SCIENTIFIC PAPERS
OF THE UNIVERSITY OF PARDUBICE
Series A
Faculty of Chemical Technology
5 (1999)

THE APPLICATION OF DERIVATIZATION AND RETENTION INDICES SYSTEM FOR IDENTIFICATION OF ALKYLPOLYETHYLENE GLYCOL ETHERS BY CAPILLARY GAS CHROMATOGRAPHY

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Received March 31, 1999

This study deals with the possibility of GC analysis of individual alkylpolyethylene glycol ethers (APEGEs) $C_4 - C_{10}$. The possibilities of derivatization reactions of these substances and the advantages of the derivative preparation are discussed. APEGEs were coverted into three types of derivatives: acetates, trifluoroacetates and trimethylsilyl ethers. The retention indices of individual oligomers of APEGEs and their derivatives for the column temperature programmed linearly were measured. The influence of an increase in the lenght of the chain in the alkyl or polyoxyethylene glycol part of molecule of non-derivatized APEGEs and their derivatives on the retention indices was studied.

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Introduction

Alkylpolyethylene glycol ethers rank among commercially important non-ionic surfactants. Surface active agents usually contain a hydrophobic hydrocarbon chain and a hydrophilic group. All these compounds exhibit asymmetry and they can adsorb at different phases and can decrease surface and interfacial tensions.

The use of non-ionic surfactants based on APEGEs is very wide spread and varied. In addition there are hundreds of polyoxyethylene alcohols produced commercially. Some of these products are designed just for a specific application, others have a variety of applications. The largest demand for APEGEs is in the formulation of detergents for household and industrial use. They can be compounded as liquids, powders and pastes. Non-ionic surfactants play a very important role in the textil-scouring operations for both natural and synthetic fibers. Polyoxyethylene alcohols are excellent emulsifiers for agricultural sprays too.

Non-ionic surfactants are usually prepared under base-catalyzed conditions by the addition of ethylene oxide to hydrophobic compounds containing one or more active hydrogen atoms, such as alkylphenols, fatty alcohols, fatty thiols, fatty amines, fatty amides and polyols. APEGEs are prepared by reactions of ethylene oxide with primary linear or branched-chain alcohols. In this reaction ethylene oxide adds to hydroxyl groups with regeneration of hydroxyl group.

During oxyethylenation of individual alcohols for example by three moles of ethylene oxide, not just one component, i.e. alkyltriethylene glycol ether arises, but a homologous series of alkylpolyethylene glycol ethers with 1-8 oxyethylene groups were found in the reaction mixtures. Compounds with more than five oxyethylene units are less common in these reaction mixtures. That is why APEGEs are complex mixtures containing unethoxylated alcohols plus series of homologous compounds that differ in the lenght of the ethoxylated as well as alkyl chain.

Lower oxyethylenated alcohols are analysed by gas chromatography or by gas chromatography — mass spectrometry. Besides the direct gas chromatography analysis of nonderivatized APEGEs it is also possible to convert them into acetates, trimethylsilyl ethers, trifluoroacetates or other volataile derivatives and analysed them afterwards, but only if they contain homologues having less than 13 – 15 oxyethylene groups. The identification of particular components is realized by means of standards, by retention index systems or by mass spectrometry with electron — impact or chemical ionization.

Reasons for Derivatization in Gas Chromatography

The presence of different polar groups in the molecules of APEGEs is the most significant source of the difficulties in their GC analysis. Hydroxyl group owing to its polarity and tendency to form hydrogen bonds, is responsible both for the low

volatility of these compounds and is the source of strong adsorption on the support of the stationary phase and asymmetry of peaks eluted from the column.

The non-quantitative elution and the losses of the sample compounds in the chromatographic system make direct GC analysis difficult or impossible. The separation of closely related compounds is another very important example of the application of derivatization in GC. Derivatives of sample compounds are commonly used also for their detection. Substances are converted into suitable derivatives for which selective and sensitive detectors can be used.

Gas chromatography analysis with electron impact ionization is shown in Vettori's [1] study. This technique is excellent for the analysis of complex mixtures of oxyethylenated fatty alcohols with a low degree of polymerization. Straight and branched-chain oxyethylenated alcohols in commercial raw materials were detected and identified by their fragmentation modes and their retention times.

Lekova and Ivanova [2] separated non-derivatized lower APEGEs. The measurements were performed with linear temperature programming and the analyses were carried out on the packed column Chromosorb P + 15% PEGS. The retention behaviour of APEGEs was described by retention indices and relative retention temperature. The polar character of APEGEs caused problems in their analyses and peak tailing and losses of sample were observed.

