Journal of Chromatography, 160 (1978) 73–80

CHROM. 11,050

DETERMINATION OF FREE POLYETHYLENE GLYCOLS IN ETHOXYLATED DERIVATIVES BY LIQUID CHROMATOGRAPHY

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(Received March 28th, 1978)

SUMMARY

For various ethoxylated derivatives that form the effective components of non-ionogenic surfactants and detergents, the determination of the fraction of free polyethylene glycol was studied by means of reversed-phase liquid chromatography. Compared with the usual extraction method according to Weibull, reversed-phase liquid chromatography with methanol–water on the polymeric sorbent Spheron 40-S yields more accurate results and is much less labour and time consuming.

INTRODUCTION

The determination of free polyethylene glycols (PEGs) in both ionogenic and non-ionogenic surfactants is an important analytical problem which can be solved by extraction or chromatographic methods. There are three reasons why free polyethylene glycols are found in ethoxylated derivatives and in the products obtained from them:

(1) free PEGs are formed as side-products in the reaction of ethylene oxide with the hydrophobic component; they are a mixture of homologous polymeric compounds with a molecular weight distribution that depends on the reaction conditions;

(2) the intentional addition of PEGs leading to the required change in properties of the final product;

(3) the presence of PEGs is a consequence of the decomposition of adducts in the synthetic reaction or during the processing. It is therefore obvious that the determination of free PEGs is important not only from the viewpoint of monitoring the products or the production process, but also as regards the determination of the suitability of surfactants or detergents for particular purposes.

Of extraction procedures used for the separation of PEGs from adducts and the unreacted starting hydrophobic component, the best results have been obtained

by employing extraction of aqueous solutions of surfactants with methyl ethyl ketone[1], or extraction of the coacervate of non-ionogenic surfactants[2] with saturated sodium chloride solution at 95°. The method most widely used is that according to Weibull[3], based on the extraction of an ethyl acetate solution of surfactants with 5 *N* sodium chloride solution, followed by extraction of the aqueous phase with chloroform, evaporation of the solvent and gravimetric determination of PEGs. The success of this method requires the strict observation of the prescribed temperature and volumes of the extractants in all operations.

Column chromatography is faster and more reproducible in the separation of free PEGs from the other components of the mixture. Silica, hydrophobized with dichlorodimethylsilane, with chlorobenzene as the stationary phase separates PEGs, which exhibit a lower retention, from their adducts; the mobile phase is acetone–water–acetic acid[4]. A similar method, utilizing reversed-phase chromatography on silanized silica gel, was suggested by Blomeyer[5]. In 30% aqueous isopropanol, free PEGs are eluted from the column, while adducts can be desorbed with 96% ethanol. An advantage of organic sorption materials is smaller non-specific interactions of the sample components with the sorbent. Elution with ethanol on a column of a cation exchanger[6] in the analysis of ethoxylated fatty amines demonstrated the inadequacy of the extraction of PEGs by the procedure according to Weibull[3].

For the determination of PEGs in adducts of fatty alcohols, alkylphenols, fatty acids and alkanolamides, Taylor[7] suggested a method based on partition chromatography with ethyl acetate as the mobile phase and cellulose as the support for the stationary phase (30% of sodium chloride solution).

This paper reports the quantitative liquid chromatographic determination of free PEGs on the organic macroporous sorbent Spheron 40-S. The results are compared with those obtained by the method according to Weibull.

EXPERIMENTAL

Materials

Model samples were prepared by adding a calculated amount of PEG 300 (Wilhelm Pieck Chemical Works, Nováky, Czechoslovakia) to an adduct of cetyl-stearyl alcohol with 30 moles of ethylene oxide, trade-name Eumulgin B-3 (Henkel, Düsseldorf, G.F.R.).

Polyethylene glycols of molecular weight 200–10,000 were obtained from Koch-Light (Colnbrook, Great Britain), Fluka (Buchs, Switzerland) and Merck (Darmstadt, G.F.R.).

