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# CORRELATIONS BETWEEN PHYSICO-CHEMICAL PROPERTIES OF UNSATURATED HYDROCARBONS AND THEIR RETENTION INDICES ON GRAPHITIZED THERMAL CARBON BLACK

As part of our study of gas adsorption chromatography on graphitized thermal carbon black (GTCB) we have correlated Kováts retention indices ($I_R$) with physico-chemical parameters, viz. boiling point ($t_B$), molar volume ($V_m$), third-order connectivity index ($\chi$) and molar refraction ($R_m$) for $C_6$—$C_{11}$ linear alkenes, alkynes, *n*-alkyl substituted cyclopentenes and cyclohexenes. We aimed at obtaining the best fitting empirical equations from which retention indices and physico-chemical properties could be predicted. This kind of information for the above systems is quite limited because in the literature property-retention relationships have been discussed mainly qualitatively. In this respect, investigations by A. V. Kiselev and K. D. Shcherbakova et al. on lower homologues [1, 2] are the most prominent. The quantitative relationships between $I$ and $n$, $I$ and $t_B$ ($n$ — carbon number of homologues, $t_B$ — boiling point of adsorbate at normal pressure, 760 mmHg, K) for compounds of these series have been discussed in [3–5].

In this study, the $I_R$ values obtained experimentally [3, 4] and the physico-chemical properties taken from [6, 7] were used. These data are given in Table 1. $V_m$ was calculated from $M/d$ ($M$ — molecular weight, $d$ — density), $R_m$ from the Lorentz-Lorenz expression: $R_m=(n_D^2-1)\times \times M/(n_D^2+2)d$. The $n_D$ (refractive index) and $d$ values were also taken from [6]. The molar refraction is linearly related to the electronic polarizability ($\alpha$) of the adsorbate ($R_m=4\pi N_A\alpha/3$, $N_A$ being Avogadro's number — $6.023\cdot10^{23}$).

The adsorption on the highly homogeneous non-specific surface of GTCB takes place mainly due to dispersion interaction [8] whose energy is determined by the distance from the adsorbent surface to the force centres of the linkages (the geometrical arrangement) of the adsorbed molecule and the polarizability of the latter. On the basis of this it may be assumed that $R_m$ accounts for the polarizability, whereas the $V_m$ and $\chi$ values of adsorbate contribute to steric factors. For the homologous series of hydrocarbons the molar refraction and molar volume are a suitable choice because these properties are responsible for dispersive interactions between different adsorbate molecules and the adsorbent surface.

The following types of correlation equations were examined:

$$y_i=A+Bx_i \quad \text{(linear)} \tag{1}$$
$$y_i=A+Bx_i+Cx_i^2 \quad \text{(quadratic)} \tag{2}$$
$$y_i=A+Bx_i+C/x_i \tag{3}$$
$$y_i=A+B/(C+x_i) \quad \text{(Antoine type equation)} \tag{4}$$

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$y_i = A \exp(Bx_i)$ (exponential) (5)

$x_i = t_B,\ R_m,\ V_m$

$y_i = A + Bx_{1i} + Cx_{2i}$ (two variables, linear) (6)

$y_i = A + Bx_{1i} + C/x_{2i}$ (7)

$y_i = A + B/x_{1i} + Cx_{2i}$ (8)

$y_i = A + Bx_{1i}^2 + Cx_{2i}$ (two variables, quadratic) (9)

$y_i = A + Bx_{1i}^2 + C/x_{2i}$ (10)

$x_{1i} = t_B \quad x_{2i} = R_m,\ V_m,\ \chi.$

The dependent variable ($y_i$) was the Kováts retention index on the graphitized thermal carbon black at 175°C. The independent variables $t_B$, $R_m$, $V_m$, $\chi$ and their reciprocal values were studied. The regression coefficients $A$, $B$ and $C$ describe quantitatively the sensitivity of the retention process to the adsorbate molecular parameters on the adsorbate-adsorbent interaction.

