

CHROM. 10,853

## Note

### Separation of close-boiling compounds on liquid-crystalline stationary phases

ZYGFRYD WITKIEWICZ and STANISŁAW POPIEL

*Institute of Chemistry and Material Engineering, Military Technical Academy, 01 489 Warsaw 49 (Poland)*

(First received October 4th, 1977; revised manuscript received December 28th, 1977)

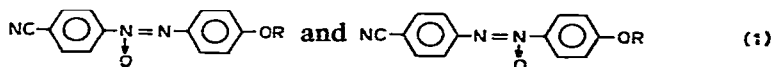
Progress in gas chromatography is dependent on the availability of improved chromatographic columns and much work has been carried out on the development of new column materials, including stationary phases. Some of the latter have been found to exhibit very interesting and unusual properties that might make them very valuable in gas chromatography, and liquid crystals belong to this category.

Liquid crystals were employed for the first time in gas chromatography in 1963<sup>1,2</sup>, since when a number of monographs have appeared<sup>3-5</sup>. Liquid crystals are used in the separation of close-boiling compounds on the basis of molecular shape. One of the most interesting separations that has been achieved on liquid crystals is the separation of optical isomers<sup>6,7</sup>. Certain liquid crystal stationary phases are suitable for programmed-temperature gas chromatography and for work at a temperature of about 300<sup>°C</sup><sup>8-10</sup>. Gas chromatography is also suitable for investigating the physico-chemical properties of liquid crystals.

In a previous paper<sup>11</sup> we have reported good separations of the isomers of several disubstituted benzenes on liquid crystals in small-bore micropacked columns (0.8 mm I.D.) of lengths 5 and 18 m. In this paper we examine the possibility of separating a number of mixtures, including isomeric disubstituted benzenes, in conventional analytical columns of 4 mm I.D., and describe the use of liquid crystalline azoxy and azo compounds as stationary phases.

## EXPERIMENTAL

Azoxy and azo compounds with the general formulae



and

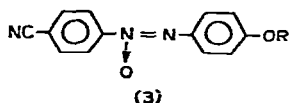


where R,R' are as given in Table I, were studied as liquid crystalline stationary phases. The phase transition temperatures and the isomeric constitution of the azoxy

TABLE I  
STATIONARY PHASES INVESTIGATED

Stationary phase No.	R or R' in formula (1 and 2)	No. of isomers	Temperature of transition to liquid (°C)		
			Smectic	Nematic	Isotropic
I	R = -C <sub>5</sub> H <sub>11</sub>	1	—	124	153
II	R = -C <sub>5</sub> H <sub>11</sub>	2	—	93.5	146.5
III	R = -C <sub>8</sub> H <sub>17</sub>	1	100.5	138.5	148.5
IV	R = -C <sub>8</sub> H <sub>17</sub>	2	71	117	135
V	R = -COC <sub>3</sub> H <sub>11</sub>	2	—	60.5	132
VI	R = $\begin{array}{c} \parallel \\ \text{O} \\ \text{---} \\ \text{COC}_8\text{H}_{17} \end{array}$	2	60.5	119.5	125.5
VII	R' = -C <sub>5</sub> H <sub>11</sub>	—	—	106	116.5
VIII	R' = -C <sub>8</sub> H <sub>17</sub>	—	—	101	111

compounds studied are also given in Table I. In the synthesis of these compounds one obtains a mixture of two isomers differing in the position of the oxygen atom on one or the other nitrogen atom. Compounds I and III are isomers that are described by formula (3):



Compounds I, II, V, VII and VIII are nematics, while compounds III, IV and VI have both a smectic and a nematic mesophase.

The preparation of liquid crystals has been described by Adamska *et al.*<sup>12</sup>. The stationary phases were deposited on supports from methylene dichloride solution. Chromosorb W AW, NAW and AW DMCS (0.102–0.2 mm) were used as the supports. The study was conducted on a Pye Unicam GCV gas chromatograph equipped with a flame-ionization detector. The columns used were 2.1 and 2.7 m × 4 mm I.D. Argon was used as the carrier gas. The injector and detector temperatures were 240° and 180°, respectively. Methane was used in the determination of the dead time. The characteristics of the columns are given in Table II. The amount of liquid crystal on the supports was determined by heating at 600° to constant weight. The columns were placed in the thermostat of the chromatograph and heated for 3 h at a temperature at which the liquid crystal concerned was an isotropic liquid. The mixtures to be separated were dissolved in cyclohexane and injected on to the column by means of a 1- $\mu$ l Hamilton syringe.

