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## GAS CHROMATOGRAPHIC PROPERTIES OF MIXED LIQUID CRYSTAL STATIONARY PHASES

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### SUMMARY

The gas chromatographic properties of six stationary phases containing various mixtures of the liquid crystals N,N'-bis(*p*-methoxybenzylidene)- $\alpha,\alpha'$ -bi-*p*-toluidine and N,N-bis(*p*-ethoxybenzylidene)- $\alpha,\alpha'$ -bi-*p*-toluidine are reported in both their supercooled and normal nematic temperature ranges. At temperatures at which all mixtures are in their nematic states, separations of 1,3- and 2,3-dimethylnaphthalene, and anthracene and phenanthrene are highest for the stationary phases containing the highest percentage of N,N'-bis(*p*-ethoxybenzylidene)- $\alpha,\alpha'$ -bi-*p*-toluidine. Since the mixed stationary phases can operate at lower temperatures than the pure compounds, it is possible to obtain better separations. Additionally, the liquid crystals interact with the support material, causing the crystal-to-nematic transition temperatures of the mixed-phase column packings to be generally lower than those of the liquid crystal mixtures themselves. This interaction also changes the eutectic composition of the mixed-phase packings. The results demonstrate that the use of mixed stationary phases improves selectivity and extends the usable temperature range of liquid crystal gas chromatographic columns.

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### INTRODUCTION

The use of nematic liquid crystals as gas chromatographic stationary phases is becoming increasingly popular<sup>1</sup>. Such phases have been successfully employed in a number of difficult separations, including those of polycyclic aromatic hydrocarbons (PAHs)<sup>2</sup>, benzene isomers<sup>3</sup>, and polychlorinated biphenyls<sup>4</sup>. However, the limited usable temperature range of such phases remains a significant problem, although several methods have been used to overcome this restriction. These include the synthesis of new phases with wider nematic temperature ranges<sup>5</sup>, the employment of lower-temperature smectic<sup>5,6</sup> and supercooled-nematic<sup>7,8</sup> thermal regions of some liquid crystalline phases, and the use of mixtures. Generally, blends of two or more liquid crystals have a lower crystal-to-nematic transition temperature than any of the components, and can operate at lower column temperatures when used as gas-liquid chromatographic (GLC) stationary phases. The value of such an approach was demonstrated by Kelker *et al.*<sup>9</sup> and later by Schroeder and co-workers<sup>3,10,11</sup>, who em-

ployed mixed liquid crystalline stationary phases for the improved separation of benzene isomers.

Since the pioneering work of Kelker *et al.* and Schroeder and co-workers, a number of new, more versatile liquid crystalline stationary phases have been developed. The liquid crystal *N,N'*-bis(*p*-methoxybenzylidene)- $\alpha,\alpha'$ -bi-*p*-toluidine (BMBT), for example, has a very wide nematic temperature range, and has been demonstrated to be a useful GLC stationary phase for the separation of 3-5-ring PAHs<sup>12</sup>, dimethylnaphthalenes<sup>7</sup>, and steroid epimers<sup>13</sup>. The use of BMBT in a mixed stationary phase thus has the potential for even greater versatility. We investigated this potential by measuring the gas chromatographic properties of mixtures of BMBT and its homolog, *N,N'*-bis(*p*-ethoxybenzylidene)- $\alpha,\alpha'$ -bi-*p*-toluidine (BEBT).

## EXPERIMENTAL

### Materials

The liquid crystal compounds BMBT and BEBT were synthesized using published methods<sup>12,14</sup> and purified to give constant transition temperatures which matched those reported. The transition temperatures and enthalpies are listed in Table I.

TABLE I

### TRANSITION TEMPERATURES AND ENTHALPIES OF THE COMPOUNDS STUDIED

*T* = transition temperature;  $\Delta H$  = enthalpy; C  $\rightarrow$  N = crystal to nematic mesophase; N  $\rightarrow$  I = nematic mesophase to isotropic liquid.

Compound	Transition	<i>T</i> ( $^{\circ}$ C)	$\Delta H$ (kcal/mole)
BMBT	C $\rightarrow$ N	181 (181)*	10.4*
	N $\rightarrow$ I	337 (337)*	1.7*
BEBT	C $\rightarrow$ N	174 (173)*	9.2*
	N $\rightarrow$ I	342 (341)*	2.2*

\* Data from ref. 14.

### Apparatus and procedure

Transition temperatures for all liquid crystal mixtures were determined by differential scanning calorimetry (DSC) using a Perkin-Elmer Model DSC-2 unit.

