

KOVATS RETENTION INDEX–BOILING POINT RELATIONSHIP OF 2–PHENYL–2–ALKYL– ACETONITRILES ON STATIONARY PHASES OF DIFFERENT POLARITY

Linear and reciprocal Kovats retention index–boiling point relationships known from the literature were used to study the Kovats retention index–boiling point dependence of 2–phenyl–2–alkylacetoneitriles on stationary phases of different polarity (OV–17, OV–210 and OV–225). The standard chemical potential of the partitioning of one methylene group of an n–alkane for the stationary phase was calculated and compared with available literature data.

Key words: 2–phenyl–2–alkylacetoneitriles, retention indices, gas chromatography, temperature dependence.

Different properties of organic compounds can be used for the characterization of their chromatographic behaviour (i.e. prediction of their retention). The physicochemical properties of the solutes (e.g. boiling points, molar volumes, molar refraction, dipole moments, or polarities, etc.) or data related to their molecular structure (e.g. topological indices) can be used.

Retention can be described using thermodynamic quantities, although it is cleverer to do the reverse, i.e. to obtain thermodynamic data by use of gas chromatography, a relatively simple analytical technique. Among the thermodynamic properties estimated are the enthalpy of vaporization, the enthalpy of solvation, the standard chemical potential of solvation, the standard chemical potential of partitioning of one methylene group or of a given solute between the stationary and mobile phases, and the enthalpy and entropy of adsorption [1].

Gas chromatographic retention can be described in many different ways, although the most frequently used is the Kovats retention index. Kovats retention index–boiling point correlations were studied using different equations [2–18]. Heberger et al. introduced the concept of applying Trouton's rule to known linear and reciprocal relationships which relate the solute Kovats retention indices with their respective boiling points [10–13, 16]. Kovats mentioned Trouton's rule in a well known paper [19], but without any quantitative results.

The quantitative definition of the Kovats retention index $I_{(i)}$ can be transformed into the form [10]:

Author address: D. Mijin, Faculty of Technology and Metallurgy, University of Belgrade, Belgrade, Karnegijeva 4, Serbia and Montenegro, E-mail: kavur@tmf.bg.ac.yu
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$$\frac{I_{(i)}}{100} = \frac{\Delta\mu_{p(i)}}{\Delta\mu_{p(\text{CH}_2)}} \quad (1)$$

where $\Delta\mu_{p(i)}$ and $\Delta\mu_{p(\text{CH}_2)}$ are, respectively, the standard chemical potential of the partitioning of the i -th solute and of one methylene group of an n -alkane between the mobile and the stationary phases.

If it is assumed that the standard chemical potential of the partitioning of one methylene group and one methyl group are practically equal [20]:

$$\frac{\Delta\mu_{p(i)}}{\Delta\mu_{p(\text{CH}_2)}} \approx z \quad (2)$$

where z refers to the number of the carbon atoms contained in the molecule of an n -alkane.

The vaporization of liquids is well characterized by Trouton's rule, which states that for the majority of liquids the entropy of vaporization is practically constant and equal to approximately $85 \text{ J mol}^{-1} \text{ K}^{-1}$ [21]:

$$\Delta S_{\text{vap}(i)} = \Delta H_{\text{vap}(i)}/T_{\text{B}(i)} = \text{const} \left(\approx 85 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) \quad (3)$$

where $T_{\text{B}(i)}$ is the boiling point of the i -th liquid and $\Delta S_{\text{vap}(i)}$ and $\Delta H_{\text{vap}(i)}$ are the entropy and enthalpy of vaporization, respectively.

The linear and reciprocal Kovats retention index–boiling points relationships are well known [10,22,23].

Linear model:

$$I_{(i)} = \left(\frac{100 \cdot 85}{\Delta\mu_{p(\text{CH}_2)}} \right) T_{\text{B}} - \frac{100 \cdot 85 \cdot T}{\Delta\mu_{p(\text{CH}_2)}} \quad (4)$$

or

$$I = a \cdot T_{\text{B}} + b \quad (5)$$

where $a = \frac{100 \cdot 85}{\Delta\mu_{p(\text{CH}_2)}}$, $b = -\frac{100 \cdot 85 \cdot T}{\Delta\mu_{p(\text{CH}_2)}}$ and T is column temperature.

Reciprocal model:

$$l_{(i)} = \frac{100 \cdot \bar{\Delta H}_{\text{vap}}}{\Delta\mu_{\text{p(CH}_2)}} - \frac{100 \cdot \bar{\Delta H}_{\text{vap}} \cdot T}{\Delta\mu_{\text{p(CH}_2)}} \cdot \frac{1}{T_{\text{B}}} \quad (6)$$

or

$$l = \frac{c}{T_{\text{B}}} + d \quad (7)$$

where $c = -\frac{100 \cdot \bar{\Delta H}_{\text{vap}} \cdot T}{\Delta\mu_{\text{p(CH}_2)}}$, $d = \frac{100 \cdot \bar{\Delta H}_{\text{vap}}}{\Delta\mu_{\text{p(CH}_2)}}$, and $\bar{\Delta H}_{\text{vap}}$ is the mean value of the enthalpy of vaporization.

