Analysis of the equations for the temperature dependence of the retention index
II. Physico-chemical meaning of the parameters

Ecaterina Tudor

Institute of Physical Chemistry "I. G. Murgulescu", Romanian Academy, Sector 6, Spl. Independenţei 202, 77208 Bucharest, Romania

Abstract

A general expression for the meaning of various parameters from the retention index-temperature equations was found. This is a linear combination of two solute dependent factors consisting of differences of enthalpies and respective entropies of solution, between the solute and the reference inferior *n*-alkane. The particular coefficients for each parameter are stationary phase dependent factors. They were calculated from methylene contributions to the thermodynamic functions of solution in SE-30 and Carbowax-20M, revealing the influence of the used temperature range. A short review of structural influences on dI/dT is included.   © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

The relation between the equations for the temperature dependence of the retention index and variation of their parameters with the mean temperature of the range were treated in Part I [1]. The equations considered here are the hyperbola and the two linear approximates:

$$I = A + \frac{B}{t + C} = A + \frac{B}{T + C'} \tag{1}$$

$$I = a + bt = a' + bT \tag{2}$$

$$I = \alpha + \frac{\beta}{T} \tag{3}$$

where t or T is the column temperature in °C or K, $C' = (C\text{-}273.15)$ and $a' = (a - 273.15b)$. The square

polynomial equation was ignored because it is less significant from the theoretical point of view [1].

The parameters of the hyperbolic Eq. (1) have a meaning deduced [2,3] from the theory of retention, based on the thermodynamics of gas-liquid partition process [4–14] and consideration of intermolecular interactions [15–17]. The simple mathematical relations between the parameters of Eqs. (2) or (3) and those of the hyperbola were used in the present paper for obtaining their thermodynamic expressions. The literature information on the physico-chemical meaning of the considered parameters is scarce or indirect [7–14,18,19]. This subject is important for understanding of *I-T* dependence in connection with molecular structure. Until now, only the linear Eq. (2) is thus applied. The parameter $b = \mathrm{d}I/\mathrm{d}T$ is used as an aid in qualitative analysis, together with the column difference ΔI and other retention correlations

[18–55]. The study of the structural effects on dI/dT on physico-chemical base is the final goal of our series of papers on this subject [1,3,20–22,57,58], including the present one. A short review on the topic is useful for evaluation of the results. The experimental application of the theory is made here only for the stationary phase dependent factors or ''phase constants'' that can be calculated from the methylene increments of the thermodynamic functions of solution [57]. The global view will be possible after the evaluation of solute dependent enthalpic and entropic factors, in Part III [58].

2. Literature information

2.1. Literature data on dI/dT behaviour

The quasi-constancy of the dI/dT value for groups of congener solutes is known [23–55]. The fact was explained in such data series through the compensation of the molecule lengthening effect by the reference to the appropriate n-alkane in the retention index definition, leaving the area of the transversal section as the decisive factor [25–30]. The acyclic solutes have the slightest temperature variation of the retention index, increasing with molecular branching [9,23–27,31–41] whatever their functionality and the stationary phase are. The dI/dT values are higher for alicyclic compounds [19,25,26,31–34,40,41] increasing with the size [25,33,42,43] and number [25,26,32,33,44,45] of the cycles. The monocyclic aromatic hydrocarbons behave similarly to the 5- or 6-membered alicyclics [25,26,28,29,32,33,40,41,46–50]. The dI/dT values increase with the number of aromatic cycles [33,51]. The temperature dependence of the retention index is generally higher on polyethylene glycol stationary phases than on non-polar dimethyl silicones [20,21,36,37,44–49], but this does not seem to be a general rule for all other polar columns. Most of the dI/dT values observed on liquid stationary phases are positive, except a for few polar solutes with relatively small molecules. Cases with negative dI/dT values are found among aliphatic alcohols, esters or ketones on Apolan-87 [33], Emulphor-O [23], SE-30 and Carbowax-20M [20,21,36,38], Carbowax-1540 [37], phenols on OV-1701 [52] and many acetylenic and $trans$-alkanes in

different conditions [25,54]. The abovementioned features were qualitatively explained mainly for hydrocarbons, by geometrical or steric structural factors as the area of the transversal section [25,27,30], rigidity or flexibility [25,54], molecular symmetry [28,54]. In the attempts to quantitatively correlate dI/dT values in groups of isomers, a quantity implying the rotation inertial moment [27], a shape parameter, or the first order molecular connectivity index [30] were used as solute descriptors.

