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Short communication

Plots of relative retention against solute boiling point indicate extra solute interactions with a liquid crystal polysiloxane stationary phase

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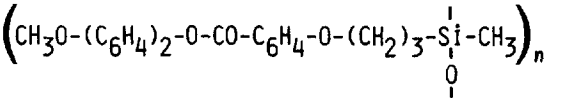
Abstract

Using a commercial liquid crystal polysiloxane phase MPMS capillary, relative retention times to *n*-tetradecane were plotted against literature boiling points (°C, 760 nm) for 26 solutes found in volatile oils. Values for five low polarity solutes were used to determine expressions for lines of best fit at 160°C (above MPMS melting point) and 130°C (below it). These expressions predicted values for some acyclic substances. Most solutes gave higher relative retentions at the higher temperature, which is different to conventional and cyclodextrin phases, so confirming a change of MPMS state. However, differences between observed and calculated (using the above expressions) values were nearly the same at both temperatures for twenty solutes, suggesting that MPMS does not always behave as an unmelted phase below its melting point. The remaining two aromatic and three acyclic monoterpenoid solutes showed more retention at the lower temperature, implying some rejection by the melted liquid crystal. Three other lines of best fit were considered for some aromatic substances and for some monoterpenoids.

Keywords: Liquid crystals; Relative retention; Boiling point; Stationary phases, GC; Mesogenic polymeric methyl siloxane

1. Introduction

This author has used the linear relationship between some low-polarity solute boiling points and relative retention times to study some modified cyclodextrin gas chromatographic phases [1]. Extra retention was noted for some solutes, which could be due to special interactions with the phases. It was now of interest to see if special responses could be observed by this method for a mesogenic liquid crystal phase, where change from unmelted solid to liquid crystalline state should be distinctive. Mesogenic polymeric methyl siloxane (MPMS) has been commercially available in capillaries, and was studied by this author, using some volatile oil constituents [2–4]. It melts at about 145°C, and its chemical composition can be represented by



MPMS has been used, for example, to separate polycyclic aromatics [5]. A second review of the use of liquid crystal phases for gas chromatography was carried out by Witkiewicz in 1989 [6].

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2. Experimental

2.1. Apparatus

A Hewlett-Packard Model 5890II gas chromatograph was used, fitted with a flame ionisation detector which was maintained at 250°C. The injection port was held at 215°C. Helium was used as the mobile phase solvent, at a capillary exit flow-rate of 0.6–0.8 ml min^{-1}, and as the make-up gas for the detector. The chromatograms were recorded on a Hewlett-Packard 3396II integrator.

A Heliflex MPMS capillary was obtained through Alltech (Homebush, N.S.W., Australia). Its dimensions are 25 m×0.25 mm I.D. It was heated and cooled at less than 5°C min^{-1} to avoid damaging the phase.

2.2. Methods

Twenty six diverse substances containing ten carbon atoms that occur in various volatile oils were studied. These substances included twenty monoterpene hydrocarbons and oxygen-containing monoterpenoids which were bicyclic, monocyclic or acyclic (see Table 1). Six aromatic constituents of

Table 1
Observed relative retention times (*n*-tetradecane = 1.00) on MPMS phase at 130 and 160°C with differences from values calculated by solute boiling point using Eqs. (1,2), respectively. Racemates used unless otherwise shown

Solute and type[a]		Boiling point[b] (°C, 760 mm.)	t_{Rrel} (130°)	Difference X [from Eq. (1)]	t_{Rrel} (160°C)	Difference Y [from Eq. (2)]	Extra retention [at 130° (X−Y)]
MYRCENE[c]	NH	167	O.17	−0.01	0.24	−0.01	0.0
3-Carene	BH	170.5	0.23	0.02	0.33	0.04	−0.02
α-TERPINENE	MH	174.2	0.25	0.01	0.34	0.01	0.0
CINEOLE	B	176.4	0.26	0.0	0.34	−0.02	0.02
LIMONENE	MH	177.7	0.28	0.0	0.37	0.0	0.0
p-Cymene	AH	177.1	0.31	0.04	0.44	0.07	−0.03
γ-TERPINENE	MH	183	0.32	−0.01	0.44	0.0	−0.01
(+)-Linalol	N	199	0.47	0.0	0.58	−0.05	0.05
Citronellal	N	207.8	0.65	0.09	0.78	0.04	0.05
Citronellol	N	244.5	(see below)		1.19	0.01	
(+)-Fenchone	B	193.5	0.56	0.14	0.72	0.15	−0.01
Thujone[c]	B	201	0.65	0.16	0.88	0.22	−0.06
Camphor	B	204	0.88	0.36	1.11	0.42	−0.06
Borneol	B	212	0.92	0.32	1.11	0.32	0.0
(−)-Menthone	M	207	1.02	0.47	1.21	0.48	−0.01
(−)-Menthol	M	216.4	1.05	0.41	1.21	0.37	0.04
4-Terpineol	M	209	1.05	0.48	1.21	0.46	0.02
α-Terpineol	M	220	1.29	0.62	1.42	0.53	0.09
Estragole	A	215	1.50	0.88	1.66	0.83	0.05
(−)-Carvone	M	231	2.56	1.79	2.79	1.77	0.02
Cuminal	A	235.5	2.64	1.82	2.85	1.78	0.04
Safrole	A	233	2.68	1.89	2.89	1.85	0.04
Citronellol	N	244.5	1.09	0.19	1.19	0.01	0.18
Geraniol	N	230	1.47	0.71	1.49	0.48	0.23
Citral[c]	N	229	2.03	1.28	2.13	1.14	0.14
Thymol[d]	A	233.5	3.62	2.82	3.48	2.43	0.39
E-Anethole[d]	A	234.5	4.19	3.38	4.17	3.11	0.27

