and cyclic peroxides decreases the nonconjugated *cis* double bonds. In fact, in fraction 2 (Figure 3), the absorption at 913 cm^{-1} arising from nonconjugated *cis* double bonds is considerably less than in fraction 1 (Fig. 3). It is presumed that, as mentioned above, fraction 2 contains the changed substance of fraction 1. Therefore, the separation of fraction 1 and fraction 2 is not good.

If partition chromatography is used to separate peroxide concs, monomeric dihydroperoxide concs can be isolated, as shown in this paper. But partition chromatography cannot be used to obtain unchanged monomeric dihydroperoxide concs from the autoxidized sample, because the amt of the dihydroperoxides is small. In fact, the monomeric dihydroperoxide concs found in this paper were not found previously (5).

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The Synthesis and Some Surface Active Properties of Alkylthioalkyl and Alkoxyalkyl Sulfates

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Abstract

A series of sodium alkylthio- and alkoxyalkyl sulfates was prepared to determine the effect of the presence, position and nature of the heteroatom on the critical micelle concentration (CMC), the surface activity and detergency of a surfactant. All of the compounds were linear and contained a total of 16 carbon atoms. Hexadecyl-1-sulfate was used as the reference compound.

Insertion of either a sulfur or oxygen atom into the hydrocarbon chain raised the CMC. In the oxygen series, the apparent trend was to a higher CMC as the oxygen atom was moved further away from the sulfate group whereas no trend was observed in the thioether series.

The surface activity of hexadecyl-1-sulfate was higher than either the ether or thioether series. The further the heteroatom from the sulfate group, the lower was the surface activity. This trend was more pronounced in the oxyether series.

All hetero-substituted compounds were generally inferior to hexadecyl sulfate in detergency.

Hydration of the oxygen atom in the oxyethers, but not the sulfur atom in the thioethers is proposed as the explanation for the observed trends.

Introduction

THE MAXIMUM PERFORMANCE of a surfactant molecule is attained at or near the critical micelle concentration (CMC) (1). At this concentration, the addition of fresh surfactant increases only the concentration of surfactant molecules in micellar form and not as discrete monomolecular species. The CMC of a surfactant solution is dependent, to a degree, on the solution's environment (e.g., temperature, ionic strength, etc.) but primarily on the structure of the surfactant. In a homologous series the CMC decreases with an increase in the length of the hydrophobic portion of the molecule (2), the CMC increases with branching on the chain (3,4) or if the hydrophilic group is moved toward the center of the chain (5); increases with polar substitution or unsaturation on the hydrophobe (2) and finally is influenced to a lesser extent by the nature of the hydrophilic group (2).

As Hartley indicated (4), only the single surfactant molecules are surface active and thus micelle formation competes with surface activity. He postulated that if the amphipathic property of the ion could be preserved and at the same time micelle formation inhibited, a greater surface response (in his case, interfacial tension) could be attained. He prepared and determined the CMC and interfacial tension of solutions of various sulfonated dialkyl esters of dihydric phenols and compared these values to those of a sulfonated alkyl ester of *para*-cresol. The former could not fit into the micelle as easily as the latter and thus had higher CMC values, but the latter, relatively straight chain compounds, had greater surface activity. Thus, although Hartley was able to inhibit micellization, he was unable at the same time, to preserve the amphipathic property of the ions.

This research was an attempt to inhibit micellization but *not* change the surface activity of the unsubstituted molecule. We expected to accomplish this by the insertion of either a sulfur or oxygen atom between two methylene groups on the carbon chain.

Sodium hexadecyl-1-sulfate was chosen as the unsubstituted compound, the model for the series. All of the compounds prepared resembled sodium hexadecyl-1-sulfate insofar as they were sodium salts of the sulfuric esters of linear primary alcohols containing 16 carbon atoms but differed from the model by the presence of a sulfur or oxygen heteroatom inserted in the hydrophobe chain. The position of the heteroatom was also varied to determine the effect of its position on the CMC, the surface activity and the cotton detergency of the surfactants.

