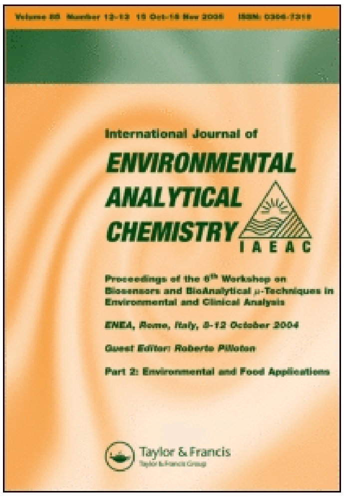

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Janssen, Frans(1982) 'Glass Capillary Columns with High Temperature Nematogenic Liquid Crystals as Stationary Phase for Polycyclic Aromatic Hydrocarbon Separations', International Journal of Environmental Analytical Chemistry, 13: 1, 37 — 54

To link to this Article: DOI: 10.1080/03067318208071582

URL: http://dx.doi.org/10.1080/03067318208071582

Intern. J. Environ. Anal. Chem., Vol. 13, pp. 37–54
0306-7319/82/1301-0037 $06.50/0

Printed in Great Britain

Glass Capillary Columns with High Temperature Nematogenic Liquid Crystals as Stationary Phase for Polycyclic Aromatic Hydrocarbon Separations†

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(*Received April 15, 1982*)

In view of the interest that has arisen during recent years about the determination of polycyclic aromatic hydrocarbons (PAH) we have carried out a study to prepare a capillary column with a special phase: a liquid crystal.

Most of the workers in the field of the analysis of PAH in environmental samples use techniques such as high performance liquid chromatography and gas chromatography with packed columns. Utilization of nematogenic liquid crystals of the type *N,N'*-Bis(*p*-methoxybenzylidene)-α,α'-bi-*p*-toluidine as stationary phase in glass capillary columns made it possible to achieve faster and more complete separation of three-, four- and five-ring PAH in comparison with packed columns. The separation properties of three liquid crystals in 20 m glass capillaries within the nematic temperature range in terms of the quality of the column and the separation system were investigated. The columns were tested with three-, four- and five-ring PAH and methylchrysene isomers and the quality of the columns evaluated with the aid of the abt-concept, which was compared with classical quality numbers as separation factor and separation number.

Furthermore, we have demonstrated in this paper that it is difficult to correlate the partial molar enthalpy of solution determined from retention measurements, with length to breadth ratio of a PAH molecule. So it is not possible to understand the separation of PAH on liquid crystals on a thermodynamic basis alone.

KEY WORDS: Gas liquid chromatography, glass capillary columns, liquid crystals, polycyclic aromatic hydrocarbons, blended stationary phases.

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†Presented at the 12th Annual Symposium on the Analytical Chemistry of Pollutants, Amsterdam, April 1982.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAH) are pollutants widely distributed in the environment. One of the probably oldest sources of PAH is nature itself, like prairy- and forest-fires, volcanic activities and even the synthesis by plants and micro-organisms. A second, more important, source are the activities of man. For instance, the increasing use of coal to produce electrical energy causes concern about the short and long term impact on the environment.

PAH are the largest known group of chemical carcinogens, some of them and their metabolites show high carcinogenic and mutagenic activities in animals. One of the most potent PAH and intensively studied carcinogen is Benzo(a)pyrene. In the period 1966–1969 the global emission over the whole world is estimated at about 5050 tons/year.[1] This number is the sum of 2600 tons/year from energy-conversion, 1050 tons/year from industrial processes, 1350 tons/year from waste burning and 50 tons/year from traffic. The carcinogenic activity of a PAH molecule depends on its structure, size and the presence of substituent groups. For instance, chrysene and its 1-, 2-, 4- and 6-methylchrysenes have moderate tumor activities, whereas 3- and 5-methylchrysenes are strong tumor initiators.[2] The differences in carcinogenic properties are one of the reasons to resolve complex mixtures of PAH completely. Another important feature which necessitates the complete separation of PAH mixtures is the strong resemblance of the mass-spectra of PAH with the same ring-number in case of GC-MS work. Also the mass-spectra of different alkyl substituted isomers do not differ sufficiently for identification and quantitation of each individual compound. So the separation efficiency and separation power of the analytical system is extremely important. A variety of methods have been used for PAH analyses over the years. Thus far, the most suitable technique for the analysis of PAH is gas chromatography and mass spectrometry. However, the best technique in trace analysis is solid probe-ms-ms. A number of workers have investigated the separation of PAH isomers on packed[3] and capillary columns with mainly polysiloxanes as stationary phase like: SE-52,[4,5] OV-17[6] and chemically bonded methylsilicone gums.[7]

However, more promising stationary phases for the resolving of closely related rigid solute isomers are liquid crystals.[8,9] The first application of liquid crystals as stationary phase in gas-liquid chromatography was published in 1963.[10] The theoretical background of liquid crystal systems is discussed in many papers[11-13] and references therein. Nematogenic liquid crystals or crystalline liquids possess a rod-like molecular structure and the alignment in the nematic range results in high solute-shape activities. It has been proved that, in accordance with predictions based on consideration of the nematic state structure that molecules with higher length to width ratios are retained longer in the column.

Janini and co-workers describe the synthesis and gas-liquid chromatographic application of the analogues and homologues of the liquid crystal *N*,*N*′-Bis(*p*-methoxybenzylidene)-α,α′-bi-*p*-toluidine (BMBT).[8,9,14–18] These high temperature nematogenic liquid crystals have been used for difficult isomer separations such as mono- and dimethoxyquinones,[19] steroid epimers and bile acids,[20] polychlorinated biphenyls,[21] aza-heterocyclic compounds,[22] etc.

