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Capillary gas chromatography of *n*-butyl and isobutyl-, *n*-amyl and isoamyl polyethylene glycol ethers and their derivatives

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Abstract

The influence of a branching and increase in the length of alkyl and polyoxyethylene chain in homologous series of *n*-butyl and isobutyl-, *n*-amyl and isoamylpolyethylene glycol ethers on the retention indices at linearly programmed temperatures of a capillary column was studied. Alkylpolyethylene glycol ethers were converted by derivatization reactions into acetates, trifluoroacetates, and trimethylsilyl ethers. The influence of the structure of the alkylpolyethylene glycol molecule and the influence of the functional groups introduced into a molecule of studied compounds were examined by means of increments of retention index. Calculated retention indices were used to identify residues of individual oligomers in the products of biodegradation. © 1998 Elsevier Science B.V.

Keywords: Retention indices; Alkylpolyethylene glycol ethers

1. Introduction

Low-molecular-mass alkylpolyethylene glycol ethers (APEGEs) are commonly used as technically important solvents, the so-called Cellosolves. Some of them are used as components of heat-carrying liquids. Medium- and higher-molecular-mass APEGEs are important surfactants. The products are produced industrially by oxyethylenation of either the individual natural or synthesized aliphatic alcohols and their mixtures. The products produced in this way are mixtures of APEGEs with various lengths of polyethylene glycol chains and/or alkyl chains. Because APEGEs with lower numbers of oxyethylene groups (EO) are degraded quickly in the environment (e.g., in water), their production is steadily increasing.

Gas chromatography (GC) is the most suitable method for analysis of the mixtures of both the lower- and medium-molecular-mass APEGEs and mixtures of this class of compounds with the other classes of compounds. GC has been used to carry out the qualitative and quantitative analysis of industrial products and compounds synthesized [1–4]. The physical properties of some homologous series of low- and medium-molecular-mass APEGEs and the relationship between retention data and molecular structure were studied by means of GC [5–10].

Attention was mostly paid to the separation of the mixtures containing APEGEs, polyethylene glycols and or aliphatic alcohols. Separations were carried out on short, packed columns [1–6,9], and recently on capillary columns [1]. Some papers were aimed at

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a study of the chromatographic and physical properties of higher-molecular-mass APEGEs [2,4,9,10] and medium-molecular-mass APEGEs, too. GC with a linearly programmed temperature of the chromatographic column (LPT-GC) was used in the majority of separations [1–4,9].

Derivatization of APEGEs with higher numbers of EO groups was carried out before the GC analysis to ensure good results. APEGEs were converted to acetates [9,10] or trimethylsilyl (TMS) derivatives [4,9,10].

This paper follows on our earlier studies dealing with an investigation of influence of the structure of organic compounds and the role of the derivatizing agent on retention indices.

2. Experimental

2.1. Analysed compounds

The following aliphatic alcohols and their derivatives were analysed.

2.1.1. Nonderivatized alcohols

(a) Aliphatic alcohols: *n*-butyl alcohol (*n*-C_4OH), *n*-amyl alcohol (*n*-C_5OH), isobutyl alcohol (i-C_4OH), isoamyl alcohol (i-C_5OH).

(b) Homologous series of *n*-butyl polyethylene glycol ethers (*n*-C_4PEGEs), and *n*-amyl polyethylene glycol ethers (*n*-C_5PEGEs) with EO numbers from 1 to 7, i.e. from *n*-C_4EO_1OH to *n*-C_4EO_7OH, from *n*-C_5EO_1OH to *n*-C_5EO_7OH.

(c) Homologous series of isobutyl polyethylene glycol ethers (i-C_4PEGEs) and isoamyl polyethylene glycol ethers (i-C_5PEGEs) with EO numbers from 1 to 7, i.e. from i-C_4EO_1OH to i-C_4EO_7OH, from i-C_5EO_1OH to i-C_5EO_7OH.

The above-mentioned homologous series of APEGEs were synthesized by oxyethylenation of individual alcohols by three moles of ethylene oxide [15].

2.1.2. Derivatized alcohols

TMS derivatives of

(a) lower aliphatic alcohols as mentioned in Section 2.1.1, i.e. *n*-C_4TMS, *n*-C_5TMS, i-C_4TMS, i-C_5TMS,

(b) homologous series of *n*-APEGEs as mentioned in Section 2.1.1, i.e. from *n*-C_4EO_1TMS to *n*-C_4EO_7TMS, from *n*-C_5EO_1TMS to *n*-C_5EO_7TMS,

(c) homologous series of iso-APEGEs mentioned in Section 2.1.1, i.e. from i-C_4EO_1TMS to i-C_4EO_7TMS, from i-C_5EO_1TMS to i-C_5EO_7TMS.

Acetates (Ac) of

(a) lower aliphatic alcohols as mentioned in Section 2.1.1, i.e. *n*-C_4Ac, *n*-C_5Ac, i-C_4Ac, i-C_5Ac,

(b) homologous series of *n*-APEGEs as mentioned in Section 2.1.1, i.e. from *n*-C_4EO_1Ac to *n*-C_4EO_7Ac, from *n*-C_5EO_1Ac to *n*-C_5EO_7Ac,

(c) homologous series of iso-APEGEs as mentioned in Section 2.1.1, i.e. from i-C_4EO_1Ac to i-C_4EO_7Ac, from i-C_5EO_1Ac to i-C_5EO_7Ac

Trifluoroacetates (TFAc) of

(a) lower aliphatic alcohols as mentioned in Section 2.1.1, i.e. *n*-C_4TFAc, *n*-C_5TFAc, i-C_4TFAc, i-C_5TFAc,

(b) homologous series of n-APEGEs as mentioned in Section 2.1.1, i.e. from *n*-C_4EO_1TFAc to *n*-C_4EO_7TFAc, from *n*-C_5EO_1TFAc to *n*-C_5EO_7TFAc,

(c) homologous series of iso-APEGEs as mentioned in Section 2.1.1, i.e. from i-C_4EO_1TFAc to i-C_4EO_7TFAc, from i-C_5EO_1TFAc to i-C_5EO_7TFAc.

