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Journal of Chromatography A, 973 (2002) 135–142

JOURNAL OF
CHROMATOGRAPHY A

www.elsevier.com/locate/chroma

Temperature dependence of Kováts indices in gas chromatography revisited

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Received 9 January 2002; received in revised form 6 August 2002; accepted 6 August 2002

Abstract

Temperature dependence of the Kováts retention index (I) was measured for some aliphatic ketones and aldehydes on a poly(dimethyl siloxane) (HP-1) stationary phase. An interesting minimum (non-linearity) was observed for the I versus isothermal column temperature (T) relationships. A novel empirical model is proposed: $I = A + B/T + C \ln T$, where A , B and C are equation constants and $B/C = T_{\min}$. A detailed statistical analysis clearly shows superiority of the extended model (i.e., of this containing the logarithm of the temperature ($\ln T$) term) over the earlier established Antoine-type reciprocal equation. The minimum temperature (and the energy like quantity $= RT_{\min}$, where R is the gas constant) changes in a systematic manner. The factors effecting the (RT_{\min}) term are as follows: (i) this term decreases with the increase of the molecular mass of the respective oxo compounds; (ii) ketones have higher absolute values of (RT_{\min}) than aldehydes; (iii) branching of the carbon chain lowers the mentioned (RT_{\min}) . This enthalpy term is unambiguously bound to the polarity of solutes. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Retention indices; Temperature dependence; Enthalpy of solution; Ketones; Aldehydes

1. Introduction

Temperature dependence of the retention data, especially of Kováts indices, has been debated for a long time [1,2], although inconclusively to a large extent. In many cases, linear approximation provides excellent results within the commonly applied temperature ranges and for the non-polar stationary

phases [2,3]. Retention indices for non-polar substances analyzed on non-polar stationary phases show an almost linear dependence on the isothermal column temperatures [1]. However, the Antoine-type relationship (which is non-linear and empirical) exhibits better performance for wide temperature ranges and for non-polar substances analyzed on polar stationary phases [1–5].

Pacáková and Feltl attributed thermodynamic significance to the equation constants of the Antoine-type equation, which couples Kováts retention indices with temperatures of the isothermally operated GC columns [6]. Their derivation is valid only if the thermodynamic quantities have no temperature de-

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pendence. However, recent examinations show that the temperature dependence of thermodynamic quantities cannot be neglected even within the narrow temperature ranges, applied in gas chromatography [7].

Our current measurements proved unambiguously that in certain cases the Kováts retention indices exhibit a minimum as a function of the isothermal column temperature (T). This minimum can be observed for polar substances on apolar stationary phases and it is certainly not an artifact. For example, it cannot be eliminated by manipulating with the column dead time, or by using alternative ways for determination of the Kováts retention indices. Earlier examinations [7–10] did not reveal the discussed minimum.

Adsorption may influence the chromatographic retention values [11–16]. Its role is enhanced, if the solute does not dissolve in the stationary liquid phase. Hence, large adsorption effects can be expected in the cases of polar substances analyzed on apolar columns [11,14,16] and vice versa [12,15]. As a consequence, retention values depend on the film thickness of the stationary liquid phases [11–16]. The adsorption finds more favorable conditions with the increasing polarity of the solute [14]. Henning and Engewald found a minimum on the Kováts index temperature curve for moderately polar compounds analyzed on an apolar stationary phase [16]. He unambiguously attributes the distortion of Kováts indices to the adsorption.

Tudor reinvestigated the temperature dependence of Kováts indices, using perfumery compounds as test solutes on SE-30 stationary phase. She studied linear [17] and hyperbolic [18] equations, as well as the relationships between these equations [19]. The relatively narrow temperature range, generally applied for examination of temperature dependency [5,17,18] does not allow discovering the existence of a minimum.