A few number of papers describe capillary columns with liquid crystals as stationary phase.[10,23–25] The liquid crystal *N*,*N*′-Bis(*p*-butoxybenzylidene)-α,α′-bi-*p*-toluidine (BBBT) was used in wide-bore (0.77 mm i.d.) stainless steel capillaries.[9,25] The same liquid crystal BBBT itself and in admixture with a gum phase SE-52[23,24] was used in small-bore glass capillary columns (0.2 mm i.d.). We previously reported the application of *N*,*N*′-Bis(*p*-phenylbenzylidene)-α,α′-bi-*p*-toluidine (BPhBT) as stationary phase in a micro-packed column.[26] Because of the very low solubility of BPhBT in various solvents with respect to the dynamic and static coating techniques we developed an *in situ* coating technique.[27] As a consequence we coated glass capillaries with the butoxy and hexyloxy analogues of BMBT, which are in contrast with BPhBT readily soluble in solvents used in the static coating technique. This paper describes the behaviour of selected standard PAH on three liquid crystals BBBT, BHxBT and BPhBT as stationary phase in small-bore (0.25 mm i.d.) capillary columns. The quality of the columns and the separation system were evaluated in terms of separation factors, the separation number, separation efficiency, the real plate number, real plate height, the utilization factor. Besides, the use of classical column parameters like theoretical and effective plate number, selectivity factor and separation number are compared with the use of the quality column numbers mentioned above.

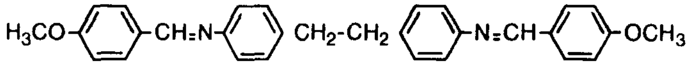
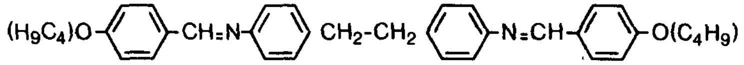
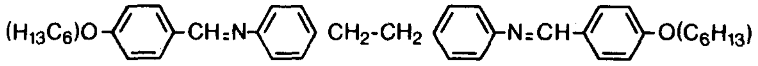
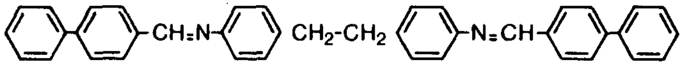
EXPERIMENTAL

Apparatus and procedure

Empty columns (o.d. 1.00 mm, i.d. 0.25 mm) of borosilicate glass (Supelco, Bellefante, PA, USA) were coated with the liquid crystals from Table I, as previously described.[27,28] BHxBT was treated in the same way as BBBT. The evaluation (see results and discussion) was carried out with the results from the columns mentioned in Table II. The gas chromatograph used in

TABLE I

Liquid crystal stationary phases in glass capillary columns

	Transition temperature[a] (°C)				
	Solid nematic C-N	Solid smectic C-S	Smectic I Smectic II S_I-S_{II}	Smectic Nematic S-N	Nematic isotropic N-I
 BMBT	181	—	—	—	332
	129; 133[b]	—	—	—	—
 BBBT	—	159	—	188	303
	—	146; 144[b]	—	185	288
 BHxBT	—	129	203	229	277
	—	177[b]	203	229	271
 BPhBT	262	—	—	—	370
	255[b]	—	—	—	—

[a] Measured by Differential Scanning Calorimetry.
[b] Transitions determined in the supercooled regions during cooling.

TABLE II

Columns used in this study

Column number	1	2	3
Stationary phase	BBBT	BHxBT	BPhBT
Substrate	$BaCO_3$	C	$BaCO_3$
Film thickness [μm]	0.1	0.1	0.1[a]
Length [m]	20.0	17.2	20.0
Outer diameter [mm]	1.0	1.0	1.0
Inner diameter [mm]	0.25	0.25	0.25
Linear flow rate H_2[b] [cm 5^{-1}]	62	52	60
Flow[c] [ml.min^{-1}]	2	3	3
Purge gas N_2 [ml.min^{-1}]	30	30	30
Inlet pressure [bar]	0.6	0.54	0.6

[a] The film thickness has been calculated on the basis of 100% yield of the reaction between α,α′-bi-*p*-toluidine and *p*-phenylbenzaldehyde.

[b] Radial average of the mobile phase linear flow velocity of methane.

[c] Volumetric flow rate measured at the column outlet measured with a soap-bubble flow meter.

this study was Varian 3700, equipped with a flame ionization detector, using an electrometer setting of 10^{-10} A full scale. The injector and detector temperature were 300 and 320°C respectively. The oven temperature was measured with a Hg-thermometer and a digital thermocouple thermometer (United Systems Corporation, Ohio, USA). An

TABLE III

Shape parameters and maximum length to breadth ratio of methyl-substituted chrysene compared with relative retention on Column 3 (Table II) and data from the literature

			Relative retention	
Compound	η[a]	L/B(max)[b]	BPhBT[c]	BBT[d]
Chrysene	1.72	1.72	1.000	—
6-methyl	1.47	1.48	1.124	1.37
5-methyl	1.34	1.48	1.164	1.44
3-methyl	1.63	1.63	1.235	1.55
4-methyl	1.35	1.51	1.253	1.62
1-methyl	1.71	1.71	1.515	1.92
2-methyl	1.85	1.85	1.720	2.17

[a] From ref. 36. η is based on the rectangle with minimum area which could envelope the molecule.

[b] From ref. 36. The rectangle eclosing the PAH-molecule, which maximizes the length to breadth ratio L/B(max).

[c] The compounds were injected spearately at 280°C.

