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Original article

Thermodynamic consistency and model correlation of isobaric vapor–liquid equilibria in binary and ternary chloroform, methanol, and benzene systems

Consistencia termodinámica y correlación de modelos de los equilibrios isobáricos vapor-líquido en sistemas binarios y ternarios de cloroformo, metanol y benceno

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Abstract

Vapor–liquid equilibrium (VLE) data are essential for the design and optimization of separation processes; however, their reliability remains a challenge, particularly for multicomponent systems, due to inconsistencies in legacy datasets. Here, we analyzed isobaric VLE data at 101.33 kPa for the binary systems chloroform(1) + benzene(2), chloroform(1) + methanol(2), and methanol(1) + benzene(2), as well as for the corresponding ternary system, using data from the Dortmund Data Bank (DDB) and the Korean Data Bank (KDB). Thermodynamic consistency was assessed using the Wisniak-modified Herington test for binaries and the Wisniak (L–W) test for the ternary system, and only consistent datasets were used to estimate thermodynamic parameters. Binary interaction parameters were determined for the Wilson, NRTL, and UNIQUAC models and evaluated through the average absolute deviation in temperature (AADT). The results indicated strong non-ideality, particularly for the chloroform(1) + methanol(2) pair, suggesting hydrogen bonding, whereas chloroform(1) + benzene(2) exhibits near-ideal behavior. On the contrary, the methanol(1) + benzene(2) interactions were highly unfavorable compared to those of the pure components, despite the possibility of association through π–dipole interactions. Additionally, the models Wilson and UNIQUAC showed the best performance for the ternary system (AADT = 0.5849 and 0.6141, respectively), while NRTL had higher deviations (AADT = 0.9896). The study presents a structured thermodynamic evaluation framework for ternary mixtures that integrates consistency testing, dataset selection, parameter optimization, and multi-model validation, thereby enhancing the reliability of VLE predictions in non-ideal multicomponent systems.

Keywords: Vapor-liquid equilibrium (VLE); thermodynamic consistency; isobaric; NRTL; Wilson; UNIQUAC.

Resumen

Los datos de equilibrio vapor–líquido (VLE) son esenciales para el diseño y la optimización de procesos de separación; sin embargo, su confiabilidad sigue siendo un desafío, particularmente para sistemas multicomponentes debido a inconsistencias en los datos experimentales reportados. En este trabajo se analizaron datos VLE isobáricos a 101.33 kPa para los sistemas binarios cloroformo(1) + benceno(2), cloroformo(1) + metanol(2) y metanol(1) + benceno(2), así como para el sistema ternario correspondiente, reportados en las bases de datos Dortmund Data Bank (DDB) y Korean Data Bank (KDB). La consistencia termodinámica se evaluó utilizando la prueba de Herington modificada por Wisniak para los sistemas binarios, y para el sistema ternario se empleó la prueba de Wisniak (L–W); se utilizaron únicamente los conjuntos de datos consistentes para la estimación de los parámetros termodinámicos. Los parámetros de interacción binaria se determinaron para los

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modelos Wilson, NRTL y UNIQUAC, y se evaluaron mediante la desviación absoluta promedio en temperatura (AADT). Los resultados indicaron una fuerte no idealidad, particularmente para el par cloroformo(1) + metanol(2), lo que sugiere la formación de enlaces de hidrógeno, mientras que el sistema cloroformo(1) + benceno(2) presentó un comportamiento cercano al ideal. Por el contrario, las interacciones metanol(1) + benceno(2) fueron altamente desfavorables en comparación con los componentes puros, a pesar de la posibilidad de asociación mediante interacciones π–dipolo. Los modelos Wilson y UNIQUAC mostraron el mejor desempeño para el modelamiento del sistema ternario (AADT = 0.5849 y 0.6141, respectivamente), mientras que el modelo NRTL presentó desviaciones mayores (AADT = 0.9896). El estudio presenta un marco estructurado de evaluación termodinámica para mezclas ternarias que integra pruebas de consistencia, selección de conjuntos de datos, optimización de parámetros y validación multimodelo, mejorando así la confiabilidad de las predicciones VLE en sistemas multicomponentes no ideales.

Palabras clave: equilibrio líquido-vapor (VLE); consistencia termodinámica; isobárico, NRTL; Wilson; UNIQUAC.