Together with some theoretical interpretation discussed below, these facts seem to indicate an entropic meaning for dI/dT. However, the importance of the enthalpic contribution cannot be excluded. Indeed, a tendency of dI/dT values in groups of related compounds to increase directly with the retention index [28] or with the solute polarity measured by the column difference ΔI [26,28,29,32,42,46] was noticed. The effect of n-alkane adsorption at the gas-liquid interface on Carbowax columns was observed [21,55] as an increase of dI/dT for thinner films. The adsorption of the hydroxylic solutes on non-polar DB-5 produces non-linear I-T curves in the range 80-110°C [56]. Nevertheless, in the range 120-150°C there is no difference in dI/dT values for 0.11 and 0.33 µm films, as calculated from the data taken from the same reference. The information on a variety of non-aliphatic polar compounds is scarce [52,53,56], but our data regarding perfumery solutes on SE-30 and Carbowax-20M [20,21] indicate the same general trends.

2.2. The physico-chemical meaning of the parameters

The retention index is the standard free energy of solution of the solute i in conventional index units (i.u.), as shown by Kováts and Weiss [4] and used for example in Refs. [7–14]:

$$I = 100z + 100 \cdot \frac{\Delta G_i^{\mathrm{S}} - \Delta G_z^{\mathrm{S}}}{\Delta G_{\mathrm{CH}_2}^{\mathrm{S}}} \qquad (4)$$

$$\Delta G_{\mathrm{CH}_2}^{\mathrm{S}} = \Delta G_{z+1}^{\mathrm{S}} - \Delta G_z^{\mathrm{S}} \qquad (5)$$

where $100z$ is the free energy of solution of the

n-alkane with z carbon atoms, in i.u. The values ΔG^S, in J mol^{-1}, are the standard free energies of solution of the solute i, reference n-alkanes with z and $(z+1)$ carbon atoms, and methylene groups. The equation:

$$\Delta G_{i.u.}^S = \frac{\Delta G_{CH_2}^S}{100} \qquad (6)$$

defines the energetic equivalent of an index unit [4,12,14,42]. This one is not explicit in the current analytical applications, but it is important for obtaining of the thermodynamic quantities from the retention indices and for understanding of the behaviour with column temperature and stationary phase polarity [8–14,42]. The absolute values of ΔG^S are not considered here. The corresponding differences of thermodynamic functions implied in Eq. (4), can be directly obtained from the relative retention of the solute against the reference n-alkane with z carbon atoms, or of the n-alkanes with $(z+1)$ and z carbon atoms. ΔG^S refers to the transfer of a mole of solute between its standard states in gas and in solution, suitable for elution gas chromatography. The differences of thermodynamic functions from Eqs. (4) and (5) can be considered as defined against the basic set of standard states, solute vapours as ideal gas with a partial pressure of 1 atm (1 atm = 101 325 Pa) and the hypothetical pure solute ($x_i = 1$) with the same interactions and environment like in the infinite dilute solution. For other concentration units, the transformation constant [5,6,12] is reduced.

Eq. (4) in terms of standard enthalpies and entropies of solution is:

$$I = 100z + 100 \cdot \frac{(\Delta H_i^S - \Delta H_z^S) - T(\Delta S_i^S - \Delta S_z^S)}{\Delta H_{CH_2}^S - T\Delta S_{CH_2}^S} \qquad (7)$$

and gives the hyperbolic form of the temperature dependence of the retention index shown in Eq. (8), where m, n, m_{CH_2} and n_{CH_2} are constants, leading ultimately [2] to Eq. (1):

$$I = \frac{mT + n}{m_{CH_2}T + n_{CH_2}} \qquad (8)$$

The deductions or commentaries about the theory of the linear temperature dependence of the retention index in the literature [7–14,18,19,31] are based on Eqs. (7) or (8). Eq. (8) was qualitatively considered to show the temperature dependence for the studied solute comparatively with the situation of an n-alkane, for example by Ettre and Billeb [18], and the approach was developed in more clear terms by Hawkes [9]. Guermouche and Vergnaud [7] suggested the reduction of Eq. (7) to Eq. (2), if the term $T\Delta S_{CH_2}^S$ is very small comparatively with $\Delta H_{CH_2}^S$. This would give the following parameters:

$$b = -100 \cdot \frac{\Delta S_i^S - \Delta S_z^S}{\Delta H_{CH_2}^S} \qquad (9)$$

$$a' = 100z + \frac{100(\Delta H_i^S - \Delta H_z^S)}{\Delta H_{CH_2}^S} \qquad (10)$$

