



## Nonaqueous Titrimetric Analysis of Sulfuric and Alkylbenzene Sulfonic Acids in Detergent Intermediates

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### ABSTRACT

A single differential nonaqueous titration method is presented for the analysis of sulfuric and alkylbenzene sulfonic acids in a detergent intermediate material. The organic and sulfuric acids in the sample were quantitatively titrated potentiometrically with standard cyclohexylamine solution. With certain specified sample compositions, approximate sulfuric acid determinations may be made without sample weighing or the use of standardized titrant. The titration is based upon the ratio of the first and second end points of the differential titration curve. Because of its simplicity, the latter method adaptation is especially useful for routine control type analyses.

### INTRODUCTION

Sulfated alcohols and sulfonic acids derived from alkylbenzene are manufactured on a wide scale as intermediates for various detergents. Their salts are used as major components of liquid and dry detergents. The amount of sulfuric acid present as a by-product has a marked effect on the color as well as the purity of the detergent intermediate. Therefore, the determination of sulfuric and organic acids ( $\text{RSO}_3\text{H}$ ) becomes an important matter. The determinations of sulfuric and sulfonic acids have been made independently by existing methods (1-3). One of the most common methods for the determination of sulfonic acid involves two phase titration with a standard solution of cationic surfactant. The end point is detected based upon the distribution of methylene blue between aqueous and chloroform phases. The classical and widely accepted methods for the determination of sulfuric acid involve titration of sulfate ion with a standard barium or lead solution (4-6).

Several examples of the differential titration of sulfonic and sulfuric acids have been reported. Yoshihara, Ishiwari, and Konishi determined sulfuric acid in the presence of sulfonic acid or sulfated alcohols by potentiometric titration with dodecyltrimethylammonium hydroxide (7). Carasik, Mausner, and Spiegelman used tetrabutylammonium hydroxides for the same purpose (8-11). A disadvantage of tetraalkylammonium hydroxides is that they contain weakly basic carbonate and tertiary amine as impurities. The titrant is also known to decompose slowly on standing to form small amounts of tertiary amine via the Hofmann reaction. In a differential titration of strong and weak acids, the impurities cause an error similar to that in an aqueous acid-base titration with sodium hydroxide that is not carbonate free. The use of an experimentally determined correction factor has been recommended to circumvent this difficulty (7). A method is reported for preparing pure titrant, however, it is a rather long and involved process (12). This paper describes an improvement in the differential titration procedure, employing a titrant which can

be easily prepared. Cyclohexylamine was chosen as a titrant since it is sufficiently basic to give sharp potential breaks. The titrant can be prepared by diluting analytical grade reagent without further purification. The normality of the titrant was determined to be constant within experimental error for at least 6 weeks, and no correction factor is required. The simple procedure described here would be of great benefit especially for routine plant analysis.

An equation which calculates only the approximate content of sulfuric acid is proposed for routine plant analysis. In the equation, exact values of titrant concentration and sample weight are not used which eliminates standardization procedures and shortens the time required for the analysis.

### EXPERIMENTAL PROCEDURES

#### Reagents and Apparatus

Reagents are of analytical grade chemicals. The cyclohexylamine titrant was prepared by diluting a weighed quantity of the amine with methanol or ethanol. The cyclohexylamine titrant was standardized against sulfamic acid by titration in methanol and ethanol. Tris(hydroxymethyl)aminomethane was used as a primary standard base for standardization of the 0.2N sulfuric acid aqueous solution used in added sulfuric acid recovery experiments. The end points were detected potentiometrically using a Metrohm automatic titrator (Model E536) equipped with a 10 ml automatic burette and a Metrohm generalpurpose combined glass-Ag/AgCl electrode EA-121.

#### Titration Procedure

Approximately 200 mg of a detergent intermediate was weighed into a 100-ml beaker, followed by addition of 50 ml of a solvent. The sample in solvent solution was titrated potentiometrically with 0.1N cyclohexylamine while stirring with a magnetic stirrer assembly. The differential end points were accurately located by the maximum peak position of the first derivatives of the titration curve. The solvent blank was less than 0.005 ml, and no correction was made.

