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Note

Improved high-performance liquid chromatographic analysis of ethylene oxide condensates by their esterification with 3,5-dinitrobenzoyl chloride

AKIO NOZAWA and TOSHIO OHNUMA

Nikkol Technical Center, Nihon Surfactant Kogyo K.K., 3-24-3 Hasune, Itabashiku, Tokyo (Japan)

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Since the character of non-ionic surfactants produced by addition of ethylene oxide to primary alcohols is very closely affected by the distribution of the condensates, its accurate and convenient analysis is indispensable. Although several column chromatographic and thin-layer chromatographic methods have been proposed for these materials¹⁻³, they are not convenient for routine work because of the lengthy chromatographic steps in the former and the complexity of the procedures in the latter. Gas chromatographic methods are also available and they can be carried out more easily than those previous chromatographic methods, but still their uses are limited only for the shorter ethylene oxide units; for example the analysis of materials containing more than 12 ethylene oxide units is difficult^{4,5}.

Recently, high-performance liquid chromatographic (HPLC) methods were proposed for the analysis of these materials. An HPLC method using a flame-ionization detector (FID) was proposed⁶ but this also seems to be inconvenient for routine work because the detector is delicate and much skill is necessary in order to obtain reproducible results. The HPLC methods using UV detectors seem to be easier than the FID method. However, their use is limited to condensates of alkylphenols having strong UV absorption^{7,8}.

Our results show that the esters of these ethylene oxide condensates, represented by $R-(O-CH_2-CH_2)_n-OH$, with 3,5-dinitrobenzoyl chloride were separated satisfactorily by HPLC under certain conditions and were detected easily by UV detector. Hence this HPLC method of esterification products can be applied to the analysis of non-ionic surfactants containing polyoxyethylene chains of different lengths.

EXPERIMENTAL

Materials and reagents

The non-ionic surfactant samples, polyoxyethylene monododecyl ethers, were prepared in our laboratory by the normal method of adding ethylene oxide to dodecanol under base-catalyzed conditions. The arithmetic average value of the ethylene oxide units was measured by determining the number of moles of the hydroxyl group per gram by an acetylation method. In this paper, the average value of the ethylene oxide units will be denoted by \bar{n} . Standard samples of 3,5-dinitrobenzoyl esters, each

having one single polyoxyethylene chain length (n of 0, 2, 4 and 6), were prepared from homogeneous polyoxyethylene monododecyl ethers (Nihon Surfactant Kogyo K.K., Tokyo, Japan). Their purity was found by means of HPLC to be higher than 98%.

Other reagents were analytical grade.

Apparatus

A liquid chromatograph system, Hitachi Model 635 (Hitachi, Tokyo, Japan), including a double-plunger type pulseless pump, a loop-type sampling valve, and a Hitachi Model 200-10 UV spectrophotometer with a micro flow-cell operated at 254 nm; was used. The columns were 250 × 4.0 mm I.D. stainless-steel tubes, packed

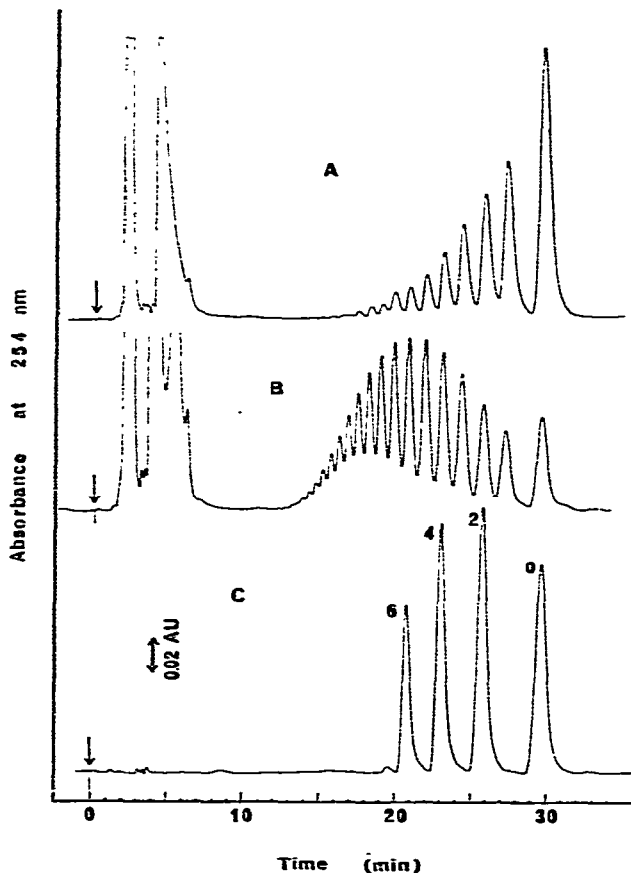


Fig. 1. Chromatograms of esterification products of polyoxyethylene monododecyl ethers with 3,5-dinitrobenzoyl chloride samples. (A) \bar{n} of the condensates was 2, the peaks were identified as materials of 0 and 1–10 ethylene oxide units from right to left; pre-peaks on the left were due to excess 3,5-dinitrobenzoyl chloride. (B) \bar{n} of the condensates was 7, the peaks were identified as materials of 0 and 1–16 ethylene oxide units from right to left; pre-peaks on the left were due to excess 3,5-dinitrobenzoyl chloride, (C) Standard sample prepared by mixing homogeneous esters having polyoxyethylene length 0, 2, 4 and 6.

with LiChrosorb RP-2, 5 μm size (Merck, Darmstadt, G.F.R.). An acetonitrile-water solvent (6:4) was used as the mobile phase at a flow-rate of 0.8 ml/min. The columns were thermostated at $50 \pm 0.2^\circ$. A Shimadzu Model C-E1B digital integrator (Shimadzu, Kyoto, Japan) was used for the analysis of the peak areas.

Procedures

About 0.1 g of the sample and twice that amount (by mole units) of 3,5-dinitrobenzoyl chloride were allowed to react in 20 ml of pyridine at 65° for 30 min. After the reaction was completed, the pyridine was evaporated. A tetrahydrofuran solution containing 2–3% of the esterification products was prepared and injected into the chromatograph system.

RESULTS AND DISCUSSION

It was found that all the samples of the esterification products whose \bar{n} was 2, 5 and 7 were well separated by HPLC. Fig. 1 shows chromatograms of samples with $\bar{n} = 2$ and 7 and also the standard sample. Polyethylene oxide units whose \bar{n} was zero to more than 20 in the sample of $\bar{n} = 7$ were effectively separated as is seen in Fig. 1. The pre-peaks are probably due to excess 3,5-dinitrobenzoyl chloride and some of the by-products, such as pyridine chloride. However, these peaks do not interfere with the analysis of the chromatograms.

The peaks in Fig. 1 were identified by comparing them with those obtained from standard samples prepared from pure polyoxyethylene monododecyl ethers.

Since the molar absorption coefficients of these 3,5-dinitrobenzoylates are for all practical purposes identical, these chromatograms should give the molar distribution of the polyoxyethylene units without making any correction. The distribution of the polyoxyethylene units in those materials was determined easily on the basis of the area of each peak which was calculated by a digital integrator applying the vertical separation method.

However, the longer the polyoxyethylenen chain, the poorer the separation, so that the analysis of high \bar{n} samples becomes difficult. The details of an improved statistical method to treat such data will be published in the near future.

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