Mitra and Saha [19] and Dwyer [8] accepted this assumption in deduction of Eq. (2). Consequently, the parameter b or dI/dT would have a meaning determined only by differences in the entropy of the solution solute-n-alkane. Nevertheless, generally the term $T\Delta S_{CH_2}^S$ cannot be neglected, because it is almost the half of the enthalpic one [57]. Aspects correlated with Eq. (3) derive indirectly from the papers [10,11].

Hawkes [9] deduced the following relationship using Eq. (7), the postulates connected with the free energy additivity for n-alkanes laying at the basis of the retention index system, and a development in McLaurin series:

$$\frac{I}{100\epsilon} = 1 - \frac{\delta}{\epsilon} + \phi \left[1 + T \cdot \frac{\Delta S_{CH_2}^S}{\Delta H_{CH_2}^S} + \left(T \cdot \frac{\Delta S_{CH_2}^S}{\Delta H_{CH_2}^S} \right)^2 + ... \right] \qquad (11)$$

The constant δ is a corrective term for the nonlinearity of the free energy relationship in the n-alkane homologous series, and for differences between methyl and methylene groups [8,9]. The constants ϵ and ϕ are defined considering the entropy and enthalpy of solution of the compound i as multiples of the respective methylene increments:

$$\epsilon = \frac{\Delta S_i^S}{\Delta S_{CH_2}^S}; \phi = \frac{\Delta H_i^S / \Delta H_{CH_2}^S}{\Delta S_i^S / \Delta S_{CH_2}^S} - 1 \qquad (12)$$

In the case of *n*-alkanes, the two entropic and enthalpic multiples are the same and equal to the carbon number, so that $\epsilon = z$, $\phi = 0$, and the retention index is $I = 100z$, independent of temperature. The constant ϕ is a measure of the structural resemblance of the solute with an *n*-alkane. For the solutes having the two multiples near equal, even if they are different from *z*, the retention index is also independent of temperature or shows a very small dI/dT value. This behaviour is expected, for example, in the case of the acyclic linear compounds. The more ϕ is different from zero, the greater the temperature dependence of the retention index. Eq. (11) is polynomial, and if the higher terms of the series are neglected, it becomes quasi-linear, but only at rather small temperatures. Although the above treatment explains much of the observed behaviour of the retention index, another point of view brings more information and generality, as follows.

3. Theory

Using the established relation between the retention index-temperature equations [1] and the meaning of hyperbola parameters, it is possible to assign a physico-chemical sense to the linear Eqs. (2) and (3).

The expressions for the thermodynamic definition of the hyperbola parameters given in Refs. [1,3] in the usual suppositions made in gas-liquid chromatography and in the retention index system, can be written in a convenient modified form:

$$A - 100z = -\kappa_1 \left(\Delta S_i^S - \Delta S_z^S \right) \qquad (13)$$

$$B = \kappa_1 \left(\Delta H_i^S - \Delta H_z^S \right) + \kappa_2 \left(\Delta S_i^S - \Delta S_z^S \right) \qquad (14)$$

$$C' = -\frac{\Delta H_{CH_2}^S}{\Delta S_{CH_2}^S}; C = 273.15 - \frac{\Delta H_{CH_2}^S}{\Delta S_{CH_2}^S} \qquad (15)$$

where

$$\kappa_1 = -\frac{100}{\Delta S_{CH_2}^S}; \kappa_2 = \frac{100 \Delta H_{CH_2}^S}{\Delta S_{CH_2}^S} \qquad (16)$$

It is obvious that the hyperbola parameter *C* or *C'* and the coefficients κ_1 and κ_2 are "phase constants" or phase dependent factors, in fact do not depend on the solute nature. They are influenced by the stationary phase, the mean temperature of the range, T_{mean} (this variable is relevant for the thermodynamic functions, and not the range itself) and the *n*-alkane pair. The phase dependent factors can be calculated from information about $\Delta H_{CH_2}^S$ and $\Delta S_{CH_2}^S$ values [57]. The differences $(\Delta H_i^S - \Delta H_z^S)$ and $(\Delta S_i^S - \Delta S_z^S)$ are solute specific factors, but not like in the concept of the linear combination of interaction forces [15–17], determined only by the solute. They also depend on the specific reference *n*-alkane, stationary phase and T_{mean}. A similar point of view is the distinction between the Kováts coefficient and the molecular structural coefficient, reported by Santiuste and Takács [13,14].

