Prediction of specific retention volumes in gas chromatography by using Kováts and molecular structural coefficients

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Abstract

The Kováts coefficients, $K_{c,z}$, of a stationary phase and the solute's molecular structural coefficients, $S_{c,i}$, depend both on the specific retention volume V_g, of a solute or homologous series and on the "log-plot" slope, b, of a chromatographic column. In view of this dependence, the feasibility of predicting V_g in three instances was investigated: (a) V_g prediction of any n-alkane from $K_{c,z}$ and retention data of n-decane; (b) V_g prediction of any solute from the temperature dependence of the above parameters and (c) V_g prediction of any term of a homologous series from the correlations of the S_c increments, ΔS_c, with the organic structural function. The possibilities of the method are evaluated in the light of the analysis of the deviations of the predicted V_g values from the measured values.

1. Introduction

The determination of specific retention volume, V_g, is very difficult as the pressure and flow of the carrier gas, column temperature, mass of the stationary phase and other parameters must be controlled. Therefore, it would be very convenient to predict V_g values from other, more easily obtained retention data. In a previous study [1], the dependence of the molecular structural coefficient of Takacs, $S_{c,i}$, of 100 solutes on temperature, polarity of the stationary phase (SP) and chemical nature of the solute was investigated. A good correlation with proposed equations was found in all cases. $K_{c,z}$ and $S_{c,i}$ are terms proposed by Takacs [2], the sum of which equals the retention index, I_t, of a solute at a given temperature and carrier gas; together with b these data are of crucial importance in the

prediction of the specific retention volumes, and can be easily determined from an n-alkane mixture (provided that these probes are used as standards) when SP of low, medium or moderately high polarity are considered.

At a given temperature, the "log-plot" slope, b, is a characteristic of a given SP. Its value depends on the polarity of the SP and on the column temperature; the effect of the latter on b is described by an Antoine-type curve, according to Hawkes [3] and Tarjan et al. [4]:

$$b(T) = A/T + B \tag{1}$$

Therefore, b also must serve for predicting V_g at variable temperatures (between 80 and 180°C) and SP polarity [retention polarity (RP) up to 72.0] [5] and, in fact, should be included in retention data libraries [4], in the same way as temperature limits or polarity data. Not much

work has been done on the effect of polarity on b. Apparently no equation for this dependence has been reported.

$K_{c,z}$ and $S_{c,i}$ [4] are a function of the V_g values of n-alkanes and non-n-alkanes, respectively, as seen in their defining equations:

$$K_{c,z} = 100[Z - \log V_{g,z}/b] \tag{2}$$

$$S_{c,i} = (100/b) \log V_{g,i} \tag{3a}$$

Replacing i by Z in Eq. 3a, we obtain

$$S_{c,z} = (100/b) \log V_{g,z} \tag{3b}$$

the Z n-alkane's molecular structural coefficient; $K_{c,z}$ has a constant value and does not depend on the Z value provided that $Z \geqslant 7$.

2. Mathematical expressions used in the predictive studies of V_g

The following three cases have been considered:

(I) Calculation of V_g of an n-alkane of carbon number Z from the V_g of decane at 120°C.

From Eq. 3b, we have

$$\log V_{g,z} = 0.01 b S_{c,z} \tag{4a}$$

and

$$\log V_{g,10} = 0.01 b S_{c,10} \tag{4b}$$

for a Z n-alkane and decane, respectively. Subtracting Eq. 4b from Eq. 4a and substituting b for its value, we obtain

$$S_{c,z} = S_{c,10} + 100(Z - 10) \tag{5}$$

Dividing Eq. 3a by Eq. 3b and bearing in mind Eq. 5, we have

$$\log V_{g,z} = F \log V_{g,10} \tag{6}$$

where

$$F = 1 + 100(Z - 10)/(1000 - K_{c,z}) \tag{7}$$

i.e., the logarithm of $V_{g,z}$ for the Z n-alkane is equal to the logarithm of the specific retention volume of decane multiplied by a factor F related to the methylene group effect.

(II) Relationship between $S_{c,i}$, $K_{c,z}$ and b and the column temperature. Application to the prediction of V_g.

