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APPLICATION OF BONDED DIOL PHASES FOR SEPARATION OF ETHOXYLATED SURFACTANTS BY HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY*

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SUMMARY

By applying hexane–isopropanol–water mobile phases containing different ratios of hexane to isopropanol, either ethylene oxide adduct (EOA) or polyethylene glycol (PEG) oligomers can be separated on a bonded diol phase and their distributions evaluated. The PEG or EOA oligomers can easily be separated up to the 30-mer even without gradient elution, and ethoxylated surfactants up to an ethoxylation degree of 20:1, *i.e.*, products of fatty alcohols, fatty acids, fatty acid monoethanolamides and alkylphenols, can be analyzed.

INTRODUCTION

Various chromatographic separations of ethoxylation products used as non-ionic surfactants a performed for the determination of the ethylene oxide adduct (EOA) distribution, for the evaluation of the free polyethylene glycol (PEG) content or for the determination of non-ethoxylated hydrophobic residues. The application of thin-layer chromatography (TLC) is limited chiefly to qualitative analysis[1,2], whereas gas–liquid chromatography (GLC) is unable to separate higher molecular weight EOAs[3–6] owing to their low volatility, in spite of derivatization. The potential of high-performance liquid chromatography (HPLC) for the separation of ethoxylates, has recently been demonstrated[7,8]. For these analyses, silica gel columns were applied under conditions of adsorption chromatography[9–14]. Attention has also been paid to the use of sorbents with bonded stationary phases of the C_2, C_8, C_{18}, CN or NH_2 types[12,15–24] using more polar mobile phases under isocratic elution[9,12,13,19], flow-rate[13] or polarity gradient elution conditions[9–12,14,15,17,18], where however differential refractometric detection is excluded. In all these papers, only the distribution of EOA is presented, not the presence and distribution of free PEG.

For the determination of the free PEG content in ethoxylation products, reversed-phase separations in polar mobile phases are sufficient[22,25–28]: under these conditions, all PEG oligomers are eluted first as a single peak without any resolution

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so that their distribution cannot be evaluated. The application of gel permeation chromatography for the determination of this distribution[29,30] or of PEG separation on a reversed phase[31] cannot provide any information on the EOA distribution. The parallel or subsequent separation of all oligomers of both PEG and EOA cannot be achieved during a single HPLC experiment even when using gradient elution.

In a search for suitable sorbents and mobile phases for the HPLC separation of fatty acid ethoxylation products, a system was found which separated the fatty acid diesters from the monoesters, and also separated the PEG oligomers[32]. Owing to the interactions between the polyether groups of the PEG chains and of the hydroxyl groups of PEG and of the fatty acid monoesters with a bonded stationary phase of the diol type, the separation is performed in *n*-hexane–isopropanol–water containing a trace of acetic acid[33]: even without gradient elution, PEG oligomers up to the 32-mer were separated and detected by differential refractometry. A similar system was recently used for ethoxylates[20], where the mobile phase was a *n*-hexane–isopropanol mixture, but the separation of PEG oligomers was incomplete. The idea to apply a bonded glycol-type phase for the HPLC separation of PEG stems from the attempt to use Carbowax 20M bonded to silica gel[15].

It followed that both the PEG and EOA distribution can be determined by changing the mobile phase polarity. Thus this paper describe the application of a diol-type bonded phase to the HPLC separation of EOA and free PEG oligomers in various ethoxylated surfactants, to the HPLC analysis of the corresponding isolated EOAs and to the monitoring of different PEG samples.

