

# **MODELING HIGH PRESSURE VAPOR-LIQUID EQUILIBRIUM OF TERNARY SYSTEMS CONTAINING SUPERCRITICAL CO<sub>2</sub> AND MIXED ORGANIC SOLVENTS USING PENG-ROBINSON EQUATION OF STATE**

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**Abstract.** High pressure vapor-liquid equilibrium (VLE) of CO<sub>2</sub>-expanded organic solvents is investigated using Peng-Robinson-LCVM-UNIFAC equation of state. Bubble pressure of ten ternary mixtures is predicted using this mixing rule and correlations are developed based only on binary experimental data. Due to the lack of experimental data for liquid phase density in the literature, it was necessary to perform a qualitative assessment of the density based on the bubble pressure behavior described by the equation of state. A sensitivity study of the LCVM parameter numerical value was done considering the coherence of the mixing rule structure and the quality of the simulation. This analysis is useful as a preliminary evaluation to predict the occurrence of liquid-liquid immiscibility and to avoid this region by selecting the appropriate temperature and pressure conditions for supercritical antisolvent micronization techniques. Further research is in progress to measure experimental data of the ternary systems and validate this approach.

**Keywords:** high pressure, cubic equation of state, vapor-liquid equilibrium, liquid density, dense carbon dioxide

## **1. Introduction**

Supercritical CO<sub>2</sub> based micronization techniques are promising for the production of nanoparticles of pharmaceuticals, catalysts, explosives and polymers [1]. Compressed carbon dioxide is an interesting process solvent, antisolvent or co-solvent because it is nonflammable, inexpensive, nontoxic, and can expand many organic solvents. CO<sub>2</sub>-expanded organic solvents can also be used as an alternate green medium for other applications such as catalyzed reactions due to its capacity to increase solubility and enhance the mass transfer of reactants. Dense CO<sub>2</sub> is also useful for recycling homogeneous catalysts by affecting a phase split of products and catalysts [2]. All of these applications require knowledge of the high-pressure vapor-liquid phase behavior and density of the systems containing carbon dioxide and organic solvent to select both the best solvent and operating conditions. For instance, the choice of solvent in an antisolvent micronization process is a key factor in controlling the solubility of the solute and particle morphology and size [3].

Supercritical antisolvent micronization techniques involve at least three components (solute, solvent and antisolvent). However, it is common to assume that the solute does not affect the phase diagram formed by the solvent-antisolvent system. Experimental measurement of phase behavior and volumetric properties of CO<sub>2</sub>-expanded organic solvent systems have been widely studied but experimental data for ternary systems are scarce in the literature [4, 5, 6]. Therefore, thermodynamic simulation is an alternative way for a preliminary evaluation of phase behavior of these systems. Further, some pharmaceutical solutes require the use of a mixture of two organic solvents to combine good dissolution and volume expansion by the antisolvent. In these cases, it is crucial to assure that both the organic solvents and the antisolvent form a single liquid phase at a given temperature and pressure [7, 8].

High pressure vapor-liquid equilibrium (VLE) data are not always available in the literature. In this case cubic equations of state such as the Peng–Robinson EOS should be used to estimate the VLE of CO<sub>2</sub> and organic solvent systems. The conventional approach is the use of PR-EOS with two-parameter van der Waals mixing rules. However, the adjustable parameters must be specifically optimized for each binary mixture using experimental data. In a previous work we successfully used the Peng–Robinson equation of state with mixing rules from LCVm method coupled with UNIFAC activity coefficient model to calculate the bubble point curve and the liquid density of several CO<sub>2</sub> and organic solvent systems [9].

In the present work we extended the application of PR-LCVm-UNIFAC model to the cases in which a mixture of two organic solvents is needed. This approach uses only the interaction parameters estimated from the solvent-antisolvent systems to predict the bubble pressure and a qualitative liquid density of the solvent-solvent-antisolvent mixtures using PR-LCVm-UNIFAC equation of state. This model is useful to calculate the volume expansion of the organic solution and to predict the occurrence of liquid-liquid immiscibility that should be avoided. As a consequence, selection of the best temperature and pressure conditions for the supercritical antisolvent micronization techniques can be done.

