Technical

The Determination of Hydrotropes in Detergent Products by Reverse-Phase and Ion-Pair High Performance Liquid Chromatography

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ABSTRACT

The three aromatic sulfonates most commonly used as hydrotropes in detergent products can be qualitatively and quantitatively determined by high performance liquid chromatography (HPLC). Reverse-phase and paired-ion methods are described for separating sodium toluene, xylene and cumene sulfonates using conventional C18, C8, hexyl, and cyano columns as well as radially compressed HPLC cartridges. Ultraviolet (UV) detection at 254 nm gives more than adequate sensitivity for hydrotropes formulated between 0.5 and 15%. Sample preparation is simple and all components can be eluted within 15 min. The quantitation has been proven precise and accurate during routine analyses of either powdered or liquid detergent products.

INTRODUCTION

Hydrotrope raw materials are sold commercially by many manufacturers and used as solubilizers and coupling agents by the detergent industry in a variety of products. Until recently, the method most commonly used for their analysis involved an adaptation of the ASTM Method D2023, Part 30. That procedure consists of an acid/ether extraction of the detergent to remove higher molecular weight sulfonates followed by determination of the remaining low molecular weight substituted benzene sulfonates by ultraviolet absorption. However, erroneous results are generated if any UV active contaminants are present after extraction; and mixtures of more than one hydrotrope cannot be individually determined. A glass column chromatographic procedure is also reported (1) which employs silica gel and elution with various organic solvents to affect a partial separation of sodium xylene sulfonate (SXS) from dodecylbenzene sulfonate and a C_{21} dicarboxylic acid. This procedure relies on gravimetric measurement, titrations and UV absorbance data for quantitation, and does not mention hydrotropes other than SXS or the various SXS isomers.

High performance liquid chromatography (HPLC) was the obvious alternative and a literature search showed four recent studies involving substituted benzene sulfonates. The first (2) concerns only benzene sulfonic acid and its disulfonic acid isomers separated by paired-ion chromatography. Jandera and Engelhardt (3) used the same technique to separate toluene sulfonic acid from several other organic acids and another Jandera paper (4) includes toluene sulfonic acid separated by reverse-phase chromatography without ion pairing. Prandi and Venturini (5) include benzene and toluene sulfonic acids in a paired-ion study of 108 aromatic sulfonic acids.

Using reverse-phase or paired-ion chromatography as described in this paper, the three most common hydrotropes (toluene, xylene and cumene sulfonates) can be determined in raw materials and detergent products on any of six columns.

These hydrotropes commonly come from the suppliers as sodium, potassium or ammonium salts in powdered form or as aqueous solutions. Their analyses are the same with only minimal change necessary due to concentrations and/or conversion in molecular weight from one salt to the other. All of the work reported in this paper will be based on the powdered sodium salts of toluene (STS), xylene (SXS) and cumene (SCS) sulfonates.

EXPERIMENTAL PROCEDURES

Instrumentation

The analyses were performed with a Waters M6000A solvent delivery system and 440 ultraviolet (UV) detector fitted with a 254 nm filter (Waters Associates, Milford, MA). Injections were made with a Rheodyne 7125 syringe injector (Rainin Inst., Woburn, MA) fitted with a 20 μL loop. The analytical columns used were Zorbax C_8 (DuPont Instruments, Wilmington, DE), phase separation spherisorb S5C6-hexyl (Rainin Inst.), octadecyl (C18) (IBM Inst., Inc., Danbury, CT), and the Waters RCM-100 radial compression module fitted with radial PAK C_{18}, C_8, and CN cartridges (8 mm id except where otherwise noted). These columns were preceded by a guard column containing pellicular C18 or CN packing meterials, depending on which analytical column was in use at the time.

