TABLE V

Effect of NAF's from Heated and Unheated Oils on Three Day Gains and Liver Size of Mice

	Soybean Oils				Cottonseed Oils			
	Three day gain (grams)		Liver, % of body wt		Three day gain (grams)		Liver, % of body wt	
	Non-heated	Heated	Non-heated	Heated	Non-Heated	Heated	Non-heated	Heated
Crude	1.3	1.7	5.9	7.6	2.4	2.8	6.5	8.3
Refined	1.3	2.1	5.9	8.2	2.0	2.6	6.9	8.2
Refined and Bleached	1.3	1.3	6.2	8.0	2.6	2.7	7.3	7.8
Ref., Bl., and Deodorized, 160C	1.6	1.8	6.2	8.3	2.9	2.7	7.1	8.2
Ref., Bl., and Deodorized, 204C	1.3	2.4	7.1	8.0	1.8	2.8	6.4	8.7
Ref., Bl., and Deodorized, 238C	1.2	1.7	6.6	8.1	1.7	2.6	6.9	8.1

deodorization.

Table V summarizes the data obtained when the NAF'S separated from the heated and non-heated oils were fed to mice at the level of 40 mgm in 360 mgm of cottonseed salad oil per mouse per day. It should be pointed out that these 40 mgm amounts represent different quantities of starting because the oils in the heated and unheated series contain varying amounts of NAF. Again the only significant differences in liver weight were those due to heating the oils. The NAF's within either the unheated or the heated series of oils were not significantly different; but the heated series did differ from the unheated. Contrary to the observation made when the oils were fed, the weight gains at the end of three days were on the whole better for the NAF's from heated oils than from unheated.

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The Analysis of Alkyl Aryl Sulfonates by Micro Desulfonation and Gas Chromatography

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Abstract

The structural analysis of micro quantities of alkyl aryl sulfonates by presently known chemical and spectroscopic techniques has been an exceedingly difficult task. The formidable nature of such analyses is due largely to the essential nonvolatility of the sulfonates, a fact which precludes the application of gas-liquid chromatography and mass spectrometric techniques.

The present paper describes an approach wherein gas chromatography is made applicable to analysis of micro quantities of sulfonates. The key to the approach is a microchemical desulfonation procedure. This process yields the parent hydrocarbon, which is volatile and hence amenable to analysis by gas-liquid chromatography and mass spectrometry.

Introduction

THE STRUCTURAL ANALYSIS of micro quantities of alkyl aryl sulfonates by presently known chemical and spectroscopic techniques has been a very difficult task. The difficulty in analyzing these materials rests on two major factors: (1) the essential nonvolatility of the sulfonates, which effectively precludes the application of such powerful techniques as gas chromatography and mass spectrometry, and (2) the great chemical complexity of the commercial alkyl aryl sulfonates, which consist of at least scores and perhaps hundreds of different molecular species.

An analytical method was required to support studies which were under way in our laboratories involving reactions of alkyl aryl sulfonates in the 10–40 ppm level. Some of the analytical requirements were as follows: (1) The method must be essentially quantitative and also yield qualitative information on structural changes of the sulfonate. (2) The method must apply to a variety of sulfonates of known structure and to commercial alkyl aryl sulfonates as well. (3) The method must be capable of dealing with one-liter samples containing from 10–40 ppm of sulfonate in the presence of a large excess of a complex reaction milieu including a variety of inorganic and organic compounds blended in an aqueous nutrient medium designed to promote growth of microorganisms.

Since an isolation procedure was essential, several schemes were developed to fractionally isolate certain components for special purposes; however for general

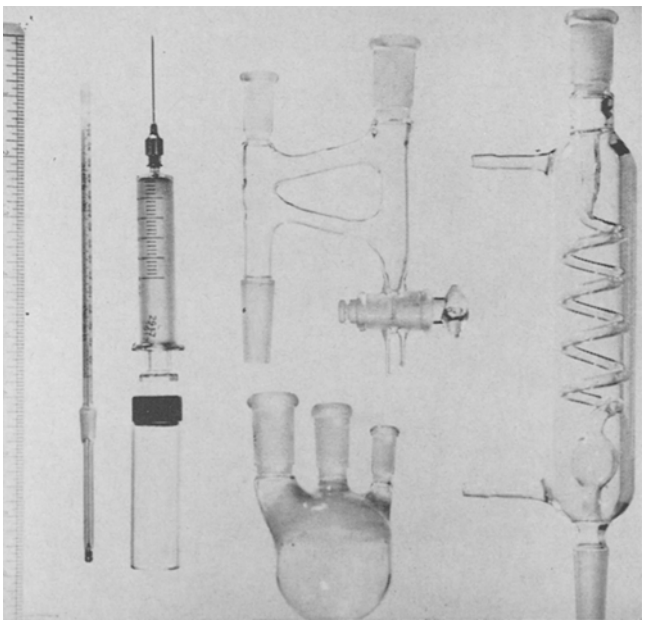

FIG. 1. Desulfonation apparatus.