[a]Solute chemical types: A = aromatic, B = bicyclic, H = hydrocarbon, M = monocyclic, N = acyclic.
[b]Taken from Handbook of Chemistry and Physics, Chemical Rubber Co., Merck Index, Merck and Co., and Encyclopaedia of the Terpenoids by J.S. Glasby, J. Wiley and Sons, 1982.
[c]Main peak used of impure sample.
[d]Solutes not plotted in Fig. 1.

oils were also used, all of which had three-carbon side chains. Some of these solutes showed minor impurities (see Table 1), but the main peak was employed, injecting trace residues from an "emptied" microsyringe. Holdup times, obtained by extrapolating to methane the retention times for *n*-heptane and *n*-hexane, on semi-logarithmic graph paper, were deducted from the observed retention times, and showed a slight increase at higher temperature. Relative retention times were used, based on *n*-tetradecane, at oven temperatures of 160 and 130°C; being about 15°C above and below the melting point of MPMS, respectively. For *n*-dodecane the relative retention times were 0.41 and 0.36, respectively.

Lines of best fit for groups of results were determined with a Novus 6030 Statistician calculator.

3. Results and discussion

Average relative retention times are given in Table 1. Most are presented in Fig. 1, where solutes can be seen to give a small increase in value as the MPMS phase changes from below its melting point (130°C, marked X) to melted liquid crystal (160°C, marked ⊙). There is hardly any change by geraniol and anethole (near the bottom of Table 1), and thymol shows a decrease. This last case is like conventional phases, where most oxygen-containing solutes show a decrease in their relative retention times as the temperature rises [7]. This also applies to modified cyclodextrin phases [8,9], so the usual MPMS response is different, and confirms a change in its physical state between 130 and 160°C. It is interesting that this liquid crystal phase operates well below its melting point, possibly by adsorption. We have