Higher oxyethylenated alcohols were analysed by Jaworski and Krogulecki [3]. They optimized the method for analysis on the packed column with Chromosorb W AW DMCS coated with OV-225. The main problems were long intervals between retention times of individual oligomers and the peaks tailing. The suitable temperature programme from 70 °C to 300 °C with a gradient of 10 °C min^{-1} removed these troubles and the dependences of retention indices on the number of oxyethylene groups were linear.

Linkiewicz and Poskrofko [4] elaborated an analytical method for oxyethylenated methanol, ethanol and butanol. Two glass columns were packed with Chromosorb G AW coated with OV-225 and OV-17 stationary phases. They measured the retention indices for linearly programmed temperature from 70 °C to 200 °C at the rate of 4 °C min^{-1}.

Acyl Derivatives

Acylation is one of the most widely used derivatization procedures for chromatography and acyl derivatives are common derivatives for hydroxy, amino and thiol groups. As they eliminate unfavourable properties of these groups, the derivatives are used in the GC of substances containing several of these functional groups. The derivatives are usually less polar than the original substances, their tendency to form hydrogen bonds decreases and their volatility increases so that non-volatile and thermally unstable compounds can be chromatographed. Halogen-

ated acyl derivatives are frequently applied in trace analysis because of their generally high ECD responses.

The preparation of acyl derivatives consists in the reaction of an excess of an acylating reagent, usually anhydride of the corresponding acid, acyl halides or reactive acyl derivatives such as acylated imidazoles in pyridine, tetrahydrofuran or another solvent capable of binding the acid produced. From among the halogenated derivatives the most frequently used are trifluoroacetates. Other perfluorinated acyl derivatives are also prepared, such as heptafluorobutyrates, pentafluoropropionates and pentafluorobenzoates.

Silver and Kalinoski [5] used capillary high temperature gas chromatography for the quantitative characterization of non-ionic oxyethylenated alcohols C_{12} – C_{18}. In their work they used two derivatization procedures: acetylation with acetic anhydride and pyridine, and silylation with *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) and pyridine. The derivatization was carried out in vials closed with teflon-lined caps and heated at approximately 60 °C for 30 min. The column temperature was 100 °C, initial time 2 min, then programmed at 4 °C min^{-1} to 375 °C and held at that temperature for 15 min. In addition, they determined flame ionization molar response factors based on the effective carbon theory.

The influence of the functional group from the derivatizating agent introduced into molecule of higher APEGEs C_{12}, C_{14} and C_{16} on the retention index was studied by Komárek, Minář and Škvarenina [6]. Alkylpolyethylene glycols were converted by derivatization reactions into acetates, monochloroacetates, trifluoroacetates and trimethylsilyl ethers. The retention indices were calculated for linearly programmed temperature from 120 °C to 370 °C at the rate 5.5 °C min^{-1}.

Szymanowski and Voelkel [7] converted APEGEs C_{12}, C_{14} and C_{16} into acetates and trimethylsilyl derivatives. The derivatives were prepared by using acetyl chloride and *N,O*-bis(trimethylsilyl)acetamide (BSA). The separation was carried out in stainless columns. Chromosorb G AW DMCS (60 – 80 mesh) was used as the support and silicone resin OV-17 (3% w/w) as the liquid phase. The analyses were started with a column temperature of 130 °C, which after 1 min was programmed for a rate of change of 4 °C min^{-1} up to 320 °C. For all the separated oligomers of acetates and TMS ethers were determined the values of the arithmetic retention indices.

The influence of a branching and increase in the lenght of alkyl and polyoxyethylene chain in homologous series of *n*-butyl, *iso*-butyl, *n*-amyl and *iso*-amylpolyethylene glycol ethers on the retention indices at linearly programmed temperature was studied by Komárek [8]. APEGEs were converted by derivatization into acetates, trifluoroacetates and trimethylsilyl ethers. The derivatives were prepared by reaction of APEGEs with acetanhydride, trifluoroacetanhydride and *N,O*-bis(trimethylsilyl)acetamide (BSA). For linearly programmed temperature from 50 °C to 350 °C at 5.5 °C min^{-1} were measured the retention indices of individual oligomers and their derivatives.

The products of oxyethylenation of 1-nonanol and 1-decanol were derivatized into acetates, trifluoroacetates and trimethylsilyl ethers by Richter, Komárek and Řezníčková [9]. The individual APEGEs were identified by the retention indices for the column temperature programmed linearly. Retention indices were used for identification of residues of APEGEs after their biodegradation.

