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A Computational Tool for Parameter Estimation in EoS: New Methodologies and Natural Gas Phase Equilibria Calculations

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Abstract

Brazilian pre-salt reservoirs represent the discovery of large amounts of light oil, but at high pressures and containing high concentration of CO_2 . Proper parameter estimation procedures are essential to perform more accurate predictions of their thermodynamic properties. Therefore, two new methodologies for such calculations have been implemented here: by applying simultaneously VLE and LLE to the metric; and by handling water content in dew point conditions. Utilizing the Cubic-Plus-Association (CPA) EoS, they were employed to obtain new parameters for water. Also, new parameters were obtained for $H_2O + CO_2$ mixtures, whose average absolute deviation in water content at high pressures fell from 24% to 3% compared to previous publications. The same procedure was performed for other aque-

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ous mixtures containing H_2S and light hydrocarbons. Finally, this study has been applied into a natural gas compressing simulation with CO_2 , studying streams properties comparing the parameters obtained in this work with the literature.

Keywords:

equations of state, parameter estimation, computational tool, natural gas production

1 1. Introduction

Pre-salt reservoirs in Brazil contain large amounts of oil inside ultra-deep
waters, with high CO₂ content at high pressures and low temperatures (Beltrao et al., 2009). Therefore, it is necessary to develop specific technologies
adapted to this challenging scenario (Santos, 2015).

In the natural gas processing, it is necessary to remove contaminants that would otherwise decrease its sale value or damage downstream equipments and lines, fitting it to commercial specifications. For example, these impurities can be water, liquid heavy hydrocarbon fractions (C_{6+}) and acid gases (Lundstrøm, 2005).

The following is a set of specific compounds and what potential damage they could cause if not removed from the natural gas (Santos, 2015):

- Hydrogen sulphide: toxic and corrosive.
- Carbon dioxide: corrosive and can crystallize at low temperature points
 of the process.
- Water: hydrate formation and corrosion.

• Heavy hydrocarbons: can condensate or form solids in transport lines.

Among these issues, the hydrate formation plays a notable role in the oil and gas production. If not prevented, it is capable to clog entire oil lines.

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The importance of aqueous mixtures is recognized worldwide in various research areas (Zirrahi et al., 2010). In the natural gas processing, the transport stage must be performed in high pressures and low temperatures, in some cases near the hydrate formation region, so the thermodynamic models must have high accuracy to minimize the costs of the design execution.

Some of the most used thermodynamic models in the oil and gas industry 25 are the cubic equations of state, due to their relative simplicity and the 26 availability of parameter values for a vast quantity of compounds in the 27 literature. However, these equations generate better predictions to non-polar 28 substances. In natural gas processing, some of the most central compounds 29 are highly polar (water, H₂S, alcohols, glycols). This raises the necessity to 30 use an improved model such as the Cubic-Plus Association (Kontogeorgis 31 et al., 1996) equation of state (CPA EoS). 32

The performance of these equations of state, in particular the CPA EoS, is related with parameter estimation from experimental data. There are well known issues in this procedure such as the possibility to obtain multiple parameter arrays, hereafter called parameter sets (Kontogeorgis et al., 2006a). Here two non-usual metrics for parameter estimation are proposed:

Saturation pressure and liquid density of a self-associating component,
 simultaneously with liquid-liquid equilibrium data with a predeter mined hydrocarbon.

• Water content calculation from dew points, knowing its temperature, pressure and dry composition (Shiguematsu, 2014).

These methodologies will be validated for water, obtaining new CPA EoS parameter values. Thereon, the binary mixture $H_2O + CO_2$ will be analysed, where new binary parameter sets will be generated and tested in a compressing simulation modelled in the Petrox[®] process simulator (Niederberger et al., 2009).

