

**Vapor-liquid equilibrium and excess properties of the binary mixtures
formed by ethyl isobutyrate and n-alkanols**

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Abstract: This contribution reports densities together with the corresponding excess molar volumes, and excess molar enthalpies of the binary mixtures formed by ethyl isobutyrate and n-alkanols (from methanol to 1-butanol) at two temperatures (303.15 and 323.15) K and at atmospheric pressure ($p = 0.1$ MPa). These excess properties were correlated with composition using the Redlich-Kister equation. Excess molar volumes and enthalpies are positive, except the excess molar volumes for the mixture ethyl isobutyrate and methanol. Furthermore, the vapor-liquid equilibrium data for these mixtures at different experimental conditions have been also presented. Both the isothermal VLE at two temperatures (303.15 and 323.15) K and isobaric VLE at two pressures (40.000 and 101.325) kPa were measured. Some of the systems exhibit azeotropic points. The VLE data were found thermodynamically consistent. From experimental data the activity coefficients along with excess Gibbs function (isothermal) and reduced excess Gibbs functions (isobaric) were obtained and correlated with composition using the Wilson equation. These excess Gibbs function and reduced excess Gibbs functions were found positive. Finally, we have used our experimental VLE data to check the reliability of modified UNIFAC predictions.

Keywords: Alkanols, Density, Enthalpy of mixing, Ethyl isobutyrate, Vapor-liquid equilibrium.

1. Introduction

Flavors and fragrances are faithful companions in daily life [1-4]. Several of them have an ester as major component [5-8]. However, the medium in which the flavor is found needs to preserve the quality and the characteristics of the molecule responsible for the scent. Therefore, the study of thermophysical properties of these esters and of its mixtures are of great importance for the design of chemical processes in which the esters are implicated. In this sense, ethyl isobutyrate is a flavoring substance [9, 10] which exists in banana, apple, wine grape, so can be found in some drinks.

In this work, we report experimental results (densities, mixing enthalpies and vapor-liquid equilibrium) for the binary systems: ethyl isobutyrate + n-alkanol (methanol, ethanol, 1-propanol or 1-butanol). Densities and mixing enthalpies were measured at two temperatures (303.15 and 323.15 K) and at atmospheric pressure (0.1 MPa). Vapor-liquid equilibrium of these mixtures was determined in two runs performed at constant temperature (303.15 and 323.15 K) and at constant pressure (40.000 and 101.325 kPa). It can be also outlined that the modified UNIFAC [11] was checked using our experimental VLE data.

To our knowledge, the properties presented here of binary mixtures involving ethyl isobutyrate and a normal alcohol at different temperatures have not been measured previously.

2. Experimental

Table 1 summarizes the information about the compounds employed in our study. With respect to the water content of the chemicals, it was determined by means of an automatic titrator Crison KF 1S-2B.

Densities of the samples, pure compounds or mixtures, were determined by means of an Anton Paar DMA 5000 vibrating tube densimeter internally thermostated at ± 0.005 K. Calibration procedure can be found elsewhere [12]. The uncertainty of density measurements can be estimated in $2 \cdot 10^{-4} \text{ g} \cdot \text{cm}^{-3}$.

The mixtures were prepared by mass using a Sartorius Semimicro balance CP225-D within $\pm 10^{-5}$ g. The corresponding estimated uncertainty in the mole fraction of the mixtures is 10^{-4} .

The thermal effect of the mixing process was registered using a Thermometric 2277 thermal activity monitor, thermostated within $\pm 2 \cdot 10^{-4}$ K, together with two Shimadzu LC-10ADVP HPLC pumps to supply the liquids. The calorimeter and the pumps were previously calibrated [13, 14], in particular the calorimeter was chemically calibrated using the well known heats of mixing of the n-hexane + cyclohexane mixture [15]. From the mixing thermal effect and the flows of the components the excess molar enthalpies at each composition can be easily calculated. The uncertainty in excess molar enthalpies is 1% while the uncertainty in the mole fractions of the mixtures is 0.001.

The vapor-liquid equilibrium of the pure compounds and systems at the different experimental conditions (isothermal and isobaric) were measured using a dynamic ebulliometer (Fischer Labodest) with recirculation of both phases provided with a Cottrell pump, this equipment has been previously described [16]. The pressure was measured with an uncertainty of 0.1 kPa by means of a Paroscientific Digiquartz 215A-102 pressure transducer and a Digiquartz 735 display unit, while the temperature was measured with an uncertainty of 0.1 K using an Automatic Systems Laboratories (model F25) thermometer with a PT100 probe. After reaching the equilibrium, samples of both liquid and condensed vapor phases were taken. The compositions of these samples were determined by densitometry, using the

previously obtained density-composition curves, the estimated uncertainty in mole fraction is 0.002.

Table 2 shows the comparison between our experimental values for the thermophysical properties of the pure compounds and the corresponding literature values [17-59]. On the other hand, a graphical comparison between our experimental values and some literature values [60-63] is shown in Fig. 1.

3. Results and discussion

There are not previous density data at our working temperatures for ethyl isobutyrate, so no comparison is possible, with respect to experimental vapour pressures and those calculated using the data of Stull [17] the concordance is reasonable with an average deviation equals to 0.176 kPa, finally the agreement between our normal boiling point and those of the literature is really good. Regarding to the alkanols the comparison between our experimental and literature values is satisfactory, the higher deviations are presented for the vapour pressures of 1-propanol and 1-butanol, these deviations are around 0.1 kPa. In general terms, we can outlined that the deviations between measured and literature values are close to the experimental uncertainties.

The experimental densities together with calculated excess molar volumes for the studied binary mixtures are collected in Table S1 of the Supplementary material, while the excess molar enthalpies are reported in Table S2.

Excess molar volume, V^E , can be obtained for each composition of the mixture from the molar masses and densities of the pure components (in the same physical state as the mixture [64]) and densities of the mixtures using standard procedures. On the other hand, as

we have mentioned above, the excess molar enthalpies at each composition can be obtained from the mixing thermal effect and the corresponding component flows.

Excess molar volumes and excess molar enthalpies have been plotted in Figs. 2 and 3, respectively. Both excess properties have been correlated with composition using the Redlich-Kister equation [65]:

$$Y^E = x_1(1-x_1)\sum_i A_i(2x_1-1)^i \quad (1)$$

being Y^E the excess property, x_1 the mole fraction of ethyl isobutyrate, and A_i the fitting parameters. Table 3 reports both Redlich-Kister parameters and standard deviations, $\sigma(Y^E)$.

The excess molar volumes, V^E , are positive over the entire composition range from ethanol to 1-butanol, while for methanol the V^E values are negative. The representation of excess molar volume against composition for all the systems is quite symmetrical. For a given temperature the V^E values follow the sequence: methanol < ethanol < 1-propanol < 1-butanol, that is, the positive contributions to excess molar volume increase with the alkanol length. Moreover, for all the mixtures the excess molar volume increases with temperature, being this increase bigger for the mixture containing ethanol and quite similar for the rest of the systems.

The excess molar enthalpies, H^E , are positive for all the binary mixtures. The corresponding H^E plots are not symmetrical, they are shifted to the ethyl isobutyrate rich region. The H^E values at both temperatures follow the same order than the V^E ones: methanol < ethanol < 1-propanol < 1-butanol. With respect to the temperature behaviour, H^E increases with temperature for all the systems, in the case of 1-propanol this increase leads to similar H^E values for the mixtures containing 1-propanol and 1-butanol at $T = 313.15$ K; on the other hand for the system ethyl isobutyrate + methanol the H^E rise is quite higher and noticeable.

The experimental data for vapor-liquid equilibrium (T , p , x_i , y_i) obtained at both conditions isothermal ($T = 303.15$ and 323.15 K) and isobaric ($p = 40.000$ and 101.325 kPa)

along with calculated activity coefficients and excess Gibbs functions, G^E , or reduced excess Gibbs functions (G^E/RT) are listed in Tables S3 to S4 of the supplementary material.

The activity coefficients γ_i of the components in the liquid phase have been calculated taking into account both the non-ideality of the vapour phase and the variation with pressure of the Gibbs functions of the pure compounds [66]:

$$\gamma_i = \frac{y_i P}{x_i p_i^\circ} \exp \left[\frac{(B_{ii} - V_i^\circ)(p - p_i^\circ) + (1 - y_i)^2 p \delta_{ij}}{RT} \right] \quad (2)$$

$$\delta_{ij} = 2B_{ij} - B_{ii} - B_{jj} \quad (3)$$

where p and T are the pressure and equilibrium temperature, respectively, R is the universal gas constant, x_i and y_i are the liquid and vapour mole fractions of component i , respectively, B_{ii} and B_{ij} are, respectively, the second virial coefficient of component i and the cross second virial coefficient, finally V_i° and p_i° are, respectively, the liquid molar volume and the vapour pressure of the pure compound i at the equilibrium temperature. The values of the virial coefficients were estimated using the Tsonopoulos method [67, 68]. The liquid molar volumes and vapour pressures of the pure compounds at the temperatures (303.15 and 323.15) K have been measured in our laboratory. These two properties of the components as a function of the temperature for isobaric data were estimated using the Rackett equation [69] for liquid molar volumes, and the Antoine equation for vapor pressures of the components:

$$\log(p / \text{kPa}) = A - \frac{B}{(T / \text{K}) + C} \quad (4)$$

the parameters of the Antoine equation given in Table S5 of the supplementary material have been taken or calculated from Riddick et al. [70] and Stull [17].

The experimental results were correlated using the Wilson model [71]: based on the following equations:

$$\ln \gamma_i = -\ln\left(\sum_j x_j \Lambda_{ij}\right) + 1 - \sum_k \frac{x_k \Lambda_{ki}}{\sum_j x_j \Lambda_{kj}} \quad (5)$$

$$\Lambda_{ij} = \frac{V_j^\circ}{V_i^\circ} \exp\left(-\frac{\lambda_{ij} - \lambda_{ii}}{RT}\right) \quad (6)$$

where V_i° is the liquid molar volume of component i at $T = 298.15$ K. The Λ_{ij} are the dimensionless model parameters, while $(\lambda_{ij} - \lambda_{ii})$ are the adjustable Wilson parameters expressed in $\text{J}\cdot\text{mol}^{-1}$. These best parameters have been obtained by minimizing the following objective function [72] that involves experimental and calculated pressures:

$$F = \sum_i \left(\frac{p^{exp} - p^{cal}}{p^{exp}} \right)_i^2 \quad (7)$$

the calculated pressures, p^{cal} , are obtained through the following expression [73]:

$$p^{cal} = \sum_i x_i \gamma_i^{cal} p_i^\circ \exp\left[\frac{(V_i^\circ - B_{ii})(p - p_i^\circ) - (1 - y_i)^2 p \delta_{ij}}{RT}\right] \quad (8)$$

Table 4 collects Wilson parameters along with deviation in pressure (isothermal data) or temperature (isobaric data) and average deviation in vapor phase composition. The biggest deviations in pressure and temperature, $\Delta p = 0.029$ kPa and $\Delta T = 0.31$ K, respectively, indicate that the correlation for these systems is adequate and that the presented VLE data are reliable. On the other hand, we have tested the thermodynamic consistency of the results using the method suggested by Van Ness et al. [74] and detailed by Fredenslund et al. [75], the experimental data are consistent if $\Delta y < 0.01$ and as it can be seen in Table 5, all the systems at the different experimental conditions satisfy this condition. We have used Legendre polynomials for the correlation of activity coefficients.

The pressure-composition, p - x_1 - y_1 , and temperature diagrams, T - x_1 - y_1 , including experimental data and Wilson equation correlation are plotted in Figs. 4-7. Some of the systems present an azeotrope whose coordinates $(T_{az}, p_{az}, x_{1,az})$ are given in Table 6; the azeotropic coordinates were obtained taking into account that the pressure-composition or temperature diagram must present an extremum and the composition of both phases must be equal, these calculated azeotropic coordinates have been plotted in the corresponding Figs. As the pressure increases, the azeotrope shifts to a lower ethyl isobutyrate composition, the same effect is also observed upon a rise in temperature. On the other hand, for a given pressure or temperature, the increase in the number of carbons in the n-alkanol causes the composition of the azeotropic point to move toward the ethyl isobutyrate rich region.

The excess Gibbs functions and the reduced excess Gibbs functions for all the binary mixtures are graphically represented in Figs. 8 and 9.

For isothermal and isobaric conditions the VLE results present positive deviation from Raoult's law, being the corresponding activity coefficients positive.

The excess Gibbs function, G^E , show positive values over the entire range of composition for all the studied mixtures with maximum values close to the equimolar composition. The G^E values show the string: methanol > ethanol > 1-propanol > 1-butanol. Excess Gibbs function decrease slightly with temperature except for the system containing methanol, for this last system, the maximum G^E value increases with rising temperature from 821.3 J·mol⁻¹ at $T= 303.15$ K to 860.5 J·mol⁻¹ at $T= 323.15$ K. On the other hand, the entropic contribution to excess Gibbs function, TS^E , is positive for all the mixtures except for the mixture involving methanol at $T = 303.15$ K which entropic contribution is sigmoidal showing a positive value from $x_1 = 0.66$. At a given temperature follows the sequence: 1-butanol > 1-propanol > ethanol > methanol. When the temperature rises the entropic contribution for all the mixtures also increases and becomes positive over the whole

composition range, at $T = 323.15$ K the entropic contribution for the systems containing 1-propanol and 1-butanol is quite similar.

