

Review

Application of capillary gas chromatography to studies on solvation thermodynamics

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Abstract

The potentiality of capillary gas chromatography (GC) as a means for research on solubility phenomena is focused. Basic thermodynamic information can be obtained in a simple and direct way from this technique relying on few parameters with their associated errors tightly controlled. An unexplored field of solvation phenomenology inaccessible to other techniques is revealed by the accuracy of capillary GC, provided that relevant chromatographic variables are utilized and an adequate treatment of the experimental information performed. The present article reviews different approaches for the attainment of basic thermodynamic information through capillary GC. Some traditional concepts on the treatment of chromatographic data for physicochemical measurement are questioned. Applications of the technique to research on solubility phenomena are depicted.

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1. Introduction

Due to states distant from phase transitions, permanent gases are the fluids allowing the widest range of temperature operation among all mobile phases (MP) employed in chromatography. This feature is of vital importance from

a physicochemical viewpoint, since it permits investigating thermodynamic behaviors in ample temperature intervals wider than 200 K. Upper limits of these intervals are mainly constrained by the thermal stability of the stationary phase (SP).

Current pressures applied in gas chromatography (GC), usually $p < 2$ bar abs, deprive the mobile phase (MP) of playing a role in selectivity, as the carrier-gas behaves

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almost ideally under these conditions. Deviations from the ideal-gas behavior, namely deviations of the compressibility factor Z from unity, are in an order $<10^{-3}$ [1]. Although this is not favorable from the analytical standpoint, it is for thermodynamic purposes. In such low pressure-range the SP undergoes insignificant variations of density, behaving practically as an incompressible fluid. Relative variations of SP density are in an order $<10^{-3}$ [2].

The ideal-carrier-gas/incompressible-SP conditions introduce convenient thermodynamic simplifications. The first condition assures that at infinite-dilution solely solute interactions with the SP have relevance, so abridging the causal basis of studied thermodynamic behaviors. Both conditions ensure that the solute partition coefficient at infinite-dilution, K , remains constant along the chromatographic column. As a consequence, thermodynamic properties are not undetermined averages in the column, but well-defined values. Measurements performed on different columns are thus reproducible when bulk-absorption is the main process governing the chromatographic retention (experimental situation also referred to as ‘pure partition’ in this text). The condition of infinite-dilution is easily accessible in GC, being verified when the retention becomes independent from the amount of solute injected.

Of the thermodynamic variables (p , T , V , N), p has not relevance in the usual practice due to the exposed reasons. For thermodynamic purposes the chromatographic process is run under isothermal conditions and the column confines the system to fixed phase-volumes V_M and V_S , subscript M denoting the MP and S the SP. It can be fairly assumed that the center of a symmetrical chromatographic band is at thermodynamic equilibrium [3,4]. If the ratio of phase-volumes, $\beta \equiv V_M/V_S$, is constant along the column, in the zone at equilibrium the fraction of solute molecules in the MP, N_M/N , will be also constant. The total number of solute molecules in this zone is $N = N_M + N_S$, where N_M and N_S , respectively, are the average number of solute molecules at the MP and SP.

In principle, gas chromatography configures convenient features for easily deriving thermodynamic information of a basic level in very wide intervals of temperature, thus being capable of expanding our empirical basis on solubility phenomena. For ‘basic level’ we mean experimental information obtained from a system having minimal non-assessable effects, making the least number of a priori assumptions and approximations.

The application of GC to physicochemical measurement is established and related literature has proliferated since technique’s dawn [5,6]. This assertion could be valid for researches carried out using packed columns, but it cannot be strictly applied to the case of wall-coated open-tubular (WCOT) capillary GC [7], despite the time elapsed since its invention by Golay [8,9] and the fact that advantages in this application were early recognized [10]. For most currently employed capillary lengths and coated film thicknesses [11], the accuracy of measurement has improved one

order of magnitude [12] relative to packed columns [13], but scant experimental work has been published providing thermodynamic information of a basic level obtained through WCOT columns. The absence of specific reviews on the subject reaffirms this. One reason for a lack of exploitation of technique’s potentiality was the apparent difficulty for a precise knowledge on phase-volumes in the tiny capillaries. Some attempts to circumvent this difficulty followed classical approaches developed for packed columns. Such endeavor makes necessary revising some traditional concepts on which chromatographic information is relevant for thermodynamic aims.

Several advantages of modern WCOT capillary columns over packed ones can be enumerated for physicochemical measurement. Having a simple geometry describable through cylindrical coordinates, it needs only of few parameters to completely define the system: column length L , internal diameter d_C and SP film thickness d_f . Explicit knowledge of them all is not necessary for thermodynamic purposes. Contrary to the tortuous and intricate geometry of porous solid supports in packed beds, incompletely described by various specifications, geometrical simplicity in capillaries allows a precise estimation of interfacial areas and the concomitant estimation of the average film thickness. More uniform films in capillaries, direct consequence of its simple geometry, minimize the contribution to peak broadening due to the delay of mass transfer at the SP [3,4,14], yielding very high column efficiencies. Even for average film thicknesses of the same order [15], packed columns have much lower efficiencies due in part to film thickening in flooded pores, a direct consequence of the complex geometry. The need in packed columns of two solid components (column wall and solid support) as confining containers for the thermodynamic system of interest (MP/SP and solute) is reduced to only one in WCOT. A different thermal expansion of the column wall and solid support, and the anisotropy in the crystalline fractions of the latter, lead to an uncertain knowledge on how phase-volumes evolve with temperature. On the other hand, a precise knowledge is possible in amorphous silica capillaries [16]. A plain chemical composition of the tube made of highly pure synthetic silica, having solely $-OH$ pendent groups in the order 10^2 ppm [17] as functions different from covalently bonded $Si-O$, simplifies the picture respect to complex siliceous materials of current supports [18]. Evaluation and control of confined-phase effects [19–27] (nanometer-scale SP regions close to interfaces yielding physical properties different from the bulk liquid) is much easier for capillaries presenting well-defined smooth surfaces, compared with packing particles having a complex size-distribution of pores with an unspecified surface chemical nature. The minute resistance to heat transfer in thin capillaries assures a rapid temperature equilibration and their efficiency allows including a vast number of solutes in the same chromatogram, notably accelerating the acquisition of data. Total flows often employed in split-injection for attaining the infinite-dilution condition

(~200 ml/min) sweep injector liners of about 0.2 ml in times of the order 10^{-3} min, turning negligible the extra-column time in capillary GC. In packed columns, where split injection is not generally applied, the extra-column time in the injector is one order higher and infinite-dilution is achieved only through careful regulation of the injected quantity.

The list of convenient features of capillary GC for physicochemical measurement could be extended, but our present concern is just to outline the possibilities the technique offers in this respect. The purpose of the present article is to review concepts involved in different approaches for making feasible the attainment of basic thermodynamic information through capillary GC.

2. Relevant chromatographic parameters

The latest IUPAC recommendations for chromatography [28] affirms: “*the thermodynamically appropriate retention parameter in chromatography is the retention volume, but times and not volumes are measured directly . . .*”. Besides expressing that officially or conventionally accepted, this seems to be a concept firmly incorporated to the discipline. In the contemporary literature (see, e.g. [29–34]) the invoked equation of chromatographic retention invariably is that proposed by Martin [35,36]:

$$V_N = KV_S + K_i A_i + K_s A_s \quad (1)$$

V_N is the net retention volume [7]. K is solute’s partition coefficient at the bulk SP of volume V_S . K_i and K_s are adsorption coefficients at the interfaces, these having areas A_i and A_s . Subscripts i and s denote, respectively, the interfaces MP–SP and SP–solid. The equation settles a relationship between elution volumes and thermodynamic intensive properties denoted by constants K ’s, factored by extensive properties of the system. Let us give a deeper insight into the implications involved.

The first aspect to mention are the implications of Eq. (1) on how the interfaces contribute to the chromatographic retention. Since interfacial areas are uniquely assumed to be relevant extensive properties of the system, only processes taking place at a definite surface are considered; i.e. solely surface adsorption is accounted for. The present knowledge on phenomena at solid–liquid interfaces, for example, shows that nanoscale regions in a liquid phase stand distinct properties respect to the bulk liquid [37,38]. The perturbing effect of a surface affects an adjacent macromolecular liquid on finite extensions. In the modern literature of interface science such effects are currently referred to as “confined-phase phenomena” [19–27,37,38]. Also absorption processes will then be affected by the proximity of an interface. In packed columns the existence of pores confining the SP should enhance these phenomena [20,37]. Eq. (1) has in consequence serious limitations in this respect.

The second and most important aspect that should be revised is expressing the retention in terms of elution volumes,

form still giving rise to dutiful interpretations in GC [39–48]. The ideal-carrier-gas/incompressible-SP usual experimental conditions turning p an irrelevant thermodynamic variable should induce the immediate question: how can compressibility correction factors and flow-rates required for the determination of elution volumes become relevant chromatographic parameters for thermodynamic aims? There is a flagrant contradiction. The utilization of elution volumes does not obey thermodynamic reasons, it is founded in historical motives. This was the variable first used by James and Martin in GC [49], following the approach from the former work on liquid chromatography (LC) [50,51]. The MP velocity in the column is a function of position for compressible fluids. Hence, the expression of GC isothermal retention in pure partition has been derived through integration along the column of the differential equation of motion for the chromatographic zone at equilibrium:

$$\frac{dz}{dt} = u(z) \frac{N_M}{N} \quad (2)$$

The variables of this ordinary differential equation are the axial variable of cylindrical coordinates, z , and the time t . The equation settles that the migration velocity of the band’s equilibrium zone at a given axial position z in the column, dz/dt , is determined by two interacting factors. First, an explicit fluid dynamic factor $u(z)$, the local MP velocity. This is the axial velocity $v_z(z, r)$ averaged in the cross-sectional area of flow at position z : $u(z) \equiv \langle v_z(z, r) \rangle_{r, \theta}$. As indicated, the average is carried out on the radial variable r , where a velocity gradient exists, and the angular variable θ of cylindrical coordinates [52]. Second, a thermodynamic factor, the fraction of solute molecules in the MP at thermodynamic equilibrium, N_M/N . This is by definition the equilibrium probability for finding the solute molecule in the MP, being directly related to the thermodynamically meaningful K . The justification of Eq. (2) is that the equilibrium zone is transported along the axial coordinate through the bulk flow of MP, i.e. by forced convection. The equation is generally taken as a starting point for isothermal GC theory. When N_M/N is assumed constant along the column, namely when K and β are constant, its solution has been obtained by integrating directly on the time variable as stated [3], or by changing variables to elution volume as in the historical procedure. The results are, respectively, Eq. (5) and Eq. (3):

$$V_R^{\circ} = V_M + KV_S \quad (3)$$

$$t_R F_c j = t_M F_c j + \frac{K t_M F_c j}{\beta} \quad (4)$$

$$t_R = t_M \left(1 + \frac{K}{\beta} \right) = t_M (1 + k) \quad (5)$$

where t_R and t_M are the retention and gas hold-up times [7]. The partition coefficient is defined as $K \equiv C_S/C_M = (V_M N_S)/(V_S N_M) = \beta k$, being the retention factor $k \equiv N_S/N_M$. The corrected retention volume V_R° is the product $t_R F_c j$, where F_c is the flow-rate at the column temperature

and outlet, and j the compressibility correction factor. The MP volume V_M is renamed the “corrected hold-up volume” and is determined as $t_M F_c j$ [7].

As shown in Eq. (4), Eq. (5) also can be derived from Eq. (3) replacing V_S by V_M/β . The common fluid dynamic factor $F_c j$ cancels out leaving K solely as function of retention times and β in Eq. (5). It should be remarked that the knowledge of the ratio of phase-volumes β is necessary for determining K through this equation, not the individual phase-volumes V_M and V_S .

