

Some Deterasive Properties of Model Straight Chain Sodium Alkylbenzenesulfonates¹

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Abstract

Model long chain sodium ortho and para alkylbenzenesulfonates having primary, secondary and tertiary carbon atoms attached to the phenyl group have been evaluated for foam, wetting and detergency. The data indicate that the surface active properties of these three classes of compounds which are primarily linear in structure are dependent upon sulfonate position, phenyl position and chain length. Each of these factors contributes to performance. Ortho sulfonates are better wetting agents than para sulfonates but the para compounds generally foam better and appear to have superior detergency properties than their respective ortho isomers. Ortho sulfonate in a detergent composition may have a greater influence on surface active properties than had been heretofore recognized.

Introduction

COMMERCIAL SODIUM (tetrapropylene) benzenesulfonate (TPBS) is prepared by treating benzene in the presence of a Friedel Crafts catalyst with polypropylene, sulfonating the alkylated product and neutralizing the sulfonic acid mixture with sodium hydroxide. The alkylated product from which the sulfonate is derived is a mixture of isomeric monoalkylbenzenes; sulfonation, although producing a useful product, adds to the complexity of this mixture. The side chain structure of these alkylates are highly branched, averaging about twelve to thirteen carbons in number. For many years the sulfonation product has been considered the ideal surfactant because of its low price, its nontoxicity, and its ability to clean and to produce abundant suds. A few years ago, difficulties and complaints attributed to the use of synthetic detergents began to arise. Large volumes of suds began to appear on streams and it was feared that water pollution would become a serious problem unless steps were taken to control the types of compounds that were entering local water supplies. It was recognized that these highly branched structures were only partially degradable by bacteria in even the most highly efficient sewage disposal systems; but that if the alkyl part of the molecule was of linear rather than of branch chain configuration, then the molecule became highly susceptible to decomposition by bacteria. To overcome this biodegradation problem, it was proposed to prepare a linear alkylbenzene; the detergent industry is currently being supplied with this type of product derived from materials such as cracked waxes and chlorinated paraffins.

Several years ago we observed that the position of the sulfonate and phenyl groups are factors which with chain length affect the deterative properties of straight chain alkylbenzenesulfonates. In order to establish a better correlation between structure and surface active properties, model sodium alkylbenzene-

sulfonates were synthesized in our laboratory and a number of their physical and chemical properties reported (1-3). In one of these articles (2) we indicated that a more detailed discussion of the surfactant properties of these compounds was in preparation. The present paper reports these data; and in addition, it more fully substantiates the earlier comparisons with the branched chain product, sodium (tetrapropylene) benzenesulfonate. Furthermore, now that linear alkylbenzenes are established commercially to overcome the sewage problem, it is interesting to note that the performance of their sulfonates (5-8) are in fairly good agreement with earlier predictions based on small quantities of laboratory prepared samples.

Experimental

Sodium Alkylbenzenesulfonates Primary Alkyl Groups

The hydrocarbons 1-phenyloctane, 1-phenyldecane and 1-phenyldodecane were prepared by converting the acid chlorides of octanoic, decanoic and dodecanoic acids to their respective alkyl phenyl ketones by means of the Friedel Crafts reaction. The carbonyl group was reduced to the methylene group by means of the Huang-Minlon modification of the Wolff-Kishner reaction. The physical properties of the alkylbenzenes were determined. These primary alkylbenzenes were sulfonated in about 98% yield. The ratio of para to ortho sodium sulfonate isomers was found to be about 5 to 1. The physical characteristics of the isomers were observed and their identification established by derivative formation and by infrared spectral data (1).

