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Temperature dependence of the retention index for perfumery compounds on a SE-30 glass capillary column

II. The hyperbolic equation

Ecaterina Tudor*, Dorel Moldovan¹

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

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Abstract

The Antoine-type hyperbolic equation of the retention index temperature dependence was reported for 82 perfumery solutes on a SE-30 capillary column. The precision was compared with that of the linear equation. The thermodynamic significance of the parameters was reconsidered and discussed. The methylene increments of the thermodynamic functions of solution were used for the prediction of the vertical asymptote position on the temperature axis at about 400–500°C, in agreement with the experimental data. Therefore, only two particular cases of this type of hyperbola should exist in a pure gas–liquid partition process. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

This work is the second part of our paper [1], where the linear equations for the temperature dependence of the retention index were reported for over 300 perfumery solutes on a SE-30 glass capillary column.

A non-linear fitting procedure can also be applied for the solutes with more than three temperature points, for the calculation of the hyperbola deduced by Takács et al. [2] from the basic retention relationships:

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

where I is the Kováts retention index, t or T is the column temperature, °C or K, $C = C' + 273.15$.

Besides the precision aspects, this may present interest for some general observations. In spite of the opinion that Eq. (1) is the general and theoretically sound one [3–6], there are very few papers containing data on larger groups of solutes. They concern, for instance, about 30 hydrocarbons and volatile solutes on Squalane [7], 147 hydrocarbons on OV-101 [8], 34 halocarbons on OV-1 and SP-1000 [9], 97 halocarbons on 5% hexafluoropropyl epoxide coated on graphitised carbon black [10] and the ten McReynolds probes on PS-255 and OV-105 [11]. Hyperbolic equations for several solutes exist also in the papers of the Takács group and in reviews

*Corresponding author.

¹Department of Physics, West Virginia University, P.O. Box 6315, Morgantown, WV 26506, USA.

[2,4,6,12]. Data and $I-t$ curves for six aroma solutes on fused-silica HP-5 capillary columns with different film thickness were reported in [13].

The reason why the hyperbolic equation was not studied in depth, seems to be the good linearity of the retention index–column temperature curve in most practical situations [1–10], sometimes even on temperature intervals as large as 100 or 120° [14–16]. Of the two equations of linear temperature dependence with t or $1/T$ as variable, the first one is generally preferred [1,3–6]:

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

It is stated that the non-linearity of the $I-t$ curve on large temperature ranges is manifest rather on polar than on non-polar columns [2–6]. Actually, a variety of situations is possible, as in the case of hydroxylic solutes on HP-5 [13]: the curve is linear for *trans*-pineol and *cis*-verbenol, hyperbolic for geraniol and with a minimum for citronellol, thymol and carvacrol. The need for more experimental and general information regarding the temperature dependence of the retention index is obvious.

Eq. (1) can be used in a formula proposed by Erdey et al. [12] for the pre-calculation of the programmed retention index, which has been evaluated comparatively with other procedures [11,16,17].

2. Theory

In literature, there is no systematic discussion of the hyperbolic processing of retention index–temperature data, based on the physico-chemical significance of the parameters of Eq. (1). The relationships given without any commentary by Takács and co-workers [7,18] are the following, obviously incomplete:

$$A = c_1 + 100z \quad (3)$$

$$B = c_2\Delta H_i - \Delta H_{z+1} + c_3\Delta H_z - \Delta H_{z+1} + c_4\Delta H_z - \Delta H_i \quad (4a)$$

or

$$B = c_2(\Delta H_i - \Delta H_{z+1}) + c_3(\Delta H_z - \Delta H_i) + c_4(\Delta H_{z+1} - \Delta H_z) \quad (4b)$$

$$C' = \frac{\Delta H_z - \Delta H_{z+1}}{c_5} \quad (5)$$

where c_1-c_5 are constants, ΔH is the differential molar heat of evaporation from solution. The subscripts i , z , $z+1$ designate the solute and the reference n -alkanes with z and $z+1$ carbon atoms, from the definition of the Kováts retention index [2–6]. The variants (a) and (b) of Eqs. (4a) and (4b) are shown, respectively, in the papers [7] and [18]. Eqs. (3)–(5) imply a simplified expression of the linear relation $\ln V_g$ on $1/T$ in terms of the thermodynamic functions of the gas–liquid partition [2]. Namely, the entropic term is included in a non-definite constant [19]. Indeed, usually the temperature dependence of the specific retention volume is expressed as:

$$\ln V_g = P\frac{1}{T} + Q \quad (6)$$

P , Q are constants with the signification [20–22]:

$$P = -\frac{\Delta H^S}{R} \quad (7)$$

$$Q = \ln \frac{273R}{M_s} + \frac{\Delta S^S}{R} \quad (8)$$

where R is the universal gas constant, M_s is the molecular mass of the stationary phase.

ΔH^S , ΔS^S are the standard molar enthalpy and entropy of solution for the transfer of a mole of solute, from the ideal gas where its partial pressure is 1 atm, in the stationary phase, where its molar fraction is $x=1$. The molecular interactions and environment are, nevertheless, as in the infinitely diluted solution. If other concentration units are used, a transformation term [22] can be added in Eq. (8). This is reduced, as the other constants in Eqs. (7) and (8), in the differences and in the ratio involved in the retention index definition:

$$I = 100z + 100\frac{\ln V_{g,i} - \ln V_{g,z}}{\ln V_{g,z+1} - \ln V_{g,z}} \quad (9)$$

The same reason permits utilisation of Eq. (6) instead of the temperature dependence of the net retention volume [23] employed by Takács et al. [2]. The main relationships in their work are as follow-

ing. Eq. (9) can be modified to that of a hyperbola with equal axes:

$$I = \frac{\alpha T + \beta}{\alpha_{\text{CH}_2} T + \beta_{\text{CH}_2}} \quad (10)$$

where

$$\alpha_{\text{CH}_2} = Q_{z+1} - Q_z \quad (11)$$

$$\beta_{\text{CH}_2} = P_{z+1} - P_z \quad (12)$$

$$\alpha = 100[(Q_i - Q_z) + z\alpha_{\text{CH}_2}] \quad (13)$$

$$\beta = 100[(P_i - P_z) + z\beta_{\text{CH}_2}] \quad (14)$$

and the subscript CH₂ is for the methylene group.