2.2. Derivatization of analysed compounds

TMS derivatives were prepared by silylation of Z alcohols and APEGEs with bis(trimethylsilyl)-acetamide (BSA), acetates and trifluoroacetates by acylation reaction with corresponding anhydrides [11].

2.3. Capillary gas chromatography

Capillary gas chromatography (cGC) separations were carried out on a MEGA 5160 gas chromatograph equipped with a flame ionization detector and with a connected LAB BASE operation system (Carlo Erba-Fisons, Milan, Italy). Fused-silica capillary column DB-5MS, 20 m×0.25 mm (J&W Scientific, Folsom, CA, USA) was used as a separation column.

GC working conditions were the following: column temperature, programmed linearly from 50°C to

350°C at 5.5°C min^{-1}; injector and detector temperatures, 350°C, injection system, split, splitting ratio 1:10, carrier gas, helium at a flow-rate of 0.8–1.1 ml min^{-1}.

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 cyclohexane and the mixture was injected into the gas chromatograph.

Intermediates appearing during biodegradation were identified by gas chromatography–mass spectrometric (GC–MS). The same gas chromatograph with the same operation system and capillary column was used but a quadrupole mass detector TRIO 1000 (Fisons, Milan, Italy) was connected. GC working conditions were the same as the above-mentioned ones. Interface temperature was 200°C.

2.4. Biodegradation

Synthesized products of oxyethylenation of aliphatic alcohols *n*-C_5OH and i-C_5OH were biodegraded [16]. Development of biodegradation in time was studied by the determination of total quantity of nondegraded APEGEs by means of chemical oxygen demand (COD) and by GC. Residues of APEGEs and some intermediates were extracted from aqueous solution by dichloromethane before the GC analysis [12]. Extracts were injected into the gas chromatograph together with the solution of *n*-alkanes for reason of identification.

3. Results and discussion

Retention indices I_{LPTx} were calculated from the measured retention data of *n*-alkanes, *n*-alcohols, APEGEs and their derivatives according to the following formula [13,14]:

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

where T_{Rx},T_{Rz}, T_{Rz+n} are the retention temperatures of component *x* and *n*-alkanes eluting before and after this component, respectively; *z* and $z+n$ are numbers of carbon atoms in *n*-alkanes eluting before and after component *x*, respectively.

The measurements were repeated five times and treated statistically. The calculation of retention indices, increments of retention index for functional groups and statistical treatment were carried out by means of the QUATRO PRO programme. The average values of I_{LPT} and their standard deviations S.D. are given in Table 1. The values of the standard deviations fluctuate mostly between 0.7 and 1. The lowest values were found for TMS derivatives and trifluoroacetates. The separation of mixtures of homologous series with an uneven mixture of individual components, especially of APEGEs and their derivatives with higher numbers of EO groups, seems to cause the fluctuation of values of standard deviation.

The relative abundance of individual oligomers of derivatives of homologous series of *n*-C_5PEGE and i-C_5PEGE is shown in Figs. 1 and 2. Peaks of *n*-alkanes are seen next to peaks of trifluoroacetates of *n*-C_5PEGE (Fig. 1) and acetates of i-C_5PEGE (Fig. 2). Fluctuations of some values of I_{LPTx} of APEGEs and *n*-alkanes occur for the compounds with very close retention times, as is evident from the results and chromatograms. The graphical dependences of I_{LPTx} values of APEGEs on the number of EO groups are linear. Fig. 3 shows these dependences for homologous series of nonderivatized APEGEs and derivatized APEGEs.

Increments of retention index for introduced acetate, trimethylsilyl and trifluoroacetate functional groups (ΔI_{Ac}, ΔI_{TMS}, ΔI_{TFAc}, respectively), are given in Table 2 and for increasing number of EO groups (ΔI_{EO}) in Table 3. Increments of retention index for three atoms of fluorine added to the acetate molecule (ΔI_{3F}) are also given in Table 2. These increments were calculated according to the following formulae:

$$\Delta I_{Ac} = I_{Ac} - I_{APEGE}$$

$$\Delta I_{TMS} = I_{TMS} - I_{APEGE}$$

$$\Delta I_{TFAc} = I_{TFAc} - I_{APEGE}$$

$$\Delta I_{3F} = I_{Ac} - I_{TFAc}$$

Table 1
Retention indices I_{LPT} and their standard deviations (S.D.) of alkylpolyethylene glycol ethers (iso-C_4, *n*-C_4, iso-C_5, *n*-C_5) and their acetates, TMS ethers and trifluoroacetates

