

Excess Molar Enthalpy of Binary Biazeotropic Ester–Carboxylic Acid systems

Farid Bedretdinov

farid.bedretdinov@gmail.com

MIREA - Russian Technological University (M.V. Lomonosov Institute of Fine Chemical Technologies)

Valentina Raeva

MIREA - Russian Technological University (M.V. Lomonosov Institute of Fine Chemical Technologies)

Tatiana Chelyuskina

MIREA - Russian Technological University (M.V. Lomonosov Institute of Fine Chemical Technologies)

Nikita Tsvetov

Murmansk Arctic State University

Yuri Anufrikov

Saint Petersburg State University

Irina Zvereva

Saint Petersburg State University

Research Article

Keywords: partial molar vaporization enthalpies, excess molar enthalpies, calorimetric study, binary azeotrope, biazeotropic mixtures, pressure swing distillation

Posted Date: September 29th, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-10975480/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Additional Declarations: No competing interests reported.

Excess Molar Enthalpy of Binary Biazeotropic Ester–Carboxylic Acid systems

Farid Bedretdinov^{1*}, Valentina Raeva¹, Tatiana Chelyuskina¹, Nikita Tsvetov², Yuri Anufrikov³, Irina Zvereva⁴

¹MIREA - Russian Technological University
(M.V. Lomonosov Institute of Fine Chemical Technologies),
78, Vernadskogo Av., 119454, Moscow, Russia

²Murmansk Arctic State University
(Department of Physics, Biology and Engineering Technologies),
29, Lesnaya st., 184209, Apatity, Russia³

³Saint Petersburg State University
(Center for Thermal Analysis and Calorimetry, Research Park)
7/9 Universitetskaya nab., 199034, St. Petersburg, Russia

⁴Saint Petersburg State University
(Department of Chemical Thermodynamics and Kinetics)
7/9 Universitetskaya nab., 199034, St. Petersburg, Russia

E-mail: Farid.bedretdinov@gmail.com

Abstract

The change in binary azeotrope composition affected by pressure change is determined by the difference in the partial vaporization enthalpies of the components. Knowledge of this dependence allows to predict azeotrope behavior and to use it for separation by pressure swing distillation without added entrainers. Precise values of the partial vaporization enthalpies is especially important for biazeotropic systems, where the same pressure change have different effects on the compositions of positive and negative azeotropes. Partial vaporization enthalpies can be obtained from the excess molar enthalpies of mixtures.

In this study, the excess molar enthalpies of three biazeotropic systems (isobutyl acetate–acetic acid, butyl propionate–propionic acid, butyl butyrate–butyric acid) were measured at about 373 K and 101.3 kPa (corresponding to the conditions of distillation) over the full concentration range using precise Calvet-type heat-flow calorimetry provided by Setaram C80 calorimeter, and correlated by a polynomial equation. The partial molar vaporization enthalpies calculated from these data showed that these values of the ester are lower than that of the carboxylic acid in all three systems. Obtained data are the basis needed to predict how azeotropes in biazeotropic systems evolve with pressure change.

Keywords: partial molar vaporization enthalpies, excess molar enthalpies, calorimetric study, binary azeotrope, biazeotropic mixtures, pressure swing distillation.

Introduction

There is an industrial relevance for the separation of binary and multicomponent azeotropic mixtures. An azeotrope is a thermodynamic limitation of the possibility of distillation in one column into pure components [1,2]. For separation of azeotropic mixtures, special methods are required. Most often, the systems contain an azeotrope over a wide pressure range. Pressure swing distillation (PSD) is used for separation of mixtures with a pressure-sensitive azeotrope [3-6].

Type of vapor liquid equilibrium (VLE) transformation determines the choice of the separation method. Usually azeotrope appears (or disappears) through a boundary tangential azeotrope. In biazeotropic systems, this can also occur through the formation of an internal tangential azeotrope [7]. The biazeotropic systems becomes zeotropic after disappearance of the internal tangential azeotrope. Systems isobutyl acetate – acetic acid, butyl propionate – propionic acid, and butyl butyrate – butyric acid may be considered as example of such behavior [8-11]. They can be separated by

ordinary distillation, if the coefficient of relative volatility of the components α is far (significantly different) from 1. In biazeotropic systems one of the azeotropes can also disappear through boundary tangential azeotrope. Then, PSD can be used to separate the monoazeotropic system.

The change of the binary azeotrope composition with varying conditions (dx_1^{Az} / dT) is uniquely determined by the thermodynamic Vreysky's law [1,12]. The sign of dx_1^{Az} / dT for any binary azeotrope composition is determined by the ratio of the partial molar vaporization enthalpies of components ($\overline{H}_{V_1}, \overline{H}_{V_2}$):

low-boiling azeotrope (min T – max P):

$$dx_1^{Az} / dT > 0 \text{ at } \overline{H}_{V_1} > \overline{H}_{V_2}; dx_1^{Az} / dT < 0 \text{ at } \overline{H}_{V_1} < \overline{H}_{V_2} \quad (1a)$$

high-boiling azeotrope (max T – min P):

$$dx_1^{Az} / dT > 0 \text{ at } \overline{H}_{V_1} < \overline{H}_{V_2}; dx_1^{Az} / dT < 0 \text{ at } \overline{H}_{V_1} > \overline{H}_{V_2} \quad (1b)$$

Theoretical studies and modeling for nontrivial cases of biazeotropic systems are desirable to confirm experimentally. The partial molar vaporization enthalpies of components can be determined from data array on the integral vaporization enthalpies H_V :

$$H_V = \overline{H}_{V_1} \cdot x_1 + \overline{H}_{V_2} \cdot x_2. \quad (2)$$

Here x_1, x_2 – mol. fraction of components. Equation (2) can be written in expanded form:

$$H_V = \left(H_{V_1} - \overline{H}_1^E \right) x_1 + \left(H_{V_2} - \overline{H}_2^E \right) x_2. \quad (3)$$

Here $\overline{H}_1^E, \overline{H}_2^E$ – partial molar excess enthalpies of components.