## 2. Modeling vapor-liquid equilibrium

Vapor-liquid equilibrium for the ternary system solvent-solvent-supercritical antisolvent is calculated by the following equations:

$$x_1 \cdot \hat{\phi}_1^L = y_1 \cdot \hat{\phi}_1^V \quad (1)$$

$$x_2 \cdot \hat{\phi}_2^L = y_2 \cdot \hat{\phi}_2^V \quad (2)$$

$$x_3 \cdot \hat{\phi}_3^L = y_3 \cdot \hat{\phi}_3^V \quad (3)$$

where  $\hat{\phi}_i^\alpha$  is the fugacity coefficient of the component  $i$  in the phase  $\alpha$ , and  $x_i$  and  $y_i$  are the molar fractions of component  $i$  in the liquid and vapor phases, respectively. Superscripts  $L$  and  $V$  denotes for liquid and vapor phases, respectively. Subscripts 1, 2 and 3 refer to antisolvent and the solvents, respectively.

Equations (1) to (3) are solved using PR-LCVm-UNIFAC model to calculate the fugacity coefficient of all components in each equilibrium phase with only one adjustable parameter in the mixing rules, as successfully done in a previous work [9]. The fugacity coefficient of component  $i$  in the mixture given by PR-LCVm-UNIFAC model is

$$\ln \hat{\phi}_i = \frac{b_i}{b} \left( \frac{Pv}{RT} - 1 \right) - \ln \frac{P(v-b)}{RT} - \frac{\bar{\alpha}_i}{2\sqrt{2}} \ln \left[ \frac{v(1+\sqrt{2})b}{v(1-\sqrt{2})b} \right] \quad (4)$$

$$b = \sum_i x_i b_i \quad (5)$$

$$\alpha = \left( \frac{\lambda}{A_V} + \frac{1-\lambda}{A_M} \right) \frac{G^E}{RT} + \frac{1-\lambda}{A_M} \sum_i x_i \ln \frac{b}{b_i} + \sum_i x_i \alpha_i \quad (6)$$

$$\bar{\alpha}_i = \left( \frac{\partial \alpha}{\partial n_i} \right)_{T,P,n_j \neq n_i} = \left( \frac{\lambda}{A_V} + \frac{1-\lambda}{A_M} \right) \ln \gamma_i + \frac{1-\lambda}{A_M} \left( \ln \frac{b}{b_i} + \frac{b_i}{b} - 1 \right) + \alpha_i \quad (7)$$

where  $A_V$  and  $A_M$  are the constants of Vidal and Michelsen mixing rules, respectively,  $\gamma_i$  is the activity coefficient calculated by the UNIFAC group contribution model and  $\lambda$  is the LCVm parameter that weights Vidal and Michelsen mixing rules. For PR-EOS,  $A_V = -0.623$  e  $A_M = -0.52$ . In this work, both the original

value of  $\lambda$  (0.36) and the value fitted to experimental binary vapor-liquid equilibrium data were used to calculate ternary VLE.

Bubble pressure calculation was performed to fit the vapor-liquid equilibrium data and the following objective function was adopted:

$$OF = \min \sum_{i=1}^{NEP} \frac{(P_i^{cal} - P_i^{exp})^2}{P_i^{exp}} \quad (8)$$

Bubble pressure calculated errors are expressed in mean relative deviation ( $\Delta P\%$ ) as follows:

$$\Delta P\% = \frac{100}{NEP} \cdot \sum_{i=1}^{NEP} \frac{|P_i^{exp} - P_i^{cal}|}{P_i^{exp}} \quad (9)$$

### 3. Results and discussion

For the LCVM mixing rule analysis several ternary systems were selected from the literature. A more comprehensive study also requires the evaluation of binary systems whose components constituted part of the ternary system. This evaluation is necessary for three reasons: i) to analyze the possibility of  $\lambda$  parameter correlations produced for ternary systems from binary systems; ii) to compare the quality of ternary simulation using the predictive value of the parameter  $\lambda = 0.36$ ; iii) to compare the predictive character of empirical correlations using two parameters one for co-volume and one for the attractive part, that is the two-parameter van der Waals mixing rules. Table 1 shows data for 21 binary systems and the relevant information regarding to the 10 ternary systems is displayed in Table 2.

