

Short Communication

Assessment of the polarity of three liquid crystals used as gas chromatographic stationary phases

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ABSTRACT

Attempts to evaluate the polarity of three liquid crystals used in packed gas chromatographic columns suggest that more than one method is required at different temperatures. At 120°C a triangular proportional plot of retention indices using three McReynolds' solute probes indicate azoxydiphenetole (ADP) and bis(methoxy-benzylideneanilchloroaniline) [(MBCA)₂] are reasonably strong in polarity. Bis(methoxybenzylideneanilbitoluidine) [(MBT)₂] is moderately polar, compared to normal-phase columns. At 160°C, however, using the sum of retention indices of three C₁₀ volatile oil constituents, ADP and (MBCA)₂ rate as only moderately polar, with (MBT)₂ now exhibiting low polarity. The polarity sequence of the three liquid crystals (unmelted, melted and supercooled) is confirmed by the second method. Their polarity rating is method-sensitive, although they change in polarity more than normal chromatographic phases with temperature alterations. The selection of a liquid crystal for particular separations is discussed.

INTRODUCTION

This author has previously studied three liquid crystals as gas chromatographic stationary phases in packed columns [1,2] for volatile oil constituents. Following this work, the question of the polarity of these phases arose. Isenberg *et al.* [3] found that some diester aromatic liquid crystals "correspond to silicone phases of low polarity" using Rohrschneider solute probes at 100°C, and our observations on bis(methoxybenzylideneanilbitoluidine) [(MBT)₂] agreed with this [4] using a comparative retention index (I_R) method we devised in 1981 [5] with linalol, estragole and carvone as "LEC" solute probes at 160°C. Betts has also used three of

McReynolds' [6] probes, *n*-butanol, pyridine and 2-octyne in connection with a triangular proportional I_R plot method of characterization [7] of a range of stationary phases. Butanol always eluted ahead of pyridine, but octyne appeared first for the group of "highly polar" phases, last from the "non-polar" phases, and between butanol and pyridine with the "intermediate polarity" phases at 120°C. This lower temperature, below all the liquid crystal melting points, allows them to be studied in the unmelted and the melted, supercooled condition. Having found that gas chromatography was readily possible with some of these supercooled liquid crystals, and having obtained interesting results with one of them at 120°C [2], it seemed appropriate to use the octyne procedure at this temperature to evaluate their polarity; supported by the higher temperature method [5] involving C₁₀ volatile oil constituents of relevance to our studies rather than the smaller mol-

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ecules (C₄–C₈) used at the lower temperature. However, only one of the liquid crystals can be evaluated at 160°C in the unmelted condition. Differing results prompted the selection of a modified set of three solute probes to allow evaluation of the polarity of these liquid crystal packed columns over a range of temperatures, with cineole instead of carvone in the LEC set.

EXPERIMENTAL

Instrumentation

A Pye-Unicam GCD gas chromatograph was used, fitted with a flame ionisation detector. This heated the columns rapidly, but on lowering the temperature setting, leaving the door closed, the oven cooled at about 4°C min⁻¹ measured with a Technoterm probe. This allowed for slow supercooling of the melted column phases. Hewlett-

Packard 3380A and 3390A recorder/integrators were used.

Columns

These were detailed in ref. 1 and contained about 3% (w/w) liquid crystal stationary phase. They were azoxy-phenetole (ADP), bis(methoxybenzylideneanilchloroaniline) [(MBCA)₂] and (MBT)₂. Normal-phase columns used are detailed in refs. 5 and 7.

Solutes

2-Octyne was obtained from T.C.I. (Tokyo). Some *n*-alkanes came from Sigma. (–)-Carvone was from Koch-Light, and sources of other solutes are as given previously [1,4] other than standard laboratory reagents.

