

Effect of Pressure on the Azeotropes of the Mixture Isobutyl Acetate–Acetic Acid: Vapor–Liquid Equilibrium at 5, 10, and 40 kPa

Valentina Schäfer-Vargas, Gabriel E. Peña-Jurado, César A. Sánchez-Correa,* Iván D. Gil-Chaves, and Gerardo Rodríguez-Niño



Cite This: *J. Chem. Eng. Data* 2026, 71, 4279–4288



Read Online

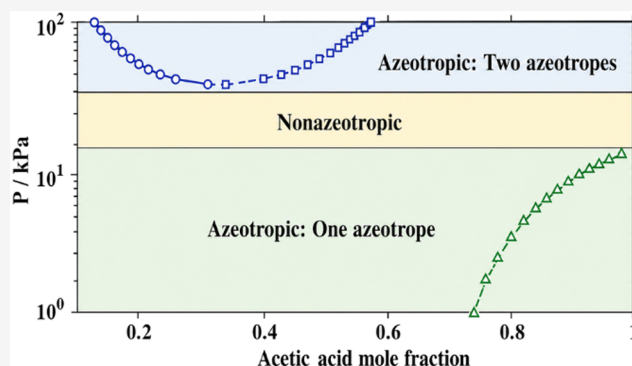
ACCESS |

Metrics & More

Article Recommendations

Supporting Information

ABSTRACT: In this work, phase equilibrium data for the binary mixture acetic acid (1) + isobutyl acetate (2) were measured at pressures of 5, 10, and 40 kPa using a dynamic recirculation cell (Fischer Labodest VLE model 602). The combined analysis of the new experimental measurements and previously reported experimental data revealed three distinct pressure-dependent regions for the system: a low-pressure region with one azeotrope, an intermediate-pressure region without azeotropes, and a high-pressure polyazeotropic region characterized by two azeotropes. The experimentally obtained data were subjected to a thermodynamic consistency analysis to validate their reliability and were subsequently employed in a regression procedure to estimate a single set of adjusted parameters for the nonrandom two-liquid (NRTL) model over the entire pressure range studied. These parameters can be directly applied in process simulation, separation process design, and the modeling of intensified operations such as reactive distillation involving the acetic acid–isobutyl acetate system.



1. INTRODUCTION

Azeotropic systems are of significant interest in chemical engineering, particularly those exhibiting double azeotropy, a rare phenomenon observed in only a few known mixtures,¹ such as benzene-hexafluorobenzene,² methanol-diethylamine,³ ammonia-pentafluoroethane⁴ and decafluoropentane and tetrahydrofuran.⁵ The isobutyl acetate-acetic acid system falls into this unique category, making its study particularly valuable for advancing the understanding of azeotropic behavior under different operating conditions. This work presents novel experimental data on the vapor-liquid equilibrium (VLE) of this system at reduced pressures of 5.00, 10.00, and 40.00 kPa. These data are scientifically unprecedented, as prior studies have only reported VLE data for this system at atmospheric pressure⁶ and at an isothermal equilibrium.⁷ Understanding this equilibrium is essential for the design and simulation of azeotropic distillation systems and the development of reactive distillation processes for the production of isobutyl acetate.

The experimental methodology involved sampling both equilibrium phases using a dynamic equilibrium cell, the FISCHER LABODEST VLE 602, followed by gas chromatography analysis to determine their compositions. The thermodynamic consistency of the obtained data was verified using the Fredenslund and Herington tests. For phase equilibrium modeling, the NRTL model was employed to represent liquid-phase activity coefficients, while fugacity

coefficients in the vapor phase were calculated using the Hayden–O’Connell equation.⁸ This approach was adopted to properly account for the highly non-ideal behavior of acetic acid in the vapor phase,⁹ which is dominated by strong molecular association effects, particularly dimerization, that cannot be adequately described by conventional equations assuming ideal or weakly non-ideal vapor behavior.

The results indicate the existence of three distinct pressure-dependent regions for this system: a low-pressure region characterized by a single azeotrope, an intermediate-pressure region without azeotropes, and a high-pressure polyazeotropic region exhibiting two azeotropes. The thermodynamic consistency of the experimental data was confirmed, reinforcing their reliability and quality. Additionally, a comprehensive thermodynamic model was developed by integrating the new experimental data generated in this work. This approach provided a robust description of the pressure-dependent azeotropic behavior of the system over a wide pressure range. These findings contribute valuable and original

Received: May 13, 2026

Revised: September 6, 2026

Accepted: September 9, 2026

Published: September 16, 2026



Table 1. Material Description

Component	Acetic acid	Isobutyl acetate	Acetone	1,4 Dioxane
Formula	C ₂ H ₄ O ₂	C ₆ H ₁₂ O ₂	C ₃ H ₆ O	C ₄ H ₈ O ₂
CAS Number	64-19-7	110-19-0	67-64-1	123-91-1
Source	PanReac	Merck KGaA	PanReac	Merck KGaA
Molecular Weight (g/mol)	60.052	116.16	58.08	88.106
Purity (GC) (area %) ^a	99.5	98.0	99.5	99.5
Water (wt %) ^a	0.2%	≤ 0.1%	≤ 0.05	≤ 0.05
T _b (K) 101.325 kPa	Exp. ^b 390.49 Lit. 391.05 ^{6,10}	390.38 389.80 ^{6,10}	- 331.44 ^{10,11}	- 374.25 ^{10,12}

^aReported by manufacturer. ^bCalculated with the experimental Antoine parameters.

data to the field of chemical engineering, enabling more accurate process simulation, optimization, and design of separation processes such as vacuum azeotropic distillation and reactive distillation.

2. EXPERIMENTAL SECTION

2.1. Materials

Analytical-grade acetic acid, isobutyl acetate, acetone, and 1,4-dioxane were obtained from the suppliers listed in Table 1 and used as received, without further purification. The vapor–liquid equilibrium measurements were carried out for the acetic acid + isobutyl acetate system. Acetone was employed as the solvent and 1,4-dioxane as the internal standard in the chromatographic method developed for the analysis; therefore, their properties are also presented. The normal boiling points listed in the table were calculated from the Antoine parameters obtained experimentally, as described in the Results and Discussion section.

2.2. VLE Apparatus and Procedure

The vapor–liquid equilibrium (VLE) measurements were performed using a Fischer Labodest VLE 602 dynamic recirculation cell (See Figure 1). The technical specifications of this apparatus have been reported in detail in previous works.^{13–15} Accuracy in measurements of temperature and pressure (certified by the manufacturer) are ± 0.01 K and 0.01 kPa, respectively. In each experiment, approximately 1.0×10^{-4} m³ (100 mL) of one pure component was initially charged into the mixing chamber, while approximately 1.0×10^{-4} m³ (100 mL) of the other component was placed in the side reservoir. Binary mixtures of the desired overall composition were then prepared by controlled addition of the second component into the cell. Subsequently, the loading sequence was reversed (i.e., the components were exchanged between the cell and the reservoir) to obtain mixtures covering the entire composition range from 0 to 1 in mole fraction.

Operation of the apparatus began by setting the desired pressure and allowing the system to stabilize, after which the heating and stirring systems were activated. The system was operated under total reflux. The heating power was adjusted to maintain a condensate return rate of approximately 1–2 drops per second, while continuously monitoring temperature and pressure. Equilibrium was assumed to be reached when the system temperature remained constant for at least 30 min. Pressure and temperature fluctuations were continuously evaluated using statistical control charts. Once equilibrium was established, samples of both the liquid and condensed vapor phases were withdrawn for chromatographic analysis. Sampling was performed using the isolation arm of the apparatus, which allows withdrawal of samples avoiding any disturbance of the equilibrium conditions within the chamber.