This paper furnishes additional proofs, which confirm the existence of a real (i.e., a non-artifact) minimum on the Kováts index—column temperature curve. A simple empirical relationship, extended by the logarithm of the temperature term ($\ln T$) is capable to describe the minimum:

$$I_{(i)} = A + B/T + C \ln T \quad (1)$$

where $I_{(i)}$ denotes the numerical value of the Kováts

retention index for the i th solute, T is the column temperature (in the isothermal GC mode), and A , B , and C are equation constants. They depend on the solute properties and thermodynamic magnitudes, but in the first approximation they are independent of temperature.

Thus, the objectives of this paper are to (i) introduce a new equation and prove its superiority over the earlier Antoine-type equation; (ii) validate the new model, extending its soundness to such cases, when the minimum appears outside the temperature window of measurements.

The reference Antoine-type reciprocal relationship is—for the sake of a reminder—given below [1–4]:

$$I_{(i)} = a + b/(T + c) \quad (2)$$

a , b , and c are the empirical constants, depending on the solutes and the stationary phases.

2. Experimental

The measurement of Kováts indices for a broad enough temperature range is particularly difficult. On the one hand, the accuracy of the dead-time determination decreases with the increasing temperature. On the other hand, a considerable peak distortion and broadening restricts determination of the exact retention time below the lower limit of the temperature range of application (generally, at the temperature of solidification). At lower temperatures, the unwanted peak broadening restricts the applicable temperature ranges.

Four aliphatic ketones (i.e., acetone, butan-2-one, pentan-2-one, and hexan-2-one) and four aldehydes (i.e., ethanal, propanal, butanal, and methyl propanal) were chosen for our experiment as the test solutes. The retention indices of these compounds established on non-polar stationary phases and plotted as functions of the isothermal column temperatures exhibited a minimum.

The Kováts retention indices (I) were measured in the 10 °C intervals at the temperatures ranging from 20 to 70 °C, and additionally at 90 and 110 °C, with at least three injections made at each working temperature. It was not expedient to carry out some of the measurements (i.e., at 20 °C with pentan-2-one and hexan-2-one). The experimental data are also

missing for 40 and 60 °C with butanal and isobutanal.

Another set of ketones and aldehydes were used for internal validation purposes. Their retention parameters were measured at 30, 50, 70, 90, and 110 °C, and there were no minima observed on the temperature dependence of the Kováts indices for these compounds within the temperature window applied. The proposed model should describe the temperature dependence also for these oxo compounds.

Aliphatic ketones and aldehydes were purchased from Fluka and Aldrich, and they were used without further purification. The column length was 50 m, its inner diameter was 0.32 mm and the film thickness was 1.05 µm. Stationary phase was dimethyl polysiloxane (producer: Hewlett-Packard, Palo Alto, CA, USA), its code HP-1. The measurements were performed with a 5890 Hewlett-Packard Series II GC with an HP 3365 ChemStation. Retention times and normal alkanes were used for determination of Kováts indices. Further details of the analysis were given in our earlier publications [7,8].

3. Results and discussion

Table 1 summarizes the averages of the multiple

determinations of the Kováts retention indices on dimethyl polysiloxane (HP-1) stationary phase.

The results of the multiple linear regression are given in Table 2. It is noteworthy that the reciprocal and the logarithm of the isothermal column temperature (i.e., $1/T$ and $\ln T$, respectively) were considered as new variables in the multilinear model.

Although the investigated temperature interval was limited by unavoidable experimental constraints, our present work unambiguously gives evidence of the existence of the minimum on the I versus T curves.

Statistical characteristics of Model 1 (shown in Table 2) confirm significance of the equations obtained, whereas those of Model 2 are significant in sporadic cases only. From these results it becomes clear that the extended new model (given by Eq. (1)) provides a much better fit than the Antoine-type reciprocal model (Eq. (2)). This statement is based on correlation coefficients, visual evaluation of residuals and residual errors.

For the sake of examples, Figs. 1 and 2 provide graphical illustration of the I versus T relationships, respectively, as obtained for acetone with aid of the extended new relationship (Model 1) and of the reciprocal, Antoine-type equation (Model 2).

