

CHROM. 13,026

CORRELATION OF GAS CHROMATOGRAPHIC SPECIFIC RETENTION VOLUMES OF HOMOLOGOUS COMPOUNDS WITH TEMPERATURE AND METHYLENE NUMBER

J. NOVÁK, J. VEJROSTA, M. ROTH and J. JANÁK*

Institute of Analytical Chemistry, Czechoslovak Academy of Sciences, 61142 Brno (Czechoslovakia)

SUMMARY

The specific retention volumes of homologous compounds can be expressed by $\log V_g = p(n/T) + q/T + nr + s$, where n is the number of methylene groups in the solute molecule, T is the absolute temperature and p , q , r and s are constants related to the thermodynamic properties of the chromatographic system. Generally, the specific retention volumes measured for four homologues at different temperatures are sufficient for determining the constants of the equation. The accuracy of the V_g values calculated for given n, T data by the equation is commensurate with the precision of replicate determinations of the V_g value of a given compound on a given instrument.

INTRODUCTION

Diverse correlations have been described between gas chromatographic retention data and the properties of the solutes, which have been applied in various ways to identify compounds by virtue of their retention behaviour¹. Most of these correlations have been based essentially on regularities that exist between the properties of homologous compounds and their number of carbon atoms and/or methylene groups. James and Martin² first observed that the logarithms of the adjusted retention volumes of homologous fatty acids yielded an almost straight line when plotted against the number of carbon atoms in the solute molecules. Constructing such a plot for groups of compounds pertaining to different homologous series results in a family of almost parallel straight lines³; this parallelism indicates that the logarithm of the homologous retention increment for a methylene group is approximately constant, independent of the kind of functional group. However, such correlations apply only to data that have been measured at the same temperature on a given sorbent. It is possible, of course, to estimate retention data at a desired temperature from the corresponding data measured at different temperatures by employing the linear relationship between the logarithm of the adjusted retention and the inverse of the absolute temperature, applicable to a given compound chromatographed on a given sorbent.

The aim of this paper is to show the possibility of correlating the logarithms of specific retention volumes of homologous compounds simultaneously with both the

number of methylene groups and temperature. This approach makes it possible to reduce the specific retention volumes measured for a group of homologous compounds at different temperatures to a single equation with four empirical constants, thus providing for a very condensed presentation of retention data and facilitating their interpolation and extrapolation to different homologues and temperatures.

THEORETICAL

In this paper, both the theoretical model and experimental data are processed in terms of specific retention volumes rather than adjusted retention volumes or distribution constants, as the specific retention volume, unlike the distribution constant, is a quantity the value of which does not reflect the dependence of the volumes of the sorbent and mobile phase on temperature. The specific retention volumes were measured and calculated by recommended methods⁴.

The standard Gibbs function of sorption, G_{sp}^0 , is related with the specific retention volume, V_g , by

$$G_{sp}^0 = -2.3RT \log(k^0 V_g) \quad (1)$$

where k^0 is a constant dependent on the choice of the standard states⁵ and R and T are the universal constant and the absolute temperature of the chromatographic column in the measurement of V_g , respectively. As $G_{sp}^0 = H_{sp}^0 - TS_{sp}^0$, where H_{sp}^0 and S_{sp}^0 are the standard enthalpy and entropy of sorption, eqn. 1 can be rewritten as

$$\log V_g = -\frac{H_{sp}^0}{2.3RT} + \frac{S_{sp}^0}{2.3R} - \log k^0 \quad (2)$$

or

$$\log V_g = (A/T) + B \quad (3)$$

where $A = -H_{sp}^0/2.3R$ and $B = (S_{sp}^0/2.3R) - \log k^0$. Within certain temperature limits the quantities A and B can be considered to be virtually constant.

Let us consider a homologous series of compounds of the type $i \equiv \text{CH}_3(\text{CH}_2)_n\text{X}$ where X is a functional group. Assuming the additivity⁶ of the contributions of the individual parts of the molecule to the values of H_{sp}^0 and S_{sp}^0 , we can write

$$H_{sp}^0 = H_{sp}^0(\text{CH}_3) + nH_{sp}^0(\text{CH}_2) + H_{sp}^0(\text{X})$$

and

$$S_{sp}^0 = S_{sp}^0(\text{CH}_3) + nS_{sp}^0(\text{CH}_2) + S_{sp}^0(\text{X})$$

so that the A and B in eqn. 3 can be expressed as

$$A = -\frac{nH_{sp}^0(\text{CH}_2) + H_{sp}^0(\text{CH}_3) + H_{sp}^0(\text{X})}{2.3R}$$

and

$$B = \frac{nS_{sp}^0(\text{CH}_2) + S_{sp}^0(\text{CH}_3) + S_{sp}^0(\text{X})}{2.3R} - \log k^0$$

