Determination of Sultones in Anionic Surfactants

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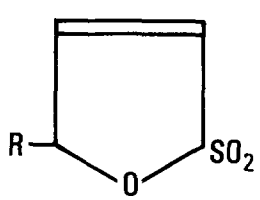
ABSTRACT AND SUMMARY

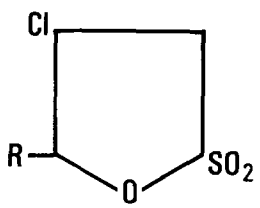
Saturated and unsaturated 1,3- and saturated 1,4-sultones in anionic surfactants are identified and measured by a series of separation maneuvers. The sultones are separated from the surfactant by ion-exchange treatment and concentrated by thin layer chromatography. By the use of high performance liquid chromatography, the sultones are identified on the basis of their retention times and are measured by comparing their peak areas with those of reference compounds. Adequate responses are obtained from 5 μg quantities of sultone, corresponding to 0.1 ppm sultone in a 50 g sample of alkylethoxy sulfate paste. All the sultones of interest are separated from each other. Chlorosultones can be determined after first treating them with collidine, which dehydrohalogenates them to the unsaturated sultones.

INTRODUCTION

Certain ring-unsaturated 1,3-sultones (I) and 2-chloro-1,3-sultones (II) have been indicted as skin sensitizers (1,2). From this indictment arose the need for a method to determine sultones in alkylethoxy sulfate (AES) and other surfactant pastes. To a lesser degree there was also a need for a specific analytical method for saturated 1,3- and 1,4-sultones in α-olefin sulfonates and other surfactants.



I.



II.

A nonspecific method has been proposed (3) in which any sultone present is hydrolyzed to the corresponding sulfonic acid, which can be determined by conventional titrimetry or colorimetry. Connor et al. (4) have described a specific analytical technique for the unsaturated sultones which uses gas chromatography and mass spectrometry with a ^{13}C-labeled sultone as an internal standard. Although the method is sensitive to 0.01 ppm, the requirement for labeled reference compounds militates against its being used widely.

The method described here uses a succession of separation techniques. Ion exchange treatment separates sultones from the bulk of the ionic surfactant. Thin layer chromatography (TLC) concentrates the sultones. Finally, high performance liquid chromatography (HPLC) provides qualitative and quantitative evaluation. In addition, fractions from the HPLC column can be trapped to provide individual, unaltered sultones for confirmatory identification or animal testing.

Although the chlorosultones can be isolated by the same procedure, the isolation is tedious at concentrations below 5 ppm. The chlorosultones are best determined by performing two analyses, one on the intact surfactant and one in which the sultone-containing concentrates are treated with collidine to dehydrohalogenate the chlorosultones before measurement of the total quantity of unsaturated sultones. Usually, however, the surfactant samples do not contain chlorosultones, or, if they do, there is no reason to distinguish them from the unsaturated sultones. When separate determination of the sultones is desired, an alternative procedure must be employed to minimize dehydrochlorination by the ion exchange resin.

MATERIALS AND METHODS

As reference materials, 1-decene-1,3-sultone, 1-dodecene-1,3-sultone, 1-tetradecene-1,3-sultone, and 1-hexadecene-1,3-sultone were synthesized by the method of Connor et al. (4). HPLC showed these materials to contain less than 1% of resolvable impurities. Saturated sultones were synthesized by liquid SO_3 sulfonation of 1-olefins followed by ethyl ether extraction of the neutralized, slightly alkaline mix. Both the 1,3- and 1,4- saturated sultones are obtained and can be separated by chromatography. The materials prepared were 1-dodecane-1,3-sultone, 1-hexadecane-1,3-sultone, 1-dodecane-1,4-sultone, and 1-hexadecane-1,4-sultone.

A mixed bed ion exchange resin, MB-1 (Rohm and Haas, Philadelphia, PA) was washed successively with distilled water, 3A ethyl alcohol (ethanol:water:methanol, ca. 90:5:5 v/v) and methylene chloride; the resin was dried and stored in closed containers.

Commercial TLC plates (EM Laboratories, Elmsford, NY) comprising a 250 μ coating of Silica Gel 60 on aluminum, were washed by ascending chromatography, first with the analytical solvent, then with ethyl ether. The dried plates were stored in covered racks.

Ethanol used in formulating the HPLC eluant was USP quality (Rossville Gold Shield, Commercial Solvents Corp., Terre Haute, IN). All other solvents were from Burdick and Jackson (Muskegon, MI). All HPLC solvents were filtered through 0.2- or 0.45-μ Millipore filters (Millipore Corp., Bedford, MA) before use.