The (G^E/RT) values of all the studied systems are positive and not too high and decrease with the increase of the pressure, although for the mixture containing methanol this decrease is low. At a given pressure, the reduced excess Gibbs function decreases according to the sequence: methanol > ethanol > 1-propanol > 1-butanol.

The excess molar enthalpy is the most adequate property in order to analyze molecular interactions. Positive contributions to excess molar enthalpy indicate that the molecular interactions are adverse from an energetic point of view, while favorable interactions have a negative contribution to H^E . To explain the excess molar enthalpies obtained it must be borne in mind that in the mixing process on one hand the interactions (dipole-dipole interactions in the ester and self-association in the alkanols) between the pure compounds can be weakened and on the other hand favorable interactions between the mixed components can be established (heteroassociation). Regarding these favorable interactions, ethyl isobutyrate presents hydrogen-bond accepting ability due to the lone-pairs on the O atoms, therefore it can establish hydrogen bond with alkanols [76, 77]. The experimental excess molar enthalpy reflects the balance between all these molecular interactions, our systems presents positive and quite high H^E values, being the lowest ones those for the mixture containing methanol because it possesses more proton donating ability than higher alkanols [78, 79].

The excess molar volume apart from energetic factors depends on structural factors, that is, V^E also depends on the more or less favorable packing of the molecules of the components in the mixture. In this sense an efficient molecular packing contributes negatively to excess molar volume. For our systems the positive excess molar volumes obtained from ethanol to 1-butanol can be explained by the weakening of dipole-dipole interactions in ethyl isobutyrate as well the dissociation of the alkanols that prevail over the heteroassociation

between ester and alkanol, together with the unfavorable packing of the molecules specially for the longer alkanols. On the other hand V^E for the system containing methanol is negative, in the case of methanol two different factors leads to the contraction in volume, on one hand his molecular size allows a better interstitial accommodation and on the other hand the above mentioned higher proton-donating ability of methanol.

With respect to vapour-liquid equilibrium positive deviations from ideal behavior resulting from unfavorable interactions between the mixed components lead to activity coefficients greater than unity and positive excess Gibbs functions. As we have previously discussed for H^E values, the unfavorable interactions in the mixture are predominant, so the excess Gibbs functions must be positive.

4. UNIFAC predictions

The modified-UNIFAC method has been used to predict the vapor-liquid equilibrium of the studied mixtures at the different experimental conditions, for the calculations we have employed the newest UNIFAC parameters available [80]. In Table 6 the coordinates of the UNIFAC-predicted azeotropes are shown while in Table 7 the deviations between the measured and predicted VLE data are given. The predicted azeotropic coordinates have been plotted in the corresponding Figs. The agreement between experimental and predicted azeotropic coordinates is quite good.

Figs. S1-S4 of the supplementary material present the comparison between the experimental and predicted isothermal VLE data at the temperatures 303.15 and 323.15 K, or predicted isobaric VLE data at the pressures 40.000 and 101.325 kPa, for the ethyl isobutyrate + n-alkanol systems.

According to Table 7 and Figs. S1-S4, the VLE data predicted by the UNIFAC model show good agreement with the experimental VLE data, being the overall average deviations $\Delta p = 0.25$ kPa and $\Delta y = 0.0141$ for isothermal conditions and $\Delta T = 0.32$ K and $\Delta y = 0.0057$ for isobaric ones. It is clear that the predictions at $T = 303.15$ K or $p = 101.325$ kPa are slightly better than at $T = 323.15$ K or $p = 40.000$ kPa. Finally, regarding the comparison of VLE predictions among the studied systems, the worst predictions correspond to the system ethyl isobutyrate + methanol, especially at isobaric conditions.

5. Conclusions

This work reported experimental density data for binary mixtures containing ethyl isobutyrate with C1-C4 n-alkanols at $p = 0.1$ MPa, and at 303.15 and 323.15 K. From experimental data, excess molar volumes and excess molar enthalpies have been determined and correlated using Redlich-Kister polynomial expansions. Both the isothermal vapor-liquid equilibria at two temperatures (303.15 and 323.15) K and isobaric vapor-liquid equilibria at two pressures (40.000 and 101.325) kPa have been determined over the whole composition range and azeotropes were observed. The VLE data were found to be thermodynamically consistent. The activity coefficients along with excess Gibbs and reduced excess Gibbs functions were obtained and correlated with composition using the Wilson equation. Positive deviations from ideality were obtained both for these excess Gibbs function and reduced excess Gibbs functions. The experimental results have been used to check the accuracy of modified UNIFAC predictions: the predictions are adequate except for the system containing 1-propanol under isothermal conditions, at $T = 323.15$ K.

Acknowledgements

Authors acknowledge the financial support from Gobierno de Aragón (grant E31_17R) Fondo de Desarrollo Regional “Construyendo Europa desde Aragón” and the Ministry of superior education and scientific research of Tunisia.

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Table 1

Sample table.

Compound	CAS number	Source	Purity ^a (mass fraction)	Analysis method	Water content / ppm	Water content method
Ethyl isobutyrate	97-62-1	Aldrich	0.998	GC	250	KF
Methanol	67-56-1	Sigma-Aldrich	0.998	GC	295	KF
Ethanol	64-17-5	Acros	0.998	GC	280	KF
1-Propanol	71-23-8	Sigma-Aldrich	0.998	GC	300	KF
1-Butanol	71-36-3	Sigma-Aldrich	0.999	GC	275	KF

^a As stated by the supplier

Table 2

Density (at $p = 0.1$ MPa), ρ , and vapour pressures, p° , at working temperatures, and normal boiling point, T_b , of the pure compounds: experimental and literature values.^a

T / K	$\rho / \text{g}\cdot\text{cm}^{-3}$			p° / kPa			T_b / K	
	Exptl.	Lit.		Exptl.	Lit.		Exptl.	Lit.
Ethyl isobutyrate								
303.15	0.85792			4.340	4.400 [17]		383.59	383.45 [18] 383.65 [19] 383.4 [20]
323.15	0.83605			11.660	11.368 [17]			
Methanol								
303.15	0.78181	0.781808 [21] 0.78186 [22] 0.78190 [23]		21.880	21.86 [25] 21.90 [26] 21.904 [27]		337.96	337.96 [28] 337.92 [29] 337.9 [30]
323.15	0.76261	0.76267 [22] 0.76270 [23] 0.76271 [24]		55.735	55.539 [25] 55.60 [26] 55.566 [27]			
Ethanol								
303.15	0.78078	0.78075 [31] 0.78073 [32] 0.78078 [33]		10.465	10.470 [37] 10.462 [38] 10.475 [39]		351.48	351.53 [41] 351.49 [42] 351.47 [43]
323.15	0.76361	0.7637 [34] 0.763643 [35] 0.76329 [36]		29.545	29.439 [37] 29.494 [38] 29.510 [40]			
1-Propanol								
303.15	0.79553	0.79548 [31] 0.79566 [44] 0.79558 [45]		3.800	3.851 [39] 3.860 [48] 3.826 [49]		370.21	370.23 [51] 370.26 [52] 370.20 [53]
323.15	0.77909	0.77911 [45] 0.77897 [46] 0.77906 [47]		12.185	12.148 [39] 12.090 [48] 12.10 [50]			
1-Butanol								
303.15	0.80191	0.80201 [31] 0.80205 [44] 0.80194 [45]		1.225	1.280 [39] 1.271 [48] 1.200 [56]		390.74	390.75 [57] 390.75 [58] 390.77 [59]
323.15	0.78662	0.78630 [45] 0.78667 [54] 0.78645 [55]		4.505	4.556 [39] 4.623 [48] 4.48 [50]			

^aStandard uncertainties u are $u(T) = 0.005$ K, $u(p) = 2.5$ kPa for density measurements, and $u(T) = 0.1$ K, $u(p) = 0.1$ kPa for vapour-liquid equilibrium measurements, and the combined expanded uncertainties U_c are $U_c(\rho) = 2 \cdot 10^{-4}$ g·cm⁻³ with 0.95 level of confidence ($k = 2$).

Table 3Parameters of the Redlich-Kister equation, A_i , and standard deviations, $\sigma(Y^E)$.

Function	T / K	A_0	A_1	A_2	A_3	$\sigma(Y^E)$
Etyhl isobutyrate (1) + methanol (2)						
$V^E / (\text{cm}^3 \cdot \text{mol}^{-1})$	303.15	-0.5111	0.0233	-0.0503		0.0014
	323.15	-0.3602	0.0066	-0.0433	0.0524	0.0009
$H^E / (\text{J} \cdot \text{mol}^{-1})$	303.15	2723	1156	871		3
	323.15	4482	1556	473	-512	5
Etyhl isobutyrate (1) + ethanol (2)						
$V^E / (\text{cm}^3 \cdot \text{mol}^{-1})$	303.15	0.2942	-0.0187	-0.166	0.0684	0.0008
	323.15	0.5316	-0.002	-0.1562	0.2114	0.0011
$H^E / (\text{J} \cdot \text{mol}^{-1})$	303.15	4713	1172	915		3
	323.15	5516	1161	882		5
Etyhl isobutyrate (1) + 1-propanol (2)						
$V^E / (\text{cm}^3 \cdot \text{mol}^{-1})$	303.15	0.3728	-0.0296	-0.1468	0.1599	0.0009
	323.15	0.5859	-0.0164	-0.0568	0.2993	0.0012
$H^E / (\text{J} \cdot \text{mol}^{-1})$	303.15	5286	1189	682	-270	4
	323.15	6095	1072	636	-145	3
Etyhl isobutyrate (1) + 1-butanol (2)						
$V^E / (\text{cm}^3 \cdot \text{mol}^{-1})$	303.15	0.4727	-0.0217	-0.1209	0.1702	0.0012
	323.15	0.6530	-0.0236	0.0175	0.2928	0.0016
$H^E / (\text{J} \cdot \text{mol}^{-1})$	303.15	5614	1176	1069	-132	4
	323.15	6222	1030	940	82	3

Table 4

Parameters of the Wilson equation, $\lambda_{ij}-\lambda_{ii}$, average deviation in pressure, Δp , or average deviation in temperature, ΔT , and average deviation in vapour phase composition, Δy .

System	T / K	$\lambda_{12}-\lambda_{11} /$ (J mol^{-1})	$\lambda_{21}-\lambda_{22} /$ (J mol^{-1})	$\Delta p / \text{kPa}$	Δy
Ethyl isobutyrate (1) + methanol (2)	303.15	-179.58	4425.06	0.024	0.0035
	323.15	-565.05	4891.93	0.026	0.0041
Ethyl isobutyrate (1) + ethanol (2)	303.15	726.70	3090.08	0.025	0.0039
	323.15	-29.75	3410.07	0.026	0.0034
Ethyl isobutyrate (1) + 1-propanol (2)	303.15	839.63	2236.45	0.023	0.0050
	323.15	591.19	2213.69	0.015	0.0037
Ethyl isobutyrate (1) + 1-butanol (2)	303.15	470.37	2165.35	0.016	0.0035
	323.15	87.49	2366.58	0.029	0.0039
	p / kPa	$\lambda_{12}-\lambda_{11} /$ (J mol^{-1})	$\lambda_{21}-\lambda_{22} /$ (J mol^{-1})	$\Delta T / \text{K}$	Δy
Ethyl isobutyrate (1) + methanol (2)	40.000	-911.66	4815.21	0.26	0.0046
	101.325	-855.55	4910.41	0.08	0.0039
Ethyl isobutyrate (1) + ethanol (2)	40.000	-829.96	3980.86	0.25	0.0043
	101.325	-782.32	3871.66	0.09	0.0031
Ethyl isobutyrate (1) + 1-propanol (2)	40.000	-274.14	2594.57	0.28	0.0045
	101.325	-536.56	2720.92	0.09	0.0043
Ethyl isobutyrate (1) + 1-butanol (2)	40.000	-1294.96	3422.54	0.31	0.0042
	101.325	-513.39	2290.45	0.10	0.0049

Table 5

Thermodynamic consistency test: average deviations in pressure, Δp , and average deviations in vapour phase composition, Δy .

System	T / K	$\Delta p / \text{kPa}$	Δy
Ethyl isobutyrate (1) + methanol (2)	303.15	0.014	0.0035
	323.15	0.016	0.0042
Ethyl isobutyrate (1) + ethanol (2)	303.15	0.025	0.0035
	323.15	0.013	0.0035
Ethyl isobutyrate (1) + 1-propanol (2)	303.15	0.018	0.0061
	323.15	0.010	0.0041
Ethyl isobutyrate (1) + 1-butanol (2)	303.15	0.016	0.0039
	323.15	0.016	0.0042
	p / kPa	$\Delta p / \text{kPa}$	Δy
Ethyl isobutyrate (1) + methanol (2)	40.000	0.46	0.0040
	101.325	0.23	0.0027
Ethyl isobutyrate (1) + ethanol (2)	40.000	0.43	0.0039
	101.325	0.31	0.0026
Ethyl isobutyrate (1) + 1-propanol (2)	40.000	0.47	0.0043
	101.325	0.28	0.0051
Ethyl isobutyrate (1) + 1-butanol (2)	40.000	0.46	0.0038
	101.325	0.21	0.0035

Table 6

Azeotropic coordinates (temperature, T_{az} , or pressure, p_{az} , and composition, $x_{1,az}$): experimental coordinates and UNIFAC predictions.

