• TECHNICAL

Rapid Method for Determination of Unsulfonated Oils

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Abstract

A primary limitation to alkylbenzene sulfonation processes has been the lack of a rapid method to sense the quality of sulfonation. This is especially true for a process using sulfur trioxide where both the level of sulfonating agent and time are critical: too little reagent results in high oils; too much reagent degrades product color; and a delay in the process also degrades color. Although steam distillation of oils from the neutralized sulfonate can be conducted in about one and one-half hours for commercial dodecylbenzene derivatives, far greater time is required for higher molecular weight homologs. Extraction of oils requires about one hour and more operator time than distillation.

The use of ethylene glycol as the principal carrier solvent, along with a small amount of water, provides oil values within 10 min distillation time. It is also applicable to longer chain alkylbenzene sulfonates besides those from dodecylbenzene. Subsequently, extracted oils are high, ca. 90%, in sulfone content. Glycol distilled oils plus subsequently extracted oils (sulfones) are slightly greater than oils obtained exclusively by extraction. It has been realized that some of the more volatile oils are lost during the usual extraction procedure.

The glycol oils distillation method has been successfully used in plants for alkylbenzene sulfonic acid quality control.

Introduction

THE PRIMARY PROPERTIES influencing the quality of alkylbenzene sulfonates are: a) the amount of unsulfonated oils and b) product color. Under-sulfonation can result in high oils which would impair functional properties, while over-sulfonation can yield an unacceptably dark-colored material. This is especially true for SO_3 sulfonation where the amount of reagent and the time of reaction are very critical. However, by a suitably rapid method for determining the level of unsulfonated oils, it should be possible to produce a high quality product even with sulfonation by SO_3.

Thus far, unsulfonated oils have been determined by extraction (2,3,4) and by steam distillation (1), either method requiring at least an hour to complete. It will be shown later that the extraction procedure alone yields sulfones as well as other oils, while steam distillation isolates only a portion of the distillable oils. To be accurate and acceptable for general use, a rapid oils method should analyze for all the volatile unsulfonated oils and leave the sulfones as distillate residue.

Experimental

Method Development

Preliminary analytical evaluations showed that ethylene glycol would act as a carrier solvent for oils distilled from alkylbenzene sulfonates. In this study, as with all succeeding oils distillations, the oil trap used consisted of a 0.4 ml lower capillary tube calibrated in 0.01 ml units which was attached to the bottom of a 10 ml large diameter column marked off in 1 ml units. The apparatus was completed by fusing a 12 in. Allihn condenser to the upper end of the 10 ml collector column. This set of equipment, which is illustrated in Figure 1, is quite similar to that developed by Eccles and described by Gilbert (1).

The recommended ethylene glycol distillation procedure is:

1. Weigh 10.0 g of alkylbenzene sulfonic acid into a 2000 ml, two-neck flask with the center neck provided with a ball joint sized to fit the trap apparatus.
2. Add 350 ml Fisher Scientific purified ethylene glycol (Catalog No. E-177).
3. Add 10 g of aqueous 40% NaOH, and several boiling stones.
4. Connect the flask to the trap and insert a thermometer through a rubber stopper and place in the side neck of the flask.
5. Heat the 2000 ml flask with an electric mantle to the boil and continue to boil at a moderate reflux for 10 min (unless otherwise specified in the accompanying data). The temperature of the vapor in the flask should be 180–185C.
6. Remove the heating mantle and allow the oils in

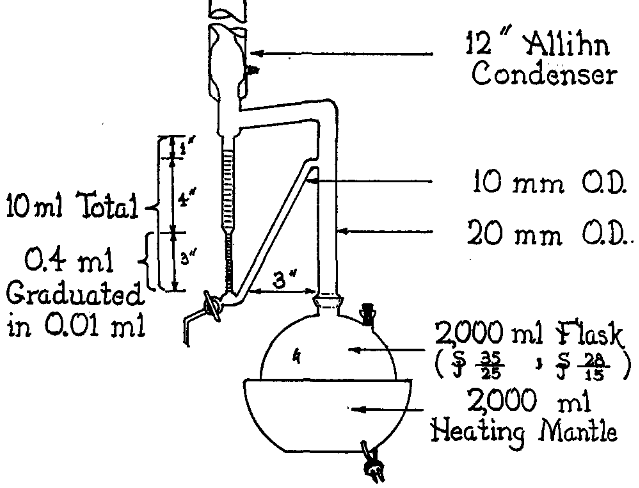

FIG. 1. Oils distillation apparatus.