[d] From ref. 36, retention relative to benz(a)anthracene.

universal capillary injection system (Chrompack, Middelburg, The Netherlands) was used in the splitless injection mode. The splitter was closed two minutes before injection; which was carried out within 5–10 seconds. The sample volume was 1 μl and was introduced using a Hamilton 701 N 10 microliter syringe. The columns were installed via Kalrez ferrules (Carlo Erba) at the detector and with graphite ferrules at the injector. Ultra high purity hydrogen was used as carrier gas and nitrogen as make-up gas. The use of hydrogen gives several advantages; there is no phase damage caused by oxygen and the gas-viscosity is smaller than of nitrogen or helium. The chromatograms were recorded on a Sigma-10 data station (Perkin Elmer). The transition temperature on heating and on cooling (Table IV) were measured by differential scanning calorimetry (DuPont).

TABLE IV

Symbols and relationships

Symbol	
a	(seconds) is the slope of the line $b_{0.5}$ vs.k'
$b_{0.5}$	(seconds) is the peak widths at half peak height (± 0.5 s)
b_0	(seconds) extrapolated $b_{0.5}$ value at $k'=0$; $b_{0.5}=ak'+b_0$
k'	(tms − tm)/tm is the capacity number
tms	(seconds) total retention time (± 0.5 s)
tm	(seconds) dead time = the retention of methane
SN_{real}	Separation efficiency number for the separation range $k'=0$ to k' is as given in Table VII. It gives the number of separable peaks in the k' range mentioned above and in a function of a, b_0 *and* t_m
SNt	Separation power number for the chromatographic range $k'=0$ till $k'=\ldots$; it gives the number of separable peaks per minute operating time
Tz	Separation number $(\mathrm{tms}(2)-\mathrm{tms}(1))/(b_{0.5(2)}+b_{0.5(1)})-1$
n_{real}	real plate number $(\mathrm{tm}/a)^2 \times 8 \log_e 2$
n_{eff}	effective plate number $(\mathrm{tms}-\mathrm{tm})/b_{0.5})^2 \times 8 \log_e 2$ $n_{\mathrm{real}}=n_{\mathrm{eff}}((k'+1)/k')^2$
h_{real}	(mm) real plate height $=L/n_{\mathrm{real}}$, L is the column length
Q_s	the utilization factor $k'a/(k'a+2b_0)$ wherein k' is the total chromatographic range (operational quality number)
ΔH	(kJ.mol^{-1}) partial molar enthalpy of solution and is calculated from the $\log_e((\mathrm{tms}-\mathrm{tm})/\mathrm{tm})$ vs $1/T$ plot
$\Delta_{i-j}(\Delta G)$	(kJ.mol^{-1}) difference in partial molar Gibbs energy of two solutes
θ	Reduced temperature; the ratio of the absolute temperature of the column and of the temperature of the phase-transition nematic-isotropic (T/T_{N-I})
σ	(%) standard deviation
r^2	Coefficient of determination (26)
α	separation factor or selectivity $=(\mathrm{tms}(2)-\mathrm{tm})/(\mathrm{tms}(1)-\mathrm{tm}) \geqq 1$

Materials

Standard polycyclic aromatic hydrocarbons purchased either from the Community Bureau of References (BCR) of the European Communities (Brussels, Belgium) or from Supelco (USA), were used without further purification and were dissolved in glass distilled cyclohexane. The sample bottles were wrapped-up in aluminium foil to prevent photolysis.

The concentration of the used compounds: phenanthrene; anthracene; fluoranthene; triphenylene; benzo(a)anthracene; chrysene and its methylchrysenes; benzo(b)fluoranthene; benzo(k)fluoranthene; benzo(e)pyrene; perylene; benzo(a)pyrene; benzo(ghi)perylene; dibenzo(a,h)anthracene; indeno(1,2,3-cd)pyrene was about 100–200 ng.μl^{-1} for each component. The structure, name and elution order is given in Figure 1.

Results and discussion

Glass capillary chromatograms of PAH mixtures are shown in Figures 2, 3, and 4. Figure 2 demonstrates the resolution of 3-, 4- and 5-ring PAH in a glass capillary column with BPhBT as stationary phase. The solutes phenanthrene and anthracene are not base-line separated on BPhBT. In Figure 3 a chromatogram is presented of 3- and 4-ring PAH on BBBT, on this phase base-line separation of phenanthrene and anthracene has been achieved. Figure 4 illustrates preliminary results of the methylchrysene isomers separation on a BPhBT column. The elution order is 6-, 5- (overlapped), 3- and 4 (overlapped) and 1- and 2-methylchrysene which are base-line separated.

From the shape-parameter L/B[29, 36] we expect the elution order 6- and 5-methylchrysene (overlapped); 4-, 3-, 1- and 2-methylchrysene. The actual elution order is 6-, 5-, 3-, 4-, 1- and 2-methylchrysene. So the more or less linear correlation between the retention and length to breadth ratio does not hold for chrysene, 3- and 4-methylchrysene. Also the column efficiency observed for methylchrysene isomers of BPhBT leaves much to be desired. Nevertheless, it is very important and necessary to separate the 3- and 5-methylchrysenes completely, because of the high carcinogenic activity, as already is pointed out in the introduction.