Eq. (5) is the same irrespective if the MP is a compressible gas or an incompressible liquid. That is to say, the result of integrating the equilibrium-zone motion is independent from the fluid dynamic aspects of the process. Then, it is evident that the explicit description of fluid mechanics, which gives rise to F_c and j , was irrelevant for reaching this result. The reason for such paradox is that Eq. (2) is not really a basic starting point. This can be understood if instead we focus the basic principle of column chromatography. This principle is developed writing only the thermodynamic factor of zone motion:

$$\frac{N_M}{N} = \lim_{n \rightarrow \infty} \frac{\sum_{i=1}^n (N_M/N)_i \Delta \tau}{\sum_{i=1}^n \Delta \tau} = \frac{\delta t_M}{\delta t} \quad (6)$$

The macroscopically observed equilibrium fraction of solute molecules in the MP, N_M/N , is not an instantaneous value. The most basic notion of statistical mechanics settles that a macroscopically observed property of a system in thermal equilibrium is an average over a sufficient long time of the dynamically unsteady microscopic states [53,54], these changing in the time scale of the femtosecond. Suppose we take a snapshot of the molecular system in the equilibrium zone and count in it the instant fraction of solute molecules that are at the MP $(N_M/N)_i$. We can then successively repeat this computation at regular intervals $\Delta \tau$ in the time scale of molecular motions and take the average as indicated in Eq. (6). The sum of the numerator has the units of time and yields the time the solute molecules were found at the MP for the total computation interval $\delta t = n \Delta \tau$. Eq. (6) then states that the macroscopic equilibrium fraction of solute molecules in the MP is equal to the fraction of time solute molecules spend at the mobile phase, $N_M/N = \delta t_M/\delta t$, in a sufficiently long interval δt . This is the most basic general principle of chromatography from which Eq. (5) directly derives with no explicit description of the nature of the MP and fluid dynamics in the system. It should be noted that, beyond thermal equilibrium, no thermodynamic hypothesis on interactions of molecules in both phases leading to the observed solute distribution was formulated, neither was formulated any hypothesis on fluid mechanics. The only hypothesis involved in Eq. (6) is statistical.

We shall firstly see how Eq. (2) derives from Eq. (6). Let us take a very short time interval δt from the standpoint of the macroscopic continuum, but sufficiently long as to comply with the statistical hypothesis, e.g. in the order of the nanosecond. Consequently, from the macroscopic viewpoint

the discrete increment δ can be changed by the continuum infinitesimal d . If we include the fluid dynamic hypothesis of convective transport in the MP, means that an element spending a differential time interval dt_M in the MP will be displaced along the axial coordinate a distance $dz = u dt_M$. Replacing $dt_M = dz/u$ in Eq. (6), Eq. (2) arises.

We shall see now how Eq. (5) derives from Eq. (6). The total interval δt is arbitrary. The unique condition is that it must be several orders of magnitude greater than the time scale of molecular motions in order to comply with the statistical hypothesis. Consequently, we can make it as long as the time it takes the equilibrium zone to migrate along the whole column length, namely it can be fixed $\delta t = t_R$. This assumption holds only if N_M/N remains constant during the chromatographic process, so K and β must be constant along the column (hypothesis of uniformity). Approaching infinite-dilution is then a prerequisite, additionally needing the requisite of ideal-gas/incompressible-SP conditions in GC, and the incompressibility of both phases in LC. Now, we can introduce the most basic fluid dynamic hypothesis: when the solute molecules are at the MP they are transported by the bulk flow. Then, for $\delta t = t_R$, the time zone-molecules spend in the MP, δt_M , is equal to the time it takes a mobile phase differential element to be transported along the whole column length during the chromatographic process. The latter is by definition t_M [7]. Thus, when $\delta t = t_R$ is $\delta t_M = t_M$, and by applying Eq. (6) is: $N_M/N = 1/(1+k) = t_M/t_R$. The equation makes no explicit reference to the fluid dynamics of the MP because all fluid dynamic aspects (described through parameters such as pressures, flow-rates, geometrical, etc.) are implicit in t_M . It clearly shows that only t_R , t_M and β are relevant for determining the thermodynamically meaningful K in pure partition. Since no hypothesis on the nature of molecular interactions was necessary for deducing this relationship, its validity for retention mechanisms simultaneously including various processes, e.g. bulk-absorption, interfacial adsorption, association, etc. is assured. In this case the retention factor will determine an apparent or effective parameter $K_{ef} \equiv k\beta$ whose exact thermodynamic significance must be inquired. Therefore, the basic retention equation for column chromatography as function of relevant parameters, in a general situation, takes the form:

$$t_R = t_M \left[1 + \frac{K_{ef}}{\beta} \right] \quad (7)$$

This equation replaces Eq. (1), or any other for different occurring processes in both phases whenever the hypothesis of uniformity is applicable.

Summarizing, the explicit fluid dynamic description in ideal-linear-isothermal chromatography is irrelevant for thermodynamic aims. One consequence of this fact is that retention volumes additionally needing of F_c and j are not relevant parameters in GC. This usage over-parameterizes the system redundantly because such information is already contained in t_M .

Working on adsorption chromatography, LeRosen in 1945 assumed valid the equality $N_M/N = t_M/(t_a + t_M)$, where t_a is the time spent by the solute molecules adsorbed on the solid surface [55]. Although this was not justified in the way is done here for Eq. (6), Giddings later perceived its importance [4]. Unfortunately, the above mentioned ultimate implications of this fundamental relationship were missed by the chromatographic literature.

The tradition of measuring retention volumes in GC, introducing experimental errors inherent to F_c and j (great errors for the former), is linked to particular characteristics of packed columns. The existence of a solid support of uncertain effective volume has not allowed the direct determination of β from the information of column construction, when current manufacturing techniques are applied. Only $V_S(T)$ has been determined from this information, or otherwise a posteriori through extraction of the SP [56–59]. $V_M(T)$ solely has been determined a posteriori of column construction through chromatographic measurement, making the approximation $V_M(T) = t_M F_c j$. It is shown in Section 5 that β can be determined exactly in capillary columns coated statically, procedure that in principle could be applied also to a column previously packed with a solid support.

Thermodynamic quantities are most currently expressed as function of specific retention volumes V_g . This parameter was introduced by Littlewood et al. [60] and is defined as:

$$V_g \equiv \frac{V_N}{W_S} \frac{273}{T} \quad (8)$$

$$V_g = \frac{K}{\rho_S} \frac{273}{T} \quad (9)$$

The net retention volume is $V_N \equiv V_R^o - V_M$. W_S and ρ_S are the mass of SP in the column and its density. Eq. (9) derives from the definition of Eq. (8) by applying Eq. (3), revealing the thermodynamic meaning of the parameter in pure partition. Since K is a very complicated function of temperature [61], it is not clear which thermodynamic interest would have introducing the factor $273/T$. Less clear is what thermodynamic significance has the quotient K/ρ_S . Also being K a complicated decreasing function of ρ_S [16,62] is obvious that this particular combination of thermodynamic functions will not have any special property deserving its determination.

Assuming V_g as the relevant chromatographic parameter for thermodynamic aims led in some cases to consider its measurement through WCOT capillary columns as an essential necessity [63–71].

3. Equation of retention

Once discussed Eq. (1), we shall inquire now on the thermodynamic significance of the measured effective constant of general Eq. (7), $K_{ef} \equiv \beta[(t_R/t_M) - 1]$, when the retention includes contributions from bulk-absorption and interfacial

phenomena of unspecified nature. Other approaches different to Eq. (1) will be revised emphasizing the application to measurement on WCOT columns.

In an early work employing capillary columns, Berezkin and Korolev [10] proposed determining K through measurement of relative retentions, utilizing non-adsorbed solutes as standards or references. The construction of columns with different SP loadings is an experimental requirement, being the same requisite for later approaches focusing the direct calculation of K without application of such standards.

More recently, a retention equation was deduced assuming that both interfaces not only introduce surface effects but also modify physical properties of the adjacent SP on depths d_i and d_s in the order of the nanometer [72], thus admitting the existence of confined-phase effects. In the deduction it was imposed the condition that the ratio A_i/A_s should be approximated to unity. The thermodynamic meaning so disclosed for K_{ef} is:

$$K_{ef} = K \left(1 + \frac{e_i d_i + e_s d_s}{d_f} \right) \quad (10)$$

The interfacial excesses are defined relative to C_S , the equilibrium numeral density of solute molecules at the bulk SP, or in a molar basis, the bulk molar concentration:

$$\begin{aligned} e_i &\equiv \frac{\langle C_i \rangle - C_S}{C_S} \equiv K_i - 1; \\ e_s &\equiv \frac{\langle C_s \rangle - C_S}{C_S} \equiv K_s - 1 \end{aligned} \quad (11)$$

$\langle C_i \rangle$ denotes an average solute concentration in the region delimited by the perturbation depth d_i , and includes all possible processes occurring within this region or subphase of the SP. $\langle C_s \rangle$ is the analogous for the other interface of the system. The term ‘excess’ applies either to a positive e indicating accumulation of solute molecules, or to a negative e due to depletion.

Although valid for packed or capillary columns, Eq. (10) presents serious practical drawbacks. The film-thickness d_f must be known with precision, so its form is unsuitable for packed columns. In the case of WCOT columns, it demands making measurements on columns of different internal diameter d_C . If d_f is diminished, d_C must be proportionally decreased in order to comply with the geometric condition [72].

For avoiding the above mentioned difficulties a more general expression must be deduced without imposing the geometric constraint of Eq. (10) ($A_i/A_s \rightarrow 1$). In this way it can be shown that (see Appendix A):

$$K_{ef} = K \left(1 + \frac{e_i V_i + e_s V_s}{V_S} \right) \quad (12)$$

V_i/V_S and V_s/V_S are the fraction of SP volume correspondent to the perturbed interfacial subphases. Like K , e_i and e_s , the perturbation depths d_i and d_s are also intensive thermodynamic properties depending only on molecular characteristics of the interacting system. If constant interfacial areas

are provided, V_i and V_s will be independent of column's SP loading V_s .

Particularly for the WCOT geometry the volume fractions in Eq. (12) can be replaced by an exact equivalence (see Appendix B):

$$K_{\text{ef}} = K \left\{ 1 + \frac{e_i \left[\frac{d_i}{d_c} - \left(\frac{d_i}{d_c} \right)^2 \left(\frac{2d_f}{d_i} - 1 \right) \right] + e_s \left[\frac{d_s}{d_c} - \left(\frac{d_s}{d_c} \right)^2 \right]}{\frac{d_f}{d_c} - \left(\frac{d_f}{d_c} \right)^2} \right\} \quad (13)$$

As should be expected, this exact expression contains the approximate Eq. (10) as a limit case. The geometric constraint $A_i/A_s \rightarrow 1$ for WCOT implies the condition $d_c \gg d_f$, so all quadratic terms of Eq. (13) can be neglected reducing it to Eq. (10).

Since d_i and d_s are in the order of the nanometer, and d_c has an order $10^2 \mu\text{m}$, the quadratic terms in the numerator of Eq. (13) are generally negligible. By using the exact relationship between the denominator and β for the WCOT geometry (see Appendix B), the equation turns to:

$$K_{\text{ef}} = K \left[1 + 4(\beta + 1) \frac{e_i d_i + e_s d_s}{d_c} \right] \quad (14)$$

Even under conditions of important interfacial phenomena, leading to significant excesses, K can still be determined accurately through Eq. (14) by making measurements on WCOT columns with the same d_c and different β (different d_f). This experimental requisite is more accessible. As in the case of pure partition, we see that only t_R , t_M and β must be known. Apart β , all other geometric parameters are irrelevant for attaining K . Given the importance of these chromatographic parameters, we dedicate subsequent sections to review the determinations of t_M and β .