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the trap to cool to room temperature. In the meantime, wash down traces of oils near the top outlet of the condenser with several small additions of ethylene glycol from a medicine dropper.

7. Slowly drain the oils in the trap into the lower calibrated capillary by removing glycol through the trap stopcock. Care must be taken to avoid a break in the oils column caused by too fast draining. Wiping the trap with a wet towel will hasten cooling.
8. Record the oils volume in the capillary.

$$\% \text{ Unsulfonated oils} = \frac{\text{ml distilled} \times 0.87 \text{ (density)} \times 100}{\text{sample weight}}$$

Where 200 g samples of alkylbenzene sulfonic acid were distilled, the above procedure was used with the following modifications:

1. The sample was neutralized with 25% aqueous NaOH in a beaker containing a liter of ethylene glycol. The contents of the beaker were rinsed into a 5 liter, two-necked flask with 250 ml of the ethylene glycol.
2. A thermometer was inserted in the side neck and the distillation was started. Water was withdrawn from the trap until the temperature reached 180–185C. The distillation was then continued for 2 hr.
3. The condenser was rinsed and the oils were recorded as previously described.

The equipment is cleaned between runs by several additions of acetone through the condenser which are then drained through the stopcock.

TABLE I

Effect of Spiking Deoiled[a] NaDDBS (In Ethylene Glycol)

No.	Additive	Ml H_2O	Min distillation time	Ml oils distilled
1	None	6	60	0.00
2	0.30 ml Steam oils[b]	0	15	0.22–Sl. turbid glycol
3	0.30 ml Steam oils[b]	6	20	0.29–Clear glycol
4	0.30 ml Glycol oils[b]	6	10	0.30
			20	0.31
5	20 g 40% NaOH	6	20	0.00
6	0.30 ml (Hi-M. W. AB)	6	180	0.29
7	0.30 ml DDB added to trap	6	30	0.30

[a] 10 g sample of sodium dodecylbenzene sulfonate deoiled by petroleum ether extraction.

[b] From previous oils distillations.

In the steam distillation, water replaces ethylene glycol and Dow Corning Antifoam A is used to defoam the solution in the flask. For a 10 g sample, two drops of defoamer are used; for a 200 g sample, 8–10 drops are required. Times for steam distillation are as indicated in the accompanying tables.

TABLE II

Reproducibility of Glycol Distillation Method

DDBSA[a] Sample No.	% Oils after 10 min distillation	
	1st Run	2nd Run
1	0.8	0.8
2	1.2	1.2
3	1.4	1.4
4	2.1	2.1

[a] 10 g.

Table I lists data showing recoveries of oils distilled from deoiled sodium alkylaryl sulfonate which had been "spiked." Ethylene glycol was the carrier solvent. According to tests 2 and 3, it was apparent that some water is required to prevent dispersion of the collected oils in the glycol phase. As noted during the studies, excess sodium hydroxide had no effect on the quantity or character of the oils collected. Even high molecular weight alkylbenzene (post-dodecylbenzene), test 6, was distilled with good recovery.

Reproducibility of the glycol distillation procedure was checked by analyzing several SO_3 based dodecylbenzene sulfonic acid samples covering a range of oil contents. Maximum oils with good test reproducibility, as shown in Table II, were obtained after 10 min distillation time.

Infrared spectra for the oils distilled with ethylene glycol showed them to be reasonably similar to the original starting alkylbenzene. No traces of contamination by ethylene glycol could be discerned.

Diethylene glycol was found unsuitable as a carrier solvent for the oils since it tended to cause partial emulsification of the oils even with some water present during the distillation.

