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DETERMINATION OF ALKYL ETHOXYLATE MIXTURES BY PROGRAMMED MULTIPLE DEVELOPMENT THIN-LAYER CHROMATOGRAPHY

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SUMMARY

A rapid method using programmed multiple development thin-layer chromatography has been developed for determining the ethylene oxide distribution in mixtures of ethoxylated fatty alcohols. This method uses only a single lane to separate the acetate esters of compounds containing from 0 to 12 ethoxy groups. The R_F values of the separated materials depend on the number of ethoxylate groups and are independent of alkyl chain length. Quantitation is achieved by spectrodensitometry. Analysis time is 19 min per sample. The weight of each ethoxylate in the mixture can be determined with 7% accuracy.

INTRODUCTION

In recent years alkyl ethoxylates [$CH_3(CH_2)_{9-21}(OCH_2CH_2)_{0-12}OH$] have found application as surfactants in a number of home laundry products. These materials are prepared by the condensation of fatty alcohols with ethylene oxide. Because the cleaning properties of these materials depend on the distribution of ethoxy groups in the surfactant mixture, a need exists for a rapid and easily interpreted method of monitoring and optimizing this reaction[1].

Both gas chromatography (GC) and circular thin-layer chromatography (TLC) have been used to determine the ethylene oxide (EO) distribution in alkyl ethoxylates[2,3]. While GC provides the distribution of both alkyl chain lengths and ethoxylate groups, the chromatograms are complex, often containing 36 peaks. Ninety minutes are required for elution of all the components and data reduction is formidable. Circular TLC provides separation of the 3,5-dinitrobenzoate esters by EO number alone. However, because each spot must be scraped from the plate and derivatized prior to spectrophotometric analysis, this method is also time consuming.

A more rapid method has been developed for determining the EO distribution in fatty alcohol–ethylene oxide condensates. Programmed multiple development (PMD) TLC enables resolution of the acetate esters of compounds containing from 0–12 ethoxy groups. A series of programmed solvent advances, each longer than the preceding one and each followed by controlled solvent removal, results in a narrowing

of spots perpendicular to the direction of development. This periodic reconcentration of sample components gives greater resolution than can be obtained with a single elution and enhanced sensitivity in the subsequent spectrodensitometric determination[4,5].

EXPERIMENTAL

Apparatus

Plate development is carried out with a Regis Model 2000 programmer and Model 222 developer. The absorbance of the charred components is quantitated with a Schoeffel Instruments Model SD3000 spectrodensitometer. Plates were scanned in the dual-beam mode at 546 nm with a slit width of 0.5 mm. For adequate resolution the length of the incident beam (in the direction of the scan) is maintained at 0.1 mm. Scanning speed is 4 in./min.

Reagents

All solvents were spectrochemical grade (Burdick & Jackson Labs., Muskegon, Mich., U.S.A.). Chloroform and acetone used in plate development were distilled immediately prior to use. Chloroform was purchased with no preservative. 20 cm × 20 cm silica gel plates [Analtech (Newark, Del., U.S.A.) silica gel G, 250 μm] were prewashed in chloroform–methanol (50:50) before prescoring into twenty 1-cm lanes parallel to the direction of development.

Alkyl ethoxylate standards ($C_{12}EO_2$, $C_{12}EO_4$, $C_{12}EO_5$, $C_{12}EO_9$, and $C_{12}EO_{12}$) and reference compounds ($C_{10}EO_2$, $C_{14}EO_2$, $C_{16}EO_2$, $C_{10}EO_4$, $C_{16}EO_4$) were prepared by condensing an alkyl bromide with the sodium salt of the particular polyoxyethylene glycol, an adaptation of the Williamson synthesis[6]. The higher polyoxyethylene glycols which are not commercially available were prepared by the method of Fordyce *et al.*[7], in which the dichloride of a polyoxyethylene glycol is reacted with the sodium salt of another polyoxyethylene glycol. Purity of the standard compounds was better than 95% by GC and TLC. Dodecyl alcohol (Procter & Gamble, Cincinnati, Ohio, U.S.A.) was also used as a standard. Its purity was better than 97% by GC and TLC.

