Considerations on the dependence of gas–liquid chromatographic retention of *n*-alkanes with the carbon number

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Abstract

The contributions to the free energy change involved in the chromatographic retention of *n*-alkanes, which are functions of the solute chain length, are discussed with the aid of recent advances in chain statistics. In the context of a simplified theoretical analysis, a discussion is promoted on the molecular nature of the observed slight deviations from linearity of $\ln t'_{\mathrm{R}}$ vs. *n*. A non-linear function $\ln t'_{\mathrm{R}}(n)$ is derived from the application of the generalized Van der Waals fluid partition function to the liquid stationary phase. The excluded volume, particularly its dependence on *n*, is analyzed through the theory of Flory for dilute solutions of chain molecules. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

The retention time of a solute, in the absence of extra-column effects, is given by:

$$t_{\mathrm{R}} = t_{\mathrm{M}} + \frac{t_{\mathrm{M}}}{\beta}\exp\left[-\Delta G/RT\right] \tag{1}$$

where t_{M} is the gas hold-up time, a function that involves the fluid dynamics of the chromatographic process. Parameter β is the phase ratio of the column. The partial molar free energy of solution ΔG concerns the thermodynamics of the process. Given a fixed stationary phase, it is a function of the molecular structure of the solute. Formally relating the molecular structure with a macroscopic thermodynamic function such as ΔG is a matter concerning

the field of classical and quantum mechanical statistics [1].

The most widely used retention parameter, the Kováts index [2], is based on the application of a relationship linking the retention to the molecular structure in an homologous series. This is the linear expression for *n*-alkanes:

$$\ln t'_{\mathrm{R}} = \ln\left[t_{\mathrm{R}}(n, p, T) - t_{\mathrm{M}}(p, T)\right]$$
$$= A(p, T) + B(T)n$$
$$\text{(constant } p \text{ and } T) \tag{2}$$

where *n* is the number of carbon atoms of the chain solute. The retention times of the different alkanes are measured on the same chromatogram, so the pressure *p* and the temperature *T* are constants, the structural factor *n* being the unique variable.

In an early work, Martin [3] proposed the parti-

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tioning of ΔG into a contribution ΔG^+ independent from the chain length, and an average monomeric contribution $\Delta G^\#$:

$$\Delta G(n) = \Delta G^+ + \Delta G^\# n \tag{3}$$

this structural interpretation of ΔG is consistent with Eq. (2). Replacing in Eq. (1):

$$t_R = t_M + \exp[A + Bn] \tag{4}$$

where:

$$A \equiv \ln\left(\frac{t_M}{\beta}\right) - \frac{\Delta G^+}{RT} \text{ and } B \equiv -\frac{\Delta G^\#}{RT} \tag{5}$$

Several interpretations of ΔG were developed in tandem with gas–liquid chromatography (GLC) (see e.g., Refs. [4–6]). In the field of statistical thermodynamics, the efforts by Martire et al. [7,8] are representative examples. Specifically, the interest on $\Delta G(n)$ of n-alkanes persists [9,10].

The application of equations with the form of Eq. (4), but containing non-linear terms of n inside the bracket of the exponential, has been focused on the necessity of determining t_M when ionization detection is used [11–15]. The t_M calculated by regression, to any empirical expression, has been designated generically as the ''mathematical gas hold-up time''. Recently, it was shown by Lebron-Aguilar et al. [14,15] that certain non-linear functions of n yield more precise curve fits of the experimental data.

The aim of this paper is to present a simplified theoretical analysis on the molecular origins for the deviations from linearity of $\Delta G(n)$ of n-alkanes. From this simplified theoretical context the expected phenomenology of the effect is deduced. Recent results from the statistical calculations of free energies in chain molecules are applied. The parameters from the regression of experimental $t_R(n)$ data are interpreted accordingly. The predicted and the experimental behaviors are contrasted.

2. General

The partial molar free energy change ΔG is the difference:

$$\Delta G = {}^L\mu_2 - {}^G\mu_2 \tag{6}$$

where ${}^G\mu_2$ is the chemical potential of the vapor of pure solute 2, hypothetically in an ideal mobile gas phase at unit molar concentration. The chemical potential of the solute in the liquid stationary phase, ${}^L\mu_2$, is that at unit molar concentration with the hypothetical behavior of the solution corresponding to infinite dilution. These definitions stem from the usual selection of hypothetical standard states (see e.g., Ref. [16]), on a molar basis, in linear-ideal chromatography.

We shall consider the free energy of a closed system at constant volume ${}^GV$ and p, T; composed by a gaseous solution with N non-interacting total molecules. This assumption, of an ideal gas phase, is only applicable to low-pressure GC. This implies that $k' = t_R'/t_M$ should remain practically constant with p [17], condition directly verifiable. Under the specified conditions, the chemical potential of a component i in the solution is related to the canonical partition function Q, of the system, by [1]:

$$-\frac{\mu_i}{kT} = \left(\frac{\partial \ln Q}{\partial N_i}\right)_{V, T, N_{j \neq i}} \tag{7}$$

The chemical potential of the solute in the low density phase is then:

$$-\frac{{}^G\mu_2}{kT} = -\frac{{}^GG_2}{N_A kT} = \ln\frac{{}^Gq_2}{N_A}$$

$$= \ln\frac{{}^Gq_2 {}^Gq_{r, v, e_2}}{N_A} \tag{8}$$

where ${}^Gq_2$ is the partition function of the solute molecule in the gas. It can be rigorously separated into the translational contribution q_t, and the rotational–vibrational–electronic, or internal partition function $q_{r,v,e}$. Eq. (8) was written for the Avogadro's number of solute molecules N_A in order to preserve a molar basis for the solute. Electronic configurations, at the relatively low GC temperatures, are assumed to be in their fundamental states [1]. Any variation between electronic densities in both phases are due to specific interactions, whose energetic effects will be accounted for from another viewpoint. For this reason, the electronic subscript will be eliminated. The translational partition function of the molecule, as a non-interacting particle, is:

$$q_{t_2} = \frac{^{\mathrm{G}}V}{\Lambda^3} \quad \text{where:} \quad \Lambda = h(2\pi m_2 kT)^{-1/2} \qquad (9)$$

m_2 is the mass of the solute molecule and h is Planck's constant.

