CHROM. 16,645

EVALUATION OF TERTIARY PHOSPHATE ESTERS AS STATIONARY PHASES FOR GAS–LIQUID CHROMATOGRAPHY

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(Received February 7th, 1984)

SUMMARY

Fifteen tertiary phosphate esters were tested for their polarity and volatility. The polarities of the phosphates investigated range from that of polyphenyl ethers to that typical of Carbowaxes, and their volatilities are by about one to three orders of magnitude lower than that of squalane. The merits of tertiary phosphate esters as stationary phases for gas–liquid chromatography are discussed.

INTRODUCTION

Tertiary phosphate esters may serve as good stationary phases for gas–liquid chromatography. The structure of tertiary phosphate esters can be represented by

$$R'O-\underset{\underset{OR'''}{|}}{\overset{\overset{O}{\|}}{P}}-OR''$$
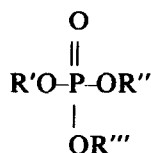
where R', R'' and R''' are any organic groups, and a great variety of compounds with different physico-chemical properties can be obtained by varying the organic moieties. Tertiary phosphate esters are chemically well defined, can easily be prepared in a very pure state and have outstanding solvent properties[1]. The volatility of tertiary phosphate esters is low compared with hydrocarbons of similar molar mass and they are high-boiling liquids or solids. The thermal stability of tertiary phosphate esters depends on their chemical constitution. Triaryl phosphates are thermally more stable than trinaphthyl phosphates, the decomposition temperatures[1] being about 510 and 476°C, respectively. Tertiary phosphate esters are non-corrosive materials and can be used with any type of column. All these properties are very advantageous with regard to both repeatability of gas chromatographic retention data and physico-chemical

measurements by gas chromatography.

Tributyl, triphenyl, tricresyl, and trixylenyl phosphates have already been employed as stationary phases to separate various classes of compounds by gas–liquid chromatography[2–6]. The aim of this work was to evaluate some tertinary phosphate esters with various aliphatic, aromatic and halogen-containing substituents. Fifteen compounds were synthesized (Table I) and their polarities and volatilities were estimated, employing squalane as a reference compound.

CHARACTERIZATION OF ORGANOPHOSPHATE STATIONARY PHASES

Polarity

The sum of the Rohrschneider–McReynolds constants[7,8] and the partial molar excess Gibbs function of solute methylene[9] were employed as polarity criteria. Whereas the sum of the Rohrschneider–McReynolds constants, $\sum_1^5 \Delta I$, may be considered as a direct measure of the contribution to solute retention due to non-dispersive solute–stationary phase interactions, the partial molar excess Gibbs function per solute methylene group, $\Delta G^E(CH_2)$, expresses the reluctance of a stationary phase to mix with a solute methylene, the latter being considered as a unit of a non-polar substance. Hence, the magnitude of $\Delta G^E(CH_2)$ is an indirect measure of the ability of the stationary phase to interact with the solute by means of non-dispersive forces, and there is a good correlation between the $\sum_1^5 \Delta I$ and $\Delta G^E(CH_2)$ values determined for different stationary phases[10]. The quantity $\sum_1^5 \Delta I$ is determined as the sum of the differential retention indices of benzene, 1-butanol, 2-pentanone, nitropropane and pyridine measured on the stationary phase under investigation and on squalane. The $\Delta G^E(CH_2)$ value can be calculated from the adjusted retention times, t_R' (and/or any other retention quantities derived from the latter), and the saturation vapour pressure, P°, of two or more homologues of a series of compounds $CH_3(CH_2)_N X$ where X is a functional group, by $\Delta G^E(CH_2) = (RT/a)\ln(t_{R,N}' P_N^\circ / t_{R,N+k}' P_{N+k}^\circ)$ and/or $\Delta G^E(CH_2) = -RT d\ln(t_R' P^\circ)/dN$, where a, R and T being the difference in the methylene number of the two homologues used to calculate $\Delta G^E(CH_2)$, the molar perfect gas constant and the absolute column temperature, respectively. Homologous C_6–C_{12} *n*-alkanes were used as solutes to determine the $\Delta G^E(CH_2)$ values for the individual stationary phases.