which can be abbreviated to

$$A = pn + q \quad (4)$$

and

$$B = rn + s \quad (5)$$

where the constants p , q , r and s have the following physical meanings: $p = -H_{sp}^0(\text{CH}_2)/2.3 R$, $q = -[H_{sp}^0(\text{CH}_3) + H_{sp}^0(\text{X})]/2.3 R$, $r = S_{sp}^0(\text{CH}_2)/2.3 R$ and $s = \{[S_{sp}^0(\text{CH}_3) + S_{sp}^0(\text{X})]/2.3 R\} - \log k^0$. Combining eqns. 3, 4 and 5, we can finally write

$$\log V_g = p(n/T) + q/T + nr + s \quad (6)$$

It can be seen from eqn. 6 that when V_g values of four homologous (or of two homologous at two different temperatures) of a given series of compounds are determined at different temperatures, it is possible to provide a set of four linear equations with four unknowns (constants p , q , r and s), the solution of which yields the values of the constants. Provided that redundant data of limited precision are available, which is usually the case, it is expedient to combine the above solution of the set of equations with regression by the least-squares method, employing a suitable computer program.

EXPERIMENTAL

In order to prove the validity of eqn. 6, homologous n -alkanes and primary n -alkanols were chromatographed on several sorbents at various temperatures, and the specific retention volumes calculated from the retention data obtained were processed as indicated above.

A home-made gas chromatograph designed for accurate measurements of specific retention volumes was employed, consisting of a cylinder packed with molecular sieve 5A (drying of the carrier gas), a pressure regulator (Porter Instrument Co., Hatfield, PA, U.S.A.), a differential flow regulator (Chemoprojekt, Satalice, Prague, Czechoslovakia), a flow meter (differential U-manometer, measuring the pressure drop across a capillary), a mercury U-manometer for measuring the column inlet excess pressure, a sample-inlet port, a chromatographic column and a flame ionization detector. The U-tube of the flow meter was filled with a silicone oil, and the flow meter was calibrated with the aid of a soap-bubble flow meter. The chromatographic column was a glass U-tube (470 \times 3.5 mm I.D.), placed in a glass jacket and thermostated by means of a water ultrathermostat (Mechanik Prüfgeräte, Medingen, G.D.R.). High-purity nitrogen was used as the carrier gas. The retention dead time was determined by the methane peak method. The standard deviation of replicate determinations of V_g , as tested with benzene on Apiezon K, was about 0.5% of the average value.

The following column packings were used: Apiezon K (Associated Electrical Industries, Manchester, Great Britain), 20 wt.-% on Chromosorb W (60–80 mesh) (Carlo Erba, Milan, Italy); Carbowax 400 (Carlo Erba), 20 wt.-% on Chromaton N AW DMCS (0.125–0.16 mm) (Lachema, Brno, Czechoslovakia); Porapak P and Q

(Waters Assoc., Milford, MA, U.S.A.); Tenax GC (Applied Science Labs., State College, PA, U.S.A.); and Carbopack A (Supelco, Bellefonte, PA, U.S.A.). The solute compounds were C_5 - C_9 *n*-alkanes and C_2 - C_4 primary *n*-alkanols; about 10- μ l samples of solute vapour with suitable contents of methane were injected into the gas chromatograph with a Hamilton 1710 gas-tight syringe (Hamilton, Bonaduz, Switzerland).

TABLE I

RESULTS OF THE PROCESSING OF EXPERIMENTAL DATA FOR *n*-ALKANES ON APIE-ZON K

n = number of methylene groups in the solute molecule $[(CH_2)_2(CH_2)_n]$; t = temperature ($^{\circ}C$) of the measurement of V_g ; $V_g(\text{calc})$ = V_g calculated by eqn. 6; $V_g(\text{exp})$ = experimentally measured V_g ; $E(\%) = 100(|V_g(\text{exp}) - V_g(\text{calc})|)/V_g(\text{calc})$; the average relative error is defined as $\sum_N E(\%)/N$, where N is the number of experimental points processed; $B(1)$, $B(2)$, $B(3)$ and $B(4)$ represent the constants s , p , q and r in eqn. 6, respectively.

