Gas Chromatographic Analysis of Nonionic Surfactants by Acid Cleavage of Ether Linkages

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ABSTRACT

The gas chromatographic analysis of various kinds of nonionic surfactants has been carried out after chemical decomposition using the mixed anhydride of acetic and p-toluene sulfonic acids which acts as a reagent for cleavage of ether linkages. The gas chromatographic peaks of the reaction products show the alkyl distributions of the hydrophobic groups of ethylene oxide adducts. The alkyl compositions closely agree with those of the starting materials. In this way, the hydrophobic groups of polyoxyethylene alkyl ether, polyoxyethylene alkyl phenol ether, polyoxyethylene alkyl amine, and polyoxyethylene alkyl thioether have been analyzed. At the same time, the hydrophilic group, namely polyoxyethylene group, can be identified in the form of ethylene glycol diacetate.

INTRODUCTION

Ethylene oxide (EO) adducts based upon fatty alcohols, alkylphenols, fatty amines, thiols, etc., generally are called surface active E.O. adducts and occupy the main parts of nonionic surfactants. They are used widely as wetting agents, emulsifiers, solubilizers, dispersants, antistatic agents, etc.

Many analytical methods have been used for the separation, identification, and determination of these surfactants. IR (1-3) and NMR (4-7) techniques often are used to determine the class of the surfact active agents. The advantage of these methods is that the analysis is carried out without prior chemical conversion. However, it is difficult to differentiate among the hydrophobic groups, because they give very similar spectra. Chromatographic techniques, such as paper (8,9), thin layer (10,11), and column chromatography (12) have been used to separate and identify these surfactants. None of these procedures, however, is effective for the analysis of the hydrophobic groups because of the interference from the polyoxyethylene (POE) groups. Pyrolysis gas chromatography (13,14) (GLC) can be used for analysis of such samples, but this method has some problem on reproducibility. Gas chromatographic analysis has been studied in combination with cleavage of ether linkages using some reagents. This technique is useful for the analysis of the hydrophobic groups, as well as the POE groups. As the cleavage reagents of ether linkages, hydriodic acid (15), hydrobromic acid (7,16), hydrochloric acid (17), phosphoric acid (18,20), lithium alminum hydride (21), etc., have been investigated. In using these reagents, the procedures are often troublesome, and the formation of by-products sometimes interferes with the quantitative analyses.

The polyol base compounds of polyurethane polyethers can be identified easily (22,23) by the gas chromatographic technique after conversion into acetylation products by the reaction with the mixed anhydride of acetic and p-toluene sulfonic acids (24,25). The procedure is simple, and the by-products are comparatively small. In this paper, this method was extended to analyze the hydrophobic and hydrophilic groups of the surface active EO adducts.

EXPERIMENTAL PROCEDURES

Reagent for Cleavage of Ether Linkages

Ca. 120 g p-toluene sulfonic acid was placed in a 300 ml four-necked round-bottomed flask, and 80 g acetic anhydride was added dropwise at room temperature. The mixture was refluxed at 120 C for 30 min. The product was used as reagent for cleavage of ether linkages without further purification.

Samples

POE alkyl ethers based upon natural alcohols and synthetic alcohols which contain oxo and ziegler alcohols, POE alkyl phenol ethers, POE alkyl amines, POE alkyl thioether, and EO-propylene oxide (PO) copolymer were used for the analysis. These samples are manufactured by our company or commercially available. The hydrophobic groups have some alkyl distributions, but they are known previously on the starting materials.

