Gas Chromatographic Analysis of Ester-type Surfactants by Using Mixed Anhydride Reagent

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ABSTRACT

Polyoxyethylene alkyl ether sulfates, polyoxyethylene alkyl ether phosphates, and polyoxyethylene fatty acid ester-type surfactants have been analyzed by gas chromatography after chemical decomposition by using the mixed anhydride of acetic and p-toluenesulfonic acids. In this way, the hydrophobic groups of the polyoxyethylene alkyl ether sulfates and polyoxyethylene alkyl ether phosphates can be identified in the form of alkyl acetates, and the alkyl compositions can be determined easily. On the other hand, the hydrophobic groups of the polyoxyethylene fatty acid ester-type surfactants, such as polyoxyethylene fatty acid ester, polyoxyethylene glycerol fatty acid ester, and polyoxyethylene sorbitan fatty acid ester, have been identified after conversion into their corresponding fatty acids. At the same time, the base compounds of the hydrophilic groups have been converted into ethylene glycol diacetate, glycerol triacetate, and isosorbide diacetate, respectively, so these surfactants may be distinguished easily,

INTRODUCTION

Polyoxyethylene (POE) alkyl ether sulfates, POE alkyl ether phosphates, and POE fatty acid ester-type surfactants are used widely as detergents, wetting agents, emulsifiers, dispersants, solubilizers, etc. In case of analyzing these surfactants, it is important to identify their hydrophobic groups, since thier physical properties depend, to a certain extent, upon the chemical structure of the hydrophobic groups, as well as the hydrophilic groups.

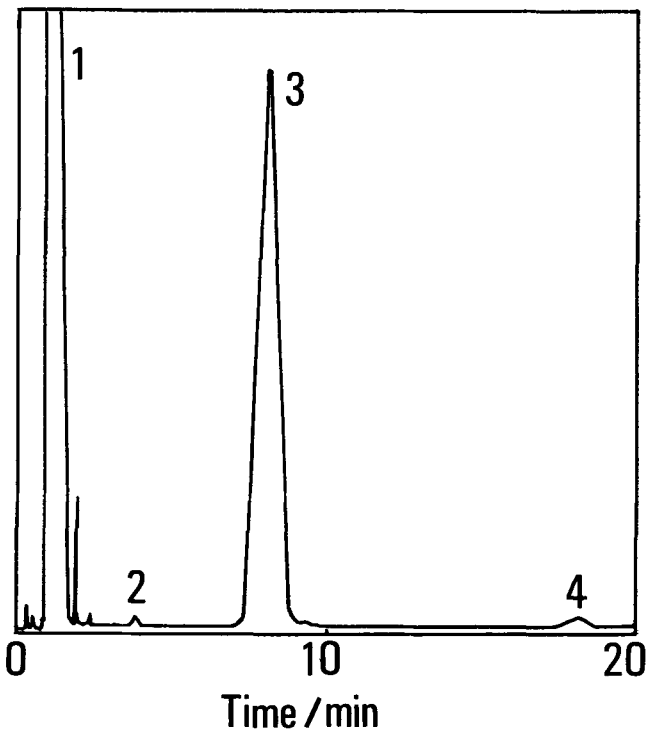

FIG. 1. Gas chromatogram of reaction products of polyoxyethylene alkyl ether sulfate. 1. Ethylene glycol diacetate. 2. Decyl acetate. 3. Dodecyl acetate. 4. Tetradecyl acetate. Gas liquid chromatographic conditions: 1 m x 3 mm, packed with 15% Apiezon grease L; oven, 145 C; and chart speed, 1 cm/min.

For the identification of the alkyl compositions of the POE alkyl ether sulfates, hydriodic acid (HI) decomposition gas liquid chromatography (GLC) method has been used (1,2). To separate and identify the POE alkyl ether phosphates, thin layer chromatography (TLC) has been employed (3). However, it seems to be impossible to determine their hydrophobic groups. When the alkyl compositions of the POE fatty acid ester-type surface-active agents are determined, samples generally are hydrolyzed with methanol and a small amount of sulfuric acid followed by the GLC analysis of methyl esters produced. On the other hand, it is also significant to differentiate among these surfactants, especially their hydrophilic groups. However, the distinction by IR spectrometry is very difficult because of their analogous IR spectra which consist of ester bands at 1740 cm^{-1}, ether bands at 1120 cm^{-1}, and hydroxyl bands at 3470 cm^{-1}. The combined use of saponification values and hydroxyl values allows some identification of the surfactants. However, it is sometimes dangerous to draw final conclusions from these data.