**Table 1.** Experimental vapor-liquid equilibria data for binary systems

Binary systems	T (K)	P (atm)	No. of data points	Reference
CO <sub>2</sub> -Methanol	313.2	6.91 – 81.03	13	[10]
CO <sub>2</sub> -Propane	270	6.33 – 27.47	18	[11]
Propane-Methanol	313.1	3.45 – 13.42	12	[12]
CO <sub>2</sub> -Methane	230	16.30 – 55.02	7	[13]
Methane- Propane	230	21.46 – 39.20	6	[11]
CO <sub>2</sub> -Ethanol	313.2	62.68 – 79.26	7	[14]
CO <sub>2</sub> -Ethyl Acetate	313.15	9.08 – 77.77	10	[15]
Ethanol-Ethyl Acetate	343.15	0.72 – 0.95	12	[16]
CO <sub>2</sub> -H <sub>2</sub> O	323.15	67.31 – 174.49	8	[17]
Methanol-H <sub>2</sub> O	233.15	0.20 – 0.83	7	[18]
Ethanol-H <sub>2</sub> O	423.15	4.51 – 8.73	17	[19]
CO <sub>2</sub> -Ethane	250	14.23 – 21.07	13	[13]
Ethane-Methane	250	15.10 – 65.39	7	[13]
CO <sub>2</sub> -Acetic Acid	323.15	55.47 – 82.60	6	[17]
H <sub>2</sub> O-Acetic Acid	253.15	0.27 – 0.47	9	[20]
CO <sub>2</sub> -n-Octane	322.39	19.87 – 84.19	7	[21]
CO <sub>2</sub> -n-Decane	319.11	34.40 – 87.88	8	[21]
n-Octane-n-Decane	373.49	0.13 – 0.47	19	[*]
CO <sub>2</sub> -n-Hexane	393.15	8.84 – 114.45	15	[22]
n-Hexane-n-Decane	393.15	0.12 – 0.87	16	[*]
H <sub>2</sub> O-Methane	375.8	107.60 – 492.60	5	[23]

\*binary data produced by Raoult's law

For each binary system using the objective function expressed by equation (8),  $\lambda$  parameter values were estimated to provide the smallest errors. Table 3 shows the  $\lambda$  parameter values obtained without any restriction on their numerical values. But a more detailed analysis reveals that for many systems the  $\lambda$  parameter values are extremely high, not consistent at all with the original formulation of the mixing rule. For this reason the simulations have been reset considering these restrictions on the numerical value and as a consequence the mean relative bubble pressure deviation  $\Delta P(\%)$  increased. Table 3 shows the re-estimated

$\lambda_{rev}$  values as well as the respective mean relative deviation  $\Delta P_{rev}$  (%). The reason for repeating values of  $\lambda$  and  $\lambda_{rev}$  in Table 3 is that a new evaluation is unnecessary since the  $\lambda$  optimal values are within the range intended as being realistic for this mixing rule. Despite this re-estimation, for methanol-H<sub>2</sub>O-and acetic acid-H<sub>2</sub>O the errors are too high and it was not possible to achieve smaller values. An additional evaluation can be performed by comparison, for the same binary data values, of the mean relative bubble pressure deviation  $\Delta P_{rev}$  (%) obtained with the more consistent  $\lambda_{rev}$  and the correlation value corresponding to empirical van der Waals  $\Delta P_{emp}$  (%), which uses two parameters for each binary pair. This is the main reason of these latter much lower values  $\Delta P_{emp}$  (%) than the respective  $\Delta P_{rev}$  (%) mixing rule LCVM. It is important to emphasize that this difference does not depend on the chemical family.

**Table 2.** Experimental vapor-liquid equilibria data for ternary systems.

Ternary systems	T (K)	P (atm)	No. of data points	Reference
CO <sub>2</sub> -Propane-Methanol	313.1	5.03 – 31.62	6	[12]
CO <sub>2</sub> -Propane-Methane	270	27.62 – 78.97	6	[11]
CO <sub>2</sub> -Ethanol-Ethyl Acetate	308.2	40.96 – 69.00	4	[24]
CO <sub>2</sub> -H <sub>2</sub> O-Methanol	298.15	5.14 – 49.90	13	[25]
CO <sub>2</sub> -H <sub>2</sub> O-Ethanol	323.2	89.34 – 116.48	4	[14]
CO <sub>2</sub> -Ethane-Methane	250	21 - 30	3	[13]
CO <sub>2</sub> -H <sub>2</sub> O-Acetic Acid	313	68.61 – 76.90	4	[26]
CO <sub>2</sub> -Octane-Decane	373.49	69.16 – 95.85	4	[27]
CO <sub>2</sub> -Hexane-Decane	312.89	20.47 – 70.85	5	[27]
CO <sub>2</sub> -H <sub>2</sub> O-Methane	324.4	486.67 – 496.54	6	[23]

**Table 3.** Binary interaction parameter regressed for the antisolvent-solvent systems using Peng-Robinson equation of state and LCVM.

