Considerations on the temperature dependence of the gas–liquid chromatographic retention

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Abstract

A discussion on the temperature dependence of the partition coefficient K is developed. This discussion embraces topics such as the limitations of conventional thermodynamic approaches followed in the chromatographic literature, qualitative theoretical notions arising from molecular thermodynamics and the experimental information that is accessible through modern capillary gas chromatography. It is shown that the heat capacity difference of solute transfer for flexible molecules has at least one maximum in the chromatographic range of temperature. As a consequence, a great amount of experimental data is required for a correct thermodynamic interpretation of the chromatographic retention. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

The understanding of the nature intrinsic to the influence of temperature on solvation is vital for gas–liquid chromatography (GLC). It is essential, for example, in temperature-programmed gas chromatography (TPGC), where high heating rates are employed for fast analysis and very wide temperature intervals of elution are thus generated for the solutes. The behavior of partition coefficients in these broad temperature intervals, $K(T)$, determines the elution order of the analytes in TPGC. Therefore, reliable thermodynamic expressions, capable of describing $K(T)$ accurately in the whole GLC range, are indispensable for a computer-assisted optimization of the TPGC separation [1].

If presently there are no rigorous explicit expressions available for describing the behavior of $K(T)$, we could then formulate an immediate question: In order to expand the empirical basis to be contrasted with the different theoretical approaches, what thermodynamic information is acquirable through accurate capillary GLC measurement? But before facing this experimental problem it may be convenient first to consider if there are some a priori basic notions on the nature of the function $K(T)$ that could contribute to efficiently focus the experimental efforts.

This paper has several objectives. The principal is

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to develop a theoretical discussion on the general properties expected for $K(T)$. It also seeks answers to the question formulated above. A complementary aim is to analyze and compare the applicability and limitations of some approaches followed in the ambit of GLC.

The approaches currently followed in the chromatographic literature for obtaining expressions of $K(T)$ may be classified into two general categories: (a) empirical and (b) based on conventional (macroscopic) thermodynamics. In the first group are included those approaches which do not seek the explicit thermodynamic meaning the parameters of the mathematical model must have. They are for satisfying practical needs, as, for example, the performance of numerical simulations for the TPGC process. On the other hand, those classified in the latter group are characterized by the explicit physical interpretation of all the parameters in the mathematical model, through the application of conventional thermodynamics. Macroscopic thermodynamics are unable to provide a theoretical description for the temperature dependence of thermodynamic functions such as the heat capacity [2,3]. Therefore, the approaches of group b are semiempirical.

A representative example for an approach comprised in group a is the empirical expression utilized by Vezzani and co-workers [4,5] in their numerical simulation of the GLC process:

$$\ln K(T) = A + \frac{B}{T} + CT \tag{1}$$

where the parameters of the model, A, B, and C, are independent of T.

The most general treatment for the temperature dependence of K in the context of conventional thermodynamics was developed by Castells et al. [6], who adapted the procedure of Clarke and Glew [7]. This involves the Taylor series expansion of the standard partial molar enthalpy of solution, ΔH_{s}^{0}, around an arbitrary reference temperature T_0. For simplicity, in the following expression are written only the first four terms for the resultant explicit form of $K(T)$:

$$\ln K(T) = A + \frac{B}{T} + C \ln T + DT + \dots \tag{2}$$

The physical meaning of the parameters depends on the number of terms that are taken. For their interpretation we shall not use the nomenclature applied in macroscopic thermodynamics. Instead, for the sake of uniformity in this paper, the nomenclature for molecular solvation thermodynamics is employed. This change is feasible due to the rigorous equality for a solvation process at infinite dilution [8]:

$$\frac{\Delta G_{s}^{0}}{RT} = \frac{\Delta G^*}{kT} = -\ln K \tag{3}$$

The standard partial molar free energy of solution, ΔG_{s}^{0}, corresponds to the usual standard states adopted in conventional thermodynamics for a solution process at infinite dilution on the molar concentration scale. These comprise a unit concentration liquid solution that hypothetically obeys Henry's law and a unit concentration vapor solution that hypothetically behaves as an ideal gas. ΔG^* is the Gibbs free energy of solute transfer for one solute molecule (the ensemble average) from the ideal gas into a fixed position in the liquid solution [8]. This molecularly defined thermodynamic function does not require settling hypothetical standard states as in conventional thermodynamics. The solute molecule placed in the ideal gas provides a reference state. In this environment the molecule does not interact beyond molecular collisions. As a consequence, ΔG^* unequivocally renders a measure of the interactions of the solute molecule in the liquid solution.

2. General

2.1. The limitations of conventional thermodynamics

If only two terms are taken in Eq. (2) the interpretation of the parameters is:

$$A = \frac{\Delta S^*}{k} \quad B = \frac{-\Delta H^*}{k} \tag{4}$$

ΔS^* and ΔH^* are, respectively, the entropy and enthalpy of solute transfer. According to Eq. (4) the preceding functions are assumed constant with T, which is equivalent to saying that the isobaric heat capacity difference of solute transfer is $\Delta C_{p}^{*} = 0$.

This has been the most commonly applied thermodynamic approximation in the chromatographic literature.

