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THE DETERMINATION OF POLYETHYLENE GLYCOL IN CERTAIN NON-IONIC SURFACE ACTIVE AGENTS

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SUMMARY

A method is described for the determination of polyethylene glycol in polyethers, referred to as condensates, derived from reaction between ethylene oxide and fatty alcohols, alkyl phenols, fatty amines and alkanolamides. The method is based on liquid partition chromatography using sodium chloride solution as the stationary phase, ethyl acetate as the moving phase, and cellulose as the column support. The conditions required for complete separation and recovery are described.

INTRODUCTION

Polyethylene glycol may be present in the above products for several reasons. (1) By deliberate mixture; (2) by the reaction of the ethylene oxide with water present either in the starting material or in the ethylene oxide; (3) by decomposition.

It is very desirable to be able to determine the amount of polyethylene glycol present both from the point of view of control of manufacture and the physical performance of the product.

Polyethylene glycol has been satisfactorily determined in a number of polyethers by the method of WEIBULL[1], and subsequent modifications[2,3]. In these methods 5 g of the sample is dissolved in 75 ml ethyl acetate and extracted three times with 50 ml 30 % brine solution, the temperature being very carefully maintained at 35° ± 1°. The combined brine extracts are washed twice with 25 ml ethyl acetate and the combined ethyl acetate washings re-extracted with 25 ml 30 % brine solution. The ethyl acetate washings are added to the original ethyl acetate solution and the final brine extract added to the three combined brine extracts. It is essential that all these operations are carried out at 35° ± 1°. The combined brine extracts are then extracted three times with 100 ml of chloroform and the chloroform evaporated to dryness and the residue dried and weighed. This gives the polyethylene glycol. If it is required to determine the condensate also, the ethyl acetate layer and washings are also evaporated to dryness and weighed. The polyethylene glycol and condensate fractions should then be checked for completeness of separation by thin-layer chromatography[4]. An ammonium sulphate impregnated silica gel is used and the plate developed with chloroform–methanol (9:1). The plate is then sprayed with Dragendorff's reagent. The method gives good results but is very tedious and lengthy and conditions have

to be adhered to very closely in order to obtain reproducible results. The proposed method uses the same principle of solvent partition but the whole operation is transferred to a liquid chromatographic column, making the operation quicker, easier to perform, particularly by an unskilled operator, and less dependent on slight variations in conditions. The necessity of examining the separated polyethylene glycol fraction by thin-layer chromatography to ensure complete separation is also avoided as the method includes a check that complete separation has been achieved.

EXPERIMENTAL

Initial experiments

An attempt was first made to transfer the modified WEIBULL determination onto a cellulose column using the same solvents and doing the experiment at room temperature. A sample of polyether based on tallow alcohols with 20 moles ethylene oxide was first tried as this had been already analysed by the WEIBULL method. A column of 30 g of cellulose mixed with 10 ml of 30 % w/v sodium chloride as the column support, was packed in ethyl acetate as the moving phase. 2 g of the sample were dissolved in ethyl acetate and added to the column and the column then eluted with 150 ml ethyl acetate. The column was then further eluted with another 300 ml of ethyl acetate and finally with 150 ml of chloroform. The three solvent portions were evaporated on the steam bath, dried at 105° for 5 min, cooled and weighed. It was found that the condensate was entirely eluted in the first 150 ml of ethyl acetate. The second 300 ml of ethyl acetate contained no residue on evaporation at all and the polyethylene glycol was eluted by the 150 ml of chloroform. The results by both this and the WEIBULL method are shown in Table I.

TABLE I

TALLOW ALCOHOLS WITH 20 MOLES ETHYLENE OXIDE
Comparison with modified WEIBULL method.

Method	*Condensate* (%)	*Polyethylene glycol* (%)
Modified Weibull	89.8	9.0
	90.6	8.8
Cellulose column	91.0	8.8
	90.8	9.1
	91.0	8.8

It was found, however, that this agreement with the WEIBULL method was not obtained with these conditions with a sample of a polyether based on cetyl alcohol containing 80 moles of ethylene oxide. The method was also unsatisfactory with polyethers based on alkyl phenols and fatty amines. The conditions were therefore varied to try to obtain good separations in these cases.