Compounds	x_{E0}	i-C_4		*n*-C_4		i-C_5		*n*-C_5	
		I_{LPT}	S.D.	I_{LPT}	S.D.	I_{LPT}	S.D.	I_{LPT}	S.D.
Alcohols	0	657.6	5.7	726.4	0.1	750.0	1.0	819.4	0.9
	1	927.0	0.5	965.4	1.3	1022.6	1.1	1060.6	0.4
	2	1220.1	0.8	1262.3	1.0	1317.0	0.7	1358.7	1.4
	3	1514.7	1.9	1557.9	0.9	1611.0	0.9	1653.7	2.2
	4	1799.6	1.2	1849.6	1.0	1896.7	0.7	1946.0	2.4
	5	2092.0	1.7	2137.8	0.4	2187.6	2.7	2234.9	3.3
	6	2380.0	1.6	2422.8	1.1	2478.0	3.1	2519.2	3.7
	7	2660.4	1.3	2696.4	0.4	2757.1	3.4	2793.8	2.4
Acetates	0	779.0	1.0	830.1	1.1	874.6	1.4	928.0	1.4
	1	1074.9	1.3	1120.2	0.7	1175.8	1.0	1216.6	1.0
	2	1366.0	1.5	1408.2	1.1	1463.5	1.6	1507.0	1.2
	3	1645.7	1.4	1690.0	1.4	1746.7	2.2	1787.2	1.4
	4	1935.5	0.5	1975.6	0.8	2034.8	2.1	2073.0	3.2
	5	2214.6	1.8	2259.8	2.8	2310.1	2.0	2358.0	3.3
	6	2494.3	0.9	2539.8	1.0	2592.8	4.0	2636.6	1.0
	7	2776.3	2.7	2816.6	0.3	2874.6	2.8	2918.3	5.0
	8	3060.6	2.0	3094.1	2.8	3162.7	3.5	3191.4	1.5
	9			3375.7	1.8	3446.4	1.9	3476.2	1.7
TMS ethers	0	751.7	1.0	793.6	1.6	842.2	1.1	890.9	2.1
	1	1012.4	2.0	1068.1	1.5	1110.9	0.2	1164.9	0.6
	2	1305.5	0.8	1341.7	0.7	1403.6	1.9	1437.2	2.3
	3	1583.5	1.0	1613.2	1.0	1681.4	2.3	1710.9	1.2
	4	1856.0	1.7	1885.0	1.0	1953.9	1.8	1981.0	1.3
	5	2128.1	1.1	2161.0	1.7	2226.6	2.8	2257.2	1.3
	6	2396.6	1.4	2430.5	1.4	2494.0	0.3	2527.1	1.4
	7	2665.4	2.8	2702.7	3.0	2763.3	1.1	2801.6	3.2
	8	2939.8	2.5	2982.4	2.4	3038.4	2.2	3077.4	1.3
Trifluoroacetates	0	656.4	4.0	678.8	1.7	752.1	1.3	776.2	0.5
	1	927.4	1.3	953.7	0.9	1022.3	1.0	1051.4	1.1
	2	1196.0	1.2	1221.8	0.4	1296.4	0.8	1319.6	1.1
	3	1451.0	2.0	1475.9	0.5	1548.0	1.4	1575.3	1.1
	4	1704.7	1.0	1735.1	0.5	1800.8	1.6	1836.2	1.0
	5	1973.1	1.0	2002.0	1.2	2070.1	1.7	2102.5	1.3
	6	2233.1	1.6	2268.6	0.5	2330.6	0.9	2366.1	1.5
	7	2498.1	0.9	2533.8	2.3	2595.1	2.2	2629.6	1.6
	8	2760.3	0.4	2804.3	0.8	2857.4	3.0	2901.2	2.6

$$\Delta I_{EO} = I_{APEGE(EO)n} - I_{APEGE(EO)n-1}$$

Increments of retention index calculated for the methylene group incoming into *n*-C_4PEGE and i-C_4PEGE, $\Delta I_{CH_2(n)}$, $\Delta I_{CH_2(i)}$, respectively, are given in Table 4. These increments were calculated as the difference of retention indices of *n*-C_5PEGE and *n*-C_4PEGE, i-C_5PEGE and i-C_4PEGE with the same number of EO groups in a molecule of APEGE according to the formulae:

