Capillary gas chromatography–mass spectrometry of lower oxyethylenated aliphatic alcohols[1]

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Abstract

This paper deals with the capillary gas chromatography–mass spectrometric (CGC–MS) analysis of alkylpoly(ethylene glycol) ethers in the products of the oxyethylenation of the individual lower aliphatic alcohols C_4–C_{10}, both in synthetic mixtures and as residues in water after their biodegradation. MS has been used for the acquisition of spectra and for the recording of retention times and the areas of eluted components. Particular alkylpoly(ethylene glycol) ethers have been identified by a combination of interpreting their electron impact (EI) mass spectra and by correlating their relative retention times with the structure of the molecules. Using these correlations, the length of both the poly(ethylene glycol) part and the alkyl part of a molecule were determined. Retention times of the eluted components were used for calculation of the relative retention characteristics. The peak areas were used to determine the concentration decreases of individual components as a function of the degradation time. Alkylpoly(ethylene glycol) ethers were analysed in both the non-derivatized form and after their conversion to trimethylsilyl derivatives and acetates. © 1997 Elsevier Science B.V.

Keywords: Relative retention data; Alcohols; Alkylpoly(ethylene glycol) ethers

1. Introduction

Oxyethylenated higher, and some lower, aliphatic alcohols belong to the technologically important group of surface-active organic compounds. They are used for the production of detergents, emulsifiers, dispersants, cosmetic preparations, etc. Lower oxy-ethylenated alcohols are used as solvents and as heat-carrying liquids.

On oxyethylenation of individual alcohols by, for example, three moles of ethylene oxide, not just one component, i.e. alkyltri(ethylene glycol) ether, arises, but an homologous series of alkylpoly(ethylene glycol) ethers with 1–8 oxyethylene groups are found in the reaction mixtures. Compounds with more than five oxyethylene units are less common in the reaction mixture. Products containing even several tens of components arise on oxyethylenation of a mixture of natural or synthetic alcohols. After using preparations containing this group of compounds,

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their residues are found, as contaminants, in waste water, sludge or surface water, where they undergo biodegradation.

The separation methods are mostly used during analyses of synthetic products obtained by oxyethylenation of aliphatic alcohols. These analyses are concerned mainly with the determination of the abundance of particular components. The separation methods are also used for the determination of these compounds in water samples.
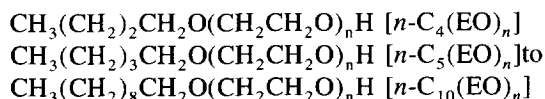
Analyses of the products of the oxyethylenation of higher aliphatic alcohols with long poly(ethylene glycol) chains, that is, with large numbers of oxyethylene groups (EO), were carried out by high-performance liquid chromatography (HPLC) [1–4], supercritical fluid chromatography (SFC) [5–7], nuclear magnetic resonance spectroscopy (NMR) [4,10], thin-layer chromatography (TLC) [8–10], TLC–flame-ionization detection (FID) [11] and liquid chromatography–mass spectrometry (LC–MS) [12]. Lower oxyethylenated alcohols were analyzed by gas chromatography (GC) or GC–MS [4,6,7,13–25]. The identification of particular components was realized by means of synthesized standards by retention indices systems and by MS with various ionization techniques [12,21,22,25,26].

In order to study the biodegradation process of particular alkyl poly(ethylene glycol) ethers (APEGEs) during batch kinetic tests [27], we used a capillary gas chromatograph with a connected quadrupole mass detector with EI ionization. We want to show how it is possible to combine the identification of particular APEGEs by the interpretation of their measured EI mass spectra in combination with correlation of their retention data (measured by the same detector) with the structure of their molecules. The simultaneously recorded areas of the identified components before and after biodegradation were used for the determination of the degree of biodegradation.

2. Experimental

2.1. Analyzed compounds

(a) n-Alkyl poly(ethylene glycol) ethers:

$CH_3(CH_2)_2CH_2O(CH_2CH_2O)_nH$ [n-$C_4(EO)_n$]
$CH_3(CH_2)_3CH_2O(CH_2CH_2O)_nH$ [n-$C_5(EO)_n$]to
$CH_3(CH_2)_8CH_2O(CH_2CH_2O)_nH$ [n-$C_{10}(EO)_n$]

where number of EO groups $n = 0-8$.