System	T / K	p_{az} / kPa		$x_{1,az}$	
		Exptl.	UNIFAC	Exptl.	UNIFAC
Ethyl isobutyrate (1) + ethanol (2)	303.15	10.87	10.56	0.144	0.096
	323.15	29.83	29.59	0.083	0.039
Ethyl isobutyrate (1) + 1-propanol (2)	303.15	5.23	5.26	0.538	0.623
	323.15	14.90	14.91	0.446	0.523
		T_{az} / K		$x_{1,az}$	
	p / kPa	Exptl.	UNIFAC	Exptl.	UNIFAC
Ethyl isobutyrate (1) + 1-propanol (2)	40.000	345.9	345.8	0.318	0.366
	101.325	369.7	369.7	0.188	0.196
Ethyl isobutyrate (1) + 1-butanol (2)	40.000	354.7	354.7	0.906	0.899
	101.325	382.5	382.6	0.773	0.794

Table 7

UNIFAC predictions: average deviation in pressure, Δp , or in temperature, ΔT , and in vapour phase composition, Δy .

System	T / K	$\Delta p / \text{kPa}$	Δy
Ethyl isobutyrate (1) + methanol (2)	303.15	0.26	0.0091
	323.15	0.47	0.0036
Ethyl isobutyrate (1) + ethanol (2)	303.15	0.30	0.0215
	323.15	0.43	0.0134
Ethyl isobutyrate (1) + 1-propanol (2)	303.15	0.11	0.0225
	323.15	0.24	0.0174
Ethyl isobutyrate (1) + 1-butanol (2)	303.15	0.08	0.0148
	323.15	0.13	0.0108
	p / kPa	$\Delta T / \text{K}$	Δy
Ethyl isobutyrate (1) + methanol (2)	40.000	0.85	0.0094
	101.325	0.75	0.0067
Ethyl isobutyrate (1) + ethanol (2)	40.000	0.19	0.0058
	101.325	0.08	0.0032
Ethyl isobutyrate (1) + 1-propanol (2)	40.000	0.31	0.0100
	101.325	0.13	0.0050
Ethyl isobutyrate (1) + 1-butanol (2)	40.000	0.09	0.0014
	101.325	0.19	0.0043

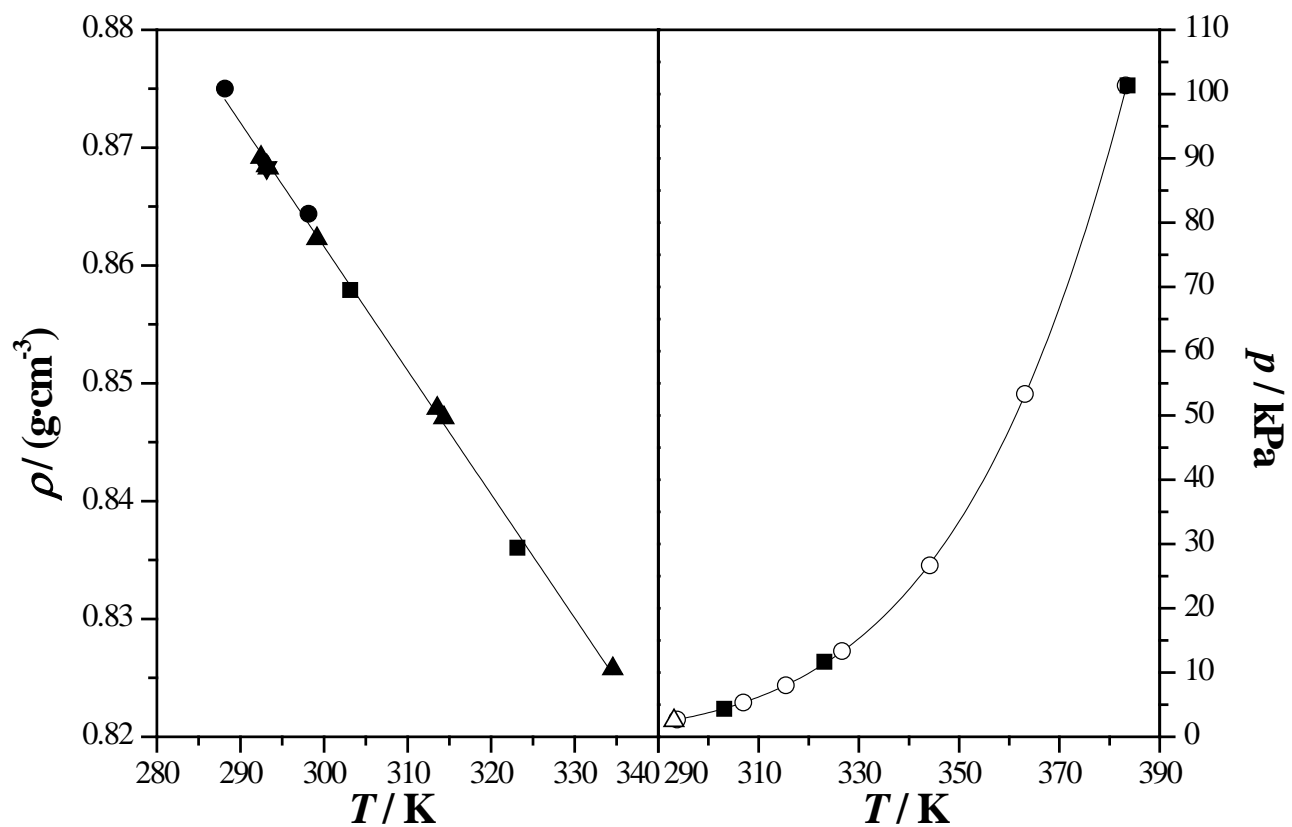


Fig. 1. Densities at $p = 0.1$ MPa, ρ , and vapour pressures, p , as a function of temperature, T , of ethyl isobutyrate: (■) experimental; (●) Ref. [60]; (▲) Ref. [62]; (▼) Ref. [63]; (○) Ref. [17]; (△) Ref. [61]; (—) correlated values.

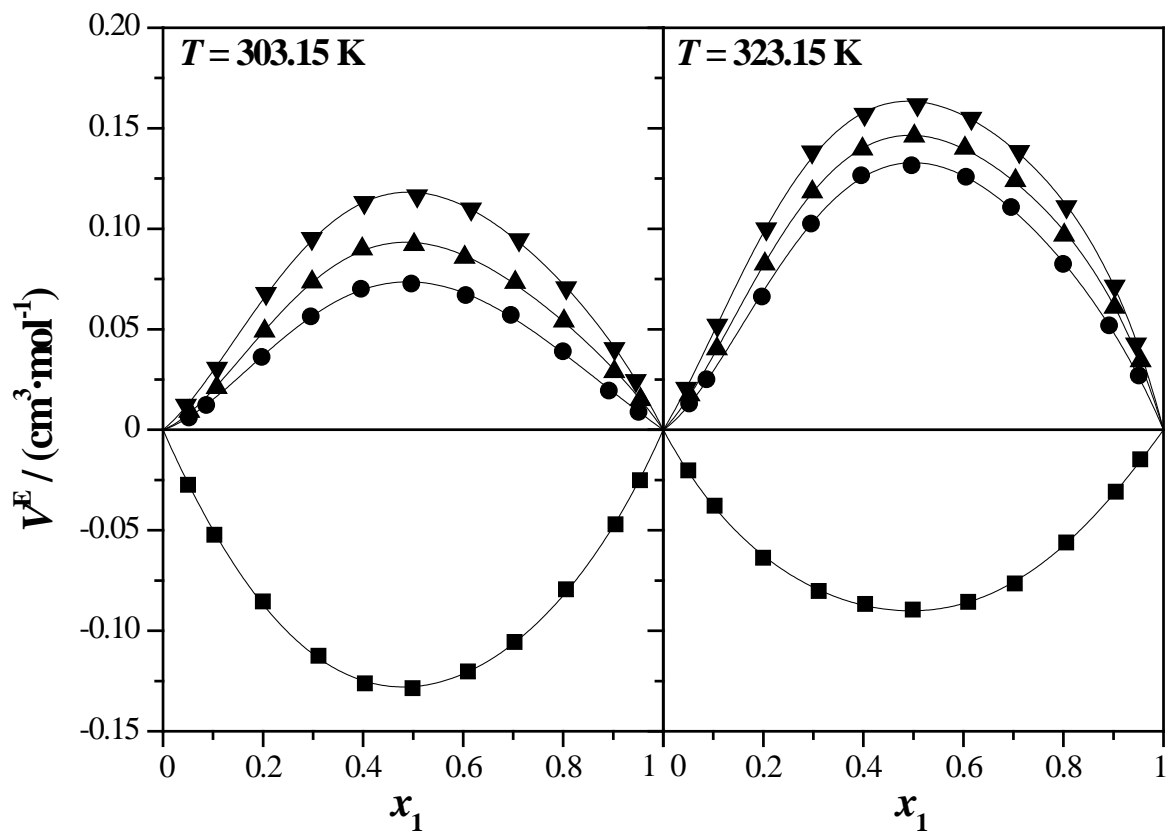


Fig. 2. Excess molar volumes, V^E , as a function of the mole fraction, x_1 , at $p = 0.1 \text{ MPa}$ and at working temperatures for the binary mixtures ethyl isobutyrate (1) + alkanol (2): (■) methanol; (●) ethanol; (▲) 1-propanol; (▼) 1-butanol; (—) Redlich-Kister equation.

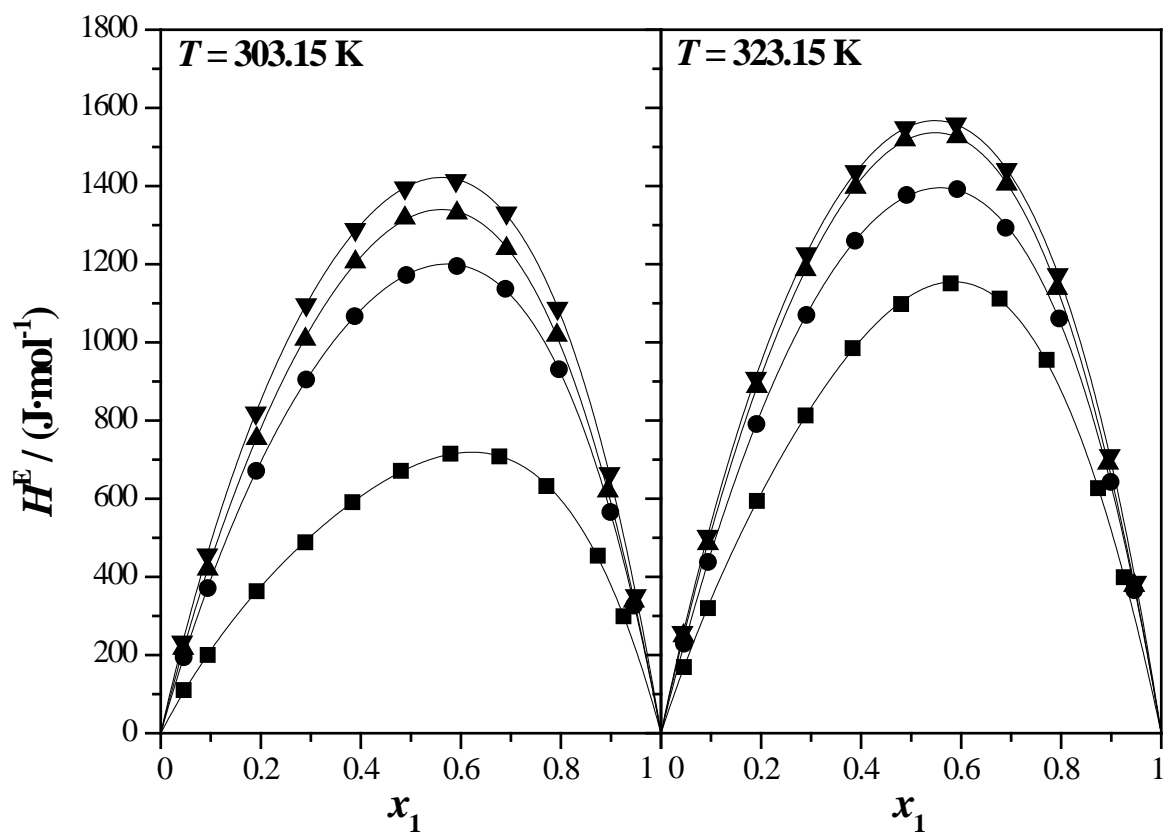


Fig. 3. Excess molar enthalpies, H^E , as a function of the mole fraction, x_1 , at $p = 0.1$ MPa and at working temperatures for the binary mixtures ethyl isobutyrate (1) + alkanol (2): (■) methanol; (●) ethanol; (▲) 1-propanol; (▼) 1-butanol; (—) Redlich-Kister equation.

