



Analysis of the equations for the temperature dependence of the retention index

I. Relation between equations

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Abstract

The relation between the parameters of several equations for the retention index temperature dependence was established, taking the hyperbola deduced from the retention theory as starting point. The transformation factors depend only on methylene contributions to the thermodynamic functions of solution and temperature. Their evolution with the mean temperature of the range was illustrated for SE-30 and Carbowax-20M glass capillary columns. On this basis the post-run standardisation of dI/dT values at a reference mean temperature is possible. Examples and statistical correlation between series of parameters from different equations for perfumery solutes were shown. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Different equations are currently used for the temperature dependence of the retention index in gas chromatography (GC) [1–8]. They are usually the hyperbolic equation deduced from the retention theory [4,5]:

$$I = A + \frac{B}{t + C} = A + \frac{B}{T + C'} \quad (1)$$

and the empirical linear equations, that are eventually approximations of the hyperbola sections on narrower temperature ranges:

$$I = a + bt = a' + bT \quad (2)$$

$$I = \alpha + \frac{\beta}{T} \quad (3)$$

where I is the retention index, t or T is the column temperature, in °C or K. The non linear I – t curves can be described also by a square or cubic polynomial regression [9,10], for example:

$$I = \gamma_0 + \gamma_1 t + \gamma_2 t^2 \quad (4)$$

Both variants of Eqs. (1) and (2) are considered, where only the parameters C , C' and a , a' are different. They are correlated by:

$$C = C' + 273.15 \quad (5)$$

$$a = a' + 273.15b \quad (6)$$

Connection between the above equations and the meaning of their parameters are subjects not very much discussed in the literature [1–3,5,11–18]. The

problem is of interest for generalisation of retention index data and quantitative retention–structure relationships. The hyperbola parameters have a physico-chemical significance [5,18]. For the other equations this information is practically absent, in spite of many observations on structural effects regarding the slope of Eq. (2), $b = dI/dT$ [19].

Our approach starts with the hyperbola, finding its mathematical relation with the other equations, and then the meaning of their parameters. In this way a larger area of interest is revealed: (1) mutual transformations between equations; (2) realising the extent of the dependence of the parameters on temperature range; (3) finding the physico-chemical sense of the parameters, especially of b and (4) possibility of standardisation of b data obtained on different temperature ranges. Parameter meanings will be shown in Part II [19], except the factors depending only on methylene increments, treated here. Data on Eqs. (1)–(3) obtained with perfumery solutes on SE-30 and Carbowax-20M glass capillary columns [18,20–22] are used as illustrations. Helpful information can be found from the values of methylene contributions to the thermodynamic functions of solution, measured for different temperatures and alkane pairs on the same columns [23].

2. Theory

2.1. General

The definition of the Kováts retention index [3,13,24,25] is an interpolation on a logarithmic retention scale of the solute i between two reference n -alkanes with z and $z+1$ carbon atoms:

$$I = 100z + 100 \frac{\ln R_i - \ln R_z}{\ln R_{z+1} - \ln R_z}; R_z < R_i < R_{z+1} \quad (7)$$

where R is any of the retention values based on the adjusted retention time. Considering the usual linear temperature dependence of the logarithm of a retention value as a function of $1/T$, this is a hyperbolic temperature function [1,2,4]. Eq. (7) was rearranged [4,5] to the Antoine type hyperbola, Eq. (1). Its parameters have the meaning [4,5,18]:

$$A = \frac{100}{\Delta S_{\text{CH}_2}^{\text{S}}} (\Delta S_i^{\text{S}} - \Delta S_z^{\text{S}}) + 100z \quad (8)$$

$$B = 100 \frac{\Delta H_{\text{CH}_2}^{\text{S}}}{(\Delta S_{\text{CH}_2}^{\text{S}})^2} (\Delta S_i^{\text{S}} - \Delta S_z^{\text{S}}) - \frac{100}{\Delta S_{\text{CH}_2}^{\text{S}}} (\Delta H_i^{\text{S}} - \Delta H_z^{\text{S}}) \quad (9)$$

$$C' = \frac{\Delta H_{\text{CH}_2}^{\text{S}}}{\Delta S_{\text{CH}_2}^{\text{S}}}; \quad C = 273.15 - \frac{\Delta H_{\text{CH}_2}^{\text{S}}}{\Delta S_{\text{CH}_2}^{\text{S}}} \quad (10)$$

where ΔH^{S} and ΔS^{S} are the enthalpy and entropy of solution, at the transfer of a mole of solute between its standard states in gas and in stationary phase for the conditions of infinite dilution existent in elution gas–liquid chromatography (GLC). Subscripts i , z and CH_2 stand for the studied solute, the reference inferior n -alkane in the retention index definition and the methylene increment. The equations are valid with the usual suppositions in definition of the retention index and for a pure gas–liquid partition process [18].

The differences of thermodynamic functions in Eqs. (8)–(10) are almost constant for ranges of different widths centred on the same mean temperature, but change with this variable [23]. The temperature effect on the enthalpy and entropy of solution is more conveniently followed considering small consecutive intervals [23,26,27], instead using non-linear expressions of the specific retention volume [16,28]. The influence of n -alkane pair at a given temperature is slight, but perceptible [23].

So, the hyperbola parameters must rely on the investigated temperature interval, not to mention those of the linear equations, dependent also on the specific range, as shown in Fig. 1. Kováts considered this aspect using the finite difference per 10°C , $\delta I/10^\circ\text{C}$, together with the retention index in the middle of the temperature range [24,25]. In the present paper a distinction is made in notation of mean temperature, as t_{mean} for the whole hyperbola range and \bar{t} for the partial ranges associated with its linear sections. The appropriate use of t or T in different equations is implied.

Based on Eq. (10), hyperbola parameter C depends only on stationary phase, t_{mean} and n -alkane

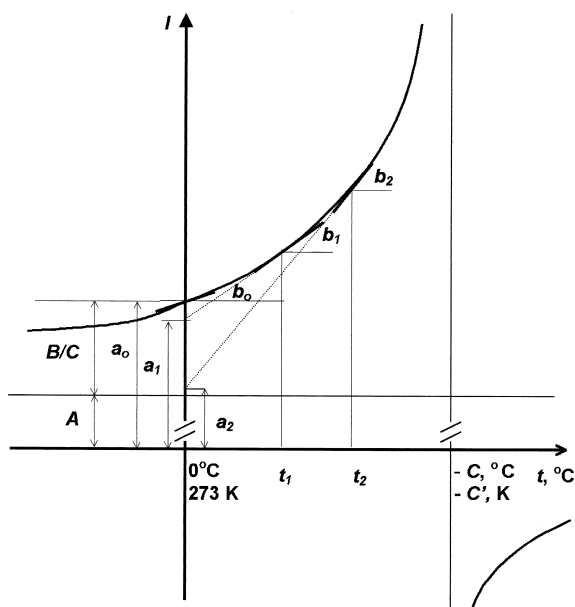


Fig. 1. Schematic representation of a case I hyperbola in the GC range, with linear sections described by Eq. (2) around temperatures 0°C , t_1 and $t_2^{\circ}\text{C}$.

pair [4,5,18,22,23]. The temperature ($-C$) of about $400\text{--}500^{\circ}\text{C}$ for SE-30 and Carbowax-20M corresponds to the vertical asymptote situated beyond the superior limit of the stationary phase. As shown in Fig. 1, only a branch of the hyperbola contains the GC range [4,18]. For the pure partition GLC, only two particular cases of Antoine-type hyperbola are normally expected [18,22], both with C around the above negative value and A positive. Case I with B negative shows a concave increasing I - t branch in the GC range and case II with B positive, has a convex decreasing branch.