$$\Delta I_{CH_2(n)} = I_{n-C_5PEGE} - I_{n-C_4PEGE}$$

$$\Delta I_{CH_2(i)} = I_{i-C_5PEGE} - I_{i-C_4PEGE}$$

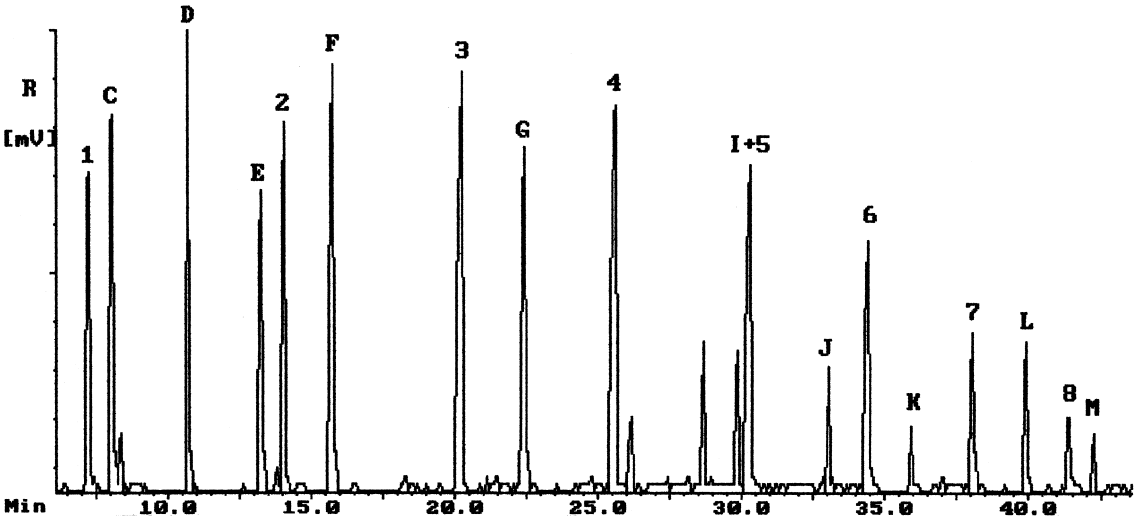


Fig. 1. Chromatogram of the separation of trifluoroacetates of *n*-amylpolyethylene glycol ethers. 1=*n*-C_5EO_1TFAc; 2=*n*-C_5EO_2TFAc; 3=*n*-C_5EO_3TFAc; 4=*n*-C_5EO_4TFAc; 5=*n*-C_5EO_5TFAc; 6=*n*-C_5EO_6TFAc; 7=*n*-C_5EO_7TFAc; 8=*n*-C_5EO_8TFAc; C, D, E, F, G, I, J, K, L, M=C_{11}, C_{12}, C_{13}, C_{14}, C_{17}, C_{23}, C_{25}, C_{28}, C_{30} *n*-alkanes.

The influence of branching of alkyl parts in APEGE molecules on a decrease in the values of retention indices was examined by means of increments of retention index $\Delta I_{(n-i)}$. Their values (Table 5) were calculated as the difference between retention indices of *n*-C_4PEGE and i-C_4PEGE, *n*-

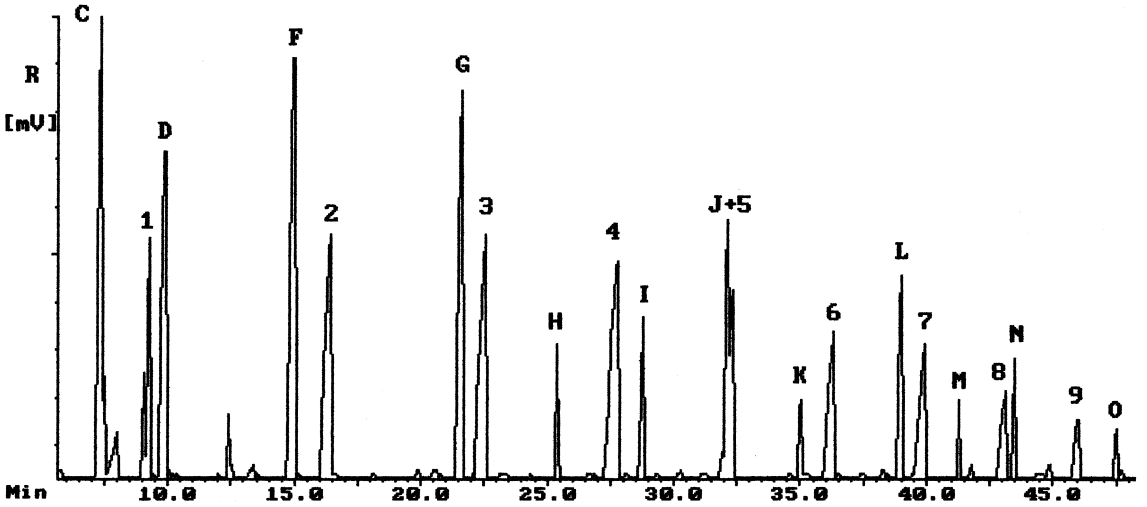


Fig. 2. Chromatogram of the separation of acetates of isoamylalkylpolyethylene glycol ethers. 1=iso-C_5EO_1Ac; 2=iso-C_5EO_2Ac; 3=iso-C_5EO_3Ac; 4=iso-C_5EO_4Ac; 5=iso-C_5EO_5Ac; 6=iso-C_5EO_6Ac; 7=iso-C_5EO_7Ac; 8=iso-C_5EO_8Ac; 9=iso-C_5EO_9Ac; C, D, F, G, H, I, J, K, L, M, N, O=C_{11}, C_{12}, C_{14}, C_{17}, C_{19}, C_{21}, C_{23}, C_{25}, C_{28}, C_{30}, C_{32}, C_{36} *n*-alkanes.

