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Hold-up time in gas chromatography V. Dependence of the retention of *n*-alkanes on the chromatographic variables in isothermal gas chromatography

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Abstract

The chromatographic behaviour of *n*-alkanes and other homologous series in isothermal gas chromatography has been shown to depart from the "linear" representation of the logarithms of the adjusted retention times vs. carbon number. One of the expressions proposed to describe this behaviour is $t_R(z) = A + \exp(B + Cz^D)$. In this paper, a regression analysis shows that three of the parameters of the equation depend on different chromatographic variables such as hold-up time, average linear gas velocity, volume and polarity of the stationary phase and temperature of the column. The fourth parameter (*D*), responsible for the departure from the "linearity", does not depend on any chromatographic variable, and represents a gradual decrease of the contribution of the methylene groups to the general properties of *n*-alkanes, with no relation to the chromatographic phenomenon. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Many chromatographic and thermodynamic parameters of the analytes, the stationary phase and their mutual interactions, and also of the chromatographic system itself, may be obtained from a chromatogram. For that purpose, the exact point where a truly non-retained analyte would appear must be known. Adjusted retention times; retention volumes; distribution constant or partition coefficient; theoretical and effective plate numbers of the

column; separation factor; relative retention of peaks; resolution of peaks; peak capacity; separation number or Trennzahl; Kovàts' retention indices, may all be obtained. Additionally, if no time or volume errors are introduced (extracolumn volumes, etc.) then, that point of the chromatogram will correspond to the true hold-up time, and so, other system-dependent parameters may be obtained: retention factor; retardation factor; phase ratio; hold-up volume and average linear mobile phase velocity.

The absence of a truly unretained substance has forced the apparition of "mathematical" procedures based on the retention of the components of homologous series. Reviews of methods available may be found in publications of Smith et al. [1] and of

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Pakákova and Felt [2]. Traditionally a fit of retention times of *n*-alkanes to Eq. (1) below has been used to calculate hold-up times, *z* being the chain length of the *n*-alkane:

$$\ln t'_R = B + Cz \quad (1)$$

For many years since the presentation of gas chromatography in 1952, it was accepted that the chromatographic behaviour of *n*-alkanes and other homologous series was such that, for an isothermal chromatogram, the plot of the left hand side of Eq. (1) vs. *z* described a straight line of slope *C*. This fact was the basis for the universally accepted Kováts' retention index system [3]. However, departures from linearity have been presented [1,4–10] and explained [4,11–13] from time to time.

One of the equations proposed to describe the behaviour of *n*-alkanes in isothermal chromatograms, is Eq. (2) below, which has been tested for capillary and packed columns, and for polar and apolar stationary phases [7,8]:

$$t_R = A + \exp(B + Cz^D) \quad (2)$$

The equation has been designed to find a better way of deducing the hold-up time in isothermal chromatograms with greater accuracy than the classical methods based on Eq. (1). The use of Eq. (2) has been referred to as the LQG method. It has also been shown that Eq. (2) describes the chromatographic behaviour of the *n*-alkanes better than any of the other 24 expressions tested [7], for *n*-alkanes from 1 to 17 carbon atoms. A possible explanation of this behaviour has been given from a structural point of view [11–13].

Eq. (2) has four adjustable parameters (*A*, *B*, *C* and *D*). The value of each one of the parameters must be associated with some of the chromatographic variables involved in the chromatogram: nature and amount of stationary phase, physical dimensions of the column and its type, chromatographic conditions, etc., as all of them affect the retention of the *n*-alkanes.

This study was undertaken in order to find out which of the chromatographic variables is associated with each one of the above parameters, and to try to explain its chromatographic meaning.

2. Experimental

2.1. Apparatus

Most experiments were carried out using nitrogen as carrier gas on a Hewlett-Packard HP 5890 A gas chromatograph fitted with a flame ionization detector. A Fisons 8035 gas chromatograph coupled to a Fisons MD 800 quadrupole mass filter operating in the electron impact mode was used for some experiments. In this case, the gas leaving the chromatographic column (helium) was fed to the mass spectrometer through a direct line of fused-silica tubing of 0.1 mm internal diameter introduced into the column end. In this way, column outlet pressure was maintained at ambient pressure (i.e., normal chromatographic conditions).

Table 1 summarises the characteristics of the capillary columns used to obtain 526 isothermal chromatograms, at temperatures between 60 and 150°C and at different carrier gas velocities. Although Eq. (2) has been tested for all *n*-alkanes from 1 to 17 carbon atoms, experimental retention times used for this study include methane, and *n*-alkanes from 5 to 17 carbon atoms, depending on the temperature of the column.

Chromatograms involving mass spectrometry were obtained in the selected ion recording mode (SIR) with a cycle time of 0.04 s for column 16 and 0.2 s for columns 17 and 18.