## RESULTS AND DISCUSSION

### Column efficiency

HETP values were measured as a function of flow-rate ( $\mu$ ) at column temperatures corresponding to the maximal retention time. Fig. 1 shows the dependences

TABLE II  
COLUMNS USED

Column No.	Stationary phase	Chromosorb	Amount of stationary phase on support (%)	Length of column (m)	Weight of filling in column (g)
1	I	W AW DMCS	2.40	2.1	7.90
2	I	W AW	2.14	2.1	9.15
3	I	W NAW	2.06	2.1	8.85
4	I	W AW DMCS	8.46	2.1	8.40
5	I	W AW	7.81	2.1	10.25
6	I	W NAW	8.02	2.1	9.05
7	II	W AW	11.52	2.1	8.40
8	VII	W AW	11.80	2.1	9.70
9	VIII	W AW	9.02	2.1	9.65
10	IV	W AW	11.01	2.1	9.50
11	III	W AW	12.44	2.1	9.65
12	V	W AW	12.10	2.1	9.30
13	VI	W AW	12.05	2.1	9.45
14	VI	W AW	12.10	2.7	12.00

obtained for compound I. It was found that with *ca.* 2% and 8% of liquid crystal on the support the lowest HETP is obtained with Chromosorb W AW. With this support the HETP decreases with increasing amount of liquid crystal.

Therefore, in the analytical studies we used columns with *ca.* 10% of liquid crystal deposited on Chromosorb W AW. With acid-washed supports, the longer

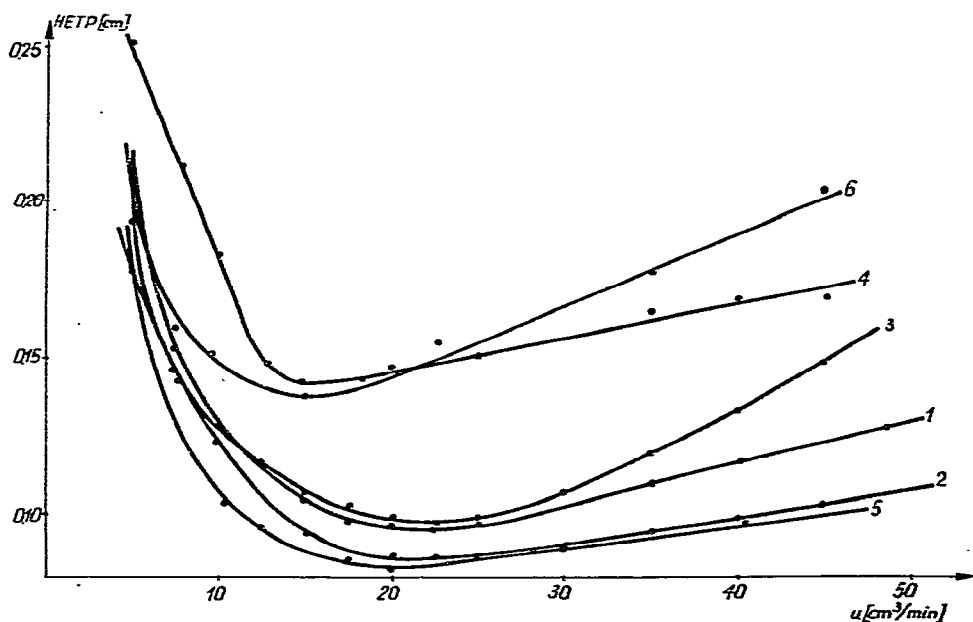


Fig. 1. HETP versus flow-rate ( $u$ ) for columns 1-6. Column temperature, 125°; test substance, *c*-di-chlorobenzene.

branches of the curves of the Van Deemter plots (Fig. 1) are flatter and parallel to each other (columns 1 and 2, and 4 and 5), whereas with Chromosorb W NAW these branches are steeper (columns 3 and 6). With the azo compounds studied, the longer branches of the curves are flat and almost coincident. The curves for compounds III and IV (a pure isomer and an isomeric mixture, respectively) are very similar and are exceptionally flat (Fig. 2). The optimal flow-rate ranged from 15 to 25 cm<sup>3</sup>/min. The lowest HETP (0.64 mm) was obtained with column 9.