Apparatus

A Hitachi gas chromatograph, model 063, equipped with a thermal conductivity detector and a temperature programer was used for the separation and the identification of reaction products. The chromatographic column mainly

TABLE I

Alkyl Compositions of Polyoxyethylene Alkyl Ethers Based Upon Natural Alcohols (Percent)[a]

Starting materials and EO adducts	C_{10}	C_{12}	C_{14}	C_{16}	C_{18}	C_{16F1}	C_{18F2}
Dodecyl alcohol	0.5	97.0	2.5	---	---	---	---
POE dodecyl ether	0.5	96.8	2.7	---	---	---	---
Tetradecyl alcohol	---	0.4	99.2	0.4	---	---	---
POE tetradecyl ether	---	0.5	99.0	0.5	---	---	---
Hexadecyl alcohol	---	3.2	5.0	71.9	---	---	---
POE hexadecyl ether	---	2.1	5.3	71.8	19.9	---	---
Octadecyl alcohol	---	---	---	12.1	87.9	---	---
POE octadecyl ether	---	---	---	12.5	87.5	---	---
Oleyl alcohol	---	1.1	7.9	27.9	1.7	17.3	44.1
POE oleyl ether	---	1.2	8.2	29.5	3.8	15.2	42.1

[a] EO = ethylene oxide; POE = polyoxyethylene.

TABLE II

Alkyl Compositions of Polyoxyehtylene Alkyl Ethers Based Upon Synthetic Alcohols (Percent)[a]

	C_{11}					C_{12}					C_{13}					C_{14}	C_{16}
Starting materials and EO adducts	n	2-C_1	2-C_2	2-C_3	2-C_4	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	n
Oxo alcohol A	46.4	34.0	9.4	6.3	4.0	---	---	---	---	---	---	---	---	---	---	---	---
A, EO adduct	46.9	33.9	8.9	5.9	4.4	---	---	---	---	---	---	---	---	---	---	---	---
Oxo alcohol B	---	---	---	---	---	36.0	9.7	3.2	2.0	2.1	27.4	10.1	2.6	1.8	5.1	---	---
B, EO adduct	---	---	---	---	---	37.1	9.0	2.9	2.1	2.1	26.8	8.9	3.4	2.7	4.8	---	---
Oxo alcohol C	---	---	---	---	---	29.9	2.9	1.1	1.2	1.4	47.4	5.5	2.4	2.5	5.7	---	---
D, EO adduct	---	---	---	---	---	30.6	2.9	1.1	1.3	1.6	47.3	5.4	2.3	2.3	5.2	---	---
Ziegler alcohol A	---	---	---	---	---	56.1	---	---	---	---	---	---	---	---	---	43.9	---
A, EO adduct	---	---	---	---	---	56.3	---	---	---	---	---	---	---	---	---	43.7	---
Ziegler alcohol B	---	---	---	---	---	69.8	---	---	---	---	---	---	---	---	---	24.3	5.9
B, EO adduct	---	---	---	---	---	70.6	---	---	---	---	---	---	---	---	---	24.0	5.4

[a] EO = ethylene oxide.