2.2. Relationship between equations

The linear Eq. (2) approximates a hyperbola section for a narrower interval around \bar{t} , from the wider range characterised by t_{mean} and corresponds to the tangent to the curve at this point. In Fig. 1, the tangents to a case I hyperbola in the points 0°C , t_1 and $t_2^{\circ}\text{C}$ are illustrated. Parameters a and b of the lines depend on \bar{t} . Decreasing intercepts on the retention index axis and increasing slopes, a_0 , b_0 , a_1 , b_1 and a_2 , b_2 , are noticed. For the case II hyperbola,

both the intercepts and the absolute values of the slopes increase.

Development of Eq. (1) in Taylor series against variable t around the point \bar{t} gives the following expression of the retention index:

$$I = \left(A + \frac{B}{\bar{t} + C} \right) - \frac{B}{(\bar{t} + C)^2} (t - \bar{t}) + \frac{2B}{(\bar{t} + C)^3} (t - \bar{t})^2 + \dots \quad (11)$$

The higher terms, including the third, can be usually neglected. For instance, if $(t - \bar{t}) = \pm 20^{\circ}\text{C}$ around 120°C and the hyperbola parameters on SE-30 and Carbowax-20M columns [18,22] are $C = -500^{\circ}\text{C}$ and B in the range $\pm 5000\text{--}50\,000$ for most solutes, the value of the third term is in the range of ± 0.07 to 0.7 index units. For B values as high as $-200\,000$ to $-400\,000$, observed only for some polycyclic compounds, this term increases to several index units.

The same approach with $1/T$ as variable and retaining only the first two terms leads to:

$$I = \left(A + \frac{B}{T + C'} \right) + B \left(\frac{1}{T} - \frac{1}{\bar{T}} \right) \left(1 + \frac{C'}{\bar{T}} \right) + \dots \quad (12)$$

The above relations can be arranged in form of linear equations corresponding to the difference of Eqs. (2) or (3), written for t and \bar{t} or for $1/T$ and $1/\bar{T}$:

$$I_t = I_{\bar{t}} + b(t - \bar{t}) \quad (13)$$

$$I_T = I_{\bar{T}} + \beta \left(\frac{1}{T} - \frac{1}{\bar{T}} \right) \quad (14)$$

In this way, the expressions of the slopes b and β as a function of hyperbola parameters result directly. As the retention index at \bar{t} is equally described by Eq. (1) and Eqs. (2) or (3), one also obtains the expressions of the intercepts a and α , and other relations. These are summarised in Table 1, where the current number continues the equation numbering in text.

The relationships between the parameters of different equations consist basically from solute-dependent hyperbola parameters as A , B and the trans-

Table 1
Relations between the parameters of Eqs. (1)–(4).

Equation ^a	Equation ^a
<i>I. Relations between equations^b</i>	
$b = -cB$ (15)	$\beta_{273} = 273.15^2(B/C^2) = -273.15^2b_0$ (24)
$a = A + dB$ (16)	$\alpha_{273} = A + C'(B/C^2) = A - C'b_0$ (25)
$a' = A + d'B$ (17)	$\beta = u\beta_{273}$ (26)
$b_0 = -B/C^2$ (18)	$\alpha - \alpha_{273} = vB$ (27)
$a_0 = I_0 = A + B/C$ (19)	$\beta = -bT^2$ (28)
$b = f_0b_0$ (20)	$\alpha = a + b(2\bar{t} + 273.15)$ (29)
$a - a_0 = g_0B$ (21)	$\gamma_0 = a + \eta_0b$ (30)
$\beta = pB$ (22)	$\gamma_1 = \eta_1b$ (31)
$\alpha = A + qB$ (23)	$\gamma_2 = \eta_2b$ (32)
<i>II. Transformation factors^c</i>	
$c = 1/(\bar{t} + C)^2 = 1/(\bar{T} + C')^{-2}$ (33)	$q = cC'$ (39)
$d = c(2\bar{t} + C)$ (34)	$u = [T(273.15 + C')]^2/[273.15(\bar{T} + C')]^2$ (40)
$d' = c(2\bar{T} + C')$ (35)	$v = C'[1/(\bar{T} + C')^2 - 1/(273.15 + C')^2]$ (41)
$f_0 = cC^2$ (36)	$\eta_0 = -2\bar{t}^2/(\bar{t} + C)$ (42)
$g_0 = d - 1/C$ (37)	$\eta_1 = (5\bar{t} + C)/(\bar{t} + C)$ (43)
$p = c\bar{T}^2$ (38)	$\eta_2 = -2/(\bar{t} + C)$ (44)
<i>III. Relative transformation factors^d</i>	
Approach 1 (t_{mean} , C and \bar{t}_{ref} – constants, \bar{t} – variable)	
$c_{\text{rel}} = f_{0,\text{rel}} = b_{\text{rel}} = (\bar{t}_{\text{ref}} + C)^2/(\bar{t} + C)^2$ (45)	
Approach 2 ($\bar{t}_{\text{ref}} = t_{\text{mean,ref}}$ and C_{ref} – constants, $\bar{t} = t_{\text{mean}}$ and C_t – variables)	
$c_{\text{rel}} = (\bar{t}_{\text{ref}} + C_{\text{ref}})^2/(\bar{t} + C_t)^2$ (46)	$f_{0,\text{rel}} = [(\bar{t}_{\text{ref}} + C_{\text{ref}})/C_{\text{ref}}]^2/[(C_t)/(\bar{t} + C_t)]^2$

^a Continues the current equation numbering in text.

^b For the transformation factors, see the second part of the table, Eqs. (33)–(44).

^c The transformation factors contain only the hyperbola parameter C and \bar{t} , the mean temperature of the partial range (°C), or respectively, C' and \bar{T} (K).

