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USE OF A NEMATIC LIQUID CRYSTAL FOR THE GAS-LIQUID CHROMATOGRAPHIC SEPARATION OF NAPHTHALENE HOMOLOGUES

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SUMMARY

The gas-liquid chromatographic separations of methyl-, ethyl-, and dimethylnaphthalene isomers on the nematic and supercooled regions of *N,N'*-bis(*p*-methoxybenzylidene)- α,α' -bi-*p*-toluidine are presented and compared with the results obtained on other materials. The unique selectivity of this liquid crystal, based upon differences in the molecular length-to-breadth ratio of the solute positional isomers, has enabled the complete separation of these naphthalene homologues.

INTRODUCTION

The alkyl-substituted naphthalenes are important in oil-spill studies because of their toxic properties¹ and their relatively high water solubilities. These compounds are harmful to marine plant and animal life at the $\mu\text{g}/\text{kg}$ concentrations. Thus, it is important to determine the amounts of these compounds in sediments, fish tissue, and sea-water in order to ascertain the effect of an oil spill on marine life.

Gas-liquid chromatographic (GLC) separation of the positional isomers of these compounds is difficult because their boiling points are nearly the same. For example, three pairs of the dimethylnaphthalenes have boiling points within 1° of each other. Most of these solute pairs can be separated by high-efficiency capillary columns, however, one or two pairs still might remain unresolved.

It has been recognized that excellent separation of positional isomers can be achieved using nematic liquid crystal as a GLC liquid phase. Because of the rodlike shape and the ordered arrangement of the molecules, liquid crystals exhibit unique solvent properties. The more rodlike a solute molecule is, the easier it fits into the liquid crystal "lattice" and hence the greater its solubility. Liquid crystal separation solvents selectively discriminate on the basis of molecular shape. For two solutes with the same boiling point, the solute with the greater length-to-breadth ratio will be retained longer on a GLC column.

Janini *et al.*² have shown that the liquid crystal *N,N'*-bis(*p*-methoxybenzylidene)- α,α' -bi-*p*-toluidine (BMBT) is a good solvent for the chromatographic separation of polyaromatic hydrocarbons. It is the object of this paper to evaluate BMBT for the separation of alkyl-substituted naphthalenes. The properties of the supercooled region of this liquid crystal will be emphasized.

EXPERIMENTAL

Because of the difficulty in finding a suitable solvent for recrystallization, the BMBT was used as it was obtained from the manufacturer. Its purity was found to be greater than 99% by differential-scanning calorimetry. The solid \rightarrow nematic transition (181°) and the nematic \rightarrow isotropic transitions (320°) were in excellent agreement with the data published by the manufacturer.

The solid support used in this study was 100–120 mesh HP Chromosorb W. The support was coated with the liquid crystal by using chloroform as the solvent, followed by gradual solvent elimination through rotary vacuum evaporation. The packing was resieved to 100–120 mesh and then packed into 2-m \times 3.2-mm-O.D. stainless-steel columns. Prior to use the columns were conditioned at 200° for 24 h with the carrier gas flow-rate set at $20 \text{ cm}^3/\text{min}$. The effluent was monitored by a hydrogen flame detector. A 1-mV recorder with a chart speed range of 0.5–15 in./min was used to record chromatograms from which retention times and column efficiencies were determined. The flow-rate was measured with a soap-film meter.

Individual liquid samples were injected with a 10- μl syringe, using the smallest detectable sample size. The solute pair adjusted retention times were determined by taking the average of at least three measurements. It was established that the solute pair adjusted retention times were independent of sample size in both the nematic and supercooled regions of the liquid crystal stationary phase.

RESULTS AND DISCUSSION

Dewar and Schroeder³, Barrall *et al.*⁴, and Kelker *et al.*⁵ have observed that packed columns containing liquid crystal stationary phases all supercool. Chow and Martire⁶ have observed, from calorimetric measurements, that the intermediate state obtained on cooling the nematic phase of 4,4'-dihexyloxyazoxybenzene was liquid crystalline. We investigated this effect by measuring the retention volume, V_R , of solute molecules eluted from a packed column containing BMBT as the stationary phase. In Fig. 1 a plot is shown of the $\log V_R$ of the solute molecules 1,5- and 2,6-dimethylnaphthalene *versus* the reciprocal temperature. The half-filled circles represent the data obtained by heating the column from room temperature to 180° . The low V_R values for the two solutes and the absence of any separation indicate that solid BMBT crystal is a poor solvent. Just before the crystal \rightarrow nematic melting point (181°) the V_R values rise sharply and the solute molecules are separated. Above the melting point V_R decreases linearly with increasing temperature. The V_R values obtained by cooling the column are shown as open circles for 2,6- and filled circles for 1,5-dimethylnaphthalene. These plots are linear to nearly 120° , 65° below the normal nematic \rightarrow crystal melting point. At 117° the V_R values drop sharply and approach the values obtained for the BMBT crystal. Grushka and Solsky⁷ have observed a similar behavior with capillary columns for the liquid crystal *p*-azoxyanisole. They discussed the possibility that this hysteresis behavior may be due to some kind of surface orientation or a supercooling of the liquid crystal. Both these phenomena are well-known from liquid crystal studies. We feel that cooling the nematic phase below the normal nematic \rightarrow crystal melting temperature results in a supercooled region that is identical to the nematic region in physical and chemical properties. The argu-