From the data of Table 2 and plots given in Figs. 1 and 2 it clearly comes out that the extended new equation is flexible enough to adequately model the experimental minimum, whereas the reciprocal, An-

Table 1
Temperature dependence of Kováts indices measured on HP-1 stationary phase

		Temperature (K)							
		293.15	303.15	313.15	323.15	333.15	343.15	363.15	383.15
Acetone	Kováts indices	470.90	470.70	470.10	469.67	469.50	469.28	469.41	470.23
Acetone	SD	0.161	0.079	0.085	0.191	0.339	0.679	0.007	0.442
Butanone	Kováts indices	575.30	575.00	574.90	574.71	574.80	574.97	574.76	575.77
Butanone	SD	0.120	0.171	0.055	0.095	0.042	0.177	0.235	0.433
Pentan-2-one	Kováts indices		665.40	665.40	665.40	665.40	665.69	666.07	666.90
Pentan-2-one	SD		0.075	0.123	0.155	0.007	0.120	0.042	0.085
Hexan-2-one	Kováts indices		766.90	766.80	766.97	767.10	767.30	768.04	769.00
Hexan-2-one	SD		0.000	0.042	0.086	0.021	0.007	0.021	0.021
Ethanal	Kováts indices	364.00	362.60	361.60	360.37	360.50	360.64	360.37	360.88
Ethanal	SD	1.468	0.370	0.463	0.375	0.304	0.846	1.028	0.546
Propanal	Kováts indices	473.70	473.50	473.30	472.71	473.10	472.74	473.04	473.63
Propanal	SD	0.203	0.159	0.081	0.323	0.198	0.807	0.643	0.927
Propanal, 2-methyl	Kováts indices	540.0	540.0		540.32		540.94	541.57	542.98
Propanal, 2-methyl	SD	0.100	0.096		0.127		0.382	0.242	0.233
Butanal	Kováts indices	570.90	570.70		571.10		571.90	572.54	573.33
Butanal	SD	0.173	0.124		0.114		0.186	0.293	0.069

Table 2

Comparison of two models describing the temperature dependence of Kováts indices: Model 1 (extended model, Eq. (1)), $I=A+B/T+C \ln T$; Model 2 (Antoine type reciprocal model, Eq. (2)), $I=a+b/(T+c)$

	A^a	B^a	C^a	r^b	F^b	S^b	$RT_{\min} = R(B/C)$ (J mol ⁻¹)	C no. ^c	a^d	b^d	c^d	r^b	S^b
Acetone	-389.8	43250	125.6	0.9649	33.7	0.189	2863	3	469.3	25.54	-278.1	0.7961	0.435
Butanone	16.40	27080	82.13	0.8891	9.43	0.191	2741	4	575.3	4.248	-377.4	0.8849	0.194
Pentan-2-one	61.65	28300	89.33	0.9951	201	0.0688	2634	5	664.7	-61.53	-411.7	0.9917	0.0893
Hexan-2-one	41.11	33550	107.7	0.9991	1160	0.0407	2591	6	765.5	-157.8	-427.9	0.9942	0.105
Ethanal	-1146	76950	219.6	0.9786	56.5	0.319	2914	2	359.8	52.30	-280.9	0.9530	0.469
Propanal	-146.8	30650	90.84	0.9032	11.1	0.194	2805	3	473.0	4.360	-286.9	0.5678	0.372
Propanal, 2-methyl	-181.6	32390	107.6	0.9956	169	0.140	2503	4	538.3	-222.1	-430.9	0.9985	0.0826
Butanal	80.83	21290	73.46	0.9937	118	0.150	2410	4	567.2	-714.1	-499.4	0.9887	0.201

^a A , B and C are fitted parameters in the Model 1 (extended model, Eq. (1)): $I=A+B/T+C \ln T$.

^b r , F , S are multiple correlation coefficients, Fisher statistics, and residual error, respectively.

^c C no. carbon atom number.