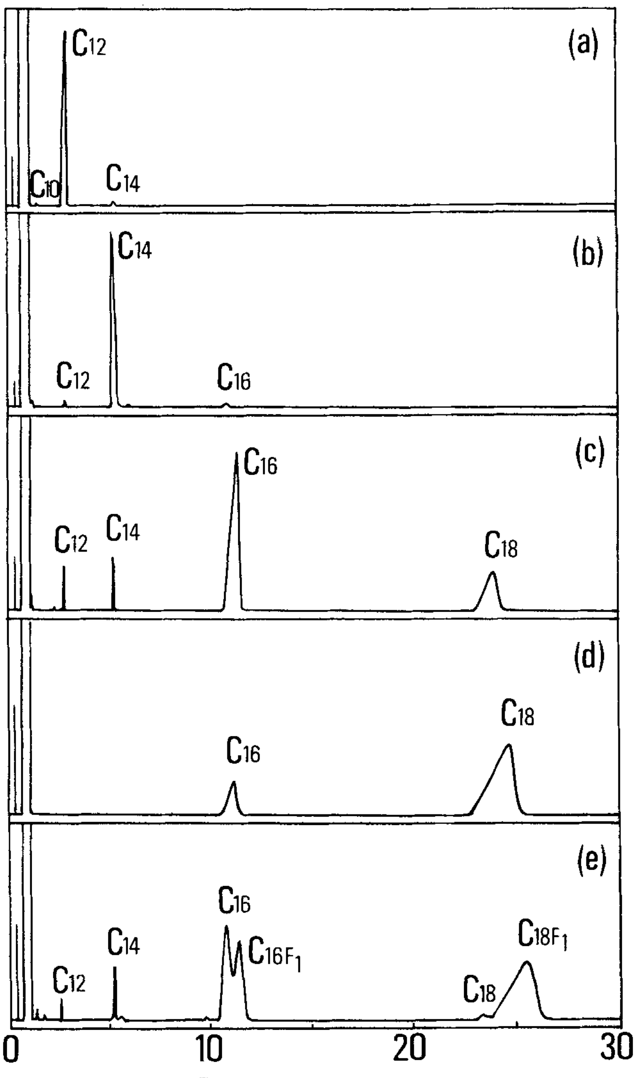


FIG. 1. Gas chromatograms of reaction products of polyoxyethylene (POE) alkyl ethers based upon natural alcohols; (A) (POE) dodecyl ether, (B) POE tetradecyl ether, (C) POE hexadecyl ether, (D) POE octadecyl ether, and (E) POE oleyl ether. Gas chromatogram conditions: column 1-m x 3-mm, packed with 15% w/w. Free fatty acid phase coated on 60-80 mesh Uniport B; oven, 165 C; and chart speed, 1 cm minute^{-1}.

employed consisted of a 1 m length of 3 mm inside diameter stainless-steel tubing packed with 15% w/w free fatty acid phase (FFAP) (carbowax 20 M terminated with 2-nitroterephthalic acid) coated on 60-80 mesh Uniport B (Gas Chro Co., Ltd., Japan). An aerograph preparative gas chromatograph, model A-700, was used for collecting the eluted component.

A Shimadzu IR spectrometer, model IR-27, Japan Electron Optics NMR spectrometer, model JNM-3H-60, and Hitachi mass spectrometer, model RMU-6D, were used for the identification of the main components.

Procedures

Ca. 100 mg sample were placed in 20 ml egg-apple type flask, and 2 g cleavage reagent was added. The mixture was heated under reflux at 120 C for 2 hr. The reaction product then was cooled to room temperature and neutralized with 50% aqueous solution of sodium carbonate followed by extraction with ca. 20 ml diethyl ether. The ether layer was washed several times with deionized water to remove the excess of reagent and then concentrated on a steam bath. The concentrate was injected into the gas chromatograph. The column was operated isomthermally 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 (helium), 60 ml/min. The compositions of the alkyl groups were determined by measuring the peak areas.

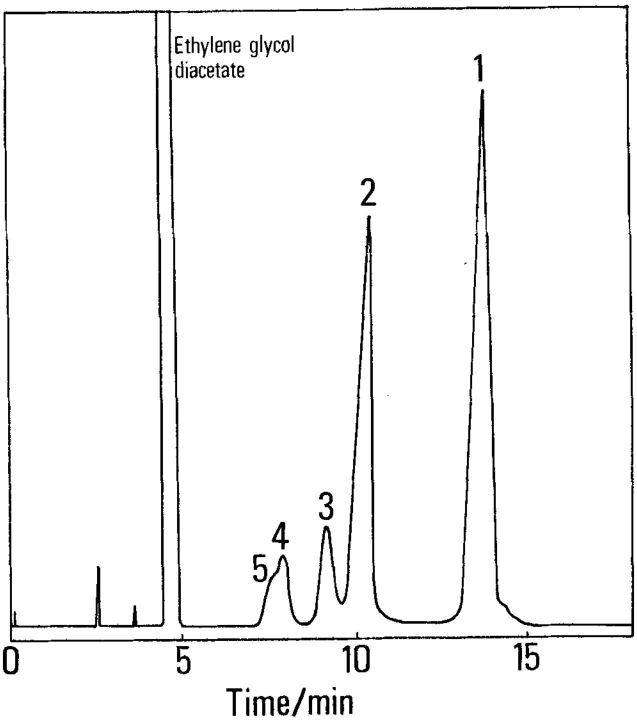


FIG. 2. Gas chromatogram of reaction products of polyoxyethylene (POE) alkyl ether based upon oxo alcohol A; 1, n-undecyl acetate; 2, 2-methyldecyl acetate; 3, 2-ethylnonyl acetate; 4, 2-propyloctyl acetate; and 5, 2-butylheptyl acetate. Gas chromatogram conditions: column, 1-m x 3-mm, pakced with 15% w/w. Free fatty acid phase coated on 60-80 mesh Uniport B; oven, 100 C → 140 C (2 C minute^{-1}); and chart speed, 1 cm minute^{-1}.

