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ANALYSIS AND IDENTIFICATION OF N-OLIGOXYETHYLENE MONO- AND DIALKYLAMINES

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SUMMARY

Gas chromatography and gas chromatography–mass spectrometry were used to analyze individual and polydisperse mixtures of mono- and dialkylamines containing up to six oxyethylene units. The products were analyzed directly and as their trimethylsilyl derivatives. Arithmetic retention indices were determined and proposed for use in identification of different homologues. The mass spectra of the trimethylsilyl derivatives of the amines are discussed.

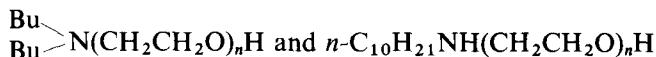
INTRODUCTION

In previous studies^{1,2} gas chromatography (GC) and mass spectrometry (MS) were used to determine the composition of product mixtures obtained in the reaction of hexylamine and some commercial alkylamines with ethylene oxide. For different mean molar ratios of the reagents, the contents of homologues having up to fourteen oxyethylene units in both polyoxyethylene chains were determined. Their structures were confirmed by GC–MS. This method was also used to estimate the ratios of the positional isomers in homologues containing up to seven oxyethylene groups.

It was found that successive homologues of N,N'-di(polyoxyethylene)alkylamines can be identified from the values of their arithmetic retention index. Some analytical problems were observed in the case of products in which the mean degree of oxyethylation did not exceed 2. In such cases the analyzed amines contained N-(2-hydroxyethyl)alkylamine which could form both the mono- and bis(trimethylsilyl) derivatives: N-(2-hydroxyethyl)alkylamine trimethylsilyl ether and N-(2-hydroxyethyl)-N-(trimethylsilyl)alkylamine trimethylsilyl ether. Thus more peaks were observed on the chromatograms and their identification and analysis were more complex.

This paper deals with analytical and especially identification problems in the

chromatographic analysis of N-oligooxyethylene alkyl- and dialkylamines containing only one oligooxyethylene chain. Contrary to the previous studies where polydisperse mixtures or even commercial products were analyzed, we have used individual compounds of the following structures



abbreviated as $\text{Bu}_2\text{NE}_n\text{H}$ (Bu = butyl) and $\text{C}_{10}\text{NE}_n\text{H}$, where $n = 1-6$. A post-reaction mixture of N-oligooxyethylene monoalkylamines containing five and six oxyethylene units was also used. Polydisperse mixtures were obtained by mixing appropriate amounts of the model compounds. These reagents and the methods of their synthesis have been described previously³.

EXPERIMENTAL

A gas-liquid chromatograph (Perkin-Elmer Model 900) with a flame ionization detector was used. The separation was carried out in stainless-steel columns (1.8 m \times 2.7 mm I.D.). Chromosorb G AW DMCS (60-80 mesh) was used as the support and silicone resin OV-17 (3%) as the liquid phase. Argon was used as the carrier gas, and its flow-rate was 15 cm³/min. The temperatures of the injector and the detector were 270 and 320°C, respectively. The column temperature was raised from 120 to 320°C at 4°/min.

Trimethylsilyl derivatives were prepared in a glass micro reaction vessel (capacity 3 cm³) having a PTFE-lined cap (Supelco, Bellefonte, PA, U.S.A.). A sample of about 0.05 g of the amine was weighed and 0.5 cm³ of N,O-di(trimethylsilyl)-acetamide (Applied Science Labs., State College, PA, U.S.A.) were added. The sealed reaction vessel containing dibutylamine derivatives was maintained at 60°C for 30 min and shaken from time to time. After this time silylation was complete and the product was analyzed. Derivatives of decylamine were maintained at different temperatures in the range of 20-120°C for 1-180 min.