The commercial samples of ethoxylated derivatives used are listed in Table II. Methanol–water (95:5) was the optimal eluent. Ethyl acetate, chloroform and sodium chloride (analytical-reagentgrade) were purchased from Lachema (Brno, Czechoslovakia).

Apparatus

An L-Chrom-50 liquid chromatograph was equipped with an RIDK 101 differential refractometer with a measuring cell volume of 10 μl. An IT-2 integrator and a PT-1 printing device were used.

The stainless-steel chromatographic column (250 × 8 mm I.D.) was packed

with Separon 40-S sorbent, spherical particle size 25–30 μm, and connected with a septum dosing valve. Separon 40-S is a C_{18} derivative of a macroporous copolymer[8] of 2-hydroxyethyl methacrylate and ethylene dimethacrylate, with substituted hydroxy groups, developed for reversed-phase chromatography on a semi-preparative scale.

All devices used in this work and the chromatographic column were manufactured by Laboratory Instruments Works (Prague, Czechoslovakia).

The apparatus used in applying Weibull's method fulfilled the requirements of the Czechoslovak Standard ČSN 681101, based on the original specification[3].

Methods

The model samples were prepared immediately before the measurement by mixing PEG 300 (molecular weight 300) with the adduct Eumulgin B-3, in which the total content of free PEG (3%) was determined in advance. In the samples thus prepared, the total content of free PEG was determined by Weibull's method while strictly observing the procedure according to ČSN 681101. The procedure is shown schematically in Fig. 1.

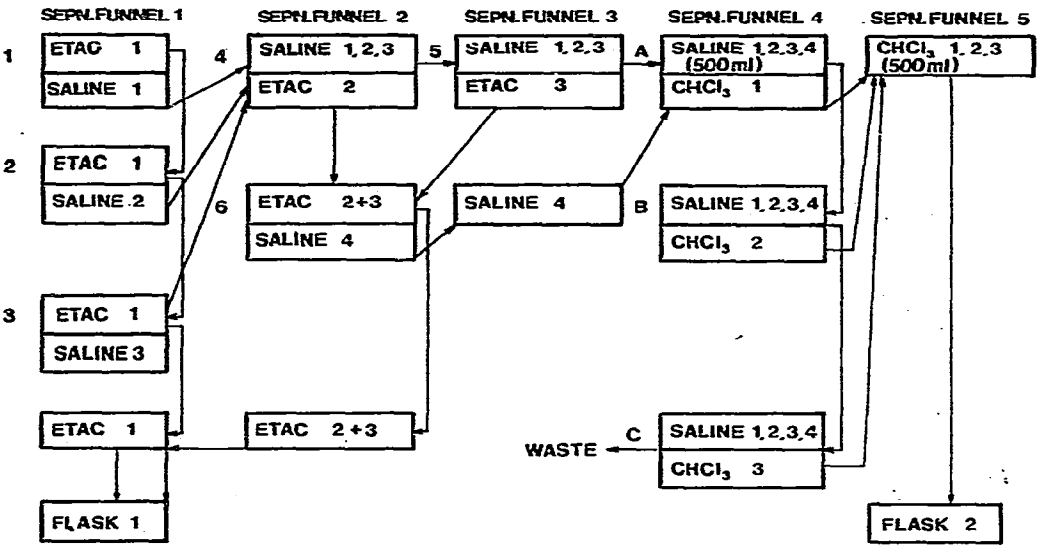

Fig. 1. Scheme of the extraction procedure according to Weibull[3]. (ETAC, ethyl acetate; saline, 300 g NaCl in 1 l water.)

For quantitative liquid chromatography, the system was calibrated with pure PEGs of molecular weight 200–10 000 with amounts injected in the range 0–500 μg (20% solution in the eluent). In this range, the concentration responses of the RIDK 101 detector were linear (Fig. 2).