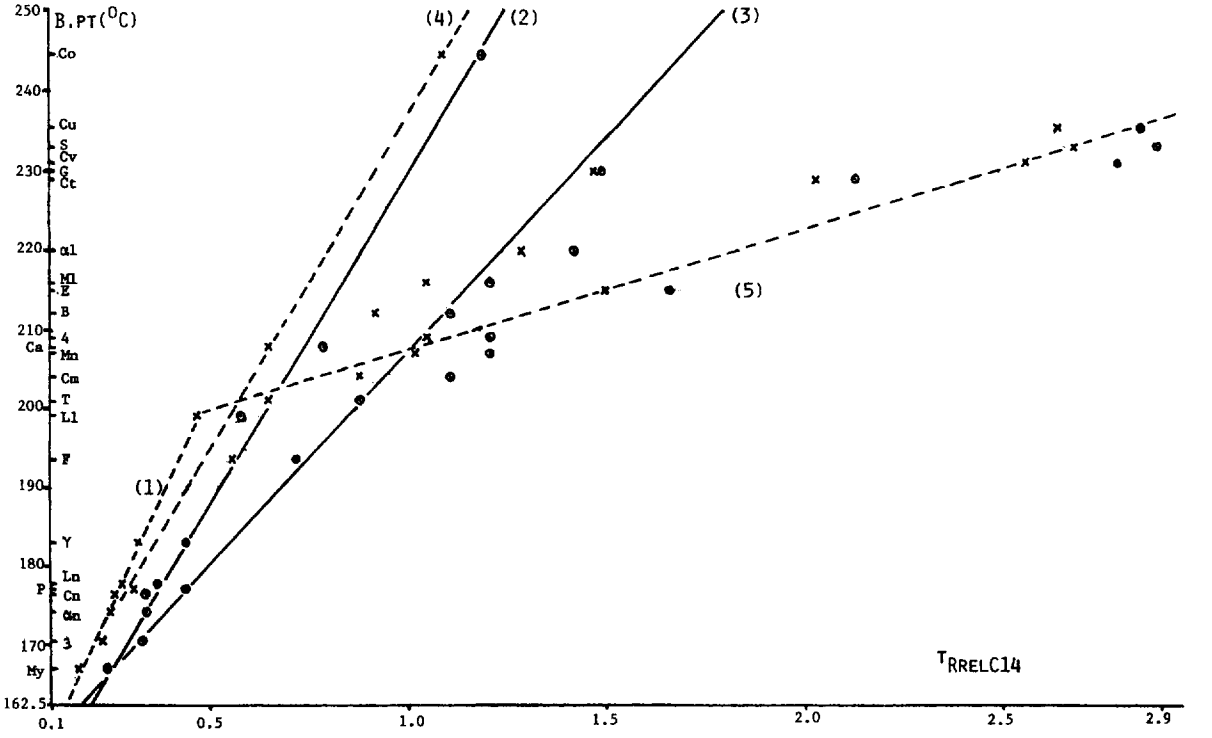

Fig. 1. Plots of solute boiling point (°C, 760 mm) against relative retention time (*n*-tetradecane = 1.00) on MPMS phase at 130 (X) and 160°C (⊙) with lines of best fit for some solutes (dashed for 130°C and continuous for 160°C). Lines (1) and (2) are derived from low polarity solutes; lines (3) and (4) from bicyclic and acyclic solutes, respectively, and line (5) involves aromatic solutes (see text). Solutes are abbreviated on the boiling point axis: αl, α-terpineol; αn, α-terpinene; γ, γ-terpinene; B, borneol; Ca, citronellal; Cm, camphor; Cn, cineole; Co, citronellol; Ct, citral; Cu, cuminal; Cv, carvone; E, estragole; F, fenchone; G, geraniol; Ll, linalol; Ln, limonene; Ml, menthol; Mn, menthone; My, myrcene; P, *p*-cymene; S, safrole; T, thujone; 3, 3-carene; 4, 4-terpineol.

observed the chromatographic ability of such phases to operate below their melting points previously [10].

By inspection of Fig. 1, as was seen for modified cyclodextrin phases [1], five low polarity solutes (named in capitals in Table 1) can be used to calculate lines of best fit at 130 and 160°C. These expressions, with correlation coefficients of at least 0.98, are

$$t_{R_{rel}C_{14}}(130°C) = 0.00932t - 1.38 \quad (1)$$

$$t_{R_{rel}C_{14}}(160°C) = 0.01207t - 1.77 \quad (2)$$

where t is the boiling point of the solute (°C, 760 mm). Differences between the observed and calculated relative retention times, using the above expressions, are given in Table 1. For the five solutes used to derive Eqs. (1,2), these differences range from 0.01 to −0.02. Eq. (1) also very accurately predicts the relative retention of linalol at 130°C, but not of any other oxygen-containing solute here. Eq. (2) also applies to some other acyclic solutes at 160°C. It is very accurate for citronellol, and quite close for citronellal (+0.04) and linalol (−0.05). With the data used to derive Eqs. (1,2), various computer programmes may produce slightly different equations which all successfully predict retention times.

Using Eqs. (1,2), differences between observed and calculated relative retention times were determined for all 26 solutes studied, and are given in Table 1. A group of nine solutes, at the top, show small differences of less than ±0.1 at both temperatures. This group includes the low polarity substances of diverse structure, with four acyclic compounds, including citronellol at 160°C. Two groups of solutes showed low to moderate increases in retention over that calculated for both temperatures. Four bicyclic substances showed a rise of 0.14–0.42, whilst four monocyclics increased by 0.37–0.62. These two ranges overlap, but provide some indication of solute structure. Interestingly, the increased retention times at the two temperatures for each solute are about the same, so there is little (<±0.1) extra retention at either temperature (see right hand column of Table 1). MPMS could be behaving as a melted phase for these solutes at 130°C, even though this is below its melting point. We have previously suggested [10] for another liquid crystal phase that this could be due to transient eutectic mixtures being formed with passing solute bands in the capillary. In support of this "catalytic" concept, larger injections of solutes were found to cause shifts in relative retention times. However, despite the problems of obtaining consistent results from MPMS at temperatures above 160°C or below 130°C, such relative retention times seem slightly changed, suggesting that the usual solute–phase weak attractions could be the reason for extra retention at lower temperatures.

