Oxyethylated Sulfonamides as Nonionic Soil Wetting Agents

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ABSTRACT

Various N-alkylbenzenesulfonamides of the type $R\phi SO_2NHR'$, where R is t-butyl, or hydrogen and R' is decyl, octyl, t-octyl, 2-ethylhexyl, hexyl, and butyl, were treated with ethylene oxide (EO) to yield polydisperse adducts $R\phi SO_2N(R')(EO)_xH$ where x is any integer from 2 to 20. Each series of adducts exhibited a range of properties and water solubility. Wetting ability, surface tension, cloud point, and hydrophilic-lipophilic balance (HLB) were related to structure and EO content to determine the most efficient wetting agent for peat moss and cotton skeins. Optimum wetting properties were found for adducts containing 5-10 EO units and in particular with $t\text{-}C_4H_9\phi SO_2N(t\text{-}C_8H_{17})(EO)_xH$. This EO chain-length region corresponded to cloud points of 25°, minimal surface tensions, and HLB values 10-12.

INTRODUCTION

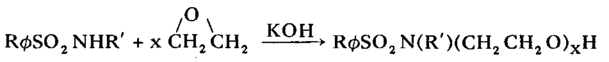
Water-repellent soils occur worldwide and are formed in various ways (1). The condition is usually associated with the presence of organic residues or compaction and is most apparent in soils from chaparral regions, old citrus groves, or forests recently devastated by fire. Hydrophobic soils are generally treated with conditioners and surface-active agents to increase water infiltration. The early literature, citing organic additives as soil conditioners, was described by Schwartz and Perry (2). The use of surfactants for this purpose has gained increasing importance since then (3-5). The application of low concentrations of surface-active agents to soil leads to stimulated growth and overall improvement in the physical properties of the soil. These agents improve soil stability by increasing water absorption, reducing runoff and evaporation (5). These effects improve soil texture and friability. The net results are the increased availability of fertilizer to the growing plant, more rapid and complete germination of seeds, and faster plant growth and maturity. The literature contains various references to commercial surfactants as soil adjuvants with very few studies specifically relating structure to wetting properties. Of the various materials studied, nonionic surfactants appear to offer the most consistent and promising results for treating hydrophobic soils. Nonionics are unaffected by hard-water ions. Chemical structures are known that are stable during acid-base hydrolysis and biodegradation. Furthermore, water solubility can be regulated within narrow limits by varying the chain length of the organic substrate or the number of ethylene oxide (EO) groups. The ability to alter the geometry and molecular weight by the above means also enables the researcher to control the adsorptivity to solubility ratio of the moisture-controlling agents in soil. Wetting agents with good solubility but low adsorptivity to soil seem to be inefficient conditioners, because repeated rainfall would simply leach them from the topsoil layer. Weil et al. (6) apparently carried out the first systematic study relating wetting properties to the structure of polyoxyethylated fatty acids and alcohols prepared from pure polyethylene glycols. They observed optimum wetting ability by a modified Draves test (7) on cotton skeins and a drop penetration test (1,8) on peat moss and natural soil with compounds containing 2-3 EO groups and acid or alcohol chain lengths of 8-10 carbon atoms. This corresponds to an EO content just short of complete water solubility. Other work at this laboratory has shown that this solubility region is the area of maximum adsorptivity on a silica soil substrate.

The broad objective of the present study was to establish the chemical structure leading to a soil wetting agent effective at low concentrations for a reasonable duration (1-2 years) and rendering improved water-retaining ability to various hydrophobic soils. The structure predicated by these requirements is known. Basically, an effective detergent consists of a hydrophilic group at the end of a long hydrocarbon chain, whereas efficient wetting properties are generated when the hydrophilic group is centrally located on this chain (9).