Effect of temperature

The column was enclosed in a water jacket and the separation attempted at different temperatures using the same sample as above. The eluate was taken in

10 ml fractions, each fraction being evaporated and weighed. The temperatures chosen were 25°, 37°, and 45° and using ethyl acetate only the elution was continued to 50 fractions (500 ml). The elution curves are shown in Figs. 1, 2 and 3. These show that at 25° the condensate is rapidly eluted and then nothing further comes off, at 45° the condensate and the polyethylene glycol are eluted together without separation, but at 37° the condensate is eluted rapidly and the polyethylene glycol eluted later in a completely separated peak. Further elution yielded only a negligible amount.

Further experiments were done with ethyl acetate as the single moving phase using commercial lauryl alcohol with 3 moles of ethylene oxide and nonyl phenol with 6 moles, 9 moles and 14 moles of ethylene oxide and similar curves were obtained. 35° was finally chosen as the optimum temperature.

Recovery of added polyethylene glycol

The amount of polyethylene glycol found in the polyethers based on the nonyl phenol was very small so it was decided to add a known amount of polyethylene glycol and check the recovery. A mixture of polyethylene glycols of mol. wts., 200, 400, 600, 800 and 1000 was made and added to nonyl phenol condensates containing 6 moles and 14 moles of ethylene oxide. The elution curves are shown in

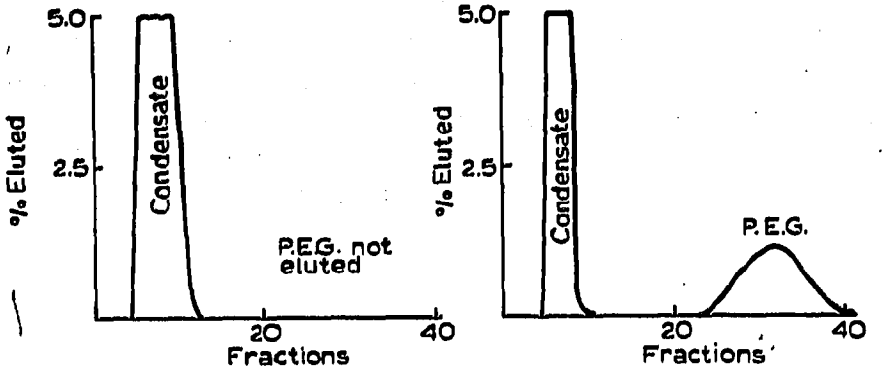

Fig. 1. Tallow alcohols + 20 moles of ethylene oxide at 25°.

Fig. 2. Tallow alcohols + 20 moles of ethylene oxide at 37°.

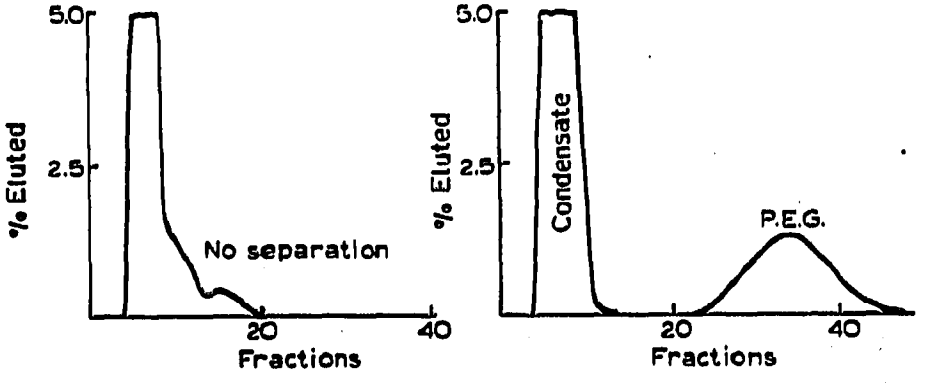

Fig. 3. Tallow alcohols + 20 moles of ethylene oxide at 45°.