2.2. Numerical calculations

In order to find out the dependence of the parameters of Eq. (2) on the various chromatographic variables, chromatograms were run on the 18 columns of Table 1 under different conditions. For each set of conditions, a minimum of five chromatograms were run, with an average of about 10 chromatograms in each case. Experimental retention times of all *n*-alkanes eluted in the same chromatogram, including methane, were fed to a computer program in order to apply the LQG method to find the values of the four parameters *A*, *B*, *C* and *D* of Eq. (2) for that chromatogram. The computer program, written in Fortran, uses a regression procedure that obtains least squares estimates of the parameters by minimising the residual sum of squares [14].

Table 1
Characteristics of the chromatographic columns

Column	Tube material	Stationary phase ^a	<i>L</i> (m)	<i>d_c</i> (mm)	<i>d_f</i> (μm)	<i>β</i>	<i>c_s</i> (mg/cm ³)	Supplier
1	Borosilicate glass	TFPS-00	22.6	0.224	0.200		3.48	Laboratory-made
2	Borosilicate glass	TFPS-00	30.1	0.225	0.300		5.20	Laboratory-made
3	Borosilicate glass	TFPS-00	22.3	0.224	0.399		6.95	Laboratory-made
4	Borosilicate glass	TFPS-12	25.7	0.207	0.200		4.12	Laboratory-made
5	Borosilicate glass	TFPS-12	24.7	0.211	0.300		6.07	Laboratory-made
6	Borosilicate glass	TFPS-12	26.7	0.209	0.403		8.24	Laboratory-made
7	Borosilicate glass	TFPS-26	26.0	0.210	0.199		4.48	Laboratory-made
8	Borosilicate glass	TFPS-26	25.3	0.214	0.300		6.61	Laboratory-made
9	Borosilicate glass	TFPS-26	24.0	0.214	0.401		8.83	Laboratory-made
10	Borosilicate glass	TFPS-35	26.4	0.214	0.200		4.63	Laboratory-made
11	Borosilicate glass	TFPS-35	25.3	0.214	0.299		6.92	Laboratory-made
12	Borosilicate glass	TFPS-35	26.1	0.211	0.399		9.36	Laboratory-made
13	Borosilicate glass	TFPS-50	25.7	0.212	0.201		4.99	Laboratory-made
14	Borosilicate glass	TFPS-50	25.7	0.216	0.300		7.32	Laboratory-made
15	Borosilicate glass	TFPS-50	26.1	0.214	0.401		9.86	Laboratory-made
16	Fused-silica	CPSIL-5CB	50.0	0.320	0.430	186		Chrompack
17	Fused-silica	HP-5	60.0	0.250	0.250	250		HP
18	Fused-silica	HP-INNOWAX	60.0	0.250	0.250	250		HP

^a TFPS-XX: Poly(3,3,3-trifluoropropylmethylsiloxane) with XX% substitution of trifluoropropyl group (synthesized in our laboratories); CPSIL-5CB: poly(dimethylsiloxane); HP-5: crosslinked poly(phenylmethyl siloxane) with 5% substitution of phenyl group; HP-INNOWAX: crosslinked poly(ethylene glycol); *L*: column length; *d_c*: column internal diameter; *d_f*: thickness of liquid phase film at 25°C; *β*: phase ratio; *c_s*: concentration of the solution of stationary phase used to prepare the capillary column [13,14]; HP: Hewlett-Packard.

The relationship between the parameters of Eq. (2) and the different chromatographic variables was investigated by applying a partial least-squares regression (PLS). PLS regression is a bilinear modeling method where information in the original *x*-data is projected onto a small number of underlying (“latent”) variables called PLS components. The *y*-data are actively used in estimating the “latent” variables to ensure that the first components are those that are most relevant for predicting the *y*-variables. This action serves to minimise the potential effects of *x*-variables having large variances but which are irrelevant to the calibration model. Interpretation of the relationship between *x*-data and *y*-data is then simplified, as this relationship is concentrated on the smallest possible number of components. Calculations were carried out using The Unscrambler 7.01 program (Camo AS).

2.3. The choice of the chromatographic variables

As it has been mentioned, the aim of this work is to find out the effect of the chromatographic con-

ditions on the values of the four parameters of Eq. (2). On selecting the variables, it was considered that they should be easily obtained with sufficient accuracy for the purpose. The choice has been made considering Eq. (2) rewritten in a different way:

$$t_R = A + \exp(B) \exp(Cz^D) \quad (3)$$

The first part of Eq. (3), $A + \exp(B)$, does not depend on the number of carbon atoms of the *n*-alkane. Therefore, it should not depend on the nature of the stationary phase, but rather on the dimensions of the column and perhaps on the temperature and flow-rate.

The second part of the expression is $\exp(Cz^D)$, obviously depending on the actual *n*-alkane considered. This term must reflect the retention of the substance, and should be affected by the variables that modify the solute–stationary phase interactions.

The final choice of the variables to be taken into account was as follows:

As variables related to the working conditions and physical characteristics of the columns, the selection

was the temperature of the column (θ_c), the average linear carrier gas velocity (\bar{u}), the volume of the stationary phase (V_S) and the hold-up time (t_M).