The above-mentioned homologous series of APEGEs were synthesized on a semi-plant scale. They were manufactured by the oxyethylenation of individual alcohols with 3 moles of ethylene oxide (Sloveca, a.s. Nováky).

(b) Trimethylsilyl (TMS) derivatives and acetates (Ac):

from n-$C_4(EO)_n$ TMS to n-$C_{10}(EO)_n$ TMS
from n-$C_4(EO)_n$ Ac to n-$C_{10}(EO)_n$ Ac.

2.2. Preparation of derivatives

TMS derivatives and acetates were prepared by the reaction of a sample of the oxyethylenation products of the individual alcohols (20 mg) with N,O-bis(trimethylsilyl)acetamide (BSA; Supelco, Bellefonte, PA, USA) and acetic anhydride (Synthesia, a.s. Pardubice, Czech Republic), respectively, in 1-ml reaction vials [28].

Extracts of residues after biodegradation were derivatized after the extraction agent was evaporated.

2.3. Instrumentation

All the analyses were carried out on a MEGA 5160 gas chromatograph with a connected QMD 1000 quadrupole mass detector (Carlo Erba-Fisons Instruments, Milan, Italy). Fused-silica capillary columns, DB-1HT, 30 m×0.32 mm (J&W Scientific, Folsom, CA, USA) were used as the separation columns.

2.4. Working conditions

The analyses of mixtures of APEGEs and their derivatives were carried out under the following conditions: column temperature, programmed linearly from 45 to 340°C at 10°C min^{-1}; injector temperature, 350°C; interface and ion source temperatures, 200°C; injection system, split, splitting ratio 1:3–15; carrier gas, helium at a flow-rate of 40–50 cm s^{-1} and an inlet pressure of 85 kPa; scanning

control parameters, mass range of 12–650 m/z and a scan time of 0.9 s. The dead retention time was measured by the injection of nitrogen.

2.5. Preparation of samples

The homologous series of synthesized oxyethylenates were diluted to 5% (v/v) in a methanol solution. TMS derivatives and acetates, after evaporation of excess reaction agent, were dissolved in about 10% (v/v) benzene solution. n-Dodecylacetate (as the standard) was diluted to 5% (v/v) in a chloroform solution.

The mixtures of oxyethylenates and standard were injected together. The volumes of injected mixtures were chosen to optimize the EI mass spectra obtained.

Chloroform extracts of residues of APEGEs after biodegradation were injected either directly into a gas chromatograph or after their derivatization. In water samples with greater than 90% biodegradation, concentration of APEGE residues was carried out by distilling off most of the chloroform and evaporating the rest using a stream of nitrogen in a graduated vial. The residue was used for the derivatization. After derivatization, excess reagent was evaporated using a stream of nitrogen and the derivatives were dissolved in 0.1 ml of benzene. When the identification of particular APEGEs was carried out, a solution containing the standard was drawn into a solution of the sample in a microsyringe before being injected into the gas chromatograph.

2.6. Biodegradability

The degree of biodegradability was determined by means of a modified batch kinetic test [27]. Solutions (1 g/l) of the oxyethylenation products of the individual alcohols, n-C_7, n-C_9 and n-C_{10}, respectively, were prepared for biodegradation. Activated sludge from the sewage treatment plant at Malenovice was used as a source of microorganisms. Sludge supernatant, with a dry weight of about 10 g/l, was used for the inoculation. The sludge contained about 1×10^5 microorganisms per ml. Water samples (100 ml) were withdrawn in the chosen time-interval for determination of residues of the starting substance by CGC–MS and for the de-

termination of total organic carbon (TOC). The APEGE residues were extracted with 3×8 ml of chloroform before their determination. Extraction was carried out in a separatory funnel and the extract was made up to 25 ml in volume. A 20-g amount of $MgSO_4 \cdot 7H_2O$ was added to the water samples before extraction. For further details on the procedure see Section 2.5.