48 2. Background

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49 2.1. Equations of State

As previously mentioned, in the Oil and Gas Industry the most used 50 models are the EoS of cubic format on the mole volume, for a number of 51 reasons. Cubic equations present a compromise between applicability and 52 simplicity, being the simplest equations capable to represent the vapour-53 liquid equilibrium behaviour (Smith et al., 2005). There are numerous cubic 54 equations of state, such as Soave-Redlich-Kwong - SRK (Soave, 1972) or 55 Peng-Robinson - PR (Peng and Robinson, 1976). As they are already well-56 known in the literature, they will not be detailed here. 57

However, these equations do not contain a term that explicitly calculates the association effects, present in mixtures containing polar components such as water. Therefore, their efficacy is limited in these systems. It may be necessary to use better equations of state.

The hydrogen bonds exert significant influence on the behaviour of the mixtures. Numerous association theories have been created along the years ⁶⁴ in order to perform such predictions. Most of them are derived from either
⁶⁵ chemical, lattice or perturbation theories (Prausnitz et al., 1998).

A perturbation theory was presented by Wertheim in four publications 66 between 1984-1986 (Wertheim, 1984a,b, 1986a,b). However, the original ver-67 sion for the EoS based on this theory (SAFT EoS - Statistical Association 68 Fluid Theory) was only presented in 1988 (Chapman et al., 1988). Diverse 69 variants of the original equation was developed and the models improved 70 from polar and quadripolar contribution additions and extension to elec-71 trolytes (Maribo-Mogensen et al., 2014). Yet, one of the most popular equa-72 tion based on association effects is the CPA EoS - simpler but as effective 73 for aqueous systems. A more comprehensive history of the main equations of 74 state throughout the twentieth century can be seen in the work of Wei and 75 Sadus (2000). 76

77 2.1.1. The CPA Equation of State

Within this context the Cubic-Plus-Association (CPA) equation of state was proposed by Kontogeorgis et al. (1996). According to the authors, it was developed to model complex mixtures with a relatively simpler approach. It is composed of two terms: the classic Soave-Redlich-Kwong equation and an association term deducted from statistical thermodynamics. These terms are explicitly additive, as it can be seen in Eq. (1):

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)} - \frac{1}{2}\frac{RT}{V}\left(1 + \rho\frac{\partial\ln g}{\partial\rho}\right)\sum_{i}x_{i}\sum_{A_{i}}\left(1 - X_{A_{i}}\right) \quad (1)$$

⁸⁴ P is the pressure of the system, T its temperature, V the mole volume of ⁸⁵ the mixture, $\rho = 1/V$ the mole density of the mixture and R the universal gas constant. The parameter a is a function of T, given by Eq. (2):

$$a(T) = a_0 \alpha(T_R, w) = a_0 [1 + c_1 (1 - T_R^{0.5})]^2$$
(2)

 $T_R = T/T_c$ is the reduced temperature and w is the acentric factor. Moreover, X_{A_i} is the mole fraction of sites A in a molecule i not bonded to any other active sites and x_i the mole fraction of the component i. X_{A_i} can be calculated using Eq. (3):

$$X_{A_i} = \frac{1}{1 + \rho \sum_j x_j \sum_{B_j} \Delta^{A_i B_j}} \tag{3}$$

In this expression, B represents a type of bonding site different to A, and j represents the index of a molecule that may or may not be different to the molecule i. $\Delta^{A_i B_j}$ is the association strength between the type A site in molecule i and the type B site in molecule j, described by Eq. (4):

$$\Delta^{A_i B_j} = g(V)^{ref} \left[\exp\left(\frac{\varepsilon^{A_i B_j}}{RT}\right) - 1 \right] b_{ij} \beta^{A_i B_j} \tag{4}$$

where $\varepsilon^{A_i B_j}$ and $\beta^{A_i B_j}$ are called, respectively, the association energy and the association volume parameter; $b_{ij} = (b_i + b_j)/2$ is the mean co-volume of the molecules *i* and *j*; and $g(V)^{ref} \equiv g$ is the radial distribution function, defined by Eq. (5) (Kontogeorgis et al., 1999):

$$g = \frac{1}{1 - 1.9\eta}, \ \eta = \frac{b\rho}{4}$$
 (5)