To estimate the above equations the multiple correlation coefficient ($R$) and residual variance ($s$) were used:

$$R = \sqrt{\sum (I^c - I^{av.})^2 / \sum (I^e - I^{av.})^2}; \quad s = \sqrt{\sum (I^e - I^c)^2 / (m - p)},$$

where $I^c$ — the retention index calculated by the correlation equation, $I^{av.}$ — arithmetic mean of experimental values ($I^e$) in the series, $m$ — the number of experimental points, and $p$ — the number of coefficients in the correlation equation. The closer the $R$ value to 1 (or 100%), the better the fit. The closer the $s$ value to zero, the better the fit.

Calculations were carried out on an Iskra 1030 computer using linear and multilinear regression programmes. For comparison also $n$-alkanes were investigated.

Among 400 fitting equations the best representatives for Kováts retention indices are summarized in Table 2. The high correlation coefficients ($R > 0.9999$) and low $s$ values show that the equations derived can be used for predicting the $I_R$ values of higher isomers. The absolute average deviations ($\Delta I$) between the experimental and calculated $I$ values

$$[\Delta I = 1/m \sum_m (I^e - I^c)]$$

vary from 0.03 to 1.25 index units that are close to the experimental error of the determination of $I_R$ values [3, 4].

For the homologous series of isomers retention index vs. boiling point plots are not linear as seen in the Figure where $I_R - t_B$ relationships for *cis*- and *trans*-2-alkenes are given. As seen from Table 2, the best equations for $I_R = f(t_B)$ relationships are those of Antoine type [(1), (5), (9), (16), (31)], quadratic equations [(13), (22), (28), (40)] and inverse ones [(25), (36)].

The introduction of $R_m$ or $V_m$ values into correlation equations of types (1)—(5) improves the results so that the $R$ values are better than 0.99997 and $s$ values are $\leqslant 1.66$.

Relationships $I_R = f(t_B, R_m)$, $I_R = f(t_B, V_m)$, $I_R = f(t_B, \chi)$ were studied and the best correlations were found by equations (6)—(10). The equations with two independent variables improve the correlation. The high regression coefficients at $R_m$ and $V_m$ in the above equations show the sensitivity of the retention process on GTCB to the polarizability and steric effects (Table 2).

The parameters presented in Table 1 describing the structure of the compounds studied depend on the carbon number and position of the multiple bond in the linear molecule as well as on the position of the side chain in the molecule of cyclenes. All the parameters increase with the increasing number of carbon atoms in the molecule.