EXPERIMENTAL

All reagents and solvents were of analytical grade (Labora, Prague, Czechoslovakia). All solvents for HPLC were redistilled from glass before use. The samples of ethoxylated fatty acids were provided by Dr. J. Šilha, Department of Milk and Fat Technology, Institute of Chemical Technology, Prague. Various other ethoxylated surfactants were prepared by Dr. M. Paulovič, Research Department, W. Pieck Chemical Plant, Nováky. All ethoxylates were prepared in closed vessels using various catalysts, *i.e.*, by ethoxylation under pressure. The PEG samples were commercial products provided by Lachema (Brno, Czechoslovakia) and W. Pieck Chemical Plant. Pure lower glycols were applied as standards for identification, namely ethylene glycol, diethylene glycol, triethylene glycol and tetraethylene glycol: they were prepared from commercial samples provided by Lachema. Other standards (lower ethylene oxide adducts) were prepared and purified by Dr. Silha.

HPLC separations were performed on a Knauer LC instrument, consisting of a pump Type 52.00, RI/UV detector Type 61.00 and a Rheodyne 7120 sample injection valve with a 20-μl sampling loop. The columns used were: 1, stainless steel, 25 cm × 4.6 mm I.D., LiChrosorb DIOL, 10 μm; 2, stainless steel, 25 cm × 4.0 mm I.D., LiChrosorb DIOL, 5 μm. The mobile phases comprised *n*-hexane, isopropanol, water and acetic acid in various ratios: A, 75:125:10:1; B, 90:110:10:1; C, 105:95:10:1; D, 120:80:10:1; E, 125:75:10:1; F, 140:60:5:1. For separations on column 1 with mobile phase C the flow-rate was 1.0 ml/min; on column 2 with all mobile phases, the flow-rate was 0.8 ml/min. In some analyses the technique of back-flushing of the PEG fraction was applied using a six-way switching valve Rheodyne 7010 connected via an apropriate column joint to the individual channels.

The identification of ethylene glycol, diethylene glycol, triethylene glycol and tetraethylene glycol peaks was performed by use of standards. The identification of higher PEG oligomers was carried out by adjusting further PEG peaks in the series on chromatograms to penta-, hexa-, heptaethylene glycol, etc. A similar procedure was used to identify higher EOA oligomers. For some samples of ethoxylated surfactants, especially those of fatty acids, a preliminary separation of EOA and PEG fractions was performed using the standard Weibull procedure[34].

The reproducibility of HPLC retention data measured for identification purposes was very good, better than 2% relative within a series of analyses and over a long period of time. For the analysis of ethoxylated surfactants on the bonded diol phases, no deterioration in column efficiency was noted.

RESULTS AND DISCUSSION

Separations of ethoxylated surfactants are illustrated in Figs. 1–3. In Fig. 1, the EOAs isolated from products of lauric acid ethoxylation (1 mol per 9 mol EO) according to Weibull[34] were separated by use of three mobile phases of different polarities, C, D and F. In these separations, where PEG oligomers were absent, the EOAs, are separated in the mobile phase of highest polarity (C) into two main peaks corresponding to diester oligomers (first unresolved peak) and to monoester oligomers (second peak showing a partial separation); using the less polar mobile phase D, the separation of the monoester oligomers is more evident and with the mobile phase of lowest polarity (F) is nearly complete. A complete separation of EOA oligomers with mobile phase F was achieved also for other ethoxylated surfactants from lauryl alcohol (1 mol per 6 mol EO) and dodecylphenol (1 mol per 6 mol EO), as is evident in Figs. 2 and 3.

An example of the complete separation of a lauric acid ethoxylate of lower ethoxylation degree in the mobile phase of moderate polarity (C) is given in Fig. 4, where mono- and diester adduct oligomers remained unresolved in two distinct peaks, whereas the PEG fraction is separated into individual oligomers. The separation of PEG oligomers is easily achieved with mobile phase B or C, where PEG oligomers up to the 30-mer can be separated. Thus, Fig. 5 shows the analyses of PEG fractions isolated by Weibull's procedure[34] from ethoxylated fatty acids of different degrees of ethoxylation, *i.e.*, 1 mol per 3, 9, 12 or 20 mol EO.

