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Sulfation with Sulfur Trioxide: Ethenoxylated Long-Chain Alcohols[1]

EVERETT E. GILBERT and BENJAMIN VELDHUIS, General Chemical Division, Allied Chemical Corporation, Morristown, New Jersey

SULFATED ETHENOXYLATED long-chain alcohols are of increasing interest as detergents because of favorable detergency, solubility, and cost (2). The preparative procedure involves reaction of a long-chain alcohol derived from animal fats, coconut oil, or petroleum with any desired ratio of ethylene oxide to form a mixture of polyether alcohols, which is then sulfated and neutralized for use.

Various reagents have been used experimentally for the sulfation step (Table I). Chlorosulfonic acid without a solvent has been most generally employed commercially. The purpose of the present study is to evaluate it in comparison with a newer reagent, sulfur trioxide vapor, which is commercially available from stabilized liquid sulfur trioxide marketed under the trade name "Sulfan" (5). Only one patent reference was noted (1) on sulfation of an ethenoxylated long-chain alcohol with sulfur trioxide in vapor form although this reagent has shown promise with long-chain alcohols and with ethenoxylated alkylphenols (3). Sulfur trioxide with liquid SO_2 solvent is used to only a minor degree industrially because of the difficulty in recovering and recycling the solvent.

TABLE I

Sulfation of Ethenoxylated Long-Chain Alcohols-Literature Summary

Alcohol	Moles ethylene oxide	Reagents used	Reference
Trimethylnonanol	3, 5	100% H_2SO_4 with dioxane	8
Butyloctanol	3–5	100% H_2SO_4; SO_3 with liquid SO_2	10, 11
Tridecyl	1–10	100% H_2SO_4; SO_3 with liquid SO_2; SO_3 vapor; $ClSO_3H$ with ethyl ether; NH_2SO_3H	1, 7
Ethylmethylundecanol	5	100% H_2SO_4 with CCl_4; SO_3 in liquid SO_2	9
Hexa-, octadecanol	2, 10	$ClSO_3H$ with tetrachloroethylene	2
Lauryl, oleyl, etc	1–3	$ClSO_3H$ (no solvent); $ClSO_3H$ with urea	13

Raw Materials

Samples used in the present study, as obtained from five different commercial sources, are listed in Table II; A–D were liquids, E and F solids, melting below 35°C.

TABLE II

Data on Raw Materials Studied

Sample	Alcohol	Mol. wt.[a]	Approx. moles oxide
A	Lauryl	334	3
B	Lauryl	338	3
C	Tridecyl	325	3
D	Tridecyl	332	3
E	Tallow[b]	440	4
F	Tallow	425	4

[a] As reported by manufacturer.
[b] Stated to comprise 65% stearyl and 35% cetyl alcohols.

Experimental Procedure

Sulfation. The sample (200–400 g.) was sulfated with sulfur trioxide vapor diluted with dry air by the method previously used by the authors for sulfating lauryl alcohol (6). Heat evolution was steady during sulfation (15 to 30 min.); external cooling was used as necessary to maintain a reaction temperature of 25–35°C. for liquid samples A–D, or 50–55°C. for solid samples E and F, which were sulfated as melts. These two samples were premelted before sulfation; below 45°C. foaming was excessive with these materials. Weight loss during sulfation was less than 2%, based on total weight of both reagents.

Chlorosulfonic acid was added dropwise with stirring and cooling to 25–35°C. for liquid samples A–D, or 40–50°C. for solid samples E and F, which were sulfated as melts. No difficulty was experienced with stirring even though no solvent was used. During the addition of the first half of the acid there was no gas evolution, but heat evolution was substantial, corresponding to the sum of the heat of sulfation and the heat of solution of hydrogen chloride. Toward the end of the acid addition, endothermic evolution of hydrogen chloride occurred, and heating was required to maintain the desired temperature range until the evolution ceased. The reaction time (20–45 min.) was somewhat longer with this reagent because of substantial foaming during the final stage of reaction.

Neutralization. To avoid gelation the acid sulfates prepared with both reagents were neutralized dif-

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[1] For previous papers in this series see (3) and other references cited therein.

