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Interpreting the gas chromatographic retention of *n*-alkanes

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Abstract

Non-linear regressions were applied to *n*-alkanes retention data for the determination of gas hold-up in a preceding paper. It was found that at temperatures over 100°C the reduced partial molar free energy of solution, $\Delta G/RT$, tends to be negligible for the solute methane in poly(dimethylsiloxane) stationary phases. A consequence of interest can be inferred from this fact. The C–H bonds from terminal methyl groups of *n*-alkane solute molecules should not contribute significantly to $\Delta G/RT$ in these conditions. The analysis of data confirms that, within the chromatographic experimental error, the contributions of *n*-alkane end C–H bonds are also negligible in this temperature range. Consequently, the regression parameter that contains the phase ratio of the column only includes the gas hold-up as the accompanying factor. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The dependence of the free energy of solution, ΔG , on the carbon number of homologue series of solutes has been a subject of considerable interest in gas chromatography. This, basically, is due to the proposal to approximate ΔG as an additive function of individual contributions of groups present in the solute molecule [1]. The early historical reference of this approach is Martin's equation for linear homologues [2]:

$$\Delta G = \Delta G^+ + n \Delta G^m \quad (1)$$

ΔG^m is a monomeric contribution to ΔG . The term independent of the carbon number *n*, ΔG^+ , was interpreted for *n*-alkanes as that contribution gener-

ated by end methyl groups. This is immediate to the observation that the terminal groups are present in all homologues, irrespective of their chain length *n*. For this interpretation of ΔG^+ , the logical consistent choice for the variable, instead of *n*, would be (*n* – 2). This defines the number of methylene monomers in the alkane molecule, excluding the end methyl groups. The selection of the variable affects the determined value of ΔG^+ .

Ample space in the chromatographic literature has been devoted to the monomeric contributions ΔG^m in different solvents. Tudor and Oncescu [3] recently reviewed this, and most precedents on this subject may be found in the bibliography cited by these authors. In contrast, less effort has been dedicated to explicitly study the behavior of the function ΔG^+ .

If an expression, such as Eq. (1), or a higher order polynomial of the molecular size variable, is employed for describing $\Delta G(n)$ of *n*-alkanes, we should

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write for the retention time of any member of the series in constant chromatographic conditions:

$$t_{\text{R}}(n) = t_{\text{M}} \left(1 + \frac{e^{-\frac{\Delta G(n)}{RT}}}{\beta} \right) \\ = t_{\text{M}} + \exp \left[A - \frac{\Delta G^{\text{m}}}{RT}(n - i) + \dots \right] \quad (2)$$

where $i=0, 1, 2, \dots$. The gas hold-up is t_{M} , and the parameter A in the exponential is:

$$A = \ln \left(\frac{t_{\text{M}}}{\beta} \right) - \frac{\Delta G^+}{RT} \quad (3)$$

The column phase ratio, β , is the volume ratio of gas and liquid phases: $\beta = V_{\text{G}}/V_{\text{L}}$. The selected value of i must be consistent with the physical interpretation of the thermodynamic parameters ΔG^{m} and ΔG^+ , as mentioned above for the example of Martin's equation.

When regressions of experimental retention times of n -alkanes are performed using equations of the type of Eq. (2), the resultant parameter A encloses information on t_{M} , β and ΔG^+ . In a former publication [4], the analysis of regressions of $t_{\text{R}}(n)$ data, obtained with poly(dimethylsiloxane) (PDMS) wall-coated capillary columns, was focused on the determination of t_{M} . This is the first parameter on the right hand side of Eq. (2). The purpose of the present article is now to apply the information derived from the preceding paper to study the behavior of ΔG^+ on PDMS stationary phases at temperatures over 100°C. This concerns the determination of the second parameter in Eq. (2), the parameter A .

When a molecular interpretation on the observed behavior of macroscopic thermodynamic properties (such as, e.g., $\Delta G(n)$) is pretended, the unavoidable theoretical context is statistical thermodynamics [5]. This provides the conceptual link between the properties of molecular systems to the macroscopic measurable thermodynamic quantities.

2. General

The statistical thermodynamics states, as a general enunciation, that the unequivocal quantification of

the solvation process is given by the logarithm of the number–density ratio of solute molecules in both phases at equilibrium [6]:

$$\ln \left(\frac{\rho_2^{\text{L}}}{\rho_2^{\text{G}}}_{\text{eq}} \right) = - \frac{\Delta G^*}{kT} \quad (4)$$

The subscript 2 denotes the solute and the left superscripts indicate the liquid and gas phases. ΔG^* is the free energy of transfer of the solute molecule from the gas to the liquid phase, this is the difference of pseudo-chemical potentials. The left hand-side of Eq. (4) is equal to $\ln K$, where K is the partition coefficient as it is currently defined for a molar concentration scale in gas–liquid chromatography.