EXPERIMENTAL PROCEDURES

Batchwise Ion-exchange

Fifty grams of detergent paste dissolved in 100 ml 3A alcohol was stirred 1 hr with 300 ml methylene chloride, 100 ml distilled water, and 700 ml purified MB-1 resin. The mixture was filtered through a fine porosity fritted glass filter, and the solvent was evaporated under vacuum at lukewarm temperatures.

Column Ion-exchange Chromatography

Three columns (28.5 x 2.2 cm) were used in series. The uppermost column was packed with 50-100 mesh cation-exchange resin (H^+ form) AG 50W-X8 (Bio-Rad Laboratories, Richmond, CA) and washed with 250 ml of the eluting solvent, 2-propanol:water:methylene chloride (85:10:5, v/v). The two lower columns were packed with anion-exchange resin BioRex 9 (Bio-Rad Laboratories, Richmond, CA) and washed with 1000 ml of eluting solvent. It was usually necessary to add additional resin after washing to offset compacting. The packed columns were joined in series and 8 g of surfactant paste was put on the top column. The system was eluted until 250 ml of solvent had been collected. The solvent was evaporated from the effluent under vacuum at lukewarm temperatures.

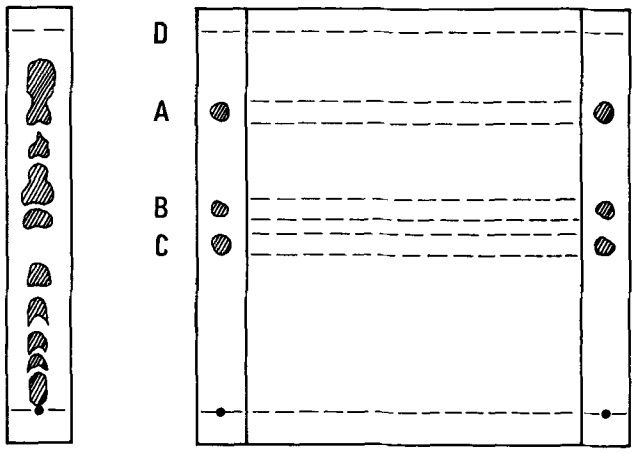


FIG. 1. Thin layer chromatography of the nonionic fraction of an alkylethoxy sulfate (AES) paste (left). Typical distribution of the nonionic components (right) illustrating the use of reference compounds and scraping to isolate sultone-containing zones. Reference compounds: A. Chlorosultones. B. Saturated 1,4-sultones. C. Saturated and unsaturated 1,3-sultones. D. Solvent front. Eluting solvent: pentane-ether-methanol (50:50:2, v/v).

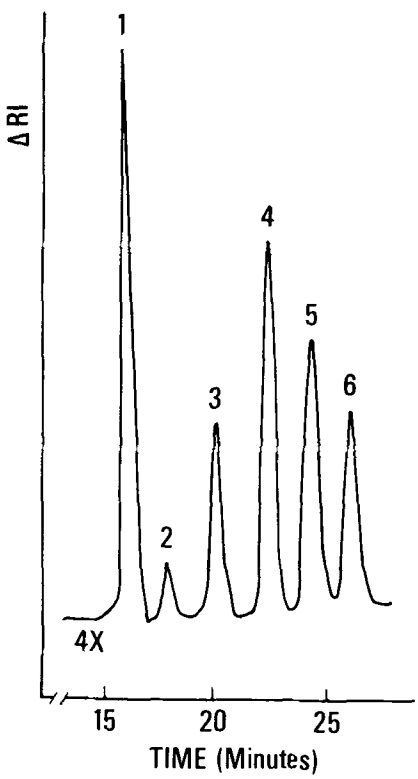


FIG. 2. High pressure liquid chromatography response and resolution of saturated and unsaturated sultones. (1) 1-hexadecane-1,4-sultone (2) 1-dodecane-1,4-sultone (3) 1-hexadecane-1,3-sultone (4) 1-dodecane-1,3-sultone (5) 1-tetradecene-1,3-sultone (6) 1-dodecene-1,3-sultone. 50 μg of each except (2) an impurity in (4). Flow, 0.5 ml/min, iso-octane:ethanol (96:4), Micro-Porasil column 30 x 0.8 cm.

