

Modeling Vapor Liquid Equilibrium of Binary and Ternary Systems of CO₂ + Hydrocarbons at High-Pressure Conditions

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In this work, binary and ternary systems composed by hydrocarbons and CO₂ in liquid-vapor equilibrium conditions (LV) were thermodynamically modeled using Peng-Robinson (PR) and Patel-Teja (PT) equations of state (EoS) in combination with van der Waals mixing rule with two adjustable parameters (vdW-2, k_{ij} and l_{ij}). The model was formulated as a minimization of the Mean Absolute Deviation (%AAD) between the predicted and experimental values for liquid and vapor phases using the simplex algorithm, through the software Phase-Equilibrium 2000 (PE-2000). Low deviations, %AAD = 2.33% for PR EoS and %AAD = 3.06% for PT EoS were observed for binary systems in the evaluation of 160 experimental points (EP). Ternary systems were modeled with low deviations too, %AAD = 1.12% for EoS PR and %AAD = 1.18% for EoS PT were observed in the evaluation of 69 EP. Both tested EoS proved to be useful to represent LV equilibrium in this kind of system.

1. Introduction

The use of CO₂ in the chemical industry has increased in recent years due to its properties as a solvent, especially at supercritical conditions. Accurate data for liquid-vapor equilibrium for systems composed by carbon dioxide, hydrocarbons, ethanol and water are important for designing separation processes and synthesis reactions from syngas, such as Fischer-Tropsch synthesis (Freitas and Guirardello, 2015) and are useful for supercritical fluids technology, applications can be found in chemical, petrochemical and food industry (Gallegos et al., 2006).

The prediction and description of thermodynamic properties and phase equilibria of multicomponent mixtures remains a major challenge in the scientific community at the same time becomes a necessity in the industrial environment. Despite the wide range of applications, the use equations of EoS to model systems composed by CO₂ and hydrocarbons are very rare in the literature. Studies that determine the parameters to represent liquid vapor equilibrium for this kind of systems using cubic EoS are scarce, however, these kind of study are essential for some applications, including the use of these equations in modeling and simulation of chemical processes with greater confidence.

In this context, the main objective of this paper was the use of Peng-Robinson (PR) and Patel-Teja (PT) equations of state in combination with van der Waals mixing rule with 2 adjustable parameters (vdW-2, k_{ij} and l_{ij}) to determine binary interaction parameters for systems composed by CO₂ and hydrocarbons in binary and ternary systems. For this, the software Phase Equilibrium 2000 (PE-2000) was used in combination with simplex Nelder-Mead algorithm to minimize an objective function based on average deviations observed between molar fractions of liquid and vapor phases.

2. Methodology

2.1. Peng-Robinson EoS (PR)

The expression for Peng-Robinson (PR) EoS (Peng and Robinson, 1976) is represented by:

$$P = \frac{RT}{V-b} - \frac{\alpha(T)}{V(V+b) + b(V-b)} \quad (1)$$

Here, P is the pressure, V is the molar volume, T is the temperature, $\alpha(T)$ is the temperature-dependent attractive parameter, b is the co-volume and R is the ideal gas constant. The co-volume parameter is temperature independent and is calculated using the critical properties of the pure component as follows:

$$b = 0,0778 \frac{RT_c}{P_c} \quad (2)$$

The attractive parameter, $\alpha(T)$, is calculated by:

$$\alpha = 0,45724 \frac{(RT_c)^2}{P_c} \left[1 + (0,37464 + 1,5422\omega - 0,26992\omega^2)(1 - T_r^{0,5}) \right]^2 \quad (3)$$

2.2. Patel-Teja EoS (PT)

The expression for Patel and Teja (PT) EoS (Patel and Teja, 1982) is represented by:

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b) + c(V-b)} \quad (4)$$

The variables are the same explained above for PR EoS. The parameters a , b and c are:

$$a = 0,66121 - 0,761057Z_c \frac{R^2T_c^2}{P_c^2} \left[1 + (0,46283 + 3,58230\omega Z_c + 8,19417(\omega Z_c)^2)(1 - \sqrt{T_r}) \right]^2 \quad (5)$$

$$b = 0,02207 - 0,20868Z_c \frac{RT_c}{P_c} \quad (6)$$

$$c = 0,57765 - 1,87080Z_c \frac{RT_c}{P_c} \quad (7)$$

2.3 van der Waals mixing rule

PR and PT EoS were applied in combination with the van der Waals mixing rule with two adjustable parameters (k_{ij} and l_{ij}) (vdW-2). The a_{mix} and b_{mix} parameters are presented in equations (8) and (9) respectively.