Volatility

The volatilities of the phosphate esters were assessed by depositing each on a chromatographic support, preparing gas chromatographic columns from the materials obtained and measuring the bleeding from the columns at different column temperatures and at a fixed carrier gas flow-rate (as measured at the detector temperature and atmospheric pressure) with a flame-ionization detector. The data obtained were used to calculate the molar enthalpies of vaporization[11], ΔH_v, of the phosphate esters, employing the equation $\Delta H_v = -\{R[d\ln R_i/d(1/T)] - RT\}$ where R, R_i and T are the molar perfect gas constant, the detector response to column bleeding and the absolute column temperature, respectively. This equation is valid

provided that the gaseous phase leaving the column behaves ideally, and the error due to gas-phase non-ideality may amount to several percent of the value calculated[11]. The data processing procedure consisted in plotting log R_i against $1/(t + 230)$, where t and 230 are the column temperature in degrees Celcius and the Calingaert–Davis constant in the Antoine equation, respectively, determining the slope (B) of the plot and calculating the value of $d\ln R_i/d(1/T)$ from $d\ln R_i/d(1/T) = 2.303\,B[T/(t+230)]^2$.

EXPERIMENTAL

Materials

The phosphate esters were used as substrates at concentrations of 10% (by wt.) on Anakrom Q support (80–90 mesh) (Analabs, North Haven, CT, U.S.A.) employing the siurry method with chloroform as a solvent, and the latter was evaporated from the packing material under vacuum in a rotary evaporator. The materials so obtained were packed in 2 m × 2.3 mm I.D. stainless-steel and/or 2 m × 2.1 mm I.D. glass columns, and the columns were conditioned at 150°C for 3 h in the column oven of the gas chromatograph at a low nitrogen carrier gas flow-rate.

All the solutes were obtained from PolyScience (U.S.A.).

Gas chromatograph

A Varian 3700 gas chromatograph with a flame-ionization detector and a Varian 9176 potentiometric recorder were employed. In order to measure accurately the column temperature, a calibrated mercury thermometer was inserted into the column oven. For the measurement of ΔH_v, the detector temperature was 170°C and the sample-port temperature was the same as the column temperature in all instances. For the measurement of ΔI and $\Delta G^E(CH_2)$, the detector and sample-port temperatures were 140 and 120°C, respectively. The flow-rates of the carrier gas (nitrogen), hydrogen, and oxygen (instead of air) were 20, 20 and 60 ml/min, as measured at the ambient temperature and pressure, respectively.

Procedure

The $\sum_1^5 \Delta I$ and $\Delta G^E(CH_2)$ values determined for the individual stationary phases refer to 100 and/or 110°C (with compounds 13, 14 and 15). About 0.1-μl charges of liquid solutes were injected into the gas chromatograph. The measurements of column bleeding (R_i) were carried out at column temperatures in the range 50–150°C in 10°C steps. In the measurements of R_i, a length of column about 10 cm at the outlet was left unpacked in order to avoid overheating of the packing by the detector body.

RESULTS AND DISCUSSION

In Table I, the stationary phases studied are arranged in order of increasing polarity. The $\sum_1^5 \Delta I$ and $\Delta G^E(CH_2)$ values for the individual phosphate esters were measured and calculated as described above, and the $\Delta G^E(CH_2)$ values for squalane were calculated by using the retention data for *n*-alkanes on squalane published by