#### Calculations

The results of the analysis were calculated as follows.

$$\% \text{H}_2\text{SO}_4 = \frac{(V_2 - V_1)N \times 98.08 \times 100}{W} \quad (I)$$

$$\% \text{RSO}_3\text{H} = \frac{(2V_1 - V_2)N \times MW \times 100}{W} \quad (II)$$

where  $V_1$ ,  $V_2$ : milliliters of titrant at the first and the second end points

N: normality of titrant

W: sample weight in milligrams

MW: average molecular weight of organic acid

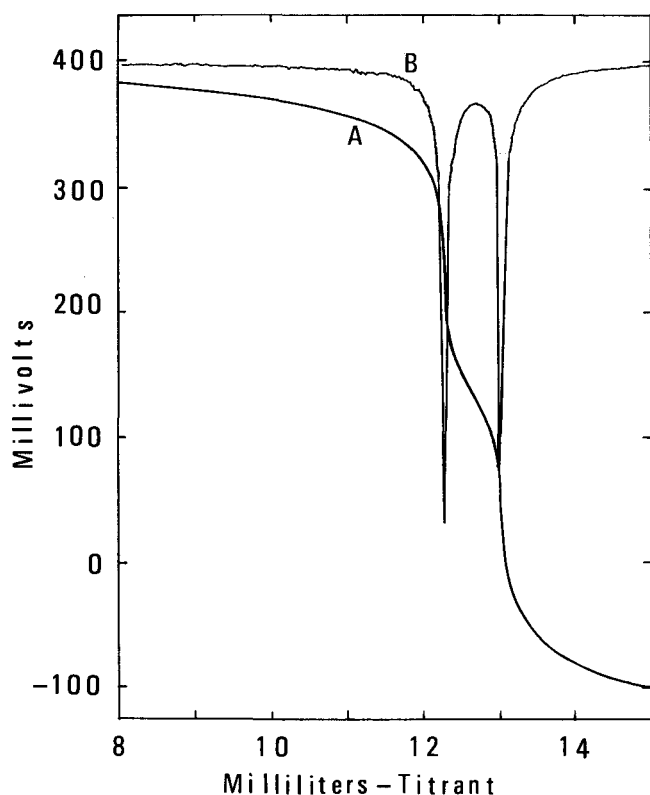


FIG. 1. Titration of a detergent intermediate containing alkylsulfonic acid and sulfuric acids. Solvent: methanol. Titrant: 0.1N cyclohexylamine. A. Differentiating titration curve, B. the first derivative curve of the curve A.

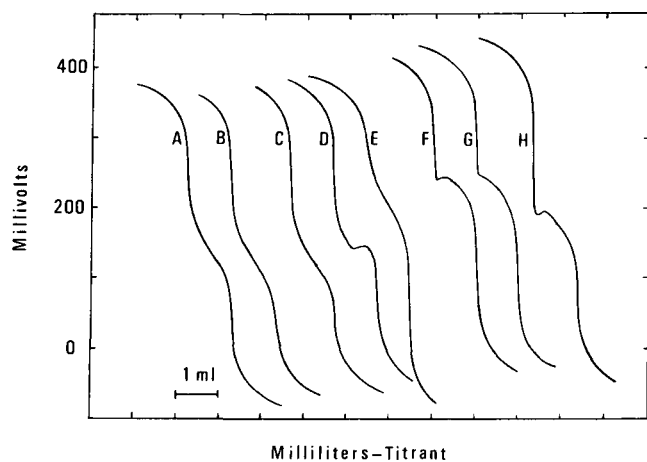


FIG. 2. Titration of alkylsulfonic and sulfuric acids with cyclohexylamine in various solvents. A. methanol, B. ethanol, C. isopropanol, D. tert-butanol, E. ethylene glycol, F. methylisobutylketone, G. acetone, H. acetonitrile.

#### Rapid Method for the Approximate Determination of Sulfuric Acid Content

The following simplified procedure can be applied for a quick determination of the approximate content of sulfuric acid in a detergent intermediate with typical levels of organic and sulfuric acids. The principle of the simplified method is to substitute exact sample weight with the calculated weight of organic and sulfuric acids. Exact sample weight and the normality of titrant are not necessary. Consequently, the experimental procedure can be greatly simplified by eliminating weighing and titrant standardization.