Eq. (10) was rearranged to the more convenient hyperbolic Eq. (1), the two series of parameters being correlated by:

$$A = \frac{\alpha}{\alpha_{\text{CH}_2}} \quad (15)$$

$$B = \frac{\alpha_{\text{CH}_2} \beta - \beta_{\text{CH}_2} \alpha}{\alpha_{\text{CH}_2}^2} \quad (16)$$

$$C' = \frac{\beta_{\text{CH}_2}}{\alpha_{\text{CH}_2}} \quad (17)$$

Using Eqs. (7) and (8) and (11)–(14) in Eqs. (15)–(17), the thermodynamic meaning of the parameters results as:

$$A = \frac{100}{\Delta S_{\text{CH}_2}^S} (\Delta S_i^S - \Delta S_z^S) + 100z \quad (18)$$

$$B = 100 \frac{\Delta H_{\text{CH}_2}^S}{(\Delta S_{\text{CH}_2}^S)^2} (\Delta S_i^S - \Delta S_z^S) - \frac{100}{\Delta S_{\text{CH}_2}^S} (\Delta H_i^S - \Delta H_z^S) \quad (19)$$

$$C' = \frac{\Delta H_{\text{CH}_2}^S}{\Delta S_{\text{CH}_2}^S} \quad C = 273.15 - \frac{\Delta H_{\text{CH}_2}^S}{\Delta S_{\text{CH}_2}^S} \quad (20)$$

The new Eqs. (18)–(20) compared with Eqs. (3)–(5), show a similarity for *A* and *C'*, except that *A*, and not only *B*, is in fact dependent on the solute and

n-alkane nature; however, *B* in Eqs. (4a) or (4b) seems meaningless.

The validity of Eqs. (18)–(20) and of the entire approach, depends on the basic assumptions in Eqs. (6)–(8): a pure gas–liquid partition process and the constancy of the functions ΔH^S , ΔS^S , on the employed temperature range. The existence of mixed distribution processes having a different sensitivity against temperature, can eventually modify the hyperbolic curve [13]. On the other hand, on large temperature ranges where the hyperbola must actually be defined, the $\ln V_g$ vs. $1/T$ relationship becomes non-linear, due to a slight but distinct temperature dependence of ΔH^S and ΔS^S . Besides the Antoine-type hyperbolic relationship used in [24], this may be expressed for example [25], with the equation:

$$\ln V_g = Q' + P' \frac{1}{T} + S' \left(\frac{1}{T} \right)^2 \quad (21)$$

or [26], with the equation:

$$\ln V_g = Q'' + P'' \frac{1}{T} + S'' \ln T \quad (22)$$

where Q' , P' , S' , Q'' , P'' , S'' are constant coefficients. Some of them include ΔC_p^S , the solution standard molar heat capacity at constant pressure. Another approach is the measurement of ΔH^S , ΔS^S defined for narrow different temperature ranges, and consideration of their variation [27]. This effect is in a great measure reduced in Eqs. (18)–(20), by the ΔH – ΔS compensation [28] and by the differences between the thermodynamic functions of the solute and the reference *n*-alkane. These differences can be considered constant for reasonably wide ranges centred on the same mean. More details and references on these aspects are given in [29]. However, the practical consequence is a certain dependence of the hyperbola parameters on the used temperature interval, if this is shifted against the fixed mean.

3. Experimental and calculation method

The experimental procedure was reported in Part I [1]. The retention indices were measured on a SE-30 glass capillary column with a film thickness of 0.35 μm . The calculation of the parameters of Eq. (1) was done with a personal computer program of iterative

non-linear fitting. This was based on the general features shown in [7] and on a minimisation algorithm Nelder–Mead type simplex, applied for n experimental points (I_j, t_j) to the function:

$$F_{ABC} = \sum_{j=1}^n \left(I_j - A - \frac{B}{t_j + C} \right)^2 \quad (23)$$

The start set A_o, B_o, C_o , is delivered by the solution of a system of three equations written for three experimental (I, t) points [2,7]:

$$C_o = \frac{(t_2 - t_1)(I_3 t_3 - I_1 t_1) + (t_3 - t_1)(I_1 t_1 - I_2 t_2)}{(t_3 - t_1)(I_2 - I_1) - (t_2 - t_1)(I_3 - I_1)} \quad (24)$$

$$A_o = \frac{I_3 t_3 - I_1 t_1 + C_o(I_3 - I_1)}{t_3 - t_1} \quad (25)$$

$$B_o = I_3 t_3 + I_3 C_o - A_o(t_3 + C_o) \quad (26)$$

The program stipulates five combinations of three points, to be used at choice for a trial and error approach, until a plausible regression curve with the smallest standard deviation is obtained. As the hyperbola has three parameters, the standard deviation was calculated with $(n-3)$ degrees of freedom:

$$\sigma = \sqrt{\frac{\sum_{j=1}^n (I_j - \hat{I}_j)^2}{n-3}} \quad (27)$$

unlike the $(n-2)$ degrees of freedom for Eq. (2) [1,30]. The correlation coefficient was obtained by linear regression between the experimental retention indices I_j and the calculated ones, \hat{I}_j .

4. Results and discussion

The parameters, temperature ranges, statistical evaluation and the particular case of the hyperbolic curves for 82 perfumery solutes, are reported in Table 1, together with the raw formula as a primary structural information. The standard deviation and the correlation coefficient of the linear Eq. (2), taken from [1], are included for comparison.

Before the discussion of results, an examination of

Eq. (1) and of the theoretical Eqs. (18)–(20) will help establish some guidelines. The equilateral hyperbola described by Eq. (1) has mutual perpendicular asymptotes, parallel with the co-ordinate axes. The vertical asymptote crosses the temperature axis at $-C$ °C, and the horizontal asymptote crosses the retention index axis at the value A . The parameter B is correlated with the sign and curvature of the $I-t$ curve. The derivative of Eq. (1) in a point laying in the middle of a linear section described by Eq. (2), is:

$$\frac{dI}{dt} = -\frac{B}{(\bar{t} + C)^2} = b_{\bar{t}} \quad (28)$$

The subscript of the b value indicates its dependence on the mean temperature of the considered linear range.

Considering the physico-chemical significance of the parameters, it can be seen that A and B depend on differences during the solution process between the solute and the reference n -alkane with z carbon atoms. The parameter C is a constant for the given stationary phase and temperature range, because it contains only the methylene increments of the thermodynamic functions.