Method

Injections were made from a microsyringe which

TABLE I

I_R , x AND McREYNOLDS VALUES FOR PACKED COLUMNS OF LIQUID CRYSTAL AND SOME CONVENTIONAL STATIONARY PHASES AT 120°C

$x = (I_R \text{ of solute}) / \sum(I_R \text{ three solutes})$. $McR = I_R \text{ of solute on phase minus its } I_R \text{ on squalane}$. Data in italics from ref. 7. Phases below the break show solute sequence of butanol–octyne–pyridine (last).

Stationary phase	Solute									$\sum(I_R)_3$	$\sum(McR)_3$
	2-Octyne			<i>n</i> -Butanol			Pyridine				
	I_R	McR	x	I_R	McR	x	I_R	McR	x		
PEG 20M polyglycol	1041	200		1104	514		1180	481		3325	1195
ADP UNmelted	854	13	0.281 ^a	1090	500	0.358 ^b	1098	399	0.361	3042	912
(MBCA) ₂ new UNmelted	873	32	0.291	1010	420	0.337	1117	418	0.372	3000	870
SP-2330 PSX ^c CN-propyl			0.292 ^d			0.336			0.372 ^e		
ADP melted ^f	917	76	0.307	1009	419	0.338	1059	360	0.355	2985	855
PEG 1000 polyglycol			0.306			0.337 ^e			0.357		
(MBCA) ₂ old UN- or melt	909	68	0.309	922	332	0.314	1109	410	0.377 ^b	2940	810
OV-225 PSX ^c CN-pr, Ph, Me	980	139	0.330	939	349	0.317	1046	347	0.353	2965	835
(MBT) ₂ melted ^f	890	49	0.331	858	268	0.319	940	241	0.350	2688	558
OV-210 PSX ^c F ₃ -pr, Me	891	50	0.332	815	225	0.304	977	278	0.364	2683	553
(MBT) ₂ UNmelted	892	51	0.340	813	223	0.309	922	223	0.351	2627	497

^a Lower x value than observed previously [7]. See ^d.

^b Higher x value than observed previously. See ^e.

^c Polysiloxane (PSX). Side chains Methyl, Phenyl, F₃-pr = trifluoropropyl.

^d Lowest x value observed previously.

^e Highest x value observed previously.

^f Slowly cooled from above liquid crystal melting point at about 4°C min⁻¹. [Above 138°C for ADP, above 154°C for (MBCA)₂, above 181°C for (MBT)₂].

TABLE II
 I_R VALUES FOR PACKED COLUMNS OF LIQUID CRYSTAL AND SOME CONVENTIONAL STATIONARY PHASES

P rating = $\sum(I_R)_3$ for phase minus $\sum(I_R)_3$ for "base" SP-2250, all divided by three [5]. Data in italics from conventional phases.

Cineole	Stationary phase			120°C			
	Linalol	Estragole	$\sum(I_R)_3$ P rating	Cineole	Linalol	Estragole	$\sum(I_R)_3$
1216	1363	1531	4110 + 137	<i>OV-225 PSX CN-pr, Ph, Me</i>	1082	1307	3796
1125	1284	1453	+ 55	← melted ADP	1076	1363	3682
1125	1321	1391	+ 46	← melted (MBCA) ₂	1106	1309	3741
1139	1198 ^c	1361 ^c	3698	<i>SP-2250 PSX^d Ph, Me (BASE)</i>			
[1054	1230	1423	3707	← melted (MBT) ₂ at 190°C]			
960	1183	1352	3495	← melted ^a (MBT) ₂	1016	1208	3554
1010	1177	1246	3433	← UNmelted (MBT) ₂	1004	1191	3407
1048	1100 ^c	1197 ^c	3345	<i>SP-2100 PSX Me</i>			

^a Slowly cooled from above liquid crystal melting point at about 4°C min⁻¹.

^b Estragole precedes linalol (only case observed).

^c Values a little different to those recorded over ten years ago [5] reflecting use of columns.

^d PSX see Table I footnote c.

had been filled, then “emptied”, apart from larger alkanes which required about 0.1 μ l. Retention indices were obtained by a graphic method, plotting retention times of *n*-alkanes on a logarithmic scale against their carbon numbers, and then entering retention times of the probe solutes.