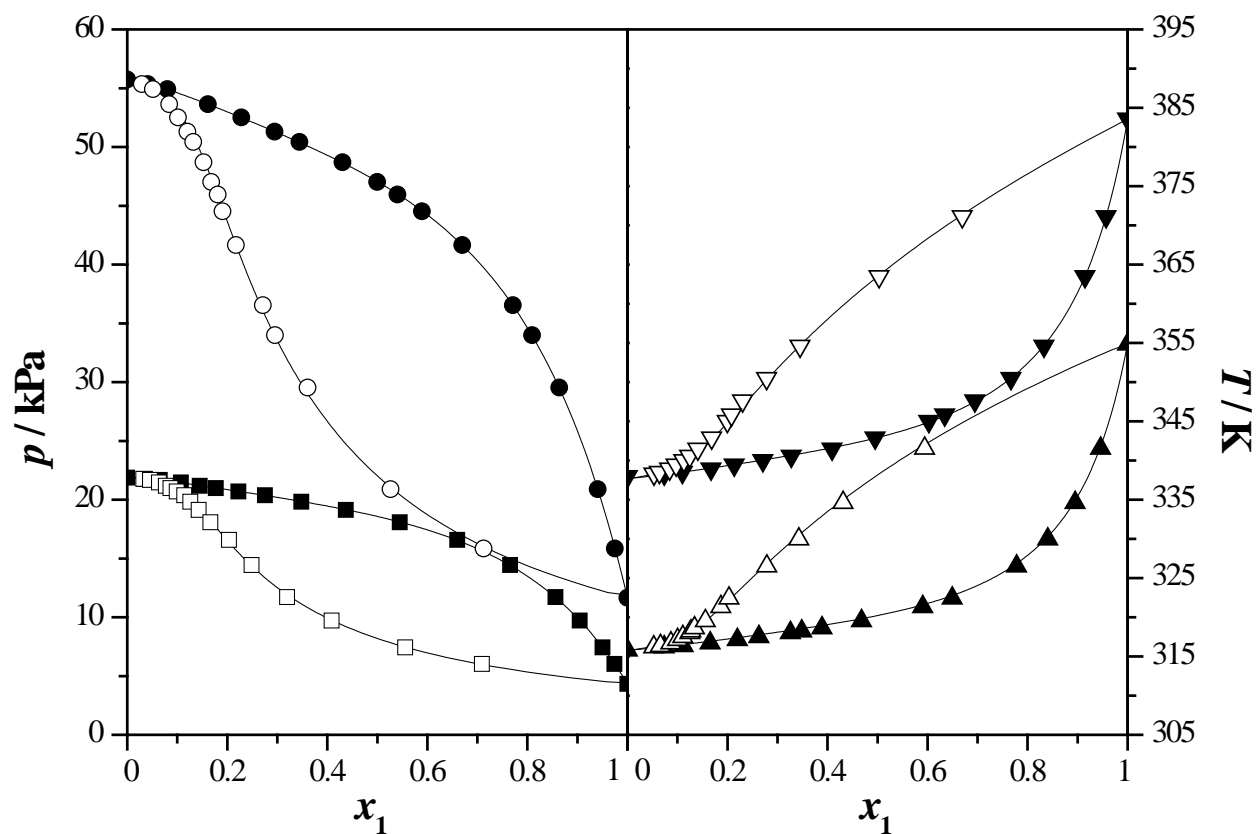


Fig. 4. p - x_1 - y_1 and T - x_1 - y_1 diagrams for the binary mixture ethyl isobutyrate (1) + methanol (2): (■, □) experimental data at $T = 303.15$ K; (●, ○) experimental data at $T = 323.15$ K; (▲, △) experimental data at $p = 40.000$ kPa; (▼, ▽) experimental data at $p = 101.325$ kPa; (—) Wilson correlation.

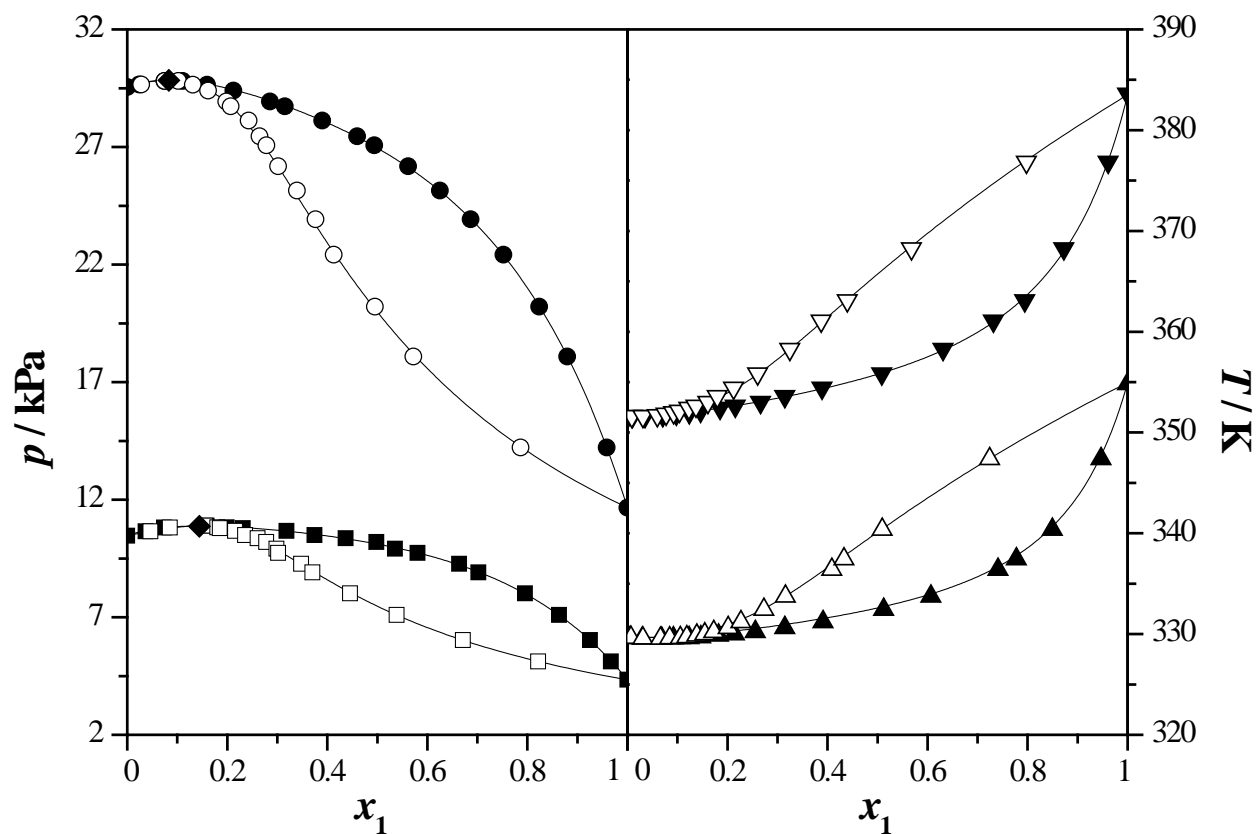


Fig. 5. p - x_1 - y_1 and T - x_1 - y_1 diagrams for the binary mixture ethyl isobutyrate (1) + ethanol (2): (■, □) experimental data at $T = 303.15$ K; (●, ○) experimental data at $T = 323.15$ K; (▲, △) experimental data at $p = 40.000$ kPa; (▼, ▽) experimental data at $p = 101.325$ kPa; (◆) calculated azeotropes; (—) Wilson correlation.

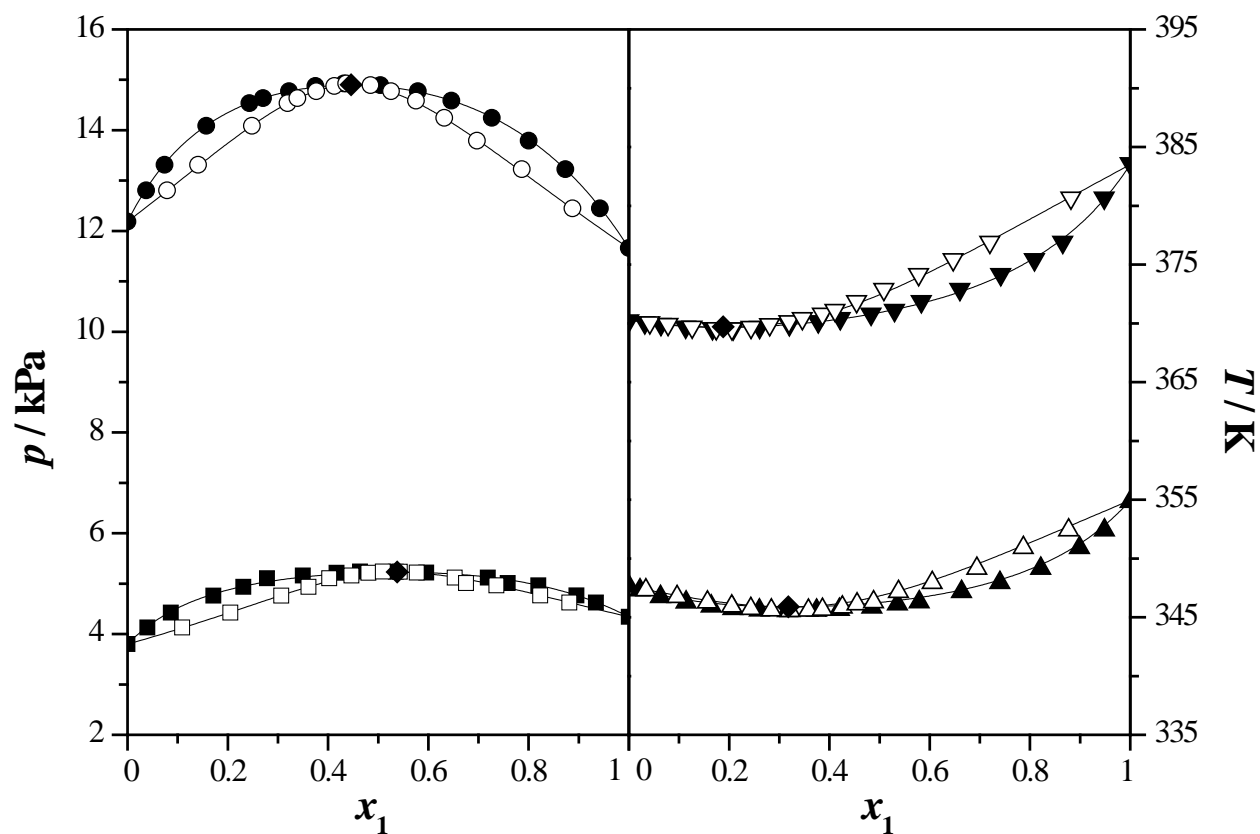


Fig. 6. p - x_1 - y_1 and T - x_1 - y_1 diagrams for the binary mixture ethyl isobutyrate (1) + 1-propanol (2): (■, □) experimental data at $T = 303.15$ K; (●, ○) experimental data at $T = 323.15$ K; (▲, △) experimental data at $p = 40.000$ kPa; (▼, ▽) experimental data at $p = 101.325$ kPa; (◆) calculated azeotropes; (—) Wilson correlation.

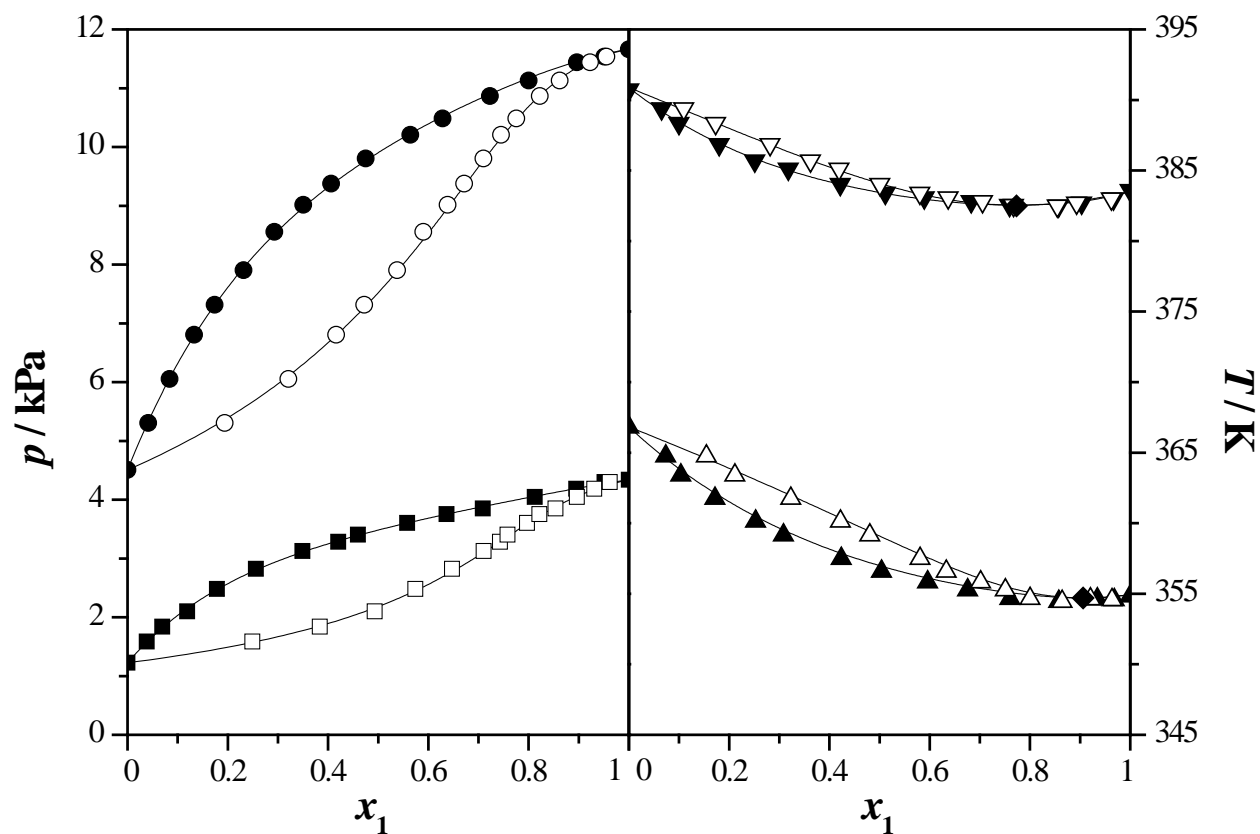


Fig. 7. p - x_1 - y_1 and T - x_1 - y_1 diagrams for the binary mixture ethyl isobutyrate (1) + 1-butanol (2): (■, □) experimental data at $T = 303.15$ K; (●, ○) experimental data at $T = 323.15$ K; (▲, △) experimental data at $p = 40.000$ kPa; (▼, ▽) experimental data at $p = 101.325$ kPa; (◆) calculated azeotropes; (—) Wilson correlation.