Secondary Alkyl Groups, 2-Phenylalkanes

The hydrocarbons, 2-phenylundecane, 2-phenyltridecane, 2-phenylpentadecane and 2-phenylheptadecane were prepared from alkyl phenyl ketones derived from acid chlorides and benzene by the Friedel Crafts reaction. Tertiary alcohols were prepared by the appropriate Grignard reaction, then dehydrated to yield phenylalkenes. Catalytic hydrogenation of the unsaturated hydrocarbons with palladium as catalyst at slightly elevated pressure gave the desired 2-phenylalkanes. The physical properties of these alkylbenzenes were determined. The 2-phenylalkanes prepared were sulfonated in about 98% yields. The ratio of para to ortho sulfonate isomers was found to be about 13 to 1. The physical characteristics of the isomers were observed, and their identification established by derivative formation and by infrared spectral data (2).

Secondary Alkyl Group, 5-Phenyldodecane

The hydrocarbon 5-phenyldodecane was prepared from butyl magnesium bromide and n-heptyl phenyl ketone by a sequence of reactions similar to those used to prepare 2-phenylalkanes. The sulfonation of 5-phenyldodecane yields predominantly para isomer with a very small amount, if any, of ortho isomer. The purified para 5-phenylsulfonate isomer in con-

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TABLE I
 Ross-Miles Pour Foam, mm (Distilled Water, 60C)

$\begin{array}{c} R' \\ \\ R-C_6H_4SO_3Na \\ \\ R'' \end{array}$				Foam height at various concentrations						
Abbreviation	Orien- tation	R	R', R''	0.015	.030	.075	.150	.300	.450	.600
p-1 ϕ -C ₈	p	C ₇ H ₁₅	H, H	24	41	79	134	152	163	163
o-1 ϕ -C ₈	o	C ₇ H ₁₅	H, H	27	38	124	148
p-1 ϕ -C ₁₀	p	C ₉ H ₁₉	H, H	112	121	141	186	182	184
o-1 ϕ -C ₁₀	o	C ₉ H ₁₉	H, H	12	35	105	125	130
p-1 ϕ -C ₁₂	p	C ₁₁ H ₂₃	H, H	81	163	196	201
o-1 ϕ -C ₁₂	o	C ₁₁ H ₂₃	H, H	137	157	179	206	208	193
p-2 ϕ -C ₁₁	p	C ₉ H ₁₉	CH ₃ , H	86	136	157	162	182	192	188
o-2 ϕ -C ₁₁	o	C ₉ H ₁₉	CH ₃ , H	10	50	155	165	170	155
p-2 ϕ -C ₁₃	p	C ₁₁ H ₂₃	CH ₃ , H	164	184	192	210	215	211
o-2 ϕ -C ₁₃	o	C ₁₁ H ₂₃	CH ₃ , H	115	140	165	196	195	195
p-2 ϕ -C ₁₅	p	C ₁₃ H ₂₇	CH ₃ , H	152	162	170	174	176	176
o-2 ϕ -C ₁₅	o	C ₁₃ H ₂₇	CH ₃ , H	25	60	40
p-2 ϕ -C ₁₇	p	C ₁₅ H ₃₁	CH ₃ , H	116	126	126	129	131	141	135
o-2 ϕ -C ₁₇	o	C ₁₅ H ₃₁	CH ₃ , H	65	85	100	105	90	105
p-5 ϕ -C ₁₂	p	C ₇ H ₁₅	C ₆ H ₅ , H	139	165	191	219	227	232	227
p-2 ϕ -2Me-C ₁₂	p	C ₉ H ₁₉	CH ₃ , CH ₃	122	194	212	215	210	210
TPBS				86	144	160	201	213	222

trast to the crystalline para 1-phenyl and 2-phenyl sulfonates is amorphous in nature (1).

Tertiary Alkyl Group, 2-Phenyl-2-methylundecane

Benzene was alkylated with methallyl chloride to form neophyl chloride. The Grignard reagent, prepared from the chloride, was treated with octanal. The resulting carbinol was dehydrated and then reduced to 2-phenyl-2-methylundecane. Its sulfonation product was isolated as crystalline sodium p-(1,1-dimethyldecyl) benzenesulfonate (2).