Method Applicability

The next step in this study was to evaluate the glycol versus steam distillation methods and to determine the effects of sample size, sulfonating agent, and type of sulfonate. The dodecylbenzene sulfonic acids used were based on commercial dodecylbenzene and were prepared by 100% H_2SO_4, 105% H_2SO_4 (20% oleum) and SO_3 sulfonation. A sample of TeDBSA (tetradecylbenzene sulfonic acid) by 100% H_2SO_4 sulfonation of commercial tetradecylbenzene was also analyzed. The sulfuric acid and oleum based products had an active ingredient range of 86–88%, sulfuric acid range of 6–9%, and a water content of 4–5%. The SO_3 sulfonated acid had been diluted with water to about 85% active and its sulfuric acid content was 1.4%. All sulfonic acids tested were readily available commercial products. Oil values were reported on an "as received" basis.

Table III shows fair agreement, within 0.1%, for glycol oils obtained from 10 g and 200 g samples.

TABLE III

Oils Distilled vs. Sample Size, Time, and Extraction

Sulfonic acid	Sulf. agent	% Oils by glycol distillation		% Oils by steam distillation			% Oils by extraction[c]
		10 g/ 10 min[a]	200 g/ 2 hr[a]	10 g/ 1.5 hr	10 g/ 16–20 hr	200 g/ 16–20 hr	
DDBSA	100% H_2SO_4	0.87 0.87	0.97	0.35 0.44	0.47 0.52	0.55	0.70 0.66
DDBSA	105% H_2SO_4	0.64 0.65	0.68	0.26 0.30	0.45 0.49	0.39	0.88 0.84
DDBSA	Air—SO_3	0.70	0.70[b]	0.26	0.43	0.30	0.90 0.78
TeDBSA	100% H_2SO_4	1.48 1.48	1.35	0.58 0.56	0.78 0.83	0.96	1.20 1.12

[a] Maximum oil obtained.

[b] 75 g sample.

[c] 5 g sample via ASTM D 1568-60T.

TABLE IV
Oils Distilled vs. Solvent Carrier

Sulfonic acid[a]	Sulf. agents	% Oils by			
		Sequential solvents			Glycol alone
		Water	Glycol	Total	
DDBSA	100% H_2SO_4	0.55	0.43	0.98	0.97
DDBSA	105% H_2SO_4	0.39	0.30	0.69	0.68
DDBSA	Air—SO_3	0.30	0.39	0.69	0.70
TeDBSA	100% H_2SO_4	0.96	0.48	1.44	1.35

200 g samples except for No. 3—75 g.

Good agreement was found for oils from duplicate 10 g samples that yielded maximum oil volumes after 10 min distillation time.

Steam distilled oils, listed in Table III, for the same samples show that maximum oils are not obtained until after 16–20 hr distillation. Although agreement within duplicate sets is good, there are some differences between small and large samples.

When comparing oils by distillation versus those obtained by petroleum ether extraction, the following comments appear applicable. Glycol distillation yields more oils than steam distillation. Petroleum ether extraction yields less oils than glycol distillation for sulfuric acid based sulfonics, but more oils for those sulfonic acids made via oleum and SO_3 sulfonation. In the first case, undoubtedly, some of the more volatile oils are lost during extraction.

In order to more clearly define the nature of the oils obtained, the water left in the pot after steam distillation was replaced with ethylene glycol. This change was carried out by adding an appropriate volume of glycol to the flask and withdrawing water from the trap until the boiling point reached 180–185C. Then the solution was distilled for 2 hr to complete the removal of oils by ethylene glycol. Table IV lists amounts of oils obtained by sequential steam-glycol distillation versus glycol alone. Indices of refraction presented in Table V for the oils show them to be less aromatic than the starting alkylbenzenes. Average molecular weights (also listed in Table V) measured by a Mechrolab osmometer show the steam distilled oils to be of a slightly lower molecular weight than the starting alkylbenzenes, while the sequential glycol oils are appreciably higher molecular weight materials. Where glycol alone was used, the molecular weight of the oil from SO_3 sulfonated DDBSA was higher than the others, probably due to the loss of more volatile oils through vapor sparging during sulfonation.

