Distribution coefficients of *n*-alkanes measured on wall-coated capillary columns

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Abstract

Distribution coefficients K of *n*-alkanes were determined in wide ranges of temperature and carbon numbers from gas chromatographic retention data measured on wall-coated poly(dimethylsiloxane) commercial capillary columns. A discussion is centered on how to mitigate the difficulties for an accurate determination of K when using weakly retentive columns, as those bearing very high phase ratios or short lengths. Particularly, the errors associated with the estimation of the gas hold-up and the phase ratio of the column are considered. The chromatographic importance for determining K of *n*-alkanes relies on the fact that these are the most commonly applied references for reporting relative thermodynamic parameters such as the Kovats Index and the relative retention. A great amount of information has been compiled in this form. If K of the reference is known, absolute values of distribution coefficients for a myriad of substances are readily obtainable. The knowledge of $K(T)$ functions of solutes in wide ranges of temperature is a primary necessity in temperature-programmed gas chromatography. This knowledge is needed for the prediction of absolute retention times and for computing separation optimizations of mixtures containing several critical pairs of analytes.   © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

At the thermodynamic equilibrium, the solvation of a solute in the bulk solvent is quantified by the logarithm of solute molecule's numeral density ratio in both phases [1,2]:

$$\ln\left(\frac{^{L}\rho_2}{^{G}\rho_2}\right)_{eq} = \ln K_L = -\frac{\Delta G^*}{kT} \qquad (1)$$

The number density ratio of solute molecules in the liquid and gas solutions, $^{L}\rho_2 / ^{G}\rho_2$, is equal to the gas–liquid distribution coefficient K_L. The pseudo-chemical potential difference ΔG^* is the average Gibbs free energy for the process of transferring one solute molecule from the ideal gas into a fixed position in the bulk liquid solution. This is a statistical ensemble average over all possible configurations of molecules around the solute and possible conformations of solute and solvent [1].

Since $\ln K_L$ is the relevant thermodynamic quantity of solvation, it must be the parameter to be compared between systems when the bulk solution is the principal occurring process. The purpose of the

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present article is to report and compare chromato-graphically determined related values, that we shall denote ln K. The studied system is *n*-alkane solutes in poly(dimethylsiloxane) (PDMS) solvent. This study is realized employing commercial wall-coated capillary columns with different lengths and phase ratios, in order to cover a wide range of temperatures and chain lengths of the solutes. The value of K_L of present interest is that involving ideal behavior of the gas phase and infinite dilution. That is to say, it must be ensured that the interactions in the gas phase are negligible. The solute should mainly interact with the liquid stationary phase, with [solute–solute] and [solute–dissolved carrier gas] interactions in this phase also being negligible. The applied pressures and the injected quantity into the column must correspond to these conditions.

Beside its intrinsic physicochemical importance, the function $K_L(T)$ of *n*-alkanes in the studied solvent holds a particular chromatographic relevance. This homologous series of solutes was the most widely applied reference system for the determi-nation of relative thermodynamic parameters such as the Kovats Index and the relative retention. A great amount of information has been compiled under these forms [3,4]. For translating this information into absolute values of K_L, the distribution coeffi-cient of the reference ought to be known. Determin-ing the $K_L(T)$ functions of solutes in wide range of temperatures is a primary chromatographic need. In temperature-programmed gas chromatography (TPGC), it enables the numerical prediction of absolute retention times and the performance of computational optimizations for the separation of mixtures containing several critical pairs of analytes (see e.g., Ref. [5] and the references cited therein).

Notwithstanding the great advantages of silicone capillary columns, there is scarce published infor-mation on K_L, covering the wide T intervals applied in current analysis. This fact is originated in diverse experimental difficulties inherent to the determina-tion of absolute K_L from chromatographic retention data (see e.g., Ref. [6]). One basic objective of the present paper is to discuss and illustrate how these difficulties can be circumvented. Firstly, we shall introduce a brief review of these difficulties.