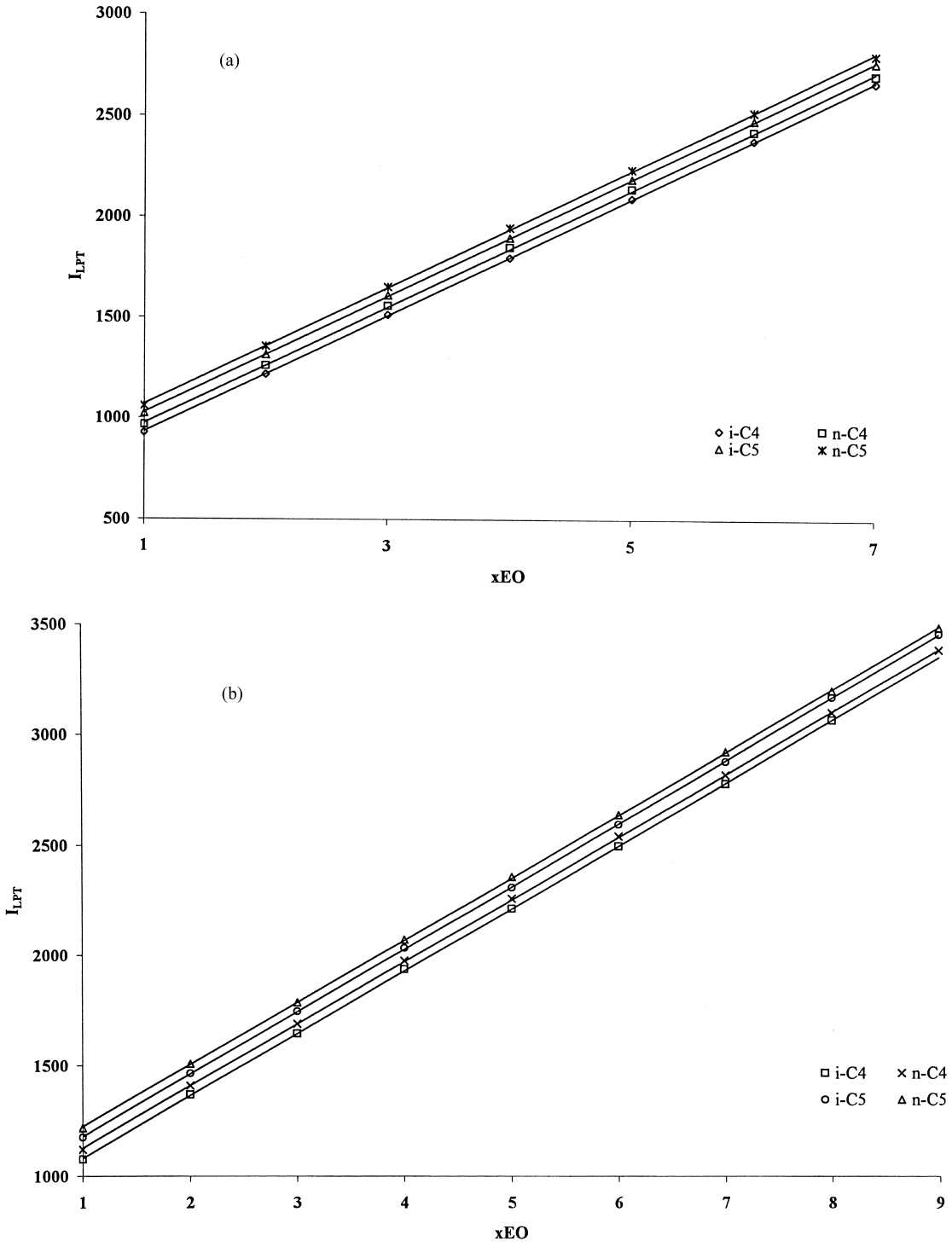
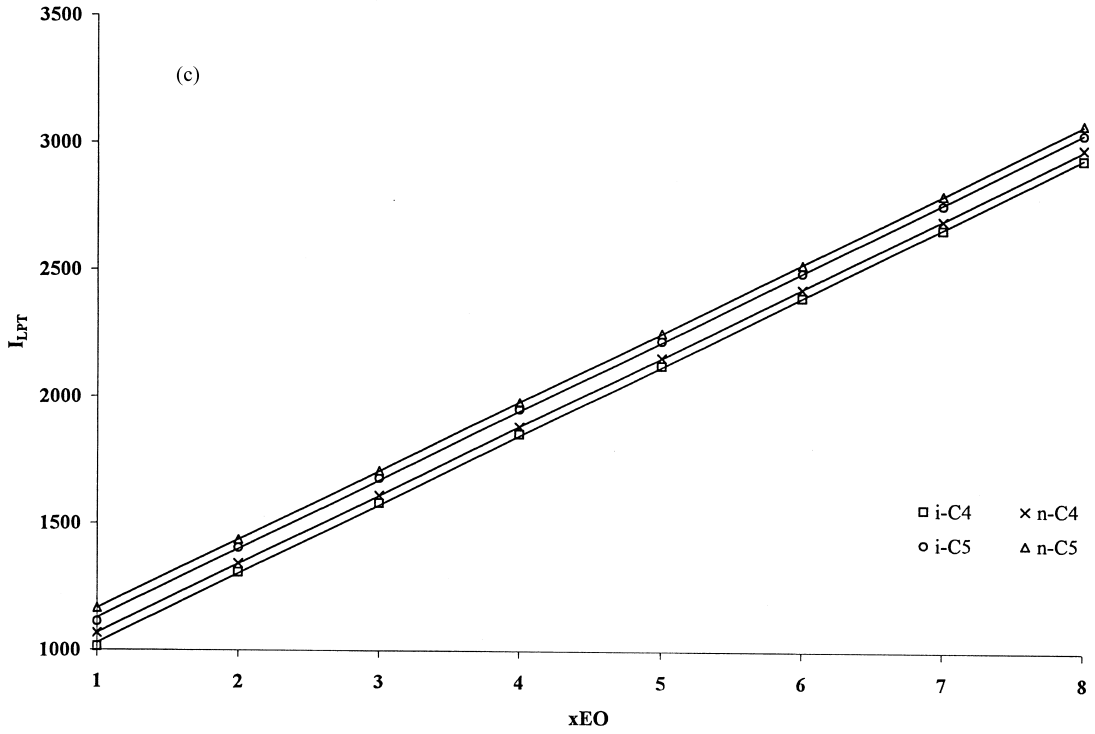


Fig. 3. Dependences of retention indices (I_{LPT}) of nonderivatized and derivatized APEGEs on the number of EO groups (*x*EO). (a) alcohols, (b) acetates; (c) TMS derivatives; (d) trifluoroacetates.