For currently employed d_f in WCOT–GC columns it was shown for a system where important interfacial effects are expected that these contributions do not introduce significant discrepancies between K_{ef} and K over 393 K [72]. The temperature range at which interfacial excesses become negligible is similar to that observed in packed columns [33,73–78]. For most experimental approaches through WCOT columns, K_{ef} can be practically approximated to K .

Wick et al. recently carried out a theoretical study through Monte Carlo simulations of squalane's gas–liquid interphase [34]. They calculated the gas–liquid distribution of polar and non-polar-solutes along this region, comparing it with bulk squalane. The simulation displays a liquid subphase i with a depth $d_i \sim 1$ nm, yielding $K_i \sim 1.4$ for 1-butanol at 363 K. Although the perturbation originated by the interface really affects a depth of about 3 nm in the liquid, there is a compensation effect on K_i in this deeper region. According to Eq. (14), these results imply that in current capillary GC conditions the excess of subphase i would make a contribution to K_{ef} in an order less than 1%. The factor $4(\beta + 1)$ has an order 10^3 and d_i/d_c an order 10^{-5} . Then we see by applying Eq. (14) that for an excess $e_i \sim 0.4$, K_{ef} would

be less than 1% greater than K . This is the order of the experimental net-excess (due to both interfaces) found for the system of polar-SP/non-polar-solute previously studied in [72].

4. Determination of t_M

The basic equation of column chromatography, Eq. (7), states that the fluid dynamic parameter t_M is equal to the retention time of an ideal probe holding $K_{\text{ef}} = 0$, so it must be $K = 0$ in accordance with Eq. (12). This thermodynamic definition of a hypothetical t_M marker is consistent with the real fluid dynamic meaning of t_M , because the MP convective flow takes place in the cross-section delimited by the MP–SP interfacial surface A_i , so the SP must be completely impermeable to the hypothetical marker [79].

Substances bearing very low solubility on liquids are noble and permanent gases generally presenting K in the range 10^{-1} – 10^0 [80–84]. This experimental situation is closer to the theoretical entity of the 'ideal inert solute' of $K = 1$, than to the 'ideal unretained solute' of $K = 0$ [79]. Therefore, a dependable direct t_M determination in GC through a marker is not feasible in all cases. Important errors are committed for columns with $\beta < 10^2$ when using current markers [85].

Although the exact fluid dynamic description of Poiseuille flow is possible in the laminar regime [52], calculation of t_M through fluid mechanics in WCOT columns is impractical and leads to great errors due to the numerous parameters involved [12,86,87].

A reliable but laborious alternative of t_M determination is the regression method of n -alkanes retention. This method is based on solution properties of the linear-chain hydrocarbons, and so is convenient to introduce it through the observed thermodynamic phenomena. Fig. 1 shows $\ln K$ of n -alkanes having more than five carbon atoms ($n \geq 5$), measured on poly(dimethylsiloxane) (PDMS) and poly(ethylene glycol) (PEG) stationary phases, as examples of a non-polar and polar solvent. The data were taken from [72,88]. These correspond to averages performed, respectively, on five and six WCOT columns with β in the range (60–850), taking into account the variation with temperature of this parameter. Values for $n = 1$ –4 are not included, since below pentane the ordinates do not lie on a smooth curve [89–91]. Methane was used as a t_M marker only for columns with very high β . According to Eq. (5) is $t_M = t_R \beta / (\beta + K)$; if $K(\text{CH}_4) \leq 1$, then, errors $< 0.2\%$ are committed assuming $t_M = t_R(\text{CH}_4)$ when $\beta > 600$.

The curves accurately fitting the experimental data of Fig. 1 are slightly downward concave. Some non-linear

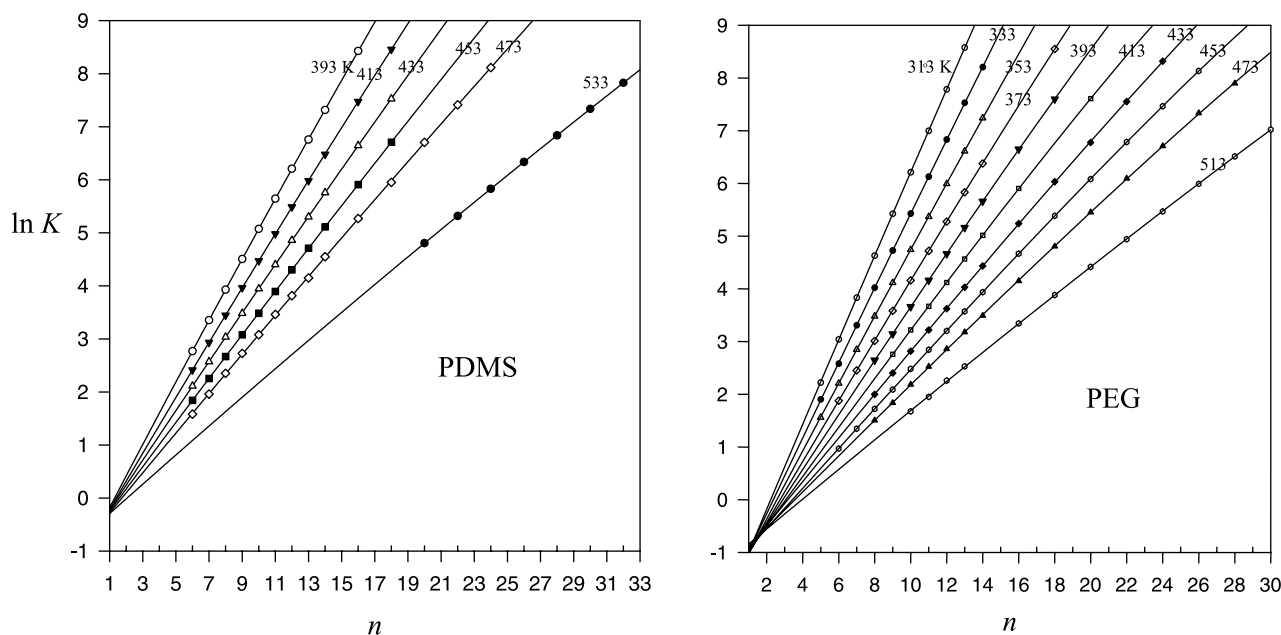


Fig. 1. Isotherms of $\ln K$ are plotted for n -alkanes as function of the number of carbon atoms n on poly(dimethylsiloxane) (PDMS) and poly(ethylene glycol) (PEG) stationary phases. Only the ordinate for pentane and higher homologues are plotted. Non-linear least-square regression curves are extrapolated to $n = 1$.

equations, or a second-order polynomial, are apt for describing this small curvature. If for example a second-order polynomial is employed, considering that K is usually the major contribution to K_{ef} , we may express also the latter as a polynomial: $\ln K_{\text{ef}}(n) = A + Bn + Cn^2$. Applying this to the equation of retention, Eq. (7) can be written as:

$$t_{\text{R}}(n) = t_{\text{M}} + \exp[\underbrace{\ln(t_{\text{M}}/\beta) + A}_{A'} + Bn + Cn^2] \quad (15)$$

This expression or any other accounting for the small curvature are suited for performing a multiparametric least-square regression of $t_{\text{R}}(n)$ data measured on the same chromatogram. In this way the parameters t_{M} , A' , B and C can be determined. Both terms that are independent of n in the exponential must be enclosed into a single parameter, $A' = \ln(t_{\text{M}}/\beta) + A$, because these have the same mathematical effect on the curve fit and in consequence are indeterminable separately. The relative weight of t_{M} decreases as all other terms of Eq. (15) increase. For this reason, low n (but $n \geq 5$) must be included for an accurate t_{M} determination. Other homologous series different to alkanes are not generally applicable owing to high values of the thermodynamic parameter A , the ordinate $\ln K_{\text{ef}}$ at the origin.

Standard errors of about $\pm 2 \times 10^{-3}$ min are obtained for t_{M} through this method, provided the following conditions. More than six alkanes are included in the chromatogram. Retention times are over 1 min and are measured with a precision of 10^{-3} min. All peaks have widths at half the height $w_{\text{h}} < 0.1$ min. The extra-column time is kept in the order 10^{-3} min (total flows of split injection are >100 ml/min and the injector liner has a volume lower than 0.5 ml).

Notwithstanding the basic importance of t_{M} and its clear physical meaning, still is evident a great deal of confusion in the literature. Let us analyze for example the concepts sustained officially. IUPAC states that through the regression function $t_{\text{R}}(n) = \mathbf{A} + \exp(\mathbf{B} + \mathbf{C}n^{\mathbf{D}})$, “the hold-up time is obtained for a value of $n = 0$ ” [28,92–94]. Accordingly, it would be $t_{\text{M}} = \mathbf{A} + e^{\mathbf{B}}$, where by comparison with Eq. (15) arises that the physical meaning of the first exponential term is $\mathbf{B} = \ln(t_{\text{M}}/\beta) + A$, where A is a thermodynamic parameter. Therefore, this interpretation contradicts the most basic equation of chromatography; Eq. (5) in the case of pure partition, or Eq. (7) for more general conditions.

Linked to the endeavor of seeking empirical equations of $t_{\text{R}}(n)$, also attention was paid in the ambit of GC to possible explanations for the solvation behavior of chain molecules stemming from different theoretical contexts [95–98]. Specifically, the observed curvature of Fig. 1 was ascribed to an effect of entropy, originated in the dependence of the solution free-volume on solute’s chain-length [98]. Through hard sphere molecular theories of free-volume, the Van der Waals fluid and the scaled-particle theory (SPT) [99–103], a free-volume entropy contribution to $\ln K$ arises for small solutes [98]:

$$\frac{\Delta S_{\text{fV}}}{k_{\text{B}}} = \ln \left[1 - \frac{V_{\text{e}}}{V_{\text{S}}} \right] \quad (16)$$

where k_{B} is Boltzmann’s constant. V_{e} is the excluded volume generated by the process of transferring the solute molecule into the solvent, thus depending on shape and size differences between solute and solvent segments. $V_{\text{e}}/N = v_{\text{c}}$ is usually interpreted in the context of SPT as the volume

of an empty cavity necessary to create in the solvent (this having a density of particles N/V_S) for making feasible the solute transfer process. The volume pervaded by chain segments does not grow linearly with the number of monomers, due to monomer connectivity complying with bond lengths and angles. For example, hydrodynamic volumes of linear polymers in solution scale as $V_h \propto [\eta]M \propto n^\delta$, where $\delta \sim (1.5\text{--}2.1)$ [104,105]. The intrinsic viscosity of the solution is $[\eta]$, and M polymer's molar mass. Short chain molecules have higher exponents, so it is expected $V_e \propto n^\delta$ with $\delta \sim 2$. Considering this fact, and the linear dependence of n -alkanes energy on n for different environments found through Monte Carlo calculations [106] (this seems to be corroborated by experimental data; see Section 7), the following semiempirical expression was proposed for $t_R(n)$ [85,98]:

$$t_R(n) = t_M + \exp[A' + B(n - 1) + \ln(1 - Cn^\delta)] \quad (17)$$

The last term in the exponential is the entropy term accounting for solute's excluded volume contribution, that responsible of the curvature of $\ln K(n)$.

5. Determination of β

The ratio of phase-volumes is essential for comparing measurements on different columns, when absolute values of K are required and for determining entropies of solute transfer. The apparent difficulty for attaining a precise knowledge on β in capillaries led in some cases to avoid its direct determination.

