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LIQUID CRYSTALS

III. APPLICATION OF LATERALLY SUBSTITUTED LIQUID CRYSTALS FOR THE SEPARATION OF ALKYLBENZENES COMPARED WITH CONVENTIONAL STATIONARY PHASES IN GAS CHROMATOGRAPHY*

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SUMMARY

The retention behaviours of 26 alkylbenzenes on a laterally substituted liquid crystalline stationary phase and on conventional stationary phases in gas chromatography have been compared. Elution of alkylbenzenes in the nematic state of liquid crystalline substrates is dependent on the linearity and planarity of the probe molecules, whereas on conventional stationary phases they elute on the basis of their boiling points. The relative retention values (α) for close-boiling positional isomers on conventional stationary phases are near unity, but their separation can be achieved on liquid crystalline substrates. The variation of the relative retention value with respect to the chain length of the alkyl substituents is discussed.

INTRODUCTION

The importance of nematic liquid crystals as stationary phases in gas–liquid chromatography (GLC) depends on their ability to separate positional isomers irrespective of their boiling points. The topic was first reviewed by Kelker and Von Schivizhoffen[1], subsequently by Schöeder[2] and more recently by Janini[3], with up-to-date uses of liquid crystals for the separation of different classes of compounds.

The separation and identification of structural and positional isomers of mono, di- and tri-substituted alkylbenzenes has industrial importance. Retention indices[4,5], Kováts retention indices[6] and a linear free energy relationship[7] have been used for structural determinations of alkylbenzenes. Several workers have attempted to separate alkylbenzenes using different commercially available stationary phases, with columns of varying length[8–12] and material.

The separation of benzene, toluene, ethylbenzene and *o*-, *m*- and *p*-xylenes using a polar solid stationary phase was carried out by Belyakova *et al.*[13]. Di Corcia *et al.*[14] used Carbopack C modified with 2,4,5,7-tetranitrofluorenone (TeNF) as a

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stationary phase to separate alkylbenzenes. There are several references[15-18] to the use of Bentone-34 in a modified form as a stationary phase giving improved resolution and separation, but here too, the columns used are of considerable length[17], and the analyses time is long.

Vernon and Khakoo[19] found liquid crystalline stationary phases to be superior to Bentone-34 and Maidachenko *et al.*[20] have patented the use of liquid crystals as a stationary phase for alkylbenzene separations.

Work in our laboratory is concerned with isomerization of xylenes, ethylation and isopropylation of benzene and aromatization of ethylene, which give rise to different alkylbenzenes. This prompted us to investigate the suitability of the liquid crystal phases developed by us[21,22] for the separation and identification of alkylbenzenes using gas chromatography, and to compare the application of a liquid crystalline statationary phase with the conventional stationary phases SE-30 and OV-17.

EXPERIMENTAL

Materials

The commercially available stationary phases used were the methylsilicone SE-30 (Analabs, North Haven, CT, U.S.A.) and the phenylsilicone OV-17 (Varian Aerograph, Walnut Creek, CA, U.S.A.).

The liquid crystalline compound 2-methyl-4′-*n*-butyl-4-[4″-ethoxybenzoyloxy]azobenzene (C–N transition temperature 107°C, N–I transition temperature 199°C; nematic range 92°C) was synthesized.

The solid supports used were Chromosorb W DMCS (60–80 mesh) for SE-30 and OV-17 and Celite (80–120 mesh) (BDH, Poole, Great Britain) for the liquid crystalline compound.

The column parameters are given in Table I.

TABLE I

COLUMN PARAMETERS

Column No.	*Stationary phase used*	*Length of column (m)*	*Total weight of packing (g)*	*Amount of stationary phase used (%, w/w)*
I	SE-30	2.28	11.5103	5
II	OV-17	2.26	9.6122	5
III	Liquid crystalline compound	1.84	9.7990	8

The stationary phases were coated on supports using appropriate solvents (chloroform for SE-30 and OV-17 and benzene for the liquid crystalline compound), followed by gradual elimination of the solvent by evaporation on a hot water-bath. The coated phases were dried in an oven at 100°C and then packed in previously washed and dried aluminium columns of 4.00 mm I.D.

Solutes

Alkylbenzene positional isomer samples were GLC pure, most of them from BDH. A few samples were synthesized in our laboratory using standard methods.

Apparatus

An AIMIL [Associated Instrument Manufacturers (India) Private Ltd.] dual-column chromatograph equipped with a thermal conductivity detector (TCD) with hydrogen as the carrier gas was used to measure the retention times of the alkylbenzenes. The chromatograms shown in Figs. 2 and 3 were obtained on a Hewlett-Packard 5730A gas chromatograph.