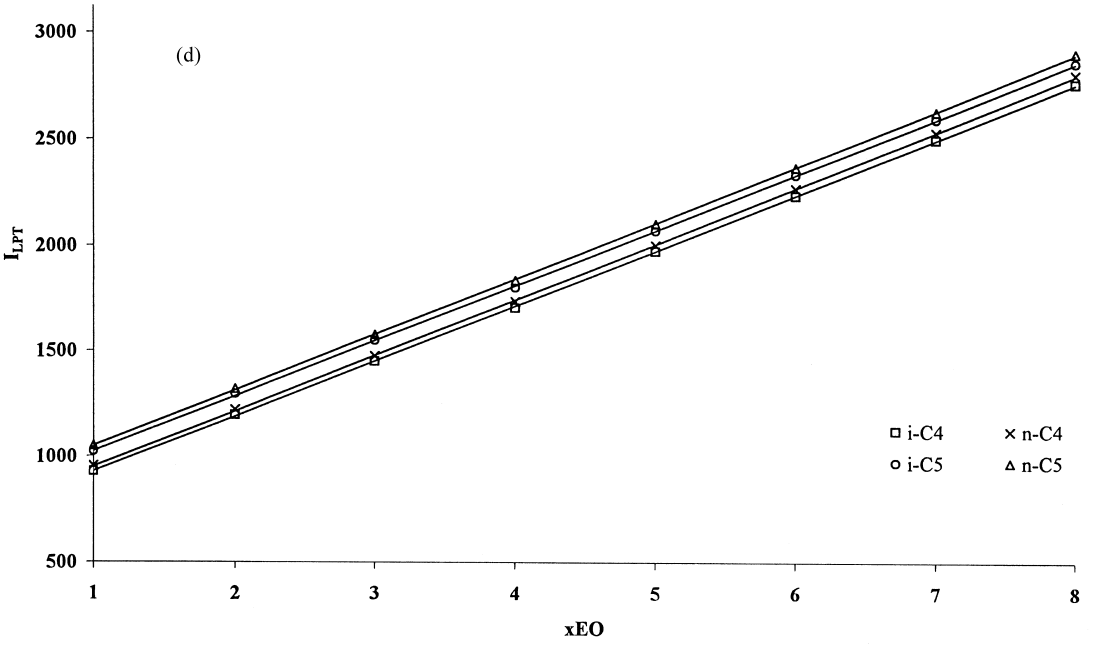


Fig. 3. (*continued*)

Table 2
Increments of retention index ΔI for introduced functional groups

Alcohol	*x*EO	ΔI_{Ac}	ΔI_{TMS}	ΔI_{TFAc}	ΔI_{3F}
i-C_4	0	121.4	94.1	1.2	122.6
	1	147.9	85.4	−0.4	147.5
	2	145.9	85.4	24.1	170.0
	3	131.0	68.8	63.7	194.7
	4	135.9	56.4	94.9	230.8
	5	122.6	36.1	118.9	241.5
	6	114.3	16.6	146.9	261.2
	7	115.9	5.0	162.3	278.2
	8				300.3
n-C_4	0	103.7	67.2	47.6	151.3
	1	155.7	104.0	10.8	166.5
	2	145.9	79.4	40.5	186.4
	3	132.1	55.3	82.0	214.1
	4	126.0	35.4	114.5	240.5
	5	122.0	23.2	135.8	257.8
	6	117.0	7.7	154.2	271.2
	7	120.2	6.3	162.6	282.8
	8				289.8
i-C_5	0	124.6	92.2	−2.1	122.5
	1	153.2	88.3	0.3	153.5
	2	146.5	86.6	20.6	167.1
	3	135.7	70.4	63.0	198.7
	4	138.1	57.2	95.9	234.8
	5	122.5	39.0	117.5	240.0
	6	114.8	16.0	147.4	262.2
	7	117.5	6.2	162.0	279.5
	8				305.3
n-C_5	0	108.6	71.5	43.2	151.8
	1	156.0	104.3	9.2	165.2
	2	148.3	78.5	39.1	187.4
	3	133.5	57.2	78.4	211.9
	4	127.0	35.0	109.8	236.8
	5	123.1	22.3	132.4	255.5
	6	117.4	7.9	1153.1	270.5
	7	124.5	7.8	164.2	288.7
	8				290.2

Table 3
Increments of retention index ΔI_{EO} for introduced oxyethylene group

Substances	*x*EO	ΔI_{EO}			
		i-C_4	*n*-C_4	i-C_5	*n*-C_5
Alcohols	1	269.3	238.1	272.5	241.2
	2	293.2	297.8	294.4	298.1
	3	294.6	295.6	294.0	295.0
	4	284.9	291.7	285.7	292.2
	5	292.4	288.2	290.9	288.9
	6	288.0	285.0	290.4	284.3
	7	280.4	273.6	279.1	274.6
Acetates	1	295.6	290.1	301.2	288.6
	2	291.0	288.0	287.7	290.4
	3	279.7	281.8	283.2	280.2
	4	289.8	285.6	288.1	285.8
	5	279.2	284.3	275.3	285.0
	6	279.6	279.9	282.7	278.6
	7	282.1	276.8	281.9	281.8
	8	284.3	277.6	288.0	273.1
	9		281.6	283.7	284.8
TMS ethers	1	260.7	274.5	268.7	274.0
	2	293.1	273.6	292.7	272.3
	3	277.9	271.5	277.8	273.7
	4	272.5	271.8	272.4	270.0
	5	272.2	276.0	272.7	276.3
	6	268.5	269.5	267.5	269.9
	7	268.8	272.1	269.2	274.5
	8	274.3	279.7	275.2	275.8
Trifluoroacetates	1	271.0	274.8	270.2	275.1
	2	268.5	268.1	274.1	268.2
	3	255.0	254.1	251.6	255.7
	4	253.7	259.3	252.7	261.0
	5	268.4	266.9	269.3	266.2
	6	260.1	266.6	260.5	263.6
	7	265.0	265.2	264.5	263.5
	8	262.2	270.5	262.3	271.6