How to explain the dependence of $\ln K$ for small molecules (e.g., methane) on the chain length of short n -alkanes as solvent aroused controversy in the ambit of physical chemistry. Some authors have suggested that Eq. (4) is incomplete, and that a Flory–Huggins-like term, accounting for the mixing entropy, should be included [7–9]. This term would consider size and shape differences between the solute and solvent. Ben-Naim et al. [10–12] showed that the observed n dependence of K does not result from the formulation of an additional term in Eq. (4). Generally, the problems associated with the statistical ensembles of particles are extremely complex, and the only way to elucidate them is with the aid of molecular simulations using molecular dynamics or Monte Carlo samplings of the phase space. Computational chemistry provides a privileged perspective for the understanding of solvation processes. By implementing Monte Carlo simulations for different models of the short chain solvent, Martin et al. [13] concluded that the repulsive forces, i.e., that part of ΔG^* related to the work of cavity formation, are mainly responsible of this n dependence of $\ln K$. Therefore, an additional Flory–Huggins entropy term on the right hand side of Eq. (4) is not justified.

In the ambit of gas chromatography it was shown that, when the short n -alkanes are the solutes, the etiology for the observed non-additive n dependence of $\ln K$ also is due to the repulsive forces [14,15]. It was found that, actually, a Flory–Huggins term is already contained in the work of cavity formation contribution to ΔG^* (viz. the excluded volume contribution):

$$-\frac{\Delta G^*}{kT} = -\frac{W_{\text{attr}}}{kT} + \ln \frac{q_{2r,v}^L}{q_{2r,v}^G} + \ln(1 - u_e) \quad (5)$$

The first term on the right hand side corresponds to the attractive part of the solute potential function for its insertion into the solvent lattice, as a rigid particle [15]. This provides a positive contribution to $\ln K$, i.e., a contribution to the partitioning of the solute favorable to the liquid. The second term contains the ratio of the internal partition functions, $q_{r,v}$, of the solute molecule in the liquid and gas solutions. This takes into consideration the internal degrees of freedom of the molecule, rotational and vibrational. From the viewpoint of classical statistical mechanics, these are separable from the translational degrees of freedom [5]. In an approximation, the mentioned first two terms are additive with respect to the monomeric contributions in the n -alkane molecule [14]. The last term, the reduced work of cavity formation $\ln(1 - u_e)$, accounts for the repulsive part of the solute insertion potential function, approximated as a hard sphere potential ($U_{21} = +\infty$, when $r \leq r_{21}^*$) [15]. This is a negative contribution to $\ln K$, i.e., favorable for the partitioning of the solute into the gas phase, and is responsible for its non-linear independence. The excluded volume fraction in the liquid solution is $u_e = \rho v_{\text{cav}}^L$, where v_{cav}^L is the volume of the solute cavity, that volume pervaded by the solute molecule that is excluded to all other particles [15]. For a chain molecule, the dependence of u_e on n can be derived applying the excluded volume theory of Flory [14,16]:

$$u_e(n) = \frac{v_{m_2}}{v_{m_1}} (2\Phi - c\Phi^2 + \dots) n^2 \quad (6)$$

The volumes of the solute and solvent monomers, or structural units, respectively, are v_{m_2} and v_{m_1} . The dimensionless function Φ is the product: $\Phi = \psi_1 [1 - (\Theta/T)] (v_{m_2}/v_{m_1})$, Θ being the temperature at which the Θ state of the liquid solution is attained [16], and ψ_1 is a dimensionless function of the partial molar entropy of dilution at infinite dilution. Eq. (6) derives from the Flory–Huggins theory of mixing entropy of chain molecules and accounts for size differences between solute and solvent molecules and their monomers. The number of different possible arrays, for a chain molecule that is inserted into

a lattice, is the direct consequence of repulsive forces: the excluded volume rejects the possibility that two monomers may occupy the same lattice site, and therefore defines which arrays are possible. From a more basic standpoint, short-range repulsive forces between atoms, derived from Pauli's exclusion principle, are the most elemental origin for the configurational entropy contributions to ΔG^* due to size and shape differences between the solute and solvent. The atoms excluded volume in conjunction to their connectivity in the molecule, i.e., the preservation of bond lengths and angles, determines the effective pervaded volume by the molecules and their shape. It also determines the final number density of particles, ρ , defining the environment perceived by any other particle in the condensed phase.

The excluded volume fraction of polymeric solutions (Eq. (6)) will depend on how much flexible are the chains. The longer the persistence length the more pronounced excluded volume effects in the liquid solution [17], and the more important the n dependence of $\ln K$ when the chain is the solvent; or greater the deviation from linearity of $\ln K(n)$ when the n -alkane is the solute. This can be visualized from the results of Martin et al. [13]. The more articulated the solvent chain model, as, e.g., the freely jointed (FJ) chain, the weaker the n dependence of K .

For a solute presenting a low K there will be a condition, when the temperature is raised, where the positive and negative contributions to $\ln K$ must compensate each other making $\ln K = 0$, namely $K = 1$ (see Eqs. (4)–(5)). This is the condition of an 'inert solute' [4], because there is no net difference between the solute molecule free energy in the liquid solution and in the ideal gas phase where it does not interact. Then, the solute thermodynamically behaves as a free particle in the liquid. This condition, of mutually compensated attractive and repulsive forces, is essentially analogous to the Θ state of the solution. The difference with the latter is that is reached gradually through an increase of T , while the Θ state is reached abruptly when T is decreased toward Θ .