When three terms are taken in Eq. (2), the physical meaning of the parameters is:

$$A = \frac{\Delta S^*(T)}{k} - \frac{\Delta C_p^*}{k} \cdot (1 + \ln T) \tag{5}$$

$$B = -\frac{\Delta H^*(T)}{k} + \frac{\Delta C_p^*}{k} \cdot T \tag{6}$$

$$C = \frac{\Delta C_p^*}{k} \tag{7}$$

As stated in Eq. (7), this model assumes that ΔC_p^* is constant with T. The other approximated thermodynamic functions, from which the parameters A and B stem, are[1]:

$$\Delta S^*(T) = \Delta S^*(T_0) + \Delta C_p^* \ln (T/T_0) \tag{8}$$

$$\Delta H^*(T) = \Delta H^*(T_0) + \Delta C_p^*(T - T_0) \tag{9}$$

Eq. (9) is the two-term approach in the Taylor development of $\Delta H^*(T)$, where we must read $\Delta C_p^* = (\partial \Delta H^*/\partial T)_{p, T=T_0}$. We see that a two-term $\Delta H^*(T)$ corresponds to a three-term explicit expression for $K(T)$. In general, if ΔH^* is developed in x terms, there are $x+1$ terms for K.

When four terms are taken in Eq. (2), the physical meaning of the parameters is:

$$A = \frac{\Delta S^*(T)}{k} - \frac{\Delta C_p^*(T)}{k} \cdot (1 + \ln T) + \frac{1}{k} \cdot \frac{\partial \Delta C_p^*}{\partial T} \cdot T \ln T \tag{10}$$

$$B = -\frac{\Delta H^*(T)}{k} + \frac{\Delta C_p^*(T)}{k} \cdot T - \frac{1}{2k} \cdot \frac{\partial \Delta C_p^*}{\partial T} \cdot T^2 \tag{11}$$

$$C = \frac{\Delta C_p^*(T)}{k} - \frac{1}{k} \cdot \frac{\partial \Delta C_p^*}{\partial T} \cdot T \tag{12}$$

$$D = \frac{1}{2k} \cdot \frac{\partial \Delta C_p^*}{\partial T} \tag{13}$$

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[1]The function $\Delta S^*(T)$ can be recovered by applying the expression of A simultaneously to T and T_0 and equaling. Also for $\Delta H^*(T)$, using the expression of B.

As stated in Eq. (13), this four-parameter approximation to K physically implies that a constant variation of ΔC_p^* with T is assumed. By applying Eq. (12) to T and T_0 and equaling:

$$\Delta C_p^*(T) = \Delta C_p^*(T_0) + (\partial \Delta C_p^*/\partial T) \cdot (T - T_0)$$

which is equivalent to:

$$\Delta C_p^*(T) = a + bT \tag{14}$$

Incrementing successively the number of terms in the development of ΔH^* means that more terms in a polynomial describing ΔC_p^* are considered, as is shown below:

$$\Delta H^*(T) = \Delta H^*(T_0) + \left(\frac{\partial \Delta H^*}{\partial T}\right)_{T_0} \cdot (T - T_0) + \frac{1}{2}$$
$$\cdot \left(\frac{\partial^2 \Delta H^*}{\partial T^2}\right)_{T_0} \cdot (T - T_0)^2 + \frac{1}{3}$$
$$\cdot \left(\frac{\partial^2 \Delta H^*}{\partial T^3}\right)_{T_0} \cdot (T - T_0)^3 + \dots \tag{15}$$

Since $\Delta C_p^* = (\partial \Delta H^*/\partial T)_p$, taking x terms for ΔH^* implies taking $x-1$ for ΔC_p^*:

$$\Delta C_p^*(T) = \Delta C_p^*(T_0) + \left(\frac{\partial \Delta C_p^*}{\partial T}\right)_{T_0} \cdot (T - T_0)$$
$$+ \left(\frac{\partial^2 \Delta C_p^*}{\partial T^2}\right)_{T_0} \cdot (T - T_0)^2 + \dots \tag{16}$$

which is the same as saying that ΔC_p^* will be given by the polynomial:

$$\Delta C_p^*(T) = a + bT + cT^2 + \dots \tag{17}$$

Hence, Eq. (2) and its physical meaning could have been obtained also by postulating Eq. (17) (namely Eq. (16)) as the starting point and by applying the three basic relationships:

$$\Delta S^*(T) = \Delta S^*(T_0) + \int_{T_0}^{T} \Delta C_p^*(T) \, \mathrm{d} \ln T \tag{18}$$

$$\Delta H^*(T) = \Delta H^*(T_0) + \int_{T_0}^{T} \Delta C_p^*(T) \, \mathrm{d}T \tag{19}$$