External calibration standards for quantitative analysis were prepared by dissolving a known amount of an oxyethylenate mixture to a biological medium. APEGEs were extracted from these solutions using chloroform and were further processed in the same way as for APEGE residues from water after biodegradation (see Section 2.5).

3. Results and discussion

The identification of particular APEGEs with one and two EO groups was carried out by a computer comparison of their measured EI mass spectra with data-bank spectra that were obtained commercially. There are some spectra of non-derivatized APEGEs and some their derivatives in the data-bank. The interpretation of measured spectra was carried out in the same way as described Vettori et al. [22] for the identification of lower oxyethylenated aliphatic alcohols, C_{12}–C_{15}. In our case, there were characteristic fragmentation ions of the APEGE molecule, which arose according to the following scheme:

$$R - CH_2 - CH_2 \mid O - CH_2 - CH_2 - O \mid CH_2 - CH_2 - O \ldots$$
$$ a b c$$
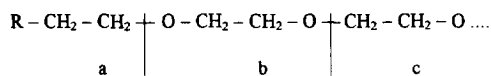
For the identification of alkyl groups, there are diagnostic ions arising by the fragmentation of the first part of the APEGE molecule (part a). Fragments arising from the second and third parts of the APEGE molecule (part b and c) are important for the determination of a number of EO groups. The fragmentation of TMS derivatives and acetates proceeded analogously [29,30]. Likewise, it was possible to identify particular APEGEs with three and four EO groups. The correlation of relative retentions for a number of EO groups in a molecule was used for the identification of higher oxyethylenated APEGEs with more than four EO groups.

Table 1

Relative retention values ($r_{i,s}$) for an homologous series of APEGEs

nEO	Compound						
	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}
0	0.010	0.025	0.068	0.140	0.247	0.388	0.540
1	0.085	0.167	0.293	0.443	0.580	0.731	0.875
2	0.403	0.541	0.690	0.828	0.962	1.093	1.223
3	0.793	0.925	1.056	1.178	1.292	1.407	1.525
4	1.148	1.266	1.479	1.486	1.588	1.689	1.796
5	1.459	1.564	1.667	1.763	1.851	1.943	2.041
6	1.731	1.832	1.923	2.008	2.094	2.174	2.255
7	1.980	2.073	2.157	2.237	2.308	2.389	
8	2.220		2.375				

Relative retentions were calculated from data obtained according to the following formula, which is used commonly in gas chromatographic analysis with FID, thermal conductivity detector (TCD), etc. under isothermal conditions:

$$r_{i,s} = \frac{t_{Ri} - t_{RM}}{t_{Rs} - t_{RM}}$$

where t_{Ri} and t_{Rs} are the retention times of component, i, and standard, s, respectively, t_{RM} is the dead retention time.

The standard used was n-dodecyl acetate (C_{12}Ac), a middle polar substance. The measurements of retention times for all the of homologous series of oxyethylenated alcohols were repeated three times. The average values, $r_{i,s}$, are given in Table 1 Table 2

Table 3. Table 1 shows the $r_{i,s}$ values of non-derivatized APEGEs, Table 2 shows the $r_{i,s}$ values for TMS derivatives and Table 3 shows the $r_{i,s}$ values of acetates. Standard deviations fluctuated from 0.0005 to 0.004 for 90% of results given in the tables and from 0.005 to 0.014 for the remainder, where $r_{i,s} > 1.5$.

In Fig. 1, the correlation between $r_{i,s}$ and the number of EO groups (nEO) for non-derivatized APEGEs and their TMS derivatives and acetates, respectively, are shown. All the correlation curves show linearity from nEO = 4. The dependence was used for the determination of the number of EO groups in a molecule of identified APEGE.

The identification of alkyl groups from MS–EI spectra was combined with the determination of carbon chain length of alkyl groups in a molecule of APEGE with the same number of EO groups from the retention data. The carbon chain length was determined by the correlation dependence of $r_{i,s}$ values on the number of carbon atoms (nC) in the alkyl chain. The correlation dependences are shown in Fig. 2. The figures illustrate that the linear dependence allows us to determine correctly the alkyl carbon chain length for both non-derivatized and derivatized APEGEs with the same number of EO groups.