n	t ($^{\circ}C$)	$V_g(\text{exp})$	$V_g(\text{calc})$	$V_g(\text{exp}) - V_g(\text{calc})$	$E(\%)$
3	57.4	26.09	26.41	-0.31	1.219
3	66.3	20.80	21.03	-0.22	1.083
3	75.7	16.80	16.74	0.06	0.376
3	85.0	13.24	13.51	-0.26	2.058
3	93.9	10.99	11.12	-0.12	1.224
4	66.3	52.69	51.98	0.71	1.353
4	75.7	40.76	39.48	1.28	3.137
4	85.0	30.90	30.51	0.39	1.270
4	93.9	24.46	24.13	0.33	1.350
5	57.4	176.74	177.23	-0.48	0.280
5	66.3	130.00	128.49	1.51	1.159
5	75.7	94.44	93.13	1.31	1.383
5	85.0	68.97	68.87	0.10	0.143
5	93.9	51.68	52.34	-0.65	1.276
6	57.4	454.64	459.15	-4.50	0.992
6	66.3	315.52	317.65	-2.12	0.675
6	75.7	219.25	219.70	-0.44	0.203
6	85.0	154.10	155.48	-1.37	0.894
6	93.9	113.06	113.53	-0.46	0.413

AVERAGE RELATIVE ERROR = 1.079%

CONSTANTS OF EQUATION: $B(1) = -1.267100E + 00$

$B(2) = 2.563962E + 02$

$B(3) = 4.788411E + 02$

$B(4) = -3.622592E - 01$

REGRESSION TABLE

SOURCE	SUM OF SQ.	DEG. FREEDOM	MEAN SQ.
REGRESSION	4.119320323007	3	1.373106774336
RESIDUAL	5.91740733E - 04	15	3.94493822E - 05
TOTAL	4.119911206375	18	

$F = 34806.8004557$

COEFF. OF DETERMINATION = 0.9998563705429

COEFF. OF MULTIPLE CORRELATION = 0.9999281827

STANDARD ERROR OF ESTIMATE = 6.28087431E - 03

RESULTS AND DISCUSSION

In order to determine the constants, p , q , r and s in eqn. 6 for the selected model systems, the experimental data were processed by a modified program of multiple linear regression, taken from the library for the Wang 2200 calculator⁷. An abbreviated description of the computation procedure is given in the Appendix. The constants in eqn. 6 are designated in the following way in the program: $B(1) = s$, $B(2) = p$, $B(3) = q$ and $B(4) = r$. After having completed the calculation, the calculator prints out the results in the form of a table; an example of the processing of data for n -alkanes on Apiezon K is shown in Table I. In addition to the data referring to the individual measurements, Table I also provides the average relative error of the data, the constants in eqn. 6 and a regression table. The program further provides for the printing out of a table of interpolated and/or extrapolated data for selected homologues at desired temperatures, together with the constants in eqn. 6. An example of this form of data presentation is shown in Table II. In Table III the constants in eqn. 6 are summarized together with the corresponding correlation coefficients (Z) and average relative errors (*cf.*, Table I) for n -alkanes and primary n -alkanols on all of the stationary phases employed.

TABLE II

V_g VALUES OF n -ALKANES ON APIEZON K, CALCULATED BY EQN. 6 FOR SELECTED n AND t VALUES

CONSTANTS OF EQUATION: $B(1) = -1.267100E + 00$ $B(2) = 2.563962E + 02$ $B(3) = 4.788411E + 02$ $B(4) = -3.622592E - 01$			
t ($^{\circ}C$)	V_g	t ($^{\circ}C$)	V_g
$n = 3$ (exp. temp. 57.4–93.9 $^{\circ}C$)		$n = 4$ (exp. temp. 66.3–93.9 $^{\circ}C$)	
20.00	80.06	20.00	260.49
25.00	67.93	25.00	213.66
30.00	57.94	30.00	176.40
35.00	49.68	35.00	146.55
$n = 5$ (exp. temp. 57.4–93.9 $^{\circ}C$)		$n = 6$ (exp. temp. 57.4–93.9 $^{\circ}C$)	
20.00	847.54	20.00	2757.55
25.00	672.09	25.00	2114.10
30.00	537.06	30.00	1635.06
35.00	432.29	35.00	1275.16

It can be seen from Table III that the values of the average relative errors are, generally, commensurate with the relative standard deviation of replicate determinations of V_g , *i.e.*, the average relative error is largely due to random errors of measurement rather than systematic errors of data processing. The concept described makes it possible to determine the V_g of any homologue at a desired temperature from the data measured for four homologues at different temperatures. However, a set of V_g values measured for any number of homologues at the same temperature and/or for a single homologue at any number of temperatures would, of course, be insufficient. The reliability of the interpolated and/or extrapolated V_g values obviously depends on

TABLE III
 CONSTANTS OF EQN. 6 DETERMINED FOR *n*-ALKANES AND PRIMARY *n*-ALKANOLS ON DIFFERENT SORBENTS

1 = Alkanes [(CH₂)_n(CH₂)_n]; 2 = alkanols [CH₃(CH₂)_nCH₂OH]; R(CH₂) = range of the experimentally embraced number of methylene groups; experimental temperature interval = temperature interval within which the V_g values were measured; Z = correlation coefficient; N = no. of experimental points processed; for the meaning of the B terms and the average relative error, see Table I.