Procedure

SE-30 and OV-17 columns were conditioned at 200°C for 12 h and the liquid crystal column was conditioned at 180°C for 4 h. The injector and detector temperatures were 150°C and 225°C, respectively. Individual samples were injected with a 10-μl syringe using the smallest detectable sample volume. The flow-rate of the carrier gas was measured using a soap-film flow meter. For obtaining the chromatograms on the Hewlett-Packard 5730A gas chromatograph the mixture of alkylbenzenes was diluted with carbon disulphide (GLC pure).

RESULTS AND DISCUSSION

Differences in retention times (t'_R) are a measure of the separating power of a stationary phase. Retention times of the alkylbenzenes studied are given in Table II. At a particular temperature, the retention times of the alkylbenzenes increase with increase in their boiling points on columns I and II, but column III shows abnormal behaviour in this respect. For instance, of the C_6–C_8 mono- and dialkylbenzenes, *p*-xylene, with a lower boiling point than *m*-xylene, elutes more slowly, with a longer retention time. This behaviour of alkylbenzenes on liquid crystalline stationary phases can be explained on the basis of the size and shape of the eluting molecules. Considering the *m*- and *p*-xylene isomers, the molecular length to width ratio is higher for *p*-xylene than *m*-xylene.

In the nematic state of the liquid crystalline phase the molecules are highly oriented and possess a rod-like molecular structure[23]. When an alkylbenzene passes through this oriented state in the gas chromatographic column, the more linear molecules (*e.g.*, *p*-xylene of *p*- and *m*-xylene isomers) fit readily into the nematic "lattice" and thus have a longer retention time than less linear molecules (*m*-xylene in this instance). *o*-Xylene isomer, which has a higher boiling point than the close-boiling *m*- and *p*-xylenes, is eluted after *p*-xylene. Thus the elution behaviour of alkylbenzenes with respecto their boiling points can be seen on columns I and II and with respects to their size and shape on column III (Fig. 1).

The higher boiling structural isomer *n*-propylbenzene has a longer retention time than isopropylbenzene on all three columns. However, the relative retention time (α) of *n*-propylbenzene (for isopropyl benzene $\alpha = 1$) is very high on column III. This might be due to the slow elution of *n*-propylbenzene (more linear) compared with isopropylbenzene.

The alkyl chain length in alkylbenzenes has a profound effect on their retention

TABLE II

RETENTION TIMES FOR ALKYLBENZENES ON COLUMNS I, II AND III AT 107°C

Flow-rate of carrier gas: columns I and II, 37.91 ml/min; column III, 25.20 ml/min.

Compound	*Boiling point (°C)*	*t'_R (min)*		
		Column I	*Column II*	*Column III*
Benzene	80.10	1.21	1.30	1.68
Toluene	110.60	1.61	1.81	2.47
Ethylbenzene	136.25	2.26	2.71	3.56
p-Xylene	137–138	2.34	2.77	4.31
m-Xylene	139	2.32	2.78	3.97
o-Xylene	144	2.55	3.28	4.73
Styrene	145–146	2.48	3.44	5.56
Isopropylbenzene	152–153	2.90	3.57	4.40
n-Propylbenzene	159.20	3.33	4.23	5.73
m-Ethyltoluene	161.30	3.39	4.48	5.98
p-Ethyltoluene	161.98	3.43	4.57	6.73
1,3,5-Trimethylbenzene	164.71	3.56	4.65	6.78
1,2,4-Trimethylbenzene	169.4	–	–	–
m-Cymene	175	4.67	6.10	6.76
1,2,3-Trimethylbenzene	176.08	–	–	–
p-Cymene	177	4.67	6.10	8.21
m-Diethylbenzene	181.25	5.23	7.06	8.57
p-Diethylbenzene	183.75	5.40	7.34	10.83
2,5-Dimethylethylbenzene	186.91	6.35	8.64	12.62
2,4-Dimethylethylbenzene	188.41	6.13	8.87	13.12
3,4-Dimethylethylbenzene	189.75	6.35	9.21	13.13
3,5-Diethyltoluene	200.71	8.62	12.51	13.92
m-Diisopropylbenzene	203.18	9.40	12.25	11.96
p-Diisopropylbenzene	210.36	10.66	14.40	17.30
1,3,5-Triethylbenzene	215.92	13.65	20.56	21.94
3,5-Diisopropyltoluene	218	14.71	20.16	15.54
p-Ethylvinylbenzene	73/10 mmHg	5.45	9.76	14.85
m-Divinylbenzene	52/3 mmHg	7.92	13.60	19.97
p-Divinylbenzene	52/4 mmHg	7.52	12.68	24.50

behaviour. The retention of *meta*- and *para*-isomers of ethyltoluenes, cymenes, diethylbenzenes and diisopropylbenzenes depends solely on their boiling points for columns I and II, giving nearly identical retention times (see *m*- and *p*-isomers in Table II). However, as the alkyl chain length increases, the difference in retention time $(t'_{R_{para}} - t'_{R_{meta}})$ increases on column III.

