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SEPARATION OF FLUOROBROMOBENZENES
BY GAS-LIQUID CHROMATOGRAPHY

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SUMMARY

Fluorobromobenzenes were separated on squalane, silicone oil, polyethylene glycol (1500), polyethylene glycol succinate, polyoxyethylene sorbitan monostearate, di-*n*-decyl phthalate and polypropylene glycol. Specific retention volumes, band impurities, and electron polarisabilities were calculated and reported.

INTRODUCTION

There has been no quantitative separation and study of fluorobromobenzenes by gas-liquid chromatography. HABBOUSH AND NORMAN¹ could resolve these isomers on dinonyl phthalate, polyethylene glycol stearic acid, and tritoyl phosphate, but with band impurity not lower than 10^{-3} .

In the present work, a complete analysis of fluorobromobenzene isomers was made on squalane, silicone oil, polyethylene glycol (1500), polyethylene glycol succinate, polyoxyethylene sorbitan monostearate, di-*n*-decyl phthalate and polypropylene glycol. The specific retention volumes, separation factors, and band impurities were calculated. The forces which could affect the separations and elution orders of these isomers were discussed.

EXPERIMENTAL AND RESULTS

Materials and methods

Apparatus. A Perkin-Elmer Model 451 fractometer equipped with a thermistor-type thermal conductivity detector was used. The recorder was a 2.5 mV Honeywell Brown Electronic unit. Nitrogen was used as the carrier gas. The average column temperature was controlled to within $\pm 0.2^\circ$.

Columns. These were specially ordered from Perkin Elmer, Great Britain. The columns used were stainless-steel tubing (2 m long and 1/4 in. O.D.) bent into a U shape and surrounded by asbestos sleeves to ensure uniform heating. The chemical composition of the liquid phases used are shown in Table I. Packing specifications of all columns used were identical. The weight of pure liquid phase per column was 3.40 g and the liquid on support was 20 % w/w. These were certified in this laboratory

TABLE I

THE CHEMICAL COMPOSITIONS OF THE LIQUID PHASES USED^a

Chemical name	Formula	Density 20°C (g/ml)	Mol. wt.	MOT ^b (°C)
Polyethylene glycol	$(\text{CH}_2)_4(\text{OH})_2\text{O}(\text{OCH}_2\text{CH}_2)_n$	1.152	1500	225
Polypropylene glycol (Ucon-LB-550-x)	$(\text{CH}_2)_6(\text{OH})_2\text{O}(\text{O}(\text{CH}_2)_3)_n$	0.984 ^b	550	200
Di- <i>n</i> -decyl phthalate	$\text{C}_{20}\text{H}_{40}[\text{COO}(\text{CH}_2)_9\text{CH}_3]_2$	0.960	446.68	200
Polyethylene glycol succinate	$[\text{O}(\text{CH}_2\text{CH}_2\text{O})_2\text{COCH}_2\text{CH}_2\text{CO-}]_n$	—	$(188.2)_n$	225
Polyoxyethylene sorbitan monostearate	—	—	—	160
2,6,10,15,19,23-Hexamethyl- tetracosane (squalane)	$\text{C}_{30}\text{H}_{62}$	0.829	422.5	160
Silicone oil (MS 200/50)	$(\text{CH}_3)_3\text{Si}[\text{OSi}(\text{CH}_3)_2]_n\text{O-}$ $\text{Si}(\text{CH}_3)_3$	0.971	—	200

^a Maximum operating temperature when they were packed in columns.^b Density at 100°F.

using a solvent extraction technique. The solid support was 60–80 mesh Chromosorb P.

Materials. Pure *o*-, *m*-, and *p*-fluorobromobenzenes were obtained from T. J. Sas & Son Ltd., London.

Sampling. Equal weights of the isomers were blended in a 3-ml cylindrical pyrex glass cell made in this laboratory. Sample sizes ranged from 0.5 to 1 μl . The injections were done using a 10- μl Hamilton 1 in. fixed needle syringe. An optimum flow rate of 20 ml/min at NTP was encountered throughout the investigations. The average inlet pressures was 6 ± 1 p.s.i. The specific retention volumes, V_g^0 , were calculated following the well-known procedure given by LITTLEWOOD *et al.*². The retention volume for the air peak was taken to be zero. Specific retention volumes for

TABLE II

SPECIFIC RETENTION VOLUMES, V_g^0 (ml/g) FOR FLUOROBROMOBENZENES AT DIFFERENT TEMPERATURES

Phase	Temperature (°C)	Fluorobromobenzene isomer		
		Meta	Para	Ortho
Polypropylene glycol	140	174	193	225
Di- <i>n</i> -decyl phthalate	120	307	354	448
Squalane	120	429	474	577
	140	200	223	295
Silicone oil	120	195	204	235
	140	132	139	160
	180	64	64	73
Polyethylene glycol	100	47	52	60
	120	38	38	44
Polyethylene glycol succinate	100	147	173	211
	140	115	134	159
	180	88	102	121
Polyoxyethylene sorbitan monostearate	100	135	158	195
	120	77	89	108
	140	52	59	70