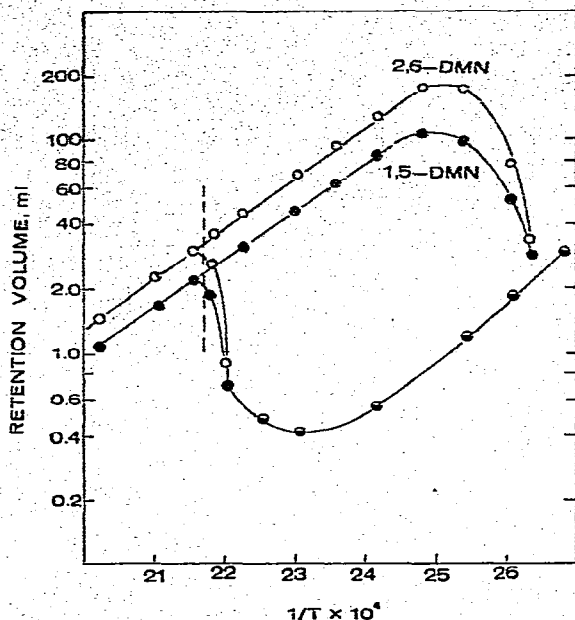


Fig. 1. Dependence of the retention volume of 1,5- and 2,6-dimethylnaphthalene (1,5-DMN and 2,6-DMN) on the column temperature in *N,N'*-bis(*p*-methoxybenzylidene)- α,α' -bi-*p*-toluidine nematic and supercooled phases. \bullet , 1,5- and 2,6-dimethylnaphthalene, heating; \circ , 1,5-dimethylnaphthalene, cooling; \circ , 2,6-dimethylnaphthalene, cooling.

ment against the existence of a supercooled region as stated by Grushka and Solsky⁷ is that the mesophase should not solidify at a given temperature, but should depend upon the cooling rate. We found, in numerous repetitions of the experiment with variations in the duration of the cooling process, that the mesophase always solidified at a temperature between 118 and 117.2°.

EFFICIENCY STUDIES

The existence of a supercooled region essentially extends the temperature range of the liquid crystal column. In order to evaluate the solvent properties of this temperature region we measured the separation factor, α , for the solute pair 1-ethylnaphthalene (b.p. 259°) and 2-ethylnaphthalene (b.p. 258°) in the nematic and supercooled regions of BMBT. The results of these measurements are shown in Fig. 2 as a plot of α versus the column temperature. The interesting feature of this plot is that there is no abrupt change in α at or near 181° (dashed line), indicating that the supercooled region acts as an extension of the nematic phase.

In Fig. 3 a plot is shown of the number of theoretical plates versus the column temperature for 2-ethylnaphthalene being eluted from a BMBT column at a constant carrier flow-rate of 22 cm³/min. This flow-rate was chosen because it represented the flow at the minima of Van Deemter plots at 220°, 180°, 150°, and 130°. A decrease in column efficiency with decreasing temperature is typical of columns containing liquid

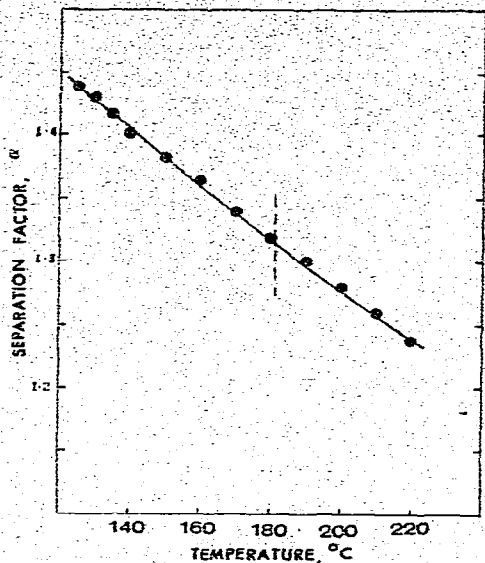


Fig. 2. Dependence of the separation factor, α , of 1- and 2-ethylnaphthalene on the column temperature.

