

Short Communication

Two-solute method for indicating polarity changes of conventional and novel gas chromatographic stationary phases with temperature increase

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ABSTRACT

This author's previous work suggested that a ratio of corrected retention times for cuminal (cu) against caryophyllene (cy) pragmatically indicated the polarity of a gas chromatographic stationary phase. A c ratio of $3c_{cu}/4c_{cy}$ below 0.8 corresponded to low-polarity phases, and above 1.2 to high-polarity ones. Changes in the c ratio for liquid crystal, toroid molecular and conventional phases were observed with increases in temperature, particularly for Carbowax 20M, which appeared to decline considerably in polarity. Some high-polarity liquid crystals were reduced to intermediate polarity c ratios (0.8–1.2). Previous anomalous observations by this author can now be explained.

INTRODUCTION

Since 1981 [1,2] this author has been interested in finding a simple method for determining the polarity of stationary phases used for gas chromatography. It became more urgent during recent studies of novel phases [3,4]. Kollie and Poole [5] recently remarked that "the general concept of polarity is a measure of the capacity of a stationary phase to enter into all intermolecular interactions. No exact method has emerged for calculating or determining this term". The general concept has been reviewed since 1989 [6,7].

McReynolds values [8] are often used as indicators of phase polarity—usually by placing them in

sequence of the sum of the values for say five (of the full ten) solute probes. However, all McReynolds values have a non-polar bias, as they are the retention index of each probe rated against non-polar normal alkanes on the phase, minus the index of the same probe on non-polar squalane phase. Logically, a "polar" phase should retain the polar solute *n*-butanol much more than low-polarity benzene. However, various phases all have McReynolds values for benzene which form a consistent about 40% of the sum of their butanol and benzene values. The respective values, for example are 158 and 119 (43%) on the phenylmethylpolysiloxane OV-17; 536 and 322 (38%) on polyethyleneglycol 20M; and 751 and 499 (40%) on diethyleneglycol succinate (DEGS). These diverse phases, and others, appear to show hardly any difference in their relative affinity for these two distinct solutes. A further limitation of the McReynolds system is that determina-

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tions should be made at the low temperature of 120°C. Other deficiencies have been observed [5].

We proposed in 1981 a system [1], subsequently [3] named "LEC", using the retention indices on the test phase of three typical volatile oil constituents; linalol, estragole and carvone (two terpenoids and an aromatic) at the more generally used temperature of 160°C. These indices were determined against polar normal alcohols as well as alkanes, and compared to values from a "standard" phenyl-methylpolysiloxane phase. The test phase was then numerically more or less polar than the standard [1]. Castello *et al.* [9,10] later devised a system in 1988 which also used both normal alcohols and alkanes; taking the difference in apparent carbon number between an alkane and an alcohol with the same retention time on a capillary phase.

Our "LEC" method was later modified [3] by the replacement of the carvone by cineole (both terpenoids), and by omission of the alcohol-based indices. It then indicated three liquid crystal phases in packed columns as being of low polarity, although by another lower-temperature method used in these laboratories, they confusingly rated much higher. This [2] utilises three McReynolds probe solutes, including the uncommon low-polarity 2-octyne (O). *n*-Butanol (B) always emerged before pyridine (P), but the sequence O-B-P was given by high-polarity phases, B-P-O by low-polarity ones, and B-O-P by intermediate polarities. These same solute sequences were later hidden in Kollie and Poole's Table II [11] amongst the values of partial molal Gibbs free energy of solution for 18 solutes on 23 phases. Here, the sequences of values show 20M and DEGS to be highly polar, whilst the "problem" phases OV-225 (cyanopropyl,phenyl,dimethylpolysiloxane) and QF-1 (trifluoropropyl,methylpolysiloxane) are appropriately indicated by B-O-P to be of intermediate polarity. Principal component analysis extracting eigenvectors confirmed these solutes to be in three different groups, but gave five classes of phases, with some behaving "independently". Cluster analysis reduced these to four classes, but grouped squalane with OV-225 and 20M! Their later paper [5], using the same procedures on a new free energy of solution parameter, did put 20M with DEGS, with a separate group of various polysiloxanes, and could thus "provide a logical and intuitive(!) classification of phases". A complex mathematical way

of achieving something quite evident to chromatographers who use these phases!

