The Relationship of Structure to Properties in Surfactants: V. Synthesis and Properties of α,ω-bis (Sodium p-Sulfophenoxy)alkanes

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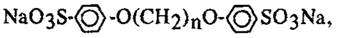
ABSTRACT

A series of symmetrical surfactants containing two arylsulfonate groups in the molecule, of general structure,

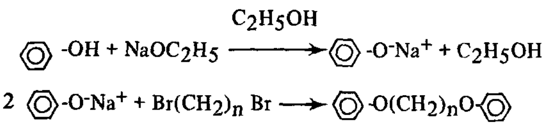


where n = 4, 6, 8, 10 and 12, has been synthesized. The synthesis involves sulfonation of the corresponding diaryl ethers, isolation, purification, and characterization of the free para-disulfonic acids, followed by conversion of the latter to the disodium salts. The nuclear magnetic resonance (NMR) spectra of the products indicate that they are the para-sulfonated compounds substantially free of the ortho isomers. The Krafft points, surface tension-log concentration curves, critical micelle concentrations, and areas/molecule at the liquid/air interface have been determined. The surface area/molecule indicate that these compounds are lying flat in the liquid/air interface.

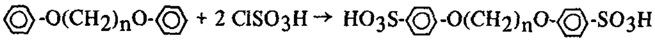
INTRODUCTION

Although materials containing multiple arylsulfonate groups are widely used to disperse finely-divided solids in aqueous media, and although it is generally accepted that the stability of such dispersions in aqueous media results from the adsorption of the sulfonate ions onto the solid particles, producing electrical and steric barriers to coalescence (1,2), almost nothing is known about the surface properties of this type of material.

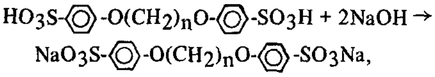
In an effort to obtain insights into the relationship between the structure of this type of material and its surface properties, a series of symmetrical α,ω-dibenzenesulfonates have been synthesized in which the distance between the two sulfonate groups is varied. The compounds synthesized are of the general structure, NaO_3S-⌬-$O(CH_2)_nO$-⌬-SO_3Na, in which n is 4, 6, 8, 10, and 12. They are prepared first by synthesizing the α,ω-bis (phenoxy) alkanes via a Williamson synthesis from sodium phenoxide and an α,ω-dibromoalkane,



and then by sulfonating the diaryl ether with chlorosulfonic acid,



The free sulfonic acids have been isolated, purified, and characterized by melting point, equivalent weight, and nuclear magnetic resonance (NMR) spectrum. They have then been neutralized with sodium hydroxide to produce the disodium salts,



which are precipitated from aqueous solution by the addition of ethanol.

EXPERIMENTAL PROCEDURES AND DATA

Preparation of the α,ω-bis (phenoxy) alkanes, $C_6H_5O(CH_2)_nOC_6H_5$

A solution of sodium ethoxide is prepared by adding 12.65 g (0.55 moles) of clean sodium metal to 250 ml of absolute ethanol in a one-liter, 3-necked, round-bottom flask equipped with a dropping funnel and a reflux condenser protected by calcium chloride drying tubes and cooled in an ice-water bath. A solution of 51.7 g (0.55 moles) of phenol in 50 ml of absolute ethanol is added to the well-stirred sodium ethoxide solution in the flask. The mixture in the flask is then heated to reflux while 0.25 moles of the appropriate α,ω-dibromide (dissolved in absolute ethanol, if the dihalide is a solid) is added dropwise to the well-stirred mixture over a period of 2-4 hr. After addition of the dihalide is complete, the mixture is stirred and heated under reflux for an additional 16 hr.

The hot mixture is slowly treated with 200 ml of hot water (80 C) and stirred while hot to dissolve precipitated sodium bromide. The mixture is then cooled to 5-10 C in an ice-water bath and filtered through a Buchner funnel. The product on the funnel is washed well with water to remove any remaining sodium bromide and then recrystallized from 95% ethanol or isopropyl alcohol to constant melting point in agreement with the literature value (3). Yields are better than 90% of the theoretical.