$$\ln K(T) = \frac{\Delta S^*(T)}{k} - \frac{\Delta H^*(T)}{kT} \tag{20}$$

One way of allowing the thermodynamic interpretation of the chromatographic retention is to carry out a least-square regression of experimental $K(T)$ data to any of the equations, e.g., that taking three terms in Eq. (2). Severe difficulties will arise in doing so when the number of parameters is incremented. Besides the natural mathematical difficulties for attaining a well convergent regression in a model of many parameters, let us analyze these difficulties from a physical viewpoint. Up to the three-parameter description of $K(T)$ there are no major difficulties [6,9]. The physical reason is that as the model assumes a constant ΔC_p^* (see Eq. (7)), this value can be considered an average in the experimental temperature interval. This is a physical assumption of general character that offers no problem in a discrete T interval. When we shift to four parameters the variation of ΔC_p^* is assumed constant (see Eq. (14)), consequently, only data corresponding to a monotonously linearly decreasing, or increasing, real $\Delta C_p^*(T)$ can be correctly interpreted. But what would occur if the real $\Delta C_p^*(T)$ has an exponential growth or decay, or what is worse, one or several maximums and minimums? The parameters will be meaningless. A complicated real $\Delta C_p^*(T)$ can be approximated by a linear function such as Eq. (14) only in a narrow temperature interval. But the narrower the interval, the greater the difficulties for attaining regression convergence in a four-parameter $K(T)$ model.

We should then guess if it is possible to inquire a priori on the nature of $\Delta C_p^*(T)$. If this would be feasible, the number of parameters for the correct description of the thermodynamic functions could be optimized. Unfortunately, macroscopic thermodynamics do not admit an insight into the nature of $\Delta C_p^*(T)$ because the ways the matter can store energy are inherently related to its structure. Therefore, any approach to the nature of $\Delta C_p^*(T)$ demands a molecular theory.

Summarizing, conventional thermodynamics can reveal the physical meaning of the parameters of a mathematical model for $K(T)$ in relation to the thermodynamic solvation functions $\Delta H^*(T)$, $\Delta S^*(T)$ or $\Delta C_p^*(T)$, but it cannot inquire on the behavior of these functions and their link to the solute structure. So the natural context for a discussion on this issue is molecular (statistical) thermodynamics.

2.2. A qualitative approach to the behavior of the solvation functions

We shall adopt here a simplified phenomenological approach for discussing the problem of the temperature dependence of the solvation functions. This is done with the aim to reveal some qualitative features of these functions, a necessary a priori knowledge for designing experiments efficiently in the study of the retention dependence with T.

Statistical thermodynamics settle the following contributions to K [8,10,11]:

$$\ln K = \ln\frac{^{L}q_{r,v_2}}{^{G}q_{r,v_2}} - \frac{W(2/1)}{kT} \tag{21}$$

where the symbols $^{L}q_{r,v_2}$ and $^{G}q_{r,v_2}$ denote the rotational–vibrational partition functions of the solute molecule in the liquid and gas phases. These are the contributions of the internal degrees of freedom of the molecule. The partition functions for the momentum of translation cancel out and do not contribute in Eq. (21). The work for coupling solute 2 to solvent 1, $W(2/1)$, includes all the other contributions not considered by the first term, e.g., the work of formation for the cavity hosting the solute molecule in the liquid. For small solutes, the nature of the latter is mainly entropic. In the present discussion we shall focus on the first term of the sum.

The first term in Eq. (21) should have importance when rotations and vibrations in the solute molecule are affected by the transfer process. We can illustrate schematically this effect with a classical oscillator, represented by a spring-bead model in Fig. 1. This is transferred from in-vacuo (the ideal gas G) to the force field generated by the surrounding solvent particles in the liquid lattice L (atoms, molecules or solvent monomers represented by white circles). If the solvent particles exert net attractive forces (arrows), the process can be viewed as a change in the effective force constant of the oscillator. This translates into a shift in the oscillator's vibration frequencies from $^{G}\nu$ to a lower frequency $^{L}\nu$.

A flexible molecule of n' atoms has $3n'-6$ internal degrees of freedom. The potential energy surface for molecules having many degrees of freedom, as, for example, linear flexible ones [12], are
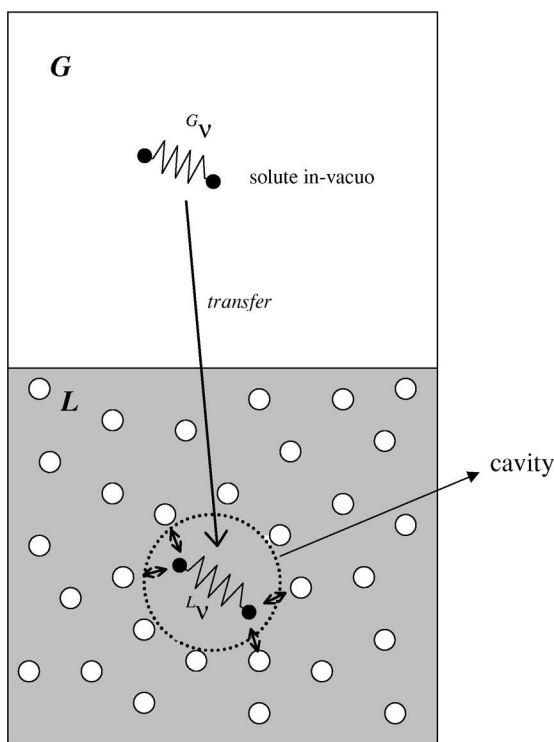
Fig. 1. Scheme illustrating the effect of the solvation process on a classical oscillator. The vibration frequency of the solute in-vacuo, $^{G}\nu$, is shifted to $^{L}\nu$ by the force field exerted by the solvent molecules in the liquid lattice L.

