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Research Article

Gas Chromatography/Electron Ionization Mass Spectrometric Analysis of Oligomeric Polyethylene Glycol Mono Alkyl Ethers

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Abstract: Polyethylene Glycol Monoalkyl Ethers, C_xH_{2x+1} $(OC_2H_4)_n$ OH, (PEGMAE), are polar compounds like Polyethylene Glycols (PEG) and they undergo microbial degradation which produces toxic substances that are potentially dangerous to the environment. Therefore, the purpose of this study is to carry out proper identification and characterization of these compounds. The Electron Ionization (EI) and Chemical Ionization (CI) spectra of various PEGMAE were obtained by Gas Chromatography/Mass Spectrometry (GC/MS) and were used to identify and characterize these compounds. The characteristic cleavages in the EI and CI reactions of PEGMAEs were also studied. The results obtained showed that the methane CI mass spectra of the PEGMAE contain MH^+ ions and fragment ions similar to those found in their EI mass spectra. The relative abundances of the MH^+ ions are low, variable and increase with increasing sample size across the chromatographic peaks; but do not increase with increasing x or n. The base peaks of the low mass oligomers ($x \leq 3$) are PEG related (e.g., m/z 45, 59) but those of higher mass oligomers ($x \geq 4$) include the ion at m/z 63 $(HOC_2H_4OH)\ H^+$ or m/z 107 $(HO\ (C_2H_4O)_2\ H)\ H^+$. There are no $(MH\text{-}H_2O)^+$ ions or protonated dimer ions ($n \geq 2$, $x \geq 2$) in the spectra of PEGMAE. The Relative Molar Sensitivities (RMS) or the Relative Sensitivity per Gram (RSG) increases linearly with molecular polarizabilty or molecular weight with a non-zero intercept.

Keywords: Electron, methane chemical ionization, polyethylene glycol ethers

INTRODUCTION

Polyethylene Glycol Monoalkyl Ethers, C_xH_{2x+1} $(OC_2H_4)_n$ OH (PEGMAE), are polar compounds like Polyethylene Glycols (PEG) and are extensively used for many industrial purposes: in cleaning formulations, detergents, agriculture (Coble and Brumbaugh, 1993; Steber and Wierich, 1985) pharmaceuticals, alkaline batteries, tin electroplating, lubricants, coating agents and in textile fibres (Forkner *et al.*, 1994; Aronstein *et al.*, 1991). However, the widest application of PEGMAE is in the field of surfactants where they are used in formulating PEG based anionic, cationic or non ionic surfactants (Evans *et al.*, 1994). Because of the large production of PEGMAE, some oligomers have been found in environmental samples but are considered less environmentally harmful than ionic surfactants, but they still undergo microbial degradation that produces toxic substances that are potentially dangerous to the environment. Ethylene glycol and its oligomers are readily biodegradable and are not considered as persistent in the environment (Forkner *et al.*, 1994) but ethylene glycol derivatives have been observed in environmental samples (Sheldon and Hites, 1979). Evidence has been presented that ethylene glycol and ethylene glycol alkyl monomers have tetratogenic effects (Nadeau, 1964) if consumed in high doses. The metabolites of PEG ethers are usually aldehydes and carboxylic acids which are responsible for their toxic effects in animals (Nadeau, 1964). The wide usage of and inappropriate disposal of containers of polyethylene glycols and the corresponding ethers makes them inevitable pollutants. Despite the attempts to degrade industrial effluents, some still find their way into rivers, water, wells and the soil, suggesting that some of them are bioresistant (Cox, 1978; Kloster *et al.*, 1993; Watson and Jones, 1977). Allgood *et al.* (1990) reported that separation of higher molecular weight oligomers of PEGMAE ($x \geq 6$, $n \geq 5$) by Gas Chromatography (GC) and Mass Spectrometry (MS) are difficult because of their low volatility. Puthoff and Benedict (1961), separated some phenyl-azo derivatives of PEGMAE's (n = 1 - 2) oligomers and report of GC separation of nonylphenol ethoxylates was also made in earlier studies (Anghel *et al.*, 1994; Favretto *et al.*, 1978; Stephanou and Giger, 1982). The Electron Ionization (EI) spectra of low mass PEGMAE, like