The need was apparent for a simple procedure which could be applied over a range of temperatures, unlike McReynolds', and other methods. Consideration of my recent work on volatile oil constituents [4] suggested that this could be provided by the pair of solutes polar aromatic cuminal [$\text{CHO}-\text{C}_6\text{H}_4-\text{CH}(\text{CH}_3)_2$], and non-polar bicyclic non-aromatic diene sesquiterpene caryophyllene [$\text{CH}_2 = \text{C}_{11}\text{H}_{13}(\text{CH}_3)_3$] with a nine-carbon ring system. Having made previous records of their relative retention times on novel phases [4,12,13], it only needed some new observations on traditional phases. The use of just two solute probes to evaluate stationary phases goes back to 1959, when Rohrschneider [14] used butane and butadiene. Abraham *et al.* [15] currently claim that a "single parameter cannot possibly reflect the various solute-(phase) interactions". They feel the need for a complex equation of five terms with six constants, although they previously acknowledged [16] that three of their constants were "not very useful", "minor" or "not significant". Their tables listing calculations for various phases of the surviving three terms (ref. 15, Table IV; ref. 16, Table XII) reveal they cannot discriminate five different probe solutes. All phases show lowest value of one term along with highest values for the other two terms, and the same pattern of values for each solute. Their equation, deduced from a hypothetical model involving the creation of cavities in the phase to receive solute molecules [16], seems unable to reflect phase polarity differences. A later paper [17] uses, for two low polarity phases, a "truncated" equation involving just two terms for molar refraction and a partition coefficient in hexadecane at the impractical temperature of 25°C; seemingly distant from actual gas chromatography! It seems sense to use two appropriate probe solutes, as is done in the present pragmatic work.

EXPERIMENTAL

Apparatus

A Hewlett-Packard 5790A gas chromatograph was used, fitted with a capillary control unit, and a splitter injection port and flame ionisation detector both set at 235°C. A Hewlett-Packard 3380A recorder/integrator was attached.

Materials and methods

Details of the capillaries used have been recorded previously [18]. Helium was used as mobile phase at about 1 ml min⁻¹ except for the “Chiraldex-A-DA” toroid phase, where double this flow-rate was needed. Injections were made of trace residues from an “emptied” microsyringe. Holdup times were obtained by extrapolating to methane the retention times of *n*-heptane and *n*-hexane plotted on semi-logarithmic graph paper.

Details of the packed columns have been given previously. The liquid crystal phases, (all 3%, w/w) [13] were bis(methoxybenzylideneanilchloroaniline) [(MBCA)₂], bis(methoxybenzylideneanilbitoluidine) [(MBT)₂] and azoxydiphenetol (ADP), all from T.C.I. (Tokyo, Japan). The toroid molecular phases (both 3%, w/w) [4] dicyclohexano- and dibenzo-24-crown-8 ethers were from Aldrich. Cholesteryl acetate (10%, w/w), was from Sigma, and although a liquid crystal at about 115°C, had been found to function best as a normal isotropic liquid above this temperature [19]. The linalol used was from Sigma, the cuminal (*p*-isopropylbenzaldehyde) from Eastman, and the (impure) caryophyllene from Koch-Light.

RESULTS AND DISCUSSION

Average results, newly obtained for this work, and from my previous studies [4,12,13] are given in Table I as relative retention times to linalol, after deducting holdup times. The ratio of these values for cuminal (cu) against caryophyllene (cy) presented best if reduced by three-quarters, and this is included in Table I as an indicator of phase polarity. If its “*c* ratio” of 3cu/4cy was about unity (say 0.80–1.20) a phase had intermediate polarity like the cyanopropyl,phenyl,dimethylpolysiloxane OV-225 [2]. A bigger *c* ratio (up to almost 1.60 was observed) indicated a strongly polar phase; whilst a lower ratio (down to near 0.25 was observed), with caryophyllene emerging after cuminal, indicated a low-polarity phase. Of course, simple corrected retention times gave the same *c* ratios, but relative times are quoted in Table I as these are what have been published before.