C_5PEGE and i-C_5PEGE according to the following formula:

$$\Delta I_{(n-\mathrm{i})\mathrm{C}_4} = I_{n-\mathrm{C}_4\mathrm{PEGE}} - I_{i-\mathrm{C}_4\mathrm{PEGE}}$$

$$\Delta I_{(n-\mathrm{i})\mathrm{C}_5} = I_{n-\mathrm{C}_5\mathrm{PEGE}} - I_{\mathrm{i}-\mathrm{C}_5\mathrm{PEGE}}$$

The influence of the functional group from the derivatizing agent introduced into a molecule of APEGEs on the retention indices is shown very well from the values of ΔI (Table 2). As is evident, the values of ΔI for the functional groups are similar for homologous series of *n*-C_4PEGE and *n*-C_5PEGE, or i-C_4PEGE and i-C_5PEGE. For derivatives with an increasing number of EO groups, the ΔI values of acetates and TMS derivatives decrease gradually to values of 115–125 and 5–8 retention units, respectively. Therefore, the used methods of derivatization do not lengthen the time of analysis either for lower APEGEs. Values of ΔI_{TFAc} decrease gradually by 162–164 units for all the homologous series of TFAc (Table 2). This means that the time of analysis can be shortened. The decrease of I_{LPT} values of

Table 4
Increments of retention index for methylene group introduced into iso- and *n*-butylpolyethylene glycol ether molecules, respectively

Compounds	*x*EO	$\Delta I_{CH_2(i)}$	$\Delta I_{CH_2(n)}$
Alcohols	0	92. 4	93. 0
	1	95.6	96.1
	2	96.5	96.5
	3	96.2	95.8
	4	97.1	96.4
	5	95.6	97.1
	6	98.0	96.4
	7	96.7	97.4
Acetates	0	95.6	97.9
	1	100.9	96.3
	2	97.5	98.8
	3	101.0	97.2
	4	99.3	97.4
	5	95.5	98.1
	6	98.5	96.8
	7	98.3	101.8
	8	102.1	97.3
	9		100.5
TMS ethers	0	90.5	97.3
	1	98.5	96.8
	2	98.1	95.5
	3	98.0	97.7
	4	97.9	95.9
	5	98.5	96.2
	6	97.4	96.6
	7	97.8	99.0
	8	98.7	95.0
Trifluoroacetates	0	95.6	97.4
	1	94.8	97.7
	2	100.4	97,8
	3	97.0	99.4
	4	96.1	101.1
	5	97.0	100.5
	6	97.5	97.5
	7	97.0	95.8
	8	97.1	96.9

Table 5
Increments of retention index characteristic of branched alkyl chains

Compounds	*x*EO	$\Delta I(n-\mathrm{i})C_4$	$\Delta I(n-\mathrm{i})C_5$
Alcohols	0	68. 8	69.4
	1	37.5	38.0
	2	42.2	41.7
	3	43.2	42.7
	4	50.0	49.3
	5	45.8	47.3
	6	42.8	41.2
	7	36.0	36.7
Acetates	0	51.1	53.4
	1	45.3	40.8
	2	42.2	43.5
	3	44.3	40.5
	4	40.1	38.2
	5	45.2	47.9
	6	45.5	43.8
	7	40.3	43.7
	8	33.5	28.7
	9		29.8
TMS ethers	0	41.9	48.7
	1	55.7	54.0
	2	36.2	33.6
	3	29.7	29.5
	4	29.0	27.1
	5	32.9	34.6
	6	33.9	33.1
	7	37.3	38.3
	8	42.6	39.0
Trifluoroacetates	0	22.4	24.1
	1	26.3	29.1
	2	25.8	23.2
	3	24.9	27.3
	4	30.4	35.4
	5	28.9	32.4
	6	35.5	35.5
	7	35.7	34.5
	8	44.0	43.8

APEGEs after the introduction of the trifluoroacetate functional group is evident from the linear dependence of I_{LPT} on the number of EO groups (Fig. 3).

The influence of fluorine atoms introduced into the molecule of acetates on the retention indices is very positive and the retention indices of the compounds with eight EO groups are decreased by 290–305 units.

The values of the increments of retention index for the introduced methylene group, $\Delta I_{CH_2(n)}$ and $\Delta I_{CH_2(i)}$ (Table 4), fluctuate mostly in the interval from 96 to 99 retention units. No difference can be seen between the values of $\Delta I_{CH_2(n)}$ calculated from retention indices (I_{LPT}) for homologous series of *n*-APEGEs and $\Delta I_{CH_2(i)}$ calculated from retention indices (I_{LPT}) for homologous series of i-APEGEs.