In the study of specific contributions to enantiomeric separations [107–111], Schurig and coworkers eliminated β through the utilization of relative retentions in a procedure that resembles Berezkin's one for mixed retention mechanisms [10]. In this case, the procedure relies on a standard solute whose K is supposed not to vary with the addition of an enantiomeric selector to a silicone SP. This condition is much harder to achieve than the invariance of a standard's K with SP loadings in Berezkin's application of relative retentions. Even in the case of a low affinity of the standard solute to the additive, the selector will modify the SP density and so standard's K .

Through the comparison with values of K obtained with other techniques for a standard solute, Carr and coworkers eluded the direct determination of column's β from the information of construction due to the volatility of the SP (hexadecane) [31,112]. The WCOT chromatographic measurement in this case is converted into a relative method needing of a 'calibration' tied to the error of other techniques. Its capacity of being an absolute method of K determination has to be neglected. Although small standard deviations were reported for specific measurements of K carried out through different methods [112], this is not generally the case. For example, measurements performed on different packed columns usually render standard deviations between 2 and 5% [13]. Static determinations of K

carried out through GC analysis of a vial's head-space have standard deviations of about 5% [113–118]. It should be remarked that, with this level of precision, part of a studied solvation phenomenology would be missed. For example, the detailed behavior of $\ln K(n)$ would remain unnoticed because error bars will overcome the curvature of this function in Fig. 1. In fact this is the reason why this curvature was not detected through packed-columns or WCOT columns when specific retention volumes V_g were measured [79,119].

Other approaches to the determination of β a posteriori from column construction have been proposed for the specific case of low-density PDMS stationary phases. The thermodynamic parameter A was neglected in [85] based on the fact that $A \equiv \ln K(n = 1)$ has the same order of $\ln K(\text{CH}_4)$ when $A \leq 0$, and that on low-density PDMS it was observed $K \sim 1$ for methane at $T \geq 393$ K [79]. If A is eliminated, also the determination of β becomes feasible through the least-square regression of $t_R(n)$ data to Eq. (17). Further research later showed that neglecting A leads to a systematic 6% overestimation of β , with respect to that arising from information of column construction, if the variation of β with T is not considered [88]. Taking into account the thermal expansion in the column, an average value of $A = -0.22$ was determined for low-density PDMS at temperatures over 393 K, using five capillary columns of different β .

If the WCOT column is manufactured through the static coating procedure [120], it was shown that it is possible to determine β exactly at any temperature [16,62]:

$$\beta(T) = \frac{\rho_S(T)}{C_0} e^{\alpha_{\text{SiO}_2}(T-T_0)} - 1 \quad (18)$$

$\rho_S(T)$ is the SP density at temperature T , C_0 is the mass-concentration of the coating solution at column's filling temperature T_0 , and α_{SiO_2} the volume thermal expansion coefficient of the solid capillary wall. At T_0 , the first term measures the reciprocal volume fraction of pure SP in the coating solution: $\phi(T_0) \equiv V_S/V_{\text{sol}} = V_S/V_C = C_0/\rho_S(T_0)$.

It can be easily shown that Eq. (18) is valid also for a packed-column, if the thermal expansion coefficient of tube's wall approximates that of the solid support. For example, in the case of borosilicate-glass or fused silica tubes filled with a deactivated siliceous support, prior to a static coating.

Although the static procedure is time consuming owing to the long-term evaporation of coating solutions, it is the manufacturing method adopted by the industry. One reason is that the dynamic coating, a faster alternative [120], does not allow a reliable estimation of the amount of SP deposited in a capillary. Only two significant digits are usually provided for d_f and β of commercial WCOT columns. The precision of these specifications can be greatly improved through the application of Eq. (18) and the exact geometric relationship

(see Appendix B):

$$d_f = \frac{dC}{2} \left[1 - \left(\frac{\beta}{\beta + 1} \right)^{1/2} \right] \quad (19)$$

The number of significant digits of measured C_o and ρ_S obviously determines the level of precision in the estimation of β . The exactitude of C_o can be increased by preparing a larger amount of solution than needed, generally leaving $\rho_S(T)$ as the sensitive measurement.

Two methods of density measurement have been currently applied, classical pycnometry (see, e.g. [16,59,121–124]) and electronic measurement through a vibrating tube transducer [125–127]. This device provides a relative method demanding its calibration by using appropriate standards of known density [128]. Electronic measurement can provide two orders of magnitude greater precision than current pycnometry. In principle, β can be estimated with the same number of significant digits as t_R , and t_M , generally four.

Times required for the evaporation of coating solutions in the static method have been reduced drastically through the application of liquid butane and fluorocarbons (freons) as coating solvents for silicones [129,130]. The utilization of vacuum is not indispensable for these solvents, and its associated problems can be eliminated. Vacuum evaporation is hard to control, presenting several drawbacks. For example, it requires a very careful previous column treatment such to collapse any micro-bubble in the solution, in order to avoid posterior events of ‘bubble projections’. If a gas bubble remains in the coating solution, this grows when vacuum is applied from the open-end of the capillary, expelling out the solution from the column, so spoiling it.

Nardi [131] recently calculated β for the static coating approximating V_M to column’s internal volume V_C . The procedure allows the calculation at the column filling temperature through direct measurement of the volume fraction of pure SP in the coating solution. The phase-volume ratio for this approximation is simply $\beta(T_o) = 1/\phi(T_o)$. Committed errors for different β can be assessed by comparison with Eq. (18).

SP volume measurements have very low accuracy with respect to weighting. Therefore, it is not generally advisable to elude the determination of densities. Moreover, being the density a relevant thermodynamic specification for a polymeric SP [16,62], its measurement should be an indispensable task in research laboratories.

6. Measurement of basic thermodynamic functions

In this section are reviewed concepts involved in current procedures of the literature for deriving basic thermodynamic functions from chromatographic data. Two formalisms for defining thermodynamic quantities have been applied, based on conventional (macroscopic) thermodynamics, and that relying on notions from statistical

mechanics. The macroscopic thermodynamic viewpoint presents limitations in two aspects. (a) It is incapable to inquire on the temperature dependence of the thermodynamic functions [53,54]. (b) Hypothetical standard states are used when defining these functions for a solvation process. Not being physically consistent entities, such references give rise to ill-defined functions [132,133]. Molecular (statistical) thermodynamics on the other hand provides a theoretical framework for studying the temperature dependence of the thermodynamic functions and makes possible an unequivocal physically consistent definition of these quantities for a solvation process [133,134].

The relevant concentration scale in statistical thermodynamics is the number density of interacting particles, $C \equiv N/V$, or in a molar basis, the molar concentration. This is the variable directly related to the system’s free-energy [53,54].

A general definition for the solvation process was given by Ben-Naim in the statistical thermodynamic context by taking the solute molecule placed in the ideal-gas as a reference-state [133]. There it does not interact with other molecules beyond collisions. The solvation process is defined as that of transferring one solute molecule from a fixed position in the ideal-gas (in our case the MP), into a fixed position in the phase of interest (in our case the SP). The process corresponds to a macroscopic one, so the ensemble average is considered. The definition was given for the (p, T, N) statistical ensemble. It is shown that:

$$\frac{-\Delta G^*}{k_B T} = \ln K \quad (20)$$

The Gibbs free-energy of solute transfer, ΔG^* , is the difference for system’s final and initial states mentioned above. As stated previously, the distribution coefficient is the quotient of numeral densities: $K = C_S/C_M$, where $C_S = N_S/V_S$ and $C_M = N_M/V_M$. Related thermodynamic quantities of the process, the entropy of solute transfer ΔS^* , the enthalpy ΔH^* , the isobaric heat capacity difference ΔC_p^* and the volume difference of transfer ΔV^* , are obtained through the application of basic thermodynamic relationships:

$$\Delta S^* = - \left(\frac{\partial \Delta G^*}{\partial T} \right)_p \quad (21)$$

$$\Delta H^* = \Delta G^* + T \Delta S^* \quad (22)$$

$$\Delta C_p^* = \left(\frac{\partial \Delta H^*}{\partial T} \right)_p \quad (23)$$

$$\Delta V^* = \left(\frac{\partial \Delta G^*}{\partial p} \right)_T \quad (24)$$

Eq. (20) can be derived also through explicit molecular models of the dense phase. One particular example discussed in the chromatographic literature was the solute transfer from the ideal-gas into a Van der Waals fluid [98]. Although the Van der Waals theory simplifies interactions to pair of particles, and approximates repulsive forces by the infinite potential of hard spheres, the model contains

all conceptual elements for describing the phenomenology of the transfer process. This application of the model was induced by its simplicity and the impressive qualitative capacity of prediction of the generalized Van der Waals theory of fluids, which has been amply recognized in contemporary physics [135,136]. Other authors later employed the model for some theoretical discussions pertinent also to chromatography [137]. In this ambit, it was argued that the solute placed in the ideal-gas is a “true zero-energy level point” [138]. Such concept could lead to confusion, so it is convenient to examine this aspect of the reference-state.

According to molecular thermodynamics, the solute chemical potential in the ideal-gas is [53,133]:

$$\frac{\mu_M}{k_B T} = -\ln q_M + \ln \left(\frac{N_M \Lambda^3}{V_M} \right) \quad (25)$$

In our discrete molecular picture the chemical potential, $\mu_i \equiv (\partial G / \partial N_i)_{p,T,N_j} = (\partial A / \partial N_i)_{V,T,N_j}$, is the variation of system's free-energy by adding one molecule of solute i , while keeping constant all other components j . q_M is the canonical partition function for solute's molecule internal degrees of freedom (d.f.); electronic, rotational and vibrational. The reciprocal partition function of solute's momentum of translation is the cube of de Broglie's thermal wavelength, $\Lambda = h / (2\pi m_i k_B T)^{1/2}$, where m_i is the solute molecular mass. The chemical potential in the dense phase contains both terms of Eq. (25) plus interaction terms. Λ is irrelevant for the solvation process, since at thermodynamic equilibrium the solute chemical potential is the same in both phases, $\mu_M = \mu_S$, so Λ^3 cancels out. Therefore, only $-\ln q_M$ is relevant for our reference in the transfer process (C_M will be contained in K). In a solute molecule having internal degrees of freedom, intramolecular potentials yield different energies according to the molecular conformation adopted. Then, the ideal-gas reference-state cannot be “zero-energy”, neither a “level point”. Instead, it provides a defined ensemble average free-energy of reference $\langle G \rangle_M$.

Through the application of conventional thermodynamics, the use of different concentration scales has been frequent in chromatography, generating divers standard states for defining the thermodynamic quantities that describe the solvation process [139]. The most commonly applied is the molar scale, taking as standard states a hypothetical unit molar concentration of solute in the gas phase behaving ideally, and a one molar concentration SP that hypothetically is assumed to behave as an ideal infinite diluted solution (i.e. complying with Henry's law). The following equality, originated in the use of the same concentration scale, holds for these definitions and that derived from molecular thermodynamics:

$$\frac{\Delta G_s^\circ}{RT} = \frac{\Delta G^*}{k_B T} \quad (26)$$

ΔG_s° is solute's chemical potential difference for the standard states defined above. It must be remarked that this equality is only numerical, not conceptual, since the solvation process of transferring one mole of solute from the

mentioned initial to final states is physically different than the molecularly defined. Ben-Naim showed that differences arise between the derived functions (ΔS_s° , ΔH_s° , ΔC_{ps}°) on the one hand, and (ΔS^* , ΔH^* , ΔC_p^*) on the other. For example, ΔS_s° contains the additional term $\alpha_S k_B T$, where α_S is the isobaric volume thermal expansion coefficient of the dense phase. This is not relevant for an isothermal solvation process [133].

