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RESEARCH ARTICLE

Determination of the enthalpy of evaporation of pentaerythritol esters of various structures using gas chromatographic retention characteristics

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Abstract

Objectives. The work set out to prepare and chromatographically analyze pentaerythritol esters, use gas chromatography to determine the Kováts logarithmic retention indices and enthalpies of sorption, and evaluate the enthalpy of evaporation of pentaerythritol tetraesters based on linear correlations with enthalpies of sorption and logarithmic retention indices.

Methods. The synthesis was carried out in an isothermal stirred reactor at $T = 393.2$ K at a molar ratio of pentaerythritol to carboxylic acid of 1 : 4 in self-catalysis mode to avoid side reactions that occur during aggressive acid catalysis. The obtained samples were analyzed using Chromatec Analytic hardware and software complex based on a Kristall-2000M chromatograph equipped with a capillary column (60 m × 0.32 mm × 0.5 μm) having BP-1 grafted stationary phase (100% dimethylpolysiloxane). The analysis conditions were as follows: isothermal mode; column temperature, 433.2–603.2 K; evaporator and detector temperatures, 623.2 K; gas flow split, 1 : 50; carrier gas, helium; volume of injected sample, 0.15 μL; diluent of reaction samples, methanol.

Results. For the first time, the values of the Kováts retention indices and enthalpies of sorption were found for 31 pentaerythritol esters of various structures (mono-, di-, tri-, and tetramethanoates; 2-methylpentanoates; 4-methylpentanoates; 2,2-dimethylbutanoates; 2-ethylbutanoates; octanoates; nanoates; and decanoates). The obtained correlation equations were used to estimate the enthalpy of evaporation of pentaerythritol tetraesters (for 7 compounds, data were obtained for the first time).

Conclusions. The retention parameters were found as linear dependencies with a high degree of correlation ($R^2 > 0.99$) in the studied temperature range (433.2–603.2 K). The enthalpies of evaporation calculated based on the enthalpies of sorption and logarithmic retention indices within the limits of error of the correlation dependencies coincide with the literature data and the values predicted by the quantitative structure–property relationship method. The obtained data can be used to design units for separating multicomponent mixtures and identify these compounds.

Keywords

pentaerythritol esters, retention indices, enthalpy of evaporation, esterification, sorption

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НАУЧНАЯ СТАТЬЯ

Определение энтальпии испарения сложных эфиров пентаэритрита различного строения с использованием газохроматографических характеристик удерживания

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Аннотация

Цели. Получение и хроматографический анализ сложных эфиров пентаэритрита; определение логарифмических индексов удерживания Ковача и энтальпий сорбции с помощью газовой хроматографии; оценка энтальпии испарения тетраэфиров пентаэритрита на основе линейных корреляций с энтальпиями сорбции и логарифмическими индексами удерживания.

Методы. Синтез проводили в изотермическом реакторе смешения при соотношении пентаэритрит : карбоновая кислота = 1 : 4 (мольн.), в режиме самокатализа во избежание протекания побочных превращений, имеющих место при агрессивном кислотном катализе, при $T = 393.2$ K. Анализ полученных образцов проводили с использованием программно-аппаратного комплекса «Хроматэк-Аналитик» на базе хроматографа «Кристалл-2000М», оснащенного капиллярной колонкой (60 м × 0.32 мм × 0.5 мкм) с привитой неподвижной фазой ВР-1 (100% диметилполисилоксан). Условия анализа: изотермический режим; температура колонки 433.2–603.2 K; температуры испарителя и детектора одинаковы и равны 623.2 K; деление газового потока 1 : 50; газ носитель — гелий; объем вводимой пробы — 0.15 мкл; для разбавления реакционных проб применяли метанол.

Результаты. Впервые получены значения индексов удерживания Ковача и энтальпий сорбции для 31 сложного эфира пентаэритрита различной структуры (моно-, ди-, три- и тетраформиатов, 2-метилпентаноатов, 4-метилпентаноатов, 2,2-диметилбутаноатов, 2-этилбутаноатов, октаноатов, наноатов, деканоатов). Получены корреляционные уравнения, позволившие оценить энтальпию испарения для тетраэфиров пентаэритрита (для 7 соединений данные получены впервые).