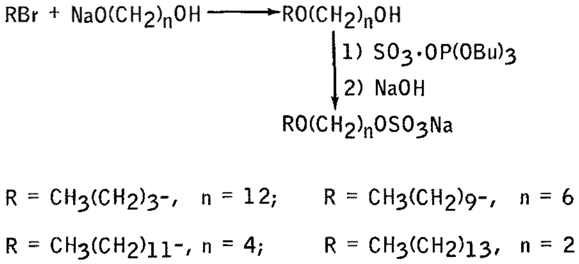

FIG. 1. Synthesis of alkoxyalkyl sulfates.

Experimental

The preparation of the alcohols will be the subject of another publication. The sulfates were prepared by a modified method of Turbak and Livingston (11).

A solution of sulfur trioxide and tributyl phosphate was prepared by the addition of 80 g (1 mole) of sulfur dioxide to 266 g (1 mole) of tributyl phosphate in 400 ml of methylene chloride at 0–5C.

3-Oxaheptadecanol-1 (15 g, 0.058 mole) dissolved in 50 ml of methylene chloride was added to 42.9 g (0.058 mole) of the sulfur trioxide phosphate complex at 10–15C. Stirring was continued for 10 min and then the mixture was neutralized with 50% sodium hydroxide solution. The mixture was extracted with a 50:50 water isopropyl alcohol mixture and then the aqueous layer re-extracted with petroleum ether. The aqueous layer was concentrated on a steam bath and the sulfate precipitated by the addition of acetone, filtered, and, after drying, recrystallized from absolute ethanol. Sodium-3-oxaheptadecyl-1-sulfate (I) 11.0 g, 53% was recovered.

Results and Discussion

The detailed synthesis of the alcohols from which the sulfates were prepared will be the subject of another publication. The general method of preparation and the compounds prepared are outlined in Figures 1 and 2. All of the sulfates were recrystallized from ethanol until satisfactory purity was indicated by elemental analyses. A more exacting criterion of purity (minima in the surface tension curves) showed that the sulfates still contained small amounts of impurities.

Melting Points of Alcohols

Evidence that crystalline packing (6) is affected by the presence and position of the heteroatom in the carbon chain is shown in Figure 3—a comparison of the melting points of the alcohols from which the sulfates were prepared. In both the oxygen and sulfur series the hetero-substituted alcohol has a lower melting point than the unsubstituted model, 1-hexadecanol. As the heteroatom is located a greater distance from the primary hydroxyl group, the melting point of the molecule becomes lower indicating that the attractive forces between molecules in the crystal have been decreased. A much greater effect is seen for the oxyalcohols than for the thiaalcohols. Although the cause (polarity of the heteroatom, steric inhibition to packing, etc.) of the vast difference in melting points between the sulfur and oxygen series is not clear, it obviously must be due to some difference in the molecule caused by the heteroatom.

Critical Micelle Concentration

The aggregation of surface active molecules into micelles occurs because it lowers the total free energy of the surfactant solution. Micelle growth continues until the energy factors favoring micellization are overcome by those opposing micellization. Among the factors favoring micellization are the cohesive force between water molecules which tend to "force" the hydrophobic part of the surfactant out of solution, and the weak attractive forces between the hydrocarbon chains of the surfactant in the micelle. Factors opposing micellization are the electrostatic repulsion of charged hydrophilic groups and the decrease in entropy of the surfactant molecules caused by aggregation (7).

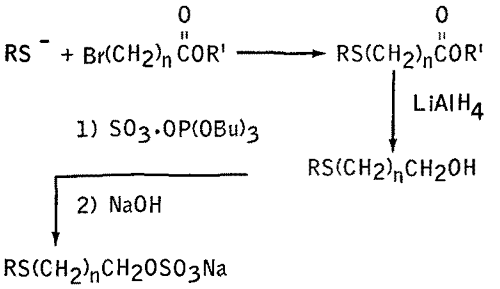

FIG. 2. Synthesis of alkylthioalkyl sulfates.

Although there is disagreement concerning the exact shape of a micelle, in aqueous systems, the polar, hydrophilic portion of the surfactant is always considered to be located on the periphery of the micelle and the nonpolar lipophilic portion in the inside of the micelle. Since micellization and micelle growth is dependent on an energy balance, any change in intermolecular forces due either to the structure or the polarity of the hydrophobe will influence the CMC. For instance, if the attractive forces between the carbon chains are decreased and if all else is equal, the CMC will be increased. In like manner, if a polar moiety is forced into the nonpolar medium of the micelle interior, the CMC should also be increased.