The treatment of the liquid stationary phase will be placed in the theoretical context of the generalized Van der Waals (VW) fluid. In this model, the canonical partition function for a system of N total molecules [18,19] is given by:

$$Q = \frac{1}{N!}\left(\frac{V_{\mathrm{f}}}{\Lambda^3}\right)^N \left[\exp -\frac{E_{\mathrm{t}}}{2kT}\right]^N [q_{\mathrm{r,\,v}}]^N \qquad (10)$$

The theory assumes that the molecules move independently in a uniform potential field. The field is generated by the interacting forces between molecules. Due to the independence of movements the form $Q = q^N/N!$ is retained for a system of independent particles, but with two modifications [1]. First, the volume where the molecules can move in the system is reduced by excluded volume effects to a free volume V_{f}. For example, in the liquid phase with total volume $^{\mathrm{L}}V$ and excluded volume U_{e}: $^{\mathrm{L}}V_{\mathrm{f}} = {}^{\mathrm{L}}V - U_{\mathrm{e}}$. Second, a Boltzmann factor $(\exp - E_{\mathrm{t}}/2kT)$ is inserted to take into account the resultant intermolecular forces. The total potential energy of interaction E_{t} is that between a given molecule (the "central molecule") and the others of the system taken as a sum of two-body interactions. Each molecule is considered a unique rigid interacting particle. Therefore, this term neglects the inner molecular structure. The last term in Eq. (10) contains the partition function $q_{\mathrm{r,v}}$, associated with the internal degrees of freedom of the molecule.

By applying Eq. (7), the chemical potential of the solute in the dense phase is:

$$-\frac{^{\mathrm{L}}\mu_2}{kT} = \frac{^{\mathrm{L}}G_2}{N_{\mathrm{A}}kT} = \ln\frac{^{\mathrm{L}}q_2}{N_{\mathrm{A}}} = \ln\frac{^{\mathrm{L}}q_{t_2}{}^{\mathrm{L}}q_{\mathrm{r,\,v_2}}}{N_{\mathrm{A}}}$$

$$= \ln\left[\frac{^{\mathrm{L}}V_{\mathrm{f}}}{\Lambda^3 N_{\mathrm{A}}}\exp(-E_{\mathrm{t}}/2kT)^{\mathrm{L}}q_{\mathrm{r,\,v_2}}\right] \qquad (11)$$

The difference between both phases is, by using Eqs. (6), (8), (11):

$$-\frac{\Delta G}{RT} = \ln\frac{^{\mathrm{L}}V_{\mathrm{f}}}{^{\mathrm{G}}V} - \frac{E_{\mathrm{t}}}{2kT} + \ln\frac{^{\mathrm{L}}q_{\mathrm{r,\,v_2}}}{^{\mathrm{G}}q_{\mathrm{r,\,v_2}}} \qquad (12)$$

The first term of the sum is the contribution arising from the isothermal volume work performed along the compression of one mole of the ideal solute vapor, from $^{\mathrm{G}}V$ at the low density phase, to the free volume $^{\mathrm{L}}V_{\mathrm{f}}$ in the dense phase. The second term is the contribution from the potential energy of intermolecular interactions between the solute molecule and the liquid stationary phase, at infinite dilution. In this term the molecule is considered a unique spherical rigid interacting particle. Only the five degrees of freedom of the linear molecule moving as a whole are considered here. The last term arises from the energetic difference, between both environments, due to the $(3n-5)$ internal degrees of freedom of the linear molecule. These variables describe the molecular configuration and conformation.

Rigorously, the last two terms of Eq. (12) cannot be determined separately. As the linear molecule has flexibility, the monomers are in some degree individual interacting units. Although their motions are correlated by the connectivity of the chain, this correlation between two given monomers vanishes rapidly as their separation along the chain contour increases [20]. The contribution to ΔG arising from energetic interactions of interconnected monomers, and accounting for only the $(3n-5)$ internal degrees of freedom of the molecule, constitutes the conformational free energy contribution ΔG_{c}. It is related to the last term of Eq. (12):

$$-\frac{\Delta G_{\mathrm{c}}}{RT} = \ln\frac{^{\mathrm{L}}q_{\mathrm{r,\,v_2}}}{^{\mathrm{G}}q_{\mathrm{r,\,v_2}}} = \ln\frac{^{\mathrm{L}}<\exp(-U/kT)>_{\mathrm{c}}}{^{\mathrm{G}}<\exp(-U/kT)>_{\mathrm{c}}} \qquad (13)$$

where U is the two-body potential function, describing the interaction of the "central monomer" with another particle. The indicated averages are performed for overall conformations of the solute molecule, pondered by their statistical weights, with monomers in total interaction. This means we are simultaneously considering intra-molecular interactions between bonded monomers, as well as intermolecular interactions between non-bonded monomers. The averages involve multidimensional integrations. For each type of monomeric interaction, there will be a particular potential function U. The intramolecular interactions between bonded monomers are also denominated "long range intramolecu-

lar interactions'' meaning that the interacting pair is distantly separated along the chain contour, but physically close so the interaction is feasible.

In fact, the first term of Eq. (12) is also linked to the conformational properties of the solute molecule, through the excluded volume U_e. Although not rigorous, we shall preserve the generalized VW partition approximation in this discussion. Its simplicity is specially suited for our present purposes. Several aspects of chromatographic interest can be pointed out from this formalism. A more rigorous partitioning, such as Ben Naim's and those arising from the extension of Flory–Huggins lattice theory (see e.g., Refs. [21,22]) would not admit a simple overview.

Long range interactions between segments in chain molecules frustrates the possibility of expressing the potential energy of the molecule as a sum of contributions associated to each monomer and first neighbors along the chain [23]. The total two-body potential energy of a chain molecule has to be calculated by summation over all pair interactions (monomer–monomer and monomer–solvent) in the system, considering its connectivity. With such conditions, the average properties of the system can only be obtained by means of molecular dynamics or Monte Carlo (MC) calculations [23]. Contemporary advances in MC calculations of chain molecules free energies [24,25] allows an insight into our specific questioning, the nature of the ΔG dependence on n.

