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The temperature dependence of the retention index for *n*-alkyl esters of acetic, propionic, cyclohexanecarboxylic, benzoic and phenylacetic acid on DB-1 and DB-5 capillary columns

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Abstract: The temperature dependence of the retention index was studied for *n*-alkyl esters of acetic, propionic, cyclohexanecarboxylic, benzoic and phenylacetic acid on DB-1 and DB-5 capillary columns. The study was performed over various temperature ranges depending on the volatility of the ester. Two linear equations of the temperature dependence of the retention data on the column temperature and its reciprocal as variables were studied. A good linearity of the retention index *versus* column temperature was found.

Keywords: retention indices, alkyl esters, temperature dependence.

INTRODUCTION

In 1952 James and Martin introduced gas-liquid chromatography.[1] Six years later, Kovats published a work in which he elaborated a universal retention system.[2] The Kovats retention index I has become a useful analytical tool for the identification of a compound by gas chromatography, and since these indices are not sensitive to the gas chromatographic conditions, it can be reproduced in various laboratories.

The temperature dependence of the retention index against column temperature t, °C or $1/T$, K^{-1}, is given by:

$$I = a + bt \tag{1}$$

$$I = A + B/T \tag{2}$$

where $b = dI/dT$, Eq. (1), corresponds (as $10\ dI/dT$) to the initially introduced Kovats retention index increments per 10 °C obtained by finite differences, $\Delta I/10$ °C.

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n-Alkyl esters of carboxylic acids are compounds widely used thanks to their odour and taste. They are also used as perfumery compounds. Some of the esters have been studied by Tudor, who made a detailed evaluation of Eqs. (1) and (2).[3,4] Some authors only indicated the Kovats retention index increment for some alkyl ester of certain carboxylic acids.[5]

As a part of our study[6–11] of chemical structure–retention index relationships, a study of the temperature dependence of the retention indices of a series of *n*-alkyl esters of acetic, propionic, cyclohexanecarboxylic, benzoic and phenylacetic acid (Table I) on DB-1 and DB-5 capillary columns is reported here.

TABLE I. Investigated compounds

R	CH_3COOR	CH_3CH_2COOR	$C_6H_{11}COOR$	C_6H_5COOR	$C_6H_5CH_2COOR$
Me	1	11	21	31	41
Et	2	12	22	32	42
n-Pr	3	13	23	33	43
n-Bu	4	14	24	34	44
n-Pe	5	15	25	35	45
n-He	6	16	26	36	46
n-Hp	7	17	27	37	47
n-Oc	8	18	28	38	48
n-No	9	19	29	39	49
n-De	10	20	30	40	50

EXPERIMENTAL

The GC analyses were performed on a Varian 3400 gas chromatograph equipped with a flame ionization detector and an all-glass split-splitless sample injector (1071 capillary injector). Data handling was provided by a Varian 4720 data system.

The employed capillary columns were as follows. DB-1: obtained from J & W Scientific, Folsom, CA, USA, dimensions 30 m × 0.256 mm, film thickness 0.25 μm, theoretical plates/meter 4554 for tridecane, coating efficiency 100.3 for tridecane. DB-5: obtained from J & W Scientific, Folsom, CA, USA, dimensions 60 m × 0.321 mm, film thickness 0.25 μm, theoretical plates/meter 3409 for tridecane, coating efficiency 94.5 for tridecane.

Both columns were operated under isothermal conditions as given in the tables.

The carrier gas was nitrogen, carrier gas flow 1 ml/min, injector temperature 250 °C, split ratio 1:60, detector temperature 300 °C, attenuation 1 and range 10^{-10} A/mV.

The investigated esters were obtained commercially by Fluka or prepared from *n*-alcohols and carboxylic acids by the general procedure given in ref. 12. The obtained compounds were then purified by distillation and/or microdistillation until GC purity was obtained. All products were characterized by IR and ^{1}H NMR spectroscopy.

The other used compounds were obtained commercially.

The hydrocarbons used in this study as standards were obtained from Fluka (Switzerland).