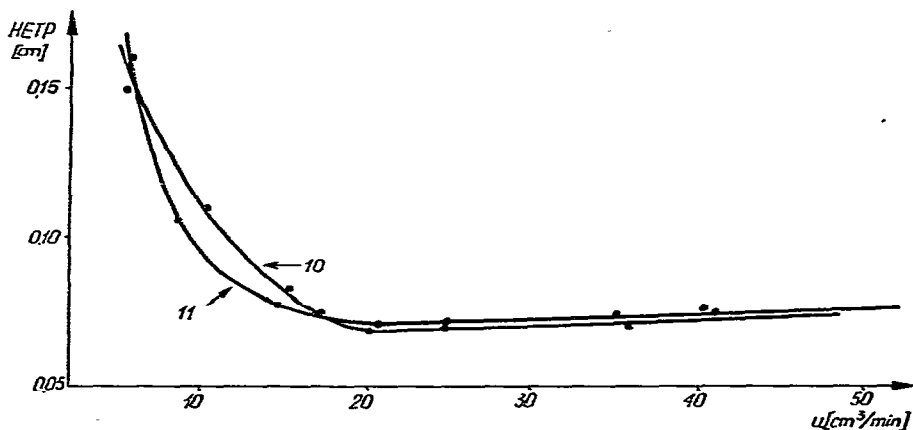


Fig. 2. HETP versus flow-rate ( $u$ ) for columns 10 and 11. Column temperature 77° (column 10) and 104° (column 11); test substance, *p*-xylene.

#### Relative retention times

The relative retention time,  $\alpha = t'_{r_1}/t'_{r_2}$ , where  $t'_{r_1} > t'_{r_2}$ , was calculated for all of the columns using xylene isomers. The dependences  $\alpha = f(T)$  obtained by heating the columns were either similar to the curve in Fig. 3, which is characteristic of nematic

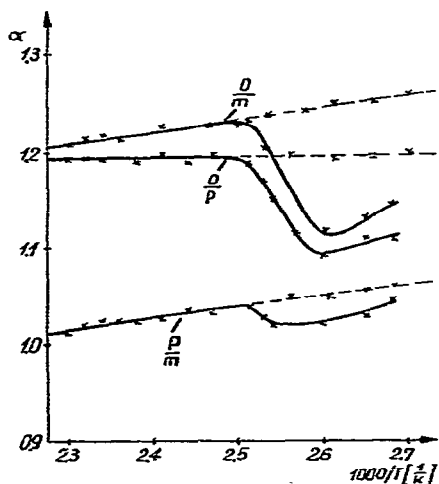


Fig. 3.  $\alpha$  versus  $1000/T$  for column 2. Broken line: cooling of column. *o*, *m*, *p* = isomers of xylene.

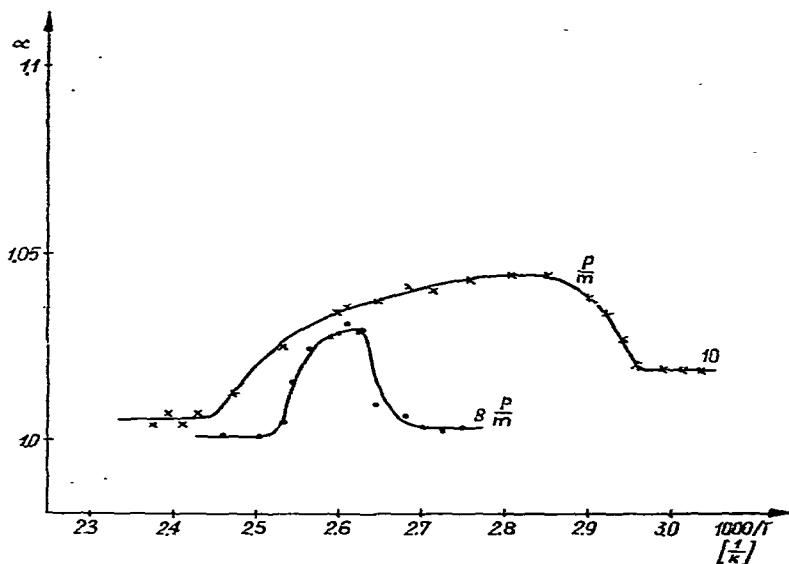


Fig. 4.  $\alpha$  versus  $1000/T$  for columns 8 and 10.  $p, m$  = isomers of xylene.

azoxy compounds, or to that in Fig. 4, which is characteristic of azo and azoxy compounds that have both a smectic and a nematic phase. Fig. 3 also shows the change in  $\alpha$  obtained by cooling the column. It can be seen that this part of the dependence differs from that obtained by heating the column. This can be explained by the ability of nematic azoxy compounds to become supercooled. Liquid crystals that will not supercool exhibit the same values of  $\alpha$  during both heating and cooling of the column. During heating, the maximal value of  $\alpha$  is obtained at temperatures cor-