The description of the stationary phase may be done in several ways. For the purpose of this discussion, it was considered essential to choose variables that represented both its chemical nature and perhaps its appearance. The final decision was to use the density (ρ_S) and the retention polarity (\bar{P}_R) at 120°C:

$$\bar{P}_R = 20 \sum_{i=1}^5 \frac{\Delta I_i}{I_i^{SQ}} = 20 \sum_{i=1}^5 \frac{I_i^P - I_i^{SQ}}{I_i^{SQ}} \quad (4)$$

where: ΔI_i = McReynolds' constant of probe i ; I_i^P = retention index of the McReynolds' probe i in the stationary phase and I_i^{SQ} = retention index of the McReynolds' probe i in squalane.

As an estimate of t_M , the experimental retention time of methane [$t_R(\text{CH}_4)$] was used. This gas has been shown to be retained on stationary phases under any condition, but for the purpose of the work presented in this paper, this retention is irrelevant. The retention time of methane was also used to deduce \bar{u} . The volume of stationary phase was deduced as follows: for columns made in our laboratory, it was calculated from density (ρ_S) and mass (W_S) data [15,16]; for commercial columns, V_S was deduced from the density and the phase ratio (β) as reported by the manufacturers. Densities of the stationary phases were determined by a picnometric method, except for columns 17 and 18, which were taken from Ref. [17].

The values of the chromatographic variables selected are gathered in Table 2. Values of \bar{u} , $t_R(\text{CH}_4)$, A , B , C and D are in all cases the mean value of the various chromatograms run under identical conditions (between 5 and 27 injections).

3. Results and discussion

Values of the parameters A , B , C and D , from Table 2, corresponding to capillary columns of various film thickness, taken from chromatograms run at different temperatures and linear carrier gas velocities, were correlated by a PLS method to the

six chromatographic variables mentioned above (Table 2). The correlation is carried out in such a way, that all six variables are used for each parameter.

Results may be explained by examination of Figs. 1–4, each one divided into three parts:

(i) In all figures, part (a) represents the variance explained with the number of PLS components used in the regression. This allows us to take the decision on the number of PLS components needed to build the model. This decision must be made bearing in mind that the model should include the number of PLS components that explain most of the variance.

(ii) Part (b) is a representation of the experimental value of the parameter (from Table 2) versus the value deduced from the model, which has been built with the number of PLS components deduced according to Figure (a). Part (b) gives an idea of the goodness of fit obtained.

(iii) Part (c) of the figures, shows the values of the regression coefficients for the different chromatographic variables. The higher the absolute value of one of those coefficients, the greater the effect of the variable on the corresponding parameter of the equation.

3.1. Parameter A

Fig. 1a shows that one of the PLS components explains almost 100% of the variance of the values of this parameter in Table 2. This is confirmed with Fig. 1b, which presents an excellent agreement between experimental and theoretical values when only one PLS component is used for the model, with a regression coefficient of 0.9996. Fig. 1c indicates that, according to the model, parameter A depends almost exclusively on the retention time of methane, something that, in a way, should have been expected.

The dependence of A on $t_R(\text{CH}_4)$ is direct (positive coefficient): the higher $t_R(\text{CH}_4)$, the higher the value of A . In a way, it may be interpreted that A gives an idea of the time that the mobile phase would take to pass through the part of the column not occupied by the stationary phase. An examination of Table 2 shows that A is always slightly smaller than the retention time of methane, which has been shown to be retained in all cases [7,8].

Table 2

Mean values of the chromatographic variables and the parameters of Eq. (2) under different conditions^a