^d See Eqs. (50)–(54).

formation factors reported in the second part of the Table 1. The transformation factors depend only on \bar{t} , hyperbola parameter C and the implicit influences on it introduced by $\Delta H_{\text{CH}_2}^{\text{S}}$ and $\Delta S_{\text{CH}_2}^{\text{S}}$ increments (stationary phase, t_{mean} , and n -alkane pair). The parameters of Eqs. (2) and (3) in frames of a hyperbola, given by Eqs. (15)–(17) and (22)–(23), vary with the mean temperature of the linear range through the transformation factors. The parameters at $\bar{t}=0^\circ\text{C}$ (b_0 , a_0 , β_{273} , α_{273}) contain exclusively hyperbola data, as seen in Eqs. (18)–(19) and (24)–(25). Such values must be taken only as a formal tool for separation of the intrinsic hyperbola contribution from the partial temperature range effect, in the manner described by Eqs. (20)–(21) and (26)–(27). However, the hyperbola parameters imply t_{mean} and the situation has no connection with the real

physical state of the stationary phase at 0°C . Although without new essential aspects, Eq. (20) as an alternative to Eq. (15) has some practical advantages when the experimental hyperbolae are used in transformations. So, b_0 is a better solute characteristic than B , because of the relative compensation of the errors associated with hyperbola parameters B and C in Eq. (18), and the factor f_0 is in fact the relative slope b/b_0 .

The transformation factors and parameter C are “phase constants” for the given conditions of temperature in which hyperbola and the linear sections are defined. They can be calculated at different temperatures from the existent general information on methylene increments of the thermodynamic functions [18,22,23]. Their thermodynamic meaning derives from Table 1 and Eq. (10). For instance, the

transformation factor c defined by Eq. (33) and contained in the expressions of the other factors, Eqs. (34)–(39), has the sense:

$$c = \frac{(\Delta S_{\text{CH}_2}^{\text{S}})_{T_{\text{mean}}}^2}{\left[(\Delta H_{\text{CH}_2}^{\text{S}})_{T_{\text{mean}}} - \bar{T}(\Delta S_{\text{CH}_2}^{\text{S}})_{T_{\text{mean}}} \right]^2} \quad (48)$$

The transformation factor f_0 from Eqs. (20) and (36) is:

$$f_0 = \frac{\left[(\Delta H_{\text{CH}_2}^{\text{S}})_{T_{\text{mean}}} - 273.15(\Delta S_{\text{CH}_2}^{\text{S}})_{T_{\text{mean}}} \right]^2}{\left[(\Delta H_{\text{CH}_2}^{\text{S}})_{T_{\text{mean}}} - \bar{T}(\Delta S_{\text{CH}_2}^{\text{S}})_{T_{\text{mean}}} \right]^2} \quad (49)$$

Expressions of the free energy from the square brackets in Eqs. (48) and (49) were kept in the developed form, to highlight the role of the two kinds of temperature ranges and because the $\Delta H_{\text{CH}_2}^{\text{S}}$ and $\Delta S_{\text{CH}_2}^{\text{S}}$ increments from Ref. [23] were used in the subsequent calculations.

2.3. Standardisation of the slope value, b from Eq. (2), against a reference temperature range

Since parameter b is the one used in correlation with molecular structure, its standardisation against the mean temperature of the range is important when different solutes are compared. Ideally, all measurements must be done using the same temperature range, or ranges centred on the same mean. For various reasons, such as high disparities in solute volatility or use of particular columns, b values can be obtained on different ranges. It is important to investigate the possibility of subsequent normalisation of data to a reference temperature, \bar{t}_{ref} . If experimental hyperbola is previously defined, Eqs. (15) or (20) can be directly used for the calculation of b value at any \bar{t} inside the larger interval or for short-range extrapolation. Otherwise, experimental and theoretical observations on the values and trends of variation of the solute- and phase-dependent factors and involved thermodynamic functions with column temperature are useful.

The relative slope of two straight lines defined in the ranges described by \bar{t} and \bar{t}_{ref} for a solute is:

$$b_{\text{rel}} = b_{\bar{t}}/b_{\bar{t}_{\text{ref}}} \quad (50)$$

Under given conditions b_{rel} can be predicted at

different temperatures and used to calculate $b_{\bar{t}_{\text{ref}}}$ from the experimental $b_{\bar{t}}$.

Theoretically, b_{rel} can be described in different ways, depending on how the straight lines are considered. These ways will be designated approaches 1 and 2. In approach 1, the lines are in the limits of a given hyperbola, as in Fig. 1 and as discussed until now. So, t_{mean} , \bar{t}_{ref} and the thermodynamic functions or parameter C defined at t_{mean} are constant, the only variable being \bar{t} . In approach 2, the lines are self-consistent; each is attached to a virtual hyperbola defined on the same temperature range, so that no distinction exists between \bar{t} and t_{mean} . Only \bar{t}_{ref} ($=t_{\text{mean,ref}}$) and the thermodynamic functions for the line of reference are kept constant, whereas for the current lines, \bar{t} ($=t_{\text{mean}}$) and the corresponding thermodynamic functions varies. The two equivalent notations here for the mean temperature of the range will be used, depending whether the accent is on the quality of line or of hyperbola, respectively. The formal relations concerning Eq. (2) are the same in the two situations.

Definition of b_{rel} for approach 2 and at the same time the general one, is:

$$b_{\text{rel}} = c_{\text{rel}}B_{\text{rel}} \quad (51)$$

or alternatively:

$$b_{\text{rel}} = f_{0,\text{rel}}b_{0,\text{rel}} \quad (52)$$

with

$$f_{0,\text{rel}} = c_{\text{rel}}C_{\text{rel}}^2 \quad (53)$$

All relative quantities are ratios of the value at \bar{t} against the value at \bar{t}_{ref} . The expressions of the relative transformation factors c_{rel} and $f_{0,\text{rel}}$ as a function of C and temperature are included in the third part of Table 1, as Eqs. (46) and (47). In terms of methylene increments, they are of the kind of Eqs. (48) or (49), multiplied by a constant factor (reciprocal of these equations at the reference temperature). However, in prediction of the relative slope in approach 2, the use of Eqs. (52) and (53) has no advantage and complicates the situation, so these will not be discussed in detail. The relative values B_{rel} and $b_{0,\text{rel}}$ are in principle different from unity because of the dependence of the functions $(\Delta H_i^{\text{S}} - \Delta H_z^{\text{S}})$ and $(\Delta S_i^{\text{S}} - \Delta S_z^{\text{S}})$ and of their coefficients from

Eq. (9) on temperature range. In consequence, use of approach 2 implies besides the calculation of transformation factors from methylene increments, a study for each solute. It would be better to avoid this difficulty.