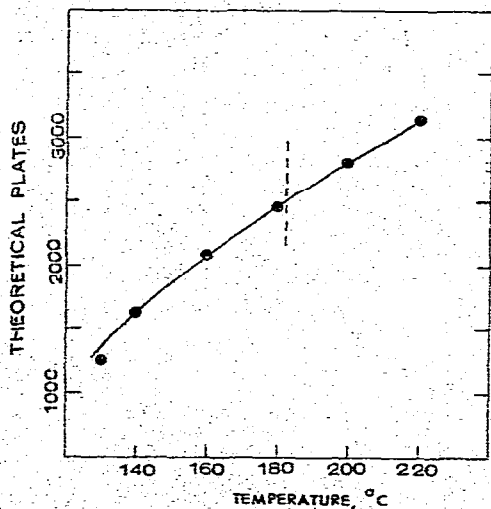


Fig. 3. Dependence of the number of theoretical plates on the column temperature for 2-ethylnaphthalene. Flow-rate, 22 cm³/min.

crystal stationary phases. This is probably due to the increase in viscosity of the liquid phase.

Figs. 2 and 3 indicate that in operating BMBT columns at lower elution temperatures there is a compromise between the advantages of higher α values and the disadvantage of lower column efficiency. In Fig. 4 the results of this compromise are shown as a plot of the ratio of the theoretical plates of the column to the required

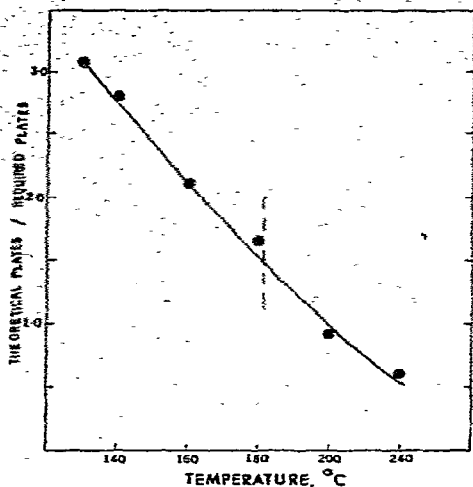


Fig. 4. Dependence of the ratio of theoretical plates to required plates on the column temperature for the solute pair 1-ethylnaphthalene/2-ethylnaphthalene.

theoretical plates versus temperature for the solute pair 1-ethylnaphthalene/2-ethylnaphthalene. In the nematic region (195°) this ratio is equal to unity, which indicates that at this temperature the column has a just sufficient number of plates to give a baseline separation of the solute pair, whereas at 125°, in the supercooled region, the number of theoretical plates is three times that required for separation. The number of theoretical plates required to separate two peaks, $N_{\text{req.}}$, was calculated from an expression derived by Purnell⁸

$$N_{\text{req.}} = 36\alpha^2 (\alpha - 1)^2 \left(1 + \frac{V_D}{V_R}\right)^2 \quad (1)$$

where V_D is the dead volume of the column and V_R is the retention volume of the more retained peak.

In Table I the relative retention data (naphthalene = 1) are given for some alkyl-substituted naphthalenes measured on a BMBT column at 130°. Previously published retention data on DC-500 phenylmethylsilicone⁹, a *p',p'*-azoxyphenetole¹⁰, and a graphitized carbon black¹² are included for comparison. In addition, retention data on polyphenyl ether (6 rings), obtained in this laboratory, are presented.

Table I shows that for the conventional liquid phase (DC-500) the elution order for the isomeric naphthalene homologues corresponds to their boiling points. The elution order is different on solvents which are able to establish specific interaction with π -electron systems of the naphthalene homologues or which have steric effects due to "fitting in" of the solute molecules in the liquid crystal "lattice". The elution order from BMBT is typical of that from a nematic liquid crystal in that for two solutes with similar boiling points the solute with the larger length-to-breadth ratio is retained longer. The lower-boiling 1-methylnaphthalene is eluted after 2-methylnaphthalene. This is also true for 1- and 2-ethylnaphthalene. Another example is that of 2,6-dimethylnaphthalene (b.p. 262°) and 1,4-dimethylnaphthalene (b.p. 268°).

TABLE I
RELATIVE RETENTION DATA OF NAPHTHALENE HOMOLOGUES ON DIFFERENT MATERIALS

Compound	B.p. (°C)	DC-500 phenylmethylsilicone at 160°	<i>p,p'</i> -Azoxyphenetole at 137° ¹⁰	Carbon black at 220° ¹¹	Polyphenyl ether (6 rings) at 210°	DMBT at 130°
Naphthalene	218	1.0	1.00	1.00	1.00	1.00
2-Methylnaphthalene	241	1.66	2.01	3.03	1.58	2.17
1-Methylnaphthalene	245	1.83	1.95	2.78	1.88	1.74
2-Ethyl-naphthalene	258	2.55	—	4.52	—	2.86
1-Ethyl-naphthalene	259	2.65	—	4.19	—	2.02
2,6-Dimethylnaphthalene	262	2.70	4.26	10.66	2.48	5.25
1,3-Dimethylnaphthalene	265	2.97	3.70	9.14	2.73	3.12
2,3-Dimethylnaphthalene	268	3.24	4.57	10.77	3.09	4.69
1,4-Dimethylnaphthalene	268	3.28	3.80	8.26	3.03	2.63
1,5-Dimethylnaphthalene	269	3.35	4.03	8.54	3.18	3.67
1,2-Dimethylnaphthalene	271	3.54	4.66	10.42	3.72	4.35