3. The conformational free energy

3.1. Representation of categories of interaction. The monomeric potential functions

Herein, we shall refer exclusively to the work by Collet and Premilat [24], who studied three situations for the chain molecule, those earlier described by Flory [20].

(1) The unperturbed condition. In this condition the monomers are only affected by the preservation of bond lengths, angles and first neighbor rotation potentials. These are designated as ''short range interactions'', and are denoted by the subscript o. This condition solely expresses the effect of the monomeric connectivity, deprived of any other exter-

nal forces or perturbations. It corresponds to Flory's Θ condition in a solution. Θ is the temperature at which solute–solvent segmental interactions compensate the intramolecular repulsion. Then, the molecule adopts the unperturbed conformations. The excluded volume effect vanishes under such conditions, and the monomers behave as punctual particles [20].

(2) Extended conformations in a good solvent. In a solution comprising a good solvent the molecule adopts extended conformations with respect to the unperturbed molecular dimensions. The expansion of the molecule is a consequence of the particular solute–solvent monomeric potential function. This will present an important attractive term. In Ref. [24] the expansion of the molecular dimensions is modeled by a hard sphere potential function, identified by the subscript hs, avoiding the explicit representation of the solvent.

(3) Intramolecular long range interactions in a poor solvent. In a dense environment, with weak intermolecular attractive forces, segments of the molecule well separated along the chain contour are brought together. In this way, intramolecular segment–segment attractions become feasible. As a result, a long chain molecule adopts more folded conformations in comparison to the good solvent condition. The Van der Waals potential function was used by Premilat to simulate these intramolecular attractions. The subscript vw will identify the potential function for this specific interaction. According to Flory, two conditions are necessary for the occurrence of these interactions. Besides the intramolecular segment–segment attraction, a relatively high density is necessary for bringing portions of the molecule together, by the exclusion effect exerted by the surrounding molecules. This is the result of an energy balance between the entropic trend of the molecule to pervade the available volume, the intramolecular monomer–monomer attraction, and the intermolecular exclusion. As an illustration for such conditions, Fig. 1 shows the experimental critical volumes of n-alkanes as function of chain length, taken from Ref. [26]. All critical pressures are over 46 bar. It can be clearly seen that this is an additive property for $n \le 5$, namely for the alkanes where intramolecular interactions are not possible (dotted line). Five is the least number of methylenes
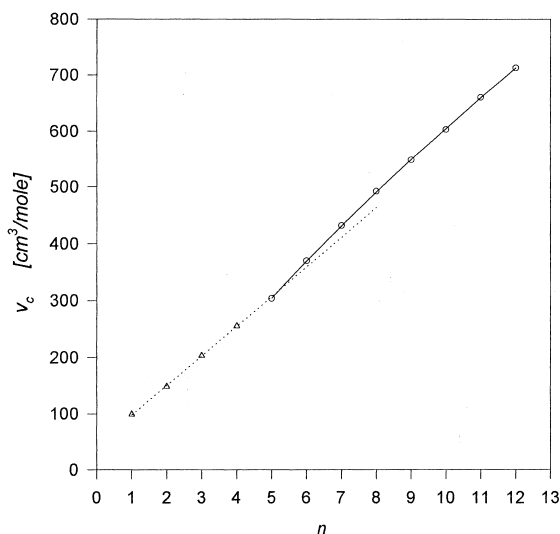
Fig. 1. Critical volumes of n-alkanes as a function of chain length. When the carbon number surpasses $n = 5$, long range intramolecular interactions become feasible, playing an important role in the properties of a dense phase.

necessary to form a loop such that the ends of this part of the molecule can interact. A different behavior is observed for those alkanes with $n \geq 5$, when these interactions become feasible. This fact reveals the importance of long range intramolecular interactions at a high density, but sufficiently low to maintain intermolecular attractions as not dominant. Intramolecular interactions will be hindered in the good solvent by the strong intermolecular attractions, causers of the molecular expansion.

3.2. The perturbed system

Short range interactions (o) define the connectivity of the chain. Then, any practical situation will be necessarily the sum of this contribution plus a perturbation indicated by p. Under the conditions described in points (2) and (3) in Section 3.1 the monomeric potential functions will be: p≡hs and p≡vw, respectively. The total conformational potential energy of the molecule is the sum of the unperturbed term and the perturbation: $E_c = E_o + E_p$.

The rotational isomeric state (RIS) model of Flory [27] is applied to the calculation of the molecular partition function q_o in the unperturbed condition. In this ideal condition the conformational free energy G_o is a linear function of n [24,27]:

$$-\frac{G_o}{RT} = \ln q_o = \overline{G_o}(n - 2) \tag{14}$$

where $\overline{G_o}$ is an average contribution per C–C bond to $-G_o/RT$.

Collet and Premilat's results, which are based on Refs. [28,29], indicate that the conformational free energy is also a linear function of n in the studied perturbed systems:

$$\frac{\Delta G_p}{RT} \equiv \frac{G_{o+p}}{RT} - \frac{G_o}{RT}$$

$$= \ln \frac{q_o}{q_{o+p}} = \overline{G_p}(n - 2) \tag{15}$$

with p=hs for the good solvent and p=vw for the poor solvent condition.

3.3. The GLC conformational free energy

By definition, intermolecular interactions are non existent in the ideal gas phase. We shall also neglect intramolecular interactions, due to the low density of the gas. This assumption implies that $^{G}q_{r,v2} = q_o$.

The roles are inverted in the GLC stationary phase, with respect to what is usual in polymer science. The solute is a low-molecular-mass substance, while the solvent is a relatively high-molecular-mass polymer. Notwithstanding, the Θ temperature of the conjugate solution is a parameter reflecting the segmental thermodynamic interaction in the system. With few exceptions, we can consider normal alkanes to be poor or bad solvents for most polymers used as stationary phases. The poorer the solvent, the higher is Θ of the system, and conversely for good solvents. At a temperature $T < \Theta$, phase segregation is likely to occur, due to the solute–solvent repulsion [20]. At $T = \Theta$ the unperturbed condition in the stationary phase solution is accomplished, then: $^{L}q_{r,v2} = q_0$. Consequently, there will be no chromatographic retention at $T \leq \Theta$.

