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The Relationship of Structure to Properties in Surfactants: VII. Synthesis and Properties of Some Sodium 1,4- and 2,6-Alkoxynaphthalenesulfonates[1]

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ABSTRACT

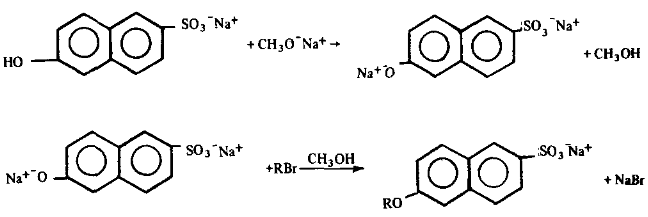
A number of surface-active alkoxynaphthalenesulfonates, $ROC_{10}H_6SO_3Na$, have been synthesized, and some of their surface properties determined. The synthesis involved a Williamson reaction of an alkyl halide with the disodium salt of a naphtholsulfonic acid. The Krafft points, surface tension-log concentration curves, critical micelle concentrations, and areas/molecule at the air/liquid interface of the purified and characterized alkoxynaphthalenesulfonates have been determined. Their surface areas/molecule indicate that the oxynaphthalenesulfonate portion of these compounds is lying flat in the air/liquid interface with the alkyl group vertical to the plane of the naphthalene. Their surface tension reduction efficiencies and critical micelle concentrations indicate that an α- or β-naphthoxy gruop in the hydrophobic portion of the molecule at 60 C is equivalent to about eight carbons in a straight alkyl chain and about six carbons at 25 C. These compounds, in contrast to other surfactants without an aryl ether linkage in the molecule, show greater efficiency and effectiveness in surface tension reduction with increase in temperature.

INTRODUCTION

Surfactants based on coal tar and containing the naphthalenesulfonate group, e.g., Nekal A, sodium diisopropylnaphthalenesulfonate, were invented in Germany during World War I (1) and widely used as textile wetting agents. The advent of cheap petroleum as a source of raw materials for the chemical industry caused a decline in the use of coal tar for that purpose, and surfactants based on benzene from petroleum replaced those based on naphthalene from coal tar. The recent large increases in the price of crude oil have fostered re-examination of naphthalene from coal tar as an alternative raw material for surfactants.

Since almost no information is available on the surface properties of well-defined naphthalenesulfonate derivatives, the current investigation was undertaken to examine the relationship between the chemical structures of some well-defined materials of that type and their surface peoperties. Two isomeric series of sodium alkoxynaphthalenesulfonates have been synthesized, the 1,4- and 2,6-compounds of general structure $ROC_{10}H_6SO_3Na$, where R is $n\text{-}C_4H_9$, iso-C_4H_9, or $n\text{-}C_6H_{13}$. The compounds were prepared via a Williamson synthesis from an alkyl bromide and the disodium salt of a naphtholsulfonic acid. The synthetic scheme, illustrated for the 2,6-compounds, was as follows:

$$Na(metal) + CH_3OH \rightarrow CH_3O^-Na^+ + \tfrac{1}{2}H_2$$



(R = n-C_4H_9, iso-C_4H_9, or n-C_6H_{13})

The 1,4-compounds were synthesized by a similar procedure.

After purification and analysis, the molar absorptivity in the ultraviolet region, the Krafft point, and the surface tension of aqueous solutions of the compounds were measured. From the surface tension-log concentration curves, the surface excess concentration, surface area/molecule at the liquid/air interface, the critical micelle concentration, and the efficiency (2) and effectiveness (3) of surface tension reduction of the individual compounds were calculated.

EXPERIMENTAL PROCEDURES AND DATA

Preparation of the Sodium Alkoxynaphthalenesulfonates

A methanolic solution of 0.1 mole of sodium 1,4- or 2,6-naphtholsulfonate (Eastman Kodak Co., Rochester, NY) is prepared by dissolving the salt in 250 ml of anhydrous methanol in a 1-liter, 3-necked, round-bottom flask equipped with a magnetic stirrer, a dropping funnel, a reflux condenser protected by a calcium chloride drying tube, and a heating mantle. A methanolic solution of 0.1 mole of sodium methoxide is prepared by accurately weighing out 2.3 g (0.1 moles) of freshly cut sodium metal, dividing it into small pieces, and dissolving it in 50 ml of methanol in a Erlenmeyer flask previously cooled in an ice-bath. After all the sodium metal has reacted, the $NaOCH_3$ solution is poured into the stirred naphtholsulfonate solution. The mixture is stirred and heated to 60 C to dissolve any precipitated material.