Eq. (4) can be rearranged using the corrected boiling point ($T_{\text{B}}-T$) instead of T_{B} [11]:

$$l_{(i)} = \frac{100 \cdot 85}{\Delta\mu_{\text{p(CH}_2)} (T_{\text{B}(i)} - T)} \quad (8)$$

or

$$l = b_0 + b_1 (T_{\text{B}(i)} - T) \quad (9)$$

Additionally, Eq. (6) can be rearranged using the corrected boiling point ($T_{\text{B}}-T$) instead of T_{B} [11]:

$$l_{(i)} = \frac{100 \cdot \bar{\Delta H}_{\text{vap}}}{\Delta\mu_{\text{p(CH}_2)}} \left(1 - \frac{T}{T_{\text{B}}}\right) \quad (10)$$

or

$$l = b_0 + b_1 \cdot \left(1 - \frac{T}{T_{\text{B}}}\right) \quad (11)$$

where only b_1 has physico-chemical meaning

$$b_1 = \frac{100 \cdot \bar{\Delta H}_{\text{vap}}}{\Delta\mu_{\text{p(CH}_2)}}$$

The parameter $\Delta\mu_{\text{p(CH}_2)}$ can be evaluated from these constants (except b_0).

In this study $\Delta\mu_{\text{p(CH}_2)}$ were calculated using the Kovats retention indices of previously synthesized 2-phenyl-2-alkylacetonitriles [24] obtained at 433 K on stationary phases of different polarity (OV-17, OV-210 and OV-225). The obtained results were compared with available literature data.

EXPERIMENTAL

The GC analyses were performed on a Varian 1400 gas chromatograph equipped with a flame ionization detector. Data handling was provided by a Varian 4720 data system.

The packed columns were laboratory-prepared using 2 m stainless steel columns, i.d. 2 mm, and commercially available materials were obtained from Varian:

1. 3% OV-17 on Chromosorb W HP 80/100,
2. 3% OV-210 on Chromosorb W HP 80/100 and
3. 3% OV-225 on Chromosorb W HP 80/100.

All the columns were operated under isothermal (160°C) conditions. The carrier gas was nitrogen, the carrier gas flow 20 ml/min, injector temperature 250°C, detector temperature 300°C.

RESULTS AND DISCUSSION

The experimental values of the Kovats retention indices of 2-phenyl-2-alkylacetonitriles and the calculated boiling points are given in Table 1.

The statistical evaluation of the quality of the fits of the experimental retention index l and calculated T_{B} values to the linear and reciprocal models is given in Tables 2 and 3. Table 2 summarize the results of the fits

Table 1. The Kovats retention indices of 2-phenyl-2-alkylacetonitriles on three packed columns at 160°C (433 K).

R	Column			T _B *, K
	OV-17	OV-210	OV-225	
H	1430.72	1574.95	1624.95	506.65
Me	1443.56	1613.61	1663.02	504.15
Et	1477.89	1647.28	1685.56	510.15
n-Pr	1567.95	1742.93	1771.12	528.35
n-Bu	1665.12	1813.35	1846.07	545.95
n-Pe	1787.08	1951.64	1977.18	563.15
n-He	1889.08	2056.73	2084.43	579.85
n-Hp	1995.93	2157.99	2179.54	596.25
n-Oc	2098.23	2260.29	2253.77	612.15
n-No	2190.25	2352.8	2343.13	627.65

*T_B data are calculated boiling points at atmospheric pressure taken from Scifinder database-data calculated using Advanced Chemistry Development (ACD) Software Solaris V4.67

Table 2. Kovats retention index vs. boiling point. Regression summary for the linear models $l = aT_{\text{B}} + b$ (Eq. 4) and $l = b_0 + b_1(T_{\text{B}} - T)$ (Eq.9) ($T = 433$ K, R -regression coefficient, n -number of points = 10, S -standard error)

	OV-17	OV-210	OV-225
a, slope	6.16	6.16	5.75
b, intercept	-1677.96	-1518.09	-1264.30
b ₁ , slope	6.16	6.16	5.75
b ₀ , intercept	989.29	1151.26	1227.83
R	0.9992	0.9978	0.9976
S	11.80	19.68	19.12

Table 3. Kovats retention index vs. boiling point. Regression summary for the reciprocal models $l = c/T_{\text{B}} + d$ (Eq.7) and $l = b_0 + b_1(1 - T/T_{\text{B}})$ (Eq.11) ($T = 433$ K, R -regression coefficient, n -number of points = 10, S -standard error)

