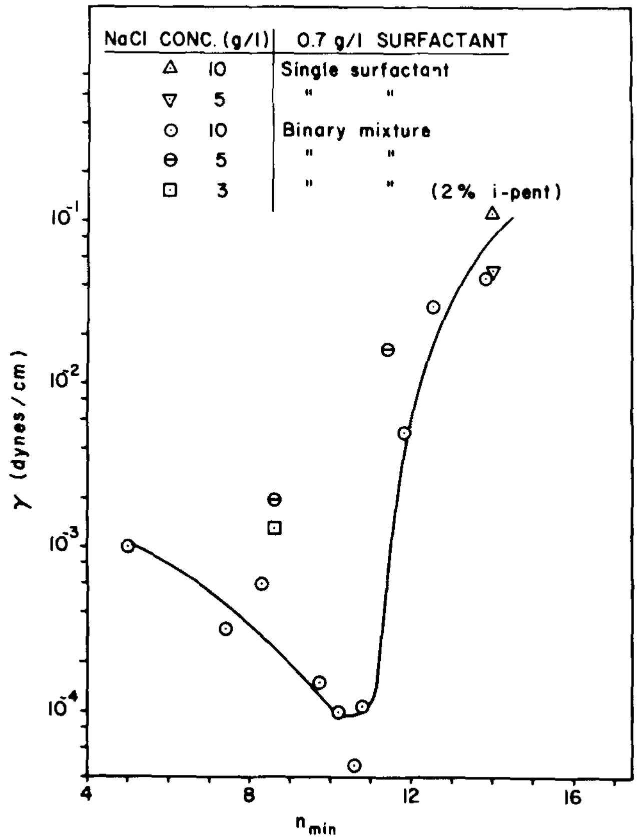

FIG. 11. Alkane preference curve for trialkyl sulfonates with C_{12} major chain.

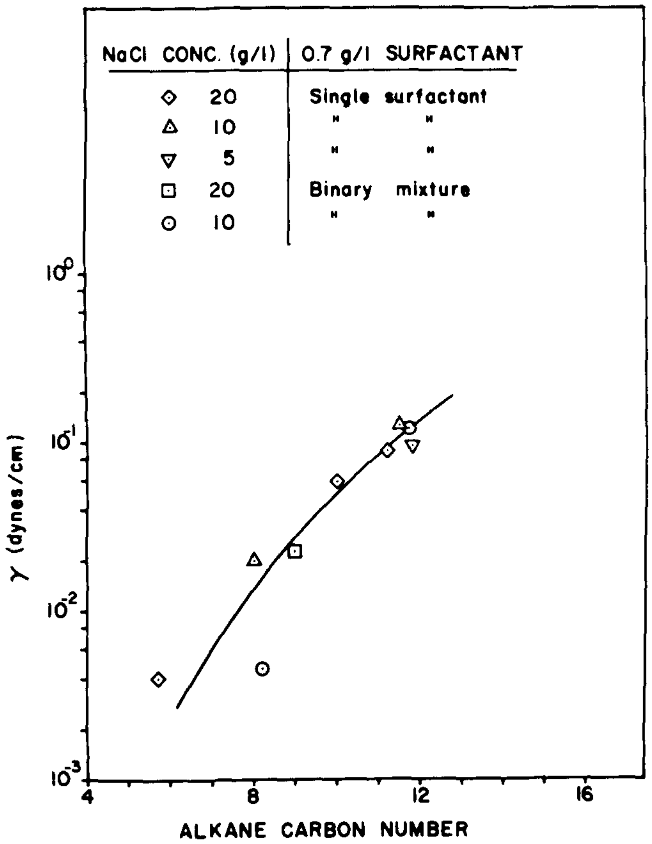

FIG. 12. Alkane preference curve for trialkyl surfactants with C_8, C_9, or C_{10} major chain.

typical set of scans for one series of mixtures is shown in Figure 8.

When we assemble the preference data for the dialkylbenzenesulfonates, we find that they fall very distinctly into two groups, indicating two kinds of alkane preference. In the first group (Fig. 9) are the surfactants with a C_{12} or C_{16} major chain and a minor chain of C_3 or less. The second group (Fig. 10) includes all those surfactants with a p butyl or p t-butyl substituent. Clearly, except at the extreme ends of the liquid alkane range, the first group are giving much lower interfacial tensions.