Preparation of the Disulfonic Acids, $HO_3SC_6H_4O(CH_2)_nOC_6H_4SO_3H$

A solution of 0.1 mole of the appropriate α,ω-bis (phenoxy) alkane in 250 ml of dry chloroform is placed in a 1-liter, 3-necked, round-bottom flask equipped with a dropping funnel and a reflux condenser protected by calcium chloride drying tubes and cooled in an ice-water bath. The solution in the flask is stirred and cooled to 20 C and then 26.7 g (0.23 moles) of chlorosulfonic acid is added dropwise over a period of 2 hr. The mixture is then stirred for an additional 16-20 hr at room temperature.

The reaction mixture is filtered through a coarse sintered glass funnel and washed well on the funnel with chloroform. The crude disulfonic acid on the funnel is dissolved in no more than 100 ml of water and the aqueous solution extracted three or four times with 30 ml portions of chloroform in a separatory funnel. The aqueous solution is then transferred to an Erlenmeyer flask immersed in an ice water bath and saturated with hydrogen chloride gas to precipitate the free disulfonic acid. The free sulfonic acid is removed by filtration using a sintered glass funnel. Yield: 50-60% of theory.

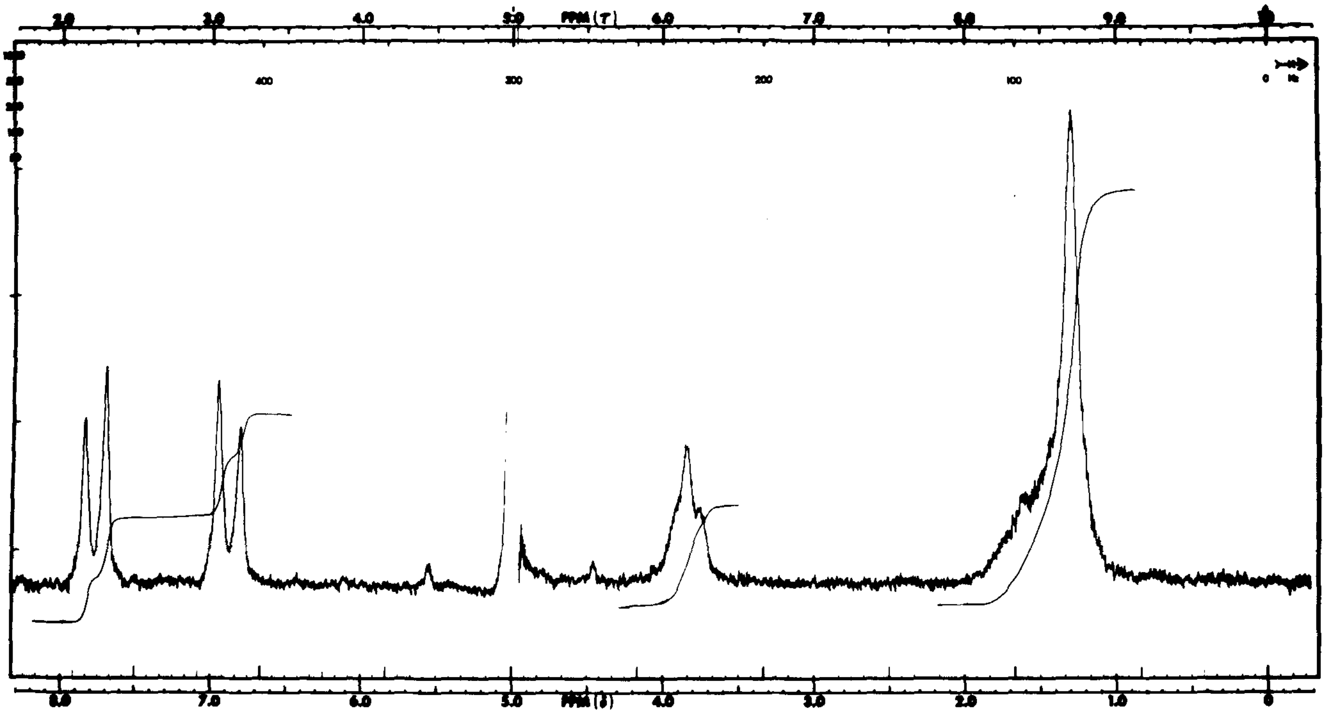


FIG. 1. Proton magnetic resonance spectrum of HO_3S-⌬-$O(CH_2)_{10}O$-⌬-SO_3H in D_2O.

Solution of the precipitated free disulfonic acid in water and precipitation by saturating the aqueous solution with hydrogen chloride gas is repeated, usually three to four times, until, after drying the material first over NaOH and then over P_2O_5 in a vacuum dessicator, constant melting point is attained. The free disulfonic acids are white, very hygroscopic, crystalline solids. They become discolored (pink, purple) upon standing, even in vacuo. Their equivalent weights were determined by titration with sodium hydroxide solution.

