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OPTIMIZATION OF THE GAS CHROMATOGRAPHIC SEPARATION OF FIVE-MEMBERED RING POLYARENES WITH AN ADMIXED BPhBT LIQUID CRYSTAL–DEXSIL 300 STATIONARY PHASE

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SUMMARY

A window diagram constructed with the liquid crystal BPhBT in admixtures with the gum phase Dexsil 300 gave the optimum mixing ratio for the gas chromatographic resolution of five-membered ring polycyclic aromatic hydrocarbon solutes. The window diagram was constructed from relative retention data obtained from specific retention volume measurements. Plots of the specific retention volumes *versus* percentage of BPhBT in the blend were linear to within ±5% for all solutes. Further, intimately blended phases gave specific retention volumes virtually identical with those of mechanically mixed phases, within experimental error, when the same mixing ratios were compared. This suggests that the liquid crystal is only dispersed (as opposed to dissolved) in Dexsil 300 and that the two phases act independently of each other in the blends. This contention is supported by differential scanning calorimetric measurements. The use of the retention index scheme for the purpose of window diagram construction is shown not to be a valid option for this system.

INTRODUCTION

Comprehensive theoretical and experimental studies by Laub, Purnell and co-workers[1–9] have established that solute retention with mixed gas chromatographic stationary phases can be predicted from retention data with each of the pure phases. The subject has been comprehensively reviewed by Laub[10] and by Laub and Wellington[11]. The theoretical basis of this approach rests on a solution model in which the mixed phases are considered to be mutually immiscible. Thus,

$$K_{R(M)} = \varphi_A K_{R(A)}^0 + \varphi_B K_{R(B)}^0 \tag{1}$$

where K_R^0 is the partition coefficient of a solute with pure phases A and B, $K_{R(M)}$ is the partition coefficient with any combination of the two pure phases and φ_i is the volume fraction of component i.

As was first deduced by Primavesi[12], eqn. 1 can be put alternatively in terms of solute specific retention volume (V_g^0):

$$V_{g(M)}^0 = w_A V_{g(A)}^0 + w_B V_{g(B)}^0 \tag{2}$$

where w_i is the mass fraction of component i.

Pecsok and Apffel[13] have also shown that for several binary stationary phases, eqn. 1 can be cast in terms of the retention index, I:

$$I_{(M)} = \varphi_{(A)} I_{(A)}^0 + \varphi_{(B)} I_{(B)}^0 \tag{3}$$

Further, for columns of equal phase ratio per unit length, eqn. 1 can be put in terms of capacity factors, k':

$$k'_{(M)} = w_{(A)} k'_{(A)} + w_{(B)} k'_{(B)} \tag{4}$$

However, some modification of eqn. 4 is required when the capacity factor data are obtained with packings of unequal liquid loadings and/or particle size[8,9].

Any variant of eqn. 1 can be used for the prediction of the optimum mixed phase for the resolution of a given solute mixture. For example, employing eqn. 2 the relative retention of two solutes $(\alpha_{2/1})$ is given by

$$\alpha(2/1) = \frac{[w_{(A)} V_{g(A)}^0 + w_{(B)} V_{g(B)}^0]_2}{[w_{(A)} V_{g(A)}^0 + w_{(B)} V_{g(B)}^0]_1} \tag{5}$$

Thus plots of $\alpha(2/1)$ *versus* $w_{(A)}$ (window diagram) allows the prediction of the optimum α value for the most difficult solute pair. Consequently, the number of theoretical plates and, hence, the column length required to affect the resolution can then be calculated[14].

Examination of eqn. 1 and its variants by several workers showed that it is valid for a wide variety of mixed solvents and solute classes[10,11]. However, several studies[15-20] have shown that the relationship is accurate to no better than 20% for several systems examined with intimately blended stationary phases. For example, curvature of the plots of $K_{(M)}$ *versus* φ_A was observed for a number of solutes with squalane in admixture with dinonyl phthalate as stationary phase at 30°C[21]. On the other hand, and as argued by many workers[3,11,20], retention with mechanically mixed stationary phases must conform with eqn. 1 and its variants because the phases are physically separated in the column.