It is important to mention that if $\varepsilon^{A_i B_j} = \beta^{A_i B_j} = 0$ (i.e. there is no association effect in the compound) then the CPA EoS automatically reduces to the functionality of the SRK EoS. In the CPA EoS for mixtures, the classical mixing rules in Eqs. (6) and (7) are applied for the physical part and the CR-1 rule in Eqs. (8) and (9) for the cross-association term (Kontogeorgis and Folas, 2010). An exception lies when it is considered that there is a cross-association effect between a selfassociative component such as H₂O and a component without self-association such as CO₂. In this case only Eq. (8) applies and the parameter $\beta^{A_iB_j}$ becomes manipulated (Li and Firoozabadi, 2009).

$$a = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j (a_i a_j)^{0.5} (1 - k_{ij})$$
(6)

$$b = \sum_{i=1}^{n} x_i b_i \tag{7}$$

$$\varepsilon^{A_i B_j} = \frac{\varepsilon^{A_i B_i} + \varepsilon^{A_j B_j}}{2} \tag{8}$$

$$\beta^{A_i B_j} = \sqrt{\beta^{A_i B_i} \beta^{A_j B_j}} \tag{9}$$

The parameters k_{ij} are called binary interaction parameters, and they are usually calculated by estimation fitting experimental data.

Therefore, when applied to the parameter estimation procedure, there are five parameters to be manipulated in this equation of state for pure components: three in the physical term $(a_0, b \text{ and } c_1)$ and two in the association term (ε and β). For mixtures, the parameters are k_{ij} and, alternatively to Eqs. (8) and (9), $\varepsilon^{A_i B_j}$ and $\beta^{A_i B_j}$.

116 2.2. Parameter Estimation

The parameter estimation procedure is defined as an optimization prob-117 lem where a model is used as a reference and the parameters are modified 118 until the values obtained by this model become as closer to the experimental 119 data as possible. In order to assure the attainment of the best values, the 120 objective function and the optimization methods must be studied carefully. 121 This method is characterized by a minimization of an objective function S(X)122 (Eq. (10)), subject to the restrictions h(X), defined here by the thermody-123 namic model. The vector \underline{X} contains the parameters to be manipulated. 124

$$S(\underline{X}) = \sum_{k}^{n_v} \left[\frac{1}{n_e} \sum_{i}^{n_e} \frac{(y_{k,i}^e - y_{k,i}^*)^2}{\sigma_{k,i}^2} \right]$$
(10)

 y_k are the variables to be analysed, n_e is the number of experiments and n_v 125 is the number of calculated variables; the superscript e means 'experimental' 126 and * means 'calculated'; and $\sigma_{k,i}$ is the variance of the experimental variable. 127 This procedure is specially applied to CPA parameter estimation, in which 128 there are a wide variety of possible solutions (i.e. sets of parameters that 129 result in similar deviations from experimental data). The usual methodology 130 is to apply the variables saturation pressure and liquid density (or volume) 131 into the objective function $S(\underline{X})$ to estimate the parameters of the equation 132 of state for pure components $(a_0, b, c_1, \varepsilon \text{ and } \beta)$. 133

¹³⁴ Moreover, in Thermodynamics, experimental data can be scarce and of-¹³⁵ ten there is no replica to these data, so variance values can be unavailable ¹³⁶ or unreliable. In these cases, $\sigma_{k,i}$ is commonly equalled to the experimen-¹³⁷ tal point $y_{k,i}^e$ itself (Santos, 2015; Kontogeorgis et al., 2006a; Oliveira et al., ¹³⁸ 2007). The advantage of this practice when analysing pure components is that the term becomes well-scaled numbers and takes into account that measure errors are higher in regions of high pressure, which agrees with what is
seen experimentally.

Nevertheless, analysing pure component properties may not be enough to find a proper set of parameters. For instance, when applied to mixtures with liquid-liquid equilibrium (LLE), frequently the solution set of this optimization failed to predict the experimental data (Derawi et al., 2003). Therefore, in order to select the best values, LLE experimental data is commonly used in the literature with specific hydrocarbons to 'guide' the user to the desired solution (Kontogeorgis et al., 2006a).