The melting points and equivalent weights of the free disulfonic acids obtained in this manner are:

disulfonic acid	m.p. (C)	equivalent weight observed	equivalent weight theoretical
$HO_3SC_6H_4O(CH_2)_4OC_6H_4SO_3H$	145-145.5	201.8	201.1
$HO_3SC_6H_4O(CH_2)_6OC_6H_4SO_3H$	139.2-140	216.6	215.2
$HO_3SC_6H_4O(CH_2)_8OC_6H_4SO_3H$	110.8-111.2	233.0	229.2
$HO_3SC_6H_4O(CH_2)_{10}OC_6H_4SO_3H$	121.5-123	243.1	243.2
$HO_3SC_6H_4O(CH_2)_{12}OC_6H_4SO_3H$	127-129	259.2	257.2

NMR spectra of the free sulfonic acids in D_2O indicate that the aromatic nuclei are sulfonated in the para position with little, if any, ortho isomer. The spectrum of α,ω-bis (p-sulfophenoxy) decane is given in Figure 1.

Preparation of the α,ω-bis (sodium p-sulfophenoxy) alkanes

A solution of about 0.05 moles of the disulfonic acid in 50 ml of quartz-distilled water to which 2-3 drops of 0.1% ethanolic phenolphthalein solution has been added is treated with about 0.1 moles of NaOH in quartz-distilled water until the solution has a permanent slight pink color. About 1000-1500 ml of 95% ethanol are then added to the solution to precipitate the disodium salt, which is removed by filtration, washed well with a total of several hundred ml of 95% ethanol, and dried on the filter and then over P_2O_5 in a vacuum dessicator to constant weight. The yield is essentially quantitative. C, H, and S analyses are consistent with the formulae for the anhydrous salts.

The ultraviolet spectra of the sodium salts show maxima at 232.5 and 269 nm. The molar absorptivities of the compounds are:

Compound	232.5 nm	269 nm
$NaO_3SC_6H_4O(CH_2)_4OC_6H_4SO_3Na$	-	2.01×10^3
$NaO_3SC_6H_4O(CH_2)_6OC_6H_4SO_3Na$	3.30×10^4	2.40×10^3
$NaO_3SC_6H_4O(CH_2)_8OC_6H_4SO_3Na$	3.28×10^4	2.36×10^3
$NaO_3SC_6H_4O(CH_2)_{10}OC_6H_4SO_3Na$	2.89×10^4	2.15×10^3
$NaO_3SC_6H_4O(CH_2)_{12}OC_8H_4SO_3Na$	2.71×10^4	2.02×10^3

