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ARTICLES

Retention Indices of Symmetric Dicarboxylic Acid Esters

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Abstract—Retention indices of 28 symmetric dicarboxylic acid esters containing from two to six carbon atoms in the acid residue were determined experimentally. The temperature dependences of the retention indices were linear. Equations were proposed to predict the retention indices for symmetric and mixed C2–C6 dicarboxylic acid esters.

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The widespread occurrence of polymer materials, plastics, and synthetic fuels and oils has promoted the synthesis of increasing amounts of special additives improving the quality of these products. Plasticizers and various additives are among them. As a rule, such additives are mixed products. Fractions or waste materials that have no practical importance in other fields are often used as additives. Strict requirements posed on polymer materials impose limitations on the composition and properties of the additives.

Currently, esters and, particularly, dicarboxylic acid esters are most commonly used. They have found application in the production of plasticizers, synthetic motor oils, and perfumery. The esterification of dicarboxylic acids with a corresponding alcohol or olefin is the main method for synthesizing esters. In this case, the problem of the simple and universal identification of the synthesized esters arises. The common methods for mixture analysis cannot provide the ester structure. Most of them indicate the presence of the ester group (IR spectrometry) and, at the best case, identify the acid forming the ester (chromatography–mass spectrometry). Additionally, the compound can be identified using retention indices; however, a systematized database of their values is required. There is some information in the literature for methyl and ethyl esters [1–4], but no data is available on the retention indices of esters with a more complicated structure. Moreover, all investigations were performed on various phases and in different temperature modes; therefore, the systematization of these data is impossible.

The goal of the present work was to determine the retention indices of symmetric methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, and cyclohexyl esters of dicarboxylic acids containing two to six carbon atoms; to reveal the temperature dependences of the retention indices; and to find the equations adequately describing the change in the index with the homologue number and the temperature increment.

EXPERIMENTAL

Methyl, ethyl, propyl, isopropyl, *n*-butyl, isobutyl, cyclohexyl, and some *n*-pentyl esters of C2–C6 dicarboxylic acids were studied in this work. The esters were prepared by esterifying acids with corresponding alcohols according to the procedures described in [5]. Phosphoric acid was used as a catalyst. In the case of light alcohols C1–C3, extractive esterification was performed to shift the equilibrium; tetrachloromethane was used to absorb the ester formed. In the case of heavy alcohols C4–C6, azeotropic esterification was used; that is, benzene was added to the mixture to yield an azeotropic mixture with the water formed. The azeotrope was distilled from the reaction mixture; this shifted the equilibrium and increased the yield of the product. Then, the reaction mixture was neutralized and rectified. The practical yield for normal symmetric esters was 70–98% and for branched esters, 40–60%. The purity of the esters obtained was 99.9% or higher.

Mixed esters were prepared by the transalkylation of the ester with the corresponding alcohol on sulfonic cation exchangers.

The Khromatek-Analitika chromatographic software and a hardware interface based on a Kristall-2000M chromatograph were used to analyze the mixtures and to determine the retention times. A 50 m × 0.25 mm capillary column with a bonded OV-101 phase was used in the isothermal mode. The injector temperature was 350°C and the detector temperature was 300°C. Helium was used as a carrier gas at a split ratio of 1 : 40. One-microliter samples of mixtures of the studied esters and 1 μL of *n*-alkanes were dissolved in 1 mL of methanol [6]; 1 μL of the solution obtained was injected into the chromatograph with a microsyringe. The retention indices were calculated by the Kovats equation [7]

$$J_x = \frac{\log(t_x) - \log(t_N)}{\log(t_{N+1}) - \log(t_N)} \times 100 + 100N, \qquad (1)$$