Previously two approaches were introduced [1] regarding the influence of the mean temperature of the range on the parameters of Eq. (2). A distinction was made between the mean temperatures $\bar{T}$ and T_{mean} of a linear section belonging to a hyperbola and of the general range. In the present paper only approach 2 is considered, when each straight line is associated with its own hyperbola defined on the same range ($\bar{T} = T_{mean}$). The two notations will be used when convenient, as well as *t* or *T* in °C or K.

Applying the proposed procedure, a general expression is found for the thermodynamic description of the parameters of Eqs. (1–3) and of the contributions to the retention index at the mean temperature of the range, $I_{\bar{T}}$. This relation can be written in two equivalent variants, connected with the dimension of the considered quantities:

$$Y = k_1 \left(\Delta H_i^S - \Delta H_z^S \right) + k_2 \left(\Delta S_i^S - \Delta S_z^S \right) \qquad (17)$$

$$Y = \frac{100}{\left(\Delta G_{CH_2}^S \right)_{\bar{T}}} \left[k_1' \left(\Delta H_i^S - \Delta H_z^S \right) + k_2' \left(\Delta S_i^S - \Delta S_z^S \right) \right]$$

$$= \frac{100}{\left(\Delta G_{CH_2}^S \right)_{\bar{T}}} Z \qquad (18)$$

where *Y* designates, respectively, for the three equa-

tions: the parameters B, b, β, the $(I_{\bar{T}} - 100z)$ value and the contributions to it represented by $(A-100z)$ and $B/(\bar{T} + C')$, $(a'-100z)$ and $b\bar{T}$, or $(\alpha-100z)$ and $\beta/\bar{T}$. The dimension of the different quantities named Y involves the dimensionless i.u, the enthalpy is in J mol^{-1} and the entropy in J mol^{-1} K^{-1}. Eq. (17) gives the two enthalpic and entropic terms in units based on i.u. (e.g., for b, in i.u. K^{-1}), whereas Eq. (18) emphasises in the square brackets the same terms and their sum Z, in units based on J mol^{-1} (for b, in J mol^{-1} K^{-1}). The general factor in Eq. (18) is due to the energetic equivalent of an i.u. at $\bar{T}$. Dimension of the coefficients k_1 and k_2, or k_1' and k_2' adjust to this situation.

The two series of coefficients k_1, k_2 and k_1', k_2' are "phase constants". They have different expressions and notations for each parameter and are interrelated by:

$$k_1 = \frac{100}{\left(\Delta G_{CH_2}^S\right)_{\bar{T}}} \cdot k_1'; \quad k_2 = \frac{100}{\left(\Delta G_{CH_2}^S\right)_{\bar{T}}} \cdot k_2' \tag{19}$$

where

$$\left(\Delta G_{CH_2}^S\right)_{\bar{T}} = \Delta G_{CH_2}^S - \bar{T}\Delta S_{CH_2}^S \tag{20}$$

The information on the coefficients k_1' and k_2' particularised for different cases is summarised in Table 1. Examples of their numerical values at 120°C on SE-30 are included.

For the slope b of the linear Eq. (2), the specific expression of Eq. (17) is:

$$b = \varphi_1\left(\Delta H_i^S - \Delta H_z^S\right) + \varphi_2\left(\Delta S_i^S - \Delta S_z^S\right) \tag{21}$$

with

$$\varphi_1 = \frac{100\Delta S_{CH_2}^S}{\left[\left(\Delta G_{CH_2}^S\right)_{\bar{T}}\right]^2}; \quad \varphi_2 - \frac{100\Delta H_{CH_2}^S}{\left[\left(\Delta G_{CH_2}^S\right)_{\bar{T}}\right]^2} \tag{22}$$

The experimental behaviour of this parameter reviewed above is obviously well explained by Eq. (21). The $b = dI/dT$ value increases with the differences $(\Delta H_i^S - \Delta H_z^S)$ and $(\Delta S_i^S - \Delta S_z^S)$. These are determined by the disparities in molecular features of the solute and of reference n-alkane, as pure compounds and in relation to the stationary phase. Both modifications of interaction forces and of order in solution or of energetic and steric factors are considered. Some compensation effects are possible in

series of solutes or for the same solute at different mean temperatures of the range.