The ratio of liquid phase volume to interfacial area (as e.g., the gas–liquid interfacial area) for wall-

coated capillary columns has the order $V_L/A_i \cong d_f \sim 10^{-5}$ cm, where d_f is the average film thickness of stationary phase coating in the column. This value is comparably very low with respect to that of a solution contained in a small vessel, which has an order $V_L/A_i \sim 1$ cm. The latter is the order of V_L/A_i met by other methods for determining K_L, as for example in the Ben Naim–Baer instrument [7–9]. If the solute–solvent molecular forces of interaction greatly differ from the solvent–solvent ones, the accumulation of solute in the inter-phase region, or either its depletion with respect to the bulk liquid concentration, may occur. This is the consequence of, either, the decrease or increase in the solution's interfacial free energy per unit area (viz. the surface tension) due to the presence of the solute [10]. The system evolves to the least total free energy, and the concentration of solute in this region will evolve accordingly. Therefore, we should be aware that the incidence of interfacial phenomena might be signifi-cant in capillary gas–liquid chromatography [11–14]. In the particular case of the system we study in the present paper, it is expected that the chromato-graphically measured K will not depend on $V_L/A_i \cong d_f$, namely, the interfacial effect should be negligible. Another possible reason for the depen-dence of the chromatographic K on d_f is the exist-ence of a slow mass transfer leading to non-equilib-rium conditions [6], but this effect is not expected considering the thin d_f for coatings of capillary columns.

The equation of isothermal retention, in the ab-sence of interfacial and extra-column effects, is:

$$t_R = t_M(1 + K_L\beta^{-1}) \qquad (2)$$

t_R is the retention time, β is the volume ratio of gas and liquid phases, $\beta = V_G/V_L$, and t_M is the gas hold-up. The latter is the retention time of a non-retained solute, a solute with $K_L = 0$. This is a hypothetical solute that cannot permeate into the liquid phase. All real molecules used as t_M markers actually permeate the polymers usually employed as stationary phases [15], and in some cases the fused-silica capillary wall [16].

Eq. (2) assumes that the position of the chromato-graphic peak is defined by its maximum. This condition is solely valid for perfectly symmetrical

peaks. The position of an asymmetric peak is defined by t_1, the first moment of its time-distribution function [6]. The peaks eluting from very short capillary columns are generally skewed.

As is stated in Eq. (2), the determination of K_L from chromatographic retention data demands the precise knowledge of t_M and β. The difficulties associated with the accurate determination of these two basic chromatographic parameters are, respectively, the central topics of Sections 3 and 4.

2. Experimental

Three columns were employed in this study. These are described in Table 1. The specifications in the table are nominal values reported by the manufacturer. The column identified as column 1 presents a high retention. This is a long column, bearing a length, $L = 50$ m, with a relatively low nominal phase ratio, $\beta = 151$. This column allows one to determine K of alkanes with a low carbon number n. Column 2 has the same specifications but it is very short, having an L of only 12 m. Column 3 has a very high nominal phase ratio, $\beta = 800$, with a very thin film. Columns 2 and 3 admit measuring the retention of alkanes with higher carbon numbers, n, up to 32. All measurements were run in a Hewlett-Packard 5880A chromatograph. Flame ionization detection was used in all cases. The applied split ratios ranged from 60

to 100:1, using hydrogen as the carrier gas. The retention times, t_R, were measured with a precision of 0.001 min. The injected quantities were such that, invariably, the recorded peak areas were lower than 1000 counts, and in the same order for all the n-alkanes eluted in the same chromatogram. In the employed instrument one count approximately corresponds to one detected picocoulomb. As a guideline, the response of combined detector–integrator is 5000 pC/μl of injected methane (1 μl~0.65 μg of methane at ambient p and T). The approximate upper limit of 1000 counts was found for not detecting any variation in the last digit of t_R due to the injected amount of sample. For column 1, the ratio of absolute inlet/outlet pressures was systematically varied from $P \equiv p_i/p_o = 1.4$ to 2.6. The outlet pressure p_o was the atmospheric pressure. The variation of pressures was done with a dual aim. First, to detect any dynamic effect owing to mass-transport phenomena, i.e., a dependence of the chromatographic K on the linear velocity u of carrier gas. Second, to either detect any thermodynamic effect as the pressure dependence of K caused by non-ideal behavior of the gas phase [6]. For columns 2 and 3 the range of P was 1.3–1.6. The oven temperature was monitored with three calibrated chromel–constantan thermocouples connected to a digital instrument (Omega Engineering, Stanford, CT, USA). These were located in an equilateral triangle array near to the column coil. Reported

Table 1
Columns employed in this work for the determination of K of n-alkanes[a]

Column	Commercial name	Specifications (nominal values)	β nominal	β calculated regression to Eq. (10)
1	HP-1 (crosslinked PDMS)	$L = 50$ m $d_c = 200$ μm $d_f = 0.33$ μm	151	160.4
2	HP-1 (crosslinked PDMS)	$L = 12$ m $d_c = 200$ μm $d_f = 0.33$ μm	151	157.8
3	SPB-1 (bonded PDMS)	$L = 30$ m $d_c = 320$ μm $d_f = 0.10$ μm	800	850.6

[a] Column length, L; column internal diameter, d_c; coating film thickness, d_f. The column nominal phase ratio is $\beta = d_c/4d_f$. The calculated β is the average of four values obtained by regression of $t_R(n)$ data to Eq. (10), involving four different chromatograms in the range $T = 120$ to 220°C. The lowest possible n were applied (see Tables 3–4 and Section 4).

temperatures have an error of $\pm 1°C$. Temperature gradients across the oven were such that a difference of less than $1°C$ was detected between thermocouples for $T < 200°C$, greater gradients were found for the higher temperature range.