The CMC of the various sulfates was determined by measuring the change in specific conductance of the sulfate with concentration.

The data, as summarized in Table II, indicate that the CMC is affected significantly by the presence of the oxygen atom. The presence of the sulfur atom, however, has practically no effect on the CMC. In the oxyether series the position of the oxygen atom in the chain exerts a pronounced effect on the CMC of the sulfate. The greater the separation of the hetero oxygen atom from the sulfate group, the higher is the CMC.

One explanation of this raising of the CMC can be attributed to a decrease in the attractive forces between the hydrocarbon chains. Since the attractive

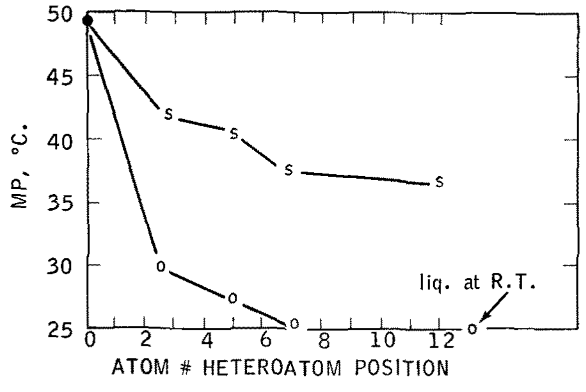

FIG. 3. Melting point of alcohol vs. heteroatom position.

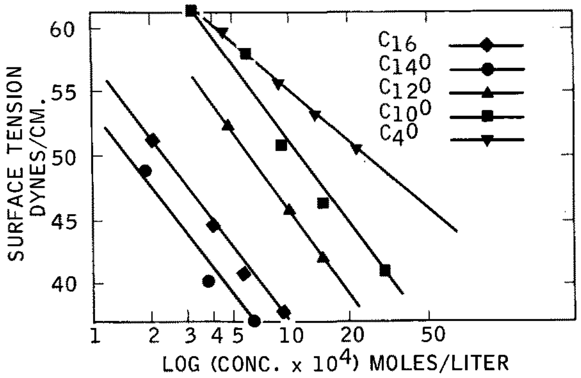

FIG. 4. Surface tension at 25C of alkoxalkyl sulfates.

forces promote micellization, any decrease in them would be reflected in a higher CMC. One piece of evidence in favor of this explanation is that the melting points of the oxyalcohols lower in the same trend as the CMC's increase. If the melting point lowering is due to a reduction in the attractive forces, so then could be the increase in the CMC's.

Another possible cause of this phenomenon may be the hydration of the heteroatom. If the heteroatom is hydrated, the water of hydration would either have to be removed or else brought into the interior of the micelle. In both extremes energy would have to be expended, either to remove the water or else to overcome an unfavorable packing situation which would be created if the water were brought into the micelle. In either case micellization would be inhibited. Evidence in support of this explanation is the relative degree to which organo-bound sulfur and oxygen atoms are hydrated. Hydration of the oxygen atom in organic molecules renders low molecular weight alcohols and other oxygenated compounds water soluble. On the other hand, sulfur atoms are not hydrated and thus diethyl sulfide is insoluble in water whereas diethyl ether has appreciable water solubility. Thus, if hydration of the heteroatom causes an increase in the CMC its effect should be more pronounced in the oxygen series—as it is.

Surface Activity

The surface activity or the degree of adsorption of the surfactants was measured by rate of change in surface tension with concentration (8,9). In these series the surface activity decreased as the CMC increased. As shown in Figure 4, there is an evident reduction in surface activity as the oxygen atom is farther removed from the sulfate group as indicated by the decreasing slope of the plot. At a given concentration, sodium 3-oxaheptadecyl-1-sulfate appears to be adsorbed to about the same extent as sodium hexadecyl-1-sulfate whereas sodium 13-oxaheptadecyl-1-sulfate is considerably less adsorbed. For instance, at a concentration of 5×10^{-4} moles/liter, the surface tension of sodium 3-oxaheptadecyl-1-sulfate solution is about 38 dynes/ cm while at the same concentration the sodium 13-oxaheptadecyl-1-sulfate is about 59 dynes/cm.