Independent measurements of the methylene increments on the present SE-30 column, for different temperatures and homologue pairs [29], permitted calculation of the C values given in the Table 2. $\Delta H_{\text{CH}_2}^S$ and $\Delta S_{\text{CH}_2}^S$ are both negative because of the heat evolved at the dispersion interaction, and of the loss of freedom, respectively, during the transfer from gas into stationary phase. In consequence, the parameter C' must be always negative for the pure gas–liquid partition, at least in the usual organic stationary phases. The parameter C is also negative and shows some variation with the column temperature. The n -alkane pair seems to have a reduced influence on C , covered by the experimental errors. The arithmetic mean for the 70 values in Table 2 is $C = -(488 \pm 53)^\circ\text{C}$. A similar approach for Carbowax-20M [31] gave a value of C of about -530°C . For other usual liquid phases, the same order of magnitude is expected, considering the comparable intensity of the dispersion interaction. The jump in retention due to the vertical asymptote would be, therefore, in the right part of the $I-t$ graph

Table 1

The hyperbola parameters A , B , C , a comparison of the correlation coefficients and standard deviations for the hyperbolic (R , σ) and linear (r , s) fitting^a, the raw formulae and the hyperbola cases I or II^b for perfumery solutes on the SE-30 glass capillary column

No.	Solute	Formula	I t (°C)	Range (°C)	n	A	$-B$	$-C$	R^2	σ	r^2	s	*
100°													
1	<i>trans</i> -2-Hexenal	C ₆ H ₁₀ O	830.6	90–150	4	741.4	53 649.1	699.0	0.994	0.6	0.989	0.6	I
2	<i>n</i> -Hexanol	C ₆ H ₁₄ O	848.2	80–150	6	888.2	-7678.0	289.7	0.984	1.1	0.967	1.4	II
3	Isoamyl acetate	C ₇ H ₁₄ O ₂	857.8	80–150	4	864.4	-506.2	176.0	1.000	0.3	0.969	1.5	II
4	Benzaldehyde	C ₇ H ₆ O	939.3	90–150	5	808.7	54 877.7	522.3	0.998	0.6	0.992	0.8	I
5	Camphene	C ₁₀ H ₁₆	957.1	70–140	5	729.9	110 736.2	587.4	0.991	1.8	0.990	1.5	I
6	<i>cis</i> -3-Hexenyl acetate	C ₈ H ₁₄ O ₂	976.4	90–160	4	869.8	60 728.8	666.8	0.991	1.2	0.991	0.8	I
7	2-Octanol	C ₈ H ₁₈ O	976.7	100–130	4	852.2	47 995.2	485.8	0.992	0.7	0.993	0.5	I
8	<i>trans</i> -2-Hexenyl acetate	C ₈ H ₁₄ O ₂	991.4	80–150	7	1020.5	-6112.4	310.3	0.998	0.3	0.985	0.5	II
9	Hexyl acetate	C ₈ H ₁₆ O ₂	993.1	80–150	5	1053.8	-43 620.1	816.7	0.989	0.3	0.994	0.2	I
10	2-Carene	C ₁₀ H ₁₆	1001.6	70–150	5	896.9	34 514.5	429.8	0.999	0.5	0.996	0.6	I
11	Benzyl alcohol	C ₇ H ₈ O	1006.8	100–150	5	989.9	1839.8	208.8	0.994	0.7	0.969	1.3	I
12	1,8-Cineole	C ₁₀ H ₁₈ O	1025.5	110–150	4	827.5	97 889.8	594.4	0.997	1.0	0.997	0.6	I
13	Limonene	C ₁₀ H ₁₆	1027.1	90–150	6	928.2	35 507.0	458.5	0.998	0.5	0.995	0.5	I
14	Diethylmalonate	C ₇ H ₁₂ O ₄	1033.3	80–150	4	1078.3	-10 573.5	334.8	0.998	0.4	0.991	0.8	II
15	<i>n</i> -Amyl isobutyrate	C ₉ H ₁₈ O ₂	1038.1	80–140	4	1045.1	-1040.8	250.1	0.999	0.1	0.986	0.2	II
120°													
16	Tetrahydromyrcenol	C ₁₀ H ₂₂ O	1088.6	90–150	4	1074.9	1585.9	235.8	0.960	1.2	0.932	1.1	I
17	Tetrahydroinalool	C ₁₀ H ₂₂ O	1088.9	90–150	4	1017.9	35 306.9	617.5	0.990	0.6	0.993	0.4	I
18	1-Octene-3-yl-acetate	C ₁₀ H ₁₈ O ₂	1089.5	90–120	4	1167.5	-32 741.6	539.1	0.995	0.3	0.995	0.2	II
19	β -Phenylethyl alcohol	C ₈ H ₁₀ O	1092.0	80–150	6	1005.9	21 924.5	374.8	0.993	1.0	0.989	1.1	I
20	Benzyl acetate	C ₉ H ₁₀ O ₂	1135.1	120–180	5	1047.6	28 552.7	446.3	0.991	1.0	0.987	1.0	I
21	Camphor	C ₁₀ H ₁₆ O	1135.1	110–150	5	875.6	105 763.2	527.5	0.998	0.6	0.998	0.6	I
22	<i>p</i> -Cresyl acetate	C ₉ H ₁₀ O ₂	1142.4	120–170	4	1115.8	2676.5	220.5	0.995	1.3	0.946	3.2	I
23	Neomenthol	C ₁₀ H ₂₀ O	1152.8	110–150	5	1070.5	14 590.6	297.2	0.983	1.6	0.978	1.4	I
24	3,5,5-Trimethyl hexyl acetate	C ₁₁ H ₂₂ O ₂	1161.7	120–180	5	1140.8	3535.5	290.2	0.990	0.6	0.982	0.7	I
25	Terpinene-4-ol	C ₁₀ H ₁₈ O	1169.6	110–150	4	1141.6	2434.9	207.1	0.998	0.6	0.984	1.3	I
26	Methyl salicylate	C ₈ H ₈ O ₃	1176.5	120–180	4	1116.1	10 564.6	295.0	1.000	0.5	0.980	2.2	I
27	α -Terpineol	C ₁₀ H ₁₈ O	1179.3	110–150	4	1112.7	11 538.9	293.2	0.993	0.8	0.990	0.7	I
28	Myrtenal	C ₁₀ H ₁₄ O	1181.3	110–150	5	1074.2	23 798.2	342.3	0.984	1.5	0.981	1.4	I
29	γ -Terpineol	C ₁₀ H ₁₈ O	1185.4	110–150	4	1065.1	43 973.5	485.4	0.995	0.5	0.994	0.5	I
30	Myrtenol	C ₁₀ H ₁₆ O	1185.8	110–150	4	1117.6	11 643.4	292.0	0.997	1.2	0.994	1.1	I
31	Verbenone	C ₁₀ H ₁₄ O	1190.9	100–160	5	1159.9	2735.9	208.3	0.988	2.1	0.951	3.5	I
32	<i>n</i> -Octyl acetate	C ₁₀ H ₂₀ O ₂	1191.9	120–160	5	1200.5	-1082.8	245.9	0.998	0.2	0.985	0.2	II
33	3-Phenylpropyl alcohol	C ₉ H ₁₂ O	1203.0	120–150	4	1165.6	5304.6	262.0	0.999	0.2	0.994	0.4	I
34	Cuminaldehyde	C ₁₀ H ₁₂ O	1218.0	110–150	5	1065.8	52 072.8	462.0	0.978	1.6	0.981	1.2	I
35	<i>p</i> -Anisaldehyde	C ₈ H ₈ O ₂	1220.4	120–150	4	1014.3	98 889.2	599.3	0.988	1.1	0.990	0.7	I
36	Carvenone	C ₁₀ H ₁₆ O	1236.2	110–150	4	1125.5	22 764.1	325.6	1.000	0.4	0.996	0.8	I
37	Methyl benzyl acetate 1	C ₁₀ H ₁₂ O ₂	1237.2	120–180	5	1211.0	3820.9	265.8	0.998	0.5	0.971	1.4	I
38	Methyl benzyl acetate 2	C ₁₀ H ₁₂ O ₂	1240.1	120–180	5	1226.7	1511.9	232.7	1.000	0.1	0.948	1.6	I
39	Ethyl salicylate	C ₉ H ₁₀ O ₃	1249.1	120–180	4	1065.1	84 800.1	580.9	0.978	3.0	0.979	2.0	I
40	<i>trans</i> -Cinnamyl alcohol	C ₉ H ₁₀ O	1271.8	120–150	4	1174.6	28 730.1	415.5	0.983	1.1	0.982	0.9	I
41	Carvacrol	C ₁₀ H ₁₄ O	1273.8	110–150	4	1269.0	294.4	182.4	0.999	0.1	0.940	0.8	I
42	Menthyl acetate	C ₁₂ H ₂₂ O ₂	1279.2	110–150	4	1269.2	710.6	190.9	1.000	0.1	0.966	0.9	I
43	Geranyl formate	C ₁₁ H ₁₈ O ₂	1281.6	120–180	4	1279.2	172.4	192.7	0.970	1.5	0.799	3.0	I
44	<i>p</i> -Cresyl isobutyrate	C ₁₁ H ₁₄ O ₂	1289.1	120–180	5	1275.1	1596.5	235.5	0.996	0.5	0.938	1.6	I
45	Dimethyl benzyl carbinyl acetate	C ₁₂ H ₁₆ O ₂	1297.5	130–180	5	1102.5	106 339.2	669.3	0.994	0.8	0.994	0.7	I

