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GAS CHROMATOGRAPHIC SEPARATION OF DIBASIC ALKANOIC ACID DIMETHYL ESTERS AND THE THREE ISOMERIC PHTHALIC ACID DIMETHYL ESTERS WITH A POLYAMIDE LIQUID PHASE

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SUMMARY

The complete gas chromatographic separation of the dimethyl esters of dibasic alkanoic acids (C_3–C_{12}) and the three isomeric phthalic acids was carried out using a fluoren-9-one and N-66/6 2-stage column. The greater degree of polarity of the stationary phases (N-66/6 > N-6I > N-12 and NGS > PEGS > PEG-6000) that was expected was in accordance with the shorter retention times of dimethyl azelate on these stationary phases. The differences in the elution order of the three isomeric phthalic acids on each stationary phase were interpreted from electronic theory and hydrogen bonding. Plotting the logarithm of the retention times of the diesters relative to adipic acid diester vs. carbon numbers on all stationary phases investigated gave the same straight lines, with negligible deviations.

INTRODUCTION

A technique recently described for the analysis of copolyamides is the gas chromatographic resolution of the polymer hydrolysate[1]. The liberated diacids in the hydrolysate were esterified with BF_3–methanol, and the diesters were gas chromatographed following the extraction. Using this technique, the esters of sebacic and terephthalic acids were not separated. The gas chromatographic separation of the three isomeric dimethyl phthalates and the dimethyl sebacate were carried out using a Benton-34–Carbowax column[2]. However, the dimethyl esters of dodecadionic acid which was frequently encountered in polyamides has not been examined.

KOMERS AND BAZANT[3,4] used Provina packing coated with 10.8% erythritol for separation of isomeric dimethyl phthalates (*o*-, *iso*- and terephthalates). The following comparative retention volumes were determined: *o*-, 1.42; *iso*-, 1.00; and tere-, 0.88. The dimethyl esters of dibasic alkanoic acids in the range C_4 to C_{13} were separated with 5% PEG-6000 on firebrick C-22 (ref. 5), and the dimethyl esters of

adipic, azelaic, sebacic and o-phthalic acids were resolved with 15% Ultramoll III or Resoflex[6]. The dibasic acid n-propyl esters in the range C_3 to C_{12} were also investigated[7]; however, they did not allow the separation of the dimethyl esters of dibasic alkanoic acids and the three isomeric phthalic acids on the same chromatogram.

BROOKS et al.[8] used a polyamide resin, Versamide 900, as stationary liquid phase for the separation of resin acid methyl esters (L-pimaric, abietic, pimaric and dehydroabietic acids). Versamide-900 was also used for the separation of dinitrobenzene isomers[9].

The primary objective of this research was the complete gas chromatographic separation of the dimethyl esters of dibasic alkanoic acids (malonic to dodecadionic acid) and the three isomeric phthalic acids using a single sample on the same chromatogram. The secondary objective was to ascertain whether any polyamides have the properties desirable for stationary liquid phases in gas chromatography.

MATERIALS AND METHODS

Stationary phases

Polyhexamethylene isophthalamide (N-6I, m.p. 175°) and polyhexamethylene adipamide–capramide copolymer (N-66/6, 30/70 w/w, m.p. 186°) were prepared from the corresponding nylon salts and caprolactam. Polylauramide (N-12, m.p. 182°) was kindly supplied by the Toyo Rayon Co. Ltd., and polyethyleneglycol 6000(PEG -6000, m.p. 63°), neopentylglycol succinate polyester (NGS, m.p. 63.5°), polyethyleneglycol succinate polyester (PEGS, m.p. 73°) and fluoren-9-one (m.p. 84°) were obtained from Nishio Kogyo Co. Ltd. The melting points of these polymers were measured with a Yanagimoto micromelting-point apparatus, model MP-S2.

Columns

For preparation of column packings, Dia-solid M (60–80 mesh) was used. The amount of liquid phases was 5% by weight in all cases. A stainless-steel tube, 2 m long and 3 mm I.D., was used for each column. In preparing the packings, polyester, polyether and fluoren-9-one phases were applied in an acetone solution and polyamide phases in a benzyl alcohol solution. All columns were conditioned at 240° for 24 h except for the fluoren-9-one column which was conditioned at 170°.