In this program, various substituted benzenesulfonamides of the type $ArSO_2NHR'$, where Ar is phenyl or p-butylphenyl, and R' is a linear or branched aliphatic group, were treated with EO to form polydisperse nonionic surfactants (10-12). The synthesis, using excess chlorosulfonic acid, is given in the following equations where x is the number of mol of EO per mol of sulfonamide.

$$R\phi + 3\ ClSO_3H \xrightarrow{\text{dichloroethane}} R\phi SO_2Cl \qquad [1]$$

$$R\phi SO_2Cl + 2\ R'NH_2 \xrightarrow{\text{dichloroethane}} R\phi SO_2NHR' + R'NH_2 \cdot HCl \qquad [2]$$



$$R\phi SO_2NHR' + x\ \overset{O}{CH_2CH_2} \xrightarrow{KOH} R\phi SO_2N(R')(CH_2CH_2O)_xH \qquad [3]$$

The structure of the polydisperse EO adduct 3 was varied by the type and size of R, R', and the EO chain length. Consequently, property variations could be observed for each sulfonamide as a function of EO content. The wetting properties of the adducts were determined using peat moss and standard cotton skeins.

EXPERIMENTAL PROCEDURES

Materials and Apparatus

Butylbenzene, decylamine, octylamine, t-octylamine, hexylamine, butylamine, benzenesulfonyl chloride, and chlorosulfonic acid were obtained from Aldrich Chemical Company, Milwaukee, WI. 1,2-Dichloroethane and 2-ethylhexylamine were Eastman white label. (Caution is required when handling solvents such as 1,2-dichloroethane as this substance has carcinogenic properties.) Benzene and hexane were reagent grade. EO was obtained from Matheson Gas Products, New York, NY. Aqua-Gro, a 50% polyoxyethylene ether and 50% polyoxyethylene ester, was obtained from Aquatrols Corporation of America, POB385, Delair, NJ. All compounds were used as received. Infrared spectra were obtained with a Perkin Elmer 257 grating infrared spectrophotometer. Oxyethylation reactions were carried out at pressures <45 psi in specially fabricated Fischer Porter heavy-walled glass 500 mL round-bottom flasks equipped with a thermometer well and an aerosol pressure coupling (#110-585). Reactions requiring less than 40 mL of reactants were performed in heavy-walled glass pressure tubes (capacity ca. 90 mL) #320-008 (inside diameter [ID] 1 in., length 8 in.), Lab-Crest Scientific Division, Fischer Porter Company, Warminster, PA.

Synthesis of (N-octyl)p-t-butylbenzenesulfonamide

The method of Shirley and Lehto (13), with minor variations, was used to prepare p-t-butylbenzenesulfonyl chloride. To 67 g (0.5 mol) t-butylbenzene in 100 mL 1,2-dichloroethane at 0 C, 175 g (1.5 mol) chlorosulfonic acid

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[1] Agricultural Research Service, U.S.D.A.

was added drop by drop, while stirring. After the chlorosulfonic acid was added, the mixture was stirred overnight and the bath was allowed to rise to room temperature. The mixture was poured on a tray of ice while being stirred vigorously. After the organic layer was removed, the aqueous layer was extracted once with 90 mL solvent. The combined organic layers were washed once with 100 mL water and evaporated at reduced pressure 0.5 mm/40 C to give 105 g (0.45 mol) crystalline p-t-butylbenzenesulfonyl chloride (90% yield).

To a liter reaction flask was added 120 g (0.9 mol) octylamine and 80 mL 1,2-dichloroethane. The solution was cooled to ca. 20 C and the previously prepared sulfonyl chloride, 105 g (0.45 mol) in 80 mL solvent, was added in 45 min. The mixture was refluxed for 1 hr, cooled to room temperature, and filtered. The amine hydrochloride was washed with 80 mL solvent. The filtrates were combined, acidified with 100 mL 6 N HCl and the organic layer separated. The organic layer was extracted with 90 mL portions of water until the aqueous liquid was neutral and free of chloride ion. Vacuum evaporation of solvent gave 135 g of crude sulfonamide. Crystallization from hexane to a constant melting solid gave 109 g (68%) of (N-octyl) p-t-butylbenzenesulfonamide m.p. 58-59 C which was characterized as follows: analyses found compared with theory—C 66.44/66.42, H 9.64/9.60, N 4.08/4.30, and S 10.12/9.85. A sharp NH band occurs at 3,260 cm^{-1}, aromatic unsaturation at 1,595 cm^{-1}, and SO_2 stretching bands at 1,325, 1,158 cm^{-1}.