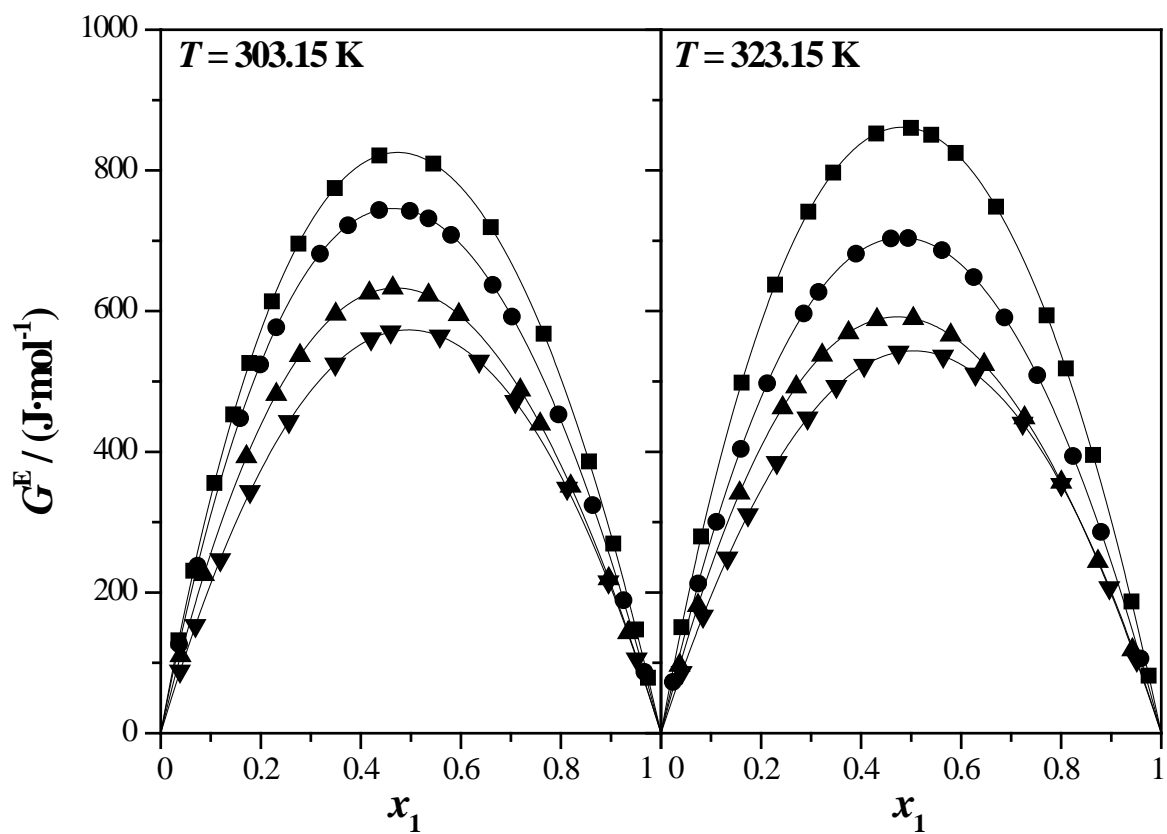


Fig. 8. Calculated excess Gibbs functions, G^E , as a function of the mole fraction, x_1 , at working temperatures for the binary mixtures ethyl isobutyrate (1) + alkanol (2): (■) methanol; (●) ethanol; (▲) 1-propanol; (▼) 1-butanol; (—) Wilson equation.

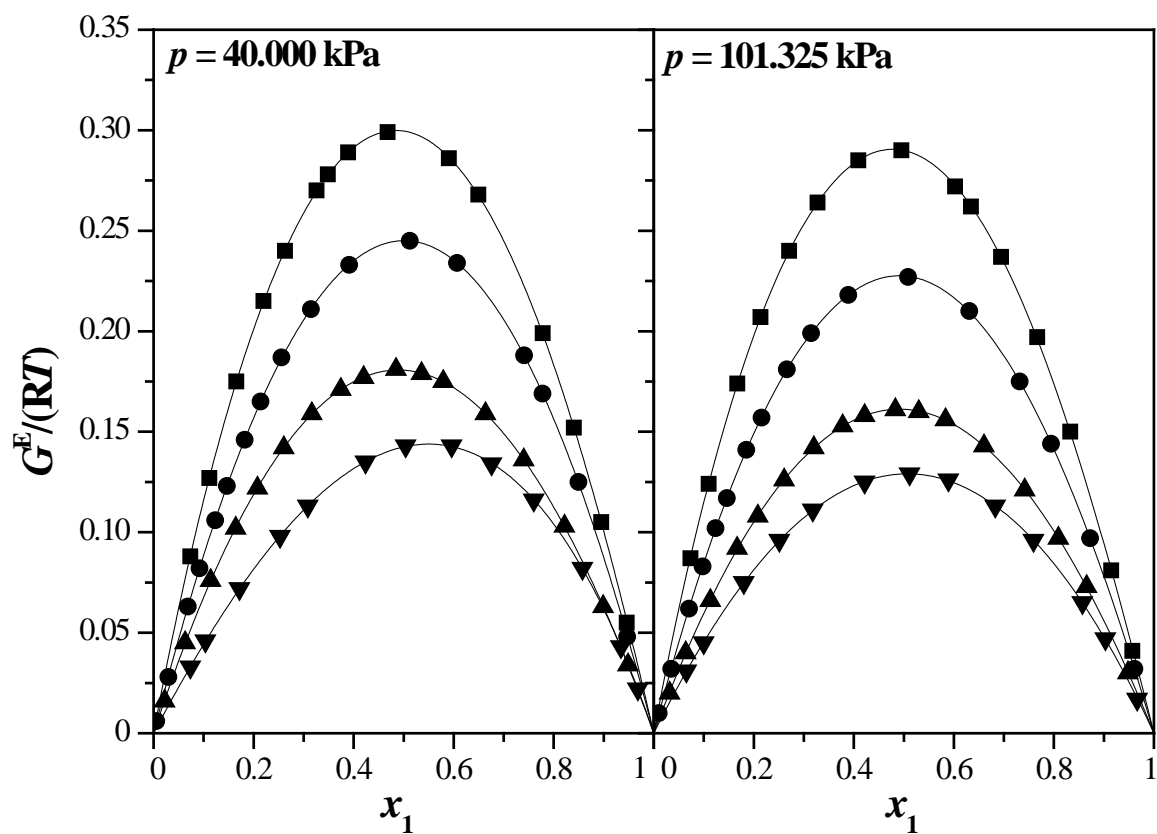


Fig. 9. Calculated reduced excess Gibbs functions, G^E , as a function of the mole fraction, x_1 , at working pressures for the binary mixtures ethyl isobutyrate (1) + alkanol (2): (■) methanol; (●) ethanol; (▲) 1-propanol; (▼) 1-butanol; (—) Wilson equation.

**Vapour-liquid equilibrium and excess properties of the binary mixtures
formed by ethyl isobutyrate and n-alkanols**

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Cristallochimie et Thermodynamique Appliquée, LR15ES01, Département de Chimie, 2092
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TABLE S1. Experimental densities, ρ , and calculated excess volumes, V^E , as function of the mole fraction, x_1 , for ethyl isobutyrate (1) + n-alkanol (2) systems at $p = 0.1$ MPa and at working temperatures.^a

x_1	$\rho / (\text{g}\cdot\text{cm}^{-3})$	$V^E / (\text{cm}^3\cdot\text{mol}^{-1})$	x_1	$\rho / (\text{g}\cdot\text{cm}^{-3})$	$V^E / (\text{cm}^3\cdot\text{mol}^{-1})$
Ethyl isobutyrate (1) + methanol (2) at $T = 303.15$ K					
0.0000	0.78181		0.6099	0.84661	-0.1203
0.0501	0.79358	-0.0274	0.7030	0.85012	-0.1056
0.1028	0.80354	-0.0523	0.8056	0.85331	-0.0794
0.1996	0.81736	-0.0854	0.9046	0.85588	-0.0471
0.3110	0.82869	-0.1125	0.9538	0.85698	-0.0251
0.4038	0.83574	-0.1262	1.0000	0.85792	
0.4990	0.84141	-0.1286			
Ethyl isobutyrate (1) + methanol (2) at $T = 323.15$ K					
0.0000	0.76261		0.6099	0.82484	-0.0856
0.0501	0.77385	-0.0202	0.7030	0.82830	-0.0765
0.1028	0.78336	-0.0378	0.8056	0.83144	-0.0561
0.1996	0.79663	-0.0637	0.9046	0.83398	-0.0308
0.3110	0.80748	-0.0802	0.9538	0.83508	-0.0147
0.4038	0.81425	-0.0867	1.0000	0.83605	
0.4990	0.81976	-0.0895			
Ethyl isobutyrate (1) + ethanol (2) at $T = 303.15$ K					
0.0000	0.78078		0.6052	0.84031	0.0670
0.0519	0.78931	0.0061	0.6952	0.84511	0.0571
0.0865	0.79440	0.0123	0.7995	0.85004	0.0390
0.1972	0.80819	0.0362	0.8912	0.85389	0.0195
0.2954	0.81804	0.0564	0.9505	0.85615	0.0089
0.3959	0.82646	0.0701	1.0000	0.85792	
0.4964	0.83364	0.0727			
Ethyl isobutyrate (1) + ethanol (2) at $T = 323.15$ K					
0.0000	0.76361		0.6052	0.81910	0.1259
0.0519	0.77156	0.0130	0.6952	0.82367	0.1108
0.0865	0.77629	0.0251	0.7995	0.82838	0.0825
0.1972	0.78909	0.0663	0.8912	0.83207	0.0519
0.2954	0.79821	0.1026	0.9505	0.83428	0.0270
0.3959	0.80606	0.1266	1.0000	0.83605	
0.4964	0.81282	0.1316			

TABLE S1. Continuation

x_1	$\rho / (\text{g}\cdot\text{cm}^{-3})$	$V^E / (\text{cm}^3\cdot\text{mol}^{-1})$	x_1	$\rho / (\text{g}\cdot\text{cm}^{-3})$	$V^E / (\text{cm}^3\cdot\text{mol}^{-1})$
Ethyl isobutyrate (1) + 1-propanol (2) at $T = 303.15$ K					
0.0000	0.79553		0.6030	0.84051	0.0858
0.0528	0.80111	0.0092	0.7040	0.84554	0.0733
0.1073	0.80638	0.0211	0.8014	0.84997	0.0541
0.2033	0.81465	0.0491	0.9021	0.85416	0.0289
0.2978	0.82183	0.0736	0.9546	0.85621	0.0150
0.3984	0.82864	0.0900	1.0000	0.85792	
0.5020	0.83496	0.0922			
Ethyl isobutyrate (1) + 1-propanol (2) at $T = 323.15$ K					
0.0000	0.77909		0.6030	0.81980	0.1401
0.0528	0.78412	0.0174	0.7040	0.82442	0.1240
0.1073	0.78885	0.0403	0.8014	0.82853	0.0969
0.2033	0.79629	0.0825	0.9021	0.83243	0.0610
0.2978	0.80276	0.1184	0.9546	0.83437	0.0344
0.3984	0.80896	0.1397	1.0000	0.83605	
0.5020	0.81472	0.1461			
Ethyl isobutyrate (1) + 1-butanol (2) at $T = 303.15$ K					
0.0000	0.80191		0.6160	0.84042	0.1099
0.0461	0.80551	0.0122	0.7116	0.84513	0.0946
0.1084	0.81012	0.0306	0.8062	0.84955	0.0706
0.2062	0.81680	0.0678	0.9025	0.85381	0.0404
0.2976	0.82262	0.0952	0.9454	0.85563	0.0245
0.4024	0.82887	0.1131	1.0000	0.85792	
0.5081	0.83478	0.1164			
Ethyl isobutyrate (1) + 1-butanol (2) at $T = 323.15$ K					
0.0000	0.78662		0.6160	0.82031	0.1550
0.0461	0.78973	0.0206	0.7116	0.82448	0.1384
0.1084	0.79371	0.0520	0.8062	0.82841	0.1110
0.2062	0.79953	0.1000	0.9025	0.83223	0.0715
0.2976	0.80459	0.1382	0.9454	0.83392	0.0427
0.4024	0.81011	0.1569	1.0000	0.83605	
0.5081	0.81533	0.1617			

^a Standard uncertainties u are $u(T) = 0.005$ K, $u(p) = 2.5$ kPa, and $u(x_1) = 0.0001$, and the combined expanded uncertainty U_c is $U_c(\rho) = 2 \cdot 10^{-4}$ g·cm⁻³ with a 0.95 level of confidence ($k = 2$).