RESULTS AND DISCUSSION

Table II lists the parameters (*a,b*) of Eq. (1) and statistical data (*r*, correlation coefficient; *s*, standard error) as well as the parameters (*A*, *B*) of Eq. (2) and statisti-

TABLE II. The parameters *a,b;* correlation coefficient *r* and standard error *s* for the linear regressions using Eq. (1) and the parameters *A, B*; correlation coefficient *R* and standard error *S* for the linear regressions using Eq. (2) on capillary columns DB-1 and DB-5 in the temperature range 80–120 °C (*eI*=experimental value of the retention index, number of experimental points = 3) for acetic acid *n*-alkyl esters

Column	DB-1									DB-5								
Comp.	*eI*	*b*	*a*	*r*	*s*	*–B*	*A*	*R*	*S*	*eI*	*b*	*a*	*r*	*s*	*–B*	*A*	*R*	*S*
No	80 °C									80 °C								
1	501.15	0.5115	460.93	0.9929	1.73	4912.74	562.57	0.9999	0.06	522.17	0.6230	472.79	0.9979	1.14	5946.32	596.21	0.9987	0.88
2	578.95	0.5262	537.46	0.9950	1.49	5043.47	641.92	0.9998	0.22	600.00	0.6010	552.24	0.9989	0.79	5724.32	671.17	0.9976	1.16
3	684.60	0.5820	638.27	0.9994	0.56	5535.47	753.36	0.9967	1.32	705.64	0.6212	656.38	0.9980	1.09	5928.00	779.44	0.9986	0.92
4	784.76	0.5825	738.28	0.9996	0.48	5546.53	853.63	0.9963	1.41	805.85	0.6235	756.43	0.9980	1.12	5950.42	879.93	0.9987	0.90
5	887.63	0.5120	847.38	0.9929	1.74	4917.79	949.12	0.9999	0.06	908.68	0.6240	859.22	0.9979	1.14	5955.79	982.94	0.9987	0.88
6	988.13	0.5140	947.72	0.9929	1.73	4936.74	1049.86	0.9999	0.06	1010.21	0.6207	961.00	0.9980	1.10	5923.58	1083.96	0.9986	0.91
7	1089.15	0.5065	1049.28	0.9939	1.59	4860.00	1149.88	0.9999	0.06	1110.21	0.6260	1060.72	0.9966	1.46	5987.05	1184.86	0.9995	0.58
8	1190.56	0.5012	1151.23	0.9912	1.89	4822.11	1250.92	0.9998	0.30	1211.65	0.6220	1162.36	0.9978	1.16	5937.79	1285.59	0.9988	0.86
9	1289.39	0.5137	1249.12	0.9925	1.79	4936.42	1351.13	0.9999	0.11	1310.45	0.6200	1261.33	0.9977	1.19	5919.79	1384.18	0.9989	0.83
10	1389.27	0.5112	1349.07	0.9930	1.72	4909.89	1450.66	0.9999	0.05	1410.32	0.6218	1361.04	0.9979	1.14	5934.63	1484.22	0.9988	0.88

TABLE III. The parameters *a,b;* correlation coefficient *r* and standard error *s* for linear regressions using Eq. (1) and the parameters *A, B;* correlation coefficient *R* and standard error *S* for linear regressions using Eq.(2) on capillary columns DB-1 and DB-5 in the temperature range 80–120 ºC (*eI* = experimental value of the retention index, number of experimental points = 3) for propionic acid *n*-alkyl esters

Column	DB-1									DB-5								
Comp.	*eI*	*b*	*a*	*r*	*s*	*–B*	*A*	*R*	*S*	*eI*	*b*	*a*	*r*	*s*	*–B*	*A*	*R*	S
No	80 ºC									80 ºC								
11	578.95	0.5120	538.69	0.9930	1.72	4917.16	640.43	0.9999	0.05	600.00	0.6077	551.73	0.9987	0.87	5791.58	672.03	0.9980	1.09
12	678.95	0.5140	638.53	0.9930	1.72	4936.11	740.66	0.9999	0.04	700.00	0.6192	650.60	0.9981	1.08	5908.42	773.55	0.9986	0.93
13	778.99	0.5217	737.96	0.9931	1.74	5010.32	841.63	0.9999	0.04	800.00	0.6065	751.84	0.9986	0.89	5780.21	871.90	0.9980	1.08
14	880.42	0.4895	842.05	0.9904	1.93	4712.21	939.43	0.9997	0.33	901.48	0.5857	854.59	0.9999	0.07	5546.53	970.17	0.9929	1.96
15	980.41	0.5050	940.68	0.9934	1.64	4847.00	1040.99	0.9999	0.02	1001.50	0.5885	954.87	0.9978	1.11	5618.21	1071.46	0.9988	0.80
16	1079.95	0.5100	1039.85	0.9931	1.70	4897.58	1141.18	0.9999	0.04	1100.99	0.6000	1053.31	0.9989	0.79	5714.84	1172.04	0.9977	1.16
17	1180.06	0.5165	1139.48	0.9923	1.82	4963.89	1242.15	0.9999	0.14	1201.11	0.5990	1153.73	0.9970	1.32	5725.89	1272.48	0.9993	0.62
18	1280.60	0.5142	1240.18	0.9927	1.76	4940.21	1342.38	0.9999	0.08	1301.68	0.5857	1255.33	0.9971	1.26	5598.00	1371.44	0.9992	0.64
19	1380.10	0.5120	1339.84	0.9931	1.71	4916.84	1441.57	0.9999	0.04	1401.13	0.5970	1353.95	0.9964	1.42	5711.05	1472.35	0.9995	0.51
20	1480.05	0.5152	1439.54	0.9928	1.75	4949.05	1541.93	0.9999	0.07	1501.10	0.5982	1453.81	0.9965	1.43	5722.42	1572.46	0.9995	0.53

