



Original Article

Liquid balance - steam for methanol mixing - Benzen using the Peng Robinson and Van-Laar models

Balance de líquidos - vapor para mezcla de metanol - Benzen usando los modelos Peng Robinson y Van-Laar

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ABSTRACT

Keywords:

Azeotrope
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This paper is related to the procedure for calculating curves dew point and bubble point of a binary system, consisting of the methanol and benzene mixture to 45°C, using the Peng-Robinson cubic equation to calculate the fugacity coefficient of gas *i* in the mixture, and Van Laar model to calculate the activity coefficient of component *i* in the liquid mixture. Then a comparison between the theoretical data with the experimental data and later with the commercial simulator Hysys-Aspen, which applies the model of Wilson. The simulation was validated with experimental data, in addition to comparing the results with a commercial simulator.

RESUMEN

Palabras clave:

Azeótropo
Coeficiente de actividad
Coeficiente de fugacidad
Equilibrio vapor-líquido

El presente artículo está relacionado con el procedimiento para obtener las curvas de punto de rocío y de punto de burbuja en un equilibrio líquido - vapor (VLE) para una mezcla binaria con azeótropo de Metanol y Benceno a 45°C, utilizando la ecuación cúbica de Peng Robinson para calcular el coeficiente de fugacidad del gas *i* en la mezcla gaseosa, y el modelo de Van Laar para calcular el coeficiente de actividad del componente *i* en la mezcla líquida. Luego se compararon los datos teóricos con datos experimentales, posteriormente con el simulador comercial, el cual aplica el modelo de Wilson, se logró validar los datos experimentales, además de comparar los resultados con un simulador comercial.

1. Introduction

Studies on the equilibrium of the mixing phase are of considerable importance for the design of thermal separation processes and theoretical understanding of molecular behavior [1]. Oxygenated compounds such as methyl tert-butyl ether (MTBE), ethyl tert-butyl ether (ETBE) and methyl tert-amyl ether (TAME) can be used as gasoline additives due to their good anti-knocking properties, VLE data of

these additives with alcohols and hydrocarbons are used to develop calculation models for the reformulation of gasoline Jong-Hyeok et al [2], [3] determined isothermal experimental results of liquid-vapor equilibrium for five binary substances among them the mixture methanol and benzene. In the last decade there has been a growing demand for the use of oxygenated compounds to produce unleaded gasoline [4] - [7]. Gramajo de Doz et al [8] analyzed the equilibrium phases of the systems

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containing hydrocarbons (benzene, isooctane, toluene, or cyclohexane) and oxygenated compounds (methanol, ethanol, or methyl tert-butyl ether), due to the physical and chemical properties of methanol, as a candidate for an oxygenated fuel additive. However, methanol has partial miscibility with aliphatic hydrocarbons, but not with aromatic hydrocarbons. Therefore, it is of great importance to study systems composed of methanol and hydrocarbon components representative of gasoline. In 2013 García et al [9], focused on studying the diagrams of hydrocarbon phases such as gasoline and methanol through tertiary and quaternary systems, (heptane + benzene + methanol), (heptane + ethylbenzene + methanol), (heptane + m-xylene + methanol), (heptane + benzene + ethylbenzene + methanol), and (heptane + Benzene + m-xylene + methanol) at temperature of 293.15K and atmospheric pressure, to define the solubility of methanol in gasoline at low temperatures. The mixture of these components is not only used for fuel alcohol additives, it has also been used as a raw material for the synthesis of other chemicals and polymers; accurate data on the phase equilibrium of mixtures of propylene oxide with hydrocarbons (methanol-benzene) are necessary for proper design and optimization of the relevant chemical processes and purification steps [10]. Subsequently, these components have been analyzed with the purpose of making an efficient and adequate selection of a solvent for the separation of azeotropes with methanol, which is why ionic liquids (ILS) have received significant interest in recent years as its application in industrial processes refers [11]. In recent years, new applications have been found for methanol derivatives such as gasoline additives, biofuels, diesel fuels etc., because mixtures of this with other substances have proven to be effective and non-toxic inhibitors of ice formation. [12].