Binary systems	$\lambda$	$\Delta P$ (%)	$\lambda_{rev}$	$\Delta P_{rev}$ (%)	$\Delta P_{emp}$ (%)
CO <sub>2</sub> -Methanol	2.3294	5.98	0.4224	11.72	1.31
CO <sub>2</sub> -Propane	1.1418	2.89	1.1418	2.89	0.09
Propane-Methanol	1.066	9.37	1.066	9.37	0.88
CO <sub>2</sub> -Methane	4.3695	4.07	0.5741	15.79	0.02
Methane- Propane	0.3602	3.67	0.3602	3.67	0.15
CO <sub>2</sub> -Ethanol	1.2029	5.32	1.2029	5.32	3.36
CO <sub>2</sub> -Ethyl Acetate	0.0345	4.99	0.0345	4.99	3.18
Ethanol-Ethyl Acetate	2.4702	7.84	1.1979	10.73	0.15
CO <sub>2</sub> -H <sub>2</sub> O	2.0011	6.16	0.2777	20.17	2.92
Methanol-H <sub>2</sub> O	28.3467	13.72	1.2015	18.83	4.64
Ethanol-H <sub>2</sub> O	1.2299	8.69	1.2299	8.69	0.43
CO <sub>2</sub> -Ethane	4.0575	7.87	1.6892	28.39	0.06
Ethane-Methane	5.2585	9.29	1.0805	13.10	3.09
CO <sub>2</sub> -Acetic Acid	3.3600	4.16	0.98	6.13	0.73
H <sub>2</sub> O-Acetic Acid	-12.0429	57.34	-12.0429	57.34	6.35
CO <sub>2</sub> -Octane	1.0894	4.17	1.0894	4.17	1.28
CO <sub>2</sub> -Decane	0.887	3.98	0.887	3.98	1.89
Octane-Decane	4.8803	2.65	1.0805	4.69	0.04
CO <sub>2</sub> -Hexane	0.1353	6.18	0.1353	6.18	0.91
Hexane-Decane	0.1296	2.33	0.1296	2.33	0.04
H <sub>2</sub> O-Methane	0.724	5.00	0.724	5.00	0.09

The same considerations about the aggregate concept of  $\lambda$  parameter observed for binary systems should be taken into account for ternary systems. This analysis was performed and the results obtained are shown in Table 4, maintaining the same nomenclature as in Table 3. In addition, Table 4 shows the mean relative bubble pressure deviation when considering the constant value  $\lambda$  (0.36) and the mean relative bubble pressure deviation  $\Delta P_{emp}$  (%) due to the use of the conventional approach with two-parameter van der Waals mixing rules. It is worth noting that two different approaches are being used in Table 4 although both being considered as predictive. The first  $\lambda$  (0.36) does not depend on any binary parameter estimation. However the second approach binary parameters were estimated and then incorporated into the ternary system directly. The results displayed in Table 4 reveals a doubt on the predictive quality of the van der Waals mixing rule. The good performance of this mixing rule for binary systems is not repeated for the ternary system as can be seen

in Table 3. This reinforces once more that the complexity of the intermolecular forces cannot be neglected and the difficulty of its description.

**Table 4.** Interaction parameter regressed for the ternary systems using Peng-Robinson equation of state and LCVM.

Ternary systems	$\lambda$	$\Delta P$ (%)	$\lambda_{rev}$	$\Delta P_{rev}$ (%)	$\Delta P_{\lambda=0.36}$ (%)	$\Delta P_{emp}$ (%)
CO <sub>2</sub> -Propane-Methanol	0.7474	14.36	0.7474	14.36	17.23	14.79
CO <sub>2</sub> -Propane-Methane	-0.9894	1.91	-0.9894	1.91	11.81	2.30
CO <sub>2</sub> -Ethanol-Ethyl Acet.	7.3297	10.81	1.0435	18.13	21.21	15.97
CO <sub>2</sub> -H <sub>2</sub> O-Methanol	2.6344	4.97	1.0299	5.02	5.03	20.27
CO <sub>2</sub> -H <sub>2</sub> O-Ethanol	4.4189	5.00	0.7313	8.44	14.98	23.83
CO <sub>2</sub> -Ethane-Methane	13.8599	9.79	0.7818	47.70	46.37	6.17
CO <sub>2</sub> -H <sub>2</sub> O-Acetic Acid	3.5317	4.62	0.6958	7.91	12.35	4.55
CO <sub>2</sub> -Octane-Decane	2.3329	5.00	1.100	9.70	21.56	10.04
CO <sub>2</sub> -Hexane-Decane	-0.1903	5.64	0.1903	5.64	21.31	25.21
CO <sub>2</sub> -H <sub>2</sub> O-Methane	2.8044	5.00	2.8044	5.00	5.02	18.91