Silyl Derivatives

These derivatives are probably the most commonly used in the GC of non-volatile substances and for blocking their functional groups. Silyl derivatives can be prepared by the reaction of silylating agent with groups containing active hydrogen atom. There are a number of silyl derivatives and silyl reagents but trimethylsilyl derivatives have maintained their high popularity. Pyridine or another solvent with a large solvation capacity (acetonitrile, dimethylformamide) are mostly used as solvents in the silylation reactions. During the derivatization, anhydrous conditions are necessary because the derivatives are decomposed by traces of water.

Conversion of oxyethylenated alcohols into trimethylsilyl ethers and subsequent high temperature gas chromatography analysis was the aim of Rasmussen's study [10]. Oxyethylenated alcohols with an excess of *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) were heated at 60 °C for 20 min. The column was temperature programmed from 50 °C 3 min a first ramp at 20 °C min^{-1} to 100 °C and the second ramp at 4 °C min^{-1} to 375 °C with a hold time of 15 min. The method was applied to the separation of oxyethylenated alcohols mixtures C_{12} – C_{15} from 1 to 17 oxyethylene groups.

Komárek, Pitthard and Kostrubaničová [11] analysed lower oxyethylenated aliphatic alcohos C_4 – C_{10}, in both the non-derivatized form and after their conversion into trimethylsilyl ethers and acetates, by GC-MS. Individual oligomers of APEGEs were identified by a combination of their electron impact mass spectra and by correlating their retention times with the structure of their molecules. Retention times of the eluted components were used for calculation of the relative retention characteristics, too.

Szymanowski and Szewczyk [12] analysed commercial APEGEs C_8 – C_{22} in the form of acetates and trimethylsilyl ethers. They separated all the polyoxyethylene homologues up to the compounds containing 13 oxyethylene units and measured their arithmetic retention indices for temperature programmed. Trimethylsilyl derivatives eluted somewhat sooner than the corresponding acetate derivatives.

Oxyethylation mixtures obtained from the reaction of dodecanol with ethylene oxide have been analysed by gas chromatography after silylation by Törnquist [13, 14]. He used a mixture of trimethylchlorsilane and hexamethy-ldisilazane as the derivatization agent. Trimethylsilyl ethers were succesfully applied in the separation

of these oxyethylenated adducts. Column temperature was programmed with a gradient of 10 °C min^{-1} from a starting temperature of 100 °C to 380 °C.

The gas chromatographic analysis of commercial APEGEs is described by Stancher and Favretto [15]. Oxyethylenated alcohols $C_{10} - C_{18}$ were converted into trimethylsilyl ethers and analysed on a glass column packed with 80 – 100 mesh Gas-Chrom Q coated with 3% (w/w) GE SE-30. Separation was carried out with a linear temperature programmed from 80 °C to 370 °C at the rate of 10 °C min^{-1}. Conversion into trimethylsilyl derivatives improved the volatility and removed peaks tailing.

Experimental

Reagents

Acetanhydride (VCHZ SYNTHESIA Pardubice), trifluoroacetanhydride and *N,O*-bis(trimethylsilyl)acetamide (Supelco, A. Rohm and HAAS Company), alkanes (Polyscience Corporation Niles, Illinois), oxyethylenated alcohols n-C_4 – n-C_{10} and *iso*-C_4 and *iso*-C_5 (Sloveca, Slovenská EniChem Augusta, Nováky).

Preparation of Derivatives

All the derivatives were prepared on milligram scale in septum closed reaction vials of 1 ml volume. Trimethylsilyl ethers were prepared by the reaction of 20 mg of APEGEs with 100 µl of *N,O*-bis(trimethylsilyl)acetamide. The reaction time was 15 min and the temperature was 40 °C. [16]. The preparation of acyl derivatives is easy and consists in the reaction of 20 mg of APEGEs with 100 µl of acetanhydride or trifluoroacetanhydride in pyridine.The reaction time was 60 min and the temperature was 60 °C [17].

Working Conditions

The studies were carried out on a gas chromatograph MEGA 5160 equipped with a flame ionization detector and with a connected LAB BASE operation system (Carlo Erba-Fisons, Milan, Italy). As a separation column was used a fused-silica capillary column DB-5MS, 20 m × 0.25 mm I. D., film thickness 0.25 µm (J &W Scientific, Folsom, CA, USA). The analyses of mixtures of APEGEs and their derivatives were carried out under following conditions: column temperature programmed linearly from 50 °C to 350 °C at the rate of 5.5 °C min^{-1}, injector and detector temperature was 350 °C, injection system, split-spliting ratio 1:10, carrier

gas helium with an inlet pressure 75 – 100 kPa. The individual oligomers of APEGEs and their derivatives were identified by GC-MS (CI).