With this approach a more complete view is obtained than a simple shape resemblance with n-alkanes.

4. Experimental

The $\Delta H_{CH_2}^S$ and $\Delta S_{CH_2}^S$ contributions at various mean temperatures of 20-30°C wide ranges on SE-30 (40 m×0.35 mm, film thickness d_f 0.35 μm) and two Carbowax-20M (one of 51 m×0.43 mm, d_f 0.45 μm, another of 46 m×0.3 mm, d_f 0.08 μm) glass capillary columns were taken from Ref. [57]. The same columns were used in our previous work and in Part III [58].

5. Results and discussion

The established relations for the thermodynamic meaning of the parameters of Eqs. (1–3) are evaluated in the present paper only in relation to the stationary phase dependent factors. The specific quantities and a study for each solute, is accomplished for several compounds in Part III [58]. Besides the numerical examples from Table 1, a more detailed view is necessary for Eqs. (1) and (2). The basic hyperbolic equation was studied on SE-30 [3] and Carbowax-20M [22] columns for different aspects, except the dependence of the parameters A and B on T_{mean}. The parameter b of the linear Eq. (2) is relevant for structural effects. The phase dependent factors κ_1 and κ_2 regarding the hyperbola and φ_1 and φ_2 concerning the parameter b were calculated in steps of 5°C for the three columns. The $\Delta H_{CH_2}^S$ and $\Delta S_{CH_2}^S$ increments were used in Eqs. (16) and (22) and in Table 1.

The effects of stationary phase nature, interfacial phenomena for Carbowax and mean temperature of the range can be so considered. The n-alkane pair influence was indirectly reflected in the $\Delta H_{CH_2}^S$ and $\Delta S_{CH_2}^S$ values, measured as averages for several n-alkane pairs on a given range, as imposed by the level of the experimental errors [57]. The specific pairs were decided by their volatility in relation with

Table 1
Expressions and examples of numerical values[a] of the coefficients k_1' and k_2'[b] in the general Eq. (18) for the parameters of Eqs. (1–3) and for the corresponding contributions to the retention index at the mean temperature of the range