Gas chromatographic analyses were performed on a Hewlett-Packard Model 7610 gas chromatograph equipped with a flame ionization detector. All of the columns were glass (6 ft.  $\times$  2 mm I.D.). The column packings were 2.5% (w/w) of the liquid crystal mixtures on 100-120 mesh Chromosorb W-HP, prepared by dissolving each mixture in chloroform and then coating the support by the solvent slurry technique. The compositions of the liquid crystal mixtures used in each column packing are listed in Table II. Chromatograms were recorded on a 1 mV f.s. strip chart recorder using an electrometer setting of  $16 \cdot 10^2$ . Carrier gas flow (helium, 20 ml/min) was monitored by a calibrated Brooks 5840 Dual-GC Mass Flow Controller, while hydrogen and air flow-rates (40 and 500 ml/min, respectively) were measured by a soap bubble flow meter. Samples (usually 1-2  $\mu$ l) were injected with a Hamilton 701 N 10- $\mu$ l syringe.

TABLE II

COMPOSITIONS OF LIQUID CRYSTAL MIXTURES USED IN EACH COLUMN PACKING

Column	Mole percent BMBT	Mole percent BEBT
1	0	100
2	26.8	73.2
3	43.1	56.9
4	61.6	38.4
5	76.3	23.7
6	100	0

The retention characteristics of 1,3- and 2,3-dimethylnaphthalene were determined while cooling the columns from 180°C to 85°C in 5° increments, while those of anthracene and phenanthrene were determined while heating the columns from 130°C to 205°C also in 5° increments. Retention times were corrected using benzene as the unretained solute, which was experimentally shown to be unretained over the temperature range used. The separation factor,  $\alpha$ , was determined by the ratio of corrected retention times ( $\alpha = t'_{R2}/t'_{R1}$ ).

## RESULTS AND DISCUSSION

In addition to its potential for increased versatility in GLC analyses, the

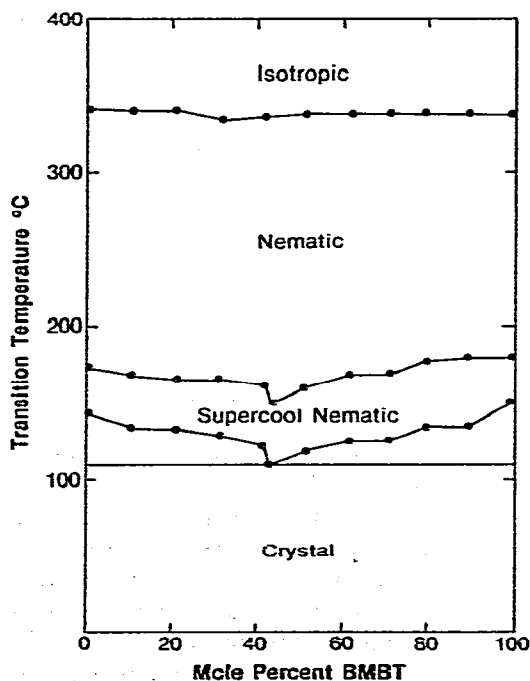


Fig. 1. Phase diagram of the BMBT-BEBT system.

BMBT-BEBT system was chosen for evaluation because it was expected to have predictable physical properties. Being homologs, the two liquid crystals have very similar structures, and therefore should be miscible. Additionally, because they are homologs, mixing of the two compounds should cause little or no disruption of liquid crystalline order. The phase diagram for the BMBT-BEBT system (Fig. 1) confirms these predictions. Both the crystal-nematic and nematic-isotropic transition temperature-composition curves are smooth, with no unexpected discontinuities. In fact, the nematic-isotropic curve is virtually linear, in contrast to the concavity of such curves with binary liquid crystal mixtures of dissimilar structure<sup>11,15</sup>.

The experimentally determined eutectic composition and transition temperature for this system is in accord with the values predicted from the Schroder-Van Laar equations<sup>16,17</sup>:

$$-\ln X_1 = \frac{\Delta H_1}{R} \left( \frac{1}{T} - \frac{1}{T_1} \right)$$

$$-\ln (1 - X_1) = \frac{\Delta H_2}{R} \left( \frac{1}{T} - \frac{1}{T_2} \right)$$

where  $\Delta H_1$ ,  $T_1$  and  $\Delta H_2$ ,  $T_2$  are the transition enthalpies and temperatures of pure components 1 and 2 from crystal to nematic mesophase, and  $T$  is the eutectic transition temperature for a system containing  $X_1$  mole fraction of component 1. Simultaneous solution of the equations using the data for BMBT and BEBT (Table I) gives a predicted eutectic composition of 43 mole percent BMBT and a transition temperature of 150°C, virtually identical to the experimentally determined values (Fig. 1). The applicability of these equations to the BMBT-BEBT system again indicates the formation of a nearly ideal solution, with little or no interactive forces between the two components.