Experimental calorimetric data for binary systems at high temperatures are scarced [13]. Experimental data for systems containing esters of carboxylic acids, usually given for low temperatures [14-17]. Therefore, excess molar enthalpies of binary mixtures are not taken into account. The following assumption is used:

$$H_V = H_{V_1} \cdot x_1 + H_{V_2} \cdot x_2 \quad (4)$$

Estimation of the legitimacy of such replacement is especially important when studying the evolution of biazeotropic systems.

Enthalpy of vaporization is a crucial thermal property of substances and mixtures. A precise assessment of vaporization enthalpy and its temperature dependence is essential in studying phase transitions [18–20]. Reliable data on the molar enthalpy of vaporization for pure substances (H_V^0) and mixtures (H_V) under various conditions of phase equilibrium are necessary for thermal balance calculations in distillation columns. In the absence of experimental data, thermodynamic methods for calculating the enthalpy of vapor formation of the mixture are used [21, 22].

It is also worth noting that the process of directly measuring the enthalpy of vaporization using calorimetry is intricate and time-consuming, therefore, experimental data are not numerous [18, 23–27]. To our knowledge, there are no arrays of necessary experimental calorimetric data for the conditions of biazeotropy existence in systems complex ether – monocarboxylic acid.

In this work the excess molar enthalpy for biazeotropic systems isobutyl acetate – acetic acid, butyl propionate – propionic acid, and butyl butyrate – butyric acid at atmospheric pressure and about 373 K were experimentally measured.

Experimental part

The method of measuring of excess molar enthalpy in binary mixtures containing carboxylic acids with the use of C80 Calorimeter was tested on the example of n-propanol – acetic acid mixture [28].

Design of the calorimeter is based on Tian and Calvet principles [29]. The main element of the Calorimeter is a calorimetric chamber which is adapted to rotations of 180° thus this mechanism is designed to increase the degree of mixing of the studied liquids. It is established that the energy resulting from the movement of liquids in the capsule is insignificant in comparison to the effect of mixing liquids.

To calibrate the calorimeter, the Joule effect, or electrical calibration was used. To simulate the experimental vessel with the sample inside, a vessel with a built-in heater were used, which was also calibrated by using a series of precise heat inputs.

To control the course of experiment we used the CALISTO software. Experimental measurements were performed with use of membrane mixing cells, which were specially designed to study the mixing of two substances in order to obtain the corresponding values of interaction heat. Cylindrical stainless cell was consisted of two cell chambers, which are isolated by membrane from each other.

The purity of all reagents was tested by gas chromatograph and was more than 99.9%. All reagents were purchased from “BASF” and “Sigma-Aldrich” (Germany). The index of refraction of substances also was measured and was confirmed to correspond to the literature data.

One sample was placed into the lower cell chamber (2.5 ml), and the other one into the upper cell chamber (3.5 ml). A sharp-edged impeller, connected to a command rod, movable along the central shaft of the cell and the cell well, was used to break the membrane in order to mix the substances.

Thus, high fidelity of obtained experimental data is ensured by modern equipment implemented in the experimental set-up. To weight our samples, a Sartorius MSU225S analytical balance (precision ± 0.01 mg) was used. The uncertainties in the mole fractions were less than 0.0002. Both measuring and reference cells were loaded with the same amount of substance. The cells were then inserted into the calorimeter thermostat and kept there for 1 hour for equilibration. Before the enthalpy of mixing measurement, the temperature and heat flow signals have been being stable during at least 30 min. By lowering the control rod of the measuring cell and breaking the separation membrane, agitating of liquids was initiated. Then the rod has been returned to an initial state. After establishing the thermal stability, which indicates the end of the experiment, we made a correction for the movement of the rod, i.e., the rod was once again lowered and raised. Integration of the heat flow peaks yields the excess enthalpy. After heat flow and temperature stabilization, the similar actions have been done with the reference cell: in this case the values of the enthalpy have to be taken with a reversed sign. For each pair of substances, we repeat the measurement at least two times.

The correction on the heat of evaporation of the liquids by the method suggested in [30] was taken into account. The necessary physical reference data have been taken in NIST [31]. Experimental values of excess molar enthalpies H_{exp}^E of system complex ether (1) – monocarboxylic acid (2) about 373 K and atmospheric pressure are presented in Tables 1-3.