At temperatures slightly over Θ ($T > \Theta$), the poor solvent condition is attained. Then, from Eqs. (13) and (15) we should write:

$$-\frac{\Delta G_c}{RT} = \ln \frac{^{\mathrm{L}}q_{\mathrm{r},\,\mathrm{v}_2}}{^{\mathrm{G}}q_{\mathrm{r},\,\mathrm{v}_2}}$$

$$= \ln \frac{q_{o+vw}}{q_o} = \overline{G}_{vw}(n-2) \tag{16}$$

(ideal poor solvent condition)

It can be expected that as the temperature is decreased toward Θ, no matter what the chemical composition of the stationary phase, the conformational free energy should tend to universal values, those given by the theoretical poor solvent. In this condition, intramolecular interactions are dominant. These are governed by the methylene–methylene potential function, irrespective of solvent's nature. We shall denote this universal limit: ''the ideal poor solvent condition''.

When the temperature of the system is raised high above Θ $(T \gg \Theta)$, or the affinity of the stationary phase for the n-alkanes improves, the actual contribution per C–C bond to the conformational free energy, that will be represented by the symbol $\overline{G}_c$, should depart from the value of the ideal poor solvent $\overline{G}_{vw}$. As the molecular dimensions expands in the good solvent, intramolecular interactions become less important. Premilat's work shows that for the good solvent $\overline{G}_{hs}$, from Eq. (15), is extremely low. This means that the difference of conformational free energy between the good solvent and the unperturbed state is negligible. However, the molecular dimensions in both conditions differ substantially. Then, we can assume for the good solvent condition:

$$-\frac{\Delta G_c}{RT} = \ln \frac{q_{o+hs}}{q_o} = -\overline{G}_{hs}(n-2)$$

$$\approx 0 \quad \text{(good solvent condition)} \tag{17}$$

4. The intermolecular energy of interaction for the rigid molecule

As mentioned previously, the term $E_t/2RT$ in Eq. (12) cannot be determined independently from the conformational free energy. Therefore, its dependence on n has to be analyzed in conjunction with the last term of Eq. (12). Spyriouni et al. [30] reported an MC calculation for the excess chemical potential of short n-alkanes (C_6 to C_{15}), dissolved in C_{16} at infinite dilution. The simulation was performed in a low density vapor and in the liquid. These calculations also involve the five degrees of freedom of the molecule as a rigid particle. Two reference states were used, the unperturbed condition, and the low density gas retaining intramolecular interactions. Whatever the reference state being used, the results display a linear dependence on n in the vapor and the liquid. By applying the Soave–Redlich–Kwong equation of state and the ideal gas reference, they showed that also a linear function is obtained for the liquid at 450 K: $\mu_2^e = \overline{G}_2^e(n-2)$. From this report it follows that the consideration of the five degrees of freedom of the molecule as a rigid particle also leads to a linear dependence of the calculated free energies. In view of these results, and those from Premilat's work, we shall assume a linear dependence for the last two terms of Eq. (12):

$$-\frac{E_t}{2RT} + \ln \frac{^{\mathrm{L}}q_{\mathrm{r},\,\mathrm{v}_2}}{^{\mathrm{G}}q_{\mathrm{r},\,\mathrm{v}_2}} \equiv -(\overline{G}_t + \overline{G}_c)(n-2) - \frac{\Delta G^+}{RT}$$

$$\tag{18}$$

where ΔG^+ is the free energy contribution independent from chain length, that accounts for the ordinate displacements that may exist in the plots of ΔG_c or vs. $(n-2)$. This displacement arises, in part, from the energies of rotation concerning hydrogen. These energetic contributions are neglected by the united atoms formalism, which considers the methylene monomer the least interacting unit.

Under the good solvent condition $\overline{G}_c$ should be negligible, while it is expected that $\overline{G}_t$ be important. The inverse situation will occur in the poor solvent condition.

MC calculations, described so far, cannot detect systematic deviations from linearity in the studied properties. One major problem with these calculations is the error arising from the specific MC sampling techniques. If the deviations from linearity to be determined are too small, within the magnitude of this error, the effect would pass unnoticed. Also, it should be remarked that these are first-order perturbation estimations.

5. The dependence of the isothermal volume work with n

The aim of this section is the evaluation of the dependence of the first term in Eq. (12) on n. This term can be expressed as function of volume fractions in the liquid and the phase ratio of the column:

$$\ln \frac{^{L}V_{f}}{^{G}V} = \ln \left(\frac{^{L}V - U_{e}(n)}{^{G}V} \right)$$

$$= \ln \left(1 - \frac{U_{e}(n)}{^{L}V} \right) - \ln \beta \qquad (19)$$

Consequently, the first task to face is to determine the form of the excluded volume function, corresponding to the solution volume ^{L}V.

5.1. The excluded volume in dilute solutions of chain molecules

The notion of excluded volume effects in solutions of chain molecules does not retain the simplicity derived from the VW hard spheres. It is a rather complex thermodynamic notion concerning solute–solvent interactions. In this evaluation we shall follow Flory's theory of excluded volume in dilute solution [20], in order to deduce the expected phenomenology for the effect. It is based on the estimation of the free energy change taking place when two distant molecules are brought together to a given close separation. The free energy associated to the process of bringing two molecular segments to a shared volume element is then integrated over the total volume. It is assumed a Gaussian radial distribution for the chain segment density around its center of mass. The estimated free energy is related to the probability of finding another molecular center of mass in the vicinity of the central molecule. The domain where this probability falls to be negligible, defines the excluded volume. Although the theory is developed for long coiling chain molecules, the basic concepts are applicable to our relatively short n-alkanes solutes, by adapting the theoretical notions to our specific necessities. The details of the derivations of final equations are given in Appendix A.