Sodium (Tetrapropylene)benzenesulfonate (TPBS)

This material is a commercial product from which inorganic salt and free oil (or extraneous material) was removed by extraction. Its molecular weight (345) corresponds to a side chain averaging twelve carbon atoms.

Foam Height. The foam heights given in Table I were determined by the Ross-Miles method (4) in distilled water at 60C.

Wetting Time. In Table II, the wetting power of the various sulfonates is indicated by the time in

seconds for a canvas disk, 1 inch in diameter to sink beneath the surface of liquid at 60C (1).

Detergency. The procedure and means for obtaining detergency values on Test Fabric #26 with a maximum probable error of ± 1.9 brightness gain units is given in our previous paper (1). The data are summarized in Table III.

Results and Discussion

Foam (Table 1)

In the 12 carbon chain para sulfonate series, the effect of phenyl position is most pronounced at the lowest concentrations studied. The p-5 ϕ -C₁₂ and p-2 ϕ -2Me-C₁₂ isomers are superior to p-1 ϕ -C₁₂. Secondary 2-phenyl ortho and para sulfonates having a C₁₂ side chain were not synthesized, but it is evident from a comparison of the three C₁₂ isomers mentioned above with p-2 ϕ -C₁₁ and p-2 ϕ -C₁₃ that there is considerable interdependence of phenyl position with concentration and chain length. The 11-carbon compound gives a foam height much less than obtained with p-5 ϕ -C₁₂ or p-2 ϕ -2Me-C₁₂ but equivalent to that of p-1 ϕ -C₁₂. On

 TABLE II
 Wetting Time, Seconds (Distilled Water, 60C)

$\begin{array}{c} R' \\ \\ R-C_6H_4SO_3Na \\ \\ R'' \end{array}$				Wetting time, seconds at various concentrations			
Abbreviation	Orien- tation	R	R', R''	0.015	0.030	0.075	0.150
p-1 ϕ -C ₈	p	C ₇ H ₁₅	H, H	300 +	300 +	300 +	300 +
o-1 ϕ -C ₈	o	C ₇ H ₁₅	H, H	300 +	300 +	300 +	103
p-1 ϕ -C ₁₀	p	C ₉ H ₁₉	H, H	300 +	300 +	300 +	145
o-1 ϕ -C ₁₀	o	C ₉ H ₁₉	H, H	300 +	300 +	221	73
p-1 ϕ -C ₁₂	p	C ₁₁ H ₂₃	H, H	300 +	300 +	300 +	300 +
o-1 ϕ -C ₁₂	o	C ₁₁ H ₂₃	H, H	300 +	300 +	300 +	33
p-2 ϕ -C ₁₁	p	C ₉ H ₁₉	CH ₃ , H	300 +	300 +	300 +	300 +
o-2 ϕ -C ₁₁	o	C ₉ H ₁₉	CH ₃ , H	300 +	300 +	90	58
p-2 ϕ -C ₁₃	p	C ₁₁ H ₂₃	CH ₃ , H	300 +	300 +	159	28
o-2 ϕ -C ₁₃	o	C ₁₁ H ₂₃	CH ₃ , H	300 +	104	35	32
p-2 ϕ -C ₁₅	p	C ₁₃ H ₂₇	CH ₃ , H	300 +	300 +	208	58
o-2 ϕ -C ₁₅	o	C ₁₃ H ₂₇	CH ₃ , H	32	21
p-2 ϕ -C ₁₇	p	C ₁₅ H ₃₁	CH ₃ , H	300 +	300 +	300 +	134
o-2 ϕ -C ₁₇	o	C ₁₅ H ₃₁	CH ₃ , H	300 +	300 +	300 +	151
p-5 ϕ -C ₁₂	p	C ₇ H ₁₅	C ₆ H ₅ , H	300 +	187	15	8
p-2 ϕ -2Me-C ₁₂	p	C ₉ H ₁₉	CH ₃ , CH ₃	300	79	48	14
TPBS				176	46	8	6