In order to evaluate the quality of the column and the separation system and to compare the performances of the capillaries with different liquid crystal stationary phases we used the so-called abt-concept.[30, 31] We calculated the separation number SN_{real} (Table IV) and the separation number/time SNt, which refer to the separation efficiency and the separation power of the separation system (the combination of column and instrumentation) respectively. The quality of the column has been

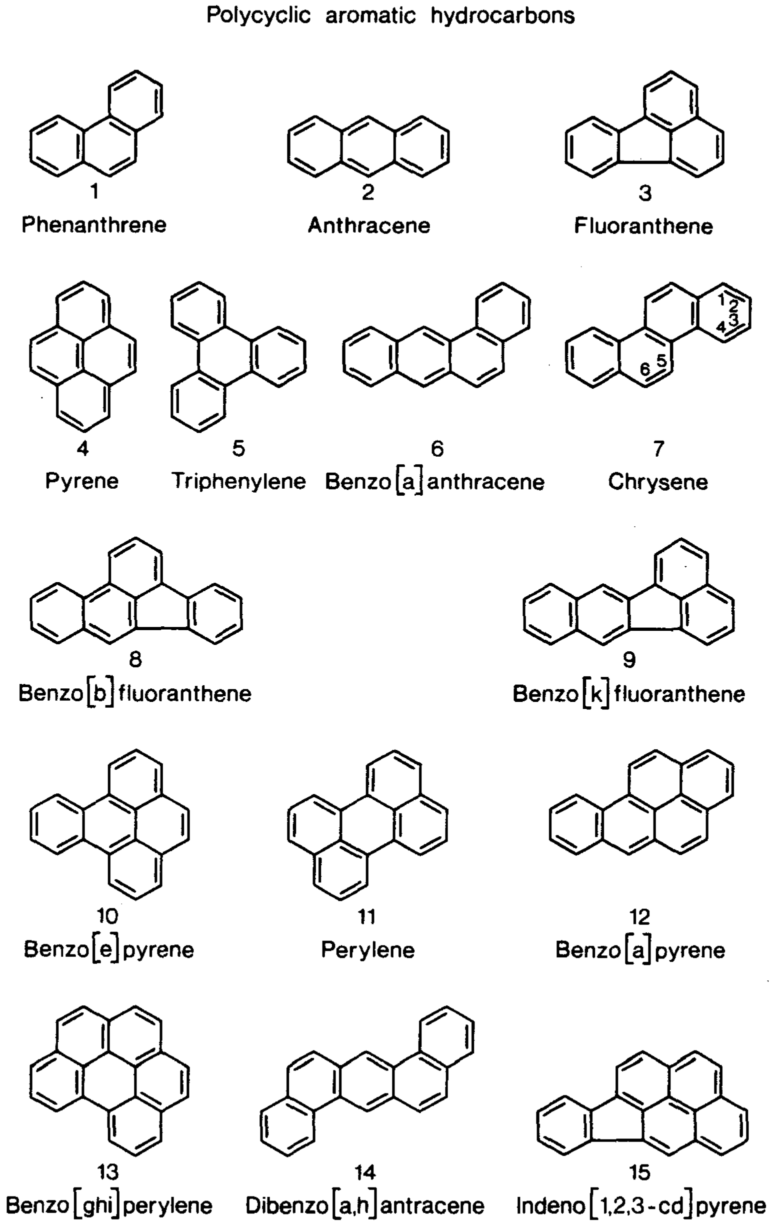


FIGURE 1 Polycyclic aromatic hydrocarbons used in this study. The number indicates the retention order on nematogenic liquid crystals.

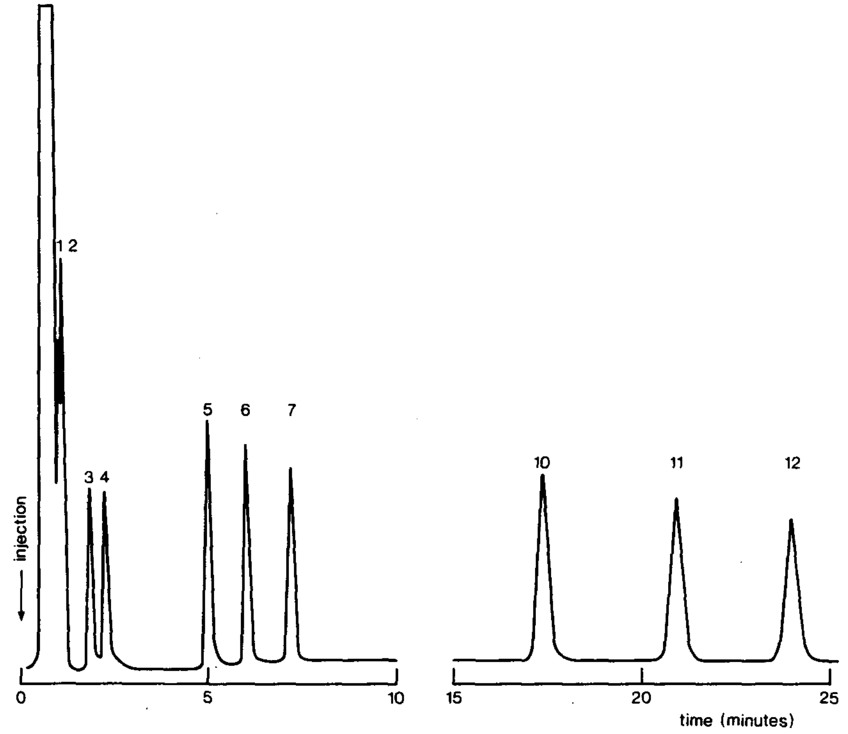


FIGURE 2 Glass capillary chromatograms of PAH, BPhBT as stationary phase. Peak assignment in Figure 1.

described by the real plate number n_{real} and the corresponding real plate height h_{real}. Table V summarizes the results of the evaluation of three columns. We have selected those temperatures at which the abt approach is permissible, this is when there exists a linear correlation between the capacity number and the peak width at half height. From the linear correlation we can deduce from Table V that the measured PAH family behaves like "homologues" on a liquid crystal column. This important feature is advantageous because the test mixture resembles the environmental samples to be analyzed. Furthermore, it can be seen from Table V that the quality of the column (n_{real} and h_{real}) and the quality of the separation system (SN_{real} and SNt) remains more or less constant within the nematic range for the BBBT and the BPhBT columns. Moreover, n_{real} is independant of the capacity number. The column with BPhBT shows the best "abt" results.