Introduction

The thermodynamic interest in the mixture of methanol, chloroform, and benzene lies in its complex molecular interactions, making it a system of both industrial and academic interest (**Kijevčanin *et al.***, 2007). Mixtures of methanol and chloroform are commonly used in protein purification chloroform and benzene mixtures are used as insecticides (**Sahayaraj & Jeeva**, 2011), and methanol and benzene mixtures are present in industrial wastewater (**Rajamohan *et al.***, 2021; **Thanekar *et al.,*** 2021). The ternary system under study was selected as no previous reports have proposed thermodynamic correlation models that adequately describe the behavior of the chloroform(1) + methanol(2) + benzene(3) mixture, which is likely to exhibit azeotropic behavior (**Wisniak & Tamir**, 1978). Therefore, we aimed to provide insights into the reliability of experimental vapor–liquid equilibrium (VLE) data compiled from databases and to determine the interaction parameters required for modeling the activity coefficients essential to describe the behavior of the analyzed ternary mixture.

The modeling of activity coefficients is key to describing the ideality and non-ideality of various mixtures in the vapor-liquid equilibrium (VLE) (**Belvèze *et al.***, 2004). Reliability in the experimental equilibrium data is necessary, since they constitute a fundamental tool in the simulation of processes (**Han *et al.***, 2021). Usually, the random errors present in isothermal and isobaric systems are found with graphic techniques (e.g., P-x-y and T-x-y) (**McDermott & Ellis**, 1965); in the case of systematic errors, consistency tests play an important role (**Wisniak *et al.***, 2017).

Our sources were the international thermodynamic databases known as the Dortmund Data Bank (DDB 2022) and the Korean Data Bank (KDB 2022), and the Dortmund Data Bank (DDB 2022) and the Korean Data Bank (KDB 2022), hosted by the Chemical Engineering Materials Research Information Center (CHERIC), for all systems at atmospheric pressure conditions (isobaric). Thermodynamic consistency was checked by the Herington method modified by Wisniak and the Wisniak (L-W tests) for ternary systems (**Wisniak**, 1993; **Wisniak *et al.,*** 1997). Wilson (**Grant**, 1964), NRTL (**Renon & Prausnitz**, 1968), and UNIQUAC (**Fredenslund *et al.***, 1975) models were used for data correlation and prediction of interaction parameters for both binary and ternary systems.

The design and optimization of separation processes depend fundamentally on the availability of reliable vapor–liquid equilibrium (VLE) data (**Mathias**, 2017). However, a large amount of the literature data was reported decades ago and has not been re-evaluated for internal consistency (**Kang *et al.***, 2010). The absence of systematic validation may cause uncertainty in process simulations and can lead to significant inefficiencies in industrial applications including distillation, solvent recovery, and wastewater treatment (**Marcilla *et al.***, 2024). Therefore, identifying and rectifying inconsistencies in published VLE data is a fundamental advance towards improving both the scientific reliability and the applied utility of thermodynamic models.

The chloroform(1) + methanol(2) + benzene(3) system is one of the most complicated case studies. Each binary pair has strong non-idealities that correspond to different kinds of molecular interactions: hydrogen bonding in methanol, dipole interactions in chloroform, and dispersive interactions in benzene (**Marcilla *et al.***, 2024). These competing forces then lead to a complex phase behavior with both positive and negative deviations from Raoult's law that may explain the potential azeotropic phenomena (**Wisniak & Tamir**, 1978). These mixtures are relevant from an industrial viewpoint: chloroform(1) + methanol(2) is involved in protein purification, chloroform(1) + benzene(2) is found in pesticide mixtures, and methanol(1) + benzene(2) mixtures appear in industrial effluents (**Kijevčanin *et al.***, 2007; **Rajamohan *et al.***, 2021; **Sahayaraj & Jeeva**, 2011; **Thanekar *et al.***, 2021; **Vertommen *et al.***, 2010). However, many available VLE data for these systems are patchy and usually not accurate. For this reason, the current work strives to establish the thermodynamic consistency of binary and ternary VLE data for the chloroform(1) + methanol(2) + benzene(3) system and correlate them with three broadly used models of excess Gibbs free energy, namely, Wilson, NRTL, and UNIQUAC models. Our study used well-known consistency checking (the Wisniak-modified Herington area test for binary systems and the Wisniak point test for ternary ones) to justify the reliability of the chosen data. The interaction coefficients resulting from harmonized binary data were then used to model the behavior of ternary mixtures and, hence, ensure reliable interdependency in terms of model performance. Our work contributes to filling the large gap in thermodynamic data on the chloroform(1) + methanol(2) + benzene(3) system by combining systematic consistency analysis and a rigorous model correlation mechanism. Moreover, our results could be used as a standard for further studies, and some practical guidance is also proposed for process engineers and researchers working with non-ideal mixtures.

In addition to data validation, this work moves beyond conventional thermodynamic consistency analysis by proposing an integrated evaluation platform that combines consistency testing, dataset selection, parameter optimization, and multimodel validation into a unified methodology for assessing VLE datasets and quantifying their predictive performance. This approach enables a critical reassessment of legacy thermodynamic data and provides transferable criteria for evaluating multicomponent equilibrium systems. By integrating these steps into a structured workflow, the present study aims to identify reliable datasets and improve predictive capability in multicomponent systems.