Samples whose oil content was distilled with ethylene glycol (no silicone defoamer present) were analyzed by extraction for any residual oils and sulfones. The large samples which had been distilled were subsequently mixed with 500 ml 3-A alcohol and 1100 ml water, and were then extracted seven times with 200 ml portions of petroleum ether (30–60C bp). The combined ether extractions were washed four times with 150 ml portions of 50% aqueous 3-A alcohol. Following this, the ether was carefully evaporated and the residue was finally heated to constant weight at 105C. Table VI lists the amounts of materials extracted. (The extraction blank was insignificant and no correction was required.) The smallest amounts were recovered from sulfuric acid based sulfonates, while extracts from 20% oleum and SO_3 based sulfonates were considerable greater. The same order of differences were found for their calculated sulfone contents based on sulfur analysis. The extracts from oleum and SO_3 sulfonates were greater than 90% sulfone purity (calculated). In all cases, the amounts of impurities present, i.e., the difference between ''as received'' sulfones extracted and the calculated sulfone content based on sulfur analysis, were 0.05% or less. Infrared analysis confirmed the identity of sulfones by strong absorptions at 7.52 and 8.6 μ. In addition, strong bands near 8.95 and 11.95 μ showed that these sulfones are para substituted as would be expected.

Discussion

The ethylene glycol oils distillation method has been successfully and routinely used in plants for monitoring alkylbenzene sulfonic acid quality. It has proved extremely helpful in SO_3 sulfonation plant operation in that it has enabled rapid batch trimming with incremental amounts of SO_3. Otherwise, prolonged delay caused by slower analytical methods would have impaired the final product color and would have reduced plant output. To hold the test time to a minimum in the plant, the sulfonic acid sample was introduced with a 10 ml syringe (Becton, Dickinson and Co., ''Yale,'' 10Y) through a small hole in a rubber stopper fitted into the side neck of the flask containing the boiling solution of ethylene glycol and 10 g of 40% aqueous NaOH. The stopper hole was quickly rinsed with glycol from a second syringe and was plugged with a smaller stopper. In this manner, the entire analysis required no more than 15 min. Afterwards, the trap was drained, rinsed several times with

TABLE VI
Sulfone Analysis

Sulfonic acid[a]	Sulf. agent	% ''as is'' sulfone extracted	% Avg sulfur	Calc. avg mol wt	% Calc. sulfone purity	% Calc. pure sulfone in sample
DDBSA	100% H_2SO_4	0.11	3.85	823	67.3[b]	0.074[b]
DDBSA	105% H_2SO_4	0.54	5.25	610	90.8[b]	0.49[b]
DDBSA	Air—SO_3	0.56	5.35	598	92.7[b]	0.52[b]
TeDBSA	100% H_2SO_4	0.22	4.14	767	77.8[c]	0.17[c]

[a] From 200 g samples except for No. 3—75 g.
[b] Theoretical mol wt = 554.
[c] Theoretical mol wt = 598.

TABLE V
Average Molecular Weights and Index of Refraction of Distilled Oils

Sulfonic acid	Sulf. agent	Oils avg molecular weights for distillation with			Oils index of refraction for distillation with		
		Sequential solvents		Glycol alone	Sequential solvents		Glycol alone
		Water	Glycol		Water	Glycol	
DDBSA[a]................	100% H_2SO_4	219	300	240	1.4514	1.4604	1.4555
DDBSA[a]................	105% H_2SO_4	230	288	243	1.4437	1.4504	1.4478
DDBSA[a]................	Air—SO_3	242	290	261	1.4642	1.4515	1.4566
TeDBSA[b]...............	100% H_2SO_4	237	314	251	1.4562	1.4731	1.4614

Starting alkylbenzenes:

	Avg mol wt	n_D^{25}
[a] DDB =	246	ca. 1.4859
[b] TeDB =	265	ca. 1.4870

acetone, and dried. Care was taken to prevent acetone entering the flask. Thus, the glycol in the boiling flask could be used for several analyses simply by adding 10 g additional 40% NaOH for each succeeding test.