If further increments to the temperature are attained, and if the excluded volume effects are still being important, K will be reduced below 1. This is

the case of the partition of small inert gas molecules into short *n*-alkane solvents. Hesse et al. [18] studied these systems experimentally at ambient *T* using the Ben Naim-Baer instrument. The reason for *K* yielding values below 1 relies in two facts. First, the ratio v_{m_2}/v_{m_1} is high, having an order of 1, giving rise to important excluded volume effects (see Eqs. (5)–(6)). Second, due to the low affinity of the solute to the liquid phase, represented by a low value of the enthalpic interaction term ($-W_{\text{attr}}/kT$), the condition $K=1$ is reached below ambient temperature. For an almost athermal solvation, $\Theta \rightarrow 0$ K [16], thus the excluded volume fraction u_e is practically independent of *T* (see Eq. (6)). Therefore, at higher temperatures the excluded volume effect is still important and the reduction of $\ln K$ below 0 is attained, due to its negative contribution.

3. What can be inferred from previous results

In the preceding paper [4] the partitioning of methane on PDMS stationary phases was studied. In this case the ratio v_{m_2}/v_{m_1} has an order 10^{-1} . The temperature at which the repulsive and attractive terms of Eq. (5) grossly compensate each other, reaching the same order ($\ln K \sim 0$), is relatively high, about 100°C. The temperature Θ for this system is expected to be close to 100 K [14], so in this case u_e decreases with an increasing *T* (see Eqs. (5)–(6)). At temperatures over 100°C the excluded volume effect is unimportant due to the decrease of u_e , and *K* is not reduced significantly below 1, leveling nearby to this value. This issue can be understood better in the following way. In a compact packing of hard spheres of the same volume v_{m_1} (the solvent monomers) there is a void volume fraction, the free volume of the system. The cavities of the packing may be occupied by spheres of a smaller volume v_{m_2} , the solute. The latter would not perturb the packing of the bigger ones if the ratio v_{m_2}/v_{m_1} is lower than a certain value (<1) which depends on the efficiency of the packing. Therefore, for lower values of v_{m_2}/v_{m_1} the work of cavity formation for inserting the smaller sphere is null, because the cavity already exists in the packing. Polymeric liquids are far from being efficient packing of monomers, so the free

volume fraction ($1-u_e$) is always important in infinitely diluted solutions, as those studied here with $v_{m_2}/v_{m_1} \sim 10^{-1}$.

If *K* of methane levels near a constant value of 1 at $T > 100^\circ\text{C}$, this means that the first two terms on the right hand side of Eq. (5) must also be negligible; considering that both are functions of *T*. This molecule has internal degrees of freedom due to the C–H bonds. We may roughly assimilate each vibration mode to an independent harmonic oscillator. The classical partition function of the harmonic oscillator is [5]:

$$q = \frac{kT}{h\nu} \quad (7)$$

where ν is the vibration frequency of the oscillator, which is related to its effective force constant, *f*, generated by the mean field potential, as $\nu = 1/2\pi(f/m)^{1/2}$. Therefore, the contribution of each mode will be:

$$\ln \frac{q^L}{q^G} = \ln \frac{G \nu}{L \nu} \quad (8)$$

A negligible contribution to ΔG^* from the C–H bonds of methane at $T > 100^\circ\text{C}$ means, in addition to other implications, that their vibration frequencies in the gas and in the solvent are very similar. The same applies to the quantum partition function [5].

If overall the above exposed issues are true for methane, then we may conjecture if these could be applicable to C–H in terminal methyl groups of *n*-alkanes, those in principle responsible for the existence of ΔG^+ , our present matter of study. We must be aware that the excluded volume effects are different for methane in PDMS than when the solutes are *n*-alkanes. The latter, in addition, can undergo intramolecular interactions when $n \geq 5$. Thus, the environment (the mean field potential) felt by the C–H in methane must be different than the one felt in the alkanes methyl groups. Precisely, this is the point we try to elucidate here.

There is another energetic contribution of methyl groups in *n*-alkanes. The rotation around the end C–C bond is exposed to potential barriers. At our relatively high temperatures, these are largely surpassed by the thermal energy of the molecules in both phases, making them irrelevant.

If it is admitted that the terminal C–H would not contribute to ΔG^* for *n*-alkanes solutes in PDMS over 100°C, then we may analyze which are the observable consequences of this hypothesis and see if the experimental results confirm or refute them.