TABLE I

Analytical Data

Compound	Mp of corres. alcohol ° C	S calc.	S found
Sodium-3-oxaheptadecyl-1-sulfate (I)	29–30.5	8.90	9.02
Sodium-5-oxaheptadecyl-1-sulfate (II)	26.5–27.5	8.90	8.72, 8.67
Sodium-7-oxaheptadecyl-1-sulfate (III)	25°	8.90	913, 9.20
Sodium-13-oxaheptadecyl-1-sulfate (IV)	Liquid	8.90	8.93
Sodium-3-thiaheptadecyl-1-sulfate (V)	41.5–42.5	17.03	17.07, 17.15
Sodium-5-thiaheptadecyl-1-sulfate (VI)	40–41.5	17.03	16.84
Sodium-7-thiaheptadecyl-1-sulfate (VII)	37–38	17.03	17.08, 16.90
Sodium-12-thiaheptadecyl-1-sulfate (VIII)	36.5–37.5	17.03	16.88, 16.83

Note: The carbon and hydrogen microanalyses were found to be unreliable because of incomplete burning of the sulfate. The sulfur anayses were found to be reliable and are cited here in the absence of the carbon-hydrogen analyses. Elemental analysis were carried out by the Analytical Research Division of Esso Research and Engineering Company.

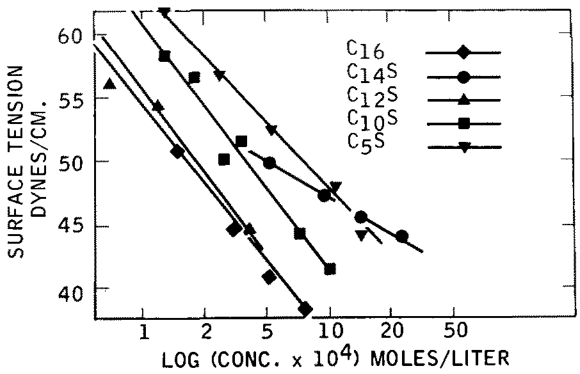

FIG. 5. Surface tension at 25C of alkylthioalkyl sulfates.

Figure 5 summarizes the surface tension data on the thioether series. Sodium 3-thiaheptadecyl-1-sulfate inexplicably appears to be less surface active than any of the other compounds in the series. The other thioethers are closer in activity and degree of adsorption than are the oxyethers. For instance, at the point of widest separation, a 5×10^{-4} molar concentration of sodium 5-thiaheptadecyl-1-sulfate has a surface tension of about 42 dynes/cm while the sodium 12-thiaheptadecyl-1-sulfate at the same concentration has a surface tension of 53 dynes/cm—a difference of only 11 dynes/cm. At this concentration, the oxygen series has a maximum difference of 21 dynes/cm—about twice as much as the thioethers.

It is apparent that even in these compounds of very similar structure, the surface activity is varied significantly by small changes in structure just as is the CMC. That the surface activity should vary to such a degree is inexplicable solely on the basis of changes in intermolecular forces between the hydrophobic chains or steric hindrance to interfacial packing. It further supports the argument that the hydration effect is the real cause of the difference in the series. The farther removed the two hydrated or hydrophilic groups, the shorter is the effective chain length of the hydrophobe and thus the lower is the surface activity (4).

TABLE II

Critical Micelle Concentration and Cotton Detergency

Compound	CMC[a] Moles/liter $\times 10^3$	Cotton detergency[b] Δ Reflectance
I	1.1 [lit. 1.5 (12)]	6.75
II	2.9	6.30
III	3.95	5.05
IV	7.1	3.60
V	2.95	7.45
VI	0.6	7.10
VII	1.45	6.80
VIII	1.15	7.45
Sodium hexadecyl-1-sulfate	0.50 [lit. 0.67 (12) 0.40 (13)]	7.21

[a] The CMC's were determined from conductance measurements at 25.0C. A cell with a 1.51 cell constant was used in conjunction with an RD-16B2 conductivity bridge manufactured by Industrial Instruments Inc., Cedar Grove, New Jersey.