Alkanes which are necessary for the calculation of retention indices were injected together with the solution of the homologous series of analysed compounds. Particular APEGEs were dissolved in methanol and their derivatives in benzene. Then these solutions were mixed with the solution of *n*-alkanes in cyklohexane and the mixture was injected into the gas chromatograph.

Results and Discussion

From the measured retention data of *n*-alkanes, APEGEs and their derivatives the retention indices for linearly programmed temperature (I_{LPTx}) were calculated according to the following formula

$$I_{LPTx} = 100z + 100n \frac{T_{Rx} - T_{Rz}}{T_{Rz+n} - T_{Rz}}$$

where T_{Rx}, T_{Rz} and T_{Rz+n} are retention temperatures of component x and *n*-alkanes eluting before and after this component, z and $z + n$ are the number of carbon atoms in *n*-alkanes eluting before and after component x. Retention temperature T_R is defined by equation

$$T_R = T_0 + rt_R$$

where T_0 is the starting temperature, r is the temperature gradient and t_r is the retention time.

The average values of I_{LPTx} of oxyethylenated alcohols $C_4 - C_{10}$ and their acetates, trifluoroacetates and TMS ethers are given in Table I. The measurements were repeated five times and treated statistically by a QUATTRO PRO programme. The I_{LPTx} for trifluoroacetates of APEGEs are lower than I_{LPTx} for non-derivatized APEGEs. For quantitative analysis of these compounds a highly sensitive electron capture detector can be used too. The conversion of APEGEs into acetates or trimethylsilyl ethers does not result in shortening of the analyses time, but makes possible a perfect elution of oligomers with higher number of oxyethylene groups. The chromatogram of the separation of non-derivatized *n*-hexylpolyethylene glycol ethers is shown in Fig. 1. Figure 2 shows the separation of acetates of *n*-hexylpolyethylene glycol ethers with *n*-alkanes.

Table I Retention indices I_{LPTx} of alkylpolyethylene glycol ethers (i-C_4, n-C_4, i-C_5, n-C_5, n-C_6, n-C_7, n-C_8, n-C_9 and n-C_{10}) and their acetates, TMS ethers and trifluoracetates

Substances	*xEO*	I_{LPTx}								
		i-C_4	n-C_4	i-C_5	n-C_5	n-C_6	n-C_7	n-C_8	n-C_9	n-C_{10}
Alcohols	0	657.6	726.4	750.0	819.4	921.5	1024.6	1127.8	1230.0	1333.5
	1	927.0	964.5	1022.6	1060.6	1159.9	1263.6	1359.1	1463.5	1566.7
	2	1220.1	1262.3	1317.0	1358.7	1461.6	1557.5	1657.6	1761.7	1864.1
	3	1514.7	1557.9	1611.0	1653.7	1753.2	1852.3	1949.6	2047.2	2148.2
	4	1799.6	1849.6	1896.7	1946.0	2047.7	2143.9	2240.9	2339.0	2442.0
	5	2092.0	2137.8	2187.6	2234.9	2331.5	2434.3	2532.5	2635.9	2733.7
	6	2380.0	2422.8	2478.0	2519.2	2618.1	2716.2	2814.5	2912.8	3016.4
	7	2660.4	2696.4	2757.1	2793.8	2896.5				
Acetates	0	779.0	830.1	874.6	928.0	1030.4	1133.2	1234.1	1336.1	1437.6
	1	1074.9	1120.2	1175.8	1216.6	1315.4	1411.5	1515.6	1615.5	1717.0
	2	1366.0	1408.2	1463.5	1507.0	1609.0	1713.3	1810.8	1908.7	2007.1
	3	1645.7	1690.0	1746.7	1787.2	1889.5	1992.9	2089.4	2187.5	2287.1
	4	1935.5	1975.6	2034.8	2073.0	2171.4	2275.1	2377.1	2474.2	2576.8
	5	2214.6	2259.8	2310.1	2358.0	2456.3	2554.5	2655.0	2759.3	2855.2
	6	2494.3	2539.8	2592.8	2636.6	2732.9	2834.8	2933.9	3036.6	3140.3
	7	2776.3	2816.6	2874.6	2918.3	3014.0	3114.1	3212.9	3312.4	3415.2
	8	3060.6	3094.1	3162.7	3291.4	3295.1	3395.3	3493.8	3590.3	
	9		3375.7	3446.4	3476.2	3573.8	3676.3			
TMS ethers	0	751.7	793.6	842.2	890.9	987.7	1085.4	1185.8	1289.8	1393.4
	1	1012.4	1068.1	1110.9	1164.9	1262.6	1359.3	1460.9	1557.3	1654.4
	2	1305.5	1341.7	1403.6	1437.2	1535.4	1633.3	1729.0	1826.5	1923.3
	3	1583.5	1613.2	1681.4	1710.9	1808.6	1905.0	2002.2	2096.2	2196.4
	4	1856.0	1885.0	1953.9	1981.0	2078.9	2176.6	2273.6	2371.6	2467.3
	5	2128.1	2161.0	2226.6	2257.2	2353.6	2450.4	2548.3	2643.9	2740.8
	6	2396.6	2430.5	2494.0	2527.1	2623.6	2721.0	2817.2	2912.6	3010.2
	7	2665.4	2702.7	2763.3	2801.6	2898.3	3001.8	3097.4	3194.9	3297.4
	8	2939.8	2982.4	3038.4	3077.4	3174.1	3271.1			
TFA	0	656.4	678.8	752.1	776.2	873.1	973.6	1075.4	1176.3	1273.6
	1	927.4	953.7	1022.3	1051.4	1154.4	1252.4	1348.6	1444.8	1542.0
	2	1196.0	1221.8	1296.4	1319.6	1416.9	1513.3	1609.9	1707.1	1804.3
	3	1451.0	1475.9	1548.0	1575.3	1674.3	1773.5	1872.2	1970.0	2067.8
	4	1704.7	1735.1	1800.8	1836.2	1935.1	2034.8	2131.9	2229.8	2326.0
	5	1973.1	2002.0	2070.1	2102.5	2205.3	2305.3	2402.6	2497.0	2597.0
	6	2233.1	2268.6	2330.6	2366.1	2468.0	2568.5	2668.6	2766.0	2862.7
	7	2498.1	2533.8	2595.1	2629.6	2726.2	2828.7	2925.9	3025.3	3123.1
	8	2760.3	2804.3	2857.4	2901.2	2996.3	3099.3	3196.5		

