# PHYSICAL CHEMISTRY OF SEPARATION PROCESSES. CHROMATOGRAPHY

# Retention Indices and Sorption Enthalpies of Pentaerythritol and C<sub>2</sub>-C<sub>8</sub> Acid Esters on Nonpolar Stationary Phases

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Abstract—The retention and sorption enthalpy characteristics of 38 pentaerythritol esters of  $C_2-C_8$  carboxylic acids of different structures were determined by gas-liquid chromatography on a nonpolar phase in the temperature range 433.2–563.2 K. The molecular structure was shown to affect the temperature dependence of the retention indices of the esters. The average change in the sorption enthalpy of pentaerythritol tetraesters per CH<sub>2</sub> group is lower in magnitude than the similar contribution for normal alkanes. The excess mixing enthalpy at 298.2 K was evaluated for four fully substituted pentaerythritol esters.

Keywords: pentaerythritol esters, gas-liquid chromatography, logarithmic retention indices, sorption enthalpy

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Pentaerythritol (2,2-bis(hydroxymethyl)propan-1,3-diol) esters are used to produce plasticizers, varnishes, paints, and cosmetic products. They are of greatest interest for the production of synthetic oils for various purposes. Pentaerythritol esters of monocarboxylic acids have good thermal oxidative stability [1, 2]; low crystallization temperatures allow the use of synthetic oils based on them in the Arctic zone [3-5]. These oils are mixtures based on pentaerythritol esters of monocarboxylic acids with various additives [4, 5]. Their quantitative analysis is performed by gas-liquid chromatography, and the components are identified using logarithmic retention indices [6–9]. The retention indices obtained by gas-liquid chromatography on a capillary column with a nonpolar stationary phase are widely used in practice; in addition to identification, these values can be used to calculate the boiling point [10, 11] and vapor pressure [12, 13]. Correlations between the retention indices and enthalpies of vaporization within the same homologous series make it possible to evaluate the enthalpies of vaporization for compounds for which experimental data are unavailable [14-18].

Chromatographic analysis allows us to obtain not only the retention indices, but also the thermodynamic characteristics of sorption. The sorption enthalpy is important for understanding the mechanism of chromatographic retention and investigating the intermolecular sorbate—sorbent interactions [11]. The correlation between the sorption enthalpy and the enthalpy of vaporization of compounds makes it possible to evaluate the enthalpies of vaporization of complex organic compounds [19-23].

An analysis of the literature data showed that for pentaerythritol esters, the characteristics of retention on a nonpolar stationary phase under gas-liquid chromatography conditions were not studied. Therefore, the goal of this study was to determine the retention indices and sorption enthalpies and analyze their temperature dependences and changes in the homologous series of pentaerythritol esters of  $C_2-C_8$  acids with different structures. This paper is a continuation of the series of publications on sorption under conditions of gas-liquid chromatography on the nonpolar phase of esters of carboxylic acids and polyhydric alcohols with different contents of ester and hydroxyl groups in the molecule [24–29].

## EXPERIMENTAL

The esters were synthesized by esterification of the corresponding carboxylic acids with pentaerythritol using an eightfold molar excess of acid [1]. The reaction was performed in an inert gas (nitrogen) atmosphere without a catalyst to reduce the possibility of formation of condensation products and to prevent the oxidation of pentaerythritol. The synthesis temperature corresponded to the boiling point of the carboxylic acid used. The water formed during esterification was removed using a Dean–Stark trap. The reaction mixture was sampled (20  $\mu$ L) with a syringe in 1–1.5 h

after the start of water separation, diluted with methanol (1 mL), and analyzed by GLC. All the samples were in a liquid state. *n*-Alkanes (1  $\mu$ L of each alkane) were added to the sample; they were chosen such that the retention time of the test compounds was between the retention times of alkanes. The sample was introduced in the chromatograph using a syringe. The volume of the injected sample was 0.2  $\mu$ L.

The reaction mass was analyzed and retention times were determined using the Chromatech-Analytic hardware-software complex based on the Crystal-2000M chromatograph. For analysis of pentaerythritol esters of  $C_2$ - $C_6$  acids, a capillary column of 100 m  $\times$  0.2 mm  $\times$  0.5 µm with a grafted DB-1 stationary liquid phase was used. For analysis of pentaerythritol esters of  $C_7$ – $C_8$  acids, a capillary column of 30 m  $\times$  0.32 mm  $\times$  0.5  $\mu$ m with a grafted BP-1 stationary liquid phase was used. The DB-1 and BP-1 phases have the same chemical composition (100% polydimethylsiloxane) and are nonpolar. Analysis conditions: helium carrier gas, split ratio 1/50, flame ionization detector, injector temperature 623.2 K, detector temperature 573.2 K, column temperature 433.2–563.2 K, sample volume 0.2 µL.