4. The observable consequences

The first consequence for accepting that there are no contributions from terminal C–H for *n*-alkanes is that $\Delta G^+ / kT = 0$ when $T > 100^\circ\text{C}$. This situation will be manifested in the *A* regression parameter obtained from experimental $t_R(n)$ data (see Eqs. (2)–(3)). The immediate question is which is the size variable consistent with this hypothesis? If there are no contributions from C–H, the only contributions to ΔG^* arise from C–C. There are $(n - 1)$ C–C, so this would be the variable for the additive average monomeric contributions; those corresponding to the first two terms of Eq. (5): $[-W_{\text{attr}}/kT + \ln({}^L q_{2r,v} / {}^G q_{2r,v})]$ [14]. The condition for the average contributions from C–C to $\ln({}^L q_{2r,v} / {}^G q_{2r,v})$ of being approximately additive, property corroborated by Monte Carlo calculations (see Ref. [14] and the bibliography cited therein), implies that the molecule may be assumed to be composed by independent hypothetical oscillators. The reduced work of cavity formation, $\ln(1 - u_e)$, is not additive as follows from Eq. (6). In consequence, the theoretical equation $t_R(n)$ for the regression of *n*-alkanes retention data in these experimental conditions should be:

$$t_R(n) = t_M \left(1 + \frac{e^{-\frac{\Delta G^*}{kT}}}{\beta} \right) \\ = t_M + \frac{t_M}{\beta} \exp [B(n - 1) + \ln(1 - Cn^2)] \quad (9)$$

where $B = [-W_{\text{attr}}/kT + \ln({}^L q_{2r,v} / {}^G q_{2r,v})]$ and $C = (v_{m_2} / v_{m_1}) (2\Phi - c\Phi^2 + \dots)$. If the hypothesis inherent to Eq. (9) is correct, the parameter β calculated by regression of experimental $t_R(n)$ data to this expression must be a constant independent of *T*, and must present a close value to the one reported by the manufacturers of the chromatographic column. In addition, the other calculated parameters (t_M , *B* and *C*) should be exactly the same as those calculated without the hypothesis $\Delta G^+ / kT = 0$, that is to say,

assuming a priori that $\Delta G^+ / kT$ might not be null. In this latter case the regression equation is [14,15]:

$$t_R = t_M + \exp [A + B(n - 2) + \ln(1 - Cn^2)] \quad (10)$$

Our next task is to confirm or refute the deduced constraints.

5. Results

In this section we shall analyze the results of published retention data. The designations and specifications of the columns employed for obtaining these data are given in Table 1. The retention of *n*-alkanes on capillary Columns 1 and 2, and the packed Column 4 was measured by the research group headed by García-Domínguez and co-workers [19–21]. The published data of Column 3 [4] are from the author's laboratory. The regressions were performed with commercial software applying the algorithm of Marquardt (Sigma Plot, Jandel Scientific, CA, USA).

The experimental retention times utilized in the regressions are reported in the third columns of Tables 2–5. The parameters, and their standard errors, obtained from the regression to Eq. (9) are shown in the fifth column. The t_R values calculated with these parameters are tabulated next to the experimental, for an easier comparison. An X on the right indicates when the residues are not zero, so the curve fit is not perfect. The calculated retentions and parameters are all rounded to four digits for a more rapid follow-up of the results. The applied program uses 15 characters in the calculations.

It can be seen, for a given table, that the calculated parameter β is constant with *T*, within the chromatographic error, when $T > 120^\circ\text{C}$ for all the columns. Table 6 compares the average value of β , obtained from the regressions, with the phase ratio estimated from the specifications of the chromatographic column. The latter are nominal values provided by the manufacturer. The discrepancy is important for Column 1. For the other columns it is within expectation, since only two digits are significant for the nominal β . The remaining constraint, the condition that t_M , *B* and *C* should be the same for the regression to Eq. (10), is fulfilled. Table 7 compares

Table 1
Columns utilized for obtaining retention data for $t_R(n)$ [4,19–21]^a

Column designation	Type	Stationary phase	Specifications nominal values	β nominal
1	Capillary WCOT	Crosslinked PDMS 5% phenyl groups HP-5	$L = 60$ m $d_c = 250$ μm $d_f = 0.25$ μm	250
2	Capillary WCOT	PDMS CPSIL-5CB	$L = 50$ m $d_c = 320$ μm $d_f = 0.43$ μm	186
3	Capillary WCOT	Crosslinked PDMS HP-1	$L = 50$ m $d_c = 200$ μm $d_f = 0.33$ μm	151
4	Packed	PDMS 1–3% vinyl groups PS-255	$L = 4$ m $d_c = 2.2$ mm $w_L = 0.194$ SS: ChromosorbW AW DMCS	10

^a L , column length; d_c , column internal diameter; d_f , film thickness; w_L , weight fraction of liquid in the packing; SS, solid support; WCOT, wall-coated open tubular. The phase ratio of capillary columns was estimated from the specified parameters as $\beta = d_c/4d_f$. This value has only two significant digits. The packed column data were estimated as indicated in Appendix A.

the parameters for both curve fits, in order to illustrate the agreement of values.

