



Vapor pressure and enthalpy of vaporization of trimethylolpropane and carboxylic acids esters



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ABSTRACT

Vapor pressure and molar standard enthalpies of vaporization of esters of 2-ethyl-2-(hydroxymethyl)-1,3-propanediol (trimethylolpropane, TMP) and straight and branched carboxylic acids with chain length C_1 , C_3 – C_6 , were determined by the transpiration method. A linear correlation of vaporization enthalpies of trimethylolpropane esters with the number of carbon atoms and with the Kovat's indices on the non-polar DB-1 GC column has been found. Enthalpies of vaporization of tested compounds were also calculated by QSPR-method. These results were checked by experimental values.

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1. Introduction

Esters of 2-ethyl-2-(hydroxymethyl)-1,3-propanediol (trimethylolpropane, TMP) and carboxylic acids are extensively used for industrial production of pigments, synthetic oils, dispersants, emollients and plasticizers [1,2]. Optimization of industrial synthetic and separation technologies require reliable vapor pressure and vaporization enthalpies data. The analysis of the literature shows that there are no experimentally determinate data of vapor pressure and molar standard enthalpies of vaporization of tested compounds. Available calculated values are scarce [3].

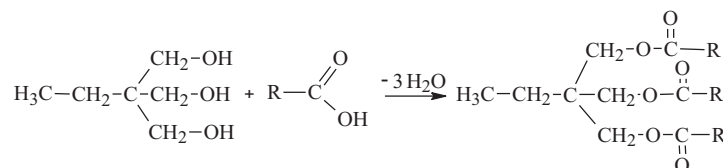
In this work, vapor pressure and vaporization enthalpies of

esters of trimethylolpropane and straight and branched carboxylic acids with chain length C_1 , C_3 – C_6 were obtained by the transpiration method. New enthalpies of vaporization at 298 K were used for developing of QSPR method.

2. Experimental

2.1. Materials

The samples esters of trimethylolpropane were synthesized by esterification in the presence of benzene (for triacetate TMP), of toluene (for others esters) and of phosphoric acid as a catalyst.



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Straight and branched carboxylic acids with chain length C₁, C₃–C₆ were used. Molar relation TMP to acid was 1: 6–8. An excess of acid was evaporated and reaction mass was neutralized by solution of sodium carbonate. All samples were purified by a repeated distillation in vacuum. Purities of samples were determined by the gas chromatography. The degree of purity of the samples was determined using a Khromatek-Analitika chromatographic program-apparatus complex based on a Kristall-2000M chromatograph equipped with a flame ionization detector. A capillary column DB-1 (stationary phase dimethylpolysiloxane) was used with a column length of 100 m and inside diameter of 0.2 mm and a film thickness of 0.5 μm. We used isothermal conditions with column temperature 493.15–553.15 K, vaporizer temperature 623 K, detector temperature 573 K, carrier gas helium, and flow splitting 1/100. The purity of samples was obtained more than 99.5% mass (see Table 1).

Determination of retention times of the esters was performed using a Kristall-2000M chromatograph equipped with a flame ionization detector. A capillary column DB-1 was used with a column length of 100 m an inside diameter of 0.2 mm and a film thickness of 0.5 μm.

2.2. Vapor pressure and vaporization enthalpy measurements

Vapor pressures of esters were determined using the method of transpiration [4,5] in a saturated helium stream. About 0.5 g of the sample was mixed with glass beads and placed in a temperature-controlled U-shaped tube with a length of 20 cm and a diameter of 0.5 cm. Glass beads with a diameter of the glass spheres of 1 mm provide the surface large enough for rapid vapor-liquid equilibration. At constant temperature (±0.1 K), a helium stream was passed through the U-tube and the transported amount of gaseous material was collected in a cooling trap. The flow rate of the helium stream was measured using a soap bubble flow meter and was optimized in order to reach the saturation equilibrium of the transporting gas at each temperature under study. The amount of condensed substance was determined by GC analysis using an external standard. The external standard was hydrocarbon n-C_nH_{2n+2} eluted close to the ester. The saturation vapor pressure p_i at each temperature T_i was calculated from the amount of the product collected within a definite period of time. Assuming that Dalton's law of partial pressures applied to the helium stream saturated with the substance of interest is valid, values of p_i were calculated with equation:

$$p_i = \frac{m_i \times R \times T_a}{V \times M_i}; \quad V = V_{He} + V_i; \quad V_{He} \gg V_i \quad (1)$$

where R = 8.314472 J K⁻¹ mol⁻¹; m_i is the mass of the transported compound, M_i is the molar mass of the compound, and V_i is the volume contribution to the gaseous phase. V_{He} is the volume of the carrier gas and T_a is the temperature of the soap bubble meter. The volume of the carrier gas V_{He} was determined from the flow rate and the time measurement.