Table 1. Continued

No.	Solute	Formula	I t (°C)	Range (°C)	n	A	$-B$	$-C$	R^2	σ	r^2	s	*
46	Methyl anthranilate	C ₈ H ₉ NO ₂	1306.3	120–180	4	1131.8	72 449.5	535.0	1.000	0.4	0.997	0.8	I
47	Benzyl <i>n</i> -butyrate	C ₁₁ H ₁₄ O ₂	1315.8	120–180	4	1286.2	4670.7	277.8	0.998	0.5	0.971	1.6	I
48	<i>p</i> - <i>tert</i> -Butylcyclohexyl acetate 1	C ₁₂ H ₂₂ O ₂	1315.8	130–170	4	1283.1	4249.8	245.4	0.996	0.9	0.978	1.5	I
49	Linalyl <i>n</i> -propionate	C ₁₃ H ₂₂ O ₂	1321.4	120–170	4	1320.4	60.8	182.6	0.999	0.1	0.968	0.1	I
50	Benzilydene acetate	C ₁₀ H ₂₀ O ₂	1322.3	130–170	4	1300.8	2051.9	215.8	0.998	0.7	0.958	2.2	I
51	Vanillin	C ₈ H ₈ O ₃	1347.9	120–200	4	1228.4	36 329.1	424.1	1.000	0.1	0.996	1.5	I
52	<i>p</i> - <i>tert</i> -Butylcyclohexyl acetate 2	C ₁₂ H ₂₂ O ₂	1352.0	130–170	4	1302.9	7038.5	267.8	0.992	1.1	0.980	1.5	I
150°													
53	Linalyl isobutyrate	C ₁₄ H ₂₄ O ₂	1361.7	120–150	4	1538.6	68.6	162.8	0.997	0.2	0.881	0.7	I
54	Phenylethyl isobutyrate	C ₁₂ H ₁₆ O ₂	1375.3	120–180	5	1318.0	9324.5	312.5	0.967	2.2	0.950	2.2	I
55	Anisyl acetate	C ₁₀ H ₁₂ O ₃	1382.5	150–180	4	1248.1	53 396.6	547.3	0.998	0.6	0.996	0.3	I
56	<i>n</i> -Decyl acetate	C ₁₂ H ₂₄ O ₂	1391.3	130–190	6	1391.1	5.4	175.6	0.736	0.6	0.510	0.6	I
57	Dihydro- <i>nor</i> -dicyclopentadienyl acetate	C ₁₂ H ₁₄ O ₂	1406.7	150–180	4	1354.0	5510.2	254.6	0.997	0.9	0.988	1.2	I
58	Allyl-3-cyclohexyl propionate	C ₁₂ H ₂₀ O ₂	1406.7	150–190	5	1215.3	100 683.6	676.0	0.994	0.7	0.994	0.6	I
59	Nopyl acetate	C ₁₃ H ₂₀ O ₂	1413.1	130–180	4	1320.0	16 319.7	325.2	1.000	0.4	0.990	1.5	I
60	Cinnamyl acetate	C ₁₁ H ₂₂ O ₂	1413.2	150–190	5	1313.4	46 140.7	612.5	0.995	1.0	0.957	0.9	I
61	Isoamylbenzoate	C ₁₂ H ₁₆ O ₂	1418.2	150–190	4	1369.2	6424.3	281.2	0.998	0.8	0.988	1.3	I
62	Dimethyl phenylethyl carbonyl acetate	C ₁₃ H ₁₈ O ₂	1423.7	150–180	4	1291.7	39 207.4	447.1	0.998	0.6	0.994	0.6	I
63	Longifolene	C ₁₅ H ₂₄	1427.0	110–170	5	956.4	252 655.7	690.0	0.986	3.6	0.999	0.9	I
64	Ethyl cinnamate	C ₁₁ H ₁₂ O ₂	1437.2	150–190	5	1211.7	106 174.6	620.7	0.994	0.9	0.997	0.5	I
65	Anisyl acetone	C ₁₁ H ₁₄ O ₂	1462.0	160–220	4	1400.1	12 008.5	343.9	0.977	2.0	0.973	1.6	I
66	γ -Cadinene	C ₁₅ H ₂₄	1496.6	120–150	4	1383.6	13 333.7	268.1	0.999	0.5	0.995	0.9	I
67	Dihydro- <i>nor</i> -dicyclopentadienyl propionate	C ₁₃ H ₁₆ O ₂	1498.6	150–190	5	1199.0	162 295.6	691.8	0.990	1.3	0.990	1.1	I
68	Ledene	C ₁₅ H ₂₄	1501.0	120–160	4	1203.4	139 141.6	617.5	0.989	1.9	0.990	1.3	I
69	Isoamyl salicylate	C ₁₂ H ₁₆ O ₃	1515.4	150–190	5	1160.6	215 945.2	758.7	0.993	1.1	0.995	0.7	I
70	<i>cis</i> -Nerolidol	C ₁₅ H ₂₆ O	1517.1	120–160	4	1505.4	508.8	193.4	0.993	0.5	0.929	1.2	I
71	γ -Undecalactone	C ₁₁ H ₂₀ O ₂	1532.6	140–180	4	1501.8	2968.8	246.3	1.000	0.2	0.982	1.2	I
72	<i>trans</i> -Nerolidol	C ₁₅ H ₂₆ O	1546.4	120–160	4	1534.5	521.0	193.8	0.989	0.7	0.924	1.2	I
73	<i>n</i> -Amyl salicylate	C ₁₂ H ₁₆ O ₃	1552.0	150–180	4	1272.8	150 464.5	688.5	0.997	0.7	0.998	0.4	I
74	α -Cedrene epoxide	C ₁₅ H ₂₄ O	1568.7	150–190	4	1332.1	64 866.5	424.2	1.000	0.5	0.998	1.0	I
75	Methyl dihydrogalenonate	C ₁₃ H ₁₈ O ₃	1614.9	150–190	5	1507.4	38 023.1	503.2	0.995	0.6	0.993	0.5	I
76	Patchouli alcohol	C ₁₅ H ₂₆ O	1639.8	140–210	4	1281.0	124 163.5	496.1	0.999	1.9	0.997	2.5	I
77	<i>n</i> -Hexyl salicylate	C ₁₃ H ₁₈ O ₃	1651.5	150–180	4	1445.1	83 203.5	553.2	0.993	1.1	0.995	0.6	I
78	Allyl- α -ionone	C ₁₆ H ₂₄ O	1664.5	140–180	4	1596.0	12 085.7	326.4	0.978	2.0	0.974	1.5	I
180°													
79	Cedroxide	C ₁₆ H ₂₈ O	1711.0	150–180	4	877.2	728 613.0	1053.8	0.999	0.6	1.000	0.3	I
80	Cedryl acetate	C ₁₇ H ₂₈ O ₂	1768.3	160–190	4	1531.2	50 790.1	394.5	1.000	0.3	0.998	0.7	I
81	Linalyl benzoate	C ₁₇ H ₂₂ O ₂	1780.8	150–190	4	1546.2	122 543.7	702.5	0.997	0.7	0.998	0.4	I
82	Styrallyl phenylacetate	C ₁₆ H ₁₈ O ₂	1820.4	160–190	4	1763.7	6836.6	300.6	0.998	0.5	0.993	0.6	I