TABLE III
 Detergency (Units Soil Removal)

Abbreviation	Orientation	R	R', R''	Units brightness gain at various concentrations						
				.015	.030	.075	.150	.300	.450	.600
p-1 ϕ -C ₈	p	C ₇ H ₁₅	H, H	11.3	15.5	19.9	24.6	26.6
o-1 ϕ -C ₈	o	C ₇ H ₁₅	H, H	10.3	16.2	19.6
p-1 ϕ -C ₁₀	p	C ₉ H ₁₉	H, H	10.9	10.6	13.6	19.4	21.6	22.3	24.6
o-1 ϕ -C ₁₀	o	C ₉ H ₁₉	H, H	7.7	10.2	10.4	15.4	22.6	20.7
p-1 ϕ -C ₁₂	p	C ₁₁ H ₂₃	H, H	11.2	27.9	30.7	33.3
o-1 ϕ -C ₁₂	o	C ₁₁ H ₂₃	H, H	10.5	16.9	24.6	25.9
p-2 ϕ -C ₁₁	p	C ₉ H ₁₉	CH ₃ , H	9.0	10.6	19.6	19.7	19.2	21.6
o-2 ϕ -C ₁₁	o	C ₉ H ₁₉	CH ₃ , H	3.1	4.0	7.0	9.2	10.7	8.3
p-2 ϕ -C ₁₃	p	C ₁₁ H ₂₃	CH ₃ , H	14.8	27.4	29.2	29.7	27.4	29.1
o-2 ϕ -C ₁₃	o	C ₁₁ H ₂₃	CH ₃ , H	4.2	7.9	9.7	8.0	8.6	8.4
p-2 ϕ -C ₁₅	p	C ₁₃ H ₂₇	CH ₃ , H	22.2	27.1	29.0	30.2	32.9	37.8	37.6
o-2 ϕ -C ₁₅	o	C ₁₃ H ₂₇	CH ₃ , H	8.1	8.9	8.8
p-2 ϕ -C ₁₇	p	C ₁₅ H ₃₁	CH ₃ , H	27.9	27.5	35.4	38.9	39.4	39.8
o-2 ϕ -C ₁₇	o	C ₁₅ H ₃₁	CH ₃ , H	8.0	8.8	8.4	8.2	8.9	9.3
p-5 ϕ -C ₁₂	p	C ₇ H ₁₅	C ₄ H ₉ , H	9.3	13.9	23.0	22.8
p-2 ϕ -2Me-C ₁₂	p	C ₉ H ₁₉	CH ₃ , CH ₃	7.8	20.3	26.3	26.1	23.1	19.1
TPBS				9.8	12.2	15.8	26.1	24.3	20.9

the other hand, the 13-carbon compound produces far greater foam than all other compounds at lowest concentration. Moreover its foam capacity is greater than other secondary 2-phenyl compounds, is the equivalent of p-2 ϕ -2Me-C₁₂ and approaches that of p-5 ϕ -C₁₂ at higher concentrations.

Other investigators have prepared 2-phenylalkanes but have not reported the effect of the isomerization produced by sulfonation (5,7,8). In addition to phenyl position and chain length, sulfonate position appears to have a major effect on foam. Wherever possible to compare respective ortho and para isomers, the para isomer is usually superior to the ortho isomer. A major exception appears to be the o-1 ϕ -C₁₂ at low concentrations; but for all 2-phenyl compounds the para isomers are superior to their respective ortho compounds. Unfortunately, both isomers could not be compared when the phenyl group was more centrally located, since sulfonation of 5-phenyldodecane did not yield any isolatable quantity of ortho isomer.

Wetting (Table II)

Ortho isomers are better wetting agents than para isomers, but the most dramatic effect seems to result from changing the structure of the hydrophobic part of the molecule. Central location of the phenyl group or tertiary hydrocarbon structure produces sulfonates of superior wetting ability.