2. Materials and methods

Initially to calculate this curve the study temperature must be defined, for this case it is 45 ° C, the compositions of the liquid phase are assumed and

all Φ_i is set equal to one, which will be used to calculate an estimated value of the pressure of the system as initial data; the critical properties of each component and acentric factor (ω) are determined, which were taken from the book by Reid et al [13] and are summarized in Table 1.

Table I. Critical properties of the pure components Methanol and Benzene

	Tc [K]	Pc [KPa]	Vc [m ³ .Kmol ⁻¹]	Zc	ω
Methanol	512.6	8090	0.118	0.22	0.56
Benzene	562.2	4890	0.259	0.27	0.21

The procedure to calculate the bubble point curve, part of the liquid-vapor equilibrium equation at low pressures:

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

First step (Bubble Point): The saturation pressure of each component is calculated at a temperature of 45 ° C using the Antoine equation for base logarithm 10, where the temperature units for equation number 2 are in degrees Celsius and the units of pressure are Torr, which is subsequently converted to KPa by multiplying by the factor 0.133322. The Antoine coefficients for each component are found in Table II.

$$\log(P_i^{sat}) = A - \frac{B}{(T^\circ + C)} \quad (2)$$

Table II. Antoine constants (A, B, C)

	A	B	C
Methanol	8.08097	1582.271	239.726
Benzene	6.87987	1196.76	219.161

Second step (Bubble Point): The activity coefficients are calculated using the Van Laar model at the temperature and composition of the given liquid phase, the constants for the Methanol-Benzene mixture at 45°C are $A_{12}=2.1623$ and $A_{21}=1.7925$.

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

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

Third step (Bubble Point): The initial system pressure at temperature and established liquid phase compositions is calculated assuming a Φ_i equal to one, using the following expression:

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

Fourth step (Bubble Point): Steam fractions are calculated by clearing y_i from equation number 1, the following expression is obtained from this process:

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

Fifth step (Bubble Point): With the vapor fractions, the transience coefficients for Methanol and Benzene are calculated using equation number 7 and the cubic state equation of Peng Robinson:

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

Using Peng-Robinson to calculate the transience coefficient requires several calculations:

$$\alpha = [1 + (0.37464 + 1.54226w - 0.26992w^2)(1 - Tr^{0.5})]^2 \quad (8)$$

$$a = \frac{0.45724R^2 T_c^2}{P_c} \alpha \quad (9)$$

$$b = \frac{0.0778RT_c}{P_c} \quad (10)$$

Polynomial shape:

$$A = \frac{aP}{R^2 T^2} \quad (11)$$

$$B = \frac{bP}{RT} \quad (12)$$

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

Mixing rules:

$$a_{ij} = \sqrt{a_i a_j} (1 - k_{ij}) \quad (14)$$

$$a = \sum \sum Y_i Y_j a_{ij} \quad (15)$$

$$b = \sum Y_i b_i \quad (16)$$

Fugue coefficients for components in solution:

$$\ln \hat{\varphi}_i = \frac{b_i}{b} (z - 1) - \ln(z - B) + \frac{A}{B2\sqrt{2}} \dots \\ \dots \left(\frac{b_i}{b} - \sigma_i \right) \ln \frac{z + B(1 + \sqrt{2})}{z + B(1 - \sqrt{2})} \quad (17)$$

$$\sigma_i = 2 \left(\frac{a_i}{a} \right) \quad (18)$$

The fugacity coefficient equation for pure substances is applied to find the φ_i^{sat} of each component of the mixture, recalculating equations 11, 12 and 13, with the saturation pressure and using them in the following expression:

$$\ln \Phi_i = (z - 1) - \ln(z - B) - \frac{A}{2\sqrt{2}B} \dots \\ \dots \ln \frac{z + 2.414B}{z - 0.414B} \quad (19)$$

Sixth step (Bubble Point): The system pressure is recalculated with equation number 5 using the calculated Φ_i of each component in the previous step, this procedure or iteration is performed several times until the difference between the initially defined system pressure and the system pressure recalculated

with the Φ_i new, be less than the tolerance $\varepsilon = 0.01$ established.

$$\Delta P = \text{abs}(P_{\text{initially}} - P_{\text{System}}) < \varepsilon \quad (20)$$

After the above condition is met, the bubble pressure curve is constructed by plotting P system vs X_i .