The separation factor (α), separation number (Tz) in Table VI and the

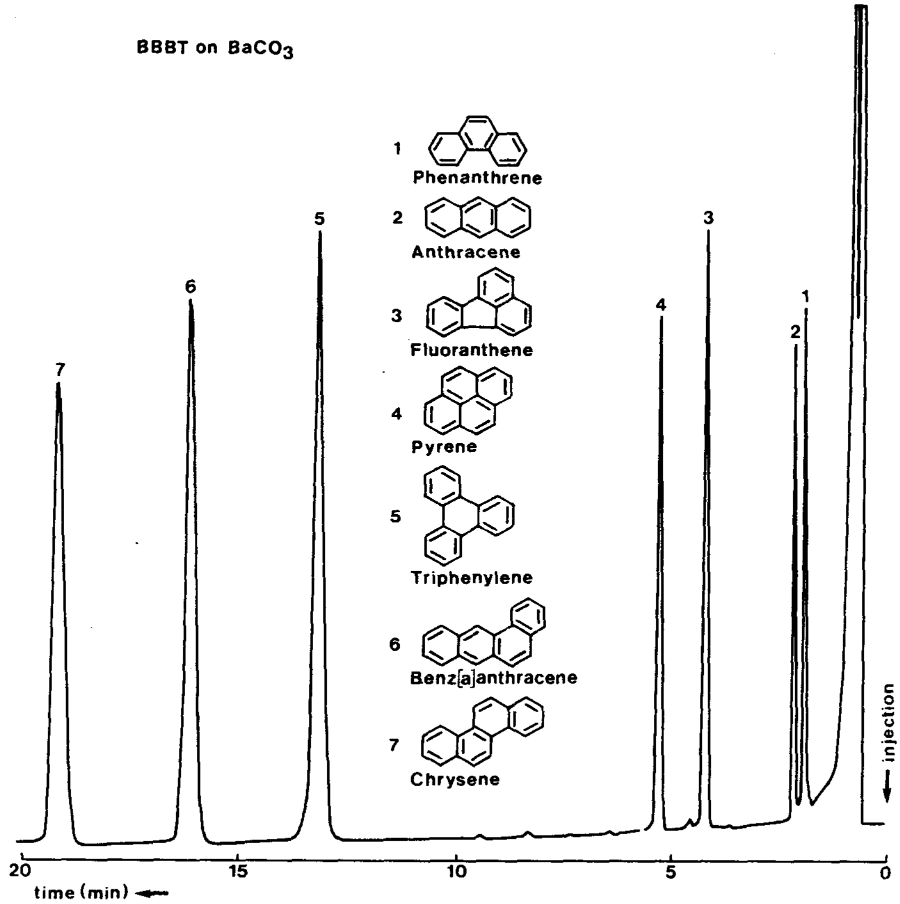


FIGURE 3 Glass capillary chromatogram of three- and four-ring PAH on BBBT.

effective plate number in Table VII increase as the temperature decreases in case of BPhBT. We found the same effect in previous work.[27]

With BHxBT and BBBT this tendency is not clear. So the α, Tz and n_{eff} values are not suitable for comparing liquid crystal columns because they depend largely on experimental conditions. However, the increase in α on cooling emphasizes the conclusion that optimum selectivity of a nematic liquid crystal is obtained at the lowest possible operating temperature: so in the vicinity of the transition temperature. The quality numbers of the BHxBT columns differ very strongly. It is surprising that in the isotropic region the numbers are larger than in the nematic region and it is difficult to interpret the preliminary results at this moment.

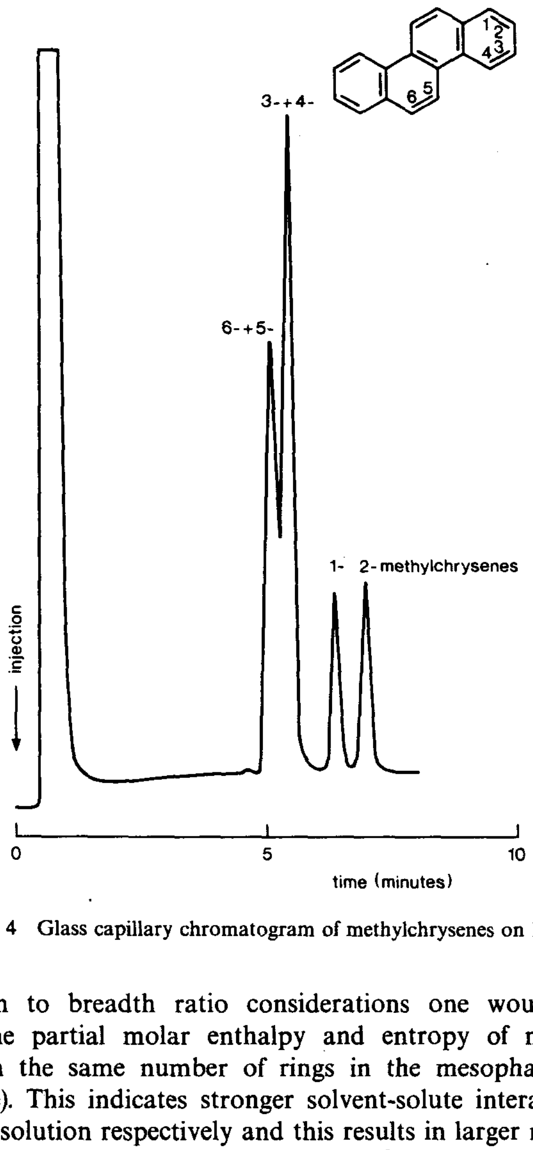


FIGURE 4 Glass capillary chromatogram of methylchrysenes on BPhBT.