In an analogous manner, linear dependence of the retention time on the number of carbon groups was found for aliphatic alcohols C_4–C_{12} [31] and oxyethylenated higher aliphatic alcohols [14] using a linear temperature programme. Studies describing

Table 2

Relative retention values ($r_{i,s}$) for an homologous series of TMS derivatives of APEGE

nEO	Compound						
	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}
0	0.039	0.090	0.165	0.284	0.421	0.571	0.718
1	0.270	0.392	0.526	0.664	0.802	0.938	1.068
2	0.646	0.775	0.902	1.024	1.143	1.255	1.374
3	1.000	1.121	1.235	1.336	1.443	1.549	1.654
4	1.309	1.420	1.518	1.613	1.712	2.032	2.113
5	1.587	1.688	1.775	1.863	1.980	2.032	2.113
6	1.846	1.931	2.009	2.092	2.185	2.242	2.301
7	2.072	2.152	2.231	2.303	2.411	2.447	
8		2.362	2.460				

Table 3

Relative retention values ($r_{i,s}$) for an homologous series of acetates of APEGE

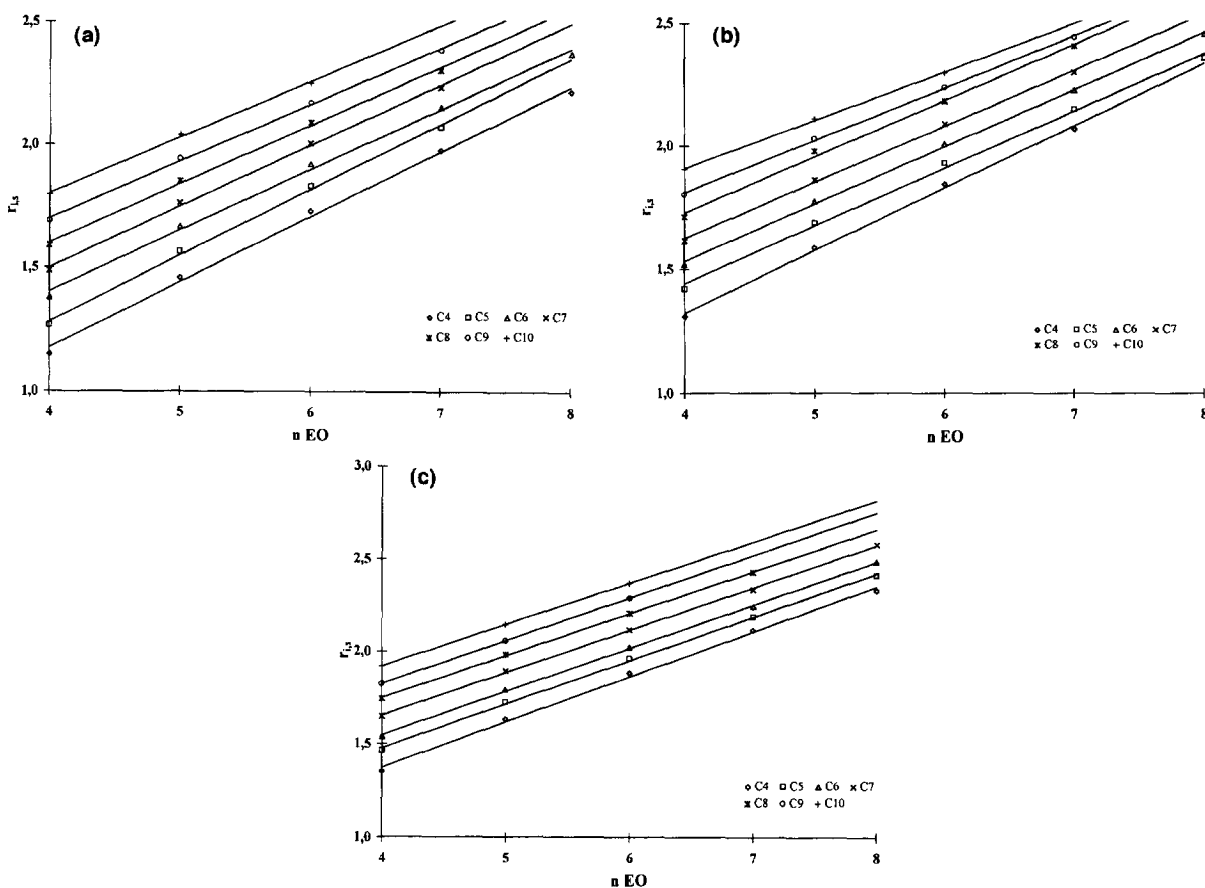| nEO	Compound						
	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}
0	0.041		0.175	0.312	0.451	0.594	0.748
1	0.271	0.411	0.542	0.697	0.827	0.958	1.094
2	0.665	0.807	0.924	1.059	1.174	1.283	1.401
3	1.031	1.155	1.256	1.370	1.475	1.567	1.675
4	1.351	1.462	1.539	1.647	1.742	1.824	1.920
5	1.631	1.724	1.792	1.893	1.983	2.058	2.145
6	1.883	1.963	2.024	2.118	2.206	2.289	2.370
7	2.117	2.187	2.245	2.336	2.432		
8	2.333	2.414	2.489	2.582			

