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THE ANALYSIS OF ALKYLENE OXIDE–FATTY ALCOHOL CONDENSATES BY GAS–LIQUID CHROMATOGRAPHY

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SUMMARY

The ether groups of ethylene oxide, and/or propylene oxide–fatty alcohol condensates were cleaved by reaction with 50% hydrobromic acid (in glacial acetic acid) in sealed Pyrex glass tubes. The resulting alkyl bromides were extracted with carbon disulphide and chromatographed on 5% OV-210 columns. Peak areas were used to determine the number of moles of alkylene oxide in the condensate. A series of ethylene oxide–fatty alcohol condensates were tested, and the results were in good agreement with those obtained from nuclear magnetic resonance methods. A further series of products consisting of mixed alkylene (ethylene and propylene) oxide–fatty alcohol condensates were also examined.

INTRODUCTION

Ethylene oxide–fatty alcohol condensates are used as general purpose detergents, emulsifiers in cosmetic and agricultural formulations, and softening agents for textile fibres.

Ethylene oxide/propylene oxide–fatty alcohol condensates can be used as lubricants and are often added to modify solubilities in detergent formulations.

In a study of fatty alcohol distribution in fatty alcohol ethoxylates, Bore and Gataud[1] refluxed these condensates with HBr at 135° and chromatographed the purified bromides on DEGS and Apiezon L columns at 190° and 230°, respectively. Components detected were 1,2-dibromoethane, β,β'-dibromoethyl ether, plus the alkyl bromides from the fatty alcohols. Products formed from propylene oxide–fatty alcohol condensates were not resolved from those of the former condensates, and therefore interfered in the procedure.

Work by Mathias and Mellor[2] indicated that temperatures of 150° were necessary to bring about fission of polyether chains in ethylene oxide–propylene oxide copolymers, and recommended a reaction time of 2 h. Stead and Hindley[3] extended the reaction times to 3 h and achieved almost complete fission of the ether linkages.

When the reaction conditions proposed by Stead and Hindley were applied to alkylene oxide–fatty alcohol condensates, and the products analysed by gas–liquid chromatography (GLC), it was possible to determine the molar proportions of the components.

EXPERIMENTAL

Commercial products

The products used in this investigation were supplied by I.C.I. (Australia), and consisted of :

(1) Teric 17A Series —These are ethylene oxide–fatty alcohol condensates, the mixed fatty alcohol hydrophobe having an average molecular weight of 256 corresponding to $C_{17}H_{35}OH$. Further details are given in Table I.

(2) A series of mixed alkylene oxides (with varying ethylene and propylene oxide ratios)–fatty alcohol condensates based on fatty alcohols having an average molecular weight of 206. These products are shown in Table II and include both block and random copolymers.

Reagents

Hydrobromic acid, 50% in glacial acetic acid, was supplied by Hopkin and Williams, Great Britain. The carbon disulphide used was of A.R. grade.

Gas–liquid chromatography

A Varian Aerograph 1200 with 6 ft. × $\frac{1}{8}$ in. O.D. stainless-steel columns containing 5% OV-210 on 80–100 mesh silanized Chromosorb W was used. Detection was carried out by means of a flame ionization detector with an injector temperature of 250° and a detector temperature of 260°. The carrier gas was nitrogen, at a flow-rate of 15 ml/min, measured at the outlet of the column. Measurements were carried out with a Varian Aerograph Model 20 recorder, and a Hewlett-Packard Model 3370B electronic integrator.

Nuclear magnetic resonance spectroscopy

5% solutions of samples in A.R. grade carbon tetrachloride with D_2O were subjected to spectroscopy using a Varian A-60 spectrometer.

Procedure

The anhydrous samples, if liquid, were drawn up into a capillary tube (a melting point tube is suitable) such that 15 ± 4 mg was obtained. The capillary tube was then placed into a Pyrex glass tube (approximately 6 in. × $\frac{1}{4}$ in. I.D.). Solid samples, which could not easily be rendered liquid by warming, were added directly to the Pyrex tube.

A graduated pipette was used to add 0.4 ml HBr–glacial acetic acid (1:1) reagent to the Pyrex tube which was then carefully sealed. After allowing the tube to cool, the contents were thoroughly mixed by inverting the tube several times. It was then placed in an oven at 150 ± 1° for 3 h.