Krafft points: These were determined from the discontinuity in the specific conductivity vs. temperature curve of a saturated aqueous solution of the compound in the presence of excess solid using a Wayne-Kerr Universal Bridge model B221A. Since the rate of solution of these compounds in water is very slow, to ensure equilibrium the mixture was first heated to about 80 C for some time and conductivities measured as the temperature of the well-stirred mixture was slowly decreased in a thermostatted bath over a period of 2-4 hr. The following Krafft points were observed:

Compound	Krafft point
NaO_3-⌬-$O(CH_2)_6O$-⌬-SO_3Na	< 20 C
NaO_3S-⌬-$O(CH_2)_8O$-⌬-SO_3Na	28 C
NaO_3S-⌬-$O(CH_2)_{10}O$-⌬-SO_3Na	59 C
NaO_3S-⌬-$O(CH_2)_{12}O$-⌬-SO_3Na	70 C

Surface tension measurements: All surface tension measurements were made by the Wilhemy vertical plate technique, using a sand-blasted platinum plate of ca. 5 cm perimeter, which was calibrated against quartz-distilled water (conductivity, $<2.0 \times 10^{-6}$ ohm^{-1} cm^{-1}) each day measurements were made. The plate was suspended from a dial-type torsion balance capable of being read to 0.2 mg.

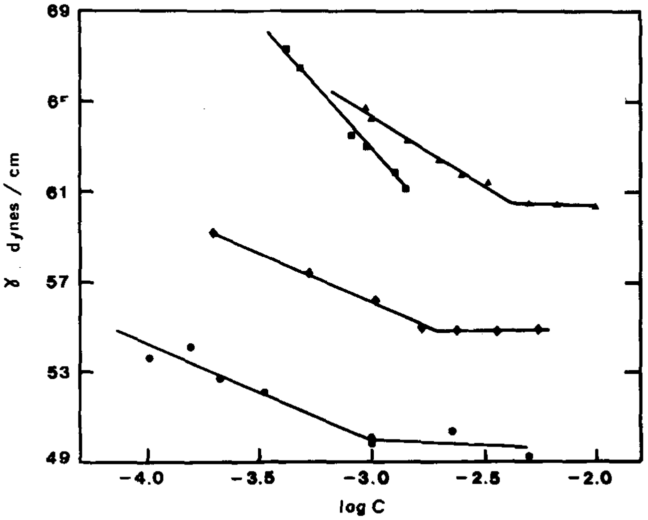


FIG. 2. Surface tension vs. log of the concentration of the surfactant in aqueous solution. ▲ NaO_3S-⌬-$O(CH_2)_6O$-⌬-SO_3Na at 25 C. ■ NaO_3S-⌬-$O(CH_2)_{10}O$-⌬-SO_3Na at 40 C. ◆ NaO_3S-⌬-$O(CH_2)_{10}O$-⌬-SO_3Na at 60 C. ● NaO_3S-⌬-$O(CH_2)_{12}O$-⌬-SO_3Na at 70 C.

All solutions to be tested were immersed in a constant temperature bath at the desired temperature ± 0.05 C and aged for at least 0.5 hr before measurements were made. Measurements were repeated at 30 min intervals until no significant changes occurred. Plots of the surface tension of aqueous solutions of some of these disulfonates vs. the log of the surfactant concentration in moles/liter are shown in Figure 2.

Critical micelle concentrations and areas/molecule at the liquid/air interface were determined from the surface tension-log concentration plots. The critical micelle concentrations (CMCs) were taken as the concentrations at the points of intersection of the two linear portions of the curves. The areas/molecule, A, in nm² (= 10^2 square Angstroms) at the liquid/air interface were calculated from the relationships

$$\Gamma = -\frac{1}{6.9\,RT}\left(\frac{\delta\gamma}{\delta \log c}\right)_T$$

and

$$A = \frac{10^{14}}{N\Gamma}$$

where $\left(\frac{\delta\gamma}{\delta \log c}\right)_T$ is the slope of the surface tension - log concentration curve at constant (absolute) temperature, T, R = 8.31×10^7 ergs $mole^{-1}$ degree $Kelvin^{-1}$, and N = Avogadro's number. The values obtained for the CMCs and areas/molecule are listed in Table I, together with cross-sectional areas of the compounds as determined from molecular models.