To minimize heat losses to the surroundings, the VLE 602 apparatus is equipped with a heating mantle covering the equilibrium chamber and heating tape wrapped around the condensate return line. During each experimental run, the set-point temperatures of the heating mantle and heating tape were adjusted to match the temperatures of the equilibrium chamber and mixing chamber,

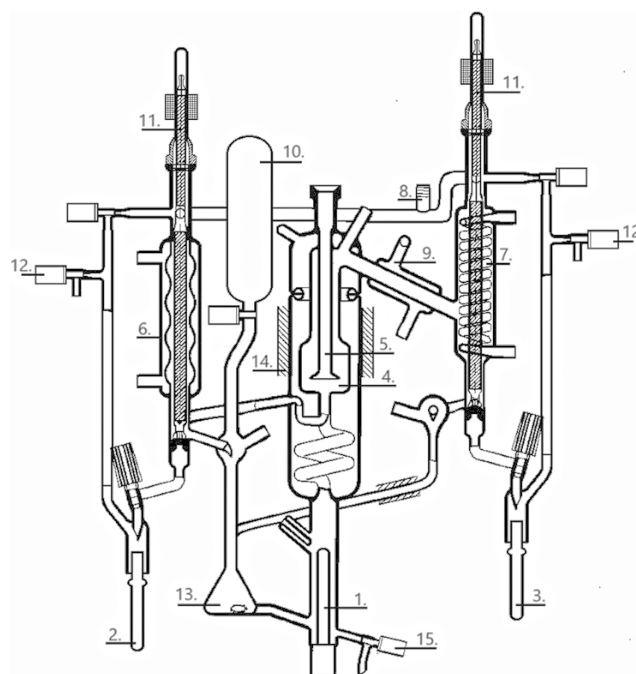


Figure 1. VLE apparatus used in this work: 1, heating rod; 2, Receiver (liquid sample); 3, Receiver (vapor sample); 4, Equilibrium Chamber; 5, Pt-100 (vapor temperature); 6, Security cooler liquid phase; 7, Security cooler vapor phase; 8, Connection to buffer vessel; 9, Condenser; 10, mixture reservoir; 11, controlled solenoid valves; 12, Ventilation valve; 13, Mixing Chamber; 14, Heated isolation jacket; 15, Drain valve.

respectively, thereby minimizing heat transfer between the apparatus and the surroundings.

The Fischer Labodest VLE apparatus and the general measurement protocol used in this work have been previously described and applied in peer-reviewed studies from our research group, in which the same experimental setup and methodology were employed.^{13–19} More specifically, the experimental procedure has been verified and validated using reference systems for which independent literature data are available, including the propyl propanoate (1) + water (2)¹⁶ and ethanol (1) + water (2)¹⁹ systems. Accordingly, the reliability of the apparatus, sampling procedure, and measurement protocol used in the present work is supported by prior validation studies performed under the same methodological framework.

2.3. Analytical Method

The composition of the liquid and vapor samples from the VLE experiments was determined by gas chromatography (GC) using a Shimadzu 2010 Plus instrument equipped with a flame ionization detector (FID). Each sample was prepared by dissolving 100 μ L of the analyzed phase in 900 μ L of acetone and adding 50 μ L of 1,4-dioxane as the internal standard. Separation was carried out on an

SGE Analytical Science capillary column (30 m × 0.32 mm × 0.25 μm) coated with BP-20 (polyethylene glycol) as the stationary phase. High-purity helium (chromatography grade) was used as the carrier gas. The injector and detector temperatures were both maintained at 513.15 K (240 °C).

The oven temperature program started at 100 °C, followed by a heating rate of 5 °C min⁻¹ up to 137 °C (1 min hold), and subsequently 20 °C min⁻¹ up to 165 °C with a final hold of 2.2 min, resulting in a total run time of approximately 12 min. Under these conditions, the retention times were approximately 5.47 min for acetone, 6.14 min for isobutyl acetate, 6.41 min for 1,4-dioxane (internal standard), and 9.69 min for acetic acid.

Calibration curves were established by analyzing standard mixtures of known composition prepared gravimetrically using an analytical balance (±0.001 g). The resulting calibration curves are presented in Figure S.1 of the Supporting Information.

3. RESULTS AND DISCUSSION

3.1. Vapor-Liquid Equilibrium Data

The experimental saturated vapor pressures of pure acetic acid and isobutyl acetate are presented in Table 2. The Antoine

Table 2. Experimental Data of Saturated Vapor Pressures of the Pure Components^a

Acetic acid		Isobutyl acetate	
T/K	P/kPa	T/K	P/kPa
302.75	2.50	313.21	5.01
314.78	5.01	321.02	7.50
322.64	7.51	327.06	10.01
328.46	10.01	343.16	20.00
337.39	15.00	353.48	30.00
344.15	20.00	361.27	40.00
354.35	30.00	367.65	50.00
362.16	40.01	373.10	60.00
368.37	50.00	377.83	69.99
373.72	60.01	380.08	75.20
378.35	70.00		
380.55	75.19		

^aExpanded uncertainties (0.95 level of confidence) U are $U(T) = 0.06$ K and $U_r(P) = 0.03$.

constants for each component were determined through nonlinear regression using Aspen Plus V12,²⁰ and the resulting parameters are reported in Table 3. The regression framework

Table 3. Adjusted Values of Antoine Equation^a Constants of the Pure Components at the Temperature Interval and the Corresponding Standard Deviation, σ

Component	A (σ)	B (σ)	C (σ)	T range (K)
Acetic acid	20.059 (0.125)	-2477.038 (60.402)	-100.224 (2.912)	302.75–380.55
Isobutyl acetate	20.526 (0.206)	-2762.638 (108.250)	-83.024 (5.110)	313.21 – 380.08

^aThe constants are fitted for use with temperature in K and pressure in Pa.

implemented in Aspen Plus is based on the Britt–Luecke algorithm in combination with a Maximum-Likelihood objective function. The regression was performed based on eq (1)

$$\ln(p) = A + \frac{B}{T + C} \quad (1)$$

In eq (1), temperature is expressed in K and pressure in Pa.

Figure 2 shows the linear relationship between $\ln(P)$ and $1/T$ for both pure substances. The experimental vapor pressure data and literature correlations exhibit excellent agreement with the model regressed from the experimental measurements, both for acetic acid and isobutyl acetate. The strong agreement between literature data and the experimentally obtained correlation not only validates the regressed Antoine parameters, but also provides additional evidence that the vapor–liquid equilibrium cell was operated properly and that reliable equilibrium measurements were achieved.

3.2. Thermodynamic Consistency

The activity coefficient was calculated through eq (2), which correspond to the general equilibrium equation²²

$$y_i \phi_i^p = x_i \gamma_i^{\text{sat}} p_i^{\text{sat}} \phi_i^{\text{sat}} \exp \left[\frac{1}{RT} \int_{p_i^{\text{sat}}}^p v_i^l dp \right] \quad (2)$$

Since the pressures established for the experiments are relatively low, the Poynting correction can be assumed to be unity. The fugacity coefficients of the pure components at saturation conditions (ϕ_i^{sat}), as well as those of the components in the vapor phase mixture (ϕ_i), were calculated using the Hayden–O’Connell method,⁸ as implemented in a custom MATLAB code developed in this work. It should be noted that the parameters required for the implementation of this model were obtained from Aspen Plus and are reported in Tables 4 and 5.

This code was also used to determine the activity coefficients of each component from the experimentally measured equilibrium data and the calculated variables. The resulting activity coefficients are reported in Tables 7, 8, and 9.