Indeed, in approach 1, which is a particular case of approach 2, the ratios B_{rel} , $b_{0,\text{rel}}$ and C_{rel}^2 , all defined at $T_{\text{mean}} = \text{constant}$, are equal to unity, so that $b_{\text{rel}} = c_{\text{rel}} = f_{0,\text{rel}}$ and can be calculated with Eq. (45) or from methylene increments, as:

$$b_{\text{rel}} = c_{\text{rel}} = f_{0,\text{rel}} = \frac{[(\Delta H_{\text{CH}_2}^S)_{T_{\text{mean}}} - \bar{T}_{\text{ref}}(\Delta S_{\text{CH}_2}^S)_{T_{\text{mean}}}]^2}{[(\Delta H_{\text{CH}_2}^S)_{T_{\text{mean}}} - \bar{T}(\Delta S_{\text{CH}_2}^S)_{T_{\text{mean}}}]^2} \quad (54)$$

3. Experimental

The experimental data were previously reported. An SE-30 glass capillary column 40 m × 0.35 mm with the film thickness d_f of 0.35 μm was used for establishing the linear Eqs. (2) and (3) for 343 perfumery solutes [20] and the hyperbolic Eq. (1) for 82 solutes [18]. Similar work was done on two Carbowax-20M glass capillary columns obtained by barium carbonate procedure, one of 51 m × 0.43 mm, d_f 0.45 μm and another of 46 m × 0.3 mm, d_f 0.08 μm. Sets of linear Eq. (2) for about 230–240 solutes [21] and hyperbolae for about 40 solutes [22] were obtained for each of them. The hyperbolic equations were calculated for selected sets of compounds

where more temperature points were available, using the same experimental data as for linear equations. The $\Delta H_{\text{CH}_2}^S$ and $\Delta S_{\text{CH}_2}^S$ contributions were determined for successive 20–30°C wide temperature ranges, with the same columns and conditions [23]. The B data were calculated with Eq. (9) from the differences of thermodynamic functions ($\Delta H_i^S - \Delta H_z^S$) and ($\Delta S_i^S - \Delta S_z^S$) for some typical solutes on different temperature ranges, taken together with the experimental b_{rel} values from Ref. [29].

4. Results and discussion

In the present paper the attention is focused on the “phase constant” components of the parameters of I vs. t equations, namely C and the transformation factors. The solute-dependent factors are considered in detail in Part III [29] and only illustratively mentioned regarding the relative slope in approach 2.

In Table 2, the essential information on the order of magnitude and extent of systematic modification of hyperbola parameter C [18,22] and of the methylene contributions [23] with t_{mean} is recalled. These values are rather similar for SE-30 and Carbowax-20M 0.45 μm columns. Influence of the Carbowax film thickness is mainly on the $\Delta S_{\text{CH}_2}^S$ increment. The n -alkane pair effect was indirectly considered in the $\Delta H_{\text{CH}_2}^S$ and $\Delta S_{\text{CH}_2}^S$ values. They are the averages of a number of particular pairs, corresponding to the

Table 2

Average values of the hyperbola parameter C found experimentally^a and calculated^{b,c} together with the extent of the systematic variation of the increments $\Delta H_{\text{CH}_2}^S$ and $\Delta S_{\text{CH}_2}^S$ with the mean temperature of the range^{c,d} for SE-30 and Carbowax-20M glass capillary columns

Column	– C (°C)				– $\Delta H_{\text{CH}_2}^S$ (kJ mol ⁻¹)	– $\Delta S_{\text{CH}_2}^S$ (J mol ⁻¹ K ⁻¹)
	Experimental ^a	n	Calculated ^{b,c}	n		
SE-30, d_f 0.35 μm	407 ± 189	82	488 ± 53 (387 to 577) (487 to 539)	70	4.5 to 3.1 3.8 to 3.5	6.8 to 3.6 5.0 to 4.3
Carbowax-20M d_f 0.45 μm	531 ± 234	43	534 ± 31 (490 to 557)	42	3.5 to 3.1	4.6 to 3.7
Carbowax-20M d_f 0.08 μm	463 ± 174	41	532 ± 55 (459 to 572)	45	3.8 to 3.0	5.1 to 3.6

^a Averages of the parameter C from hyperbolic regression of I – t data, for the corresponding number of solutes [18,22].

^b Averages of the indicated number of values calculated with Eq. (10) from $\Delta H_{\text{CH}_2}^S$ and $\Delta S_{\text{CH}_2}^S$ increments for different temperatures t_{mean} and n -alkane pairs [18,22,23]; the extent of variation is given in parentheses.

^c The extent of systematic variation of the individual values in the following t_{mean} intervals: SE-30, in the first row between 90 and 215°C and in the second row, 130 and 190°C; Carbowax-20M d_f 0.45 μm, 130–190°C, and Carbowax-20M d_f 0.08 μm, 130–210°C.

^d Methylene contributions obtained on 20 to 30°C wide ranges, as the arithmetic means of the values for several specific n -alkane pairs [23].

evolution of their volatility with the optimum retention factor. Influences of t_{mean} and homologue pairs on the average experimental parameter C of different solutes are generally overwhelmed by statistical and model errors [18,22]. Consequently, for realising the trends derived from Eqs. (8)–(10) and theory, the C values calculated from methylene increments were used in Eqs. (33)–(47).

4.1. Transformation factors, their dependence on the mean temperature of the range and the standardisation of b

Besides the conversion aspects, the transformation factors concerning Eqs. (2) and (3), defined in terms of C and \bar{t} in Eqs. (33)–(37) or in terms of methylene increments in Eqs. (48), (49), and (54) are important for revealing the extent of the temperature range influence on the parameters. The linear Eq. (2), particularly its parameter $b = dI/dt$ is especially considered. All data used in the following illustrations were calculated with the $\Delta H_{\text{CH}_2}^{\text{S}}$ and $\Delta S_{\text{CH}_2}^{\text{S}}$ values reported in steps of mean temperature of 5°C in Tables 5 and 6 from Ref. [23].

Table 3 contains numerical examples of transformation factors regarding Eq. (2) in approach 1. Different lines are considered, in the limits of an hypothetical hyperbola defined for $t_{\text{mean}} = 140^\circ\text{C}$ on

SE-30, when the calculated parameter C is -496.5°C . This information alone is sufficient for obtaining the factors at different partial mean temperatures, indifferently on the sense of the $I-t$ variation (hyperbola of the kind I or II). The \bar{t} influence is obvious and better seen with the relative slopes, f_0 (against $\bar{t}_{\text{ref}} = 0^\circ\text{C}$) or b_{rel} (against a practical $\bar{t}_{\text{ref}} = 120^\circ\text{C}$). For realizing more directly the effect of \bar{t} on the intercept, the difference $(a - a_0)$ was calculated, using as supplementary information the hyperbola parameter B taken as $-25\,000$ (case I hyperbola) or $25\,000$ (case II hyperbola). This was chosen to correspond with a parameter b of about 0.2 or -0.2 , respectively, to agree with the order of magnitude of the observed maximum negative b value for perfumery solutes on SE-30 [20]. Nevertheless, the retention index usually increases with temperature, so that $-B$ can range between 0 and 250 000. Correspondingly the $(a - a_0)$ values are higher or lower as in Table 3, according to Eq. (21).

In Table 4, similar examples of absolute and relative factors regarding the slope and intercept of Eq. (3) are given, in the frame of the same hyperbola as in Table 3. These factors and parameters are more sensible against the mean temperature of the linear range than in the case of Eq. (2), as follows from Eqs. (28) and (29).