In this work, we have examined the linearity of plots of $V_{g(M)}^0$ *versus* $w_{(A)}$ for mixed liquid crystal–polymeric gum phases. Two sets of columns were constructed to asses this effect, one with mechanically mixed phases and the other with intimately blended phases. A window diagram constructed from the data generated by these columns gave the optimum mixed-bed composition for the separation of five-membered ring polycyclic aromatic hydrocarbons.

EXPERIMENTAL

N,N'-Bis(p-phenylbenzylidene)-α,α'-bi-p-toluidine (BPhBT) was synthesized by the reaction of 2 mol of p-phenylbenzaldehyde with 1 mol of α,α'-bi-p-toluidine. The mixture was allowed to reflux in absolute ethanol for 24 h, then the product was

recrystalized twice from hot chloroform. The solid–nematic transition temperature (257°C) and the nematic–isotropic transition temperature (403°C) were measured by differential scanning calorimetry (DSC) and were confirmed by hot-stage microscopy. Dexsil 300 and Chromosorb W HP (100–120 mesh) were purchased from Applied Science Labs. (State College, PA, U.S.A.).

The column packings were prepared by dissolving weighed amounts of the appropriate stationary phase in chloroform and transferring it into a chloroform slurry of weighed solid support in a round-bottomed flask. Excess of solvent was gently removed using a rotary evaporator and the slurry was then sieved to the appropriate mesh size. The percentage loading (10–11%) of each packing was determined to ±2% by exhaustive duplicate extractions. The columns used were 1/4 in. O.D. Pyrex glass.

A Perkin-Elmer Sigma 1B gas chromatograph equipped with dual column, forced-air oven, two flame ionization detectors, electronic carrier gas flow controllers and a Sigma 10 data station was employed. The column outlet pressure was read off a barometer and the column inlet pressure was measured with an auxiliary pressure gauge to ±0.2 p.s.i. The oven temperature was independently calibrated with a thermocouple. The temperature control at 265°C was accurate to within ±3°C.

Retention data were directly recorded by the on-line data station. An average of three measurements were taken for each point. The retention time of benzene was used to correct for the dead time. The minimum sample size was used to ensure that all peaks are symmetric. Helium carrier gas flow-rates were read off the digital display and were also checked with a calibrated soap-bubble flow meter.

Specific retention volumes were calculated from primary chromatographic data by the expression

$$V_g^0 = t' F_c^0 / g \qquad (6)$$

where t' is the corrected solute retention time, F_c^0 is the volume flow rate of the carrier gas adjusted to the mean column pressure and 0°C and g is the mass of the liquid stationary phase in the column.

RESULTS AND DISCUSSION

The use of liquid crystals as stationary phases for the separation of rigid geometric isomers is gaining interest, especially after the introduction of polymeric varieties of these materials[22,23]. A considerable improvement in column efficiency is achieved when liquid crystals are used in admixtures with gum phases[24]. Of particular importance is the fact that dispersion of the liquid crystalline material in the gum solvent (up to 25%, w/w) does not destroy but only dilutes the ordered molecular orientation of the liquid crystal, which is responsible for its unique selectivity towards rigid geometric isomers[24]. This suggests that at least for the systems studied so far[24,25] the liquid crystal phase is immiscible in the gum solvent. Hence eqns. 1 and 2 ought to be valid for such systems despite the fact that the two phases differ widely in their solvent properties.