Fully methylpolysiloxane is a classic very low-polarity phase, and gave very low *c* ratios around 0.30, which went from 0.27 to 0.33 as the oven temper-

ature increased from 140 to 200°C. This phase thus behaved in a slightly less non-polar fashion with temperature rise. Isotropic (normal liquid) cholesteryl acetate (not functioning as a liquid crystal) showed less low-polar *c* ratios, around 0.40, which also rose slightly with temperature increase. Two toroid (ring) molecular phases showed very consistent values around 0.65, and so were not as low-polar as those above, but still could not be considered to be up to intermediate polarity. These phases all gave the B–P–O (see Introduction) low polarity sequence [2,4,19] except the dicyclohexane crown ether, which probably did not behave “normally” at the low 120°C used for this method. Its *c* ratios indicated that it was very similar to the Chiraldex phase, and at 140°C this latter yielded the same sequence of eight chemically different solutes as the crown ether at 170°C [4].

OV-225 gave *c* ratios around 1.00, which decreased from 1.03 to 0.94 with oven temperature increase from 140°C to 200°C. The liquid crystal (MBCA)₂ showed similar ratios, also decreasing from 1.07 to 1.00 as the temperature went from 145 to 175°C—the reverse of the small rises in polarity shown by the low-polarity phases. Another liquid crystal, mesogenic polymeric methyl siloxane “MPMS” showed constant ratios, when melted, of 1.19 (more polar than OV-225 or (MBCA)₂ and almost falling into the high-polarity category), with a similar ratio when unmelted. OV-225 and “MPMS” showed the intermediate solute sequence of B–O–P [2,18] but not (MBCA)₂ [3]. However, the 120°C used with these three solutes was well below the melting point of (MBCA)₂, so it was probably not behaving typically then.

Carbowax 20M is a typical high-polarity phase and gave higher *c* ratios which decreased from almost 1.6 at 120°C to 1.4 at 160°C, indicating a rapid decrease in polarity with oven temperature increases. This had been used for some years, and was possibly partly oxidized. ADP also suffered a big fall in *c* ratios from 140 to 165°C, due particularly to increase in caryophyllene relative retention times, taking it down to an intermediate polarity phase at the higher temperature. At 140°C it rates as more polar than Carbowax 20M and, like the other liquid crystal “MPMS”, this polarity is mostly maintained in the unmelted condition—in contrast to (MBT)₂.

The melted liquid crystal (MBT)₂ also showed

TABLE I

AVERAGE RELATIVE RETENTION TIMES (LINALOL = 1.00) FOR THREE GROUPS OF STATIONARY PHASES IN PACKED COLUMNS OR CAPILLARIES AT TEMPERATURES (°C) INDICATED

Phase	Temperature (°C)	Cuminal (cu)	Caryophyllene (cy)	c ratio (3cu/4cy)	
<i>Low polarity</i>					
Methylpolysiloxane capillary	200	1.89	4.10 ^a	0.33	
	160	2.01	4.97	0.30	
	140	2.10	5.75	0.27	
Cholesteryl acetate packed column [15]					
	isotropic	155	2.69	5.08 ^a	0.40
	isotropic	140	2.69	5.26	0.38
"Chiraldex-A-DA" ring capillary [4]	140	3.22	3.61 ^a	0.67	
	125	3.28	3.75	0.66	
	110	3.25	3.77	0.65	
Dicyclohexano-24-crown-8 ether ring packed column [4]	170	2.68	3.04 ^a	0.66	
	155	2.69	3.12	0.65	
<i>Intermediate polarity</i>					
Cyanopropyl (25%)–phenyl (25%)–methyl (50%) polysiloxane OV-225 packed column	200	3.44	2.75	0.94	
	160	3.60	2.72	0.99	
	140	3.78	2.75	1.03	
(MBCA) ₂ liquid crystal packed column [11]	175	3.25	2.43	1.00	
	160	3.48	2.51	1.04	
	supercool	145	3.61	2.53	1.07
"MPMS" polysiloxane liquid crystal capillary [11]	160	4.97	3.12	1.19	
	140	5.50	3.47	1.19	
	unmelted	120	5.91	3.82	1.16
<i>High polarity</i>					
Carbowax 20 M polyethylene glycol capillary	160	2.97	1.60	1.39	
	140	2.90	1.45	1.50	
	120	3.03	1.44	1.58	
(MBT) ₂ liquid crystal packed column [10,11]	200	4.38	2.22	1.48	
	175	4.62	2.41	1.44	
	unmelted	160	3.35	2.80	0.90 ^b
unmelted	150	3.30	2.87	0.86 ^b	
Dibenzo-24-crown-8 ether ring packed column [4]	170	4.21	2.52	1.25	
	155	4.30	2.43	1.33	
ADP liquid crystal packed column [11]	165	4.20	3.00	1.05 ^b	
	140	4.64	2.22	1.57	
	unmelted	130	2.81	1.47	1.43