A general picture on the variation of the transformation factors connected with b values with the

Table 3

Examples of transformation factors between Eqs. (1) and (2)^a as a function of the mean temperature of the partial range, in the frame of a case I or II hyperbola defined for $t_{\text{mean}} = 140^\circ\text{C}$ on the SE-30 column^{b,c}: c and f_0 describing the slope, b_{rel} – the relative slope, d and g_0 , describing the intercept, and the difference of intercepts $(a - a_0)$ ^d

\bar{t} (°C)	$c \cdot 10^6$, Eqs. (15), (33)	f_0 , Eqs. (18), (36)	$b_{\text{rel}} = c_{\text{rel}} = f_{0,\text{rel}}$ $\bar{t} = 120^\circ\text{C}$; Eqs. (45), (50), (54)	$d \cdot 10^3$, Eqs. (16), (34)	$g_0 \cdot 10^4$, Eqs. (21), (37)	$\pm(a - a_0)$, Eq. (21)
0	4.0566	1.000	0.58	2.014	0.00	0.0
100	6.3608	1.568	0.90	1.886	1.28	3.2
120	7.0546	1.739	1.00	1.810	2.05	5.1
140	7.8683	1.940	1.12	1.668	3.10	7.8
160	8.8314	2.177	1.25	1.559	4.56	11.4
180	9.9828	2.461	1.42	1.363	6.51	16.3

^a Defined and calculated with the indicated equations.

^b Hyperbola characterised by parameter $C = -496.5^\circ\text{C}$ and by an arbitrary value of the parameter B of $-25\,000$ (case I) or $25\,000$ (case II).

^c The used C value is the mean of the individual values calculated from methylene increments for a range of alkane pairs among 8 and 15 carbon atoms, taken from Table 2, Ref. [18].

^d The negative values of $(a - a_0)$ are for case I, the positive values for the case II hyperbola.

Table 4

Examples of transformation factors between Eqs. (1) and (3)^a as a function of the mean temperature of the partial range, in frame of a case I or II hyperbola as defined in Table 3: p and u regarding the slope, q and v regarding the intercept and the difference of intercepts ($\alpha - \alpha_{273}$)^b

T (K)	p , Eqs. (22), (38)	u , Eqs. (26), (40)	$-q \cdot 10^3$, Eqs. (23), (39)	$-v \cdot 10^3$, Eqs. (27), (41)	$\pm(\alpha - \alpha_{273})$ Eq. (27)
273	0.3027	1.0000	3.122	0.0000	0.0
373	0.8857	2.9262	4.896	1.773	44.3
393	1.0905	3.6025	5.430	2.307	57.7
413	1.3431	4.4382	6.056	2.933	73.3
433	1.6570	5.4742	6.798	3.674	91.9
453	2.0500	6.7730	7.684	4.559	114.0

^a Defined and calculated with the indicated equations and with the C' value given by Eq. (10) as in Table 3.

^b The positive values for case I, the negative values for the case II hyperbola.

mean temperature of the range is shown in Figs. 2–4. The factor c is considered in Fig. 2, in approach 1 on SE-30 with as \bar{t} variable and t_{mean} as parameter and in approach 2 with t_{mean} as variable, on the three used columns. Fig. 3 contains a similar picture for the factor f_0 in the two approaches on SE-30.

In Fig. 4 the evolution of c_{rel} in approaches 1 and 2 on the columns SE-30 with $\bar{t}_{\text{ref}} = 130^\circ\text{C}$ and medium film Carbowax-20M with $\bar{t}_{\text{ref}} = 150^\circ\text{C}$ is shown. The chosen temperatures of reference are convenient for most of the studied perfumery solutes [20]. The revealed tendencies are useful in connection with slope standardisation.

In approach 1, the dependence of the factors c , f_0

and $c_{\text{rel}} = f_{0,\text{rel}} = b_{\text{rel}}$ on \bar{t} is a truly square polynomial, as results from Eqs. (33), (36), (45) and (48), (49), (54). For each factor there is a family of curves (noted as 1 in Figs. 2–4), corresponding to different hyperbolae characterised by the inscribed t_{mean} values. The numerical example from Table 3 was for one of them. These curves arise from the systematic variation of C values or methylene increments with t_{mean} . The mutual distance between the individual curves, affected in some measure by the experimental errors, is greater for t_{mean} between 90 and 120°C and after 200°C and smaller between 120 and 200°C . The reason is the non-linear third- or fourth-polynomial decrease of the absolute values of $\Delta H_{\text{CH}_2}^S$ and

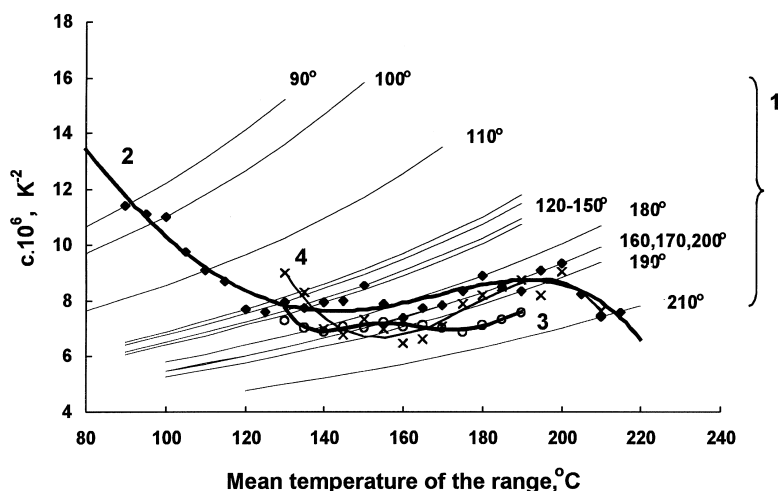


Fig. 2. The transformation factor c from Eqs. (15), (33), (48) against the mean temperature of the partial or whole range, in approach 1 on SE-30 and approach 2 on the three used columns. 1=The approach 1 curves c vs. \bar{t} , with t_{mean} as parameter ($^\circ\text{C}$) on the SE-30 column; 2–4=the approach 2 curves (c) _{t_{mean}} vs. t_{mean} for the columns: 2=SE-30 (\blacklozenge), 3=Carbowax-20M d_f 0.45 μm (\circ) and 4=Carbowax-20M d_f 0.08 μm (\times).