The identification of the polyol base compounds of polyurethane polyethers based upon propylene glycol, glycerol, trimethylol propane, sorbitol, etc., was carried out by GLC after conversion into their corresponding acetates by using the mixed anhydride of acetic and p-toluenesulfonic acids as a reagent for cleavage of ether linkages (4,5). Moreover, the hydrophobic groups of the POE alkyl ethers, POE alkyl phenyl ethers, POE alkyl amines, etc., have been analyzed (6) in the similar manner. In the present study, this method is extended to identify the hydrophobic groups of the ester-type surfactants containing POE groups and differentiates the POE fatty acid ester-type surface-active agents.

EXPERIMENTAL PROCEDURES

Reagent

p-Toluenesulfonic acid (120 g) was placed in a 300 ml 4-necked round-bottomed flask at room temperature, and 80 g acetic anhydride was added dropwise and with stirring. The mixture then was heated under reflux on an oil-bath maintained at 120 C for 30 min and cooled to room temperature. The product was used as the reagent without removal of acetic acid produced, an excess of acetic anhydride and remaining p-toluenesulfonic acid. The reagent should be stored in a brown bottle and will keep ca. 1 month.

Samples

POE alkyl ether sulfates and POE alkyl ether phosphates based upon natural and synthetic alcohols were employed for the determination of the alkyl compositions of hydrophobic groups. POE fatty acid ester, POE glycerol fatty acid ester, and POE sorbitan fatty acid ester were employed for the analysis of the hydrophobic groups and the distinction of the base compounds of the hydrophilic groups.

These samples are manufactured by our company and

TABLE I

Alkyl Compositions of Polyoxyethylene (POE) Alkyl Ether Sulfates (%)

Starting materials and POE alkyl ether sulfates	C_{10}	C_{12}					C_{13}					C_{14}
	n	n	2-C_1	2-C_2	2-C_3	2-$C_{4,5}$	n	2-C_1	2-C_2	2-C_3	2-$C_{4,5}$	n
Dodecyl alcohol	0.3	97.1	---	---	---	---	---	---	---	---	---	2.6
POE dodecyl ether sulfate	0.3	97.2	---	---	---	---	---	---	---	---	---	2.5
Oxo-alcohol A	---	36.0	9.7	3.2	2.0	2.1	27.4	10.1	2.6	1.8	5.1	---
POE alkyl ether sulfate (A)	---	36.1	9.5	2.9	2.3	2.4	25.0	9.5	3.7	3.3	5.5	---
Oxo-alcohol B	---	29.9	2.9	1.1	1.2	1.4	47.4	5.5	2.4	2.5	5.7	---
POE alkyl ether sulfate (B)	---	30.4	2.5	1.1	1.3	1.6	47.1	5.5	2.5	2.7	5.4	---

used without further purification.

Apparatus

The separation of acetates and fatty acids produced was carried out on a Hitachi gas chromatograph, model 063, equipped with a thermal conductivity detector. The column consisted of a 1 m length of 3 mm inside diameter stainless steel tubing packed with 15%. w/w Free fatty acid phase (FFAP) (or Apiezon grease L) coated on 60-80 mesh Uniport B (Gas Chromatographic Co., Tokyo). Helium gas was used as carrier gas. The sample was injected with a 10 μliter Jintan Terumo syringe, model MS-10. A shimadzu IR spectrometer, model IR-27, and a Hitachi mass spectrometer, model RMU-6D, were used for identifying the main components.

