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ANALYSIS OF FATTY ACID ETHOXYLATES BY PREPARATIVE HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

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SUMMARY

A method for the determination of poly(ethylene glycols) and poly(oxyethylene) mono- and dialkyl esters in fatty acid ethoxylates by preparative reversed-phase high-performance liquid chromatography is described. The complete separation of these non-ionic compounds has been obtained on a 500 × 20 mm I.D. column packed with C_{18} bonded phase with acetone–water as the mobile phase. The separated compounds were subsequently determined by gravimetry.

INTRODUCTION

Fatty acid ethoxylates are used as emulisifiers for pharmaceuticals, colorants and non-ionic detergents. They are synthesized by two different methods: addition of ethylene oxide (EO) to the fatty acid or esterification between the fatty acid and poly(ethylene glycols). These fatty acid ethoxylates are mixtures of poly(ethylene glycols) and poly(oxyethylene) mono- and dialkyl esters. The contents of these non-ionic compounds vary depending on the molar ratio in the reaction[1], and they have a marked effect on the performance characteristics of the product mixture.

Thin-layer chromatography (TLC)[2], paper chromatography (PC)[3] and column liquid chromatography[4,5] have been used for the analysis of these non-ionic compounds. Although TLC and PC are simple and easy to perform, they cannot be used for quantitation. Column liquid chromatography is slow and tedious. Gas chromatography can also be used for the determination of polyglycols in fatty acid ethoxylates via their acetate esters[6], but non-volatile poly(oxyethylene) mono- and dialkyl esters cannot be determined.

Others methods are indirect, *e.g.*, based on acid values, saponification values and solvent extraction. The primary problems often encountered with these methods are lack of specifity, difficulty of quantitation and limited application.

More recently, high-performance liquid chromatographic (HPLC) methods have been reported for the analysis of polyglycerol esters of fatty acids[7] and fatty acid esters of mono- and polyhydric alcohols[8,9]. These HPLC methods are the most suitable for the analysis of these non-volatile fatty acid esters.

This paper describes a method for the determination of poly(ethylene glycols)

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and poly(oxyethylene) mono- and dialkyl esters in fatty acid ethoxylates by preparative HPLC. The separation of these non-ionic compounds was obtained on a 500 × 20 mm I.D. column packed with C_{18} bonded phase and subsequently determined by gravimetry. The long analysis time usual in preparative HPLC was reduced by using a back-flush elution method.

The proposed method provides a simple determination of these non-ionic compounds in fatty acid ethoxylates and was extended to various alkyl groups and degrees of ethoxylation.

EXPERIMENTAL

Chemicals

Fatty acid ethoxylates were purchased from Nihon Yushi (Tokyo, Japan) or synthesized in our laboratories, and were used without further purification.

Acetone, used for preparing the mobile phase, was of analytical-reagent grade. Water was first de-ionized with an ion-exchange resin and further purified through a column packed with ODS resin (LiChroprep RP-18; Merck, Darmstadt, F.R.G).

Preparative HPLC apparatus and operating conditions

The preparative HPLC apparatus was as described previously[10]. Acetone–water (70:30) was used as the mobile phase at a flow-rate of 10 ml/min. Sample solutions were prepared at concentrations of *ca.* 10–20% using the mobile phase and the injection volume was 7.87 ml.

To determine the amounts of poly(ethylene glycols) and mono- and dialkyl esters, the eluates containing these compounds were collected manually with the aid of a refractive index detector (Waters R-403). After collection of the eluate, the solvent was evaporated to dryness and the amounts of the non-ionic compounds were measured gravimetrically.

Field desorption mass spectrometry apparatus and operating conditions

Field desorption (FD) mass spectra were measured on a Hitachi M-80 double focusing mass spectrometer with a combined field desorption–field ionization–chemical ionization–electron impact ion source (Hitachi Scientific Instruments, Tokyo, Japan). The emitter was tungsten wire with carbon needles (20–40 μm) and the emitter current was programmed from 0 to 45 mA at 3 mA/min. The potential between the electrodes was 6 kV and the sample was loaded by the microsyringe technique[11]. FD mass spectra were obtained by the integration of repetitive scans over the range 100–1500 m/z at intervals of 8 sec.

RESULTS AND DISCUSSION

The advantages of the gravimetric determination of these fatty acid ethoxylates and their prior separation by preparative HPLC are lack of necessity for any standards for the determination, and the ease of operation for the separation and determination of poly(ethylene glycols) and mono- and dialkyl esters using the back-flush elution method. In practice, the former advantage is important for the determination of product mixtures.

A typical chromatogram showing the separation of poly(ethylene glycols) and poly(oxyethylene) mono- and dilauryl esters in lauric acid ethoxylate (average 10 EO units) is shown in Fig. 1. Poly(ethylene glycols) eluted first and poly(oxyethylene) mono- and dilauryl esters next. After elution of the monolauryl ester, the back-flush elution method was used to reduce the long analysis time.

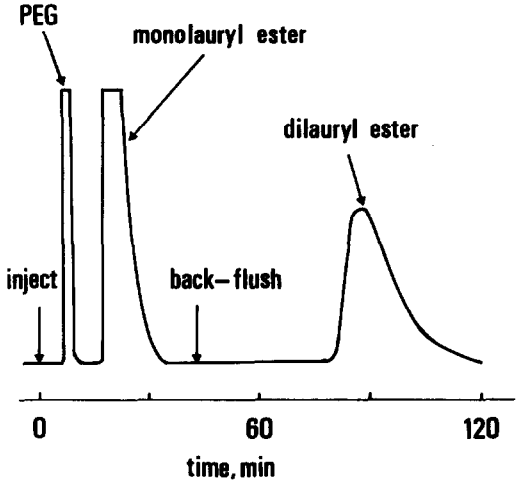

Fig. 1. Typical chromatogram of lauric acid ethoxylate (average 10 EO units).