TABLE III
Summarized Sulfation Data

Sample	A						B						
From SO_3[a]	91	94	97	100	....	....	94	97	100	107[b]	....	....	....
From $ClSO_3$[a]	....	....	....	....	100	105	....	....	....	....	95	100	105[b]
Color[d]	75	95	160	170	17	15	115	110	130	215	33	37	35
Yield[d]	81	85	87	87	90	93	84	87	88	91	85	90	93

	C			D									
From SO_3	95	100	....	95	100	105[b,c]	110	115	....	....	....	....	....
From $ClSO_3$	....	....	100	....	....	....	....	....	100	105[b,c]	110	115	120
Color	175	185	75	90	110	165	280	400	25	30	30	30	32
Yield	85	90	88	84	87	91	90	91	90	94	94	94	94

	E							F								
From SO_3	105	110[b,c]	117	....	....	....	....	95	100	105	110	115	....	....	....	....
From $ClSO_3$	....	....	....	92	96	104	110[b,c]	....	....	....	....	....	100	105	110	115
Color	125	150	185	50	50	50	70	115	125	140	300	460	50	55	50	50
Yield	84	86	92	72	77	83	87	84	87	92	93	94	89	91	96	96

[a] Expressed as mole percentage of the reagent used, based on molecular weight given in Table II.
[b] Performance data on this sample given in Table IV.
[c] Inorganic salt analysis of these samples given in text.
[d] See text for significance of color and yield values.

ferently from the procedure used for lauryl sulfate (6). Typically 450 g. of acid sulfate from Sample B and 208 g. of 20% aqueous sodium hydroxide were added simultaneously, over 30 min., with stirring and cooling to 50°C., to 100 ml. of water and 200 ml. of 95% ethanol in a beaker. The pH was maintained at 7 to 10. Finally 10 ml. of saturated aqueous sodium bicarbonate were added to pH 9 to 10. The resulting solution contained about 50% of sodium organic sulfate.

Product Analysis. Color values were determined on 15% aqueous solutions (active-ingredient basis) in a Klett-Summerson Photoelectric Colorimeter, Test Tube Model, using No. 42 filter. (The products from samples E and F were diluted with 50% aqueous ethanol because of a tendency to gel.) The lower the number, the lighter the color (0 = colorless; 200 = light yellow). Colors were measured immediately after preparation since the samples bleach spontaneously on standing.

Active-ingredient content, used as the basis for yield-calculation, was obtained by quaternary titration following the method of Epton (4) except that a 0.0054 molal solution of Hyamine 1622 (Rohm and Haas Company) (14) was substituted for cetyl pyridinium bromide, which is less stable.

Sodium chloride content was determined by the Volhard method (12). Sodium sulfate content was obtained by ethanol precipitation (12), followed by resolution in water and precipitation as barium sulfate to eliminate the chloride ion present as sodium chloride.

Experimental Results

The experimental data obtained at varying ratios of sulfating agent are given in Table III. The following conclusions were drawn.

Color. Chlorosulfonic acid gives lighter product colors than sulfur trioxide with all samples tested. However the latter reagent in all cases at optimum yield forms products considered suitable for household detergent use. With chlorosulfonic acid, product color is independent of the ratio used while with *sulfur trioxide the color darkened with increasing* percentage.

Yield. Chlorosulfonic acid gave a slightly better (2 to 5%) yield of active ingredient with four samples, about the same with one, and slightly less with one.

Inorganic Salt Content. Sulfur trioxide gave products with considerably lower sodium sulfate content than the other reagent, possibly because of the diluent air stream. Thus Sample D, sulfated with 105% sulfur trioxide, analyzed 0.3% sodium sulfate based on active ingredient; the same sample, sulfated with 105% chlorosulfonic acid, analyzed 8.5% sodium chloride and 2.0% sodium sulfate. Sample E, sulfated with 110% sulfur trioxide, had 0.3% sodium sulfate; 110% chlorosulfonic acid gave 7.0% sodium chloride and 0.9% sodium sulfate. This substantial difference in the content of inorganic salts was not reflected in performance tests however. As might be expected, hydrogen chloride retention in reaction mixtures prepared with chlorosulfonic acid is substantial. Judging from weight loss for 19 runs, hydrogen chloride evolved varied from 31% to 66% of theory. A final product analyses of 7.0% and 8.5% sodium chloride (on active) corresponded to 47% and 43% evolution of hydrogen chloride.

Use of a reaction solvent in which hydrogen chloride is slightly soluble (such as chloroform) would undoubtedly result in more complete evolution.

Performance Tests

Comparative performance data on products, obtained by reacting the same weight percentage of each reagent with one of each of the three types of condensate studied, are summarized in Table IV. It is noted that the results show that the two reagents yield sulfates of closely similar performance in all cases except the Draves Wetting Time for Sample E. This difference is not considered significant since both numbers are large.

Sulfating Agents Compared

Comparison of the two reagents, chlorosulfonic acid and sulfur trioxide vapor, shows the following based on the results obtained in the present study.