A new form of predicting parameter was developed from the parameter obtained with binary system data. Considering that the nature of the chemical functions is very important, we selected two groups: systems involving only hydrocarbons and CO<sub>2</sub> and systems involving CO<sub>2</sub>, water and alcohol. We selected all binaries involving CO<sub>2</sub> and hydrocarbons. A correlation was generated from this set of binary data and the corresponding ternary systems, as expressed by Equation (10).

The  $\lambda$  parameter involving hydrocarbons and CO<sub>2</sub> namely  $\lambda_{correl}$  is a function of the binary system parameter and is expressed as

$$\lambda_{correl} = \frac{0.5384 + \lambda_{12}}{2.4218 \cdot \lambda_{13}} \quad (10)$$

where  $\lambda_{12}$  is the parameter related to interactions between CO<sub>2</sub> and hydrocarbons and  $\lambda_{13}$  is the average parameter related to the two involved hydrocarbons.

The same procedure was developed for systems containing CO<sub>2</sub>, water and alcohol and the correlation obtained is shown in Equation (11).

The  $\lambda$  parameter involving CO<sub>2</sub>, water and alcohol  $\lambda_{correl}$  as a function of the binary system parameter is expressed as

$$\lambda_{correl} = \frac{\lambda_{12}}{0.9993 + 2.3188 \cdot \lambda_{13}^2} + 3.0806 \quad (11)$$

where  $\lambda_{12}$  is the parameter related to CO<sub>2</sub> and alcohol and  $\lambda_{13}$  is the average parameter related to the two other components: water and alcohol.

For an evaluation of predictive ability of Equations (10) and (11), Table 5 shows the results of applying these correlations  $\lambda_{correl}$  and the corresponding value of the the mean relative bubble pressure deviation  $\Delta P_{correl}$  (%). An interesting comparison concerns the mean relative bubble pressure deviation obtained from the correlation  $\Delta P_{correl}$  (%) and the error obtained using the parameter  $\lambda$  constant. This comparison is shown in Table 5. The results displayed in Table 5 show a very defensible estimation of  $\lambda_{correl}$  for ternary system from binary systems. This procedure constitutes an embryo that might be useful in future procedures from a larger universe of binary data.

Another relevant assessment is concerning the optimum value of the parameter  $\lambda$  to be used in a temperature different from that in which it was estimated. This study is shown in Table 6 and highlighted the temperature (T) at which the estimated values were previously used and a new temperature T<sub>new</sub>. The results displayed in Table 6 clearly show the difficulty of quality estimation for the bubble pressure even at temperatures very close to the values in which the parameters were estimated.

**Table 5.** Interaction parameter correlation for the ternary systems using Peng-Robinson equation of state and LCVm.

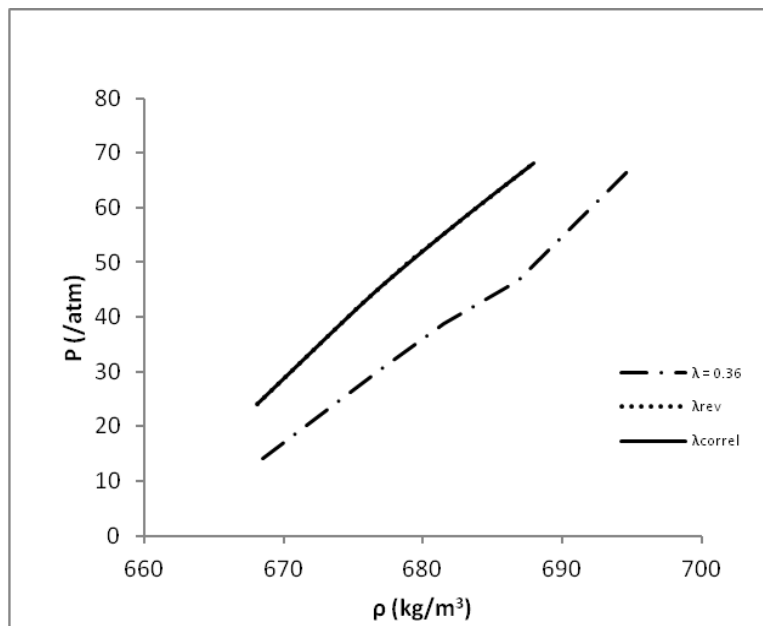
Ternary systems	$\lambda_{\text{correl}}$	$\Delta P_{\text{correl}}(\%)$	$\Delta P_{\lambda=0.36}(\%)$
CO <sub>2</sub> -Propane-Methane	-0.1768	8.05	11.81
CO <sub>2</sub> -H <sub>2</sub> O-Methanol	4.0027	5.00	5.03
CO <sub>2</sub> -H <sub>2</sub> O-Ethanol	3.7193	5.00	14.98
CO <sub>2</sub> -Ethane-Methane	18.1172	17.47	46.37
CO <sub>2</sub> -Octane-Decane	0.2830	16.07	21.56
CO <sub>2</sub> -Hexane-Decane	-0.1893	5.66	21.31