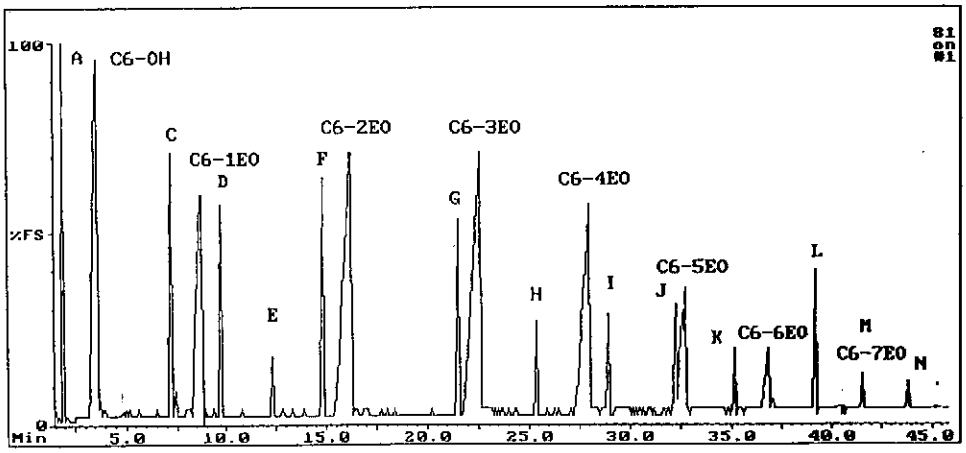

Fig. 1 Chromatogram of the separation of non-derivatized *n*-hexylpolyethylene glycol ethers: C6–OH ..... $CH_3(CH_2)_4CH_2$–OH, C6–1EO – C6–7EO ..... $CH_3(CH_2)_4CH_2$–O–CH_2CH_2OH ..... $CH_3(CH_2)_4CH_2$–O–$(CH_2CH_2O)_6$–CH_2CH_2OH, A – octane, C – undecane, D – dodecane, E – tridecane, F – tetradecane, G – heptadecane, H – nonadecane, I – heneicosane, J – tricosane, K – pentacosane, L – oktacosane, M – triacontane, N – dotriacontane