^a r , s taken from Ref. [1].

^b *Indicates hyperbola cases I or II.

and out of the practical temperature range. For SE-30, this is 50–350°C.

The parameter A is dominated by the term $100z$

and was found always positive, in present work and in literature. At the first sight, the order of magnitude and the sign of the parameter B are difficult to

Table 2

The hyperbola coefficient C , calculated from the methylene group increments to the enthalpy and entropy of the solution, in function of temperature and n -alkane pair^a

T (°C)	90	100	110	120	130	140	150	160	170	180	190	200	210
Pair $z+1, z$	– C (°C)												
8,7	389	400											
9,8	397	442	457	477	514	492							
10,9	414	417	436	444	447	488							
11,10	359	373	440	467	504	525							
12,11	378	380	451	504	495	507	500	520	569				
13,12		402	433	498	487	526	502	518	542				
14,13				505	505	471	496	580	520	537			
15,14					454	481	466	515	497	486	582	544	
16,15						482	501	566	564	529	543	552	
18,16/2								528	538	524	516	505	
19,18								482	485	513	514	519	577
Mean	387	402	443	483	487	497	493	529	531	517	539	530	577
σ	21	25	10	24	26	21	15	33	32	20	32	22	

^a Determined on 20°C wide ranges, for the SE-30 glass capillary column used in present work [29].

anticipate from Eq. (19). The observed B parameters are negative or positive, and have absolute values of the order $0-1 \times 10^7$.

The eight possibilities resulted from the different combinations of signs of the parameters A , B , C , are reduced at two. So, in the pure gas–liquid chromatography, only the hyperbolae having A positive and C negative, with the vertical asymptote beyond the superior limit of the used range, can be expected. This situation leads to only two particular cases, namely: *case I*, with B negative and a concave increasing $I-t$ curve and *case II*, with B positive, and a decreasing convex $I-t$ curve. Experimental examples are shown in Figs. 1 and 2.

The great sensitivity of hyperbola parameters against the experimental errors and imperfections of the calculation method modify these basic patterns in practice. Various start sets of A_o , B_o , C_o values produce rather different results if the precision of the retention index data is not indeed very good. The model errors, as a curve too linear or presenting a minimum or plateau due to the concurrent interfacial phenomena [13], are another causes of possible distortions. Remaining in the frame of hyperbola cases I and II, an obvious symptom is a numerical value of C rather different from the above value. This is illustrated bellow by the data from the Tables 1 and 3. Besides, in practice two categories of ‘false

hyperbolae’ can arise. The first is with the vertical asymptote beyond the lower limit of the used temperature range, because C is positive or takes a too small negative value. This corresponds with convex increasing or concave decreasing $I-t$ graphics. The second is with the vertical asymptote inside the used temperature range. This is actually an improbable circumstance, because it would produce a huge retention jump around $-C$. The above two situations can be generated, respectively, by experimental errors affecting a little an extreme or a middle point. Namely, the first category is frequent for quasi-linear curves and the second, when there is a low temperature dependence of the retention index. The literature data illustrates well the above considerations, with a certain predomination of the expected hyperbola cases I and II [2–13].