Eq. 1 allows the calculation of b at any temperature. In addition there is one equation

$$K_{c,z}(T) = a_1 T + a_2 \tag{8}$$

for each stationary phase, and one equation

$$S_{c,i}(T) = \alpha T + \beta \tag{9}$$

for each solute, where a_1, a_2, α and β are LSR parameters. Therefore, V_g can be calculated from the equation

$$\log V_{g,i}(T) = 0.01 b(T) S_{c,i}(T) \tag{10a}$$

for non-n-alkane solutes, and from the equation

$$\log V_{g,z}(T) = 0.01 b(T) K_{c,z}(T) \tag{10b}$$

for n-alkanes.

(III) ΔS_c and solute chemical functions.

The dependence of ΔS_c of a series of solutes [1] with a given functional group on the stationary phase RP, calculated according to Szentirmai et al. [5], is linear:

$$\Delta S_c(\text{function}) = m RP + n \tag{11}$$

where m and n are obtained by a least-squares fit. As $\Delta S_c(\text{function}) = S_{c,i} - S_{c,z}$, we have

$$S_{c,i} = S_{c,z} + \Delta S_c(\text{function})$$
$$= (m RP + n) + (100Z - K_{c,z}) \tag{12}$$

(bearing in mind Eqs. 2 and 3b). $S_{c,i}$ is the S_c of the term of the homologous series with functional group to be determined. Hence the V_g of a solute i will be given by

$$\log V_{g,i} = 0.01 b[(100Z - K_{c,z}) + (m RP + n)] \tag{13}$$

Eq. 13 gives $V_{g,i}$ as a sum of two terms: a first term that decreases with increasing $K_{c,z}$, which in turn increases with increasing SP polarity, and a second term that increases with the polarity of both the stationary phase and the solute. $V_{g,i}$ also depends on the b value, which renders a good prediction difficult, since it depends on too many parameters, each with its own uncertainty.

Indirect determinations of V_g were tried by Fernández Sanchez et al. [6], who calculated V_g values for 24 silicone-type SPs from relative retention data for n-C_{10}, n-C_{12} and the ten McReynolds probes, with an error of 1.2%. In a second calculation [7], the retention indices of the ten McReynolds probes had a mean error of 2.2%.

Abraham et al. [8] reported an equation for calculating $\log V_g$ of a series of solutes in a given SP as a sum of a constant and five terms, each consisting of a coefficient multiplied by a parameter. Hence they could account for each solute–stationary phase interaction: a molar refractive term, a solute dipolarity moment term, two H-bond terms (acidity and basicity) and a structural term containing the solvation model on which they assume interactions occur. The coefficients were calculated by an MLRA fit. The results were very good, as was to be expected from a five-parameter equation.

3. Experimental

The apparatus, solutes, stationary phases, carrier gas, etc., have been described elsewhere [1]. Retention data used in the calculations were taken from Refs. [9–13].

4. Results and discussion

Some V_g predictions for the above three cases are discussed. The agreement between the calculated or predicted and the measured V_g values is evaluated from both absolute deviations and percentage relative errors. Eqs. 6, 10a, 10b and 13 were used in calculations.

4.1. Prediction of V_g of any n-alkane from decane at 120°C

Eq. 6 was used for this prediction. $S_{c,10}$ is the S_c of decane. Table 1 gives the parameters RP, $K_{c,Z}$, $S_{c,10}$ and F necessary for the calculation of V_g and the V_g absolute deviations, δ, for dodecane for 21 stationary phases of different

polarities. It is seen that F tends to increase with increasing polarity. The calculated and measured V_gs are in good agreement, the V_g mean absolute deviation being 0.2 unit. The V_g δ values for other n-alkanes (averaged for all the stationary phases) were found to be as follows: hexane, -0.07; heptane, -0.08; octane, -0.07; nonane, $+0.09$; and undecane, $+0.18$ unit.

Table 2 presents calculated V_g values for n-alkanes from $Z = 6$ to 12 on OV-22. δ was -0.12 unit.

Fig. 1 shows the plots of the V_g mean absolute deviations of the n-alkanes, excluding the decane reference, for each column versus the column retention polarity. A straight line can be drawn at zero δ, showing that most stationary phases have negligible V_g mean absolute deviations, with the exception of the polyethylene glycols (Carbowax, Superox, etc.), which are the most polar of the SPs and, therefore, show the worst reproducibility. In Fig. 1 the V_g mean deviations for heptane are also included.