Alkyl bromide (0.11 moles) is added from the dropping funnel over a period of 5-6 hr. After addition of the alkyl bromide is complete, the mixture is stirred and heated at reflux temperature for an additional 16 hr. The reaction mixture is cooled in an ice-bath, and the precipitated product removed by filtration. The filtrate is evaporated to half volume, cooled, and filtered to remove additional product. The combined yield of crude product is ca. 50% of the theoretical value.

The crude product is washed with hexane several times and recrystallized twice from 95% ethyl alcohol and twice from 1:3 (v/v) isopropyl alcohol-ethyl alcohol, using de-

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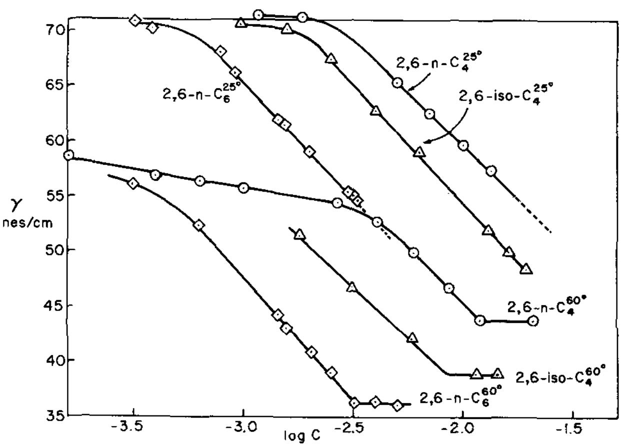

FIG. 1. Surface tension vs. log of the concentration of the 2,6-alkoxynaphthalenesulfonates in aqueous solution at 25 C and 60 C.

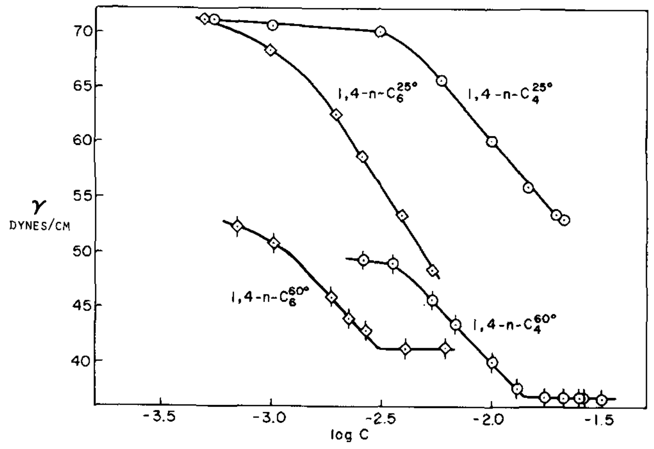

FIG. 2. Surface tension vs. log of the concentration of the 1,4-alkoxynaphthalenesulfonates in aqueous solution at 25 C and 60 C.

colorizing carbon when necessary. Finally, the purified product is recrystallized twice from quartz-distilled water.

The pure sodium alkoxynaphthalenesulfonates are white, hygroscopic, crystalline solids. After purification, they are dried over phosphorous pentoxide in a vacuum dissicator to constant weight. The yield of purified product is ca. 30% of the theoretical value.

Elemental analyses of the compounds are:

Compound[a]	Calculated C	Calculated H	Calculated S	Found C	Found H	Found S
2,6-n-C_4	55.62	5.00	10.60	55.89	5.16	10.95
2,6-n-C_6	58.17	5.80	9.70	58.42	5.92	9.78
2,6-iso-C_4	55.62	5.00	10.60	55.64	5.20	10.48
1,4-n-C_4 • ½H_2O	54.00	5.18	10.30	54.19	5.31	10.66
1,4-n-C_6 • ½H_2O	56.62	5.94	9.45	56.25	5.96	9.24

[a] 2,6-n-C_4 : Sodium 6-n-butoxy-2-naphthalanesulfonate.
2,6-n-C_6 : Sodium 6-n-hexoxy-2-naphthalenesulfonate.
2,6-iso-C_4 : Sodium 6-iso-butoxy-2-naphthalenesulfonate.
1,4-n-C_4 : Sodium 4-n-butoxy-1-naphthalenesulfonate.
1,4-n-C_6 : Sodium 4-n-hexoxy-1-naphthalenesulfonate.