TABLE III

MAXIMAL RELATIVE RETENTION TIMES FOR *p*- AND *m*-XYLENE

Column No.	Temperature of column ( $^{\circ}\text{C}$ )	$\alpha_{\text{max.}}$
1	127 (heating)	1.040
	90 (cooling)	1.088
2	127 (heating)	1.038
	90 (cooling)	1.052
3	127 (heating)	1.040
	90 (cooling)	1.072
4	127 (heating)	1.044
	90 (cooling)	1.090
5	127 (heating)	1.042
6	127 (heating)	1.044
7	93 (heating)	1.058
8	108 (heating)	1.030
9	107 (heating)	1.027
10	81 (heating)	1.043
11	108 (heating)	1.033
12	63 (heating)	1.078

responding to the maximal retention time. When nematic azoxy compounds are supercooled,  $\alpha$  increases, but so does the analysis time. Also, the ability of a liquid crystal to stay in the supercooled state is limited. Below a certain temperature, the state of supercooling rapidly disappears. Table III gives the maximal values of  $\alpha$  for *m*- and *p*-xylene on several columns.

### Separations

With the liquid crystals studied, complete separations of ethyltoluenes, chlorotoluenes, bromotoluenes and dichlorobenzenes were achieved. Complete separations of ethylbenzene from xylenes and of propylbenzene from ethyltoluenes were also achieved. It was also possible to separate a mixture of cyclohexane, cyclohexene and benzene. Almost complete separations of xylenes were achieved.

The separations obtained on different columns are listed in Table IV and a typical separation is shown in Fig. 5. Of the liquid crystals studied, the best separations were achieved with compounds II and V, which are mixtures of isomers. The azoxy compounds were found to be better stationary phases than the corresponding azo compounds.

TABLE IV

## SOME SEPARATIONS OBTAINED ON DIFFERENT COLUMNS

Column No.	Good separation of mixture	Time of separation (min)	Flow-rate of argon (cm <sup>3</sup> /min)	Temperature of column (°C)
4	Dichlorobenzenes	40	20	85
5	Dichlorobenzenes	13	20	128
	Bromotoluenes	24	20	85
6	Dichlorobenzenes	27	15	105
7	Bromotoluenes	62	16	90
	Dichlorobenzenes	25	17.5	96
10	Ethyltoluenes	45	20	78
11	Benzene, cyclohexane, cyclohexene	3.5	20	105
12	Xylenes	62	17.5	50
	Ethyltoluenes	50	17.5	70
14	Xylenes	50	20	60
	Ethyltoluenes	35	20	85
	Benzene, cyclohexane, cyclohexene	8	20	60
	Bromotoluenes	83	20	85
	Chlorotoluenes	40	20	85

No separations of *o*- and *p*-diethylbenzenes were achieved on any of the columns, although previously we had been able to separate these isomers using a micropacked column with a liquid crystal deposited on Polsorb B<sup>11</sup>. The failure to achieve a separation in the present work could have been caused by the use of a shorter column with a greater HETP and of a different type of support that orientates the liquid crystal molecules in a different manner. With Polsorb B, better properties were obtained with acid-washed than with untreated supports; with Chromosorb the reverse was the case.

Isopropylbenzene could not be separated from xylenes; it was coincident with *p*-xylene. This is due to the shape of the isopropylbenzene molecule and to its small