Table 1. Excess molar enthalpy (H^E , J mol⁻¹) of isobutyl acetate (1) – acetic acid (2) at 373.21 and 101,3 kPa

x_1	H_{exp}^E	H_{calc}^E
0.10004	-8.7	-2.45
0.20032	-5.2	-10.3
0.20051	-6.8	-10.3
0.39987	21.5	22.9
0.40015	18.5	23.0
0.50106	61.8	62.0
0.50371	58.9	63.1
0.59935	105.3	98.4
0.59979	101.7	98.6

0.69899	121.4	118.5
0.79766	100.9	109.9
0.80084	105.1	109.0
0.89949	71.3	67.4
0.89950	71.1	67.4

Standard uncertainties of temperature T and mole fraction x are as follows: $u(T) = 0.05$ K, $u(x) = 0.0001$, and the relative expanded standard uncertainty U_r for the excess enthalpies is $U_r(H^E) = 0.03$ (95% level of confidence)

Table 2. Excess molar enthalpy (H^E , J mol⁻¹) of butyl propionate (1) – propionic acid (2) at 373.15 K and 101,3 kPa

x_1	H^E_{exp}	H^E_{calc}
0.09825	1.7	-1.6
0.10191	-2.4	1.1
0.19914	24.3	25.0
0.20142	24.7	25.8
0.29177	60.7	59.0
0.29261	60.9	59.3
0.29798	57.9	61.6
0.30069	61.0	62.4
0.38490	97.0	94.7
0.39845	101.2	99.8
0.39979	100.4	100.2
0.40014	96.3	104.0
0.49734	140.1	135.7
0.50065	139.7	136.9
0.60013	161.3	168.7
0.60165	175.4	169.3
0.69930	190.3	190.8
0.70023	194.2	191.0
0.79964	191.7	190.1
0.80004	189.2	190.1
0.90152	140.0	139.3
0.90247	135.3	138.3

Standard uncertainties of temperature T and mole fraction x are as follows: $u(T) = 0.05$ K, $u(x) = 0.0001$, and the relative expanded standard uncertainty U_r for the excess enthalpies is $U_r(H^E) = 0.03$ (95% level of confidence)

Table 3. Excess molar enthalpy (H^E , J mol⁻¹) of butyl butyrate (1) – butyric acid (2) at 373.12 K and 101,3 kPa

x_1	H^E_{exp}	H^E_{calc}
0.05028	3.0	3.05
0.05036	3.1	3.15
0.10063	16.4	15.1
0.10235	17.3	15.65
0.19645	52.0	52.0
0.19896	52.6	53.0
0.29816	95	96.2
0.2999	95.4	97.0
0.39133	133.8	134.0
0.39529	132.6	135.5
0.49564	174.3	171.2
0.49822	175.8	172.0
0.58994	200.9	199.6
0.59557	202.3	201.0
0.69468	218.8	220.9
0.69637	217.7	221.1
0.79698	217.3	217.3
0.79982	214.3	216.6
0.89626	163.9	162.8

Standard uncertainties of temperature T and mole fraction x are as follows: $u(T) = 0.05$ K, $u(x) = 0.0001$, and the relative expanded standard uncertainty U_r for the excess enthalpies is $U_r(H^E) = 0.03$ (95% level of confidence)

Results and discussion

Experimental data $H^E(x)$ is described by polynomial:

$$H^E = ax^5 + bx^4 + cx^3 + dx^2 + xe + f \quad (5)$$

The coefficients of Eq. 5 are listed in Table 4 for each system.

Table 4. Coefficients of Eq. (5)

	a	b	c	d	e	f
Isobutyl acetate – acetic acid	4228.4	-11265	9297.2	-2405.7	148.41	-1.4105
Butyl propionate – propionic acid	-3637.7	7701.3	-6789.9	2982.95	-257.01	0.5714
Butyl butyrate – butyric acid	-4319.9	9126	-7678.6	2961.9	-88.895	0.9959

Calculated by equation 5 values are presented in Figs. 1-3 and Tables 1-3.

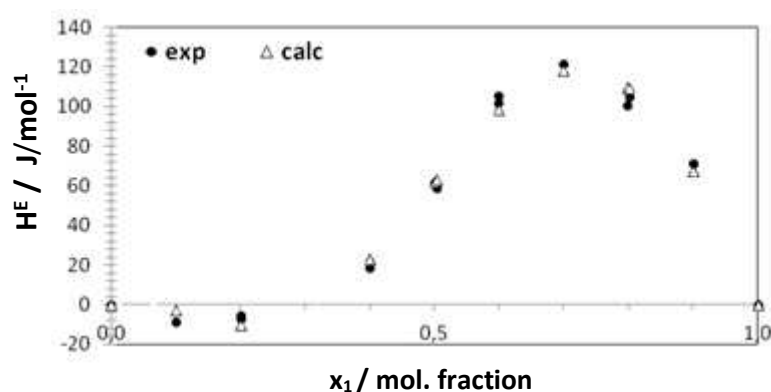


Fig.1. Excess molar enthalpies of system isobutyl acetate (1) – acetic acid (2) at 373.21 K

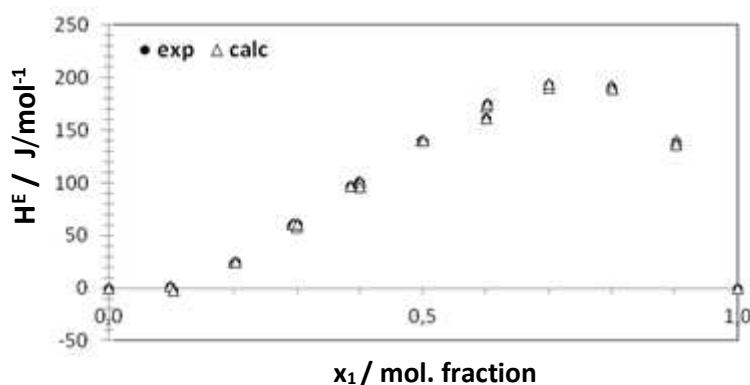


Fig.2. Excess molar enthalpies of butyl propionate (1) – propionic acid (2) at 373.15 K