The ultraviolet spectra of the sodium 6-alkoxy-2-naphthalenesulfonates show absorption maxima at ~277 nm and ~314 nm; the sodium 4-alkoxy-1-naphthalenesulfonates show absorption maxima at 297.5 nm and absorption minima at 251 nm.

The molar absorptivities of the compounds are:

Compound	251 nm	277 nm	278 nm	297.5 nm	313.5 nm	314 nm
2,6-n-C_4	—	5890	—	—	—	1186
2,6-iso-C_4	—	—	5780	—	1174	—
2,6-n-C_6	—	—	5910	—	1194	—
1,4-n-C_4	641	—	—	8750	—	—
1,4-n-C_6	658	—	—	9500	—	—

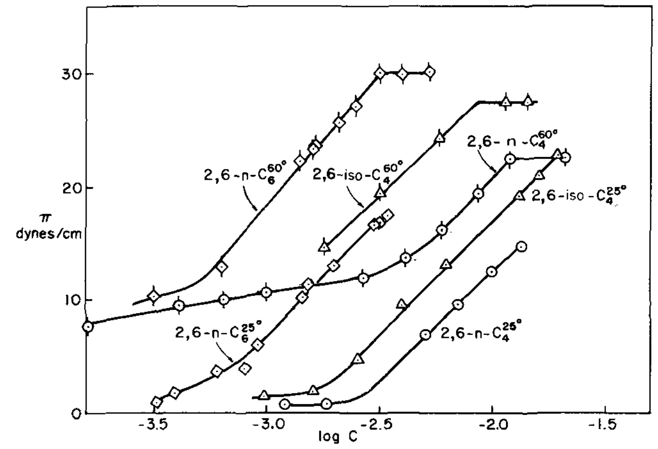

FIG. 3. Surface pressure vs. log of the concentration of the 2,6-alkoxynaphthalenesulfonates in aqueous solution at 25 C and 60 C.

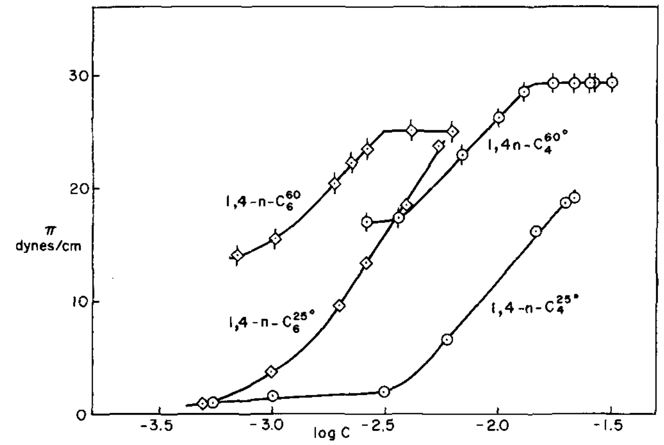

FIG. 4. Surface pressure vs. log of the concentration of the 1,4-alkoxynaphthalenesulfonates in aqueous solution at 25 C and 60 C.

Two-phase dye transfer titration of these compounds with Hyamine 1622 (4-6) using acid mixed indicator (Dimidium bromide and Disulphine Blue VN in dilute sulfuric acid) indicates that, with the possible exception of the isobutoxy derivative, this titration procedure is suitable for determining the concentration of aqueous solutions of these surfactants with a deviation of less than 1% from that obtained by use of molar absorptivities.

Krafft Points

These were determined from the discontinuity in the specific conductivity versus temperature curve of a saturated aqueous solution of the compound in the presence of excess solid (7). Since the discontinuity in the curves is slight for these compounds, the Krafft points are somewhat indefinite. The following Krafft points were observed:

Compound	Krafft point
2,6-n-C_4	~ 42 C
2,6-iso-C_4	~ 26 C
2,6-n-C_6	~ 57 C
1,4-n-C_4	~ 43 C
1,4-n-C_6	~ 57 C

Surface Tension Measurements

All surface tension measurements were made by Wilhelmy vertical plate technique, using a sand-blasted platinum plate of ca. 5 cm perimeter calibrated against quartz-

TABLE I

Critical Micelle Concentration (CMC) and Area/Molecule at the Liquid/Air Interface at 60 C

Compound	CMC (moles/liter)	Areas/molecule, in nm^2 x 100	
		From γ-log C curve	From molecular models
2,6-n-C_4	1.3 x 10^{-2}	119	100^a; 123^b; 44^c
2,6-iso-C_4	8.4 x 10^{-3}	114	110^a; 120^b; 45^c
2,6-n-C_6	3.2 x 10^{-3}	95	100^a; 135^b; 46^c
1,4-n-C_4	1.4 x 10^{-2}	102	95^a; 118^b; 52^c
1,4-n-C_6	3.1 x 10^{-3}	100	96^a; 131^b; 53^c

[a] For only the oxynaphthalenesulfonate portion lying flat in the interface.