Moreover, the saturation pressures of the pure components were calculated using the extended Antoine vapor pressure eq (eq 3), with parameters obtained from the Aspen Plus chemical process simulator database²⁰ and presented in Table 6

$$\ln(p_i) = C_{1i} + \frac{C_{2i}}{T + C_{3i}} + C_{4i}T + C_{5i}\ln(T) + C_{6i}T^{C_{7i}} \quad (3)$$

Although Antoine parameters were independently regressed from the experimental vapor-pressure data of the pure substances (Table 2), the extended Antoine equation and Aspen Plus parameters were ultimately adopted for the activity-coefficient calculations. This choice was made because the experimentally regressed parameters are only valid within the pressure range covered by the measurements (up to approximately 75.00 kPa), whereas the Aspen Plus correlation is applicable over a significantly wider temperature and pressure range, thereby providing greater robustness and consistency for the thermodynamic calculations.

Then, according to eq 2 and applying the general law of propagation of experimental uncertainties,²³ the uncertainty of the activity coefficient of component k was evaluated with the following equation

$$(\Delta \gamma_k)^2 = \left(\frac{\partial \gamma_k}{\partial p} \right)^2 (\Delta p)^2 + \left(\frac{\partial \gamma_k}{\partial T} \right)^2 (\Delta T)^2 + \left(\frac{\partial \gamma_k}{\partial x_1} \right)^2 (\Delta x_1)^2 + \left(\frac{\partial \gamma_k}{\partial y_1} \right)^2 (\Delta y_1)^2 \quad (4)$$

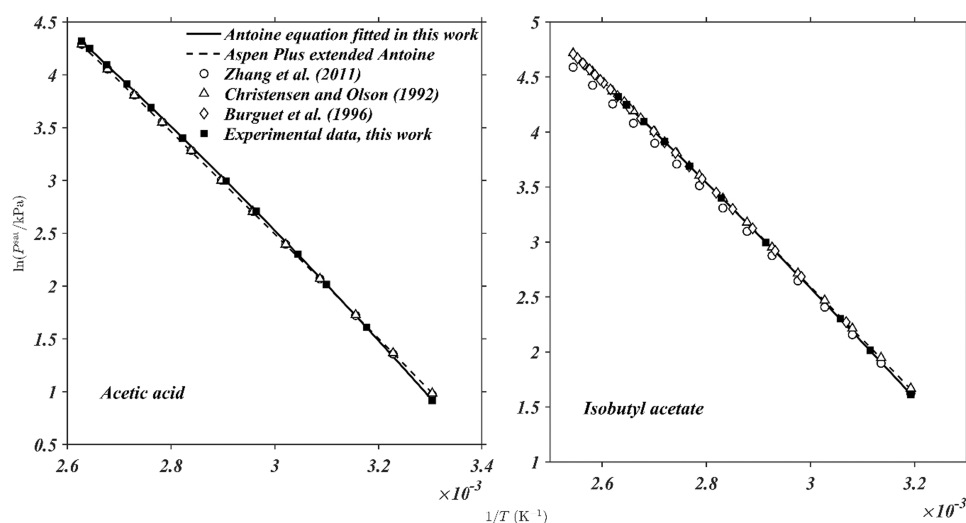


Figure 2. Vapor pressure temperature dependence for acetic acid and isobutyl acetate. Experimental data from this work (■), Burguet et al.⁷ (◇), Antoine equation from Zhang et al.⁶ (○), Christensen & Olson.²¹ (△), Aspen Plus (---), fitted in this work (—).

Table 4. Association and Solvation Parameters for the Acetic Acid (1) and Isobutyl Acetate (2) System²⁰

	Acetic acid	Isobutyl acetate
Acetic acid	4.5	2
Isobutyl acetate	2	0.53

Table 5. Pure-Component Properties^a Used in the Hayden–O’Connell Method²⁰

Component	T_C (K)	P_C (bar)	R_D (Å)	μ (D)	M (g mol ⁻¹)
Acetic acid	591.95	57.86	2.61	1.73880051	60.05256
Isobutyl acetate	560.8	30.1	4.276	1.87071	116.16

^aGiven are the critical temperature T_C , critical pressure P_C , molecular diameter R_D , dipole moment μ and molecular weight M .

For the mole fraction, the uncertainty was considered as the maximum error associated with the chromatography, $u(x_1) = u(y_1) = 0.002$. For temperature, the measurement uncertainty was evaluated following the recommendations of the Guide to the Expression of Uncertainty in Measurement (GUM).²⁴ The resulting combined standard uncertainty was $u_c(T) = 0.03$ K. For pressure, a relative expanded uncertainty of $U_r(P) = 0.03$ was adopted, as recommended by the Statistical Reviewer based on the NIST comparison of the measured vapor-pressure data with literature values represented by the Wagner correlation. Accordingly, the pressure uncertainty was calculated as $\Delta P = 0.03P$. The procedure used to calculate the temperature uncertainty is provided in the [Supporting Information](#).

Tables 7, 8, and 9 also include the relative volatility of acetic acid (α) and its associated uncertainty. The procedure used to propagate the experimental uncertainties to α is described in

the [Supporting Information](#) and follows an approach analogous to that used for the activity coefficients.

The thermodynamic consistency of the experimental data was assessed using the Fredenslund test.^{25–27} In this approach, the excess Gibbs energy is expressed as a linear combination of Legendre polynomials truncated to four terms, according to

$$g^E = \frac{G^E}{RT} = x_1(1 - x_1)\sum_{k=0}^n a_k L_k(x_1) \quad (5)$$

Where a_k are adjustable model parameters and L_k denotes the Legendre polynomial of order k . The activity coefficients were subsequently obtained from the numerical differentiation of the excess Gibbs energy with respect to composition. For component 1, the activity coefficient is given by

$$\ln(\gamma_1) = g^E + x_2 \frac{dg^E}{dx_1} \quad (6)$$

$$\ln(\gamma_2) = g^E - x_1 \frac{dg^E}{dx_1} \quad (7)$$

Once the activity coefficients were determined, the vapor-phase mole fractions were recalculated using the general phase equilibrium equation. The parameters a_k were then adjusted by minimizing the deviations between experimental and calculated values, thereby allowing the consistency of the experimental data to be evaluated.

The performance of the test was quantified in terms of the relative deviation in pressure (δp) and the average absolute deviation (AAD) of the vapor-phase mole fraction (Δy_1), defined as

Table 6. Aspen Plus Parameters for the Extended Antoine Vapor-Pressure Equation (Equation 3)^a

Component	C_{1i}	C_{2i}	C_{3i}	C_{4i}	C_{5i}	C_{6i}	C_{7i}
Acetic acid	46.36224472	−6304.50	0	0	−4.298500	8.886500×10^{-18}	6
Isobutyl acetate	65.40224472	−6944.30	0	0	−7.29800	3.789200×10^{-06}	2

^aIn eq 3, T is expressed in K and P in kPa.