Table 1. Retention indices on the OV-101 phase at different temperatures

Homologous series	Homologue no., *n*C	Temperature				
Methyl esters	*T*, °C	120	130	140	150	220
$CH_3OOC(CH_2)_nCOOCH_3$	0					727*
	1	914	917	918	921	
	2	1012	1014	1015	1017	957*
	T, °C	90	100	110	120	
	3	1109	1108	1107	1106	
	4	1215	1213	1212	1211	1234*
Ethyl esters	*T*, °C	120	130	140	150	220
$C_2H_5OOC(CH_2)_nCOOC_2H_5$	0					877*
	1	1034	1034	1032	1029	1033 [4]
	2	1148	1149	1147	1145	1149*
	4	1354	1353	1352	1350	1368
Propyl esters	*T*, °C	130	140	150	160	220
$C_3H_7OOC(CH_2)_nCOOC_3H_7$	0	1130	1131	1126	1128	
	1	1220	1221	1218	1220	1153
	2	1338	1339	1336	1338	1357
	3	1439	1440	1438	1439	
	4	1544	1545	1543	1544	1569
Isopropyl esters	*T*, °C	120	130	140	150	220*
$C_3H_7OOC(CH_2)_nCOOC_3H_7$	1	1115	1113	1111	1108	
	2	1226	1225	1223	1220	
	3	1323	1321	1319	1317	
	4	1430	1429	1427	1424	
Butyl esters	*T*, °C	170	180	190	200	220*
$C_4H_9OOC(CH_2)_nCOOC_4H_9$	0	1322	1320	1320	1319	1359
	1	1406	1406	1406	1406	
	2	1529	1528	1528	1528	1560
	3	1628	1627	1628	1628	
	4	1734	1733	1734	1734	1727 [3] (150°C)
Isobutyl esters	*T*, °C	150	160	170	180	
$C_4H_9OOC(CH_2)_nCOOC_4H_9$	2	1452	1451	1451	1450	
	4	1657	1656	1656	1655	
Cyclohexyl esters	*T*, °C	200	210	220	230	240
$C_6H_{11}OOC(CH_2)_nCOOC_6H_{11}$	0		1846	1853	1860	1866
	1		1925	1932	1939	1947
	2		2053	2060	2068	2076
	3		2133	2140	2148	2158
	4	2247	2254	2261	2269	

* Data reported in [2].

where t_x, t_N, and t_{N+1} were the adjusted retention times of the ester and *n*-alkanes with the numbers of carbon atoms of *N* and *N* + 1, respectively.

The experimental values of the retention indices determined after 5–7 measurements are presented in Table 1. The confidence interval was 0.2–2 index units. The literature data on the retention indices on the nonpolar SE-30 and OV-101 phases are also given in Table 1. One can compare the retention indices obtained on these phases, because the Rohrschneider and McRey-

Table 2. Coefficients of the dependence of the retention indices on temperature $J = a + bT$ (2)

Homologous series	Homologue no., n	b	a
Methyl esters	1	0.201	890.6
$CH_3OOC(CH_2)_nCOOCH_3$	2	0.181	990.3
	3	–0.105	1118.6
	4	–0.107	1224.1
Ethyl esters	1	–0.172	1055.4
$C_2H_5OOC(CH_2)_nCOOC_2H_5$	2	–0.110	1162.2
	4	–0.108	1366.9
Propyl esters	0	–0.087	1141.2
$C_3H_7OOC(CH_2)_nCOOC_3H_7$	1	–0.033	1224.8
	2	–0.027	1341.5
	3	–0.008	1440.3
	4	–0.005	1545.1
Isopropyl esters	1	–0.228	1142.7
$C_3H_7OOC(CH_2)_nCOOC_3H_7$	2	–0.205	1250.9
	3	–0.198	1346.8
	4	–0.211	1455.7
Butyl esters	0	–0.089	1336.4
$C_4H_9OOC(CH_2)_nCOOC_4H_9$	1	–0.015	1408.9
	2	–0.019	1531.7
	3	–0.009	1629.3
	4	0.017	1730.8
Isobutyl esters	2	0.068	1439.7
$C_4H_9OOC(CH_2)_nCOOC_4H_9$	4	0.057	1646.8
Cyclohexyl esters	0	0.678	1703.6
$C_6H_{11}OOC(CH_2)_nCOOC_6H_{11}$	1	0.717	1774.7
	2	0.757	1893.8
	3	0.806	1963.6
	4	0.735	2100.0
Ethyl propyl adipate $C_2H_5OOC(CH)_6COOC_3H_7$	6	–0.109	1459.7
Ethyl butyl adipate $C_2H_5OOC(CH)_6COOC_4H_9$	6	–0.011	1542.3
Ethyl propyl malonate $C_2H_5OOCCH_2COOC_3H_7$	1	–0.091	1139.8

nolds constants for them are equal [8]. In the literature, there are data on the retention indices for the SE-54 phase [1]. This phase is weakly polar; therefore, those data were not considered in this work.

RESULTS AND DISCUSSION

The analysis of the results shows that, for all esters, the change in the index with the temperature ($\Delta I/\Delta T$) does not exceed 3 index units per 10 K except for cyclohexyl esters, for which the change is 10 index units. The temperature dependences of the indices are linear in the studied temperature range. The coefficients of linear regression are presented in Table 2.

