Modeling the liquid-vapor balance of the chloroform-methane system using the Van Laar model and Peng Robinson equation

Modelación del equilibrio líquido-vapor del sistema cloroformo-metano usando Van Laar y Peng Robinson

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Resumen

La modelación matemática del equilibrio de fases es la base de la descripción de la destilación, usada para refinar productos de poder adquisitivo. La habilidad de entender, modelar y predecir el equilibrio de fases es necesaria para el diseño de procesos de separación industrial. El presente artículo tiene como finalidad presentar el modelo termodinámico y la metodología descrita paso a paso, para la construcción de las curvas de burbuja y rocío, del sistema cloroformo-metanol. Los programas realizados en Matlab predijeron adecuadamente el azeótropo, utilizando la ecuación cúbica de *Peng Robinson* y el modelo de *Van Laar*. Finalmente, fueron comparadas las simulaciones con Aspen Hysys y se validaron con datos experimentales reportados en la literatura, encontrándose porcentajes de error inferiores al 5 %.

Palabras clave: equilibrio vapor-líquido; azeótropo; cloroformo; methanol; *Peng Robinson*; *Van Laar*.

Abstract

Mathematical modeling of the phase balance is the basis of the description of distillation, used to refine products of purchasing potential. The ability to understand, model and predict the balance of phases is necessary for the design of industrial separation processes. The purpose of this article is to present the thermodynamic model and the methodology described step by step, for the construction of the bubble and dew curves, of the chloroform-methanol system. Matlab programs adequately predicted the azeotrope, using Peng's cubic equation Robinson and the Van Laar model. Finally, the simulations were compared with Aspen Hysys and validated with experimental data reports reported in the literature, with error rates below 5 %.

Keywords: vapor-liquid balance; azeotrope; chloroform; methanol; *Peng Robinson*; *Van Laar*.

Introduction

Distillation is one of the most important operations in the industry, as it is used to obtain the refinement and separation of mixtures due to differences in boiling points (Hosgor; Kucuk; Oksal; Kaymak, 2014). The separation of compounds and phases requires a thorough knowledge of the behavior of phases and thermodynamic properties (Del Castillo, 2015; Rubio-Ramírez; Martheyn-Lizarazo; Rolón-Ortiz; Vera-Duarte, 2018), thus, the analysis Numerical and mathematical modeling is essential for the study of physical-chemical parameters in real-time or in extreme conditions, since it is possible to reduce the dangers of experimentation and avoid high costs (González-Silva; Matos; Martignoni; Mori, 2012; Prieto -Jiménez; González-Silva, 2019). On the other hand, the study of the experimental data of Liquid-Vapor Equilibrium (ELV) at isothermal conditions, contributes decisively to the development of precise methods in predicting the behavior of properties at equilibrium (Constantinescu; Wichterle, 2002; Zaitseva; Pokki; Le; Alopaeus; Sixta, 2016).

In this investigation, the modeling and coding through *Matlab* ELV of the chloroform-methanol system at 35 and 49 °C is proposed; This binary mixture is widely used for the purification and quantification of membrane lipids, as well as for oil extraction from seeds (Santana-Brum; Arruda; Bismara, 2009; Elliott; Elliott, 2016). Regarding the construction of the P-x-y curves, the Van Laar model is used due to its simplicity and versatility, in addition to its applicability in binary mixtures were positive or negative deviations are shown from Raoult's law (Gmehling; Onken; Arlt, 1997). On the other hand, using the Peng Robinson cubic equation, the fugacity coefficient of the gas in the gaseous mixture is calculated. Additionally, simulations are compared with experimental data (Kireev; Sitnikov, 1941; Nagata, 1962), and with *Aspen Hysys.*

Materials and methods

To validate the simulations, the experimental conditions reported by (Kireev; Sitnikov, 1941; Nagata, 1962) were used, where the temperatures were 35 and 49 °C together with the physical properties of each compound (chloroform-methanol) shown in Table 1.

Table 1.
Properties of pure compounds

	Chloroform	Methanol
Tc [k]	536,4	512,6
Pc [kPa]	5370	8090
Vc	0,239	0,118
Zc	0,293	0,224

Source: Poling; Prausnitz; Connell (2000).

Regarding the algorithm used for the construction of the bubble curves, it began by assuming all the Φi to the unit and assuming the compositions of the liquid phase, in this way, the initial pressure of the system was calculated, information that was used as data to start the simulation. Furthermore, the equation of the vapor-liquid equilibrium at low pressures (Huerta-Quiñones, 2015; Smith, Ness; Abbott, 2005) was given by:

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

i. For the calculation of the saturation pressure of each compound, the Antoine equation was used (see Table 2).

Table 2.