TABLE III

COLUMN EFFICIENCIES FOR FLUOROBROMOBENZENES AT DIFFERENT COLUMN TEMPERATURES^a

Fluorobromo- benzene isomer	<i>n</i>	α	η	<i>n</i>	α	η
	Polypropylene glycol (140°C)			Di- <i>n</i> -decyl phthalate (120°C)		
<i>Meta</i>	2830	1.11	6×10^{-8}	2350	1.15	5×10^{-4}
<i>Para</i>	2530	1.16	1×10^{-4}	2110	1.27	1×10^{-8}
<i>Ortho</i>	2820			2170		
	Squalane (120°C)			Silicone oil (120°C)		
<i>Meta</i>	2280	1.11	4×10^{-9}	3730	1.04	8×10^{-2}
<i>Para</i>	2620	1.22	1×10^{-7}	3440	1.15	2×10^{-5}
<i>Ortho</i>	2500			3900		
	Polyethylene glycol (100°C)			Polyethylene glycol succinate (100°C)		
<i>Meta</i>	120	1.1	10^{-1}	2130	1.18	5×10^{-5}
<i>Para</i>	325	1.15	10^{-1}	2130	1.22	6×10^{-5}
<i>Ortho</i>	680			2360		
	Polyoxyethylene sorbitan monostearate (100°C)					
<i>Meta</i>	2200	1.17	8×10^{-5}			
<i>Para</i>	2200	1.23	5×10^{-7}			
<i>Ortho</i>	2700					

^a When a set of isomers was examined at more than one temperature, values of *n*, α , and η are recorded for the temperature at which resolution was more satisfactory.

fluorobromobenzene isomers at different column temperatures on the liquid phases examined are listed in Table II. The number of theoretical plates, *n*, was calculated as recommended by JOHNSON AND STROSS³. Table III gives the number of theoretical plates, separation factors and fractional band impurities for the isomers.

Electron polarisabilities per unit volume, α_e^v , were calculated using the Clausius-Mosotti equation:

$$\alpha_e^v = 3(n^2 - 1)/4\pi N(n^2 + 2)$$

Where *n* is the refractive index and *N* is Avogadro's number.

Refractive indices of fluorobromobenzenes at 30°C were measured in this laboratory using an Ape refractometer. Dipole moments were calculated as given by SMITH⁵. These physical constants are tabulated in Table IV.

Fluorobromobenzenes were selectively resolved on polyoxyethylene sorbitan monostearate, polyethylene glycol succinate, and di-*n*-decyl phthalate (as seen from Fig. 1 and Table III).

TABLE IV

SOME PHYSICAL CONSTANTS OF FLUOROBROMOBENZENE ISOMERS

Fluorobromo- benzene isomer	n_D^{30}	$E.P.$ ($cm^3 \times 10^{20}$)	$B.p.$ ^a ($^{\circ}C$)	$D.M.$ (Debye)
Ortho	1.5294	12.227	151-2	2.56
Meta	1.5229	12.100	149-51/764 mm	1.48
Para	1.5243	12.129	153.5/756 mm	0.08