Besides, Santos et al. (2015c) suggested, in their work, a creation of a 149 single objective function which considers not only the metric based on the 150 pure component's saturation pressure and liquid density, but also the metric 151 based on the compositions in LLE with a pre-selected hydrocarbon. Con-152 sequently, there would be a multi-objective optimization problem to solve, 153 weighted by a specified value. One of the methodologies proposed in this 154 work is based on this procedure, so that the parameters are obtained in a 155 more rigorous systematic way by putting the LLE data in the metric. 156

For binary parameters, they are usually estimated by bubble pressure or compositions in LLE (Folas et al., 2006). Also, when aiming the flow assurance by hydrate prevention in gas processing, these parameters can be estimated by gas solubility in the liquid phase (Haghighi et al., 2009). However, in this work, another procedure is proposed, based on the water content in a gas in dew point condition (Shiguematsu, 2014). Section 3 will provide more details in these calculations.

9

¹⁶⁴ 3. Methodology

165 3.1. Thermodynamic Calculations

¹⁶⁶ 3.1.1. Saturation Pressure and Liquid Density for Pure Components

Before calculating these variables, the system in Eqs. (1) to (5) must firstly be solved by V and X_{A_i} . As this involves two connected convergence loops, a special strategy of calculation is needed (Michelsen, 2006). Thereon, its compressibility factor and fugacity coefficients may be calculated via the respective equation of state (Prausnitz et al., 1998). Thus, solving Eq. (11) the saturation pressure is obtained.

$$P_{sat}^{(k+1)} = \frac{\phi_L(T, P_{sat}^{(k)})}{\phi_V(T, P_{sat}^{(k)})} P_{sat}^{(k)}$$
(11)

¹⁷³ T is the temperature of the system, ϕ_L and ϕ_V are respectively the liquid ¹⁷⁴ and vapour fugacity coefficients, and $P_{sat}^{(k)}$ is the saturation pressure obtained ¹⁷⁵ at iteration k. When the difference between the saturation pressures in two ¹⁷⁶ consecutive iterations are lower than a predefined tolerance, the calculation is ¹⁷⁷ assumed to converge and then the density ρ_{liq} may be determined by Eq. (12).

$$\rho_{liq} = \frac{P_{sat}}{RTZ(T, P_{sat})} \tag{12}$$

R is the universal gas constant and Z is the compressibility factor of the liquid phase.

3.1.2. Compositions of Each Phase for Binary Mixtures in Liquid-Liquid Equilibrium (LLE)

The conditions at LLE can be directly calculated by solving the Rachford-Rice flash calculation. Moreover, as this is a binary two-phase system, Gibbs' Phase Rule shows that there is only one solution to the compositions (Prausnitz et al., 1998). They are analytical and defined in Eqs. (13) and (14).

$$x_{1(2)} = \frac{K_2 - 1}{K_2 - K_1} \tag{13}$$

$$x_{2(1)} = \frac{K_2(1 - K_1)}{K_2 - K_1} \tag{14}$$

 $x_{i(j)}$ stands for the composition of *i* in the phase *j*, and $K_i \equiv \hat{\phi}_{i(2)}/\hat{\phi}_{i(1)}$ is the liquid-liquid equilibrium constant, with $\hat{\phi}_{i(j)}$ being the respective phase fugacity coefficient, function of *T*, *P* and $x_{i(j)}$.

If the pressure P is unknown, it is assumed to be the bubble pressure of a equimolar system of these components.

¹⁹¹ 3.1.3. Water Content for Mixtures Between Water and a Gas in Dew Point
¹⁹² This calculation was based on the work of Shiguematsu (2014), according
¹⁹³ to Eq. (15):

$$y_{H_2O} = y_{H_2O} \left(T, P, \underline{y}_{DG} \right) \tag{15}$$

 y_{H_2O} is the required water content to bring the system to its dew point, Tthe system temperature, P the system pressure and \underline{y}_{DG} stands for the dry gas composition. Considering that the system is already at dew point condition in (T, P), the program calculates the liquid composition in equilibrium \underline{x} and solves the expression in Eq. (16).

$$F \equiv \sum_{i=1}^{n_c} x_i - 1 = 0$$
 (16)

 n_c is the total number of components. This is an implicit calculation, which can be solved by bisection or secant numerical methods.