Antoine's constants for components

	A	B	C
Chloroform	14,5014	2938,55	-36,9972
Methanol	16,4948	3593,39	-35,2249

Source: Reklaitis; Schneider (1990).

$$\ln\left(P_i^{sat}\right) = A - \frac{B}{(T + C)} \quad (2)$$

Where P is given in kPa and T in K.

ii. Activity coefficients were calculated with the Van Laar model.

$$\ln(\gamma_1) = A_{12}\left(\frac{A_{21}x_2}{A_{12}x_1 + A_{21}x_2}\right)^2 \quad (3)$$

$$\ln(\gamma_2) = A_{21}\left(\frac{A_{12}x_1}{A_{12}x_1 + A_{21}x_2}\right)^2 \quad (4)$$

The binary parameters for the chloroform-methanol mixture correspond to:

A_{12}= 0,9356 y A_{21}= 1,8860 (Nagata, 1962)

iii. Next, the initial pressure of the system and steam fractions were calculated:

$$\mathrm{P} = \sum \frac{x_i \gamma_i P_i^{sat}}{\Phi_i} \quad (5)$$

$$y_i = \frac{x_i \gamma_i P_i^{sat}}{\mathrm{P}\Phi_i} \quad (6)$$

Subsequently, the fugacity and fugacity coefficients of each component in the mixture were calculated.

$$\Phi_i = \frac{\widehat{\varphi_i}}{\varphi_i^{sat}} exp\left[\frac{-v_i^L(P - P_i^{sat}}{RT}\right] \quad (7)$$

$$ln\widehat{\emptyset_i} = \frac{b_i}{b}(z-1) - \ln(z-B) \ldots + \frac{A}{B2\sqrt{2}}\left(\frac{b_i}{b} - \sigma_i\right) \ldots \quad (8)$$

$$ln\frac{z + B(1+\sqrt{2})}{z + B(1-\sqrt{2})}$$

$$\sigma_i = 2\left(\frac{a_i}{a}\right) \quad (9)$$

Where the parameters of the equation were defined as:

$$b = \sum Y_i b_i \quad (10)$$

$$a = \sum\sum Y_i Y_j a_{ij} \quad (11)$$

$$a_{ij} = \sqrt{a_i a_j}(1 - k_{ij}) \quad (12)$$

Thus, the interaction parameter was assumed as zero.

iv. The Peng-Robinson equation was used to calculate the compressibility factor.

$$Z^3 - (1 - B)Z^2 + (A - 3B^2 - 2B)Z - (AB - B^2 - B^3) = 0 \ldots \quad (13)$$

$$\alpha = \left[1 + \left(0{,}37464 + 1{,}54226w - 0{,}26992w^2\right)\left(1 - Tr^{0,5}\right)\right]^2 \quad (14)$$

$$a = \frac{0{,}45724R^2Tc^2}{Pc}\alpha \quad (15)$$

$$b = \frac{0{,}0778RTc}{Pc} \quad (16)$$

$$A = \frac{aP}{R^2T^2} \quad (17)$$

$$B = \frac{bP}{RT} \quad (18)$$

$$ln\emptyset = (z - 1) - \ln(z - B) - \frac{A}{2\sqrt{2B}} ln \frac{z + 2{,}414B}{z - 0{,}414B}, , \quad (19)$$

v. Finally, with the calculation of the fugacity coefficient of each component in the mixture using equation 8, equation 19 was applied to calculate the ϕ_i^{sat}, then equations 16, 17, and 19 were recalculated, replacing the pressure with saturation pressure. In this way, all the necessary terms were obtained to use equation 8 and thus, the φ_i for each compound were recalculated. Likewise, it was necessary to recalculate the system pressure with the φ_i previously calculated and the mathematical iterations were performed up to a value, the difference between the initial and recalculated system pressure was less than a previously established tolerance.

$$\Delta P = abs(P_{Initial} - P_{System}) < tol \quad (20)$$

In this way, the tolerance was reached and the iterations were stopped, then the bubble pressure graph, (P-X), was built. In the case of the Rocío curves, the algorithm proposed by (Sandler, 2017) was implemented).

Results

The algorithms of the *Van Laar and Peng* Robinson model were programmed in Matlab for the binary mixture chloroform-methanol at 35 °C, where it was observed that the pressure at the azeotropic point was 47 kPa (see Figure 1). In the ELV at 49 °C, the pressure in the azeotrope was 85 kPa (see Figure 2).