Materials and methods

Sources and evaluation of binary and ternary VLE data

Experimental vapor–liquid equilibrium (VLE) data for the binary systems chloroform(1) + benzene(2), chloroform(1) + methanol(2), and methanol(1) + benzene(2), and for the ternary system chloroform(1) + methanol(2) + benzene(3) the data were collected from the Dortmund Data Bank (DDB) and the Korea Thermophysical Properties Data Bank (KDB) at 101.3 kPa (**Tables S1 and S2,** https://www.raccefyn.co/index.php/raccefyn/article/view/3349/5363).

The consistency of the binary and ternary datasets was assessed using the Wisniak-modified Herington area test for binary systems and the Wisniak point test for ternary systems. Only the datasets that satisfied the thermodynamic consistency criteria described in the section "Thermodynamic consistency test of experimental data" (Results) were retained for parameter estimation and model validation.

Theoretical basis of thermodynamic correlation models

The basic VLE relationship for the activity coefficients (γ_i) was calculated using the modified Raoult's law (Equation 1).

$$y_i \Phi_i P = x_i \gamma_i P^{sat} \quad (1),$$

where y_i, x_i, P^{sat}, Φ_i, γ_i and P refer to the vapor phase composition, the liquid phase composition, the vapor pressure of pure components, the fugacity coefficient, the activity

coefficient, and the equilibrium pressure, respectively. Since the pressure of the collected experimental data is less than 1 bar, the gas phase can be assumed to exhibit ideal behavior; thus, $\Phi_i = 1$ (**Smith *et al.***, 2005; **Zhou *et al.,*** 2017).

The Antoine parameters, obtained from the DDB physical properties databank (DDB Online 2022), are shown in **Table S3,** https://www.raccefyn.co/index.php/raccefyn/article/view/3349/5363. The VLE data reported for the binary systems were correlated by the Wilson, NRTL, and UNIQUAC models. These models were defined as follows:

Wilson model equation:

$$ln(\gamma_1) = -ln(x_1 + \Lambda_{12}x_2) + x_2\left(\frac{\Lambda_{12}}{x_1+\Lambda_{12}x_2} - \frac{\Lambda_{21}}{x_2+\Lambda_{21}x_1}\right) \quad (2)$$

$$ln(\gamma_2) = -ln(x_2 + \Lambda_{21}x_1) + x_1\left(\frac{\Lambda_{21}}{x_2+\Lambda_{21}x_1} - \frac{\Lambda_{12}}{x_1+\Lambda_{12}x_2}\right) \quad (3)$$

Equations 2 and 3 correspond to the activity coefficients of components in the binary mixture, where Λ_{ij} (Λ_{12}, Λ_{21}) is the adjustable parameter of the Wilson model.

The non-random two-liquid (NRTL) model equation:

$$ln\gamma_1 = x_2^2\left[\tau_{21}\left(\frac{G_{21}}{x_1+x_2G_{21}}\right)^2 + \frac{G_{12}\tau_{12}}{(x_2+x_1G_{12})^2}\right] \quad (4)$$

$$ln\gamma_2 = x_1^2\left[\tau_{12}\left(\frac{G_{12}}{x_2+x_1G_{12}}\right)^2 + \frac{G_{21}*\tau_{21}}{(x_1+x_2G_{21})^2}\right] \quad (5)$$

The equation for multicomponent systems:

$$ln(\gamma_1) = \frac{\sum_{j=1}^{n}\tau_{ji}G_{ji}x_j}{\sum_{k=1}^{n}G_{ki}x_k} + \sum_{j=1}^{n}\frac{x_jG_{ij}}{\sum_{k=1}^{n}G_{kj}x_k}\left(\tau_{ij} - \frac{\sum_{i=1}^{n}x_i\tau_{ij}G_{ij}}{\sum_{k=1}^{n}G_{kj}x_k}\right) \quad (6)$$

The universal quasi-chemical theory (UNIQUAC) model equation:

$$ln\,\gamma_i = ln\,\gamma_{i,combinatorial} + ln\,\gamma_{i,residual} \quad (7)$$

$$ln\,\gamma_{i,combinatorial} = 1 - J_i + lnJ_i - 5q_i\left(1 - \frac{J_i}{L_i} + ln\frac{J_i}{L_i}\right) \quad (8)$$

$$ln\,\gamma_{i,residual} = q_i(1 - lns_i - \sum_j \frac{\theta_j\tau_{ki}}{s_j}) \quad (9)$$