Column	θ_c (°C)	\bar{u} (cm/s)	ρ_s (g/cm ³)	V_s (mm ³)	\bar{P}_R	t_R (CH ₄) (s)	A	B	C	D
1	120	9.2	0.889	3.49	6.33	245.5	244.80	-0.9474	0.6797	0.9847
2	80	16.1	0.926	6.72	6.33	187.4	186.47	-0.9244	0.8489	0.9478
	100	16.1	0.907	6.86	6.33	186.5	185.61	-0.8938	0.7586	0.9476
	120	8.1	0.889	7.00	6.33	371.6	369.93	-0.1679	0.6790	0.9477
	120	15.7	0.889	7.00	6.33	191.8	190.94	-0.8406	0.6837	0.9455
	120	16.1	0.889	7.00	6.33	187.4	186.57	-0.8635	0.6840	0.9457
	120	20.8	0.889	7.00	6.33	144.6	143.93	-1.1295	0.6866	0.9441
	140	16.0	0.871	7.15	6.33	187.9	187.14	-0.8573	0.6271	0.9396
3	120	13.7	0.889	6.87	6.33	163.0	162.00	-0.6884	0.6764	0.9488
4	120	13.5	0.980	3.64	15.21	191.0	190.43	-1.2083	0.6781	0.9397
5	80	13.4	1.017	5.15	15.21	184.3	183.38	-0.8982	0.8308	0.9460
	100	13.4	0.999	5.25	15.21	184.2	183.29	-0.8538	0.7389	0.9469
	120	10.2	0.980	5.35	15.21	242.9	241.79	-0.5451	0.6649	0.9454
	120	13.4	0.980	5.35	15.21	184.2	183.32	-0.8392	0.6697	0.9430
	140	13.4	0.961	5.45	15.21	183.7	182.86	-0.8137	0.6059	0.9403
6	120	13.4	0.980	7.70	15.21	199.7	198.47	-0.4253	0.6615	0.9467
7	120	11.3	1.073	3.76	26.89	231.1	230.41	-1.0836	0.6469	0.9369
8	80	12.3	1.118	5.38	26.89	205.4	204.39	-0.8166	0.7798	0.9493
	100	12.3	1.095	5.49	26.89	205.6	204.76	-0.8424	0.7182	0.9398
	120	10.4	1.073	5.61	26.89	242.3	241.32	-0.6239	0.6390	0.9408
	120	12.4	1.073	5.61	26.89	204.3	203.47	-0.7998	0.6419	0.9395
	140	12.3	1.050	5.73	26.89	205.5	204.63	-0.7419	0.5738	0.9397
9	120	11.5	1.073	7.09	26.89	208.1	206.96	-0.4669	0.6283	0.9454
10	120	7.4	1.110	3.96	35.01	356.6	355.65	-0.6851	0.6056	0.9445
11	80	11.5	1.163	5.41	35.01	220.7	219.70	-0.8469	0.7549	0.9474
	100	11.5	1.137	5.54	35.01	219.6	218.70	-0.8132	0.6750	0.9458
	120	9.8	1.110	5.67	35.01	259.0	258.02	-0.6018	0.6031	0.9453
	120	11.5	1.110	5.67	35.01	220.5	219.65	-0.7878	0.6107	0.9416
	140	11.5	1.084	5.81	35.01	220.0	219.20	-0.7763	0.5566	0.9364
12	120	9.9	1.110	7.68	35.01	264.2	262.87	-0.2953	0.6150	0.9397
13	120	10.0	1.193	3.79	49.16	256.9	256.38	-1.2092	0.5831	0.9333
14	80	9.7	1.245	5.54	49.16	264.9	263.97	-0.8196	0.7084	0.9450
	100	9.6	1.219	5.66	49.16	266.6	265.72	-0.7928	0.6395	0.9400
	120	6.4	1.193	5.78	49.16	400.0	398.70	-0.3289	0.5675	0.9406
	120	9.7	1.193	5.78	49.16	265.8	265.04	-0.7737	0.5793	0.9348
	120	9.9	1.193	5.78	49.16	258.8	258.01	-0.7934	0.5755	0.9367
	120	16.5	1.193	5.78	49.16	155.8	155.32	-1.2413	0.5592	0.9444
	140	9.6	1.167	5.91	49.16	267.0	266.19	-0.7623	0.5324	0.9264
15	120	9.9	1.193	7.76	49.16	262.8	261.70	-0.4607	0.5656	0.9413
16	60	25.6	0.944	22.78	6.33	195.3	194.01	-0.8103	0.9553	0.9520
	90	23.7	0.916	23.47	6.33	211.4	210.22	-0.6953	0.8070	0.9506
	120	22.3	0.889	24.19	6.33	224.6	223.56	-0.6093	0.6939	0.9460
	150	21.2	0.861	24.97	6.33	236.0	235.02	-0.5225	0.5995	0.9417

Table 2 (continued)

Column	θ_c (°C)	\bar{u} (cm/s)	ρ_s (g/cm ³)	V_s (mm ³)	\bar{P}_R	t_R (CH ₄) (s)	A	B	C	D
17	60	18.6	0.955	12.29	10.51	322.8	321.65	-0.8902	0.9895	0.9445
	90	17.4	0.920	12.75	10.51	344.0	342.89	-0.7589	0.8291	0.9463
	120	16.6	0.885	13.25	10.51	361.8	360.78	-0.6537	0.7056	0.9452
	150	15.9	0.851	13.79	10.51	377.4	376.39	-0.5986	0.6174	0.9379
18	90	17.6	1.064	11.03	71.91	340.8	340.46	-1.8787	0.6541	0.9787
	120	16.7	1.035	11.34	71.91	358.3	358.07	-1.8364	0.5986	0.9566

^a θ_c : Column temperature; \bar{u} : average linear gas velocity; ρ_s : stationary phase density; V_s : volume of stationary phase in column; \bar{P}_R : retention polarity at 120°C; t_R (CH₄): retention time of methane; A, B, C and D, adjustable parameters of Eq. (2).

3.2. Parameter B

Fig. 2a shows that the five PLS components are needed for the model, to explain almost 70% of the variance for parameter B of Eq. (2). Fig. 2c makes it clear that B depends mainly on the volume of stationary phase and the average linear velocity of the mobile phase, increasing with V_s (positive coefficient) and decreasing when the linear gas velocity increases (negative coefficient).