Выводы. Значения параметров удерживания представляют собой линейные зависимости с высокой степенью корреляции ($R^2 > 0.99$) в исследованном температурном диапазоне (433.2–603.2 K). Рассчитанные энтальпии испарения в пределах погрешности корреляционных зависимостей на основе энтальпий сорбции и логарифмических индексов удерживания совпадают с литературными и прогнозируемыми по методу Quantitative Structure-Property Relationship значениями. Полученные данные могут быть использованы для проектирования узлов разделения многокомпонентных смесей и идентификации данных соединений.

Ключевые слова

сложные эфиры пентаэритрита, индексы удерживания, энтальпии испарения, этерификация, сорбция

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INTRODUCTION

Pentaerythritol esters are of great interest to various sectors of global industry. This is mainly due to the possibility of varying the chemical and/or physical properties of these esters by introducing various numbers of acid fragments of a particular structure to permit their use as plasticizers for polymer products, alkyd resins, lubricants, stationary chromatographic phases, and nonionic surfactants [1–6].

The mass application of plasticizers is limited by a number of requirements imposed by technical and economic standards: absence of odor and color, commercial availability, and thermodynamic compatibility with the polymer material [7]. As a rule, such requirements are met by pentaerythritol esters of linear and an iso structure having an average molecular weight in the range of 400–800 g/mol [8]. In this case, the most significant effect is exhibited by compounds of branched structure, which have a higher resistance to emission from the polymer in comparison with their isomers of linear structure.

To create optimal technologies for obtaining ester products, reliable data on the enthalpies of evaporation are required, which are used in the design of reaction units or separation units [9]. Experimental determination is based on obtaining the saturated vapor pressure by various methods: direct (ebulliometry), indirect (transpiration), etc. However, this entails certain difficulties, since the classical ebulliometric method is unsuitable for compounds with low thermal stability (which clearly manifests itself for branched ester structures); moreover, when using the transpiration method, the experiment can be extremely lengthy due to the high molecular weight of the ester [10, 11].

Recently, modeling methods have become increasingly important, allowing for rapid estimation of the enthalpy of evaporation with a sufficient accuracy based on reliable retention parameters of compounds obtained under gas chromatography conditions [12].

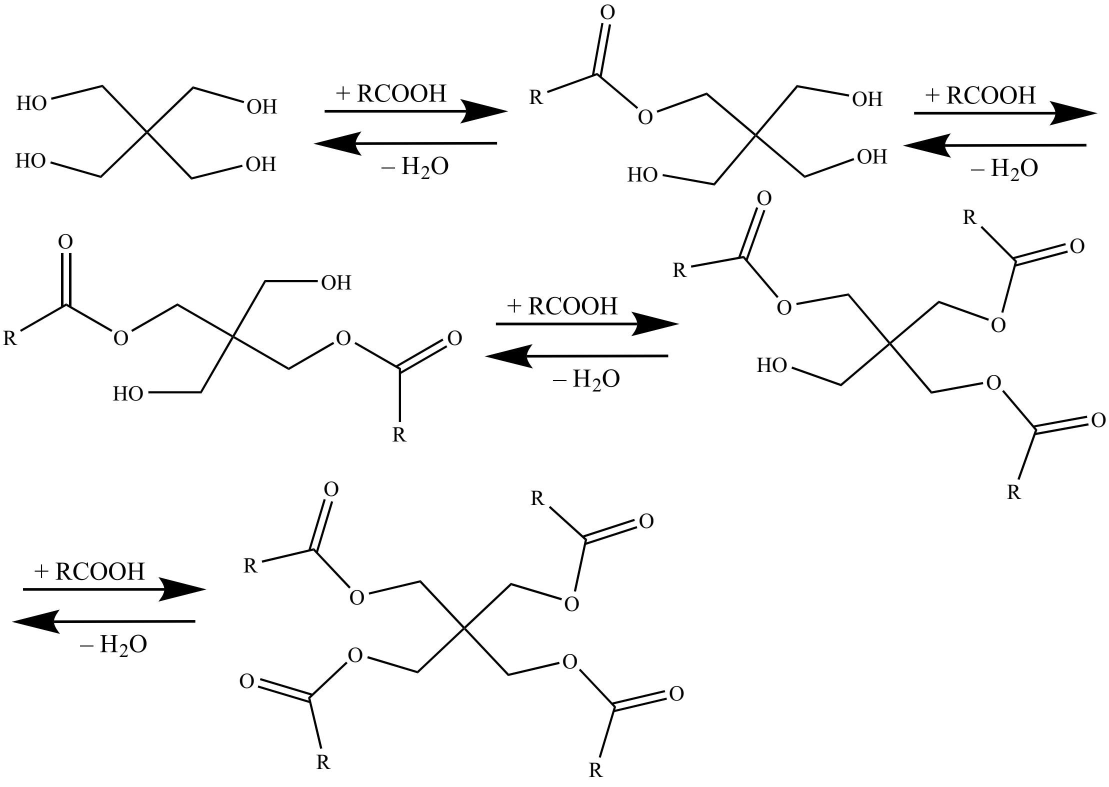
The purpose of this work was to obtain and chromatographically analyze pentaerythritol esters, determine the Kováts retention indices for a number of unstudied pentaerythritol esters of various structures, determine the enthalpies of sorption, and estimate the enthalpies of evaporation for tetraethers by prediction based on experimental correlations.