The identification of the separated components was carried out by means of a mass spectrometer, coupled to a gas-liquid chromatograph (GC-MS 2091; LKB, Bromma, Sweden). The chromatographic column and separation conditions were the same as the GC analysis. The mass spectra were taken at the tops of the chromatographic peaks. An ionization energy of 70 eV, an ion-source temperature of 250°C, a pressure of $5 \cdot 10^{-7}$ mmHg and a sweep time of 9 s were employed. The products were analyzed in the form of their trimethylsilyl derivatives.

RESULTS AND DISCUSSION

Separation and identification of N-oligooxyethylene dibutylamines

The model compounds can be analyzed both directly and as their trimethylsilyl derivatives. The homologues having longer oligooxyethylene chains must be analyzed in the form of volatile derivatives. The chromatograms obtained directly for the compounds (dissolved in ethanol) illustrate their purity. Single peaks were also obtained when other liquid phases were used. The chromatograms of trimethylsilyl

derivatives are similar, but small peaks of impurities are observed. The contents of impurities, estimated from the surface area of the peaks and assuming correction coefficients equal to 1, are in the range of 0.5–5%. A typical chromatogram for a mixture of the amines is shown in Fig. 1.

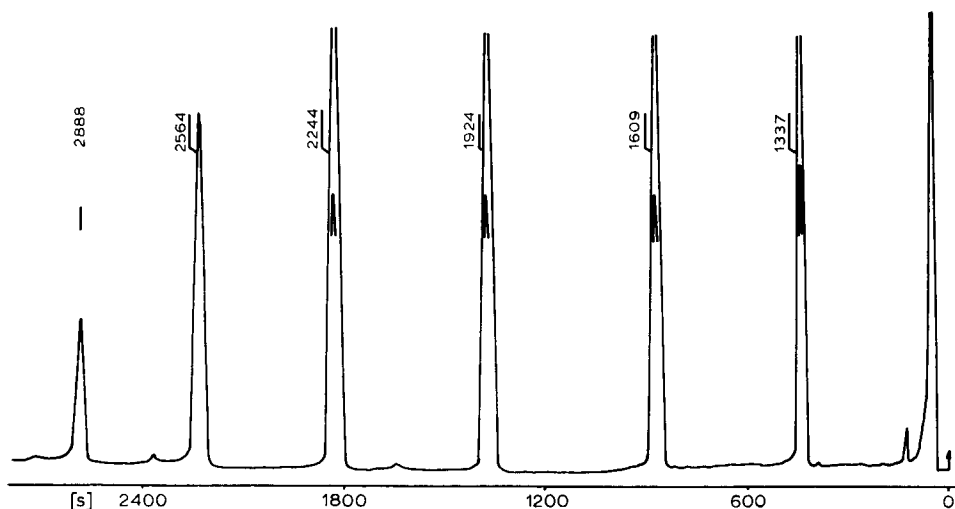


Fig. 1. A gas chromatogram of a polydisperse mixture of N-oligooxyethylene dibutylamines.

The mass spectra of the trimethylsilyl derivatives of the amines containing up to three oxyethylene units are given in Fig. 2. In all these spectra parent ions are present: at m/e 245, 289 and 333 for homologues containing one, two and three oxyethylene units, respectively. The main fragment ion at m/e 142, $[\text{Bu}_2\text{NCH}_2]^+$, is formed as a result of the splitting of the C–C bond in the oxyethylene unit linked to the nitrogen atom. Partial splitting of the C–O bond also occurs in this oxyethylene group, and an ion at m/e 156, $[\text{Bu}_2\text{NCH}_2\text{CH}_2]^+$, is observed. The next characteristic ion, $[\text{M} - 43]^+$, is formed by splitting off the propyl radical from a hydrocarbon chain. Ions at m/e 73, $[\text{Si}(\text{CH}_3)]^+$, and m/e 100 are also observed.

The mass spectra obtained fully confirm the structure and purity of the investigated homologues and the completeness of silylation.