Table 7. Experimental Vapor–Liquid Equilibrium Data for the System of Acetic acid (1) and Isobutyl Acetate (2) at 5.00 kPa^a

<i>T</i> /K	<i>x</i> ₁	<i>y</i> ₁	<i>γ</i> ₁	<i>γ</i> ₂	$\Delta\gamma_1/\gamma_1$	$\Delta\gamma_2/\gamma_2$	<i>α</i>	$\Delta\alpha/\alpha$
312.79	0.051	0.034	1.925	0.993	0.118	0.031	0.655	0.058
313.52	0.169	0.136	1.456	1.014	0.036	0.031	0.774	0.0201
314.14	0.395	0.357	1.150	1.112	0.022	0.032	0.850	0.012
314.26	0.429	0.394	1.128	1.125	0.021	0.032	0.865	0.012
314.34	0.462	0.426	1.103	1.145	0.021	0.032	0.864	0.011
314.67	0.614	0.601	1.053	1.206	0.019	0.034	0.947	0.012
314.76	0.644	0.635	1.044	1.216	0.019	0.034	0.962	0.012
314.77	0.678	0.668	1.032	1.248	0.019	0.035	0.956	0.013
314.81	0.722	0.716	1.023	1.274	0.019	0.036	0.971	0.014
315.19	0.890	0.893	0.992	1.353	0.018	0.059	1.031	0.029

^aGiven are the liquid-phase mole fraction *x*, vapor-phase mole fraction *y*, temperature *T*, the calculated results for activity coefficient *γ*, relative uncertainty $\Delta\gamma/\gamma$, relative volatility *α*, and the relative uncertainty $\Delta\alpha/\alpha$. Expanded uncertainties (0.95 level of confidence) *U* are *U*(*T*) = 0.06 K; *U*(*P*) = 0.15 kPa; *U*(*x*₁) = *U*(*y*₁) = 0.004.

Table 8. Experimental Vapor–Liquid Equilibrium Data for the System of Acetic Acid and Isobutyl Acetate at 10.00 kPa^a

<i>T</i> /K	<i>x</i> ₁	<i>y</i> ₁	<i>γ</i> ₁	<i>γ</i> ₂	$\Delta\gamma_1/\gamma_1$	$\Delta\gamma_2/\gamma_2$	<i>α</i>	$\Delta\alpha/\alpha$
327.13	0.082	0.060	1.725	1.018	0.071	0.030	0.715	0.038
327.37	0.119	0.091	1.575	1.025	0.049	0.031	0.741	0.027
327.65	0.173	0.142	1.450	1.038	0.035	0.031	0.791	0.020
327.83	0.219	0.185	1.358	1.053	0.030	0.031	0.809	0.016
327.98	0.270	0.233	1.278	1.075	0.026	0.031	0.821	0.014
328.15	0.416	0.386	1.161	1.147	0.022	0.032	0.882	0.012
328.25	0.472	0.442	1.121	1.181	0.021	0.032	0.886	0.011
328.38	0.540	0.523	1.102	1.204	0.020	0.033	0.934	0.011
328.43	0.580	0.565	1.085	1.229	0.020	0.033	0.941	0.012
328.48	0.618	0.602	1.066	1.261	0.019	0.034	0.935	0.012
328.49	0.661	0.653	1.061	1.278	0.019	0.034	0.965	0.013
328.62	0.707	0.705	1.051	1.291	0.019	0.036	0.990	0.014
328.65	0.765	0.760	1.032	1.357	0.019	0.038	0.973	0.016
328.96	0.913	0.911	1.006	1.498	0.018	0.070	0.975	0.036

^aGiven are the liquid-phase mole fraction *x*, vapor-phase mole fraction *y*, temperature *T*, the calculated results for activity coefficient *γ*, relative uncertainty $\Delta\gamma/\gamma$, relative volatility *α*, and the relative uncertainty $\Delta\alpha/\alpha$. Expanded uncertainties (0.95 level of confidence) *U* are *U*(*T*) = 0.06 K; *U*(*P*) = 0.30 kPa; *U*(*x*₁) = *U*(*y*₁) = 0.004.

Table 9. Experimental Vapor–Liquid Equilibrium Data for the System of Acetic Acid and Isobutyl Acetate at 40.00 kPa^a

<i>T</i> /K	<i>x</i> ₁	<i>y</i> ₁	<i>γ</i> ₁	<i>γ</i> ₂	$\Delta\gamma_1/\gamma_1$	$\Delta\gamma_2/\gamma_2$	<i>α</i>	$\Delta\alpha/\alpha$
361.57	0.178	0.161	1.469	1.049	0.035	0.030	0.886	0.019
361.64	0.228	0.212	1.389	1.066	0.030	0.030	0.911	0.016
361.65	0.272	0.254	1.320	1.088	0.027	0.031	0.911	0.014
361.73	0.427	0.419	1.196	1.155	0.022	0.032	0.968	0.012
361.88	0.480	0.475	1.161	1.176	0.021	0.032	0.980	0.011
361.98	0.520	0.516	1.137	1.195	0.021	0.032	0.984	0.011
361.98	0.569	0.554	1.096	1.251	0.021	0.033	0.941	0.011
362.1	0.702	0.695	1.058	1.337	0.020	0.036	0.967	0.013
362.13	0.738	0.728	1.045	1.383	0.020	0.037	0.950	0.015
362.28	0.821	0.811	1.026	1.478	0.019	0.043	0.935	0.019
362.38	0.896	0.892	1.021	1.535	0.019	0.060	0.959	0.030
362.7	0.962	0.958	1.010	1.698	0.019	0.143	0.901	0.077

^aGiven are the liquid-phase mole fraction *x*, vapor-phase mole fraction *y*, temperature *T*, the calculated results for activity coefficient *γ*, relative uncertainty $\Delta\gamma/\gamma$, relative volatility *α*, and the relative uncertainty $\Delta\alpha/\alpha$. Expanded uncertainties (0.95 level of confidence) *U* are *U*(*T*) = 0.06 K; *U*(*P*) = 1.20 kPa; *U*(*x*₁) = *U*(*y*₁) = 0.004.

$$\delta p = \frac{1}{N} \sum_{i=1}^N \left| \frac{p_i^{\text{exp}} - p_i^{\text{cal}}}{p_i^{\text{exp}}} \right| \leq 0.01 \quad (8)$$

$$\Delta y_1 = \frac{1}{N} \sum_{i=1}^N |y_i^{\text{exp}} - y_i^{\text{cal}}| \leq 0.01 \quad (9)$$

where *N* is the number of experimental data points, and *p_i* and *y_i* denote the pressure and vapor-phase mole fraction of the *i*-th data point, respectively. The superscripts “exp” and “cal” refer to experimental and calculated values.

According to the results summarized in Table 10, the data sets at 5.00, 10.00, and 40.00 kPa satisfy the Fredenslund criteria of $\delta p < 1\%$ and $\delta y_i < 1\%$, indicating satisfactory

Table 10. Thermodynamic Consistency of the Experimental VLE Data by Fredenslund Test

Pressure (kPa)	δp	δy_1	δy_2
5.00	0.002	0.007	0.006
10.00	0.002	0.003	0.004
40.00	0.002	0.005	0.004

thermodynamic consistency.²⁸ To further assess possible local inconsistencies, the randomness of the pressure residuals was evaluated using an exact two-sided runs test about zero. At a significance level of $\alpha = 0.05$, the null hypothesis of random ordering of the residuals was not rejected at 5.00, 10.00, or 40.00 kPa, with p -values of 0.810, 0.056, and 0.218, respectively. The individual pressure residuals, together with the activity coefficients obtained from the Legendre-polynomial representation of g^E/RT , are provided in the [Supporting Information](#).