Fig. 6, shows a semilogarithmic plot the retention of PEG oligomers against the number of ether groups in the molecules. The influence of the mobile phase polarity is substantial: whereas in mobile phases of lower polarity (E, F) only lower PEG oligomers can be separated, optimum separation is achieved in mobile phases of moderate polarity (B and especially C), where PEG oligomers even higher than the 30-mer are sufficiently separated in a reasonable time; in more polar mobile phases such as A the separation of PEG oligomers is incomplete, but on the other hand, fractions of broader distribution or higher mean molecular mass can be analyzed, at least up to MW 4000.

The nature of the separation in the present system evidently involves the interaction of free hydroxyl and polyether groups: it is determined by the relative number of these groups in EOA and PEG oligomers. This is the reason for the increasing retention in the series non-ethoxylated hydrophobic residues (without PEG chain),

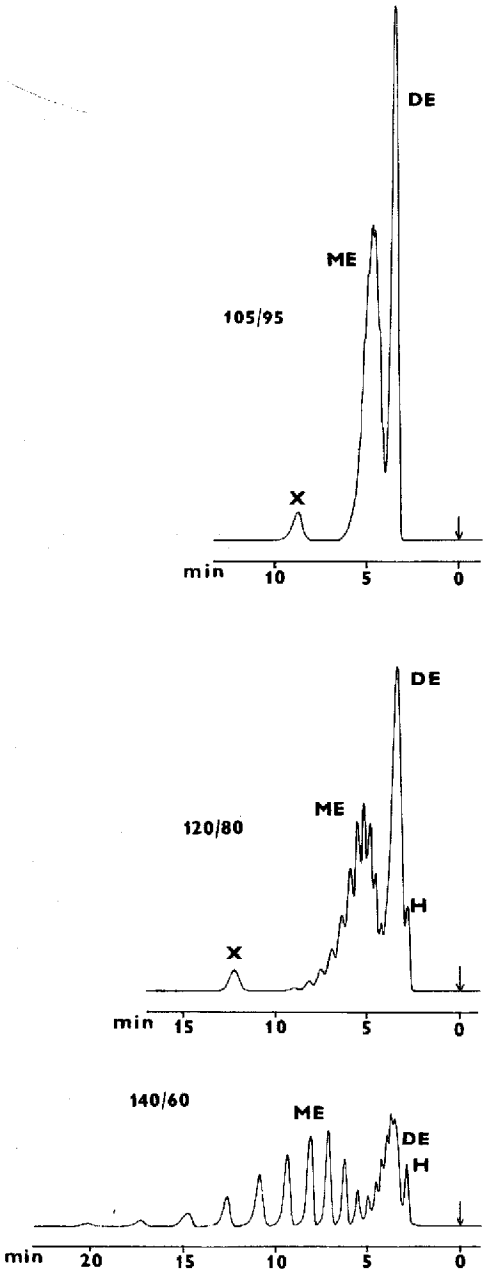

Fig. 1. Separation of EOAs isolated from products of lauric acid ethoxylation in three different mobile phases: C, 105:95; D, 120:80 and F, 140:60 The (hexane–isopropanol ratio) ethoxylation degree was 9 mol EO per mol acid. H = Non-ethoxylated residue; DE = unresolved diester oligomers; ME = monoester oligomers; X = unidentified component.

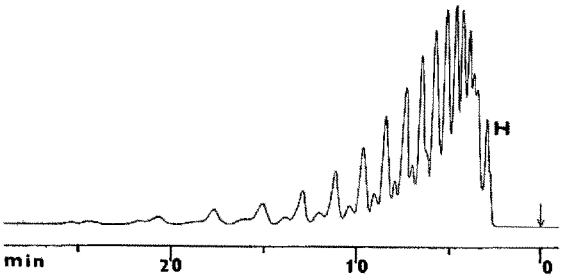

Fig. 2. Separation of lauryl alcohol ethoxylated by 6 mol EO: the higher peaks are due to EOAs of C_{12} chain length, the small peaks between them are due to C_{14} EOA present as impurity. The first leading peak is unreacted fatty alcohol. The separation was performed using mobile phase F.