On the other hand, according to the model described by Eq. (2), the hold-up time would be the retention time of a hypothetical *n*-alkane of zero carbon atoms [7,8], as follows:

$$t_M = A + \exp B \quad (5)$$

involving both parameters A and B. Therefore, the hold-up time, as deduced from Eq. (5), is the sum of the time required for the mobile phase to pass through the volume of column outside the stationary phase (parameter A) plus an additional term ($\exp B$). The latter might be interpreted bearing in mind that polymers are most permeable to permanent gases [18]. Therefore, the mobile phase molecules will penetrate the stationary phase by a purely mechanical effect. When these molecules return to the mobile phase, their velocity component in the axial direction will be zero, and this will retard slightly the overall movement of the gas, increasing the residence time of the mobile phase in the column. The effect will be more pronounced for columns with larger volumes of stationary phase but less noticeable at high linear gas velocities (Fig. 2c). This penetration of the mobile phase does not imply any affinity or interaction solute–stationary phase, which will be present only

in the case of retained solutes. It may be observed that the value of t_M calculated for all cases of Table 2 by Eq. (5) is still shorter than the retention time of methane.

3.3. Parameter C

According to Fig. 3a, two PLS components explain more than 90% of the variance of this parameter, with a reasonable correlation between theoretical and experimental values ($r=0.9678$, Fig. 3b). Fig. 3c shows that C depends mainly on the temperature of the column and the polarity of the stationary phase, decreasing as any of them increases. It may be deduced from Eq. (2), that parameter C represents an increase of the retention time due to the interaction of the methylene groups of the *n*-alkane with the stationary phase. Fig. 3c shows clearly something which is well known to all chromatographers: retention of *n*-alkanes increases with the number of carbon atoms (Eq. (2)), but in all cases decreases with increasing temperature and polarity of the stationary phase.

This parameter is equivalent to parameter C of the classical equation generally accepted up to recently to explain the behaviour of *n*-alkanes in isothermal chromatograms (Eq. (1)), and has been explained by several authors as representing the mean contribution of the methylene group to the interactions of solute–stationary phase [19,20].

3.4. Parameter D

The result of the correlation of this parameter with the chromatographic variables, shown as Fig. 4a, indicates that none of the independent variables tried