²⁰¹ 3.2. Optimization Methods and Strategies

The optimization procedures performed in this work consist of multivariable search methods, due to the complexity of the thermodynamic calculations. The approach adopted is common to various authors such as Santos et al. (2015c), which is divided in two stages:

- A stochastic method. It was decided to implement the Particle Swarm
 Optimization PSO (Kennedy and Eberhart, 1995) because it is widely
 applied in the subject of this work and there are several published improvements to this method available in the literature (Shi and Eberhart,
 1998; Schwaab et al., 2008; Moraes et al., 2015).
- A deterministic method. Although derivative-based optimization meth-211 ods could provide more robust results, it was decided to implement a 212 more traditional method in this work which is the Simplex (Nelder 213 and Mead, 1965). This method is of simple implementation and does 214 not need to compute derivatives of the objective function. This al-215 lows for greater flexibility of thermodynamic models if a new model 216 would be inserted into the computational tool. Due to the fast calcu-217 lations in each iteration, its maximum number is set to a high enough 218 value to ensure that the generated result becomes independent of the 219 selected optimization method. For this work, an improvement to the 220 generation of its initial cluster was implemented, due to thermody-221 namic limitations. Nelder and Mead (1965) recommended to select the 222

vortexes at the bounds of the variables, but this frequently leaded to non-convergence issues. Therefore, here these points are arbitrated from random values inside a predefined region around the initial guess. After that each point is tested and the first (n + 1) that converged are selected to be part of the cluster (n is the number of manipulated variables).

Usually, these methods are implemented sequentially, using the PSO solution as the initial estimation for the Simplex, which acts merely as a refiner of the former (Santos et al., 2015c). However, in this work, an alternative hybridization approach is also performed, based on the work of Das et al. (2006). It consists of a parallel combination between both optimization strategies, briefly described as follows:

²³⁵ 1. Run one regular iteration of PSO.

236
2. From the best current point of the swarm, generate a cluster and exe237 cute the Simplex method.

²³⁸ 3. Replace the worst point of the swarm with the Simplex solution.

4. Evaluate the convergence criteria. If not satisfied, go back to Step 1.
Else, the solution is achieved and exit routine.

As mentioned previously, this implementation is based on the work of Das et al. (2006). However, these methods are not the same. Their 'tandem' approach consists of creating several simplex clusters in each iteration, solving them simultaneously, while in this work they are still solved separately.

245 3.3. Metrics for Parameter Estimation

The metrics studied in this work follow the thermodynamic calculations previously described. Each of them are detailed below.

248 3.3.1. Estimation of Parameters for Pure Components

For pure components, the calculated variables studied for this work are saturation vapour pressure (P) and liquid density (ρ). Thus, the objective function is defined by Eq. (17), with its manipulated variables listed in Eq. (18).

$$S(\underline{X}) = \frac{1}{n_e} \left[\sum_{i=1}^{n_e} \frac{(P_i^e - P_i^*)^2}{\sigma_{P,i}^2} + \sum_{i=1}^{n_e} \frac{(\rho_i^e - \rho_i^*)^2}{\sigma_{\rho,i}^2} \right]$$
(17)

$$\underline{X} = \begin{bmatrix} a_0 & b & c_1 & \varepsilon/R & \beta \end{bmatrix}^T \tag{18}$$

²⁵³ The following data are needed to accomplish this parameter estimation:

• Critical properties
$$(T_c, P_c)$$
 and the acentric factor w ;

• Experimental temperature data
$$(T)$$
;

• Experimental pressure data (P^e) and their variances (σ_P) , if available;

• Experimental liquid density data (ρ^e) and their variances (σ_{ρ}) , if available (optional).

If there is no liquid density data available, calculations may proceed using only pressure as calculated variable. The experimental variances are not obligatory data either. It is possible to select an option which will make the program assume that $\sigma_{P,i} = P_i^e$ and $\sigma_{\rho,i} = \rho_i^e$ (i.e. the respective experimental variables). This applies to all metrics described in this work.