The tube was cooled to room temperature before being carefully opened, and the contents were then quickly transferred to a 10- to 15-ml test tube. The Pyrex reaction tube was rinsed with a total of 4 ml of water, followed by 2 ml of carbon disulphide, and the washings transferred to the test tube.

The stoppered test tube was shaken for 1 min and then centrifuged at between 500 and 1000 r.p.m. (78 × g) for 2 min. 1–2 μl of the carbon disulphide layer was injected into the gas chromatograph and the areas of the alkyl and alkylene bromide peaks measured using the electronic integrator.

CALCULATIONS*

Ethylene oxide–fatty alcohol condensates

The number of moles ethylene oxide is

$$\frac{\text{average mol. wt. fatty alcohol} \times A_E}{44(100-A_E)}$$

where A_E=% peak area ratio $EBr_2/(EBr_2+\Sigma RBr)$.

The peak areas of the various fatty alkyl bromides are used to determine the proportions of the corresponding fatty alcohols, and hence the average molecular weight of the alcohols.

Ethylene oxide/propylene oxide–fatty alcohol condensates

The total number of moles ethylene oxide + propylene oxide in the condensate is

$$\frac{\text{average mol. wt. fatty alcohol} \times A_T}{\text{average mol. wt. alkylene oxide } (100-A_T)}$$

where A_T =% peak area ratio $(EBr_2+PBr_2)/(EBr_2+PBr_2+\Sigma RBr)$.

The average molecular weight of the fatty alcohol is obtained similarly to that discussed earlier.

Whilst investigating the work of Stead and Hindley on ethylene oxide–propylene oxide copolymers, it was found[4] that, contrary to their findings, the peak area ratio $EBr_2/(EBr_2+PBr_2)$ varied linearly with the mole fraction of ethylene oxide (Fig. 1). This led to a simplification of their procedure, in that the mole fraction of ethylene oxide could be obtained directly from a calibration graph.

Thus, in considering the alkylene oxide portion of the condensate, the weight percentage of ethylene oxide is

$$\frac{78.4A_{EP}}{1-0.250A_{EP}}$$

where

A_{EP}= peak area ratio $EBr_2/(EBr_2+PBr_2)$.

Knowing the weight percentages of ethylene oxide and propylene oxide, the average molecular weight of the alkylene oxide portion can be readily calculated.

The mole ratio EO/(EO+PO) is obtained from the graph (Fig. 1), prepared by subjecting mixtures of known molar ratios of polyethylene and polypropylene glycols to the procedure as outlined. Having determined the total number of moles

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* EBr_2 = 1,2-ethylenedibromide; PBr_2 = 1,2-propylenedibromide; R = alkyl > C_4; EO = ethylene oxide; PO = propylene oxide.

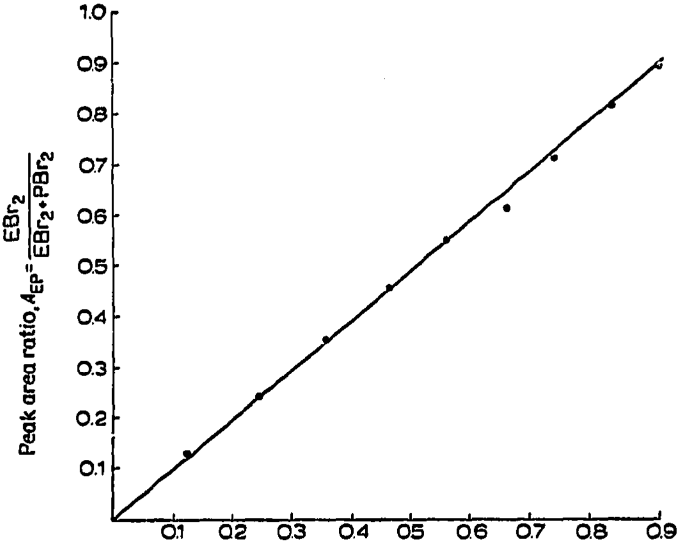


Fig. 1. Graph of mole fraction of ethylene oxide in the alkylene oxide portion of the condensate *versus* the peak area ratio, $A_{EP}=EBr_2/(EBr_2+PBr_2)$.

of ethylene oxide and propylene oxide, the number of moles of each individual alkylene oxide can now be calculated.