Separation and identification of N-oligooxyethylene decylamines

A typical chromatogram obtained directly for a mixture of the amines, *i.e.*, without silylation, is shown in Fig. 3. Some small peaks of impurities are also present; their contents in the amines containing up to four oxyethylene units, as determined for individual amines, are in the range of 1.8–8.5%. The post-reaction mixture of N-oligooxyethylene monoalkylamines contains 45.7% and 26.5% of the homologues having five and six oxyethylene units, as well as 22 other unidentified compounds present in small quantities, in the range of 0.1–5.1%.

Chromatograms for trimethylsilyl derivatives are usually more complex. In the reaction with N,O-di(trimethylsilyl)acetamide the considered N-oligooxyethylene de-

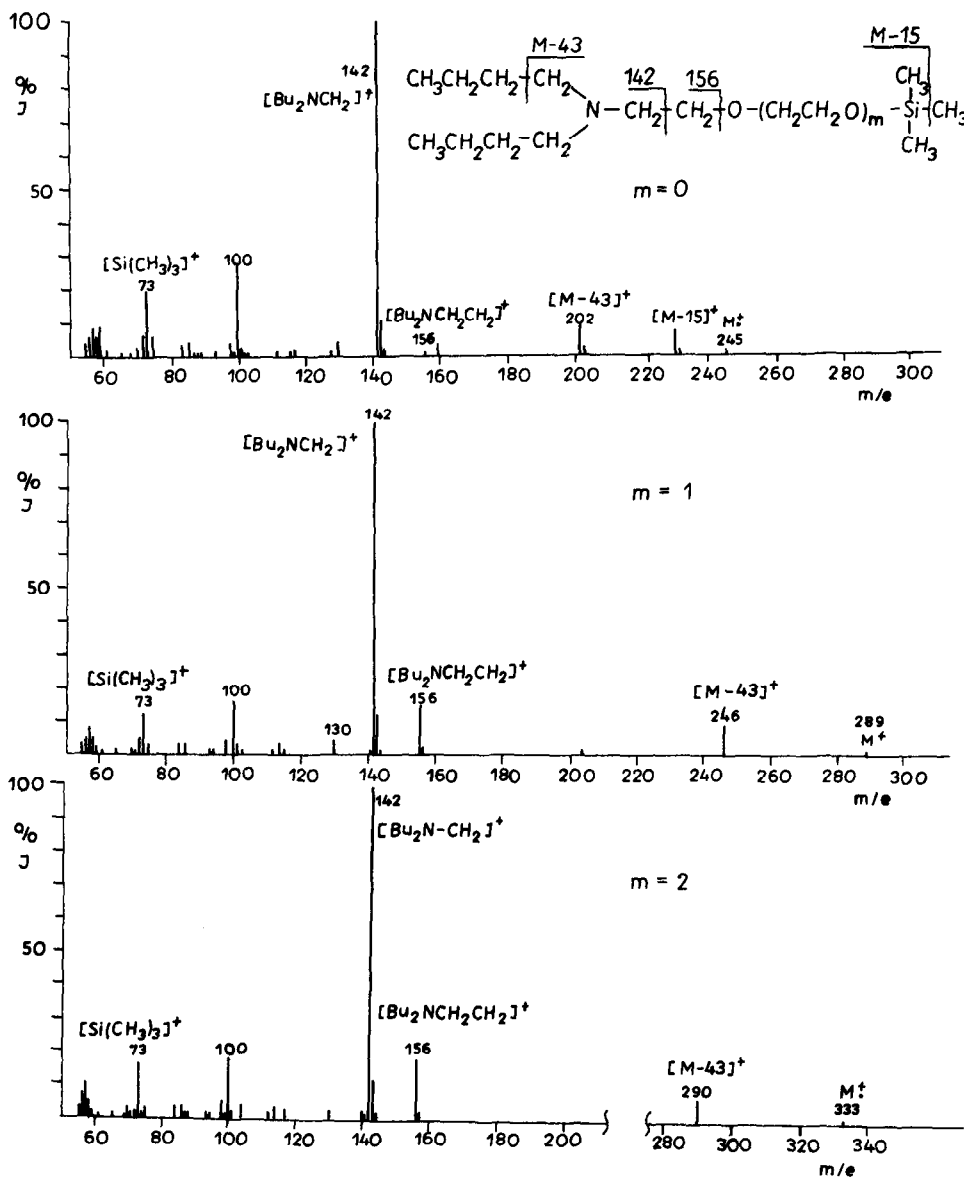
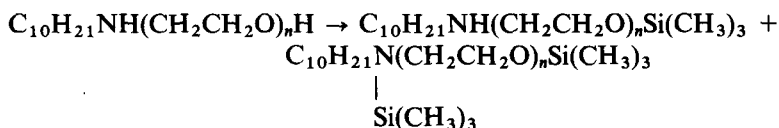