The mixture components were identified using a Finnigan Trace DSQ mass spectrometer with NIST 2002, Xcalibur 1.31.Sp 5 software. Conditions of analysis: capillary column ZB-5MS with a weakly polar phase, length 30 m; inner diameter 0.32 mm; injector temperature 623.2 K; transfer line temperature 573.2 K; column temperature control mode  $t_{init} = 353$  K, 1 min, temperature rise rate 10 K/min to 573.2 K; helium carrier gas; carrier gas flow rate 1.3 mL/min.

The following expected products were identified in the reaction mixture:

$$\begin{array}{c} H_2C-OH \\ I \\ HO-CH_2-C \\ -CH_2-O-C-R \\ HO-CH_2 \\ Pentaerythritol monoester \end{array}$$

$$\begin{array}{c} O & H_2C-OH & O \\ \parallel & \mid & \mid \\ R-C-O-CH_2-C-CH_2-O-C-R \\ HO-CH_2 \\ Pentaerythritol diester \end{array}$$

$$\begin{array}{c} O\\ O\\ R-C-O-CH_2\\ R-C-O-CH_2-C-CH_2-O-C-R\\ HO-CH_2 O\\ Pentaerythritol triester \end{array}$$

where  $R = n-C_nH_{2n-1}$  (n = 1-6), iso- $C_3H_7$ , iso- $C_4H_9$ , tert- $C_4H_9$ , 2-ethyl- $C_5H_{11}$ .

The retention times were determined in an isothermal mode using the procedures presented in [24, 25].

The retention indices were calculated by the Kovats equation [30]:

$$I_x = \frac{\log(t'_x) - \log(t'_z)}{\log(t'_{z+1}) - \log(t'_z)} 100 + 100z,$$
(1)

where  $t'_x$ ,  $t'_z$ ,  $t'_{z+1}$  is the reduced elution time of the compound and *n*-alkanes with *z* and *z* + 1 carbon atoms, respectively.

The experimental retention indices were determined from three to seven measurements; the reliable range of indices was no more than  $\pm 1.0$  index units (i.u.).

The changes in the internal energy  $\Delta_{\text{sorp}}\overline{U}$  (kJ/mol) and sorption enthalpy  $\Delta_{\text{sorp}}\overline{H}$  (kJ/mol) at the average temperature of experiment were determined by the equations [26, 31]

$$\ln\left(\frac{k}{T}\right) = C - \frac{\Delta_{\rm sorp}U}{RT},\tag{2}$$

$$\Delta_{\rm sorp}\bar{H} = \Delta_{\rm sorp}\bar{U} - RT, \qquad (3)$$

where *R* is the gas constant (8.314 J/(mol K)), and *k* is the retention index calculated by the equation

$$k = \frac{t_R - t_M}{t_M},\tag{4}$$

where  $t_R$  is the elution time of the compound under study, and  $t_M$  is the elution time of the nonsorbing compound.

The sorption enthalpies obtained by Eq. (2) correspond to the average temperature of experiment. Reduction to the standard temperature (298.2 K) was performed by Eq. (5) [26]:

$$\Delta_{\rm sorp} H(298.2) = \Delta_{\rm sorp} H(T_{\rm av}) + (-\Delta_1^{\rm v} C_p^{\circ})(298.2 - T_{\rm av}),$$
(5)

where  $\Delta_1^v C_p^o$  is the change in the heat capacity of the liquid–gas transition determined by the procedure proposed in [32].

RUSSIAN JOURNAL OF PHYSICAL CHEMISTRY A Vol. 94 No. 10 2020

The excess mixing enthalpy  $\Delta H^{E,\infty}(298.2)$  was calculated by the equation [31]

$$\Delta H^{L,\infty}(298.2) = \Delta_{\rm vap} H^{\circ}(298.2) + \Delta_{\rm sorp} H^{\circ}(298.2).$$
(6)

#### **RESULTS AND DISCUSSION**

#### **Retention Indices**

The obtained retention indices of pentaerythritol esters and the coefficients of the equation of the temperature dependence of retention indices are presented in Table 1.

The temperature dependences of retention indices in the given temperature range are linear, which is confirmed by the high correlation coefficients  $R^2$ (Table 1). This indicates that there is no interaction between the sorbate molecules on the sorbent surface [33].

An analysis of changes in the indices at a temperature increased by 10 K ( $\Delta I/\Delta T$ ), calculated for the homologous series of mono-, di-, tri-, and fully substituted pentaerythritol esters, showed that the average increment of the retention index decreases when the hydroxyl group is replaced by an ester group and becomes negative in the case of fully substituted tetraesters (Table 2).