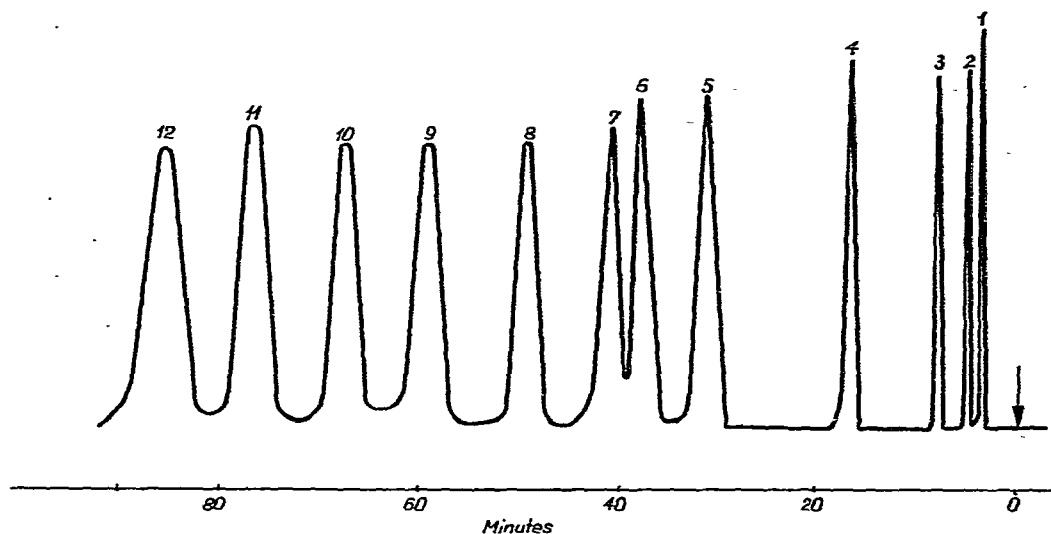


Fig. 5. Separation of a mixture on column 14. Temperature,  $60^{\circ}$ ; carrier gas, argon at  $20 \text{ cm}^3/\text{min}$ . Peaks: 1 = cyclohexane; 2 = cyclohexene; 3 = benzene; 4 = toluene; 5 = ethylbenzene; 6 = *m*-xylene; 7 = *p*-xylene; 8 = *o*-xylene; 9 = propylbenzene; 10 = *m*-ethyltoluene; 11 = *p*-ethyltoluene; 12 = *o*-ethyltoluene.

length-to-width ratio. Molecules of this type are eluted from the column at an earlier stage than molecules with a greater length-to-width ratio.

One should consider whether the improvement in the separation of *meta* and *para* isomers that is achieved at higher relative retention times is caused by delayed elution of the *para* isomer or by accelerated elution of the *meta* isomer. From Fig. 3 it can be seen that the relative retention time of *ortho* and *para* isomers remains constant, while those of *ortho* and *meta* and of *para* and *meta* isomers increase. Hence it can be concluded that at higher relative retention times the *meta* isomer is eluted from the column earlier than the *para* isomer.

Also of interest is the order in which cyclohexane, cyclohexene and benzene are eluted from the column. On most of the conventional stationary phases this order is different and corresponds to their boiling points, *viz.*, benzene, cyclohexane and cyclohexene. This leads to the conclusion that on a liquid crystal the separation of these compounds is determined by the planarity of the ring. Being the most planar of the three, the benzene ring fits into the structure of the liquid crystal with the greatest ease and is therefore retained the longest. The cyclohexane ring is the least planar, does not fit easily into the structure of the liquid crystal and is therefore eluted from the column in the shortest time.

#### ACKNOWLEDGEMENT

The authors thank Dr. R. Dąbrowski for providing the liquid crystals.

## REFERENCES

- 1 H. Kelker, *Ber. Bunsenges. Phys. Chem.*, 67 (1963) 698.
- 2 H. Kelker, *Z. Anal. Chem.*, 198 (1963) 254.
- 3 H. Kelker and E. von Schivizhoffen, *Advan. Chromatogr.*, 6 (1968) 247.
- 4 J. P. Schroeder, in G. W. Gray and P. A. Winsor (Editors), *Liquid Crystals and Plastic Crystals*, Vol. I, Ellis Horwood, Chichester, 1974, p. 356.
- 5 Z. Witkiewicz, *Wiad. Chem.*, 31 (1977) 19.
- 6 C. H. Lochmüller and R. W. Souter, *J. Chromatogr.*, 87 (1973) 243.
- 7 C. H. Lochmüller and R. W. Souter, *J. Chromatogr.*, 113 (1975) 283.
- 8 H. Kelker, B. Scheurle, J. Sabel, J. Jainz and H. Winterscheidt, *Mol. Cryst. Liq. Cryst.*, 12 (1971) 113.
- 9 G. M. Janini, G. M. Muschik, J. A. Schroer and W. L. Zielinski, *Anal. Chem.*, 48 (1976) 1879.
- 10 G. M. Janini, B. Shaikh and W. L. Zielinski, Jr., *J. Chromatogr.*, 132 (1977) 136.
- 11 Z. Witkiewicz, Z. Suprynowicz, J. Wójcik and R. Dąbrowski, *J. Chromatogr.*, 152 (1978) 323.
- 12 G. Adamska, R. Dąbrowski, M. Ptaszyńska and Z. Witkiewicz, *Biul. Wojsk. Akad. Tech.*, 26, No. 7 (1977) 105.