*Table 1*

**$I_R$ on graphitized thermal carbon black at 175 °C and physico-chemical properties of hydrocarbons**

| Compound | $I_R$ | $t_B$, °C | $R_m$, cm³/mol | $V_m$, cm³/mol | $n_D$ | $d \cdot 10^3$ g/cm³ | $\varkappa$ |
|---|---|---|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| $C_6$ | | | | | | | |
| 3-Methylcyclopentene | 522.12 | 65.07 | 27.312 | 107.767 | 1.4207 | 762.2 | |
| 1-Methylcyclopentene | 554.20 | 75.78 | 27.362 | 105.281 | 1.4330 | 780.2 | |
| 1-Hexyne | 563.61 | 71.38 | 27.790 | 114.929 | 1.39884 | 714.7 | |
| 2-Hexyne | 567.40 | 84.52 | 28.056 | 112.290 | 1.41394 | 731.5 | |
| 3-Hexyne | 550.47 | 81.43 | 28.207 | 113.531 | 1.41129 | 723.5 | |
| *n*-1-Hexene | 576.96 | 63.49 | 29.491 | 125.014 | 1.38788 | 673.17 | 0.7618 |
| *cis*-2-Hexene | 569.64 | 68.84 | 29.531 | 122.468 | 1.39761 | 687.2 | 0.6910 |
| *cis*-3-Hexene | 564.67 | 66.45 | 29.661 | 123.783 | 1.39479 | 679.9 | 0.6381 |
| *trans*-2-Hexene | 590.48 | 67.88 | 29.668 | 124.133 | 1.39363 | 677.95 | |
| *trans*-3-Hexene | 576.56 | 67.09 | 29.749 | 124.287 | 1.39429 | 677.11 | |
| *n*-Hexane | 600 | 68.74 | 29.922 | 130.688 | 1.37508 | 659.37 | |
| $C_7$ | | | | | | | |
| 3-Ethylcyclopentene | 622.22 | 97.81 | 31.849 | 122.817 | 1.4319 | 783.0 | |
| 1-Ethylcyclopentene | 633.12 | 106.11 | 31.954 | 120.766 | 1.4420 | 796.3 | |
| 1-Methylcyclohexene | 633.53 | 110.02 | 31.908 | 118.709 | 1.4501 | 810.1 | |
| 1-Heptyne | 655.96 | 99.78 | 32.425 | 131.231 | 1.40873 | 732.8 | |
| 2-Heptyne | 661.26 | 111.25 | 32.664 | 128.633 | 1.42165 | 747.6 | |
| 3-Heptyne | 648.22 | 107.00 | 32.889 | 130.306 | 1.41874 | 738.0 | |
| *n*-1-Heptene | 680.79 | 93.64 | 34.135 | 140.868 | 1.39980 | 696.98 | 1.0118 |
| *cis*-2-Heptene | 671.08 | 98.50 | 34.161 | 138.452 | 1.40811 | 709.2 | 0.9600 |
| *cis*-3-Heptene | 661.46 | 95.75 | 34.211 | 139.217 | 1.40610 | 705.1 | 0.8577 |
| *trans*-2-Heptene | 685.26 | 97.95 | 34.311 | 140.080 | 1.40470 | 700.9 | |
| *trans*-3-Heptene | 675.39 | 95.67 | 34.389 | 140.461 | 1.40450 | 699.0 | |
| *n*-Heptane | 700 | 98.43 | 34.566 | 146.574 | 1.38774 | 683.6 | |
| $C_8$ | | | | | | | |
| 3-Ethylcyclohexene | 717.32 | 134.45 | 36.161 | 134.430 | 1.4505 | 819.7 | |
| 1-Ethylcyclohexene | 716.66 | 136.66 | 36.419 | 133.647 | 1.4573 | 824.5 | |
| 3-*n*-Propylcyclopentene | 722.47 | 126.00 | 36.417 | 139.307 | 1.4359 | 791.0 | |
| 1-*n*-Propylcyclopentene | 730.57 | 131.19 | 36.455 | 136.455 | 1.4461 | 806.2 | |

*Table 1* (continued)