From length to breadth ratio considerations one would intuitively expect that the partial molar enthalpy and entropy of more-rod like molecules with the same number of rings in the mesophase are larger (more negative). This indicates stronger solvent-solute interactions and a better ordered solution respectively and this results in larger retentions.

This effect has been found by Zielinsky *et al.*[32] in their thermodynamic study of divinylbenzenes separation on the liquid crystal 4,4′-dihexoxyazoxybenzene. They calculated the partial molar enthalpy and entropy of solution and found for the para isomers larger (more negative) values than for the meta isomers. In contrast with their findings we find the opposite effect (in case of BPhBT) and no correlation in the sense

TABLE V

Results of evaluation of three columns by the abt-concept.[a] The meaning of the symbols is explained in Table VI

Column Stationary phase	1 BBBT			2 BHxBT		3 BPhBT		
Temperature (°C)	258.2	238.2	209.4	290.0	260.0	396.8	290.0	280.0
$k'=0\rightarrow k'=$	37	70	112	17	19.2	27	37	51
a (s)	0.407	0.391	0.502	0.610	1.134	0.318	0.341	0.291
$\pm\sigma_a$ (%)	4.3	5.2	0.4	9.1	11.1	5.9	4.7	3.5
b_0 (s)	2.89	8.00	3.61	5.42	6.30	8.07	7.82	7.17
$\pm\sigma_{b_0}$	13.0	10.6	3.4	11.9	25.8	3.8	4.2	3.9
tm (s)	30.0	30.0	38.4	34.2	33.6	30.6	31.2	28.2
SN_{real}	31.4	14.2	32.3	20.1	14.2	14.9	15.5	15.5
SNt	5.7	2.6	4.6	3.2	2.3	2.7	2.7	3.0
n_{real}	30127	32644	32446	17430	4868	51345	46341	52074
h_{real} (mm)	0.663	0.612	0.616	0.986	3.53	0.389	0.430	0.384
Q_s	0.41	0.20	0.41	0.36	0.47	0.16	0.18	0.17
r^2	0.99	0.99	0.99	0.98	0.98	0.98	0.99	0.99
Compound nrs.[b]	1–7	1–7	1–7	1–4	1–4	4–7 10–12	4–7 10–12	4–7 10–12

[a] The parameters are calculated with the aid of a computer program developed by the Institute of Chromatography, Bad Dürkheim, Germany.

[b] See Figure 1.

mentioned above between the length to breadth ratio and the partial molar enthalpy and entropy of solution (Table VIII). The enthalpies are smaller (less negative) while the retentions are larger. For instance Benzo(a)pyrene has a higher length to breadth ratio, a lower (less negative) partial molar enthalpy and entropy, but a higher retention on BPhBT than Benzo(e)pyrene. The same appears with the four-ring PAH and the methylchrysenes. So our results do not support the postulate that the more rod-like isomer should be more soluble in a liquid crystal and we agree with Chow and Martire[33] that this postulate is misleading. Factors as size, shape and charge distribution and charge symmetry of the π-system of the molecules play a not unimportant role in the gas chromatographic behaviour of PAH on liquid crystals. For instance, the influence of the methyl group in PAH molecules on retention is not predictable on the basis of length to breadth ratio considerations as already has been pointed out. However, these considerations should be handled with care because one should keep in mind that the partial molar heats of solution are obtained from retention time measurements over a relatively large temperature interval of about 16.8 K in case of BPhBT. Blu *et al.*[34] showed that an accuracy in ΔH of better than 1% could be

Liquid phase	BHxBT					BBBT				
Temperature (°C)	296.8	290.0	280.0	270.0	260.0	258.2	238.2	228.5	218.9	209.4
k' max		17		19	21	27	70	94	102	112
Solute pair										
2/1		10.7		1.08	1.13	1.12	1.21	1.24	1.26	1.30
		—		—	—	0.9	0.4	1.9	4.1	3.7
3/2		2.46		2.51	2.44	2.34	2.40	2.46	2.51	2.58
		11.5		9.4	6.8	11.4	8.3	15.2	22.7	14.7
4/3		1.23		1.24	1.27	1.29	1.30	1.31	1.33	1.33
		2.7		2.0	1.6	4.1	3.1	5.2	7.1	7.1
Liquid phase	BPhBT									
k' max	28	37	51							
5/4	2.45	2.52	2.56			2.68	2.84	2.99	1.96	—
	4.7	6.3	7.9			21.8	20.6	26.5	10.4	—
6/5	1.17	1.19	1.23			1.23	1.29	1.32	1.57	—
	0.6	1.3	2.2			4.7	5.7	7.7	9.4	—
7/6	1.19	1.19	1.21			1.19	1.22	1.24	1.36	1.39
	0.9	1.6	2.4			4.5	4.9	9.4	10.2	10.6
7/5	1.39	1.42	1.49			1.46	1.58	1.63	2.14	
	2.6	3.8	5.6			10.2	11.7	21.0	17.1	
8/7	—	—	2.16							
	—	—	16.5							
9/8	—	—	1.10							
	—	—	1.71							
11/10	1.19	1.20	1.21							
	2.9	3.7	4.7							
12/11	1.11	1.12	1.15							
	1.6	2.2	3.4							
12/10	1.32	1.34	1.39							
	5.5	6.6	9.9							
13/12	—	—	2.35							
	—	—	28.5							
14/13	—	—	1.09							