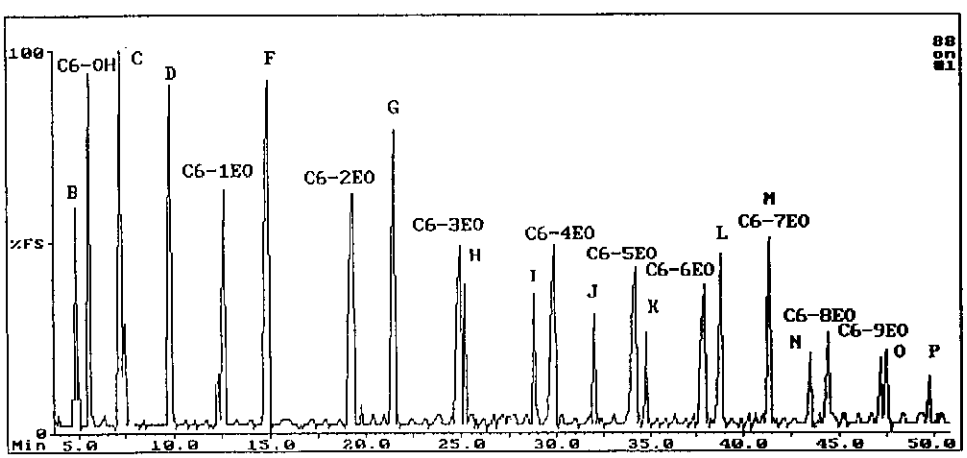

Fig. 2 Chromatogram of the separation of acetates of *n*-hexylpolyethylene glycol ethers: C6–OH ..... $CH_3(CH_2)_4CH_2$–OH, C6–1EO – C6–9EO ..... $CH_3(CH_2)_4CH_2$–O– CH_2CH_2OAc ..... $CH_3(CH_2)_4CH_2$–O–$(CH_2CH_2O)_8$–CH_2CH_2OAc, B – decane, C – undecane, D – dodecane, F – tetradecane, G – heptadecane, H – nonadecane, I – heneicosane, J – tricosane, K – pentacosane, L – oktacosane, M – triacontane, N – dotriacontane, O – hexatriacontane, P – tetracontane

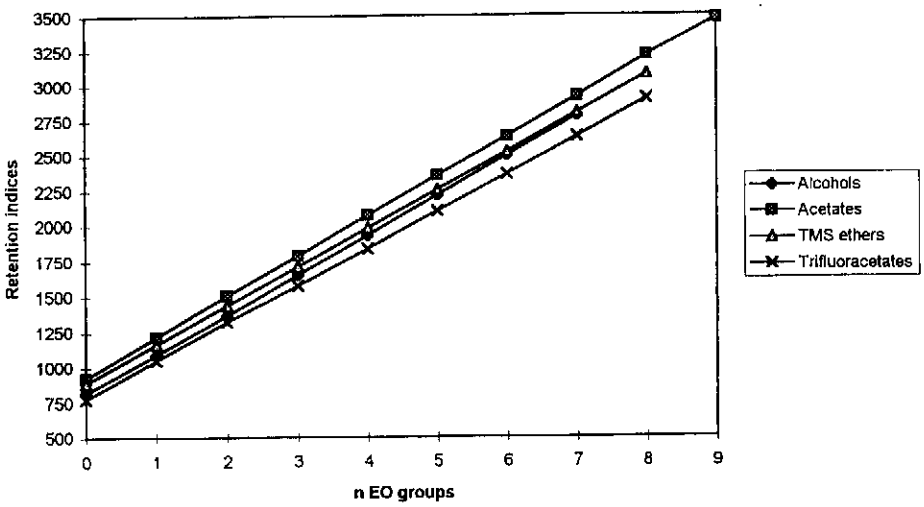

Fig. 3 The dependencies of retention indices of *n*-amylpolyethylene glycol ethers and their derivatives on the number of oxyethylene groups

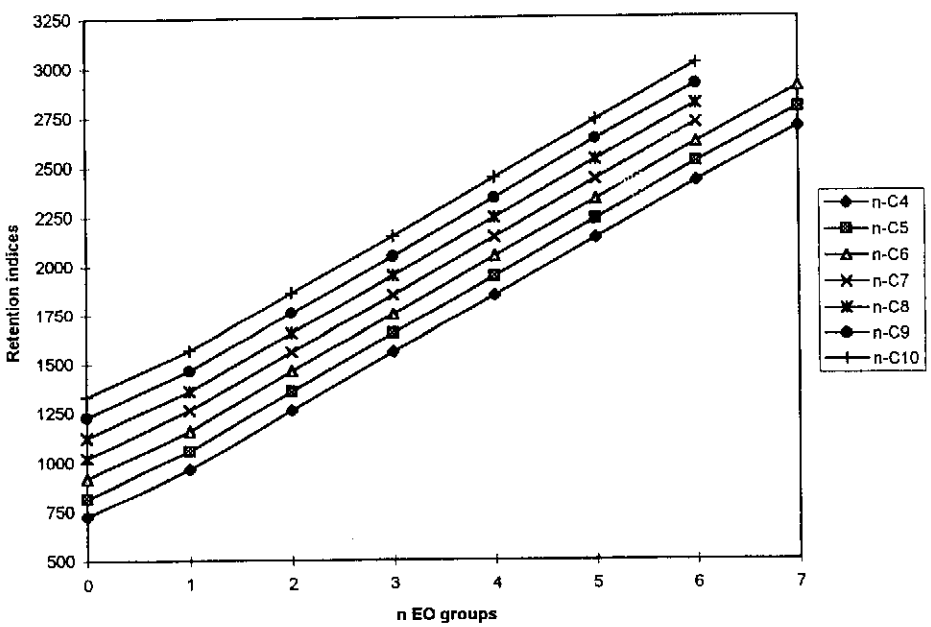

Fig. 4 The dependencies of retention indices of non-derivatized APEGEs n-C_4, n-C_5, n-C_6, n-C_7, n-C_8, n-C_9 and n-C_{10} on the number of oxyethylene groups