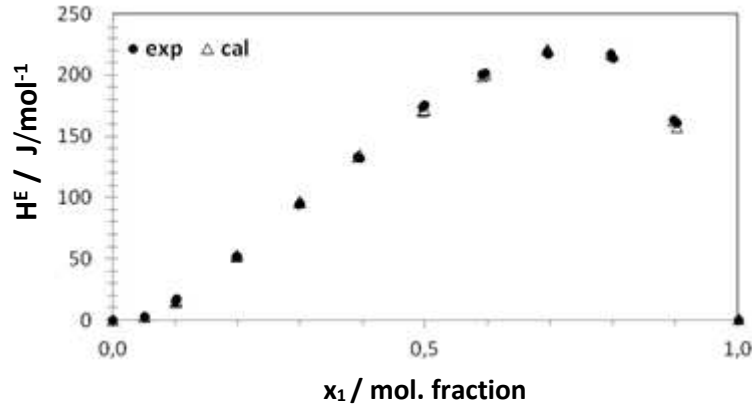


Fig.3. Excess molar enthalpies of butyl butyrate (1) – butyric acid (2) at 373.12 K

The quality of the excess molar enthalpies description has been estimated via average relative deviation (ARD, %) and standard deviation (STD) given as:

$$ARD = \frac{100}{n} \sum_{i=1}^n \frac{|H_{\text{exp}}^E - H_{\text{calc}}^E|}{|H_{\text{exp}}^E|} \quad (6)$$

$$STD = \sqrt{\frac{1}{n-N} \sum_{i=1}^n (H_{\text{exp}}^E - H_{\text{calc}}^E)^2} \quad (7)$$

and are listed in Table 5. Here n is number of experimental points, $N=6$ is total number of coefficients Eq. (5).

Table 5. Average relative deviation ARD (%), and standard deviation STD of H^E (J mol⁻¹).

System	STD	ARD
Isobutyl acetate – acetic acid	6.2	21.0
Butyl propionate – propionic acid	3.5	13.2
Butyl butyrate – butyric acid	0.64	1.9

The accuracy of the description of S-shaped curves $H^E(x)$ with small regions of negative values for binary system is 8.04–22.5% (ARD) [28,32], 7.2 [33], 3.5 [34], 24% [35]. The values STD (H^E) for these curves make up the ranges 14.2–16.6 [28,32], 9.9–43.5 [33], 10–15 [34]. The region of negative values H^E for system ethyl acetate (1) – acetic acid (2) is larger, the value $H^E = 0$ is about at $x_1 = 0.51$ –0.6 mol. fraction, STD (H^E) is 3.24 [36]. The curves $H^E(x)$ of binary systems of acetic or propionic acid with ethyl alkanooates (C₃–C₁₀) are almost symmetric, therefore values STD (H^E) are much lower 0.6–2.7 [37].

The S-shape of curves $H^E(x)$ takes place in isobutyl acetate (1) – acetic acid (2) (Fig. 1) and butyl propionate (1) – propionic acid (2) (Fig. 2). Negative values of excess molar enthalpies recorded in the field of acid-rich compositions in both systems. The biggest region of negative enthalpy is in system isobutyl acetate (1) – acetic acid (2) (Fig. 1). The maximum $H^E(x)$ is about 122 J mol⁻¹ at $x_1 = 0.7$, the minimum of excess molar enthalpy is not less -10 J mol⁻¹ at $x_1 = 0.1$ mol. fraction. The calculated value $H^E = 0$ is observed at $x_1 = 0.32$ mol. fraction.

In system butyl propionate (1) – propionic acid (2) (Fig. 2) the maximum $H^E(x)$ is about 195 J mol⁻¹ at $x_1 = 0.7$, the minimum of excess molar enthalpy is not less -5 J mol⁻¹ at $x_1 = 0.05$, and the calculated value $H^E = 0$ is observed at $x_1 = 0.1$ mol. fraction.

At the same time excess molar enthalpies of butyl butyrate (1) – butyric acid (2) are positive in the whole range of compositions (Fig. 3), with maximum value about 222 J mol⁻¹ at x₁= 0.75 mol. fraction. Partial values ($\overline{H}_1^E, \overline{H}_2^E$) were calculated using equation of tangent line to the dependencies $H^E(x)$ (5) at the experimental points:

$$H^E = \overline{H}_1^E \cdot x_1 + \overline{H}_2^E \cdot x_2 \quad (8)$$

Calculated values of partial ($\overline{H}_{V_1}, \overline{H}_{V_2}$) and integral molar enthalpies of vaporization (H_V) are represented in Tables 6-8. Molar vaporization enthalpies for pure components (H_{V_1}, H_{V_2}) are presented in [38]. In every system it takes place the ratio ($H_{V_1} < H_{V_2}$): 36872 < 39050 for isobutyl acetate (1) – acetic acid (2); 38183 < 42998 for butyl propionate (1) – propionic acid (2); 40102 < 46841 for butyl butyrate (1) – butyric acid (2).