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those of similar hydrocarbons, alcohols and ethers, show low abundance of molecular ions ($x \leq 3$, n = 1-4) while the higher members of this series ($x \geq 4$ for al n) do not contain molecular ions. Most of the mass spectra of PEGMAE available in the literature are spectra of phenyl, methyl, trimethylsilyl derivatives (Cross, 1987; Stein, 1997) including the EI mass spectra of mixtures of C_{12}-C_{14} ethoxylated alcohols, with up to twenty units of ethylene oxide, obtained by direct insertion into the source of the mass spectrometer (Julia-Danes and Casanovas, 1979). Because of the low volatility of these compounds, other techniques such as potentiometer, High Pressure Liquid Chromatography (HPLC), Thin Layer Chromatography (TLC) etc., have been used to analyze mixtures of PEGMAE (Cross, 1987). Proper identification of these compounds is impossible except other methods such as Chemical Ionization (CI) are used to obtain molecular weight information.

PEGMAE have a hydrophobic group and a hydrophilic group with an ether group sandwiched between them. The focal point of removing an electron from these compounds is either from the internal oxygen (ether) or the terminal (hydroxyl) oxygen. Other results given by McLafferty and Turecek (1993) and Williams and Howe (1972) have shown that the EI mass spectrum of PEGMAE include fragments produced by the general fragmentation pattern of the three classes of compounds such as: σ-cleavages ($C_xH_{2x+1}^+$, $C_xH_{2x-1}^+$, $C_xH_{2x}^+$), hydrogen rearrangements (hydrocarbons, alcohols, ethers), inductive or charge-site cleavages (alcohols and ethers, $C_xH_{2x+1}O^+$, $C_xH_{2x-1}O^+$, $C_xH_{2x}O^+$) and α-cleavages (alcohols, ethers, $RCH_2 = OH^+$).

Few EI mass spectra of PEGMAE are available in the literature. In this present study, the EI and methane chemical ionization (CH_4 CI) mass spectra of several PEGMAE will be obtained for proper identification and characterization and a comparison with the few EI spectra found in the NIST spectral data (Stein, 1997) base will be made with those obtained in our laboratory. Attempt will also be made to identify characteristic cleavages that occur with EI and CI of PEGMAE's.

MATERIALS AND METHODS

EI mass spectra of the PEGMAE were obtained by GC/MS using Hewlett Packard (HP) 5970 Mass Selective Detector (MSD) attached to an HP5980 gas chromatograph, an HP 5972 MSD attached to an HP 5980A gas chromatograph and a Micro Mass/VG Auto specQ mass spectrometer attached to an HP 5980 Series II gas chromatograph. Each MSD was calibrated using the automatic tuning procedure (Auto tune) with peflurotributylamine, PFTBA as the standard. Peflurokerosene, PFK was used to calibrate the Auto SpecQ mass spectrometer.

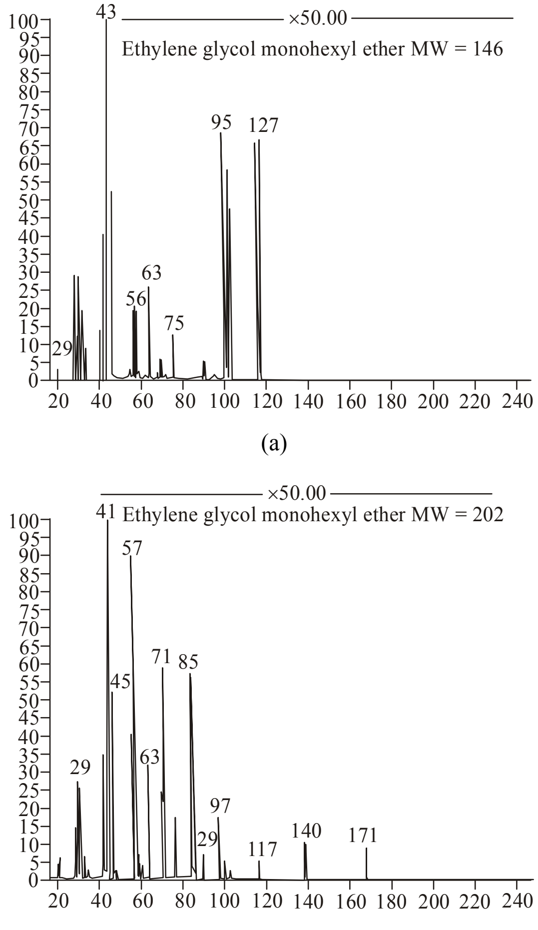
Source temperatures of the MSD were ~250°C and the transfer lines were ~280°C. A source temperature of ~200°C was used with the Auto SpecQ mass spectrometer and Helium was used as the carrier gas at a flow rate of 1 mL/min. EI ionization was done with nominal electron energy of 70 eV. Separation of mixtures of known concentrations of the lower oligomers (n = 1-6) were achieved with 30×0.25 mm cross-linked methyl silicone capillary columns (Alltech SE-30, SE54) using temperature programs of ~35-250°C at 5°C/min. Split less injections of 0.05-0.5 μL sample were used for these experiments.