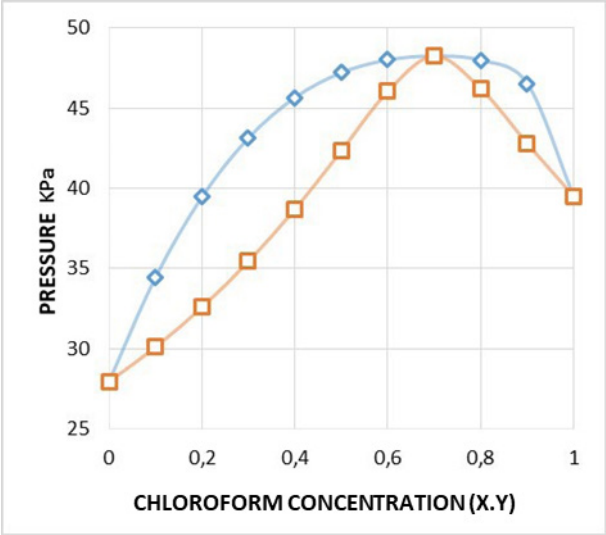

Figure 1. P-X-Y diagram for the chloroform-methanol mixture at 35 °C (bubble line in blue, dew line in orange).
Source: self-made.

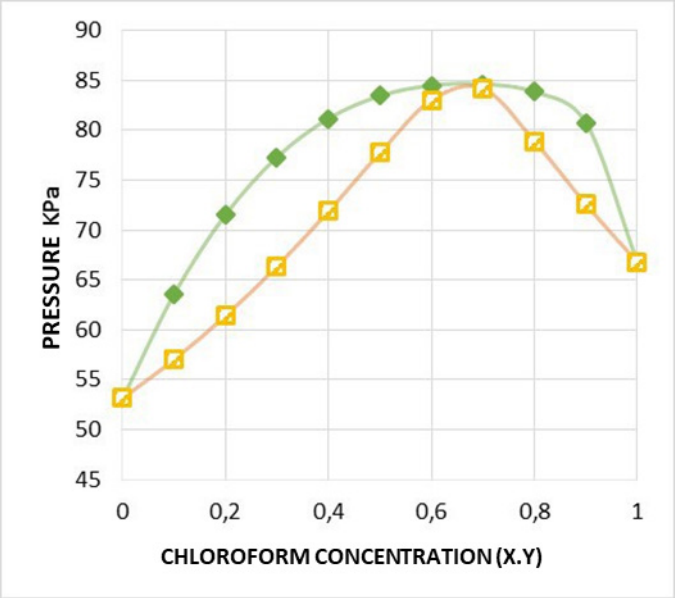

Figure 2. P-X-Y diagram for the chloroform-methanol mixture at 49 °C (bubble line in green, dew line in yellow).
Source: self-made.

Regarding the calculation of the bubble pressure, this showed relative errors of less than 5 %. When comparing the behavior of the relative errors for both temperatures, a similar trend was observed for the case of 49 °C, except for the liquid fraction value of 0.95; regarding the 35 °C case, the relative errors were less than 2.5 % (see Figure 3).

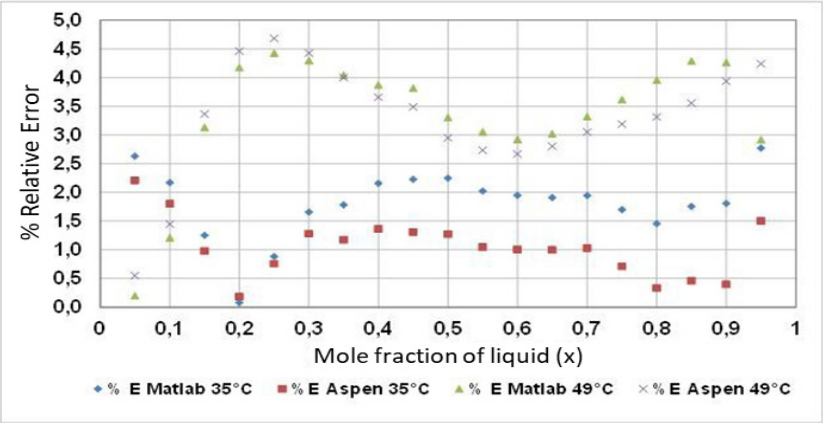

Figure 3. Relative error percentage for calculating bubble pressure for temperatures of 35 °C and 49 °C
Source: self-made.

On the other hand, in the calculation of the dew pressure with *Aspen-Hysys* at 49 and 35 °C in Matlab, there were relative errors between 5 and 25 % in the region of 0.1 to a 0.6-mole fraction of gas; however, the error fell to values below 3% for the complementary region, these results allowed to describe the azeotropic point with this precision. For their part, the simulations for dew pressure with Matlab at 49 °C and *Aspen-Hysys* at 35 °C, had relative errors of less than 4 % (see Figure 4).

Figure 5 shows the comparison and validation of the simulations with experimental data taken from Kireev; Sitnikov (1941) and Nagata (1962), where it is observed that there was no significant difference between the simulated data in Matlab, Aspen Hysys and experimental data; it is important to clarify that the same models were used in both Aspen and Matlab.