TABLE IV. The parameters *a,b;* correlation coefficient *r* and standard error *s* for linear regressions using Eq. (1) and the parameters *A, B;* correlation coefficient *R* and standard error *S* for linear regressions using Eq.(2) on capillary columns DB-1 and DB-5 in the temperature range 160–220 °C (*eI* = experimental value of the retention index, number of experimental points = 3) for cyclohexanecarboxylic acid *n*-alkyl esters

Column	DB-1									DB-5								
Comp.	*eI*	*b*	*a*	*r*	*s*	*–B*	*A*	*R*	*S*	*eI*	*b*	*a*	*r*	*s*	*–B*	*A*	*R*	S
No	160 °C									160 °C								
21	1005.17	0.2965	957.44	0.9985	0.68	10299.00	1068.91	0.9894	1.82	1009.57	0.3525	956.16	0.8982	7.31	12854.80	1091.94	0.9343	5.93
22	1105.82	0.2838	1060.46	0.9999	0.15	9919.92	1164.49	0.9969	0.94	1108.49	0.3675	1052.87	0.8931	7.85	13424.40	1194.58	0.9303	6.40
23	1205.98	0.2625	1164.10	0.9996	0.30	9186.81	1263.15	0.9980	0.70	1209.00	0.3621	1154.04	0.9024	7.33	13193.50	1293.48	0.9378	5.91
24	1305.46	0.2748	1261.62	0.9996	0.35	9620.43	1365.34	0.9981	0.71	1309.75	0.3395	1258.55	0.8830	7.65	1246.10	1389.57	0.9220	6.31
25	1405.39	0.2776	1361.20	0.9988	0.60	9736.80	1466.07	0.9991	0.49	1408.57	0.3595	1354.24	0.8897	7.82	13137.10	1492.87	0.9275	6.40
26	1506.12	0.2736	1462.40	0.9999	0.18	9567.15	1565.61	0.9971	0.87	1509.71	0.3433	1457.70	0.8976	7.15	12522.20	1589.96	0.9339	5.80
27	1606.09	0.2671	1563.54	0.9990	0.50	9364.42	1664.43	0.9989	0.52	1609.01	0.3550	1555.66	0.8721	8.45	13026.90	1692.84	0.9129	7.04
28	1706.03	0.3676	1663.43	0.9987	0.57	9387.04	1764.54	0.9992	0.46	1709.83	0.3382	1658.84	0.8826	7.63	12378.30	1789.35	0.9217	6.30
29	1806.51	0.2716	1763.14	0.9998	0.24	9502.23	1865.62	0.9976	0.80	1808.99	0.3565	1754.86	0.9046	7.12	12979.70	1892.07	0.9396	5.72
30	1905.95	0.2753	1861.98	0.9998	0.21	9627.78	1965.83	0.9973	0.85	1909.72	0.3375	1858.81	0.8837	7.58	12350.80	1989.92	0.9226	6.24

TABLE V. The parameters *a, b;* correlation coefficient *r* and standard error *s* for linear regressions using Eq. (1) and the parameters *A, B;* correlation coefficient *R* and standard error *S* for linear regressions using Eq.(2) on capillary columns DB-1 and DB-5 in the temperature range 170–210 °C (*eI* = experimental value of the retention index, number of experimental points = 3) for benzoic acid *n*-alkyl esters