The main components also were separated and collected by using a preparative gas chromatograph and identified by IR, NMR, mass spectrometry (MS), and elementary analysis.

RESULTS

POE Alkyl Ethers

The gas chromatograms of the reaction products of the POE dodecyl ether, POE tetradecyl ether, POE hexadecyl ether, POE octadecyl ether, and POE oleyl ether at 165 C are shown in Figure 1. The alkyl acetate peaks appear correspondingly to the carbon number distribution of the alkyl groups together with the peaks of ethylene glycol (EG) diacetates which are produced by the cleavage of POE groups. The alkyl compositions of hydrophobic groups are compared with those of starting materials, and it has become apparent that the agreement between them is satisfactory as shown in Table I.

The POE alkyl ethers based upon oxo alcohol A, B, and C also were investigated in the same way. The typical chromatogram of the reaction products of the POE alkyl ether based upon oxo alcohol A is shown in Figure 2. The reaction products of POE alkyl ethers based on ziegler alcohol A and B were similarly analyzed. The alkyl compositions obtained closely agree with those of the initiating higher alcohols, as given in Table II. In conclusion the alkyl compositions of the hydrophobic groups of the POE alkyl ethers are determined satisfactorily.

POE Alkyl Phenol Ethers

The gas chromatograms of reaction products of EO adducts of p-octyl phenol (from diisobutene) and nonyl phenol (from tripropene) at 165 C are shown in Figure 3.