Multi-parametric non-linear regressions of n-alkane isothermal retention data $t_R(n)$ were performed with commercial software (Sigma Plot, Jandel Scientific, CA, USA). This applies the algorithm of Marquardt.

3. On the determination of gas hold-up

The correct determination of the parameter t_M has been a controversial issue since the initiation of GC [17–26]. Great confusion in the literature has originated in the relationship between its physical significance and those experimental entities that may be correlative [26]. Three general approaches for t_M determination have been described: (a) calculation by fluid mechanics; (b) calculation through the retention of markers supposedly being completely insoluble, i.e., assuming that the marker's t_R would practically coincide with t_M; (c) calculation through multi-parametric regression of isothermal $t_R(n)$ data of homologous series, as e.g., the n-alkanes.

Approach (a) is based upon the application of basic relationships from fluid mechanics. The expression of t_M is obtained by integration of the differential form of Hagen–Poiseulle's equation, leading to [27]:

$$t_M = \frac{128\eta}{3p_o} \cdot \left(\frac{L}{d_c}\right)^2 \cdot \left[\frac{P^3 - 1}{(P^2 - 1)^2}\right] \qquad (3)$$

This, or the equivalent expression in terms of flow-rates, will not permit an accurate determination of t_M due to the intrinsic errors of measurement in the average internal column diameter d_c, the gas viscosity η, or the flow-rate. Experimental results show that even when d_c is specified by electronic microscopy, considerable discrepancy of results is computed between flow-rate [28] and pressure [25] measurements. Excessively high values of t_M, close to t_R of methane, have been reported by this method [25].

Method (b) cannot be applied since all gases used

as t_M markers permeate the PDMS polymer, and therefore, are invariably retained to some extent [15].

Method (c) is based on the property of $\ln K_L$ (or $-\Delta G^*/kT$), for homologous series such as the n-alkanes, of being a smoothly increasing function of the carbon number n when $n \geq 5$. This assertion is valid under constant chromatographic conditions. According to Eqs. (1) and (2), in isothermal and perfectly constant conditions, and in the absence of interfacial effects, the retention time of any n-alkane is given by:

$$t_R(n) = t_M + \frac{t_M}{\beta} \cdot \exp\left[\frac{-\Delta G^*(n)}{kT}\right] \quad (\text{const. } p, T)$$

$$(4)$$

If a functional form is provided for $\Delta G^*(n)$, the corresponding multi-parametric regression of experimental $t_R(n)$ data will render the values for the parameters of the equation, i.e., t_M and the parameters contained in the second term of the right hand side. Function $-\Delta G^*(n)/kT$, viz. $\ln K_L(n)$, very slightly deviates from linearity [29]. In consequence, any appropriate empirical non-linear expression contained in the exponential of Eq. (4) will accurately represent the experimental behavior of $t_R(n)$, yielding the correct calculated value of t_M. A theoretical expression of $\Delta G^*(n)$ has been derived from elementary concepts of statistical thermodynamics [2], leading to:

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

$$(5)$$

In this, or in any empirical expression [21,23,24], the exponential term gains importance at increasing n, becoming relatively less important as the contribution to $t_R(n)$ from the first term t_M. Hence, in the determination of the parameter t_M by curve fitting, the statistical weights for t_R values of low n are more significant. When a low retention column is used, like those with a great phase ratio or a short length, the smaller n-alkanes cannot be included in the chromatogram. Consequently, the determination of t_M by the n-alkane regression method loses exactitude. Another reason for the lack of reliability of the calculated t_M in these types of columns is their lower magnitudes, introducing greater percentage

Table 2
Short column 2[a]