One of the reasons for the decrease in the index at elevated temperature may be the overloading of the chromatographic column [34]. However, this is not so because the peak asymmetry factor is close to unity for all esters. Another reason may be a change in the properties of the stationary phase because of its dynamic modification by the analytes [35]. However, as indicated above, the analyte concentration was minimum due to dilution; therefore, phase modification is unlikely.

The temperature dependences of the retention indices of the homologous series of mono-, di-, and fully substituted esters of three polyhydric alcohols (glycerol, neopentylglycol, and trimethylolpropane) determined on a capillary column with a nonpolar stationary phase were analyzed (Table 2) [24, 27, 28]. The obtained values confirm the tendency toward a decrease in the average value of  $\Delta I/\Delta T$  for the case with hydroxyl groups replaced by ester ones.

The temperature dependences of retention indices were studied on a capillary column with a TBR-1 nonpolar stationary phase (100% polydimethylsiloxane) in a wide temperature range (333–423 K) for various classes of organic compounds, including monocarboxylic esters [36]. An analysis of the results of the study reported in [36] revealed that the retention indices for esters decrease at elevated temperatures, and  $\Delta I/\Delta T$  is, on the average, -1.1...-0.5 i.u. Earlier, we determined the retention indices of dicarboxylic acid esters on a capillary column with an OV-101 nonpolar stationary phase in the temperature range of 30 K [29]. It was shown that the retention indices also decreased at elevated temperature in the given temperature ranges for the majority of linear esters ( $\Delta I/\Delta T$  is from -1.7 to -0.5 i.u. on the average), except for dimethyl oxalate and malonate.

On the other hand, for hydroxycarboxylic esters obtained on a capillary column with a DB-1 nonpolar stationary phase, the retention indices increase in the given temperature range [25]. For glycolic and lactic esters,  $\Delta I/\Delta T$  is small and amounts to 0.2–1 i.u., while for malic and tartaric esters the increase in the retention index at elevated temperatures is more pronounced ( $\Delta I/\Delta T$  is in the range 1.7–4.0 i.u.).

Thus, it can be assumed that for compounds containing hydroxyl and ester functional groups, the retention index increases with temperature. This tendency is associated with the presence of a hydroxyl group in the molecule because for completely substituted esters, the retention index changes slightly or decreases with increasing temperature.

The dependences of the retention indices of esters on the number of carbon atoms ( $n_c$ ) in a linear alkyl substituent at a column temperature of 513.2 K are described by the following equations:

$$I_{513,2} = 96.0n_{\rm C} + 1387, \quad R^2 = 0.999 \tag{7}$$

for monoesters;

$$I_{513,2} = 184.2n_{\rm C} + 1385, \quad R^2 = 0.999$$
 (8)

for diesters;

$$I_{513,2} = 264.6n_{\rm C} + 1380, \quad R^2 = 0.999 \tag{9}$$

for triesters; and

$$I_{513,2} = 341.1n_{\rm C} + 1350, \quad R^2 = 0.998$$
 (10)

for tetraesters.

In the method for calculating the retention index it is postulated that the change in the retention index per carbon atom ( $\Delta I/n_{\rm C}$ ) for normal alkanes is 100. As is known, for some mono- and dicarboxylic esters, the retention index increases by 90–95 i.u. per CH<sub>2</sub> group [29, 37]. The change in retention indices for pentaerythritol esters with the alkyl substituent (R) increased by one CH<sub>2</sub> group was 95.8 i.u. for monoesters, 92.1 i.u. for diesters, 88.2 i.u. for triesters, and 85.3 i.u. for tetraesters. In this case, the dependence of the index change by a CH<sub>2</sub> group is almost linear (Fig. 1), which confirms the absence of interactions between ester molecules on the phase surface. A simi-