Table 6. Calculated values (J mol⁻¹) for isobutyl acetate (1) – acetic acid (2) at 373.21 K and 101,3 kPa

x_1	$\overline{H}_1^E$	$\overline{H}_2^E$	$\overline{H}_{V_1}$	$\overline{H}_{V_2}$	H_V
0.10004	-89.7	7.3	36928.5	39006.2	38798.4
0.20032	-29.7	-5.4	36868.5	39018.9	38588.1
0.20051	-29.5	-5.4	36868.3	39018.9	38587.7
0.39987	229.2	-114.5	36609.6	39128.0	38121.0
0.40015	229.4	-114.7	36609.4	39128.2	38120.3
0.50106	263.8	-140.6	36575.0	39154.1	37861.8
0.50371	263.5	-140.3	36575.3	39153.8	37855.0
0.59935	222.9	-87.8	36615.9	39101.3	37611.7
0.59979	222.6	-87.3	36616.2	39100.8	37610.6
0.69899	139.9	68.9	36698.9	38944.6	37374.9
0.79766	58.6	312.0	36780.2	38693.1	37167.3
0.80084	56.5	320.4	36782.3	38693.1	37162.9
0.89949	10.5	576.4	36828.3	38437.2	36990.0
0.89950	10.5	576.4	36828.3	38437.1	36990.0

Table 7. Calculated values (J mol⁻¹) for butyl propionate (1) – propionic acid (2) at 373.15 K and 101,3 kPa

x_1	$\overline{H}_1^E$	$\overline{H}_2^E$	$\overline{H}_{V_1}$	$\overline{H}_{V_2}$	H_V
0.09825	142.6	-17.4	38040.4	43015.4	42526.6
0.10191	151.6	-18.4	38031.4	43016.4	42508.4
0.19914	295.5	-42.2	37887.5	43040.2	42014.1
0.20142	297.2	-42.7	37885.8	43040.7	42002.4
0.29177	330.0	-52.7	37853.0	43050.7	41534.2
0.29261	325.0	-57.7	37858.0	43055.7	41534.8
0.29798	331.5	-52.9	37851.5	43050.9	41501.6
0.30069	330.7	-53.0	37852.3	43051.0	41487.8
0.38490	327.5	-51.1	37855.5	43049.1	41050.1
0.39845	326.0	-50.1	37857.0	43048.1	40979.7
0.39979	325.8	-50.0	37857.2	43048.0	40972.8
0.40014	325.75	-50.0	37857.3	43048.0	40971.0
0.49734	310.6	-37.4	37872.4	43035.4	40467.6
0.50065	310.0	-36.7	37873.0	43034.7	40450.5
0.60013	282.9	-2.6	37900.1	43000.6	39939.6
0.60165	282.7	-2.34	37900.3	43000.3	39937.1
0.69930	282.3	-1.8	37900.7	42999.8	39931.9
0.70023	232.3	94.2	37950.7	42903.8	39440.1
0.79964	231.6	95.7	37951.4	42902.3	39435.5
0.80004	150.3	347.9	38032.7	42650.1	38957.8
0.90152	149.9	349.4	38033.1	42648.6	38956.0
0.90247	52.3	930.3	38130.7	42067.7	38518.4

Table 8. Calculated values (J mol^{-1}) for butyl butyrate (1) – butyric acid (2) at 373.12 K and 101,3 kPa

x_1	$\bar{H}_1^E$	$\bar{H}_2^E$	$\bar{H}_{V_1}$	$\bar{H}_{V_2}$	H_V
0.05028	150.55	-4.71	39951.5	46845.7	46499.1
0.05036	150.8	-4.73	39951.2	46845.7	46498.5
0.10063	293	-15.98	39809.0	46857.0	46147.7
0.10235	296.5	-16.38	39805.5	46857.4	46135.6
0.19645	397.8	-32.6	39704.2	46873.6	45465.2
0.19896	398.7	-32.81	39703.3	46873.8	45447.2
0.29816	395.5	-30.91	39706.5	46871.9	44735.5
0.2999	395	-30.71	39707.0	46871.7	44723.0
0.39133	366.95	-15.74	39735.1	46856.7	44069.8
0.39529	365.7	-14.94	39736.3	46855.9	44041.6
0.49564	337.3	7.88	39764.7	46833.1	43329.7
0.49822	336.6	8.56	39765.4	46832.4	43311.5
0.58994	309.2	41.84	39792.8	46799.2	42665.8
0.59557	307.1	44.85	39794.9	46796.2	42626.4
0.69468	256.6	139.6	39845.4	46701.4	41938.7
0.69637	255.5	142.2	39846.5	46698.8	41927.1
0.79698	169.6	404.3	39932.4	46436.7	41252.9
0.79982	166.8	415.7	39935.2	46425.3	41234.4
0.89626	65.23	1005.4	40036.8	45835.6	40638.3
0.90137	60.19	1050.15	40041.8	45790.9	40608.8

The differences ($H_{V_1} - H_{V_2}$) are -2174, -4815 and -6709 J mol^{-1} for isobutyl acetate (1) – acetic acid (2), butyl propionate (1) – propionic acid (2); and butyl butyrate (1) – butyric acid (2), respectively. These differences significantly exceed ($\bar{H}_1^E - \bar{H}_2^E$) in these biazeotropic systems (Tables 6-8). Thus, value of vaporization enthalpies (3) are close to additive values (4) (Fig. 4-6).