extremely complex, presenting a great amount of local minimums. The simplest example familiar to all chemists is the potential of rotation around the dihedral angle of butane [13], which presents three total minimums. If the potential is developed around each minimum and only the first two no-null terms are taken, we then have the potential of a harmonic oscillator [3]:

$$U_i(\phi_i) = U(\phi_{i\,\min}) + (1/2)\kappa\,(\phi_i - \phi_{i\,\min})^2 + \ldots \tag{22}$$

where ϕ_i denotes generalized coordinates (the dihedral angle in the example). The force constant of the oscillator is $\kappa = (\partial^2 U_i / \partial \phi_i^{\,2})_{\min}$. Then, we have for small displacements around a local minimum that each $U_i(\phi_i)$ corresponds to the potential of a monodimensional harmonic oscillator. This holds for rotational and vibrational degrees of freedom. There-

fore, concerning its $(3n'-6)$ internal degrees of freedom, we can roughly assimilate the molecule to a subsystem composed of harmonic oscillators. Let us admit that n oscillators are active at a given temperature range (i.e., that their potentials functions are thermally accessible), and that their motions can be mathematically transformed into a total number of m normal modes (i.e., m independent monodimensional harmonic oscillators). The quantum partition function for such a subsystem is [3]:

$$q_{r,v_2} = \prod_m \frac{e^{-\theta_m/2T}}{1 - e^{-\theta_m/T}} \tag{23}$$

where the characteristic temperature is defined by: $\theta \equiv (h/k)\nu = (ch/k)\tilde{\nu} = 1.439\ (\text{cm K})\ \tilde{\nu}\ (\text{cm}^{-1})$. So we have for the rotational–vibrational (r,v) contributions to K:

$$
\begin{aligned}
\ln K_{r,v} &= \ln \frac{^{L}q_{r,v_2}}{^{G}q_{r,v_2}} \\
&= \sum_m \left[\frac{^{G}\theta_m - {}^{L}\theta_m}{2T} + \ln \frac{1 - e^{-{}^{G}\theta_m/T}}{1 - e^{-{}^{L}\theta_m/T}} \right]
\end{aligned} \tag{24}
$$

For obtaining the associated thermodynamic functions, the derivatives of $\ln K_{r,v}$ are needed:

$$\frac{\Delta S^*}{k} = \frac{-\partial \Delta G^*}{k\,\partial T} = \ln K + T \cdot \frac{\partial \ln K}{\partial T} \tag{25}$$

$$\frac{\Delta H^*}{k} = T^2 \cdot \frac{\partial \ln K}{\partial T} \tag{26}$$

$$\frac{\Delta C_p^*}{k} = 2T \cdot \frac{\partial \ln K}{\partial T} + T^2 \cdot \frac{\partial^2 \ln K}{\partial T^2} \tag{27}$$

where for simplicity the subscripts r, v were omitted, as well as the indications for a constant pressure p. The latter simplification is justified by the negligible dependence of K with p in the usual chromatographic conditions [15], so the partial derivatives of Eqs. (25)–(27) can be replaced by total derivatives. The application of Eqs. (20), (25)–(27) renders:

$$\frac{\Delta S_{r,v}^*}{k} = \sum_m \frac{(^{L}\theta_m/T)}{e^{^{L}\theta_m/T} - 1} - \frac{(^{G}\theta_m/T)}{e^{^{G}\theta_m/T} - 1} + \ln \frac{1 - e^{-{}^{G}\theta_m/T}}{1 - e^{-{}^{L}\theta_m/T}} \tag{28}$$

$$\frac{\Delta H^*_{r,v}}{k} = \sum_m \frac{{}^L\theta_m - {}^G\theta_m}{2} + \frac{{}^L\theta_m}{e^{{}^L\theta_m/T} - 1} - \frac{{}^G\theta_m}{e^{{}^G\theta_m/T} - 1}$$

$$(29)$$

$$\frac{\Delta C^*_{p\,r,v}}{k} = \sum_m \frac{({}^L\theta_m/T)^2 e^{{}^L\theta_m/T}}{\left(e^{{}^L\theta_m/T} - 1\right)^2} - \frac{({}^G\theta_m/T)^2 e^{{}^G\theta_m/T}}{\left(e^{{}^G\theta_m/T} - 1\right)^2} \quad (30)$$

Fig. 2 reveals the basic phenomenology expected for the solvation functions of some few vibration modes of an alkane molecule in the chromatographic range of T. These are bending normal modes of $-CH_2-$ and C–H stretching. Function $\ln K(1/T)$ is slightly upward concave, function $\Delta H^*(T)$ is slightly sigmoidal, with its inflexion point in the chromatographic range, and so $\Delta C^*_p(T)$ is a distribution with its maximum in the same position. If we analyze

each contribution separately, we will see that the position of the maximum shifts to a higher T as higher is $\tilde{\nu}$ of the normal mode. For example, the contribution of the highly energetic vibration mode of C–H stretching is shown in Fig. 3, where solely the chromatographic range is displayed. In this case the maximum of ΔC^*_p shifts to a very high T. We see that this mode makes a negligible contribution to ΔC^*_p in the range shown. It contributes with a small, almost constant, value of ΔH^*, so $\ln K(1/T)$ is practically linear. This situation would be describable by the two-parameter model of Section 2.1. For modes with lower $\tilde{\nu}$ the same analysis can be performed.