264 3.3.2. Estimation of Binary Parameters by LLE

This case is similar to the previous metric, with the main difference being the calculated variables in the objective function, related to the liquid-liquid equilibrium (LLE) of the system, according to Eqs. (19) and (20).

$$S(\underline{X}) = \frac{1}{n_e} \left[\sum_{i=1}^{n_e} \frac{(x_{1(2),i}^e - x_{1(2),i}^*)^2}{\sigma_{x_{1(2)},i}^2} + \sum_{i=1}^{n_e} \frac{(x_{2(1),i}^e - x_{2(1),i}^*)^2}{\sigma_{x_{2(1)},i}^2} \right]$$
(19)

$$\underline{X} = \begin{bmatrix} k_{12} \ \varepsilon^{A_1 B_2} / R \ \beta^{A_1 B_2} \end{bmatrix}^T$$
(20)

- Components 1 and 2's pure parameters and critical data;
- Experimental temperature data (T);
- Experimental pressure data (P_i^e , optional). If not given, the program will calculate internally the bubble pressure of the corresponding equimolar system;
- Experimental composition data of component 1 in the phase rich in component 2 $(x_{1(2)}^e)$ and vice-versa $(x_{2(1)}^e)$, as well as their variances $(\sigma_{x_{1(2)}} \text{ and } \sigma_{x_{2(1)}}, \text{ respectively}), \text{ if available.}$

277 3.3.3. The VLE-LLE Methodology

As previously described in this work, a number of authors recommended to use LLE calculations with specific compounds to help the selection of the best CPA parameter values for pure components (Kontogeorgis et al., 281 2006a). This work proposes an improvement to this analysis, enabling its automation. It consists in unifying both previous objective functions into
Eq. (21):

$$S(\underline{X}) = S_{pure}(\underline{X1}) + \omega S_{LLE}(\underline{X2}) \tag{21}$$

 S_{pure} is the objective function defined by Eq. (17), S_{LLE} is the objective function defined by Eq. (19) and ω is a user-defined weight. All pure (<u>X1</u>) and binary (<u>X2</u>) parameters can be manipulated at once in this approach, i.e. <u>X</u> = [<u>X1 X2</u>]. Henceforward, this procedure will be called here the VLE-LLE Methodology.

The proposed algorithm starts from estimating parameter values with $\omega_0 = 0$. Thereafter, they are used as initial guesses to estimate new values for $\omega_i = \omega_{i-1} + \delta \omega$. This procedure is then repeated iteratively until a desired ω value is achieved. For more details, see Abunahman (2018).

With this method, it is possible to analyse simultaneously the behaviour of S_{pure} and S_{LLE} for various values of weight, enabling analysis such as Pareto (Schwaab and Pinto, 2007). Also, once there always is an initial guess which is relatively close to the following solution, the Simplex method can be used without a previous global search, greatly accelerating the calculations. Results of this procedure for water will be shown and discussed in the Section 4.

300 3.3.4. Estimation of Binary Parameters from Water Content Data

In this case there is also only one calculated variable, which is the water content in dew point condition, as previously described in this work. Thus, the objective function is given by Eqs. (22) and (23).

$$S(\underline{X}) = \frac{1}{n_e} \sum_{i=1}^{n_e} \frac{(y_{H_2O}^e - y_{H_2O}^*)^2}{\sigma_{y,i}^2}$$
(22)

$$\underline{X} = [k_{i-H_2O} \ \varepsilon^{A_i B_{H_2O}} / R \ \beta^{A_i B_{H_2O}}]^T$$
(23)

where i is the component that forms the respective binary mixture with water. The difference in this approach is that it can be also applied to multicomponent mixtures, being able to manipulate parameters of more than one pair at once. The user is allowed to select which pair(s) whose parameters are desired to be estimated, as long as one of the components is water.

Also, due to the complexity of this calculation, it was decided to implement only the Simplex method with this metric, using predetermined initial guesses. Usually parameter values obtained in the literature by bubble pressure based metrics (Yakoumis et al., 1997) are adequate to initialize the optimizer.