Calculation of the dew point curve

To find this curve, several of the algebraic expressions written above were used, but the procedure varied somewhat with respect to the process explained in section 2. In the first step, the vapor phase compositions are assumed, the saturation pressure is calculated with the Antoine equation, equation number 2; it is assumed $\Phi_i=1$ for the first evaluation of the iterative process and in the same way the $\gamma_i=1$ (since they cannot be calculated and depend on the composition of the liquid phase). With the data and parameters established above, the initial dew pressure of the system is calculated.

$$P = \frac{1}{\sum \frac{y_i \Phi_i}{\gamma_i P_i^{\text{sat}}}} \quad (21)$$

Second step (Dew Point): With the estimated initial system pressure, the compositions of the liquid phase are determined, rearranging equation number 1.

$$x_i = \frac{y_i P \Phi_i}{\gamma_i P_i^{\text{sat}}} \quad (22)$$

Third step (Dew Point): With the determined liquid fractions the activity coefficients are calculated $\gamma_{\text{initially}}$ using the Van Laar model expressed in equations number 3 and 4.

Fourth step (Dew Point): System pressure is recalculated P_{Sist2} using equation number 21 with the initial $\gamma_{\text{initially}}$ calculated in the previous step

Fifth step (Dew Point): Φ_i is determined for each component using the expressions given from equation number 7 to number 19.

Sixth step (Dew Point): With the parameters obtained in steps three, four and five the fractions of the liquid phase are recalculated using equation number 22 and they are normalized. With the normalized X_i the activity coefficients are recalculated again $\gamma_{\text{recalculated}}$ for the Van Laar model with equations number 3 and 4.

Seventh step (Dew Point): The γ_i delta is evaluated to be less than the tolerance $\varepsilon = 0.01$. If this is not fulfilled, the fractions of the liquid phase with the last phase are calculated $\gamma_{\text{recalculated}}$, the X_i are normalized and the activity coefficient is recalculated to find the new $\gamma_{\text{recalculated}}$ this procedure is performed until condition $\Delta\gamma_i < \varepsilon$ is met.

$$\Delta\gamma_i = \text{abs}(\gamma_{\text{initially}} - \gamma_{\text{recalculated}}) < \varepsilon \quad (23)$$

Eighth step (Dew Point): Finally with the $\gamma_{\text{recalculated}}$ the final system pressure is calculated P_{Sist3} with equation 21 and it is evaluated that ΔP is less than the tolerance $\varepsilon = 0.01$.

$$\Delta P = \text{abs}(P_{\text{Sist2}} - P_{\text{Sist3}}) < \varepsilon \quad (24)$$

If the previous condition is not satisfied, the whole process is performed again but using $\gamma_{\text{recalculated}}$ to determine the system pressure P_{Sist2} and recalculate all parameters, the iterations will continue until the condition $\Delta P < \varepsilon$ is met. Then the dew pressure curve is constructed by graphing P_{Sist3} vs Y_i .

3. Results and Discussion

Comparison between the peng Robinson-Van Laar model theoretically calculated, experimental data and simulation in hysys-aspens de la mix

The procedures described in numeral 2 and 3 were the basis of the algorithm for programming the Matlab code and obtaining the dew point and bubble point curves using the Peng Robinson - Van Laar model to calculate the transience coefficients and the coefficients of activity of the binary mixture

Methanol-Benzene at 45 ° C, the calculated data can be seen in Figure 1 and Table III.

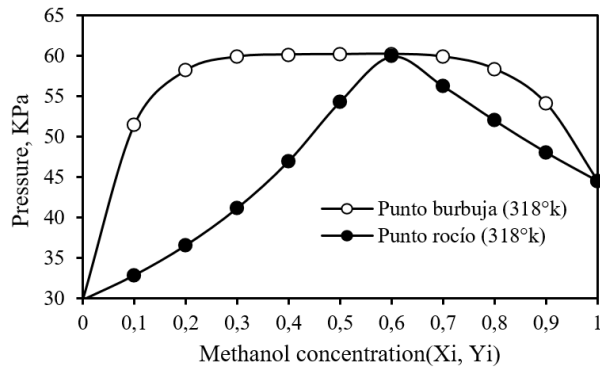


Figure 1. P-X-Y diagram for the Methanol-Benzene mixture at 45°C (318.15 ° K)