[b] Cotton detergency measurements were made by the U.S. Testing Company in the Terg-O-Tometer Test with U.S. Testing Company standard soiled cloth. The conditions used were 0.04% actives in a standard heavy duty formulation * containing no foam boosters at 130F.

* Heavy duty formulation
Actives—20%
Phosphates—40%
Sodium sulfate—34%
Sodium metasilicate—5%
Carboxymethyl cellulose—1%

Cotton Detergency

The cotton detergency of the sulfates was determined with a Terg-O-Tometer using U.S. Testing Company soiled cloth. The cleaning ability of the detergent is reported in terms of ΔR, the difference in percent reflectance between the washed cloth and the original soiled cloth. The greater the increase in percent reflectance, the more efficient is the cleaning agent.

A comparison of the relative cotton detergency of the various sulfates was made and is outlined in Table II. The thioether sulfates exhibited approximately the same cotton detergency regardless of the hetero sulfur atom position. They were also equivalent to the standard, 1-hexadecyl sulfate.

The oxyethers decreased in cotton detergency performance with increasing distance of the oxygen atom from the sulfate group and were inferior to hexadecyl-1-sulfate. It was noted above that the CMC's and the surface activities of the thioether series were not affected to nearly the same degree by the presence and position of the sulfur heteroatom as in the oxyether series. In general, the sulfates which have the lowest CMC's were found to be the most surface active and to be the most effective cotton detergents.

A plot of the change in reflectance vs. the surface activity of the surfactant shows an apparent relationship between the two. There seems to be only a certain level of surface activity needed for cotton detergency (as seen in Figure 6) because as the surface activity increases above this level, the change in reflectance does not increase. Since solubilization, wetting ability and deflocculation (10) all play major roles in cotton detergency and since the relationship of these properties to heteroatom positions has not yet been determined, a firm conclusion concerning the relationship between surface activity and detergency cannot yet be drawn.

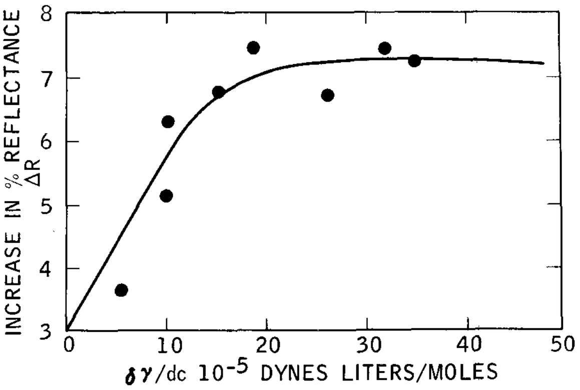

FIG. 6. Δ Reflectance vs slope of surface tension curve.

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A Laboratory Method for Testing Laundry Products for Detergency

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Abstract

A laboratory screening test for fabric detergency has been developed, which closely parallels practical laundry operations. Natural airborne particulate is used so that the argument for and against carbon soil is eliminated. The oily soil consists of synthetic sebum, thereby simulating the surface film that covers the human integument. The particulate and fatty matter are combined into an aqueous suspension and padded onto the fabric. Variables can be measured in a minimum of time because the entire procedure is carried out in the laboratory and is not dependent on a panel of subjects as is the case in most practical testing. The procedure for this test as generally employed consists of multiple washes and measures brightener build up and redeposition in addition to detergency. Precision of the method is ± 0.4% at the 95% confidence level. Evaluations are made both visually and instrumentally.

Introduction

"THE POWER TO REMOVE SOIL by a colloidal chemical process that is possessed by certain materials or systems is called detergency." (1) A laboratory test that is designed to measure this phenomenon should relate to practical testing. The most common practice today is to wash standard soiled swatches and measure the reflectance before and after washing. These reflectance data are translated into soil content or soil removal in many instances. However, the results obtained from different commercially prepared artificially soiled cloths are not always in agreement with each other (2) and interpretations must be made with perspicacity. Since a great deal of time and manpower are being used in tailoring molecules for soft detergents, the measurement of detergency takes on added importance. It is for this reason that this study was made.

The choice of soil to use for detergency measurements and the method of application have been the subject of many publications. A total review of the