Fig. 2. The mass spectra of trimethylsilyl derivatives of N-oligooxyethylene dibutylamines containing one, two and three oxyethylene units ($M = 245, 289$ and 333).

cyamines can form mono- and bis(trimethylsilyl) derivatives, which in some cases are eluted together and in other cases separately:



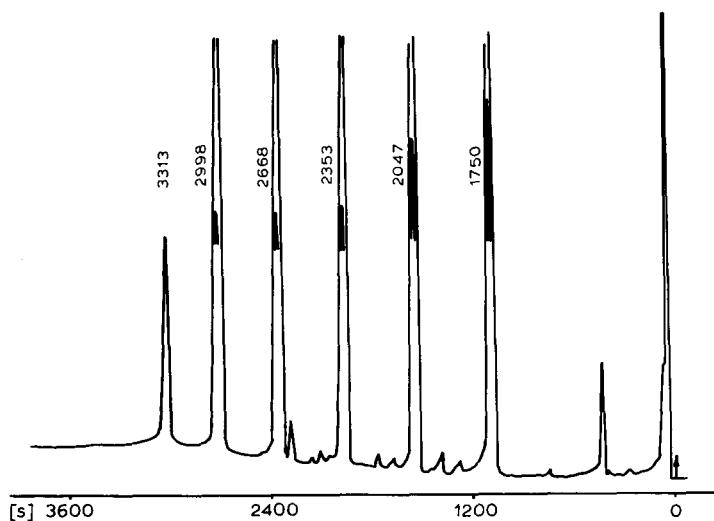


Fig. 3. A gas chromatogram of a polydisperse mixture of N-oligooxyethylene decylamines.

We succeeded in the separation of mono- and bis(trimethylsilyl) derivatives of homologues containing up to four oxyethylene units (Fig. 4). The relative ratio of mono- to bis(trimethylsilyl) derivatives depends upon the silylation conditions, especially

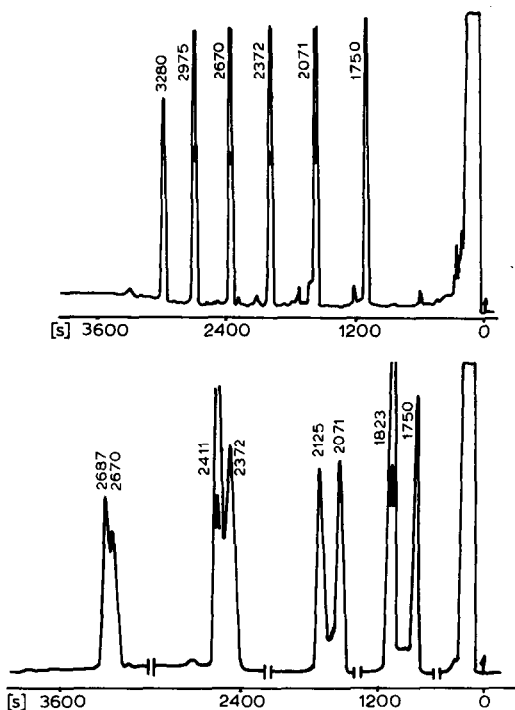


Fig. 4. Gas chromatograms of silyl derivatives of N-oligooxyethylene decylamines; monotrimethylsilyl derivatives at the top, mono- and bis(trimethylsilyl) derivatives at the bottom.