T (°C)	n	$t_R(n)$ exp. (min)	$t_R(n)$ calc.[b] (min)	Parameters obtained by regression to Eq. (5)	t_M calculated from t_R and K_L of methane Eq. (8)	t_R of methane (exp.)
280	20	1.434	1.434	$t_M = 0.875 \pm 0.0014$	0.879	0.885
	22	1.762	1.762	$A = -4.842 \pm 0.0094$		
	24	2.280	2.280	$B = 0.242 \pm 0.0005$		
	26	3.094	3.094	$C = 0.00024 \pm 0.000005$		
	30	6.354	6.354			
	32	9.439	9.439			
300	20	1.067	1.067	$t_M = 0.763 \pm 0.0026$	0.758	0.763
	22	1.228	1.228	$A = -5.097 \pm 0.031$		
	24	1.470	1.470	$B = 0.223 \pm 0.0017$		
	26	1.834	1.835	$C = 0.00025 \pm 0.000015$		
	28	2.382	2.382			
	30	3.200	3.200			
	32	4.415	4.415			

[a] Due to the application of excessively high n, two anomalous values of t_M are obtained by the n-alkanes regression method. These are compared with t_M calculated from the retention of methane and its K_L. At 280°C the t_M obtained by regression is too low. At 300°C the inverse situation is attained; t_M obtained by regression is equal to t_R of methane, thus exceeding the expected value.

[b] $t_R(n)$ calc. values are calculated with the parameters of the regression. The applied software uses 15 characters for the calculations. In all tables the parameters are rounded to 3 or 4 digits for an easier comparison.

standard errors. In order to illustrate this situation, Table 2 indicates the retention times used in the regressions and the calculated parameters for the short column 2. These only include values of $n > 20$, which are excessively high for an accurate determination of t_M, particularly considering the errors originated by peak asymmetry in this column. Strictly, t_R should be replaced by t_1 in Eqs. (2) or (4). In one case the calculated t_M is excessively low compared to t_M derived from the retention of methane and its K_L. On the other case the calculated t_M is equal to the retention of methane, a condition that has no physical sense [26]. These two chromatograms were unique examples where significant deviations were detected, but are illustrative of what could occur in principle in other cases.

The described regression method for t_M determination is only applicable when the retention times of the shorter n-alkanes are included in the chromatogram, i.e., for long columns having a reduced phase ratio, in the order $\beta \sim 100$. This situation demands seeking another way of estimating t_M in weakly retentive columns, especially for the short columns where peak asymmetry is important. To overcome this difficulty, one possibility is to use a t_M marker whose $K(T)$ function has been previously established

through adequate experimental conditions. We shall employ here the ln $K(T)$ function of methane reported in a preceding publication [29]. This was determined in the 50 m column with nominal $\beta = 151$. Although for a more accurate determination of K of methane a column of at least 100 m with $\beta \sim 100$ would be needed at temperatures between 80 and 120°C, the lack of data from the current literature covering this issue compels us to adopt $K(T)$ reported in Ref. [29][1]. The behavior in the range 40–120°C is described by the following polynomial of the reciprocal absolute temperature:

$$\ln K(CH_4) = 1.401 - 2106(1/T) + 616\,275(1/T)^2$$
$$(313 \leq T \leq 393 \text{ K}) \qquad (6)$$

For the practical purpose of determining t_M, the behavior at temperatures over 120°C may be approximated to [26]:

$$K(CH_4) \cong 1 \quad (T \geq 393 \text{ K}) \qquad (7)$$

[1] More accurate determinations of methane's K_L near ambient temperature should be obtained by using other methods, rather than GC, such as measuring it in the Ben Naim–Baer apparatus.

By using the relationships given by Eqs.(6) and (7), t_M can then be estimated through Eq. (2):

$$t_M = t_R(CH_4) \cdot \frac{\beta}{\beta + K(CH_4)} \qquad (8)$$

When the retention times are measured with a precision of 0.001 min, it can be checked easily that for $K \sim 1$ and $\beta > 250$, variations of almost 10% in β do not induce any change in the last digit of the calculated t_M. Therefore, nominal values of β can be used in Eq. (8) as a first approximation, provided this β will be corrected a posteriori applying some appropriate estimation of the parameter.

The latter described procedure is the one employed for determining t_M in the chromatograms of columns 2 and 3. The regression to Eq. (5) was the method employed for column 1, and this generated the reported $K(CH_4)$ function.