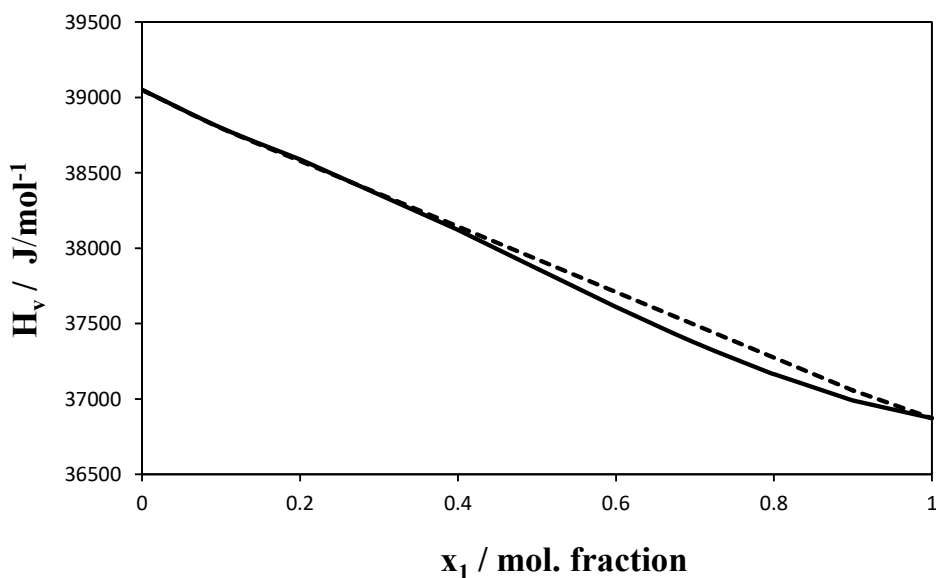


Fig.4. Vaporization enthalpies for isobutyl acetate (1) – acetic acid (2) at 373.21 K (Table. 6): (solid line - calculated by equation 3; dotted line - calculated by equation 4 (additivity)).

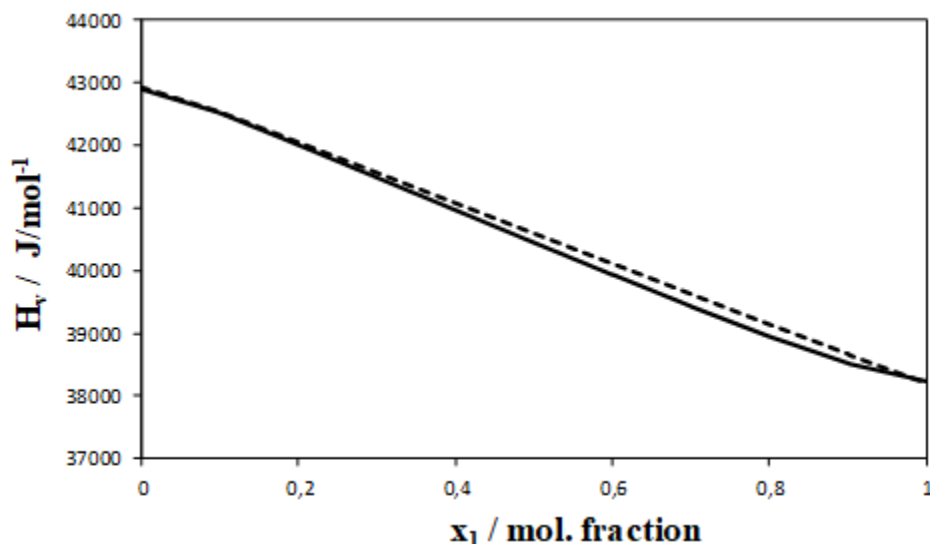


Fig.5. Vaporization enthalpies for butyl propionate (1) – propionic acid (2) at 373.15 K (Table. 7): (solid line - calculated by equation 3; dotted line - calculated by equation 4 (additivity)).

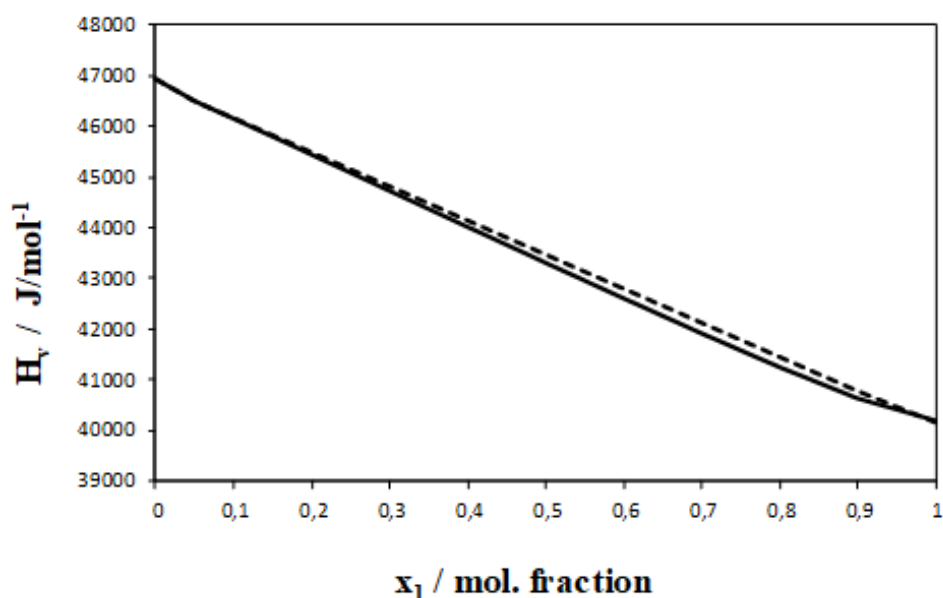


Fig.6. Vaporization enthalpies for butyl butyrate (1) – butyric acid (2) at 373.12 K (Table. 6): (solid line - calculated by equation 3; dotted line - calculated by equation 4 (additivity)).

Conclusion

Experimental data of excess molar enthalpies for whole concentration range were obtained for three systems (isobutyl acetate – acetic acid; butyl propionate – propionic acid; butyl butyrate – butyric acid) about 373 K. This data array is important for study evolution of biazeotropic systems.