Reagent cost, per unit weight of sulfur trioxide

TABLE IV
Summary of Performance Data

Sample	B		D		E	
Reagent	SO_3	$ClSO_3H$	SO_3	$ClSO_3H$	SO_3	$ClSO_3H$
Percentage	107	105	105	105	110	110
Wetting time[a]	52	49	28	32	173	132
Foaming power						
DW[b]	145	145	135	145	110	115
HW[c]	185	185	210	205	15	15
Detergency[d]						
DW[e] 0.1	17	14	11	11	25	25
0.2	15	13	11	9	22	26
0.3	12	12	11	10	20	21
HW[f] 0.1	3	7	4	4	18	22
0.2	3	5	6	2	13	16
0.3	0	0	4	4	11	13

[a] Draves (Synthron Tape Method) in seconds at 25°C., 0.1%solution.
[b] Ross-Miles in distilled water at 0.05%.
[c] Ross-Miles in 15-degree hard water at 0.2%.
[d] Expressed as percentage of brightness increase in Launder-Ometer.
[e] In distilled water containing 0.5% added sodium chloride, at percentages given.
[f] In 15-degree hard water containing 0.5% added sodium chloride, at percentages given.

introduced, is approximately half for sulfur trioxide compared with chlorosulfonic acid at current bulk prices.

With sulfur trioxide there is no formation of hydrogen chloride, the reaction time is shorter, and heat evolution and foaming are balanced while these of chlorosulfonic acid are unbalanced. Total evolution of heat is greater with sulfur trioxide, and vaporization of this reagent is required.

Sulfur trioxide gives no sodium chloride and considerably less sodium sulfate. This reagent gives products of darker but acceptable color in yields which are the same or slightly lower. Product performance with the two reagents is the same.

A practical alternative process to the use of either pure reagent comprises employing chlorosulfonic acid as the sulfating reagent, with collection of the evolved hydrogen chloride in a tail tower charged with Sulfan, thereby regenerating chlorosulfonic acid for re-use. The engineering factors involved in this modification have been discussed by the authors in an earlier publication (6). This approach is often well suited to existing installations using chlorosulfonic acid since reagent cost is reduced, plant and process changes are minor, hydrogen chloride disposal is eliminated, and product quality is unchanged. Obviously the extent to which this substitution can be effected depends upon the efficiency of hydrogen chloride evolution, which in the present process is at most about two-thirds of theoretical.

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Composition of Zelkova Seed Oil[1,2]

C. Y. HOPKINS and MARY J. CHISHOLM, National Research Council (Canada), Ottawa, Canada

THE Japanese Zelkova tree, which grows to a height of 100 feet, is native in Eastern Asia. It is hardy in the northern hemisphere and is grown as a shade tree in North America. The greyish-brown seeds are about 3–4 mm. long, roughly tetrahedral in shape, and wingless. The kernel is white, soft, and oily. There appears to be no published information on the oil.

The tree is known botanically as *Zelkova serrata* and belongs to the genus *Zelkova* of the family *Ulmaceae.* It was chosen for this investigation because one genus of *Ulmaceae,* namely *Ulmus,* which includes the common elm tree, has been regarded as unique in having capric acid as the chief fatty acid in the seed oil. Three species of *Ulmus* have been shown to exhibit this characteristic, *U. campestris* (1), Manchurian elm (2), and *U. americana* (3). A complete analysis of the seed oil of the last-named species was reported (4). Capric acid amounted to 61% of the total fatty acids.

Examples of two other genera of *Ulmaceae, Celtis* and *Trema,* did not yield capric acid or any acids of chain length shorter than C_{16} (5).

In the present work the seed oil of *Zelkova serrata* was found to contain capric acid to the extent of 73% of the total fatty acids, the highest proportion found up to the present time in any natural oil or fat. All of the even-numbered carbon saturated acids from C_8 to C_{18} were present. The general composition was similar to that of the oil of *Ulmus americana.* Thus these two genera, *Ulmus* and *Zelkova,* share the distinction of high capric acid content.

Experimental

Seed of *Zelkova serrata,* Makino (grown in Japan), was obtained from a commercial seed house. The seed was ground in a Wiley mill, the moisture content was determined, and the oil was extracted with petroleum ether. The oil content was 21.7% on a 10% moisture basis. The constants were as follows:

Iodine value	12.9	Acid value	11.2
Saponification value	292.1	Free acid as capric, %	3.4
Unsaponifiable matter, %	0.57	Glycerol yield, %	13.6

The petroleum ether distilled from the extracted oil was examined and found to contain no acid. The oil was washed with water, and the washings were also neutral. Thus there was no free water-soluble acid in the oil. On saponification a small amount of volatile water-soluble acid was found. The Reichert-Meissl value was 4.8. If calculated as caproic acid, this is equivalent to 1.2% of the total fatty acids. The Polenske value was 43 8, indicating a considerable content of acid in the C_8–C_{12} range.

A portion of the oil was converted to methyl esters and examined by gas chromatography. The column was one meter in length and was packed with Apiezon M vacuum grease on Celite. The detector was a thermistor type of thermal conductivity cell. The lower-boiling esters were chromatographed at 150° and a helium flow rate of 75 ml./min. The higher

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[2] Issued as N.R.C. No. 5176.