Column	DB-1									DB-5								
Comp.	*eI*	*b*	*a*	*r*	*s*	*–B*	*A*	*R*	*S*	*eI*	*b*	*a*	*r*	*s*	*–B*	*A*	*R*	*S*
No	170 °C									170 °C								
31	1036.37	0.5412	944.19	0.9997	0.38	19221.90	1148.96	0.9963	1.31	1053.63	0.4707	973.38	0.9992	0.52	16703.70	1151.40	0.9950	1.33
32	1133.38	0.5650	1036.96	0.9984	0.88	20028.30	1250.51	0.9932	1.85	1153.14	0.4655	1073.61	0.9974	0.95	16484.20	1249.46	0.9912	1.75
33	1266.05	0.5572	1171.11	0.9995	0.49	19782.90	1381.89	0.9958	1.44	1287.24	0.4112	1216.81	0.9942	1.26	14531.20	1372.00	0.9858	0.96
34	1383.13	0.5447	1289.92	0.9996	0.46	19447.50	1497.01	0.9959	1.40	1404.06	0.3810	1338.33	0.9772	2.34	13372.60	1481.63	0.9625	2.99
35	1440.46	0.5497	1346.70	0.9989	0.74	19497.40	1554.53	0.9942	1.68	1462.27	0.4112	1392.25	0.9998	0.25	14608.60	1547.85	0.9966	0.95
36	1575.95	0.5517	1481.82	0.9986	0.80	19563.50	1690.39	0.9937	1.75	1595.76	0.4007	1526.89	0.9874	1.81	14115.30	1677.88	0.9760	2.50
37	1663.10	0.5462	1569.96	0.9990	0.68	19377.30	1776.49	0.9945	1.61	1682.49	0.4155	1611.43	0.9962	1.02	14700.80	1768.33	0.9892	1.73
38	1778.79	0.5292	1688.63	0.9995	0.45	18790.10	1888.82	0.9959	1.36	1792.23	0.5157	1704.00	0.9957	1.35	18241.20	1898.71	0.9883	2.23
39	1885.24	0.5577	1790.13	0.9990	0.69	19785.10	2001.02	0.9945	1.65	1909.71	0.3445	1851.05	0.9997	0.22	12235.90	1981.38	0.9964	0.81
40	1977.32	0.5580	1882.33	0.9998	0.31	19823.00	2093.46	0.9967	1.27	2003.36	0.3137	1949.87	0.9991	0.37	11131.30	2068.50	0.9947	0.91

TABLE VI. The parameters *a,b;* correlation coefficient *r* and standard error *s* for linear regressions using Eq. (1) and the parameters *A, B;* correlation coefficient *R* and standard error *S* for linear regressions using Eq.(2) on capillary columns DB-1 and DB-5 in the temperature range 160–220 ºC (*eI = experimental value of the retention index, number of experimental points = 3) for phenylacetic acid n*-alkyl esters

Column	DB-1									DB-5								
Comp.	*eI*	*b*	*a*	*r*	*s*	*–B*	*A*	*R*	*S*	*eI*	*b*	*a*	*r*	*s*	*–B*	*A*	*R*	*S*
No	160 ºC									160 °*C*								
41	1107.45	0.5645	1018.34	0.9924	2.96	19929.30	1232.27	0.9995	0.78	1128.84	0.6675	1022.64	0.9987	1.46	23412.30	1274.78	0.9992	1.11
42	1207.77	0.5382	1122.44	0.9965	1.92	18931.10	1326.03	0.9999	0.16	1230.68	0.6523	1126.92	0.9985	1.51	22886.80	1373.38	0.9993	1.00
43	1309.25	0.5253	1225.25	0.9999	0.15	18350.40	1423.29	0.9964	1.87	1331.02	0.6525	1227.64	0.9960	2.49	22965.80	1474.54	0.9999	0.03
44	1407.64	0.5866	1313.66	0.9999	0.27	20460.30	1534.65	0.9948	2.52	1433.00	0.6446	1329.90	0.9960	0.10	22513.20	1572.89	0.9962	2.37
45	1507.65	0.5348	1422.76	0.9972	1.69	18798.10	1625.01	0.9998	0.37	1529.29	0.6916	1419.39	0.9999	1.87	24286.90	1680.81	0.9996	0.79
46	1605.59	0.5785	1515.63	0.9677	6.38	20674.60	1736.22	0.9866	4.13	1627.92	0.7178	1515.21	0.9980	5.26	25454.20	1787.85	0.9968	2.47
47	1707.67	0.5416	1621.58	0.9981	1.42	19016.10	1826.29	0.9996	0.67	1733.01	0.5953	1638.14	0.9854	0.93	20853.50	1862.88	0.9986	1.35
48	1800.30	0.6590	1696.32	0.9918	3.58	23274.50	1946.12	0.9993	1.03	1830.31	0.6128	1732.73	0.9993	1.17	21481.80	1964.16	0.9989	1.19
49	1906.65	0.5465	1818.60	0.9800	1.47	18967.70	2023.97	0.9881	3.57	1935.31	0.5011	1855.04	0.9990	0.18	17481.90	2043.85	0.9950	2.11
50	2005.97	0.5660	1914.25	0.9929	2.86	19544.00	2126.40	0.9781	5.03	2035.66	0.4958	1956.06	0.9995	0.65	17260.80	2142.66	0.9926	2.55