To verify the validity of the theoretically calculated data with the Matlab algorithm, a simulation of the liquid-vapor balance of the mixture was performed using the “Hysys-Aspen” program with the Wilson model to the conditions of the case study, the results are shown in Table 4, a comparison was also made with the experimental data of the Methanol-Benzene mixture that he used as a model of transience, the Redlich-Kwong equation, and for the liquid phase he uses the Wilson activity model the results are summarized in Table 5, both models were selected for their degree of reliability for the analyzed system. The comparative graphs (P-X-Y) of the 45° Methanol Benzene mixture with the three models mentioned are shown in Figures 2, 3 and 4.

Table III. Theoretical data calculated for the VLE Isotherm at 45°C for the Methanol-Benzene mixture

Bubble Curve		Dew Curve	
P _b [KPa]	X ₁	P _r [KPa]	Y ₁
29.799	0	29.799	0
51.425	0.1	32.841	0.1
58.162	0.2	36.551	0.2
59.871	0.3	41.158	0.3
60.137	0.4	46.975	0.4
60.177	0.5	54.331	0.5
60.208	0.6	59.921	0.6
59.885	0.7	56.252	0.7
58.355	0.8	52.013	0.8
54.092	0.9	48.058	0.9
44.523	1	44.523	1

The theoretically calculated data were subjected to analysis with the data of the other models used to verify the validity of the algorithm and its results; The standard deviation of the theoretical calculations with respect to the other models were (0.146 theoretical vs. experimental), (theoretical 0.0974 vs. simulation program).

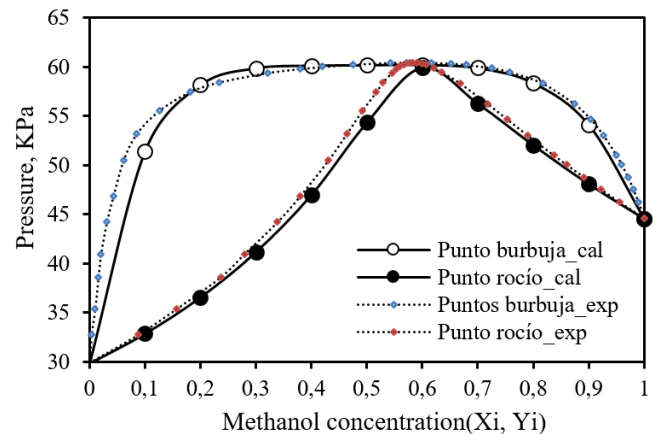


Figure 2. P-X-Y diagram for the mixture Methanol - Benzene at 45°C, comparison between theoretically calculated data and experimental data of Marian Góral et al (2004)

Figure 2 shows that the theoretical curve of the bubble and dew points is slightly out of phase with respect to the experimental values, a result that was expected due to the standard deviation previously analyzed between these two curves, however the algorithm used to obtaining these theoretical data can be useful as an approximation to analyze the behavior of these curves at different temperatures.

Table IV. Data calculated with Hysys-Aspen simulator for the Methanol-Benzene mixture at 45°C. Applying the Wilson model

P[KPa]	X ₁	Y ₁
29.72411	0	0
41.01448	0.0344827	0.2969302
47.48603	0.0689655	0.4070656
51.45286	0.1034483	0.4632581
54.01323	0.137931	0.4968534
55.73548	0.1724138	0.5190207
56.93424	0.2068966	0.5347086
57.79334	0.2413793	0.5464344
58.42496	0.2758621	0.5556109
58.90002	0.3103448	0.563093
59.26462	0.3448276	0.5694312

59.54913	0.3793103	0.5750016
59.77394	0.4137931	0.5800757
59.95251	0.4482759	0.5848628
60.09332	0.4827586	0.5895356
60.20106	0.5172414	0.5942489
60.27724	0.5517241	0.5991536
60.32031	0.5862069	0.6044095
60.32547	0.6206897	0.6101994
60.28407	0.6551724	0.6167462
60.18242	0.6896552	0.6243365
59.99986	0.7241379	0.6333568
59.70566	0.7586207	0.6443501
59.25388	0.7931034	0.6581118
58.57502	0.8275862	0.6758612
57.5617	0.862069	0.6995675
56.04355	0.8965517	0.7326236
53.74102	0.9310345	0.7813901
50.1766	0.9655172	0.8592741
44.49296	1	1