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|
| 1-Octyne | 757.34 | 126.30 | 37.057 | 147.651 | 1.41606 | 746.3 | |
| 2-Octyne | 768.27 | 138.09 | 37.325 | 145.123 | 1.42785 | 759.3 | |
| 3-Octyne | 741.32 | 133.32 | 37.507 | 146.590 | 1.42531 | 751.7 | |
| 4-Octyne | 735.05 | 131.41 | 37.526 | 146.864 | 1.42465 | 750.3 | |
| *n*-1-Octene | 777.76 | 121.30 | 38.756 | 156.847 | 1.40874 | 715.4 | 1.2618 |
| *cis*-2-Octene | 768.64 | 125.63 | 38.860 | 154.855 | 1.41600 | 724.6 | 1.2100 |
| *cis*-3-Octene | 760.78 | 122.96 | 38.897 | 155.542 | 1.41435 | 721.4 | 1.1267 |
| *cis*-4-Octene | 751.09 | 122.55 | 38.927 | 155.434 | 1.41505 | 721.9 | 1.0744 |
| *trans*-2-Octene | 787.61 | 124.95 | 38.904 | 155.953 | 1.41320 | 719.5 | |
| *trans*-3-Octene | 769.84 | 123.28 | 39.036 | 156.606 | 1.41282 | 716.5 | |
| *trans*-4-Octene | 774.90 | 122.32 | 39.044 | 156.847 | 1.41220 | 715.4 | |
| *n*-Octane | 800 | 124.67 | 39.203 | 162.573 | 1.39761 | 702.6 | |
| $C_9$ | | | | | | | |
| 1-*n*-Propylcyclohexene | 804.58 | 154.65 | 40.954 | 150.149 | 1.4578 | 827.3 | |
| 1-*n*-Butylcyclopentene | 822.94 | 156.73 | 40.989 | 152.639 | 1.4496 | 813.8 | |
| 3-*n*-Butylcyclopentene | 823.80 | 151.91 | 41.038 | 155.467 | 1.4408 | 799.0 | |
| 1-Nonyne | 856.54 | 150.80 | 41.673 | 163.984 | 1.42202 | 757.5 | |
| 2-Nonyne | 861.55 | 161.37 | 41.931 | 161.574 | 1.43227 | 768.8 | |
| 3-Nonyne | 842.81 | 156.67 | 42.107 | 162.930 | 1.43021 | 762.4 | |
| 4-Nonyne | 832.35 | 155.12 | 42.129 | 163.144 | 1.42982 | 761.4 | |
| *n*-1-Nonene | 878.27 | 146.87 | 43.415 | 173.108 | 1.41572 | 729.22 | 1.5118 |
| *cis*-2-Nonene | 868.58 | 150.79 | 43.436 | 170.887 | 1.42212 | 738.7 | 1.4600 |
| *cis*-3-Nonene | 856.66 | 147.98 | 43.579 | 171.958 | 1.42069 | 734.1 | 1.3767 |
| *cis*-4-Nonene | 847.60 | 147.39 | 43.595 | 171.840 | 1.42120 | 734.6 | 1.3464 |
| *trans*-2-Nonene | 885.57 | 150.06 | 43.576 | 172.286 | 1.41975 | 732.7 | |
| *trans*-3-Nonene | 872.35 | 148.18 | 43.690 | 172.876 | 1.41937 | 730.2 | |
| *trans*-4-Nonene | 871.00 | 147.77 | 43.728 | 173.208 | 1.41886 | 728.8 | |
| *n*-Nonane | 900 | 150.80 | 43.843 | 178.696 | 1.40547 | 717.7 | |
| $C_{10}$ | | | | | | | |
| 1-*n*-Butylcyclohexene | 902.80 | 180.85 | 45.677 | 166.961 | 1.4594 | 828.0 | |
| 3-*n*-Butylcyclohexene | 919.17 | — | 45.373 | 166.599 | 1.4570 | 829.8 | |
| 3-*n*-Pentylcyclopentene | 921.42 | — | 45.866 | 172.331 | 1.4450 | 802.2 | |
| 1-*n*-Pentylcyclopentene | 925.82 | 179.85 | 45.962 | 171.689 | 1.4480 | 805.2 | |
| 1-Decyne | 957.24 | 173.87 | 46.302 | 180.310 | 1.42708 | 766.7 | |
| 2-Decyne | 962.23 | 183.65 | 46.582 | 178.058 | 1.43628 | 776.4 | |

*Table 1* (continued)