Fig. 4. Nonyl phenol + 6 moles of ethylene oxide with 9.6% added polyethylene glycol at 35°.

Figs. 4 and 5. 9.6 % of polyethylene glycol was added to the first sample and 8.5 % recovered. 12.6 % was added to the second sample and 13.5 % recovered. These figures were, however, obtained by adding together the residues on evaporation from about 12 fractions and therefore a high accuracy could not be expected. In both cases the column was further eluted with chloroform and less than 0.1 % polyethylene glycol obtained.

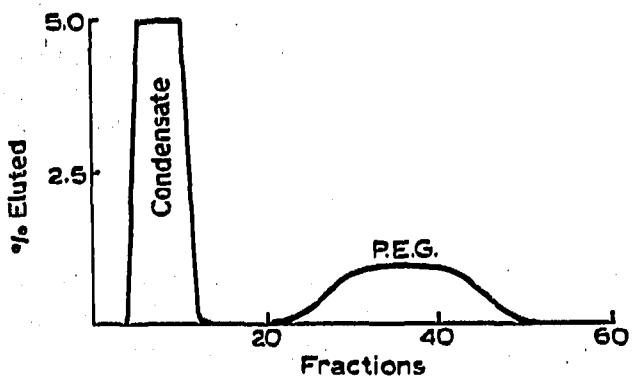

Fig. 5. Nonyl phenol + 14 moles of ethylene oxide with 12.6% of added polyethylene glycol at 35°.

The second sample with 12.6 % of added mixed polyethylene glycols was then determined a number of times by two different operators by taking blocks of eluate for evaporation and weighing. The first 150 ml was taken for the first block which should contain the condensate, the next 60 ml was taken for the second block which should contain nothing and therefore indicates complete separation of the peaks and then a third block of 300 ml was taken which should contain the polyethylene glycol. The results are shown in Table II.

These results show that with these types of sample satisfactory results are obtained using ethyl acetate only at 35°.

TABLE II

RECOVERY OF POLYETHYLENE GLYCOL FROM NONYL PHENOL CONDENSATE CONTAINING 14 MOLES OF ETHYLENE OXIDE WITH 12.6% OF ADDED POLYETHYLENE GLYCOL

First portion 150 ml	*Second portion 60 ml*	*Third portion 300 ml*
85.8%	0.3%	12.5%
85.6%	0.1%	13.3%
85.9%[a]	negligible	12.7%
86.7%	do	12.6%
84.6%[a]	do	12.8%

[a] Second operator.

Separations with various other types of polyether

Reaction products of fatty amines and ethylene oxide containing 2 moles and 15 moles of ethylene oxide were then tried and found to be almost identical with previous separations. A fatty amine with 2 moles of ethylene oxide was found to

contain 0.5 % of polyethylene glycol and when 10.3 % of the mixed polyethylene glycol was added the recovery was 10.5 %. A sample containing 15 moles of ethylene oxide gave 10.1 % of polyethylene glycol. The shape of the elution curve was identical with the nonyl phenol condensate separations.

A sample of the polyether based on cetyl alcohol with 80 moles of ethylene oxide was attempted with the above conditions. The condensate was eluted sharply as in all the other materials tried but the elution of the polythelene glycol was delayed and after 50 fractions had been taken only 92 % of the total sample had been recovered. Further elution with ethyl acetate did not remove any more polyethylene glycol. Elution with chloroform removed another 5 % but the last traces were only eluted with ethanol.

A cocomonoethanolamide with 2 moles of ethylene oxide was then attempted. The major component was eluted in the same pattern from fractions 4 to 14 and then nothing further was eluted with ethyl acetate up to 50 fractions. The experiment was done twice and the main peak amounted to 95.7 % and 96.2 %. 12 % of the mixed polyethylene glycol was then added to the sample and the determination repeated. 11.6 % of polyethylene glycol was recovered with exactly the same type of curve as Fig. 4. This showed that the original material contains a negligible amount of polyethylene glycol. At this stage, however, only 96.4 % of the sample had been recovered. The original ethanolamide before ethoxylation may, however, contain some free monoethanolamine so the elution was continued with chloroform and ethanol and the fractions also checked for alkalinity to bromophenol blue. A further 0.6 % was eluted with 250 ml of chloroform, this material being neutral, and finally 3.2 % was eluted with ethanol which was titratable to bromophenol blue.