The reported EI and CI mass spectra are averages of 3-5 spectra across the tops of the chromatographic peaks, with background subtraction. The Total Ion Current (TIC), was obtained by summing the ion currents of all the sample ions over the mass range, 10-500 μ. Solvent delay times (0.5-2.2 sec) were applied for the analyses of some mixtures, but most of the experiments were done with no solvent delay times. Chemical Ionization (CI) mass spectra were obtained using a VG MM-16 and the VG Auto SpecQ mass spectrometers. Source pressures was measured as ~0.3 torr with a capacitance manometer (MKS Instruments, Burlington, MA), connected directly into the source of the mass spectrometer by a glass tube through the inlet for the direct insertion probe. The ratios of the major ions in the methane reagent gas with the 2 instruments used in this study are similar: m/z 29/17 = 1, 19/17 = 0.02, 41/17 = 0.03 and 43/17 = 0.02 with the VG MM-16 and m/z 29/17 = 0.65, 19/17 = 0.02, 41/17 = 0.11 and 43/17 = 0.04 with the VG Auto Spec Q mass spectrometer (little H_3O^+ in the source).

RESULTS AND DISCUSSION

GC/EIMS of ethylene glycol monoalkyl ethers: The EI mass spectra of ethylene glycol monohexyl ether and ethylene glycol monodactyl ether are shown in Fig. 1.

The fragmentation patterns are similar to those in the mass spectra of Ethoxylated Fatty Amines (EFA) obtained by field desorption mass spectrometry, FD (Weber *et al.*, 1982). The major ions for both classes of compounds (PEGMAE and EFA) occur in the lower mass region and consist of ions with nominal composition: $C_xH_{2x+1}^+$ (15, 29, 43,...), $C_xH_{2x-1}^+$ (27, 41, 55,...), $C_xH_{2x}^+$ (28, 42, 56,...), $C_xH_{2x+1}O^+$ (31, 45, 59,...), $C_xH_{2x-1}O^+$ (29, 43, 57,...), $C_xH_{2x+2}OH^+$ (19, 33, 47, 61,...), $C_xH_{2x}O^+$ (30, 44, 58,...), $(HO\ (C_2H_4O)_n\ H)\ H^+$ (63, 107, 151,...). The EI mass spectra of low molecular weight hydrocarbons, alcohols and ethers have been shown to contain low abundant molecular ions (McLafferty and Turecek, 1993) but those of the corresponding high molecular weight homologs do not

