The Analytical Separation of Surface Active Agents

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Abstract

Methods for the separation of typical mixtures of surfactants are described. These procedures facilitate the separation and subsequent determination of individual surface active agents present in many commercial products.

Introduction

NUMEROUS ANALYTICAL methods are available for the determination of surface active agents occurring singly in commercial syndet formulations. A comprehensive review of available procedures is given by Spangler (1). Excellent bibliographical abstracts of the field have been published by the American Society for Testing Materials (2).

Although general procedures for the separation of mixtures of surface active agents are described by Rosen and Goldsmith (3), the need exists for methods of separation applicable to specific mixtures of such surfactants as are generally encountered in commercial products.

This paper presents a summary of analytical separations useful in the separation of specific mixtures of surfactants, together with critical comments based on experience in our laboratories. The methods are not given in detail, but the principle of the separation is stressed to enable an experienced worker to apply to his particular problem such of the separations as may be of value.

Preliminary to the successful separation of mixtures of surfactants is the removal of inorganic salts which complicate the problem. The usual method of elimination involves their removal as alcohol insoluble material by acceptable procedures (4–6).

Significant amounts of NaCl are found in the filtrate when the alcohol insoluble method is employed. Fortunately, the presence of NaCl does not interfere in most separation procedures. Traces of sodium carbonate, bicarbonate, and borax contaminate the filtrate when appreciable quantities are present in the original sample. Ross and Blank (7) recommend a re-extraction of the alcohol soluble material with 1:1 ethyl ether and acetone to remove the latter three compounds.

Determination of the types of surface active agents present in an unknown mixture is required before the selection of a quantitative method. Schemes for qualitative identification have been published (6, 8–10). An IR absorption method utilizing the water insoluble barium salts for identification has been described by Jenkins and Kellenbach (11). The components of some mixtures may be identified by direct examination of the alcohol soluble extract employing an IR spectrophotometer (12,13). Certain types of surfactants may be identified by UV spectrophotometry (14).

Separation Procedures

Procedures for separation of the following frequently encountered mixtures of surface active agents are described:

1. Soap and surface active agents.
2. High and low molecular weight sulfonates.
3. Alkyl aryl sulfonates and fatty alcohol sulfates.
4. Alkyl aryl sulfonates and sulfated fatty acid monoglycerides.
5. Alkyl aryl sulfonates and nonionic surfactants.
6. Fatty alcohol sulfates and sulfated fatty acid monoglycerides.
7. Fatty alcohol sulfates, alkyl aryl sulfonates and alkanolamides.
8. Alkyl aryl sulfonates, polyoxyethylated anionic sulfates and nonionics.

1. *The Separation of Soap from Surfactants.* The determination of soap in admixture with surfactants may be accomplished in several ways.

A. Titration of an ethyl alcohol extract of the sample with a standard solution of acid in G-H mix, 1:1 Ethylene Glycol-Isopropanol Alcohol (15).

B. Titration of an aqueous solution of the sample with standard acid using methyl orange-xylene cyanol mixed indicator. Alkali salts, if present, must be removed prior to titration. The error introduced by free alkali may be avoided by titration with $N/10$ HCl to a phenolphthalein endpoint.

C. The soap fatty acids may be split with acid, extracted with petroleum ether and titrated.

D. The soap fatty acids may be isolated by precipitation with magnesium salts.

2. *Separation of High Mol wt (Long Chain) Sulfonates from Low Mol wt (Short Chain) Sulfonates.* High mol wt alkyl aryl sulfonates (alkyl chain lengths of 4 carbons or more) can be separated from short chain sulfonates, such as toluene sulfonate, by extraction from an acidified aqueous solution with ethyl ether (16). The alkyl benzene sulfonate content of the ether layer may be determined by UV spectrophotometry (17) or by cationic titration (18, 19).

The amount of toluene sulfonate remaining in the extracted water layer can be determined by UV absorption after removal of the residual ether. Measurement of the absorbance at 220 mμ and background at 240 mμ provide data for calculation of toluene sulfonate content. The absorptivity value used in the calculation may be derived by determination on a sample of the toluene sulfonate used, or by calculation from the known absorbances of the pure ortho- and para- isomers.

The latter approach is used in this laboratory. The total toluene sulfonate is determined by measuring the respective absorbances at 220 mμ and 240 mμ and calculated, using a predetermined absorptivity value of 54.1 for *p*-toluene sulfonate. The para/ortho ratio of the sample is calculated from measured absorbances at 267 and 274 mμ and predetermined absorptivity values of the pure isomers. The calculated para/ortho ratio is then employed to correct the original absorbance of the para isomer measured at 220 mμ.

Most commercial surface active agents of alkyl benzene sulfonate type contain tailings (low mol wt entities) which interfere in this determination and result in the toluene sulfonate content being high by 0.2–0.5%. If the original alkyl benzene sulfonate is available for examination a blank can be established.