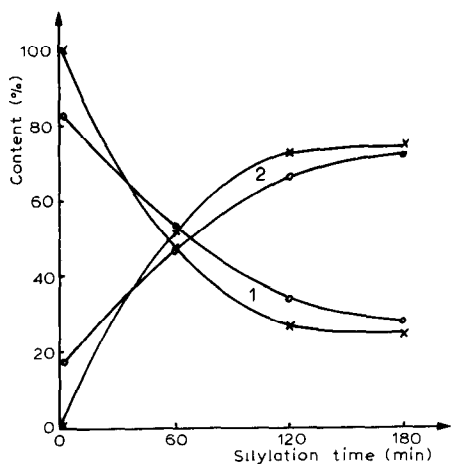
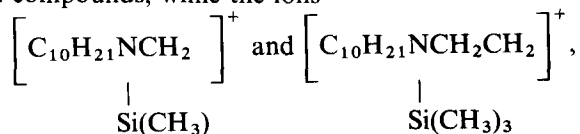


Fig. 5. The content of mono- and bis(trimethylsilyl) derivatives during the silylation of *N*-oligooxyethylene decylamines: O—O, C₁₀NE₂; ×—×, C₁₀NE₄; 1, 2 = mono- and bis(trimethylsilyl) derivatives, respectively. Amounts of reagents: amine, 0.02 g; *N,O*-di(trimethylsilyl)acetamide, 0.2 cm³.

the time of silylation (Fig. 5). At room temperature, directly after mixing of the reagents, mainly mono derivatives are formed, whose content is above 80%. The content of bis(trimethylsilyl) derivatives increases as the silylation time increases, achieving an equilibrium value after 3 h. At this time the content of mono derivatives is about 25–30%. Further changes in the silylation time and heating reaction mixtures up to 120°C did not result in a higher content of bis(trimethylsilyl) derivatives. In the case of the post-reaction mixture (it was impossible to carry out a distillation) of *N*-oligooxyethylene monodecylamines containing homologues having five and six oxyethylene units, bis(trimethylsilyl) derivatives were not formed. Moreover, when this product was added to other pure model compounds the formation of bis(trimethylsilyl) derivatives of these compounds also ceased. This was not caused by the pH of the sample, the acidity being similar to those of the other products.

The mass spectra of the separated mono(trimethylsilyl) derivatives are given in Fig. 6. With the exception of the spectrum obtained for the homologue containing five oxyethylene groups, parent ions are present: at *m/e* 273, 317, 361 and 405 for compounds having one, two, three and four oxyethylene units, respectively. The other main fragment ions are analogous to those observed for *N*-oligooxyethylene dibutylamines. Those at *m/e* 170 and 184 ions prove that the trimethylsilyl group is not bonded to the nitrogen atom. The ions at *m/e* 242 and 256, characteristic for bis(trimethylsilyl) derivatives or for mono derivatives in which the trimethylsilyl group is bonded to the nitrogen atom, are not observed.

The mass spectra of the bis(trimethylsilyl) derivatives (Fig. 7) confirm their structures. The parent and [M - 15]⁺ ions yield the molecular masses of the separated compounds, while the ions