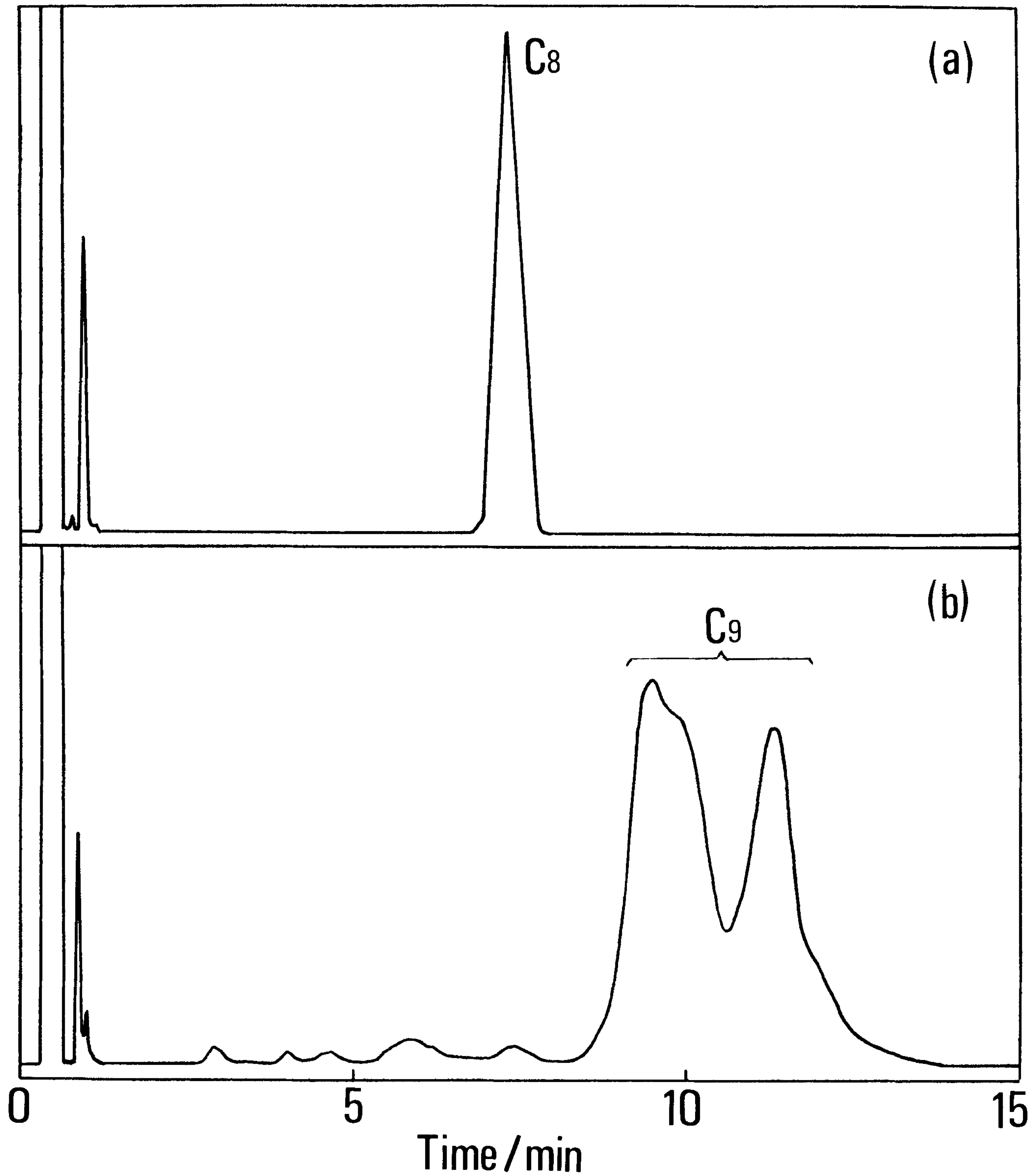


FIG. 3. Gas chromatogram of reaction products of polyoxyethylene POE alkyl phenol ether; (A) POE octyl phenol ether and (B) POE nonylphenol ether. Gas chromatogram conditions: column, 1-m x 3-mm, packed with 15% w/w. Free fatty acid phase on Uniport B; oven, 200 C; and chart speed, 1 cm minute^{-1}.

Besides EG diacetate, the peaks of alkyl phenols appear at different positions. The complicated peak of nonyl phenol results from the existance of the alkyl group isomers formed when it is synthesized. Consequently, the POE octyl phenol ether and the POE nonyl phenol ether can be distinguished easily.

POE Alkyl Amines

The reaction products of the POE dodecyl amine, POE octadecyl amine, and POE oleyl amine were analyzed at 235 C. The gas chromatographic peaks due to the alkyl bis-(2-hydroxy ethyl) amine diacetates appear according to the carbon number distribution. The alkyl compositions of the reaction products and the starting materials are shown in Table III.

In case of POE alkyl amines, the hydrophobic groups can also be identified and their alkyl compositions determined.