n <sub>C</sub>	I, units			<i>I</i> <sub>513.2</sub> , units*	$\Delta I / \Delta T$	а	Ь	<i>R</i> <sup>2</sup>	
Pentaerythritol monoesters									
1	433.2	443.2	453.2	463.2					
	$1451.9\pm0.1$	$1455.7\pm0.1$	$1459.7\pm0.1$	$1464.2\pm0.1$	1483.4	4.1	0.409	1274.6	0.998
2	453.2	463.2	473.2	483.2					
	$1551.5\pm0.1$	$1556.1\pm0.1$	$1561.0\pm0.1$	$1566.2\pm0.1$	1580.8	4.9	0.492	1329.3	0.999
3	493.2	503.2	513.2	523.2					
	$1660.3\pm0.1$	$1666.3\pm0.1$	$1672.8\pm0.1$	$1679.9\pm0.1$	1673.0	6.5	0.65	1338.0	0.999
4	513.2	523.2	533.2	543.2					
	$1772.8\pm0.1$	$1778.4\pm0.1$	$1784.5\pm0.1$	$1795.2\pm0.1$	1771.4	7.3	0.732	1395.6	0.974
5	503.2	513.2	523.2	533.2					
	$1862.2\pm0.1$	$1868.9\pm0.1$	$1875.3\pm0.1$	$1882.2\pm0.1$	1868.1	6.7	0.664	1528.1	0.999
3	493.2	503.2	513.2	523.2					
iso-	$1617.0\pm0.1$	$1622.9\pm0.1$	$1629.1\pm0.1$	$1635.5\pm0.1$	1629.1	6.2	0.619	1311.8	0.999
4	503.2	513.2	523.2	533.2					
tert-	$1359.1\pm0.1$	$1364.0\pm0.1$	$1369.3\pm0.1$	$1374.3\pm0.1$	1364.5	5.1	0.508	1103.7	0.999
4	513.2	523.2	533.2	543.2					
iso-	$1726.91\pm0.1$	$1733.2\pm0.1$	$1739.9\pm0.1$	$1746.9\pm0.1$	1726.1	6.7	0.667	1384.5	0.999
5	533.2	543.2	553.2	563.2					
2-ethyl-	$2285.7\pm0.1$	$2290.4\pm0.1$	$2295.4\pm0.1$	_	2276.2	4.7	0.486	2026.4	0.999
Pentaerythritol diesters									
1	433.2	443.2	453.2	463.2					
	$1549.4\pm0.1$	$1552.8\pm0.1$	$1555.4\pm0.1$	$1559.6\pm0.1$	1575.9	3.3	0.332	1405.5	0.992
2	453.2	463.2	473.2	483.2					
	$1734.5\pm0.1$	$1738.6\pm0.1$	$1742.6\pm0.1$	$1746.9\pm0.1$	1758.2	4.1	0.412	1547.8	0.999
3	493.2	503.2	513.2	523.2					
	$1918.5\pm0.1$	$1923.1\pm0.1$	$1927.5\pm0.1$	$1932.6\pm0.1$	1927.6	4.7	0.467	1688.1	0.999
4	513.2	523.2	533.2	543.2					
	$2116.8\pm0.1$	$2120.8\pm0.1$	$2125.3\pm0.1$	$2135.2\pm0.1$	2114.5	6.0	0.597	1809.2	0.947
5	503.2	513.2	523.2	533.2					
	$2304.6\pm0.1$	$2306.1\pm0.1$	$2311.2\pm0.1$	$2316.1\pm0.1$	2307.5	3.4	0.396	2104.3	0.957
6	533.2	553.2	263.2						
	$2509.7\pm0.1$	$2521.6\pm0.1$	$2526.5\pm0.1$	—	2498.4	5.6	0.564	2208.6	0.998
3	493.2	503.2	513.2	523.2					
iso-	$1828.9\pm0.1$	$1833.8\pm0.1$	$1838.8\pm0.1$	$1844.1\pm0.1$	1838.7	5.1	0.506	1579.3	0.999
4	503.2	513.2	523.2	533.2					
tert-	$1551.6\pm0.1$	$1556.2\pm0.1$	$1561.2\pm0.1$	$1566.4\pm0.1$	1556.12	4.9	0.494	1302.9	0.999
4	513.2	523.2	533.2	543.2					
iso-	$2023.8\pm0.1$	$2028.9\pm0.1$	$2033.8\pm0.1$	$2039.2\pm0.1$	2023.4	5.1	0.510	1761.5	0.999
5	533.2	543.2	553.2						
2-ethyl-	$2484.7\pm0.1$	$2489.6\pm0.1$	$2496.3\pm0.1$	_	2472.7	5.8	0.580	2175.1	0.993

**Table 1.** Experimental retention indices and coefficients of the temperature dependences of pentaerythritol esters ( $I = aT_c + b$ ;  $T_c$  is the column temperature, K. The values are italicized)