It has been argued for a long time that the molal concentration scale would be appropriate for describing the solution on a polymeric SP [140,141]. The standard states adopted in this case are the solute at a partial pressure of 1 atm in a gas phase hypothetically behaving ideally, and its unit molality liquid solution hypothetically complying with the properties of infinite-dilution (Henry's law). Invoking these definitions, it is often written [141]:

$$\frac{\Delta G_m^\circ}{RT} \equiv \frac{\mu_S^\circ - \mu_M^\circ}{RT} = -\ln g \quad (27)$$

ΔG_m° is the Gibbs free-energy for the solvation process of transferring one mole of solute from the MP to the SP under the mentioned hypothetical standard conditions. μ_M° and μ_S° are the respective standard chemical potentials of the solute. The molal Henry's coefficient is $g = p/m$, where p is solute's partial pressure in the MP (atm) and m its molality in the SP. Since by definition the chemical potential has the units of energy, the left-hand side of Eq. (27) is dimensionless, while the argument of the logarithm has units. It is usually indicated that the argument must be factored by the combination of units yielding dimensional coherence [141], but the fact is that for achieving such condition the argument must be factored by explicit entities or parameters having these dimensions, if not, the dimensional inconsistency persists. This free use of expressions in the context of macroscopic thermodynamics has led for example to the derivation of dimensionally inconsistent chromatographic equations [142,143]. Dimensional inconsistency is of course the utterance of logical and, so, physical inconsistency. Ben-Naim showed that the physical behavior of ΔG_m° , even correctly expressed dimensionally, is inconsistent because it diverges to minus infinite when ρ_S tends to zero, this being an unacceptable behavior for a function that it is supposed to measure the interactions of the solute with the solvating medium [133].

Due to the numerous difficulties arising in the context of conventional thermodynamics, clearly pointed out by Ben-Naim and illustrated through a couple of examples in the preceding paragraphs, in the following we utilize for the review of concepts only the molecular definitions of solvation quantities.

The treatment given to chromatographic data obtained at different temperatures is crucial for determining thermodynamic functions, because these involve the first and second derivative of the free-energy of solution with respect to T (see the Eqs. (20)–(23)). The strategy implicitly adopted by all procedures carried out in the context of conventional

thermodynamics can be concisely summarized as the following physical concept [61]. A small number of terms in a polynomial describing the temperature dependence of the heat capacity difference of solution are taken:

$$\Delta C_p^*(T) = a + bT + cT^2 + \dots \quad (28)$$

Examples in the chromatographic literature range only from the roughest and most usual procedure of implicitly imposing the condition $\Delta C_p^* = 0$, so neglecting the temperature dependence of ΔH^* and ΔS^* , to the crude approximation of imposing $\Delta C_p^* = a = \text{const.}$ (see, e.g. [144–149]). A regression of chromatographic data, expressed either as V_g or K , to the corresponding equation of the model is then performed. In the case of assuming $\Delta C_p^*(T) = a + bT$ in a regular temperature interval, Castells et al. [150] found through the least-square regression of V_g data that the parameter b , taking into account the temperature variation of ΔC_p^* , was not statistically significant. This result sometimes has been misinterpreted as experimental evidence (see, e.g. [141,149]) that neglecting the variation of ΔC_p^* with T is substantive in the practice. It was later shown with the aid of molecular thermodynamics and WCOT experimental data [61] that Castells results stems from the fact that a polynomial is not appropriate for describing with few parameters the expected complicated exponential behavior of $\Delta C_p^*(T)$. For example, this function presents two maximums in the chromatographic range of T in the case of *n*-dodecane [16]. The statistical significance of parameters obtained through regression of experimental data to an imposed mathematical behavior of $\Delta C_p^*(T)$ evaluates the goodness of the prescribed mathematical model in relation to the data. But in case of a negative result, nothing can be said on how is the real behavior.

In view of the limitations intrinsic to the conventional thermodynamic approach, a completely different strategy was proposed for the treatment of chromatographic data in [61]. This simply consists in determining $\ln K$ directly from WCOT columns retention times in order to assure sufficient precision, compiling such an amount of experimental information to allow the numerical determination of significant values of its first and second derivatives. The thermodynamic functions are then calculated by direct application of Eqs. (20)–(23):

$$\frac{\Delta S^*}{k_B} = \ln K + T \frac{\partial \ln K}{\partial T} \quad (29)$$

$$\frac{\Delta H^*}{k_B} = T^2 \frac{\partial \ln K}{\partial T} \quad (30)$$

$$\frac{\Delta C_p^*}{k_B} = 2T \frac{\partial \ln K}{\partial T} + T^2 \frac{\partial^2 \ln K}{\partial T^2} \quad (31)$$

The temperature derivative of a function f is determined numerically as

$$\left(\frac{df}{dT} \right)_{T=T_i} = \frac{1}{2} \left(\frac{f_{i+1} - f_i}{T_{i+1} - T_i} + \frac{f_i - f_{i-1}}{T_i - T_{i-1}} \right) \quad (32)$$

In this way no prescribed behavior, as e.g. Eq. (28), is imposed a priori to the solvation functions. Instead, the procedure just let the experimental data to express themselves through the thermodynamic functions, provided the sufficient precision and required amount of data. For obtaining information on functional behavior, temperature intervals wider than 200 K must be covered measuring tens of data.

The knowledge on the real behavior of $\Delta C_p^*(T)$ is of paramount thermodynamic importance since it provides vital information on molecular mechanisms responsible of solubility's variation with temperature. The interpretation of the observed phenomena indispensably needs of the molecular theory, and therefore, of the application of statistical mechanics. For this reason, it is convenient to review some elementary notions derived from this theoretical context.

7. Some elementary concepts on solvation from molecular thermodynamics

According to the statistical mechanical viewpoint two main contributions to the solubility can be considered [98,133,134]:

$$\ln K = \ln \frac{q_S}{q_M} - \frac{W}{k_B T} \quad (33)$$

The quotient of canonical partition functions in both phases, q_S/q_M , measures how solute's internal degrees of freedom in vacuo are modified, via transfer, by the force field generated by the surrounding solvent particles. Qualitative features originated by this term are predominantly due to the solute's structure, the solvent force field affecting mainly the quantitative aspects. The force field may be of any sort; being originated by dispersion forces, dipole–dipole coupling forces, permanent dipole–induced dipole, etc. W denotes all other works required for introducing the solute molecule into the solvent, thus comprising the work of formation for the cavity hosting it and the correspondent modifications in the solvent lattice.

The transfer does not modify electronic states of a solute molecule, unless highly energetic processes take place. In the usual chromatographic conditions, q_S/q_M only involves the modification of low energy modes of rotation and vibration (r, v). If these internal molecular motions are approximated through the description of i normal modes of harmonic oscillators, the ratio of quantum partition functions leads to the following thermodynamic quantities [61]:

$$\ln \frac{q_S}{q_M} = \sum_i \left(\frac{\theta_M - \theta_S}{2T} + \ln \frac{1 - e^{-\theta_M/T}}{1 - e^{-\theta_S/T}} \right)_i \quad (34)$$

$$\frac{\Delta S_{r,v}}{k_B} = \sum_i \left(\frac{(\theta_S/T)}{e^{\theta_S/T} - 1} - \frac{(\theta_M/T)}{e^{\theta_M/T} - 1} + \ln \frac{1 - e^{-\theta_M/T}}{1 - e^{-\theta_S/T}} \right)_i \quad (35)$$

$$\frac{\Delta H_{r,v}}{k_B} = \sum_i \left(\frac{\theta_S - \theta_M}{2} + \frac{\theta_S}{e^{\theta_S/T} - 1} - \frac{\theta_M}{e^{\theta_M/T} - 1} \right)_i \quad (36)$$

$$\frac{\Delta C_{pr,v}}{k_B} = \sum_i \left(\frac{(\theta_S/T)^2 e^{\theta_S/T}}{(e^{\theta_S/T} - 1)^2} - \frac{(\theta_M/T)^2 e^{\theta_M/T}}{(e^{\theta_M/T} - 1)^2} \right)_i \quad (37)$$

The characteristic temperature is $\theta \equiv (h/k_B)\nu = (ch/k_B)\tilde{\nu} = 1.439 \text{ (cm K)} \times \tilde{\nu} \text{ (cm}^{-1}\text{)}$, where ν is the vibration frequency of the harmonic oscillator.

The observation of $\Delta C_p^*(T)$ maximums in the chromatographic range are explained in this context through the modification of the r , v , molecular degrees of freedom by the solute–solvent attractive forces in the dense phase [61]. Assigning such ‘bands’ of $\Delta C_p^*(T)$ to modes of vibration requires a theoretical analysis as the assignation of bands in IR spectroscopy.

The solute–solvent attractive forces make a positive contribution on the first term in the right-hand side of Eq. (33). This is the case of $\Delta S_{r,v}$ and $\Delta H_{r,v}$. While the former is positive, the latter is negative [61], then both contribute positively to $\ln K$ (see Eqs. (20)–(22)). In the same way, the repulsive forces will contribute to $\ln K$ with a negative term. Nonetheless, due to the short range nature of repulsive forces, a simpler analysis can be carried out from another viewpoint, so their effect will not be analyzed through Eqs. (34)–(37).

When solute–solvent repulsive forces overcome the attractive is $K < 1$ ($\Delta G^* > 0$), and conversely if the attractive ones dominate. When the attractive and repulsive forces compensate each other is $K = 1$ ($\Delta G^* = 0$), and the solute behaves as an inert entity. So the probability of finding it only depends on volume, $N_M/N = V_M/(V_M + V_S)$ (79), because the confining volume is the only constraint for a molecule that does not perceive any difference of free-energy.

An athermal contribution to the work of cavity formation can be envisioned for a small rigid solute if the repulsive forces are considered as the effect of hard spheres and if the solvent free-volume is sufficient for generating the cavity by simple fluctuations in the position of the solvent particles. These fluctuations must lead to the same final macroscopic energy of the system. For making this feasible, the solute should have small dimensions in relation to the solvent particles, so the system can accommodate the molecule. W is given in this case by the free-volume entropy, Eq. (16), which would provide a negative contribution to the right-hand side of Eq. (33). Eq. (16) can be rewritten as:

$$\frac{\Delta S_{fv}}{k_B} = \ln \left(1 - \frac{N}{V_S} v_c \right) \quad (38)$$

N/V_S is the numeral density of particles in the solvent and v_c is the volume of the cavity. Being the solute a hard particle, the pressure affects only the density. The free-volume in the solvent decreases as the pressure increases. The thermal expansion affects both factors, so ΔS_{fv} has a negligible variation with T . This leads to $\partial \ln K_{fv}/\partial T \rightarrow 0$ and

$\partial^2 \ln K_{fv}/\partial T^2 \rightarrow 0$. Therefore, the enthalpy and heat capacity contributions associated with ΔS_{fv} , namely ΔH_{fv} and ΔC_{Pfv} , are negligible in this case.

According to Eq. (24) ΔV^* can be calculated through the variation of solubility with pressure. The pressure modifies the density of particles in the solvent increasing it according to the respective equation of state [2], reducing the free-volume. Playing the solute the role of a sensing probe, ΔV^* monitors both, the free-volume in the solvent and the increment in V_S necessary to accommodate the molecule. When the transfer of a solute of considerable size involves a variation in V_S , this evidently requires a work against the solvent cohesive forces and an associated enthalpy and heat capacity arise.