RESULTS AND DISCUSSION

Average results at 120°C for the octyne method are presented in Table I in sequence of decreasing sum of their I_R for the three solute probes. This indicates decreasing polarity, as it corresponds to increasing x values (proportion of I_R sum) for the lowest polarity probe octyne. (MBCA)₂ and ADP exhibit high polarity, shown by their elution sequence of solutes: octyne–butanol–pyridine (last). Their I_R sums are below that of polyethylene glycol 20M, however.

A new, never-melted column of (MBCA)₂ shows x values (not the actual I_R) very close to those of the highly polar cyanopropyl polysiloxane SP-2330 (see Table I and Fig. 1). After melting, a well-used mature column of (MBCA)₂ gives no change between melted and unmelted states (unlike the other two liquid crystals here) and has lower polarity than initially, particularly due to lower retention of butanol and stronger affinity for octyne. But it retains the same probe sequence indicating it is in the “highly polar” group of phases. It now exhibits a higher x value for pyridine than any seen previously [7], although this has increased only slightly (Table I, Fig. 1).

The other two mature liquid crystal columns always show different behaviour on changing from unmelted to melted (supercooled) condition. Previous study of volatile oil constituents with short retention times [2] also revealed this changing behaviour, again differing from (MBCA)₂. ADP decreases in polarity on melting, from having considerably the highest x value ever observed by this author for butanol (and the lowest for octyne) on any phase, to a set of x values very close to those of polyethylene glycol 1000. It retains the “highly polar” probe sequence.

(MBT)₂ in contrast increases in polarity on melting and exhibits the different probe sequence of butanol–octyne–pyridine, indicating only moderate polarity. Unmelted, it has I_R for octyne and butanol

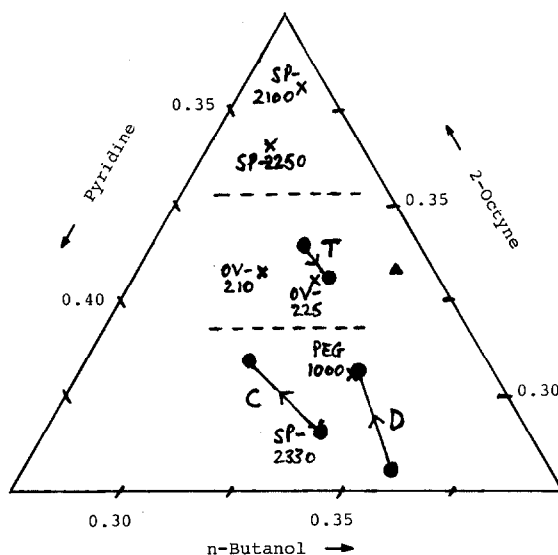


Fig. 1. Plot of relative I_R values of gas chromatographic stationary phases using solute probes of 2-octyne (right), pyridine (left) and *n*-butanol (base). \blacktriangle = Centre of full triangular plot; \bullet = experimental values for liquid crystals (MBCA)₂ (C), ADP (D), and (MBT)₂ (T); \times = values from ref. 7 for conventional phases explained in Tables I and II. Arrowed lines show changes from unmelted to melted liquid crystal condition. Dashed lines separate the strongly polar phases at the base of the triangle from the moderately polar phases across the middle and the low polarity phases at the top.

similar to the trifluoropropyl methyl polysiloxane OV-210 (see Table I). After melting, (MBT)₂ shows x values very close to the quarter-cyanopropyl polysiloxane OV-225 (Fig. 1), and slightly increased polarity, although x values for pyridine hardly alter. McReynolds' values are all low for octyne, but otherwise confirm the reasonably high polarities of the three liquid crystals (Table I).