EXPERIMENTAL

Synthesis of pentaerythritol esters

The objects of the study were pentaerythritol esters for which there are no reference descriptions of retention indices under gas-liquid chromatography conditions. Pentaerythritol esters of the following acids were studied: formic (98%, *neoFroxx GmbH*, Germany), 2-methylpentanoic (98%, *Merck*, Germany), 4-methylpentanoic (99%, *Sigma-Aldrich*, USA), 2,2-dimethylbutanoic (98%, *Acros Organics*, USA), 2-ethylbutanoic (99%, *Acros Organics*, USA), octanoic (99%, *Sigma-Aldrich*, USA), nonanoic (99%, *Sigma-Aldrich*, USA), and decanoic (99%, *Sigma-Aldrich*, USA), which were synthesized according to the following scheme:

The syntheses were carried out at a molar ratio of alcohol to carboxylic acid of 1 : 4 in order to obtain products of all degrees of substitution. The experimental equipment was a jacketed reactor (*RULLAB*, Russia) connected to a reflux condenser. The reactor was thermostated by circulating PMS-200 polymethylsiloxane (*Acros Organics*, USA) using a circulating oil thermostat (*Huber*, Germany). The reaction temperature was 393 K. The process was conducted in the self-catalysis mode to avoid side reactions that occur during aggressive acid catalysis.



Scheme. Synthesis of pentaerythritol esters

The reaction system was stirred with a magnetic stirrer (*Heidolph*, Germany). The reaction was performed until the signals of all four possible products appeared (monoesters, diesters, triesters, and tetraesters). The conversion of pentaerythritol was determined by kinetic monitoring of the reaction by changing the chromatographic signals with time (gradual depletion of alcohol and increase and decrease in concentrations in a series of mono-, di-, tri- and tetrasubstituted products).

Analysis of reaction mixture

The obtained samples were analyzed using the Chromatec Analytic hardware and software complex based on a Kristall-2000M chromatograph (*Chromatec*, Russia) equipped with a capillary column (60 m × 0.32 mm × 0.5 μm) with BP-1 grafted stationary phase (100% dimethylpolysiloxane, *Chromatec*, Russia). Analysis conditions were as follows: isothermal mode; column temperature, 433.2–603.2 K; injector temperature, 623.2 K; detector temperature, 623.2 K; gas flow split, 1 : 50; carrier gas, helium; injected sample volume, 0.15 μL; diluent for reaction samples, methanol (*Acros Organics*, USA); concentration range of the measured compounds, 0.2–0.6 mg/mL. The asymmetry factor of chromatographic peaks was 1, thus eliminating the possibility of overloading the chromatographic column, as well as its physical modification, which could lead to distortion of retention index values [13, 14].