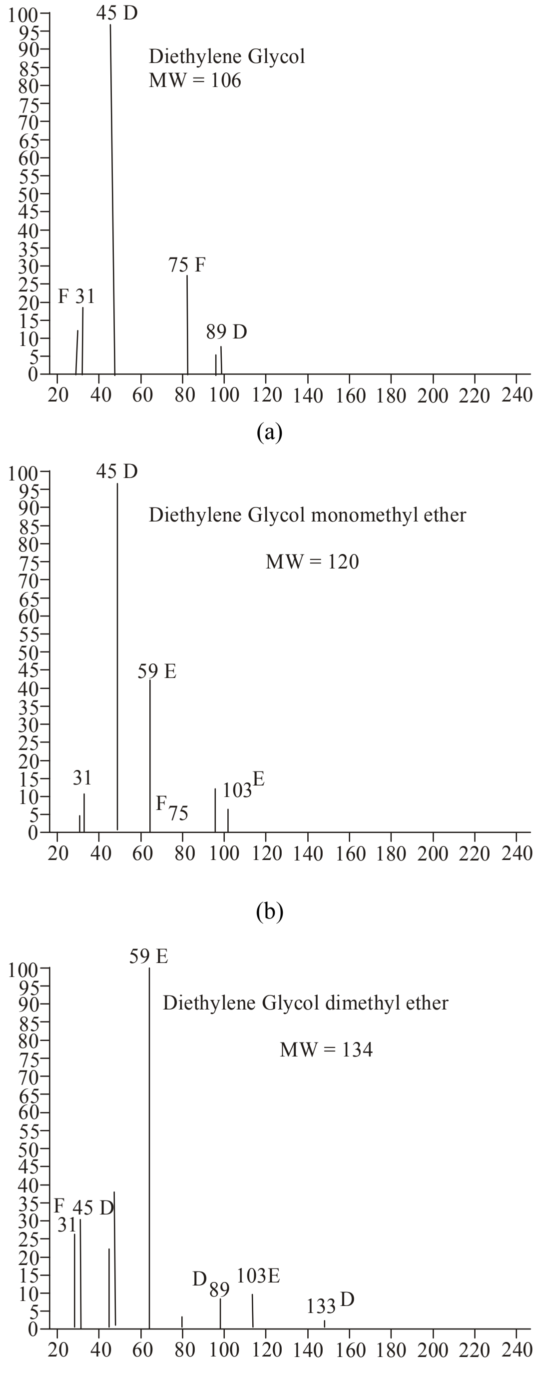


(a)

(b)

Fig. 1: 70 eV GC/EI mass spectra of (a) ethylene glycol monohexyl ether (b) ethylene glycol monodactyl ether on VG auto SpecQ

contain detectable molecular ions (Stein, 1997; Weber *et al*., 1982). Similarly, the EI spectra of PEGMAE ($x \geq 4$) consist mostly of low mass fragment ions and no high mass fragment ions of significant abundance to allow unambiguous determination of their molecular weights. However, the $(M+1)^+$ ions reported by Tanaka and Igarashi (2004); in the EI mass spectra of a mixture of ethoxylated fatty alcohols (C_{12}-C_{14}) must have resulted from ion-molecule reactions.



(a)

(b)

(c)

Fig. 2: GC/EI 70 eV mass spectra of (a) diethylene glycol, (b) diethylene glycol monomethyl ether, (c) diethylene glycol dimethyl ether; ($D = (C_2H_4O)_n H^+$, $E = CH_3 (OC_2H_4)_n^+$, $F = CH_3O (C_2H_4O)_n^+$)

For short alky chain PEGMAE, ($x = 1$-2), the EI spectra are similar to the mass spectra of the analogous PEG oligomers and their dimethyl ethers reported by Favretto *et al*. (1978) (Fig. 2). The 70 eV EI mass spectra of EGMAE, $C_xH_{2x+1}OC_2H_4OH$, obtained by two instruments in our laboratory and the literature data (Coble and Brumbaugh, 1993) for the lower oligomers ($x = 1$-9), are similar to each other. However, there are significant differences among the relative abundances of the major ions in the spectra obtained in this laboratory and those of the literature (although there is no obvious pattern to the differences).

The spectra of the ethylene glycol monomethyl ether, its ethyl and propyl analog (x = 1, 2, 3) do not contain detectable molecular ions but show distributions of ions similar to those of the analogous hydrocarbons ($C_xH_{2x+1}^+$, $C_xH_{2x-1}^+$, $C_xH_{2x}^+$, $C_xH_{2x-2}^+$) with additional oxygen containing ions derived from the ethylene oxide units ($C_xH_{2x+1}O^+$, $C_xH_{2x}O^+$, $C_xH_{2x-1}O^+$, $C_2H_4OH^+$, (HOC_2H_4OH) H^+). However, the alkyl fragment ions, oxygen containing fragment ions and fragment ions separated by 44 mass units, will allow the identification of these compounds as polyethylene glycol derivatives. Alkyl ions with the same carbon number as the alkyl groups attached to the ethylene glycol unit are relatively abundant and therefore, allow for a differentiation of each PEGMAE from each other (x≤6).