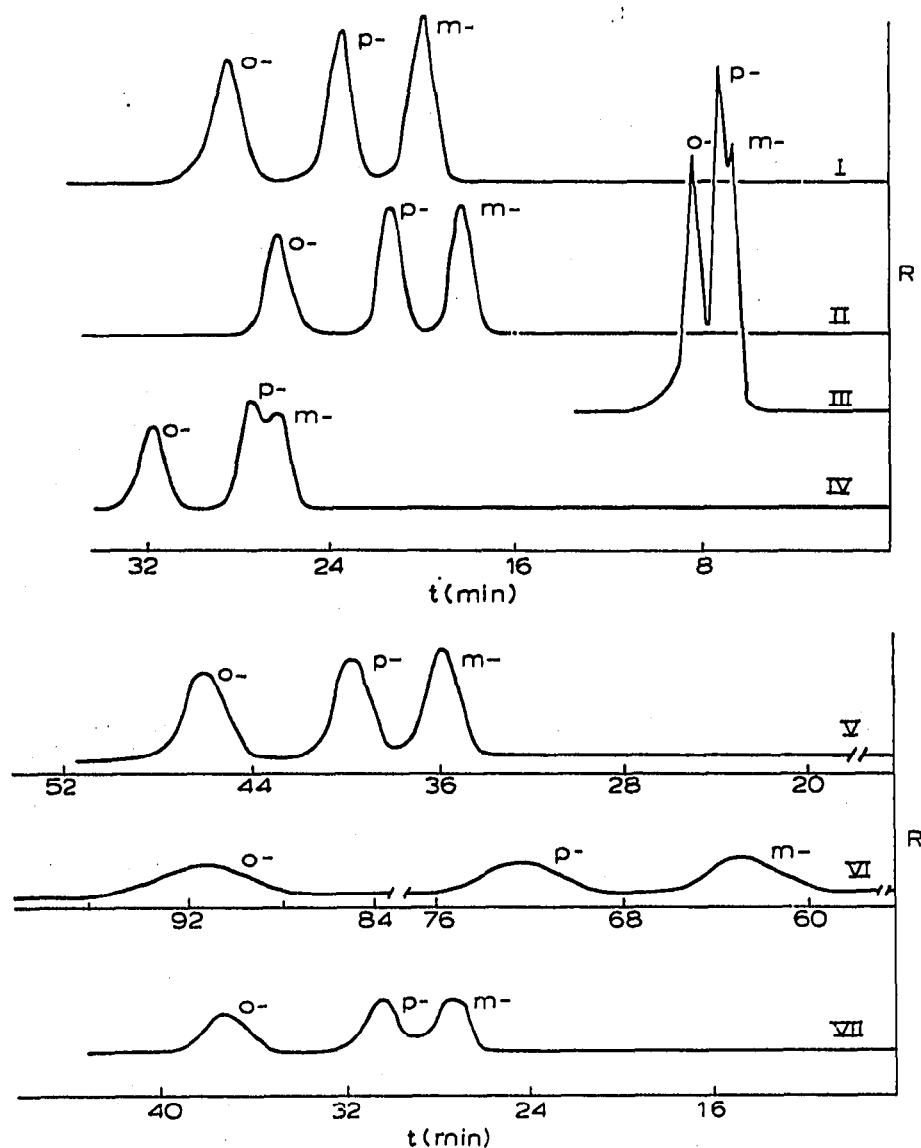
^a Ref. 6.

Fig. 1. Chromatograms showing the separation of fluorobromobenzene isomers on: I = Polyethylene glycol succinate at $100^{\circ}C$; II = polyoxyethylenesorbitani monostearate at $100^{\circ}C$; III = polyethylene glycol at $100^{\circ}C$; IV = silicone oil at $120^{\circ}C$; V = polypropylene glycol at $140^{\circ}C$; VI = di-*n*-decyl phthalate at $120^{\circ}C$; VII = squalane at $140^{\circ}C$. *R* is the recorder deflection, and *t* is the retention time in min.

DISCUSSION

The order of elution of fluorobromobenzenes on all the columns was *meta*, *para*, and then *ortho*. This order is not the order of the increase of the calculated dipole moments of these isomers. It seems that the polarisation of the *p*-isomer is higher than the corresponding *m*-isomer, *i.e.* the *p*-isomer would exert higher polarity than the calculated polarity, this being due to the polarising effect of the solvent (or the induced dipoles to the solvent). The *ortho* derivative has an effectively larger dipole moment, leading to a stronger interaction with the solvent. The calculated electron polarisabilities per unit volume for these isomers support the above mechanism (see Table IV).

The most selective liquid phases for the separation and quantitative determination of these isomers are the polyglycols. When an ester group (succinate, stearate or phthalate) is introduced to the structure of a polyglycol-type liquid phase, the selectivity is much increased (as seen in Table III, Fig. 1). The carbonyl groups present in such structures may act as good polarising groups leading to better resolutions.

The results obtained in this work can be utilised successfully in the quantitative determinations and in following the kinetics of the reactions involving these isomers.

REFERENCES

- 1 A. E. HABBOUSH AND R. O. C. NORMAN, *J. Chromatog.*, 7 (1962) 438.
- 3 A. B. LITTLEWOOD, C. S. G. PHILLIPS AND D. T. PRICE, *J. Chem. Soc.*, (1955) 1480.
- 2 H. W. JOHNSON AND F. H. STROSS, *Anal. Chem.*, 30 (1958) 1586.
- 4 G. W. HINE, Perkin Elmer Ltd., Beaconsfield, Bucks., Great Britain, private communication.
- 5 J. W. SMITH (Editor), *Electrical Dipole Moments*, Butterworths, London, 1955, p. 96.
- 6 J. R. A. POLLOCK AND R. STEVENS (Editors), *Dictionary of Organic Compounds*, Eyre & Spottiswoode, London, Vol. 1, p. 445.

J. Chromatog., 54 (1971) 145-149