4. On the determination of the phase ratio

In the current method the volume ratio of gas to liquid phases can be guessed through the information on the column's construction. From this information the geometric parameters of the column may be estimated roughly. For wall-coated capillary columns the phase ratio can be approximated to:

$$\beta \equiv \frac{V_G}{V_L} \cong \frac{d_c}{4d_f} \qquad (9)$$

Great difficulties for a direct accurate determination of the average column internal diameter d_c and film thickness d_f are evident. Usually, d_f is estimated indirectly through information from the coating method [30–34]. When the dynamic method is utilized, the film thickness is a function of the passage velocity of the solution containing the stationary phase. A perfectly uniform film thickness

Table 3
Column 2[a]

T (°C)	n	$t_R(n)$ exp. (min)	$t_R(n)$ calc.[b] (min)	Parameters obtained by regression to Eq. (10)	t_M calculated from t_R and K_L of methane Eq. (8)	t_R of methane (exp.)
120	9	0.871	0.871	$\beta = 157.6 \pm 0.8$	0.525	0.528
	10	1.137	1.137	$B = 0.593 \pm 0.0010$		
	11	1.604	1.604	$C = 0.00111 \pm 0.00003$		
	12	2.420	2.420			
200	14	1.392	1.390	$\beta = 156.8 \pm 1.9$	0.792	0.797
	16	2.020	2.023	$B = 0.373 \pm 0.0010$		
	20	5.938	5.937	$C = 0.000378 \pm 0.000015$		
	22	11.237	11.238			
	24	21.887	21.887			
220	12	1.003	1.003	$\beta = 157.7 \pm 1.2$	0.906	0.912
	13	1.079	1.079	$B = 0.337 \pm 0.0008$		
	14	1.182	1.183	$C = 0.000390 \pm 0.000013$		
	16	1.526	1.526			
	18	2.175	2.175			
	20	3.397	3.397			
	22	5.689	5.689			
220	18	1.755	1.757	$\beta = 159.0 \pm 2.2$	0.653	0.657
	20	2.746	2.744	$B = 0.337 \pm 0.001$		
	22	4.592	4.592	$C = 0.00040 \pm 0.000012$		
	24	8.027	8.028			
	26	14.367	14.367			

[a] Estimation of β by curve fitting to Eq. (10), using t_M calculated from the retention of methane and its K_L.
[b] $t_R(n)$ calc. values are calculated with the parameters of the regression and t_M reported in the sixth column. The latter is a constant for the curve fit to Eq. (10). The applied software uses 15 characters for the calculations. In all tables the parameters are rounded to 3 or 4 digits for an easier comparison.

along the whole column length cannot be assured [30]. Therefore, in these estimations of the parameters great uncertainty is attained, even when the time consuming static method of coating is applied [30].

In Ref. [29] was shown that for the retention of n-alkanes on PDMS at temperatures over 120°C, the contribution to $\Delta G^*(n)/kT$ independent of n becomes negligible. This absent contribution is ascribed to end methyl C–H bonds. With this condition, Eq. (4) is reduced to:

$$t_R(n) = t_M + \frac{t_M}{\beta} \cdot \exp\left[B(n-1) + \ln\left(1 - Cn^2\right)\right]$$

(10)

where $(n-1)$ is the number of C–C bonds in the alkane molecule. If t_M is determined by other means than curve fitting, as e.g., using methane as the marker and its previously determined $K(T)$ function, the unknown parameters are β, B and C. Hence, the n-alkane regression method can now be applied for calculating only β, B and C.

Tables 3 and 4 show the results obtained by the regressions of $t_R(n)$ data to Eq. (10), respectively, in columns 2 and 3. Temperatures are between 120 and 220°C. The chromatograms containing the lowest n possible were included (recalling that n must be ≥ 5). The gas hold-up is not a parameter to be determined; it is a constant in the curve fitting

Table 4
Column 3[a]

T (°C)	n	$t_R(n)$ exp. (min)	$t_R(n)$ calc.[b] (min)	Parameters obtained by regression to Eq. (10)	t_M calculated from t_R and K_L of methane Eq. (8)	t_R of methane (exp.)
120	8	1.669	1.669	$\beta = 849.8 \pm 7.2$	1.561	1.563
	9	1.753	1.753	$B = 0.591 \pm 0.0014$		
	10	1.900	1.900	$C = 0.000998 \pm 0.000039$		
	11	2.159	2.159			
	12	2.614	2.614			
	14	4.789	4.789			
140	8	1.686	1.687	$\beta = 852.5 \pm 5.1$	1.616	1.618
	9	1.734	1.734	$B = 0.524 \pm 0.0007$		
	10	1.812	1.812	$C = 0.000738 \pm 0.000014$		
	11	1.942	1.942			
	12	2.156	2.156			
	13	2.511	2.510			
	14	3.090	3.091			
	16	5.605	5.605			
	18	12.290	12.290			
160	8	1.723	1.723	$\beta = 850.0 \pm 5.4$	1.673	1.675
	9	1.751	1.751	$B = 0.467 \pm 0.00076$		
	10	1.796	1.796	$C = 0.000610 \pm 0.000016$		
	11	1.867	1.867			
	13	2.152	2.152			
	14	2.423	2.423			
	16	3.501	3.501			
	18	6.096	6.096			
180	12	1.915	1.915	$\beta = 850.3 \pm 3.4$	1.730	1.732
	13	2.008	2.008	$B = 0.418 \pm 0.0014$		
	14	2.145	2.145	$C = 0.000518 \pm 0.000015$		
	16	2.656	2.656			
	18	3.779	3.779			