According to the results summarized in [Table 10](#), the data set of the different equilibrium pressures meet the criteria of $\delta p < 1\%$ and $\delta y < 1\%$, indicating high-quality experimental data.²⁸

The Herington test^{26,29} was additionally applied as a complementary and qualitative assessment. The parameters D and J were calculated as follows

$$D = 100 \frac{\left| \int_0^1 \ln \frac{y_1}{y_2} dx_1 \right|}{\int_0^1 \left| \ln \frac{y_1}{y_2} \right| dx_1} \quad (10)$$

$$J = 150 \frac{T_{\max} - T_{\min}}{T_{\min}} \quad (11)$$

Where $T_{\min}$ and $T_{\max}$ are the lowest and highest recorded in the binary equilibrium data. According to the classical Herington criterion, thermodynamic consistency is expected when the difference $|D - J|$ is lower than 10,²⁸ which is fulfilled for all pressure levels as shown in [Table 11](#), despite the strong non-ideal behavior of the acetic acid–isobutyl acetate system, mainly associated with acetic acid dimerization in the vapor phase.

Table 11. Thermodynamic Consistency of the Experimental VLE Data by Herington Test

Pressure (kPa)	D	J	$ D - J $
5.00	12.2072	9.7629	2.4444
10.00	4.3631	6.7406	2.3775
40.00	9.3437	3.8721	5.4716

3.3. Data Correlation

The activity coefficients were correlated using the non-random two-liquid (NRTL) model.³⁰ This model was selected due to its flexibility, robustness, and extensive use in industrial applications, particularly for the design and simulation of separation units governed by vapor–liquid equilibrium behavior. In the present work, the NRTL formulation is expressed as follows:

$$\ln(\gamma_i) = \frac{\sum_j x_j \tau_{ji} G_{ji}}{\sum_k x_k G_{ki}} + \sum_j \frac{x_j G_{ij}}{\sum_k x_k G_{kj}} \left(\tau_{ij} - \frac{\sum_m x_m \tau_{mj} G_{mj}}{\sum_k x_k G_{kj}} \right) \quad (12)$$

Where $G_{ji} = e^{-\alpha_{ij} \tau_{ij}}$, $\tau_{ij} = \frac{b_{ij}}{T}$ and $\alpha_{ij} = c_{ij} + d_{ij}(T - 273.15 \text{ K})$. The value of c_{ij} was fixed at 0.47 according to the Aspen Plus recommendations for mixtures exhibiting molecular association behavior.

The parameters of the NRTL model were estimated by regressing the experimental vapor–liquid equilibrium data using Aspen Plus (V12). The regression was performed by selecting an objective function based on the activity coefficients, which provides an appropriate representation of the phase-equilibrium behavior for highly non-ideal systems. This formulation accounts for both the liquid-phase non-idealities through the activity coefficients and the vapor-phase non-idealities through the fugacity coefficients included in the equilibrium calculations. Furthermore, the optimization was carried out using the Britt–Luecke algorithm.

Regarding the experimental data employed for the parameter estimation, a single regression was performed using the three experimental datasets obtained at the different operating pressures. This approach was adopted in order to obtain a single set of model parameters capable of accurately representing the vapor–liquid equilibrium behavior over a broader pressure range. The obtained parameters are reported in [Table 12](#).

Table 12. NRTL Model Parameters, Associated Standard Deviations (σ), and Root Mean Square Deviations of Temperature and Vapor-Phase Composition for Bubble-Point Calculations

Parameter	Value	
$b_{12}/K (\pm \sigma)$	$-163.5491 (\pm 12.2825)$	
$b_{21}/K (\pm \sigma)$	$417.9162 (\pm 19.3609)$	
$d_{12} = d_{21} (\pm \sigma)$	$-0.0036 (\pm 0.0002)$	
Pressure/kPa	RMSD (T) ^a /K	RMSD (y ₁) ^a
5.00	0.181	0.00694
10.00	0.267	0.00670
40.00	0.372	0.00706

^aRMSD (Root Mean Square Deviation) values were obtained from bubble-point calculations using the experimental pressure and liquid-phase composition as specified variables, with temperature and vapor-phase composition as calculated variables.

The predictive performance of the fitted NRTL model was further evaluated through bubble-point calculations, using the experimental pressure and liquid-phase composition as specified variables. As shown in [Table 12](#), the RMSD values for temperature were 0.181, 0.267, and 0.372 K at 5.00, 10.00, and 40.00 kPa, respectively, while the corresponding RMSD values for the vapor-phase mole fraction were 0.00694, 0.00670, and 0.00706. These results indicate that the single set of NRTL parameters provides a consistent representation of the experimental VLE data over the investigated pressure range.

[Figure 3](#) presents the experimentally determined activity coefficients together with those calculated using the thermodynamic model at 5.00, 10.00, and 40.00 kPa. As can be observed, the NRTL model successfully reproduces the behavior of both components over the entire composition range and at all investigated pressures. Furthermore, the figure shows the opposite trends exhibited by the activity coefficients of both components as the liquid composition changes, which

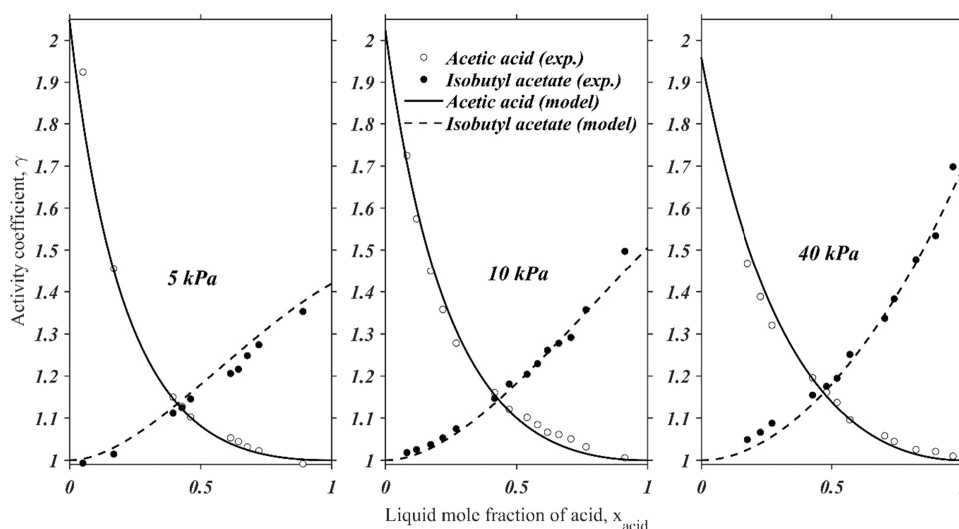


Figure 3. x – γ diagram of the VLE of the binary system acetic acid (1) + isobutyl acetate (2).

reflects the complex intermolecular interactions present in the mixture.

As can be observed in Figure 4, despite the highly non-ideal behaviour of the mixture, the experimental activity-coefficient

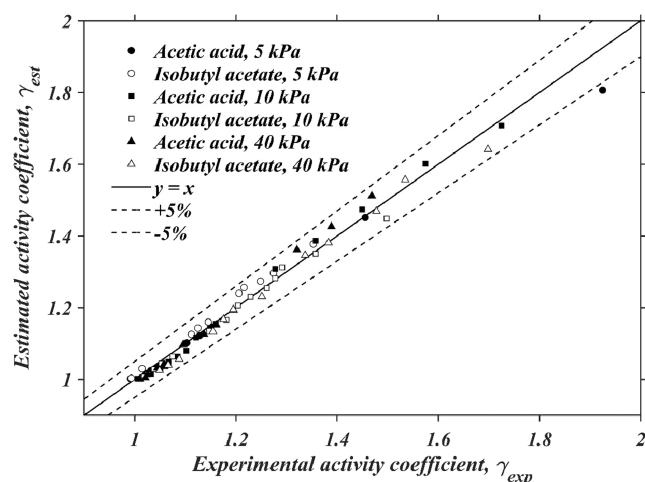


Figure 4. Parity plot for activity coefficients of the binary system acetic acid (1) + isobutyl acetate (2) obtained with the NRTL model.

data for both components show excellent agreement with the thermodynamic model at all investigated pressures, with most deviations remaining within $\pm 5\%$.