	OV-17	OV-210	OV-225
c, slope	-1917142	-1918742	-1792497
d, intercept	5214.28	5379.74	5177.64
b ₁ , slope	4226.05	4429.74	4138.28
b ₀ , intercept	788.23	950.00	1039.36
R	0.9962	0.9949	0.9953
S	25.77	30.03	26.76

Table 4. Comparison of calculated $\Delta\mu_{p(CH_2)}$ values using Eq.(5, 7, 9 and 11) for packed column

$\Delta\mu_{p(CH_2)}$, J mol ⁻¹												
	from a Eq. (4)	from b Eq. (4)	from c Eq. (6)*	from c Eq. (6)**	from d Eq. (6)*	from d Eq. (6)**	from b ₁ Eq. (8)	from b ₁ Eq. (10)*	from b ₁ Eq. (10)**	average value	literature value	
OV-17	1379	2194	1184	1070	1005	908	1380	1240	1121	1275	2224***	1966***
OV-210	1379	2425	1182	1069	974	881	1380	1182	1069	1282	1456****	1158*****
OV-225	1478	2912	1265	1144	1012	915	1478	1266	1162	1403	1645****	1397*****

*the $\Delta\bar{H}_{vap}$ value was obtained using ΔH_{vap} values taken from Scifinder database–data calculated using Advanced Chemistry Development (ACD) Software Solaris V4.67; $\Delta\bar{H}_{vap} = 52,39$ kJ mol⁻¹

**the ΔH_{vap} value was obtained using Eq.(4); $\Delta H_{vap} = 47.38$ kJ mol⁻¹

*** at T=333 K (ref. 11)

****at T=373 K (ref. 11)

*****at T=423 K (ref. 11)

by the linear models in the form of Eqs. (5) and (9). Table 3 summarize the results of the fit by the reciprocal models in the form of Eqs.(7) and (11). The description of the linear model is slightly better than that of the reciprocal models.

Table 4 summarizes the results of a comparison for $\Delta\mu_{p(CH_2)}$ obtained using parameters a, b, c, d and b₁ according to Eqs. (4, 5, 8 and 10) and from the literature. The average values are also given. The fairness of the results depends on the precision of the $\Delta\bar{H}_{vap}$ value, which was obtained using ΔH_{vap} values taken from the Scifinder database for the investigated 2-phenyl-2-alkyl- acetonitriles, and the $\Delta\bar{H}_{vap}$ value, which was obtained using Eq. (3). The values from Trouton's rule, as well as from the Scifinder database should be treated only as approximate, because they are independent of the chemical nature and polarity of the stationary phase and of the temperature of the gas chromatographic analysis.

The calculated $\Delta\mu_{p(CH_2)}$ values show a large scatter. Values obtained from a, b (Eq.4) and b₁ (Eq.8) are independent of $\Delta\bar{H}_{vap}$. Values obtained from other constants depend on the used value of $\Delta\bar{H}_{vap}$. These values of $\Delta\mu_{p(CH_2)}$ show smaller scatter than the ones obtained from constants independent of $\Delta\bar{H}_{vap}$. The recommended practise is to use the average value of all the obtained $\Delta\mu_{p(CH_2)}$ values. As can be seen from Table 4, the obtained average values of $\Delta\mu_{p(CH_2)}$ fit the literature data for OV-210 and OV-225 stationary phase quite well, while for OV-17 this value is much lower, probably due to the fact that the literature value is obtained from only one set of data and mostly resembles the $\Delta\mu_{p(CH_2)}$ obtained from constant b.

CONCLUSION

The Kovats retention index –boiling point relationship of 2-phenyl-2-alkylacetonitriles was used to determine $\Delta\mu_{p(CH_2)}$ on stationary phases of different

polarity. The obtained values are in good agreement with the literature data.

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IZVOD

ZAVISNOST KOVAČEVOG RETENCIONOG INDEKSA OD TEMPERATURE KLJUČANJA 2-FENIL-2-ALKILACETONITRILA NA STACIONARNIM FAZAMA RAZLIČITE POLARNOSTI

(rad)

Dušan Ž. Mijin, Dušan G. Antonović

Katedra za organsku hemiju, Tehnološko-metalurški fakultet, Univerzitet u Beogradu,
Beograd, Srbija i Crna Gora

Poznati linearni izrazi zavisnosti Kovačevog retencionog indeksa od temperature ključanja su korišćeni za proučavanje zavisnosti Kovačevog retencionog indeksa od temperature ključanja prethodno sintetizovanih 2-fenil-2-alkilacetoneitrila. Kovačev retencioni indeks je dobijen na stacionarnim fazama različite polarnosti (OV-17, OV-210 i OV-225). Upotrebom linearnih i recipročnih modela izračunat je particioni hemijski potencijal metilenske grupe za ispitivane stacionarne faze i dobijene vrednosti su upoređene sa podacima iz literature.

Ključne reči: 2-fenil-2-alkilacetoneitrili, retencioni indeksi, gasna gromatografija, temperaturna zavisnost.