[a] Estimation of β by curve fitting to Eq. (10), using t_M calculated from the retention of methane and its K_L.

[b] $t_R(n)$ calc. values are calculated with the parameters of the regression and t_M reported in the sixth column. The latter is a constant for the curve fit to Eq. (10). The applied software uses 15 characters for the calculations. In all tables the parameters are rounded to 3 or 4 digits for an easier comparison.

Table 5
Ln K tabulated as function of T

T (°C)	$n=6$			$n=7$			$n=8$			$n=9$			$n=10$			$n=11$			$n=12$			$n=13$			$n=14$			$n=16$		
	Column 1	Column 2	Column 3	Column 1	Column 2	Column 3	Column 1	Column 2	Column 3	Column 1	Column 2	Column 3	Column 1	Column 2	Column 3	Column 1	Column 2	Column 3	Column 1	Column 2	Column 3	Column 1	Column 2	Column 3	Column 1	Column 2	Column 3	Column 1	Column 2	Column 3
40	4.979			5.900			6.815		6.794	7.724		7.702																			
50	4.646	4.64		5.510	5.501		6.372	6.363		7.229	7.220																			
60	4.338			5.155		4.324	5.967	5.953	5.950	6.775	6.757	6.756	7.573	7.557	7.558		8.359				9.152			9.938						
70	4.059			4.825	4.81		5.593	5.576		6.353	6.339		7.112	7.098			7.852			8.604										
80	3.794			4.520		3.768	5.241	5.224	5.223	5.960		5.941	6.675	6.655	6.655	7.390	7.368	7.367		8.077	8.074			8.779						
90	3.560			4.244			4.924			5.602			6.277																	
100	3.330			3.976		3.960	4.621		4.607	5.261	5.243	5.245	5.898	5.882	5.883	6.533	6.514	6.516	7.166	7.145	7.147			7.774			8.404			9.647
120	2.926			3.509		3.501	4.083		4.073	4.661	4.65	4.648	5.230	5.217	5.217	5.800	5.782	5.786	6.364	6.346	6.350			6.912			7.472			8.584
140	2.587			3.107			3.620		3.613	4.137	4.12	4.124	4.646	4.64	4.635	5.154	5.142	5.144	5.661	5.647	5.650			6.155	6.660		6.654			7.650
160	2.305			2.764			3.229		3.236	3.676	3.68	3.680	4.138	4.13	4.136	4.594	4.58	4.591	5.051	5.038	5.039	5.494		5.494	5.949	5.945	5.942		6.839	6.834
180	2.052			2.464			2.878			3.288	3.29		3.694			4.104	4.10		4.511	4.51	4.515	4.920		4.918	5.322		5.318			6.120
200	1.809			2.188			2.580			2.955			3.308			3.689			4.043		4.035		4.37	4.378	4.778		4.777		5.500	5.498
220	1.617			1.939			2.262			2.613			2.952			3.291			3.624				3.97	4.035	4.283	4.287			4.940	
240				1.756						2.364																3.88			4.453	4.449

Table 6
Measured ln K of n-alkanes in the range of chain lengths from $n = 18$ to 32

T (°C)	Ln K							
	$n = 18$	$n = 20$	$n = 22$	$n = 24$	$n = 26$	$n = 28$	$n = 30$	$n = 32$
140	8.633, column 3							
160	7.721, column 2							
	7.718, column 3							
180	6.917, column 3							
200	6.180, column 3	6.933, column 2	7.641, column 3	8.344, column 3				
220	5.587, column 2	6.226, column 2	6.860, column 2	7.489, column 2	8.111, column 2			
240	5.049, column 2	5.621, column 2	6.192, column 2	6.752, column 2	7.322, column 2	7.864, column 2	8.421, column2	
	5.051, column 3					7.853, column 3	8.436, column 3	
260		5.081, column 2	5.594, column 2	6.105, column 2	6.611, column 2	7.113, column 2	7.611, column 2	8.103, column 2
280		4.596, column 2	5.060, column 2	5.522, column 2	5.981, column 2	6.432, column 2	6.886, column 2	7.332, column 2
300		4.209, column 2	4.618, column 2	5.026, column 2	5.434, column 2	5.843, column 2	6.249, column 2	6.651, column 2

calculation. The employed t_M are reported in the sixth column of these tables. In Ref. [29] β and t_M were simultaneously determined for column 1 by the regression method.