Fig. 1 shows the plots of experimental $\ln K$ as function of the number of C–C bonds for the n -alkanes using different columns as examples. K was calculated as $K = [(t_R/t_M) - 1]\beta$ using t_M obtained by regression and the average β for all temperatures where constancy is confirmed. The filled line is the representation of theoretical Eq. (9), i.e., $\ln K(n) = B(n-1) + \ln(1 - Cn^2)$. If the results are extrapolated to $(n-1)=0$, the ordinate must be equal to $\ln(1 - C)$, which has the order -10^{-4} in this range of T . Consequently, we graphically observe that all curves practically converge to zero. This is what should be expected for a consistent behavior. For the hypothetical extrapolated C_1 there are no more C–C, and the remaining C–H should not contribute to $\ln K$ as was postulated. In addition, the excluded volume contribution $\ln(1 - u_c)$ of this hypothetical C_1 is negligible. Fig. 2 shows the plot of $\ln K$ versus $1/T$ for methane in the different columns. The parameters of a curve fit to the experimental $\ln K$, corresponding to Column 3, are indicated. This curve is represented as a filled line in Fig. 1. The knowledge of function $\ln K(T)$ for methane is of extreme importance for chromatographers. In chromatograms where there are insufficient numbers of n -alkane peaks to permit a reliable regression $t_R(n)$, or in the absence of them,

the accurate determination of t_M is impeded [4]. Otherwise, methane can generally be injected without interference in the chromatogram. The correct gas hold-up can be easily determined from its retention time $t_R(C_1)$ and its known distribution coefficient $K(C_1)$:

$$t_M = t_R(C_1) \frac{\beta}{\beta + K(C_1)} \quad (11)$$

6. Discussion

The reported experimental data seem to corroborate our hypothesis, yielding consistent results. All the constraints deduced from this hypothesis are confirmed. The only strong discrepancy is for β of Column 1. But the calculated β for this column is constant when $T > 120^\circ\text{C}$, confirming that $\Delta G^+/kT$ cannot be contained in this parameter.

From the inspection of results in Tables 2–5, it is seen that the capillary columns render perfect curve fits in most cases. The absence of Xs on the right is the indicator for this fact. This is not the case for the packed Column 4. This situation will be a constant for all packed columns and the reason may be understood a priori. In the preceding paper [4] it was shown that, if a bigaussian distribution is assumed

Table 2
Experimental and calculated data for Column 1

T (°C)	n	t_R (n)	t_R (n) _{calc}	Regr. to Eq. (9) parameters
120	6	384.9 s	384.9	$t_M = 360.3 \pm 0.05$ $\beta = 293.5 \pm 1.0$ $B = 0.606 \pm 0.0005$ $C = 0.00088 \pm 0.000016$
	7	404.9	404.9	
	8	440.9	440.9	
	9	505.7	505.7	
	10	622.0	622.0	
	11	830.2	830.2	
	12	1202.2	1202.2	
150	6	391.5	391.5	$t_M = 376.1 \pm 0.09$ $\beta = 321.6 \pm 4.5$ $B = 0.522 \pm 0.0024$ $C = 0.00097 \pm 0.00008$
	7	401.7	401.7	
	8	418.6	418.6	
	9	446.4	446.4	
	10	492.3	492.3	
	11	567.5	567.5	
150	12	690.6	690.6	$t_M = 14.55 \pm 0.01$ $\beta = 320.8 \pm 6.8$ $B = 0.512 \pm 0.003$ $C = 0.00084 \pm 0.000065$
	7	15.49 min	15.49	
	8	16.10	16.10	
	9	17.10	17.10	
	10	18.73	18.73	
	11	21.39	21.39	
	12	25.72	25.72	
	13	32.73	32.74 X	
160	14	44.12	44.11 X	$t_M = 14.92 \pm 0.004$ $\beta = 315.6 \pm 3.0$ $B = 0.482 \pm 0.0013$ $C = 0.00072 \pm 0.000032$
	15	62.45	62.45	
	7	15.74	15.74	
	8	16.23	16.23	
	9	17.02	17.02	
	10	18.28	18.28	
	11	20.27	20.27	
	12	23.43	23.43	
200	13	28.43	28.43	$t_M = 15.87 \pm 0.0059$ $\beta = 319.5 \pm 5.9$ $B = 0.390 \pm 0.0021$ $C = 0.00054 \pm 0.000048$
	14	36.32	36.32	
	15	48.74	48.74	
	7	16.37	16.37	
	8	16.60	16.60	
	9	16.94	16.94	
	10	17.43	17.43	
	11	18.15	18.15	
	12	19.20	19.20	
	13	20.71	20.71	
14	22.91	22.91		
15	26.08	26.08		
16	30.65	30.65		
17	37.25	37.25		

for accounting peak asymmetry, the difference between the residence time t_1 corresponding the first moment of the distribution (which defines the peak position) and the peak maximum is given by:

Table 3
Experimental and calculated data for Column 2

T (°C)	n	t_R (n)	t_R (n) _{calc}	Regr. to Eq. (9) parameters		
120	5	236.7 s	236.7	$t_M = 223.3 \pm 0.05$ $\beta = 179.5 \pm 0.7$ $B = 0.600 \pm 0.0006$ $C = 0.00094 \pm 0.000018$		
	6	247.4	247.4			
	7	266.7	266.7			
	8	301.2	301.2			
	9	362.9	362.9			
	10	472.7	472.7			
	11	667.7	667.8 X			
	12	1013.4	1013.4			
	13	1623.7	1623.7			
	150	5	244.1		244.1	$t_M = 234.8 \pm 0.04$ $\beta = 188.8 \pm 0.9$ $B = 0.509 \pm 0.0007$ $C = 0.00079 \pm 0.000019$
		6	250.2		250.2	
		7	260.2		260.2	
		8	276.6		276.6	
9		303.3	303.3			
10		347.1	347.1			
11		418.3	418.3			
12		534.2	534.2			
13		722.1	722.1			
14		1026.0	1026.0			

$$t_1 - t_R = (\pi \ln 2)^{-1/2} \cdot \frac{(x^2 - 1)}{(x + 1)^2} \cdot w_h \quad (12)$$

