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–alkylacetonitriles 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–alkylacetonitriles; 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 \( I_0 \) can be transformed into the form [10]:

\[
I_0 = \frac{\Delta \mu_{p(i)} - \Delta \mu_{p(CH_3)}}{100 - \Delta \mu_{p(CH_3)}}
\]

where \( \Delta \mu_{p(i)} \) and \( \Delta \mu_{p(CH_3)} \) 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]:

\[
\frac{\Delta \mu_{p(i)}}{\Delta \mu_{p(CH_3)}} = z
\]

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 J mol\(^{-1}\) K\(^{-1}\) [21]:

\[
\Delta S_{vap(i)} = \Delta H_{vap(i)} / T_B(i) = \text{const} \times \left( \frac{85}{\text{J mol}^{-1} \text{K}^{-1}} \right)
\]

where \( T_B(i) \) is the boiling point of the i-th liquid and \( \Delta S_{vap(i)} \) and \( \Delta H_{vap(i)} \) 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:

\[
I_0 = \left( \frac{100 \cdot 85}{\Delta \mu_{p(CH_3)}} \right) T_B - \frac{100 \cdot 85 \cdot T}{\Delta \mu_{p(CH_3)}}
\]

or

\[
I = a \cdot T_B + b
\]

where \( a = \frac{100 \cdot 85}{\Delta \mu_{p(CH_3)}} \), \( b = - \frac{100 \cdot 85 \cdot T}{\Delta \mu_{p(CH_3)}} \) and \( T \) is column temperature.
Reciprocal model:

\[ l_b = \frac{100 \cdot \Delta H_{\text{vap}}}{\Delta H_{\text{p}(CH_2)}} - \frac{100 \cdot \Delta H_{\text{vap}} \cdot T}{\Delta H_{\text{p}(CH_2)} \cdot T_{B}} \]  \hspace{1cm} \text{(6)}

or

\[ l = \frac{c}{T_{B}} + d \]  \hspace{1cm} \text{(7)}

where \( c = -\frac{100 \cdot \Delta H_{\text{vap}} \cdot T}{\Delta H_{\text{p}(CH_2)}} \), \( d = \frac{100 \cdot \Delta H_{\text{vap}}}{\Delta H_{\text{p}(CH_2)}} \), and \( \Delta H_{\text{vap}} \) is the mean value of the enthalpy of vaporization.

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

\[ l(i) = \frac{100 \cdot \Delta H_{\text{vap}}}{\Delta H_{\text{p}(CH_2)}} \left( 1 - \frac{T}{T_{B}} \right) \]  \hspace{1cm} \text{(10)}

or

\[ l = b_0 + b_1 \left( 1 - \frac{T}{T_{B}} \right) \]  \hspace{1cm} \text{(11)}

where only \( b_1 \) has physico-chemical meaning

\[ b_1 = \frac{100 \cdot \Delta H_{\text{vap}}}{\Delta H_{\text{p}(CH_2)}} \]

The parameter \( \Delta H_{\text{p}(CH_2)} \) can be evaluated from these constants (except \( b_0 \)).

In this study \( \Delta H_{\text{p}(CH_2)} \) were calculated using the Kovats retention indices of previously synthesized 2-phenyl-2-alkyloctanetolines [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 HP80/100,
2. 2% OV-210 on Chromosorb W HP80/100 and
3. 3% OV-225 on Chromosorb W HP80/100.

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-alkyloctanetolines and the calculated boiling points are given in Table 1.

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

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

<table>
<thead>
<tr>
<th>R</th>
<th>Column</th>
<th>Tb*, K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>OV-17</td>
<td>OV-210</td>
</tr>
<tr>
<td>H</td>
<td>1430.72</td>
<td>1574.95</td>
</tr>
<tr>
<td>Me</td>
<td>1443.56</td>
<td>1613.61</td>
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<td>Et</td>
<td>1477.89</td>
<td>1647.28</td>
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<tr>
<td>n-Pr</td>
<td>1567.95</td>
<td>1742.93</td>
</tr>
<tr>
<td>n-Bu</td>
<td>1665.12</td>
<td>1813.35</td>
</tr>
<tr>
<td>n-Pe</td>
<td>1787.08</td>
<td>1951.64</td>
</tr>
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<td>n-He</td>
<td>1889.08</td>
<td>2056.73</td>
</tr>
<tr>
<td>n-Hp</td>
<td>1995.93</td>
<td>2157.99</td>
</tr>
<tr>
<td>n-Oct</td>
<td>1980.23</td>
<td>2260.29</td>
</tr>
<tr>
<td>n-No</td>
<td>2190.25</td>
<td>2352.82</td>
</tr>
</tbody>
</table>

*\( T_{B} \) 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 model \( I = a + b \cdot T_{B} \) (Eq. 4) and \( I = b_0 + b_1 \cdot T_{B} \) (Eq. 9) (\( T_{B} = 433 \text{ K}, R = \text{regression coefficient}, \text{n-number of points} = 10, \text{S-standard error} \)).