cal data (*R*, correlation coefficient; *S*, standard error) for the *n*-alkyl esters of acetic acid in the temperature range 80–120 °C (at 80, 100 and 120 °C) on the DB-1 and DB-5 capillary columns. Good linear temperature dependencies of the retention indices were noticed for the investigated columns. Eq. (2) shows similar or slightly better precision in comparison to Eq. (1).

Table III lists the parameters and statistical data of Eqs. (1) and (2), respectively, for *n*-alkyl esters of propionic acid in the temperature range 80–120 °C (at 80, 100 and 120 °C) on the DB-1 and DB-5 capillary columns. Although high linear temperature dependencies of the retention data were observed, it was lower for Eq. (1) on the DB-1 capillary column in comparison to the *n*-alkyl esters of acetic acid. Better precision was obtained using Eq. (2) in comparison to Eq. (1) on both columns.

Table IV gives the parameter and statistical data of Eqs. (1) and (2), respectively, in the temperature range 160–220 °C (at 160, 190 and 220 °C) for DB-1 and DB-5 capillary columns for the *n*-alkyl esters of cyclohexanecarboxylic acid. Although this temperature dependence was studied over a wider temperature range than was the case for the *n*-alkyl esters of propionic and acetic acid, very good linear precision was obtained for the DB-1 capillary column with both equations. In this case, Eq. (1) showed slightly better or similar precision in comparison to Eq. (2). With the DB-5 capillary column, the temperature dependence of the retention indices using Eq. (1), showed high non-linearity. On the other hand, some but not high linearity was obtained using Eq. (2).

Table V gives the parameters and statistical data of Eqs. (1) and (2), respectively, for *n*-alkyl esters of benzoic acid in the temperature range 170–210 °C (at 170, 190 and 210 °C) on DB-1 and DB-5 capillary columns. Once again good linear temperature dependencies of the retention data was observed. Eq. (1) showed better precision in comparison to Eq. (2).

The parameters and statistical data for Eqs. (1) and (2) are listed in Table VI for the *n*-alkyl esters of phenylacetic acid in the temperature range 160–220 °C (at 160, 190 and 220 °C) on DB-1 and DB-5 capillary columns. Good linear temperature dependencies of the retention data were once again observed. Moreover, Eq. (2) showed better or similar precision in comparison to Eq. (1).

Although the regression coefficients in this study are generally very high, except for the *n*-alkyl esters of cyclohexanecarboxylic acid on the DB-5 column, the standard error was in some cases higher than 1.00, indicating a hyperbolic curve. This study was performed using only three experimental points which is insufficient to study a hyperbolic temperature dependence of the retention index. In future work, such a study will be performed.

CONCLUSION

The linear temperature dependencies of the retention indices were established for *n*-alkyl esters of acetic, propionic, cyclohexanecarboxylic, benzoic and phe-

nylacetic acid on DB-1 and DB-5 capillary columns. A good linearity of the retention indices *versus* column temperature was found.

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И З В О Д

УТИЦАЈ ТЕМПЕРАТУРЕ НА РЕТЕНЦИОНИ ИНДЕКС *n*-АЛКИЛ-ЕСТАРА СИРЋЕТНЕ, ПРОПИОНСКЕ, ЦИКЛОХЕКСАНКАРБОНСКЕ, БЕНЗОЕВЕ И ФЕНИЛСИРЋЕТНЕ КИСЕЛИНЕ НА DB-1 И DB-5 КАПИЛАРНИМ КОЛОНАМА

ДУШАН Ж. МИЈИН и ДУШАН Г. АНТОНОВИЋ

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У раду је приказана линеарна зависност ретенционог индекса од температуре коришћењем линеарних зависности ретенционог индекса у функцији температуре колоне t, °C или $1/T$, K^{-1} за *n*-алкил естре сирћетне, пропионске, циклохексанкарбонске, бензоеве и фенилсирћетне киселине на капиларним колонама DB-1 и DB-5.

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