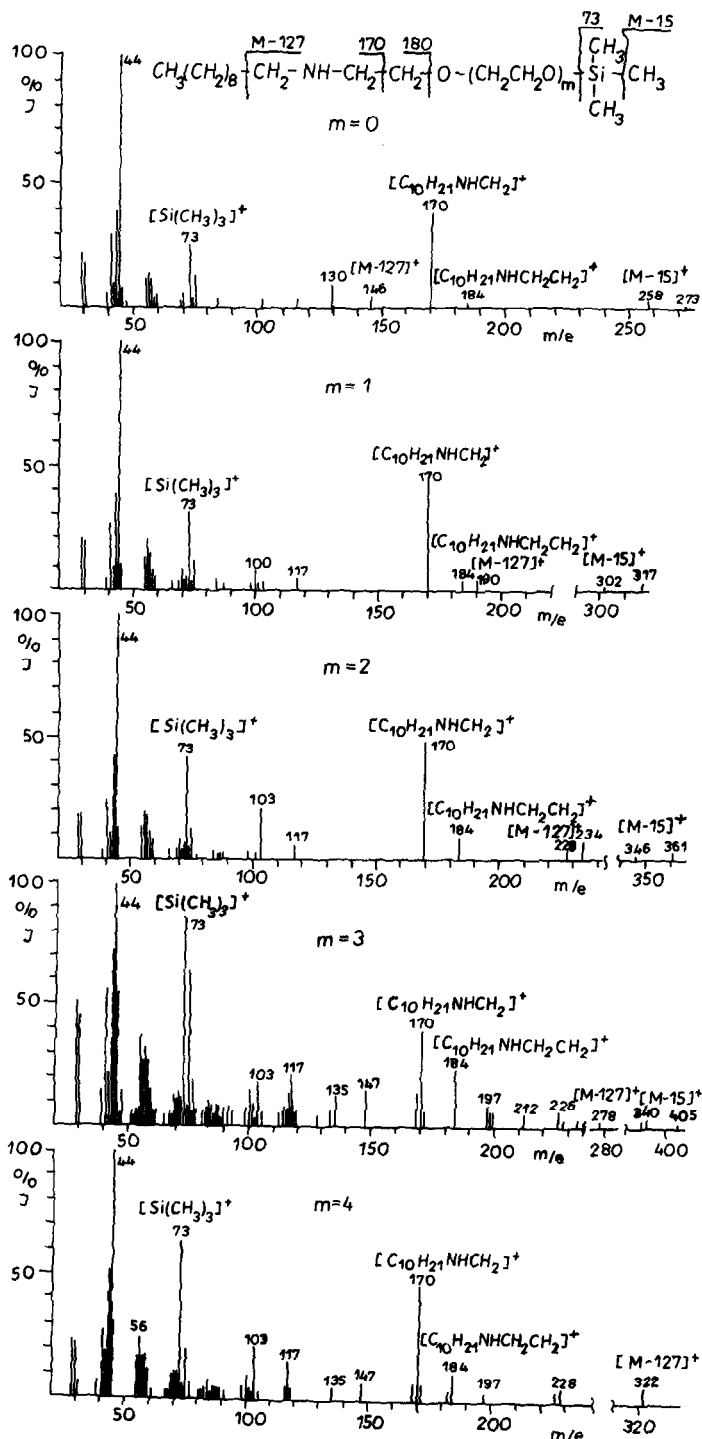


Fig. 6. The mass spectra of mono(trimethylsilyl) derivatives of N-oligooxyethylene decylamines.