Similarly, Figure 5 presents the x – y diagrams for the system at the three investigated pressures, together with the corresponding thermodynamic model correlations.

As a complementary validation of the model developed in the present work, experimental equilibrium data for the system at 101.33 kPa available in the literature⁶ were compared with the predictions obtained using the regressed NRTL model. As shown in Figure 6, although 101.33 kPa is significantly higher than the maximum experimental pressure investigated in this study (40.00 kPa), the model is still able to reproduce the experimental equilibrium data and accurately predict the two azeotropes at this pressure. The predictive capability obtained is comparable to that reported in the literature using the UNIQUAC model fitted directly to data at atmospheric

pressure. The average absolute relative deviation (AARD) and the maximum absolute relative deviation (MARD) were calculated for the temperatures presented in Figure 6, using the experimental values as the reference. For the NRTL model, the AARD and MARD were 0.043% and 0.076%, respectively, whereas for the UNIQUAC model, they were 0.031% and 0.069%, respectively. These results further confirm the robustness and reliability of the thermodynamic model developed in this work.

To further assess the predictive capability of the model at 101.33 kPa, Figure 7 compares the experimental vapor-phase compositions reported by Zhang et al. with the NRTL predictions obtained in this work in an x_1 – y_1 diagram. Good agreement is observed over the investigated composition range, with a root mean square deviation (RMSD) of 0.00816 and an average absolute deviation (AAD) of 0.00698 for y_1 . These results provide additional evidence that the NRTL model maintains a satisfactory predictive performance when extrapolated from the pressure range used for parameter estimation to atmospheric pressure.

Likewise, the NRTL model obtained in this work made it possible to predict the azeotropic behavior of the mixture over a wide pressure range. As shown in Figure 8, at low pressures the acetic acid (1) + isobutyl acetate (2) system exhibits a single azeotrope. As the pressure increases, the system enters a pressure region in which no azeotropes are present. However, upon further increasing the pressure, the system evolves into a polyazeotropic region characterized by the presence of two azeotropes. It should be noted that Figure 8 also includes the predictions obtained using UNIFAC, which are in qualitative agreement with the conclusions of the present work. Table 13 presents the azeotropic temperatures and compositions predicted by the NRTL model at the pressures investigated in this work.

The azeotropic pressure–composition curves shown in Figure 8 were generated in Aspen Plus using a two-phase flash separator with a specified vapor fraction close to zero. For each pressure, the feed composition was iteratively adjusted using a Design Specification, which manipulated the component feed flow rates until the vapor-phase composition matched the overall feed composition. The pressure was then varied through a Sensitivity Analysis to trace the azeotropic

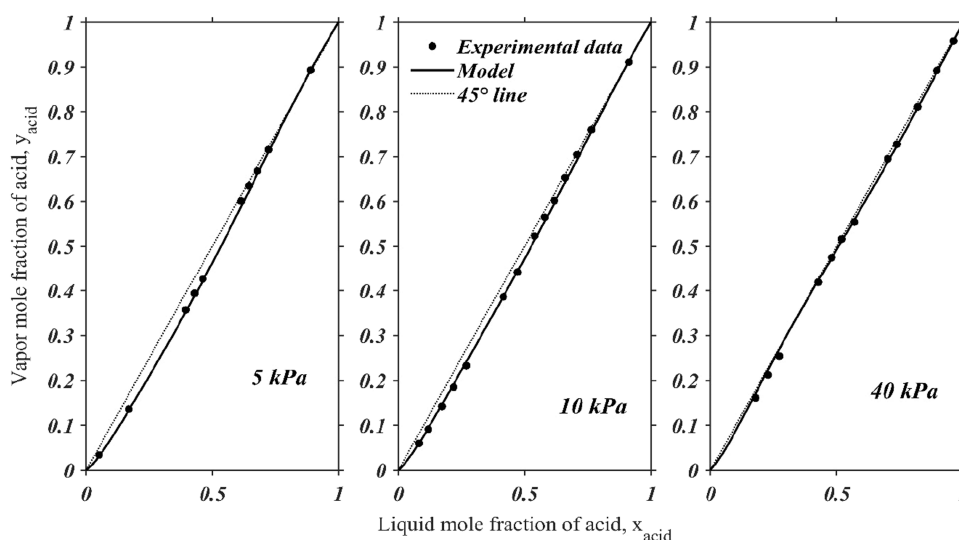


Figure 5. x – y diagrams of the VLE of the binary system acetic acid (1) + isobutyl acetate (2).

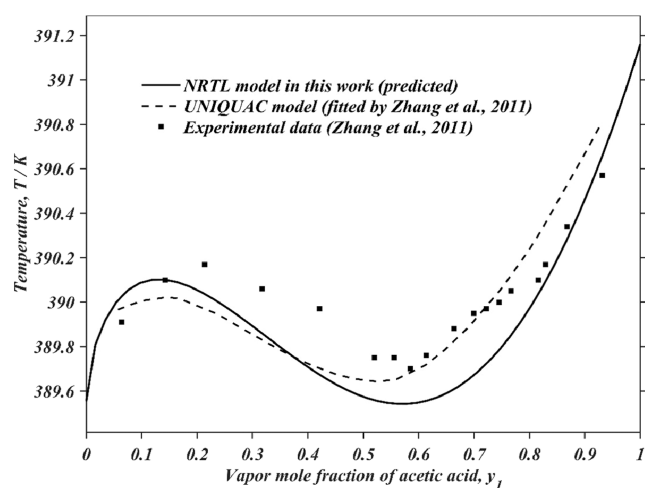


Figure 6. T – y diagram at 101.33 kPa of the acetic acid (1) + isobutyl acetate (2) system.⁶

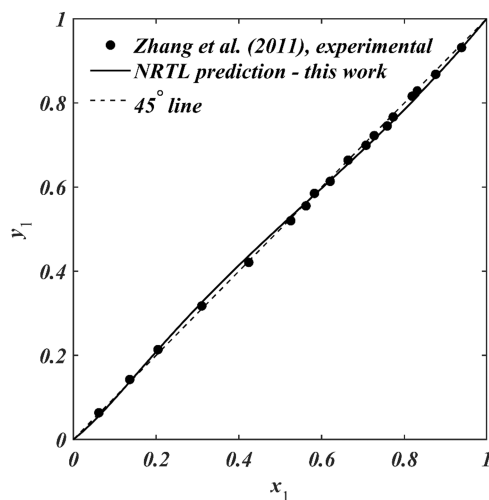


Figure 7. x – y diagram of the VLE of the binary system acetic acid (1) + isobutyl acetate (2) at 101.33 kPa.

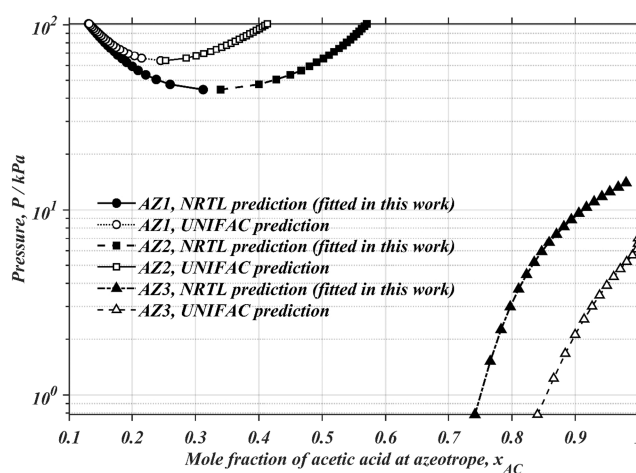


Figure 8. Azeotropic pressure as a function of mole fraction.