A large difference in retention time is observed between close-boiling 1,3,5-triethylbenzene and 3,5-diisopropyltoluene. The interesting point here is that 3,5-diisopropyltoluene has both a higher boiling point and molecular weight than 1,3,5-triethylbenzene, but in spite of that, the former elutes faster than the latter. This might be due to the planarity of the molecules of 1,3,5-triethylbenzene which fit tightly in the oriented molecules of the liquid crystalline compound and hence elute slowly.

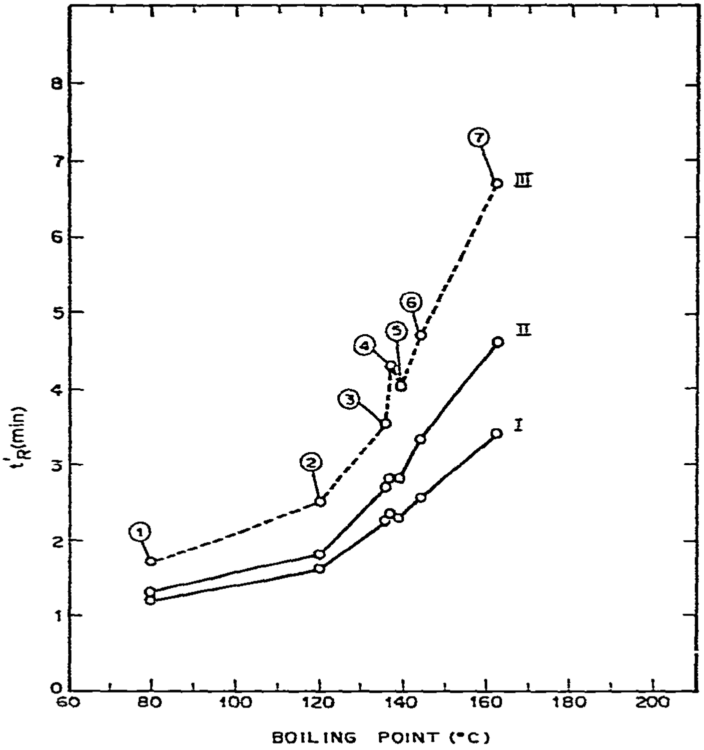

Fig. 1. t'_R *versus* boiling point for columns I. II and III. Compounds: 1 = benzene; 2 = toluene; 3 = ethylbenzene; 4 = *p*-xylene; 5 = *m*-xylene; 6 = *o*-xylene; 7 = *p*-ethyltoluene.

Relative retention times (α values)

The relative retention times (for *para*-isomers relative to the corresponding *meta*-isomer = 1) calculated from Table II are presented in Table III.

The separation of all the three xylene isomers from lower boiling ethylbenzene

TABLE III

RELATIVE RETENTIONS (α) OF *p*-DIALKYLBENZENES (*m*-ISOMER = 1.00)

Compound	α		
	Column I	*Column II*	*Column III*
p-Xylene	1.009	1.00	1.104
n-Propylbenzene*	1.148	1.185	1.302
p-Ethyltoluene	1.012	1.022	1.126
p-Cymene	1.00	1.00	1.213
p-Diethylbenzene	1.032	1.040	1.264
2,4-Dimethylethylbenzene**	1.01	1.020	1.01
p-Diisopropylbenzene	1.140	1.164	1.44

* Isopropylbenzene = 1.

** 3,4-Dimethylethylbenzene = 1.

and higher boiling styrene is very difficult on the conventional columns I and II. These separations have been tried by many workers using different stationary phases and varying column lengths[17]. Bentone-34 giving good resolution when mixed with silicone stationary phases[15]. We have obtained their rapid separation on column III (Fig. 2).