Determination of retention indices

The retention indices and enthalpies of sorption were determined by the following equations [15]:

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

$$\ln(k) = \frac{\Delta\bar{S}_{\text{sorb}}}{R} - \frac{\Delta\bar{U}_{\text{sorb}}}{RT}, \tag{2}$$

$$k = \frac{t_{\text{R}} - t_{\text{D}}}{t_{\text{D}}}, \tag{3}$$

$$\Delta\bar{H}_{\text{sorb}}\left(T_{\text{av}}\right) = \Delta\bar{U}_{\text{sorb}}\left(T_{\text{av}}\right) - RT, \tag{4}$$

where I_x is the retention index of the substance under study; t'_x, t'_z, and t'_{z+1} are the reduced retention times of the sample under study (subscript x) and normal alkanes with the number of carbon atoms z and $z + 1$, respectively; $R = 8.3145$ J/(mol · K) is the universal gas constant; t_{R} is the absolute retention time of the substance under study; t_{D} is the dead retention time; k is the retention factor; $\Delta\bar{U}_{\text{sorb}}$ is the internal energy of sorption at the average temperature of the experiment; $\Delta\bar{S}_{\text{sorb}}$ is the entropy of sorption at the average temperature of the experiment; $\Delta\bar{H}_{\text{sorb}}$ is the enthalpy of sorption at the average temperature of the experiment; and T_{av} is the average temperature of the experiment.

The experimental values of the enthalpies of sorption were reduced to a temperature of 298.2 K using the equation

$$\begin{aligned}&\Delta H_{\text{sorb}}(298.2\text{K}) = \\ &= \Delta\bar{H}_{\text{sorb}}\left(T_{\text{av}}\right) + \left(-\Delta_{\text{liq}}^{\text{vap}} C_P^{\circ}\right)\left(298.2 - T_{\text{av}}\right),\end{aligned} \tag{5}$$

where $\Delta_{\text{liq}}^{\text{vap}} C_P^{\circ}$ is the heat capacity of the liquid–vapor phase transition, predicted using the method that we proposed previously [16] based on modified Randić indices.

RESULTS AND DISCUSSION

Retention indices

For all compounds in the temperature range of 433.2–603.2 K (all studied temperature modes are given in Table 1), it was possible to achieve a clear separation of the components of the analyzed samples. The only exception was pentaerythritol monodecanoates, which may be due to the similar retention times of normal alkanes.

The confidence interval in determining the retention indices as determined in 3–4 measurements was no more than 0.2.

Table 1 presents the experimental values of the logarithmic retention indices and their temperature dependencies.

One of the known dependencies relating the logarithmic retention index with the structure of the compound is the correlation relative to the number of carbon atoms in the acid fragment of the ester in the case of linear structure. For this, it is necessary to have data for determining the retention index at the same temperature. As such a temperature, the value of 513.2 K was chosen based on the published data [17], as well as due to the fact that this temperature is within the studied range (433.2–603.2 K), which allows for a satisfactory approximation to 513.2 K.

The dependence of the retention indices on the number of carbon atoms in the acid fragment (Fig. 1) demonstrates good linearization ($R^2 = 0.999$), indicating the adequacy of the obtained results.