Temperature dependence of vapor pressures from experimental data was determined by the equation [5]:

$$R \times \ln p_i = a + \frac{b}{T} + \Delta_f^g C_p \times \ln \left[\frac{T}{T_0} \right] \quad (2)$$

where a and b are adjustable parameters and is the difference of the isobaric molar heat capacities of the gaseous and the liquid phase respectively. T₀ appearing in Eq. (2) is an arbitrarily chosen

reference temperature (which has been chosen to be 298.15 K).

Vaporization enthalpy at temperature T was derived from temperature dependence of vapor pressures using equation (3):

$$\Delta_f^g H_m(T) = -b + \Delta_f^g C_p \times T \quad (3)$$

The difference of the isobaric molar heat capacities of the gaseous and the liquid phase were estimated by the QSPR-method [6].

Procedure for calculation of the combined uncertainties of the vaporization enthalpy was described elsewhere [4,5]. They include uncertainties from the transpiration experimental conditions, uncertainties of vapor pressure, and uncertainties from temperature adjustment to T = 298.15 K.

2.3. QSPR method of calculation of Δ_f^gH_m(298.15 K) and Δ_f^gC_p

A calculation procedure for the enthalpies of vaporization Δ_f^gH_m(298.15 K) and Δ_f^gC_p by the topological method based on the modified Randić indices was described in the previous works [5,6]. In the proposed QSPR method based on the principles of graph theory non-hydrogen atoms being graph vertices (descriptors) and bonds being the edges are used. Based on the descriptors, molecular connectivity indices from zero to the third order are determined, which are summed up and correlated with the sought property.

Vaporization enthalpy Δ_f^gH_m(298.15 K) and difference of the isobaric molar heat capacities of the gaseous and the liquid phase Δ_f^gC_p were estimated by equations [6,7]:

$$\Delta_f^g H_m(298.15) = 1.6883 \times 0^{-3} \chi + 2.0781 \quad (4)$$

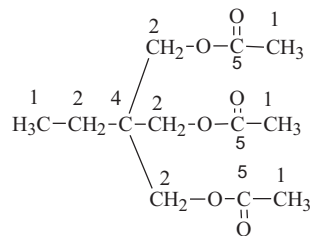
$$\Delta_f^g C_p(298.15) = -2.416 \times 0^{-3} \chi - 11.0 \quad (5)$$

where 0⁻³χ is the total index calculated by the formula

$$0^{-3} \chi = 0 \chi + \frac{1 \chi}{2} + \frac{3 \chi}{3} + \frac{3 \chi}{4} + \chi_{mm} \quad (6)$$

where 0χ = ∑₁ⁿ 1/ln(δ_i) is the zero order connectivity index and determines the contribution of atoms or a group of atoms; 1χ = ∑₁^m 1/ln(δ_i × δ_j) is the first order connectivity index and determines the contribution of two valently bonded atoms; 2χ = ∑₁^p 1/ln(δ_i × δ_j × δ_k) is the second order connectivity index and determines the contribution to the three successively located atoms; 3χ = ∑₁^r 1/ln(δ_i × δ_j × δ_k × δ_l) is the third order connectivity index and determines the contribution to the four successively located atoms; χ_{mm} – intermolecular interaction, calculated by formula χ_{mm} = (-3.249 * ln(m * 0⁻³χ_{alk}) + 14.806) * (n - 1) [7], where m is the number of carbon atoms in the molecule, n is the number of ester groups in the molecule, 0⁻³χ is total index of alkane relevant acid (for acetate this is ethane).

For example, the calculation of molecular indices triethanoate TMP is as the following:



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