Table II Increments of retention index ΔI_{EO} for an incoming oxyethylene groups into the molecule of APEGEs

Substances	xEO	ΔI_{EO}								
		i-C_4	n-C_4	i-C_5	n-C_5	n-C_6	n-C_7	n-C_8	n-C_9	n-C_{10}
Alcohols	1	269.3	238.1	272.5	241.2	238.4	239.0	231.3	233.5	233.2
	2	293.2	297.8	294.4	298.1	301.7	293.9	298.4	298.2	297.4
	3	294.6	295.6	294.0	295.0	291.6	294.8	292.0	285.5	284.0
	4	284.9	291.7	285.7	292.2	294.5	291.6	291.3	291.7	293.9
	5	292.4	288.2	290.9	288.9	283.8	290.4	291.6	296.9	291.7
	6	288.0	285.0	290.4	284.3	286.5	281.8	282.0	277.0	282.7
	7	280.4	273.6	279.1	274.6	278.4				
Acetates	1	295.9	290.1	301.2	288.6	285.0	278.3	281.5	279.4	279.4
	2	291.0	288.0	287.7	290.4	293.6	301.8	295.2	293.2	290.1
	3	279.7	281.8	283.2	280.2	280.5	279.5	278.5	278.8	280.3
	4	289.8	285.6	288.1	285.8	281.9	282.2	287.7	286.7	289.4
	5	279.2	284.3	275.3	285.0	285.0	279.4	278.0	284.9	278.4
	6	279.6	279.9	282.7	278.6	276.5	280.3	278.9	277.3	285.0
	7	282.1	276.8	281.9	281.8	281.1	279.3	279.0	275.9	275.0
	8	284.3	277.6	288.0	273.1	281.1	281.2	278.9	277.9	
	9		281.6	283.7	284.8	278.7	281.0			
TMS ethers	1	260.7	274.5	268.7	274.0	274.9	273.9	275.2	267.5	261.0
	2	293.1	273.6	292.7	272.3	272.8	274.0	268.1	269.2	268.9
	3	277.9	271.5	277.8	273.7	273.2	271.7	273.2	269.8	273.2
	4	272.5	271.8	272.4	270.0	270.3	271.6	271.4	275.4	270.9
	5	272.2	276.0	272.7	276.3	274.7	273.8	274.7	272.2	273.5
	6	268.5	269.5	267.5	269.9	269.9	270.6	268.9	268.7	269.4
	7	268.8	272.1	269.2	274.5	274.7	280.8	280.2	282.3	287.2
	8	274.3	279.7	275.2	275.8	275.8	269.3			
Trifluoracetates	1	271.0	274.8	270.2	275.1	281.3	278.7	273.2	268.5	268.4
	2	268.5	268.1	274.1	268.2	262.5	261.0	261.3	262.5	262.3
	3	255.0	254.1	251.6	255.7	257.4	260.1	262.3	262.9	263.5
	4	253.7	259.3	252.7	261.0	260.8	261.3	259.7	259.8	258.1
	5	268.4	266.9	269.3	266.2	270.3	270.5	270.7	267.1	271.0
	6	260.1	266.6	260.5	263.6	259.7	263.2	266.0	269.0	265.7
	7	265.0	265.2	264.5	263.5	261.2	260.2	257.3	259.3	260.4
	8	262.2	270.5	262.3	271.6	270.0	270.6	270.6		

The graphical dependences of I_{LPTx} values of APEGEs and their derivatives on the number of oxyethylene groups are linear. Figure 3 shows these dependences for homologous series of non-derivatized *n*-amylpolyethylene glycol ethers and their derivatives. In Fig. 4 are shown the correlations between I_{LPTx} and the number of oxyethylene groups for non-derivatized APEGEs C_4, C_5, C_6, C_7, C_8, C_9 and C_{10}. All the correlation curves show linearity from the first oxyethylene group. These dependences were used for the determination of the number of oxyethylene groups in the molecule of higher APEGEs.

