Separation and Quantitative Determination of Active Ingredients in Detergent Formulations

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ABSTRACT

During the past few years, the increasing complexity of detergent formulations has required the analytical detergent chemists to devise many new and complicated separation schemes. This paper describes a method which allows the separation and quantitative determination of linear alkylbenzene sulfonate (LAS), ethoxylated alcohol sulfate (AES), alcohol sulfate (AS), free nonionic and amine oxide in detergent formulations. A combination of ion exchange, chemical separations, and gas chromatography is used in the described method. In addition to quantitating the types of "active" material listed, the ethylene oxide content of the ethoxylated alcohol sulfate and the homolog distribution of the alcohol hydrophobe in both the ethoxylated alcohol sulfate and the alcohol sulfate are obtained. This separation scheme is applicable to either liquid or powdered detergent formulations.

INTRODUCTION

Shortly before World War II, the first soapless detergent powder, DREFT, was introduced in the United States by Procter & Gamble. The original DREFT formulation consisted of sodium alkyl sulfate as the active ingredient (at a level of 40 weight percent) with sodium sulfate as a diluent (1). The introduction of this product was the basis or beginning of the present day detergent industry. The shortage of fats during the war led to research from which alkyl aryl sulfonates were developed. The first product of this type used in this country was an alkyltoluene sulfonate. This compound, however, gave detergent powders which caked very badly. The alkyl toluene sulfonates were quickly replaced by alkylbenzene sulfonates based on tetrapropylene. About this time sodium tripolyphosphate became commercially available, and it was soon found that sodium tripolyphosphate addition not only enhanced the detergency of alkylbenzene sulfonates but also gave rise to a free-flowing, noncaking powder. So was born the built detergent powder.

During the 1950s the branched chain alkylbenzene sulfonates, being nonbiodegradable, or "hard," caused foaming problems in sewage plants and in many streams. This prompted the development and marketing of biodegradable or "soft" linear alkylate sulfonates (LAS) during the early 1960s. Formulations based on LAS were the main product of the detergent industry until governmental legislation against the use of phosphates appeared. This caused major changes in the active ingredients used in detergent powders. Ethoxylated alcohols, fatty alcohol sulfates (AS), sulfated ethoxylated alcohols (AES), amine oxides, and other active ingredients suddenly began to appear in detergent formulations.

With these more complex formulations, the life of the analytical detergent chemist became more and more complicated and at times very frustrating. With this in mind, we have attempted to develop a general detergent separation scheme which will handle the major types of active materials presently being used in commercial liquid and

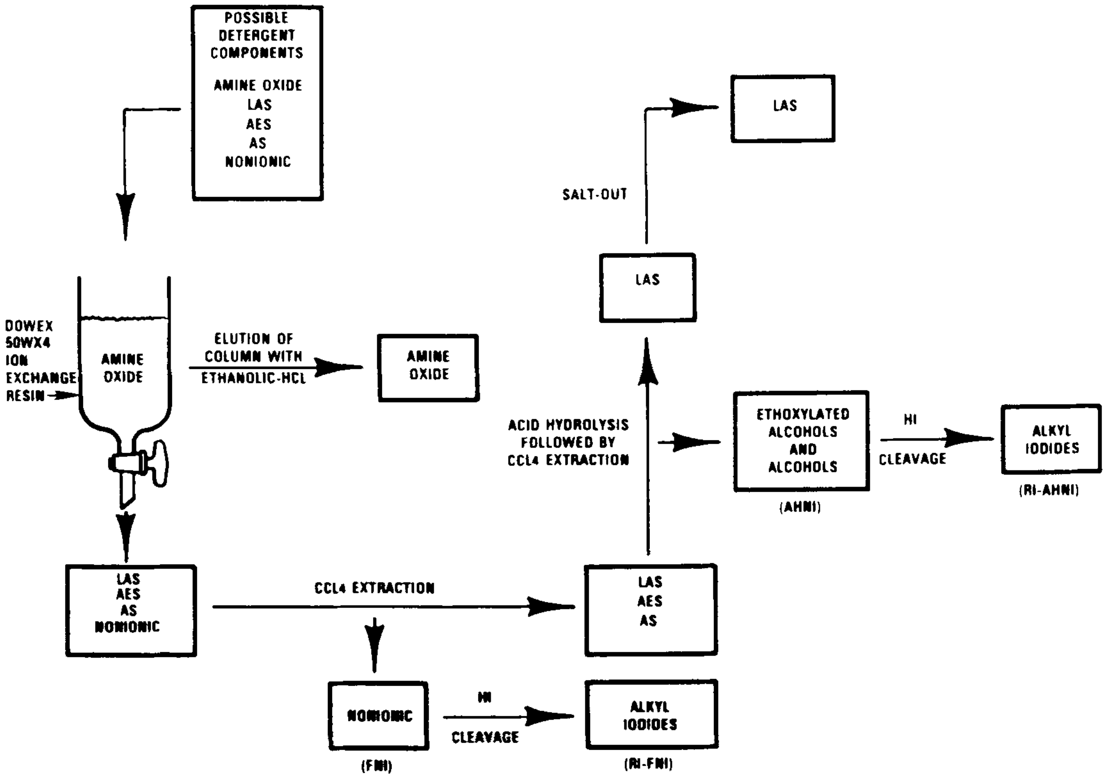

FIG. 1. Flow chart showing the isolation procedure for various detergent fractions.