Y		Expression		Example	
		k_1'	k_2'	k_1'	k_2'
		Retention index at the mean temperature of the range			
$(I_{\bar{T}}\text{-}100z)$	i.u.	1	$-\bar{T}$	1	-393.1 K
Coefficients and contributions in Eq. (1)					
B	i.u. K	$\kappa_1' = \dfrac{-(\Delta G^{\mathrm{S}}_{\mathrm{CH_2}})_{\bar{T}}}{\Delta S^{\mathrm{S}}_{\mathrm{CH_2}}}$	$\kappa_2' = \dfrac{\Delta H^{\mathrm{S}}_{\mathrm{CH_2}}(\Delta G^{\mathrm{S}}_{\mathrm{CH_2}})_{\bar{T}}}{(\Delta S^{\mathrm{S}}_{\mathrm{CH_2}})^2}$	-361.26 K	$2.752\cdot10^5$ K^2
$B/(\bar{T}+C')$	i.u.	1	$-\dfrac{\Delta H^{\mathrm{S}}_{\mathrm{CH_2}}}{\Delta S^{\mathrm{S}}_{\mathrm{CH_2}}}$	1	-754.4 K
$(A\text{-}100z)$	i.u.		$\dfrac{(\Delta G^{\mathrm{S}}_{\mathrm{CH_2}})_{\bar{T}}}{\Delta S^{\mathrm{S}}_{\mathrm{CH_2}}}$		361.3 K
Coefficients and contributions in Eq. (2)					
b	i.u. K^{-1}	$\varphi_1' = \dfrac{\Delta S^{\mathrm{S}}_{\mathrm{CH_2}}}{(\Delta G^{\mathrm{S}}_{\mathrm{CH_2}})_{\bar{T}}}$	$\varphi_2' = \dfrac{-\Delta H^{\mathrm{S}}_{\mathrm{CH_2}}}{(\Delta G^{\mathrm{S}}_{\mathrm{CH_2}})_{\bar{T}}}$	0.0028 K^{-1}	-2.0883
$b\bar{T}$	i.u.			1.0883	-821.0 K
$(a'\text{-}100z)$	i.u.	$\lambda_1' = \dfrac{\Delta H^{\mathrm{S}}_{\mathrm{CH_2}} - 2\bar{T}\Delta S^{\mathrm{S}}_{\mathrm{CH_2}}}{(\Delta G^{\mathrm{S}}_{\mathrm{CH_2}})_{\bar{T}}}$	$\lambda_2' = \dfrac{\bar{T}^2\Delta S^{\mathrm{S}}_{\mathrm{CH_2}}}{(\Delta G^{\mathrm{S}}_{\mathrm{CH_2}})_{\bar{T}}}$	-0.0883	427.9 K
Coefficients and contributions in Eq. (3)					
β	i.u. K	$\theta_1' = \dfrac{-\bar{T}^2\Delta S^{\mathrm{S}}_{\mathrm{CH_2}}}{(\Delta G^{\mathrm{S}}_{\mathrm{CH_2}})_{\bar{T}}}$	$\theta_2' = \dfrac{\bar{T}^2\Delta H^{\mathrm{S}}_{\mathrm{CH_2}}}{(\Delta G^{\mathrm{S}}_{\mathrm{CH_2}})_{\bar{T}}}$	-427.88 K	$3.228\cdot10^5$ K^2
$\beta/\bar{T}$	i.u.			-1.0883	821.0 K
$(\alpha\text{-}100z)$	i.u.	$\omega_1' = -\varphi_2' = \dfrac{\Delta H^{\mathrm{S}}_{\mathrm{CH_2}}}{(\Delta G^{\mathrm{S}}_{\mathrm{CH_2}})_{\bar{T}}}$	$\omega_2' = \dfrac{-\bar{T}\left[(\Delta G^{\mathrm{S}}_{\mathrm{CH_2}})_{\bar{T}} + \Delta H^{\mathrm{S}}_{\mathrm{CH_2}}\right]}{(\Delta G^{\mathrm{S}}_{\mathrm{CH_2}})_{\bar{T}}}$	2.0883	-1214.2 K

[a] The numerical values are calculated at $\bar{T}=393.15$ K from $\Delta H^{\mathrm{S}}_{\mathrm{CH_2}}$ and $\Delta S^{\mathrm{S}}_{\mathrm{CH_2}}$ increments for the glass capillary column SE-30 [57]. The sum of the coefficients k_i' ($i=1$ or 2) for the two terms of Eqs. (1–3): $(A\text{-}100z)$ and $B/(\bar{T}+C')$; $(a'\text{-}100z)$ and $b\bar{T}$; $(\alpha\text{-}100z)$ and $\beta/\bar{T}$, must be equal with the coefficients of $(I_{\bar{T}}\text{-}100z)$ value, that means with unity for k_1' and with $-\bar{T}$ for k_2'. See Eq. (24).

[b] The corresponding coefficients k_1 and k_2 from the general Eqs. (17) and (19) have the following particular notations for the parameters of Eqs. (1–3): κ_1 and κ_2 for $(A\text{-}100z)$ and B, φ_1 and φ_2 for b, λ_1 and λ_2 for $(a'-100z)$, θ_1 and θ_2 for β, and ω_1 and ω_2 for $(\alpha\text{-}100z)$.

the optimum retention factor. To assure data uniformity, the $(\Delta G^{\mathrm{S}}_{\mathrm{CH_2}})_{\bar{T}}$ values necessary in Eq. (22) and in Table 1 were calculated with Eq. (20), although the free energy increments for each temperature and *n*-alkane pair were available.

The results of the variation of the coefficients with T_{mean} are shown in Figs. 1 and 2. The patterns and sequence of the curves for the three columns are determined by the values (influenced by the stationary phase polarity) and by the non-linear behaviour

of the $\Delta H^{\mathrm{S}}_{\mathrm{CH_2}}$ and $\Delta S^{\mathrm{S}}_{\mathrm{CH_2}}$ contributions, as shown in Ref. [57]. Both increments are negative. The fourth- or third-polynomial parallel decrease of their absolute values with T_{mean} seems to be explained by differences in the heat capacity of the *n*-alkane pairs involved at each point. The parallel trends of the two quantities at different temperatures induce compensation effects in their ratios or in the free energy.