TABLE I

POLARITY CRITERIA OF ORGANOPHOSPHATE ESTER STATIONARY PHASES

No.	Ester	Column temperature (°C)	$\overset{5}{\underset{1}{\Sigma}} \Delta I$	$\Delta G^E(CH_2)$ (J/mole)
1	Tris(2-methoxy-4-propylphenyl) phosphate	100	1572	433.83
2	Bis(o-cresyl)-2-methoxy-4-propylphenyl phosphate	100	1564	408.33
3	Diphenyl-2-methoxy-4-propylphenyl phosphate	100	1935	523.05
4	Diphenyl-4-chloro-m-cresyl phosphate	100	1479	355.56
5	Bis(o-cresyl)-4-chloro-m-cresyl phosphate	100	1343	331.11
6	Diphenyl-2-methoxy-4-(2,3-dichloropropyl)phenyl phosphate	100	1931	515.27
7	Bis(o-cresyl)-2-methoxy-4-(2,3-dichloropropyl)phenyl phosphate	100	1790	489.44
8	Tris(4-chloro-m-cresyl) phosphate	100	1195	315.28
9	Tris(2,4-dichlorophenyl) phosphate	100	1330	334.16
10	Tris(2,5-xylenyl) phosphate	100	1241	324.44
11	Tris(p-tert.-butylphenyl) phosphate	100	1012	282.21
12	Tris(3,5,5-trimethylhexyl) phosphate	100	791	219.44
—	Squalane	100	0	114.86
13	Tris(β-naphthyl) phosphate	110	1704	456.94
14	Tris(p-chlorophenyl) phosphate	110	1339	335.55
15	Tris(p-bromophenyl) phosphate	110	1467	362.50
—	Squalane	110	0	143.96

McReynolds[8]. In our earlier work[10], retention data for several types of solute were employed to determine the $\Delta G^E(CH_2)$ values, which is why the $\Delta G^E(CH_2)$ value obtained earlier for squalane differs from that obtained in this work. The data in Table I show that the phosphate esters investigated have low or medium polarity.

In Fig. 1, the $\Delta G^E(CH_2)$ data are correlated with those of $\overset{5}{\underset{1}{\Sigma}} \Delta I$. The graph was constructed using data measured at 100°C. Figs. 2 and 3 show the plots of $-RT$
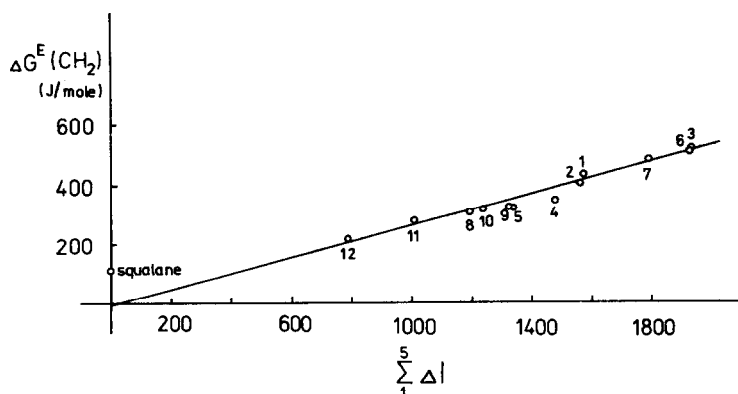

Fig. 1. Plot of $\Delta G^E(CH_2)$ against $\Sigma \Delta I$ for phosphate stationary phases and squalane at 100°C. The numbers designate the individual phosphate esters specified in Table I. $\Delta G^E(CH_2)$ is the partial molar excess Gibbs function of solute methylene in the given solvent and $\Sigma \Delta I$ is the sum of the Rohrschneider-McReynolds constants.
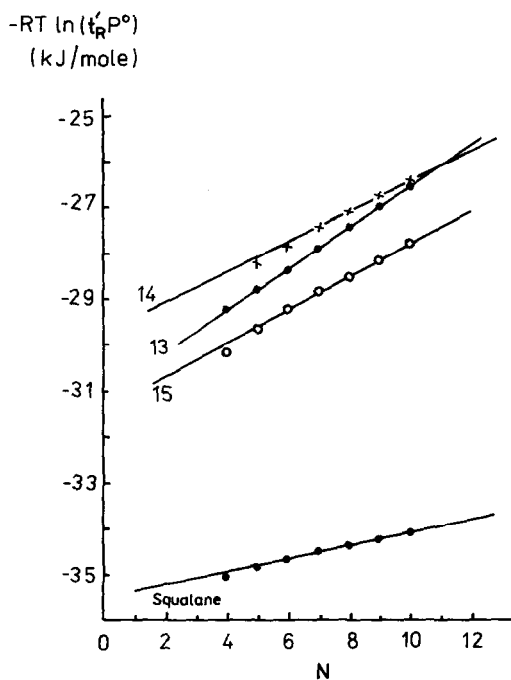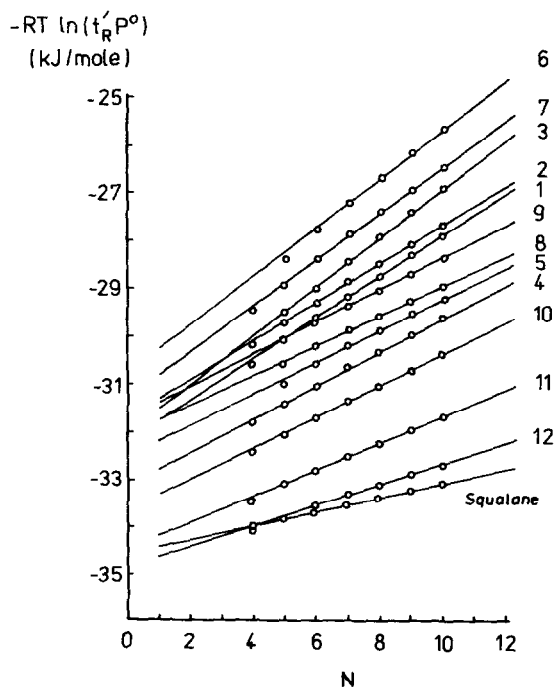
Fig. 2. Plot of $-RT \ln(t'_R P°)$ against N for phosphate stationary phases and squalane at 100°C. t'_R and $P°$ are, respectively, the corrected retention times and the saturated vapour pressures of the solutes (n-alkanes) and N is the methylene number of the solutes.