These theoretical facts explain why rigid molecules having mainly highly energetic stretching possibilities present a different temperature depen-
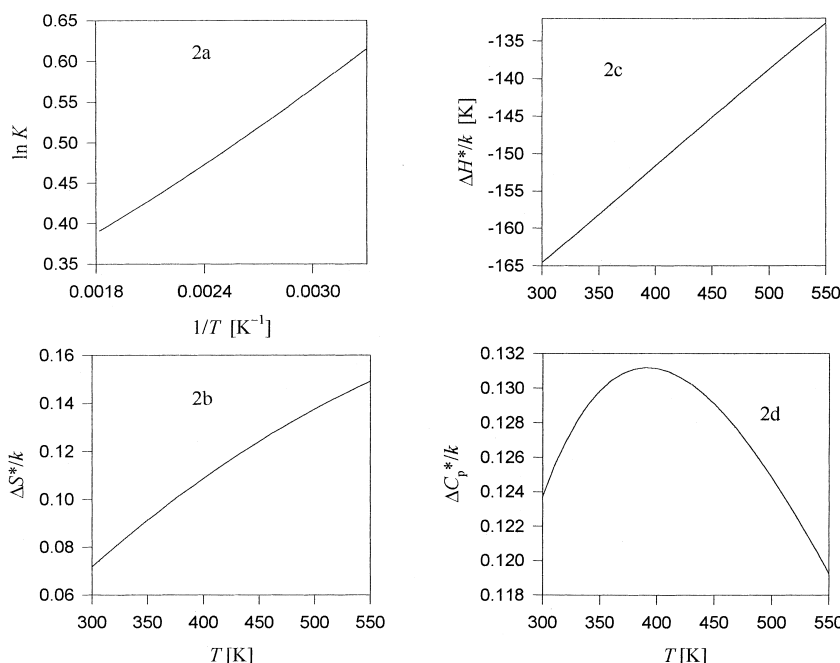

Fig. 2. Qualitative behaviors of the rotational–vibrational solvation functions for some vibration frequencies contributing in the chromatographic range of T. In the example the spectroscopic reported $\tilde{\nu}$ for alkanes [14], currently assigned to bending and stretching modes, were applied to Eqs. (24), (28)–(30). Only the principal bands were considered. These are: ${}^G\tilde{\nu} = 2850$ cm^{-1} (C–H stretching); 1470, 1380, 725 cm^{-1} ($-CH_2-$ and $-CH_3$ bending). Shifts were taken of the order of the experimental range for the reported frequencies. They were increased as the force constant decreased. These, respectively are: $\Delta\tilde{\nu} = -25, -50, -55, -100$ cm^{-1}. (a) The function $\ln K_{r,v}$ vs. $1/T$ is slightly upward concave. (b) $\Delta S^*_{r,v}$ is sigmoidal (not visible in the range displayed). (c) $\Delta H^*_{r,v}$ is slightly sigmoidal. (d) $\Delta C^*_{p\,r,v}$ has a maximum at the inflexion point of $\Delta H^*_{r,v}$.
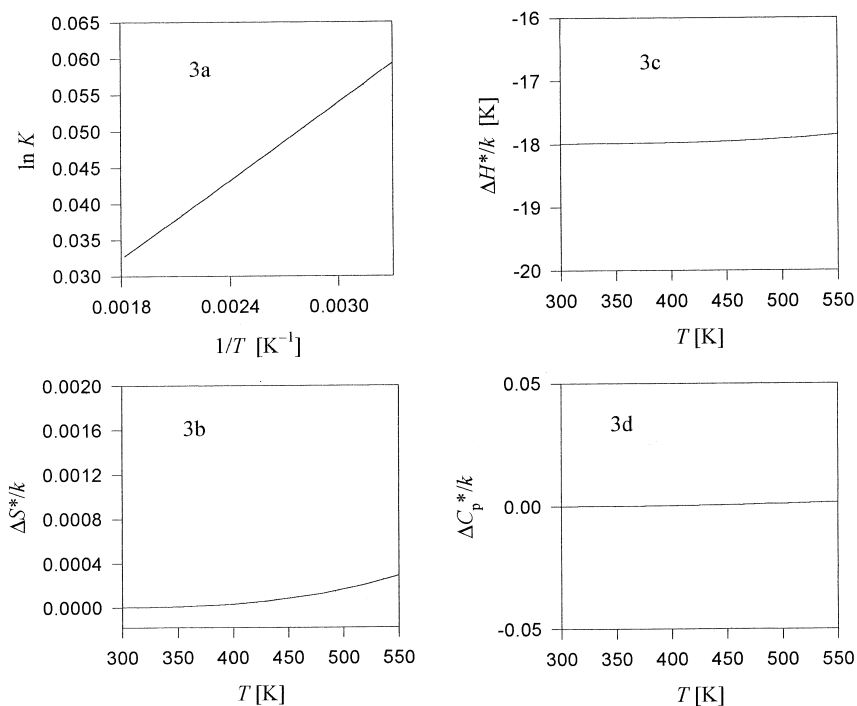
Fig. 3. As Fig. 2, considering only the C–H stretching mode. (a) The function $\ln K_{r,v}$ vs. $1/T$ is practically linear in the chromatographic range. (b) An almost null $\Delta S^*_{r,v}$ is observed. (c) A small contribution to $\Delta H^*_{r,v}$ is observed. (d) There is an almost null contribution to $\Delta C^*_{p\,r,v}$ in the chromatographic range.