TABLE S2. Excess enthalpies, H^E , as function of the mole fraction, x_1 , for ethyl isobutyrate (1) + n-alkanol (2) systems at $p = 0.1$ MPa and at working temperatures.^a

x_1	$H^E / (\text{J}\cdot\text{mol}^{-1})$	x_1	$H^E / (\text{J}\cdot\text{mol}^{-1})$	x_1	$H^E / (\text{J}\cdot\text{mol}^{-1})$
Ethyl isobutyrate (1) + methanol (2) at $T = 303.15$ K					
0.046	110	0.383	591	0.771	632
0.094	200	0.480	671	0.874	454
0.192	363	0.579	715	0.925	299
0.289	488	0.677	708		
Ethyl isobutyrate (1) + methanol (2) at $T = 323.15$ K					
0.046	169	0.383	985	0.771	955
0.094	320	0.480	1098	0.874	627
0.192	594	0.579	1150	0.925	399
0.289	813	0.677	1112		
Ethyl isobutyrate (1) + ethanol (2) at $T = 303.15$ K					
0.046	194	0.388	1067	0.796	931
0.094	371	0.491	1172	0.899	566
0.191	671	0.592	1195	0.946	326
0.291	905	0.689	1137		
Ethyl isobutyrate (1) + ethanol (2) at $T = 323.15$ K					
0.046	229	0.388	1260	0.796	1061
0.094	438	0.491	1377	0.899	643
0.191	791	0.592	1392	0.946	366
0.291	1070	0.689	1293		
Ethyl isobutyrate (1) + 1-propanol (2) at $T = 303.15$ K					
0.045	217	0.389	1206	0.792	1018
0.094	420	0.488	1318	0.894	620
0.192	754	0.592	1331	0.946	338
0.289	1008	0.691	1240		
Ethyl isobutyrate (1) + 1-propanol (2) at $T = 323.15$ K					
0.045	249	0.389	1397	0.792	1138
0.094	485	0.488	1518	0.894	691
0.192	887	0.592	1526	0.946	378
0.289	1186	0.691	1405		

TABLE S2. Continuation

x_1	$H^E / (\text{J}\cdot\text{mol}^{-1})$	x_1	$H^E / (\text{J}\cdot\text{mol}^{-1})$	x_1	$H^E / (\text{J}\cdot\text{mol}^{-1})$
Ethyl isobutyrate (1) + 1-butanol (2) at $T = 303.15$ K					
0.043	233	0.389	1289	0.793	1087
0.093	456	0.488	1395	0.897	664
0.190	819	0.590	1414	0.950	352
0.291	1096	0.691	1331		
Ethyl isobutyrate (1) + 1-butanol (2) at $T = 323.15$ K					
0.043	258	0.389	1437	0.793	1173
0.093	504	0.488	1549	0.897	710
0.190	908	0.590	1559	0.950	386
0.291	1227	0.691	1442		

^a Standard uncertainties u are $u(T) = 0.0002$ K, $u(p) = 2.5$ kPa, and $u(x_1) = 0.001$, and the combined expanded uncertainty U_c is $U_c(H^E) = 1$ % with a 0.95 level of confidence ($k = 2$).

Table S3. Isothermal VLE data for ethyl isobutyrate (1) + n-alkanol (2) systems at several temperatures, T : experimental pressure, p , liquid-phase, x_1 , and vapor-phase, y_1 mole fractions, calculated activity coefficients γ_i , and calculated excess Gibbs functions, G^E .^a

p / kPa	x_1	y_1	γ_1	γ_2	G^E / (J·mol ⁻¹)
Ethyl isobutyrate (1) + methanol (2) at $T = 303.15$ K					
21.880	0.0000	0.0000			
21.765	0.0356	0.0321	4.020	1.003	131.8
21.675	0.0652	0.0455	3.565	1.009	230.7
21.455	0.1073	0.0634	3.060	1.024	355.6
21.185	0.1451	0.0775	2.710	1.042	453.2
20.975	0.1773	0.0867	2.468	1.061	526.2
20.690	0.2225	0.0992	2.193	1.093	613.9
20.380	0.2753	0.1139	1.942	1.137	695.7
19.820	0.3483	0.1262	1.683	1.213	774.8
19.125	0.4369	0.1429	1.459	1.330	821.3
18.075	0.5450	0.1663	1.273	1.517	809.6
16.575	0.6600	0.2034	1.143	1.786	719.2
14.445	0.7657	0.2487	1.065	2.125	567.6
11.710	0.8563	0.3195	1.024	2.516	386.2
9.715	0.9048	0.4089	1.011	2.778	269.5
7.440	0.9503	0.5558	1.003	3.067	147.4
6.025	0.9741	0.7092	1.001	3.238	78.7
4.340	1.0000	1.0000			
Ethyl isobutyrate (1) + methanol (2) at $T = 323.15$ K					
55.735	0.0000	0.0000			
55.350	0.0410	0.0294	3.642	1.003	150.7
54.915	0.0804	0.0513	3.182	1.012	279.5
53.645	0.1611	0.0840	2.512	1.045	498.2
52.510	0.2282	0.1016	2.132	1.087	637.7
51.310	0.2947	0.1205	1.855	1.142	741.1
50.425	0.3442	0.1322	1.694	1.192	796.7
48.695	0.4304	0.1525	1.479	1.298	852.3
47.025	0.4996	0.1678	1.350	1.406	860.5
45.960	0.5405	0.1810	1.287	1.480	850.5
44.530	0.5891	0.1905	1.223	1.581	824.7
41.650	0.6697	0.2175	1.140	1.783	748.5
36.535	0.7711	0.2710	1.066	2.119	593.9

Table S3. Continuation.

p / kPa	x_1	y_1	γ_1	γ_2	G^E / (J·mol ⁻¹)
33.985	0.8095	0.2955	1.045	2.279	518.3
29.535	0.8637	0.3606	1.023	2.543	395.3
20.890	0.9408	0.5266	1.004	3.021	187.1
15.845	0.9751	0.7126	1.001	3.284	81.6
11.660	1.0000	1.0000			
Ethyl isobutyrate (1) + ethanol (2) at $T = 303.15$ K					
10.465	0.0000	0.0000			
10.650	0.0369	0.0464	3.611	1.003	126.7
10.815	0.0736	0.0851	3.135	1.011	238.1
10.895	0.1589	0.1564	2.391	1.048	447.6
10.825	0.1988	0.1799	2.153	1.072	524.1
10.785	0.2311	0.1850	1.994	1.094	576.9
10.670	0.3183	0.2157	1.672	1.170	681.6
10.495	0.3745	0.2358	1.522	1.229	721.9
10.360	0.4368	0.2607	1.392	1.306	743.6
10.200	0.4983	0.2778	1.292	1.395	742.5
9.915	0.5355	0.2982	1.242	1.455	731.6
9.735	0.5804	0.3016	1.191	1.534	708.3
9.270	0.6634	0.3475	1.116	1.706	637.2
8.905	0.7020	0.3701	1.089	1.799	592.1
8.015	0.7951	0.4454	1.041	2.060	453.0
7.100	0.8634	0.5386	1.018	2.295	324.2
6.030	0.9250	0.6712	1.005	2.546	188.9
5.115	0.9668	0.8215	1.001	2.741	86.9
4.340	1.0000	1.0000			
Ethyl isobutyrate (1) + ethanol (2) at $T = 323.15$ K					
29.545	0.0000	0.0000			
29.660	0.0238	0.0281	3.010	1.001	72.7
29.810	0.0745	0.0748	2.615	1.008	212.6
29.805	0.1107	0.1018	2.389	1.017	300.4
29.645	0.1596	0.1313	2.137	1.035	404.0
29.400	0.2123	0.1616	1.919	1.061	497.2
28.935	0.2855	0.1982	1.685	1.108	596.6
28.725	0.3151	0.2069	1.608	1.130	627.3
28.120	0.3899	0.2426	1.446	1.197	681.6

Table S3. Continuation.

p / kPa	x_1	y_1	γ_1	γ_2	$G^E / (\text{J} \cdot \text{mol}^{-1})$
27.455	0.4598	0.2647	1.329	1.274	703.3
27.070	0.4939	0.2783	1.282	1.317	703.9
26.180	0.5617	0.3017	1.202	1.415	686.6
25.145	0.6252	0.3395	1.143	1.523	648.2
23.925	0.6866	0.3767	1.097	1.646	591.0
22.415	0.7521	0.4130	1.060	1.800	508.8
20.210	0.8237	0.4952	1.030	2.002	393.8
18.090	0.8796	0.5720	1.014	2.190	286.0
14.220	0.9588	0.7864	1.002	2.514	106.2
11.660	1.0000	1.0000			
Ethyl isobutyrate (1) + 1-propanol (2) at $T = 303.15 \text{ K}$					
3.800	0.0000	0.0000			
4.130	0.0395	0.1092	2.847	1.003	110.2
4.425	0.0866	0.2051	2.491	1.012	225.6
4.760	0.1715	0.3068	2.032	1.042	392.9
4.935	0.2310	0.3611	1.804	1.074	481.7
5.105	0.2784	0.4024	1.659	1.105	536.9
5.160	0.3498	0.4468	1.488	1.161	595.7
5.215	0.4171	0.4807	1.364	1.226	625.6
5.240	0.4639	0.5096	1.294	1.277	632.7
5.235	0.5352	0.5433	1.209	1.368	622.6
5.220	0.5959	0.5773	1.151	1.458	595.1
5.120	0.7189	0.6526	1.068	1.681	487.9
5.010	0.7583	0.6751	1.050	1.767	439.5
4.965	0.8195	0.7357	1.027	1.916	351.2
4.765	0.8956	0.8234	1.009	2.134	219.5
4.625	0.9345	0.8813	1.003	2.262	142.9
4.340	1.0000	1.0000			
Ethyl isobutyrate (1) + 1-propanol (2) at $T = 323.15 \text{ K}$					
12.185	0.0000	0.0000			
12.805	0.0374	0.0789	2.491	1.002	96.6
13.315	0.0740	0.1407	2.280	1.007	181.5
14.085	0.1571	0.2481	1.913	1.030	341.4
14.535	0.2432	0.3193	1.648	1.069	462.7
14.635	0.2705	0.3387	1.581	1.085	492.4

Table S3. Continuation.

p / kPa	x_1	y_1	γ_1	γ_2	$G^E / (\text{J} \cdot \text{mol}^{-1})$
14.775	0.3221	0.3766	1.471	1.118	537.5
14.875	0.3748	0.4125	1.378	1.158	569.2
14.925	0.4316	0.4363	1.296	1.207	587.9
14.895	0.5045	0.4848	1.212	1.280	589.4
14.775	0.5790	0.5259	1.145	1.369	565.9
14.585	0.6461	0.5756	1.098	1.462	524.0
14.245	0.7268	0.6319	1.056	1.592	448.4
13.790	0.8001	0.6971	1.029	1.731	356.8
13.225	0.8732	0.7864	1.012	1.892	244.2
12.450	0.9424	0.8875	1.002	2.070	118.5
11.660	1.0000	1.0000			
Ethyl isobutyrate (1) + 1-butanol (2) at $T = 303.15 \text{ K}$					
1.225	0.0000	0.0000			
1.585	0.0386	0.2489	2.380	1.002	88.2
1.840	0.0694	0.3737	2.241	1.005	152.9
2.100	0.1189	0.4929	2.047	1.015	246.7
2.480	0.1786	0.5743	1.852	1.032	343.4
2.825	0.2562	0.6475	1.649	1.066	443.1
3.125	0.3490	0.7106	1.462	1.123	524.8
3.285	0.4203	0.7430	1.350	1.180	560.6
3.405	0.4597	0.7582	1.298	1.218	570.4
3.605	0.5580	0.7969	1.191	1.331	564.4
3.755	0.6363	0.8215	1.126	1.446	528.8
3.850	0.7086	0.8539	1.080	1.577	471.5
4.045	0.8124	0.8962	1.033	1.816	348.2
4.185	0.8950	0.9312	1.010	2.065	215.1
4.300	0.9517	0.9618	1.002	2.276	105.4
4.340	1.0000	1.0000			
Ethyl isobutyrate (1) + 1-butanol (2) at $T = 323.15 \text{ K}$					
4.505	0.0000	0.0000			
5.305	0.0415	0.1938	2.095	1.001	86.1
6.055	0.0839	0.3210	1.964	1.006	166.3
6.805	0.1328	0.4161	1.830	1.014	249.0
7.315	0.1738	0.4724	1.731	1.025	310.4
7.905	0.2315	0.5377	1.609	1.044	384.6

Table S3. Continuation.

p / kPa	x_1	y_1	γ_1	γ_2	$G^E / (\text{J} \cdot \text{mol}^{-1})$
8.555	0.2929	0.5901	1.498	1.071	447.9
9.015	0.3508	0.6386	1.407	1.103	493.0
9.375	0.4063	0.6716	1.333	1.140	522.8
10.865	0.7228	0.8222	1.068	1.521	440.7
11.130	0.8003	0.8622	1.036	1.680	353.5
11.440	0.8965	0.9226	1.010	1.936	206.9
11.535	0.9512	0.9552	1.002	2.120	104.1
11.660	1.0000	1.0000			

^aStandard uncertainties u are $u(T) = 0.1 \text{ K}$, $u(p) = 0.1 \text{ kPa}$, $u(x_1) = 0.002$, and $u(y_1) = 0.002$.