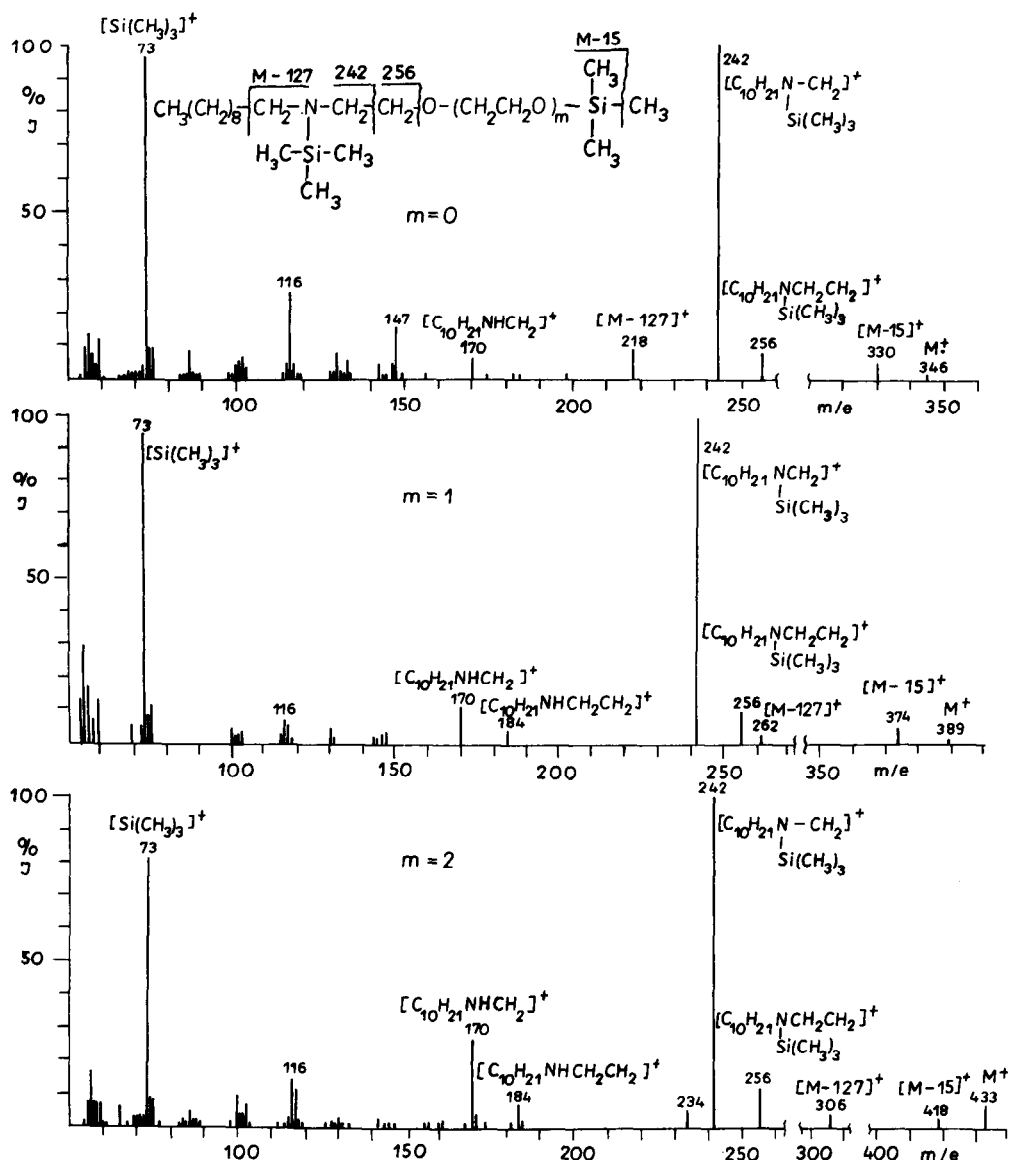


Fig. 7. The mass spectra of bis(trimethylsilyl) derivatives of N-oligooxyethylene decylamines.

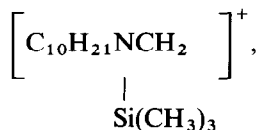
at m/e 242 and 256, show that the hydrogen bonded with the nitrogen atom has also been replaced by a trimethylsilyl group. However, the less intense ions at m/e 170 and 184, characteristic for mono(trimethylsilyl) derivatives, are also present. Thus, the separation was not complete. The intensity of the ion $[\text{C}_{10}\text{H}_{21}\text{NHCH}_2]^+$, m/e

TABLE I

ARITHMETIC RETENTION INDEX FOR N-OLIGOXYETHYLENE DIBUTYLAMINES AND THEIR TRIMETHYLSILYL DERIVATIVES

No. of oxyethylene units	$\text{Bu}_2\text{N}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$		$\text{Bu}_2\text{N}(\text{CH}_2\text{CH}_2\text{O})_n\text{Si}(\text{CH}_3)_3$	
	Found	Calculated	Found	Calculated
1	1337	1330	1361	1340
2	1609	1638	1660	1648
3	1924	1946	1966	1956
4	2244	2254	2270	2264
5	2564	2561	2570	2573
6	2888	2871	2870	2881
Mean absolute error		14		11
Mean relative error (%)		0.8		0.6