Table 13. Azeotropes of the System at the Different Pressures

Pressure (kPa)	$T_{az,1}$ (K)	$x_{1,az,1}$	$T_{az,2}$ (K)	$x_{1,az,2}$
5.00	314.87	0.832	-	-
10.00	329.19	0.912	-	-
101.33 (predicted)	390.09	0.131	389.50	0.570
101.33 ⁶	390.16	0.238	389.70	0.591

branches shown in Figure 8. This procedure was applied using both the regressed NRTL parameters and the UNIFAC model.

4. ANALYSIS

The acetic acid + isobutyl acetate system exhibits a highly complex vapor–liquid equilibrium behavior, primarily characterized by the presence of two azeotropes and a remarkably narrow vapor–liquid region. This pronounced non-ideality, already discussed in the Introduction section, arises from strong molecular interactions in the liquid phase and association effects in the vapor phase.

The evolution of the y – x diagrams with pressure (see Figures 5 and 7) reveals a qualitative change in relative volatility and, consequently, a redistribution of the distillation regions. At low pressures, such as 5.00 and 10.00 kPa in Figure

5, a single azeotrope divides the composition range into two distillation regions. At the intermediate pressure of 40.00 kPa, the azeotrope disappears and the entire composition range constitutes a single distillation region. At higher pressure, as illustrated by the results at 101.33 kPa in Figure 7, two azeotropes are present, dividing the composition range into three distillation regions. This pressure-dependent behavior results from changes in equilibrium temperature and in the relative volatility of the components, leading to the appearance, disappearance, and formation of multiple azeotropes as pressure varies. These predictions are consistent with literature reports. Zhang et al.⁶ presented experimental evidence for the existence of both azeotropes at 101.33 kPa, whereas Burguet et al.⁷ showed, based on isothermal experiments, that there are temperatures at which both azeotropes are present and temperatures at which no azeotrope exists. According to the predictions of the regressed model, if azeotrope-free separation is desired, the process should ideally be operated at moderately reduced pressures, specifically within the pressure region between approximately 20.00 and 40.00 kPa, as shown in Figure 8. Nevertheless, despite this improvement, the system remains intrinsically difficult to separate, since the vapor and liquid compositions remain very similar over the entire composition range, corresponding to relative volatilities close to unity.

The activity coefficient diagrams as a function of liquid composition (x_i) reflect the expected thermodynamic trends associated with highly non-ideal systems, including strong composition dependence and significant departures from unity. The consistency and smooth behavior of these profiles further support the reliability and internal coherence of the experimental data.

Regarding thermodynamic consistency, the experimental data sets were rigorously evaluated using several established methods. Among them, the Herrington test and the Fredenslund test confirmed the internal consistency of the data at all studied pressures. These results indicate that the experimental measurements are reliable and free from significant systematic errors, despite the intrinsic difficulty of working with such a highly non-ideal system. The agreement obtained with these independent consistency tests reinforces the robustness of both the experimental procedure and the subsequent data treatment.

The correlation of the experimental data using the NRTL model further demonstrated the quality and value of the generated data. The fitted parameters provided an accurate representation of the phase behavior across the entire composition range. Importantly, the relatively large and well-distributed data set not only enabled a reliable parameter estimation but also allowed for the reproduction of the experimental pressures through simulation. Furthermore, although the experimental measurements were carried out only at 5.00, 10.00, and 40.00 kPa, the obtained model also demonstrated a good predictive capability at significantly higher pressures, successfully reproducing literature equilibrium data and azeotropic behavior at atmospheric pressure (101.33 kPa). This highlights the robustness and reliability of the regressed parameters over a broad pressure range. These results emphasize the importance of generating comprehensive and high-quality experimental equilibrium data, as they significantly enhance the predictive capability of thermodynamic models and support their application in process

simulation and design, particularly for complex separation processes such as reactive distillation.

5. CONCLUSIONS

Vapor–liquid equilibrium data for the acetic acid + isobutyl acetate system were measured at 5.00, 10.00, and 40.00 kPa using a dynamic recirculation cell. It was observed that this system exhibits strong non-ideal behavior, including a narrow vapor–liquid region and a pressure dependent azeotropic behaviour.

Thermodynamic consistency of the data was verified using the Herrington and Fredenslund tests, confirming the reliability of the experimental measurements. The NRTL model provided an accurate correlation of the data across the entire composition range and successfully reproduced the pressure dependence of the system.

On the other hand, the predictive analysis revealed the existence of three distinct pressure-dependent regions for the system: a low-pressure region with one azeotrope, an intermediate-pressure region without azeotropes, and a high-pressure polyazeotropic region characterized by two azeotropes. The results suggest that operating at moderately reduced pressures, approximately between 20.00 and 40.00 kPa, could be advantageous for separation processes, since the system is predicted to exhibit no azeotropic behavior within this pressure range. Nevertheless, despite this improvement, the system remains intrinsically difficult to separate, since the vapor and liquid compositions remain very similar over the entire composition range, corresponding to relative volatilities close to unity.

These results provide scarce and valuable experimental data for a complex polyazeotropic system and supply a robust thermodynamic model for process simulation and design.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jced.6c00287>.

Uncertainty propagation for relative volatility; gas chromatography calibration curves; uncertainty calculation procedure; and Fredenslund consistency test based on pressure residuals (PDF)

■ AUTHOR INFORMATION

Corresponding Author

César A. Sánchez-Correa – Grupo de Procesos Químicos y Bioquímicos, Department of Chemical and Environmental Engineering, Universidad Nacional de Colombia, Bogotá 111321, Colombia; orcid.org/0000-0002-7826-9582; Email: casanchezc@unal.edu.co

Authors

Valentina Schäfer-Vargas – Grupo de Procesos Químicos y Bioquímicos, Department of Chemical and Environmental Engineering, Universidad Nacional de Colombia, Bogotá 111321, Colombia

Gabriel E. Peña-Jurado – Grupo de Procesos Químicos y Bioquímicos, Department of Chemical and Environmental Engineering, Universidad Nacional de Colombia, Bogotá 111321, Colombia; orcid.org/0009-0009-7000-6145

Iván D. Gil-Chaves – Grupo de Procesos Químicos y Bioquímicos, Department of Chemical and Environmental Engineering, Universidad Nacional de Colombia, Bogotá 111321, Colombia; orcid.org/0000-0002-0638-0222

Gerardo Rodríguez-Niño – Grupo de Procesos Químicos y Bioquímicos, Department of Chemical and Environmental Engineering, Universidad Nacional de Colombia, Bogotá 111321, Colombia

Complete contact information is available at:
<https://pubs.acs.org/10.1021/acs.jced.6c00287>

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. V.S.-V.: Experimentation, investigation, software, writing—original draft, writing—review and editing. G.E.P.-J.: Experimentation, writing—review and editing. C.A.S.-C.: Investigation, conceptualization, software, visualization, writing—review and editing. I.D.G.-C.: Conceptualization, resources, writing—review and editing. G.R.-N.: Methodology, supervision, writing—review and editing.

Notes

The authors declare no competing financial interest.