The same lack of *extra* retention at either temperature is seen in Table 1 (near the bottom) for three aromatics, plus another monocyclic solute with high (>0.8) increased retentions at both temperatures. However, the remaining solutes, two aromatics and three acyclic monoterpenoids, exhibit distinctively greater relative retention times at 130°C than at 160°C, in the range of 0.14–0.39 extra (see right hand column of Table 1). Thus the aromatic solutes cuminal, safrole, thymol and anethole resolve into different groups, although they have very similar boiling points. The calculated differences from observed values which contribute to this include some very large differences (3.38 for anethole at 130°C). These extra increases in relative retention at 130°C imply some rejection of these solute molecules by MPMS at 160°C after melting to a liquid crystal. This is unexpected for anethole and thymol on a poly-aromatic phase. A plot (shown in Fig. 2) of these extra retentions at 130°C compared to 160°C, against solute boiling points, emphasises that only six of the 26 substances studied exhibited an increased retention time of more than 0.06. If this is taken as virtually no change, the monocyclic α-terpineol joins the group of solutes exhibiting some rejection by melted MPMS. The remaining thirteen oxygen-containing solutes give perfect correlation between their relative retentions at 130 and 160°C, and so confirm the concept of MPMS behaving in a melted fashion below its melting point.

From inspection of Fig. 1, it is interesting that Eq. (2), which was determined from values at 160°C, accurately predicts the relative retentions at 130°C for the bicyclic solutes fenchone (difference 0.0) and thujone (+0.01), but not for borneol (−0.13). Borneol and three other bicyclics at 160°C do give another linear plot with the high correlation coefficient of 0.998

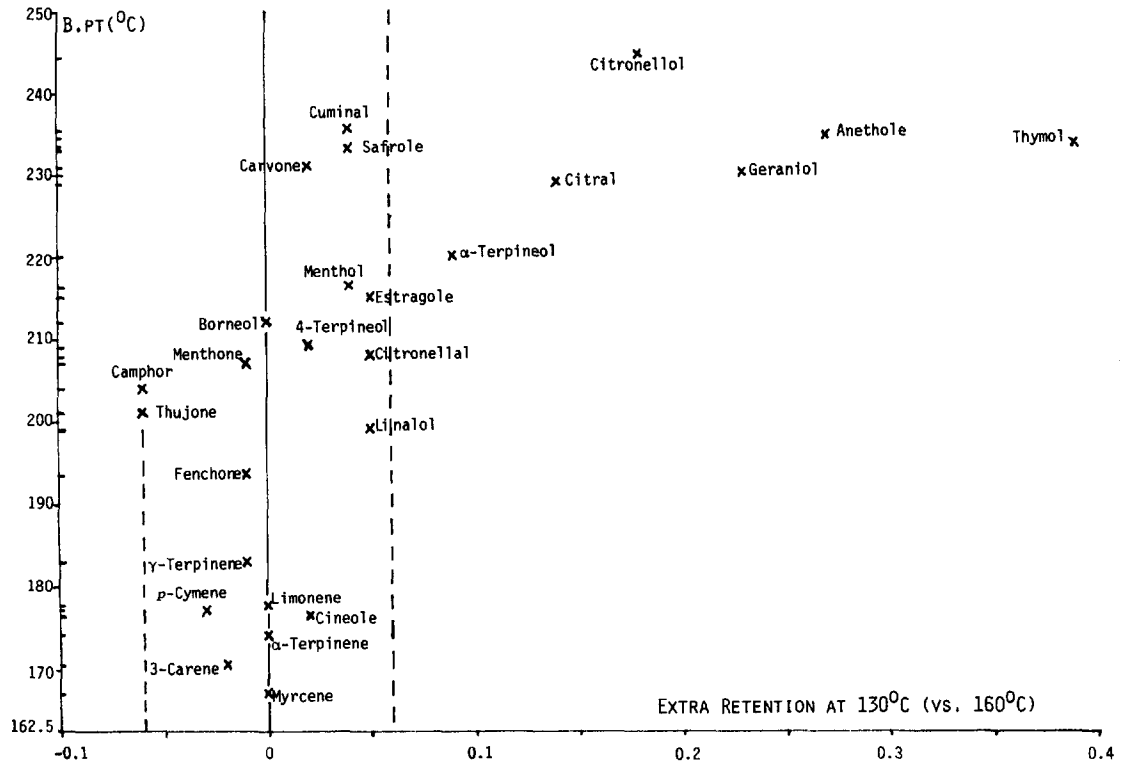

Fig. 2. Plots for all 26 named solutes, of extra retention seen on MPMS phase at 130°C, after deducting that observed at 160°C, against their boiling points (°C, 760 mm). Dashed lines enclose points taken to represent "no change" (±0.06).