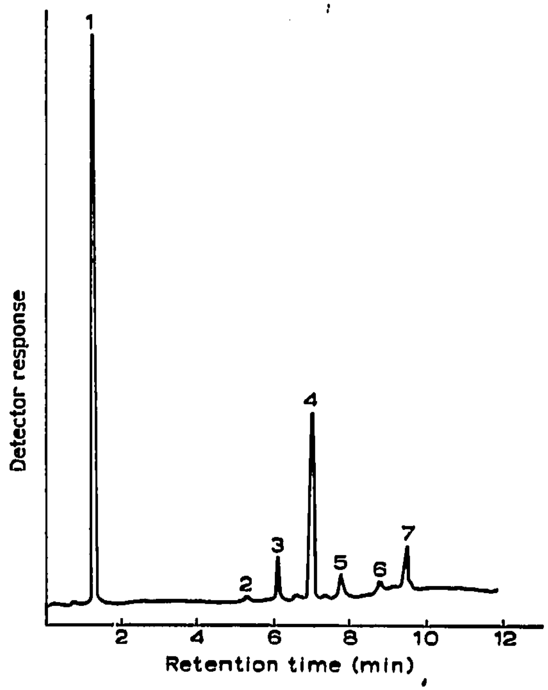
RESULTS AND DISCUSSION

When treated as described in the procedure, polyethylene glycol (PEG 400) and polypropylene glycol (PPG 400) each produced only one peak corresponding to 1,2-ethylenedibromide and 1,2-propylenedibromide, respectively. Similarly the fatty alcohols C_8, C_{12}, C_{14}, C_{16} and $C_{18:0}$ each gave only one peak, and were consistent with the corresponding alkyl bromide. Oleyl alcohol gave one major peak preceded by a smaller one. These were probably due to di- and tribromo derivatives produced by bromination of the unsaturated $C_9=C_{10}$ bond in the fatty alkyl chain.

With the exception of Teric 17A8 the range of molecular weights of the fatty alcohols of the Teric 17A series was found to be 255–260. In the case of Teric 17A8 the average molecular weight was 240, and this lower value was accounted for by the fact that the raw materials originated from a different supplier.

A typical chromatogram of an ethylene oxide–fatty alcohol condensate is shown in Fig. 2. It shows peaks for 1,2-ethylenedibromide and C_{12}, C_{14}, C_{16} and $C_{18:0}$ alkyl bromides. Peaks Nos. 6 and 7 had retention times the same as those produced by bromination of oleyl alcohol.

That normalization of peak areas is suitable for calculations of alkylene oxide content is seen by the agreement with the results obtained using nuclear magnetic resonance (NMR) spectroscopy (Table I). Further, this procedure has been used on products from different manufacturers having a variety of fatty alcohol distributions. In all cases the results were consistent with the manufacturer's stated



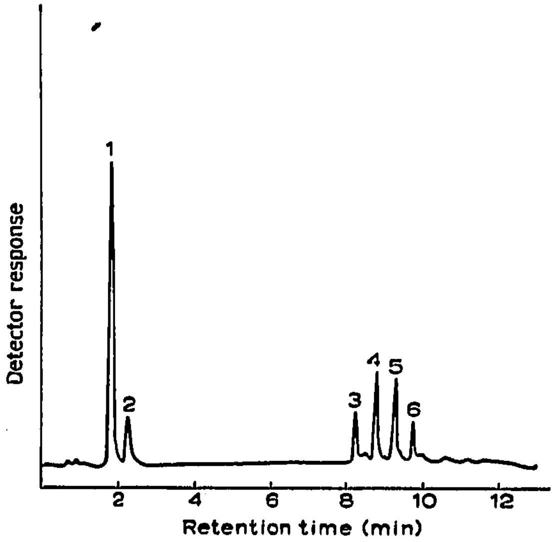


Fig. 2. Chromatogram of an ethylene oxide-fatty alcohol condensate (Teric 17A3). Column, 5% OV-210, temperature programmed from 55° to 260° at 20°/min. 1 = 1,2-Ethylenedibromide; 2 = lauryl bromide; 3 = myristyl bromide; 4 = cetyl bromide; 5 = stearyl bromide; 6 and 7 = bromides derived from oleyl alcohol.