According to the two-term approximation of the theory, the excluded volume per unit solution volume, at infinite dilution, is:

$$\frac{U_{e}(n)}{^{L}V} \approx \left(\frac{V_{2}}{V_{1}} \right) \{ 2\Phi - c'\Phi^{2} \} n^{2}$$

$$\equiv \overline{G_{u}} n^{2} \qquad (20)$$

where the dimensionless function Φ is composed by three dimensionless factors describing the monomeric solute–solvent interaction: $\Phi = \psi_{1}[1 - (\Theta/T)](V_{2}/V_{1})$. The first factor ψ_{1} depends on the partial molar entropy of dilution, at infinite dilution. The second is a function of the reduced temperature T/Θ. The third, is the ratio of the monomeric volume of the alkane solute, V_{2}, to that of the interacting segment of the stationary phase, V_{1}. The first term of Θ, in Eq. (20), corresponds to the second coefficient in a virial expansion. Fig. 2 shows the two-term approximation of $\overline{G_{u}}$, plotted as function of the reduced temperature. The solute/solvent segmental volume ratio is assumed to be: $V_{2}/V_{1} = 0.1$, and ψ_{1} in the order of unity. Currently, the methylene will be much smaller than the structural units of most stationary phase polymers [e.g., poly-(methylphenylsiloxane)]. $\overline{G_{u}}$ has a maximum at: $T|_{max} = \Theta/\{1 - [c'\psi_{1}(V_{2}/V_{1})]^{-1}\}$

For assumed values, the maximum lies in the order of $T = 2\Theta$. This complex behavior implies that if the temperature of the system is raised high above
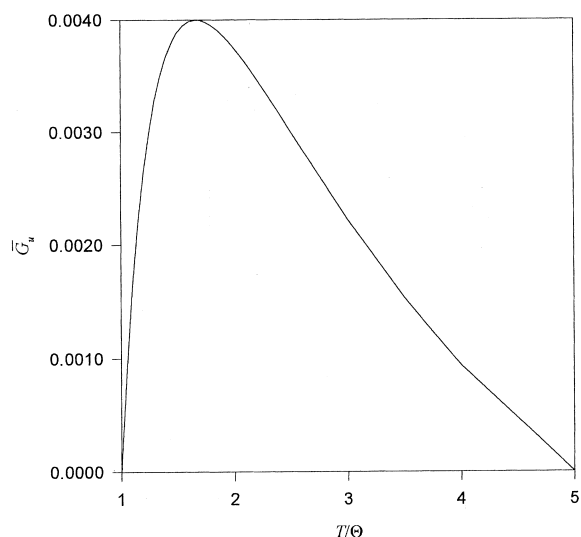

Fig. 2. The theoretical $\overline{G_{u}}$ function from the two-term approximation for F(X). This approximation erroneously predicts $\overline{G_{u}}$ returning to zero at finite high temperatures.

the Θ point, there should be a change in the sign of the temperature coefficient for the excluded volume effect. The expected monotonically increasing excluded volume U_e for better solvent conditions (increasing T) can change to a decreasing function if the temperature is sufficiently high. Theoretically, $\overline{G_u}$ can only return to zero at infinite T, when the thermal energy of the monomers is so high that these are unaffected by the potential barriers. In this situation these will behave, once more, as punctual particles. $\overline{G_u}$ erroneously reaching zero at finite T/Θ in Fig. 2 is the consequence of the limitation imposed by the two-term approximation. The theory expects that $\overline{G_u}$ should tend to zero in a bad solvent when the temperature is decreased toward Θ, and should increase for a good solvent. Generally speaking, at lower Θ temperatures for the system, the greater will be the excluded volume effects and the deviations from linearity of $\Delta G(n)$.

6. Retention time dependence on n

Finally, by using Eqs. (1), (12), (18)–(20), the retention time of n-alkanes as function of chain length will have the form:

$$
\begin{aligned}
t_R = t_M \\
+ \exp\Bigg[\left(\ln \frac{t_M}{\beta^2} - \frac{\Delta G^+}{RT} \right) - (\overline{G_t} + \overline{G_c})(n-2) \\
+ \ln\left(1 - \overline{G_u}n^2\right) \Bigg] \equiv t_M \\
+ \exp\left[A + B(n-2) + \ln\left(1 - Cn^2\right) \right]
\end{aligned} \tag{21}
$$

This theoretically derived expression is consistent with the empirical regression equation proposed by Lebron-Aguilar et al. [14,15]. When $\overline{G_u}n^2 < 0.2$, by taking only the first term in the series expansion of the logarithm in Eq. (21), this is reduced to[1]:

$$
t_R = t_M + \exp\left[A + B(n-2) - Cn^2 \right] \tag{22}
$$

$C = G_n$ is always positive. The regression of ex-

perimental data $t_R(n)$ to Eq. (21) or Eq. (22) provides a perfect curve fit with $r^2 = 1$.

7. Discussion of the theoretical consequences

We shall analyze here the theoretical behavior of $t_R(n)$. These theoretical predictions will be compared with the available experimental information, through the parameters derived from the regressions of the experimental data $t_R(n)$ to Eq. (21). The experimental data to be examined in this discussion will be restricted to that obtained from capillary columns, where the specific surface area is reduced to a minimum. Packed columns will not be considered, as adsorption effects might be important.

7.1. The dependence of t_R with the phase ratio of the column

Whatever the rigor given to the treatment of the partition functions, the isothermal volume work contribution to ΔG will always be present, leading to a dependence of parameter A with, $-2\ln \beta$ instead of the classical dependence given in Eq. (5). We should remark that in some solution theories the volume work is neglected, being viewed as a trifling contribution [21].

Since parameter $A = \ln (t_M/\beta^2) - \Delta G^+/RT$ also contains the thermodynamic factor ΔG^+, in the assessment of its dependence with the phase ratio we must correlate regression parameters obtained from columns with different β, same type of stationary phase, all measured at the same temperature. In this way ΔG^+ is reduced to a constant. Under these conditions, t_M/e^A plotted against the phase ratio of the columns should be a parabola, instead of being a straight line in accordance with Eq. (5). Fig. 3 presents data, from Refs. [14,15] and from our laboratory, for poly(dimethylsiloxane) columns. Although the β^2 representation will provide a better fit, the curve does not pass through the origin as expected.