To test this hypothesis we selected the liquid crystal BPhBT and the gum phase Dexsil 300. Fig. 1 shows DSC thermograms for (a) neat BPhBT, (b) a 10% (w/w)
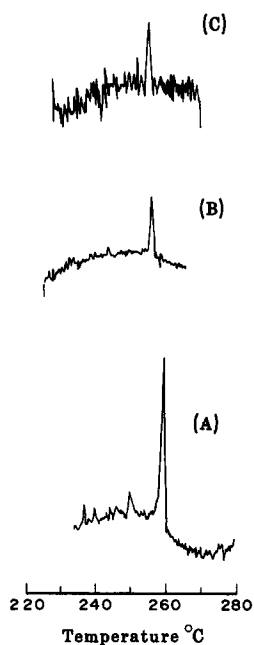
Fig. 1. DSC scans of (A) bulk BPhBT, (B) 10% (w/w) coating of BPhBT on Chromosorb W HP and (C) 10% (w/w) coating of a blend of BPhBT–Dexsil 300 (55.6:44.4) on Chromosorb W HP. Scan rate, 10°C/min.
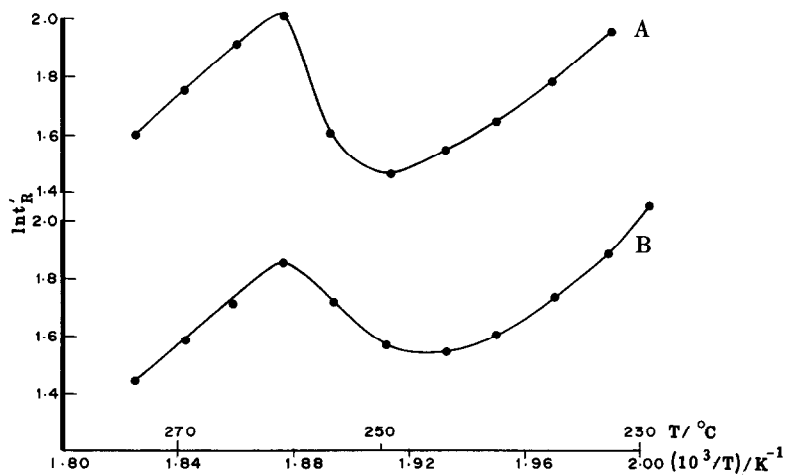

Fig. 2. Plots of the logarithm of the retention time (t'_R) of benzo[a]pyrene as a function of reciprocal temperature on (A) mechanically mixed and (B) intimately blended columns of BPhBT–Dexsil 300. Each packing contained 56.6% BPhBT.

TABLE I

SPECIFIC RETENTION VOLUMES OF SOLUTES [$V_g^0 \pm 5\%$ (ml g^{-1})] WITH NEAT BPhBT, NEAT DEXSIL 300 AND INTIMATE BLENDS OF THE TWO PHASES AT 265°C

Solute	BPhBT (mass%)					
	0	9.5	23.9	55.6	73.9	100
Triphenylene	247.6	264.3	298.1	322.2	337.9	404.4
Benz[a]anthracene	242.2	260.4	316.8	409.9	478.7	547.2
Chrysene	243.2	280.6	376.0	502.3	584.9	709.7
Benzo[k]fluoranthene	530.0	632.5	831.8	1153	1306	1644
Benzo[e]pyrene	644.5	760.5	890.1	1146	1298	1504
Perylene	702.7	832.7	1037	1350	1659	1918
Benzo[a]pyrene	658.7	818.2	1129	1633	2097	2483

coating of BPhBT on Chromosorb W HP (100–120 mesh) and (c) a 10% (w/w) coating of BPhBT–Dexsil 300 (55.6:44.4) on Chromosorb W HP (100–120 mesh). There is a slight shift in the solid–nematic transition temperature of coated BPhBT in comparison with neat BPhBT. However, no difference is observed between coatings of neat BPhBT and those of its blend with Dexsil 300, indicating that the liquid crystal is only dispersed in Dexsil 300 because real solution behaviour would shift the BPhBT transition temperature to lower values and eventually disrupt the mesomorphic order as the percentage of Dexsil 300 is increased. Further evidence is provided in Fig. 2, which presents Van 't Hoff plots of the logarithm of the retention time of a solute (benz[a]anthracene) as a function of reciprocal temperature on two admixed BPhBT–Dexsil 300 columns, one mechanically mixed and the other intimately blended. The two curves are essentially identical, showing no appreciable difference in the BPhBT phase transition for the two types of phase mixing.