Materials

J.T. Baker anhydrous sodium sulfate, dibasic ammonium phosphate, and HPLC grade methanol, acetonitrile and 2-propanol were purchased from Sargent-Welch Sci., (Springfield, NJ). The tetrabutylammonium hydrogen sulfate and tetraethylammonium bromide were purchased from Aldrich Chemical Co., (Metuchen, NJ). Hexadecyltrimethylammonium bromide was purchased from Mallinckrodt, Inc. (Paris, KY). Tetramethylammonium nitrate was purchased from Eastman Kodak Co. (Rochester, NY). Pure reference hydrotropes were synthesized by the method described by Weber (6), converted to their sodium salts, and recrystallized from ethyl alcohol.

Sample and Standard Preparation

Samples were prepared by vigorously stirring 2.5 g detergent in 100 mL of mobile phase and filtering when necessary. Standards were prepared by weighing 50 mg of hydrotrope into a 100 mL volumetric flask and filling to the mark with mobile phase. Specific concentration changes may be necessary for samples of very high or low levels.

HPLC

All mobile phases were filtered through a 5 μm millipore

filter before use. Flow rates varied from 1 to 2.5 mL/min and 20 μL injections were used throughout.

In order to know what to expect in finished products, the first problem was to characterize the raw materials which vary in active ingredient content and isomers formed during their synthesis. STS and SCS were relatively straightforward because their synthesis involves only the sulfonation of a "pure" monosubstituted benzene: toluene and cumene (*iso*-propylbenzene), respectively. All STS and SCS samples monitored yielded single major peaks (see Figs. 1 and 2) with insignificant minor impurities occasionally detected, although STS could be separated into the characteristic 4:1 ratio of *para/ortho* toluene sulfonates which are formed during the sulfonation (see Fig. 3).

SXS was by far the most complex and unpredictable of the hydrotropes to characterize because the xylene starting material is subject to several isomeric and chemical variables. Initial investigations produced chromatograms with two to three peaks which were assumed to be the *meta, para* and *ortho* isomers. However, an additional (fourth) component was found to be present in relatively large quantities when known SXS isomers were synthesized and found to coelute under some of the conditions employed.

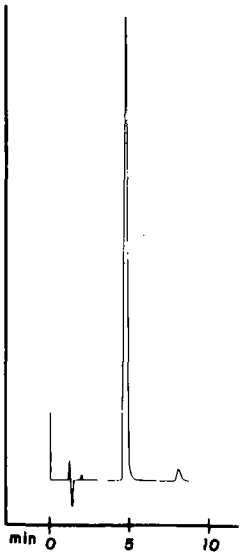

FIG. 1. Chromatogram of STS raw material on a radially compressed C_{18} cartridge with 55:45 acetonitrile/water containing 0.01M hexadecyltrimethylammonium bromide at pH 7.5 with dibasic ammonium phosphate; flow rate 1.5mL/min.

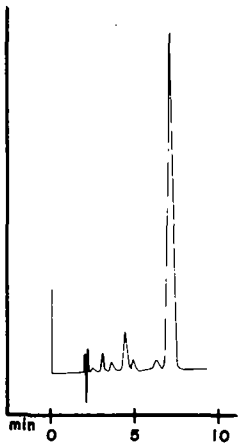

FIG. 2. Chromatogram of SCS raw material on a radially compressed C_{18} cartridge with 35:65 acetonitrile/water containing 0.01M tetrabutylammonium hydrogen sulfate at pH 7.5 with dibasic ammonium phosphate; flow rate 1.5 mL/min.

Assuming that it derived from the xylene starting material which has been known to contain ethylbenzene, a pure standard of sodium-4-ethylbenzene sulfonate (SEBS) was synthesized and chromatographed to match the fourth SXS component under all conditions studied.

Using the conditions described in Figure 1, only the *ortho*-xylene sulfonate is separated from the coeluting *meta*-xylene, *para*-xylene and ethylbenzene sulfonates (see Fig. 4). to isolate ethylbenzene sulfonate, a Zorbax C8 column was used with a mobile phase of 25:75 2-propanol/water containing 0.01M tetrabutylammonium hydrogen sulfate at pH 7.5 with dibasic ammonium phosphate as shown in Figure 5.

With a hexyl column as described in Figure 6, *meta*- and *para*-xylene sulfonate coelute, followed by *ortho*-xylene sulfonate and then ethylbenzene sulfonate.