n <sub>C</sub>	<i>I</i> , units			<i>I</i> <sub>513.2</sub> , units*	$\Delta I / \Delta T$	а	b	$R^2$	
Pentaerythritol triesters									
1	433.2	443.2	463.2						
	$1648.5\pm0.1$	$1649.4\pm0.1$	$1651.3\pm0.1$	_	1655.3	1.0	0.094	1608.0	0.998
2	453.2	463.2	473.2	483.2					
	$1908.1\pm0.1$	$1909.6\pm0.1$	$1911.1\pm0.1$	$1912.9\pm0.1$	1917.2	1.6	0.159	1836.0	0.998
3	493.2	503.2	513.2	523.2					
	$2154.7\pm0.1$	$2156.4\pm0.1$	$2157.9\pm0.1$	$2159.8\pm0.1$	2157.6	1.7	0.168	2071.8	0.998
4	513.2	523.2	533.2						
	$2425.7\pm0.1$	$2427.2\pm0.1$	$2428.7\pm0.1$	_	2425.0	1.5	0.15	2348.7	0.997
5	503.2	513.2	523.2	533.2					
	$2703.8\pm0.1$	$2704.2\pm0.1$	$2705.8\pm0.1$	$2707.1\pm0.1$	2704.3	1.2	0.115	2645.6	0.955
6	533.2	543.2	553.2	263.2					
	$2986.6\pm0.1$	$2987.5\pm0.1$	$2989.4\pm0.1$	$2991.8\pm0.1$	2982.0	1.8	0.175	2892.9	0.964
3	493.2	503.2	513.2	523.2					
iso-	$2020.8\pm0.1$	$2022.9\pm0.1$	$2025.2\pm0.1$	$2027.5\pm0.1$	2025.24	2.3	0.224	1910.3	0.999
4	503.2	513.2	523.2	533.2					
tert-	$1734.6\pm0.1$	$1738.7\pm0.1$	$1742.7\pm0.1$	$1746.9\pm0.1$	1738.4	4.1	0.409	1528.8	0.999
4	513.2	523.2	533.2	543.2					
iso-	$2287.1\pm0.1$	$2288.9\pm0.1$	$2290.5\pm0.1$	$2292.8\pm0.1$	2286.4	1.9	0.187	2191.1	0.994
5	533.2	543.2	553.2	563.2					
2-ethyl-	$2918.4\pm0.1$	$2919.4\pm0.1$	$2920.4\pm0.1$	$2922.3\pm0.1$	2916.2	1.3	0.127	2850.5	0.971
Pentaerythritol tetraesters									
1	433.2	443.2	453.2	463.2					
	$1721.5 \pm 0.1$	$1719.8 \pm 0.1$	$1718.2 \pm 0.1$	$1717.1 \pm 0.1$	1709.0	-1.5	-0.148	1785.5	0.991
2	453.2	463.2	473.2	483.2					
	$2053.1\pm0.1$	$2052.2\pm0.1$	$2051.5\pm0.1$	$2050.8\pm0.1$	2050.0	-0.8	-0.076	2089.0	0.993
3	493.2	503.2	513.2	523.2					
	$2350.4 \pm 0.1$	$2348.5 \pm 0.1$	$2346.8 \pm 0.1$	$2345.2 \pm 0.1$	2346.2	-1.7	-0.173	2435.6	0.999
4	513.2	523.2	533.2	—					
	$2687.5 \pm 0.1$	$2685.1 \pm 0.1$	$2682.5 \pm 0.1$	—	2686.2	-2.4	-0.250	2815.8	0.997
5	503.2	513.2	523.2	533.2					
	$3042.0 \pm 0.1$	$3039.3 \pm 0.1$	$3036.3 \pm 0.1$	$3033.4 \pm 0.1$	3039.1	-2.9	-0.288	3187.0	0.999
6	543.2	563.2	—	—					
_	$3445.1 \pm 0.1$	$3438.1 \pm 0.1$	—	_	3455.7	-3.5	-0.347	3593.0	_
3	493.2	503.2	513.2	523.2					
iso-	$2174.6 \pm 0.1$	$2173.7 \pm 0.1$	$2172.8 \pm 0.1$	$2172.0 \pm 0.1$	2172.9	-0.9	-0.087	2217.5	0.999
4	503.2	513.2	523.2	533.2					
tert-	$2223.7 \pm 0.1$	$2224.1 \pm 0.1$	$2224.8 \pm 0.1$	$2225.7 \pm 0.1$	2223.8	0.7	0.067	2208.2	0.973
4	533.2	543.2	—	—	<b>2</b> 407 0		0.10		
1SO-	$2494.4 \pm 0.1$	$2492.6 \pm 0.1$	_	_	2497.8	-1.8	-0.18	2541.2	_
5	533.2	543.2	553.2	563.2	2255		0.010	2447.2	0.000
2-ethyl-	3259.6 ± 0.1	$3255.9 \pm 0.1$	$3252.3 \pm 0.1$	$3249.2 \pm 0.1$	3266.4	-3.5	-0.348	3445.0	0.998

Alcohol	Pentaerythritol	Glycerol [27]	Trimethylolpropane [24]	Neopentylglycol [28]
Ester				
Mono-	5.9	2.3	4.1	2.7
Di-	4.5	0.9	3.7	1.0
Tri-	1.5	-0.9	0.6	—
Tetra-	-2.1	—	—	—

Table 2. Average increment of retention indices at a temperature raised by 10 K for esters of polyhydric alcohols

lar increase (of less than 100 per  $CH_2$  group) was obtained for glycerol esters (88–95 units) [27], neopentylglycol (91–96 units) [28], and trimethylol-propane (82–90 units) [24] (Fig. 1).