TABLE VII

Effective plate number (n_{eff}) and capacity number on three liquid crystal stationary phases as function of temperature

Liquid phase	BHxBT					BBBT				
Temperature (°C)	296.8	290.0	280.0	270.0	260.0	258.2	238.2	228.5	218.8	209.4
Compound										
Phenanthrene		2260		2035	1271	2722	927	3218	8426	5999
		5.3		6.2	5.5	2.7	4.8	4.8	5.8	5.7
Anthracene		2949		3890	1394	2787	1363	4920	13438	8462
		5.7		6.6	6.2	3.1	5.0	6.0	7.3	9.6
Fluoranthene		6094		3014	2269	7502	4162	10328	18674	16819
		14.0		16.7	15.2	7.4	12.1	14.7	18.3	24.5
Pyrene		7887		6415	3191	10330	7035	12871	18027	19674
		17.2		20.7	19.3	9.5	15.7	19.3	24.3	32.5
Liquid phase	BPhBT									
Triphenylene	1961	3036	4480			15611	13580	18457	4832	
	5.9	7.7	9.7			25.5	44.6	57.7	47.6	

Benzo(a)anthracene	2389	4335	5990	19970	16911	26390	29936	27699
	6.9	9.1	11.9	31.2	57.5	75.9	74.9	103.5
Chrysene	3365	5203	7860	22912	21103	112856	29728	81891
	8.2	10.9	14.4	37.3	70.4	94.2	101.7	111.8
Benzo(b)fluoranthene	—	—	15603					
	—	—	29.7					
Benzo(k)fluoranthene	—	—	18959					
	—	—	32.8					
Benzo(e)perylene	10624	11691	17999					
	20.6	27.6	36.4					
Perylene	11893	12894	21735					
	24 5	32.9	44.0					
Benzo(a)perylene	13673	14707	22865					
	27.3	37.0	50.6					
Benzo(ghi)perylene	—	—	36232					
	—	—	113.0					
Dibenzo(a,h)anthracene	—	—	26555					
	—	—	123.6					
Indeno(1,2,2-cd)pyrene	—	—	27070					

TABLE VIII

Partial molar enthalpy of solution of PAH on BPhBT (Column 3, Table II)

Number of rings	Compound	$-\Delta H^{a}$ kJ.mol^{-1}	$-C^{b}$
3	Phenanthrene	29.75	6.62
3	Anthracene	29.45	6.46
4	Fluoranthene	38.85	7.63
4	Pyrene	38.30	7.25
4	Triphenylene	50.24	8.87
4	Benzo(a)anthracene	44.85	7.59
4	Chrysene	43.93	7.23
	6-methylchrysene	51.84	8.80
	5-methylchrysene	51.84	8.80
	3-methylchrysene	48.51	8.01
	4-methylchrysene	48.51	8.01
	1-methylchrysene	54.52	9.17
	2-methylchrysene	43.80	6.76
5	Benzo(e)pyrene	56.95	9.03
5	Perylene	58.74	9.23
5	Benzo(a)pyrene	52.14	7.75

[a] ΔH is calculated from the $\log_e$ ((tms − tm)/tm) vs $1/T$plot with coefficient of determination $r^2 \geqq 0.98$.

[b] C is a constant and a measure for the enthropy of equation $\log_e$ ((tms-tm)/tm) $= -\Delta H/RT + C$.

reached when ΔH is measured over an interval of temperature of one degree. They calculated the relative error on ΔH with the relationship

$$\frac{\theta(\Delta H)}{\Delta H} = \frac{\theta(\partial T)}{\partial T} + \frac{\theta(\partial \tau)}{\partial \tau}$$

where θ denotes absolute error. The error on the absolute temperature in our case is about 0.2 K and at a column temperature of 553 K the relative error is about 8.10^{-3}. If the relative error on the net retention of Benzo(a)pyrene at $T = 553$ K (1450 s ± 10 s) is about 7.10^{-3} then the absolute error on $\partial\tau$ will be $\theta(\partial\tau) = 14.10^{-3}$ (tms − tm). According to the relationship derived by Blu *et al.*[34]

$$\frac{\theta(\partial \tau)}{\partial \tau} = 14.10^{-3} \frac{RT^2}{\Delta H . \partial T}$$

and if $T = 553$ K, $\partial T = 16.8$ K, $\Delta H = 52.1 \times 10^3$ [J.mol^{-1}] we find a relative error on $\partial\tau$ of 4%. So the accuracy in ΔH is better than 5% and this justifies the assumption that there is no relationship between the partial molar enthalpy of solution and the length to breadth ratio.

From Table VIII it follows that as the entropy term C increases then the partial molar enthalpy of solution increases. So there is a more or less linear correlation for the PAH series. Similar linear correlations have been found for a series of homologues like *n*-1-chloroalkanes, *n*-alkanes and *n*-alkenes on a liquid crystal.[33]

CONCLUSIONS

Thus far one of the best columns suitable for the separation of PAH is the glass capillary column with BPhBT as stationary phase on $BaCO_3$ as substrate. However the columns have to be improved, because of the very low Q_s (the operational quality number) values (Table V).

The best way to express the quality of a liquid crystal glass capillary column and the quality of the separation system are the numbers n_{real} and its corresponding h_{real}, and SN_{real} and SNt respectively.

The separation number (Tz) as well as the effective plate number (n_{eff}) are poor indices to describe the quality of a glass capillary liquid crystal column.

There exists no relationship between the partial molar enthalpy of solution and the shape parameter (length to breadth ratio) when BPhBT is used as stationary phase. This enthalpy is measured within an accuracy of 5%, which is reasonable for thermodynamic measurements with gas-liquid chromatography over a large temperature interval (20°C).