EOAs with one hydroxy group and several ether groups and PEGs with two hydroxy groups and several ether groups. For EOA and PEG oligomers, the separation is determined by the number of ether groups. On the other hand, the retention of ethylene glycol and diethylene glycol in these mobile phases is nearly the same.

This general retention order of ethoxylation products on bonded diol phases using mobile phases of controlled polarity is the reverse of that on alkyl bonded phases using polar, *e.g.*, methanol–water, mobile phases[22,25–28]. Whereas the analysis of ethoxylates on alkyl bonded phases may be suitable for determining the free PEG content, the present system may be more advantageous because the complete distribution of the PEG fraction can be recorded. Thus the calibration problem for PEG can be solved by use of the dependence of the relative response of the differential refractometric detector on n_D data for the PEG oligomers[33], whereas the corresponding calibration on alkyl bonded phases is dependent on the mean molecular mass, which cannot be exactly determined in the given system[27].

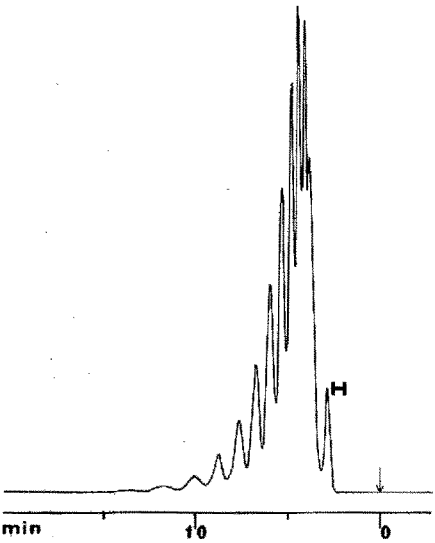

Fig. 3. Separation of EOA from dodecylphenol ethoxylated by 6 mol EO using mobile phase F. The first peak is unreacted dodecylphenol residue.

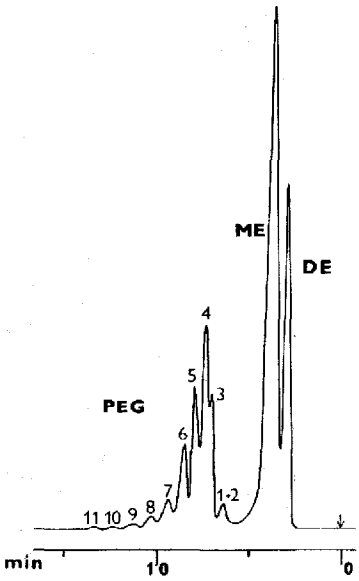

Fig. 4. Separation of the ethoxylation products of lauric acid with 20 mol EO using a polymer catalyst. DE = Diester oligomers; ME = monoester oligomers; PEG = distribution of PEG oligomers.