Thin Layer Chromatography

The nonionic residue from either ion-exchange procedure was streaked across the center portion of several TLC plates. Space was left along each vertical edge to spot 50 μg of reference sultone (Fig. 1). Each plate accommodated 25 mg residue in ethyl ether. The plates were developed by ascending chromatography in pentane:ether:methanol (50:50:2, v/v). The solvent was allowed to reach just to the top of the plate. After the plates dried, the side strips were cut off, sprayed with 25% sulfuric acid, and charred. Those zones in the center portions of the plate that corresponded to the sultone spots at the edge were scraped, and the silica gel was extracted with ether. After clarification by passage through a Millipore filter, the extracts were transferred gradually and quantitatively to cone-shaped vials and evaporated. The residue (usually about 20 mg total) was taken up in 50 μl of the HPLC eluting solvent, and the solution was drawn into a syringe for injection into the HPLC column.

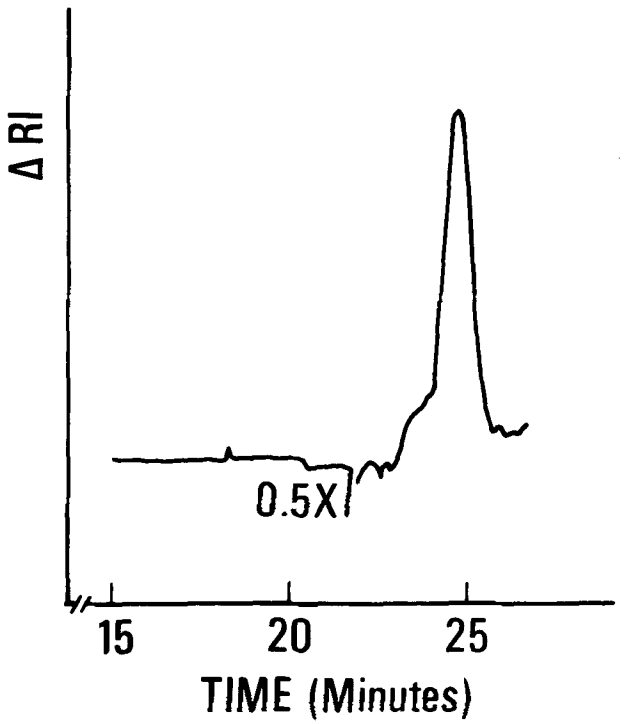


FIG. 3. High pressure liquid chromatography response of 5 μg 1-dodecene-1,3-sultone, (0.1 ppm in 50 g alkylethoxy sulfate). Flow rate: 0.5 ml/min, iso-octane:ethanol (96:4, v/v) on Micro-Porasil column 30 x 0.8 cm.

High Performance Liquid Chromatography

HPLC was carried out on a Waters, Assoc. Inc. (Milford, MA) ALC/GPC 202-401 unit fitted with a 30 x 0.8 cm Micro-Porasil column and Model R-401 refractometer. One column was sufficient for residues from the batch-wise ion exchange procedure; two columns in series were needed for adequate resolution of residues from the ion-exchange column. Materials were eluted with iso-octane:ethanol (96:4, v/v) at 0.5 ml/min, and were detected by the refractometer (Fig. 2). Peaks were identified by comparing their retention times to those of the reference sultones, or, in doubtful cases, the individual materials were trapped, and their identities were confirmed by gas chromatography and mass spectrometry.

If the chromatogram indicated that the separation was not clean, individual peaks were trapped and rechromatographed. In this event, the reference sultones used for quantification were treated similarly, since some sultone was lost with each passage through the column.

The quantity of each sultone was established by comparing the area under its peak with the area under the peak for a known quantity of reference material that had been handled through the same procedures.

Chlorosultones

Chlorosultones could be identified and determined directly by scraping the appropriate region from the TLC

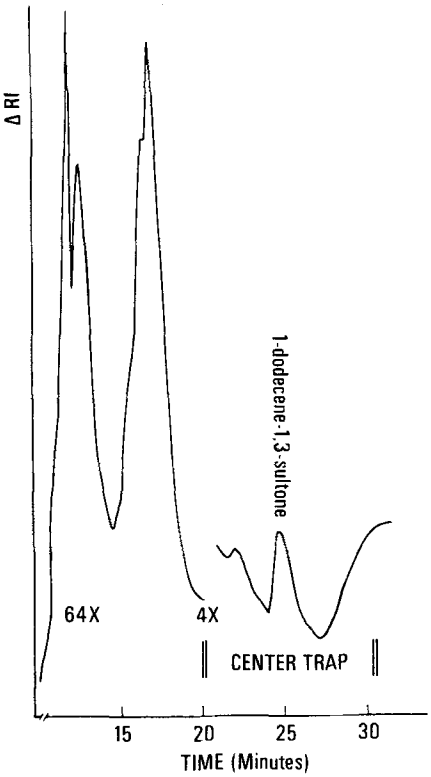


FIG. 4. Typical high pressure liquid chromatogram from a mixture of 50 μg 1-dodecene-1,3-sultone and 50 g AES after concentration by batch-wise ion-exchange and thin layer chromatography. Flow rate: 0.5 ml/min, iso-octane:ethanol (96:4, v/v) on Micro-Porasil column. Material emerging in the 20-30 min interval was collected for rechromatographing (see Fig. 5).