The inductive cleavage reactions at the ether oxygen of EGMAE can give four ionic products Eq. (1) to (4), viz: Two α-cleavage product ions Eq. (5) to (7) which produce alkyl ions. The $C_2H_4OH^+$ ion (m/z 45) becomes more abundant with increasing size of the alkyl group. The ratio:

$$RO^{+\cdot}C_2H_4OH \rightarrow R^+ + {}^{\cdot}OC_2H_4OH \quad (1)$$

$$\rightarrow {}^{+}OC_2H_4OH + R \quad (2)$$

$$\rightarrow C_2H_4OH^+ + RO^+ \quad (3)$$

$$\rightarrow RO^+ + {}^{\cdot}C_2H_4OH \quad (4)$$

$$\rightarrow RO^+ = CH_2 + {}^{\cdot}CH_2OH \quad (5)$$

$$\rightarrow CH_2 = OH^+ + ROCH_{2.} \quad (6)$$

$$R^+ \rightarrow \text{lower alkyl fragment ions} \quad (7)$$

of the I (R^+) /I (RO^+) ions Eq. (1), (7), increases with increasing value of x for x = 1 - 6 and becomes very small for x = 10 and 12 because of the subsequent decomposition of the R^+ ion to lower mass fragment ions. These observations suggest: that the cleavage of the R--O^+ bond is favored over the cleavage of the RO--C bond.

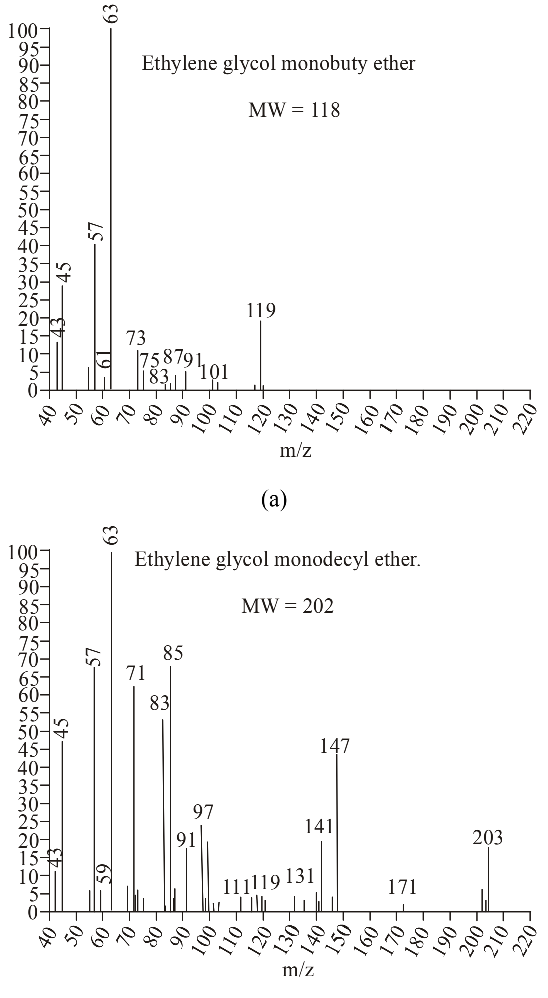
The base peak in the spectrum of ethylene glycol monomethyl ether is the ion at m/z 45, which is probably both $CH_3O^+ = CH_2$ (α-cleavage) and or protonated ethylene oxide (inductive cleavage). The base peak of ethylene glycol monoethyl ether is the ion at m/z 31, which is probably formed from the terminal CH_2OH Eq. (6), cleavage of the C-O bond). As the size of the alkyl group increases (x≥3), there are consecutive decompositions of the saturated hydrocarbon ions which resulted into lower alkyl fragment ions. The abundances of these alkyl fragments reaches a maximum at C_3 (m/z 43) or C_4 (m/z 57). The base peak of EGMAE is either m/z 43 or 57 except that of ethylene glycol mono nonlethal (m/z 69 ($C_xH_{2x-1}^+$). The lower mass $C_xH_{2x+1}^+$ and $C_xH_{2x-1}^+$ ions are also major ions in the mass spectra of decanol and dodecanol (the base peak at m/z 43). However, the $C_xH_{2x-1}^+$ and $C_xH_{2x}^+$ ions are more prominent in the mass spectra of decanol and dodecanol than in those of EGMAE (Stein, 1997).

The ions in the series $C_xH_{2x+1}^+$ are isobaric with the ions in $C_xH_{2x-1}O^+$ series. The $C_xH_{2x+1}^+$ ion are formed by charge-site cleavages of the ether C-O bond followed by σ-cleavages of the C-C bonds. The $C_xH_{2x-1}O^+$ ions are also formed by charge-site cleavage of the ether C-O bond followed by decompositions into lower mass oxygen containing fragment ions or becomes dehydrated to form $C_xH_{2x-1}^+$ ions. In the EI mass spectra of alcohols, McLafferty and Turecek (1993) showed that ions such as $C_2H_5^+$, CHO^+ and $C_3H_7^+$, $C_2H_3O^+$ contributes to the relative abundance of ions at mass m/z 29 and 43, respectively. The relative abundance of m/z 29 (% total ionization) in this experiment decreases with increasing x. This observation suggests that most of m/z 29 ions are CHO^+ ions and with some contributions from $C_2H_5^+$.