Procedure

Samples are esterified after having been warmed to 65° for 10 min and shaken vigorously to ensure homogeneity. 200 ± 0.5 mg are weighed into a 5-ml tapered bottom vial (Reacti-Vial®, Pierce) and 1 ml each of toluene, pyridine, and acetic anhydride are added. The vials are capped and heated to 110° for 35 min.

The contents of the Reacti-Vial are transferred to a warmed (60–70°) 30-ml separatory funnel and washed with two 20-ml portions of warm distilled water. After extraction, the toluene layer is transferred to a 25-ml volumetric flask and diluted to volume with toluene.

The standards, weighing out 50 ± 0.01 mg each, are similarly esterified. Solutions are spotted on the thin-layer plate using Corning disposable pipets. Mixtures containing 1, 2, 4, and 6 μg of each standard are spotted on lanes 5, 8, 13, and 16, respectively. Samples are spotted on lanes 2, 4, 7, 10, 11, 14, 17, and 19. Sample weight is 40 μg.

The programmer is set to provide eight cycles (each cycle consists of one solvent

advance and removal). Using program "Mode 3", the time of each solvent advance (elution) is controlled so that

$$\text{elution time} = (\text{cycle number})^2(\text{elution time for cycle one})$$

Solvent advance time is set at 40 sec (elution time for cycle one). Removal time is constant throughout the program at 100 sec. Solvent removal is accomplished by infrared irradiation using setting 9 (360 W). Interim power used to retard elution after development is set at 8 (320 W). The eluent is changed from 70%:30% (v/v) chloroform–acetone to first 90%:10% chloroform–acetone and then to 100% chloroform according to the time line shown in Fig. 1. The "pause" mode is employed while changing solvents.

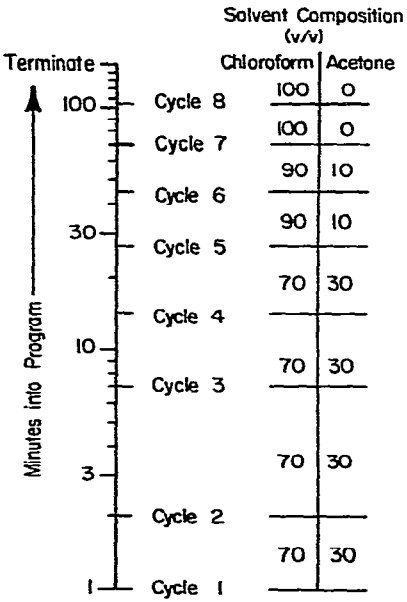

Fig. 1. A time line relating cycle number, duration of cycle, and solvent composition.

The separated ethoxylates are visualized by spraying the plates with 25% aqueous H_2SO_4 and heating at 260° for 30 min.

Integrated peak areas are converted to a weight distribution in two steps. Using a best second-order fit, it is possible to relate EO number and the integrated peak area for each of the standards at the four levels spotted, as shown graphically in Fig. 2. Areas for compounds with EO numbers intermediate to those of the standards are then calculated. These data are used to generate a calibration curve (best first-order fit) of μg ethoxylate *versus* peak area for EO values from 0 to 12 (Fig. 3). The weight of the particular ethoxylate is then calculated from its integrated peak area.