³¹⁴ Thus, the input data required in this approach are:

- All components' pure parameters, critical data (T_c, P_c) and the acentric factor w.
- All binary parameters. The ones to be estimated will be used as initial guess by the program. If not given, they will be considered equal to zero.
- Experimental temperatures (T) and pressures (P), as well as the composition of the dry gas in each point (\underline{y}_{DG}) .
- Experimental water contents (y_{H_2O}) and their variances $(\sigma_{y,i})$, if available.

The main advantage of this procedure is that the convergence is guaranteed because the system is already considered to be in dew point conditions. On the other hand, when pressure is calculated from a defined composition, there may be several inconsistencies regarding multiple dew point conditions or formation of distinct liquid phases. This metric presents as an alternative to calculate natural gas properties in high pressure, commonly observed in the Brazilian Pre-Salt area oil production.

331 3.4. Computational Aspects

All the aforementioned calculations have been implemented in a program written in the languages C# and Fortran, which was named *ThermOptimizer*, or *ThermOpt* for short. This program contains various features to help the user in various thermodynamic analyses such as:

- Generation of output plots of each variable behaviour versus the respective objective function value, as well as tables of them, if the user wishes to export these data to an Excel application, for example.
- Execution of parametric and statistical analysis from the results of the PSO method implemented in this software.
- Presentation of general charts such as phase equilibria diagrams, vari able deviations and isotherms containing pressure versus water content.
- Generation of histogram charts from successive PSO executions in order
 to evaluate its effectiveness from a fixed set of PSO's internal variables.
- Organization of the results of the VLE-LLE Methodology in exportable
 tables.

It is important to state that the items in the interface change dynamically as the user modifies the thermodynamic model, the association schemes or the internal options of the program. Thus, it can be considered a friendlyuser tool.

As it can be seen from these figures, *ThermOpt* is capable of doing numerous analysis. In this example, the water parameters were optimized by the hybrid optimization method in parallel described earlier in this work. It is a reliable method, of which successive executions lead essentially to the same solution.

356 4. Results and Discussion

357 4.1. Parameter Estimation for Water

Firstly, a parameter estimation using the metric defined by Eq. (17) was 358 performed for the component water, selected due to its key relevance to the 359 natural gas processing units. Its association scheme was set as '4C' (Huang 360 and Radosz, 1990), as recommended in the literature (Kontogeorgis et al., 361 2006a). Table S.1, in the Supplementary Material (SM) indicated in Ap-362 pendix A, resumes the data inserted into *ThermOpt*. Table S.2, also in 363 SM, presents each variable bounds. Finally, Table 1 shows the optimized 364 parameter values using pressure and density data for water. 365

The average absolute deviations for pressure (AAP) and density (AAD)are defined by Eqs. (24) and (25), respectively.

$$AAP = \frac{100\%}{n_e} \sum_{i=1}^{n_e} \frac{|P_i^e - P_i^*|}{P_i^e}$$
(24)

Table 1: Water parameters estimated from *ThermOpt*, using saturation pressure and liquid density using DIPPR experimental data from $T_R = 0.42$ to $T_R = 0.95$, comparing to the parameters published by Kontogeorgis et al. (1999).

Parameter	Literature Kontogeorgis et al. (1999)	This Work
$a_0 $ [bar L ² mol ⁻²]	1.2278	1.1534
$b \; [\text{mol } \mathbf{L}^{-1}]$	0.0145	0.01468
c_1	0.6736	1.2323
$\varepsilon/R~[{ m K}]$	2003.25	1758.06
1000β	69.20	108.66
S_{pure}	3.45e-4	1.96e-4
$AAP \ [\%]$	0.78	0.32
$AAD \ [\%]$	1.20	1.14

$$AAD = \frac{100\%}{n_e} \sum_{i=1}^{n_e} \frac{|\rho_i^e - \rho_i^*|}{\rho_i^e}$$
(25)

368 4.2. Validation with LLE Data

As already stated, parameter estimation based only on pure component properties, such as saturation pressure and liquid density, is not enough to attain a set of parameters that is capable to correctly predict the behaviour of mixtures, specially when they are in liquid-liquid equilibrium (LLE).