Procedure

Sample (100 mg) and 2 g reagent were placed in a 20 ml egg-apple type flask, and the mixture was heated under reflux on a oil-bath at 120 C for 2 hr. The reaction product then was cooled to room temperature and extracted 3 or 4 times with ca. 20 ml portions of diethyl ether. The extracts were combined and washed with deionized water several times until the washings were no longer acid to methyl orange. They are dried over anhydrous sodium sulfate and evaporated on a steam-bath. The concentrate then was injected into gas chromatograph. The chromatographic column was operated isothermally or with programed temperature. The conditions used were: injector temperature, 280 C; detector temperature, 260 C; detector current, 100 mA; and flow rate of carrier gas, 60 ml/min. The composition of the alkyl groups was determined by measuring the peak areas.

RESULTS

Analysis of POE Alkyl Ether Sulfates

First, the reaction product of the POE alkyl ether based upon dodecyl alcohol was analyzed. The Apiezon grease L column was operated at 145 C, and the flow rate of carrier gas was regulated at 60 ml/min. A typical gas chromatogram is shown in Figure 1. The alkyl acetate peaks appear correspondingly to the carbon number distribution of the alkyl group together with the peak of ethylene glycol diacetate produced by the cleavage of the POE group. The POE alkyl ethers based upon oxo-alcohol A and B also were investigated in the same procedure. The gas chromatograms obtained showed the existance of 2-alkyl, such as 2-methyl-, 2-ethyl-, 2-propyl-, and 2-butyl, branched isomers. The alkyl compositions of the hydrophobic groups agree closely with those of the initiating higher alcohols as given in Table I.

Analysis of POE Alkyl Ether Phosphates

The gas chromatograms of the reaction products of the POE alkyl ether phosphates based upon dodecanol, tetradecanol, hexadecanol, and octadecanol are shown in Figure 2. The column temperature was held at 185 C, and the flow rate of the carrier gas was regulated at 60 ml/min. In Figure 2A the peaks of decyl acetate, dodecyl acetate, and tetradecyl acetate appear with those of ethylene glycol diacetate and small amounts of by-products. The by-products were identified by combined GLC-mass spectrometry method, and they were proved to be chiefly dodecene-1 and its isomers. In Figures 2B, 2C, and 2D the peaks of acetates and some olefins also appear according to the alkyl distributions. The alkyl compositions of the hydrophobic groups calculated from the peak areas of alkyl acetates are summarized in Table II. The formation of olefins did not interfere with the determination. The reaction products of the POE alkyl ether phosphate based upon oxo-alcohol A

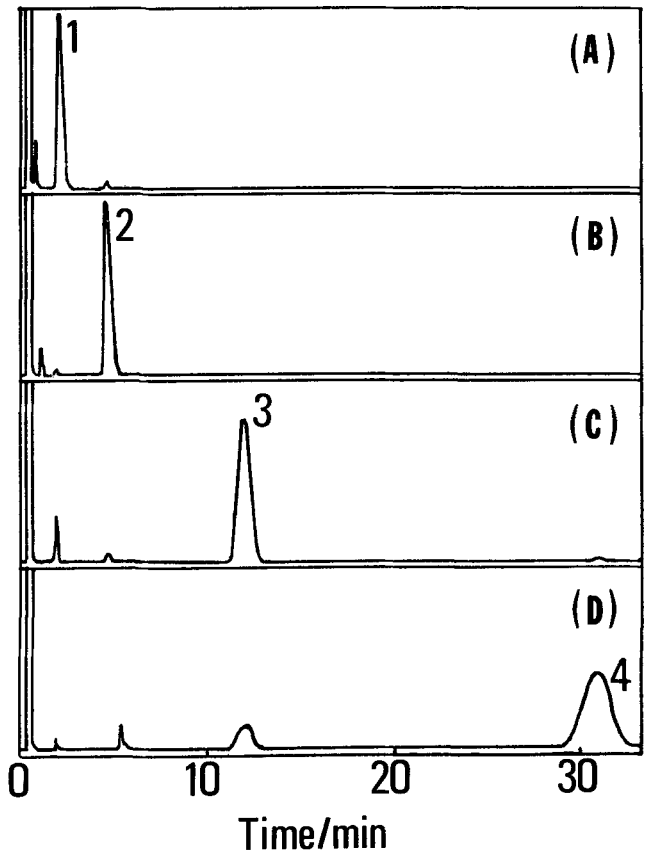

FIG. 2. Gas chromatogram of reaction products of polyoxyethylene (POE) alkyl ether phosphates: A POE dodecyl ether phosphate; B POE tetradecyl ether phosphate; C POE hexadecyl ether phosphate; and D POE octadecyl ether phosphate. 1. Dodecyl acetate. 2. Tetradecyl acetate. 3. Hexadecyl acetate. 4. Octadecyl acetate. Gas liquid chromatographic conditions: column, Apiezon grease L, 15% 1 m, 185 C; carrier gas, He, 60 ml/min.