DISCUSSION

The method of isolating the free disulfonic acid ensures that only the para isomer will be present in the final product, since the ortho isomer is much more water-soluble than the para. The proton magnetic resonance spectra (Fig. 1) of the compounds confirm this. The two downfield doublets are characteristic of para-disubstituted benzenes. The doublets are rather widely separated, reflecting the very different deshielding effects of the $-SO_3H$ and $-OCH_2-$ groups.

The UV spectra of these compounds, with their two absorption maxima, provide a rapid, convenient method for analyzing solutions of these materials down to 1×10^{-6} molar. The ease with which solutions in the micromolar range can be analyzed makes these molecules particularly suitable for adsorption studies.

The Krafft points of these compounds follow the usual pattern of increase with increase in the chain length of the hydrophobic group. The Krafft points of some α,ω-bis (sodium sulfato) alkanes have been reported by Ueno (4): $NaO_4S(CH_2)_{14}SO_4Na$, 24.8 C; $NaO_4S(CH_2)_{16}SO_4Na$, 39.1 C; $NaO_4S(CH_2)_{18}SO_4Na$, 44.9 C. It is apparent that the Krafft points of the present compounds increase more rapidly with increase in the length of the polymethylene chain than do those of the alkane disulfates.

The surface tension - log concentration curves given in Figure 2 and the surface areas/molecules calculated from them (Table I) show that these compounds are lying flat in the liquid/air interface as would be expected from their structure with hydrophilic groups at opposite ends of the molecule. The data also indicate that the longer chain compounds are more closely packed at the interface than their shorter-chain homologs and may be close packed at room temperature. The reason for their large areas/molecules is probably the elevated temperatures at which the data were taken because of their high Krafft points.

The large surface areas/molecule and the consequent low surface excess concentrations of these molecules make these compounds rather ineffective for reducing the surface tension of water. The longest chain compound is somewhat more effective than the others, producing a reduction of close to 15 dynes/cm @ 70 C, compared to reductions of about 11 dynes/cm for the other two compounds shown in Figure 2. The efficiency of surface tension reduction

TABLE I

CMCs[a] and Areas/molecule at the L/A Interface

Compound	Temp. (C)	CMC (moles/ℓ)	Areas/molecule, in nm² x 10^2 From γ-log C curves	Areas/molecule, in nm² x 10^2 From molecular models[b]
NaO_3S-⌬-$O(CH_2)_4O$-⌬-SO_3Na	25	>1.0×10^{-2}	-	165
NaO_3S-⌬-$O(CH_2)_6O$-⌬-SO_3Na	25	4.3×10^{-3}	460	185
NaO_3S-⌬-$O(CH_2)_{10}O$-⌬-SO_3Na	40[c]	-	260	224
NaO_3S-⌬-$O(CH_2)_{10}O$-⌬-SO_3Na	60	2.0×10^{-3}	750	224
NaO_3S-⌬-$O(CH_2)_{12}O$-⌬-SO_3Na	70	1.0×10^{-3}	760	244

[a] Critical micelle concentration.
[b] For molecule lying flat in the interface.
[c] Below Krafft point of compound.

increases, as usual (5), with increase in the length of the hydrophobic group, the bulk concentrations of compound required to achieve a 10 dynes/cm reduction in surface tension being ca. 1×10^{-4}, 1×10^{-3}, and 6×10^{-3} molar for the dodecane, decane, and hexane derivatives, respectively.

The CMCs also decrease with increase in length of the polymethylene portion of the molecule, but since the temperatures at which the CMCs were determined vary with the compound, the effect of an additional methylene group is not determinable from the current data.

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