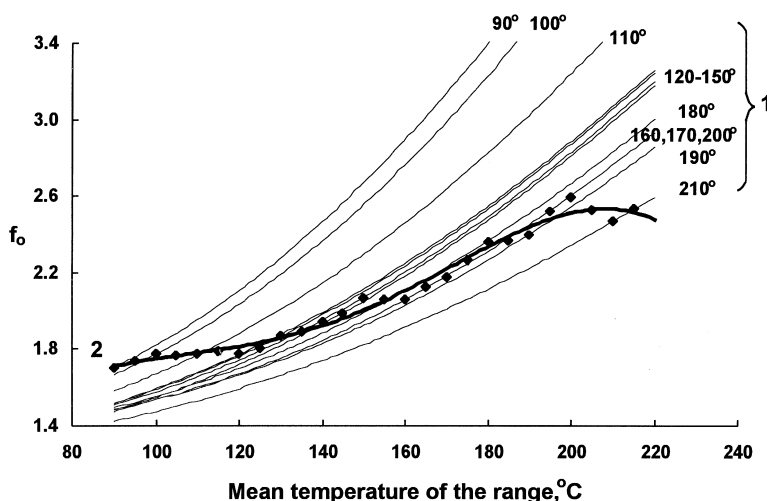


Fig. 3. The transformation factor f_0 from Eqs. (20) and (36) as a function of the mean temperature of the partial or whole range on the SE-30 column. 1=The approach 1 curves f_0 vs. \bar{t} , with t_{mean} ($^{\circ}\text{C}$) as parameter; 2=the approach 2 curve $(f_0)_{\bar{t}_{\text{mean}}}$ vs. t_{mean} .

$\Delta S_{\text{CH}_2}^{\text{S}}$ with this variable, influenced by the involved n -alkane pairs and their heat capacities [23]. Some inversion of the curves order in the t_{mean} range of 160 to 200 $^{\circ}\text{C}$ is due to the same causes.

The standardisation at \bar{t}_{ref} with approach 1 is simple if the appropriate C value is used for each solute, namely at a mean temperature of the range near that of the processed b data, and if very large extrapolation of the hyperbola is avoided. As seen in Fig. 4, the curves $c_{\text{rel}} = f_{0,\text{rel}} = b_{\text{rel}}$ are almost superimposed in the t_{mean} interval of 120 to 170 $^{\circ}\text{C}$ on SE-30 and 125 to 190 $^{\circ}\text{C}$ on Carbowax d_f 0.45 μm columns, so that the situation is very favourable.

Approach 2 is more laborious, but it must be mentioned to have a general view on the subject and to avoid subsequent confusions. From the equivalent in this case designation of mean temperature of the range as \bar{t} or t_{mean} , here is convenient t_{mean} for an easier connection with the above discussion of approach 1 curves. Dependence of c and c_{rel} on t_{mean} (curves 2–4 in Fig. 2 and curve 2 in Fig. 4) has a fourth-polynomial decreasing form ($r=0.92$ – 0.93). Its origin is revealed by Eq. (48), where the mentioned polynomial dependence of $\Delta S_{\text{CH}_2}^{\text{S}}$ and $\Delta H_{\text{CH}_2}^{\text{S}}$, their compensation effect and the linear decrease of $\Delta G_{\text{CH}_2}^{\text{S}}$ absolute value vs. t_{mean} , lead to this pattern. It is characterised by an almost constant section in the middle part of the curve for the 120–200 $^{\circ}\text{C}$

range, corresponding to the close or superposed approach 1 curves. The behaviour of the factor f_0 in approach 2 (curve 2, Fig. 3) is the result of the compensatory variation of the factors in Eqs. (36) and (49). A quasi-linear increase with t_{mean} in the most part of the graphic, yet fitted as fourth-polynomial on a wide range ($r=0.98$ – 0.99) is observed. As shown in Figs. 2 and 3, the approach 2 curves of c and f_0 join the particular points $t = t_{\text{mean}}$ lying on the approach 1 curves, following Eqs. (48) or (49). On the contrary, the corresponding curves of the c_{rel} values from Fig. 4 have any connection, except the formal reference point. In this case the thermodynamic definitions, Eq. (54) in approach 1 and Eq. (48) multiplied with a constant in approach 2, are different. Moreover, each of the approach 1 curves has its own line of reference and only one of them (with $\bar{t} = \bar{t}_{\text{ref}}$ on the curve $t_{\text{mean ref}}$) is common with approach 2.

Unlike approach 1 where $b_{\text{rel}} = c_{\text{rel}}$, the graphic of the relative slope in approach 2 is according to Eq. (51), the resultant of the temperature variation of c_{rel} and solute dependent factor B_{rel} . This situation is illustrated for several solutes on SE-30 in Fig. 5. The temperature trend of B_{rel} was obtained using the $(\Delta H_i^{\text{S}} - \Delta H_z^{\text{S}})$ and $(\Delta S_i^{\text{S}} - \Delta S_z^{\text{S}})$ data on different temperature ranges and Eq. (9). Table 5 contains examples of experimental and predicted b_{rel} values

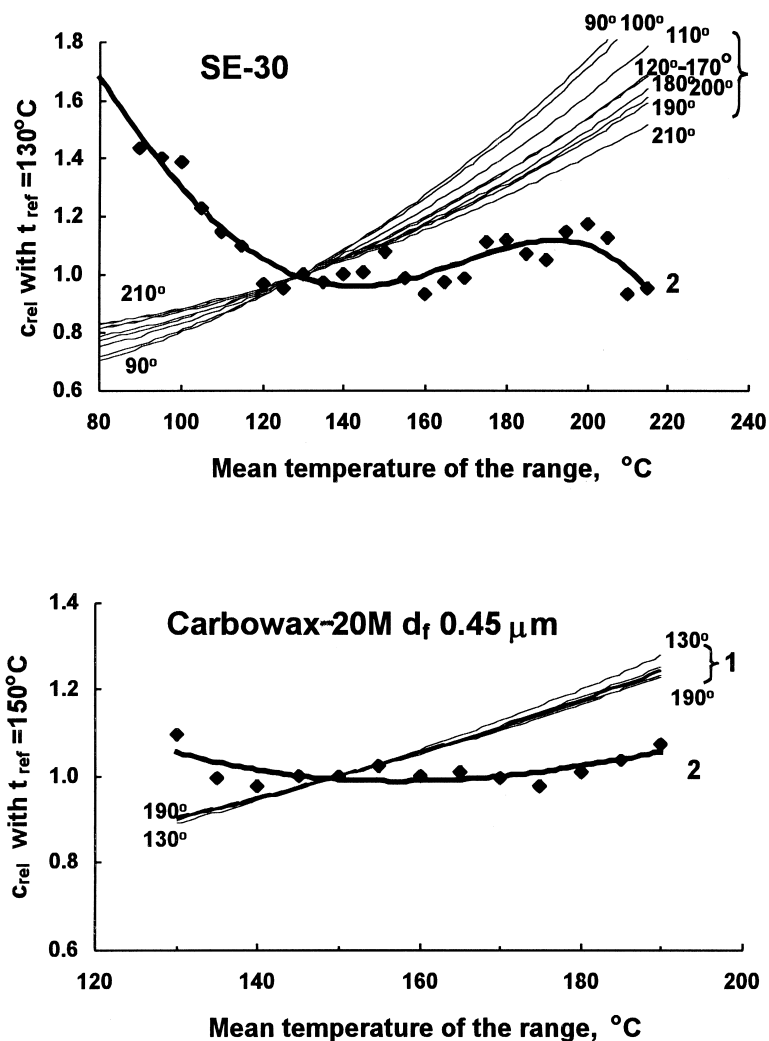


Fig. 4. The relative value c_{rel} as a function of the mean temperature of the partial or whole range for SE-30 and Carbowax-20M d_f 0.45 μm columns. The mean temperature of reference is 130°C for SE-30 and 150°C for Carbowax-20M; 1 = the approach 1 curves $c_{rel} = f_{0,rel} = b_{rel}$ vs. \bar{t} , with t_{mean} (°C) as parameter; 2 = the approach 2 curve c_{rel} vs. t_{mean} .

