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Determination of Sodium Sulfate in Anionic Surfactants by Nonaqueous Titration

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ABSTRACT

A convenient and easy method was developed for nonaqueous titrimetric determination of sodium sulfate in the presence of sulfonate and sulfate type anionic surfactants. Sodium sulfate and the anionic surfactants were converted to sulfuric acid and the corresponding organo-sulfonic or organo-sulfuric acids by the addition of an excess of perchloric acid. The resulting acid mixture was then titrated in methanol with cyclohexylamine. The sulfate content was calculated from the difference of the two end points of the differentiating titration curve. For the determination of sodium sulfate in typical anionic surfactants, the relative standard deviation varied from 0.7 to 2.0% at the 0.3-10% sodium sulfate levels. The method provides a rapid and precise determination of inorganic sulfates in sulfonated or sulfated materials.

Sulfonate and sulfate type anionic surfactants usually contain small amounts of sodium sulfate. Therefore, a simple and easy determination of sodium sulfate in the anionic surfactants is a primary concern to process analysts in the detergent industry. The common gravimetric method for inorganic sulfate determination is usually complicated by co-precipitation. Many titrimetric procedures which involve the formation of barium or lead sulfate have been reported (1-3). However, none of these methods is satisfactory for routine determination in speed and simplicity.

The present study describes a nonaqueous titration procedure for determining sodium sulfate in anionic surfactants. Upon addition of an excess perchloric acid to a sample containing sodium sulfate and anionic surfactants, the reactions shown below occur:

$$Na_2SO_4 + 2HClO_4 = H_2SO_4 + 2NaClO_4$$
$$RSO_3Na + HClO_4 = RSO_3H + NaClO_4$$
$$ROSO_3Na + HClO_4 = ROSO_3H + NaClO_4$$

The resulting acid mixture was analyzed for bisulfate anion by potentiometric titration in nonaqueous solvent. The usefulness of the nonaqueous differentiation of bisulfate anion has been presented earlier (4). The simple titrimetric method should be useful in many cases where rapid determination of sodium sulfate is required.

EXPERIMENTAL PROCEDURES

Reagent and Apparatus

Reagent grade chemicals were used without further purification.

0.2N Perchloric acid: Perchloric acid solution in methanol was prepared by adding 9.0 ml of 70% perchloric acid to methanol in a 500 ml volumetric flask. The solution was diluted to the mark with methanol. The perchloric acid solution thus obtained was approximately two-tenths normal.

0.05N Cyclohexylamine: Cyclohexylamine in methanol was prepared by diluting 5 g of reagent grade cyclohexylamine to 1 liter with methanol. The exact normality of the cyclohexylamine solution was determined by standardization aginst sulfamic acid. A 0.01N cyclohexylamine solution was prepared in a similar way.

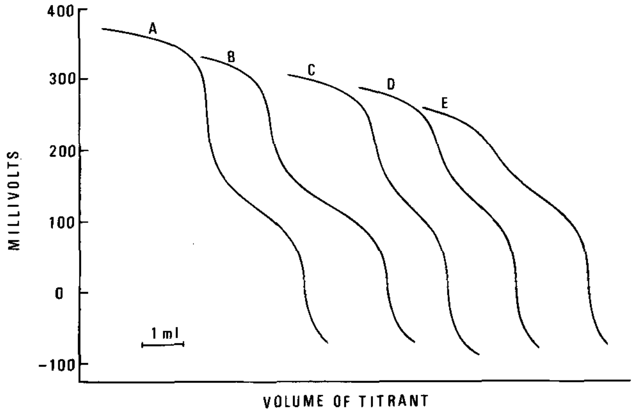

FIG. 1. Titration of sulfate in anionic surfactants after conversion to the corresponding acids. Water content in methanol: A-0%, B-1%, C-3%, D-5%, E-10%.

TABLE I

Determination of Na_2SO_4 in Anionic Surfactants

Anionic surfactants	% Na_2SO_4 Calculated	% Na_2SO_4 Found	Relative std. dev. (n=5) (%)
Salts of sulfonic acids			
RSO_3Na (C_{15}, 3-jydroxy)	9.9	9.8	0.7
RC_6H_4 SO_3Na (C_{12})	6.0	5.9	1.0
Salts of acid sulfuric acid ester			
R OSO_3Na (C_{12})	10.2	10.2	0.9
	0.56	0.56	1.9
	0.29	0.29	1.7
RO $(CH_2CH_2O)_mSO_3Na$	10.5	10.3	1.1

A Metrohm Potentiograph Model E536, automatic recording titrator, equipped with a 20 ml buret was used to record the titration curve. A combination type glass and Ag/AgCl electrode (Metrohm EA121) was used without modification.

Titration Procedure

About 0.2 g of sample containing sodium sulfate was weighed directly into a 200-ml beaker. Five milliliters of 0.2N perchloric acid solution was added with a pipet to dissolve the sample followed by dilution with methanol to 100 ml. Potentiometric titration was carried out in a conventional way. The two end points were detected from the inflections of the titration curve. Cyclohexylamine (0.01N) was used to titrate near the end points for the determination of low concentrations (1% or less) of sodium sulfate.

RESULTS AND DISCUSSION

A potentiometric titration curve, typical in this experiment, is given in Figure 1. The first inflection represents the neutralization of strong acids, unreacted perchloric acid, the first hydrogen of sulfuric acid, and the organo-sulfonic acid. The second inflection represents the neutralization of the second hydrogen of sulfuric acid. The amount of sodium sulfate is calculated based upon the titrant volume between the two inflections, which is equivalent to the amount of base required for neutralization of the bisulfate anion. The influence of water in the solvent is shown in Figure 1. Here, the samples were titrated in methanol containing increasing concentrations of water. The differentiation of two inflections becomes more poorly defined as the concentration of water increases. The differentiation was not useful for the analytical purpose when more than 5% of water was present in the methanol solvent. The upper limit of water concentration should be taken into consideration, if samples in dilute aqueous solutions are analyzed. Typical results of the determinations are given in Table I for anionic surfactants mixed with known amount of sodium sulfate. Good agreement was obtained between the calculated and experimental results. The relative standard deviation for replicate synthetic mixture was found to be between 0.7-2.0% at the 0.3-10% sodium sulfate levels.

Anions which can be converted to moderately weak acids upon addition of perchloric acid should be absent. Phosphate, for example, will interfere with the determination. The presence of chloride and nitrate does not interfere with the determination. The method can be applied to various sulfonated or sulfated materials as well as anionic surfactants.

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