The same consideration, as described in the preceding section, is applicable to the determination of β by regression. If the exponential factor of Eq. (10) is excessively high, great standard errors on the calculated β will be attained. Therefore, it is advisable that an adequate range of n should be included in the chromatogram. This means that chromatograms obtained at temperatures greater than 200°C should not be considered in the case of columns 2 and 3.

The average value of β from the reported four curve fits in Tables 3 and 4 are shown in the last column of Table 1. The comparison of the nominal and calculated β reveals discrepancies of about 6% for columns 1 and 3, while the difference is lower for column 2, though this was produced by the same manufacturer of column 1.

5. Results and discussion

Tables 5 and 6 reports values of ln K as function of T for each solute. At a given temperature, K was calculated from the retention time t_R of the solute according to:

$$K = \left(\frac{t_R}{t_M} - 1 \right) \cdot \beta \qquad (11)$$

As was mentioned in Section 3, t_M in columns 2 and 3 was determined through Eq. (8) using the t_R of methane, its reported $K(T)$ and β reported in the last column of Table 1. In most cases methane could be injected in the same chromatogram. When the sample contained higher homologues, the presence of solvent deprived us from injecting the marker in the same chromatogram owing to lack of resolution of marker and solvent. In these cases methane was injected alone immediately previous or posterior to the sample chromatogram.

Through the systematic variation of the head pressure in column 1, from $P = 1.4$ to 2.6, no significant changes were detected on the measured ln K beyond the experimental error. Table 7 illustrates this observation through representative examples.

Table 7
Examples of ln K data measured at different pressures in column 1 [a]

T (°C)	P	Measured ln K	Average	Standard deviation
60	1.4	4.342	4.338	0.003
	1.7	4.333		
	1.8	4.343		
	1.9	4.341		
	2.0	4.336		
	2.1	4.336		
	2.2	4.337		
	2.6	4.339		
80	1.4	3.797	3.794	0.005
	1.7	3.786		
	1.8	3.798		
	1.9	3.797		
	2.6	3.790		
100	1.4	3.329	3.330	0.006
	1.8	3.335		
	2.0	3.335		
	2.2	3.323		
	2.2	3.333		
	2.6	3.323		
120	1.4	2.933	2.926	0.008
	1.7	2.916		
	1.8	2.933		
	2.4	2.920		
	2.6	2.928		

[a] The reported data belong to $n = 6$.

Differences between runs present random fluctuations that reveal the precision of measurement in the employed chromatograph, not a systematic effect of pressure on K. Therefore, in the context of the present accuracy of measurement, ideal behavior of the gas phase can be assumed in the applied pressure interval. The average of measured ln K at different P, are the values reported in Table 5 for column 1. The reported ln K for columns 2 and 3 are also the average of different measurements, in many cases. Generally, the dispersion increases when T is incremented, as can be observed in the column of standard deviations of Table 7. The increasing temperature gradients in the oven, and the consequent reduction of temperature control, is the cause of this expected result.

From $n = 8$ to 12 the solutes could be measured in all three columns in relatively wide T intervals, without greatly differing intrinsic errors, i.e., without

too extreme differences in the orders of measured ratios t_R / t_M. This allows the comparison between columns. It can be seen in Table 5 that there are no discrepancies between columns 2 and 3, greater than the experimental dispersion. Since there is a threefold relation in their d_f, interfacial effects can also be assumed to be negligible. The discrepancies between column 1 and the others fluctuate around 0.3–0.6% at temperatures below 140°C. In principle, this could be ascribed to the greater errors in the determination of β for this column, considering that four parameters were determined by the regressions, not three as in the other cases. But the discrepancies

vanish at temperatures over 140°C. Both columns 1 and 2 belong to the same manufacturer, even though, differences in the cross-linking of the polymer may occur, considering that this process is carried out in situ. A difference in the composition might be the origin for the discrepancy [35].