In the case of linear flexible molecules the dimensions of the molecular coil, measured by the mean square end-to-end distance $\langle r^2 \rangle^{1/2}$ or the radius of gyration [151], depend on T and the solute–solvent interactions. The solute–solute, solute–solvent forces and T determine how folded are the molecular conformations and then how segregated from their environment are chain segments. Therefore, the excluded volume depends on T . However, the effect of the force field on the solute is already accounted for by the first term of Eq. (33). Then, if the segregated chain segments are small enough, ΔS_{fv} in this case will not have a specific associated enthalpy that could be discriminated, although the size of the cavity varies with T .

A simplified qualitative analysis on the behavior of the solubility can be carried out by considering only the effects of solute–solvent attractive forces on the first term of Eq. (33), and the effects of repulsive ones on the second term W . The latter can be roughly approximated for small rigid solutes as the work of cavity formation in a solvent of hard spheres by using Eq. (38). From this theoretical standpoint the following observable consequences are derived:

- A weak dependence of K with T is expected for small solutes (relative to the size of solvent particles) when $K < 1$. If the solubility is mainly controlled by W , it must be mostly an entropic process. For an athermal solution ($\Delta H^* \rightarrow 0$) must be $\partial \ln K/\partial T \rightarrow 0$ according to Eq. (30). According to Eqs. (29) and (38) is $\ln K \approx \Delta S^*/k_B \approx \Delta S_{fv}/k_B$.
- When $K < 1$, for a given small solute in different solvents of the same chemical nature, it is expected the solvent density to be the relevant property controlling its solubility. According to Eq. (38) v_c and the numeral density of particles in the solvent control the process. N/V_S is proportional to the solvent density ρ_S .
- For a small solute in different solvents of the same chemical nature, if a variation of solubility is controlled by the free-volume in the dense phase, even when $K > 1$ this must lead to a decrease with the solvent density, and these changes must be due only to entropy, as states Eq. (38).

From this simplified viewpoint, the contributions to the transfer entropy are

$$\Delta S^* = \Delta S_{r,v} + \Delta S_{fv} \quad (39)$$

$\Delta S_{r,v}$ is positive, as only attractive forces are considered in Eq. (34). This function presents a complex behavior with T according to Eq. (35), and so has an associated enthalpy, $\Delta H_{r,v}$, given by Eq. (36). On the other hand, ΔS_{fv} is negative. For a small rigid solute, ΔS_{fv} is practically independent of T and in consequence has not an associated enthalpy. Therefore, the shape of function $\Delta S^*(T)$ should be determined principally by the complex behavior of $\Delta S_{r,v}$. Instead, the absolute value of ΔS^* is determined by both contributions. It is found experimentally that $\Delta S^*(T)$ is generally negative, so ΔS_{fv} should overcome $\Delta S_{r,v}$.

8. Solubility phenomena studied through capillary GC

Different orientations may be given to the application of GC to physicochemical measurement. One is the compilation of specific thermodynamic information as a goal itself. In this case, the objects of study are particular systems having some special interest. In another order can be inscribed the application of GC to studies on solubility phenomena. We utilize this idiom here for those researches whose aim is seeking general behaviors of solvation processes; namely those phenomena that are common to many systems, being the expression of essential features or general mechanisms. In the first case the interest is focused on the particular and in the second on what is general.

Through capillary GC measurement in ample intervals of T it has been observed for methane a behavior approach-

ing that expected in the observable consequence (a) of the preceding section. Fig. 2 shows data obtained from low- β capillary columns of two different solvents in [72,79]. In the latter reference, the dependence of β with T was neglected, so the data had to be corrected. The behavior expected theoretically is reached by methane in PDMS at $T \geq 393$ K, while in PEG it seems to cover all the chromatographic range. A great dispersion of data is observed for PEG in comparison with PDMS. Besides the lower values of K in PEG, another reason is that 30 m columns were used for this, while only a 50 m column for PDMS. The technique is not appropriate for studying small K 's, due to the little difference between t_R and t_M and difficulties arising in the determination of the second parameter for columns of low β and large L . Solely the range $K > 1$ can be studied accurately through capillary GC. Static measurement through GC analysis of a vial's head-space would be suitable for studying these phenomena, but unfortunately not enough experimental information at different temperatures has been published.

Great interest since the beginning of GC has drawn in the chromatographic literature the solvation behavior of homologous series of solutes, and particularly the n -alkanes (see, e.g. [152–164]). Beside the properties of solution observed at a glance in Fig. 1, presenting essential features that are independent from the solvent nature, and so are intrinsic to the solute chain structure, there are other general aspects of interest. ΔH^* isotherms as function of the number of C–C bonds at different temperatures are shown in Fig. 3. These are linear functions tending to zero when are extrapolated to zero C–C bonds, namely when the chain's backbone disappears. It can be inferred that the alkanes backbone degrees of freedom are responsible in determining the energetics

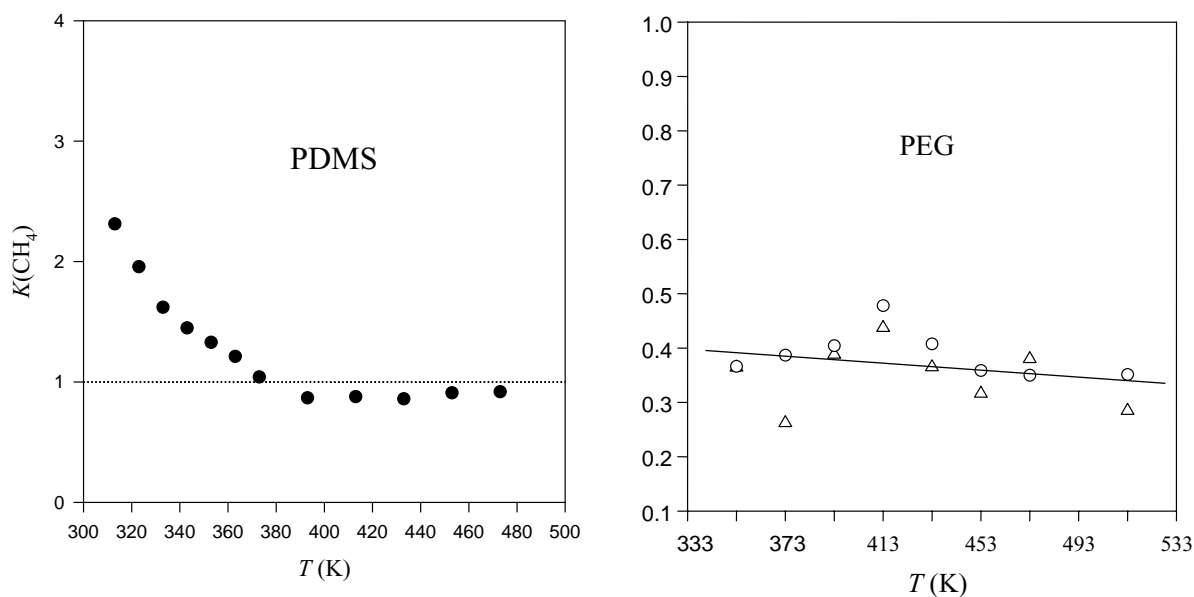


Fig. 2. Dependence of methane's partition coefficient with the temperature T , measured on low β WCOT columns of poly(dimethylsiloxane) and poly(ethylene glycol) stationary phases. When $K < 1$ the solubility becomes rather insensitive to T .

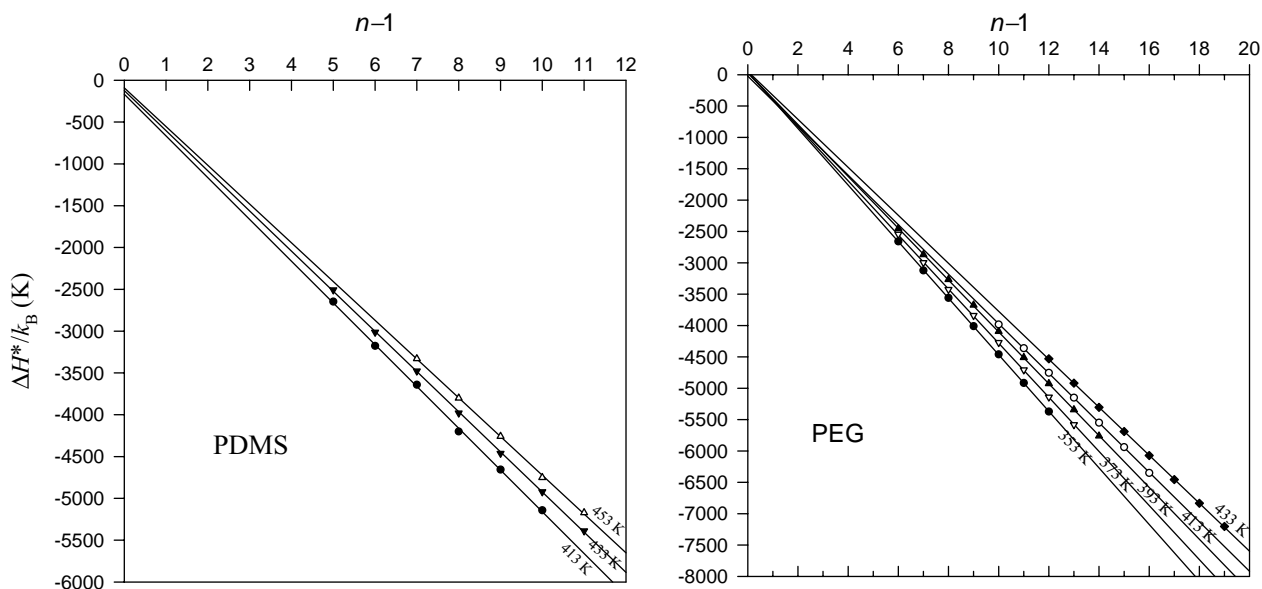


Fig. 3. Isotherms of the solute transfer enthalpy are plotted as function of the number of C–C bonds in the n -alkane molecule. Linear least-square regressions of the experimental data are extrapolated to zero C–C bonds.

of the solvation process at the shown conditions. There must be a corresponding manifestation in other functions consistent with this viewpoint. Fig. 4 shows in the example of n -dodecane that $\Delta C_p^*(T)$ presents two maximums in the chromatographic range of temperatures. The characteristic temperatures θ of these bands would correspond to bending motions of solute's carbon backbone [61], what contributes to explain why ΔH^* in this range of T tends

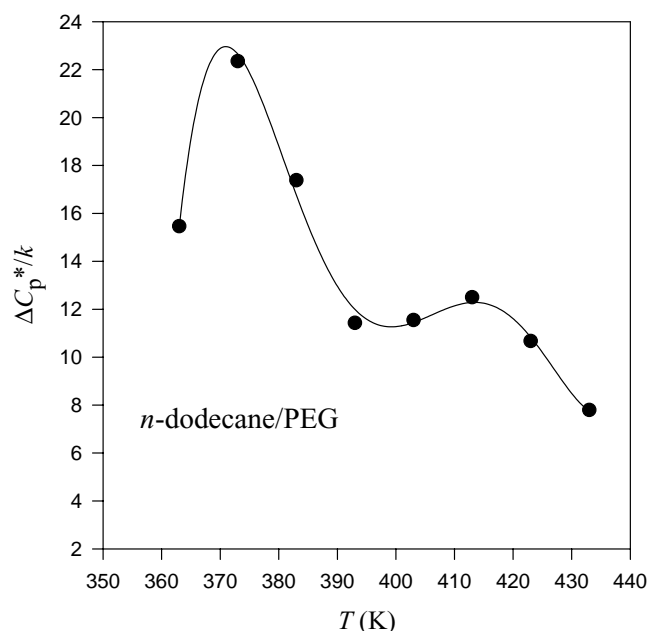


Fig. 4. The heat capacity difference of solute transfer for n -dodecane is plotted against the temperature. The characteristic temperatures θ of both maximums are in the range of energies corresponding to the carbon backbone bending motions.

to zero when the number of C–C bonds are zero. This linear energetic dependence justifies the $B(n - 1)$ term in Eq. (17).