There is a series of nominal α-cleavage ions, $C_xH_{2x+1}O = CH_2^+$, (31, 45, 59, 73, 87 and 101 m/z, respectively) which are probably carbocations. These carbocations may undergo hydrogen rearrangement to the carbon atom of the oxonium double bond. The rearrangement also involves loss of C_xH_{2x} ions to form more CH_3O^+ or higher mass oxonium ions. The relative abundances of these ions depend on the relative abundance of its primary ions (Levin and Lias, 1971). The ion at m/z 31 is the most abundant in this series and its relative abundance (% Total Ionization, TIC) decreases with increasing size of the alkyl group. This observation suggests that the ions at m/z 31 are formed mostly from the terminal $HOCH_2$ with minimal contribution from CH_3O^+ (Stephanou and Giger, 1982).

Ions at m/z 63, $HOC_2H_4OH_2^+$, only occur when x≥3 and are likely to be formed by double hydrogen rearrangement reactions. Its relative abundance (% TIC) increases with increasing x and reaches a limiting value of ~3.3% with ethylene glycol dodecyl ether.

There is another series of ions with nominal composition of $C_xH_{2x-1}^+$ (41, 55 and 69 m/z, respectively) formed from the decomposition of the alkyl fragment ion ($C_xH_{2x+1}^{+\cdot}$) or from the dehydration of the $C_xH_{2x-1}O^+$ ions. The relative abundances of these ions (% TIC) increase with increasing value of x and



(a)

(b)

Fig. 3: CH_4/CI mass spectra of (a) ethylene glycol monobutyl ether (b) ethylene glycol monodactyl ether

m/z 69 is the base peak in the spectrum of ethylene glycol monononyl ether. The sum of the relative abundances of these ions varies from ~10% of the total ionization for ethylene glycol monomethyl ether to ~30% in ethylene glycol dodecyl ether and are more abundant in the mass spectra of decanol and dodecanol than in the spectra of the corresponding ethylene glycol monodactyl and dodecyl ethers (Stein, 1997).

Another decomposition pathway observed with the lower mass ethylene glycol monoalkyl ethers (x = 1 - 4) is the elimination of water (1-5% of total ionization). The spectra of the higher EGMAE (x≥6) do not contain $(M\text{-}H_2O)^+$ ions in contrast to the mass spectra of n-decanol and n-dodecanol (Harrison *et al.*, 1971).

Series of ions formed by the loss of neutral (H_2O + C_xH_{2x}) molecules (m/z 30, 44, 58...) were also observed. These ions are formed in decreasing amounts with increasing value of x for each of the monoalkyl ethers and constitute ~2-7% of the total sample ionization. A series of olefinic ions, $C_xH_{2x}^+$ (m/z 42, 56, 70…) were also present in the spectra of these monoalkyl ethers. The relative abundances of these ions vary between ~3-8% of the total ionization.

The major ions in the EI mass spectra of polyethylene glycol monodactyl and dodecyl ethers, C_xH_{2x+1} $(OC_2H_4)_n$ OH (x = 10,12; n = 1- 3), consist mostly of low mass hydrocarbon homolog's (~56-65%, $C_xH_{2x+1}^+$, $C_xH_{2x}^+$, $C_xH_{2x-1}^+$, $C_xH_{2x-2}^+$, etc.) with additional oxygen containing ions derived from ethylene oxide units (~26-28%, $CxH_{2x-1}O^+$, $CxH_{2x}O^+$, $(C_2H_4O)_n$ H^+, HO $(C_2H_4O)_n$ H_2^+) and no molecular ions. The base peaks in the spectra of these compounds are variable and are determined by the hydrocarbon part of the oligomer when n≤2, x≥3 and by the ethylene oxide moiety when n≥3. The dominant cleavages in all spectra of the monodactyl ethers are a chimerically assisted charge-site cleavages and σ-cleavages. The simple α-cleavage ions accompanied by hydrogen rearrangement (31, 75, 119 and 163 m/z, respectively) are not as prominent as those in the spectrum of PEG's, 1-decanol and other alcohols (Onigbinde *et al.*, 2001).