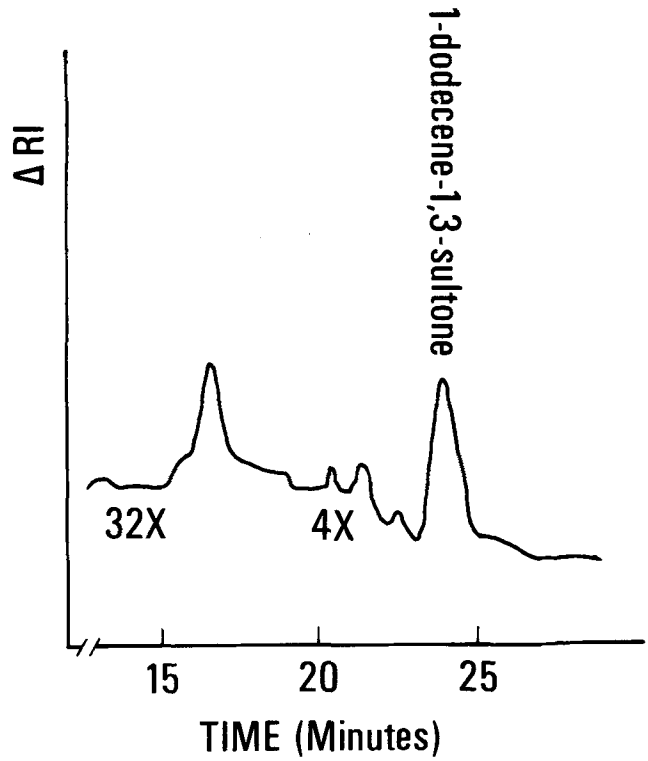


FIG. 5. High pressure liquid chromatogram of material collected from Fig. 4. Flow rate: 0.5 ml/min, iso-octane:ethanol (96:4, v/v) on Micro-Porasil column 30 x 0.8 cm.

plate (Fig. 1) and analyzing the adsorbed material by HPLC. This procedure was not satisfactory for chlorosultone levels below 5 ppm, however, since the chlorosultone region of the TLC plate contains many other low-polarity components. For lower levels, the chlorosultone was converted to unsaturated sultone by dehydrohalogenation with collidine.

Dehydrohalogenation was effected by heating the residue from the ion-exchange separation with an equal weight of 2,3,6-trimethylpyridine under nitrogen for 2 hr at 95-100 C. After it cooled, the mixture was dissolved in 200 ml hexane:ether (1:1, v/v) and washed with 5 x 50 ml 0.01N HCl and 3 x 50 ml distilled water. The organic layer was dried over sodium sulfate, filtered, and evaporated on the steam bath. The residue was then examined by HPLC. The result was the sum of unsaturated sultone plus chlorosultone in the original sample.

RESULTS AND DISCUSSION

Selectivity and Sensitivity

The method described is essentially one of concentration, 10^6 times or greater, depending on the sultone level of the surfactant. It nondestructively determines individual unsaturated sultones down to the 0.2 ppm level in alkylethoxy sulfate pastes, and levels as low as 0.01 ppm may be determined when the background does not interfere. Figure 3 shows the refractive index response of 5 μg of 1-dodecene-1,3-sultone, an amount equivalent to 0.1 ppm in 50 g of surfactant.

The column ion-exchange procedure, using only 8 g of surfactant instead of 50 g, is correspondingly less sensitive, and the lower limit of its usefulness is about 0.2 ppm. The column procedure is faster than the batch procedure and better suited for routine screening, but its chief advantage is that it causes very little dehydrohalogenation of the chlorosultones.

Since all of the sultones of interest are well resolved (Fig. 2), the method can be used for determination of saturated or unsaturated sultones, and of either 1,3- or 1,4-sultones. In practice, the 1,4-sultones do not appear on the same chromatograms as the 1,3-sultones, for they concentrate in a different region of the TLC plate (Fig. 1) and are injected separately into the HPLC column.

The shapes and resolution of the sultone peaks may be affected by other components of some samples; large quantities of hydrophilic components tend to tail into the sultone area. Low levels of sultones in such samples should be trapped and rechromatographed for maximum accuracy, as shown in Figure 4 and Figure 5.