The model samples containing a known amount of free PEGs, and samples of commercial mixtures, were weighed, diluted with the eluent methanol–water (95:5) to give a *ca.* 20% solution, and 0.5–2.5 μl of the solution were injected by means of

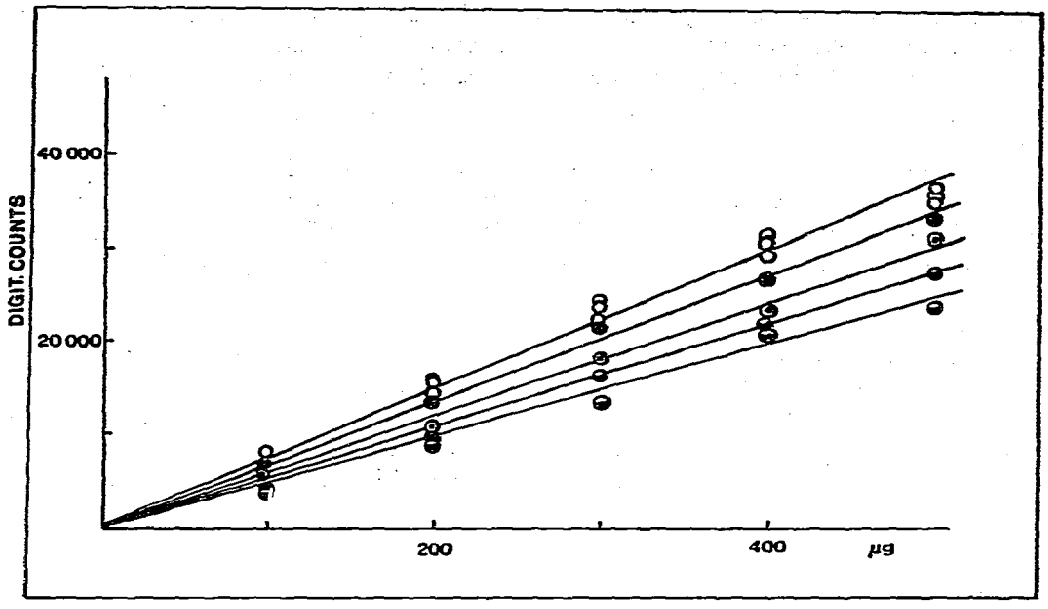

Fig. 2. Calibration graph for pure PEGs. Column: 250 × 8 mm I.D. Sorbent: Separon 40-S (25–30 µm). Eluent: methanol–water (95:5). Flow-rate: 100 ml/h. ◒, PEG 200; ⊗, PEG 300; ⊙, PEG 1000; ●, PEG 2000; ○, PEG 4000, 6000, 10,000.

the septum valve directly into the chromatographic column. The detector response was recorded with a TZ 21 S recorder (Laboratory Instruments Works) and evaluated by the triangular method or with an integrator.

RESULTS AND DISCUSSION

The liquid chromatographic method for the determination of free PEGs is based on the isolation of the PEG fraction from adducts and unreacted hydrophilic components and on a refractometric determination of this fraction in the sample. A typical chromatogram is shown in Fig. 3. In non-ionogenic surfactants and detergents, PEGs are the most polar fraction, and under the conditions described in Experimental, are the first to be eluted from the column. The more hydrophobic molecules of the adduct or of unreacted starting compounds are retarded on the Separon 40-S sorbent for a longer time. An insufficient separation of the PEG fraction from the accompanying components has a negative effect on the accuracy of the determination. However, the separation can be greatly improved at the expense of prolonging the analysis if the polarity of the mobile phase is altered by increasing the water content.