## Sorption Enthalpy

The results of calculation of sorption enthalpy for pentaerythritol esters are presented in Table 3. An analysis of these data shows that the sorption enthalpies at 298.2 K depend linearly on the number of carbon atoms ( $n_c$ ) in the linear alkyl substituent for mono-, di-, tri-, and tetraesters (Fig. 2).

The change in the sorption enthalpies calculated for the homologous series of mono-, di-, tri-, and completely substituted pentaerythritol esters per carbon atom in the alkyl substituent  $\Delta(\Delta_{sorp}H^{\circ})/n_{C}$ depending on the number of COOR groups in the ester molecule is also linear (Fig. 3). which is indicative of the additive contribution of hydroxyl and ester groups to the sorption enthalpy. A similar dependence was also observed for trimethylolpropane and neopentylglycol esters [24, 28] (Fig. 3), and the numerical



**Fig. 1.** Dependences of the change in the retention index per carbon atom in a linear alkyl substituent on the number of COOR groups in the molecule of pentaerythritol (PE), trimethylolpropane (TMP), glycerol (GL), and neopen-tylglycol (NPG) esters.

values of  $\Delta(\Delta_{sorp}H^{\circ})/n_{C}$  coincide almost completely for these compounds.

The average change in the sorption enthalpies per methylene fragment is 6.9, 5.1, 4.3, and 3.9 kJ/mol for mono-, di-, tri-, and fully substituted pentaerythritol esters, respectively. It was shown [31] that in the temperature range 323–328 K, the sorption enthalpy for normal alkanes on the nonpolar phase (HP-1) decreases on average by 4.4–4.5 kJ/mol per CH<sub>2</sub> group. In our previous work, we determined a similar contribution to the sorption enthalpy (298.2 K) for linear alkanes, which amounted to 5.4 kJ/mol [28]. Thus, a lower contribution of the methylene fragment to the sorption enthalpy of fully substituted pentaerythritol esters is most likely responsible for the decrease in the retention index at elevated temperature.

To evaluate the excess enthalpy of mixing  $\Delta H^{E,\infty}(298.2)$  based on the literature data on saturated vapor pressures [38], the enthalpies of vaporization at 298.2 K were calculated for four pentaerythritol esters. The excess mixing enthalpy is a negative value (Table 4); i.e., the intermolecular interactions



**Fig. 2.** Dependences of  $\Delta_{\text{sorp}} H^{\circ}(298.2)$  on the number of carbon atoms in a linear alkyl substituent for pentaerythritol (1) mono-, (2) di-, (3) tri-, and (4) tetraesters.

RUSSIAN JOURNAL OF PHYSICAL CHEMISTRY A Vol. 94 No. 10 2020

n <sub>C</sub>	$-\Delta_1^{\mathrm{v}} C_p^{\circ},$ J/(mol K)	<i>T</i> <sub>av</sub> , K	$-\Delta_{ m sorp}\overline{H}(T_{ m av}),$ kJ/mol	$-\Delta_{ m sorp}H^{\circ}(298.2),$ kJ/mol				
Pentaerythritol monoesters								
1	193.2	448.2	$57.5 \pm 0.3$	86.5				
2	200.4	468.2	$58.7 \pm 0.2$	92.8				
3	207.6	508.2	$58.5 \pm 0.4$	102.1				
4	214.7	528.2	$60.4\pm0.5$	109.8				
5	221.8	518.2	$63.9\pm0.3$	112.7				
3, <i>iso</i> -	205.1	508.2	$57.2 \pm 0.4$	100.3				
4, <i>iso</i> -	212.5	528.2	$59.0 \pm 0.4$	107.8				
4, <i>tert</i> -	208.4	518.2	$56.1 \pm 0.1$	94.2				
5, 2-ethyl-	233.9	548.2	$73.3\pm2.1$	131.7				
	ļ	Pentaerythritol diesters	ļ	ļ				
1	185.2	448.2	$61.5\pm0.3$	89.2				
2	194.9	468.2	$65.2\pm0.2$	98.4				
3	205.6	508.2	$67.6\pm0.4$	110.8				
4	216.9	528.2	$71.9\pm0.5$	121.8				
5	228.7	518.2	$78.2\pm0.3$	128.6				
6	240.9	548.2	$79.7\pm2.6$	139.9				
3, <i>iso</i> -	201.2	508.2	$64.6\pm0.4$	106.9				
4, <i>iso</i> -	213.1	528.2	$68.9\pm0.4$	117.9				
4, <i>tert</i> -	205.7	518.2	$56.1\pm2.3$	101.3				
5, 2-ethyl-	249.2	548.2	$96.2\pm0.5$	158.5				
Pentaerythritol triesters								
1	174.1	448.2	$66.6\pm0.4$	92.7				
2	185.6	468.2	$72.6\pm0.3$	104.1				
3	199.4	508.2	$76.9\pm0.5$	118.7				
4	214.6	528.2	$83.3 \pm 0.4$	132.6				
5	230.9	518.2	$92.3\pm0.5$	143.1				
6	247.9	548.2	$95.8 \pm 0.7$	157.7				
3, <i>iso</i> -	193.2	508.2	$72.4\pm0.5$	112.9				
4, <i>iso</i> -	209.1	528.2	$78.5 \pm 0.4$	126.6				
4, <i>tert</i> -	259.5	548.2	$94.8\pm2.8$	159.7				
	Pentaerythritol tetraesters							
1	160.6	448.2	$70.6\pm0.4$	94.7				
2	173.6	488.2	$77.0 \pm 0.3$	110.0				
3	190.3	508.2	$84.9\pm0.6$	124.9				
4	209.3	528.2	$93.2\pm0.5$	141.4				
5	230.0	518.2	$104.8\pm0.5$	155.4				
6	251.8	548.2	$109.6 \pm 0.4$	172.6				
3, <i>iso</i> -	182.3	508.2	$79.1\pm0.5$	117.4				
4, <i>iso</i> -	202.2	528.2	$84.6\pm0.7$	131.1				
4, <i>tert</i> -	188.1	518.2	$79.0\pm0.3$	120.4				
5, 2-ethyl-	266.6	548.2	$106.8 \pm 1.2$	173.4				