^d a , b and c are fitted parameters in the Model 2 (Antoine type reciprocal model, Eq. (2)): $I=a+b/(T+c)$.

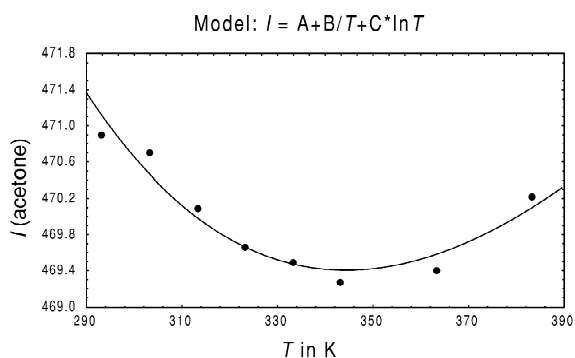


Fig. 1. Regression plots of the I versus isothermal column temperature for acetone (Model 1, Eq. (1)).

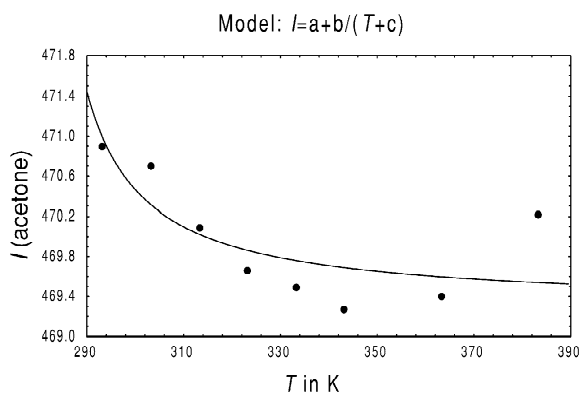


Fig. 2. Regression plots of the I versus isothermal column temperature for acetone (Model 2, Eq. (2)).

toine-type, equation evidently lacks this important feature.

The correctness of the new (i.e., extended) model is justified by the better theoretical description, granted by this model to the experimental link between the Kováts retention indices and the isothermal column temperatures for all the test solutes considered.

Derivation of Eq. (1) provides the temperature at the minimum of the I versus T curve ($T_{\min} = B/C$). At the first approximation we may express the minimum-temperature values on another scale, e.g., in energy-like quantities. Therefore T_{\min} is multiplied with the gas constant “ R ”. The RT_{\min} term reveals a physicochemical process. The RT_{\min} term values for the eight solutes investigated are quite close to each

other and they decrease with the increasing number of carbon atoms. In the other words, the RT_{\min} term becomes less significant with the increasing carbon chain. The order of magnitude for the RT_{\min} term is smaller than for chemical reactions and in this way it well corresponds with weak intermolecular interactions. Moreover, the B and C constants (Eq. (1)) are needed for its calculation. They do not change in the same direction with the increase of the carbon atom number of the analytes. However, the RT_{\min} term does change and exhibits very small differences only (Table 2).

4. Validation and interpretation

Another set of oxo compounds can be used for validation of the findings. They do not have a minimum within the experimental temperature-window applied. The temperature dependencies of the Kováts indices are summarized in Table 3.

All the statistical characteristics (multiple correlation coefficients, Fisher statistics, and residual error) suggest that Model 1 provides a highly significant description of the retention data (Table 4). Moreover, all conclusions drawn from the study with the eight oxo compounds showing a minimum, remain true for the validation set.

Some interesting tendencies can be observed for the minimum. The RT_{\min} term for aldehydes is noticeably lower than for the corresponding ketones.

Another tendency can also be observed, namely that the branching of the carbon chain causes a similar lowering of the values of the RT_{\min} term.

Generally speaking, the straight-line species show higher RT_{\min} values than their mono- and double-branched counterparts.