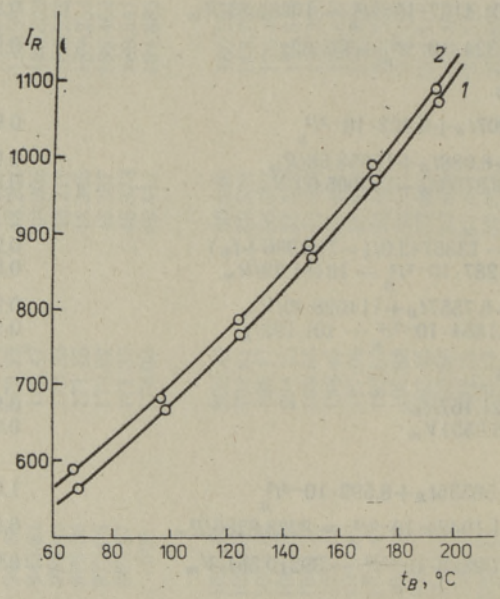
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|
| 3-Decyne | 939.02 | 178.82 | 46.726 | 179.328 | 1.43427 | 770.9 | |
| 4-Decyne | 932.87 | 177.37 | 46.760 | 179.538 | 1.43405 | 770.0 | |
| 5-Decyne | 922.90 | 177.33 | 46.794 | 179.748 | 1.43383 | 769.1 | |
| *n*-1-Decene | 977.59 | 170.57 | 48.059 | 189.333 | 1.42146 | 740.81 | 1.7618 |
| *cis*-2-Decene | 968.18 | 174.24 | 48.077 | 187.213 | 1.42710 | 749.2 | 1.7100 |
| *cis*-3-Decene | 956.51 | 171.34 | 48.236 | 188.370 | 1.42571 | 744.6 | 1.6267 |
| *cis*-4-Decene | 947.86 | 170.72 | 48.201 | 187.991 | 1.42633 | 746.1 | 1.5964 |
| *cis*-5-Decene | 945.61 | 170.47 | 48.208 | 188.092 | 1.42614 | 745.7 | 1.6154 |
| *trans*-2-Decene | 986.43 | 173.33 | 48.219 | 188.572 | 1.42501 | 743.8 | |
| *trans*-3-Decene | 970.36 | 171.45 | 48.345 | 189.234 | 1.42458 | 741.2 | |
| *trans*-4-Decene | 972.06 | 170.82 | 48.357 | 189.464 | 1.42411 | 740.3 | |
| *trans*-5-Decene | 965.57 | 171.32 | 48.373 | 189.541 | 1.42408 | 740.0 | |
| *n*-Decane | 1000 | 174.00 | 48.481 | 194.885 | 1.41189 | 730.05 | |
| $C_{11}$ | | | | | | | |
| 1-*n*-Hexylcyclopentene | 1021.11 | 202.42 | 50.546 | 186.651 | 1.4540 | 815.8 | |
| 3-*n*-Hexylcyclopentene | 1023.96 | 198.61 | 50.531 | 188.757 | 1.4480 | 806.7 | |
| 1-Undecyne | 1055.85 | 195.17 | 50.873 | 196.401 | 1.43134 | 775.3 | |
| 2-Undecyne | 1060.52 | 204.25 | 51.212 | 194.545 | 1.4394 | 782.7 | |
| 3-Undecyne | 1041.73 | 199.85 | 51.466 | 196.250 | 1.4375 | 775.9 | |
| 4-Undecyne | 1033.18 | 198.45 | 51.451 | 196.427 | 1.4369 | 775.2 | |
| 5-Undecyne | 1027.62 | 197.99 | 51.444 | 196.401 | 1.43691 | 775.3 | |
| 1-Undecene | 1076.48 | 192.67 | 52.672 | 205.523 | 1.42611 | 750.7 | 2.0118 |
| *cis*-2-Undecene | 1071.30 | 195.88 | 52.721 | 203.705 | 1.43093 | 757.4 | 1.9600 |
| *cis*-3-Undecene | 1060.76 | 193.45 | 52.822 | 204.515 | 1.42991 | 754.4 | 1.8767 |
| *cis*-4-Undecene | 1050.72 | 192.66 | 52.852 | 204.407 | 1.43045 | 754.8 | 1.8464 |
| *cis*-5-Undecene | 1045.35 | 192.15 | 52.891 | 204.678 | 1.43016 | 753.8 | 1.8654 |
| *trans*-2-Undecene | 1084.74 | 195.19 | 52.858 | 204.895 | 1.42933 | 753.0 | |
| *trans*-3-Undecene | 1067.20 | 193.31 | 52.954 | 205.413 | 1.42898 | 751.1 | |
| *trans*-4-Undecene | 1069.73 | 192.90 | 52.992 | 205.770 | 1.42849 | 749.8 | |
| *trans*-5-Undecene | 1065.30 | 192.86 | 53.027 | 205.907 | 1.42848 | 749.3 | |
| *n*-Undecane | 1100 | 195.89 | 53.133 | 211.150 | 1.4173 | 740.24 | |

**The best representatives among the fitting equations for Kováts retention indices on graphitized thermal carbon black at 175° C**