Finally, the conditions necessary for the separation of all four components were found and are shown in Figure 7. Here an IBM octadecyl column was used with a mobile phase of 0.01 M tetramethylammonium nitrate in 35:65 methanol/water at pH 7.5 with dibasic ammonium phosphate.

When this mobile phase was used with the hexyl or the Zorbax C8 columns (the radially compressed columns were not attempted), complete resolution of isomers did not occur. The resulting chromatogram in both cases was similar to that displayed in Figure 5. Apparently the increased "power" of the C18 was necessary to achieve this separation – we did not have an alternative to try.

Although the raw materials were found to vary slightly from batch to batch, they were consistent or characteristic enough to be used as "standards" once they had been assayed for moisture, inorganic sulfate, and other hydrotropes present, if measurable. For the determination of SXS in finished products, we generally added the individual isomer peak heights together to produce a total SXS percentage based on the same treatment for the isomers in the standard.

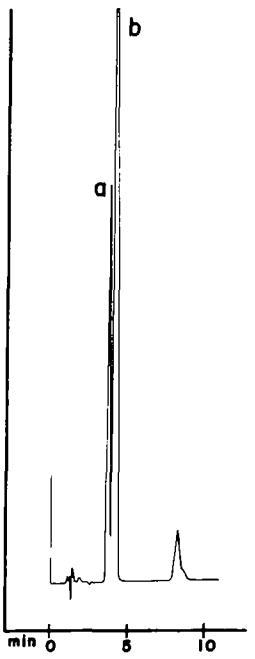

FIG. 3. Chromatogram of *ortho* and *para* STS on a radially compressed C_8 cartridge with 20:80 methanol/water containing 0.1M Na_2SO_4; flow rate 2.5mL/min. (a) *ortho* STS; (b) *para* STS.

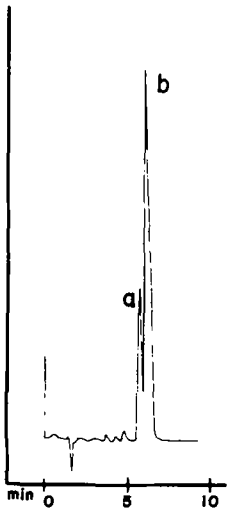

FIG.4. Chromatogram of SXS raw material; conditions the same as Fig. 1. (a) *ortho* SXS; (b) *para* and *meta* SXS and SEBS.

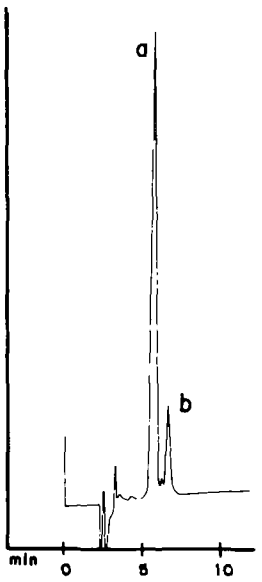

FIG. 5. Chromatogram of SXS raw material on Zorbax C_8 with 25:75 2-propanol/water containing 0.01M tetrabutylammonium hydrogen sulfate at pH 7.5 with dibasic ammonium phosphate; flow rate 1.0 mL/min. (a) *ortho, meta* and *para* SXS; (b) SEBS.

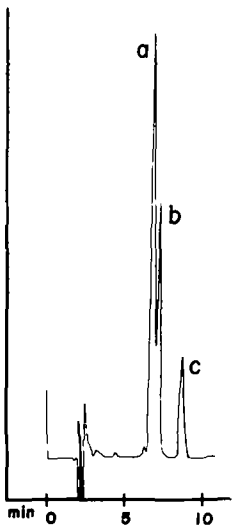

FIG. 6. Chromatogram of commercial SXS on a hexyl column with 10% 2-propanol in water containing 0.01M tetraethylammonium bromide at pH 7.5 with dibasic ammonium phosphate; flow rate 1.2 mL/min. (a) *meta* and *para* SXS; (b) *ortho* SXS; (c) SEBS.