**Table 6:** Evaluation of the temperature on the value of interaction parameter lambda.

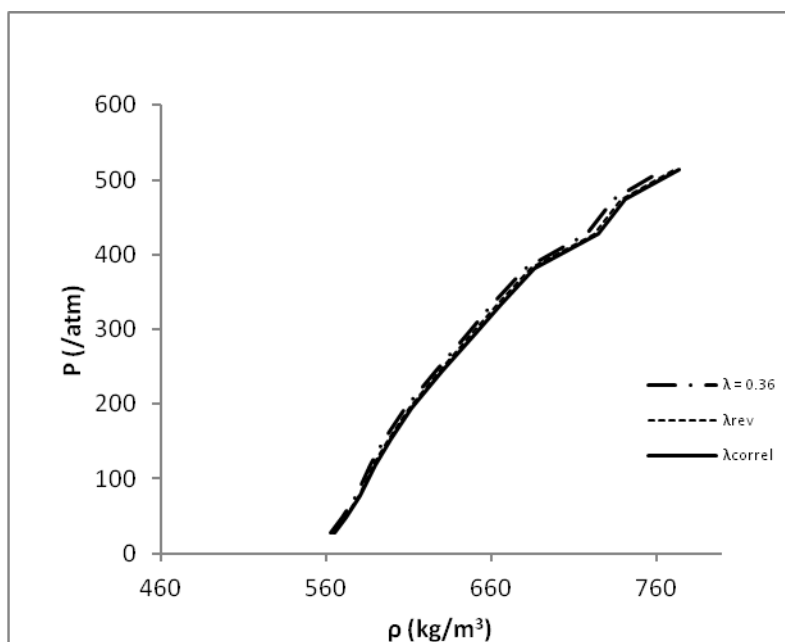
Ternary systems	T (K)	$\lambda_{\text{rev}}$	$\Delta P(\%)$	T <sub>new</sub> (K)	$\Delta P_{\text{new}}(\%)$
CO <sub>2</sub> -Propane-Methanol	313.1	0.7474	14.36	343.1	18.71
CO <sub>2</sub> -Propane-Methane	270.0	-0.9894	1.91	230	3.99
CO <sub>2</sub> -Ethanol-Ethyl Acetate	308.2	1.0435	10.81	313.2	25.84
CO <sub>2</sub> -H <sub>2</sub> O-Ethanol	323.2	4.4189	5.00	313.2	7.87
CO <sub>2</sub> -H <sub>2</sub> O-Acetic Acid	313	0.6958	4.62	323.15	10.80
CO <sub>2</sub> -Octane-Decane	373.49	2.3329	5.00	344.28	21.13
CO <sub>2</sub> -Hexane-Decane	312.89	-0.1903	5.64	376.2	51.86

Despite the fact that density of ternary studied systems is not available in the literature, a qualitative evaluation can be performed from the bubble pressure experimental data. There are three assessment options: one corresponding to the  $\lambda=0.36$ , another through the  $\lambda_{\text{correl}}$  and the third one obtained with the best  $\lambda_{\text{rev}}$  adjustment parameter. For the three evaluations due to its structure estimation, the nearest experimental density should be the one corresponding to the best adjustment. Figure 1 shows the results of this evaluation for the system CO<sub>2</sub>-hexane-decane at 312.89 K. The results for this system indicate that there is no difference between the density calculated by the correlation compared to the density obtained by  $\lambda_{\text{rev}}$ . For the entire pressure range investigated the density obtained with  $\lambda$  constant always provides the lowest value, that is the corresponding value of the compressibility factor is always oversized.