| Equation | $R$ | $s$ |
|---|---|---|
| *n*-Alkanes | | |
| (1) $I_R = -1929.1 - 1948113.0/(-839.07+t_B)$ | 0.99998 | 1.64 |
| (2) $I_R = -46.032+21.612R_m - 7.814\cdot 10^{-4}R_m^2$ | 0.99999 | 0.09 |
| (3) $I_R = -146.31+6.022V_m - 5318.43/V_m$ | 1 | 0.04 |
| (4) $I_R = -250.51 - 76.704\cdot 10^{-5}t_B^2 + 6.536V_m$ | 0.99999 | 0.07 |
| 1-Alkenes | | |
| (5) $I_R = -1943.6 - 1972943.0/(-845.97+t_B)$ | 0.99998 | 1.41 |
| (6) $I_R = -37.871 - 654.80/t_B + 21.213R_m$ | 0.99999 | 1.18 |
| (7) $I_R = -156.66 - 1257.58/t_B + 6.0300V_m$ | 0.99999 | 1.08 |
| (8) $I_R = 288.30 - 673.40/t_B + 393.40\chi$ | 0.99999 | 1.28 |
| *cis*-2-Alkenes | | |
| (9) $I_R = -1593.03 - 1464234.0/(-745.62+t_B)$ | 0.99998 | 1.35 |
| (10) $I_R = -183.38+6.1557V_m$ | 0.99998 | 1.44 |
| (11) $I_R = 883.618+101.4107\cdot 10^{-4}t_B^2 - 10669.85/R_m$ | 0.99998 | 1.43 |
| (12) $I_R = 327.04+22.324\cdot 10^{-4}t_B^2 + 335.82\chi$ | 0.99999 | 0.63 |
| *trans*-2-Alkenes | | |
| (13) $I_R = 410.07+2.207t_B+6.422\cdot 10^{-3}t_B^2$ | 0.99997 | 1.96 |
| (14) $I_R = -462.172+6.088t_B+18958.58/R_m$ | 0.99998 | 1.44 |
| (15) $I_R = -815.07+6.8100t_B+117005.02/V_m$ | 0.99998 | 1.58 |
| *cis*-3-Alkenes | | |
| (16) $I_R = -1483.42 - 1336742.0/(-718.996+t_B)$ | 0.99999 | 1.22 |
| (17) $I_R = 873.15+10.287\cdot 10^{-2}t_B^2 - 10481.99/R_m$ | 0.99998 | 1.57 |
| (18) $I_R = -804.849+6.7557t_B+114028.40/V_m$ | 0.99997 | 1.76 |
| (19) $I_R = 670.911+1.1854\cdot 10^{-2}t_B^2 - 101.192/\chi$ | 0.99999 | 0.37 |
| *trans*-3-Alkenes | | |
| (20) $I_R = -53.544+21.167R_m$ | 0.99997 | 1.66 |
| (21) $I_R = -176.01+6.0551V_m$ | 0.99997 | 1.56 |
| *cis*-4-Alkenes | | |
| (22) $I_R = 430.222+1.56536t_B+8.592\cdot 10^{-3}t_B^2$ | 1.0 | 0.02 |
| (23) $I_R = 796.6016+1.10424\cdot 10^{-2}t_B^2 - 8228.8286/R_m$ | 0.99999 | 0.21 |
| (24) $I_R = 840.6966+1.0828\cdot 10^{-2}t_B^2 - 39210.561/V_m$ | 0.99999 | 0.22 |
| *trans*-4-Alkenes | | |
| (25) $I_R = -103.328+5.34925t_B+27350.810/t_B$ | 0.99996 | 2.06 |
| (26) $I_R = -54.1928+21.2059R_m$ | 0.99994 | 1.78 |
| (27) $I_R = -174.228+6.0453V_m$ | 0.99995 | 1.62 |
| 1-Alkynes | | |
| (28) $I_R = 370.65+2.21665t_B+6.644\cdot 10^{-3}t_B^2$ | 0.99998 | 1.42 |
| (29) $I_R = -378.798+5.8855t_B+14517.08/R_m$ | 0.99999 | 0.91 |
| (30) $I_R = -560.322+6.2465t_B+77912.76/V_m$ | 0.99999 | 0.85 |
| 2-Alkynes | | |
| (31) $I_R = -1938.95 - 1824244.0/(-812.463+t_B)$ | 0.99998 | 1.65 |
| (32) $I_R = 801.410+1.0262\cdot 10^{-2}t_B^2 - 8643.165/R_m$ | 0.99995 | 2.28 |
| (33) $I_R = 847.420+9.9807\cdot 10^{-3}t_B^2 - 39523.88/V_m$ | 0.99995 | 2.31 |
| 3-Alkynes | | |
| (34) $I_R = -94.9185 - 0.78685t_B+25.14631R_m$ | 0.99997 | 1.74 |
| (35) $I_R = -166.955+1949.350/t_B+6.10960V_m$ | 0.99998 | 1.67 |