$$\tau_{ji} = \exp\left(-\frac{u_{ji}-u_{ii}}{RT}\right) \quad (10)$$

$$J_i = \frac{r_i}{\sum_j^i r_jx_j} \quad (11)$$

$$L_i = \frac{q_i}{\sum_j^i q_jx_j} \quad (12)$$

$$s_i = \sum_k^i \theta_k\tau_{ki} \quad (13)$$

$$\theta_i = \frac{x_iq_i}{\sum_j^i q_jx_j} \quad (14)$$

$$r_i = \sum_k^i v_k^{(i)}R_k \quad (15)$$

$$q_i = \sum_k^i v_k^{(i)}Q_k \quad (16)$$

The parameters of equations 8 and 9 were defined from equations 10 to 16, where r_i is a parameter representing a relative molecular volume and q_i another one representing a relative molecular surface area, each of which is given by the sum of the R_k and Q_k functional group parameters comprising the component (**Table S4,** https://www.raccefyn.co/index.php/raccefyn/article/view/3349/5363).

Atomic and molecular properties of solvents

The macroscopic thermodynamic behavior and deviations from ideality of the mixtures under study are governed by the molecular properties of the pure components. Intermolecular interactions play a key role in determining non-ideal vapor–liquid equilibrium (VLE) behavior (Li ***et al.***, 2026). **Table S5,** https://www.raccefyn.co/index.php/raccefyn/article/view/3349/5363 summarizes the physicochemical properties of methanol, chloroform, and benzene. These properties explain the deviations from ideality. The relationship between permanent and induced dipoles governs intermolecular forces in these mixtures.

The dipole moment (μ) represents a permanent charge separation, dictating strong electrostatic interactions and hydrogen bonding. Methanol is the most polar component, with a dipole moment (μ) of 1.71 D, which allows it to form extensive self-associated networks via hydrogen bonding. Chloroform, with a dipole moment (μ) of 1.01 D, acts as a significant hydrogen bond donor due to its acidic proton. Conversely, polarizability measures the extent to which a molecule's electron cloud can be distorted to form an induced dipole (Atkins, 1998). Benzene is non-polar but presents a high polarizability (α) due to its electron cloud, allowing it to engage in dipole-induced dipole interactions when exposed to the permanent electric fields of methanol or chloroform (**Figure 1**).

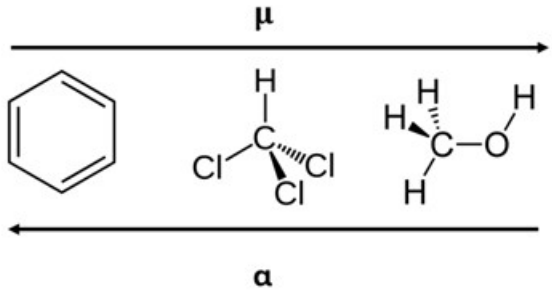

Figure 1. Trend of μ and α in the benzene, chloroform, and methanol, respectively

Results and discussion

Thermodynamic consistency test of experimental data

The consistency of experimental vapor-liquid equilibrium (VLE) data for binary systems can be evaluated by correlating it with appropriate mathematical models, a process known as a thermodynamic consistency test. This implies that the values estimated by the test must agree with the experimental values within their uncertainty range (**Jackson & Wilsak**, 1995). T, P, and x variables, and even the activity coefficient of a system, are linked by the phase rule of thermodynamics (**Fedele *et al.***, 2005; **Marrufo *et al.***, 2009). Consequently, the fundamental equation of thermodynamics, the Gibbs-Duhem equation for activity coefficients, is used to check the reliability of experimental data (**Li *et al.***, 2018; **Martínez-Baños *et al.***, 2015). We performed a thermodynamic consistency test to verify this reliability. For the binary system, the Herington approach was applied (Equation 17).

$$D = 100\left|\frac{S_+ - S_-}{S_+ + S_-}\right| = \frac{\left|\int_{x_1=0}^{x_1=1} ln\frac{\gamma_1}{\gamma_2} dx_1\right|}{\int_{x_1=0}^{x_1=1}\left|ln\frac{\gamma_1}{\gamma_2}\right| dx_1} \quad (17)$$

$$J_{modified} = 34\, X \left|\frac{\Delta H_m}{\Delta G_m^E}\right| X \left|\frac{T_1^\circ - T_2^\circ}{T_i}\right| \quad (18)$$

The variables S_+ and S- are the areas in positive and negative ordinates of the Redlich-Kister plots only for the binary data of mixtures (**Das *et al.***, 2021). The boiling points of the pure components (1) and (2) are represented by T_1° and T_2°, respectively. T_i is the lowest

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point (Equation 18). (**Liu *et al***., 2017). The ratio $\frac{\Delta H_m}{\Delta G_m^E}$ could vary between 0 and 28.640, as calculated in Equation 19.

$$\Delta H_m(Jmol^{-1}) = -237.02 + 1.3863\ X\ \Delta G_m^E(Jmol^{-1}) \quad (19)$$