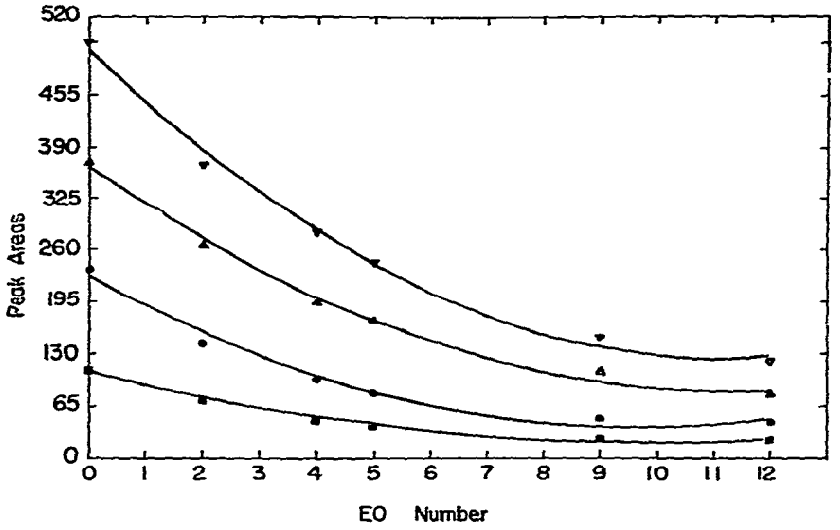

Fig. 2. Graphic display of second-order equations used to generate ethoxylate response curves. ■, 1 μg; ●, 2 μg; ▲, 4 μg; ▼, 6 μg.

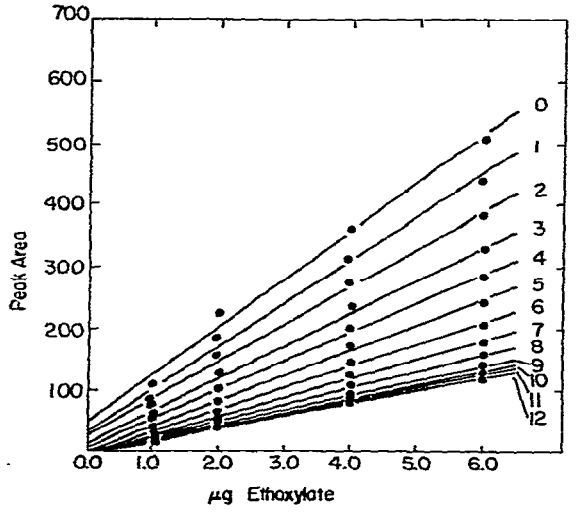

Fig. 3. Response curves for alkyl ethoxylates. Numbers refer to number of ethoxy units.

RESULTS AND DISCUSSION

Approach

Initial experiments using conventional TLC indicated that separation of alkyl ethoxylates was possible on silica gel plates if acetate esters were formed to prevent "streaking". Using increasing concentrations of ethanol in chloroform, multiple developments were performed after spotting the sample on three different plates. Compounds were separated by EO number alone and could be easily visualized by

sulfuric acid charring. This process, however, required almost constant operator manipulation and development time was more than 3 h. PMD promised advantages in speed, simplicity, and unattended operation.

Eluent optimization

A short program was employed to screen eluent systems for the best PMD separation. The program consisted of four cycles (solvent advances and removals). Advance times were 40, 160, 360, and 640 sec, respectively, followed by a 100-sec removal period. Mixtures of ethanol and chloroform, effective in resolving alkyl ethoxylates by conventional multiple development, exhibited a double solvent front with PMD. This was caused by the different rates of evaporation of these two solvents during infrared irradiation of the plate in the eluent removal cycle. It resulted in skewing of the separated component bands toward the direction of development (Fig. 4). Even though individual components remained separated, quantitation by spectrodensitometry was impossible. Acetone proved a suitable substitute for ethanol. Compounds with EO numbers 12 to 8 were separated in 70%:30% chloroform–acetone, compounds with EO numbers 8 to 5 were separated with a 90%:10% mixture, and compounds with EO numbers 4 to 0 were separated in chloroform alone.