*Table 2* (continued)

| Equation | $R$ | $s$ |
|---|---|---|
| 4-Alkynes | | |
| (36) $I_R = -251.6296 + 5.66701 t_B + 31796.050/t_B$ | 0.99999 | 0.11 |
| (37) $I_R = -738.223 + 6.79338 t_B + 21782.911/R_m$ | 0.99999 | 0.43 |
| (38) $I_R = -978.266 + 7.29108 t_B + 110904.101/V_m$ | 0.99999 | 0.28 |
| 1-*n*-Alkyl-1-cyclopentenes | | |
| (39) $I_R = -90.2556 + 3883.487/t_B + 21.6331 R_m$ | 0.99990 | 3.31 |
| 3-*n*-Alkyl-1-cyclopentenes | | |
| (40) $I_R = 359.13525 + 2.07767 t_B + 6.4038 \cdot 10^{-3} t_B^2$ | 0.999986 | 1.45 |
| (41) $I_R = -114.20575 + 24.17689 R_m - 3.26354 \cdot 10^{-2} R_m^2$ | 0.999996 | 0.79 |
| (42) $I_R = 900.45654 + 9.1751 \cdot 10^{-3} t_B^2 - 44967.1959/V_m$ | 0.999995 | 0.87 |
| 1-*n*-Alkyl-1-cyclohexenes | | |
| (43) $I_R = -2168.78 - 440400.9/(-189.0597 + R_m)$ | 0.999999 | 0.32 |
| (44) $I_R = 68.99719 + 2.5564 \cdot 10^{-3} t_B^2 + 4.492184 V_m$ | 0.999996 | 0.58 |




Retention indices on graphitized thermal carbon black at 175 °C vs. boiling points for the $C_6$—$C_{11}$ homologs of *cis*-2-alkenes (*1*) and *trans*-2-alkenes (*2*).

*Table 3*

**Dependence of $I_R$ values at 175° C of $C_6$ hydrocarbons on their physico-chemical properties**

| Compound | $I_R$ | $t_B$, °C | $R_m$, cm³/mol | $V_m$, cm³/mol |
|---|---|---|---|---|
| 1-Methylcyclopentene | 554.20 | 75.78 | 27.362 | 105.281 |
| 2-Hexyne | 567.40 | 84.52 | 28.056 | 112.290 |
| *cis*-2-Hexene | 569.64 | 68.84 | 29.531 | 122.468 |
| *trans*-2-Hexene | 590.48 | 67.88 | 29.668 | 124.133 |
| *n*-Hexane | 600 | 68.74 | 29.922 | 130.688 |

In case of the same number of carbon atoms in the adsorbate molecule, the $I_R$ values do not increase with the boiling point, but with the increasing molar refraction and molar volume as shown in Table 3. *n*-Alkanes with the highest molar refraction and therefore the highest electronic polarizability are most strongly retained on GTCB. The boiling points of *n*-alkynes are higher than those of *cis*-alkenes and *trans*-alkenes (by the same carbon number and position of the multiple bond), but their elution order from GTCB is as follows: *n*-alkyne, *cis*-alkene, *trans*-alkene, *n*-alkane. The elution order of $C_9$ compounds with close boiling points is the following: 1-nonyne (150.80 °C), *cis*-2-nonene (150.79 °C), *n*-nonane (150.80 °C). The differences in their retention indices are: 1-nonyne/*n*-nonane 43.5 e. u., *cis*-2-nonene/*n*-nonane 31.4 e. u. They may be explained by the changes in their molar refraction (1-nonyne/*n*-nonane 2.17 $cm^3$/mol, *cis*-2-nonene/*n*-nonane 0.41 $cm^3$/mol) and molar volume values (1-nonyne/*n*-nonane 14.71 $cm^3$/mol, *cis*-2-nonene/*n*-nonane 7.81 $cm^3$/mol). Analogous regularities are observed for the other compounds having close boiling points and they are explained by differences between the intermolecular interactions of adsorbates in the liquid phase (boiling point) and the adsorbent on a low surface coverage on GTCB in the case of adsorption.