Oxyethylation of (N-octyl)p-t-butylbenzenesulfonamide

In a 500-mL thick-walled glass pressure flask was weighed 0.1 mol purified sulfonamide, 0.5 mol liquified ethylene oxide, and 0.1-0.2 g anhydrous potassium hydroxide. An aerosol coupling equipped with a pressure gauge (0-60 psi) and a release valve was hand tightened onto the flask. The mixture was heated in an oil bath, with vigorous stirring and adequate shielding, to a pressure not exceeding 45 psi. The temperature was maintained at 55-70 C until a pressure drop occurred, then the clear mixture was heated to 115 C until the pressure decreased to zero. The flask was weighed to determine if any EO was lost. A sample of the 5 molar adduct was removed, sufficient EO and a trace of catalyst were added, and the oxyethylation was repeated to form the next higher adduct.

Evaluation

A modified Draves wetting test was used to determine the wetting properties of EO adducts. The test was carried out with 0.1% solutions at room temperature and is the time in seconds required for a 5 g cotton skein to sink.

The drop-penetration time (DPT) method (1,8) was employed as a screening test on Canadian sphagnum peat moss ground in a Wiley mill to pass through a No. 10 screen. About 1 g ground peat moss was placed on a watch glass and given a concave surface. Two drops of 0.1% aqueous solution of EO adduct from a medicine dropper were applied to the surface and the time recorded for the liquid to penetrate the sample. Rewetting time was determined with distilled water after the samples had dried overnight at room temperature.

Surface tension measurements were made on 0.1% aqueous solutions with a duNoüy tensiometer. All curves were corrected to 25 C.

Cloud point was determined on 1% aqueous solutions and is the temperature (°C) at which the sample becomes turbid.

RESULTS AND DISCUSSION

Synthesis

The synthesis of oxyethylated N-alkylbenzenesulfonamides is shown in equations 1-3. The intermediate sulfonamides, Table I, are constant melting solids purified by crystallization from hexane or hexane-benzene. They melt from 25-126 C and yielded well (50-85%). Purifiable sulfonamides were obtained only when excess alkylamine was used as an HCl scavenger. Pyridine and other bases gave products not easily purified. The use of crude sulfonyl chloride preparations gave sulfonamides that were always contaminated with sulfone and the low-melting ortho isomer. The by-products constituted 5-20%, by weight, of the pure sulfonamide, with the sulfone being the minor component (less than 4%). These contaminants were removed by crystallization. IR spectra for the sulfonamides showed a characteristic NH band at 3,240-3,280 cm^{-1}, unsaturation at 1,580-1,595 cm^{-1}, and SO_2 stretching 1,155-1,160 cm^{-1}, 1,310-1,330 cm^{-1}. Analyses for carbon, hydrogen, nitrogen, and sulfur agreed to within ±0.3% of theory.

The polydisperse oxyethylated N-alkylbenzenesulfonamides were used without purification and obtained without loss of EO reagent. Reaction periods generally ranged from 1-12 hr, yielding colorless to amber oils, some of which solidified on standing. Initial reaction between EO and the sulfonamide usually required the longest time and generated the highest pressures. Subsequent EO additions occurred readily (1-3 hr or less), and at lower pressures, because of mutual solubilization. The reaction rate between EO and the sulfonamide decreased as the branching of the N-alkyl group increased. The adducts showed broad OH absorption at 3,450-3,470 cm^{-1} and sharp unsaturation at 1,595 cm^{-1}. They are stable during acid-base hydrolysis and presumably the branched structures are stable during biodegradation.

Properties of Polydisperse EO Adducts

Data for (N-hexyl)(N-polyethoxyethanol)p-t-butylbenzenesulfonamide are listed in Table II to exemplify the information generated with these systems. The EO chain length x varies from 3-19 with partial to complete water solubility at these levels. Reaction rates of 1-12 hr differ from the usually observed pattern in being quite erratic. Cloud point increases smoothly from less than 0 C to 83 C. Complete solution above 0 C occurred at the 9 molar EO level. The hydrophilic-lipophilic balance (14) from Griffin's formula (HLB = wt % EO/5) was used to define adduct type. The best wetting properties were observed with HLB = 10-12, a