Mixtures of BMBT and BEBT, as well as the pure liquid crystalline components, exhibit supercooling from the nematic to crystalline state. The supercooling transition temperatures are independent of the cooling rate, in accord with observations by Janini *et al.*<sup>8</sup> and others<sup>7,18</sup> for other supercooled liquid crystals. Additionally, the supercooling nematic-to-crystal transition temperature-composition curve (Fig. 1) parallels that of the normal crystal-to-nematic curve. The eutectic mixture of 43 mole percent BMBT and 57 mole percent BEBT can be supercooled to a temperature of 111°C before it crystallizes.

The existence of supercooled nematic thermal regions in mixtures of BMBT and BEBT gives such mixtures the potential for use of GLC stationary phases at lower column temperatures. The GLC properties of the mixed liquid crystal columns in these supercooled regions were evaluated by determination of the retention characteristics of 1,3- and 2,3-dimethylnaphthalene, solutes which have reasonable retention times at these lower temperatures, and have been successfully separated on other supercooled liquid crystalline phases<sup>7</sup>. At the higher temperatures near the normal (non-supercooled) crystal-to-nematic transitions, the columns were studied by investigation of the retention behavior of anthracene and phenanthrene.

Fig. 2 displays the retention behavior of 1,3- and 2,3-dimethylnaphthalenes (Fig. 2A) and anthracene-phenanthrene (Fig. 2B) in the supercooled and normal

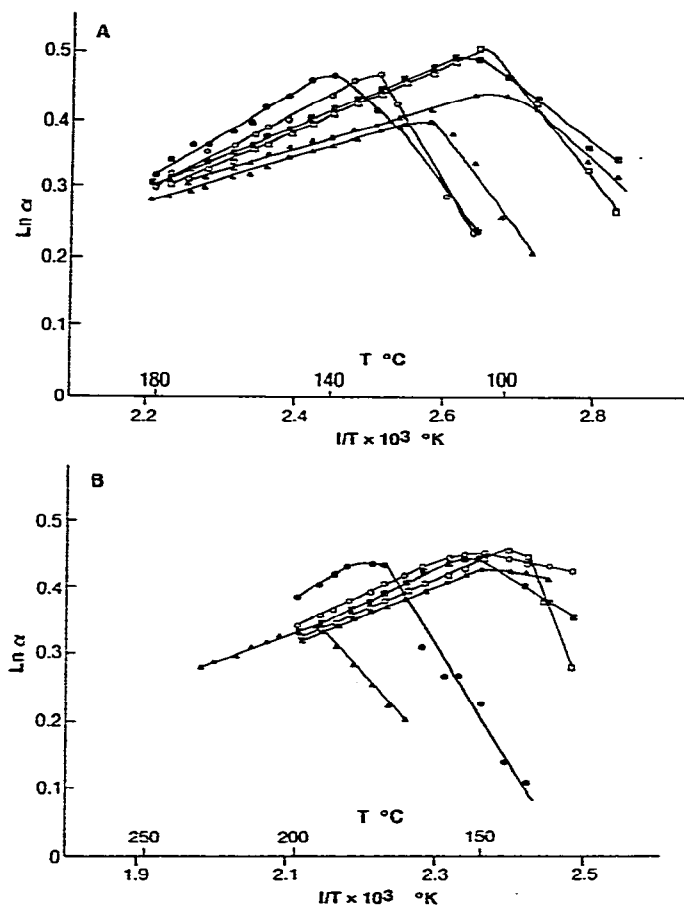


Fig. 2. Behavior of the separation factor with temperature for columns 1-6 for (A) 1,3-dimethylnaphthalene and 2,3-dimethylnaphthalene in the supercooled nematic regions of the columns and (B) anthracene and phenanthrene in the normal nematic regions. ●, Column 1; ○, column 2; ■, column 3; □, column 4; ▲, column 5; △, column 6.