$$t_{R_{rel}C_{14}}(160°C) = 0.01865t - 2.86 \quad (3)$$

Differences, for the solutes involved, from this expression are 3-carene (−0.01), fenchone (+0.03), thujone (+0.01) and borneol (−0.02). Eq. (3) also predicts observed relative retentions at 160°C for the diverse, non-bicyclic substances *p*-cymene (0.0), menthol (−0.03) and geraniol (−0.06), which were selected by review of Fig. 1.

As in the case of Eq. (2), Eq. (3) is also capable of predicting some lower temperature results at 130°C. These are for menthone (−0.02), 4-terpineol (−0.01) and α-terpineol (−0.05). If these predictions, using "wrong" temperature data, are more than coincidence for some cyclic solutes, they support the concept of MPMS being able to behave as though it were melted at 130°C, with some passing substances.

Having considered two equations at 160°C, another one appears relevant at 130°C, to predict for three acyclic solutes. This has the perfect correlation coefficient of 0.999 and is

$$t_{R_{rel}C_{14}}(130°C) = 0.01187t - 1.81 \quad (4)$$

This very accurately predicts relative retentions for citronellol, citronellal and myrcene, suggesting that their flexible linear molecules can fit the surface of unmelted MPMS to give slight extra retention over that provided using Eq. (1). However, *p*-cymene also fits Eq. (4) with a difference of −0.01.

In Fig. 1, there remain some unaccounted-for solutes on the right hand side, including aromatic substances. Whilst an exponential plot might look acceptable for these solutes, linear plots are to be expected according to Saura-Calixto et al. [11]. Possible linear relationships can be seen from Fig. 1, but they are likely to be fortuitous, and not meaningful. Four non-aromatic substances, together with two

aromatics with allyl side chains, give a perfect correlation coefficient for

$$t_{R_{rel}C_{14}}(130°C) = 0.06539t - 12.55 \quad (5)$$

This gives very good predictions for safrole, estragole, carvone and linalol with small differences for menthone (−0.03) and 4-terpineol (+0.07). The relatively high constants in Eq. (5) reflect the strong affinity between the tri-aromatic liquid crystal side chains of MPMS and the aromatics.

Considering Eqs. (1,2) at 130 and 160°C, respectively, to represent normal expected relative retentions by MPMS, without exhibiting any special solute interactions, 20 of the 26 solutes examined showed the same retention (±0.06) enhanced or not, at the two temperatures. These substances respond equally to this liquid crystal phase above or below its melting point. They may show no delay at either temperature, as for limonene; small delays, as for fenchone (about 0.15); larger delays, as for 4-terpineol (about 0.47); or similar big delays at both temperatures, as for cuminal (about 1.80). This is not so for two aromatic substances, nor for three acyclic monoterpenoids. It does not seem possible to define a relationship between the five oxygen-containing aromatic substances studied, but in Table 1, groups of bicyclic solutes (apart from cineole) and monocyclic compounds (apart from carvone) can be seen. This is unexpected, considering the tri-aromatic nature of MPMS side-chains. It is not unexpected that this phase has difficulty resolving menthol, 4-terpineol and menthone. The last two conform to Eq. (5), whilst menthol at 160°C approaches Eq. (3). In summary, on MPMS phase:

1. Five low polarity solutes show linear relationship expressions at 130 and 160°C, along with some oxygen-containing acyclic substances.
2. Other acyclic molecules may fit the surface of unmelted MPMS to provide slight extra retention over 1 above.
3. Some cyclic monoterpenoids give relative retentions at 130°C which can be predicted by equations determined at 160°C, suggesting that they transiently melt the phase.
4. Some bicyclic solutes show a linear relationship at 160°C.
5. Some aromatic substances show linear relationship expressions with larger constants than those in 1 above, reflecting the tri-aromatic nature of MPMS, but also predicting values for some monoterpenoids.
6. Solutes containing oxygen which show about the same increased retention over the expressions in 1 above for both temperatures, are bicyclic terpenoids if these increases are in the range 0.14–0.32, or are monocyclics if the increases are between 0.46 and 0.62. Exceptions are cineole, camphor, menthol and carvone.

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