Intriguingly, the preference data for the trialkylbenzenesulfonates divides along similar lines. The first group here contains the three surfactants with a C_{12} major substituent and the second group those with C_8, C_9, or C_{10} major chains. The preference data are shown, respectively, in Figures 11 and 12.

All four of these preference curves include results for single surfactants and for binary mixtures. They also use results from runs conducted at more than one salinity. In each case, the mixture and pure surfactant data correspond within experimental error. Five grams per liter sodium chloride is too low a concentration for optimum performance with the trialkyl group one surfactants, hence the points for 5 g/liter salt on Figure 11 lie above the preference line drawn. Otherwise, the preference curves are not significantly shifted by these variations in salt concentration. We believe that the curves drawn represent the optimum low tension behavior for the surfactant structures they represent, making them useful in choosing surfactants for particular low tension applications.

Over most of the alkane range there is an order of magnitude or more difference in interfacial tension between a Group one and a Group two surfactant. This is much larger than the scatter in the results within each group. Hence, there can be no doubt that two distinct types of behavior are being observed. Some of the observed scatter is due to the difficulty of accurately interpolating the minimum tension from an experimental alkane scan. Some of it is undoubtedly due to real differences in performance between the surfactants in a particular group. What the preference curves tell us is that these differences are small compared to the gross differences that distinguish the two groups. In other words, in a practical low tension application, ignoring any considerations other than interfacial tension, any surfactant formulation of a given group will, at the same n_{min}, perform almost the same as any other formulation. The criteria which decide which will be used are likely to be other than their absolute optimum in low tension behavior, such as solubility, adsorption characteristics, or salt tolerance.

With the preference curves represented in Figures 9 to 12, three types have been observed in all.

(a) The Group one (Figs. 9 and 11), or broad molecular weight selective, which show tensions below 10^{-3} dyne cm^{-1} for all alkanes from pentane to dodecane. Group one surfactants prefere EACNs between 5 and 12.

(b) Group two (Figs. 10 and 12). These surfactants are generally bad performers, but show some preference for the lowest alkanes – EACNs from 5 to 7, perhaps. They are low molecular weight selective.

(c) The linear alkylbenzenesulfonates (10), which gave tensions below 10^{-3} dyne cm^{-1} only for the alkanes decane to tridecane. Their preferred EACNs are 10 to 13, making them high molecular weight selective.

The trend as we go from LABS to Group one to Group two is for the number of minor chain alkyl carbons to increase relative to the number of major chain carbons. This is probably the major factor determining a surfactant's alkane preference, but it is not the whole story. Notice that the diethyl C_{12} sulfonate is a Group one surfactant, whereas the p butyl C_{12} is Group two. Thus the single C_4

chain, which is mostly ortho to the sulfonate group, has a larger effect on the alkane preference than the two C_2 chains, only one of which can be ortho to the sulfonate. This could well be because the longer chain interferes more drastically with the sulfonate-water interactions.

Notice also that the butyl group increases n_{mins}, more than the two ethyl groups. It is dangerous to draw conclusions from such limited information, but it is possible that the two observations – an increase in n_{min} at a fixed surfactant molecular weight and a decrease in preferred EACN – are related. Thus the idea advanced in the introduction may be of very limited applicability. Perhaps we cannot increase n_{mins}, by more than a small amount by structural modifications at a fixed molecular weight, without losing the low tension performance in the desired EACN range. This idea will be followed up in subsequent publications.

The results described above and earlier (11) have implications for the selection of a surfactant for tertiary oil recovery. Since crude oils usually have EACNs in the range from 6 to 9 (6), we have suggested (10) that surfactants which give low tensions against the alkanes hexane to nonane are likely to give the best performance against a crude oil. This means a group one surfactant – an ABS with one or two minor alkyl chains and a relatively long major chain. Petroleum (4,5) and xylene (1-3) sulfonates fall into this class and they do give low tensions against crude oils. Interestingly, our present results indicate that a dialkyl surfactant gives lower tensions over much of the alkane range. So far as we are aware, no such material is being used commercially.

We have, therefore, in this paper, identified some alkylbenzenesulfonate structures which are very good for obtaining ultra-low interfacial tensions and have perhaps found a structure which is better than those of currently used commercial surfactants. We have, of course, by no means exhausted the possible structural variations, some of which might prove beneficial. For this reason, work is currently in progress using surfactants which do not have the basic linear alkylbenzene structure of the materials reported on so far.

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