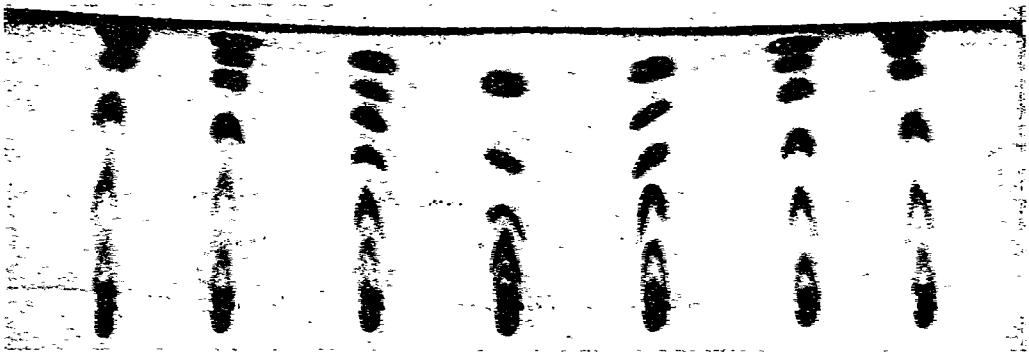

Fig. 4. Plate developed on short screen program illustrating effect of secondary solvent front.

Solvent purity was found to be critical for subsequent spectrodensitometric quantitation of the resolved bands. Minor organic impurities on the silica gel plates or in the eluent itself were concentrated in bands with characteristic R_F values. After sulfuric acid charring, these bands interfered with quantitation of the ethoxylate esters. This necessitated prewashing of the silica gel plates, as well as distillation of solvents. Chloroform was purchased with no preservative to eliminate interferences.

Program selection

A program was developed that combined the three eluents from the rapid screen program. To optimize resolution of all twelve bands on a single plate, various programming "modes" were explored. Of the three modes available (dictated by instrument design) only mode 3 provided efficient resolution of all constituents. This mode provides the greatest center-to-center separation of a homologous series of