TABLE I

Melting Points and Yields of N-alkylbenzenesulfonamides $ArSO_2NHR$

Ar	R	m.p.°C	% Yield
t-Butylphenyl	Decyl	61-2	48
t-Butylphenyl	Octyl	58-9	68
t-Butylphenyl	2-Ethylhexyl	33-4	58
t-Butylphenyl	t-Octyl[a]	126-7	44
t-Butylphenyl	Hexyl	57-8	62
t-Butylphenyl	Butyl	80-1	69
n-Butylphenyl	Octyl	36	63
Phenyl	Decyl	46-7	75
Phenyl	Octyl	48	66
Phenyl	2-Ethylhexyl	39	85
Phenyl	Hexyl	25-6	83

[a] 1,1,3,3-tetramethylbutyl.

TABLE II

Surfactant Properties of $t\text{-}C_4H_9\phi SO_2N(C_6H_{13})(CH_2CH_2O)_xH$

x^a	R.T.(hr)[b]	Cloud pt[c] (C)	Wet time[d] (secs)	γ^e (mN/m)	HLB[f]	Wet time (secs)[g] Wet	Wet time (secs)[g] Rewet
3	2.3	<0	>300	35.2	6	10^3	10^3
5	1.8	<0	28	31.2	8	10^3	240
7	12	<0	8	31.3	10	60	80
9	1	17	10	31.6	11	90	80
12	2	50	11	33.2	12	180	160
14	2.5	63	19	34.3	13	10^3	10^3
16	7.3	72	20	35.6	14	10^3	10^3
19	1.8	83	70	36.4	15	10^3	10^3

[a] Mol EO/mol sulfonamide.

[b] Reaction time in hr for the oxyethylation.

[c] Determined with 1% solutions.

[d] Draves test, wetting time in secs (0.1% solution) for cotton skein to sink.

[e] Surface tension at 25 C for 0.1% solution with duNoüy tensiometer.

[f] Hydrophilic-lipophilic balance by Griffin's formula.

[g] Drop penetration wetting test on peat moss (0.1% solution).

somewhat higher range than previously found (6). Draves test showed decreasing wetting times at 3-5 EO units, minimum values at 7-12 EO units, and steadily deteriorating wetting properties beyond this chain length. An analogous pattern of activity was found for wet-rewet times on peat moss by the drop-penetration method (1,8). The results are an order of magnitude larger than those obtained with the cotton skeins, but the same basic pattern is found with 7-12 EO units. A commercial soil wetting agent, Aqua-Gro, gave drop penetration wetting times of ca. 750 sec. The surface activity of these adducts is reflected in surface tension values that correlate well with wetting properties because minimum surface tension values are found in the same EO chain-length region (x = 5-12) exhibiting the highest wetting activity.

Figure 1 shows Draves wetting time profiles for EO adducts $R\phi SO_2N(R')(EO)_xH$ where R is hydrogen in the upper series and t-butyl in the lower series. Wetting time (seconds) is plotted against EO chain length x. The R′ groups are shown above the wetting profiles. N-butyl and N-t-octyl adducts of benzenesulfonamides were not prepared. Based on the limits set, wetting times greater than 100 sec would lead to rectangular plots while wetting times less than 100 sec would give truncated rectangles as shown by these profiles. Therefore, the smaller the profile area, the better the wetting properties of the given series. The results suggest that the best wetting profile was found with $t\text{-}C_4H_9\phi SO_2N(t\text{-octyl})(EO)_xH$ where x = 11. Each profile shows an EO chain length with optimum wetting properties. Where R is t-butyl and R′ decreased from C_{10} to C_4 optimum values of x decreased from 14 to 6. Minimum wetting profiles below 20 sec occur with $R' = C_8 - C_6$ with increasing profile areas at C_{10} or C_4. Branching of the R′ group has little effect on the wetting profiles of the isomeric octyl adducts. The wetting profile for oxyethylated (N-octyl)p-n-butylbenzenesulfonamide was not included because the plot is comparable to that for the series where R′ is decyl. However, wetting times for these adducts, where x = 13-15, were less than 8 sec.