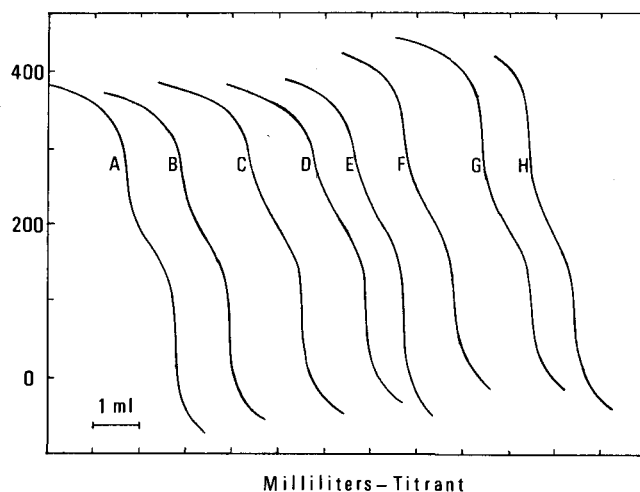


FIG. 3. Titration of alkylsulfonic and sulfuric acids with 1,3-diphenylguanidine in various solvents. A. methanol, B. ethanol, C. isopropanol, D. tert-butanol, E. ethylene glycol, F. methylisobutylketone, G. acetone, H. acetonitrile.

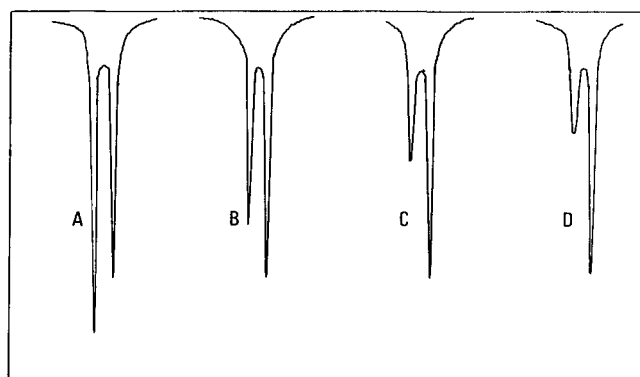


FIG. 4. Effect of water addition on the resolution of alkylsulfonic and sulfuric acids in methanol. % water added: A, none; B, 1; C, 3; D, 5.

$$W \text{ (mg)} = \text{RSO}_3\text{H (mg)} + \text{H}_2\text{SO}_4 \text{ (mg)} \quad \text{(III)}$$

Equation (I) can be rewritten as

$$\begin{aligned} \% \text{H}_2\text{SO}_4 &= \frac{\text{H}_2\text{SO}_4 \text{ (mg)} \times 100}{\text{RSO}_3\text{H (mg)} + \text{H}_2\text{SO}_4 \text{ (mg)}} \\ &= \frac{98.08(V_2 - V_1)N \times 100}{\text{MW}(2V_1 - V_2)N + 98.08(V_2 - V_1)N} \\ &= \frac{98.08(V_2/V_1 - 1) \times 100}{\text{MW}(2 - V_2/V_1) + 98.08(V_2/V_1 - 1)} \quad \text{(IV)} \end{aligned}$$

Equation (IV) does not include the terms for titrant concentration and sample weight. Percent sulfuric acid depends solely on the ratio of  $V_1$  and  $V_2$ . Therefore, sulfuric acid content can be determined quickly by dissolving small amounts of sample without weighing. The methanolic or ethanolic sample solution is then titrated potentiometrically. After the titration, the percent sulfuric acid is calculated based upon the ratio of the first and the second end points. Generally, the average molecular weight (MW) of the organic acid required in the calculation is known.

#### RESULTS AND DISCUSSION

Acid mixtures to be titrated in this experiment are strongly acidic and do not require strongly basic titrant such as tetraalkylammonium hydroxide. Cyclohexylamine and 1,3-diphenylguanidine were investigated as possible

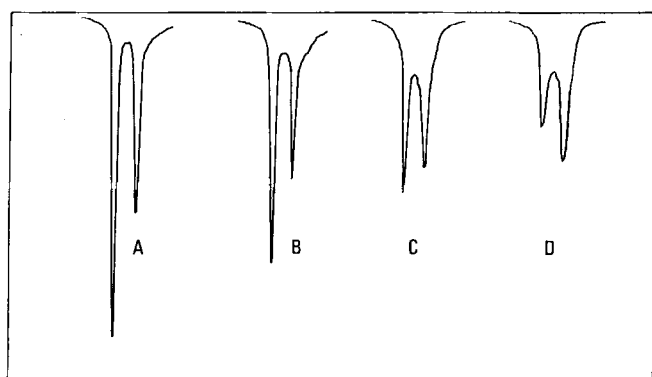


FIG. 5. Effect of water addition on the resolution of alkylsulfonic and sulfuric acids in ethanol. % water added: A, none; B, 1; C, 3; D, 5.