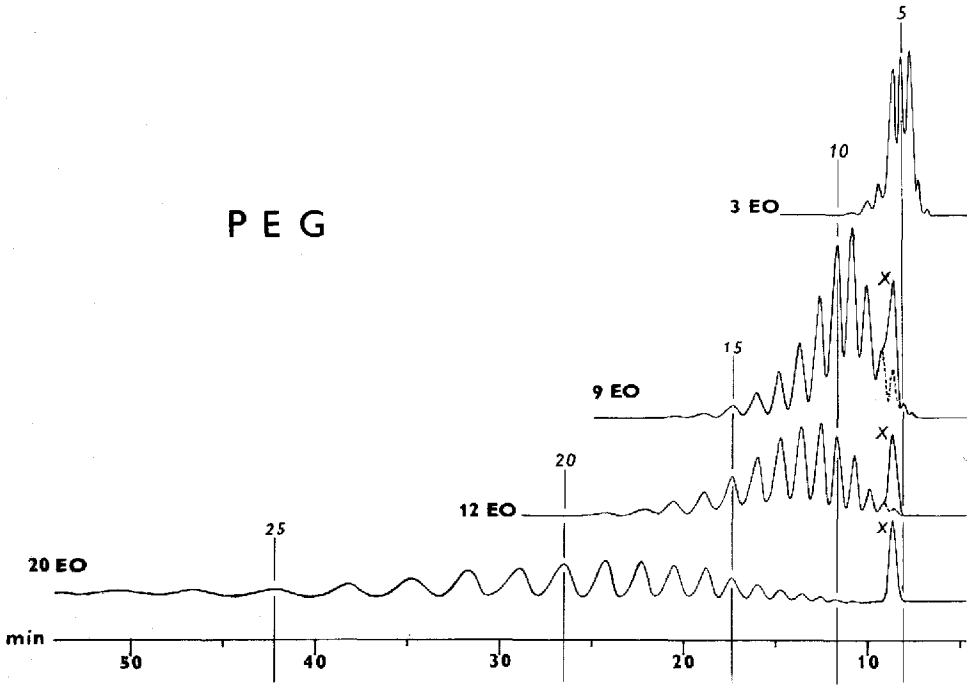

Fig. 5. Separation of PEG fractions, isolated from lauric acid ethoxylates with 3, 9, 12 and 20 mol EO, using mobile phase C. The 5-, 10-, 15-, 20- and 25-mer are indicated. X represents an unidentified component in the region of the 6-mer.

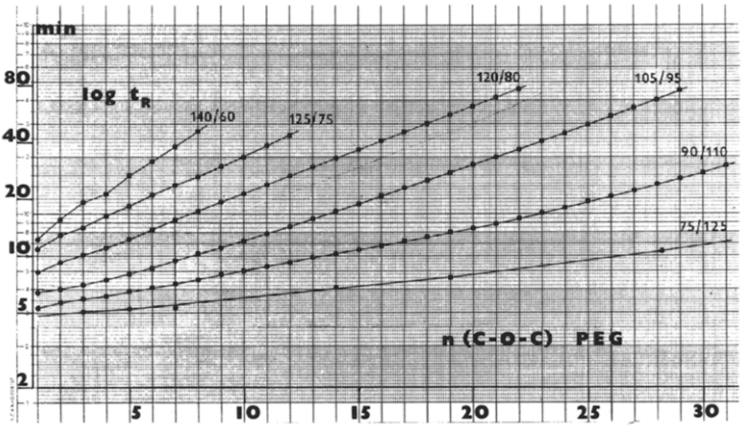

Fig. 6. Dependence of the retention of PEG oligomers, log t_R (min), on the number of ether groups in the molecules for mobile phases A–F of different polarities. The *n*-hexane–isopropanol ratios are indicated.

Thus for the complete analysis of ethoxylated surfactants on a diol phase two procedures can be applied: (a) two analyses are performed one for the determination of the EOA distribution using mobile phase F with elution of the PEG fraction as a single peak by back-flushing and a second for the determination of the PEG distribution using mobile phase C where EOAs remain unresolved; or (b) the EOA and PEG fractions are pre-separated by an appropriate procedure[34] and then analyzed separately using mobile phase F for the EOA fraction and mobile phase C for the PEG fraction. On alkyl and other bonded phases or on bare silica gel, such combinations even with gradient elution have not been described till now[9–24].

CONCLUSION

The application of a bonded diol phase and *n*-hexane–isopropanol–water mobile phases of controlled polarity seems to be a valuable procedure for the analysis of different ethoxylated surfactants without gradient elution. Samples up to an ethoxylation degree of 20 mol EO per mol hydrophobic compound can be separated in isocratic systems with refractometric detection, encompassing the distribution of EOA and PEG oligomers higher than the 30-mer. The distribution of both the EOA and PEG fractions can be determined in two analyses in mobile phases of different polarities either by use of the original samples and applying back-flushing, or after preseparation of both fractions. This system can also be used for the determination of the free PEG content in ethoxylated surfactants.

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