[b] For the entire molecule lying flat in the interface.

[c] For the entire molecule standing vertical to the interface.

TABLE II

Surface Excess Concentration (Γ), Efficiency, and Effectiveness of Surface Tension Reduction

Compound	Temp. (C)	Γ x 10^{10} (moles/cm^2)	Efficiency pC_{20}	Effectiveness (π at 3.2 x 10^{-3}M conc.)
2,6-n-C_4	25	1.7	$(1.60)^a$	3.0
	60	1.4	2.03	12.0
2,6-iso-C_4	25	1.9	2.89	6.8
	60	1.5	2.45	19.3
2,6-n-C_6	25	1.8	$(2.35)^a$	17.1
	60	1.8	2.93	29.7
1,4-n-C_4	25	2.1	1.64	2.0
	60	1.6	2.30	17.1
1,4-n-C_6	25	2.7	2.37	16.4
	60	1.7	2.74	24.9

[a] By extrapolation.

distilled water (specific conductivity 1.1 x 10^{-6} ohm^{-1} cm^{-1} at 25 C) each time measurements were made (7).

Plots of the surface tension (γ) of aqueous solutions of these alkoxynaphthalenesulfonates versus the log of their bulk concentrations in moles/liter (log C) are shown in Figures 1 and 2. Plots of the surface pressure, π, where $\pi = \gamma_o - \gamma$ and γ_o = the surface tension of the pure water at that temperture, versus the log of the bulk concentrations of the surfactants, are shown in Figures 3 and 4.

Critical micelle concentrations (CMCs) were taken as the concentrations at the points of intersection of the two linear portions of the γ - log C curves. Surface excess concentrations, Γ, in moles/cm^2, and surface areas/molecule, A, in nm^2, at the liquid/air interface were calculated from the relationships

$$\Gamma = -\frac{1}{4.61\ RT}\left(\frac{\partial\gamma}{\partial \log C}\right)_T$$

and

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

where $\left(\frac{\partial\gamma}{\partial \log C}\right)_T$ is the slope of the surface tension-log concentration curve at constant (absolute) temperature, T, R = 8.31 x 10^7 ergs $mole^{-1}$ degree $Kelvin^{-1}$ and N = Avogadro's number. The values obtained for the CMCs and minimum surface areas/molecule, together with cross-sectional areas of the compounds as determined from molecular models, are listed in Table I. The minimum values of A were calculated from the linear portion of the γ-log C curves (maximum values of Γ), just below the CMC.

The efficiency of surface tension reduction of a surfactant (2) is measured by the negative log of the concentration required to depress the surface tension of the solvent by 20 dynes/cm, $-(\log C)_{\pi=20}$, symbolized pC_{20}. The effectiveness of surface tension reduction of a surfactant (3) is measured by the amount of reduction of the surface tension of the solvent at the critical micelle concentration of the surfactant, π_{cmc}. Since these compounds are too insoluble in water at 25 C to reach their CMCs (i.e., their Krafft points are above 25 C), π_{cmc} cannot be used as a measure of the effectiveness of these compounds at 25 C. In order to compare the effectiveness of these compounds at 25 C and 60 C, the amount of surface tension reduction, π, of the solvent attained at an arbitrary molar concentration of 3.2 x 10^{-3} (where data are available for all the compounds) was used.

Values of the maximum surface excess concentration, Γ, the efficiency of surface tension reduction, pC_{20}, and π at 3.2 x 10^{-3} M concentration of each of these alkoxynaphthalenesulfonates are listed in Table II.

DISCUSSION

The Krafft points of these compounds increase with increase in the chain length of the hydrophobic group, as is usually the case, and as expected, the isobutyl compound has a lower Krafft point than its n-butyl isomer. Since the electrical conductance-temperature curves of these surfactants show an unusually small discontinuity, the Krafft points are rather indefinite. In the two series investigated, the relative positions of the alkoxy and sulfonate groups on the naphthalene nucleus appear to have little effect on the Krafft point.