Gas chromatography

A Shimadzu gas chromatograph, model GC-4APTF, with dual flame ionization detectors and a linear temperature programmer was used. The injection port and the detector oven were maintained at 240°; the flow rate of the carrier gas was 60 ml of N_2 per min. The column temperature was maintained isothermally at 120, 140, 160, 180 and 200°, or programmed from 80 or 100° at a rate of 2°/min.

Dibasic alkanoic acids (malonic acid (C_3) to dodecadionic acid (C_{12})) and the three isomeric phthalic acids were commercial products of reagent grade and esterified with a dry HCl-methanol mixture. For the determination of retention times, all these esters were analyzed either separately or in various mixtures on prepared packings.

RESULTS AND DISCUSSION

The main results of the measurements and calculations are recorded in Figs. 1 and 2 and Tables I–III. The corrected retention times of dimethyl azelate on the stationary phases investigated at different temperatures are listed in Table I. Considering the data in Table I, it could be stated that the retention times on N-66/6 and NGS were shorter than on N-12 and PEG-6000. This was in accordance with the expected greater degree of polarity of N-66/6 and NGS, which could be explained by differences in the structures of these stationary phases[10].

The relative retention times of the dimethyl esters of the three isomeric phthalic acids and sebacic acid vs. azelaic acid are given in Table II. The gas chromatograms of

TABLE I

RETENTION TIMES OF DIMETHYL AZELATE

Stationary phase	Retention time (min)	
	140°	160°
PEG-6000	38.3	14.5
PEGS	32.0	13.1
NGS	10.9	4.5
N-12	21.0	11.9
N-61	12.7	5.6
N-66/6	9.7	4.1
Fluoren-9-one	6.0	—

TABLE II

RELATIVE RETENTION TIMES OF THE THREE ISOMERIC PHTHALIC ACIDS AND SEBACIC ACID DIMETHYL ESTERS

Stationary phase	Programmed temperature (2°/min)	Relative retention time				
		Az[a]	p-[b]	o-[c]	m-[d]	Se[e]
PEG-6000	100–200	1.00	1.09	m- + o- 1.15		1.13
NGS	80–180	1.00	1.03	m- + o- 1.06		1.14
PEGS	100–200	1.00	o- + p- 1.07		1.12	1.15
N-66/6	80–160	1.00	1.06	1.16	1.11	1.17
N-12	80–180	1.00	p- + o- 1.09		Se + m- 1.15	
N-61	100–180	1.00	1.11	m- + o- 1.17		1.21
Fluoren-9-one	80–150	Az + p- 1.00		m- + o- 1.06		1.18

[a] Azelaic acid dimethyl ester.
[b] Terephthalic acid dimethyl ester.
[c] Phthalic acid dimethyl ester.
[d] Isophthalic acid dimethyl ester.
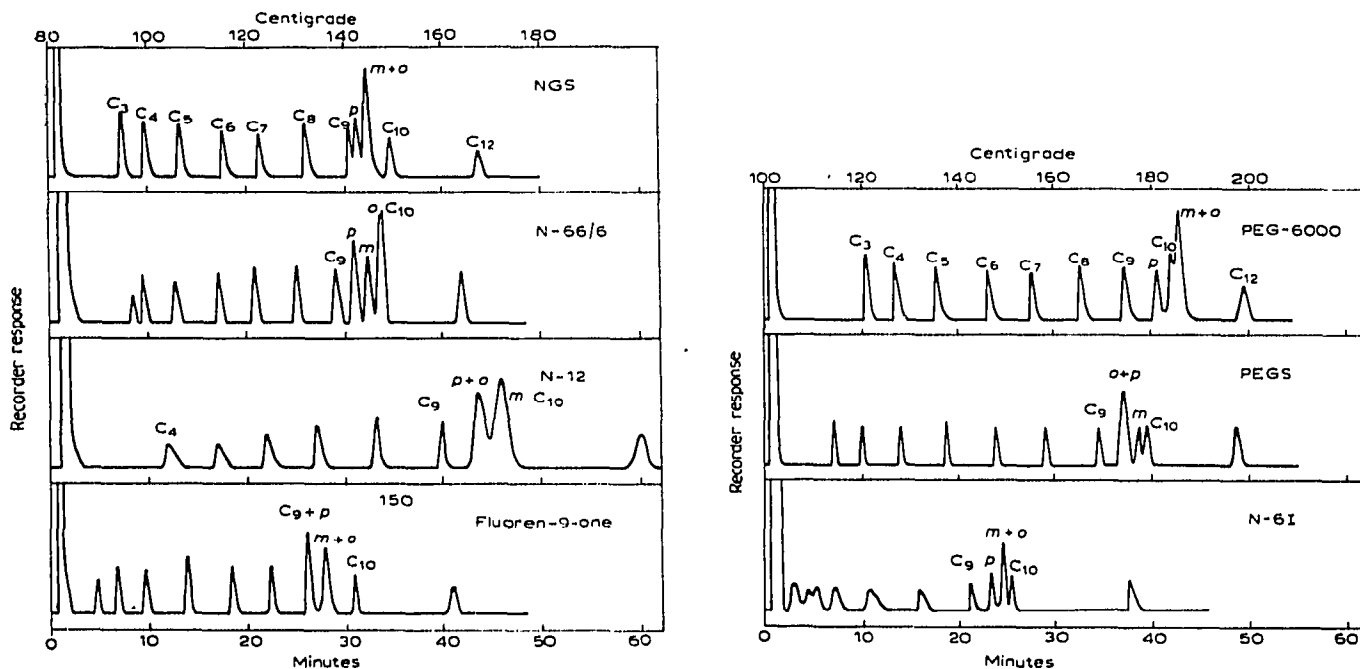[e] Sebacic acid dimethyl ester.