The same analysis was performed for the system CO<sub>2</sub>-H<sub>2</sub>O-methanol at 298.15 K. Unlike the previous ternary system the difference in density calculated by anyone of the three methods in which the parameter was obtained is minimal.



**Figure 1.** Comparison of density for CO<sub>2</sub>-hexane-decane at 312.89° K calculated from the PR-EOS with three different values of  $\lambda$  parameter.



**Figure 2.** Comparison of density for CO<sub>2</sub>-H<sub>2</sub>O-methanol at 298.15° K calculated from the PR-EOS with three different values of  $\lambda$  parameter.

#### 4. Conclusion

High pressure vapor-liquid equilibrium (VLE) of CO<sub>2</sub>-expanded organic solvents is investigated using Peng-Robinson-LCVM-UNIFAC equation of state. For ternary systems several comparisons were performed and the mean relative pressure bubble deviation was investigated. We evaluated the performance of the optimal parameter LCVM rule  $\lambda_{rev}$ , the constant parameter  $\lambda$  (0.36) and a correlation  $\lambda_{correl}$  developed for use in ternary systems from binary systems. A comparison with the empirical van der Waals mixing rule showed that despite two parameters were used for each binary pair, this rule does not provide good results when applied to ternary systems.

#### Acknowledgements

The authors wish to thank CNPq (Brazilian National Science Foundation) for the financial support (grant numbers 563933/2008-9, 470980/2010-9, and 201127/2011-3).

#### References

- [1] E. Reverchon, R. Adami, Nanomaterials and supercritical fluids – Review, *J. Supercritical Fluids* 37 (2006) 1–22.
- [2] A.M. Scurto, K. Hutchenson, B. Subramaniam, Gas-Expanded Liquids: Fundamentals and Applications, In *Gas-Expanded Liquids and Near-Critical Media*; Hutchenson, K., et al., ACS Symposium Series, American Chemical Society: Washington, DC, 2009, p. 3-37.
- [3] Su, C.-S., Prediction of volumetric properties of carbon dioxide-expanded organic solvents using the Predictive Soave–Redlich–Kwong (PSRK) equation of state, *J. Supercrit. Fluids* 72 (2012) 223-231.
- [4] A. Kordikowski, A.P. Schenk, R.M. Van Nielen, C.J. Peters, Volume expansions and vapor-liquid equilibria of binary mixtures of a variety of polar solvents and certain near-critical solvents, *J. Supercritical Fluids* 8 (1995) 205-216.
- [5] M. Christov, R. Dohm, High-pressure fluid phase equilibria experimental methods and systems investigated (1994-1999), *Fluid Phase Equilibria* 202 (2002) 153-218.
- [6] J. Chen, W. Wu, B. Han, L. Gao, T. Mu, Z. Liu, T. Jiang, J. Du, Phase behavior, densities, and isothermal compressibility of CO<sub>2</sub> + pentane and CO<sub>2</sub> + acetone systems in various phase regions. *J. Chemical Engineering Data*, 48 (2003) 1544-1548.