The temperature dependence of the coefficients κ_1 and κ_2 is illustrated in Fig. 1. The data are fitted with
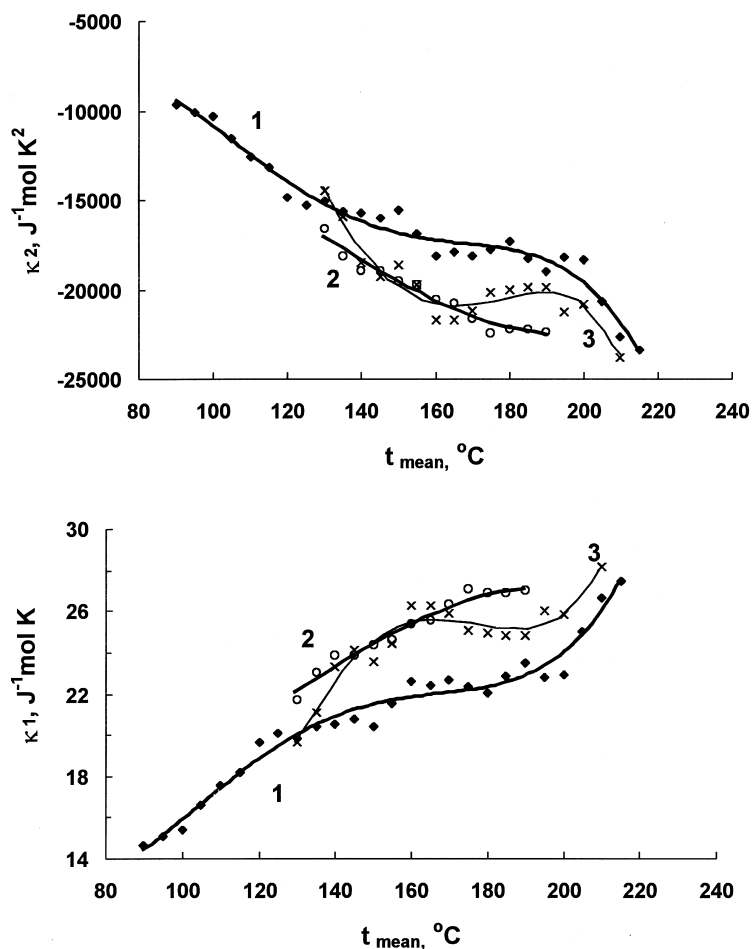
Fig. 1. The coefficients κ_1 and κ_2 from the theoretical expressions of the hyperbola parameters A and B as a function of the mean temperature of the range, for the glass capillary columns: (1) SE-30 (♦); (2) Carbowax-20M with film thickness 0.45 μm (○), and (3) Carbowax-20M with film thickness 0.08 μm (×). See Eq. (16).

fourth-order polynomial equations for the SE-30 (the mean correlation coefficient for κ_1 and κ_2 curves, $r_{mean} = 0.987$) and thin film Carbowax ($r_{mean} = 0.964$) columns, and with third-order ones for the medium film Carbowax column ($r_{mean} = 0.984$).

As revealed by Eq. (16), the dependence is due even for κ_2 mainly to the reciprocal of $\Delta S_{CH_2}^{S}$. Indeed, the ratio $\Delta H_{CH_2}^{S} / \Delta S_{CH_2}^{S}$ or the hyperbola parameter C have a much slighter variation [3,22]. The modification of hyperbola parameters with T_{mean} can be dominated by the rather high opposite symmetrical change of the factors κ_1 and κ_2 because the solute dependent factors vary to a lesser extent

[58]. If the parameter A with a single term increase or decrease with T_{mean}, for the parameter B a relative compensation effect is expected between the two terms in Eq. (17).