A maximum was obtained by simple derivation of Equation 20.

$$\Delta G^E = RT \sum x_i\ ln\ \gamma_i \quad (20).$$

According to Wisniak's modified Herington area test, VLE data can be thermodynamically consistent if |D-Jmodified |<10. The thermodynamic consistency of the experimental VLE data for the ternary system chloroform(1) + methanol(2) + benzene(3), retrieved from the DDB (data sets 2578, 6481, and 18035), was assessed using the Wisniak point test. The Wisniak point test (L-W test) method has been widely used in the thermodynamic consistency test of binary and multicomponent VLE data (**Duran *et al.***, 2013; **Parsana *et al.***, 2020; **Shen *et al.***, 2018). The L-W test is described by the following equations:

$$F_k = 100\ X\ \frac{|L_k - W_k|}{L_k + W_k} \quad (21)$$

$$L_k = \frac{\sum T_i^{\circ} x_i \Delta s_i^0}{\Delta s} - T = \frac{G^E}{\Delta s} - \frac{RTw}{\Delta s} = W_k \quad (22)$$

$$\Delta s = \sum x_i \Delta s_i^{\circ} \quad (23)$$

$$w = \sum x_i\ \ln\left(\frac{\gamma_i}{x_i}\right) \quad (24)$$

The VLE data can be considered to be thermodynamically consistent if the average and maximum values of Fk< 5. Therefore, the VLE experimental data for the binary mixtures with best results were ID 4500, ID 4121, and ID 2724 for chloroform(1) + benzene(2), chloroform(1) + methanol(2), and methanol(1) + benzene(2) systems, respectively, and data set 18035 for ternary system (**Tables 1, 2, 3, 4**).

Table 1. Results of the modified Herington for chloroform(1) + benzene(2)

Parameters	Data set 408	Data set 410	ID 3565	ID 4500
D	27.6770	23.3813	2.6344	5.1554
$J_{corrected}$	3.4363	5.3548	5.1769	5.1613
Result	24.2407 failed	18.0265 failed	2.5425 passed	0.0059 passed

Table 2. Results of the modified Herington for chloroform(1) + methanol(2)

Parameters	ID 3114	ID 4121
D	2.7429	0.2716
$J_{corrected}$	0.4041	0.4003
Result	2.3389 passed	0.1288 passed

Table 3. Results of the modified Herington for methanol(1) + benzene(2)

Parameters	Data set 39	ID 2724	ID 2749	ID 3711
D	0.02787	0.9524	0.4784	2.8765
$J_{corrected}$	1.8733	1.8733	1.8698	1.0306
Result	1.8455 passed	0.9209 passed	1.3914 passed	1.8459 passed

Table 4. Results of L-W test for chloroform(1) + methanol(2) + benzene(3)

Parameters	Data set 2578	Data set 6481	Data set 18035
$(F_K)_{average}$	1.3891	1.1533	1.0798
$(F_K)_{maximum}$	2.0496	3.7333	2.0088
Result	passed	passed	passed

The VLE data for the ternary system of chloroform(1) + methanol(2) + benzene(3) data from the DDB were predicted by chloroform(1) + benzene(2) (DDB), chloroform(1) + methanol(2) (KDB), and methanol(1) + benzene(2) (KDB), and correlated parameters from UNIQUAC, Wilson, and NRTL.

Correlation of VLE data

To optimize the interaction parameters (obtaining the minimum value) (**Rodrigues *et al.***, 2023; **Timmermann & Muzzio**, 2017) for each model, calculations were developed using the GRG nonlinear solver in Microsoft Excel (**Fernández *et al.***, 2021). The binary parameters were estimated based on the objective function (OF) (Equation 25) in terms of the calculated (Wilson, NRTL, UNIQUAC) and experimental (Equation 1) activity coefficient. These parameters are used for the prediction of the activity coefficient of ternary systems.

$$OF = \sum_{i=i}^{N} \sum_{j=1}^{2} \left| \left(\frac{\gamma_j^{exp} - \gamma_j^{cal}}{\gamma_j^{exp}} \right) \right|^2 \quad (25),$$

where i represents the amount of data from 1 to N and j denotes the number of components in the system. Binary interaction parameters of Wilson, NRTL, and UNIQUAC models with the objective function (OF) are listed in **Table 5**.

Average absolute deviations of the boiling temperature (AADT) between experimental and calculated data should be as minimal as possible to obtain the optimal interaction parameters for each model (**Table 6**).

The comparison between experimental data and the thermodynamic model predictions (Wilson, NRTL, and UNIQUAC models) for the binary mixtures of chloroform(1) + benzene(2), chloroform(1) + methanol(2), and methanol(1) + benzene(2) is presented in **Figures 2, 3,** and **4** for each binary system, respectively.