If the peak width at half height, w_h , is in the order of those usually encountered with packed columns, even for a very low skew factor x , the difference $t_1 - t_R$ will have the order of the last significant digit of a measured t_R . For example, if $w_h = 30$ s, and if a skew factor x is assumed to be $x = 1.01$, the difference is within the last digit ($t_1 - t_R = 0.1$ s). This value of x provides a tailing distribution almost indistinguishable from a gaussian distribution. Since w_h varies along the chromatogram, ($t_1 - t_R$) will not keep constant proportions for all the eluted n -alkanes. Thus, it is expected that the chromatograms from packed columns will be systematically affected, even when very symmetrical peak patterns are observed. The same concept is applicable to largely retained peaks in capillary columns. If these are not symmetrical, it is preferable not to include them in the regressions. The only way to circumvent this problem is by applying the values of $t_1(n)$ instead of $t_R(n)$ in the regressions, demanding a computer assisted record of the chromatogram.

There is another important consideration concerning packed columns. Due to the smaller values

Table 4
Experimental and calculated data for Column 3

T (°C)	n	t_R (n)	t_R (n) _{calc}	Regr. to Eq. (9) parameters
120	5	5.119 min	5.119	$t_M = 4.805 \pm 0.002$
	6	5.368	5.368	$\beta = 159.9 \pm 1.6$
	7	5.810	5.809 X	$B = 0.594 \pm 0.0019$
	8	6.593	6.593	$C = 0.00111 \pm$
	9	7.978	7.979 X	0.000067
	10	10.422	10.422	
140	7	5.687	5.687	$t_M = 4.987 \pm 0.0036$
	8	6.156	6.157 X	$\beta = 160.6 \pm 3.0$
	9	6.939	6.939	$B = 0.526 \pm 0.003$
	10	8.238	8.238	$C = 0.00076 \pm$
	11	10.390	10.390	0.00015
	12	13.950	13.950	
160	7	5.662	5.662	$t_M = 5.150 \pm 0.002$
	8	5.960	5.960	$\beta = 161.4 \pm 2.6$
	9	6.431	6.431	$B = 0.467 \pm 0.0027$
	10	7.173	7.173	$C = 0.00051 \pm$
	11	8.340	8.340	0.000097
	12	10.175	10.175	
180	7	5.710	5.710	$t_M = 5.315 \pm 0.007$
	8	5.909	5.909	$\beta = 158.8 \pm 1.1$
	9	6.210	6.210	$B = 0.414 \pm 0.012$
	10	6.662	6.661 X	$C = 0.00027 \pm$
	11	7.339	7.339	0.00044
	12	8.357	8.357	

of β , with respect to capillary columns, the corrections to the retention of gases used as t_M markers are one order higher (see Eq. (11)). If these corrections are not applied, great errors in the determination of thermodynamic parameters may be committed. Sometimes contradictory situations are produced when sophisticated corrections for non-ideal behavior of the vapor phase are introduced in the determination of the specific retention volume, even at relatively low pressures, and no reliable corrections to the determination of t_M from markers are attained. For doing the latter, firstly, the $\ln K(T)$ function for the marker should be determined in appropriate experimental conditions.

We can identify a priori several problems for the comparison of determined values of $\ln K$ for n -alkanes in different columns and from different laboratories (see, e.g., Ref. [22]). The dependence of t_R on the amount of the injected sample will lead to differences between measured $\ln K$. In the case of

Table 5
Experimental and calculated data for Column 4

T (°C)	n	t_R (n)	t_R (n) _{calc}	Regr. to Eq. (9) parameters
120	5	321.0 s	321.0	$t_M = 145.2 \pm 1.4$
	6	465.3	465.2 X	$\beta = 9.36 \pm 0.30$
	7	725.0	725.1 X	$B = 0.617 \pm 0.0054$
	8	1191.9	1191.9	$C = 0.00163 \pm$
	9	2025.7	2025.7	0.00023
	150	5	276.8	276.8
6		358.5	358.5	$\beta = 9.50 \pm 0.10$
7		493.0	493.1 X	$B = 0.518 \pm 0.0015$
8		714.3	714.3	$C = 0.00110 \pm$
9		1076.9	1076.7 X	0.000052
10		1668.4	1668.5 X	
150	5	277.3	277.4 X	$t_M = 154.5 \pm 0.6$
	6	358.9	358.9	$\beta = 9.84 \pm 0.20$
	7	493.7	493.3 X	$B = 0.522 \pm 0.0027$
	8	714.1	714.4 X	$C = 0.0012 \pm$
	9	1076.6	1076.8 X	0.000097
	10	1668.7	1668.5 X	
11	2630.8	2630.8		