POE Alkyl Thioether

The gas chromatogram of the reaction products of the

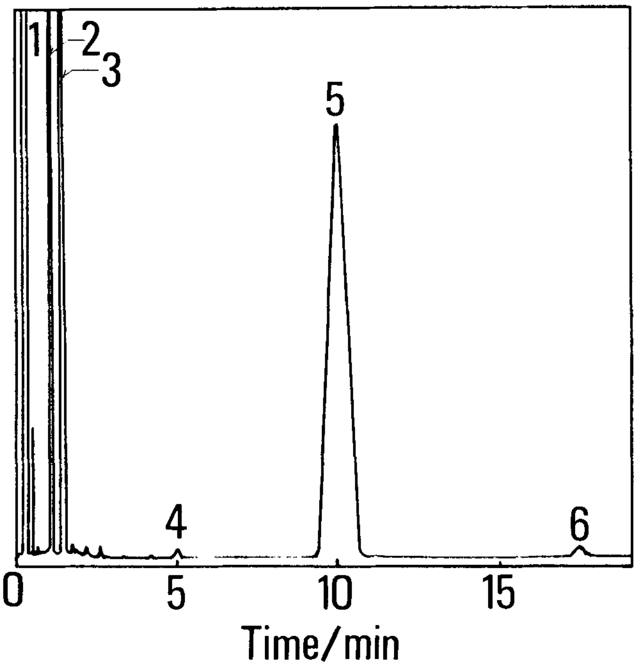


FIG. 4. Gas chromatogram of reaction products of polyoxyethylene (POE) dodecyl thioether; 1, ethylene glycol diacetate; 2, dodecyl methyl ketone; 3, 1,4-thioxane; 4, 2-(decylthio)ethyl acetate; 5, 2-(dodecylthio)ethyl acetate; and 6, 2-(tetradecyl)ethyl acetate. Gas chromatogram conditions: column, 1-m x 3-mm, packed with 15% w/w. Free fatty acid phase on Uniport B; oven, 185 C; and chart speed, 1 cm minute^{-1}.

POE dodecyl thioether is shown in Figure 4. Several peaks of the by-products appear after EG diacetate peak, and the peaks of 2-(alkyl thio) ethyl acetates appeared according to the alkyl group distribution. The by-products have been analyzed by the combined GLC-MS method, and it has been ascertained that dodecyl methyl ketone and 1,4-thioxane were produced. In spite of the formation of these by-products, the alkyl composition agrees with that of the starting material.

EO-PO Copolymer

Figure 5 shows the typical gas chromatogram of reaction product of EO-PO copolymer. The column temperature was held at 65 C. Two peaks of EG diacetate and propylene glycol (PG) diacetate produced from POE and polyoxypropylene (POP) groups, respectively, are separated completely. The bp of the EG diacetate and PG diacetate are ca. equal (190-191 C) at the pressure of 1 atm. But PG diacetate is more polar, so it elutes before EG diacetate.

The proportion of oxyethylene and oxypropylene of the copolymer could be determined readily from the relative areas of these peaks. Results for EO contents by this method and by NMR spectrometry are shown in Table IV. All values are averages of three determinations.

DISCUSSION

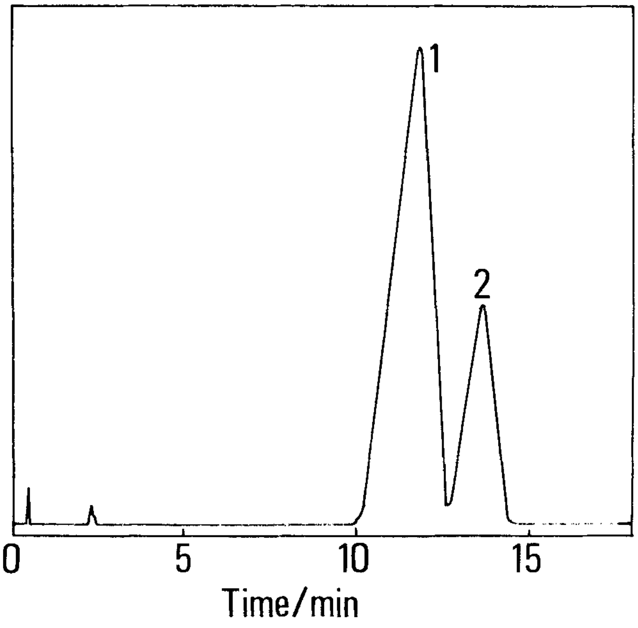


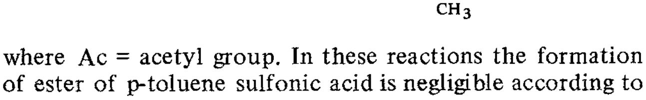
FIG. 5. Gas chromatogram of reaction products of ethylene oxide/propylene oxide copolymer; 1, propylene glycol diacetate; and 2, ethylene glycol diacetate. Gas chromatogram conditions: column, 1-m x 3-mm, packed with 15% w/w. Free fatty acid phase on Uniport B; oven, 65 C; and chart speed, 1 cm minute^{-1}.