The RT_{\min} term is connected to polarity. Ketones are more polar compounds than aldehydes. If we compare the dipole moments of the respective pairs of compounds (e.g., butan-2-one and butanal; 3-methyl butan-2-one and 3-methyl butanal; hexan-2-one and hexanal, etc.) calculated by the semiempirical PM3 method [20], it is always the more polar compound that has the larger enthalpy. The RT_{\min} enthalpies for almost equally polar molecules are almost equal as well (e.g., for 3,3-dimethyl butan-2-

Table 3
Temperature dependence of Kováts indices measured on HP-1 stationary phase

		Temperature (K)				
		303.15	323.15	343.15	363.15	383.15
Pentan-3-one	Kováts indices	675.75	675.42	675.52	675.84	676.91
Pentan-3-one	SD	0.130	0.134	0.170	0.057	0.216
Butan-2-one, 3-methyl	Kováts indices	639.36	639.89	640.49	641.53	642.78
Butan-2-one, 3-methyl	SD	0.050	0.101	0.028	0.014	0.29
Hexan-3-one	Kováts indices	764.11	764.10	764.37	765.00	765.97
Hexan-3-one	SD	0.053	0.037	0.007	0.000	0.042
Pentan-2-one, 4-methyl	Kováts indices	719.78	720.12	720.65	721.70	722.94
Pentan-2-one, 4-methyl	SD	0.029	0.102	0.014	0.007	0.007
Butan-2-one, 3,3-dimethyl	Kováts indices	690.48	691.81	693.30	695.47	697.44
Butan-2-one, 3,3-dimethyl	SD	0.115	0.070	0.007	0.255	0.049
Pentan-2-one, 3-methyl	Kováts indices	732.26	733.49	734.94	736.84	738.96
Pentan-2-one, 3-methyl	SD	0.134	0.035	0.000	0.014	0.014
Pentan-3-one, 2,4-dimethyl	Kováts indices	776.47	777.67	779.36	781.05	783.11
Pentan-3-one, 2,4-dimethyl	SD	0.014	0.075	0.078	0.014	0.028
Butanal, 3-methyl	Kováts indices	633.83	634.98	636.40	637.46	639.23
Butanal, 3-methyl	SD	0.299	0.127	0.057	0.035	0.021
Butanal, 2-methyl	Kováts indices	644.21	645.33	646.90	648.21	650.03
Butanal, 2-methyl	SD	0.122	0.091	0.072	0.110	0.065
Pentanal	Kováts indices	673.91	674.37	675.18	676.24	677.34
Pentanal	SD	0.192	0.093	0.000	0.064	0.134
Propanal, 2,2-dimethyl	Kováts indices	580.50	581.71	583.28	584.49	586.08
Propanal, 2,2-dimethyl	SD	0.135	0.012	0.015	0.164	0.050
Hexanal	Kováts indices	776.06	776.45	777.23	778.46	780.00
Hexanal	SD	0.271	0.163	0.007	0.042	0.170
Butanal, 2-ethyl	Kováts indices	740.26	742.07	743.96	746.25	748.85
Butanal, 2-ethyl	SD	0.038	0.095	0.007	0.014	0.014
Butanal, 3,3-dimethyl	Kováts indices	687.24	689.09	691.42	694.01	697.02
Butanal, 3,3-dimethyl	SD	0.071	0.087	0.106	0.099	0.262

Table 4
Temperature dependence of Kováts indices according to Model 1 for the validation set (Extended model, Eq. (1)): $I = A + B/T + C \ln T$