Table S4. Isobaric VLE data for ethyl isobutyrate (1) + n-alkanol (2) systems at several pressures, p : experimental temperature, T , liquid-phase, x_1 , and vapor-phase, y_1 mole fractions, calculated activity coefficients γ_i , and calculated reduced excess Gibbs functions, $G^E/(RT)$.^a

T/K	x_1	y_1	γ_1	γ_2	$G^E/(RT)$
Ethyl isobutyrate (1) + methanol (2) at $p = 40.000$ kPa					
315.81	0.0000	0.0000			
316.20	0.0734	0.0528	2.976	1.009	0.088
316.37	0.1117	0.0662	2.679	1.019	0.127
316.72	0.1655	0.0869	2.343	1.041	0.175
317.13	0.2197	0.1004	2.078	1.071	0.215
317.51	0.2629	0.1107	1.906	1.101	0.240
318.01	0.3259	0.1250	1.702	1.154	0.270
318.24	0.3487	0.1271	1.639	1.176	0.278
318.63	0.3889	0.1342	1.541	1.218	0.289
319.55	0.4680	0.1557	1.383	1.319	0.299
321.35	0.5906	0.1866	1.210	1.528	0.286
322.44	0.6493	0.2029	1.150	1.656	0.268
326.52	0.7783	0.2788	1.057	2.020	0.199
329.97	0.8405	0.3427	1.029	2.239	0.152
334.63	0.8953	0.4314	1.012	2.451	0.105
341.55	0.9463	0.5944	1.003	2.644	0.055
354.84	1.0000	1.0000			
Ethyl isobutyrate (1) + methanol (2) at $p = 101.325$ kPa					
337.96	0.0000	0.0000			
338.29	0.0734	0.0532	2.937	1.009	0.087
338.50	0.1097	0.0641	2.650	1.019	0.124
338.94	0.1672	0.0844	2.290	1.043	0.174
339.43	0.2137	0.0975	2.063	1.069	0.207
340.01	0.2706	0.1128	1.840	1.108	0.240
340.56	0.3276	0.1247	1.663	1.157	0.264
341.47	0.4090	0.1407	1.468	1.242	0.285
342.89	0.4953	0.1682	1.316	1.357	0.290
345.01	0.6027	0.1996	1.182	1.541	0.272
345.84	0.6345	0.2079	1.151	1.606	0.262
347.61	0.6946	0.2304	1.102	1.742	0.237

Table S4. Continuation.

T / K	x_1	y_1	γ_1	γ_2	$G^E/(RT)$
350.47	0.7667	0.2783	1.057	1.933	0.197
354.59	0.8328	0.3450	1.028	2.132	0.150
363.47	0.9148	0.5030	1.007	2.393	0.081
371.12	0.9569	0.6695	1.002	2.511	0.041
383.59	1.0000	1.0000			
Ethyl isobutyrate (1) + ethanol (2) at $p = 40.000$ kPa					
329.61	0.0000	0.0000			
329.64	0.0056	0.0070	2.661	1.000	0.006
329.58	0.0295	0.0310	2.534	1.001	0.028
329.56	0.0685	0.0661	2.348	1.005	0.063
329.60	0.0920	0.0844	2.247	1.009	0.082
329.63	0.1234	0.1056	2.123	1.016	0.106
329.71	0.1465	0.1187	2.040	1.022	0.123
329.87	0.1824	0.1389	1.923	1.034	0.146
330.01	0.2141	0.1548	1.829	1.047	0.165
330.23	0.2557	0.1725	1.719	1.067	0.187
330.62	0.3148	0.2013	1.584	1.102	0.211
331.21	0.3911	0.2269	1.440	1.160	0.233
332.44	0.5124	0.2728	1.267	1.287	0.245
333.74	0.6066	0.3161	1.169	1.424	0.234
336.41	0.7409	0.4085	1.072	1.696	0.188
337.44	0.7775	0.4331	1.053	1.790	0.169
340.39	0.8496	0.5095	1.024	2.005	0.125
347.39	0.9470	0.7242	1.003	2.359	0.048
354.84	1.0000	1.0000			
Ethyl isobutyrate (1) + ethanol (2) at $p = 101.325$ kPa					
351.48	0.0000	0.0000			
351.60	0.0102	0.0086	2.537	1.000	0.010
351.61	0.0350	0.0308	2.410	1.001	0.032
351.70	0.0705	0.0598	2.248	1.005	0.062
351.83	0.0978	0.0772	2.136	1.010	0.083
351.99	0.1237	0.0924	2.039	1.016	0.102
352.12	0.1462	0.1041	1.961	1.022	0.117
352.42	0.1850	0.1229	1.840	1.035	0.141
352.62	0.2157	0.1369	1.755	1.047	0.157

Table S4. Continuation.

T / K	x_1	y_1	γ_1	γ_2	$G^E/(RT)$
353.01	0.2662	0.1609	1.631	1.071	0.181
353.59	0.3145	0.1798	1.529	1.100	0.199
354.41	0.3890	0.2121	1.398	1.154	0.218
355.84	0.5085	0.2604	1.240	1.270	0.227
358.26	0.6309	0.3247	1.129	1.434	0.210
361.07	0.7317	0.3872	1.066	1.613	0.175
363.10	0.7944	0.4397	1.038	1.748	0.144
368.24	0.8727	0.5678	1.014	1.943	0.097
376.83	0.9611	0.7979	1.001	2.185	0.032
383.59	1.0000	1.0000			
Ethyl isobutyrate (1) + 1-propanol (2) at $p = 40.000$ kPa					
347.66	0.0000	0.0000			
347.31	0.0221	0.0340	2.056	1.000	0.016
346.74	0.0633	0.0963	1.925	1.003	0.045
346.28	0.1141	0.1567	1.785	1.011	0.076
345.94	0.1641	0.2052	1.667	1.022	0.102
345.73	0.2075	0.2431	1.577	1.035	0.122
345.60	0.2604	0.2840	1.481	1.055	0.142
345.56	0.3164	0.3217	1.395	1.081	0.159
345.58	0.3744	0.3583	1.318	1.114	0.171
345.66	0.4198	0.3863	1.267	1.144	0.177
345.85	0.4846	0.4257	1.203	1.193	0.181
346.12	0.5358	0.4550	1.161	1.238	0.179
346.30	0.5792	0.4881	1.130	1.281	0.175
347.18	0.6635	0.5378	1.081	1.377	0.159
347.95	0.7399	0.6050	1.047	1.481	0.136
349.16	0.8216	0.6940	1.022	1.612	0.103
350.92	0.8988	0.7870	1.007	1.758	0.063
352.42	0.9485	0.8772	1.002	1.863	0.034
354.84	1.0000	1.0000			
Ethyl isobutyrate (1) + 1-propanol (2) at $p = 101.325$ kPa					
370.21	0.0000	0.0000			
370.07	0.0316	0.0418	1.865	1.001	0.020
369.92	0.0639	0.0780	1.785	1.003	0.040
369.69	0.1131	0.1262	1.676	1.009	0.066

Table S4. Continuation.

T / K	x_1	y_1	γ_1	γ_2	$G^E/(RT)$
369.56	0.1666	0.1744	1.572	1.020	0.092
369.54	0.2079	0.2054	1.502	1.031	0.108
369.67	0.2609	0.2435	1.421	1.048	0.126
369.91	0.3201	0.2809	1.344	1.072	0.142
370.15	0.3777	0.3194	1.279	1.101	0.153
370.42	0.4217	0.3461	1.236	1.126	0.158
370.80	0.4829	0.3861	1.183	1.167	0.161
371.11	0.5299	0.4111	1.149	1.203	0.160
371.86	0.5835	0.4544	1.114	1.249	0.156
372.89	0.6601	0.5086	1.074	1.325	0.143
374.16	0.7419	0.5778	1.042	1.421	0.121
375.42	0.8092	0.6469	1.023	1.513	0.097
376.90	0.8654	0.7199	1.011	1.599	0.073
380.66	0.9483	0.8819	1.002	1.742	0.030
383.59	1.0000	1.0000			
Ethyl isobutyrate (1) + 1-butanol (2) at $p = 40.000$ kPa					
366.80	0.0000	0.0000			
364.76	0.0737	0.1545	1.537	1.002	0.033
363.40	0.1035	0.2114	1.507	1.004	0.046
361.75	0.1719	0.3229	1.442	1.011	0.072
360.13	0.2528	0.4220	1.370	1.025	0.098
359.15	0.3083	0.4804	1.324	1.039	0.113
357.49	0.4238	0.5810	1.236	1.082	0.135
356.58	0.5038	0.6330	1.183	1.125	0.143
355.83	0.5960	0.7015	1.128	1.193	0.143
355.27	0.6759	0.7509	1.087	1.273	0.134
354.66	0.7601	0.8004	1.051	1.388	0.116
354.45	0.8573	0.8643	1.020	1.578	0.082
354.62	0.9344	0.9208	1.004	1.796	0.043
354.57	0.9682	0.9635	1.001	1.918	0.022
354.84	1.0000	1.0000			
Ethyl isobutyrate (1) + 1-butanol (2) at $p = 101.325$ kPa					
390.74	0.0000	0.0000			
389.38	0.0653	0.1094	1.551	1.002	0.031
388.35	0.0998	0.1730	1.505	1.005	0.045

Table S4. Continuation.

T / K	x_1	y_1	γ_1	γ_2	$G^E/(RT)$
386.84	0.1802	0.2817	1.408	1.016	0.075
385.68	0.2513	0.3622	1.333	1.032	0.096
385.10	0.3182	0.4193	1.272	1.051	0.111
384.02	0.4215	0.5007	1.192	1.093	0.125
383.40	0.5116	0.5806	1.135	1.141	0.129
383.07	0.5893	0.6370	1.095	1.193	0.126
382.81	0.6827	0.7054	1.057	1.270	0.113
382.54	0.7591	0.7671	1.033	1.348	0.096
382.49	0.8571	0.8547	1.012	1.470	0.065
382.70	0.9030	0.8929	1.005	1.538	0.047
383.00	0.9664	0.9624	1.001	1.644	0.017
383.59	1.0000	1.0000			

^aStandard uncertainties u are $u(T) = 0.1 \text{ K}$, $u(p) = 0.1 \text{ kPa}$, $u(x_1) = 0.002$, and $u(y_1) = 0.002$.

Table S5. Parameters of Antoine's equation for vapour pressures of the pure compounds (pressure in kPa, temperature in K).

Compound	Reference	<i>A</i>	<i>B</i>	<i>C</i>
Ethyl isobutyrate	[17]	6.42839	1509.7627	-42.134
Methanol	[70]	7.20519	1581.993	-33.439
Ethanol	[70]	7.16879	1552.601	-50.731
1-Propanol	[70]	6.87613	1441.705	-74.291
1-Butanol	[70]	6.54743	1338.769	-96.108

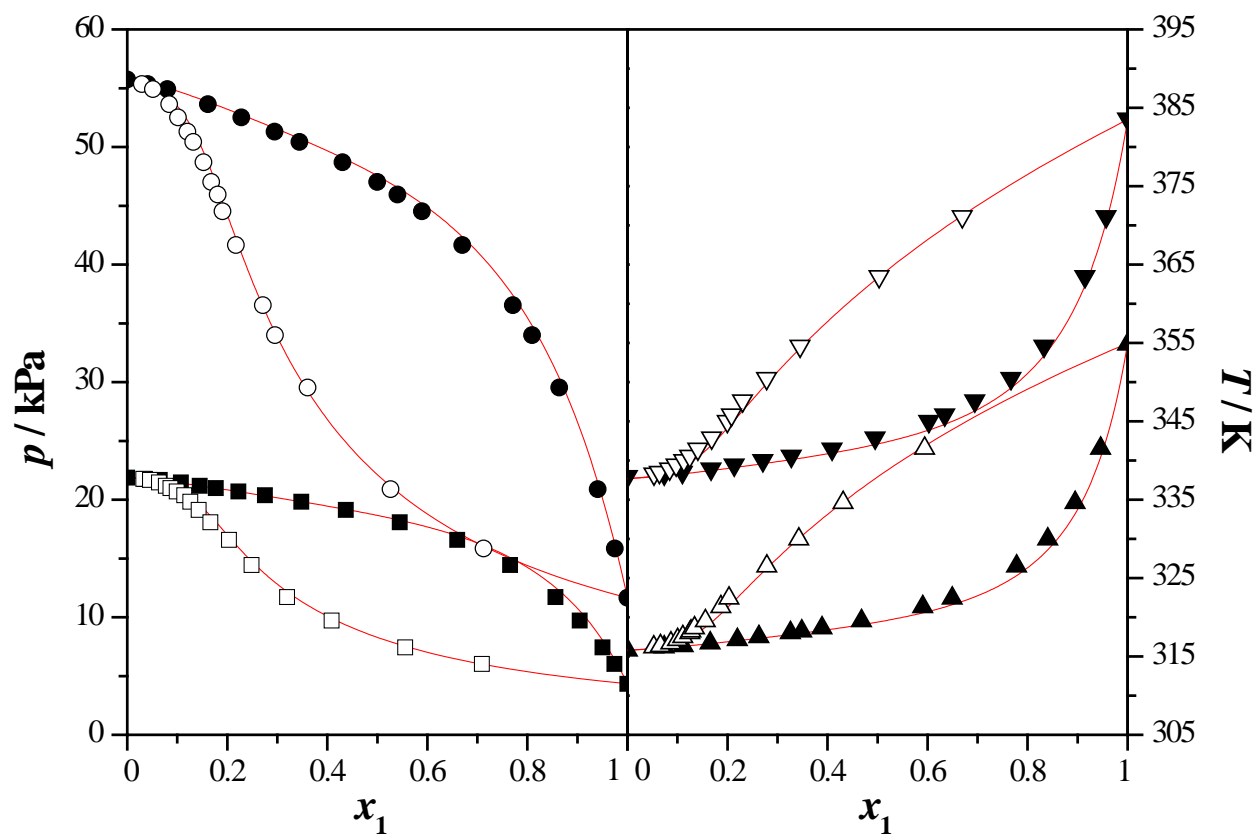


Fig. S1. p - x_1 - y_1 and T - x_1 - y_1 diagrams for the binary mixture ethyl isobutyrate (1) + methanol (2): (■, □) experimental data at $T = 303.15$ K; (●, ○) experimental data at $T = 323.15$ K; (▲, △) experimental data at $p = 40.000$ kPa; (▼, ▽) experimental data at $p = 101.325$ kPa; (—) UNIFAC prediction.