REFERENCES

- (1) Anjum, N.; Oba, S.; Hiaki, T.; Hsieh, C.-J.; Chen, C.-C. Thermodynamic modeling of double azeotropy systems. *Fluid Phase Equilib.* **2024**, 578, No. 113993.
- (2) GAW, W. J.; Swinton, F. Occurrence of a Double Azeotrope in the Binary System Hexafluorobenzene+Benzene. *Nature* **1966**, 212, 283–284.
- (3) Aucejo, A.; Loras, S.; Muñoz, R.; Wisniak, J.; Segura, H. Phase Equilibria and Multiple Azeotropy in the Associating System Methanol + Diethylamine. *J. Chem. Eng. Data* **1997**, 42 (6), 1201–1207.
- (4) Chai Kao, C.-P.; Paulaitis, M. E.; Yokozeki, A. Double azeotropy in binary mixtures of NH₃ and CHF₂CF₃. *Fluid Phase Equilib.* **1997**, 127, 191–203.
- (5) Kao, C.-P. C.; Sievert, A. C.; Schiller, M.; Sturgis, J. F. Double Azeotropy in Binary Mixtures 1,1,1,2,3,4,4,5,5,5-Decafluoropentane High-Boiling Diastereomer + Tetrahydrofuran. *Chem. Eng. Data* **2004**, 49, 532–536.
- (6) Zhang, C.; Wan, H.; Xue, L.; Guan, G. Investigation on isobaric vapor liquid equilibrium for acetic acid+water+(n-propyl acetate or iso-butyl acetate). *Fluid Phase Equilib.* **2011**, 305 (1), 68–75.
- (7) Burguet, M. C.; Montón, J. B.; Muñoz, R.; Wisniak, J.; Segura, H. Polyazeotropy in Associating Systems: The 2-Methylpropyl Ethanoate + Ethanoic Acid System. *J. Chem. Eng. Data* **1996**, 41 (5), 1191–1195.
- (8) Hayden, J. G.; O'Connell, J. P. A Generalized Method for Predicting Second Virial Coefficients. *Ind. Eng. Chem. Process Des. Dev.* **1975**, 14 (3), 209–216.
- (9) Chen, W.-L.; Hsu, C.-C.; Lin, S.-T. Prediction of phase behaviors of acetic acid containing fluids. *Fluid Phase Equilib.* **2013**, 353, 61–68.
- (10) L, P. J.; M, E. W. G. Thermodynamics Research Center, NIST Chemistry WebBook *Thermodynamics Source Database* [Online].
- (11) Gan, Y.; Xu, J.; Yan, Y. An experimental study of two-phase pressure drop of acetone in triangular silicon micro-channels. *Appl. Therm. Eng.* **2015**, 80, 76–86.
- (12) Hayes, D. G.; Williams, M.; Pechacek, N.; Hebert, B.; Stanton, K. Precise measurement of 1, 4-DIOXANE concentration in cleaning products: A review of the current state-of-the-art. *J. Surfactants Deterg.* **2022**, 25 (6), 729–741.
- (13) Duran, J. A.; Córdoba, F. P.; Gil, I. D.; Rodríguez, G.; Orjuela, A. Vapor–liquid equilibrium of the ethanol+3-methyl-1-butanol system at 50.66, 101.33 and 151.99 kPa. *Fluid Phase Equilib.* **2013**, 338, 128–134.
- (14) Leyva, F.; Orjuela, A.; Gil, I.; Vargas, J.; Rodríguez, G. Vapor–liquid equilibrium of isoamyl alcohol+isoamyl propionate and propionic acid+isoamyl propionate systems at 50.00, 101.33 and 150.00 kPa. *Fluid Phase Equilib.* **2013**, 356, 56–62.
- (15) Sánchez, C. A.; Sánchez, O. A.; Orjuela, A.; Gil, I. D.; Rodríguez, G. Vapor–Liquid Equilibrium for Binary Mixtures of Acetates in the Direct Esterification of Fusel Oil. *J. Chem. Eng. Data* **2017**, 62 (1), 11–19.
- (16) Velandia, J. J.; Fonseca, J. D.; Rodríguez Niño, G.; Gil Chaves, I. D. Isobaric Vapor–Liquid–Liquid Equilibrium for the 1-Propanol–Propyl Propanoate–Water Ternary System at 80.00 and 101.32 kPa. *J. Chem. Eng. Data* **2023**, 68 (9), 2353–2363.
- (17) García, C. A.; Velandia, J. J.; Céspedes, M. A.; Rodríguez, G.; Gil, I. D. Isobaric Vapor–Liquid Equilibrium for the Binary Mixture of 1-Butanol + Butyl L-Lactate at 1 and 5 kPa. *J. Chem. Eng. Data* **2021**, 66 (5), 2006–2011.
- (18) Sánchez, C. A.; Herrera, A. A.; Vargas, J. C.; Gil, I. D.; Rodríguez, G. Isobaric Vapor Liquid Equilibria for Binary Mixtures of Isoamyl Acetate + Ethyl Acetate at 50 and 100 kPa. *J. Chem. Eng. Data* **2019**, 64 (5), 2110–2115.
- (19) Rojas, O.; Salazar, A.; Gil, I.; Rodríguez, G. Effect of Pressure on the Azeotrope of the Mixture Isoamyl Acetate–Isoamyl Alcohol at 50.00, 101.32, 250.00, and 350.00 kPa. *J. Chem. Eng. Data* **2016**, 61 (9), 3109–3115.
- (20) Aspen Technology, Inc.. *Aspen Properties physical property database* [Physical property database], AspenTech.
- (21) Christensen, S. P.; Olson, J. Phase Equilibria and Multiple Azeotropy of the Acetic Acid–Isobutyl Acetate System. *Fluid Phase Equilib.* **1992**, 79, 187–199.
- (22) Smith, J. M.; Van Ness, H.; Abbott, M. M. *Introduction to Chemical Engineering Thermodynamics*; McGraw-Hill Education, 2005.
- (23) Andraos, J. On the Propagation of Statistical Errors for a Function of Several Variables. *Chem. Educ.* **1996**, 73 (2), No. 150.
- (24) Joint Committee for Guides in Metrology (JCGM). *Evaluation of Measurement Data—Guide to the Expression of Uncertainty in Measurement* 2008:100:2008(E) DOI: 10.59161/JCGM100-2008E.
- (25) Fredenslund, A.; Gmehling, J.; Rasmussen, P. *Vapor-Liquid Equilibria using UNIFAC. A Group-Contribution Method*; Elsevier, 1977; p 380.
- (26) Sommer, T.; Strnad, V.; Zapletal, M.; Vostrá, J.; Zbytovský, J.; Trejbal, J. Experimental Determination of Isobaric Vapor–Liquid Equilibria for the Binary Systems Containing Toluene and Isomers of 1,4-Dimethylcyclohexane at 15, 25, and 40 kPa. *J. Chem. Eng. Data* **2025**, 70 (11), 4625–4636.
- (27) Hartanto, D.; Schuur, B.; Schuttevaer, T.; Kiss, A. A.; de Haan, A. B. Isobaric Vapor–Liquid Equilibrium of Methylcyclohexane + Toluene with Gamma-Valerolactone as a Biobased Entrainer and 1-Methylpyrrolidin-2-one as a Conventional Entrainer. *J. Chem. Eng. Data* **2025**, 70 (3), 1339–1351.
- (28) Wisniak, J.; Ortega, J.; Fernández, L. A fresh look at the thermodynamic consistency of vapour-liquid equilibria data. *J. Chem. Thermodyn.* **2017**, 105, 385–395.
- (29) Wisniak, J. The Herington Test for Thermodynamic Consistency. *Ind. Eng. Chem. Res.* **1994**, 33, 177–180.
- (30) Renon, H.; Prausnitz, J. M. Local compositions in thermodynamic excess functions for liquid mixtures. *AIChE J.* **1968**, 14 (1), 135–144.