	A^a	B^a	C^a	r^b	F^b	S^b	$RT_{\min} = R(B/C)$ (J mol ⁻¹)
Pentan-3-one	-231.6	43850	133.5	0.9877	39.95	0.132	2732
Butan-2-one, 3-methyl	-71.61	31280	106.4	0.9991	568.4	0.0808	2445
Hexan-3-one	8.611	35380	111.8	0.9990	496.2	0.0503	2631
Pentan-2-one, 4-methyl	-107.3	37350	123.2	0.9993	706.8	0.0685	2521
Butan-3-one, 2,2-dimethyl	-251.0	38340	142.6	0.9995	943.6	0.129	2235
Pentan-2-one, 3-methyl	-258.9	41220	149.7	0.9999	4534	0.0560	2290
Pentan-3-one, 2,4-dimethyl	-71.99	34150	128.8	0.9998	2760	0.0712	2205
Butanal, 3-methyl	110.6	19600	80.26	0.9981	262.7	0.183	2030
Butanal, 2-methyl	10.61	24490	96.74	0.9992	638.8	0.129	2105
Pentanal	44.66	27090	94.48	0.9997	1928	0.0450	2384
Propanal, 2,2-dimethyl	168.2	13750	64.21	0.9992	635.5	0.124	1781
Hexanal	-218.0	44690	148.2	0.9999	4934	0.0323	2508
Butanal, 2-ethyl	-272.7	40060	154.1	0.9998	2567	0.0946	2161
Butanal, 3,3-dimethyl	-570.9	50750	190.9	1.0000	15560	0.0440	2210

^a A , B and C are fitted parameters in the Model 1 (extended model, Eq. (1)): $I = A + B/T + C \ln T$.

^b r , F , S are multiple correlation coefficients, Fisher statistics, and residual error, respectively.

one and 3,3-dimethyl butanal), still the larger—smaller relationship is preserved.

As the polarity of solutes diminishes, less and less enthalpy can be observed gradually. According to the arguments outlined in the introduction it would be easy to attribute physical meaning to this term as adsorption. However, this term must not be confused with the heat of adsorption in gas–solid chromatography. The heat of adsorption is at least by one magnitude order higher [21–23] than our effect. Dernovaya and Eltekhov evaluated adsorption heats of acetone and butan-2-one as equal to 50.6 and 54.7 kJ mol⁻¹, respectively [21]. The contribution of this “polar term” to the entire adsorption process can be calculated from the RT_{\min} values determined in this study (Table 3). The results are 5.7% for acetone and 5.0% for butan-2-one. Berezkin and Korolev investigated the role of adsorption on the same polydimethyl siloxane stationary phase, as we did. They attribute 6.0 and 7.1% for nonan-5-one, depending on the cross-linking [13]. The coincidence is surprisingly good but it can be accidental. Orav et al. studied the effect of adsorption on *polar* stationary phases. They obtained smaller values (0.7–1.3%) for the contribution of adsorption on OV-225 and PEG 20M columns, as expected [15]. For apolar solutes on polar stationary phase they established a large adsorption contribution (15–33%), which agrees with bad solubility of apolar compounds.

Hennig and Engewald [16] observed a similar distortion (minimum) of the Kováts indices as a function of temperature, using alcohols and phenols as the test compounds and an apolar stationary phase (HP-5). The distortion was due to the adsorption effects, however, without any quantitative evaluation. Their observation supports our findings that the minimum found is not an artifact.

A logarithmic equation similar to our new model (1) has already been suggested by Castells et al. They used the specific retention volumes instead of the Kováts indices and discussed the equation constants in the context of the molar heat capacity [24].

Dallos et al. describes the temperature dependence of standard chemical potential difference with parabolic equations [25]. As Kováts indices can thermodynamically be defined by chemical potentials, the analogy is obvious: the logarithmic equa-

tion (Model 1) can be expanded by a Taylor series expansion using quadratic terms.

5. Conclusions

Temperature dependence of the Kováts retention indices can adequately be described by a new equation: $I = A + B/T + C \ln T$ (Model 1). Statistical analysis based on correlation coefficients, Fisher statistics and residual errors suggests that this is not only a fully acceptable description, but also a superior one to the earlier Antoine-type equation.

The RT_{\min} enthalpy term is unambiguously bounded to the polarity of solutes.

Several interesting trends are observed, namely (i) with the increasing molecular masses of oxo compounds, the respective enthalpies decrease, (ii) ketones have higher enthalpy values than aldehydes, and (iii) branching of the carbon chain lowers the magnitude of the RT_{\min} term.

Acknowledgements

This work was supported by the Hungarian Research Foundation: OTKA T 029748 and OTKA C 307-8.

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