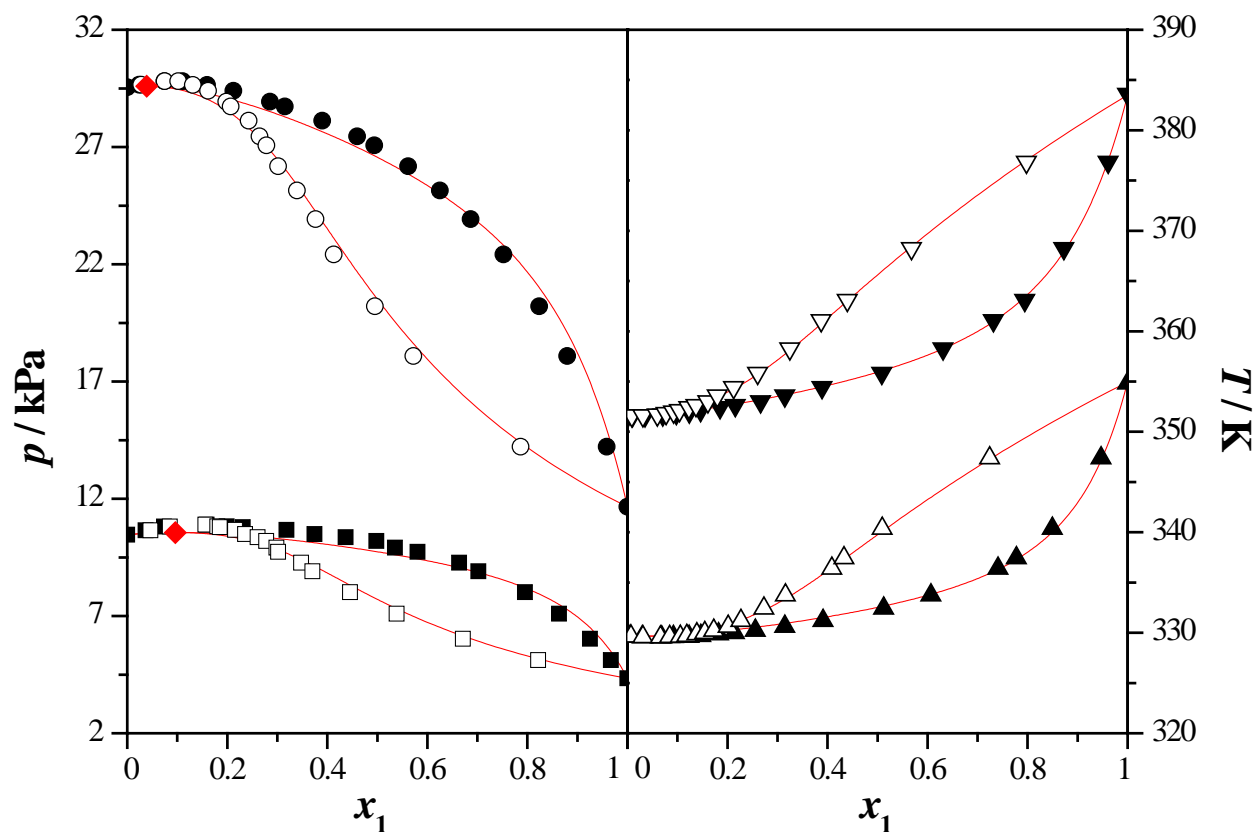


Fig. S2. p - x_1 - y_1 and T - x_1 - y_1 diagrams for the binary mixture ethyl isobutyrate (1) + ethanol (2): (■, □) experimental data at $T = 303.15$ K; (●, ○) experimental data at $T = 323.15$ K; (▲, △) experimental data at $p = 40.000$ kPa; (▼, ▽) experimental data at $p = 101.325$ kPa; (◆) UNIFAC predicted azeotropes; (—) UNIFAC prediction.

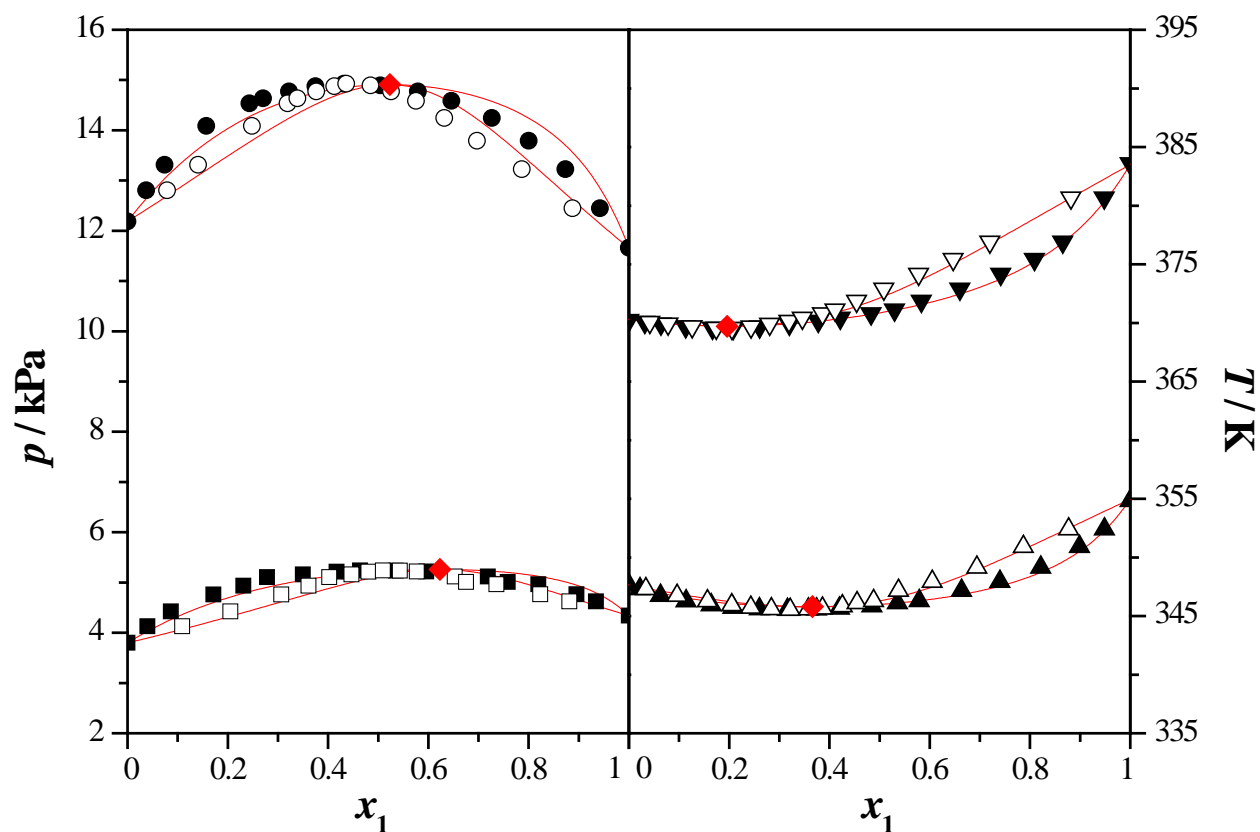


Fig. S3. p - x_1 - y_1 and T - x_1 - y_1 diagrams for the binary mixture ethyl isobutyrate (1) + 1-propanol (2): (■, □) experimental data at $T = 303.15$ K; (●, ○) experimental data at $T = 323.15$ K; (▲, △) experimental data at $p = 40.000$ kPa; (▼, ▽) experimental data at $p = 101.325$ kPa; (◆) UNIFAC predicted azeotropes; (—) UNIFAC prediction.

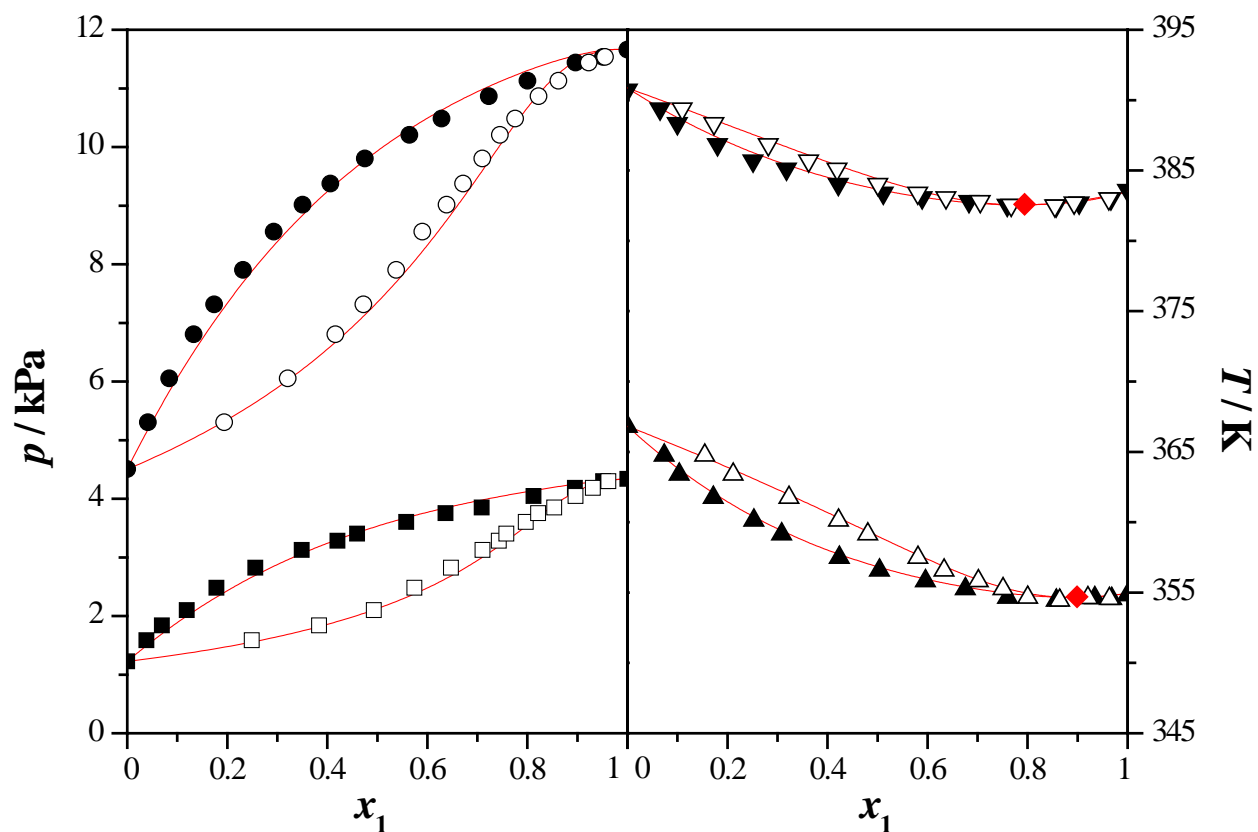


Fig. S4. p - x_1 - y_1 and T - x_1 - y_1 diagrams for the binary mixture ethyl isobutyrate (1) + 1-butanol (2): (■, □) experimental data at $T = 303.15$ K; (●, ○) experimental data at $T = 323.15$ K; (▲, △) experimental data at $p = 40.000$ kPa; (▼, ▽) experimental data at $p = 101.325$ kPa; (◆) UNIFAC predicted azeotropes; (—) UNIFAC prediction.