Results obtained in the analysis of model samples using the PEG 300 standard by liquid chromatography and by the procedure according to Weibull are summarized in Table I. In agreement with the results presented earlier for ethoxylated fatty amines[6], Weibull's extraction method yielded values more than 10% lower than the actual values in the determination of PEGs in the presence of ethoxylated fatty alcohols. On the other hand, the results obtained by liquid chromatography were within ±5%

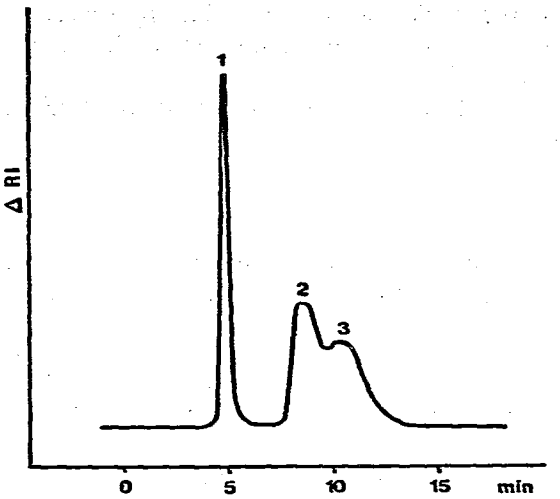

Fig. 3. Chromatogram of a surfactant containing free PEG Eumulgin B-3. Column 250 × 8 mm I.D.; Separon 40-S (25–30 μm); methanol–water (95:5); flow-rate 100 ml/h; refractive index detector. Peaks: 1 = PEG 300; 2 = adduct; 3 = unreacted starting hydrophobic component.

TABLE I

COMPARISON OF RESULTS OF THE DETERMINATION OF THE CONTENT OF FREE POLYETHYLENE GLYCOLS IN MODEL SAMPLES (EUMULGIN B-3 + PEG 300) BY THE METHOD ACCORDING TO WEIBULL AND BY LIQUID CHROMATOGRAPHY

Sample	*Actual PEG content (%)*	*Liquid chromatography*		*Weibull's method*[3]	
		PEG (%)	*Rel. error (%)*	*PEG (%)*	*Rel. error (%)*
1	7.93	8.30	+4.64	6.49	−17.53
2	9.69	9.56	−1.33	8.62	−13.28
3	13.70	13.12	−4.20	10.94	−14.39
4	17.47	16.87	−3.48	15.40	−12.45
5	22.83	23.81	+4.27	20.13	−10.33
6	27.77	28.46	+2.47	23.96	−11.93
7	32.07	31.84	−0.72	27.79	−13.67

of the actual values. Table I also clearly shows the systematic error involved in Weibull's method, which we attribute to the inadequate efficiency of extraction.

From the quantitative standpoint, however, it may be objected that the results based on a calibration with the standard PEG and on an analysis of a mixture of the standard and ethoxylated derivatives do not take into account sufficiently the possible dependence of the retention volume of the PEG fraction, or of the refractive index, on the molecular weight of the PEGs. We therefore examined these aspects also. The chromatography of PEG standards with different average molecular weights showed that under the conditions described in Experimental, the elution times are independent of the molecular weight of the samples.

With increasing molecular weight, the peaks become broader, however, so that a quantitative determination must be carried out by evaluating its surface area; measurement of the peak height alone is insufficient.

Heitz *et al.*[9] determined the dependence of the refractive index of defined PEGs on molecular weight, which can be expressed by

$$n_D = A - B/M_w$$

where n_D is the refractive index, M_w molecular weight and A and B are constants. This dependence permits a quantitative correction of the chromatogram to be made if required.

From the dependence of the detector response on the concentration and molecular weight of the PEG standards in Fig. 2, it follows that an exact determination of PEGs in real samples requires a knowledge of the degree of polyaddition. To meet the requirement of an exact quantitative determination, it is possible to collect the PEG fraction of an unknown sample eluted from the column, to determine its average molecular weight by employing one of the usual methods and to carry out a correlation using Fig. 2.

The determination of free PEGs by liquid chromatography was also applied to various types of ethylene oxide adducts differing in the hydrophobic component. The suitability of the method is illustrated in Table II.

Using the eluent methanol–water (95:5), a complete separation of the polyglycol fraction from the other components was achieved with derivatives of fatty alcohols, alkylphenols, fatty acids and glycerides. An incomplete separation was observed with sorbitans and alkanolamide. However, by using an integrator even chromatograms with an incompletely separated PEG fraction can be quantitatively evaluated satisfactorily.