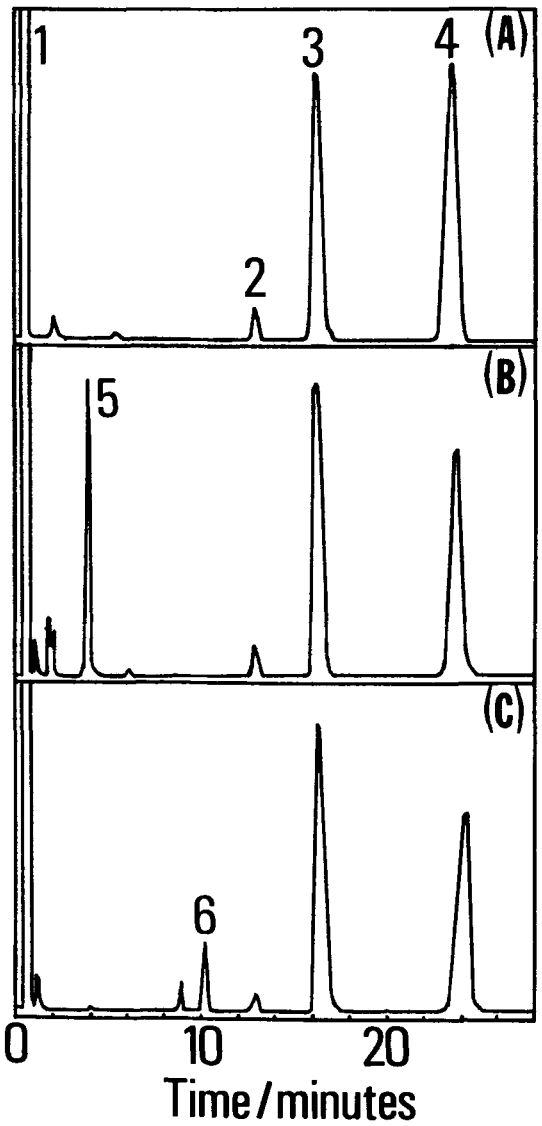

FIG. 3. Gas chromatograms of reaction products of polyoxyethylene (POE) fatty acid ester-type surfactants. A POE fatty acid ester; B POE glycerol fatty acid ester; and C POE sorbitan fatty acid ester. 1. Ethylene glycol diacetate. 2. Tetradecanoic acid. 3. Hexadecanoic acid. 4. Octadecanoic acid. 5. Glyerol triacetate. and 6. 1,4,3,6-Sorbide diacetate. Gas liquid chromatographic conditions: column 1 m x 3 mm, packed with 15% free fatty acid phase on Uniport B; oven 140 → 220 C (5 C/min); and chart speed, 1 cm/min.

resulted in the similar data.

Analysis of POE Fatty Acid Ester-Type Surfactants

The gas chromatograms of the reaction products of the POE fatty acid ester, POE glycerol fatty acid ester, and POE sorbitan fatty acid ester, respectively, are shown in Figure 3. The FFAP column was programed at 5 C/min, 140-220 C.

In Figure 3A, the peak of ethylene glycol diacetate produced by cleavage of the POE group appears, followed by the peaks of tetradecanoic acid, hexadecanoic acid, and octadecanoic acid corresponding to the alkyl distribution of the hydrophoibc groups. In Figure 3B, the peak of glycerol triacetate appears with the peaks of ethylene glycol diacetate and fatty acids. In Figure 3C, the peak of 1,4,3,6-sorbide (isosorbide) diacetate and its isomer appear.