The ratio of partial vaporization enthalpies ($\overline{H}_{V_1} < \overline{H}_{V_2}$) is preserved over whole composition range in every system. According to Vrevsky's law, at temperature rise in every system azeotrope (min T) is enriched with acid, while azeotrope (max T) – with ether.

Thus, dependences $H_V(x)$ have no extremum. Consequently, in the considered biazeotropic systems, the replacement of partial molar vaporization enthalpies by vaporization enthalpies of pure substances is acceptable. Thus, while choosing conditions for PSD, its acceptable to take molar vaporization enthalpies of pure substances.

Acknowledgments: This research has been carried out with use of the equipment of Saint Petersburg State University Research Park: Center for Thermal Analysis and Calorimetry. The authors acknowledge Saint-Petersburg State University for a research project 125021902439–8 and Russian Foundation for Basic Research for a research project 18-03-01224-a.

References

1. Zharov V, Serafimov L. Fiziko-khimicheskie osnovy distillyatsii i rektifikatsii (Physicochemical Fundamentals of Distillation Processes), Leningrad: Khimiya; 1975.
2. Gorak A, Sorensen E (eds). Distillation: Fundamentals and Principles, Elsevier; 2014.
3. Kiva VN, Hilmen EK, Skogestad S. Azeotropic phase equilibrium diagrams: a survey. Chem. Eng. Sci. 2003. [https://doi.org/10.1016/S0009-2509\(03\)00018-6](https://doi.org/10.1016/S0009-2509(03)00018-6)
4. Petlyuk FB. Distillation Theory and Its Application to Optimal Design of Separation Units. Cambridge: Cambridge Univ. 2004. <https://doi.org/10.1017/CBO9780511547102>
5. Seader J, Henley E. Separation Process Principles. 2nd ed. New York: Wiley; 2006
6. Luyben L, Chien IL. Design and Control of Distillation Systems for Separating Azeotropes. New York: Wiley; 2010.
7. Serafimov LA, Chelyuskina TV. Complex singular points of the Tie-Line vector field diagrams of ternary mixtures. Theor. Found. Chem. Eng. 2005. <https://doi.org/10.1007/s11236-005-0123-3>
8. Christensen SP, Olson JD. Phase equilibria and multiple azeotropy of the acetic acid-isobutyl acetate system. Fluid Phase Equilib. 1992. [https://doi.org/10.1016/0378-3812\(92\)85129-V](https://doi.org/10.1016/0378-3812(92)85129-V)
9. Burguet MC, Monton JB, Munoz R, Wisniak J, Segura H. Polyazeotropy in Associating Systems: The 2 – Methylpropyl Ethanoate + Ethanoic Acid System. J. Chem. Eng. Data. 1996/ <https://doi.org/10.1021/je960159k>
10. Serafimov LA, Chelyuskina TV, Polkovnichenko AV, Yakushev RA. The Analysis of the Mutual Transformations of the Structures of Diagrams of Ternary Systems via the Formation of Binary Internal Tangential Azeotropes. Theor. Found. Chem. Eng. 2018. <https://doi.org/10.1134/S0040579518040401>
11. Bedretdinov FN, Chelyuskina TV. Research of various iso-manifolds in four component systems containing biazotropic binary constituents. Fine Chemical Technologies. 2018. <https://doi.org/10.32362/2410-6593-2018-13-1-45-54>
12. Morachevsky A. (ed). Termodinamika ravnovesiya zhidkost-par (Thermodynamic of vapor-liquid equilibrium). Leningrad: Khimiya; 1989.
13. Tsvetov NS, Sadaeva AA, Toikka MA, Zvereva IA, Toikka AM. Excess molar heat capacity for the binary system n propyl alcohol+water in the temperature range 278.15–358.15 K: new data and application for excess enthalpy calculation. J. Therm. Anal. Calorim. 2020. <https://doi.org/10.1007/s10973-020-09605-y>
14. Dipak Sen, Moon Gab Kim. Excess molar volumes and excess molar enthalpies for binary mixtures of 1,2-dichloropropane with methyl ethanoate, methyl propanoate, and methyl butanoate at T = 298.15 K. Fluid Phase Equilib. 2011. <https://doi.org/10.1016/j.fluid.2011.01.005>
15. Kiyofumi K, Yoshinobu N, Takafumi O, Yuta I, Hiroyuki M, Katsumi T. Determination and correlation of excess molar enthalpies of the binary carbon dioxide + ethyl acetate system at 298.15 to 308.15 K and 5.0 to 7.0 MPa. Fluid Phase Equilib. 2013. <https://doi.org/10.1016/j.fluid.2013.10.038>
16. Casas H, Segade L, Franjo C, Jiménez E. Excess Molar Enthalpies of Propyl Propanoate + Hexane + Benzene at 298.15 K and 308.15 K. J. Chem. Eng. Data. 2000. <https://doi.org/10.1021/je990265x>