The branching of the alkyl chain in APEGEs cause a decrease of I_{LPT} values by 23–56 retention units. Values of $\Delta I_{(n-i)C_4}$ and $\Delta I_{(n-i)C_5}$ are close to one another for the oligomers with the same number of

Table 6
Biodegradation of the oxyethylenation products of iso- and *n*-amyl alcohols

Time of biodegradation (h)	Biodegradation by COD (%)		Biodegradation by GC (%)	
	iso-C_5	*n*-C_5	iso-C_5	*n*-C_5
0.0	0.0	0.0	0.0	0.0
21.0	3.8	5.5	28.2	19.9
117.0	14.8	22.5	64.5	57.4
189.0	31.4	43.8	67.4	80.9
309.0	59.1	73.8	85.7	89.9
356.0	68.0	74.5	98.1	97.1
452.0	76.0	80.9	98.9	98.7
620.5	93.6	91.7	–	–

EO groups (Table 5). The decrease of the I_{LPT} values caused by branching of alkyl parts can be easily seen from the linear dependences of I_{LPT} on the number of EO groups (Fig. 3).

The EO groups introduced into a molecule of APEGEs caused an increase of I_{LPT} values by 240–295 retention units (Table 3). The ΔI_{EO} values of all the homologs of *n*-C_4PEGE and *n*-C_5PEGE or i-C_4PEGE and i-C_5PEGE and their derivatives, respectively are similar. The ΔI_{EO} values decrease very slowly with the increasing number of EO groups in a molecule of all the derivatized APEGEs. These values for the nonderivatized APEGEs decrease from oligomers with the EO numbers higher than two. The lesser abundance of oligomers with a higher number of EO groups in the analysed homologous series causes the fluctuation of some values of ΔI.

The I_{LPT} values and the linear dependences of I_{LPT} values on the number of EO groups in a molecule of APEGEs were used for the identification of individual oligomers in both the synthesized mixtures of oxyethylenated alcohols and their residues arising from the compounds in the course of the biodegradation process. The degree of biodegradation was calculated from the determination of residues of individual oligomers by GC (primary degradation) compared with the degree of biodegradation calculated from the COD values determined (total degradation), see Table 6. The biodegradation of APEGEs was finished within 350 h and then the intermediates were degraded (Table 6). The chromatogram in Fig. 4 shows the peaks of nondegraded APEGEs and the peaks of intermediates arising during biodegradation. Homologs of *n*-amylpolyethylenoxy carboxylic acids $CH_3(CH_2)_3CH_2O–(CH_2CH_2O)_x–CH_2COOH$ (x= 0–6) were found in the products of biodegradation,

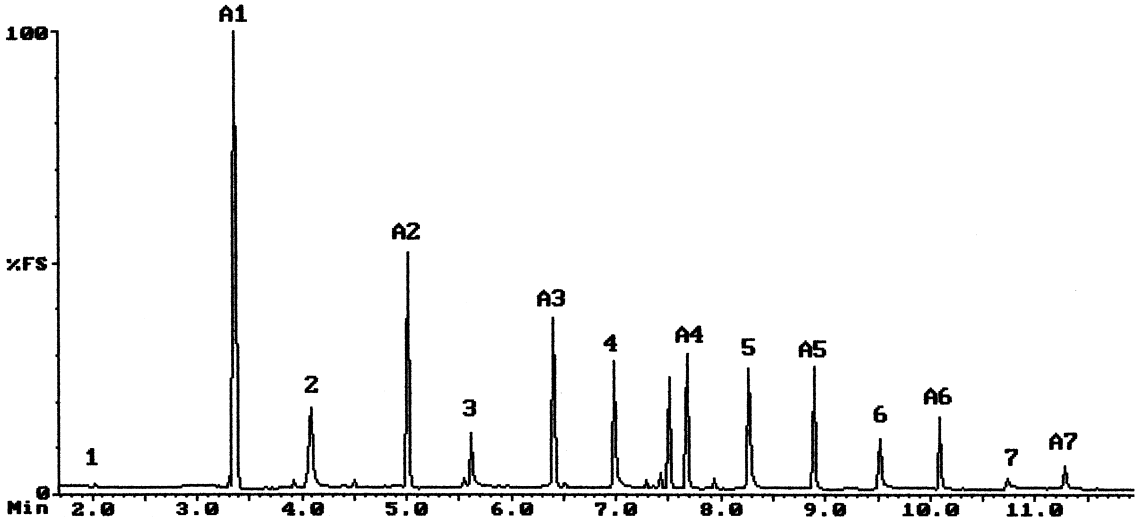


Fig. 4. Total ion current (TIC) chromatogram of the separation of dichloromethane extract of residues of *n*-amylpolyethylene glycol ethers after biodegradation. 1=*n*-C_5EO_1OH; 2=*n*-C_5EO_2OH; 3=*n*-C_5EO_3OH; 4=*n*-C_5EO_4OH; 5=*n*-C_5EO_5OH; 6=*n*-C_6EO_2OH; 7=*n*-C_5EO_7OH; A1–A7=$CH_3(CH_2)_3CH_2O–(CH_2CH_2O)_xCH_2COOH$, where x=0–6, respectively.

which was evidenced by GC–MS analysis, i.e. by their fragmentation mode and by the fragmentation mode of their methyl esters.

The calculated retention indices and linear dependences of I_{LPT} values on the number of EO groups are to be used for the identification of the compounds in commercial products, in waste water, or in slurries after their isolation from the analysed sample. After the conversion of APEGEs into their derivatives such as acetates or TMS derivatives, the polar character of the original compounds is decreased. The formation of hydrogen bond between the hydroxyl group of APEGEs and a stationary phase is prevented. After the conversion of APEGEs into trifluoroacetates, the time of analysis is shorter. In addition, a highly sensitive electron-capture detector can be used for quantitative analysis of the compounds.

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