We would like to draw attention to the fact that an increase in the number of carbon atoms in the acid residue causes the increase in the retention indices by 80 to 125 index units per CH_2 group (with the same alkyl substituents). The difference in indices between the acid residues with even numbers and the preceding residues with odd numbers of carbon atoms is always considerably larger than the difference between the acid residues with an odd number and the preceding residues with even numbers of carbon atoms. This allows the conclusion that the studied esters exhibit the properties of dicarboxylic acids [9], whose physicochemical properties considerably depend on the multiplicity of the carbon chain. Thus, the simultaneous analysis of esters with even and odd numbers of carbon atoms in

Table 3. Coefficients of the dependence of the retention indices on the number of carbon atoms in the molecule $J = bn + a$ (3) at 150°C

Homologous series	b	a
Oxalic acid esters $H_3C(CH_2)_nOOCCOO(CH_2)_nCH_3$	99.6	327.1
Malonic acid esters $H_3C(CH_2)_nOOCCH_2COO(CH_2)_nCH_3$	94.4	368.6
Succinic acid esters $H_3C(CH_2)_nOOC(CH_2)_2COO(CH_2)_nCH_3$	95.9	378.0
Glutaric acid esters $H_3C(CH_2)_nOOC(CH_2)_3COO(CH_2)_nCH_3$	96.0	381.0
Adipic acid esters $H_3C(CH_2)_nOOC(CH_2)_4COO(CH_2)_nCH_3$	96.1	389.7

Table 4. Retention indices of the mixed esters on the OV-101 phase

Compound	J_{150} exp.	J_{150} calc.	ΔJ
Ethyl propyl adipate $C_2H_5OOC(CH)_6COOC_3H_7$	1443	1446	3
Ethyl propyl malonate $C_2H_5OOCCH_2COOC_3H_7$	1126	1124	2
Ethylbutyl adipate $C_2H_5OOC(CH)_6COOC_4H_9$	1540	1543	3

the acid residue can give incorrect results. For example, the difference between the calculated and experimental values of the retention index in constructing the dependence of J on the number of carbon atoms for cyclohexyl esters was as great as from 5 to 25 index units, which was unacceptable for identification.

We performed an analysis of esters containing one and the same acid residue and different alkyl groups. For this purpose, the retention indices at 150°C were calculated using the data in Table 1, and the dependences of the indices on the number of carbon atoms were constructed for each group of esters. For all groups of esters, the dependence was linear. The coefficients of the equations are presented in Table 3. The equations obtained can be used to predict the retention indices of any linear symmetric ester of an acid containing two to six carbon atoms.

To test the potentials of the derived equations for the identification of mixed symmetric esters, we synthesized ethyl butyl adipate, ethyl propyl adipate, and ethyl propyl malonate. The experimental retention indices adjusted to 150°C and the corresponding values calculated by Eq. (1) are presented in Table 4. The deviation between the calculated data and experimental data does not exceed three index units, and, consequently, the proposed equations can be used to predict the retention indices of linear mixed esters except for methyl esters.

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REFERENCES

1. Grigor'eva, D.N., Vasil'eva, A.V., and Golovnya, R.V., *Zh. Anal. Khim.*, 1993, vol. 48, no. 7, p. 1167.
2. Zulaica, J. and Guiochon, G., *Bull. Soc. Chim. Fr.*, 1963, no. 6, p. 1242.
3. Delley, R. and Friedrich, K., *Chromatographia*, 1977, vol. 10, no. 10, p. 593.
4. Tudor, E. and Moldovan, D., *J. Chromatogr.,* 1999, vol. 848, nos. 1–2, p. 215.
5. Becker, H., Berger, W., and Domschke, G., *Organikum. Organisch-chemisches Grundpraktikum*, Berlin: VEB Deutsche Verlag der Wissenschaften, 1976, vol. 2.
6. Chickos, J., Hosseini, S., and Hesse, D., *Thermochimica acta*, 1995, vol. 249, nos. 1–2, p. 41.
7. Stolyarov, B.V., Savinov, I.M., and Vitternberg, A.G., *Prakticheskaya gazovaya i zhidkostnaya khromatografiya* (Practical Gas and Liquid Chromatography), St. Petersburg: S.-Peterburg. Univ., 2002.
8. *Handbuch der Gaschromatographie*, Leibnitz, E. and Struppe, H.G., Eds., Leipzig: Akademische Verlagsgesellschaft Geest & Portig K.-G., 1984.
9. Traven', V.F., *Organicheskaya khimiya* (Organic Chemistry), Moscow: IKTs Akademkniga, 2004.