Fig. 1. Gas chromatograms of diesters on single columns. Programmed at 2°/min; flow rate of carrier gas 60 ml N_2/min. C_3 = malonic acid dimethyl ester; C_4 = succinic acid dimethyl ester; C_5 = glutaric acid dimethyl ester; C_6 = adipic acid dimethyl ester; C_7 = pimelic acid dimethyl ester; C_8 = suberic acid dimethyl ester; C_9 = azelaic acid dimethyl ester; C_{10} = sebacic acid dimethyl ester; C_{12} = dodecadionic acid dimethyl ester; o = phthalic acid dimethyl ester; m = isophthalic acid dimethyl ester; p = terephthalic acid dimethyl ester.

all dibasic acid dimethyl esters on the stationary phases studied are shown in Fig. 1.

On PEG-6000, NGS and PEGS, the retention times of sebacic acid dimethyl ester relative to those of azelaic acid dimethyl ester were almost identical using these three stationary phases; however, those of each of the three isomeric phthalic acid (o-, iso- and tere-) dimethyl esters were different on each phase. Isophthalic and o-phthalic acids or terephthalic and o-phthalic acids were not separated using programmed gas chromatography, although they were incompletely separated by isothermal gas chromatography. The elution order is as follows: tere-, iso- and o- on PEG-6000; tere-, o- and iso- on NGS; and o-, tere- and iso- on PEGS. This phenomenon could be interpreted by electronic theory, and the differences among the coherences of the stationary phases with o-phthalic acid dimethyl ester might be greater than with iso- or terephthalic acids.

On N-66/6, N-6I and N-12, the elution order using isothermal gas chromatography is as follows: tere-, iso- and o- on N-66/6 and N-6I; and tere-, o- and iso- on N-12. As the melting points of the polyamide stationary phases were close to each other, this elution difference was perhaps related to the stereo structure of the phthalic isomers and to the distance between adjoining amide linkages of the polyamide stationary phases. The hydrogen bonding of o-phthalic acid dimethyl ester with the N-12 liquid phase might be so weak that the retention time for o-phthalic acid dimethyl ester was shorter than that for isophthalic acid dimethyl ester.