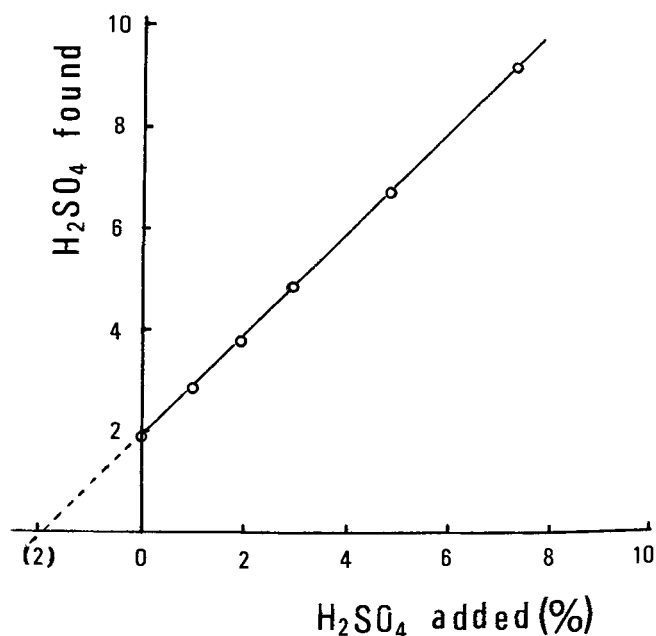


FIG. 6. Recovery of sulfuric acid added to a detergent intermediate in methanol.

titrant bases which are sufficiently basic to give sharp end points in a potentiometric titration of the acid mixture. The amines have advantages over tetraalkylammonium hydroxide in purity, stability, reagent cost, and less reactivity with carbon dioxide in the air. In addition, the preparation of the titrant is very easy.

A typical potentiometric titration curve together with the first derivatives is shown in Figure 1. The first replaceable hydrogen of sulfuric acid, the strongest acid in the mixture, will be titrated initially and the organic acid, the second strongest acid next. Therefore, the first end point corresponds to the neutralization of the first replaceable hydrogen of sulfuric acid and the organic acid. The second end point corresponds to the neutralization of bisulfate ion, the moderately strong acid. The difference between the two end points represents the base required to titrate the bisulfate ion.

Various solvents were examined for the differential titration of acid mixtures with 0.1N cyclohexylamine or 1,3-diphenylguanidine. The results are shown in Figures 2 and 3. It can be seen from the potentiometric titration curves in Figure 2 that methanol, ethanol, isopropanol, and ethylene glycol give well resolved two end points, while titration curves are distorted by precipitate formations in tert-

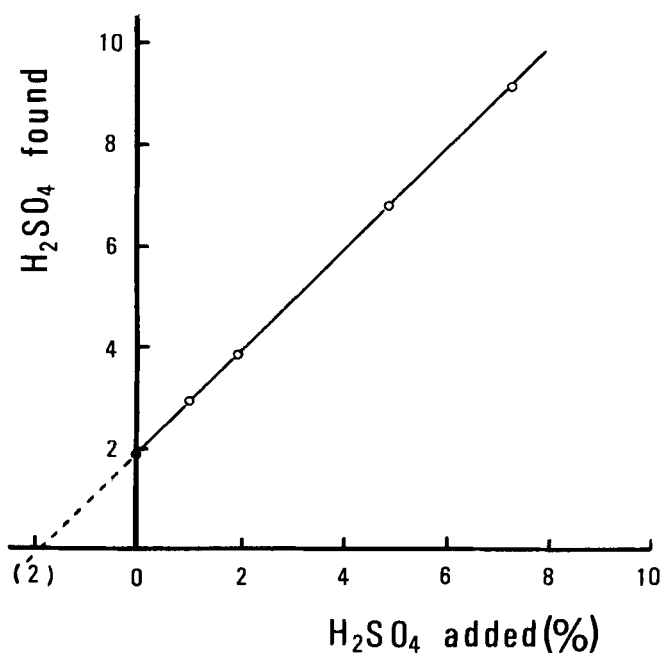


FIG. 7. Recovery of sulfuric acid added to a detergent intermediate in ethanol.