dence of K or Kovats indices than flexible molecules. Elution order inversions with T between these two types of substances is the chromatographic consequence (see Ref. [1] and references cited therein).

The total r,v contribution to K is the summation overall internal degrees of freedom. The resultant function $\Delta C^*_p(T)$ might be a complicated one if the solute molecule presents a great number of normal modes with different frequencies. A certain thermal distribution of active modes is expected. In real molecules the panorama is even more complicated if we consider anharmonic modes due to roto–vibrational coupling. In addition, in real systems $^L\theta$ is a function of T, because the thermal expansion of the solvent affects the density and distribution of the surrounding solvent particles which exert the force field on the solute molecule. As the solvent density decreases, the shift on ν will decrease very rapidly, so leading to a more abrupt decay of ΔC^*_p (namely a

more pronounced sigmoidal behavior of ΔH^*) than that described by Eqs. (28)–(30) and observed in Fig. 2.

It is observed in Fig. 2b that the r,v entropy contribution to solvation is small and positive, if the solute–solvent attractive forces are dominating. But a more important entropic contribution to $\ln K$ arises from the work of cavity formation, which is included in the second term of Eq. (21) [11]. This is invariably negative, and so will be the net ΔS^*. As the latter is associated also with the first derivative of $\ln K$, it has generally a shape similar to that of ΔH^*, but displaced. Hence, for comparing thermodynamic behaviors the interest is principally focused on the analysis of the shape of $\Delta H^*(T)$, which provides immediate information on $\Delta C^*_p(T)$.

Summarizing, in the case of flexible molecules, as, e.g., n-alkanes, the molecular thermodynamics tells us that $\Delta C^*_p(T)$ must be a function of exponential

nature with at least one maximum in the chromato-graphic range. So it is telling us that a great amount of experimental data will be required for correctly assessing the thermodynamic behavior of the re-tention.

3. Thermodynamic information acquirable through capillary GLC measurement

We shall now face the task of seeking answers to the question formulated in the Introduction. For the thermodynamic analysis of the retention data we need to determine the first and second derivatives of ln $K(T)$ (see Eqs. (25)–(27)). The derivatives can be calculated numerically directly from the raw ex-perimental data as:

$$\left(\frac{dy}{dT}\right)_{T=T_i} = \frac{1}{2} \cdot \left(\frac{y_{i+1} - y_i}{T_{i+1} - T_i} + \frac{y_i - y_{i-1}}{T_i - T_{i-1}}\right) \qquad (31)$$
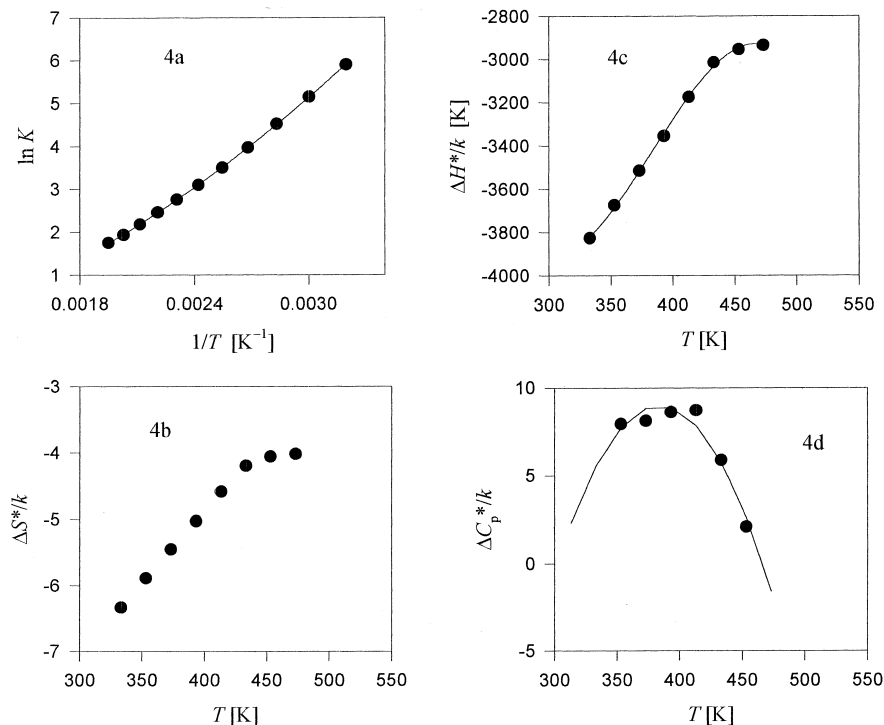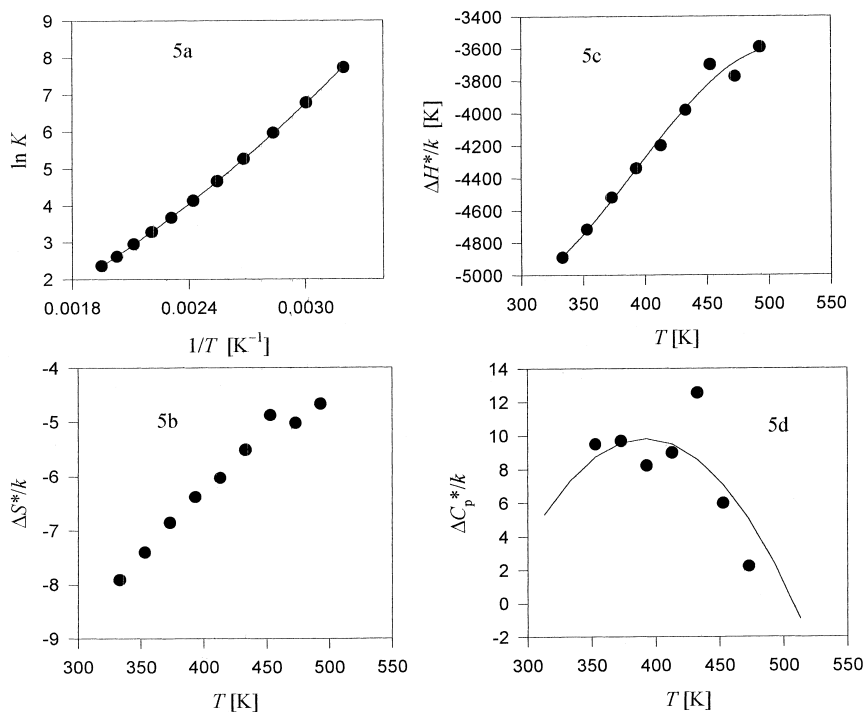
For these calculations it is important that the K data correspond to evenly spaced temperatures (i.e., $T_{i+1} - T_i = \text{const.}$). Within the same capillary column, the standard deviation of measurement for ln K in commercial chromatographs has the order 0.1% and steeply increases with the oven temperature [15]. This level of accuracy allows one to determine the first derivative, but it will make difficult the direct numerical determination (from the raw data) of significant values of the second derivative, particu-larly at high T. Nevertheless, from the form of $\Delta H^*(T)$ information on $\Delta C_p^*(T)$ can be inferred immediately.

Figs. 4 and 5 show the analysis of published K data for n-heptane and n-nonane [15], by using Eqs. (25)–(27) and (31). These data were measured on a poly(dimethylsiloxane) capillary column in the range 40–240°C, at constant intervals of 20°C. Figs. 4c and 5c reveal a sigmoidal nature for $\Delta H^*(T)$. In both figures the least-square regression of the ΔH^* data to

Fig. 4. (a) Experimental ln $K(T)$ data reported for n-heptane in Ref. [15]. (b) ΔS^* determined through the application of Eq. (25), calculating the derivative numerically from the experimental data. (c) As for ΔH^* using Eq. (26); the filled line is the regression to a polynomial of order 3. (d) As for ΔC_p^* using Eq. (27); the filled line is the derivative of the polynomial in (c).

Fig. 5. As Fig. 4 for *n*-nonane.

a polynomial (filled line) renders a sigmoidal shape. Unfortunately, the amount of data and its precision results insufficient for assessing ΔC_p^* accurately. The filled lines in plots Figs. 4d and 5d are those obtained from the derivative of the filled lines in Figs. 4c and 5c.

The analyzed experimental information clearly suggests that direct determination of $\Delta C_p^*(T)$ through capillary GLC measurement will be feasible if the interval of data acquisition is reduced to 10°C, or lower, and if the control of temperature is done within ±0.1°C, or better.

4. Discussion

We shall compare here the two cited approaches to the behavior of $K(T)$ with the experimental data employed in Section 3. These approaches are Eq. (1) of Vezzani et al. and that taking three terms from Eq. (2) (Castells et al.), so the comparison is done on the basis of an equal number of parameters. The least-square regression of the experimental K data to these

equations provides the respective parameters. The curve fits are shown in Fig. 6a. These fits are in excellent mutual agreement and with the data. The residuals typically involve the fourth digit in both cases and are thus in the order of the experimental errors. No differences between the equations can be discriminated graphically in the experimental range.