Phosphates and sterols do not dissolve in the above system without leaving a residue.

The liquid chromatographic determination was compared with the extraction procedure using real samples of ethoxylated glycerides (Table III). Here also it can be seen that in most instances the values obtained by liquid chromatography are higher than those obtained by Weibull's method.

Both the sorbent and eluent were chosen with the aim that in the chromatographic analysis the elution time of the PEG fraction should not depend on either the average molecular weight or its distribution. This property of the system is attributable to the relatively weak interactions between the copolymeric sorbent and the dissolved compounds. Unlike silica sorbents, Separon 40-S can be regenerated very readily by washing the column with methanol–diethyl ether (1:1). In routine analyses, such a regeneration is recommended after 100–150 samples have been examined. The high stability of the adsorption properties of Separon 40-S, together with simple and efficient regeneration, is one of the main advantages of this sorption material. These advantages become particularly pronounced when one passes from the analysis of artificial mixtures of standard compounds to real samples. The eluent in the isocratic system was chosen bearing in mind refractometric detection of PEGs and the inexpensive solvents used.

Compared with the extraction procedures, the liquid chromatography of free

TABLE II

UTILIZATION OF LIQUID CHROMATOGRAPHY IN THE DETERMINATION OF FREE POLYGLYCOLS IN VARIOUS TYPES OF ETHOXYLATED DERIVATIVES

Group	*Sample (and representative of the group)*	*PEG determined by liquid chromatography (%)*	*Manufacturer*	*Note**
EO alcohols	Eumulgin 05 (EO cetyloleyl alcohol)	4.2	Henkel (Düsseldorf, G.F.R.)	
EO alkylphenols	Tergitol NP 35 (EO nonylphenol), 15 EO	5.2	Union Carbide (New York, N.Y., U.S.A.)	
EO fatty acids	MYRJ 59 (POE stearate)	53.1	Atlas Chemie (Wilmington, Del., U.S.A.)	
EO sorbitans	Tween 20 SD (POE sorbitan monolaurate)	31.2	Atlas Chemie	A
EO glycerides	Tagat O-2 (EO glycerine monooleate)	22.4	Th. Goldschmidt (Essen, G.F.R.)	
Glycerine polyglycol ether esters	Tagat TO (glycerine polyglycol ether trioleate)	4.5	Th. Goldschmidt	
EO alkanolamides	Ethylane CRS (EO alkanolamide of coconut acid)	17.3	Albright and Wilson, Marchon Div. (Whitehaven, Great Britain)	A
EO phosphates	Hostaphat KO 380N (EO oleyl alcohol–phosphoric acid tertiary ester), 8 EO	—	Hoechst (Frankfurt/M, G.F.R.)	B
EO sterols	Generol TM 122 E16 (EO refined phytosterol from soya oil), 16 EO	—	General Mills (Tucson, Ariz., U.S.A.)	B

* A: the peak of free PEG is not separated from the adduct down to the baseline. B: the sample does not dissolve without leaving a residue in the system used.

TABLE III

DETERMINATION OF THE CONTENT OF FREE PEGs IN ETHOXYLATED GLYCERIDES

Sample	*PEG content (%)*		*Difference (%)*
	By liquid chromatography	*By Weibull method*	
Tagat O	27.8	24.5	+3.3
Tagat O-2	20.9	17.4	+3.5
Tagat L	18.1	12.7	+5.3
Tagat L-2	19.6	15.4	+4.2
Tagat S	26.8	21.8	+4.9
Tagat S-2	19.4	18.1	+1.3
Tagat R-1	26.6	21.6	+5.0
G-1288	20.2	19.8	+0.4
G-1292	8.4	10.5	−2.1
Arlaton G	11.6	13.4	−1.8

PEGs is much faster, yields more reliable results, is less labour consuming and permits routine analysis. Its scope of application is wider; with automatic data evaluation, the results obtained are more exact.

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