$$a_{mix} = \sum_i \sum_j x_i x_j (\alpha_i \alpha_j)^{0,5} (1 - k_{ij}) \quad (8)$$

$$b_{mix} = \sum_i \sum_j x_i x_j \frac{1}{2} (b_i + b_j) (1 - l_{ij}) \quad (9)$$

with $k_{ij} = k_{ji}$ and $l_{ij} = l_{ji}$.

2.4. PE 2000 software

The software Phase Equilibrium 2000 (PE-2000), developed by Brunner and coworkers (Pfohl and Petkov, 2000), uses the Simplex modified algorithm to regression of interaction parameters, minimizing the objective function of the absolute average deviation (%AAD) to molar fractions of liquid and vapor phase, as shown in:

$$\%AAD = \frac{100}{NP} \left(\sum_{i=1}^N |x_i^{exp} - x_i^{pred}| + \sum_{i=1}^N |y_i^{exp} - y_i^{pred}| \right) \quad (10)$$

Here, x_i^{exp} is the experimental liquid mole fraction data; x_i^{pred} is the predicted value; y_i^{exp} is the experimental vapor mole fraction data; y_i^{pred} is the predicted value and NP is the number of experimental data points used in the regression procedure. Several initial estimates were used to avoid the local minima in the regression in order to guarantee that the obtained values are the global minimum to evaluated parameters (k_{ij} and l_{ij}).

The software PE 2000 has already been used in other studies with excellent results to correlate and predict phase behavior for different systems under conditions of liquid-liquid-vapor and liquid-vapor equilibrium (Freitas et al., 2013).

2.5. CO₂+hydrocarbons systems

The 7 binary and 2 ternary systems studied in this work and the source of experimental data are presented in Table 1. The characteristics of the studied systems, including pressure, temperature and composition range of the experimental data are presented in this table as well.

The experimental data were taken from the literature as presented in Table 1 for all studied binary and ternary systems. The critical properties of all compounds studied in this work are obtained in literature as well (Poling et al., 2001).

Table 1: Identification of binary and ternary systems studied in this work.

| System | | EP | Range of data | | | References |
|-----------------|---|----|---------------|--------------|------------------|---------------------------|
| | | | T (K) | P (bar) | X _{CO2} | |
| Binary Systems | CO ₂ + CH ₄ | 24 | 240.35-261.25 | 18.3-82.4 | 0.0193-0.4206 | Nasir et al. (2015) |
| | CO ₂ + C ₃ H ₈ | 20 | 252.95-273.15 | 3.3-33.9 | 0.013-0.953 | Nagahama et al. (1969) |
| | CO ₂ + C ₄ H ₁₀ | 13 | 273.15 | 2.4-31.5 | 0.03-0.911 | Nagahama et al. (1969) |
| | CO ₂ + C ₈ H ₁₈ | 28 | 322.39-372.53 | 20.13-137.72 | 0.1422-0.8892 | Gallegos et al. (2006) |
| | CO ₂ + C ₁₀ H ₂₂ | 29 | 319.11-372.94 | 32.41-160.6 | 0.2146-0.9731 | Gallegos et al. (2006) |
| | CO ₂ + C ₅ H ₁₀ | 27 | 323.15-344.65 | 6.3-96.2 | 0.0442-0.855 | Sima et al. (2016) |
| | CO ₂ + C ₆ H ₁₂ | 19 | 323.15-353.15 | 10-110.1 | 0.108-0.7754 | Sima et al. (2016) |
| Ternary Systems | CO ₂ + CH ₄ + C ₃ H ₈ | 54 | 230-270 | 8-80 | 0.0021-0.7377 | Webster and Kidnay (2001) |
| | CO ₂ + CH ₄ + C ₂ H ₆ | 15 | 250 | 21-30 | 0.0812-0.8992 | Davalos et al. (1976) |

3. Results and discussion

3.1 Binary systems

The determined adjustable parameters, k_{ij} and l_{ij} and the %AAD as function of systems temperature are shown in Table 2 for all 7 binary systems analyzed here (17 isotherms with a total of 160 EP). Figures 1-2 shows the comparison between calculated and experimental data for the mole fraction of liquid and vapor phase for all seven systems at all temperatures and deviations in calculated pressure for both EoS analyzed. Figure 1 shows the results for PR-vdW-2 EoS determinations and Figure 2 shows the results for PT-vdW-2 EoS determinations.