Ion Exchange

When the chlorosultones are exposed to the pyridinium sites of the anion-exchange resin, they are partially dehydrochlorinated to unsaturated sultones. Approximately 40% of a chlorosultone is dehydrohalogenated during the batch-wise procedure. This is not objectionable when the collidine treatment is being used or when the sample's history indicates that no chlorosultone could be present, but if a separate determination of chlorosultones at levels above 0.2 ppm is necessary, the column ion-exchange procedure should be used, since it results in less than 8% dehydrohalogenation (Fig. 6). Attempts to scale up the column procedure caused unsatisfactory increases in dehydrohalogenation.

Extraction of sultones from AES with hexane is a logical alternative to ion exchange—one that would avoid dehydrochlorination—and was explored, but it did not provide reliably quantitative separation.

Thin Layer Chromatography

Several workers have used hydrocarbon-ether solvent

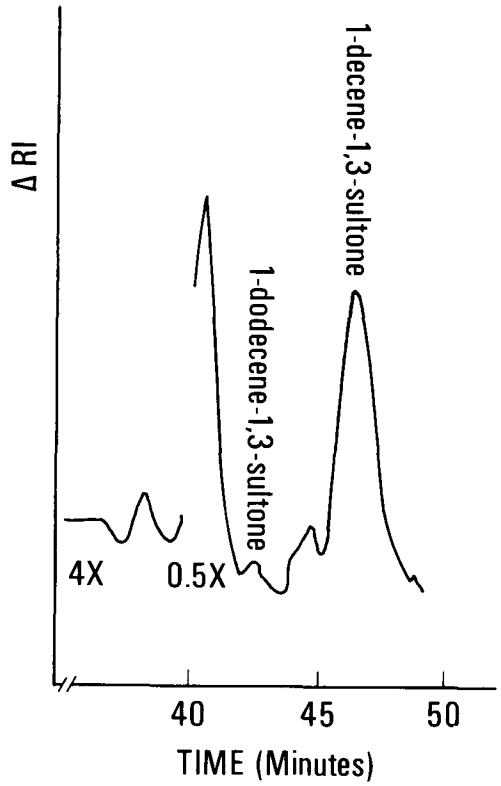


FIG. 6. High pressure liquid chromatogram from a mixture of 8 μg 2-chlorododecane-1,3-sultone, 8 μg 1-decene-1,3-sultone, and 8 g alkylethoxy sulfate after concentration by column ion exchange and thin layer chromatography (which eliminates the chlorosultone). Some 8% of the chlorosultone has been converted to 1-dodecene-1,3-sultone by the ion-exchange column. Flow rate: 0.5 ml/min iso-octane:ethanol (96:4, v/v) on two Micro-porasil columns, 30 x 0.8 cm.

systems for TLC of sultones. In this work we have found that pentane-ether is preferable to the usual hexane-ether system, and that the addition of a little methanol sharpens the separations.

Although charring with sulfuric acid was the preferred method for visualization, spraying the margins of the plates with Rhodamine B solution (0.05% w/w in water) revealed the typical pattern of the nonionic components. Although Rhodamine B does not make microgram quantities of sultone visible, it is possible with routine samples to associate the pattern of nonionics with the R_f values of the sultones and be guided by their pattern in recovering sultones from the plate. Visualization with Rhodamine B is faster than charring and conserves sultone standards.

The number of TLC plates needed to accomodate the nonionic fraction of a surfactant paste will vary with the type of surfactant and the completeness of its sulfation. As many as 32 plates have been necessary for certain samples, although 8 plates are normally sufficient for the 50-g samples of surfactant. Preparative layer plates, 1000 μ or more in thickness, carry more material but do not give comparable resolution.

High Performance Liquid Chromatography

For elution of the silica gel column, iso-octane:ethanol was preferable to several other solvent mixtures, including hexane or pentane combined with alcohol, or hydrocarbon-ether mixtures. A reversed phase column (μ Bondapak C_{18}, Water Assoc. Inc. Framingham, MA) gave nearly comparable separations when used with acetone-methanol-water mixtures, but losses of sultone occurred during evaporation of the aqueous solvent from trapped components.

During several months of experimentation there was no evidence that the columns were being deactivated by the ethanol used in eluting them. Periodic flushing of the columns with ether is advisable to remove extraneous materials that gradually build up during use.

Applicability

The method described has been used successfully for the analyses of alkylethoxy sulfates, α-olefin sulfonates, alkyl sulfates, and mixtures of those surfactants with linear alkylbenzene sulfonate.

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