Chemical Ionization (CI): The methane CI (CH_4) of ethylene glycol monohexyl and monodactyl ether is shown in Fig. 3. The methane CI mass spectra of these compounds contain MH^+ ions and fragment ions similar to those found in their EI mass spectra. The relative abundances of the MH^+ ions are low, variable and increase with increasing sample size across the chromatographic peaks; hence, a major portion of these ions are formed by sample ion/sample molecular reactions. The relative abundances of the MH^+ ions do not increase with increasing x or n. The base peaks in the spectra of these compounds under methane CI are also variable and are determined by the ethylene oxide moiety. For the low mass oligomers (x≤3), the base peak are PEG related (e.g., m/z 45, 59) but those of higher mass oligomers (x≥4) are MH^+ ions (n≥3) and sometimes ions formed by hydrogen rearrangement decompositions of the MH^+ ions (m/z 63 and 107, (HO $(C_2H_4O)_2$ H) H^+ (n = 1 - 2)). There are no $(MH\text{-}H_2O)^+$ ion or protonated dimer Ions (n≥2, x≥2) in the spectra of PEGMAE. The relative abundances of the major Ions decrease in the order of m/z 89>45>133>177 and are different from the order in methane CI of PEG oligomers (Onigbinde *et al.*, 2001).

Table 1: Relative molar sensitivities of polyethylene glycol monoalkyl Ethers (EI)

Compound	GC	MW	MW ratio	[c]α	[d]P	[e]RMS	[f]RSG
Methoxy ethanol	a	76.1	0.31	7.42	0.26	0.28 (0.03)	0.91 (0.10)
	b					0.30 (0.04)	0.97 (0.13)
Ethoxy ethanol	a	90.1	0.37	9.24	0.33	0.36 (0.05)	0.98 (0.14)
	b					0.38 (0.04)	1.03 (0.11)
2-butoxy ethanol	a	118.1	0.48	12.90	0.46	0.48 (0.04)	1.00 (0.08)
	b					0.46 (0.03)	0.96 (0.06)
Diethylene glycol mono methyl ether	a	120.2	0.49	11.69	0.42	0.43 (0.07)	0.88 (0.14)
	b					0.45 (0.03)	0.92 (0.06)
Diethylene glycol mono ethyl ether	a	134.2	0.55	13.51	0.48	0.51 (0.05)	0.94 (0.09)
	b					0.51 (0.03)	0.94 (0.06)
Ethylene glycol mono hexyl ether	b	146.2	0.59	16.56	0.58	0.58 (0.03)	0.91 (0.05)
Diethylene glycol mono butyl ether	a	162.1	0.66	17.16	0.61	0.58 (0.01)	0.88 (0.02)
	b					0.55 (0.04)	0.84 (0.06)
Diethylene glycol mono pentyl ether	a	176.1	0.72	18.97	0.68	0.63 (0.05)	0.88 (0.07)
	b					0.75 (0.09)	1.05 (0.13)
Diethylene glycol mono hexyl ether	a	190.2	0.77	20.79	0.74	0.71 (0.05)	0.92 (0.06)
Ethylene glycol mono decyl ether	a	202.2	0.82	23.95	0.85	0.73 (0.06)	0.89 (0.07)
	b					0.69 (0.02)	0.84 (0.02)
Ethylene glycol dodecyl ether	a	230.2	0.94	27.63	0.99	0.82 (0.01)	0.88 (0.01)
	b					0.84 (0.04)	0.90 (0.04)
Diethylene glycol mono decyl ether	a	246.2	1.00	28.19	1.00	1.00	1.00
	b					1.00	1.00
Diethylene glycol dodecyl ether	a	274.2	1.11	31.87	1.13	1.08 (0.07)	0.96 (0.06)
	b					1.12 (0.04)	1.01 (0.04)
Triethylene glycol mono decyl ether	a	290.2	1.18	32.40	1.11	1.04 (0.05)	0.97 (0.05)
	b					1.17 (0.03)	1.14 (0.03)
Triethylene glycol dodecyl ether	a	318.2	1.29	36.11	1.28	1.27 (0.08)	0.98 (0.06)
	b					1.28 (0.05)	0.99 (0.04)
Tetraethylene glycol dodecyl ether	a	362.2	1.47	40.36	1.44	1.31 (0.06)	0.89 (0.04)
	b					1.36 (0.04)	0.92 (0.03)