From these results it seems that the method works well, especially for low-polarity SPs; in
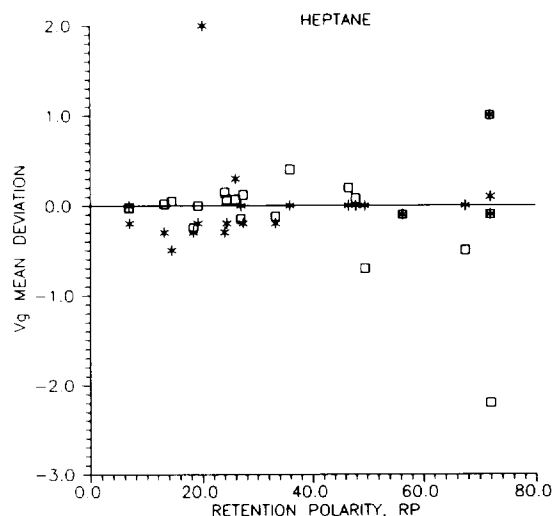

Fig. 1. V_g prediction for n-alkanes. Plots of the absolute deviations V_g(exp.) $- V_g$(calc.) vs. retention polarity of the 21 stationary phases listed on Table 1. V_g calculated from Eq. 6. $* = \delta$ values for heptane and $\square =$ averaged δ value for the n-alkanes $Z = 6,7,8,9,11$ and 12 averaged for each stationary phase.

Table 1

Retention polarities (*RP*) and Kováts coefficients ($K_{c,Z}$) for 21 stationary phases, molecular structural coefficients, $S_{c,10}$, of *n*-decane, *F* factors and V_g absolute deviations for dodecane

Stationary phase[a]	*RP*	$K_{c,Z}$	$S_{c,10}$	*F*	δ (dodecane)
OV-101	6.8	170	830	1.241	0.0
PS-255	6.9	139	861	1.232	0.9
OV-3	13.2	173	827	1.242	0.7
OV-105	14.5	149	851	1.235	1.9
OV-7	18.4	193	807	1.248	−0.4
DC-550	19.2	193	807	1.248	0.7
OV-61	24.0	229	771	1.259	1.7
OV-11	24.4	223	777	1.257	1.1
TFPS26%	26.0	212	788	1.254	−0.6
DIOPH	26.0	219	781	1.256	−2.4
OV-17	27.4	244	756	1.264	0.9
OV-22	33.3	278	722	1.277	−0.2
OV-25	35.9	302	698	1.286	1.8
QF-1	46.6	303	697	1.287	0.5
OV-215	47.9	267	733	1.273	0.0
Ucon 50HB-2000	49.6	329	671	1.298	−1.1
OV-225	56.4	284	716	1.279	−0.3
Igepal Co-990	67.5	527	472	1.424	0.0
CW 6000	72.0	416	584	1.342	−0.6
CW 20M	72.0	430	570	1.351	−0.4
Superox 20M	71.9	354	646	1.309	0.0

RP = Retention polarity of Szentirmai et al. [5]; $K_{c,Z}$, calculated from Eq. 2; S_c of decane, calculated from $S_{c,10} = 1000 - K_{c,Z}$; $F = 1 + 100(Z - 10)/S_{c,10}$.

[a] DIOPH = Diisooctyl phthalate; TFPS26% = 26% trifluoroporpylsiloxane.

Table 2

Prediction of V_g of the *n*-alkanes $Z = 6$–12 on OV-22 from decane data

Z	F	V_g(exp.)	V_g(calc.)	Deviation, δ
6	0.4464	6.2	6.3	−0.1
7	0.5848	11.0	11.2	−0.2
8	0.7232	19.6	19.7	−0.1
9	0.8616	34.9	34.9	0.0
10	1.0	61.9		
11	1.1384	109.4	109.5	−0.15
12	1.2768	193.6	193.8	−0.2
				Mean: −0.12

Data: $K_{c,Z} = 277.5$; $S_{c,10} = 722.5$; log $V_{g,10} = 1.7915$; $F = 1 + 100(Z - 10)/722.5$.