58.427	0.2334	0.5288
59.402	0.3217	0.545
59.802	0.3805	0.5538
60.015	0.4201	0.559
60.242	0.4746	0.5673
60.416	0.542	0.5783
60.443	0.5716	0.5821
60.416	0.6164	0.5908
60.35	0.6509	0.599
60.215	0.6793	0.6067
59.868	0.7259	0.6216
59.482	0.7575	0.6346
58.321	0.8171	0.6681
56.213	0.8744	0.7181
54.692	0.9033	0.7525
53.037	0.9264	0.7896
51.009	0.9497	0.8368
50.048	0.9594	0.8599
48.767	0.9707	0.8916
47.54	0.9804	0.9222
46.232	0.9895	0.9558
44.608	1	1

The data simulated with “Hysys-Aspen” recorded in Table 4, show a similar behavior to the experimental data in Table V, which is why at some points the curves overlap; the standard deviation between these two curves was 0.0654, this behavior infers that the simulator data can be reliable to adjust and calibrate the theoretical model calculated with Peng-Robinson and Van Laar used in the Matlab algorithm.

Table V. Experimental data for the vapor-liquid equilibrium of the Methanol-Benzene mixture at 45°C, from Góral et al (2004)

P[KPa]	X ₁	Y ₁
29.894	0	0
32.744	0.0037	0.0882
35.358	0.0102	0.1567
38.587	0.0161	0.2364
40.962	0.0207	0.2794
44.231	0.0314	0.3391
46.832	0.0431	0.3794
50.488	0.0613	0.4306
53.224	0.0854	0.4642
55.571	0.1263	0.4921
57.454	0.1811	0.5171

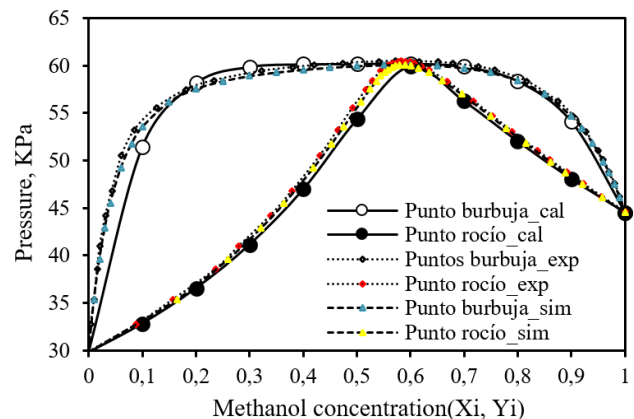


Figure 3. P-X-Y diagram for the Methanol-Benzene mixture at 45°C, with experimental data, data theoretically calculated by the algorithm and simulated with “Hysys-Aspen”

In Figure 3 a comparison of the experimental and simulated data is made with the theoretical data calculated by the algorithm designed for this article following the procedure explained in numeral 2 and 3; all the aforementioned analyzes are consolidated and the similarity between the experimental data and those simulated by “Hysys-Aspen” in which the standard deviation analyzed was 0.0654 between these two curves is clearly observed.

A similar behavior is observed in Figure 3, the theoretical data are outdated with respect to the results shown by the simulator, but in this case the standard deviation was 0.0974 which is slightly smaller than that observed in the curves of Figure 2.

4. Conclusions

The theoretical model proposed in the algorithm made for this article using the Peng Robinson cubic equation to calculate the transience coefficient and the Van Laar model to determine the activity coefficient, can be used as an approximate method to determine the point curves of dew and bubble point of a binary mixture at low pressures. After analyzing the theoretical calculations thrown by the Matlab algorithm, with the experimental and simulator data respectively, it is observed that the standard deviation of the program is between 0.0974 and 0.146 at the points farthest from the curves, this error may be associated with the tolerance used during programming. The standard deviation obtained from the analysis of the curves between experimental and simulator data was 0.0654, so the reliability of the simulator data can be inferred to adjust and calibrate the theoretical model calculated with Peng-Robinson and Van Laar used in the Matlab algorithm.

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