Solute	Stationary phase	R(CH ₂)	Experimental temperature interval (°C)	B(1)	B(2)	B(3)	B(4)	Z	Average relative error (%)	N
1	Apiezon K	<3,6>	57-94	-1,2671	256,396	478,841	-0,36226	0,9999	1,08	19
1	Carbowax 400	<3,6>	54-91	0,0258	264,031	-168,448	-0,48121	0,9995	2,10	19
1	Porapak P	<3,4>	55-94	-4,2784	409,398	1671,61	-0,63244	0,9999	0,65	14
1	Porapak Q	<3,4>	65-94	-3,3775	446,160	1480,80	-0,66438	0,9999	0,33	11
1	Tenax GC	<3,4>	75-95	-5,4550	340,363	2052,74	-0,42981	0,9999	0,59	8
1	Carbopack A	<3,4>	56-94	-3,1347	379,985	800,197	-0,41867	0,9999	0,40	12
2	Apiezon K	<0,2>	57-94	-3,9774	111,544	1780,80	0,05251	0,9994	2,45	15
2	Carbowax 400	<0,2>	55-91	-3,7538	183,670	2009,71	-0,25504	0,9998	1,35	15
2	Tenax GC	<0,2>	75-95	-5,4882	444,214	2517,04	-0,68501	0,9999	1,03	15
2	Porapak P	<0,2>	55-94	-5,1692	444,314	2406,31	-0,71733	0,9998	1,27	23

the experimentally embraced range of methylene group numbers and temperatures, the number of the experimental V_g, n, T points and the extent of extrapolation. For data processing without employing the concept represented by eqn. 6, the necessary minimum would be a set of V_g values for two homologues, each measured at two different temperatures.

The constants in eqn. 6 are characteristic of the given homologous series-stationary phase system. Hence, by determining on a given stationary phase the specific retention volumes of a deliberately chosen set of homologous series at different temperatures and processing the data to obtain the corresponding set of p, q, r and s constants, it is possible to obtain a very specific characterization of the stationary phase.

CONCLUSION

The specific retention volumes of homologous compounds on a given stationary phase can be expressed as a function of the number of methylene groups and the inverse of the absolute temperature by means of a linear equation with four empirical constants. The constants of the equation have a specific thermodynamic meaning; with the given homologous series of solute compounds the constants are characteristic of the stationary phase employed. The equation constitutes a consistent means of presentation of retention data of homologous compounds and makes it possible to provide a table of selected data for desired homologues and temperatures. The accuracy of specific retention volumes calculated by the equation is commensurate with the precision of replicate determinations of specific retention volumes on a given instrument.

APPENDIX

Abbreviated description of the computation procedure

1. Start: program description (display).
2. Stop: enter first ($n1$) and last ($n2$) methylene number of homologous series.
3. Stop: enter $K1$ (number of T, V_g measurements for $n1$).
4. Stop: enter $K1$ values of T, V_g for $n1$.
(Steps 3 and 4 are repeated for all values of n .)
5. Solution of system of linear equations.
(Stop if "there is no unique solution".)
6. Print Table I.
7. Stop for insertion of new typewriter paper.
8. Print constants of eqn. 6 and general headings of Table II.
9. Stop: enter first ($n1$) and last ($n2'$) methylene number of homologous series.
10. Print detailed headings for pair $n1, n1 + 1$.
11. Stop: enter number of temperatures (L) for which you want to calculate V_g from eqn. 6.
12. Stop: enter first $T1$.
13. Print calculated ($T1, V_g$) values for pair $n1, n1 + 1$.
(Steps 12 and 13 are repeated L times for all pairs of $n2' + 1 - n1$ values).

REFERENCES

- 1 D. A. Leathard and B. C. Shurlock, in J. H. Purnell (Editor), *Progress in Chromatography*, Wiley-Interscience, New York, 1968, p. 1.
- 2 A. T. James and A. J. P. Martin, *Biochem. J.*, 50 (1952) 679.
- 3 N. H. Ray, *J. Appl. Chem. (London)*, 4 (1954) 21.
- 4 D. H. Desty, E. Glueckauf, A. T. James, A. I. M. Keulemans, A. J. P. Martin and C. S. G. Phillips, in D. H. Desty (Editor), *Nomenclature Recommendations: Vapour Phase Chromatography*, Butterworths, London, 1957, p. 11.
- 5 M. R. James, J. C. Giddings and R. A. Keller, *J. Gas Chromatogr.*, 3, No. 2 (1965) 57.
- 6 A. J. P. Martin, *Biochem. Soc. Symp.*, 3 (1949) 4.
- 7 Wang 2200 General Library, Statistics/Engineering, Wang Laboratories, Tewksbury, MA, U.S.A., 1973.