7.2. The behavior of $\overline{G_u}$

The exposed theory predicts that the excluded volume effects should be more important in good

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[1]The interpretation of t_M in Refs. [14,15] is not that given in Eq. (22).
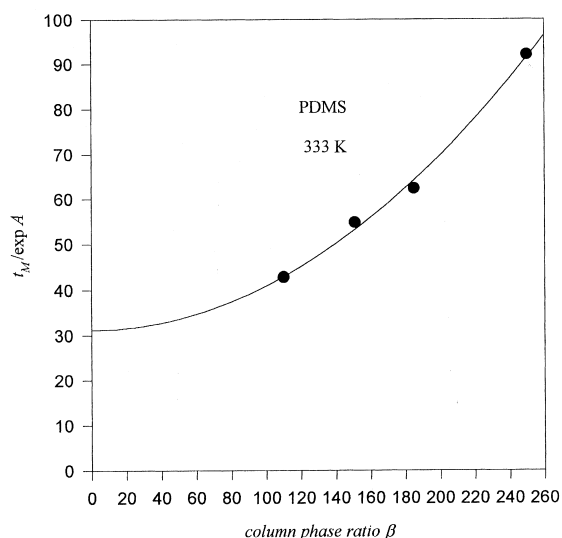
Fig. 3. The ratio of the first regression parameter (t_M), from Eq. (21), to the exponential of the second (exp A), as a function of the phase ratio β of the column. Measurements were performed at the same constant temperature (333 K) in poly(dimethylsiloxane) columns. The type of column and the ratio (diameter/film thickness) in μm: AT-1 (530/1.2), HP-1 (200/0.33), CPSIL (320/0.43), AT-1 (250/0.25).

solvents, at not extremely high temperatures over Θ. Therefore, $\overline{G_u}$, or otherwise the order of magnitude of the non-linear term, should be greater on stationary phases with good solvating properties for the n-alkanes. This will be the necessary condition for more prominent deviations from linearity of $\ln t_R'(n)$. In principle, a representative example could be given by the widely used silicone stationary phases. Poly-(dimethylsiloxane) solutions in n-alkanes display low Θ temperatures. For C_6 and C_7 it has been reported

to be 100 K [31,32], increasing for higher homologues. Table 1 presents values obtained through the regression to Eq. (21) of published data from Refs. [14,15]. The order of magnitude of $\overline{G_u}$ is 10^{-3}.

On the other hand, normal paraffins are reported to be non-solvents for poly(oxyethylene) [31,33]. This means that the point Θ for this system is over room temperature, with the consequent difficulty of determination by limiting viscometry when the low boiling alkanes are used. But GC retention occurs over 333 K in Carbowax 20M type columns. Then, Θ for these stationary phases should be slightly lower than this temperature ($\Theta \sim 323$ K). Table 1 indicates the values of $\overline{G_u}$ for this solvent, again using data from Refs. [14,15] (chromatographic column 9). It can be seen that it is an order lower than that of silicone at 333 K. Besides, the behavior with temperature is inverted, with respect to the former example. Fig. 4 displays these values, represented as a function of T/Θ, assuming $\Theta = 323$ K for poly(oxyethylene).

Comparison of Figs. 4 and 2 indicates a qualitative agreement between the expected and the observed phenomenon. Those systems in which Θ is such that 2Θ lies in the range of chromatographic measurement, should present a maximum in $\overline{G_u}(T)$. This would be the case of silicones substituted with nitrile or phenyl groups, to an adequate extent. Unfortunately, there is always a lack of information on low Θ points, due to the intrinsic difficulty of its determination.

7.3. $\overline{G_c}$ and ΔG^+ in the poor solvent

As mentioned in Section 3 Section 4, the con-

Table 1
Thermodynamic parameters from the regression of experimental $t_R(n)$ data from Refs. [14,15] to Eq. (21)

T (K)	1. PDMS, $\beta = 185$			2. PDMS, $\beta = 250$			3. PEG, $\beta = 250$		
	$\overline{G_u}$ ($\cdot 10^3$)	$-(\overline{G_t}+\overline{G_c})$	$-\Delta G^+/RT$	$\overline{G_u}$ ($\cdot 10^3$)	$-(\overline{G_t}+\overline{G_c})$	$-\Delta G^+/RT$	$\overline{G_u}$ ($\cdot 10^3$)	$(\overline{G_t}+\overline{G_c})$	$-\Delta G^+/RT$
333	1.307	0.844	6.309	1.662	0.861	6.380	0.115	0.730	4.773
363	1.138	0.710	6.043	1.138	0.719	6.149	0.360	0.616	4.673
393	0.938	0.600	5.851	0.884	0.606	5.967	0.503	0.526	4.590
423	0.786	0.510	5.709	0.724	0.515	5.827			

Columns: 1 = Poly(dimethylsiloxane) 100%. 2 = Crosslinked poly(dimethylsiloxane), 5% substitution with phenyl. 3 = Crosslinked poly(oxyethylene).
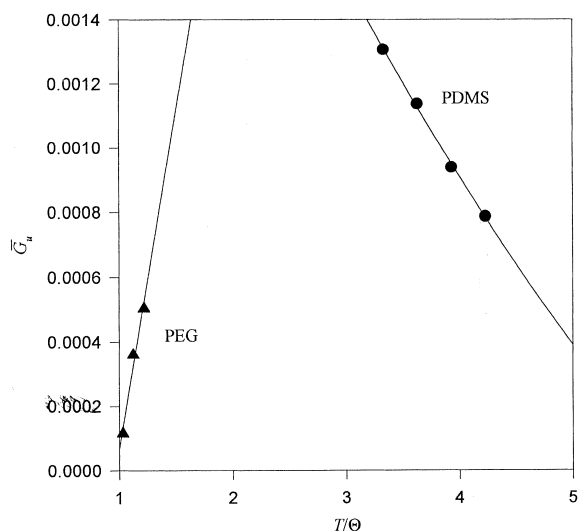
Fig. 4. Experimental $\overline{G}_u$ for poly(oxyethylene) and poly(dimethylsiloxane) as a function of the reduced temperature. Data from Refs. [14,15], columns 7 and 9.