Table 1. Experimental values of retention indices of pentaerythritol esters

No.	T, K / I_i				$I_{513.2}$	$\Delta I/\Delta T$	a^*	b^*	R^2
Monoesters									
Methanoate	*433.2* 1272.2	*443.2* 1279.5	*453.2* 1285.0	*463.2* 1290.4	1320.8	6.1	0.6011	1012.4	0.994
2-Methylpentanoate	*523.2* 1912.7	*533.2* 1920.5	*543.2* 1928.3	*553.2* 1935.2	1905.3	7.5	0.7533	1518.8	0.999
4-Methylpentanoate	*523.2* 1989.0	*533.2* 1997.0	*543.2* 2004.9	*553.2* 2014.1	1980.5	8.4	0.8323	1553.4	0.999
2,2-Dimethylbutanoate	*503.2* 1750.6	*513.2* 1750.6	*523.2* 1750.7	*533.2* 1750.8	1750.6	0.1	0.0067	1747.2	0.999
2-Ethylbutanoate	*513.2* 1572.2	*523.2* 1576.4	*533.2* 1581.3	*543.2* 1585.3	1572.2	4.4	0.4438	1344.4	0.999
Octanoate	*573.2* 2113.2	*583.2* 2122.1	*593.2* 2130.7	*603.2* 2139.8	2060.1	8.9	0.8848	1606.0	0.999
Nanoate	*573.2* 2233.0	*583.2* 2242.6	*593.2* 2252.0	*603.2* 2262.4	2174.4	9.8	0.9759	1673.5	0.999
Diesters									
Methanoate	*433.2* 1452.6	*443.2* 1457.4	*453.2* 1461.7	*463.2* 1466.8	1490.1	4.7	0.4680	1249.9	0.999
2-Methylpentanoate	*513.2* 2166.7	*523.2* 2172.9	*533.2* 2183.4	*543.2* 2188.9	2166.7	7.4	0.7720	1770.3	0.985
4-Methylpentanoate	*523.2* 2285.4	*533.2* 2289.8	*543.2* 2293.9	*553.2* 2299.4	2280.6	4.7	0.4603	2044.4	0.996
2,2-Dimethylbutanoate	*503.2* 2092.6	*513.2* 2102.6	*523.2* 2110.8	*533.2* 2121.6	2102.6	9.7	0.9528	1613.2	0.998
2-Ethylbutanoate	*513.2* 2067.5	*523.2* 2074.3	*533.2* 2079.7	*543.2* 2086.8	2067.5	6.4	0.6337	1742.4	0.997
Octanoate	*573.2* 2723.4	*583.2* 2729.3	*593.2* 2735.1	*603.2* 2742.3	2685.7	6.3	0.6253	2364.8	0.997
Nanoate	*573.2* 2919.4	*583.2* 2925.7	*593.2* 2932.0	*603.2* 2938.2	2881.8	6.3	0.6280	2559.4	0.999
Decanoate	–	–	*593.2* 3113.0	*603.2* 3119.7	3059.7	2.7	0.6670	2117.4	–
Triesters									
Methanoate	*433.2* 1506.7	*443.2* 1509.7	*453.2* 1512.7	*463.2* 1516.2	1532.0	3.2	0.3178	1368.9	0.999
2-Methylpentanoate	*513.2* 2491.7	*523.2* 2494.6	*533.2* 2497.1	*543.2* 2499.6	2491.7	2.6	0.2617	2357.5	0.999
4-Methylpentanoate	*523.2* 2588.9	*233.2* 2591.0	*543.2* 2593.5	*553.2* 2595.7	2586.6	2.3	0.2292	2469.0	0.999
2,2-Dimethylbutanoate	*503.2* 2385.7	*513.2* 2391.2	*523.2* 2396.3	*533.2* 2401.7	2391.2	5.3	0.5318	2118.1	0.999