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Preparation of Glycerides by Controlled Esterification[1]

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Abstract

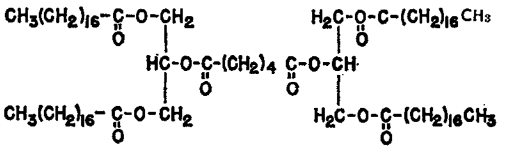
A simple procedure for esterifying glycerides without interesterification occurring would be highly useful for preparing on a large scale a number of tailor-made fats, including cocoa butter-like fats. Such esterifications were carried out by employing *p*-toluenesulfonic acid as catalyst and continuously removing the water of esterification by azeotropic distillation with aliphatic hydrocarbons or by stripping with vaporized hydrocarbons. Even though *p*-toluenesulfonic acid rapidly disproportionated 1-monostearin, even at 120C, apparently esterification was faster and only a moderate amount of ester-ester interchange and acidolysis occurred. Diacid glycerides might be prepared from monoglycerides by the procedure which was employed. Saturated diglycerides were esterified with oleic acid with little ester-ester interchange or acidolysis occurring; however, intraesterification was extensive. The reaction between 1,3-distearin and oleic acid yielded approximately 75% 1-oleodistearin and 25% 2-oleodistearin. Saturated diglycerides were esterified wtih sebacic acid, again with little or no interesterification occurring.

Introduction

VARIOUS FAT and fat-type products which are actually or potentially of considerable economic importance cannot be produced readily on a large scale. Cocoa butter-like fats belong in this category. Much effort has been devoted by research workers toward devising a process for making a fat product resembling closely the mixture of 2-oleodisaturated glycerides of palmitic and stearic acids predominating in cocoa butter. The problem of preparing by a simple procedure a di- or triacid triglyceride of reasonably high purity has not been solved satisfactorily.

In this laboratory a series of dibasic acid-containing glycerides as exemplified by

BIS/1-(STEAROYLOXYMETHYL)-2-(STEAROYLOXY)ETHYL/ADIPATE,



have been prepared and found to have potentially useful properties (9,10,25). The compounds cannot be readily prepared on a large scale by presently available processes.

A number of other new-type fat products, including the acetoglycerides (8), could be mentioned as examples of products whose preparation by a simplified procedure would be desirable.

A survey of the literature reveals that the catalysts commonly used to promote esterification also promote one or more types of interesterification, which includes acidolysis, alcoholysis, and ester interchange (2,18).

Various metals or compounds of these metals have been claimed to be esterification catalysts. Stannous chloride and zinc chloride have been found to be particularly effective (7). Again many of these compounds have been found to promote interesterifications.

Hydrochloric, sulfuric, and sulfonic acids are among the most widely used esterification catalysts, but they also are recognized as alcoholysis and ester interchange catalysts. Van Loon (24) patented the use of aromatic sulfonic acids to bring about ester interchange in triglyceride mixtures. Normann (20) carried out an ester interchange between tristearin and coconut oil by adding 1% of β-naphthalenesulfonic acid and heating the mixture for 2.5 hr at 250C.

Despite the evidence that esterification is accompanied by interesterification, and that some catalysts are good for both types of reactions, there are indications that esterification without interesterification should be possible. Even though acid catalysts are used in interesterification reactions, their activity is far below that of equivalent amounts of sodium alkoxides, at least in some systems. The methanolysis of a highly refined vegetable oil in boiling methanol under anhydrous conditions has been found by the authors to proceed quite slowly in the presence of small amounts of anhydrous hydrochloric or sulfuric acids. Presumably when interesterification occurs in some acid-catalyzed esterifications, it is caused by the water which is formed. Water in small amounts is a good interesterification catalyst (22). By continuously distilling water and some acetic acid out of the reacting mixture Grummitt and Fleming (12) succeeded in repressing the hydrolysis of castor oil during acetylation with acetic acid in the presence of *p*-toluenesulfonic acid.

While evidence is available that strong acids are generally poor interesterification catalysts and that triglycerides in the absence of water are relatively unaffected by such acids, it has not been shown heretofore that acid-catalyzed esterifications of mono- and

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