using the two approaches. Approach 1 was applied in two variants, with parameter C from the experimental hyperbola or calculated with the methylene increments defined for a suitable temperature range (usually where the parameter b_i to be standardised was measured). The first variant is equivalent in practice with the direct use of Eq. (15), because the experimental hyperbola is known. The agreement is good, except *trans*-2-hexenyl acetate on SE-30 in approach 2, due to the higher errors in the implied thermodynamic functions at low temperatures. More

details about the origin of these data will be given in Part III [29].

4.2. Conversion and statistical correlation between series of parameters

Inter-conversion of Eqs. (1)–(4) parameters can be useful occasionally for compilation and data smoothing in the preferred manner. An example of transformation of Eq. (3) to Eq. (2) is given in Table 6.

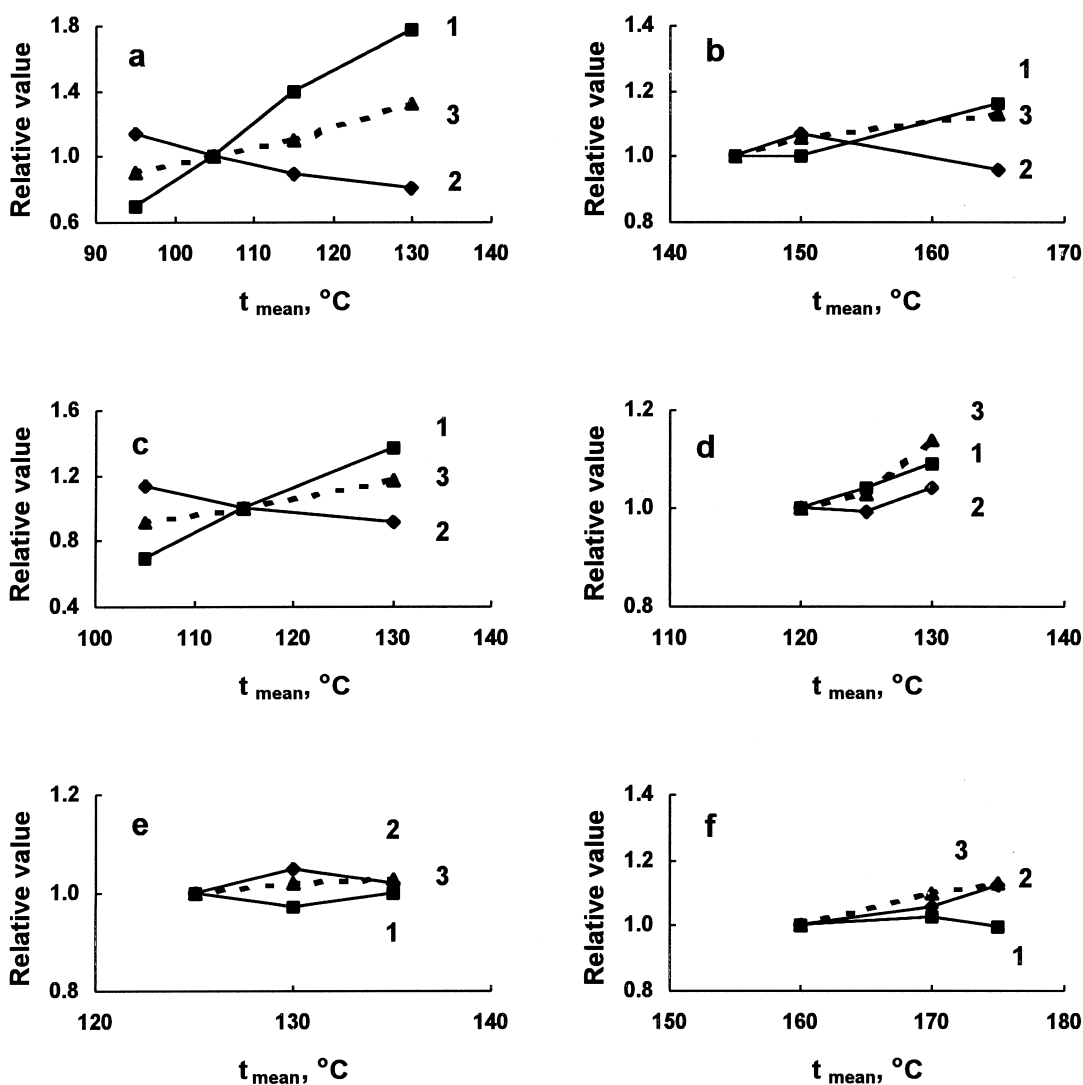


Fig. 5. The trends of evolution of the relative slope b_{rel} and of its components c_{rel} and B_{rel} in approach 2, with the mean temperature of the range. 1 = B_{rel} (■); 2 = c_{rel} (◆); 3 = b_{rel} (▲, interrupted curve); (a) *trans*-2-hexenyl acetate, (b) benzyl acetate, (c) β -phenylethanol, (d) α -terpineol, (e) camphor, (f) α -cedrene epoxide.

Statistical correlation for groups of solutes between series of regression parameters obtained with the same experimental data and temperature range, directly or converted with the established relations from those of another equation, cross-validates the results and confirm the theory. So is the comparison of parameter b obtained with Eq. (2) and calculated with Eq. (15) from hyperbola parameters. For the Carbowax-20M d_f 0.45 μ m column with data from Refs. [21,22], the correlation is:

$$b = 0.9909 \left[-\frac{B}{(\bar{t} + C)^2} \right] + 0.022; \quad (55)$$

$$r = 0.9978, n = 43$$

Similar examples for the other columns are given in Refs. [20,22]. The very important influence of the mean temperature of the range is highlighted by the drop of the correlation coefficient to 0.7–0.8 if a direct connection of b with $b_0 = -B/C^2$ is tried.