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studies a charcoal adsorption-desorption technique was used similar to that developed by the AASGP subcommittee for the analysis of ABS (1). Careful attention was given to the work of Brown and Knobloch (2) on desulfonation of petroleum sulfonates using 30% aqueous phosphoric acid at 375F in an autoclave; however this approach did not appear promising because of problems in handling our milligram quantities of sample and also because of the relatively high volatility of the hydrocarbon entities which would be used in our studies. Shortly after the inception of our program, Knight and House (3) published their valuable work on the analysis of macro quantities of surfactant mixtures based on decomposition of the surfactant in hot phosphoric acid and subsequent characterization of the hydrophobic oil by instrumental techniques. This information was of great help to us; however the many problems involved in isolating, desulfonating, and completing structural studies of sulfonates at the 10–40 ppm concentration level were still present.

The present paper describes the initial phases of a successful attack upon this problem. The key to success was the development and application of a micro-chemical isolation and desulfonation procedure, a process which yields the parent hydrocarbon which is volatile and hence amenable to analysis by gas-liquid chromatography and mass spectrometry.

Experimental

The desulfonation apparatus is shown in Figure 1. The desulfonation procedure is essentially that of Knight and House with modifications in design to handle samples down to 10 mg or less.

The sample for analysis is normally received in one liter of aqueous solution containing 10–40 mg of the sulfonate under study, several grams of inorganic salts, and 0.3–0.4 g of organic nutrient. The solution is made I N with HCl and hydrolyzed for 15 min at the boiling point to clarify the solution and remove possible adsorbed sulfonate from organic matter and from glass surfaces. After cooling, the solution is neutralized to pH 8–9 with NaOH. The sample is then passed through a glass column approximately 8 by 1.3 in. containing 15–20 g of Nuchar C-190 charcoal. By means of a stopcock at the bottom of the column, the flow rate is adjusted to about 3 ml/min. After the adsorption, the column is rinsed with about 300 ml of distilled water to remove inorganic salts and lightly adsorbed organic compounds. The sulfonate (plus some adsorbed organic matter) is then eluted from the column with 100 ml of methanol followed by 500 ml of 1% ammonium hydroxide in 1:1 benzene-methanol (4). The charcoal is then removed from the column, slurried with an additonal 500 ml of the elution solvent, and heated at the boiling point for 15–20 min on a steam bath. The slurry is then filtered to remove the charcoal, and the filtrate and any rinses are combined with the 600 ml of column eluant; and the entire solution is evaporated to dryness. The solid material is then dissolved in a minimum quantity of distilled water and transferred to the 50-ml desulfonation flask, using several increments of water to complete a quantitative transfer. The small desulfonation flask is then placed under an air jet on a steam bath to evaporate the water used in transfer. Thirty ml of H_3PO_4 boiling at about 210C (previously prepared by distillation of contained water until the BP of the H_3PO_4 reaches about 210C) is then added to the flask, carborundum boiling chips added, and the apparatus (Fig. 1) is assembled. After adding water to the modified distillation head to just below the point of return to the 3-necked flask, heat is applied; and a temperature of 215-220C is maintained by adjustment of the water level in the distillation head. The reaction is continued for 60–90 min. Upon completion of the reaction, the water in the distilling head is drawn into a 15-ml screw cap vial. The condenser and distilling head are then flushed with 4 ml of ethanol and the ethanol added to the vial. Using the vial as an extraction cylinder, the oil is extracted from the alcohol-water solution with 5 separate extractions of pentane, using approximately 2–3 ml of pentane for each extraction. The condenser and distilling head are flushed several times with the pentane used in making the extractions. Each pentane extract is removed from the vial and added to a 4½ by ½-in. test tube, using a hypodermic syringe to make the transfer. The test tube is then attached to a house vacuum line and the pentane evaporated by careful adjustment of vacuum to prevent bumping or bubbling. It was found that this method of solvent removal could be safely used with materials too volatile to allow solvent removal by any other conveniently available laboratory method.