The application of Eq. (26) to Vezzani's expression yields a parabolic enthalpic behavior, $\Delta H^*(T) = -B + CT^2$, and a linear behavior for Castells: $\Delta H^*(T) = -B + CT$. In Fig. 6b these predictions are compared with the experimental data. The mathematical models are in mutual agreement within the interval where the parameters were determined, but they rapidly diverge beyond this range. By deriving the preceding functions, or by applying Eq. (27), the prediction for the heat capacity in the first model is linear, $\Delta C_p^*(T) = 2CT$, while it is constant for the second (see Eq. (7)). These predicted behaviors are compared with the experimental data in Fig. 6c. If $\Delta C_p^*(T)$ has a maximum, it is easy to see through Eqs. (18)–(20) that the extrapolation of the mathematical models out of the range where the parame-
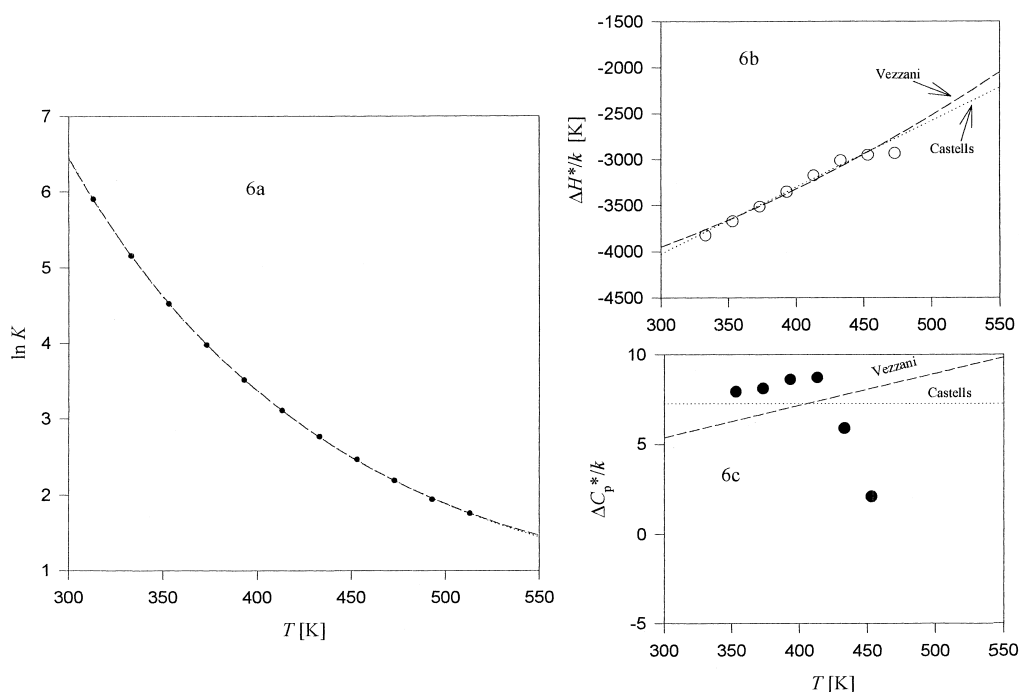
Fig. 6. (a) Regression of the experimental data of Fig. 4 (circles) to Eq. (1) of Vezzani et al. (dashed line) and to that taking three terms in Eq. (2) (Castells et al., dotted line). (b) Representation of the experimental ΔH^* (circles) in conjunction with the predictions of the cited mathematical models. (c) Comparison of the experimental ΔC_p^* (circles) with the predictions of the cited mathematical models.

ters were determined will lead to systematic errors in the predicted values of K.

Tudor and Oncescu reviewed the literature concerning the thermodynamic assessment of n-alkanes in different solvents [16]. They also performed measurements on poly(dimethylsiloxane) covering the range 363–488 K. Their ΔH_s^0 data per methylene group reproduces in part the shape of Figs. 4 and 5, so the preceding mathematical models neither can represent the subtle behavior of these data.

It has been shown, for the conditions of the data employed here, that ln K of the n-alkanes plotted as a function of the number of C–C bonds tends to be very small when it is extrapolated to zero at $T > 393$ K [17]. This experimental fact may be interpreted as a small contribution from C–H in this region, which in the context of Section 2.2 would mean negligible discrepancies between $^L\nu$ and $^G\nu$ (a negligible shift) for its associated normal modes. If this would be correct an abrupt decay should be observed for ΔC_p^* around 400 K, unless other modes than those considered in Fig. 2 would contribute significantly. How-

ever, there is no way for elucidating questions like this experimentally because taking the IR spectrum of a solute at infinite dilution in a solvent having the same chemical groups is naturally impossible. Understanding of these issues only can be obtained with the aid of molecular simulations.

5. Conclusions

There is theoretical and experimental evidence that for flexible solute molecules, such as the n-alkanes, the heat capacity of solute transfer is a function with at least one maximum in the chromatographic range of temperatures. This is equivalent to state that the enthalpy difference of transfer is sigmoidal with its inflexion point in this range. Current empirical mathematical models are unable to describe this behavior unless equations are developed ad-hoc.

Direct quantitative determination of the heat capacity difference of transfer through modern capillary GLC measurement is feasible if the interval of

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experimental data acquisition is reduced to 10°C, or less, provided a temperature control within ±0.1°C, or better. The behavior analysis of the function $\Delta C_p^*(T)$ contributes with important information on the molecular aspects of the retention.

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