Our study was initially intended to the practical interpolations and short-range extrapolations in routine conditions [1]. Retention indices were measured with a precision of 0.1–1 i.u. on scattered temperature ranges having an extension of 30–80° and temperature means between 110 and 175°C. The solutes with only three temperature points, even many with an apparent favourable pattern, were omitted. From the 170 cases with the number of temperature points ≥ 4 , 117 gave hyperbolae belonging to the cases I and II. The 82 equations summa-

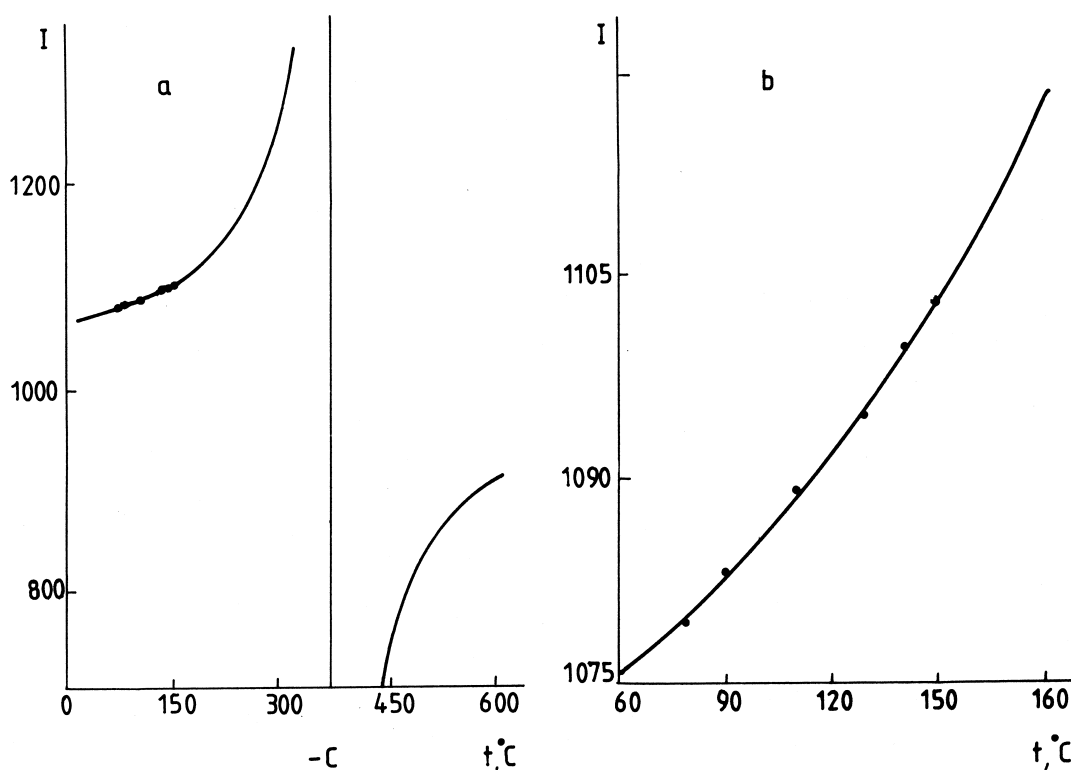


Fig. 1. Example of an experimental 'case I' hyperbola for β -phenylethyl alcohol (solute 19, Table 1) on a SE-30 glass capillary column; (a) general view; (b) detail on the used temperature range.

rised in the Table 1 are selected from these, to have a good precision. Several cases with a worse behaviour were, nevertheless, maintained as examples.

The quality of fitting was compared in Table 1, for the same data processed with Eqs. (1) and (2). Considering the correlation coefficients, about 70% from the solutes fit better the hyperbola. However, only about 40% of solutes show lower standard deviations from the hyperbolic regression curve comparatively with the linear case. Indeed, for the hyperbolic equation, the gain regarding the systematic errors is partially lost because of the smaller number of the degrees of freedom in Eq. (27). Therefore, for interpolations of the retention index data at different temperatures, the use of the linear equation is satisfactory in many cases. On the contrary, the hyperbolic equation is superior for extrapolations, but with the essential condition to be of the correct type. For example, the results can be worse than in linear approximation if a convex quasi-

linear increasing $I-t$ hyperbola is used instead of the correct hyperbola described by case I. The square polynomial fitting of $I-t$ data [16] gives also good results, but the hyperbola has the advantage of the known physico-chemical meaning.

In the following, a discussion of the observed hyperbola parameters is tried. The mean value of parameters C for the 82 solutes from the Table 1 is $-(407 \pm 189)$, compatible with the above 'theoretical' value of $-(488 \pm 53)^\circ\text{C}$. Considering all the 117 hyperbolae of the kinds I and II, this value is $C = -(382 \pm 196)^\circ\text{C}$. The experimental and model errors in the observed hyperbolae, obscure the trend described in Table 2, regarding the increasing of $-C$ with the mean temperature of the range. A clear propagation of errors between the parameters A , B and C is observed, taking as reference point the 'theoretical' C value.

The solute molecular structure is reflected in the parameters A and B , as described by Eqs. (18) and