After solvent removal, the oil is ready for structural analysis. For GLC about 30 μl of pure hexane is added to the test tube as a diluent to provide sufficient sample volume for convenient handling. When sample quantity is very small, any sample used for infrared analysis may usually be recovered for subsequent GLC analysis. Most of the chromatographic analyses were made using a 14 ft column containing 28 wt % of Resoflex 728 on 42–60 firebrick at column temperatures of 190–225C.

TABLE I

Accuracy and Repeatability Data from the Desulfonation of the Mixed Isomers of Phenyl Octane, Decane, and Dodecane Sulfonates

Sample	Alkylate yield [a] % theory	Isomer composition % total			
		2-Phenyl	3-Phenyl	4-Phenyl	5-Phenyl
Phenyl octane:					
Original alkylate	....	49.5	28.6	21.9	.....
After desulfonation 1	86	50.4	28.4	21.2	.....
2	86	50.6	28.2	21.2	.....
3	82	50.5	28.2	21.3	.....
Phenyl decane:					
Original alkylate	....	35.1	23.6	20.9	20.4
After desulfonation 1	91	35.3	23.6	20.9	20.2
2	89	35.3	23.9	20.9	19.9
3	91	35.2	23.4	20.9	20.5
Phenyl dodecane					
Original alkylate	....	30.2	22.4	19.4	28.0 [b]
After desulfonation 1	90	28.8	22.0	20.2	29.0 [b]
2	89	28.5	21.9	20.4	29.2 [b]
3	91	28.6	21.6	20.2	29.6 [b]

[a] Alkylate yield from 20 mg sodium sulfonate samples.
[b] Value includes the 6-phenyl isomer.

TABLE II

Desulfonation of a Blend of the Mixed Isomers of Phenyl Hexane, Octane, Decane, and Dodecane Sodium Sulfonate

Sample [a]	Isomer composition % total			
	2-Phenyl	3-Phenyl	4-Phenyl	5-Phenyl
Phenyl hexane:				
Original alkylate	62.7	37.3	.....	.....
After desulfonation	71.4	28.6	.....	.....
Phenyl octane:				
Original alkylate	49.4	28.9	21.7	.....
After desulfonation	50.1	28.6	21.3	.....
Phenyl Decane:				
Original alkylate	35.6	24.0	20.4	20.0
After desulfonation	36.4	23.2	20.6	19.8
Phenyl Dodecane:				
Original alkylate	29.1	21.5	20.5	28.9 [b]
After desulfonation	29.7	21.0	20.2	29.1 [b]

[a] Alkylate yield from 40 mg of sulfonate was 84% of theory.
[b] Includes 6-phenyl dodecane isomer.

TABLE III
Accuracy and Repeatability Data from 40 mg Sample of a Blend of the Mixed Isomers of Phenyl Hexane, Octane, Decane, and Dodecane Sodium Sulfonates after Sulfonation, Charcoal Adsorption, Desorption, and Desulfonation

Sample	Isomer composition % total			
	2-Phenyl	3-Phenyl	4-Phenyl	5-Phenyl
Phenyl hexane:				
Original alkylate	62.7	37.3	.....	.....
Recovered alkylate from				
Run 1	71.4	28.6	.....	.....
Run 2	71.1	28.9	.....	.....
Phenyl octane:				
Original alkylate	49.5	28.9	21.6	.....
Recovered alkylate from				
Run 1	49.9	28.6	21.5	.....
Run 2	49.7	28.7	21.6	.....
Phenyl decane:				
Original alkylate	35.2	23.9	20.6	20.3
Recovered alkylate from				
Run 1	34.7	23.9	21.1	20.3
Run 2	34.5	24.0	21.2	20.3
Phenyl dodecane:				
Original alkylate	29.1	21.8	20.3	28.8 [a]
Recovered alkylate from				
Run 1	28.4	21.4	21.0	29.2 [a]
Run 2	29.0	21.4	20.8	28.8 [a]

[a] Includes the 6-phenyl dodecane isomer.

Results and Discussion

Table I indicates the approximate yields and relative freedom from structural rearrangements from desulfonations and GLC analyses of the isomeric mixtures of 2, 3, and 4 phenyl octane sulfonate; 2, 3, 4, and 5 phenyl decane sulfonate; and 2, 3, 4, 5, and 6 phenyl dodecane sulfonate. The data also indicate repeatability of yields and isomer ratio values. The individual isomer content is expressed in percentage terms and is obtained by comparing the peak height of an isomer to the sum of the peak heights of all isomers in the sample. The GLC data indicate no significant changes in isomer ratios through the sulfonation-desulfonation reactions when the desulfonated alkylate is compared to the original alkylate.

Figure 2 shows a chromatogram of 2, 3, 4, and 5 phenyl decane alkylate and the chromatogram after sulfonation and subsequent desulfonation of this alkylate.