As the study at 120°C indicated surprisingly high polarity, there was a need to assess this at another temperature. Davies [8] remarks that “temperature has ... quite marked effects on the (retention) indices on (polyethylene glycol) 20M” and records an increase of about 20 units over 20°C rise for caryophyllene on a methyl silicone. The probe solute carvone, previously used at 160°C [5] gave unsatisfactory broad peaks on two of these liquid crystal phases, as did some of the *n*-alcohols originally used as the basis for one set of I_R . Cineole, a low polarity terpenoid ether, replaced carvone and the three I_R were only determined against the traditional *n*-alkanes.

Table II gives the results for these revised LEC solute probes at 160°C in decreasing polarity, as indicated by their I_R sum; and at 120°C for comparison. They emerge in the sequence cineole-linalol-estragole apart from unmelted ADP, where linalol is last. From the sum of their three solute I_R (MBCA)₂ and ADP are distinctly more polar than (MBT)₂, confirming the sequence in Table I. They indicate an overall lower polarity than before, however, as the pair are only a little more polar than a low-polarity phenyl, methyl polysiloxane SP-2250 at 160°C, and (MBT)₂ a little more than a non-polar fully methyl polysiloxane SP-2100, which agrees with our earlier report [4]. At 160°C, melted ADP shows higher I_R for cineole and estragole than at 120°C in either its supercooled, or its unmelted condition: the latter is distinctively lower for estragole. Melted (MBCA)₂ at 160°C also shows the higher I_R compared to lower temperature values. There is thus no evidence that the polarity of these two phases is lower at 160°C than at 120°C. However, the LEC values at 160°C, and the derived P values in Table II, indicate considerably lower polarity than by the octyne method.

At 160°C, melted, supercooled (MBT)₂ has I_R lower than at 120°C for cineole and linalol and overall is slightly less polar. At both these temperatures, (MBT)₂ can be studied in the unmelted condition. It then has the lowest polarity observed here, especially at 120°C. Properly melted, at 190°C, it shows considerably higher polarity like the other two liquid crystals, with I_R close to a phenyl, methyl polysiloxane. Whilst there are some changes in I_R for LEC between 120° and 160°C for all three liquid crystals they do not account for the octyne procedure giving high polarity ratings at 120°C. Yet the results here are compared in each procedure with those of authentic normal phases of various polarities. The discrepancy can be illustrated in relation to the moderately polar cyanopropyl(25), phenyl (25), methyl(50)-polysiloxane OV-225. The octyne procedure sums (of I_R or McReynolds values) in Table I indicate the overall similar polarity of ADP and (MBCA)₂ to OV-225. With the LEC method at 160°C, the sums indicate these two liquid crystals to be considerably less polar than OV-225 (Table II). This is despite the three solute probes being, in both cases, an aromatic substance, an aliphatic alcohol, and a low polarity material. One method of polarity

rating alone is apparently insufficient for liquid crystal phase assessment, probably because they change with alteration of temperature more than normal phases.

As it is the least polar liquid crystal here, (MBT)₂ should be the choice for studies of hydrocarbons, and it was previously found by Betts [2] to provide on melting a distinctive relative retention change for identifying terpinolene from other cyclic monoterpenes. However, it gave less resolution of a group of five such compounds when unmelted than the other two liquid crystals. None of these three liquid crystals gave the “non-polar” solute sequence butanol–pyridine–octyne, which would be optimum for such hydrocarbon studies.

From its results with estragole melted ADP should be the choice for studies of aromatics. However, previous studies made [1] show that relative to estragole the similarly linear aromatic safrole has a nearly constant retention time of about 1.6 on all three liquid crystals at various temperatures, with ADP showing the slightly highest value. (MBCA)₂ retains pyridine most strongly in the proportional plot (Fig. 1) and gives the best resolution of the “terpene-shaped” aromatic cuminal from safrole, but the worst separation of cuminal from the linear aromatic anethole. The “terpene-shaped” phenol thymol cannot be handled on ADP and is best resolved by (MBT)₂. Thus predictions of the appropriate phase for an analysis are not successful from I_R considerations.

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