Fig. 3. Plot of $-RT \ln(t'_R P°)$ against N for phosphate stationary phases and squalane at 110°C.

TABLE II

MELTING POINTS, BOILING POINTS, HEATS OF VAPORIZATION AND VAPOUR PRES-
SURES AT 100°C OF ORGANOPHOSPHATE ESTERS AND SQUALANE

The melting and boiling points of the phosphate esters were determined by common laboratory techniques
and those of squalane were taken from ref. 12.

Stationary phase	Melting point (°C)	Boiling point (°C)	$\dfrac{d \ln R_i}{d(1/T)}$ (°K)	ΔH_v (kJ/mole)	$P_l^0 \cdot 10^4$ (kPa)
1		257/40 Pa	8747.39	69.63	3.1
2		210–220/53 Pa	8283.98	65.77	5.4
3		230–245/53 Pa	11665.25	93.89	0.18
4		198–200/53 Pa	7150.91	56.35	24
5		209–211/53 Pa	10344.90	82.91	0.59
6		252–254/53 Pa	10658.10	85.51	0.44
7		247–252/53 Pa	9942.25	79.56	0.87
8	90–92		8271.33	65.67	5.5
9	89–91		11769.11	94.75	0.16
10		202–206/53 Pa	11268.28	90.59	0.25
11	97–98		6181.05	48.29	105
12		206–208/107 Pa	7601.96	60.10	13
Squalane	−80	274/1333 Pa	11513.42	92.62	560

$\ln(t'_R P°)$ versus solute (n-alkane) methylene number (N) for the phosphate esters stud-
ied and for squalane at 100 and 110°C, respectively. It is apparent from these graphs
that the slopes, i.e., $\Delta G^E(CH_2)$ values, can be determined with fairly high precision.
Table II gives the melting and/or boiling points, the slopes of the ln R_i versus $1/T$
lines, the ΔH_v values calculated from the slopes and estimates of the saturated vapour
pressures for the phosphate esters studied and for squalane. The vapour pressures
were determined by correlating graphically the known[13] vapour pressures and ΔH_v
values for eight trisubstituted phosphate esters and reading off the $P°$ data for the
phosphate esters investigated from the plot according to the ΔH_v values measured
by the gas chromatograph as described above. Hence, the $P°$ data quoted in Table
II are very rough estimates only.

CONCLUSIONS

        The tertiary phosphate esters investigated appear to have certain merits as
stationary phases for gas–liquid chromatography. They are stable, chemically well
defined and can easily be prepared in a pure state. Their volatilities are about one to
three orders of magnitude lower than that of squalane. The polarities of the phos-
phate esters tested range from that of polyphenyl ethers to that typical of Carbowaxes
(see the plot in Fig. 2 in ref. 10).

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