Analyzing Figures 1, 2, and Table 2, it can be verified that a good correlation between experimental and calculated data was obtained for most part of systems analyzed, with low computational time (less than 5 minutes) for all cases. Larger deviations were observed for PT EoS.

The phase behavior of all analyzed systems showed an increase in the solubility of CO₂ in hydrocarbons with increasing in system pressure. This behavior was observed for all compounds evaluated in this work, and the increase in temperature resulted in a decrease in CO₂ composition in the vapor phase, this trend was observed for all studied systems too. In general was observed that liquid phase predictions from EoS are worse than that observed for vapor phase. The most dissonant points for the upper curve, in both cases, refer to the system C₅H₁₀ + CO₂, which may indicate some deviations in experimental data obtained by Sima et al. (2016). In addition, there is a higher concentration of the experimental data in the region of higher to vapor phase compositions. This behavior can be explained by the lower solubility of CO₂ in hydrocarbons with more than 4 carbons in chain. Similar trends were described in Freitas et al. (2013) for systems composed by ionic liquids and CO₂ at high pressure conditions.

Table 2: Binary interaction parameters and deviation at different temperatures for PR and PT EoS combined with vdW-2 mixing rule.

| System | PR | | | | PT | | | |
|---|--------|-----------------|-----------------|-------------|--------|-----------------|-----------------|-------------|
| | T (K) | k _{ij} | l _{ij} | %AAD | T (K) | k _{ij} | l _{ij} | %AAD |
| CO ₂ + CH ₄ | 240.35 | 0.0567 | -0.0615 | 3.87 | 240.35 | 0.0595 | -0.0575 | 4.01 |
| | 250.00 | 0.0691 | -0.0514 | 2.70 | 250.00 | 0.0723 | -0.0465 | 2.89 |
| | 261.25 | 0.0555 | -0.0571 | 1.70 | 261.25 | 0.0587 | -0.0536 | 1.90 |
| CO ₂ + C ₃ H ₈ | 252.95 | 0.0786 | -0.0384 | 2.90 | 252.95 | -0.0150 | -0.2256 | 3.90 |
| | 273.15 | -0.0226 | -0.2066 | 3.81 | 273.15 | 0.0769 | -0.0502 | 2.94 |
| CO ₂ + C ₄ H ₁₀ | 273.15 | 0.0795 | -0.0365 | 1.28 | 273.15 | 0.0825 | -0.0393 | 3.40 |
| CO ₂ + C ₈ H ₁₈ | 322.39 | 0.0931 | -0.0099 | 1.16 | 322.39 | 0.1006 | -5.36E-5 | 1.72 |
| | 348.25 | 0.1117 | -0.0033 | 1.71 | 348.25 | 0.0825 | -0.0096 | 0.08 |
| | 372.53 | 0.1149 | -0.0082 | 2.31 | 372.53 | 0.1036 | -0.0048 | 2.26 |
| CO ₂ + C ₁₀ H ₂₂ | 319.11 | 0.0885 | -0.0268 | 1.06 | 319.11 | 0.0489 | -0.0356 | 4.15 |
| | 344.74 | 0.0883 | 0.0122 | 3.42 | 344.74 | 0.0687 | 0.0248 | 3.64 |
| | 372.94 | 0.0985 | 0.0001 | 1.64 | 372.94 | 0.0790 | 0.0115 | 1.72 |
| CO ₂ + C ₅ H ₁₀ | 323.15 | 0.1159 | 0.1131 | 6.17 | 323.15 | 0.1131 | 0.1209 | 6.11 |
| | 333.15 | 0.1234 | 0.1630 | 8.19 | 333.15 | 0.1179 | 0.1752 | 8.16 |
| | 344.65 | 0.1638 | 0.1999 | 8.16 | 344.65 | 0.1669 | 0.2281 | 8.16 |
| CO ₂ + C ₆ H ₁₂ | 323.15 | 0.1006 | -0.0287 | 1.54 | 323.15 | 0.1031 | -0.0328 | 1.63 |
| | 353.15 | 0.1101 | 0.0301 | 2.36 | 353.15 | 0.1099 | 0.0296 | 3.06 |
| Mean deviation | - | - | - | 2.36 | - | - | - | 3.06 |