The retention time of poly(ethylene glycols) is almost independent of their molecular weight because of their hydrophilic properties. However, the retention times of the mono- and dialkyl esters were influenced by the degree of ethoxylation and the alkyl chain length. Therefore, the mobile phase composition should be changed for the determination and /or long alkyl groups.

The complete elution of the dialkyl esters required long analysis times under the chromatographic conditions used for the separation of poly(ethylene glycols) and monoalkyl esters. The back-flush elution method was therefore employed to reduce the analysis time and to effect the accurate determination of dialkyl esters by preventing peak broading.

The identification of poly(ethylene glycols) and mono- and dialkyl esters in lauric acid ethoxylate (average 10 EO units) was carried out by FD mass spectrometry using collected fractions. Fig. 2 shows an FD mass spectrum of fractionated

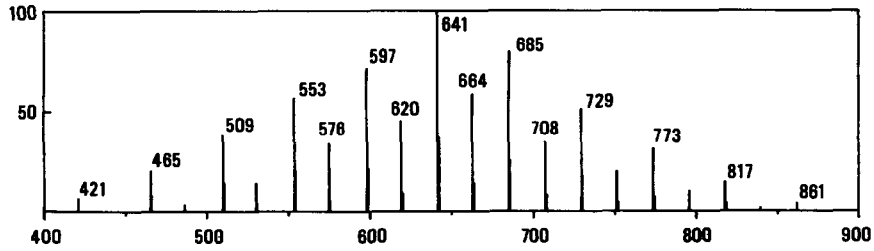

Fig. 2. FD mass spectrum of fractionated poly(oxyethylene) monolauryl ester.

poly(oxyethylene) monolauryl ester. Each peaks is due to a protonated molecular ion and a sodium cluster with a different degree of ethoxylation. The difference between two peaks corresponds to the difference in the molecular weight of EO, 44 *m/z*. The peak at *m/z* 641 is equivalent to the protonated molecular ion $(M+1)^+$ of poly(oxyethylene) monolauryl ester with a degree of ethoxylation of 10. The peak at *m/z* 664 is equivalent to the sodium cluster ion $(M+Na)^+$ of poly(oxyethylene) monolauryl ester with a degree of ethoxylation of 10. Therre were no peaks corresponding to poly(etylene glycols) or the dilauryl ester.

Fig. 3 shows the FD mass spectrum of collected poly(oxyethylene) dilauryl ester. The peak at *m/z* 845 corresponds to the sodium cluster ion of poly(oxyethylene) dilauryl ester with a degree of ethoxylation of 10. The peak at *m/z* 823 represents the protonated molecular ion of poly(oxyethylene) dilauryl ester with a degree of ethoxylation of 10. There was no peak corresponding to the monolauryl ester.

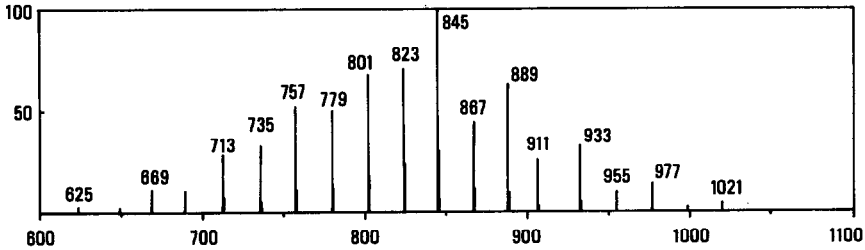

Fig. 3. FD mass spectrum of fractionated poly(oxyethylene) dilauryl ester.

The reproducibility of the gravimetric determination of poly(ethylene glycols) and mono- and dialkyl esters in fatty acid ethoxylates was determined. Two samples were chosen from lauric and oleic acid ethoxylates, the degree of ethoxylation of the samples being 5 and 10, respectively. The determination was repeated five times and the relative standard deviation for each non-ionic compound was less than 1.0%. The results were satisfactory.

The recovery of poly(ethylene glycols) and mono- and dialkyl esters was examined in order to confirm that they were completely recovered from the separation

TABLE I

ANALYSIS OF FATTY ACID ETHOXYLATES

Sample	*Poly(ethylene glycols) content (%)*	*Monoester content (%)*	*Diester content (%)*
Lauric acid, 5 EO units	15	49	36
Lauric acid, 10 EO units	19	50	31
Oleic acid, 10 EO units	17	50	33
Lauric acid–PEG 400*	23	49	28
Oleic acid–PEG 400	20	45	35
Oleic acid–PEG 600**	20	46	34
Stearic acid–PEG 200***	15	49	36

* Poly(ethylene glycol), MW = 400.
** Poly(ethylene glycol), MW = 600.
*** Poly(ethylene glycol), MW = 200.

column. The content of poly(ethylene glycols) in fatty acid ethoxylates was determined before and after the addition of known amount of commercially available poly(ethylene glycols). As there were no standards available for poly(oxyethylene) mono- and dialkyl eesters, their recoveries were calculated from the difference between the amounts of fatty acid ethoxylates injected and recovered. The runs were repeated five times and the result in every test was a recovery of over 97%; also, there was no adsorption of these non-ionic compounds in the separation column.

Table I shows the results for the determination of poly(ethylene glycols) and mono- and dialkyl esters in various kinds of fatty acid ethoxylates having various degrees of ethoxylation and various alkyl groups.

There were no apparent differences in the contents of poly(ethylene glycols) and mono- and dialkyl esters obtained by methods of synthesis. Also, the alkyl groups and the degree of ethoxylation had no effect.

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