170, is equal to 7, 11 and 26%, while that of



m/e 242, is 100%. Making a rough simplifying assumption that the intensities of these ions are proportional to the fractional vapour pressures of the components in the analyzed mixture of mono- and bis(trimethylsilyl) derivatives, and that these fractional pressures are proportional to the concentrations, the contents of mono- and bis(trimethylsilyl) derivatives were estimated as about 7 and 93%, 10 and 90%, and 20 and 80% for homologues containing one, two and three oxyethylene units, respectively.

The arithmetic retention index

The arithmetic retention indices for N-oligoxyethylene dibutyl- and decylamine and for their trimethylsilyl derivatives are given in Tables I and II. The values for the amines obtained directly are similar to those obtained for the trimethylsilyl derivatives. An oxyethylene group corresponds to about 300 units on the arithmetic retention scale. Thus, the successive homologues in the technical polydisperse products can be identified from their arithmetic retention index without the use of GC-MS.

When the additivity of the arithmetic retention index is assumed, increments for the characteristic groups present in the amines can be calculated according to

$$I_R = I_R^0 + \sum_{i=1}^k n_i \Delta I_{Ri}$$

TABLE II
ARITHMETIC RETENTION INDEX FOR N-OLIGOXYETHYLENE DECYLAMINES AND THEIR TRIMETHYLSILYL DERIVATIVES

No. of oxyethylene units	$C_{10}H_{21}NH(CH_2CH_2O)_nH$		$C_{10}H_{21}NH(CH_2CH_2O)_nSi(CH_3)_3$		$C_{10}H_{21}N(CH_2CH_2O)_nSi(CH_3)_3$ Si(CH ₃) ₃	
	Found	Calculated	Found	Calculated	Found	Calculated
1	1750	1745	1750	1755	1823	1815
2	2047	2053	2071	2063	2125	2123
3	2353	2361	2372	2371	2411	2431
4	2668	2670	2670	2680	2687	2740
5	2998	2978	2975	2988	—	—
6	3313	3286	3280	3296	—	—
Mean absolute error		11	—	9	—	21
Mean relative error (%)		0.4	—	0.3	—	0.8

where I_R^0 = constant residual value of the arithmetic retention index, n_i = number of a characteristic group i present in the amine, ΔI_{Ri} = increment of I_R for the group i and k = number of the characteristic groups. The values calculated for ΔI_{Ri} are as follows: $I_R^0 = 0$, $\Delta I_R(\text{CH}_2) = \Delta I_R(\text{CH}_3) = 100$, $\Delta I_R(\text{N}) = 237$, $\Delta I_R(\text{NH}) = 452$, $\Delta I_R(\text{O}) = 108$, $\Delta I_R(\text{OH}) = 92$, $\Delta I_R[\text{OSi}(\text{CH}_3)_3] = 102$, $\Delta I_R[\text{NSi}(\text{CH}_3)_3] = 512$ and $\Delta I_R(\text{OCH}_2\text{CH}_2) = 308$.

Using the values of ΔI_{Ri} obtained, the arithmetic retention indices of the compounds can be estimated with satisfactory agreement to experimental data. The mean absolute and relative errors of the arithmetic retention index estimation are in the ranges of 10–20 and 0.3–0.8%, respectively.

CONCLUSIONS

N-Oligoxyethylene mono- and dialkylamines can be separated directly or as their trimethylsilyl derivatives by means of GC. The trimethylsilyl derivatives can be obtained quantitatively from N-polyoxyethylene dialkylamines. However, in the case of N-polyoxyethylene monoalkylamines the silylation products are mixtures of mono- and bis(trimethylsilyl) derivatives.

Successive homologues of N-oligoxyethylene mono- and dialkylamines can be identified from the values of their retention indices. The determined increments in retention indices can be used to estimate the values of the arithmetic retention index for the compounds considered, with an error not exceeding 1%.

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