 Table 3. Calculated sorption enthalpies

RUSSIAN JOURNAL OF PHYSICAL CHEMISTRY A Vol. 94 No. 10 2020

#### RETENTION INDICES AND SORPTION ENTHALPIES

n <sub>C</sub>	$\Delta_{\rm vap}H^{\circ}(298.2)$ , exp., kJ/mol	$-\Delta_{\rm sorp}H^{\circ}(298.2),  \rm kJ/mol$	$\Delta H^{E,\infty}(298.2), \text{kJ/mol}$
4	134.0	141.4	-7.4
6	167.5	172.6	-5.1
8	193.6	206.1*	-12.5
5, 2-ethyl-	151.6	173.4	-21.8

**Table 4.** Calculated excess mixing enthalpies  $\Delta H^{E,\infty}(298.2)$  for pentaerythritol esters

\* Evaluated from the dependence of the sorption enthalpy of pentaerhythritol tetraesters on the number of carbon atoms in the linear alkyl substituent (Fig. 2).

between the ester and the nonpolar phase are greater than those between the fully substituted pentaerythritol ester molecules during evaporation. Evaluation of these interactions requires more data on the enthalpies of vaporization of pentaerythritol esters.

To summarize, the retention and sorption characteristics of pentaerythritol and  $C_1-C_8$  acid esters of various structures were determined by gas-liquid chromatography on a nonpolar phase in the temperature range 433.2–563.2 K. The retention indices and sorption enthalpies were analyzed for esters containing different numbers of ester and hydroxyl groups. For fully substituted esters, the retention index changes insignificantly or decreases at elevated temperatures. For homologous series of mono-, di-, tri-, and fully substituted pentaerythritol esters, the change in the index per methylene fragment decreases from 95.8 to 85.3 i.u.

The average change in the sorption enthalpies per methylene fragment for fully substituted pentaerythritol esters is 3.9 kJ/mol, which is lower (in magnitude) than the similar contribution for normal alkanes (4.4– 4.5 kJ/mol [31] and 5.4 kJ/mol [28]). This is probably



Fig. 3. Variation of the sorption enthalpy  $\Delta(\Delta_{sorp} H^{\circ}(298.2))/n_{C}$  depending on the number of COOR groups in the pentaerythritol (PE), trimethylolpropane (TMP), and neopentylglycol (NPH) ester molecules.

responsible for the decrease in the retention index at elevated temperatures in fully substituted pentaerythritol esters.

The intermolecular interactions between pentaerythritol tetraesters and the nonpolar phase are greater than those between the ester molecules during evaporation, which is proved by the negative values of excess mixing enthalpies.