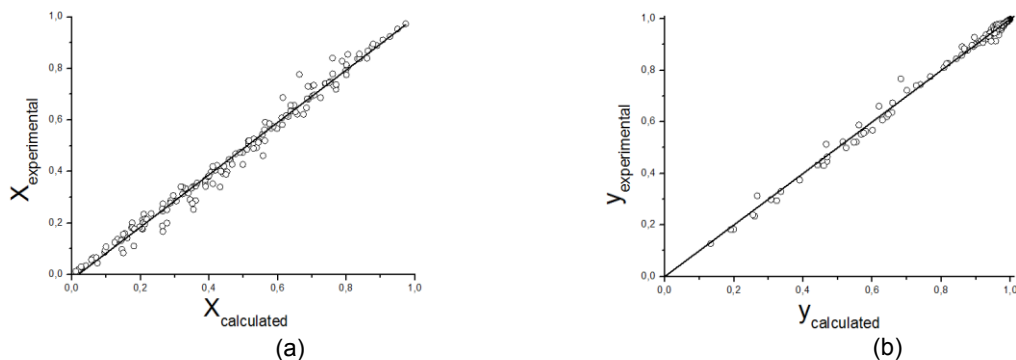


Figure 1. Comparison of calculated and experimental data for the mole fraction of liquid phase (a) and vapor phase (b) using PR-vdW-2 (binary systems).

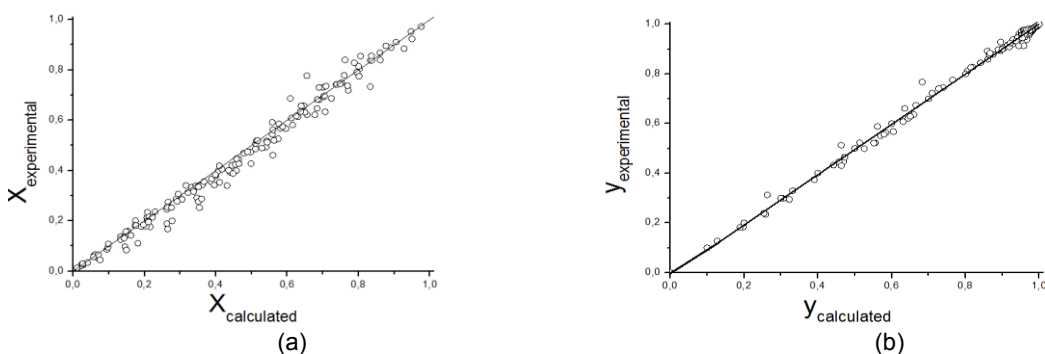


Figure 2. Comparison of calculated and experimental data for the mole fraction of liquid phase (a) and vapor phase (b) using PT-vdW-2 (binary systems).

Overall, and as expected for this type of thermodynamic model, the ability of the PR and PT EoS when combined with the vdW-2-mixing rule, for representation of vapor phase behavior was greater than that observed for the liquid phase. The results obtained by Shariati et al. (1998) for multicomponent systems formed by hydrocarbons and carbon dioxide, using PR-EoS showed similar behavior to that observed in this work.

3.2 Ternary systems

The adjustable parameters, k_{ij} and l_{ij} and the %AAD as function of pressure and temperature are presented in Table 3 (results for k_{ij}) and Table 4 (results for l_{ij}) for the 2 ternary systems analyzed in this work, totaling a total 69 experimental data points.

Table 3: Interaction parameters k_{ij} ($k_{ij} = k_{ji}$) for the two ternary systems studied at different temperatures (K) and pressures (bar) for PR and PT EoS ($k_{ij, i=j} = 0,000$).