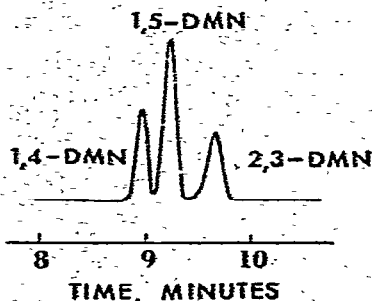


Fig. 5. Separation of 1,4-, 1,5- and 2,3-dimethylnaphthalene (1,4-, 1,5-, and 2,3-DMN, respectively). Column, 2 m \times 3.2 mm O.D. stainless steel; packing, 5% (w/w); oven temperature, 130°; injector temperature, 200°; detector temperature, 200°.

The retention ratio for this pair is equal to two, and the lower-boiling compound is eluted last. Fig. 5 shows a chromatogram of the separation of 1,4-dimethylnaphthalene (b.p. 268°), 1,5-dimethylnaphthalene (b.p. 269°), and 2,3-dimethylnaphthalene (b.p. 268°) on a BMBT column at 130°. The normally difficult separations are easily achieved because the length-to-breadth ratios of these compounds are 1.0, 1.2 and 1.5, respectively.

The elution order for the alkyl-substituted naphthalenes from the nematic liquid crystal *p,p'*-azoxyphenetole is different in some cases from that obtained with BMBT. The solute 1,3-dimethylnaphthalene is eluted before 1,4-dimethylnaphthalene, whereas 2,3- and 1,2-dimethylnaphthalene are eluted after 2,6-dimethylnaphthalene. The explanation of the elution order is more complex than one based solely on the length-to-breadth ratios of the solute molecules. Martire *et al.*¹¹ have observed similar results in comparing the retention data on two liquid crystals.

Table II gives the theoretical plate requirements for each solvent in Table I for complete resolution of the solute pairs most difficult to separate. In order to calculate $N_{req.}$ from eqn. 1 it was assumed that V_D/V_R was much less than unity. For this analysis BMBT is the best solvent, since it requires only 6,500 plates; in contrast, a column for carbon black, the least useful absorbent, would require about 190,000 theoretical plates to effect complete resolution. The retention data on BMBT were obtained at 135°, which is 46° below the nematic \rightarrow crystal melting point. The reduced

TABLE II
MOST DIFFICULT SEPARATIONS

Abbreviations: DMN = dimethylnaphthalene; EN = ethylnaphthalene; MN = methylnaphthalene.

Solvent	Difficult separation	Theoretical plates
Polyphenyl ether (6 rings)	1,4-DMN and 2,3-DMN	85,000
	2,3-DMN and 1,5-DMN	
<i>p,p'</i> -Azoxyphenetole	2,3-DMN and 1,2-DMN	92,000
	1,3-DMN and 1,4-DMN	
Carbon black	1,2-DMN and 2,6-DMN	92,000
	2,6-DMN and 2,3-DMN	
<i>N,N'</i> -Bis(<i>p</i> -methoxybenzylidene)- α,α' -bi- <i>p</i> -toluidine	1-EN and 2-MN	6,500
	2-EN and 1,3-DMN	6,500

theoretical plate requirement illustrates the advantage of the increased value of α resulting from the use of low elution temperatures.

It is interesting to note that the two most difficult separations for the BMBT column, 1-ethylnaphthalene/2-methylnaphthalene ($\alpha = 1.09$) and 2-ethylnaphthalene/1,3-dimethylnaphthalene ($\alpha = 1.09$) are relatively easy separations for the boiling-point column, DC-550 Silicone, with α values of 1.60 and 1.86, respectively. Thus 2-methylnaphthalene because of its larger length-to-breadth ratio is eluted just before the higher-boiling 1-ethylnaphthalene with a small length-to-breadth ratio. The same is true for the 2-ethylnaphthalene/1,3-dimethylnaphthalene pair. This behavior is typical of highly selective stationary phases such as liquid crystals and can be a deterrent in their use. On the other hand, difficult separations such as 1,4-, 2,3-, and 1,5-dimethylnaphthalene (Fig. 5) can be achieved with a column containing a relatively small number of theoretical plates.

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