A similar approach is applicable to the determination of xylene sulfonates, but in this case the complexity of isomers possessing varying absorptivity values complicates the analysis. If a portion of the xylene sulfonate used in a particular mixture is available, an absorptivity value representative of this material can be used in subsequent analyses. In this case no evaluation of a particular isomer is possible although a system has been developed for isomeric xylenes and ethyl benzene in hydrocarbon fuels (20).

3. *Separation of Alkyl Aryl Sulfonates from Fatty Alcohol Sulfates.* In separating mixtures of alkyl aryl sulfonate and fatty alcohol sulfate the sample should be dissolved in hot alcohol and insoluble salts removed by filtration. The alcohol-soluble material is isolated by evaporating to dryness, and the fatty alcohol sulfate hydrolyzed by refluxing with 25% HCl. The solution is cooled and barium chloride solution added to precipitate the sulfate. A volume of acetone equal to that of the solution is added to aid solubilization of the barium alkyl aryl sulfonate. The barium sulfate precipitate is filtered, ignited in the usual manner, and the sulfate content calculated to fatty alcohol sulfate (21).

Alternatively, the alkyl aryl sulfonate content can be determined by cationic titration of the acid hydrolyzed sample after neutralization or by UV spectrophotometry (17).

The desulfated fatty alcohol can be recovered from the hydrolyzed solution with *n*-pentane and qualitative identification accomplished by IR (11,22, 23) or gas chromatography.

4. *Separation of Alkyl Aryl Sulfonates from Sulfated Fatty Acid Monoglycerides.* Mixtures of alkyl aryl sulfonates and sulfated fatty acid monoglycerides can be analyzed by differential cationic titration. The mixture is dissolved in acidified aqueous ethylene glycol monobutyl ether, and an aliquot subjected to cationic titration. The total surface active titratable matter is calculated to equivalent sulfated fatty acid monoglyceride.

In a second sample, the sulfated fatty acid monoglyceride is destroyed by hydrolysis with normal KOH in ethylene glycol monobutyl ether solution and the alkyl aryl sulfonate content determined by cationic titration of an aliquot of the saponification mixture.

The sulfated fatty acid monoglyceride equivalent of the alkyl aryl sulfonate is subtracted from the total titratable matter as sulfated fatty acid monoglyceride to obtain the actual fatty acid monoglyceride.

5. *Separation of Alkyl Aryl Sulfonates from Nonionic Surfactants.* A mixture of alkyl aryl sulfonate and nonionic can be separated by a columnar or batch ion exchange method as described by Ginn and Church (24). An aqueous alcohol solution of the mixture is passed through a column packed in series with anionic and cationic exchange resins. The nonionic may be quantitatively recovered by evaporation of the eluted solution. Alternatively a mixed bed ion exchange resin may be employed, using the batch method.

The sulfonate retained by the resin may be eluted by use of a 2% NaOH solution in 1:1 isopropanol and water. Recoveries are on the order of 96%.

Nonionics of the alkyl phenoxy polyoxyethylene ethanol type can be determined in the presence of alkyl aryl sulfonate by UV spectrophotometry. The absorbance of the nonionic at 283 and 300 mμ must be determined for each nonionic or mixture of nonionics present in admixture with the alkyl aryl sulfonate.

Interference by the absorbance of alkyl aryl sulfonate at 283 mμ is avoided by the following procedure. Determine the absorbance at 283 and 300 mμ of the alkyl aryl sulfonate alone (sample blank without the addition of the nonionic) and express the ratio of the absorbances as a numerical correction factor. Multiply the background reading at 300 mμ of the nonionic and alkyl aryl sulfonate mixture by the correction factor to eliminate interference due to alkyl aryl sulfonate at the wavelength of 283 mμ.

This UV spectrophotometric procedure is also applicable to admixtures of nonionics exhibiting UV absorption and fatty alcohol sulfates.

6. *Separation of Fatty Alcohol Sulfates from Sulfated Fatty Acid Monoglycerides.* Mixtures of sulfated fatty acid monoglycerides and fatty alcohol sulfates can be separated by hydrolysis of the mixture with normal KOH in ethylene glycol monobutyl ether solution. The fatty acid monoglyceride hydrolyzes leaving the fatty alcohol sulfate unaltered. The monoglyceride sulfate can be determined by calculation from the quantity of KOH consumed in hydrolysis. The fatty alcohol sulfate is determined by cationic titration.

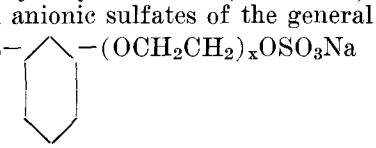
Alternatively, the differential titration technique can be applied by performing cationic titrations before and after hydrolysis, as previously described for mixtures of alkyl aryl sulfonates and sulfated fatty acid monoglycerides.