Fig. 1 represents ln K as a function of the number of C–C bonds at high temperatures. The purpose of these plots is to illustrate graphically the increasing dispersion generated by incrementing T, and the application of different chromatograms and columns. This can be compared with the same graph in Ref. [29]. Therein, data from the same chromatogram
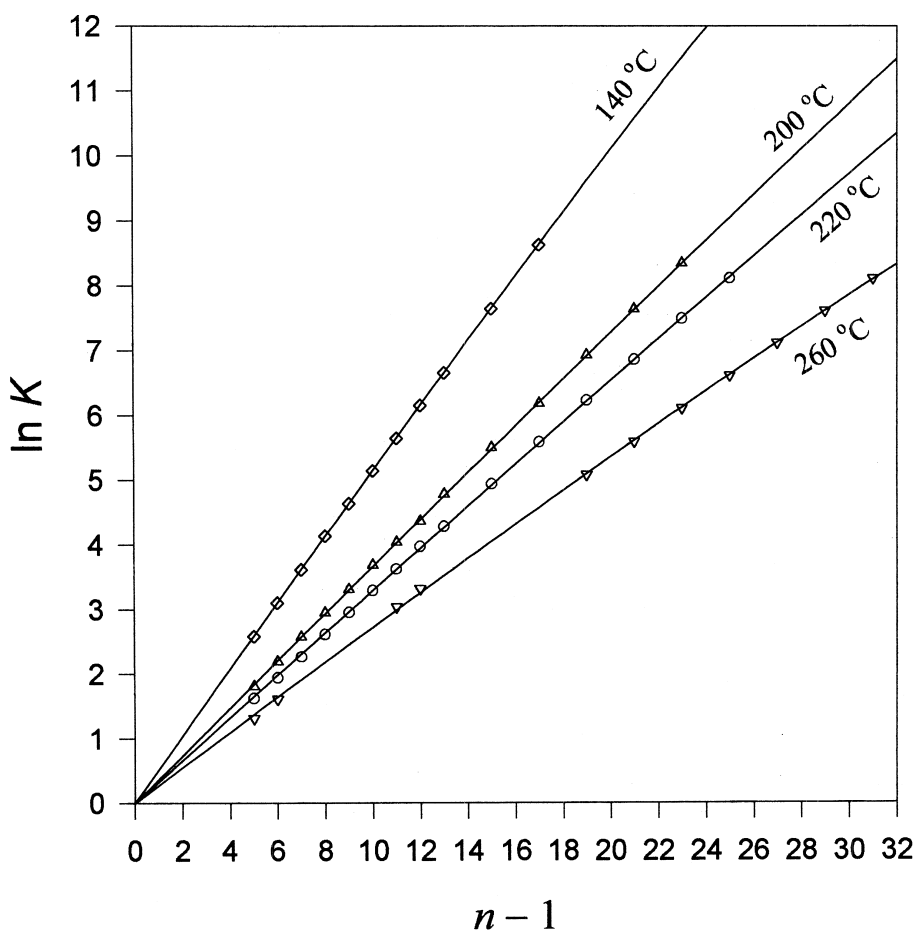

Fig. 1. Experimental ln K plotted as function of the number of C–C bonds. The same symbols are used for data obtained in different chromatograms and columns. The filled line is the theoretical expression ln $K = B(n-1) + \ln (1 - Cn^2)$. Dispersion increases dramatically with temperature due to the temperature gradients in the oven of the chromatograph.

were plotted in each curve at lower temperatures, so no dispersion could be observed graphically, and even numerically.

The theoretical physical interpretation that originated the construction of Fig. 1 in Ref. [29] is that at temperatures over 120°C C–H bonds should not contribute significantly to $-\Delta G^*(n)/kT$, and consequently, the existing contributions arise mainly from C–C bonds. This hypothesis derives from the observation on the experimental behavior of $K(T)$ of methane and the correspondent physical interpretation [26,29]. Therefore, when the number of C–C bonds in the *n*-alkane molecule tends to zero ln K should tend to be negligible.

6. Conclusions

Ln K of *n*-alkanes were measured in wide range of temperatures and carbon numbers. Commercial PDMS capillary columns with phase ratios in almost both extremes of current use were employed. The phase ratios were determined by regression. No important differences in ln K between columns were found. No pressure effect on ln K was observed using hydrogen as the carrier gas. This fact indicates that ideal behavior of the mobile phase can be assumed within the chromatographic error for pressures up to almost 3 bar (abs.). The interfacial effect was not detectable, since the film thickness had no influence on K. Therefore, we may presume that the informed ln K corresponds to ln K_L.

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