Table 6
Comparison of nominal and average calculated phase ratios

Column	β nominal	$\bar{\beta}$ regr. Eq. (9)
1	250	319
2	186	184
3	151	160
4	10	9.6

Table 7
Comparison of parameters t_M , B and C for the regression to Eqs. (9) and (10)

Chromatogram		Parameters from regr. to Eq. (9)	Parameters from regr. to Eq. (10)
Column 1 160°C	t_M	14.9155	14.9155
	B	0.4821	0.4821
	C	7.1673×10^{-4}	7.1673×10^{-4}
Column 3 120°C	t_M	4.8046	4.8046
	B	0.5943	0.5943
	C	1.1143×10^{-3}	1.1144×10^{-3}
Column 4 150°C	t_M	152.5994	152.5995
	B	0.5182	0.5182
	C	1.1034×10^{-3}	1.1034×10^{-3}

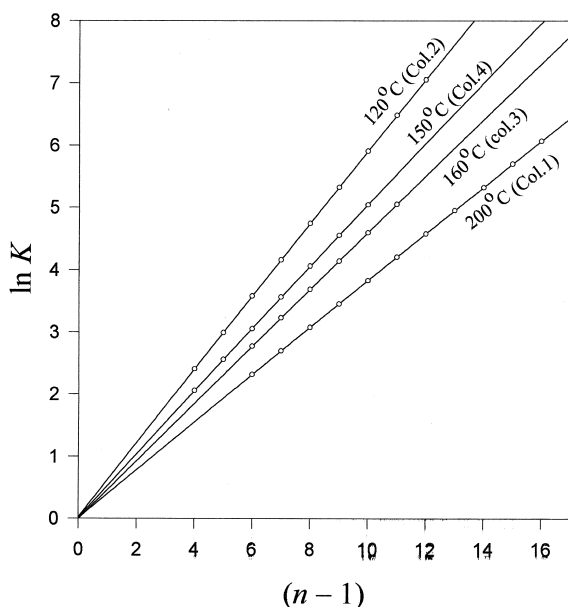


Fig. 1. $\ln K$ as function of the number of C–C bonds for n -alkanes. The phase ratio for calculating K is β . Circles are the experimental data. The filled line is the representation of theoretical Eq. (9), i.e., $\ln K = B(n-1) + \ln(1 - Cn^2)$. The ordinate when $(n-1)=0$ is $\ln(1-C)$, which has the order -10^{-4} .

column 3, from the author's laboratory, the injected amount was such that the peak area was invariably below 1000 counts in a HP5880A chromatograph. The limiting value of about 1000 counts was found for not observing differences in the last digit of t_R , between runs.

Additionally, the effect of mass-transport phenomena affecting the retention must be considered in the case of packed columns. Other reasons for the discrepancies of $\ln K$, are slight differences in the chemical compositions of the stationary phases and errors in the determination of β . While the former generates discrepancies that are variable with T , the latter generates a constant absolute difference that is independent of n and T . Finally the effects of interfacial phenomena should be accounted [22]. For pure PDMS the effect is accepted to be negligible, but this is not the case for Column 1.

Tables 8 and 9 compare $\ln K$ values obtained in different columns. The average β from the regressions was employed for calculating K . The substituted silicone stationary phases, Column 1 (5% phenyl) and Column 4 (3% vinyl), are compared in

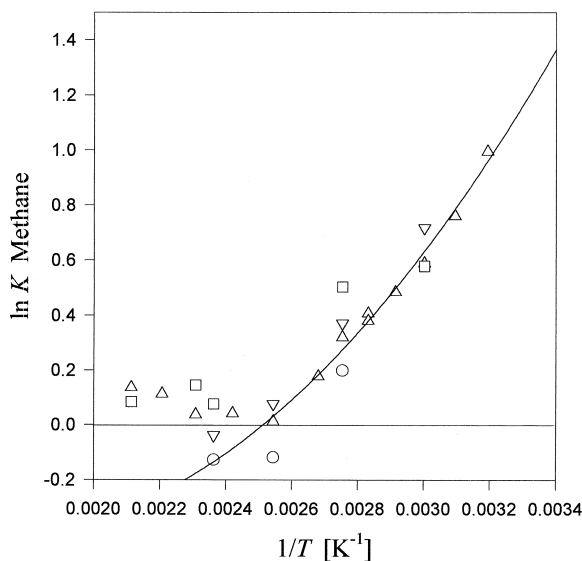


Fig. 2. Plot of $\ln K$ versus $1/T$ for the solute methane measured in four columns. The column phase ratio for determining K is β . Symbols: (□) Column 1; (▽) Column 2; (△) Column 3; (○) Column 4. The filled line is the curve fit to a quadratic polynomial for data of Column 3 in the range 40–120°C. The expression for this is: $\ln K = 1.401 - 2106(1/T) + 616\,275(1/T)^2$, where T is the absolute temperature.

Table 8 at two temperatures. The relative difference δ (%) is approximately a constant 0.8%. Therefore, the absolute difference is not constant as expected for the error attributable to β .