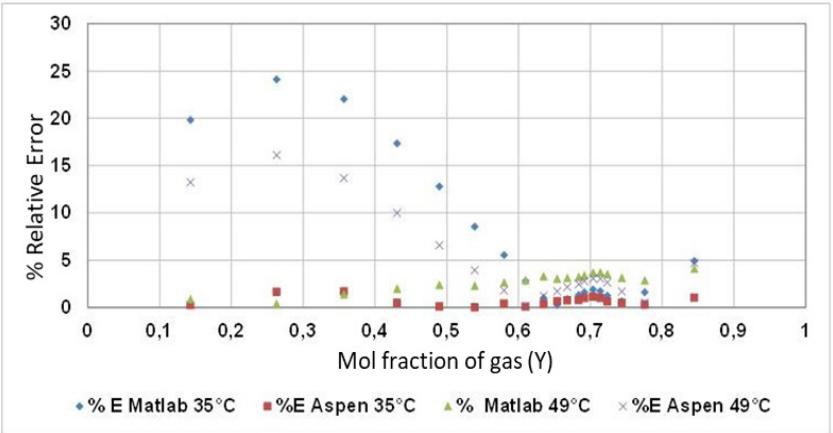

Figure 4. Relative error percentage for calculating bubble pressure for temperatures of 35 °C and 49 °C
Source: self-made.

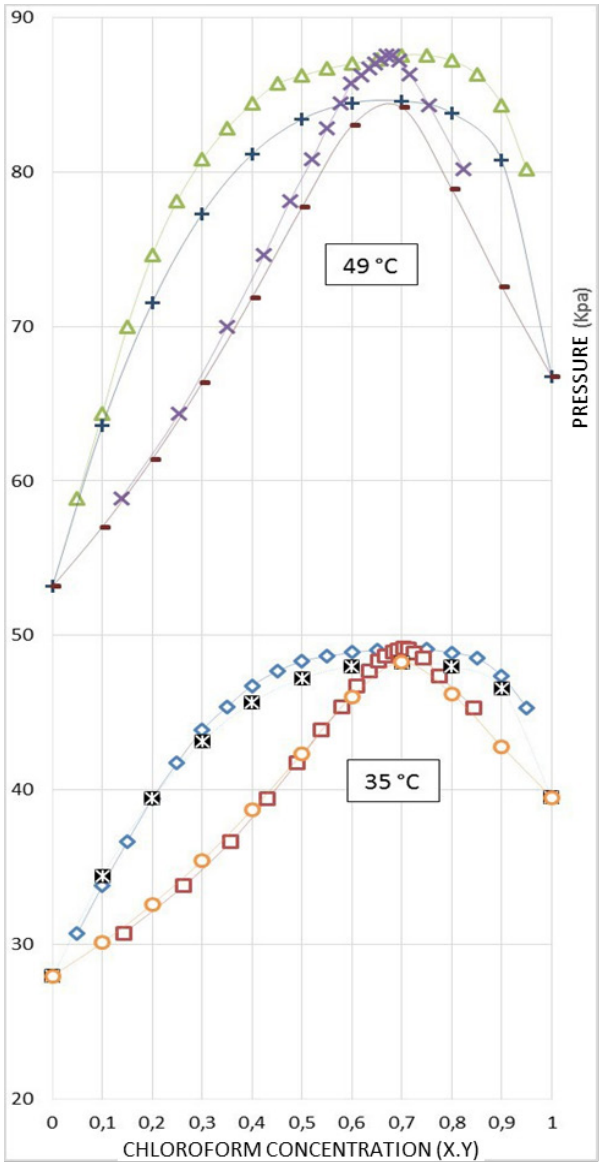

Figure 5. P-X-Y diagram for the chloroform-methanol mixture at 35 °C and 49 °C with the use of Matlab and the DDBST experimental database, –◊– Bubble curve DDBST (35 °C), –□– DDBST dew curve (35 °C) Bubble curve DDBST (49 °C) –x- Dew curve DDBST (49 °C), Matlab bubble curve (35 °C), –O– Matlab dew curve (35 °C), Matlab bubble curve (49 °C), Matlab dew curve (49 °C)
Source: self-made.

Conclusions

It is observed that the graphs made with the code programmed in Matlab for the isotherms (35 °C and 49 °C) for the liquid-vapor balance of the chloroform-methanol binary system have a similar behavior adjusting to those generated by the Aspen software, in addition to validation with experimental data, in trend and precision.

The use of the *Van Laar* model and the cubic equation of *Peng Robinson* has a good performance when applied in binary mixtures where positive or negative deviations are present, this is evidenced in the results obtained.

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