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#### REFERENCES

- 1. V. A. Gromova and Z. V. Mamarasulova, Izv. SPbGTI (TU), No. 20 (46), 64 (2013).
- N. S. Kyazimova, Khim. Tekhnol. Topl. Masel, No. 3 (547), 29 (2008).
- 3. A. M. A. Nur, Y. Robiah, R. Umer, and W. M. Z. Nurin, Tribol. Int. **93**, 43 (2016).
- L. A. Quinchia, M. A. Delgado, T. Reddyhoff, C. Gallegos, et al., Tribol. Int. 69, 110 (2014).
- R. Yunus, A. Fakhru'l-Razi, T. L. Ooi, R. Omar, et al., Ind. Eng. Chem. Res. 44, 8178 (2005).
- 6. R. L. Akhmedov, S. S. Kravtsova, K. A. Dychko, and I. V. Ramus', Anal. Kontrol' **23**, 532 (2019).
- L. A. Yatsenko, A. A. Vorontsova, and I. D. Cheshko, Teor. Prakt. Sudebn. Ekspert., No. 1, 6 (2017).
- 8. M. J. Fuentes, R. Font, M. F. Gomez-Rico, and I. Martin-Gullon, J. Anal. Appl. Pyrolys. **79**, 215 (2007).
- 9. V. I. Babushok, Trend. Anal. Chem. 69, 98 (2015).
- K. Panneerselvam, M. P. Antony, T. G. Srinivasan, and P. R. Vasudeva Rao, Thermochim. Acta 495, 1 (2009).
- 11. S. N. Yashkin and N. V. Kudasheva, Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol. **52** (7), 48 (2009).
- M. Hoskovec, D. Grygarova, J. Cvačka, et al., J. Chromatogr. 1083, 161 (2005).
- 13. A. van Roon, J. R. Parsons, and H. A. Govers, J. Chromatogr. **955**, 105 (2002).
- 14. V. N. Emel'yanenko, A. V. Yermalayeu, S. V. Portnova, et al., J. Chem. Thermodyn. **128**, 55 (2019).

- 15. V. A. Pozdeev and S. P. Verevkin, J. Chem. Thermodyn. **43**, 1791 (2011).
- 16. V. N. Emel'yanenko and S. P. Verevkin, Fluid Phase Equilib. **266**, 64 (2008).
- 17. K. V. Zaitseva, D. H. Zaitsau, M. A. Varfolomeev, and S. P. Verevkin, Fluid Phase Equilib. **494**, 228 (2019).
- 18. E. L. Krasnykh, Y. A. Druzhinina, S. V. Portnova, and Y. A. Smirnova, Fluid Phase Equilib. **462**, 111 (2018).
- J. S. Chickos, S. Hosseini, and D. G. Hesse, Thermochim. Acta 249, 41 (1995).
- K. Aryusuk, S. Lilitichan, and K. Krisnangkura, J. Chem. Thermodyn. 39, 1077 (2007).
- N. Siripoltangman and J. Chickos, J. Chem. Thermodyn. 138, 107 (2019).
- 22. C. Nelson and J. Chikos, J. Chem. Thermodyn. 121, 175 (2018).
- 23. M. Orf, M. Kurian, L. Espinosa, C. Nelson, et al., J. Chem. Thermodyn. **126**, 128 (2018).
- E. L. Krasnykh, A. Yu. Aleksandrov, A. A. Sokolova, and S. V. Levanova, Russ. J. Phys. Chem. A 91, 398 (2017).
- S. V. Portnova, Yu. F. Yamshchikova, and E. L. Krasnykh, Russ. J. Phys. Chem. A 93, 577 (2019).
- 26. A. A. Zhabina and E. L. Krasnykh, Russ. J. Phys. Chem. A **91**, 2453 (2017).
- 27. A. S. Leol'ko, E. L. Krasnykh, and S. V. Levanova, J. Anal. Chem. 64, 1126 (2009).

- O. D. Lukina, E. L. Krasnykh, S. V. Portnova, and S. V. Levanova, Russ. J. Phys. Chem. A 94, 659 (2020).
- S. V. Lipp, E. L. Krasnykh, and S. V. Levanova, J. Anal. Chem. 63, 349 (2008).
- 30. Ya. I. Yashin, E. Ya. Yashin, and A. Ya. Yashin, *Gas Chromatography* (TransLit, Moscow, 2009) [in Russian].
- 31. M. Görgenyi and K. Heberger, J. Chromatogr. Sci. 37, 11 (1999).
- 32. E. L. Krasnykh and S. V. Portnova, J. Struct. Chem. 58, 706 (2017).
- 33. A. A. Pavlovskii, K. Herberger, and I. G. Zenkevich, J. Chromatogr., A 1445, 126 (2016).
- I. G. Zenkevich and A. A. Pavlovskii, Anal. Kontrol' 18, 171 (2014).
- 35. I. G. Zenkevich and A. A. Pavlovskii, Russ. J. Phys. Chem. A **90**, 1074 (2016).
- J. M. Santiuste, J. E. Quintanilla-López, R. Becerra, and R. Lebrón-Aguilar, J. Chromatogr., A 1365, 204 (2014).
- 37. C. T. Peng, J. Chromatogr., A 903, 117 (2000).
- A. Razzouk, I. Mokbel, J. Garcia, J. Fernandez, et al., Fluid Phase Equilib. 260, 248 (2007).

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