TABLE IV

Dishwashing Foam for Primary, Secondary and Tertiary Para Sulfonate Compositions Versus Similarly Built TPBS
 Test product: 20% Sulfonate, 3.3% LMIPA, 40% Na₂P₂O₇, 36.7% Na₂SO₄
 Control product: 20% TPBS, 3% LMIPA, 7% Na₂SiO₃, 40% Na₂P₂O₇, 0.5% CMC, Q.S. Na₂SO₄
 (A built commercial type product)
 Conditions: Concentration, 0.15%; Temperature, 115F (46C); Hardness, 50 ppm

Sulfonate	Test product		▲ Plates
	Plates washed	Control product (TPBS) Plates washed	
p-1 ϕ -C ₈	18	19	-1
p-1 ϕ -C ₁₀	23	21	+2
p-1 ϕ -C ₁₂	19	20	-1
p-2 ϕ -C ₁₁	22	22	0
p-2 ϕ -C ₁₃	23	19	+4
p-2 ϕ -C ₁₅	17	22	-5
p-2 ϕ -C ₁₇	12	22	-10
p-5 ϕ -C ₁₂	30	24	+6
p-2 ϕ -2Me-C ₁₂	25	21	+4

Detergency (Table III)

The detergency of para isomers is markedly superior to that of the ortho isomers for the systems investigated. Moreover, for the para sulfonate C-12 series, the tertiary 2- ϕ 2Me compound is superior in detergency to the secondary 5- ϕ compound but it is inferior to the primary 1- ϕ isomer. These data support our original thesis that para sulfonates possess better detergency ability than ortho isomers and that the configurational change occasioned by shifting the phenyl position from a terminal to a central location detracts from the detergency capacity of a dodecylbenzenesulfonate (1). Sweeney and Olson (5) compared the detergency ability of a series of pure individual 2-phenylsulfonates (C₁₀ to C₁₈) with respective alkylbenzenesulfonates of the same molecular weight but having the phenyl group randomly distributed along the hydrocarbon chain. Under their experimental conditions, which included a purification step to remove inorganic material and extraneous material (free oil), the 2-phenylsulfonates were found to be superior to their respective isomers containing considerable internal phenyl content. Although Rubinfeld et al. (8) agree that detergency decreases as the phenyl group is moved from the near end to a central position in a dodecylbenzenesulfonate, they find that the exact converse is true for the tridecyl- and tetradecylbenzenesulfonates.

Examination of the experimental conditions of Sweeney and Olson to that of Rubinfeld et al. would indicate that the sulfonates tested by the former may have a lower ortho content (as well as extraneous matter) than the latter workers. If so, and on the basis of our results with isolated para and ortho isomers it is possible that the presence of ortho isomer in 2- ϕ sulfonates may have a far greater influence than had been heretofore recognized.

The performance of the secondary 2-phenylsulfonates increases with molecular weight and the same effect appears to follow for those para 1-phenyl compounds examined. The tertiary compound, 2- ϕ -2Me-C₁₂, is unusual in that a plot of its detergency values with concentration produces a maximum. This is the only model compound studied that behaved this way, and before any significance is attached to this be-

havior additional homologs and other soils should be examined.

Comparison with Branched Chain Product

Unformulated. Since TPBS is a complicated mixture whose structure is only partially known, a comparison between this commercial product and pure compounds cannot be made on structural grounds. However, the TPBS used is inferior in foam and superior in wetting ability to any of the pure para isomers of comparable molecular weight. Furthermore it is interesting that only TPBS and p-2 ϕ -2Me-C₁₂ show maxima in their detergency vs. concentration curves. This may be related to the tertiary structure in the pure isomer and to a corresponding predominating structure in the commercial product.