One important consequence derived from the linearity of the isotherms $\Delta H^*(n)$ is that the observed curvature of $\ln K(n)$ must be due to an effect of entropy.

Another universal behavior independent of the solvent nature is that mentioned in Section 4 concerning the parameter A . Its physical meaning is the value of $-\Delta G^*/k_B T$ that would correspond to a hypothetical isolated $-\text{CH}_2-$ unit, as it was defined as the extrapolation of $\ln K(n)$ data of n -alkanes with $n \geq 5$, to $n = 1$. Considering from Fig. 3 that when $A < 0$ [or $K(-\text{CH}_2-) < 1$], is observed $\Delta H^*(n - 1) \rightarrow 0$ for $n \rightarrow 1$, implies that A is entropic in nature. Under this condition, it is observed that A has the same order of $\ln K$ of methane. As the latter, A is also rather insensitive to T . The theoretical approach described in the preceding section makes the following interpretation of this fact. Although methylene has a different electronic structure and, thus, strongly modified internal degrees of freedom with respect to methane, these do not contribute significantly in the chromatographic range of T and then is $\Delta G^* > 0$ ($K < 1$). In consequence, the solubility should be controlled by ΔS_{fv} . In Eq. (38) the solute structure affects v_c as the volume of hard spheres. Methylene and methane have Van der Waals radii of the same order, hence explaining the correlation between A and $\ln K(\text{CH}_4)$ in different solvents [62,72].

From the preceding considerations it is clear that the solubility of any permanent gas presenting $K < 1$ (or A) is adequate for studying the free-volume of the different polymeric solvents most usually employed as stationary phases, and for the construction of a scale of these.

In principle, the behavior of the thermodynamic function ΔV^* should be studied through the application of Eq. (24), measuring variations of solubility with p :

$$\frac{\Delta V^*}{k_B T} = \left(\frac{-\partial \ln K}{\partial p} \right)_T \quad (40)$$

In the usual experimental conditions K is practically independent of pressure [12]. If we increase p with the aim of modifying the free-volume in the solvent, the departure from ideal behavior of the MP deprives us from measuring ΔV^* directly, and corrections must be done (see Section 9). However, we can have an approach to the problem indirectly through the study of the effect of the solvent density. The equation of state, $\rho_S(p)$, is known for many polymers [2].

Linked to the consequence (c) of the preceding section, capillary GC measurement was carried out on columns coated with PEG oligomers of different densities in [16,62]. PEG presents the rare peculiarity that ρ_S decreases by increasing its molar mass M . It was found by using different solutes having $K > 1$ that the solubility decreases with the increasing density of the solvent. The change of solubility only has associated an entropy change $\partial \Delta S^*/\partial \rho_S < 0$, remaining within the experimental error the observed variations of enthalpy, $\partial \Delta H^*/\partial \rho_S \approx 0$. Consistently, these changes are rather insensitive to T . It is thus assumed that the free-volume entropy is responsible for these experimental facts.

If the internal degrees of freedom of the solute molecule are controlling the energetics of the solvation, then the qualitative aspects of $\Delta H^*(T)$ should be similar for molecules having similar d.f., independently of the types of atoms; namely independent of the quantitative aspects of the force field. Fig. 5 compares shapes of $\Delta H^*(T)$ for two different heterocycle molecules with two different chain molecules [62]. The cycles have alike profiles between them, and so the chain molecules. The number of d.f. in a chain molecule is reduced by formation of a cycle; then cycles should have a smoother curve than chain molecules. This is what is observed in Fig. 5.

9. Equations of retention in non-uniform chromatography

When the experimental conditions are changed to those in which solute's distribution in the system, $F = C_S/C_M$, depends significantly on pressure and concentration, this ratio becomes a function of column's axial coordinate z , because p and C vary along z . Then, the hypothesis of uniformity is not applicable. The fitness of this hypothesis can be easily verified comparing K_{ef} measured on two WCOT columns of the same d_f and d_C , but greatly differing lengths L [12], so creating along the column harsh differences on pressure gradients and peak broadening, while keeping constant interfacial excesses. If the discrepancies of measured K_{ef} are beyond the standard errors, the inapplicability of the hypoth-

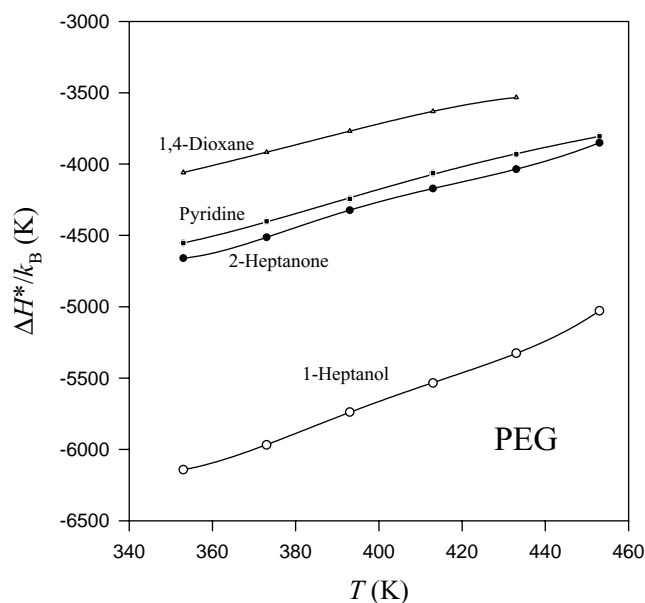


Fig. 5. Curves of transfer enthalpies plotted as function of temperature are compared for two chain molecules and two heterocycle molecules. Molecules with the same structural features have similar profiles. The heterocycles present a rather smoother curve than chain molecules.

esis of uniformity is suspected and the direct use of the principle of Eq. (6) along the whole column is no longer valid. A rigorous expression of retention, explicitly relating t_R with relevant thermodynamic constants, is then obtainable exclusively through the solution of the differential equation for the local zone motion, Eq. (2), because the principle is now applicable just locally:

$$\frac{dz}{dt} = \frac{u(z)}{1 + (F(z, t)/\beta)} \quad (41)$$

With the aim of providing some preliminary insight into the meaning of K_{ef} in non-uniform chromatography, suppose for one moment we would have the mathematical ability of writing $F(z, t)$ as function of only z , through the a priori knowledge of zone's trajectory $t(z)$. In such hypothetical situation the separation of variables in Eq. (41) would be feasible, permitting an explicit expression for the retention:

$$\int_0^{t_R} dt = \int_0^L \frac{dz}{u(z)} + \frac{1}{\beta} \int_0^L \frac{F(z)}{u(z)} dz \quad (42)$$

According to the hypothesis of convective transport, a differential element spending a time interval dt_M in the MP, at a given position z , is transported a distance $dz = u(z) dt_M$. So the first integral in the right-hand side is by definition t_M . If we rearrange the equation:

$$\left(\frac{t_R - t_M}{t_M} \right) \beta = \frac{1}{t_M} \int_0^L \frac{F(z)}{u(z)} dz \quad (43)$$

That is to say

$$K_{\text{ef}} = \frac{1}{t_M} \int_0^{t_M} F dt_M \quad (44)$$

Although the hypothesis of uniformity does not apply, Eq. (7) is still valid. The physical meaning of K_{ef} is the time-average of the thermodynamic factor F over the period spent by solute molecules at the MP. The reason is that the fluid dynamic factor dt_M is weighting at each instant the effect of the local thermodynamic factor. The functional form of this average, and thus the ultimate meaning of K_{ef} , will be obtained uniquely when an explicit solution is available. In most real circumstances it is not possible to express F as function solely of one of the variables, generally turning inaccessible the explicit solution. We shall next analyze some particular cases.

When the ideal-gas/incompressible-SP still applies but deviations from the infinite-dilution condition occur in pure partition, F becomes a function of the solute concentration in the MP. The thermodynamic equilibrium of the partition process is described by the isotherm $C_S = I(C_M)$. A small departure from infinite-dilution may be described for example by taking only the first two terms in the development of C_S in power series of C_M , around $C_M = 0$:

$$C_S = KC_M + K'C_M^2 + K''C_M^3 + \dots \quad (45)$$

K has the previous meaning of the infinite-dilution partition constant. The second thermodynamic constant, $K' = (1/2)(\partial^2 C_S / \partial C_M^2)_{C_M=0}$, is related to solute–solute pair-wise interactions in the SP. Being $F = I(C_M)/C_M = K + K'C_M$, the explicit form of functions $u(z)$ and $C_M(z)$ must be known for solving Eq. (41). The form of $u(z)$ for the ideal-gas, as function of measurable geometric and physical constants of the system, is well known [165]. Given an initial C_{M_i} at the column inlet, the evolution of the solute concentration along the column depends, apart the partition, on other factors. These are the expansion of the gas phase along the column due to the pressure gradient and the variation of concentration owing to dispersion processes. The time t is contained in the equations of diffusion [3], so dispersion processes depend on this variable. The coupled processes then give rise to a function $C_M(z, t)$ simultaneously depending on both variables, not allowing an analytical solution of the differential equation by variable separation. In consequence, Eq. (41) has to be solved numerically through algorithms of finite differences, like in programmed temperature and pressure GC [165]. For doing so, the initial concentration C_{M_i} , d_f and diffusion coefficients must be known, this being a tough experimental complication.

When the pressure p is incremented sufficiently, two effects arise. The solute develops interactions with other molecules in the MP and the SP can no longer be assumed as incompressible. Significant variations of K occur when the relative variations of ρ_S turn out to be in the order 10^{-2} [16,62]. The relationship between ρ_S and p is known for most currently employed polymeric stationary phases through precise equations of state [2]. It is seen that in the same range of p in which interactions in the MP become perceptible, manifesting in a significant departure from unity of the compressibility factor Z [1], the relative

variations of ρ_S would introduce significant changes on K . In consequence, for the sake of rationality on that concerning the assessment of the effects, if we consider the real behavior of the gas phase, we must then consider the compressibility of the SP.

Even when the solute could be at infinite-dilution in the SP, in the MP could not. If the MP behaves as a real gas, the solute–solute interactions, currently measured through the correspondent second virial coefficient B_2 in these fluids [53], leads to a concentration dependence of F . Therefore, we have $F = F(C_M) = F(z, t)$. The same mathematical and practical difficulties as mention above then arise.

For a real gas MP, F will not depend on the concentration C_M solely when the solute is at infinite-dilution in both phases. In this case is uniquely a function of pressure, $F(p)$, and thus of z . $F(z)$ will decrease with both, the increasing ρ_S and the increasing interactions of the solute in the MP. For a small departure from the ideal-gas behavior we may take the first two terms in the development of $\ln F$ in power series of p , around $p = 0$:

$$\ln F(z) = \ln K - \frac{\Delta V^*}{k_B T} p + K_2 p^2 + \dots \quad (46)$$

K has the previous meaning of the constant for the infinite-dilution/ideal-gas/incompressible-SP conditions, and the thermodynamic significance of the constant accompanying p is given by Eq. (40). Then, according to Eq. (43) we have

$$K_{\text{ef}} = \frac{K}{t_M} \int_0^L \frac{\exp((- \Delta V^* / k_B T) p(z))}{u(z)} dz \quad (47)$$

The integration demands knowledge on the fluid dynamic functions $p(z)$ and $u(z)$ for the real gas. These are obtainable through current procedures of fluid mechanics.