Table 5

The agreement between the experimental and predicted b_{rel} values on different temperature ranges^a for several solutes on SE-30 and Carbowax-20M $d_f = 0.45 \mu\text{m}$ columns

Solute	\bar{t} or t_{mean} ^b (°C)	b_{rel} exp.	b_{rel} predicted		
			Approach 1 ^c	Approach 1 ^d	Approach 2 ^e
SE-30					
α -Terpineol	120	1.00	1.00	1.00	1.00
	125*	1.03	1.06	1.03	1.03
	130	1.14	1.13	1.06	1.13
<i>trans</i> -2-Hexenyl acetate	95	0.91	0.91	0.95	0.80
	105	1.00	1.00	1.00	1.00
	115*	1.12	1.11	1.06	1.22
	130	1.32	1.30	1.16	1.44
Benzyl acetate	145	1.00	1.00	1.00	1.00
	150*	1.06	1.03	1.03	1.07
	165	1.13	1.15	1.13	1.12
α -Cedrene epoxide	160	1.00	1.00	1.00	1.00
	170*	1.10	1.08	1.06	1.09
	175	1.13	1.12	1.09	1.12
Carbowax-20M $d_f = 0.45 \mu\text{m}$					
Geranial	145	1.00	1.00	1.00	1.00
	150*	1.09	1.07	1.03	1.09
	155	1.11	1.14	1.05	1.14
Geranyl acetate	135	1.00	1.00	1.00	1.00
	140*	1.05	1.03	1.03	1.01
	150	1.10	1.10	1.08	1.12
β -Phenylethanol	165	1.00	1.00	1.00	1.00
	175*	0.99	1.05	1.05	1.00
	185	1.06	1.10	1.11	1.06
α -Cedrene epoxide	150	1.00	1.00	1.00	1.00
	155*	1.01	1.05	1.03	1.02
	160	1.06	1.11	1.06	1.15

^a b_{rel} defined by Eq. (50), with the reference line characterised by \bar{t}_{ref} chosen inside the general investigated temperature range; the experimental and predicted values obtained with data from Refs. [19,23].

^b Mean temperature of the general (t_{mean} , marked with an *,) or partial (\bar{t}) temperature range.

^c Calculated as $b_{\text{rel}} = c_{\text{rel}}$ with Eq. (45), using the experimental value of the parameter C for the hyperbola defined on the general range.

^d Obtained with Eq. (54) or using in Eq. (45) the C value calculated from methylene increments with Eq. (10) for the general range.

^e Obtained according to Eq. (51) with the c_{rel} and B_{rel} data at each $\bar{t} = t_{\text{mean}}$; c_{rel} data were calculated with Eq. (46) using the C values from the methylene increments and B data were calculated with Eq. (9) using the enthalpy and entropy differences solute–alkane from Ref. [29] and the methylene increments.

The experimental correlation of the two series of parameters β , obtained by the fitting of data with Eq. (3) and according to Eq. (28) as products $b\bar{T}^2$ for the perfumery solutes on SE-30 [18] is:

$$\beta = -0.99844b\bar{T}^2 + 371.85; \quad r = 0.98186, \\ n = 343 \quad (56)$$

The correlation is not perfect, primarily because of

the quantitative differences between the higher terms neglected in Eqs. (11) and (12).

When the information about the mean temperature of the ranges is unavailable, a direct experimental relationship between b and β might be used for the transformation of literature data.

The plot of b vs. β for the 343 perfumery solutes on the SE-30 column from Ref. [20] is scattered and with a curvature, because of the different tempera-

Table 6

Example of application of the Eqs. (28) and (29) in the calculation of the parameters a , b of Eq. (2) from the parameters α , β of Eq. (3), for a selection of compounds on the glass capillary column SE-30

Solute	\bar{t} (°C)	α	β	b			a		
				Calculated	Experimental	e^a	Calculated	Experimental	e^a
Benzaldehyde	120	1081.9	-53 353	0.345	0.347	-0.002	904.8	904.1	0.7
Camphor	130	1411.9	-108 665	0.668	0.671	-0.003	1055.3	1054.8	0.5
Benzyl acetate	150	1280.7	-57 506	0.321	0.326	-0.005	1096.5	1095.6	0.9
Methyl salicylate	150	1406.0	-90 865	0.507	0.517	-0.010	1115.0	1113.1	1.9

^a e is the absolute error.

ture ranges required by the solute volatility. So, the observed pattern is square polynomial, but the linear fitting is rather good. For instance, the following relationships have enough generality to be used as calibration curves in approximate conversion of the data for other solutes and similar dimethylsilicone capillary columns:

$$b = 0.012 - 5.9925 \cdot 10^{-6} \beta + 5.87795 \cdot 10^{-12} \beta^2;$$

$$r = 0.9872, s = 0.047 \quad (58)$$

$$b = -4.8509 \cdot 10^{-6} \beta + 0.0411;$$

$$r = 0.9819, s = 0.055 \quad (58)$$

In Table 7, the relationship between the linear and square polynomial Eqs. (2) and (4) is verified,

together with a precision comparison also including Eq. (1). The experimental and calculated square polynomial parameters are compatible, but not identical, an expected behaviour because of the general sensibility of their numerical values to slightest influences. Most probably such transformation will be not used in practice, but it is an opportunity to remind the total difference between the parameters of linear regression and the first two parameters of Eq. (4).

5. Conclusions

A general theoretical treatment illustrated with experimental data was presented for the relation between different equations used for the temperature

Table 7

Examples of experimental (e) and calculated (c) parameters of the square polynomial Eq. (4)^a, and a comparison of precision^b between the square polynomial, hyperbolic and linear fitting of the $I-t$ data on the SE-30 column

Solute	n	Range (°C)	Eq. (4)					Eq. (1)		Eq. (2)		
			γ_0	γ_1	γ_2	r^2	s	s	a	b	s	
<i>trans</i> -2-Hexenyl acetate	7	80–150	e	997.0	0.0283	-0.00084	0.998	0.2	0.3	1007.6	-0.164	0.5
			c	994.8	0.0581	-0.00097						
3,5,5-Trimethylhexyl acetate	5	120–180	e	1163.3	-0.1493	0.00112	0.989	0.7	0.7	1139.0	0.185	0.7
			c	1163.3	-0.1396	0.00108						
α -Terpineol	4	110–140	e	1172.9	-0.2765	0.00275	0.994	0.7	0.8	1130.3	0.411	0.7
			c	1165.7	-0.1545	0.00226						
β -Phenylethanol	6	80–150	e	1067.9	0.0606	0.00117	0.993	1.1	1.0	1053.4	0.328	1.1
			c	1079.0	-0.1163	0.00193						

^a Calculated with Eqs. (30)–(32) using Eqs. (42)–(44), the experimental parameters of Eq. (2) and the C values obtained with methylene increments for the corresponding mean temperature of the range.

^b s is the standard deviation against the regression curve calculated with $(n-p)$ degrees of freedom, where n is the number of points and p is the number of parameters.

dependence of the retention index. The transformation factors calculable from the $\Delta H_{\text{CH}_2}^{\text{S}}$ and $\Delta S_{\text{CH}_2}^{\text{S}}$ increments and temperature are useful in data conversion and standardisation. The important effect of the mean temperature of the used range was highlighted. The present paper continues in Part II with the physico-chemical meaning of the parameters and in Part III with aspects concerning the solute-dependent factors.

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