Table 1. Continued

No.	T, K / I_i				$I_{513.2}$	$\Delta I/\Delta T$	a^*	b^*	R^2
2-Ethylbutanoate	*513.2* 2329.7	*523.2* 2332.1	*533.2* 2334.0	*543.2* 2336.4	2329.7	2.2	0.2207	2216.5	0.999
Octanoate	*573.2* 3273.9	*583.2* 3275.0	*593.2* 3276.4	*603.2* 3277.6	3266.5	1.2	0.1236	3203.0	0.998
Nanoate	*573.2* 3555.4	*583.2* 3558.0	*593.2* 3560.6	*603.2* 3563.1	3540.2	2.6	0.2548	3409.4	0.999
Decanoate	*573.2* 3840.3	*583.2* 3841.4	*593.2* 3842.7	*603.2* 3843.7	3833.4	1.1	0.1150	3774.4	0.998
Tetraesters									
Methanoate	*433.2* 1537.3	*443.2* 1538.5	*453.2* 1540.3	*463.2* 1541.5	1548.7	1.4	0.1440	1474.8	0.995
2-Methylpentanoate	*513.2* 2751.5	*523.2* 2750.8	*533.2* 2749.7	*553.2* 2747.7	2751.5	−0.9	−0.0967	2801.3	0.996
4-Methylpentanoate	*523.2* 2881.7	*533.2* 2879.7	*543.2* 2877.5	*553.2* 2875.5	2883.8	−2.1	−0.2089	2991.0	0.999
2,2-Dimethylbutanoate	*503.2* 2616.8	*513.2* 2619.3	*523.2* 2621.8	*533.2* 2624.6	2619.3	2.6	0.2593	2486.3	0.999
2-Ethylbutanoate	*513.2* 2650.2	*523.2* 2649.8	*533.2* 2649.4	*543.2* 2649.0	2650.2	−0.4	−0.0415	2671.5	0.999
Octanoate	*573.2* 3737.9	*583.2* 3733.5	*593.2* 3729.8	*603.2* 3725.7	3761.8	−4.1	−0.4015	3967.9	0.999
Nanoate	*573.2* 4102.3	*583.2* 4098.2	*593.2* 4094.1	*603.2* 4090.0	4126.9	−4.1	−0.4072	4335.6	0.999
Decanoate	*573.2* 4430.6	*583.2* 4426.0	*593.2* 4421.2	*603.2* 4416.5	4459.1	−4.7	−0.4729	4701.7	0.999

* The coefficients a and b are derived from the temperature dependence $I = aT + b$ of the logarithmic retention indices, where T is the temperature of the chromatographic column, K.

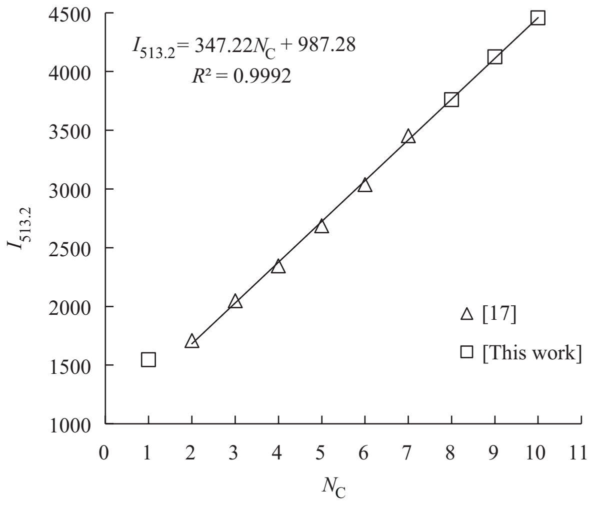


Fig. Dependence of the retention indices of pentaerythritol tetraesters of linear structure at a temperature of 513.2 K on the number of carbon atoms in the acid fragment

Enthalpies of sorption and prediction of enthalpy of evaporation

Table 2 presents the results of calculation of enthalpy of sorption.

Analysis of the enthalpies of sorption when reduced to a temperature of 298.2 K showed that the dependence of the enthalpy of sorption on the number of substituted hydroxyl groups has a linear anamorphosis for esters with different acid fragments indicating an additive contribution of the methylene fragment to the enthalpy value. At the same time, the enthalpies of sorption of pentaerythritol methanoates under error conditions have similar values, which is probably due to the absence of a methylene fragment.

The general equation (except for methanoates) describing the relationship between the retention index