Table 3

Linear regression of the "log-plot" slope, *b*, vs. the reciprocal of the absolute temperature, $b(T) = A/T + B$

Stationary phase	A[a]	B[a]	r_1
PS-255	208.3 ± 2.4	−0.2785 ± 0.006	0.9993
OV-105	207.7 ± 0.84	−0.2795 ± 0.002	0.99998
Didecyl phthalate	217.2 ± 4.0	−0.2689 ± 0.01	0.99959
QF-1	189.1 ± 3.0	−0.2749 ± 0.007	0.99985
OV-215	182.0 ± 6.1	−0.2572 ± 0.015	0.99888
Superox 20M	189.9 ± 5.4	−0.2575 ± 0.014	0.99920

[a] Values ± standard deviations ($n = 5$).

Table 4
α and β LSR parameters of $S_{c,t}$ vs. the absolute temperature and A' and B' LSR parameters of log $V_{g,i}$ vs. reciprocal of absolute temperature for five solutes in six stationary phases

Solute	Stationary phase	α	β	r_2	A'	B'	r_3
Dodecane	OV-105	−1.085	1468	0.992	2547	−3.9	0.9999
Benzene		−0.812	850	0.991	1390	−2.2	0.99995
1-Butanol		−1.204	1007	0.993	1520	−2.5	0.9996
2-Pentanone		−1.033	965	0.995	1479	−2.4	0.9978
Pyridine		−0.752	926	0.998	1578	−2.4	0.99999
Dodecane	PS-255	−1.118	1494	1.000	2750	−4.3	0.99887
Benezene		−0.781	831	0.997	1492	−2.5	0.99927
1-Butanol		−1.142	955	0.99	1496	−2.5	0.9979
2-Pentanone		−1.343	1051	0.99	1581	−2.7	0.9994
Pyridine		−0.835	935	0.971	1652	−2.7	0.99866
Dodecane	Didecyl phthalate	−1.14	1442	0.998	2665	−3.96	0.9993
Benzene		−0.84	861	0.995	1522	−2.4	0.9994
1-Butanol		−1.46	1126	0.997	1846	−3.1	0.9985
2-Pentanone		−1.19	1021	0.993	1727	−2.8	0.998
Pyridine		−0.96	1035	0.993	1866	−2.9	0.994
Dodecane	QF-1	−2.06	1710	0.999	2333	−4.1	0.9996
Benzene		−1.903	1248	0.971	1476	−2.7	0.9993
1-Butanol		−1.763	1229	0.997	1527	−2.8	0.9979
2-Pentanone		−1.69	1360	0.987	1809	−3.2	0.9995
Pyridine		−1.593	1351	0.992	1843	−3.2	0.9992
Dodecane	OV-215	−2.13	1764	0.993	2327	−4.0	0.99999
Benzene		−1.310	1053	0.95	1470	−2.6	0.99986
1-Butanol		−1.567	1181	0.999	1508	−2.7	0.99987
2-Pentanone		−1.64	1378	0.987	1780	−3.0	0.99972
Pyridine		−1.21	1228	0.992	1702	−2.8	0.99973
Dodecane	Superox 20M	−1.235	1385	0.991	2163	−3.5	0.99993
Benzene		−0.83	1001	0.990	1592	−2.5	0.99993
1-Butanol		−1.4	1378	0.990	2077	−3.4	0.99995
2-Pentanone		−1.585	1303	0.926	1859	−3.2	0.99693
Pyridine		Unavailable					

contrast, the method cannot be recommended for polar SPs owing to the known deficiencies concerning the adequacy of n-alkanes as standard probes in polar SPs, and further, the measured retention times of the smaller n-alkanes in these SPs are erratic [14,19]. Obviously, the easiest way to obtain the specific retention volume of any n-alkane is by means of the plot of log $V_{g,Z}$ vs. Z, which has to be available, but the method suggested in this paper calculates V_g values using the V_g of decane and the Kováts coefficient, $K_{c,Z}$, b not being needed. According to Eq. 2, however, b would be needed to

calculate an experimental value of $K_{c,Z}$ but the method with Eq. 6 uses an empirical value of $K_{c,Z}$ obtained by its correlation with the RP of the SP (Table 1 shows that $K_{c,Z}$ increase with increasing RP of 21 SPs). The author has worked on this correlation [15], finding a correspondence between these two magnitudes, and subsequently some empirical equations allowing $K_{c,Z}$ to be calculated were found; hence in this case it is sufficient to chromatograph decane to be able to predict the V_g of any n-alkane for any stationary phase of the known first five McReynolds constants at 120°C.