TABLE II

COMPARISON OF SPECIFIC RETENTION DATA WITH COLUMNS OF 10% (w/w) MECHANICALLY MIXED PACKING AND 10% (w/w) INTIMATELY BLENDED PACKING AT 265°C

BPhBT in each column: 55.6% (w/w).

Solute	$V_g^0 \pm 5\%$ (ml g^{-1})	
	Mechanically mixed packing[a]	Intimately blended packing[b]
Triphenelene	331.0	322.2
Benz[a]anthracene	419.0	409.9
Chrysene	497	502.3
Benzo[k]fluoranthene	1182	1153
Benzo[e]pyrene	1139	1146
Perylene	1332	1350
Benzo[a]pyrene	1701	1633

[a] Mechanically mixed 10% (w/w) BPhBT packing and 10% (w/w) Dexsil 300 packing.
[b] 10% packing of intimately blended BPhBT (56.6%) and Dexsil 300 (44.4%).

Table I gives the specific retention volumes of seven polycyclic aromatic solutes on six columns with different blending ratios of BPhBT to Dexsil 300. Although specific retention data could be measured to ± 1% with high-precision instruments, we estimate the error in our V_g^0 data to be within ± 5%. This estimate is based on the reproducibility of V_g^0 data from two independent measurements using our experimental set-up with two columns having the same proportion of 55.6% BPhBT in the blend. Also, when experimentally determined V_g^0 data were compared with smoothed values obtained from plots of V_g^0 versus mass percentage of BPhGT, a scatter well within ± 5% was observed.

Further, two columns were compared, one with a mechanically mixed and the other with an intimately blended packing. The percentage of BPhBT in each was 55.6%, and the loading of each was 10% (w/w) on Chromosorb W HP (100–200 mesh). The results presented in Table II show that the difference from solute to solute is within ± 5%. This further demonstrates that there is no systematic variation in the data generated with these two types of phase mixing.

Fig. 3 shows plots of V_g^0 values obtained with intimately blended phases versus the percentage of BPhBT, which were linear, and linear regression analysis on the data for each solute yielded correlation coefficients in excess of 0.99. Fig. 4 is a window diagram constructed by plotting the relative retention (α) values for each pair of solutes
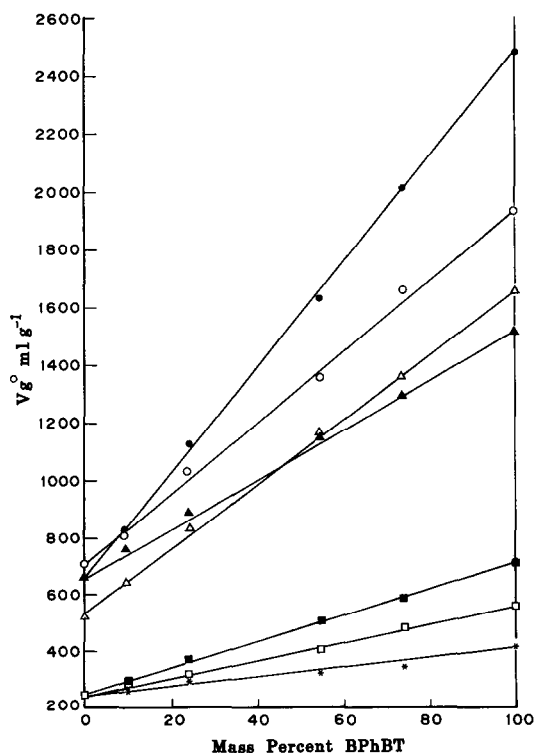

