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Gas-liquid chromatographic determination of free polyglycols in polyoxyethylated commercial stearic acid via their acetate esters

We have carried out an accurate quantitative determination of polyglycols in polyoxyethylated commercial stearic acid by gas chromatography (GC) of their oxyethylated acetyl derivatives.

The condensation of fatty acids with ethylene oxide in the presence of an alkaline catalyst yields a mixture of monoesters, diesters and polyglycols[1]. The polyglycols thus obtained do not have sufficiently long hydrophilic chain portions, and do not show the surface-active and lubricant properties of the monoesters and the diesters, which, on the contrary, have sufficiently long hydrophilic and hydrophobic chain portions. The amount of polyglycols present in the commercial oxyethylated fatty acids is therefore an important factor in determining the product properties.

Studies have been carried out in our laboratories to improve the analysis of commercial stearic acid (a mixture of stearic and palmitic acids) oxyethylated with up to 6 moles of ethylene oxide, widely used as a textile finish.

The improvement consists in the acetylation of oxyethylated stearic acid. The polyglycols are then quantitatively determined by GC in comparison with an acetylated polyglycol of molecular weight 250–300.

Experimental

The acetylation was carried out with acetic anhydride in the presence of pyridine[2]. 0.4 g of oxyethylated stearic acid or 0.1 g of polyglycols was treated in a 250-ml iodine flask at 90–95° for 1 h with 10 ml of a 25% solution of acetic anhydride in pyridine. This mixture was then analyzed by GC.

The GC was carried out with an F & M gas chromatograph, Model 720, with a filament detector, fitted with a stainless-steel column (650 mm length, 4 mm diameter), filled with 80–100 mesh, acid-washed chromosorb W containing 20% SE-30.

The operating conditions were: injector temperature, 260°; detector temperature, 270°; column temperature, programmed from 175° to 307° at a rate of 15°/min; carrier gas, nitrogen; carrier gas speed, 40 ml/min; paper speed, 0.5 in./min.

The sample of pure oxyethylated fatty acids was prepared by treating a sample of commercial stearic acid, oxyethylated with 6 moles of ethylene oxide, with a mixture of solvents of different polarities[3]. A fraction of oxyethylated, polyglycol-free products was obtained, which consisted of fatty acids oxyethylated with 3–5 moles ethylene oxide and of diesters. This fraction was then eluted through a chromatographic column[4] with an eluotropic series of solvents, to give fractions with different weights. The fraction corresponding to fatty acids oxyethylated with 4 moles of ethylene oxide, determined via the hydroxyl number[2], was acetylated.

Results and discussion

The GC of acetylated polyglycol with molecular weight 282 yielded seven peaks, which indicate the molecular distribution of the sample (Fig. 1). The same seven peaks were also present in the gas chromatogram of the acetylated sample of