formational free energy is coupled to the translational term of the interacting rigid molecule, both depending on n: $B(n-2) \equiv -(\overline{G}_t + \overline{G}_c)(n-2)$. For this reason, there are no means by which they can be determined separately from GC retention data. Nevertheless, in a poor solvent it is expected that $\overline{G}_t$ should be reduced to a minimum, while $\overline{G}_c$ should be the most important; in the order of the theoretical universal limit for the conformational free energy: $\overline{G}_{vw}$. Since the intramolecular long range interactions vanish at the Θ point, and diminishes when T/Θ is increased, there should be a characteristic range of T/Θ where these interactions are dominant. We will indicate this with the superindex vw. We can write:

$$\left| B \approx -\frac{\Delta G_c}{RT(n-2)} \equiv -\overline{G}_c \right|_{(T/\Theta)^{vw}} =$$
$$-\overline{G}_{vw} \quad \text{(ideal poor solvent)} \tag{23}$$

With the aim of comparing orders of magnitude for the regression parameters of poly(oxyethylene), the values of B obtained at reported temperatures were introduced into the calculation of its thermodynamic components, applying Clark–Glew–Castells method (for details, see Refs. [34,35]). In turn, these were employed for extrapolating B to 433 K, a temperature at which $\overline{G}_{vw}$ is reported in Ref. [24].

The results are: $-\overline{G}_c = 0.433$ (extrap. exp.) and $-\overline{G}_{vw} = 0.42$ (theor.)

However, for reasons exposed later, there should be a discrepancy in the thermodynamic components. In Ref. [24] these are calculated independently from ΔG_{vw}, and the results are not completely mutually consistent with the given value of $\overline{G}_{vw}$, as can be seen:

$$\frac{\Delta H_c}{RT(n-2)} = 0.846 \quad \text{(extrap. exp.)}$$

$$\frac{<E_{vw}>}{RT(n-2)} = -0.68 \quad \text{(theor.)}$$

$$\frac{\Delta S_c}{R(n-2)} = -0.413 \quad \text{(extrap. exp.)}$$

$$\frac{\Delta S_{vw}}{R(n-2)} = -0.22 \quad \text{(theor.)}$$

$$\frac{\Delta C_{p_c}}{R} = 1.087 \quad \text{(exp.)}$$

A major problem with the preceding comparisons can be understood from the plot illustrating the extrapolation of the experimental data of B in Fig. 5. When T is raised, the actual $\overline{G}_c$ in the solution should be lower than that corresponding to a constant density of vw interactions (the ideal poor solvent). The experimental curve is represented by the filled line. The hypothetical curve belonging to a constant density of intramolecular interactions (dashed line) should then run over the actual curve, with a slightly lower slope at higher T [lower $-\Delta H_c/R(n-2)$], and lower absolute value of the ordinate at the origin [lower $|\Delta S_c/R(n-2)|$]. There is a greater impact on the latter. Since errors on the entropic and enthalpic components are mutually compensating, the resultant effect on $\overline{G}_c$ will not be important. Obviously, the only way to avoid this problem is by measuring sufficient B points along a narrow temperature interval at $T/\Theta \sim 1.1$. The theoretical value of $\overline{G}_{vw}$ should be calculated at the median point of this interval, in order to make a proper comparison, without the intrinsic problems of the extrapolation.

From the preceding comparison in Fig. 5, we conclude that the poor solvent poly(oxyethylene) actually tends to the expected universal theoretical behavior when $T \to \Theta$.
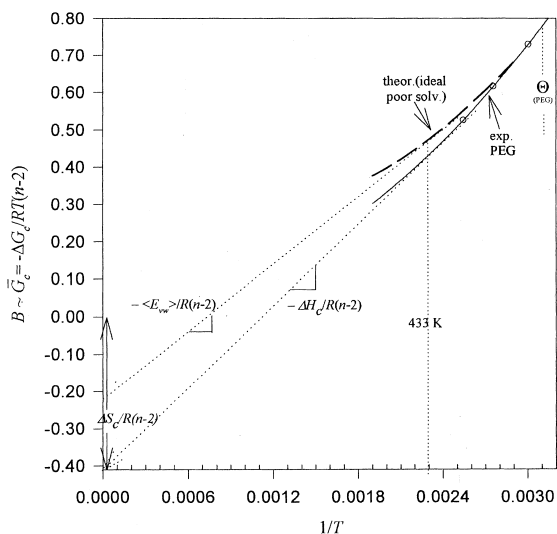
Fig. 5. Comparison of the experimental curve B vs. $1/T$ (filled line), of poly(oxyethylene), with the theoretical curve for the ideal poor solvent (dashed line). The latter is that using the reported theoretical $<E_{vw}>$ and ΔS_{vw} values at 433 K from Ref. [24], and admitting curvature by applying ΔC_{pvw} in the order of the experimental.

The results from Ref. [24] indicate that $<E_{vw}>$ is the only component to present an ordinate value at $(n-2)=0$. Therefore, this would be the only contribution to ΔG^{+} according to the poor solvent theoretical model. Once more, contrasting with the extrapolated experimental results of poly(oxyethylene) at 433 K:

$$-\frac{\Delta G^{+}}{RT} = 4.47 \quad \text{(extrap. exp.)}$$

$$-\frac{<E_{vw}>^{+}}{RT} = 5.73 \quad \text{(theor.)}$$

The theoretical model overestimates this contribution.

8. Conclusions

Present chain statistic notions can provide the elements for the interpretation of empirical expressions applied to the GLC retention of *n*-alkanes. It seems reasonable to assign the origin, for the deviations from linearity of $\ln t'_R$ vs. *n*, to excluded volume effects in the liquid stationary phase solution; effects intrinsically related to the non-ideal behavior of the solution. Whatever the theoretical context applied to treat them, these should introduce a non-linear dependence in $\Delta G(n)$. Although the deviations from linearity are small, the effects are perfectly detectable by the capillary GLC technique.