Table 2. Experimental values of enthalpies of sorption of pentaerythritol esters

No.	$-\Delta_{\text{liq}}^{\text{vap}}C_P^{\circ}$, J/(mol K)	T_{av}, K	$-\Delta\bar{H}_{\text{sorb}}(T_{\text{av}})$, kJ/mol	$-\Delta H^{\circ}_{\text{sorb}}(298.2)$, kJ/mol
Monoesters				
Methanoate	193.0	448.2	49.8 ± 3.9	80.8 ± 6.6
2-Methylpentanoate	219.5	538.2	60.1 ± 4.9	112.8 ± 9.2
4-Methylpentanoate	219.7	538.2	68.6 ± 0.4	121.4 ± 0.8
2,2-Dimethylbutanoate	215.6	518.2	63.6 ± 0.2	111.0 ± 0.3
2-Ethylbutanoate	219.7	528.2	62.0 ± 0.7	112.5 ± 1.2
Octanoate	236.1	588.2	76.6 ± 0.5	145.0 ± 0.9
Nanoate	243.2	588.2	79.8 ± 1.3	150.3 ± 2.6
Diesters				
Methanoate	180.1	448.2	54.8 ± 2.7	81.8 ± 4.1
2-Methylpentanoate	224.4	528.2	75.6 ± 1.0	127.2 ± 1.6
4-Methylpentanoate	224.9	538.2	76.2 ± 0.7	130.1 ± 1.2
2,2-Dimethylbutanoate	217.3	523.2	69.9 ± 0.4	118.8 ± 0.6
2-Ethylbutanoate	224.8	528.2	72.3 ± 0.6	124.0 ± 1.0
Octanoate	253.3	588.2	81.8 ± 0.6	155.3 ± 1.3
Nanoate	265.9	588.2	85.7 ± 1.2	162.8 ± 2.4
Decanoate	278.7	598.2	85.8	169.4
Triesters				
Methanoate	167.2	448.2	57.5 ± 3.1	82.6 ± 4.5
2-Methylpentanoate	224.7	528.2	86.2 ± 0.8	137.9 ± 1.2
4-Methylpentanoate	225.4	538.2	86.0 ± 0.6	140.1 ± 1.0
2,2-Dimethylbutanoate	214.3	518.2	80.6 ± 0.1	127.8 ± 0.1
2-Ethylbutanoate	225.2	528.2	83.9 ± 0.8	135.6 ± 1.2
Octanoate	265.5	588.2	98.2 ± 0.9	175.2 ± 1.7
Nanoate	283.4	588.2	103.6 ± 1.1	185.8 ± 2.1
Decanoate	301.8	598.2	103.7	194.3
Tetraesters				
Methanoate	154.2	448.2	60.0 ± 2.9	83.1 ± 4.1
2-Methylpentanoate	221.8	530.7	93.2 ± 0.7	144.7 ± 1.1
4-Methylpentanoate	222.8	538.2	96.7 ± 0.7	150.2 ± 1.1
2,2-Dimethylbutanoate	208.3	518.2	89.1 ± 0.1	134.9 ± 0.2
2-Ethylbutanoate	222.6	528.2	93.4 ± 0.6	144.6 ± 0.9
Octanoate	274.4	588.2	112.9 ± 0.9	192.5 ± 1.6
Nanoate	297.7	588.2	120.6 ± 1.6	206.9 ± 2.9
Decanoate	321.5	598.2	130.5 ± 1.9	227.0 ± 3.4

reduced to a single temperature and the sorption enthalpy has the form:

$$-\Delta H^\circ_{\mathrm{sorb}}(298.2) = \\ = -6.682N_i + 0.047I_{513.2} + 40.371, \left(R^2 = 0.965\right), \quad (6)$$

where N_i is the number of substituted hydroxyl groups in the pentaerythritol molecule for compound i: monoester ($N = 1$), diester ($N = 2$), triester ($N = 3$), and tetraester ($N = 4$). The characteristics of the predictive ability of the obtained equation are the following: maximum deviation, 14.3; mean error of predicted values, 4.1; and standard deviation of error, 3.9.

The enthalpies of evaporation can be found using linear correlations relative to the chromatographic retention parameters:

$$\Delta H^\circ_{\mathrm{evap}}(298) = f\left(I_T\right),$$

$$\Delta H^\circ_{\mathrm{evap}}(298) = f\left(-\Delta H^\circ_{\mathrm{sorb}}(298.2)\right),$$

where I_T is the retention index of the compound at a certain temperature T, K.

Using the literature values of enthalpies of evaporation and enthalpies of sorption of some pentaerythritol tetraesters [17, 18], we obtained the following correlation equations:

$$\Delta H^\circ_{\mathrm{evap}}(298) = \\ = 0.0367I_{513.2} + 43.387, \ \left(R^2 = 0.991\right), \quad (7)$$

$$\Delta H^\circ_{\mathrm{evap}}(298) = \\ = -0.824\Delta H^\circ_{\mathrm{sorb}}(298) + 27.055, \ \left(R^2 = 0.994\right). \quad (8)$$

Table 3 compares the values of the enthalpies of evaporation of pentaerythritol tetraesters with the values predicted by the quantitative structure–property relationship (QSPR) method [19].