Table 9 compares $\ln K$ for the pure PDMS, Columns 2 and 3. In this case the relative differences δ are constant and equal to 1.8%. For the lower homologues this is slightly higher, evidently due to errors in t_M , which has a greater impact for the early eluting solutes. The discrepancy between Columns 2 and 3 must be explained in terms of the difference in composition due to the cross-linking of the polymer [23].

7. Conclusions

Experimental results seem to corroborate the hypothesis that if C–H does not contribute to $\Delta G/RT$ in the methane solute molecule, neither does in the n -alkane end methyl groups, when using PDMS stationary phases at $T > 120^\circ\text{C}$. The consequence is

Table 8
Comparison of $\ln K$ for the substituted silicone stationary phases, Columns 1 and 4

n	$\ln K$					
	120°C			150°C		
	Column 1	Column 4	δ (%)	Column 1	Column 4	δ (%)
5		2.450			2.053	
6	3.082	3.049	1.1	2.569	2.558	0.43
7	3.677	3.643	0.92	3.078	3.053	0.81
8	4.269	4.234	0.82	3.585	3.562	0.64
9	4.859	4.820	0.81	4.089	4.060	0.71
10	5.447			4.592	4.555	0.81
11	6.032			5.091	5.046	0.88
12	6.615			5.587		
13	7.195					

that the contribution to $\Delta G(n)$ independent of n , ΔG^+ , should be negligible in this temperature range. However, this preliminary analysis of experimental results, per se, cannot close the discussion. We could be trapped in a mathematical model providing a series of self-consistent results, but with no real physical significance. If our hypothesis may also be extended to the C–H of methylene monomers, this implies that, in these conditions, molecular dynamics or Monte Carlo calculations should yield similar results using either all atoms (AA) or united atoms (UA) force fields. For the former, the molecule has $(3n' - 6)$ internal degrees of freedom contributing to ΔG , n' being the number of all atoms, including hydrogen. For the latter, these are reduced to $(3n - 6)$. The report by Martin et al. [13] shows that, in the conditions studied therein ($v_{m_2}/v_{m_1} \sim 1$, $\Theta \rightarrow 0$ K, $T = 298$ K), UA and AA force fields clearly yield different results, so there might exist contributions

from C–H to $\ln(Lq_{2r,v}/q_{2r,v}^G)$ in the case of methane. An analogous chromatographic condition would be obtained studying the retention of methane on hexadecane, and may be similar on squalane.

The comparison of Monte Carlo calculations using UA and AA for the conditions studied in the present paper ($v_{m_2}/v_{m_1} \sim 10^{-1}$, $\Theta \sim 100$ K, $T > 373$ K) will contribute in part to elucidate the verisimilitude of our hypothesis. Most important, the simulation of the vibrational spectra of solutes in both phases by ab initio and semi-empirical quantum approaches will finally contribute to this elucidation. This is an inevitable duty for the near future.

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Appendix A

We shall estimate here the phase ratio of the packed column, Column 4, by using the information provided in Refs. [19,20].

The volume of the gas phase is usually determined through the equation:

$$V_G = F_o(T) t_{Mj}$$

Table 9
Comparison of $\ln K$ for dimethylsilicones, Columns 2 and 3

n	$\ln K$, 120°C		
	Column 2	Column 3	δ (%)
5	2.404	2.350	2.2
6	2.990	2.933	1.9
7	3.578	3.512	1.8
8	4.163	4.088	1.8
9	4.746	4.662	1.8
10	5.327	5.233	1.8
11	5.904	5.800	1.8
12	6.480		
13	7.052		

where $F_o(T)$ is the flow rate at the column temperature and outlet. This latter information and the column head pressure, for determining the compressibility correction factor j , are not available in our case. So we grossly must estimate this volume as $V_G = \varepsilon_u V_{col}$. The volume of the empty column, viz. the volume of the packed bed, V_{col} , is directly obtained from the reported dimensions and is equal to 15.2 cm^3 . The inter-particle porosity for the solid support Chromosorb W was reported by Guiochon [24]: $\varepsilon_u = 0.56$. So the volume of the gas phase is estimated to be $V_G = 8.5 \text{ cm}^3$.

The volume of the liquid phase is $V_L = (w_L m_p) / \rho_L$. From this expression, the total mass of packing material in the column, m_p , is unknown. However, it can be approximately determined from the volume of the empty column and the apparent density of a packing of the same characteristics of that specified for Column 4, $m_p = \rho_{app} V_{col}$. The apparent density of a bed of packing of Chromosorb W DMCS 60–80, containing the same order of mass fraction of liquid phase is $\rho_{app} = 0.25 \text{ g/cm}^3$. This value was obtained, after the bed was compacted by tapping, as usually done when a column is filled. But, in this case, the bed was not submitted to vacuum suction. The weight fraction of liquid in Column 4 was reported to be $w_L = 0.194$, and the density of PDMS at 298 K is $\rho_L = 0.895 \text{ g/cm}^3$. Finally, by using the above given information, the estimated volume of liquid phase is $V_L = 0.82 \text{ cm}^3$.

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