(non-supercooled) nematic thermal regions, respectively, for all six columns. The data are presented as plots of the logarithm of the separation factor,  $\alpha$ , vs. the reciprocal of the absolute column temperature. Since the value  $\ln \alpha$  has been shown to be an index of relative selectivity for liquid crystal columns<sup>14,19,20</sup>, this format provides a direct comparison of column characteristics. The curves are linear for all of the columns in their nematic thermal regions, in accord with Matire's thermodynamic equations<sup>20</sup> relating relative retention and temperature for liquid crystal columns.

At temperatures in which all columns are in their nematic thermotropic regions, selectivity for both 1,3- and 2,3-dimethylnaphthalene and anthracene-phenanthrene is highest for column 1, which consists of a 100% BEBT stationary phase. Pure BEBT has the highest nematic-isotropic transition temperature of all the mixtures evaluated, and thus its superior selectivity is consistent with theories relating increased liquid crystal column selectivity with higher nematic-isotropic transition

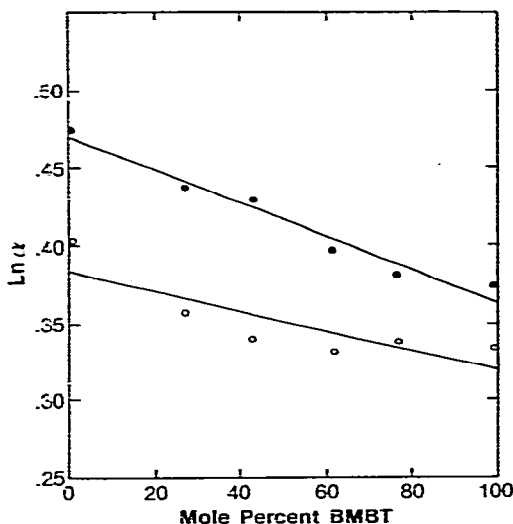


Fig. 3. Behavior of the separation factor with percentage of BMBT in the mixed stationary phase for 1,3-dimethylnaphthalene and 2,3-dimethylnaphthalene at 135°C (●) and anthracene and phenanthrene at 195°C (○).

temperatures<sup>1,14,20</sup>. Additionally, selectivity for the mixed liquid crystal columns is directly related to the composition of the mixture; at a given temperature, columns containing higher proportions of BEBT have greater selectivity. This relationship is displayed graphically in Fig. 3 as plots of the logarithm of the separation factor vs. mole percent BMBT at two column temperatures. For both the separations of 1,3- and 2,3-dimethylnaphthalenes and that of anthracene and phenanthrene, these curves are linear within experimental error (correlation coefficients greater than 0.99 for the equation below). At a given column temperature, then, the selectivity of a column composed of a mixed BMBT-BEBT stationary phase is simply a linear combination of the selectivities of the columns composed of the two pure liquid crystals. That is:

$$\ln \alpha_{1,2} = M_1 \ln \alpha_1 + M_2 \ln \alpha_2$$

where  $\alpha_1$ ,  $\alpha_2$  and  $\alpha_{1,2}$  are the separation factors for two solutes on columns consisting of pure component 1, pure component 2, and the mixture, respectively, and  $M_1$  and  $M_2$  are the mole fractions of components 1 and 2 in the mixture, respectively. The above equation allows for the prediction of the separation of solutes for any column using a mixed BMBT-BEBT stationary phase. In addition, the applicability of the equation to the BMBT-BEBT mixed system further indicates the absence of any interactive effects on the separation properties of either of the components of the mixed phases. It should be emphasized that the equation is valid only at temperatures in which all columns are in their nematic states, and only for solutes which separate by the unique geometric factors<sup>1,2,10</sup> associated with liquid crystal columns, such as those used here.

Maximum values of  $\alpha$  for both 1,3- and 2,3-dimethylnaphthalenes and anthracene-phenanthrene are shown in Table III. Despite the greater inherent selectivity of

TABLE III

## MAXIMUM SEPARATION FACTORS OBTAINED ON EACH COLUMN

$\alpha_{max}$  = maximum separation factor; AN-PH = anthracene-phenanthrene; DMN = 1,3-dimethylnaphthalene-2,3-dimethylnaphthalene;  $T$  = column temperature.