Wet and rewet profiles, solid and dashed lines, respectively, obtained by the drop-penetration method for oxyethylated p-t-butylbenzenesulfonamides on peat moss, are shown in Figure 2 where R′ is decyl, octyl, hexyl, butyl, t-octyl, or 2-ethylhexyl. The wetting times are an order of magnitude larger than for the Draves test and were limited to 1,000 sec. Wet and rewet profiles are comparable. Wetting properties slowly disappear as R′ is shortened from decyl to butyl. Isomeric octyl adducts showed comparable wetting patterns. Figure 2 shows several adducts with wetting times of less than 100 sec.

Additional wet and rewet profiles for adducts, from benzenesulfonamide, are given in Figure 3. These adducts were poorer wetting agents than those from t-butylbenzene, displaying narrower profiles with the complete disappearance of wetting properties when R′ was hexyl. Comparable wetting characteristics were found where R′ is octyl or 2-ethylhexyl. Only 3 samples have wetting times below 100 sec.

Since most of the properties described were obtained at 0.1%, knowing the wetting ability of the adducts as a func-

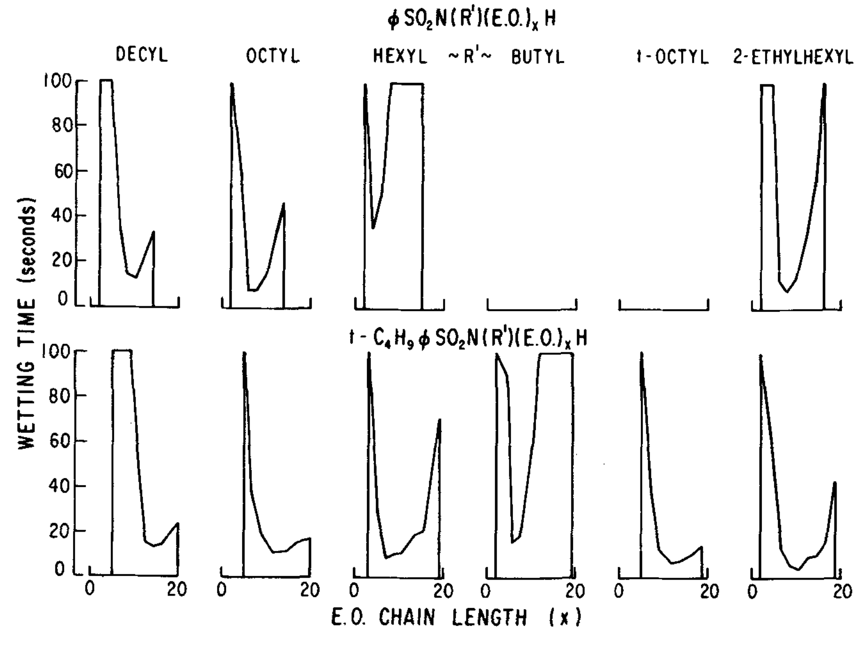

FIG. 1. Draves wetting properties of various oxyethylated benzene-sulfonamides.

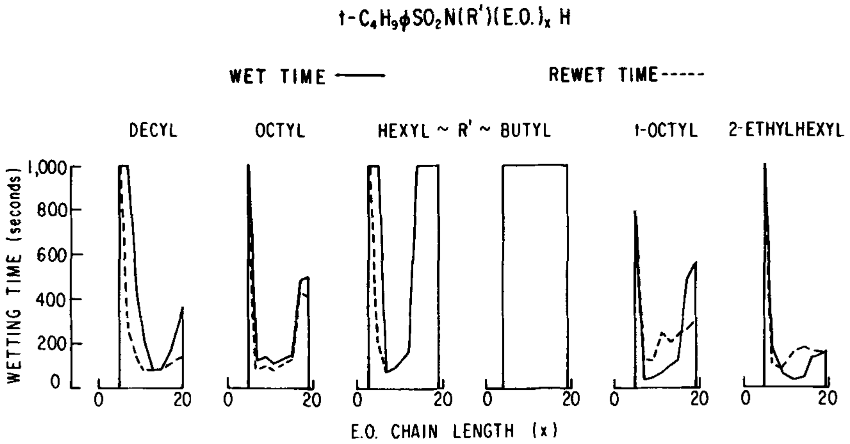

FIG. 2. Drop penetration wetting of oxyethylated t-butylbenzene-sulfonamides.