The analysis of a series of nonionics by GLC was carried out after conversion into acetates using the mixed anhydride of acetic and p-toluene sulfonic acids as a reagent for cleavage of ether linkages.

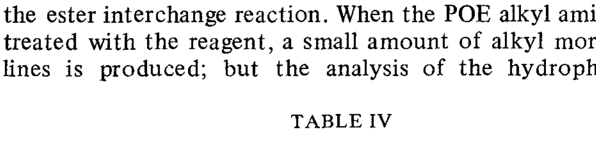
It is assumed that the main equations are:

$$RO(CH_2CH_2O)_nH \longrightarrow ROAc + nAcOCH_2CH_2OAc$$

$$RC_6H_4O(CH_2CH_2O)_nH \longrightarrow RC_6H_4OH + nAcOCH_2CH_2OAc$$


$$RN\begin{matrix}(CH_2CH_2O)_mH\\(CH_2CH_2O)_nH\end{matrix} \longrightarrow RN\begin{matrix}CH_2CH_2OAc\\CH_2CH_2OAc\end{matrix} + (m + n - 2)AcOCH_2CH_2OAc$$

$$RS(CH_2CH_2O)_nH \longrightarrow RSCH_2CH_2OAc + (n - 1)AcOCH_2CH_2OAc$$


$$HO(CH_2CH_2O)_l(\underset{CH_3}{CH_2CHO})_m(CH_2CH_2O)_nH \longrightarrow (l + n)\ AcOCH_2CH_2OAc + mAcOCH_2\underset{CH_3}{CHOAc}$$

where Ac = acetyl group. In these reactions the formation of ester of p-toluene sulfonic acid is negligible according to the IR spectra of products. It is presumed that this fact is due to conversion of sulfonates produced into acetates by the ester interchange reaction. When the POE alkyl amine is treated with the reagent, a small amount of alkyl morpholines is produced; but the analysis of the hydrophobic

TABLE III

Alkyl Compositions of Polyoxyethylene Alkyl Amines (Percent)[a]

Starting materials and EO adducts	C_{10}	C_{12}	C_{14}	C_{16}	C_{18}	C_{18F1}
Dodecyl amine	6.7	60.4	20.0	10.3	2.6	---
POE dodecyl amine	5.6	59.8	20.5	10.6	3.5	---
Octadecyl amine	---	---	4.2	37.0	58.8	---
POE octadecyl amine	---	---	4.2	37.4	58.4	---
Oleyl amine	---	---	2.6	24.2	2.9	70.3
POE oleyl amine	---	---	2.9	24.5	3.2	69.4

[a] EO = ethylene oxide; POE = polyoxyehtylene.

TABLE IV

Results for Ethylene Oxide Contents

Sample no.	Ethylene oxide / ethylene oxide + propylene oxide: Gas chromatogram result wt %[a]	NMR result wt %[a]
1	13.8	13.8
2	24.4	24.6
3	35.8	36.0
4	45.4	45.5
5	48.8	50.0

[a] Ethylene oxide/(ethylene oxide + propylene oxide.

groups are scarcely interfered. In the reaction of the POE, alkyl thioether alkyl thioacetate is expected to be produced. However, it was not detected by gas chromatography. This fact shows a clear difference in the reactivity of ether and thioether bonds.

As to POE dodecyl ether, ca. 50 mole adduct can be analyzed. In case of analysis of polyurethane polyethers, polyol base compounds, e.g. pentaerythritols, have been identified easily for even 120 mol PO adducts.

This analytical method, which is investigated by a combination of cleavage reaction and GLC, is practical to use because of its simplicity.

Besides the mixed anhydride of acetic and p-toluene sulfonic acids, some other mixed acetic-sulfonic anhydrides, such as acetyl benzene sulfonate, acetyl p-chlor benzene sulfonate, acetyl p-phenol sulfonate, and acetyl methane sulfonate have been studied. However, it has been proven that there is not a great difference among these reactivities.

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