Table 5. Results of binary parameters using the objective function

Model	Aij (J/mol)	Aji (J/mol)	αij
Chloroform(1) + Benzene(2)			
Wilson	1.1294	1.1103	0.3
NRTL	-326.4422	-326.4993	
UNIQUAC	-13.9129	-53.7918	
Chloroform(1) + Methanol(2)			
Wilson	0.8668	0.1311	0.3
NRTL	551.1252	389.0909	
UNIQUAC	976.3349	-155.6458	
Methanol(1) + Benzene(2)			
Wilson	0.1512	0.3742	0.3
NRTL	852.0765	771.4252	
UNIQUAC	-79.4477	997.1310	

Table 6. Average deviation for chloroform(1) + benzene(2), chloroform(1) + methanol(2), and methanol(1) + benzene(2)

Model	AADT
Chloroform(1) + Benzene(2)	
Wilson	0.1389
NRTL	0.3335
UNIQUAC	0.1361
Chloroform(1) + Methanol(2)	
Wilson	0.1927
NRTL	1.0022
UNIQUAC	0.1911
Methanol(1) + Benzene(2)	
Wilson	0.1427
NRTL	0.7420
UNIQUAC	0.3467

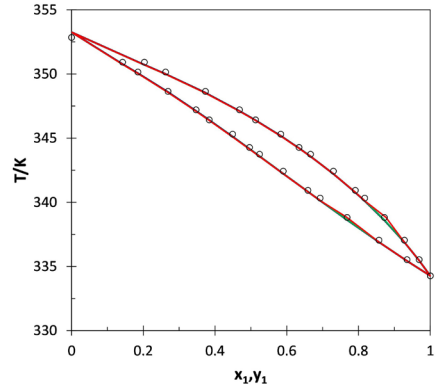

Figure 2. Temperature-composition diagram for chloroform(1) + benzene(2) at atmospheric pressure. The point (○) represents the experimental data; the solid red line (–) is the Wilson model; the solid cool green line (–) is the NRTL model, and the midnight blue line (–) is the UNIQUAC model (solid lines may overlap).

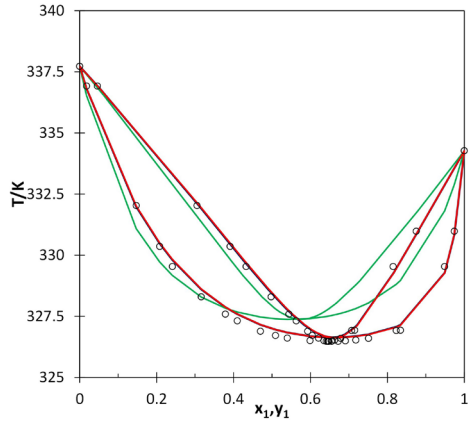

Figure 3. Temperature-composition diagram for chloroform(1) + methanol(2) at atmospheric pressure. The point (○) represents the experimental data; the solid red line (–) is the Wilson model; the solid cool green line (–) is the NRTL model, and the midnight blue line is (–) the UNIQUAC model (solid lines may overlap).

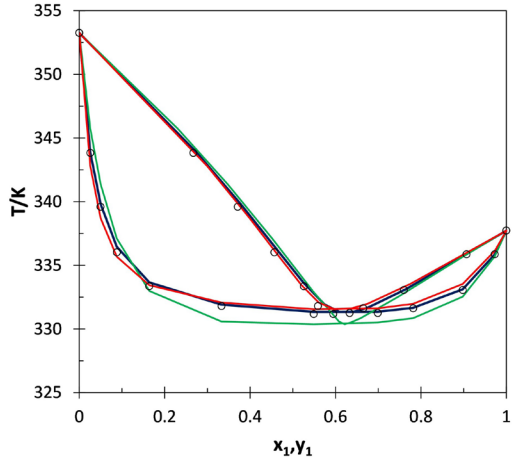

Figure 4. Temperature–composition diagram for the methanol(1) + benzene(2) system at atmospheric pressure. The point (○) represents the experimental data; the solid red line (–) is the Wilson model; the solid cool green line (–) is the NRTL model, and the midnight blue line (–) is the UNIQUAC model (solid lines may overlap).

Kurihara *et al.* (1998) measured the VLE data for the chloroform(1) + methanol(2) + benzene(3) ternary system at 101.3 kPa and recommended the Wilson model for its prediction. Our results confirmed this conclusion. The Wilson model demonstrated the best fit, as evidenced qualitatively by the data correlation in **Figure 5** and quantitatively by the lowest average deviation in dew point temperature (AADT = 0.5849) (**Table 7**).