Column	Separation	$\alpha_{max}$	$T$ ( $^{\circ}C$ )
1	DMN	1.61	135
	AN-PH	1.54	175
2	DMN	1.61	125
	AN-PH	1.56	155
3	DMN	1.66	105
	AN-PH	1.56	155
4	DMN	1.72	105
	AN-PH	1.57	140
5	DMN	1.53	95
	AN-PH	1.53	150
6	DMN	1.51	115
	AN-PH	1.41	195

the nematic phase of BEBT, lower possible operating temperatures of mixed columns 2-4 allow equal or higher values of  $\alpha$  to be achieved at these temperatures. Among the columns evaluated, the highest values of  $\alpha$  were obtained on column 4, whose composition apparently strikes a favorable balance between inherent selectivity of its nematic phase and minimum operating temperature.

For virtually all liquid crystal stationary phases, it is well established that the temperature at which the maximum value of  $\alpha$  is obtained corresponds to its liquid crystal transition temperature<sup>1,2,14</sup>. Based on this correspondence, crystal-to-nematic transition temperatures for each of the columns were obtained graphically from Fig. 2 as the temperatures of maximum  $\alpha$ , in both the supercooled and standard nematic regions. These transition temperatures are plotted as a function of mole percent BMBT in Fig. 4, along with the transition temperatures for the mixtures themselves as determined by DSC. Clearly both the supercooling (Fig. 4A) and standard (Fig. 4B) transition temperatures for the column packings as determined by GLC are different from those obtained by DSC for the liquid crystal mixtures themselves. These differences, generally resulting in lower transition temperatures for the column packings, can only be the result of the interaction of the column support material with the liquid crystalline stationary phase. The support appears to be acting as a third component, generally resulting in further depression of the transition temperatures. The change in the transition temperatures, however, is not the same for each column. As shown in Fig. 4, this results in shifts in the eutectic composition of the mixed phases toward higher percentages of BMBT. Support-liquid crystal interactions have been observed in other liquid crystal columns<sup>21,22</sup>. While the retention characteristics of the mixed BMBT-BEBT columns indicate that these interactions do not significantly alter liquid crystalline order or the separation properties of the mixed stationary phases, they clearly have an important effect on the operating temperature ranges of such phases, which must be considered in the design of any mixed liquid crystal stationary phase.

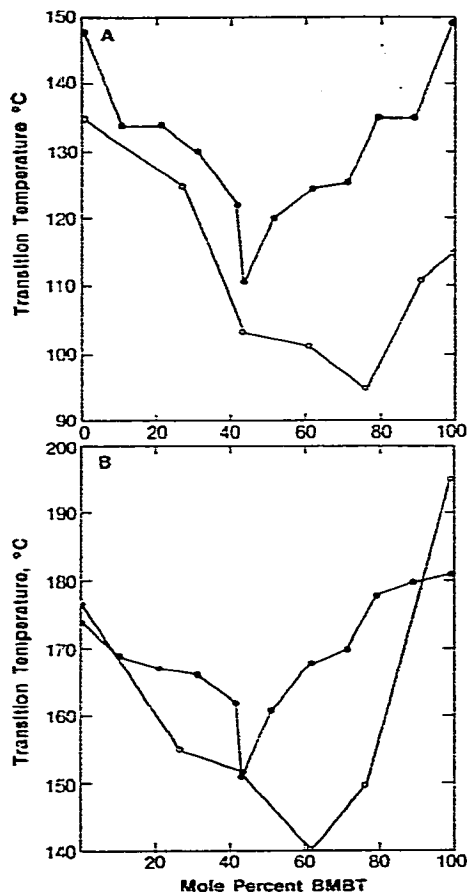


Fig. 4. Behavior of the supercooled (A) and normal (B) crystal-nematic transition temperatures with percentage of BMBT in mixtures of BMBT and BEBT, determined by DSC (●) and BMBT-BEBT mixed stationary phases on Chromosorb W-HP, determined by GC (○). An additional point is included in (A) for a column containing 91.0 mole percent BMBT.

## CONCLUSIONS

In this study, gas chromatographic columns consisting of mixed BMBT and BEBT stationary phases have been shown to have greater selectivity than columns made from either of the two liquid crystals alone, due primarily to the lower operating temperatures which are possible. While certain characteristics of such mixed liquid crystalline columns, such as the separation factors of solutes, can often be accurately predicted from data obtained from columns made from the pure components, interactions of the support with the liquid crystalline stationary phase and the existence of supercooled nematic thermal regions make the accurate prediction of minimum operating temperatures virtually impossible. Yet, because these factors generally lower the minimum operating temperatures from the predicted values, the versatility of such columns is increased even further. The use of mixed liquid crystal



stationary phases in gas chromatographic analyses thus remains a powerful tool for the extension of the working temperature range and selectivity of liquid crystal GC columns in general.

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