Table II indicates approximate yield and GLC results obtained from desulfonation of a blend containing equal parts by weight of the isomeric mixtures of phenyl hexane, octane, decane, and dodecane sulfonate. GLC analysis of a blend of the corresponding alkylates is shown to indicate the close agreement in isomer composition of the original alkylate to that obtained after the sulfonation-desulfonation process. It will be noted however, that the composition of the phenyl hexane portion of the recovered alkylate blend differs in isomer composition from its original alkylate. Values for isomer composition identical to those shown in Table II have also been obtained when this compound has been carefully desulfonated alone. There is no evidence that rearrangement occurs from desulfonation of this sulfonate. It seems more likely that this sulfonate is a product of incomplete selective sulfonation leading to the change in isomer ratio as shown.

TABLE IV
Mass Spectrometer Analysis of the Alkylate Recovered after Sulfonation and Desulfonation of a Commercial Polypropylbenzene

m/e	Compound	Original alkylate mol %	Recovered alkylate mol %
218	Phenyl-C_{10}	5.99	6.49
232	Phenyl-C_{11}	28.44	28.66
246	Phenyl-C_{12}	55.46	56.20
260	Phenyl-C_{13}	7.38	6.99
274	Phenyl-C_{14}	1.85	1.11
288	Phenyl-C_{15}	0.88	0.55

Alkylate yield after desulfonation of 30 mg sample was 71% of theory.

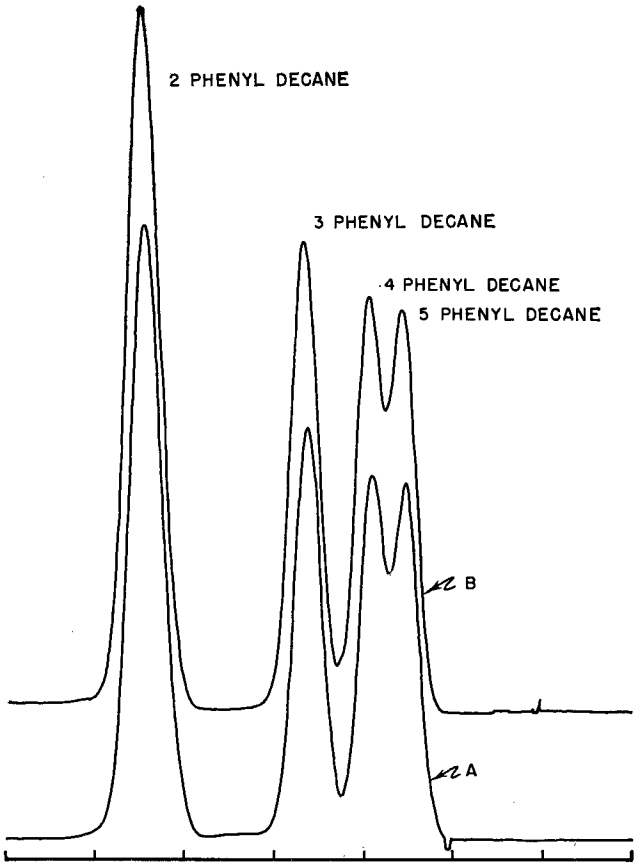

FIG. 2. (A) Mixture of the four phenyl decane isomers. (B) The four phenyl decane isomers after sulfonation-desulfonation.

Table III shows GLC results in duplicate from adsorption on charcoal and subsequent desorption and desulfonation of a 40-mg blend of the mixed isomers of phenyl hexane, octane, decane and dodecane sulfonate. The initial sample prior to processing consisted of one-liter solutions of the 40 mg of sulfonate plus the inorganic and organic compounds as described earlier in this paper. A comparison of the isomer composition of the two samples so processed to the original alkylate blend indicates the absence of selective losses or rearrangement of structural forms throughout the process.

Table IV indicates the approximate yield and mass spectrometer data from the desulfonation of commercial polypropylbenzene sulfonate.

Infrared analysis of the standard and desulfonated polypropylbenzene alkylate indicated the two to be essentially identical. GLC analysis of polypropylbenzene does not resolve individual isomers because of the large number and structural complexity of the molecular species present; however, assuming an arbitrary but fixed base line, calculations on GLC traces of polypropylbenzene alkylate indicate structural alteration of this alkylate to be relatively small through the sulfonation-desulfonation cycle. While the yield from the desulfonation of polypropylbenzene sulfonate is lower than from other structures tested, the loss apparently is not selective to molecular weight or structure as shown by mass spectrograph data in Table IV and by GLC analysis.

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