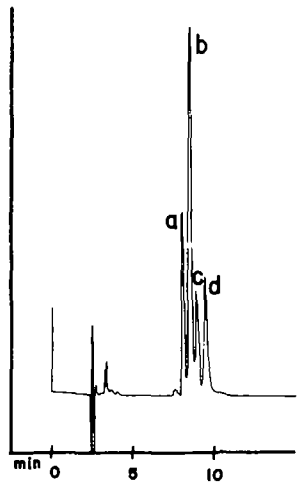

FIG. 7. Chromatogram of commerical SXS isomers on an IBM octadecyl column with 35:65 methanol/water containing 0.01M tetramethylammonium nitrate at pH 7.5 with dibasic ammonium phosphate; flow rate 1.0 mL/min. (a) *ortho* SXS; (b) *meta* SXS; (c) *para* SXS; (d) SEBS.

The conditions recommended for a fast qualitative check of unknown finished products require a 5 mm id radially compressed C8 cartridge with 0.01M tetrabutylammonium hydrogen sulfate in 35:65 acetonitrile/water at pH 7.5 with dibasic ammonium phosphate. As shown in Figure 8, STS elutes in less than 3 min, followed by the combined SXS isomers with ethylbenzene sulfonate close behind, and finally SCS in less than 5 min. As can be seen in Figure 9, an "off the shelf" powdered laundry detergent chromatographed under these conditions was found to contain STS at approximately the same concentration as the standard, so subsequent analyses for accurate quantitation could follow when desired using these or any of the other chromatographic conditions reported.

Alternative conditions for the determination of unknown finished products consist of a radially compressed CN cartridge with a mobile phase of 0.1M Na_2SO_4 in 15:85 methanol/water. As shown in Figure 10, the STS elutes within 3 min, followed by SXS (two peaks: *para* and *meta* first, then *ortho*-xylene and ethylbenzene sulfonates) and then SCS within 10 min. Using these conditions, an "off the shelf" liquid dishwashing detergent was chromatographed and found to contain 5.3% SXS (all SXS and SEBS peaks totaled) as shown in Figure 11.

RESULTS AND DISCUSSION

Through the versatility of reverse-phase and paired-ion chromatography, these hydrotropes are separated on any of six different column types and six mobile phases can be used. Depending on the applications, qualitative and quantitative work is done easily and quickly on all types of detergent products. If the hydrotropes are known prior to the analysis, simply choose the column and mobile phase with which those hydrotropes separate and elute the quickest. If they are unknown, the conditions described in

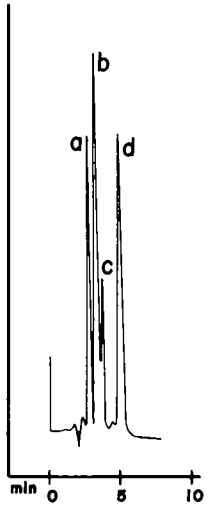

FIG. 8. Chromatogram of hydrotrope mixture on 5 mm id radially compressed C_8 cartridge with 35:65 acetonitrile/water containing 0.01M tetrabutylammonium hydrogen sulfate at pH 7.5 with dibasic ammonium phosphate; flow rate 1.0 mL/min. (a) STS; (b) SXS (all isomers); (c) SEBS; (d) SCS.

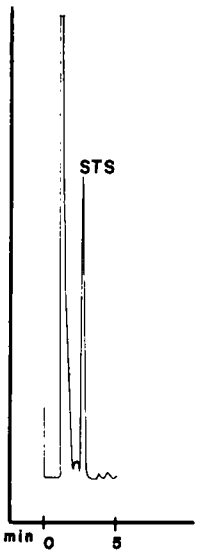

FIG. 9. Chromatogram of "off the shelf" powdered laundry detergent run under same conditions as Fig. 8 and found to contain ca. 2% STS.