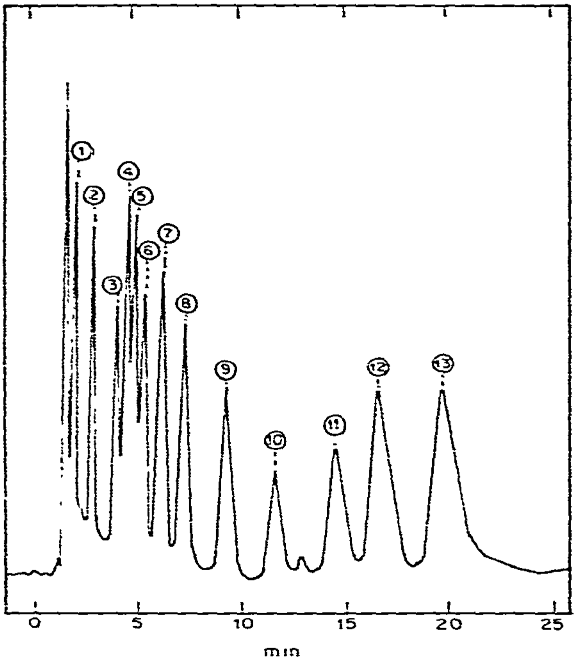

Fig. 2. Gas chromatogram of a mixture of alkylbenzenes on column III. Oven temperature, 107°C; injector temperature, 200°C; detector temperature, 300°C; flame-ionization detector; nitrogen flow-rate, 40 ml min. Peaks: 1 = benzene; 2 toluene; 3 = ethylbenzene; 4 = *m*-xylene; 5 = *p*-xylene; 6 = *o*-xylene; 7 = styrene; 8 = 1,3,5-trimethylbenzene; 9 = 1,2,4-trimethylbenzene; 10 = 1,2,3-trimethylbenzene; 11 = 3,5-diethyltoluene; 12 = *p*-diisopropylbenzene; 13 = 1,3,5-triethylbenzene.

In certain industrial processes the separation not only of benzene, toluene, xylenes and styrene is required, but also that of *n*-propylbenzene and isopropylbenzene from C_8 alkylbenzenes is essential. For this separation, if column III is used, isopropylbenzene will coincide with *p*-xylene and *n*-propylbenzene with styrene, but all four compounds can be separated on column II. Thus, using two columns in the same instrument at a particular temperature (in this instance 107°C) one can rapidly achieve an effective separation of all components.

The methylation of *p*-cymene using methyl triflate in the presence of aluminium chloride gives rise to a number of products[24] due to alkylation, isomerization and dialkylation. The determination of these products is very difficult, unless they can be resolved by gas chromatography. Of the nine products (benzene, toluene, *o*-, *m*- and *p*-xylene, isopropylbenzene, *p*- and *m*-cymene and 3,5-diisopropyltoluene) only six can be resolved using columns I and II, whereas eight components are resolved using column III.

Several reactions based on the interactions[25] and isomerization[26–28] of alkylbenzenes have been carried out in which the product analyses by infrared and GLC techniques were time consuming and presented several difficulties in identification and determination. Similarly, Olah and co-workers while carrying out Friedel–Crafts isomerization of *tert.*-butyltoluenes[29], diisopropylbenzenes[30] and the aluminium chloride-catalysed Friedel–Crafts alkylation of benzene and toluene with esters and haloesters[31], analysed the products by GLC using 150-ft. Golay-type capilliary columns coated with modified conventional stationary phases. Column III with the liquid crystal phase is promising for the analysis of the products of reactions similar to these.

The clear separation of *m*- and *p*-diisopropylbenzenes ($\alpha = 1.44$), *m*-diethylbenzene from *p*-diethylbenzene ($\alpha = 1.26$) and of *m*- and *p*-ethyltoluenes is obtained within a very short time on column III.

The separation of ethylvinylbenzene, *m*-divinylbenzene and *p*-divinylbenzene is commercially important. Their separation on columns I and II is difficult, but a complete baseline separation is achieved on column III (Fig. 3).

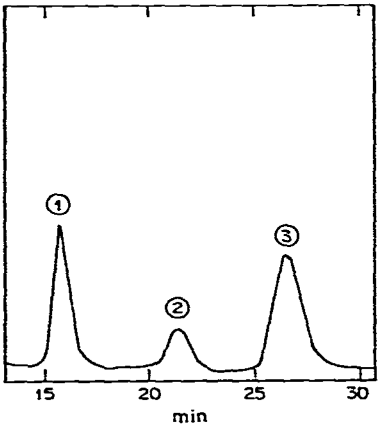

Fig. 3. Gas chromatogram of a mixture of vinylbenzenes on column III. Oven temperature, 107°C; injector temperature, 200°C; detector temperature, 300°C; flame-ionization detector; nitrogen flow-rate, 40 ml/min. Peaks: 1 = *p*-ethylvinylbenzene; 2 = *m*-divinylbenzene; 3 = *p*-divinylbenzene.

The three dimethylethylbenzene isomers considered cannot be separated on any of the three columns, possibly because they have very close boiling points and their molecular length to width ratios do not differ significantly. Development of new stationary phases for their separation is in progress.

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