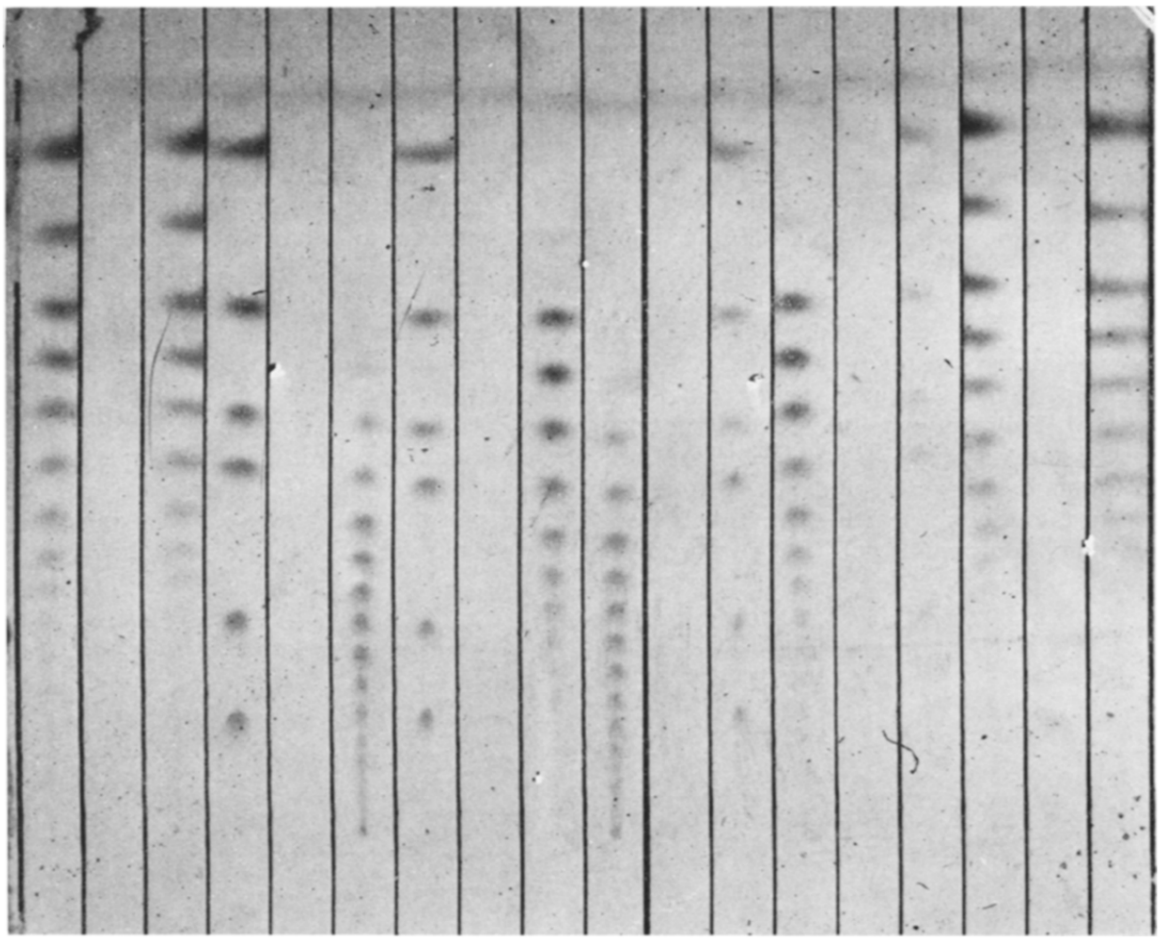

Fig. 5. Plate developed by PMD program, showing separation of the entire alkyl ethoxylate series.

moderately polar compounds (Fig. 5). Compounds with high EO numbers were separated in cycles 1 to 4, the moderately polar compounds in cycles 5 and 6, and the least polar compounds in cycles 7 and 8.

Quantitation

Neither the position nor the absorbance of the charred spots varied with alkyl chain length. A series of compounds each with two EO groups but differing in carbon number ($C_{10}EO_2$, $C_{12}EO_2$, $C_{14}EO_2$, and $C_{16}EO_2$) was analyzed. Five replicates were obtained for 6 μg of each compound. The relative standard deviations of the mean values for each alkyl chain length were 2.4 and 4.1 % for R_F and absorbance, respectively. Similar results were obtained for $C_{10}EO_4$, $C_{12}EO_4$, and $C_{16}EO_4$. Absorbance as integrated peak area varied linearly with concentration below 6 μg (0.4 a.u.f.s.). The optimum sample weight for a mixture was 40 μg with individual ethoxylates in the 1–5 μg range.

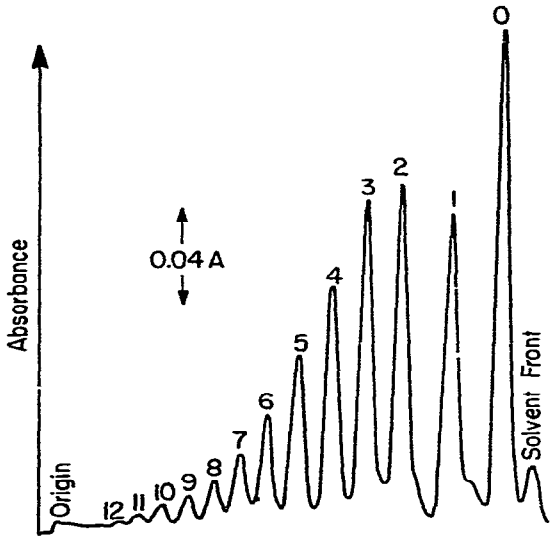

Fig. 6. Densitometer scan of PMD developed plate. Numbers refer to number of ethoxy units.

While charred spots absorb radiation throughout the available spectral region, 546 nm provides maximum intensity for sample and reference beams. Incident beam length was a trade-off between optical resolution and signal-to-noise ratio. The center-to-center distance between separated bands ranged from 14 to 7 mm. Recording absorbance at a beam length of 0.1 mm provided near baseline resolution of the separated components and typical peak half widths of 3 mm (Fig. 6).

Accuracy and precision data are shown in Table I. These data were obtained from analyses of mixtures of the standards at varied ratios. Similar precision was obtained with dodecanol–ethylene oxide condensates.

TABLE I

ACCURACY AND PRECISION DATA

Ethoxy No.	*Accuracy (%)*	*Precision (R.S.D.)*
0	7.0	3.0
2	4.8	4.8
4	6.2	2.4
5	5.9	6.8
9	6.6	5.8
12	5.1	5.3

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