These results of testing the stationary phases enabled us to conclude that the newly introduced stationary phase N-66/6 was efficient enough to separate the three

TABLE III

RELATIVE RETENTION TIMES ON A 2-STAGE COLUMN

| Stationary phase		Programmed temperature (2°/min)	Relative retention time						
First	Second		Az[a]	p-[b]	m-[c]	o-[d]	o-+m-	Se[e]	o-+Se
NGS	N-66/6	100–200	1.00	1.04			1.10	1.16	
N-66/6	NGS		1.00	1.06	1.10	1.15		1.16	
Fluoren-9-one	N-66/6	100–160	1.00	1.03	1.08	1.12		1.17	
N-66/6	Fluoren-9-one		1.00	1.06	1.11				1.16

[a] Azelaic acid dimethyl ester.
[b] Terephthalic acid dimethyl ester.
[c] Isophthalic acid dimethyl ester.
[d] Phthalic acid dimethyl ester.
[e] Sebacic acid dimethyl ester.
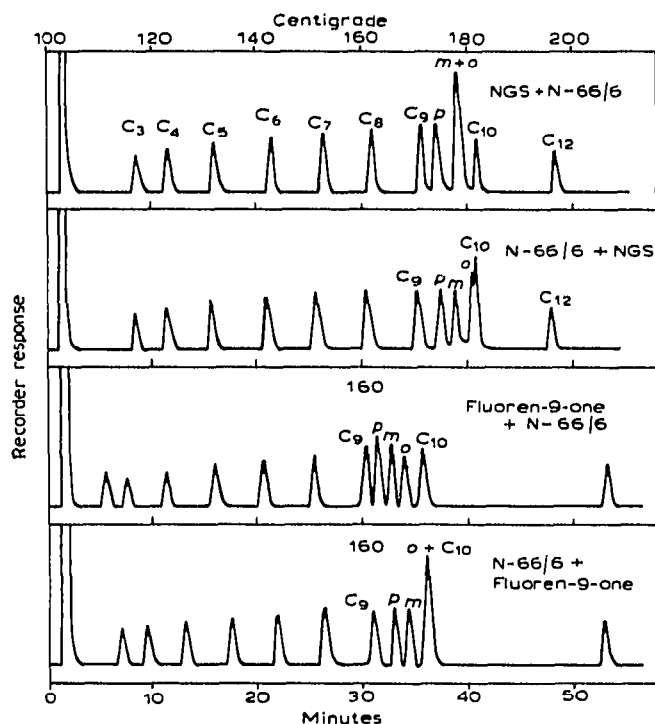
Fig. 2. Gas chromatograms of diesters on 2-stage columns. Conditions and abbreviations are identical to those in Fig. 1.

isomeric phthalic acid dimethyl esters. For separation of dibasic alkanoic acids, a 2-stage column was needed. The results are shown in Table III and Fig. 2. Complete separation of dibasic acid dimethyl esters was attained with the 2-stage column of fluoren-9-one (first stage) and N-66/6 (second stage). The column length of each stage was 2 m. Reverse combination of these stages resulted in different separations. This phenomenon could be attributed to the difference of the carrier gas flow distribution inside the column caused by the gas compressibility. As the average flow rate in the first stage was lower and the retention time was longer than in the second stage, it was assumed that the retention time on the 2-stage column was strongly affected

by the first-stage column. This supposition was proved from the consideration of the relative retention times in Tables II and III. The additivity of the relative retention times between the 2-stage column and corresponding individual columns was observed on the fluoren-9-one and N-66/6 2-stage column.

The peak shapes and the separation factors of diesters on polyamide stationary phases below their melting point were nearly identical to those over the melting points; the shapes on N-12 and N-6I were rather broad and those on N-66/6 sharp. From these results we assumed the following. First, the adsorption mechanism of diesters to the stationary liquid phases rather than dissolution of diesters in the stationary phases was responsible for the separation. The dissolution mechanism in the stationary phase was also considered over the melting point. Second, below their melting point crystallinity of the polyamides might affect the peak shape of diesters. The effect of aging upon retention times on polyamide phases during the serial analyses was within the limits of reproducibility of individual determinations; for example, the N-6I phase had a good thermal stability even after 100 h at 200°.

Plotting the logarithm of the retention times of dibasic alkanoic acid diesters relative to adipic acid diester vs. carbon numbers on all phases investigated gave straight lines. The equation obtained from these lines was:

$$\log \text{(relative retention time)} = \frac{\log 5.2}{4} \times \text{(carbon number)} + \log 0.083$$

This equation was identical, with negligible deviations, for all lines on the stationary phases. This phenomenon implied that the values of the relative retention times of the homologous series (the standard was also selected among them) were not affected by any stationary phases which were efficient enough for separation of diesters. Plotting the relative retention times against the number of carbon atoms using programmed gas chromatography (Fig. 1) also produced nearly straight lines for every stationary phase used.

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