Fig. 1. Correlation dependences of relative retention $(r_{i,s})$ on the number of ethylene groups (nEO) in a molecule. (a) Non-derivatized APEGEs; (b) TMS derivatives; (c) acetates.

possible linear courses of the dependences of retention time, temperatures and indices on the number of carbon atoms in homologous series were reviewed [32,33].

The correlation curves obtained and the $r_{i,s}$ values given in the tables were used for the identification of individual APEGEs, not only in synthesized mixtures, but also in the residues obtained after biodegradation. With a very small content of APEGE residues in a chloroform extract, incomplete EI mass spectra and less intensive MS–EI spectra were obtained. Therefore, the registering of chosen ions in selected-ion monitoring (SIM) mode was used and the identification of non-degraded APEGEs was carried out by means of reported $r_{i,s}$ values and correlation dependences. At the end of biodegrada-

tion, both non-degraded APEGE residues with $nEO > 4$ and moderately degraded residues were found in the reaction mixture. The methods of derivatization used (silylation and acetylation) made not only the elution of APEGE residues with higher numbers of EO groups, but also the selective registration of prepared derivatives in SIM mode, possible.

The decreases in individual APEGEs and in the mixtures of APEGEs in water as a function of the biodegradation time were determined from the recorded areas [34].

The degrees of biodegradation of oxyethylenated n-heptylalcohol, which were calculated from TOC determination and CGC–MS, are given in Table 4. The degree of biodegradation, which was calculated