Table 5
V_g prediction for ten solutes on OV-215 and for 1-butanol on Superox 20M at four temperatures

Ten solutes on OV-215

Solute	Temperature (°C)	V_g(exp)	V_g(calc.)	Rel. error (%)
Nonane	100	35.2	34.9	0.8
Benzene	100	20.5	20.1	1.9
Pyridine	100	63.5	61.9	2.5
N,N-Dimethylaniline	155	52.4	51.2	2.2
1-Pentanol	160	10.0	9.7	3.2
1-Octanol	100	217.1	217.8	0.3
2-Octanone	145	57.7	55.9	3.1
Butyronitrile	130	36.9	35.2	4.6
Ethyl acetate	100	27.1	25.1	7.3
Pentylbenzene	115	142.7	145.1	−1.7
			Mean:	2.4

1-Butanol on Superox 20M

Temperature (°C)	b[a]	$S_{c,i}$[b]	V_g(exp)	V_g(calc.)	Rel. error (%)
90	0.2656	869.5	204.5	203.9	0.3
110	0.2383	841.5	102.8	101.2	1.5
130	0.2137	813.5	55.3	54.7	1.1
150	0.1914	785.5	31.6	31.9	0.9
				Mean:	0.9

[a] $b = 189.9/T - 0.2575$.
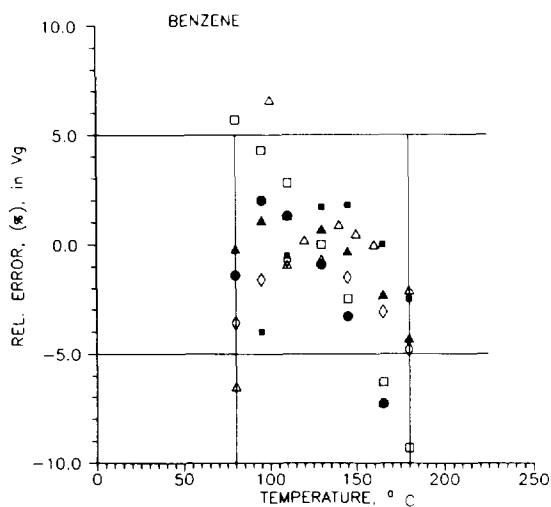[b] $S_{c,i}(T) = -1.4T + 1378$.

Fig. 2. Relative error (%) in V_g (calculated from Eq. 10a) for benzene vs. column temperature on six stationary phases: PS-255, OV-105, didecyl phthalate. QF-1, OV-215 and Superox 20M. Temperature range, 80–180°C.
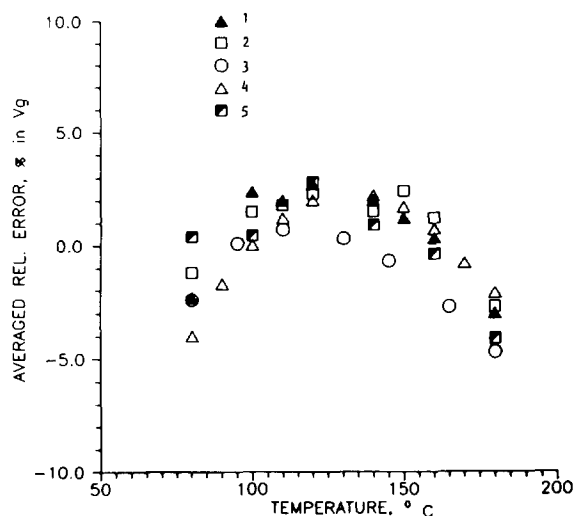

Fig. 3. Relative error (%) in V_g (calculated from Eqs. 10a and 10b) averaged for six stationary phases (PS-255, OV-105, didecyl phthalate, QF-1, OV-215 and Superox 20M) for the solutes octane (5), benzene (3), 1-butanol (1), 2-pentanone (4) and pyridine (2).

4.2. Prediction of V_g of any solute at any temperature

Retention data at several temperatures for six stationary phases are available, from which the dependences of b, $K_{c,z}$ and $S_{c,i}$ on temperature can be obtained. $V_{g,i}$ values at any temperature can be calculated from Eqs. 10a and 10b for non-n-alkanes and n-alkanes, respectively. The equations for the dependence of $K_{c,z}$ on temperature are given elsewhere [1,9]. Other data necessary for carrying out the calculations are given in Tables 3 and 4.