| System | T (K) | P (bar) | PR | | | | PT | | | |
|---|-------|---------|------------|------------|------------|-------------|------------|------------|------------|-------------|
| | | | k_{ij} | k_{ij} | k_{ij} | AAD | k_{ij} | k_{ij} | k_{ij} | AAD |
| | | | $i=1; j=2$ | $i=1; j=3$ | $i=2; j=3$ | (%) | $i=1; j=2$ | $i=1; j=3$ | $i=2; j=3$ | (%) |
| CO ₂ + CH ₄ + C ₃ H ₈ | 230 | 8 | 1.273 | 0.119 | 0.498 | 5.32 | 0.285 | 0.122 | -0.148 | 5.04 |
| | 230 | 40 | 0.098 | 0.069 | 0.011 | 0.79 | 0.103 | 0.106 | 0.006 | 0.42 |
| | 230 | 70 | 0.187 | 0.095 | -0.001 | 0.48 | 0.195 | 0.097 | -0.005 | 0.21 |
| | 270 | 28 | -0.200 | 0.216 | 0.236 | 6.81 | -0.164 | -0.374 | 0.141 | 6.84 |
| | 270 | 55 | 0.113 | 0.191 | 0.025 | 0.26 | 0.107 | 0.189 | 0.024 | 0.26 |
| | 270 | 80 | 0.143 | 0.093 | 0.007 | 0.21 | 0.150 | 0.094 | -0.0006 | 0.10 |
| CO ₂ + CH ₄ + C ₂ H ₆ | 250 | 21 | -0.017 | 0.004 | -2.332 | 3.73 | 0.004 | 0.524 | -2.761 | 3.22 |
| | 250 | 25 | 0.129 | 0.041 | -0.038 | 1.12 | 0.151 | -0.107 | -0.053 | 1.18 |
| | 250 | 30 | 0.080 | 0.284 | -0.161 | 1.56 | 0.062 | 0.451 | -0.115 | 1.54 |
| Mean deviation | - | - | - | - | - | 1.12 | - | - | - | 1.18 |

Figures 3 and 4 shows the comparison between calculated and experimental data for the mole fraction of liquid and vapor phase for both systems at all conditions analyzed. Figure 3 presents the results for PR-vdW-2 EoS determinations and Figure 4 presents the results for PT-vdW-2 EoS determinations.

The same behavior observed for binary systems was observed here for the ternary systems too. The largest deviations were observed in the description of liquid phase, this trend is common for this type of model when used to perform the calculations carried out by this work using phi-phi ($\phi - \phi$) formulation. The most dissonant points for the upper curve, in both cases, refer to lower pressure (8 and 28 bar to system 1 and 21 bar to the system 2).

Table 4: Interaction parameters l_{ij} ($l_{ij} = l_{ji}$) for the two ternary systems studied at different temperatures (K) and pressures (bar) for PR and PT EoS ($l_{ij, i=j} = 0,000$).

| System | T (K) | P (bar) | PR | | | | PT | | | |
|-----------------------|-------|---------|------------------------|------------------------|------------------------|-------------|------------------------|------------------------|------------------------|-------------|
| | | | l_{ij} $i=1; j=2$ | l_{ij} $i=1; j=3$ | l_{ij} $i=2; j=3$ | %AAD | l_{ij} $i=1; j=2$ | l_{ij} $i=1; j=3$ | l_{ij} $i=2; j=3$ | %AAD |
| | 230 | 8 | 1.092 | -0.036 | 0.353 | 5.32 | 0.215 | -0.040 | -0.127 | 5.04 |
| | 230 | 40 | -0.039 | -0.055 | 0.008 | 0.79 | -0.052 | -0.002 | 0.009 | 0.42 |
| | 230 | 70 | 0.089 | -0.028 | -0.029 | 0.48 | 0.113 | -0.028 | -0.032 | 0.21 |
| | 270 | 28 | -0.392 | -0.094 | 0.186 | 6.81 | -0.370 | -0.688 | 0.126 | 6.84 |
| | 270 | 55 | -0.020 | 0.078 | 0.022 | 0.26 | -0.042 | 0.082 | 0.033 | 0.26 |
| | 270 | 80 | 0.019 | -0.024 | -0.007 | 0.21 | 0.024 | -0.026 | -0.012 | 0.10 |
| | 250 | 21 | -0.187 | -0.280 | -2.551 | 3.73 | -0.173 | 0.247 | -3.192 | 3.22 |
| | 250 | 25 | 0.012 | -0.072 | -0.041 | 1.12 | 0.045 | -0.228 | -0.050 | 1.18 |
| | 250 | 30 | -0.050 | 0.133 | -0.187 | 1.56 | -0.095 | 0.335 | -0.133 | 1.54 |
| Mean deviation | - | - | - | - | - | 1.12 | - | - | - | 1.18 |