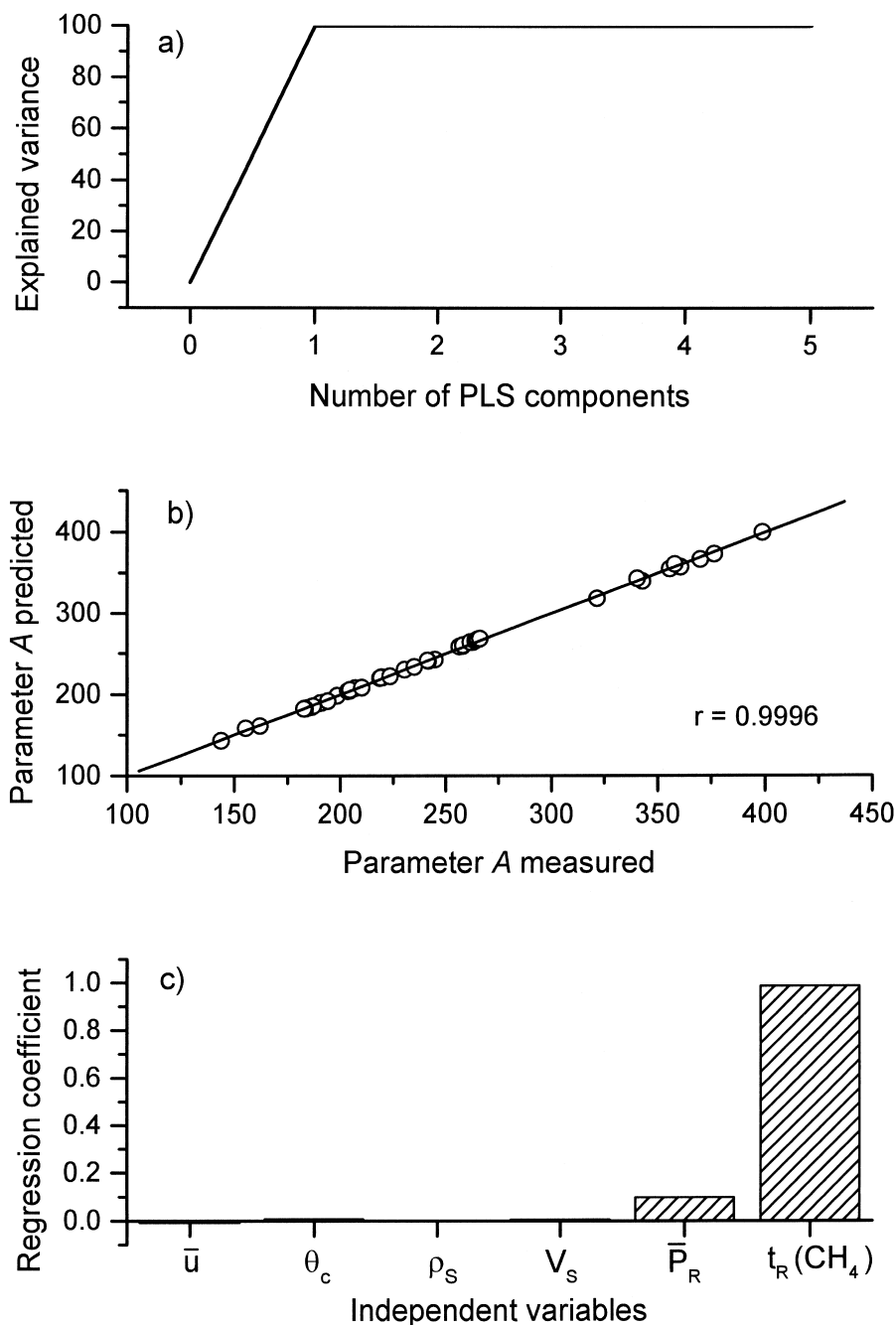


Fig. 1. Results of the PLS regression analysis for parameter A.

has any significant effect on D . It is clear that in the best case, three PLS components explain only 13% of the variance, without any improvement by in-

creasing their number. This is confirmed by the large dispersion of the points of the plot of Fig. 4b. Other chromatographic independent variables, different

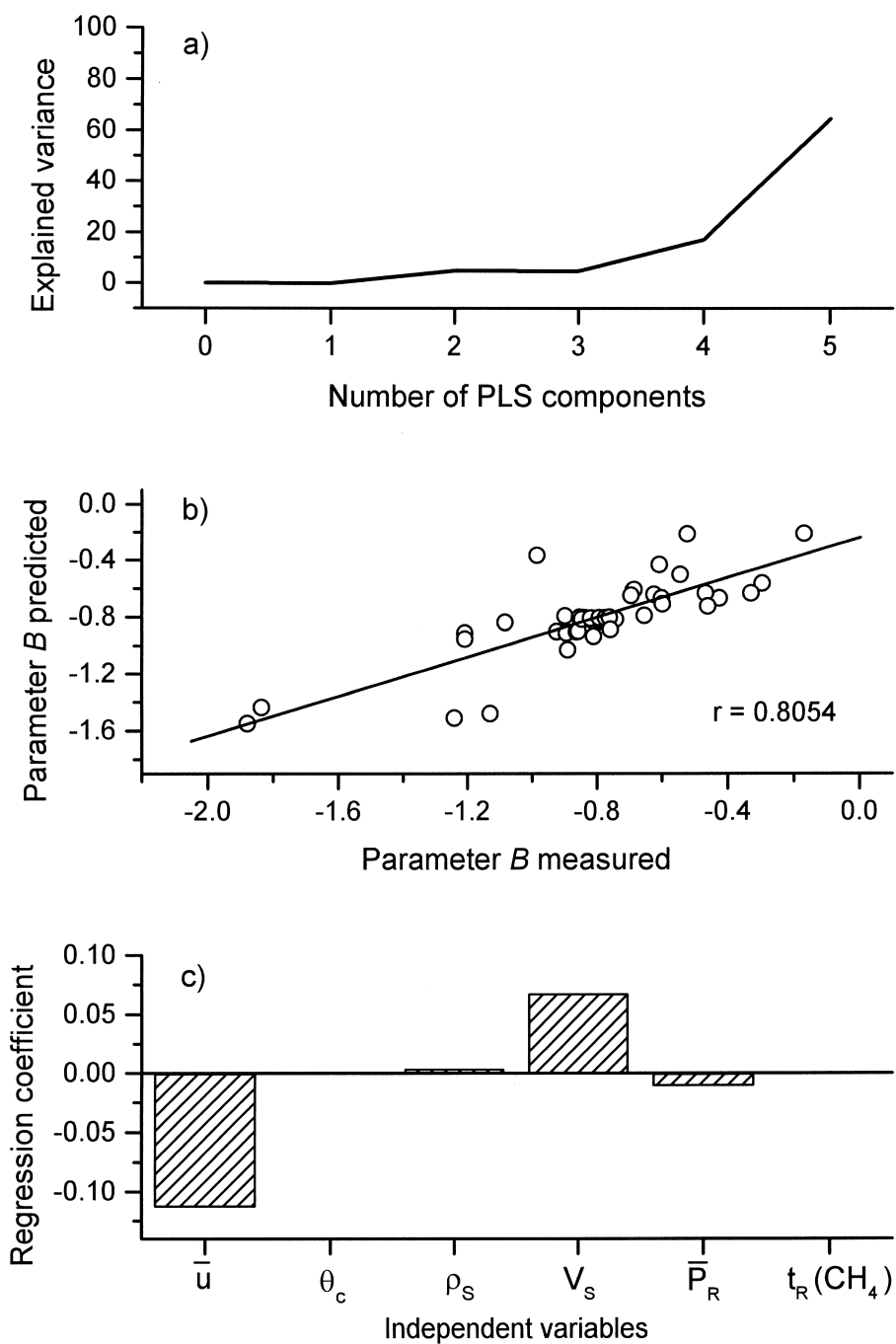


Fig. 2. Results of the PLS regression analysis for parameter B.

from the six shown in Table 2, were tried but there was no improvement.