butanol, methylisobutyl ketone, acetone, and acetonitrile. The precipitate formation was not observed in the titration with 1,3-diphenylguanidine, and the resolutions of two end points were satisfactory in all the solvents tested. No distorted titration curves were found with this titrant as shown in Figure 3. The sharpest second end point was seen in either methanol or ethanol solvent. As described above, there are many possible titrants and solvents for the differential titration of detergent intermediates. Considering the practical requirements of a solvent for routine analysis, methanol or ethanol are appropriate because these solvents are readily available, inexpensive, not excessively volatile, and without viscosity problems. Cyclohexylamine was chosen as a titrant because a little better resolution with this titrant was obtained in methanol or ethanol than with 1,3-diphenylguanidine. However, the advantage of cyclohexylamine is not decisive. The potential breaks of the first and the second end points with these solvents are both sharp and large enough for an accurate differential analysis.

#### Effect of Water

The effect of water on the differential titration is shown in Figures 4 and 5 where the first derivatives curves were drawn in solvents containing different amounts of water. The addition of water to methanol or ethanol solvent causes the peak height of the derivative curves to decrease. In methanol, only the first break becomes less sharp whereas in ethanol both breaks decrease upon addition of water to the solvent. The detergent intermediates can be titrated in methanol or ethanol containing up to 2 or 3% water. Therefore, small amounts of water originally present in a detergent intermediate do not significantly interfere in the determination. Special precautions in drying glassware or solvents are not necessary. However, if as much as 5% of water is present, the end point becomes less sharp and the result is somewhat inaccurate.

#### Precision and Accuracy

The differential titration procedure was applied in methanol and ethanol solvents to investigate the recovery of sulfuric acid added to a detergent intermediate. Standardization 0.2N sulfuric acid aqueous solution was used in

TABLE I  
Analysis of Detergent Intermediates

Sample	Sample weight (g)	H <sub>2</sub> SO <sub>4</sub> (%)	RSO <sub>3</sub> H (%)
Sulfonated alkylbenzene			
Lot A	0.2090	1.74	96.4
	0.2017	1.75	96.4
Lot B	0.2010	1.95	95.8
	0.2095	1.95	95.5
Lot C	0.1992	1.97	95.7
	0.2147	2.02	95.2
Lot D	0.2057	1.91	95.5
	0.2102	1.92	95.1
Sulfated alcohol			
Lot E	0.2219	2.04	84.0
Lot F	0.2125	1.94	84.2
Lot G	0.2020	2.24	85.0

TABLE II  
A Comparison of the H<sub>2</sub>SO<sub>4</sub> Contents with and without Approximation

With approximation	Without approximation	Difference
2.70	2.63	0.07
2.64	2.57	0.07
2.70	2.62	0.08
2.65	2.58	0.07
2.68	2.61	0.07
2.71	2.63	0.08
2.64	2.57	0.07
2.75	2.66	0.09
2.72	2.64	0.08
2.70	2.62	0.08
Mean 2.69	2.61	0.08
CV(%)1.1	1.1	0

these experiments. Slopes of 45° were obtained as shown in Figures 6 and 7, plotting sulfuric acid added versus sulfuric acid found. In all cases, recoveries of sulfuric acid were 99% or greater of the amounts added. Seven detergent intermediates were analyzed by the proposed method in methanol solvent (Table I). The coefficients of variation

were 1.1% and 0.2% for sulfuric acid and organic acid, respectively, in replicate determinations.

As can be seen in equation (III), the simplified technique can be used if the detergent intermediate contains only small amounts of materials other than organic and sulfuric acids. The organic acid content should be greater than 90%, which is ordinarily true of products made by reaction with sulfur trioxide. The comparison of sulfuric acid contents calculated by equations (I) and (IV) is shown in Table II where a detergent intermediate was analyzed repeatedly. The difference of the results was less than 0.1%, which is small enough for practical purposes to monitor a production process. If an abrupt increase of the sulfuric acid content is found, indicating low active content, the regular analytical procedure using equation (I) should be followed. The simplified procedure is very useful when analysis is required frequently to monitor a manufacturing process. The procedure described herein can be applied for the analysis of various sulfonated or sulfated materials which contain sulfuric acid as a by-product.

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