Hypothetically, if higher orders of the perturbation theory could be applied in the statistical calculations of conformational free energies, this non-linear behavior should manifest in this contribution. In this case, there would be no need to treat it separately, as done in this paper through the application of the generalized VW partition function.

The poor solvent constitutes a theoretically treatable condition, due to the dominance of intramolecular interactions. The methylene–methylene potential function is well established. On the other hand, solutions in good solvents are more difficult to study due to the unknown specific monomeric solute–solvent potential functions.

Finally, we should recommend chromatographers not to include *n*-alkanes with $n<5$ carbons in the regression of experimental data, recalling that intramolecular interactions are discontinued below pentane. This is the theoretical basis for a well known, not always followed, empirical rule.

Appendix A

According to the theory of Flory, the excluded volume in a molecular basis is:

$$u = \left(\frac{2\pi}{9}\right)^{3/2} <r^2>^{3/2} (J\xi^3) \, F(J\xi^3) \qquad \text{(A1)}$$

This equation may be viewed as correcting the proportionality of u with the solute molecular volume, by the application of the factor $XF(X)$ ($X \equiv J\xi^3$). This factor accounts for the solute–solvent

interaction. The molecular dimensions are expressed through the parameter $<r^2>$, the mean square end-to-end distance of the chain in the solution. J is a function of the segmental thermodynamic interaction between the solute monomer of mass m_o and volume V_2, and the solvent segment with volume V_1:

$$J = \psi_1 \left(1 - \frac{\Theta}{T} \right) \frac{V_2^2}{m_o^2 V_1} \qquad (A2)$$

where ψ_1 is related to the partial entropy of dilution. In our case, it will correspond to the limiting value at infinite dilution. Function ξ is related to the ratio of the square of the solute molecular mass ($m_2 = n m_o$), to its molecular volume measured in terms of $<r^2>^{3/2}$:

$$\xi^3 = \frac{9^{3/2}}{2^{1/2} \pi^{3/2}} \frac{m_o^2 n^2}{<r^2>^{3/2}} \qquad (A3)$$

The product $XF(X)$ can be developed through the series expansion of $F(X)$:

$$XF(X) = X - \frac{X^2}{2! 2^{3/2}} + \frac{X^3}{3! 3^{3/2}} - \frac{X^4}{4! 4^{3/2}} + \ldots \qquad (A4)$$

This is represented in Fig. 6 as a filled line. X is related to α, the expansion of the solute molecule, in the actual solution, over the unperturbed dimensions:
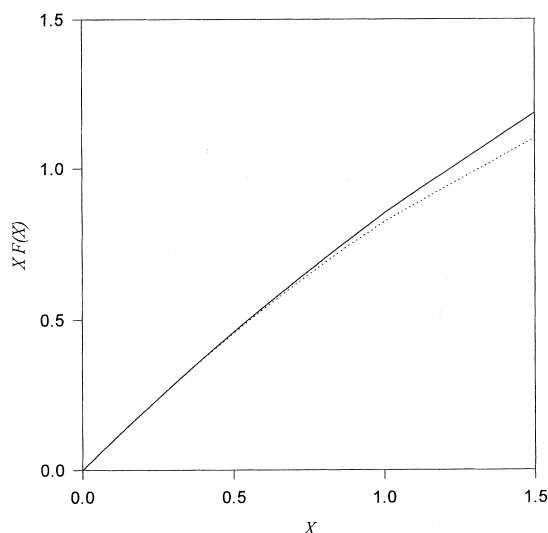

Fig. 6. Filled line: The exact product $XF(X)$ plotted as a function of X. Dotted line: the two-term approximation from the series expansion of $F(X)$.

$X = 2(\alpha^2 - 1)$, where $\alpha \equiv [<r^2>/<r^2>_o]^{1/2}$. For a very low expansion over the unperturbed dimensions ($\alpha \to 1$), namely when the system tends to the Θ temperature, by using Eqs. (A1)–(A4), the excluded volume is reduced to: $u = 2\psi_1(1 - \Theta/T)(V_2^2/V_1)n^2$. At $T = \Theta$ the excluded volume u vanishes and the monomers behave as punctual particles.

According to the results of Ref. [24], α for the good solvent (the condition with the strongest excluded volume effects) is always $\alpha < 1.1$, in the range of short chain lengths. Then, $X < 0.4$. Without committing a great error in practical conditions, we can approximate $XF(X)$ by taking only the first two terms in Eq. (A4). This approximation is shown as a dotted line in Fig. 6.

With the infinite dilution hypothesis, we can neglect the contribution of the solute to the volume of the solution. So this will be mainly given by the volume of the solvent. Recalling that V_1 is the volume of solvent associated with u, the excluded volume per unit volume of solution, at infinite dilution, will be:

$$\frac{u}{V} = 2\psi_1 \left(1 - \frac{\Theta}{T} \right) \left(\frac{V_2}{V_1} \right)^2 n^2$$

$$- 1.212 \psi_1^2 \left(1 - \frac{\Theta}{T} \right)^2 \frac{V_2^4}{V_1^3 <r^2>^{3/2}} n^4 \qquad (A5)$$

The first term of the sum corresponds to the behavior in the vicinity of the unperturbed condition, as previously described.

The "characteristic ratio" C_n is defined by: $C_n(n) \equiv <r^2>/(nl^2)$, where l is the C–C bond length. For extremely long molecules C_n tends to an asymptotic behavior. For short chains C_n is an increasing function of n that can be well represented by a potential function. This is the point in which the theory has to be adapted to the short n-alkanes condition in GLC. If we assimilate the results for the hs potential [24] to the approximation: $C_n(n) = 1.5 n^{0.423}$, applicable in the range of $n = 5$ to 40, then we may write: $<r^2>^{3/2} = 1.837 l^3 n^{2.13}$. Furthermore, we can assume the volume of the solute monomer V_2 to be in proportion to the characteristic volume given by the minimum distance between two interacting methylenes σ_{22}. Since the characteristic dimension of the monomer is taken to be: $\sigma_{22} = 3.94$ Å $= 2.56 l$ [28], we can finally write: $V_2 = cl^3$. Constant c has an

order of 10. Replacing in Eq. (A5) leads to the equivalent expression in Eq. (20).

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