The acetate peaks corresponding to each of the polyhydric alcohols appear at different positions, so that these surfactants now can be distinguished easiiy. The alkyl compositions of the hydrophobic groups, i.e. fatty acids, are given in Table III. The determination of the alkyl

TABLE II

Alkyl Compositions of Polyoxyethylene (POE) Alkyl Ether Phosphates (%)

Starting materials and POE alkyl ether phosphates	C_{10}	C_{12}	C_{14}	C_{16}	C_{18}
Dodecyl alcohol	0.5	97.2	2.3	---	---
POE dodecyl ether phosphate	0.6	97.6	1.8	---	---
Tetradecyl alcohol	---	0.8	99.2	---	---
POE tetradecyl ether phosphate	---	0.9	99.1	---	---
Hexadecyl alcohol	---	---	1.2	97.5	1.3
POE hexadecyl ether phosphate	---	---	1.3	97.7	1.0
Octadecyl alcohol	---	---	---		87.9
POE octadecyl ether phosphate	---	---	---		87.5

TABLE III

Alkyl Compositions of Polyoxyethylene (POE) Fatty Acid Ester-Type Surfactants (%)

Surfactants	C_{14}	C_{16}	C_{18}
POE fatty acid ester	3.5[a]	27.7[a]	68.8[a]
	3.5[b]	27.2[b]	69.3[b]
POE glycerol fatty acid ester	1.6[a]	42.7[a]	55.7[a]
	1.5[b]	42.8[b]	55.7[b]
POE sorbitan fatty acid ester	4.0[a]	49.1[a]	46.9[a]
	3.8[b]	49.4[b]	46.8[b]

[a]Obtained by methyl esterification method.
[b]Obtained by this method.

compositions was carried out by the conventional methyl esterification method using the FFAP column, and the results obtained also are included in the same table. The values obtained by the present method are in fair agreement with those obtained by the methyl esterification method.

DISCUSSION

An analytical method for the determination of the alkyl compositions of the ester-type surface-active agents containing the POE groups and the distinction of the POE fatty acid ester type surfactants has been established.

It has become apparent that the reagent used acts as the ester-cleavage agent as well. The main equations are assumed to be:

$$RO(CH_2CH_2O)_nSO_3H(Na) \rightarrow ROAc + nAcOCH_2CH_2OAc + H_2SO_4$$

$$RO(CH_2CH_2O)_nPO_3H(Na) \rightarrow ROAc + nAcOCH_2CH_2CH_2OAc + H_3PO_4$$

$$RCOO(CH_2CH_2O)_nH \rightarrow RCOOH + nAcOCH_2CH_2OAc$$

$$\begin{array}{l} CH_2OOCR \\ | \\ CHO(CH_2CH_2O)_mH \\ | \\ CH_2O(CH_2CH_2O)_nH \end{array} \rightarrow RCOOH + (m+n)AcOCH_2CH_2OAc + \begin{array}{l} CH_2OAc \\ | \\ CHOAc \\ | \\ CH_2OAc \end{array}$$

where Ac = acetyl group. When the POE sorbitan fatty acid ester is allowed to react with the reagent, acetates of 1,4,3,6-sorbide and its isomer chiefly are formed. They are presumed to be produced by the action of p-toluenesulfonic acid present in the reagent. Olefins are liable to be produced when oxo-alcohol derivatives or phosphates are treated with this reagent. Therefore, it is important to adjust the reagent composition, reaction temperature, and time. The mole ratio of acetic anhydride/p-toluenesulfonic acid must be at ca. 1.25. It is necessary to hold the temperature at 120 ± 5 C and the time for 2 ± 0.5 hr.

In case of identifying the hydrophilic groups of POE fatty acid ester-type surfactants, good results also can be obtained easily by using the samples previously hydrolyzed with acid catalyst. Fatty acid produced is extracted with diethyl ether, and the residue, polyether polyol, is allowed

to react with the mixed anhydride reagent. The product, acetate, is analyzed by GLC.

The present method can be extended to analyze alkyl sulfates, alkyl phosphates, glycerides, and fatty acid esters of sorbitans.

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