Fig. 3. Plots of the specific retention volume versus mass percentage of BPhBT for various solutes at 265°C. Solutes: ● = benzo[a]pyrene; ○ = perylene; △ = benzo[k]fluoranthene; ▲ = benzo[e]pyrene; ■ = chrysene; □ = benz[a]anthracene; * = triphenylene.
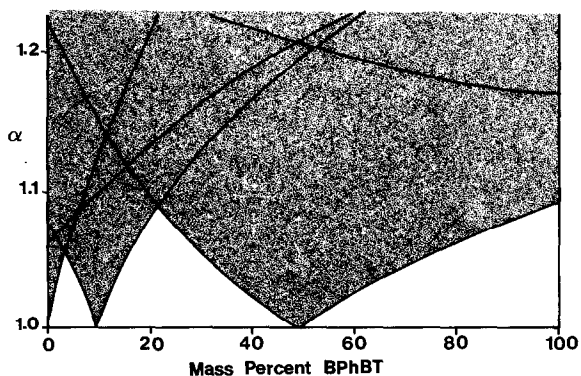
Fig. 4. Window diagram calculated from relative retention data from Table I and Fig. 3. Optimum predicted BPhBT mass percentage is 23%.

for the five-membered ring compounds. An interesting feature is that the plot shows that a column that contains only about 23% of BPhBT will easily resolve all the components of the mixture. Although neat BPhBT is more selective (*i.e.*, gives higher α values), an increase in column efficiency is gained by using columns with the optimum phase ratio. To illustrate this, Fig. 5 shows the resolution of five-membered ring polyarenes on a column packed with BPhBT–Dexsil 300 (23:77). The elution order is benzo[*k*]fluoranthene < benzo[*e*]pyrene < perylene < benzo[*a*]pyrene. The elution order of the first two compounds is the opposite of that with neat BPhBT. In
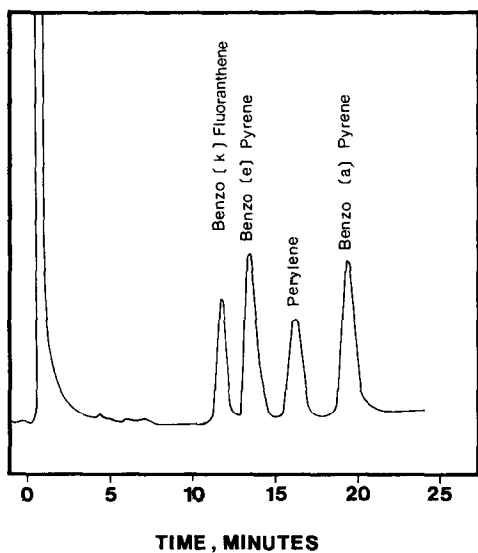

Fig. 5. Chromatogram of four pentacyclic aromatic hydrocarbons. Column: 1.8 m × 2 mm I.D. Pyrex glass. Packing: 3% (w/w) on Chromosorb W HP (100–120 mesh). Stationary phase: BPhBT–Dexsil 300 (23:77). Conditions: oven, 265°C; injector, 270°C; detector, 270°C; carrier gas, helium; flow-rate, 40 cm^3 min^{-1}.

contrast, benzo[e]pyrene and benzo[a]pyrene co-elute on neat Dexsil 300 columns and they are not resolved from the other two compounds.

It is concluded that the separation of polycyclic aromatic hydrocarbons, or for that matter any set of rigid geometric isomers, can be optimised by using admixtures of liquid crystals and gum phases. The optimization procedure requires only the measurement of V_g^0 data for each solute with the two neat phases. It should be noted that although several workers have observed systematic differences between the partition coefficient data generated with intimately blended and mechanically mixed phases[26], no such non-linear behaviour is apparent in this study, despite the wide difference in the solution properties of the liquid crystal and the gum phase.

An obvious drawback to this approach is that it requires the measurement of V_g^0 data, which may present some practical difficulties especially when gum silicone phases are used.

Window diagrams can be constructed with retention indices data via eqn. 3; however, this approach requires that the retention index of each compound should not be widely different with the two neat phases. In this work we measured the retention indices of the set of solutes with the two neat phases and found that the values for the four-membered ring compounds with BPhBT are higher than those with Dexsil 300 by more than 1500 units. For the five-membered ring compounds the difference is over 2000 units. Hence this approach is rendered impractical. Further, the alternative use of capacity factor data also requires some stringent conditions in column fabrication.

ACKNOWLEDGEMENTS

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