The obtained values of the enthalpy of evaporation are at a level acceptable for technical calculations. Deviations from the data obtained by the QSPR method and literature data on pentaerythritol tetraesters are 3–6%.

Table 3. Values of the enthalpies of evaporation of pentaerythritol tetraesters, obtained by various methods

Component	$\Delta H^\circ_{\mathrm{evap}}(298)$, kJ/mol			
	This work		Literature data	Additive method QSPR [21]
	(7)	(8)		
Methanoate	100.3 ± 2.0	95.5 ± 1.6	–	102.2 ± 2.8
Ethanoate	105.4 ± 0.8	105.0 ± 1.7	106.9 ± 1.8 [18]	106.6 ± 3.0
Propionate	118.1 ± 0.9	117.6 ± 1.9	115.0 ± 2.1 [18]	115.7 ± 3.2
Butanoate	129.8 ± 1.0	129.9 ± 2.1	129.8 ± 2.3 [18]	127.4 ± 3.6
2-Methylpropanoate	123.2 ± 1.0	123.7 ± 2.0	122.8 ± 2.5 [18]	121.8 ± 3.4
Pentanoate	142.9 ± 1.1	143.5 ± 2.4	144.2 ± 2.3 [18] 134.0 ± 1.9 [18]	141.1 ± 4.0
3-Methylbutanoate	135.7 ± 1.1	135.0 ± 2.2	137.4 ± 2.4 [18]	135.7 ± 3.8
2,2-Dimethylpropionate	125.1 ± 1.0	126.2 ± 2.1	125.2 ± 2.5 [18]	125.9 ± 3.5
Caproate	156.4 ± 1.3	155.0 ± 2.6	155.4 ± 3.0 [18]	155.1 ± 4.3
2-Methylpentanoate	144.4 ± 2.8	146.2 ± 2.4	–	149.4 ± 4.2
4-Methylpentanoate	149.3 ± 2.9	150.7 ± 2.5	–	150.1 ± 4.2
2,2-Dimethylbutanoate	139.6 ± 2.7	138.1 ± 2.3	–	139.9 ± 3.9

Table 3. Continued

Component	$\Delta H^{\circ}_{\text{evap}}(298)$, kJ/mol			
	This work		Literature data	Additive method QSPR [21]
	(7)	(8)		
2-Ethylbutanoate	140.7 ± 2.8	146.1 ± 2.4	–	149.9 ± 4.2
Heptanoate	168.5 ± 1.6	169.2 ± 2.8	168.5 ± 2.8 [18] 167.5 ± 2.3 [20]	170.3 ± 4.8
Octanoate	181.6 ± 3.6	185.6 ± 3.1	–	186.2 ± 5.2
Nanoate	195.0 ± 3.8	197.4 ± 3.3	193.6 ± 2.0 [20]	202.4 ± 5.7
Decanoate	207.2 ± 4.1	214.0 ± 3.5	–	219.1 ± 6.1

CONCLUSIONS

After experimentally determining the Kováts retention indices, the enthalpies of sorption were estimated for 31 pentaerythritol esters of various structures. The retention indices are described by linear dependencies with a high degree of correlation ($R^2 > 0.99$) in the studied temperature range (433.2–603.2 K). Using the correlation equations, the enthalpies of evaporation of pentaerythritol tetraesters were estimated (for seven of these, data were obtained for the first time). The calculated enthalpies of evaporation coincide with the literature data and the values predicted by the QSPR method within the limits of error of the correlation equations. The obtained data can be used to design units for separating multicomponent mixtures and identify these compounds.

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Authors' contributions

Yu.F. Ivanova—experiment execution, data processing, writing the article.

V.V. Emelyanov—experiment execution, data processing, writing the article.

S.V. Levanova—data processing, writing the article.

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