<table>
<thead>
<tr>
<th>R</th>
<th>Column</th>
<th>( a )</th>
<th>( b )</th>
<th>( b_0 )</th>
<th>( b_1 )</th>
<th>( R )</th>
<th>( S )</th>
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<tr>
<td></td>
<td>OV-17</td>
<td>6.16</td>
<td>6.16</td>
<td>-1677.96</td>
<td>1518.09</td>
<td>-1264.30</td>
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<tr>
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<td>OV-210</td>
<td>6.16</td>
<td>6.16</td>
<td>989.29</td>
<td>115.126</td>
<td>1227.83</td>
<td>5.75</td>
</tr>
<tr>
<td></td>
<td>OV-225</td>
<td>6.16</td>
<td>6.16</td>
<td>989.29</td>
<td>115.126</td>
<td>1227.83</td>
<td>5.75</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>R</th>
<th>Column</th>
<th>( c )</th>
<th>( b )</th>
<th>( d )</th>
<th>( b_1 )</th>
<th>( b_0 )</th>
<th>( R )</th>
<th>( S )</th>
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<tr>
<td></td>
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<td>-1917142</td>
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<td></td>
<td>OV-210</td>
<td>4226.05</td>
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<td>768.23</td>
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<tr>
<td></td>
<td>OV-225</td>
<td>4226.05</td>
<td>4429.74</td>
<td>768.23</td>
<td>950.00</td>
<td>1039.36</td>
<td>26.76</td>
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</table>
Table 4. Comparison of calculated Δμ_p(CH_2) values using Eq.(5, 7, 9 and 11) for packed column

<table>
<thead>
<tr>
<th>Δμ_p(CH_2), J mol^-1</th>
<th>from a Eq.(4)</th>
<th>from b Eq.(4)</th>
<th>from c Eq.(6)</th>
<th>from c Eq.(6)**</th>
<th>from d Eq.(6)**</th>
<th>from b Eq.(10)</th>
<th>from b Eq.(10)**</th>
<th>average value</th>
<th>literature value</th>
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<td>OV-17</td>
<td>1379</td>
<td>2194</td>
<td>1184</td>
<td>1070</td>
<td>1005</td>
<td>908</td>
<td>1360</td>
<td>1240</td>
<td>1121</td>
</tr>
<tr>
<td>OV-210</td>
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<td>2425</td>
<td>1182</td>
<td>1069</td>
<td>974</td>
<td>861</td>
<td>1380</td>
<td>1182</td>
<td>1069</td>
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<tr>
<td>OV-225</td>
<td>1478</td>
<td>2012</td>
<td>1265</td>
<td>1144</td>
<td>1012</td>
<td>915</td>
<td>1478</td>
<td>1266</td>
<td>1162</td>
</tr>
</tbody>
</table>

*the ΔH_vap value was obtained using ΔH_vap values taken from SciFinder database—data calculated using Advanced Chemistry Development (ACD) Software Solaris V4.67; ΔH_vap = 52.39 kJ mol⁻¹
** the ΔH_vap value was obtained using Eq.(4); ΔH_vap = 47.36 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 Δμ_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 ΔH_vap value, which was obtained using ΔH_vap values taken from the SciFinder database for the investigated 2-phenyl-2-alkylacetoinitriles, and the ΔH_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 Δμ_p(CH_2) values show a large scatter. Values obtained from a, b (Eq.4) and b1 (Eq.6) are independent of ΔH_vap. Values obtained from other constants depend on the used value of ΔH_vap. These values of Δμ_p(CH_2) show smaller scatter than the ones obtained from constants independent of ΔH_vap. The recommended practise is to use the average value of all the obtained Δμ_p(CH_2) values. As can be seen from Table 4, the obtained average values of Δμ_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 Δμ_p(CH_2) obtained from constant b.

CONCLUSION

The Kovats retention index-boiling point relationship of 2-phenyl-2-alkylacetoinitriles was used to determine Δμ_p(CH_2) on stationary phases of different polarity. The obtained values are in good agreement with the literature data.

ACKNOWLEDGEMENT

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REFERENCES

IZVOD

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

(red)

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