Chemical discussion

From a molecular perspective, the deviations from ideality observed can be rationalized based on the intrinsic physicochemical properties of the components. Methanol is a small polar molecule capable of acting as both hydrogen bond donor and acceptor, leading to strong self-association through extensive hydrogen-bonding networks. Although moderately polar, chloroform primarily acts as a hydrogen-bond donor through its acidic hydrogen and exhibits significant dipole–induced dipole interactions. Benzene, in contrast, is a nonpolar molecule dominated by dispersion forces and characterized by a highly polarizable π-electron cloud. The interplay of these distinct intermolecular interactions governs the non-ideal behavior observed in both binary and ternary mixtures (**Israelachvili**, 2011; **Prausnitz *et al.***, 1999).

Our results for vapor-liquid equilibrium (VLE) samples from the chloroform(1) + benzene(2), chloroform(1) + methanol(2), and methanol(1) + benzene(2) binary systems, as well as the chloroform(1) + methanol(2) + benzene(3) ternary system, showed that they were strongly representative of non-ideal behaviors. The Raoult's law deviations from ideality may be the result of different dispersion forces for different systems, with differences between the dipole and dipole interactions and the hydrogen bonds (**Israelachvili**, 2011).

We found negative deviations from ideality in the chloroform(1) + benzene(2) system, indicating stronger attractive interactions between unlike molecules. This behavior can be explained by the ability of chloroform (with a significant dipole moment) to induce polarization in the π-electron cloud of benzene, resulting in stabilizing dipole–induced dipole interactions. These interactions reduce the total vapor pressure characteristic of ideal predictions, a result that explains the marked correlations between Wilson and UNIQUAC models, and why they can be more related, and the reason for their energetic contribution related to non-ideal mixing and their association with this model (**Prausnitz *et al.***, 1999; **Orbey & Sandler**, 1998).

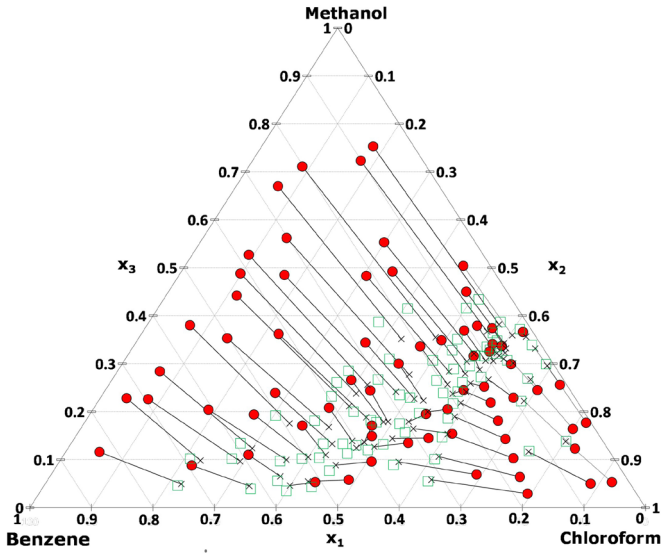

Figure 5. Diagram of the VLE for the chloroform(1) + methanol(2) + benzene(3) ternary system at atmospheric pressure. The red points (•) represent the liquid-phase experimental data; the green open squares (□) represent the vapor-phase experimental data, and the green crosses (×) represent the data predicted by the Wilson model.

Table 7. Absolute average deviation for chloroform(1) + methanol(2) + benzene(3).

Model	AADT
Wilson	0.5849
NRTL	0.9896
UNIQUAC	0.6141

$$AADT = \frac{1}{n}\sum_{i=1}^{n}\left|T_{exp} - T_{calc}\right|$$

In contrast, the chloroform(1) + methanol(2) and methanol(1) + benzene(2) systems exhibited positive deviations from Raoult's law. These deviations derive from the disruption of the hydrogen-bonding network of methanol upon mixing. Although chloroform can act as a weak hydrogen-bond donor, it does not effectively replace methanol–methanol interactions. However, benzene is incapable of participating in hydrogen bonding. In consequence, the self-association of methanol is weakened, leading to reduced cohesion in the liquid phase and increased volatility. This behavior is reflected in activity coefficients over the unity ($\gamma > 1$), which indicates that unlike interactions are weaker than interactions (**Poling *et al.***, 2001; **Prausnitz *et al.***, 1999). Our results indicate that interactions in the pure components are more favorable than in the chloroform(1) + methanol(2) and methanol(1) + benzene(2) mixtures, as evidenced by their positive deviations from ideality. However, these mixtures are stabilized by non-covalent interactions, including O–H···π interactions between benzene and methanol and hydrogen bonding between chloroform and methanol, which contribute to their miscibility (**Di Mino *et al.***, 2023).