Table 2 shows other facts. The value of D seems

to be independent of the chromatographic conditions or the nature of the stationary phase. The average value of D is 0.944 ± 0.007 . This value does not

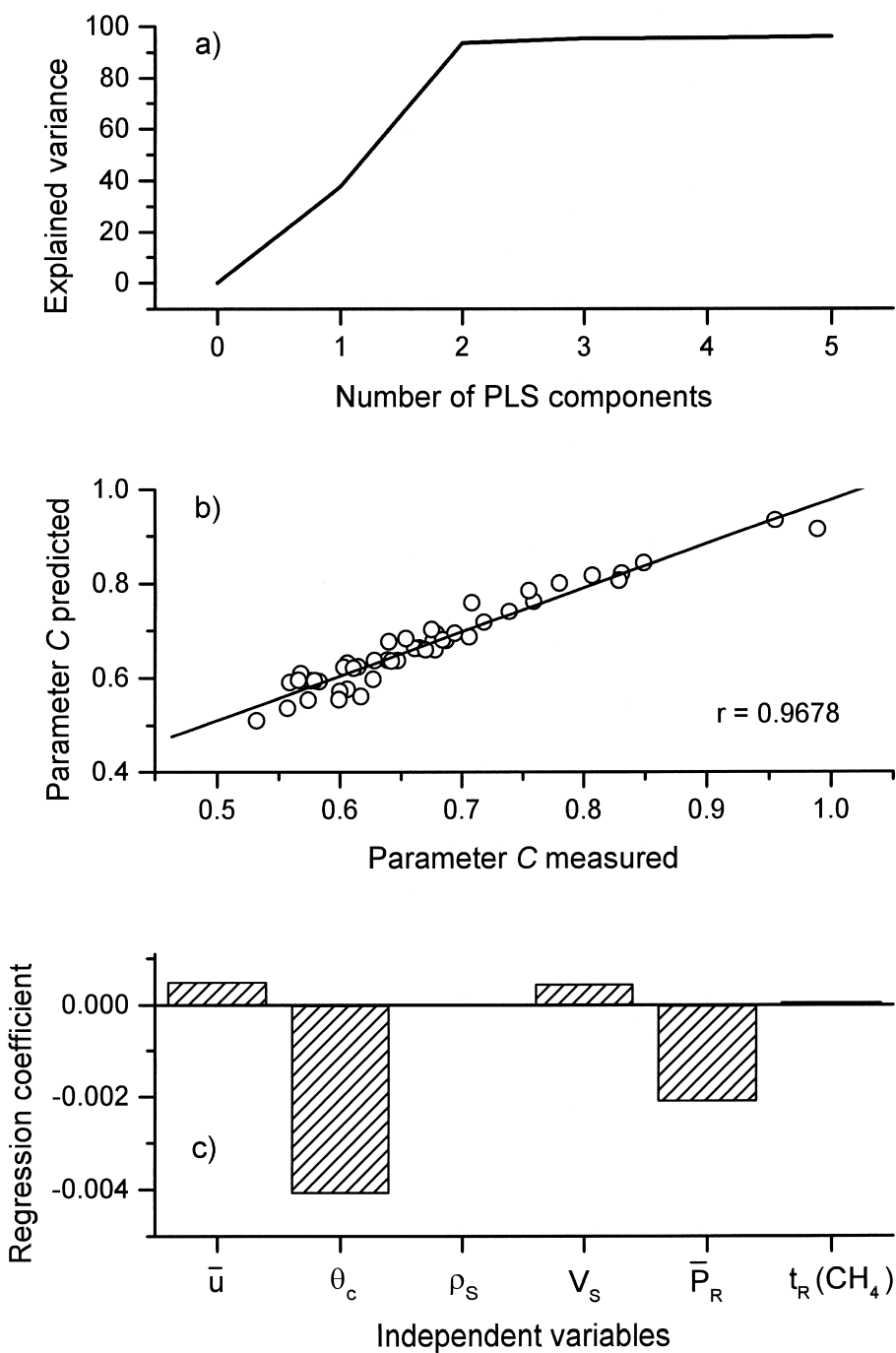


Fig. 3. Results of the PLS regression analysis for parameter C.