TABLE I

Recovery Data of Ion Exchange Experiments

Experiment		Recovery
I. Amine oxide only	AO	95%
II. Repeat of above	AO	102%
III. Amine oxide + nonionic	AO	102%
	NI	101%
IV. Amine oxide + LAS + AES	AO	103%
	LAS + AES	100%
V. Repeat of above	AO	103%
	LAS + AES	101%
VI. Amine oxide + LAS + AES + AS	AO	90%
	LAS	101%
	AES + AS	a

[a] The quantitative determination of these components are obtained from MBAS or BCG data using the GLC distributions and equivalent weight data obtained from this separation.

TABLE II

Comparison of the Amount of Amine Oxide as Determined by the Ion Exchange and Titration Method

Sample	% Amine oxide ion exchange method	% Amine oxide titration method
LDL-1	4.6	4.9
LDL-2	4.7	4.5
LDL-3	4.7-4.8	4.7

powdered detergent products found in today's marketplace.

The types of active materials considered in this paper include amine oxide, ethoxylated alcohol (nonionic), alcohol sulfate (AS), ethoxylated alcohol sulfate (AES), and linear alkylate sulfonate (LAS). A detergent could conceivably contain a combination of all of the above types of active materials. By using our routine detergent methods, we were unable to quantitatively separate amine oxides from mixtures containing amine oxide and free nonionic surfactant. The method described here overcomes this difficulty. Under basic and neutral conditions, amine oxide behaves as a nonionic material, while under acidic conditions, it behaves as a cationic material. The routine procedures we use for nonionic isolation is a carbon tetrachloride extraction from a neutral or slightly basic alcohol-water solution. In this extraction, the free oil, any nonionic material present, free amine oxide, and any amine oxide complexed with detergent anionic material may be extracted. Therefore, it was not possible for us to gravimetrically determine the quantity of amine oxide or of nonionic material present in a detergent sample if it contained both amine oxide and free nonionic. The amount of amine oxide may be estimated volumetrically by two procedures. It can be measured directly by a titration method as described by Lew (2), or it can be estimated by using the difference in meq/g of anionic active as determined by the basic brom cresol green (BCG) technique (3), and the acidic methylene blue active substance (MBAS) technqique (4,5). The acidic MBAS technique titrates only the excess anionic material present, not that complexed with the amine oxide. The basic BCG technique, however, titrates all of the anionic present.

The general detergent separation scheme which we have developed is described in the following section. Figure 1 shows a flow chart of this procedure.

EXPERIMENTAL PROCEDURE

A 4 to 6 g sample of liquid detergent or a 1 to 2 g sample of the alcohol soluble material from a powdered detergent is dissolved in a minimum volume of ethanol/water (1:1) and passed through a strong cationic ion exchange column. A polystyrene resin (DOWEX 50WX4) was selected for the column. This resin has a low divinylbenzene cross linkage factor (4% divinylbenzene). A very small particle size (200-400 mesh) was selected because experimentally it gave good separation. The sulfonic acid form of the resin was used for this work. The sample solution was followed by elution with 250-300 ml of alcohol-water solution. Amine oxide, if present, is selectively adsorbed on the resin, with the remainder of the anionic and nonionic detergent active components passing through the resin with the 250-300 ml of alcohol-water effluent. The amine oxide was eluted from the column with 250-300 ml of 1 N ethanolic-HCl solution. This eluate was evaporated to near dryness (≅5-10 ml) and neutralized to phenolphthalein indicator with 50% caustic solution. The amine oxide was extracted into carbon tetrachloride from the slightly basic alcohol-water solution. The carbon tetrachloride extract was evaporated to dryness and the recovered amine oxide dried at 60 C under vacuum and weighed. The isolated amine oxide fraction may be further characterized by a number of instrumental techniques, such as nuclear magnetic resonance (NMR), infrared spectroscopy (IR), or gas liquid chromatography (GLC), if necessary.

The aqueous alcohol effluent from the column containing free nonionic (FNI) (ethoxylated alcohols), sulfated anionic and sulfonated anionic material was then extracted by the previously described carbon tetrachloride extraction procedure to recover the FNI fraction.

The aqueous alcohol phase from the FNI extraction now containing only sulfated anionic and sulfonated anionic materials was concentrated to approximately one-half volume on a steam bath (to remove the alcohol) and then hydrolyzed with sulfuric acid (≅2 N). This acid hydrolysis step converts all of the sulfated anionic material to ethoxylated alcohol (nonionic) or fatty alcohols. The sulfonated anionic fraction is not affected by the acid hydrolysis. The nonionic and fatty alcohols resulting from the acid hydrolysis may then be extracted using carbon tetrachloride after caustic neutralization and ethanol addition to reconstitute the original solution. The remaining ethanol/water phase containing the sulfonated species was evaporated, and the sulfonate recovered and weighed by a salting out procedure as described in ASTM D-855 (6).