7. *Separation of Fatty Alcohol Sulfates, Alkyl Aryl Sulfonates and Alkanolamides.* A mixture of sulfates, sulfonates, and alkanolamides in aqueous solution may be separated by the ion exchange procedure previously described. The alkanolamide will elute. If other nonionics are present they will interfere, but frequently they can be identified by IR examination and, if they exhibit absorbance in the UV region, can be determined by UV spectrophotometry.

Alternatively, some samples can be hydrolyzed with 25% H_2SO_4 to disrupt the alkanolamide. Treatment of the neutralized solution by the ion exchange technique will result in an eluate containing the non-hydrolyzable nonionic alone. The latter may be determined and characterized by instrumental means.

Certain alkanolamides can be directly separated from admixture with fatty alcohol sulfates and alkyl aryl sulfonates by extraction with 1:1 ethyl ether/petroleum ether from solution in 1:1 ethyl alcohol/water rendered basic with caustic alkali.

8. *Separation of Alkyl Aryl Sulfonates, Polyoxyethylated Anionic Sulfates and Non-ionics.* Many detergents, particularly the liquid type, are formulated with alkyl aryl sulfonates, nonionics, and polyoxyethylated anionic sulfates of the general formula:



Such a three component system can be effectively separated by a combination of ion exchange and cationic titration techniques. The nonionic present in the sample can be quantitatively removed by employing the ion exchange method previously described.

Differential cationic titration of the sample before and after acid hydrolysis permits the determination of both anionic sulfonate and sulfate.

An alternative procedure found useful in the analysis of mixtures of alkyl aryl sulfonates, polyoxy-

ethylated anionic sulfates, and nonionics consists of the quantitative ion exchange separation of the total nonionic after hydrolysis of the mixture with acid.

The total nonionic will consist of the amount originally present in the sample as free nonionic, and the amount of nonionic derived from the hydrolysis of the anionic sulfate. Subtraction of the amount of free nonionic from the total yields the anionically combined nonionic. This may then be factored to anionic sulfate. If this approach is used, the alkyl aryl sulfonate may be determined by cationic titration of a suitable aliquot after the hydrolysis step. This method is not applicable to mixtures containing alkanolamide additives or to nonionics that are hydrolyzed under conditions of the test.

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Structure of High Melting Glycerides from the Milk Fat-Globule Membrane[1]

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Abstract

The method for determining the position of a fatty acid in triglycerides with pancreatic lipase has been applied to high-melting glycerides from the milk fat-globule membrane.

Definition of location of individual fatty acids within the membrane high-melting triglycerides indicated that the beta positions of these glycerides were occupied primarily by a saturated fatty acid of 14,16, or 18 carbon atoms.

The trisaturated glyceride content of membrane high-melting glyceride was found to be 71.2%, while those isomeric forms of disaturated-monounsaturated and monosaturated-diunsaturated glycerides which contained a saturated fatty acid in the beta position were found to predominate.

Calculation of triglyceride types and isomeric forms indicated that, while random distribution was found on the basis of saturated and unsaturated fatty acids, the individual fatty acids were not randomly distributed in the triglycerides under study.

Introduction

PALMER AND Weise (1) were the first to report the isolation of a high-melting glyceride (HMG) from the milk fat-globule membrane by precipitation from ethanol at room temperature. In 1945, Jenness and Palmer (2) isolated and characterized HMG fractions of similar properties from butterfat, washed-cream buttermilk extracts, and washed-cream serum extracts. More recently Patton and Keeney (3) and Thompson, Brunner, and Stine (4) have published the gas chromatographic analysis of the fatty acid composition of HMG fractions precipitated from acetone and ethanol respectively. This study was undertaken to determine the structure of ethanol-insoluble, high-melting glycerides isolated from membrane lipid, and to compare this fraction with the high-melting glycerides from butteroil.

Experimental

Figure 1 represents the procedure for isolating HMG from the milk fat-globule membrane. Washed cream was churned and the butterfat was separated from the buttermilk in a laboratory separator. The membrane containing buttermilk was lyophilized and the lipids were extracted with ethyl ether and 95% ethanol. Phospholipids were precipitated with acetone and the HMG fraction was purified by crystallizing from 95% ethanol.

Since the fatty acyl groups esterified at the one and three position of a triglyceride are reported to be selectively removed by pancreatic lipase, this enzyme provides a convenient approach to the determination of triglyceride structure (5,6). The procedure follows: 1) digestion of the triglyceride with pancreatic lipase; 2) isolation of the digestion products; and 3) determination of the fatty acid composition of these products.

The digestion mixture was 0.5 g triglyceride, 20 ml distilled water, 0.5 ml 45% aqueous solution $CaCl_2$, 0.2 ml 1% aqueous solution of bile salts, and 100 mg pancreatic lipase (Mann Research Laboratories, pork pancreas-crude). Digestion was at 40C with continuous agitation. The pH was held at 8 by periodic additions of 0.1 *N* NaOH, and digestion proceeded 5 min. After the hydrolysis period, pH was reduced

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