Table 3 presents the b temperature-dependence equations for six SPs [9–13]. Table 4 shows the α and β LSR parameters of the $S_{c,i}$ temperature-dependence equations and the A' and B' LSR parameters of the log V_g vs. $1/T$ dependence equations for the solutes dodecane, benzene, 1-butanol, 2-pentanone and pyridine on the same six stationary phases [9–13].

The V_g values in Table 4 are the experimental values against which the V_g values calculated from Eqs. 10a and 10b are compared.

Table 5 shows (a) calculated V_g values for ten solutes on OV-215 stationary phase, yielding a mean error of 2.4%, and (b) the predicted V_g

values of 1-butanol at four temperatures in Superox 20M. Using as data the equations in Table 3 and the equation log $V_g = 2077.5/T - 3.41$, taken from Ref. [12], a mean relative error of 0.9% is obtained. Calculated V_g values for benzene and dodecane on six SPs at 120°C [9–12] are shown in Table 6. The mean relative errors are −0.7 and −1.4%, respectively.

Hence, at 120°C and at moderate temperatures between 70–80°C and 180–200°C, the V_g prediction of the tested solutes on the studied SPs is acceptable.

To find the temperature limits for this prediction, the V_g relative errors of n-alkanes and solutes in Table 4 on the six SPs were plotted versus temperature over the range 80–180°C. Fig. 2 shows the plot for benzene. A band of permissible relative errors was obtained by drawing two horizontal lines at relative errors of 5% and −5%. If two vertical lines are drawn at the temperatures 80 and 180°C, most points fall inside the rectangle of the 5% permissible error. The solute is described by six curves, one for each stationary phase. Similar results were found when the other solutes were studied.

Fig. 3 shows the plot of the sum of the relative errors in V_g for octane and the four non-n-

Table 6
V_g prediction for benzene and dodecane on six stationary phases at 120°C

Solute	Stationary phase	V_g(exp.)	V_g(calc.)	Rel. error (%)
Benzene	PS-255[a]	32.1	32.3	−0.6
	OV-105	21.0	20.9	0.3
	DNDPH[b]	31.6	32.0	1.3
	QF-1	10.5	10.7	−1.9
	OV-215	12.6	13.0	−3.2
	Superox 20M	33.2	33.2	0.0
				Mean: −0.7
Dodecane	PS-255[a]	997.5	1034.9	−3.7
	OV-105	392.2	388.8	0.9
	DNDPH[b]	639.3	658.7	−3.0
	QF-1	70.5	71.7	−1.7
	OV-215	81.0	80.6	−0.5
	Superox 20M	106.1	106.2	−0.01
				Mean: −1.4

[a] Temperature 100°C.
[b] DNDPH = Didecyl phthalate.

alkanes, averaged over the six SPs in the same temperature range. The curves show a maximum at about 130°C, and most errors are under 5%. Hence, the method seems to be applicable from 80 to 180°C.

4.3. Prediction of V_g in a homologous series at 120°C

Theoretically, this type of prediction looks feasible, although with some reservations. Experimental data [9–13] and ΔS_c values for PS-255, QF-1, OV-215 and Superox 20M are available [1]. Therefore, V_g values of different members of some homologous series were tried. Prediction of V_g for the members $Z = 7$, 8 and 9 of the 1-alkanols on Superox 20M yields a mean relative error of 5.7%; prediction of V_g of the $Z = 3$, 6, 7 and 9 members of 1-alkanols on OV-215 yields a mean error of 3.4%, and unbranched nitriles $Z = 6$, 7 and 8 on QF-1 yield a mean error of 3.9%.

Better results are obtained for the TFPS26%

stationary phase [13], as Table 7 shows for the functional groups methyl ketones, 1-alkanols, n-alhylamines and unbranched nitriles, with mean errors of 1.8, 3.3, 4.8 and 0.3%, respectively. However, in other cases in which predictions were made testing Eq. 13 on McReynolds data [16] the predicted V_g values differed widely from the experimental values, irrespective of whether the correlations of ΔS_c with RP were fair [1]; the failure may be due to the fact of V_g may not depend only on a single variable when chemical functions are involved because the magnitudes taking part in the V_g approximate calculations, i.e., $K_{c,Z}$, b and $S_{c,i}$, may also depend on some additional factors to the SP polarity itself, e.g., the solute polarity; obviously, a multiparametric equation similar to that suggested by Abraham et al. [8] would yield much better results. The work of Takacs [17] and Peng et al. [18] shows the way in which these investigations must be carried out.

