GLC Determination of Chain Length Distribution in Fatty Alcohol Polyethoxylates and Sulfated Derivatives

FATTY ALCOHOL POLYETHOXYLATES, or their sulfated derivatives, are commonly employed as nonionics or anionics, respectively, in detergent systems. The properties of such systems are dependent not only upon the number of ethoxy groups but also upon the chain length distribution. In order to determine these chain length distributions by gas-liquid chromatography it is necessary to convert the fatty alkyl chain into a volatile derivative. Such conversion to the volatile iodo derivatives can be rapidly carried out by reaction with hydriodic acid at elevated temperature and pressure. The procedure can also be directly applied to fatty alcohols and sulfated derivatives.

Sufficient sample to contain approximately 20 to 25 mg of the fatty alcohol polyethoxylate, or sulfated derivative, is placed in a 4 in. × 7/16 in. O.D. calibrated glass stoppered test tube and 1.5 ml of hydriodic acid (sp gr 1.74) added. The head space is then purged with a stream of nitrogen for 1 to 2 min to produce an inert atmosphere. The test tube is placed in a pressure tube, which is then placed in a heating block (1) and maintained at 185C for 10 min. The pressure tube is cooled under running water and the glass tube removed. Distilled water (3 ml) is added to the tube, and after cooling, the contents are extracted with three 1 ml portions of 40–60C petroleum ether. The combined ethereal extracts are transferred, with the aid of a dropper, to a second test tube and washed twice with 1 ml portions of 20% sodium thiosulfate solution. Solvent evaporation accomplished by immersion in a water bath yields the iodo derivatives.

Gas chromatographic separations were carried out at 190C on a "Pye" Series 104 chromatograph using a 5 ft 100/120 mesh Celite column containing 10% (w/w) polyethyleneglycoladipate and nitrogen as carrier gas. Chain length distributions (relative percent) were determined from peak areas.

The results (Table I) show that fatty alcohols of all chain lengths present in the sample were equally converted to the iodo derivative, irrespective of whether the conversion was carried out on the original alcohol sulfate or on the alcohol obtained by acid hydrolysis of the sulfate, i.e. 2 hr reflux with hydrochloric acid.

Infrared examination of the product obtained from sodium lauryl 3 EO sulfate, or the polyethoxylate resulting from acid hydrolysis of this sulfate, showed it was similar in structure to that produced by treatment of an alcohol. The absence of absorptions at ca. 1120 cm^{-1} clearly showed complete removal of the ether groupings. The procedure is applicable to a formulated product (Table II); however, an additional weak broad peak due to lauric acid was present. This probably originated from hydrolysis of lauryl monoethanolamide incorporated into the product.

TABLE I

Chain Length Distribution in Fatty Alcohol Sulfate

Carbon No.	Method (a)	(b)	(c)
8	0.4	0.4	0.3
10	3.3	4.0	3.8
12	73.0	71.7	72.7
14	20.4	20.9	20.1
16	2.9	3.0	3.1

(a) By acid hydrolysis of the sulfate and GLC of the resultant alcohol.
(b) By conversion of the fatty alcohol from (a) to the iodo derivative.
(c) By direct conversion of the fatty alcohol sulfate to the iodo derivative.

TABLE II

Chain Length Distribution in Sodium Lauryl 3 EO Ether Sulfate

Carbon No.	Method (a)	(b)	(c)
8	0.2	0.2	0.3
10	5.7	5.4	5.1
12	61.5	61.6	62.1
14	19.6	19.7	19.4
16	6.9	6.7	7.2
18	6.1	6.4	5.9

(a) By direct conversion of the sulfate to the iodo derivative.
(b) By conversion of polyethoxylate, from acid hydrolysis of the sulfate, to the iodo derivative.
(c) As in (a) but on a product formulated to contain 13% of the sulfate.

The effect of the presence of unsaturation in the alkyl chain was studied by comparing the distribution (Table III) obtained by direct chromatographic examination of a commercial sample of oleyl alcohol with that for the corresponding iodo derivative. The infrared spectrum of the iodo derivative showed no evidence of absorptions due to hydroxyl or unsaturation and it was concluded that addition of HI had occurred across the double bonds to give the 1-x-diiodo derivatives. Examination of the chromatogram showed that the 1-x-diiodo derivative was eluted just after the 1-iodo derivative of the same chain length.

TABLE III

Chain Length Distribution in Oleyl Alcohol

Carbon No.	(a)	(b)
8	0.5	1.0
10	0.9	1.0
12	2.0	1.7
12(=)	1.0	1.3
12(2=)	Trace	0.1
12(3=)	Trace	Trace
14	7.0	6.7
14(=)	0.5	0.5
14(2=)	1.3	1.0
14(3=)	0.7	0.5
16	10.5	10.7
16(=)	10.5	10.8
16(2=)	1.5	1.2
16(3=)	1.5	1.5
18	2.0	2.0
18(=)	56.3	56.0
20	3.8	4.0

(a) From the alcohol.
(b) From the corresponding iodo derivative.

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