17. López M, Piñeiro MM, Salgado J, de Cominges BE, Legido JL, Paz Andrade MI. Experimental and Theoretical Study of Excess Molar Enthalpies of Ethyl Propionate + n-Hexane + 1-Butanol at 298.15 K. J. Chem. Eng. Data. 1990. <https://doi.org/10.1021/jc9900530>
18. Solomonov BN, Varfolomeev MA, Nagrimanov RN, Novikov VB, Zaitsau DH, Verevkin SP. Solution calorimetry as a complementary tool for the determination of enthalpies of vaporization and sublimation of low volatile compounds at 298.15 K. Thermochemica Acta. 2014. <https://doi.org/10.1016/j.tca.2014.05.033>
19. Yu D, Chen Z. A theoretical analysis on enthalpy of vaporization: Temperature dependence and singularity at the critical state. Fluid Phase Equilibr. 2020. <https://doi.org/10.1016/j.fluid.2020.112611>
20. Solomonov BN, Yagofarov MI. Compensation relationship in thermodynamics of solvation and vaporization: Features and applications. II. Hydrogen-bonded systems. Journal of Molecular Liquids 2023. <https://doi.org/10.1016/j.molliq.2023.121205>
21. Ryzhkin DA, Raeva VM. Comparison of methods for calculating the enthalpy of vaporization of binary azeotropic mixtures. Fine Chemical Technologies. 2024. <https://doi.org/10.32362/2410-6593-2024-19-4-279-292>
22. Kołodziejczyk E, Marczak W. Are conventional thermochemical calculations a viable alternative to measurements of vaporization enthalpy of azeotropes? Molecules. 2025. <https://doi.org/10.3390/molecules30040810>
23. Pashchenko LL, Druzhinina AI. Enthalpy of vaporization measurements by calorimetric techniques. J. Therm. Anal. Calorim. 2018. <https://doi.org/10.1007/s10973-018-7370-0>
24. Vicencio LA, López-Porfiri P, de la Fuente JC. Vapour pressure and vaporisation enthalpy for two key apple odorants, ethyl butyrate and ethyl hexanoate, at pressures from (15 to 105) kPa. J. Chem. Thermodyn. 2020. <https://doi.org/10.1016/j.jct.2019.105982>
25. Abdullah R, Solomonov BN. Sublimation/vaporization and solvation enthalpies of monosubstituted pyridine derivatives. Chem. Thermodyn. Therm. Anal. 2022. <https://doi.org/10.1016/j.ctta.2022.100087>
26. Dong J.-Q., Lin R.-S., Yen W.-H. Heats of vaporization and gaseous molar heat capacities of ethanol and the binary mixture of ethanol and benzene. Can. J. Chem. 1988. <https://doi.org/10.1139/v88-136>
27. Tamir A. Prediction of latent heat of vaporization of multicomponent mixtures. Fluid Phase Equilibr. 1982. [https://doi.org/10.1016/0378-3812\(82\)80031-9](https://doi.org/10.1016/0378-3812(82)80031-9)
28. Letyanina IA, Tsvetov NS, Zvereva IA, Samarov AA, Toikka AM. Excess molar enthalpies for binary mixtures of n-propanol, acetic acid, and n-propyl acetate at 313.15 K and atmospheric pressure. Fluid Phase Equilibr. 2014. <https://doi.org/10.1016/j.fluid.2014.08.022>
29. Calvet E, Prat H. Microcalorimétrie: Applications Physico - Chimiques et Biologiques. Paris: Masson et Cie.;1956
30. Van der Waals J, Hermans J. Thermodynamic properties of mixtures of alkanes differing in chain length. I. Heat of mixing, des Pays-Bas: Rec. Trav. Chim; 1950.
31. Frenkel M, Chirico R, Diky V, Kazakov A, Muzny C, Magee J, Abdulagatov I, Kroenlein K, Kang JW. NIST Thermo Data Engine, NIST Standard Reference Database 103b - Pure Compounds, Binary Mixtures, and Chemical Reactions, Version 5. 0, Standard Reference Data Program. National Institute of Standards and Technology, Gaithersburg, MD; 2010.
32. Letyanina IA, Tsvetov NS, Toikka AM. Excess molar enthalpies of the ternary mixture n-propanol + acetic acid + water at 313.15 K and atmospheric pressure. Fluid Phase Equilibr. 2015. <https://doi.org/10.1016/j.fluid.2015.07.053>

33. Letyanina IA, Tsvetov NS, Toikka AM. Application of the UNIFAC models for prediction and description of excess molar enthalpies for binary mixtures of n-propanol, acetic acid, n-propyl acetate, and water. *Fluid Phase Equilib.* 2016. <https://doi.org/10.1016/j.fluid.2016.07.007>
34. Tsvetov NS, Letyanina IA, Zvereva IA, Toikka AM. Excess molar enthalpies of the ternary mixture n-propanol + n-propyl acetate + water at 313.15 K. *J. Therm. Anal. Calorim.* 2018. <https://doi.org/10.1007/s10973-018-7110-5>
35. Golikova A, Shasherina A, Anufrikov Y, Misikov G, Toikka M, Zvereva I, Toikka A. Excess Enthalpies for Binary Mixtures of the Reactive System Acetic Acid + n-Butanol + n-Butyl Acetate + Water: Brief Data Review and Results at 313.15 K and Atmospheric Pressure. *Int. J. Mol. Sci.* 2023. <https://doi.org/10.3390/ijms24065137>
36. Golikova AD, Tsvetov NS, Samarov AA, Toikka MA, Zvereva IA, Trofimova M, Toikka AM. Excess enthalpies and heat of esterification reaction in ethanol + acetic acid + ethyl acetate + water system at 313.15 K. *J. Therm. Anal. Calorim.* 2020. <https://doi.org/10.1007/s10973-019-08488-y>
37. Francesconi R, Comelli R. Excess molar enthalpies of binary mixtures containing acetic or propionic acid + eight ethyl alkanoates at 298.15 K. *Thermochim. Acta.* 1998. [https://doi.org/10.1016/S0040-6031\(98\)00477-8](https://doi.org/10.1016/S0040-6031(98)00477-8)
38. Mityushkina IA. Separation of binary azeotropic mixtures with the use of additional substances of different volatility. Dissertation. Moscow, MITHT; 2011.