- [7] I. Kikic, N. De Zordi, M. Moneghini, D. Solinas, Solubility estimation of drugs in ternary systems of interest for the antisolvent precipitation processes, *J. Supercritical Fluids* 55 (2010) 616-622.
- [8] M.A. Tavares Cardoso, G.A. Monteiro, J.P. Cardoso, T.J.V. Prazeres, J.M.F. Figueiredo, J.M.G. Martinho, J.M.S. Cabral, A.M.F. Palavra, Supercritical antisolvent micronization of minocycline hydrochloride, *J. Supercritical Fluids* 44 (2008) 238-244.
- [9] G.M.N. Costa, R.L. Matos, V.J. Pereira, G.L. Santana, S.A.B. Vieira de Melo, Modeling High Pressure Phase Behavior of the Binary System Solvent/Antisolvent for SAS Processing of Pharmaceuticals Using PR-LCVM-UNIFAC Equation of State, Proceedings of the 10<sup>th</sup> International Symposium on Supercritical Fluids, San Francisco, USA, 2012.
- [10] [1] J. Yoon, H. Lee, H. Song, High-pressure Vapor-Liquid Equilibria for Carbon Dioxide + Methanol, Carbon Dioxide + Ethanol, and Carbon Dioxide + Methanol, *Journal of Chemical and Engineering Data* 38 (1993) 53-55.
- [11] L.A. Webster, A. J. Kidnay, Vapor-Liquid Equilibria for the Methane-Propane-Carbon Dioxide Systems at 230 K and 270 K, *Journal of Chemical and Engineering Data* 46 (2001) 759-764.
- [12] F.G. Solastiouk, S. Laugier, D. Richon, Vapor-Liquid equilibrium data for the Propane-methanol and propane-methanol-carbon dioxide system, *Fluid Phase Equilibria* 28 (1986) 73-85.
- [13] J. Davalos, W.R. Anderson, R.E. Phelps, A.J. Kidnay, Liquid-Vapor Equilibria at 250.00K for Systems Containing Methane, Ethane, and Carbon Dioxide, *Journal of Chemical and Engineering Data*. 21 (1976) 81-84.
- [14] J.S.Lim, Y.Y. Lee, phase Equilibria for Carbon Dioxide-Ethanol-Water System at Elevated Pressures, *The Journal of Supercritical Fluids* 7 (1994) 219-230.
- [15] A. Chrisochou, K. Schaber, U. Bolz, Phase equilibria for enzyme-catalyzed reactions in supercritical carbon dioxide, *Fluid Phase Equilibria* 108 (1995) 1-14.
- [16] J. Gmehling, U. Onken, J.R. Rarey-Nies, DECHEMA: Vapor-Liquid equilibrium data Collection- Organic Hydroxy Compounds:Alcohols (supplement3), V.1, Part 2e, pg287.
- [17] J.A. Briones, J.C. Mullins, M.C. Thies, B.U. Kim, ternary phase equilibria For Acetic Acid- Water Mixtures with supercritical carbon dioxide, *Fluid Phase Equilibria* 36 (1987) 235-246.
- [18] J. Gmehling, U. Onken, J.R. Rarey-Nies, DECHEMA: Vapor-Liquid equilibrium data Collection- Aqueous organic systems (supplement1), V.1 Part 1a, pg 57.
- [19] F. Barr-David, B.F. Dodge, Vapor-Liquid Equilibrium at High Pressures The Systems Ethanol-Water and 2-Propanol- Water, *Journal of Chemical Engineering and Data* 4 (1959) 107-121.
- [20] J. Gmehling, U. Onken, J.R. Rarey-Nies, DECHEMA: Vapor-Liquid equilibrium data Collection- Aqueous organic systems (supplement1), V.1 Part 1a, pg 89.
- [21] R. Jiménez, L.A. Galicia, O.E. Solis, Experimental Vapor-Liquid Equilibria for the Carbon Dioxide + Octane and Carbon Dioxide + Decane Systems, *Journal of Chemical Engineering and Data* 51(2006) 1624-1628.
- [22] Y.H. LI, K.H. Dillard, R.L. Robinson, Vapor-Liquid Phase Equilibrium for Carbon Dioxide-n-Hexane at 40, 80, and 120°C, *Journal of Chemical Engineering and Data* 26 (1981) 53-55.
- [23] J. Qin, R.J. Rosenbauer, Z. Duan, Experimental Measurements of Vapor-Liquid Equilibria of the H<sub>2</sub>O + CO<sub>2</sub> + CH<sub>4</sub> Ternary System, *Journal of Chemical Engineering and Data* 53 (2008) 1246-1249.
- [24] Chen-Hsi Cheng, Yan-Ping Chen, Vapor-liquid equilibria for the ternary system of carbon dioxide + ethanol + ethyl acetate at elevated pressures, *Fluid Phase Equilibria* 242 (2006) 169-175.
- [25] Jong Sung Lim, Youn Yong Lee, phase Equilibria for Carbon Dioxide-Ethanol-Water System at Elevated Pressures, *The Journal of Supercritical Fluids* 7 (1994) 219-230.
- [26] C. Sánchez-García, K. E. Vázquez-Hernandez, L. A. Galicia-Luna, O. Elizalde-Solis, Vapor-Liquid Equilibrium Measurements for the Ternary Systems of CO<sub>2</sub> + n-Hexane + n-Decane and CO<sub>2</sub> + n-Octane + n-Decane, *Ind. Eng. Chem. Res.*, 50 (2011) .
- [27] J. A. Briones, J. C. Mullins, M. C Thies, B. -U. Kim, Ternary phase equilibria for Acetic Acid-Water mixtures with supercritical carbon dioxide, *Fluid Phase Equilibria*, 36 (1987) 235-246.