The increments of retention indices for the incoming oxyethylene group (ΔI_{xEO}) and for incoming methylene group (ΔI_{CH2}) were calculated according to the following equations and the values obtained are given in Tables II and III.

$$\Delta I_{xEO} = I_{xEO} - I_{x(EO-1)}$$

$$\Delta I_{CH_2} = I_n - I_{n-1}$$

Table III Increments of retention index ΔI_{CH_2} for methylene group in the increasing aliphatic chain in the molecule of APEGEs

Compounds	xEO	ΔI_{CH_2}						
		i-C_5 - i-C_4	n-C_5 - n-C_4	n-C_6 - n-C_5	n-C_7 - n-C_6	n-C_8 - n-C_7	n-C_9 - n-C_8	n-C_{10} - n-C_9
Alcohols	0	92.4	93.0	102.1	103.1	103.2	102.2	103.5
	1	95.6	96.1	99.3	103.7	95.5	104.4	103.2
	2	96.9	96.5	102.9	95.9	100.1	104.1	102.4
	3	96.2	95.8	99.5	99.1	97.3	97.6	100.9
	4	97.1	96.4	101.8	96.2	97.0	98.0	103.0
	5	95.6	97.1	96.6	102.8	98.2	103.4	97.8
	6	98.0	96.4	98.9	98.1	98.3	98.4	103.6
	7	96.7	97.4	102.7				
Acetates	0	95.6	97.9	102.4	102.8	100.9	102.0	101.5
	1	100.9	96.3	98.8	96.1	104.1	99.8	101.5
	2	97.5	98.8	102.0	104.3	97.5	97.9	98.4
	3	101.0	97.2	102.3	103.4	96.5	98.1	99.9
	4	99.3	97.4	98.4	103.7	101.9	97.2	102.5
	5	95.5	98.1	98.4	98.2	100.5	104.3	96.1
	6	98.5	96.8	96.3	101.9	99.2	102.6	103.7
	7	98.3	101.8	95.6	100.1	98.9	99.5	102.8
	8	102.1	97.3	103.6	100.2	98.5	96.5	
	9		100.5	97.5	102.5			
TMS ethers	0	90.5	97.3	96.8	97.7	100.4	104.0	103.6
	1	98.5	96.8	97.7	96.7	101.7	96.3	97.1
	2	98.1	95.5	98.2	97.9	95.7	97.5	96.8
	3	98.0	97.7	97.6	96.4	97.2	94.0	100.2
	4	97.9	95.9	97.9	97.7	97.0	97.0	95.7
	5	98.5	96.2	96.4	96.8	97.9	95.6	97.0
	6	97.4	96.6	96.4	97.5	96.2	95.4	97.6
	7	97.8	99.0	96.7	103.5	95.5	97.5	102.5
	8	98.7	95.0	96.7	97.0			
TFA	0	95.6	97.4	96.8	100.6	101.7	100.9	97.3
	1	94.8	97.7	103.0	98.0	96.2	96.2	97.2
	2	100.4	97.8	97.3	96.5	96.5	97.2	97.2
	3	97.0	99.4	99.0	99.2	98.7	97.8	97.8
	4	96.1	101.1	98.8	99.8	97.1	97.9	96.2
	5	97.0	100.5	102.9	100.0	97.3	94.3	100.1
	6	97.5	97.5	98.9	103.5	100.1	97.3	96.7
	7	97.0	95.8	96.6	102.4	97.2	99.4	97.8
	8	97.1	96.9	95.1	103.0	97.3		

The values of the increments of retention index for introduced methylene group ΔI_{CH_2} fluctuated mostly in the interval from 96 to 103 retention units.

Increments of retention indices for the incoming oxyethylene groups ΔI_{xEO} are balanced and fluctuated between 260 and 290 retention units for both derivatized and non-derivatized APEGEs.

Conclusion

After the conversion of APEGEs into their acetates, trifluoroacetates and trimethylsilyl ethers the polar character of the original compounds is decreased. The formation of hydrogen bonds between hydroxyl groups of APEGEs and the stationary phase is prevented. After the conversion of APEGEs into trifluoroacetates a highly sensitive electron capture detector can be used for quatitative analyses of these compounds.

The influence of an increase in the lenght of alkyl and polyoxyethylene chain in homologous series of APEGEs and their derivatives on the retention indices with linearly programmed temperature was determined. The I_{LPTx} values and their linear dependences of I_{LPTx} values on the number of oxyethylene groups in the molecule of APEGEs can be used for the identification of individual oligomers in commercial mixtures as well as in residues obtained after biodegradation of these substances.

Acknowledgements

We thank the Grant Agency of the Czech Republic for financial support; Grant Project 104/95/0242.

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