The technique will therefore separate free polyethylene glycol from reaction products of monoethanolamine and ethylene oxide in addition to separation from the polyether based on cocomonoethanolamide.

The final method is as follows:

Reagents. The following reagents were used: 30 % w/v Solution of sodium chloride in water; ethyl acetate; chloroform; cellulose powder, Whatman Grade CF 11.

Apparatus. A chromatography tube, 50 cm long, 1.6 cm I.D. fitted with a tap at the lower end, and enclosed in a water jacket through which water can be circulated from a bath kept at 35° ± 1°.

Procedure. Plug the lower end of the column with cotton wool and fit the tap. Fill it with ethyl acetate by placing the tap in a beaker of ethyl acetate and sucking the ethyl acetate into the column. This procedure drives the air out of the cotton wool plug and the space below it and therefore prevents air being drawn into the column during packing.

Weigh 30 g of the cellulose and add it in small quantities at a time with thorough mixing to 10 ml of the 30 % NaCl solution. Add the mixture to the column in 1 to 2 g portions at a time, agitate thoroughly and pack down to a uniform tightness. This is rather difficult for the first 3 or 4 additions and settling is improved if the tap is slightly opened and the ethyl acetate allowed to run out. If this is done, the ethyl acetate must be collected in a beaker and then returned to the column. The column must not be refilled with fresh ethyl acetate. The tightness of packing should be such that, when all the cellulose has been added a column of about 35 cm in height is obtained.

Allow the ethyl acetate to run through until the level is about 2 cm above the level of the cellulose and circulate water at 35° through the outer jacket for at least half an hour.

Accurately weigh about 2 g of the sample to be tested. If the sample is a liquid it can be added directly to the column and stirred into the small amount of ethyl acetate on the top of the cellulose. If it is a solid, weigh in a small beaker and dissolve in the minimum quantity of ethyl acetate, warming if necessary, and add to the column. Place a measuring cylinder under the column and allow the solvent to run through until the level falls to the top of the cellulose. Add 5 ml of ethyl acetate and repeat. Fill the column with ethyl acetate and fix a reservoir above the column. A total amount of 510 ml of ethyl acetate is added to the reservoir. This 510 ml is inclusive of the small amounts that have already been used.

Collect the eluate from the column in 3 portions, 150 ml, 60 ml, and 300 ml. Evaporate them to dryness and dry in an oven at 105° for 5 min. The first portion contains the condensate and the 60-ml portion should not contain anything at all, but must be evaporated and weighed as this is the check for complete separation. The 300 ml contains the polyethylene glycol.

The polyethylene glycol elution is complete at this stage for samples containing up to about 15 moles of ethylene oxide, but if the molecular weight is higher than this the column must then be eluted with 200 ml of chloroform and this added to the 300 ml portion of ethyl acetate.

For very high molecular weights, above 40 moles of ethylene oxide, the column must be further eluted with 200 ml of ethanol. The ethanol must be evaporated to dryness, the residue dissolved in chloroform, filtered, evaporated to dryness and the final residue added to the last ethyl acetate and chloroform fractions.

In the case of ethanolamide ethoxylates the free polyethylene glycol is in the 300-ml ethyl acetate portion and further elution with chloroform or ethanol brings off ethoxylated monoethanolamine.

$$\% \text{ Polyethylene glycol} = W_1 + W_2 + W_3 \times \frac{100}{\text{weight taken}}$$

where

W_1 = weight of residue from 300-ml ethyl acetate fraction,

W_2 = weight of residue from chloroform elution where applicable,

W_3 = weight of residue from ethanol elution where applicable.

Temperature control is important as the polyethylene glycol elution shifts its position rapidly with changes in temperature.

ACKNOWLEDGEMENTS

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