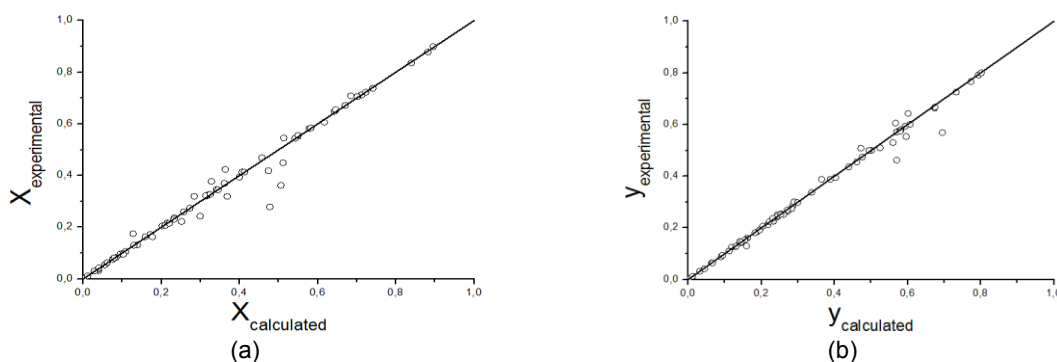


Figure 3. Comparison of calculated and experimental data for the mole fraction of liquid phase (a) and vapor phase (b) using PR-vdW-2 (ternary systems).

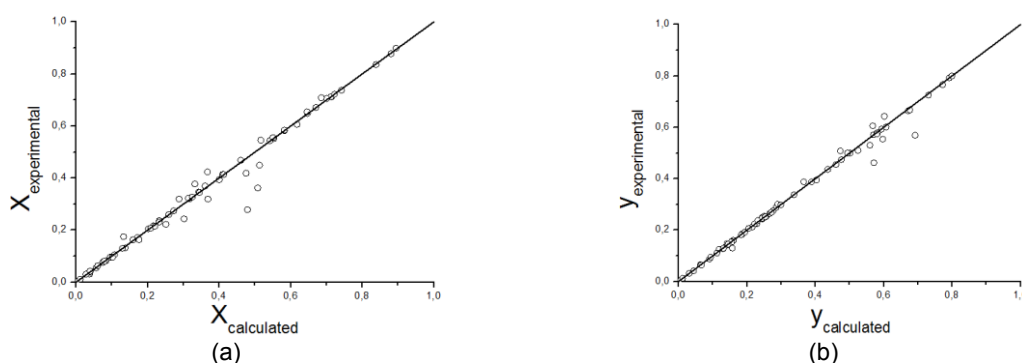


Figure 4. Comparison of calculated and experimental data for the mole fraction of liquid phase (a) and vapor phase (b) using PT-vdW-2 (ternary systems).

It is important to emphasize that the results obtained in this work are easily reproducible, since it were obtained by the use of a free software. Low deviations were observed, PR and PT EoS showed similar ability to represent this kind of experimental data in the ranges of pressure, temperature and composition tested in this work. Both EoS can be applied to describe the LV phase behavior of the systems studied with good results in further modelling and simulation of chemical processes.

4. Conclusions

In this study, binary interactions parameter for PR and PT EoS combined with vdW-2 mixing rule (k_{ij} and l_{ij}), have been optimized for 7 binary mixtures and 2 ternary mixtures composed by hydrocarbons and carbon dioxide by a minimization of %AAD function using the Nelder-Mead Simplex-algorithm implemented in free software PE2000. Experimental data were obtained from the literature, a total of 160 data points, distributed in 17 isotherms, for the binary system and 69 experimental points for the ternary systems were studied.

Good results and low computational times (less than 5 minutes) were observed for all systems examined. For binary systems, regions of higher deviations were associated with conditions of low temperatures and high pressures, especially in the liquid phase, %AAD to 2.33% for PR EoS and 3.06% for PT EoS was determined for the evaluated systems. PR EoS presented lower deviations for these systems.

In ternary systems the larger deviations regions remains in liquid phase %AAD of 1.12% for PR EoS and 1.18% for PT EoS were detected in low pressure regions. One of the reasons that could have led to this difference would be the small amount of experimental data obtained in the literature for the representation of these systems and the condition of low temperature in which these data was measured. In this way, both EoS can be applied to describe the phase LV behavior of the systems studied with good results in further modelling and simulation of chemical processes.

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