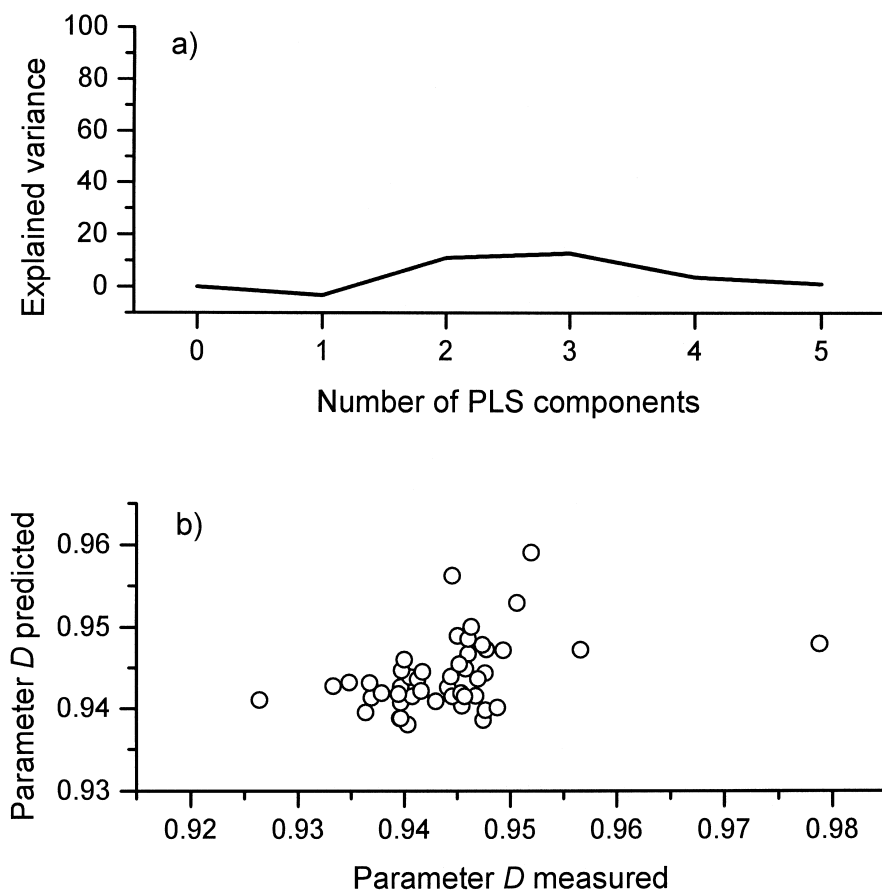


Fig. 4. Results of the PLS regression analysis for parameter D .

change if each individual value from all 526 experiments is used for the averaging. In order to check that the presence of the retention time of the first member of the homologous series (methane) does not force an artificial value for D , all 526 chromatograms were used to recalculate its value using only retention times of n -alkanes with five or more carbon atoms. No significant change on the reported value of D was found. It seems that the different individual values found in Table 2 for this parameter reflect a natural experimental variability. According to Eq. (2), this parameter modifies the real number of carbon atoms of the n -alkane by a constant factor lower than 1, in such a way that parameter D may be interpreted as a correction to the retention of the n -alkanes. It shows that the contribution of each methylene group of the molecule to the chromatographic

retention is not independent of the chain length of the n -alkane (as suggested by Eq. (1)), but rather that the contribution of the additional $-\text{CH}_2-$ group (as the chain length increases) is lower than the contribution of the previous one, with independence from the actual chain length. This interpretation is in agreement with the experimental evidence of the non-linearity of the representation of the logarithms of the adjusted retention times of the n -alkanes vs. the chain length [9]. The effect may be observed when the differences of the logarithms of the vapour pressures or boiling points of consecutive n -alkanes are plotted vs. the chain length.

The constancy of the value of D , and its independence from the chromatographic conditions, including the temperature of the column and the nature of the stationary phase, suggests that its value

is not associated to the chromatographic experiment, but rather, that it is a general property of *n*-alkanes and other homologous series, and should be reflected in a careful estimation of other molecular properties. It suggests that the “additivity” principle sometimes used to deduce molecular properties by the addition of the contributions of the methylene groups of the molecule, should be refined.

3.5. A final comment

The dependence of parameters *A*, *B* and *C* on different chromatographic variables may also be explained by a consideration of the commonly accepted chromatographic theory, summarised in this paper by Eq. (1). Eq. (2) represents only a slight modification (through parameter *D*) of the classical equation, that may be written as follows:

$$t_R = t_0 + \exp(B + Cz) \quad (6)$$

where t_0 is the hold-up time, according to the classical theory. Using known expressions for the partition constant (K_c), the dependence of parameters t_0 , *B* and *C* on different chromatographic variables may be predicted. Results thus deduced are equivalent to those presented here, obtained by a statistical procedure from experimental results. As has been mentioned on the discussion on parameter *C*, the parameters of Eq. (2) are equivalent to those of Eq. (1), with $A = t_0$.

4. Conclusions

From the evidence shown in this paper, it may be concluded that each one of the parameters *A*, *B* and *C* of Eq. (2) presents a logical and natural dependence on some chromatographic variables, all three depending on different variables, and that parameter *D* is associated with the methylene groups of the molecule and has no relation to the chromatographic system. It has also been shown that the density of the stationary phase has no effect on the retention of the *n*-alkanes, nor on the additional retention term due to penetration of the carrier gas in the stationary phase.

Results confirm that Eq. (2) is a realistic representation of the chromatographic behaviour of the *n*-alkanes under isothermal conditions.

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