Fig. 3. Chromatogram of a mixed ethylene oxide-fatty alcohol condensate (DS 6330). Column, 5% OV-210, isothermal at 50° for 3 min, then temperature programmed to 260° at 20°/min. 1 = 1,2-Ethylenedibromide; 2 = 1,2-propylenedibromide; 3 = lauryl bromide; 4 = tridecyl bromide; 5 = myristyl bromide; 6 = pentadecyl bromide.

TABLE I

DETAILS OF RESULTS OBTAINED FROM COMMERCIAL ETHYLENE OXIDE-FATTY ALCOHOL CONDENSATES

Sample	*Moles EO according to manufacturer's specification (±0.5)*	*Moles EO (NMR)*	*Wt.% EO (theoretical)*	A_E	*Moles EO (experimental)*
Teric 17A2	2.5	2.9	33.0	33.5	2.9
Teric 17A3	3.5	3.7	38.5	39.6	3.9
Teric 17A6	6.5	6.7	53.1	52.9	6.6
Teric 17A8	8.5	8.9*	62.1	62.2	9.0*
Teric 17A10	10.0	10.9	64.9	65.7	11.3

* Based on a fatty alcohol average mol. wt. of 240.

composition. These other products also included propylene oxide–fatty alcohol condensates.

In the case of mixed alkylene oxide–fatty alcohol condensates, it was necessary to operate the gas chromatograph under isothermal temperature conditions (50°) for 3 min in order to resolve 1,2-ethylenedibromide and 1,2-propylenedibromide, and follow this with temperature programming at 20°/min to elute the alkyl bromides as shown in Fig. 3. The alkyl bromides detected were C_{12}, C_{13}, C_{14} and C_{15}, the distribution of which corresponded to a fatty alcohol fraction of average molecular weight 205.

Table II lists the manufacturer's composition and specification. In each case the results of the GLC method are within the manufacturer's specifications.

The experimental results shown in Tables I and II are the average of duplicate samples, and the reproducibility of determination was ±0.15 mole for both ethylene and propylene oxides.

TABLE II

DETAILS OF RESULTS OBTAINED FROM COMMERCIAL ETHYLENE OXIDE/PROPYLENE OXIDE–FATTY ALCOHOL CONDENSATES

Sample	*Manufacturer's specification EO (±1)+PO (±1)*	A_T	A_{EP}	*Mole fraction EO in alkylene oxide*	*Experimental EO+PO*
DS 6326	8.0+2.0 (block)	70.2	0.806	0.826	8.5+1.8
DS 6327	6.0+3.0 (block)	70.8	0.658	0.673	6.8+3.3
DS 6328	8.0+4.0 (block)	69.2	0.662	0.675	8.0+3.9
DS 6330	5.4+1.0 (random)	53.2	0.836	0.855	4.3+0.7
DS 6331	8.3+1.6 (random)	67.1	0.834	0.855	7.8+1.3
DS 6332	11.3+2.1 (random)	76.1	0.838	0.860	12.1+2.0

An advantage of this method, as compared with NMR procedures[5], is that the molecular weight of the fatty alcohol portion can be determined experimentally. The use of the alkyl bromides for determining the average molecular weight of the alcohol fraction agreed within ±5 of that obtained by hydroxyl values on the raw material.

The reproducibility of triangulation and disc integration methods for peak area calculations was unsatisfactory, and the use of the electronic integrator was necessary in order to obtain reliable measurements.

Free fatty alcohols will interfere with the determination and should, if present, be removed by column chromatography on silica gel[6] prior to fission.

CONCLUSIONS

The quantitative analysis of fatty alcohol alkoxylates (ethylene and/or propylene oxide) is achieved by fission of the ether groups with 50% HBr–glacial acetic acid reagent. The procedure is rapid, requires only milligram quantities of sample, and does not require prior knowledge of the molecular weight of the fatty alcohols used. The method has been used successfully in our laboratories for the routine analysis of commercial condensates of this type.

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REFERENCES

1 P. Bore and Mme Gataud, *Rev. Fr. Corps Gras*, 10 (1963) 399.
2 A. Mathias and N. Mellor, *Anal. Chem.*, 38 (1966) 472.
3 J. B. Stead and A. H. Hindley, *J. Chromatogr.*, 42 (1969) 470.
4 B. G. Luke, 1972, unpublished work.
5 R. T. Parfitt, *Perkin-Elmer Instrument News*, 20, No. 4 (1970) 8.
6 M. J. Rosen, *Anal. Chem.*, 35 (1963) 2074.