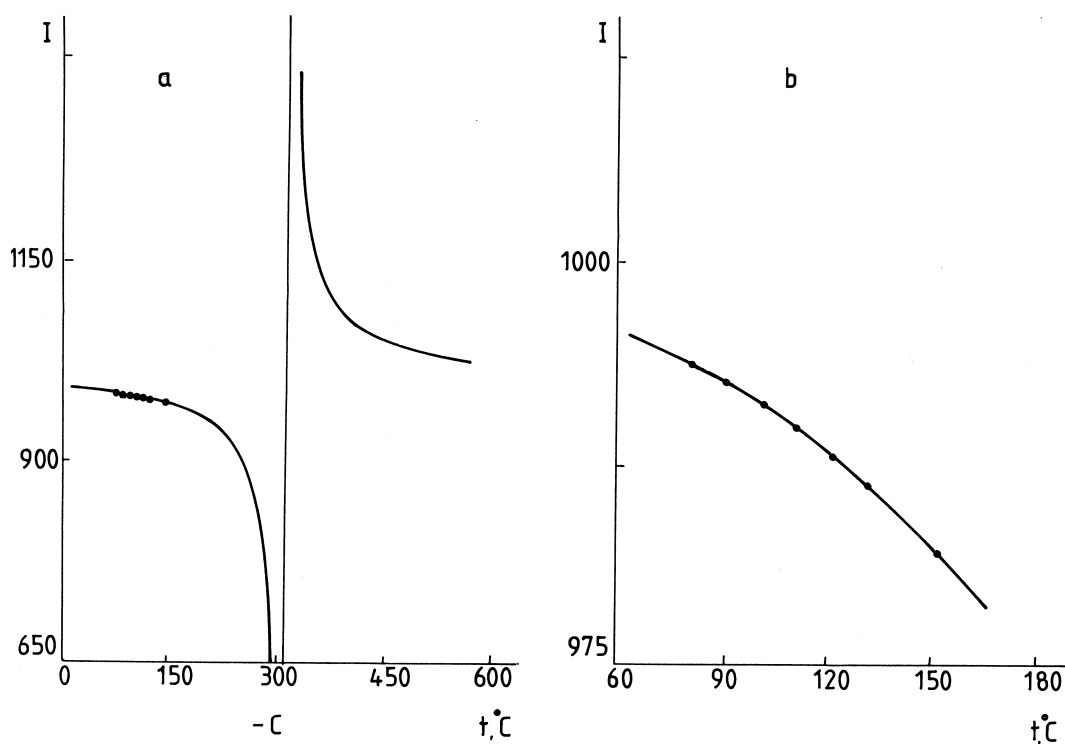


Fig. 2. Example of an experimental 'case II' hyperbola for *trans*-2-hexenyl acetate (solute 8, Table 1) on a SE-30 glass capillary column; (a) general view; (b) detail on the used temperature range.

(19). The permanent reference to an appropriate *n*-alkane for each solute, keeps about constant the $(\Delta S_i^S - \Delta S_z^S)$ and $(\Delta H_i^S - \Delta H_z^S)$ differences for a considered class and allows the discussion of the general tendencies. The same is usually done with the b or dI/dT values [3–6]. However, except a homologous or congeneric series studied in the same temperature range, this is not always a rigorous assertion. The comparison between solutes is complicated by various structural factors, temperature ranges and different reference *n*-alkanes, sometimes even for the same solute at distinct temperatures. A high scattering of the observed parameters is expected in consequence.

The quantity $(A-100z)$ has a pure entropic meaning and a simple expression, Eq. (18). So, a discussion on structural effects can be attempted, provided that it is only to see some trends. Several qualitative considerations based on thermodynamics of solution process [21,32] seem to correspond with the ob-

served data. The entropy of solution can be considered as the sum:

$$\Delta S^S = \Delta S^C + \Delta S^E \quad (29)$$

where ΔS^C is the standard entropy of condensation of the pure solute and ΔS^E is the solution excess entropy. The entropies of solution and condensation have negative values for all solutes, because of the loss of freedom at the gas–liquid transfer.

The excess entropy is the result of different positive and negative contributions. The solute–solvent disparities in molecular size and shape bring positive contributions to the excess entropy. The negative contributions are less likely. Indeed, the orientation demands for interaction are negligible in the non-polar SE-30. The interfacial effects, as apparent factors of supplementary order in solution seem to be insignificant, except for some hydroxylic solutes [13,33,34].

Table 3
The average ($A-100z$) values^a and other connected information^{b,c} for different classes of solutes from Table 1

Class of solutes	n	$A-100z$ mean	Rel. error (%)	Sign of individual ($A-z$) values	Atom number sequence ^c
Acyclic	20	64	114	17 (+), 3 (-)	16 solutes: N with 1–2 atoms $>z$ 1 solute: N with 3 atoms $>z$ 1 solute: $N=z$ 2 solutes: N with 1–2 atoms $<z$
Monocyclic alicyclic	13	-33	132	9 (-), 4 (+)	5 solutes: N with 1–2 atoms $>z$ 6 solutes: $N=z$ 2 solutes N with 1–2 atoms $<z$
Monocyclic aromatic	31	-69	125	21 (-), 10 (+)	14 solutes: N with 1–2 atoms $<z$ 11 solutes: $N=z$ 6 solutes: N with 1–2 atoms $>z$
Bicyclic alicyclic	7	-111	79	6 (-), 1 (+)	4 solutes: N with 1–2 atoms $>z$ 3 solutes: $N=z$
Tricyclic alicyclic	7	-303	66	7 (-)	6 solutes: N with 1–2 atoms $>z$ 1 solute: $N=z$

^a ($A-100z$) calculated taking as z the carbon number of the reference n -alkane in the retention indices at 120°C; the solutes Nos. 42, 31 and 57 were excluded as exceptions.

^b n is the number of solutes, rel. error is the ratio (standard deviation/average value)×100; the sign of individual ($A-100z$) values is shown for the indicated number of solutes.

^c The number N of carbon- and hetero-atoms in the solute i , comparatively with the number z of the carbon atoms in the reference n -alkane.

Then, the differences solute–reference n -alkane in relation with the solvent must be considered. The polarity of the solute has an implicit influence on the difference ($\Delta S_i^S - \Delta S_z^S$), connected with the position on the free enthalpy scale, marked by the homologues. This position determines the particular reference n -alkane with z carbon atoms. An examination in the Table 1 of the relation between the solute raw formula and the reference n -alkane is illustrative in this respect. The parameter A as the free term accumulates the most of errors, which can cover partially the structural influences. All these factors must be considered in the evaluation of relative behaviour of the pair solute–reference alkane, regarding the solution entropy.

The ($A-100z$) values were calculated, taking as z the carbon number of the reference n -alkanes in the retention indices at 120°C. A detailed discussion of individual solutes is not possible here, but some tendencies connected with the above entropy aspects can be recognised for the groups selected from the Table 1 and shown in Table 3.

The acyclic, mono-, bi- and tricyclic solutes were considered, to point out the effect of shape dissimilarity. The ($A-100z$) values were mainly positive for the polar acyclic solutes and mainly negative for the cyclic solutes, with a high incidence of exceptions for the monocyclic alicyclic and aromatic solutes. The mean values for the selected classes are shown in Table 3 as a rough indicator. As expected, the scattering for a class (described by the relative error) is high, because of the variety of molecular structure and temperature ranges. The number N of carbon- and hetero-atoms of the solute compared with z gives some information on the relation between the molecular sizes of the considered pair. A statistic on this is shown in Table 3. The solutes i are generally with only 1–2 atoms different, or equal with the reference n -alkane. This reflects the non-polar nature of the SE-30 stationary phase and the moderate polarity of the solutes. For the most cases, $N \geq z$, but at the same number of atoms, the cyclic solutes (especially aromatic) have generally lower molecular volumes than the acyclic ones. An indication on the entropies

of condensation is given by boiling points. For example, high boiling points correspond with high negative values of the enthalpy and entropy of condensation [21]. In the present case, the boiling points of the polar solutes are generally higher or close to those of the reference *n*-alkanes. So, the difference between the entropies of condensation of the pure compounds *i* and alkane *z*, is negative or close to zero. Exceptions in Table 1 are several very branched molecules.