The performance of the thermodynamic models further supports this molecular interpretation. The Wilson model, which accounts for local composition and asymmetry in molecular interactions, yielded the lowest AADT values across the systems. The UNIQUAC model, incorporating both combinatorial (size and shape effects) and residual (energy interactions) contributions, also provided reliable predictions, particularly for

the chloroform(1) + benzene(2) system where molecular size and shape differences are significant (**Abrams & Prausnitz**, 1975; **Orbey & Sandler**, 1998). In contrast, the NRTL model showed larger deviations, especially for the chloroform + methanol system, suggesting that accurate parameterization is required when modeling mixtures dominated by specific interactions such as hydrogen bonding (**Renon & Prausnitz**, 1968).

Beyond numerical fitting, these results emphasize that intermolecular forces fundamentally determine macroscopic phase behavior. Stabilizing polarization and dispersion interactions in the chloroform(1) + benzene(2) system lead to negative excess Gibbs free energies, whereas disruption of hydrogen bonding in methanol-containing mixtures results in positive excess Gibbs free energies. These thermodynamic effects are reflected in activity coefficients significantly different from unity, confirming the limitations of ideal solution models in describing such systems (**Israelachvili**, 2011; **Prausnitz *et al.***, 1999).

From an applied perspective, understanding these deviations has practical implications for process design. The ternary chloroform(1) + methanol(2) + benzene(3) system is relevant in solvent recovery, extraction, and separation processes. For example, chloroform–methanol mixtures are used in biochemical extraction processes and chloroform(1) + benzene(2) systems exist in industrial formulations. The prediction of azeotropic behavior and volatility trends is also necessary to build efficient distillation and separation unity composition systems (**Orbey & Sandler**, 1998).

Moreover, here, we found that not all experiments and observations feeding from thermodynamic databases such as DDB and KDB are very consistent, as illustrated by the Wisniak-modified Herington and L-W tests. This underscores the necessity of careful dataset selection and validation before parameter estimation. Reliable thermodynamic modeling, therefore, requires not only appropriate models but also rigorous consistency testing and data curation (**Wisniak**, 1987; **Herington**, 1951).

In summary, the deviations from Raoult's law observed in the systems under study arise from competing intermolecular forces, including dipole–induced dipole interactions in chloroform(1) + benzene(2), and hydrogen-bond disruption in methanol-containing mixtures. The better performance of Wilson and UNIQUAC models reflected their ability to capture these interaction effects more effectively than NRTL under the present conditions. Our findings reinforce the direct link between molecular-level interactions and macroscopic thermodynamic behavior, providing a physically grounded basis for the modeling and interpretation of non-ideal multicomponent systems.

Conclusions

This study presents a comprehensive thermodynamic analysis of isobaric vapor–liquid equilibrium (VLE) data for the chloroform(1) + methanol(2) + benzene(3) ternary system at 101.3 kPa, using data compiled from the DDB and KDB databases. Binary interaction parameters for Wilson, NRTL, and UNIQUAC models were determined from experimental VLE data of the corresponding binary subsystems. Thermodynamic consistency was evaluated using the Herington test modified by Wisniak, allowing the selection of the most reliable datasets (ID 4500, 4121, and 2724) for parameter estimation.

The analysis of activity coefficients revealed distinct non-ideal behavior: positive deviations from ideality were observed for the chloroform(1) + methanol(2) and methanol(1) + benzene(2) systems, while negative deviations were found for the chloroform(1) + benzene(2) system. Among the evaluated models, Wilson provided the most consistent correlation of ternary VLE data (Data Set 18035), supported by the agreement between calculated and experimental values, as reflected in low AADT deviations.

Beyond individual model performance, our study demonstrated that reliable thermodynamic modeling requires the combined application of consistency testing, dataset selection, parameter optimization, and model validation. In this context, the study established an integrated evaluation framework enabling a critical reassessment of legacy thermodynamic data and improved predictive reliability in multicomponent systems.

Overall, our results highlighted that VLE modeling should not be treated as an isolated fitting procedure but as part of a structured thermodynamic evaluation process in which data quality, model selection, and predictive performance are intrinsically interconnected.

Supplementary information

See the supplementary information in https://www.raccefyn.co/index.php/raccefyn/article/view/3349/5363

Author contributions

L.S.R.F.: Data curation; J.C.R.V., E.A.G., L.S.R.F.: Formal analysis; E.A.G., J.C.R.V., L.S.R.F.: Investigation; L.S.R.F., E.A.-G.: Methodology; L.S.R.F. Software; E.A.G., J.C.R.V.: Supervision; L.S.R.F.: Writing of the original draft; J.C.R.V., E.A.G.: Writing, review, and editing. All authors read and agreed to the published version of the manuscript.

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Data availability statement

Dortmund Data Bank Software Package (DDBSP): http://www.ddbst. de. KDB (Korea Thermophysical Properties Data Bank): http://www.cheric.org/research/kdb.

Conflicts of interest

The authors declare no conflict.

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