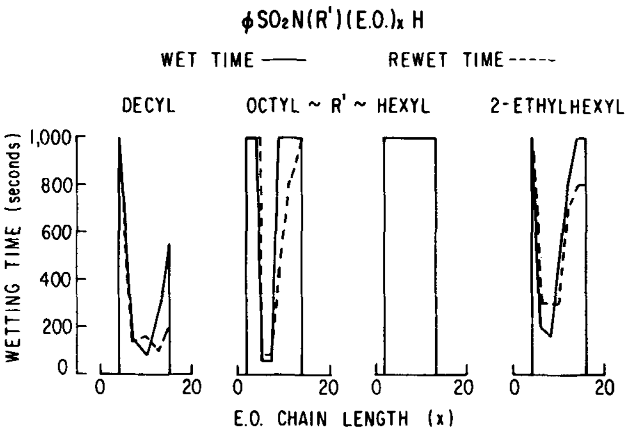

FIG. 3. Drop penetration wetting of oxyethylated benzenesulfonamides.

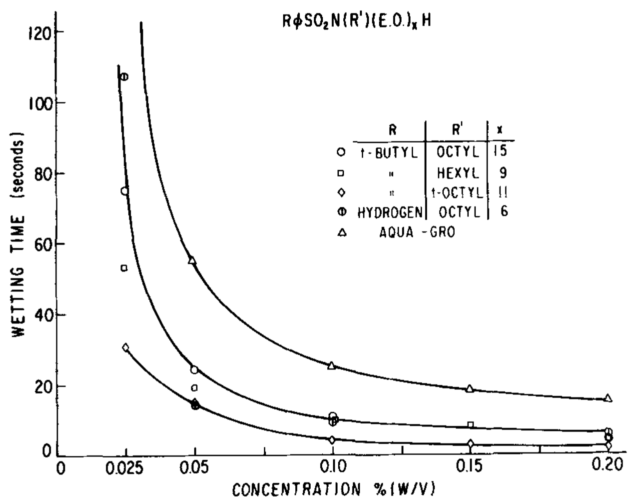

FIG. 4. Draves wetting ability vs concentration of various oxyethylated benzenesulfonamides.

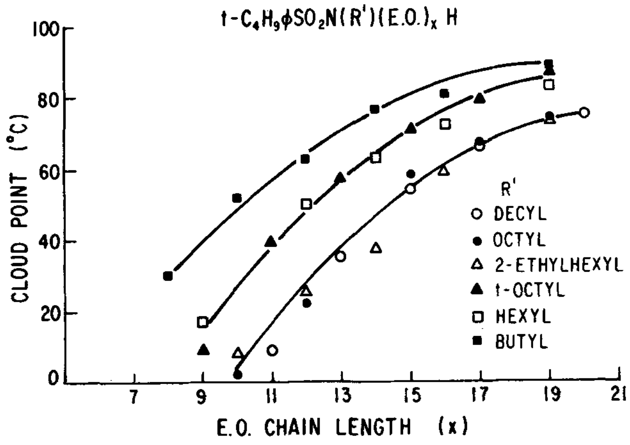

FIG. 5. Solubility of oxyethylated p-t-butylbenzenesulfonamides.

tion of concentration was considered essential. Figure 4 shows the relationship between Draves wetting time and concentrations from 0.025%-0.2% (W/V) with a commercial soil wetting agent, Aqua-Gro, as a reference. The adducts chosen had the best wetting properties as determined from the profiles in Figure 1. The curves are linear from 0.2% to 0.1%, with sharp deviations occurring at lower concentrations. Their wetting properties were superior to Aqua-Gro over the entire concentration range studied. The t-octyl adduct, where x = 11, showed the most effective wetting curve, which, in fact, is comparable to commercial anionic wetting agents (9).