Formulated (Table IV, and V)

Since all of the previous data were obtained for the unbuilt materials, we have attempted to compare the dishwashing foam (9) of formulations with these purified compounds, using a built commercial type formulation from TPBS as an internal standard. The maximum foam for the 1-phenyl compounds was at C₁₀ chain length but for the 2-phenyl compounds it was at C₁₃. However, the advantage in dishwashing foam of the tertiary isomer, p-2 ϕ -2Me-C₁₂, and central location of the phenyl group, p-5 ϕ -C₁₂, are clearly evident.

The profound effect of a detergent additive in the formulation is clearly demonstrated. The actual amount of surfactant in the formula effects the

TABLE V

Effect of LMIPA and Sodium (1-Methyldecyl) benzenesulfonate Concentrations on Dishwashing Foam
Test Product: 20-35% p-2 ϕ -C₁₁, 0-5.5% LMIPA, 40% Na₂P₂O₇ Q.S. Na₂SO₄
Control Product: 20.0% TPBS, 3% LMIPA, 7% Na₂SiO₃, 40% Na₂P₂O₇, 0.5% CMC, Q.S. Na₂SO₄
 (A built commercial type product)
Conditions: Concentration, 0.15%; Temperature, 115F (46C); Hardness, 50 ppm

Test product		Plates washed		▲ Plates
% p-2 ϕ -C ₁₁	% LMIPA	Test product	Control product	Test - Control
20	0	12	20	-8
20	3.3	22	22	0
20	4.5	26	21	+5
20	5.5	23	20	+3
23.5	0	15	24	-9
35	0	15	20	-5

dishwashing performance far less than the amount of additive, a mixture of lauroyl and myristoyl isopropanolamide in this case.

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• Letters to the Editor

A Simple and Rapid Method for the Determination of Myo-Inositol by Gas-Liquid Chromatography

THE EFFECTIVE APPLICATION of gas chromatography to the analysis of carbohydrates began with the work of Sweeley, Bentley, Makita and Wells in 1963 (1). This work yielded a simple, reliable and sensitive method for the analysis of polyhydroxy compounds with gas-liquid chromatography (GLC) through the formation of O-trimethylsilyl ether (TMS) derivatives. Three publications (2-4) have appeared recently describing methods for the quantitative determination of myo-inositol from various biological sources utilizing essentially the method of Sweeley et al. (1) mentioned above. In each of these publications the limited solubility of myo-inositol in the reaction mixture was pointed out, and, as a result, the time required for derivative formation (TMS) was 3 hr or more. We have found (5) that by the use of dimethylsulfoxide (DMSO), derivatives (TMS) can be ready for injection into the GLC instrument within 10 min after initiation of the reaction. DMSO does not interfere with quantitative trimethylsilylation as shown by parallel assays employing other methods. The derivatives, once formed, are not stable for more than 4-5 hr in DMSO unless stored in the absence of light at 0C (6). Under these latter conditions extended periods of stability are obtained.

Aliquots from aqueous solutions of tissue extracts or lipid hydrolysates containing at least 20 μ g of free myo-inositol were taken to dryness in 2.5 ml glass-stoppered conical centrifuge tubes by evaporation in vacuo. The tubes were then placed in a vacuum dessicator over NaOH pellets for several hours to remove the last traces of water. The residue was dissolved in 20 μ l of dimethylsulfoxide (DMSO) and to this was added 110 μ l of a freshly prepared reagent composed of anhydrous pyridine, hexamethyldisilazane and trimethylchlorosilane (8/2/1, v/v). The tubes were gently shaken and allowed to stand at room temperature (23C). After 5-10 min the ammonium chloride by-product was removed by centrifugation at low speed. All tubes were kept stoppered during the entire procedure except during the addition of reagents. Ten microliter aliquots were used routinely for injection into the GLC apparatus, although larger or smaller aliquots can be successfully used. Standard myo-inositol solutions for GLC were prepared in DMSO, and suitable aliquots were treated directly with TMS reagent for GLC.

The analytical data for myo-inositol in Table I were obtained by analysis of acid hydrolysates of the phosphoinositide complex (7) from kidney and tri-