In general the more rod-like the molecule the greater the retention in the nematic phase.[35] This statement does not hold for chrysene, 3- and 4-methylchrysene.

More accurate thermodynamic measurements are needed in order to understand the separation mechanism of PAH on liquid crystal on a molecular basis.

From the abt-concept and the more or less linear correlation between the partial molar enthalpy and the entropy it follows that the PAH behave like homologues.

Acknowledgements

The author is indebted to Mr. T. Kalidin for the preparation of the glass capillaries, Mr. G. Zondervan for the differential calorimetry measurements and to Miss G. de Roos for secretarial aid.

References

1. M. J. Suess, *The Sci. of the Tot. Environm.* **6**, 239 (1976).
2. D. Hoffman, W. E. Bondinell and E. L. Wyder, *Science* **183**, 215 (1974).

3. G. Grimmer and H. Böhnke, *Chromatographia* **9,** 30 (1976).
4. M. L. Lee, D. L. Vassilaros, C. M. White and M. Novotny, *Anal. Chem.* **51,** 768 (1979).
5. K. D. Bartle, M. L. Lee and S. A. Wise, *Chromatographia* **14,** 69 (1981).
6. G. Grimmer, K. W. Naujack and D. Schneider (1979), Changes in PAH-profiles in different areas of a city during the year. In: *Polynuclear Aromatic Hydrocarbons,* A. Bjørseth and A. J. Dennis, eds., pp. 107–125, Battelle Press, Columbus, Ohio.
7. U. Stenberg, T. Alsberg, L. Blomberg and T. Wannman (1979), Gas chromatographic separation of high-molecular polynuclear aromatic hydrocarbons in samples from different sources, using temperature-stable glass capillary columns. In: *Polynuclear Aromatic Hydrocarbons,* P. W. Jones and P. Leber, eds., pp. 313–326, Ann Arbor, Michigan.
8. G. M. Janini, G. M. Muschik and C. M. Hanlon, *Mol. Cryst. Liq. Cryst.* **53,** 15 (1979).
9. W. L. Zielinsky and G. M. Janini, *J. Chromatogr.* **186,** 237 (1979).
10. H. Kelker, *Z. Anal. Chem.* **198,** 254 (1963).
11. L. C. Chow and D. E. Martire, *Mol. Cryst. Liq. Cryst.* **14,** 293 (1971).
12. H. Kelker, *J. Chromatogr.* **112,** 165 (1975).
13. H. Kelker and R. Hatz (1980), *Handbook of Liquid Crystals,* Verlag Chemie, Weinheim.
14. G. M. Janini, K. Johnston and W. L. Zielinsky, *Anal. Chem.* **47,** 670 (1975).
15. G. M. Janini, G. M. Muschik and W. L. Zielinsky, *Anal. Chem.* **48,** 809 (1976).
16. G. M. Janini, G. M. Muschik, J. A. Schroer and W. L. Zielinsky, *Anal. Chem.* **48,** 1879 (1976).
17. G. M. Janini, R. I. Sato and G. M. Muschik, *Anal. Chem.* **52,** 2417 (1980).
18. W. L. Zielinsky, R. A. Scanlan and M. M. Miller, *J. Chromatogr.* **87,** 209 (1981).
19. G. M. Muschik, T. Kelly and W. B. Manning, *J. Chromatogr.* **202,** 75 (1980).
20. G. M. Janini, W. B. Manning, W. L. Zielinsky and G. M. Muschik, *J. Chromatogr.* **193,** 444 (1980).
21. H. Lamparczyk, A. Radecki and J. Falandysz, *J. High Resolut. Chromatogr. Chromatogr. Commun.* **8,** 301 (1980).
22. M. Pailer and V. Hložek, *J. Chromatogr.* **128,** 163 (1976).
23. R. J. Laub, W. L. Roberts and C. A. S. Smith, *J. High. Resolut. Chromatogr. Chromatogr. Commun.* **3,** 355 (1980).
24. R. J. Laub and W. L. Roberts (1979), Use of mixed phases for enhanced gas-chromatographic separation of polycyclic aromatic hydrocarbons: preliminary studies with liquid crystals. In: *Polynuclear Aromatic Hydrocarbons,* A. Bjørseth and A. J. Dennis, eds., pp. 25–58, Battelle Press, Columbus, Ohio.
25. G. M. Muschik and M. H. Miller (1980), "Abstracts of Papers", 179th Nat. Meet. Amer. Chem. Soc., Houston, Washington D.C., Anal. 73.
26. F. Janssen, *Anal. Chem.* **51,** 2163 (1979).
27. F. Janssen and T. Kalidin, *J. Chromatogr.* **235,** 323 (1982).
28. F. Janssen, *Chromatographia* **15,** 33 (1982).
29. A. Radecki, H. Lamparczyk and R. Kaliszan, *Chromatographia* **12,** 595 (1979).
30. R. E. Kaiser and E. Oelrich (1981), *Optimization in HPLC,* Hüthig Verlag GmbH, Heidelberg, Germany.
31. R. E. Kaiser, *Chromatographia* **9,** 337 (1976).
32. W. L. Zielinsky, D. H. Freeman, D. E. Martire and L. C. Chow, *Anal. Chem.* **42,** 176 (1970).
33. L. C. Chow and D. E. Martire, *J. Phys. Chem.* **75,** 2005 (1971).
34. G. Blu, L. Jacob and G. Guiochon, *J. Chromatogr.* **50,** 1 (1970).
35. A. Radecki, H. Lamparczyk and R. Kaliszan, *Chromatographia* **12,** 595 (1979).
36. S. A. Wise, W. J. Bonnett, F. R. Guenther and W. E. May, *J. Chromatogr. Sci.* **19,** 457 (1981).