For being consistent with preceding considerations, the equation of state for the real gas should be taken as the first two terms of the virial development [53]:

$$Z = 1 + B_2 C + B_3 C^2 + \dots \quad (48)$$

C is the numeral density of molecules in the gas and the compressibility factor is $Z \equiv p / C k_B T$. The second virial coefficient B_2 measures both, the excluded volume and pair-wise attractive interactions between gas molecules [53]. Solving the quadratic expression arising from taking the first two terms leads to:

$$C = \frac{f(p)^{1/2} - 1}{2B_2} \quad (49)$$

being $f(p) = 1 + (4B_2 p / k_B T)$.

Also the equation of continuity (the mass-balance) is needed for solving the gas motion. For a steady-state Poiseuille flow, the equation of continuity in cylindrical coordinates reduces to [52]:

$$\frac{\partial(\rho u)}{\partial z} = 0 \quad (50)$$

Since the gas density is $\rho = Cm$, where m is the mass of the carrier-gas molecule, the equation settles that $Cu = \text{const.}$, i.e. the flux of molecules is constant along the column. It should be noted that the equation of continuity for the ideal-gas, usually expressed as $pu = \text{const.}$, is no longer valid.

The balance of momentum is conveniently expressed in terms of the local cross-sectional average velocity u through the differential form of Hagen–Poiseuille’s equation:

$$u = \frac{-B}{\eta} \frac{\partial p}{\partial z} \quad (51)$$

The permeability of the column is $B = d_C^2/32$. Although Hagen–Poiseuille’s equation is valid only for incompressible Newtonian fluids, the application of its differential form is justified because in a differential element dz we have an infinitesimal pressure drop dp .

By applying the balances, $p(z)$ and $u(z)$ can be obtained only in the form of implicit functions. The simplest example is when the pressure dependence of the gas viscosity η is neglected:

$$\frac{(k_B T/6B_2)[f(p_i)^{3/2} - f(p)^{3/2}] - (p_i - p)}{(k_B T/6B_2)[f(p_i)^{3/2} - f(p_o)^{3/2}] - (p_i - p_o)} - \frac{z}{L} = 0 \quad (52)$$

p_i , p_o , respectively, denote pressures at the column inlet and outlet; p being the pressure at the axial position z . Then, an explicit analytical solution of Eq. (47) is not possible. A numerical solution of the equation becomes feasible applying Eqs. (49) and (52) and the equation of continuity. The solution involves a trial and error algorithm of successive approximations as is usually employed in the solution of implicit functions. In principle, information on ΔV^* could be obtained through measurement of K_{ef} at different pressures, including the determination of K at low pressure.

From the preceding considerations on regular deviations from the “ideal” experimental conditions (infinite-dilution/ideal-gas/incompressible-SP) the following general aspects can be summarized. In all tractable cases, the measured effective constant $K_{\text{ef}} = [(t_R/t_M) - 1]\beta$ is expressed as the product of K (the infinite-dilution/ideal-gas/incompressible-SP constant) and a correcting thermodynamic factor (\mathbf{F}), as likewise found for the mixed retention mechanism in Eq. (12):

$$K_{\text{ef}} = K(\mathbf{F}) \quad (53)$$

For thermodynamic processes varying along the column, the factor is a time average over t_M , of the mechanisms responsible of the deviations from the “ideal” condition. The exact physical meaning is not generally accessible due to the mathematical difficulties originated from the solution of the equation of zone motion. Any rigorous attempt to correct quantitatively K_{ef} with the aim of determining K invariably demands the numerical solution of the differential equation of zone motion. No easily calculable explicit factors are attainable.

Since the beginnings of GC the treatment that should be given to chromatographic data for a real carrier-gas has been an important dilemma [5,6]. The problem has been currently worked out as the determination of a compressibility correction factor for the MP that would appropriately permit the calculation of the net retention volume V_N through Eq. (3) in pure partition. These “corrections” are expressed as an explicit factor J_i^k involving different powers, i and k , of the inlet and outlet column pressures p_i and p_o . Fóti and Kováts [166] critically reviewed early approaches and criticized the official recommendations [5,6,167–170]. They pointed out common physical inconsistencies of simultaneously considering the gas real in some aspect, and ideal in another. Their approach starts replacing in the equation of zone motion dz/dt by L/t_R , $L/u(z)$ by t_M , and k by an average (\bar{k}). Since the equation of zone motion is valid only locally, this approach has not a logical justification. In their posterior development they consider the SP as incompressible.

10. Conclusions

Basic information on solvation thermodynamics can be obtained in a simple and direct way from GC measurement employing capillary WCOT columns, if only the relevant chromatographic variable, the retention time, and the relevant parameters t_M and β are utilized. The suitability of the experimental conditions is easily verifiable. A tight control of errors is possible, providing sufficient precision for studying functions like the heat capacity of transfer that are not accessible for other techniques. Important solubility phenomena not detected before, owing to the large amount and accuracy of data required, have been revealed by capillary GC. The detailed behavior of functions $\ln K(n)$, $\Delta H^*(n)$, $\Delta H^*(T)$ and $\Delta C_p^*(T)$ would not be accessible to other techniques, as for example static measurement. But static measurement still has advantages over capillary GC in the range of $K < 1$.

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Appendix A

Fig. 6 schematically represents an instant concentration profile of a chromatographic band along column’s axial coordinate. Admitting the mass-transfer delay from MP to SP implies that in the front part of the band, that finding fresh SP, the solute concentration at the MP will be greater than the equilibrium concentration. On the contrary, admitting the SP to MP mass-transfer delay in the rear part, that finding

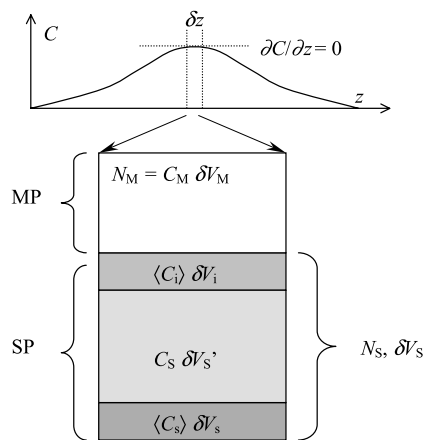


Fig. 6. Concentration profile of a chromatographic band along the axial coordinate. In the equilibrium zone, at the center of the band, three regions or subphases of the SP are discriminated.

fresh MP, solute's concentration in the MP will be lower than the equilibrium one [3]. Consequently, in the center of the band there must be a differential element δz matching the equilibrium concentration. At this zone the axial solute's concentration gradient in any of both phases is $\partial C/\partial z = 0$, and then $\partial C/\partial t = 0$. This is the so-called equilibrium-zone. As shown in the scheme, at this element we consider three subphases in the SP: the interfacial subphases with volumes δV_i , δV_s and the bulk subphase with volume $\delta V_s' = \delta V_s - (\delta V_i + \delta V_s)$. The total number of solute molecules at the SP in the equilibrium-zone can be obtained through the mass-balance:

$$N_S = C_S[\delta V_s - (\delta V_i + \delta V_s)] + \langle C_i \rangle \delta V_i + \langle C_s \rangle \delta V_s \quad (A.1)$$

Employing this expression in the definition of the retention factor k , applying the definition of K , those of Eq. (11) and

assuming a uniformly distributed SP such that volume fractions are constant along the column:

$$k \equiv \frac{N_S}{N_M} = \frac{N_S}{C_M \delta V_M} = \frac{K}{\beta} - \frac{K}{\beta} \frac{V_i}{V_S} - \frac{K}{\beta} \frac{V_s}{V_S} + \frac{K}{\beta} K_i \frac{V_i}{V_S} + \frac{K}{\beta} K_s \frac{V_s}{V_S} \quad (A.2)$$

Rearranging this equation leads to Eq. (12).

Appendix B

We summarize here all geometric relationships required by the equations of retention. The cross-section of SP film in a WCOT column is schematized in Fig. 7. Annular regions of volumes V_i and V_s are defined by the interfacial subphases. Each one is determined by the volume difference of cylinders enclosing it, whose different diameters are specified between parentheses in the equations and are indicated in the scheme. For practical reasons we express all needed volumes by taking the common factor $\pi L d_C^2$, and using the notation: $x \equiv d_f/d_C$, $y \equiv d_s/d_C$ and $y' \equiv d_i/d_C$

- Column:

$$V_C = V(d_C) = \frac{1}{4} \pi L d_C^2 \quad (B.1)$$

- MP:

$$V_M = V(d_C - 2d_f) = \pi L d_C^2 \left[\frac{1}{4} - x + x^2 \right] \quad (B.2)$$

- SP:

$$V_S = V_C - V_M = \pi L d_C^2 (x - x^2) \quad (B.3)$$

- Subphase s:

$$V_s = V_C - V(d_C - 2d_s) = \pi L d_C^2 (y - y^2) \quad (B.4)$$

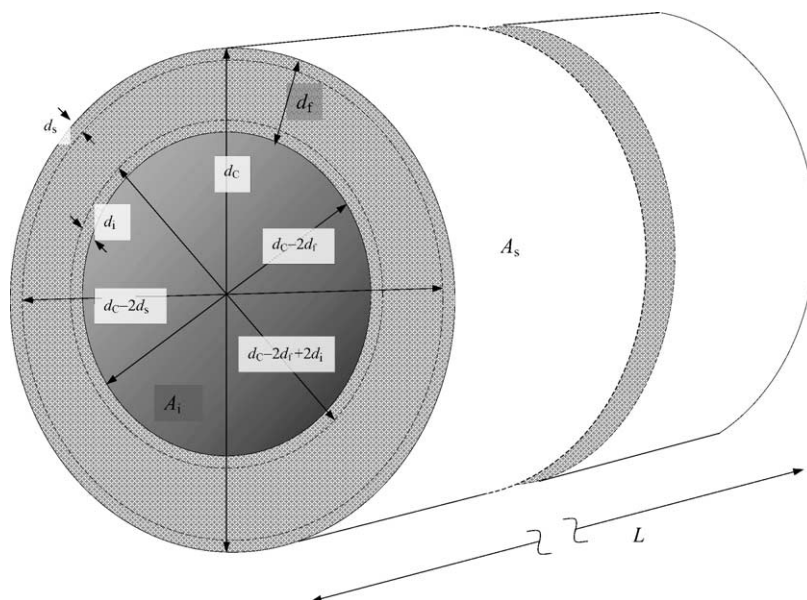


Fig. 7. The cross-section of a SP film. Annular regions are defined by the three subphases.

• Subphase i:

$$V_i = V(d_C - 2d_f + 2d_i) - V_M \\ = \pi L d_C^2 \{y' - y'^2 [2(d_f/d_i) - 1]\} \quad (\text{B.5})$$

Replacing V_i/V_S and V_s/V_S , as given by the preceding equations, into Eq. (12) yields Eq. (13). A relationship between β and x is obtained directly from its definition and Eqs. (B.1) and (B.3):

$$\beta \equiv \frac{V_M}{V_S} = \frac{V_C}{V_S} - 1 = \frac{1}{4(x - x^2)} - 1 \quad (\text{B.6})$$

Then:

$$x - x^2 = [4(\beta + 1)]^{-1} \quad (\text{B.7})$$

Eq. (B.7) is the expression needed for obtaining Eq. (14) and for deriving the relationship between β and d_f . Rearranging Eq. (B.7) yields the quadratic equation:

$$[4(\beta + 1)]^{-1} - x + x^2 = 0 \quad (\text{B.8})$$

The roots of which are

$$x = \frac{1}{2} \left[1 \pm \sqrt{\beta/(\beta + 1)} \right] \quad (\text{B.9})$$

The solution having physical sense is the one with sign (–); that is Eq. (19).

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