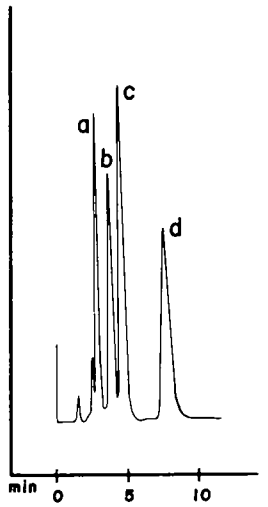

FIG. 10. Chromatogram of standard hydrotrope mixture on a radially compressed CN cartridge with 15:85 methanol/water containing 0.1M Na_2SO_4; flow rate 2.0 mL/min. (a) STS; (b) *para* and *meta* SXS; (c) *ortho* SXS and SEBS; (d) SCS.

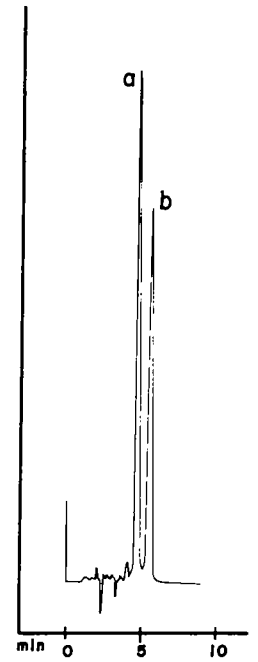

FIG. 11. Chromatogram of "off the shelf" liquid dishwashing detergent found to contain 5.3% SXS using the conditions described in Fig. 10. (a) *para* and *meta* SXS; (b) *ortho* SXS and SEBS.

TABLE I

Percent Hydrotrope Found in 6 Separate Analyses of 3 Different Detergent Products

	SCS (Powder cleanser)	SXS (Powder detergent)	STS (Powder detergent)
	0.885	2.142	1.903
	0.895	2.132	1.826
	0.880	2.177	1.901
	0.870	2.165	1.843
	0.860	2.133	1.874
	0.895	2.157	1.856
Mean	0.881	2.151	1.867
Standard deviation	0.013	0.018	0.031
Coefficient of variation (%)	1.5	0.8	1.7

Figure 10 would be the best place to start in their determination, followed by one of the paired-ion separations to back up the identifications if necessary.

The dependability of the quantitative nature of these methods has been tested through several precision and accuracy determinations. Tables I and II illustrate two studies performed on known, exactly prepared formulations. Calculations were based on peak heights vs weights of samples and standards injected.

STS and SXS are by far the most commonly found in products ranging from powdered and liquid detergents to cleansers and shampoos. The sample chromatograms are usually identical to those of the standards, since few interfering components have been detected under these conditions. Again, if an interfering component is suspected, simply use one of the alternative sets of conditions described which is different in column type and mobile phase chemistry.

As Table III shows, a random sampling of these products can contain single hydrotropes or mixtures of just about any type and level. Since there is no way to predict which will be present and at what level, the use of one or more of these HPLC methods makes the determinations fast and accurate.

TABLE II

Recovery Study of 6 Separately Prepared Detergent Samples

Sample	Formulation (% SXS)	% Recovered	% Recovery
1	2.157	2.142	99.3
2	2.144	2.132	99.4
3	2.205	2.177	98.7
4	2.184	2.165	99.1
5	2.151	2.133	99.2
6	2.163	2.157	99.7
			$\bar{X}$ 99.2

TABLE III

Percent Hydrotropes in "Off the Shelf" Detergent Products by HPLC

	Hydrotrope		
	STS	SXS	SCS
Detergent powders			
A	1.7	–	–
B	1.0	–	–
C	–	2.0	–
Liquid detergents			
D	–	1.7	–
E	1.1	4.0	–
F	–	2.5	–
Dishwashing liquids			
G	–	1.9	–
H	–	9.0	–
I	–	2.4	1.2
J	0.6	–	–
Cleansers (liquid + powder)			
K	–	–	1.1
L	–	0.5	–
All-purpose liquid cleaners			
M	–	–	4.8
N	–	1.6	–
O	7.2	–	–
P	–	1.4	14.0
Shampoo			
Q	–	2.2	–

ACKNOWLEDGMENTS

M. Camara synthesized the pure SXS and SEBS reference compounds.

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