The surface areas per molecule at the liquid/air interface (Table I) calculated from the surface tension-log concentra-

TABLE III

Number of Carbon Atoms in Straight Alkyl Chain Equivalent to Alkoxynaphthalene or Oxynaphthalene

	Group					
	Based on CMC		Based on pC_{20}			
	60 C		60 C		25 C	
Compound	Alkoxynaphthalene	Oxynaphthalene	Alkoxynaphthalene	Oxynaphthalene	Alkoxynaphthalene	Oxynaphthalene
2,6,n-C_4	11.9	7.9	11.6	7.6	(9.6)[a]	5.6
2,6-iso-C_4	12.5	---	13.0	---	10.5	---
2,6-n-C_6	14.0	8.0	14.5	8.5	(11.9)[a]	5.9
1,4-n-C_4	11.7	7.7	12.5	8.5	9.7	5.7
1,4-n-C_6	14.1	8.1	13.9	7.9	12.0	6.0

[a] By extrapolation.

tion curves, indicate that in these surfactants the oxynaphthalenesulfonate portion may be lying flat in the interface at 60 C with the alkyl group oriented perpendicular to the interface. The data also indicate somewhat closer packing of the molecules at the interface as the chain length of the alkyl portion is increased.

Critical micelle concentrations decrease, as expected, with increase in the number of carbon atoms in a straight alkyl chain attached to the oxynaphthalenesulfonate group. However, the isobutyl derivative shows unusual behavior in that its CMC is lower than that of its n-butyl isomer, contrary to the general observation that branched chain compounds generally have higher CMCs than their straight chain isomers (8). A possible explanation is that steric hindrance to hydration of the adjacent ether oxygen by the bulky isobutyl group increases the hydrophobic character of the alkoxy group compared to that of its n-butyl isomer. This steric inhibition of hydration of the adjacent ether oxygen may also account for the greater surface tension reducing efficiency of the isobutyl derivative, compared to its n-butyl isomer. This again is contrary to the observation that compounds with branched chain hydrophobic groups generally have lower surface tension reducing efficiencies than their straight chain isomers (9). As with the Krafft points, the relative positions of the alkoxy and sulfonate groups on the naphthalene nucleus appear to have little effect on the CMCs of the 1,4- and 2,6-isomers.

The efficiency of surface tension reduction, pC_{20}, increases with increase in the length of the alkyl group in both the 1,4- and 2,6-series, except for the isobutyl derivative (Table II). This is consistent with previous observations of the increase in efficiency with increase in the length of the (straight chain) hydrophobic group (2) and is also consistent with the anomalous CMC of the isobutyl derivative.

The effect of temperature change on the efficiency with which these compounds reduce surface tension is, however, unusual. All of the compounds show considerably greater surface tension reducing efficiency at 60 C than at 25 C. On the other hand, the few other ionic compounds (none of which contains an aryl ether linkage) for which data on the effect of temperature change on surface tension reduction efficiency are available (2), all show a *reduction* in efficiency with increase in temperature. The most probably cause for the increase in efficiency in the case of these alkoxynaphthalenesulfonates is a decrease in the degree of hydration of the aryl ether linkages when the temperature is increased. Such a decrease would increase the hydrophobic character of the alkoxynaphthalene group and its equivalent length as a straight chain hydrophobic group and consequently its efficiency of surface tension reduction.

The effectiveness of these compounds in reducing surface tension is also increased by an increase in temperature (Fig. 3 and 4, Table II). This, too, is unusual since the available data on the effect of temperature on the effectiveness of surface tension reduction show either no effect or a slight reduction with increase in temperature (3,10,11).

The number of carbon atoms in a straight alkyl chain to which the alkoxynaphthalene hydrophobic group in these compounds is equivalent can be estimated from either their CMCs or their pC_{20} values by comparing them with those of sodium alkanesulfonates or alkylbenzenesulfonates at the same temperature. Table III lists the carbon equivalencies of the alkoxynaphthalene groups in these compounds at both 60 C and 25 C, together with the equivalencies of the oxynaphthalene group for the four compounds containing straight alkyl chains. The carbon equivalency of the oxynaphthalene portion in the isobutyl derivative cannot be determined because the unusual surface properties of this compound make the straight chain equivalency of the isobutyl group indeterminate in this case.

The data in Table III indicate that the oxynaphthalene group, in both the 2,6- and 1,4-alkoxynaphthalenesulfonates, is equivalent to a straight chain alkyl group of about eight carbon atoms at 60 C and of about six carbon atoms at 25 C, the higher carbon equivalency at 60 C reflecting the greater hydrophobic character of the aryl oxygen atom at the higher temperature.

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