The acid hydrolyzed nonionic and/or fatty alcohol fraction (AHNI) was split into two portions. One portion was examined directly by GLC. The second portion was cleaved by the hydriodic acid method as described in ASTM D-2959 (7). Nonionics containing polyethylene oxide chains when refluxed with hydriodic acid form unstable 1,2-diiodoethane. The diiodide decomposes to form ethylene and free iodine. One mole of iodine is formed for each mole of ethylene oxide in the polyoxyalkylene chain. The free iodine was titrated with standard thiosulfate solution and the ethylene oxide content calculated. If free alcohol is found to be present in the AHNI fraction by GLC, the ethylene oxide content must be corrected accordingly. The alkyl iodides formed during the hydriodic acid reaction were isolated from the titrated solution by hexane extraction (RI-AHNI) and saved for GLC analysis.

The GLC analysis technique described by Sones et al. (8) gives the ratio of alcohol to ethoxylated alcohol and the homolog distributions of both alcohol sulfate and ethoxylated alcohol sulfate present in the original detergent sample.

RESULTS AND DISCUSSION

Because of the small resin particle size chosen, a low

TABLE III

AES/AS Ratio Data

Description		Blend No. 1	Blend No. 2	Blend No. 3
Ratio of AES/AS	Known	62:38	50:50	50:50
Ratio of AES/AS	Found	65:35	54:46	51:49
Wt. % ethylene oxide	Calculated	26.4	24.2	21.4
Wt. % ethylene oxide	Found	26.4	24.3	21.3
Percent recovery		100	100	99

TABLE IV

Homolog Distributions of Alcohol Sulfate and Ethoxylated Alcohol Sulfate Blends

Homolog distribution of alcohol sulfate	Blend No. 1		Blend No. 2		Blend No. 3	
	Known	Determined	Known	Determined	Known	Determined
C_{10}	0.2	0.2	0.2	0.3	—	—
C_{11}	0.3	0.2	—	—	0.1	0.1
C_{12}	21.0	21.2	23.0	23.1	4.1	4.0
C_{13}	8.7	9.4	—	—	5.2	5.1
C_{14}	19.0	18.8	25.7	25.5	4.8	4.5
C_{15}	3.2	4.3	—	—	1.9	2.1
C_{16}	28.4	28.8	30.5	30.8	52.8	53.2
C_{17}	—	—	—	—	—	—
C_{18}	18.2	17.1	19.6	20.3	30.5	31.0
C_{19}	—	—	—	—	—	—
C_{20}	1.0	—	1.0	—	0.6	—
Homolog distribution of ethoxylated alcohol sulfate						
C_{10}	0.1	—	0.4	—	—	—
C_{11}	0.6	—	—	—	0.6	—
C_{12}	17.6	16.0	36.9	39.0	17.6	12.0
C_{13}	42.5	40.0	—	—	42.5	45.0
C_{14}	27.1	26.0	62.1	61.0	26.7	28.0
C_{15}	11.7	18.0	—	—	11.6	15.0
C_{16}	0.4	—	0.6	—	0.5	—
C_{17}						
C_{18}						

column flow rate was experienced. Operating the columns under atmospheric pressure only, a period of several hours was required for each column run. Recent data indicate that operation of the columns with a positive pressure of ca. 10 psig will decrease the elution time required for the column to 1 hr or less.

A systematic series of experiments was conducted to evaluate the ion exchange procedure. The recovery results of these experiments are shown in Table I.

Three light duty detergents were analyzed for amine oxide content by the ion exchange method and by the titration method as described by Lew (2). Table II shows the data obtained on these samples.

The other components used in these experiments were measured by the various techniques described in the preceding Experimental Procedure section; for example, nonionic by carbon tetrachloride extraction, LAS and AES by salt out as described in ASTM D855 (6) and by the BCG technique before and after hydrolysis (3).

Three known blends of alcohol sulfate and ethoxylated alcohol sulfate were prepared to establish the validity of the separations, the hydrogen iodide cleavage and the GLC techniques. The blends were carried through the separation scheme and analyzed by GLC. Table III shows both the known and experimentally determined AES/AS ratios and ethylene oxide data for these blends. The ethylene oxide data show excellent agreement between the known blended values and the experimentally determined values. The AES/AS ratio data do not show as good agreement; however, the data are certainly adequate to guide the detergent chemist or formulation chemist.

Table IV shows the homolog distributions of the alcohol sulfates and the ethoxylated alcohol sulfates used in the same three blends both before and after blending, separation, cleavage, and analysis. The data are sufficiently accurate and adequate to allow important conclusions to be made about the original detergent composition.

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