^a Caryophyllene emerges after cuminal on this phase.

^b The phase has only intermediate polarity at this temperature.

high values until cooled to near or below its melting point, whereupon its *c* ratios became only those of an intermediate polarity phase (about 0.9). This was confirmed by its 120°C B–O–P sequence [3] that was unlike Carbowax 20M, liquid crystal ADP and the toroid dibenzo crown ether which all gave the typ-

ical high polarity sequence of O–B–P [2–4]. This crown ether again showed a decline in *c* ratios with temperature increase, like Carbowax 20M. It was clearly different to the other two toroid phases, Chiraldex and dicyclohexane crown, and gave a different solute retention sequence to them [4].

The observations above explain some of the anomalies in polarity determination that I have noted previously [3] for liquid crystal phases. It is not surprising that such substances change in polarity with temperature changes, but it is alarming that a conventional phase like Carbowax 20M appears to suffer a considerable fall in polarity with temperature increase. The c ratios for this capillary were confirmed with a packed column. Chromatographers should be warned that this polarity change is a hazard for temperature-programmed work, even with methylpolysiloxane. The latter exhibits a slight rise in polarity as the temperature rises (although it remains "low"), so these two conventional phases both approach intermediate polarity from opposite directions at higher temperatures. Abraham *et al.* [16] claim that "the effect of temperature is very important (but) it has generally been overlooked as regards characterisation of stationary phases. In general (our) main characteristic constants all decrease, often quite markedly, with temperature". The classic concept of gas-liquid chromatography is that separations are achieved by partition phenomena in the phase. However, adsorption by the polar phases is likely to contribute significantly to the retention of caryophyllene. Adsorption effects should decrease with increasing temperature, and may explain, in part, the observations here.

The O-B-P result [3] correctly indicated the high polarity of ADP, but was wrong for (MBCA)₂, which is only of intermediate polarity here. In contrast, B-O-P under-rated the polarity of (MBT)₂ as "intermediate" [3] because it was done at 120°C, well below its melting-point. The modified LEC method at 160°C greatly underestimated the polarity of all three liquid crystals, and cannot be relied on for such phases. However B-P-O correctly designated isotropic cholesteryl acetate as low polarity [19], confirmed by the LEC method. The liquid crystal "MPMS" was also properly rated as intermediate by B-O-P [18].

The toroid phases had "ChiralDEX-A-DA" correctly placed as low polarity by B-P-O [4], and the dibenzo crown ether as high-intermediate by O/B (together)-P. The dicyclohexane crown was over-rated by B-O-P, however, although octyne was only "just ahead of pyridine" [4]. If octyne had been last, it would have agreed with the c ratio here.

The simple two-solute-determination used here (it can be done without lincol) immediately shows low polarity phases by caryophyllene emerging before cuminal; and their retention time ratio then resolves the more polar phases into high- and intermediate-polarity groups. This polarity determination can be made at various temperatures, to observe any changes in polarity with heating.

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