In case of the same carbon number *cis*- and *trans*-isomers of *n*-alkenes are eluted according to the double bond displacement from the centre towards the end of the molecule (5-, 4-, 3-, 2-isomers), i. e. by an increase of the boiling point, refractive index, density and third-order connectivity index. The same regularity is observed for the isomers of *n*-alkynes. At the same time, the $R_m$ values (electronic polarizability) decrease in the same order.

## Conclusions

The retention indices of $C_6$—$C_{11}$ *n*-alkanes, *n*-alkenes, *n*-alkynes, *n*-alkyl substituted cyclopentenes and cyclohexenes at the column temperature of 175 °C on the graphitized thermal carbon black reveal the best correlation with the boiling points of hydrocarbons by the Antoine or quadratic equations. For a homologous series of hydrocarbons equations with two independent variables, including the boiling point on the one hand, and the molar refraction or the molar volume or the connectivity index on the other, describe the "property-retention" relationships more exactly than those with one independent variable.

At the same carbon number and position of the multiple bond/substituent in the molecule the retention indices increase in the order: alkylcycloalkene $<$ *n*-alkyne $<$ *cis*-alkene $<$ *trans*-alkene $<$ *n*-alkane, i. e. in accordance with the increase in their electronic polarizability, molar refraction and molar volume. The boiling point, refractive index, density and third-order connectivity index describe satisfactorily the changes of the $I_R$ values with the position of the multiple bond.

The equations obtained can be used to predict retention indices or physico-chemical properties of higher homologues of these series needed for their identification.

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## KÜLLASTUMATA SÜSIVESINIKE FÜÜSIKALIS-KEEMILISTE OMADUSTE JA TERMILISELT GRAFIIDITUD TAHMAL MÕÕDETUD RETENTSIOONIINDEKSITE VAHELISED KORRELATSIOONID


On uuritud $C_6$—$C_{11}$ *n*-alkaanide, *n*-alkeenide, *n*-alküünide, alküülasendatud tsüklopenteenide ja tsükloheksenide (kokku 90 ühendi) retentsiooniindeksite (mõõdetud termiliselt grafiiditud tahmal kolonni temperatuuril 175 °C) sõltuvust nende ühendite füüsikalis-keemilistest omadustest — keemistemperatuurist, tihedusest, murdumisnäitajast, molekulaarsest refraktsioonist, polariseeritavusest, mooli ruumalast ning konnektiivsusindeksist. On näidatud, et süsivesinike homoloogiliste ridade puhul kirjeldavad seoseid omadus—retentsiooniindeks kõige paremini kahe sõltumatu muutujaga korrelatsioonivõrrandid, mis sisaldavad ühe muutujana keemistemperatuuri ning teise muutujana kas molekulaarset refraktsiooni, mooli ruumala või konnektiivsusindeksit. Esitatud võrrandid võimaldavad arvutada kõrgemate homoloogide identifitseerimiseks vajalikke retentsiooniindekseid ja füüsikalis-keemilisi omadusi.



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## КОРРЕЛЯЦИИ МЕЖДУ ФИЗИКО-ХИМИЧЕСКИМИ СВОЙСТВАМИ НЕНАСЫЩЕННЫХ УГЛЕВОДОРОДОВ И ИХ ИНДЕКСАМИ УДЕРЖИВАНИЯ НА ГРАФИТИРОВАННОЙ ТЕРМИЧЕСКОЙ САЖЕ


Исследована связь между физико-химическими свойствами (температурой кипения, плотностью, показателем преломления, молекулярной рефракцией, поляризуемостью, молярным объемом, индексом связанности) *н*-алканов, *н*-алкенов, *н*-алкинов, *н*-алкилзамещенных циклопентенов и циклогексенов состава $C_6$—$C_{11}$ (всего 90 соединений) и их индексами удерживания на графитированной термической саже при температуре 175 °C. Показано, что для гомологических рядов углеводородов зависимости «свойство—индекс удерживания» наиболее точно описываются уравнениями, содержащими две независимые переменные величины, одной из которых является температура кипения, а другой — молекулярная рефракция, молярный объем или индекс связанности. Рекомендуемые корреляционные уравнения позволяют предсказать индексы удерживания и физико-химические характеристики, необходимые для идентификации высших гомологов.