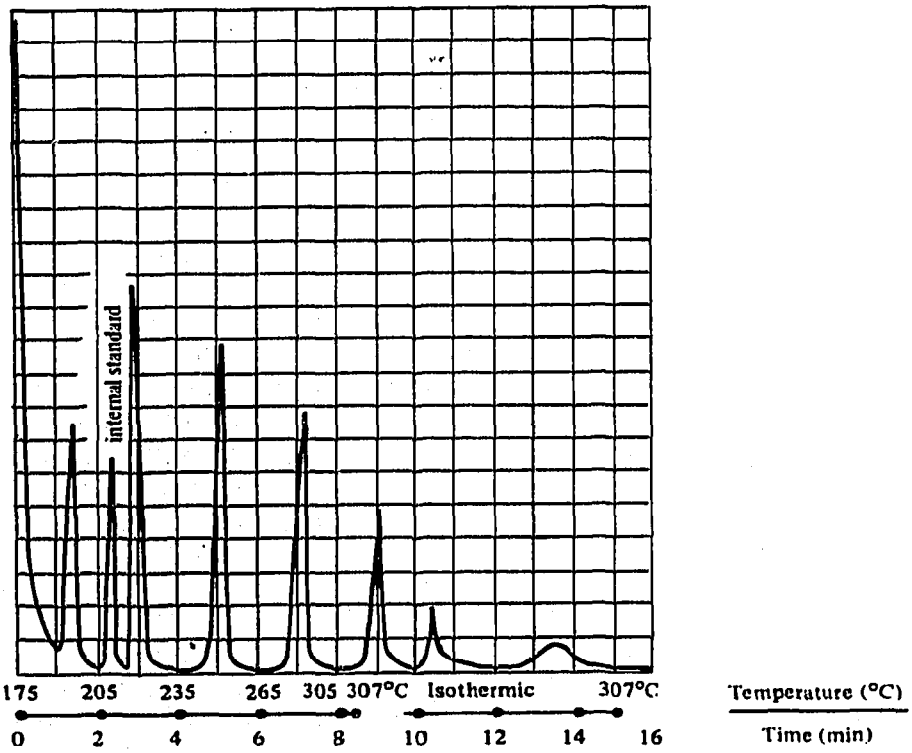

Fig. 1. Gas chromatographic distribution of acetylated polyglycol of molecular weight 282.

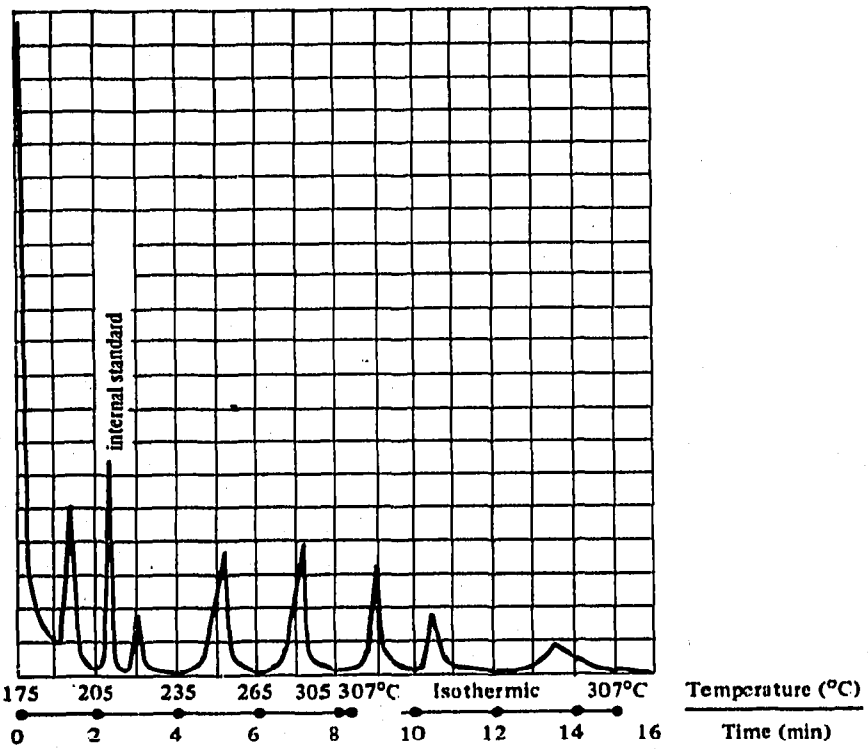

Fig. 2. Gas chromatographic distribution of an acetylated sample of commercial oxyethylated stearic acid (6 moles of ethylene oxide).

commercial oxyethylated stearic acid (6 moles of ethylene oxide) (Fig. 2). Their quantitative evaluation, using a solution of diphenylmethane in ethanol (6% v/v) as an internal standard, showed that the sample of commercial oxyethylated stearic acid contained about 10% of free polyglycol. To show that the products evolved did not decompose under the operating conditions used, a fraction of oxyethylated stearic acid was freed from polyglycols (see *Experimental*) and analyzed by GC. It did not show any peaks corresponding to polyglycols.

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