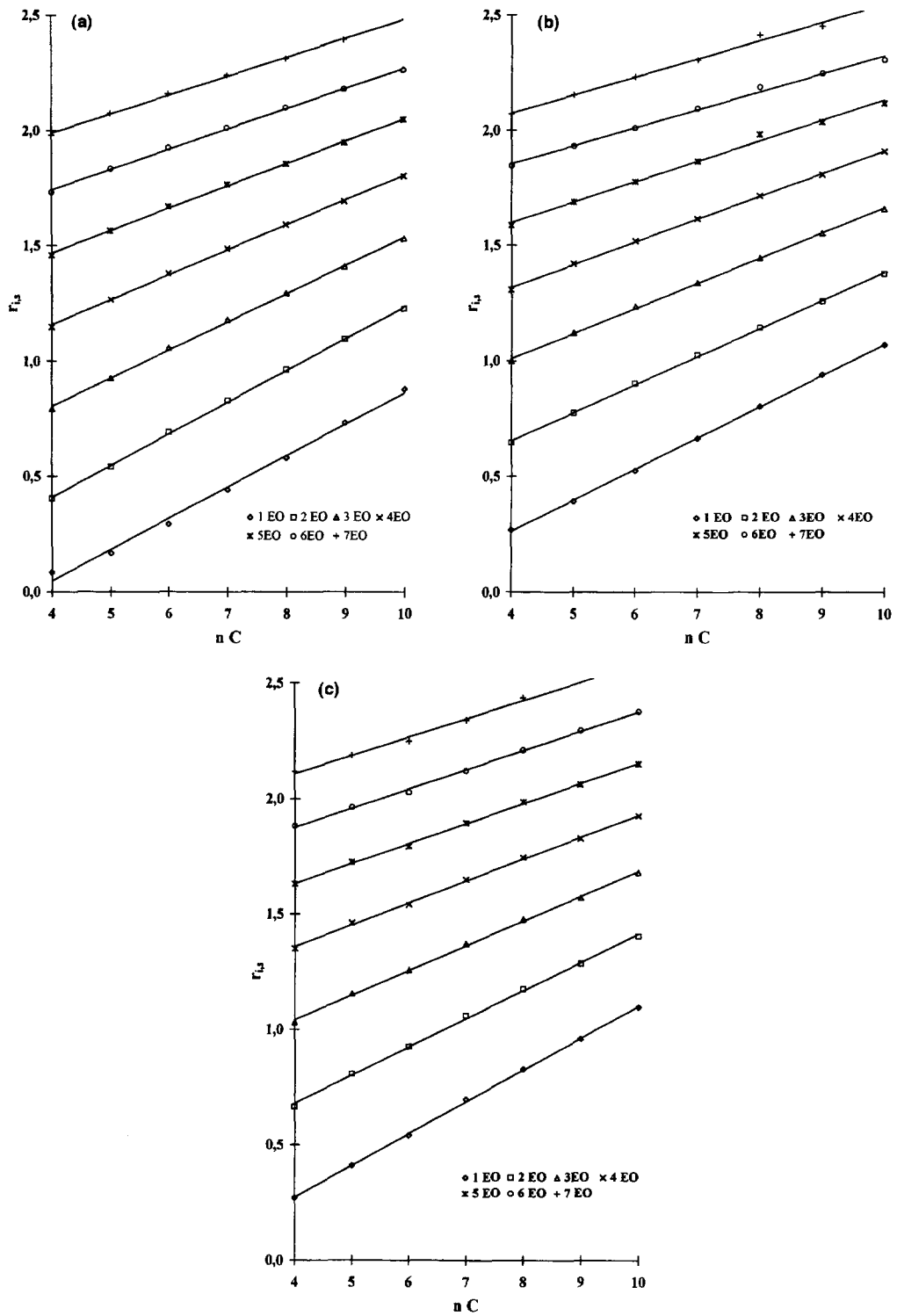Fig. 2. Correlation dependences of relative retention ($r_{i,s}$) on the number of carbon atoms (nC) in the alkyl part of APEGEs with the same number of EO groups in a molecule. (a) Non-derivatized APEGE; (b) TMS derivatives; (c) acetates.

Table 4
Biodegradation products of the oxyethylenation of n-heptylalcohol

Time of biodegradation (h)	Biodegradation by TOC (%)	Biodegradation by CGC–MS (%)
0.0	0.0	0.0
18.5	4.2	2.2
89.0	4.4	4.1
137.0	15.2	27.9
184.5	23.5	32.9
256.0	35.7	33.6
333.5	57.0	75.6
425.5	86.5	94.5
520.0	89.7	98.5

from CGC–MS determination was higher because it characterized the primary degradation of APEGEs that proceeded further via intermediates to give CO_2 and H_2O. CGC–MS analyses of residues following biodegradation showed that APEGEs with $nEO < 5$ were degraded gradually with good results. The biodegradation rate decreased with an increasing number of EO groups in the poly(ethylene glycol) part of a molecule. On the other hand, the APEGEs with $nEO > 5$ were degraded slowly, all at the same rate and with some of them not being degraded. In addition to residues of non-degraded APEGEs, intermediates were identified in extracts after biodegradation, such as monocarboxylic acids and poly(ethylene glycol)s. Analysis of these intermediates and biodegradation of APEGEs with the branched alkyl chains will be the topic of the next study.

Mass detection with EI connected to a capillary gas chromatograph makes it possible to simultaneously combine mass spectrometric and gas chromatographic identification. Therefore, it is not necessary to use more expensive equipment, such as that required for additional ionization techniques, etc., for the identification of lower APEGEs.

Acknowledgments

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