Cloud point is a reliable measure of solubility for nonionic surfactants. These results for various adducts of t-butylbenzenesulfonamide were plotted in Figure 5. Eight to 10 mol EO per mol sulfonamide was required for cloud points above 0 C. As expected, the solubility of the adducts is a function of molecular weight of the sulfonamide with the lowest molecular weight material (R' = butyl) being the most soluble at any EO chain length. In each series, cloud points increase smoothly as a function of EO content with apparent leveling at ca. 80 C. The data suggest that increased branching increases solubility. Where R' is decyl, octyl, or 2-ethylhexyl, the solubilities are essentially equal. Cloud-point curves for N-decyl, N-octyl, N-2-ethylhexyl, and N-hexylbenzenesulfonamide not shown in Figure 5 lie in close proximity above and below the uppermost curve shown for (N-butyl)p-t-butylbenzenesulfonamide.

Surface tension was related to EO chain length for polydisperse adducts from p-t-butylbenzenesulfonamides (Fig. 6) and some corresponding benzenesulfonamides (Fig. 7) in an attempt to correlate changing surface activity with the structure of the EO adducts. Invariably, the curves show minima associated with a given EO chain length and indicating the region of highest surface activity. In Figure 6, minima occur at 5-10 mol EO per mol sulfonamide. Surface tension decreased as R' was increased, reaching a minimum

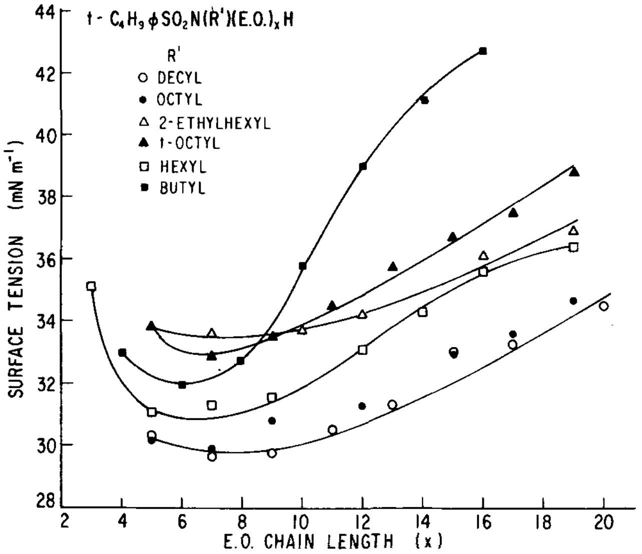

FIG. 6. Surface tension of oxyethylated p-t-butylbenzenesulfonamides.

for R' = decyl or octyl. The rate of change of surface tension with EO chain length decreased as R' increased from butyl to decyl. Curves for N-decyl, N-octyl, N-2-ethylhexyl, and N-hexylbenzenesulfonamides in Figure 7 show increasing surface-tension minima in the order given. The minima occur at 4-7 mol EO per mol sulfonamide. The lower surface activity of this series is reflected by the higher surface tension values and the rapidity of change with EO content.

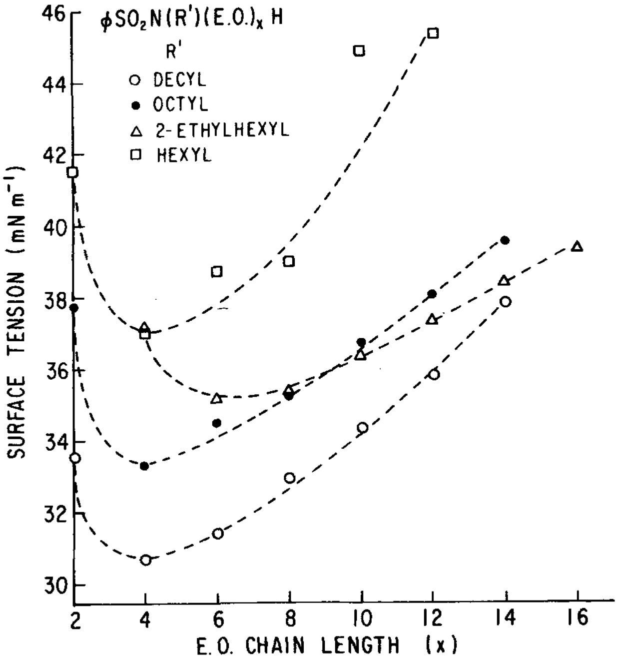

FIG. 7. Surface tension of oxyethylated benzenesulfonamides.

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