[a]: HP5970; [b]: VG auto specQ, [c]: Molecular polarizability, calculated according to reference 20; [d]: Molecular polarizability ratio; [e]: RMS = Relative molar sensitivity (calculated relative to diethylene glycol monodactyl ether = 1.00); [f]: RSG = Relative sensitivity per gram; Average of at least 5 GC/MS experiments Standard deviations given in parentheses

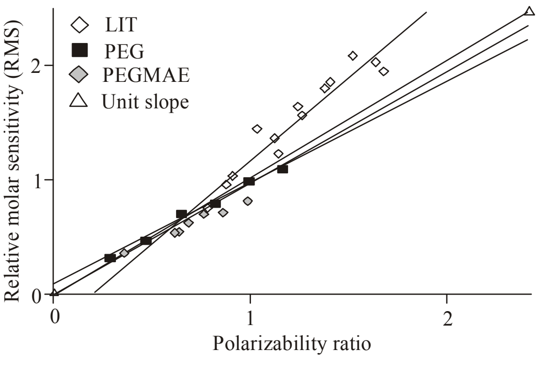


Fig. 4: Relative Molar Sensitivity (RMS) vs. polari ability ratio

Relative molar sensitivities of polyethylene glycol monoalkyl ethers: The Relative Molar Sensitivities (RMS) for some PEGMAE obtained with a quadrupole (MSD) and magnetic sector (VG Auto SpecQ) mass spectrometers are given in Table 1. The agreement between the two sets of data is satisfactory (±10%). RMS of the PEGMAE increase with increasing molecular weight or polarizability as observed previously for the polyethylene glycols, hydrocarbons and some PEGMAE (Harrison *et al*., 1971; Allgood *et al*., 1990). Figure 4 shows a plot of relative molar sensitivity, RMS, vs. polarizability ratio over the range obtained with HP 5970 (MSD). A line of unit slope, RMS = P, gives a reasonable fit (±10%) to the data. A better fit to these data is achieved, however, with a non-zero intercept and a slope which is less than one:

$$\text{RMS} = 0.96397\text{P} + 0.02387$$

The data for the relative molar sensitivities of polyethylene glycols reported by Onigbinde *et al*. (2001) is also shown in Fig. 4. The data for the PEG oligomers and the PEGMAE oligomers show essentially the same variation with polarizability ratio. The relative molar sensitivities of some PEGMAE (C_{10} - C_{12}) obtained previously in this laboratory (Allgood *et al*., 1990) were recalculated to $C_{10}H_{21}(OC_2H_4)_2OH$ and are also shown in Fig. 4. These data have a slope significantly greater than one and do not overlap the data obtained here. There is no obvious explanation for these differences.

Table 1 also lists the Relative Sensitivity per Gram (RSG) for the PEGMAE. To a reasonable approximation, one can consider the RSG to be unity; therefore, area percent from a chromatographic trace would be the same as the weight percent. The average value for the relative sensitivities per gram is 0.92 (±0.05).

CONCLUSION

The EI mass spectra of low mass PEGMAE, like those of similar hydrocarbons, alcohols and ethers, show low abundance of molecular ions ($x \leq 3$, $n = 1 - 4$). The higher members of this series ($x \geq 4$, for all n) do not contain molecular ions in their EI mass spectra. The major ions in the EI spectra of all PEGMAE are: $C_xH_{2x\pm1}^+$, $C_xH_{2x}^+$, $C_xH_{2x-2}^+$, $C_xH_{2x-1}O^+$, $C_xH_{2x}O^+$, $(C_2H_4O)_n H^+$, $HO (C_2H_4O)_n H_2^+$. There are no $(M-H_2O)^+$ ions in the mass spectra of PEGMAE for $n \geq 2$ and the relative abundances of the characteristic $C_xH_{2x+1}^+$ ions decrease with increasing x. The base peaks in the CI spectra of these compounds are variable and are determined by the hydrocarbon part of the oligomers when $n \leq 2$, $x \geq 3$ and by the ethylene oxide moiety when $n \geq 3$. The dominant cleavages in all spectra of PEGMAE are a chimerically assisted charge-site cleavages and alpha cleavages. The relative molar sensitivities, RMS, for these compounds increase linearly with increasing molecular polarizability or molecular weight. THE RMS under EI conditions shows a non-zero intercept and a slope less than one which is different from the one previously reported with a slope greater than 1.

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