Fig. 2 contains the evolution of the coefficients φ_1 and φ_2 regarding the parameter b. The points are fitted with fourth-order polynomial equations on the columns SE-30 ($r = 0.972$ for φ_1 and 0. 996 for φ_2), Carbowax 0.45 μm ($r = 0.999$-1.000) and Carbowax-20M 0.08 μm ($r = 0.980$ for φ_1 and 0. 994 for φ_2), but the square polynomial fitting is also rather good. The opposite temperature variation of the two phase dependent factors is also observed, but with a rather
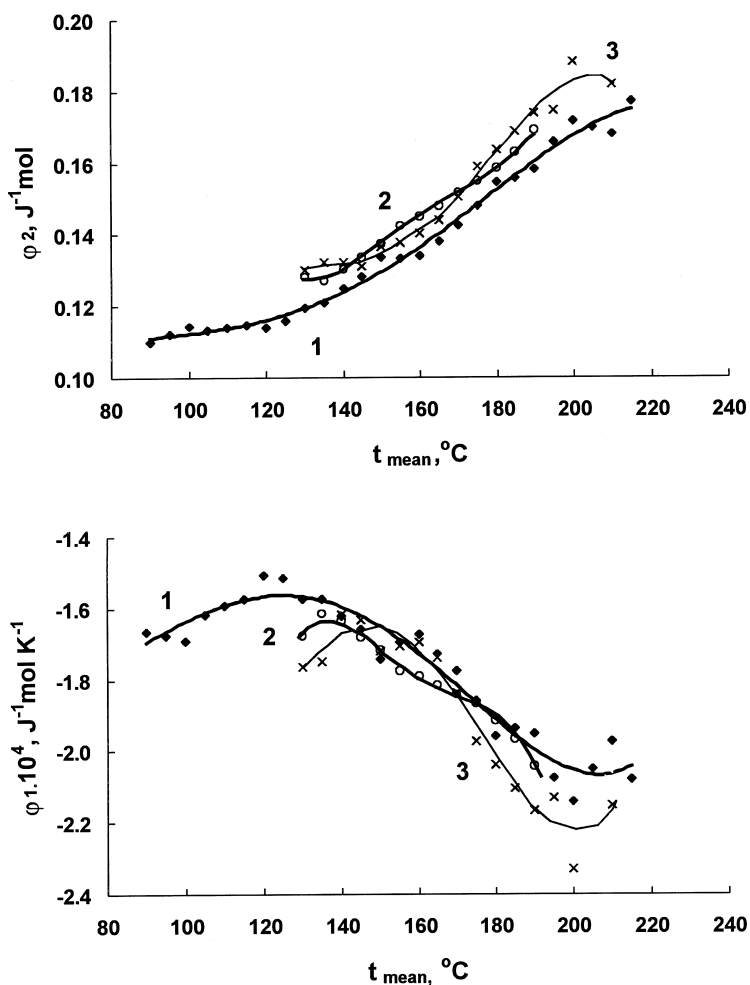
Fig. 2. The coefficients φ_1 and φ_2 from the theoretical expression of the parameter b of Eq. (2) versus the mean temperature of the range, for the same columns as in Fig. 1. See Eq. (22).

different pattern modulated by the linear decrease of $-(\Delta G_{CH_2}^S)_{\bar{T}}$ increment according to Eq. (22). So, a relative compensation effect at the shift of the temperature range must be observed in Eq. (21) for the parameter b.

Table 1, besides the expressions of the coefficients k_1' and k_2' for the different particular cases, contains examples of numerical values of these coefficients, calculated for SE-30 at $\bar{T} = 393.15$ K. In this way a balance of the different contributions to the retention index and a validation of the proposed relations can be made, both algebraically and numerical. Indeed, in Eq. (21) for $(I_{\bar{T}} - 100z)$, $k_1' = 1$ and $k_2' = -\bar{T}$. On the

other hand, the same quantity is the sum of the two contributions from Eqs. (1–3) at $\bar{T}$, each expressed with the general Eq. (21). For example in the case of Eq. (2):

$$I_{\bar{T}} - 100z = (a' - 100z) + b\bar{T} \qquad (23)$$

and considering Eqs. (19,21,22) results in:

$$\lambda_1' + \varphi_1'\bar{T} = 1; \; \lambda_2' + \varphi_2'\bar{T} = -\bar{T} \qquad (24)$$

Similar relations stand for Eqs. (1) and (3) as verified in Table 1. Obviously the distribution of the enthalpic and entropic terms in the retention index at

the current temperature is different from that at the mean temperature of the range.

6. Conclusions

The physico-chemical meaning of all parameters in Eqs. (1–3) was described by a general relation with two terms, consisting, respectively, of differences of enthalpies and entropies of solution solute-reference *n*-alkane, weighted by specific stationary phase dependent coefficients. The variation of these coefficients with the mean temperature of the range was shown on the three columns used in previous studies. The results are used in the final evaluation made in Part III [58].

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