The observed positive values of (*A*–100*z*) for most of the polar acyclic solutes indicate negative differences of entropies, that is more loss of freedom at the transfer from gas to stationary phase against the corresponding reference *n*-alkanes. The reason can be the cumulated negative contributions to ($\Delta S_i^S - \Delta S_z^S$) due to the little greater size, boiling point and to tendency of gas–liquid adsorption in case of the polar acyclic solutes. The similarity in shape with the *n*-alkanes reduces to zero this effect.

The negative (*A*–100*z*) values found for the most of the cyclic compounds, evidently increasing in absolute value with the number of cycles, are primarily due to the differences in molecular shape. This effect brings a positive contribution to ($\Delta S_i^S - \Delta S_z^S$), exceeding the contrary effects (as discussed above). In the case of monocyclic aromatic and alicyclic solutes, however, the trends are not very clear, because of their structural features.

The parameter *B* reflects most of the solute structure influence. Eq. (19) shows that besides the entropic part, the intermolecular forces involved in the enthalpic term play an essential role. The factors containing the methylene increments determine the proportion between the entropic and enthalpic contributions. However, a simple general discussion of the structural effects on *B*, is difficult. In [35], the differences ($\Delta H_i^S - \Delta H_z^S$) and ($\Delta S_i^S - \Delta S_z^S$) were determined for several typical solutes belonging to the classes from Table 3. A clearer view was obtained in an extended context, including the behaviour on Carbowax-20M.

The tendencies of the parameter *B* are easier to follow through the parameter *b* of Eq. (2), because about it there is much information on structural influences [35]. The correlation between the two series of parameters *b* and *B*, *C*, taken from Table 1 and reference [1], is according to Eq. (28):

$$b_i = 1.0060 \left[-\frac{B}{(\bar{t} + C)^2} \right] + 0.003$$

$$r = 0.9953 \quad n = 82 \quad (30)$$

The parameter *C* is basically a phase constant, so that *b* and *B* are directly related, but in a way dependent on the mean temperature of the range. Nevertheless, *B* and *C* must be considered together, because of the errors and of the slight influence of temperature on *C*. The correlation coefficient of the linear relation *b* in function of *B*/*C*² is only 0.81, due to differences in temperature ranges.

The paper of Hennig and Engewald [13] is a good example to see how the model errors disturb the hyperbolae, when the retention indices are precisely determined using an uniform temperature range. Hydroxylic solutes known as components of the essential oils were studied on a HP-5 capillary column (dimethylsilicone with 5% diphenyl). A formal processing as hyperbolic and linear regression of their data is presented in the Table 4.

In all cases, Eq. (1) shows a better fitting than Eq. (2), but the standard deviations from the regression curves are generally greater than the very small experimental error. The interfacial phenomena are reflected in a worse fitting, as can be seen for citronellol and thymol. Considering the similarity of stationary phases, the data of the linear regression are almost identical with ours on SE-30 [1]. For example, the *b* and *r*² values on SE-30 are, respectively, for citronellol 0.041 and 0.858; for geraniol 0.14 and 0.963; for carvacrol 0.115 and 0.940, for thymol 0.053 and 0.50. The good concordance with the data from Table 4, shows that the poor fitting observed in the paper [1] had, at least partially, an objective cause. The hyperbolae for carvacrol on SE-30 (No. 41 Table 1) and HP-5 are comparable. The same tendency in *C* values as in our data is observed: a mean of $-C$ of 343 with a standard deviation of about 263. Interfacial adsorption producing a plateau or minimum towards the lower temperatures, induces a decreasing of $-C$, as can be seen for citronellol, carvacrol and especially for thymol. Like the previous observations, the (*A*–100*z*) values on HP-5, based on *z* from the retention index at 120°C, are 25 and 47 for the acyclic solutes citronellol, geraniol; -351 and -140 for the

Table 4

The parameters, correlation coefficient and standard deviation of the hyperbolic Eq. (1) (A , B , C ; R , σ) and of the linear Eq. (2) (a , b ; r , s) for hydroxylic solutes on a fused-silica HP-5 capillary column with 0.33- μm film thickness, calculated from the retention index data of Hennig and Engewald [13]^{a,b}

Name	Pattern of the $I-t$ plot ^c	A	$-B$	$-C$	R^2	σ	a	b	r^2	s
β -Citronellol	Slight minimum at 90°C	1225.4	263.4	202.1	0.971	0.24	1224.1	0.039	0.898	0.35
Geraniol	Normal 'case I' hyperbola	1246.6	982.1	229.3	0.999	0.10	1246.3	0.081	0.964	0.41
<i>trans</i> -Pinocarveol	Almost linear	749.0	308026.5	872.1	1.000	0.42	1093.8	0.544	0.999	0.45
<i>cis</i> -Verbenol	Almost linear	959.8	89338.5	575.0	0.991	0.09	1105.8	0.424	0.806	0.50
Carvacrol	Slight minimum at 90°C	1295.0	548.6	190.9	0.991	0.38	1290.0	0.113	0.901	0.99
Thymol	Pronounced minimum at 100–120°C	1290.1	79.1	164.8	0.905	0.67	1286.5	0.050	0.616	1.05

^a Calculated using z from the retention index at 120°C.

^b Determined for eight temperatures in the range of 80–150°C, with a precision of 0.01–0.07 i.u.

^c On the basic pattern of a 'case I' hyperbola.

bicyclic alicyclic ones, pinocarveol, verbenol; –5 for carvacrol. The positive value of 90 for thymol seems to be irrelevant because the hyperbola is too erroneous having in view the pronounced minimum at 100–120°C.

5. Conclusions

The hyperbolic equations for the temperature dependence of the retention index were reported for a comprehensive set of solutes, having different molecular structure. The physico-chemical significance of the hyperbola parameters helps the understanding and critical evaluation of the experimental data. In gas–liquid chromatography, only two cases of hyperbolae can be expected in theory, but in practice, different causes can modify the situation. This work will be used in the evaluation of the relation between different $I-T$ equations and of the meaning of their parameters.

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