Hence the equation proposed in this paper only works when experimental data on the functional group investigated are available, and

Table 7
V_g relative errors of members of four homologous series on the TFPS26% stationary phase at 120°C

Homologous series	Compound	V_g(exp)[a]	V_g(calc.)	Rel. error (%)
Ketones	2-Pentanone	28.4	28.6	−0.7
	2-Hexanone	48.0	48.6	−1.3
	2-Nonanone	230.7	238.9	−3.5
				Mean: −1.8
1-Alkanols	Ethanol	5.3	5.5	−3.7
	1-Hexanol	46.7	46.0	−1.5
	1-Heptanol	80.5	78.2	−2.8
	1-Nonanol	238.7	225.7	−5.4
				Mean: −3.3
Amines	Ethylamine	4.6	4.8	−4.2
	n-Heptylamine	70.8	67.7	−4.3
	n-Octylamine	122.4	113.1	−5.9
				Mean: −4.8
Nitriles	n-Hexanitrile	93.7	93.9	−0.2
	n-Octanitrile	270.0	271.1	−0.4
				Mean: −0.3

$\Delta S_c = 344$ for ketones, 334 for 1-alkanols, 307 for amines and 468.5 for nitriles [1]. $RP = 27$; $K_{c,Z} = 212$; $b = 0.2303$.
[a] Measured V_g values taken from Ref. [13].

therefore its use in predictive studies of V_g in all instances cannot be recommended.

5. Conclusions

The $S_{c,i}$ values of solutes and the $K_{c,Z}$, RP and b parameters of stationary phases can be used to calculate in an approximate way the specific retention volumes of a series of solutes in two cases: (a) at 120°C, for low-polarity stationary phases, the V_g of any n-alkane if the $K_{c,Z}$ of the stationary phase (or $S_{c,10}$) and the V_g of n-decane are known; (b) at any temperature between 80 and 180°C, it is possible to predict with acceptable errors $V_{g,i}$ values for a series of solutes provided that the relevant $K_{c,Z}$, $S_{c,i}$ and b temperature dependences are known.

Extension of ΔS_c to predictive V_g determinations is not suitable for functional groups unless data on the relevant chemical function are available. It is emphasized that the model proposed in this paper is valid only if the assumption is made that the retention mechanism occurs exclusively by gas–liquid partitioning.

Symbols

SP	stationary phase
RP	retention polarity
$K_{c,Z}$	Kováts coefficient for a given SP
$S_{c,Z}$	molecular structural coefficient of a Z n-alkane
$S_{c,i}$	molecular structural coefficient of a solute i
$S_{c,10}$	S_c value for decane
I_i	retention index of a solute i
$100Z$	retention index of a Z n-alkane
$V_{g,Z}$	specific retention volume of a Z n-alkane
$V_{g,i}$	specific retention volume of a solute i
ΔS_c(function)	molecular structural coefficient increment of a functional group
b	slope of the plot of log $V_{g,Z}$ vs. the number of carbon atoms, Z
F	methylene group factor

LSR	least-squares regression
MLRA	multiple linear regression analysis
a_1, a_2	LSR parameters for the temperature dependence of $K_{c,Z}$
α, β	LSR parameters for the $S_{c,i}$ temperature dependence
A, B	LSR parameters of the b temperature dependence
A', B'	LSR parameters of the log $V_{g,i}$ temperature dependence
m, n	LSR parameters of the dependence of ΔS_c(function) on RP of a stationary phase
r_1, r_2, r_3	correlation coefficients
δ	V_g absolute deviation: $V_{g,i}$(exp) $-$ $V_{g,i}$(cal)
$V_{g,i}$(exp)	measured $V_{g,i}$
$V_{g,i}$(cal)	specific retention volume of a solute i calculated by means of Eqs. 6, 10a, 10b and 13
Rel. error (%)	Relative error of V_g: $100\{[V_{g,i}(\text{exp}) - V_{g,i}(\text{cal})]/V_{g,i}(\text{exp})\}$

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