To illustrate that, Table S.3 presents a set of parameters of water which were estimated through a different range of temperature $(T_R = [0.45 - 0.90])$, comparing to the one presented in Table 1. It also results in low deviations for pressure and density, thus it is important to include extra restrictions. The most important are the compositions of the liquid phases in equilibrium with hydrocarbons (Kontogeorgis et al., 2006a).

Therefore, the discrepancies reported in the Table S.3 proves the necessity to apply the VLE-LLE Methodology from the result presented in the Table 1. It calculates a sequence of viable sets of parameters taking into account both the VLE (saturation pressure and liquid density) and LLE properties (compositions of each liquid phase).

The objective function term S_{pure} is calculated from the Eq. (17), using the data reported in Table S.1. As for the term S_{LLE} , Eq. (19) was used.

All the variances in this work were assumed to be the respective experimental points. Even though it is not usually the recommended approach in the literature for the liquid compositions, it was observed that its optimized solutions tended to result in lower average absolute deviations for the compositions AAX then when equalizing all variances to 1.

When applied the algorithm recommended for this methodology, it has been noted that the objective function of the LLE term (S_{LLE}) and the objective function of the pure VLE term (S_{pure}) were inversely proportional. Therefore, it has been possible to determine the best sets of parameters by selecting the region in an intermediate position, where an increase of S_{pure} would result in a lower decrease of S_{LLE} and vice-versa.

The selected hydrocarbon for this LLE analysis was the n-hexane (Kontogeorgis et al., 1999; Tsonopoulos and Wilson, 1983). The main selection criteria for the parameters were based on the spectroscopic data on the measure of the hydrogen bonds' energy for water, presented by Koh et al. (1993). This property could thus be compared with the association energy parameter 402 ε/R (Kontogeorgis et al., 1996).

403 Therefore, for comparison purposes, the following parameter sets were 404 analysed:

- Set of Parameters 00 ('Set 00'): initial guess to the procedure, being
 generated by only saturation pressure and liquid density (VLE variables), as in Table 1. Its weight on Eq. (21) is equal to zero.
- Set of Parameters 01 ('Set 01'): set selected with the S_{pure} value closest to the one calculated from the parameters obtained in the literature (Kontogeorgis et al., 1999). The main objective of this set was to validate the VLE-LLE Methodology, showing that it would be possible to obtain the literature parameters' values applying this procedure.
- Set of Parameters 02 ('Set 02'): set selected with the ε/R value closest to the one reported by Koh et al. (1993) (1813 K).
- 415 416

• Set of Parameters 03 ('Set 03'): set selected with the ε/R value in an intermediary value between Set 01 and Set 02 (around 1900 K).

⁴¹⁷ When analysing the behaviour of the parameter ε/R , it was found that ⁴¹⁸ it also decreases when S_{LLE} increases, as seen in Fig. S.1, in SM. As a ⁴¹⁹ consequence, there would be a possibility of crudely predict the behaviour ⁴²⁰ of LLE in aqueous solutions of hydrocarbons using the Set 02. Therefore, it ⁴²¹ was decided to select an intermediate set, as also stated in Fig. S.1, which ⁴²² was the Set 03.

Fig. 1 presents the Pareto analysis relating S_{LLE} and S_{pure} , with the location of all parameter sets analysed in this work, and Table 2 presents the main results with the selected parameters, comparing to the literature
parameters (Kontogeorgis et al., 1999).



Figure 1: Pareto analysis containing both objective function terms of Eq. (21) for water.

From Table 2, it can be noticed that the parameters obtained in Set 01 are considerably close to the ones published by Kontogeorgis et al. (1999). If the latter was to be inserted in Fig. 1 it would be overlaid by the square symbolizing the Set 01. As a consequence, it is contained in its curve generated, that is, one of the optimal solutions calculated by the VLE-LLE Methodology is the literature set.

⁴³³ Moreover, these parameters sets were compared to literature parameters ⁴³⁴ when applying to various LLE binary mixtures, as stated in Tables S.4 to S.7 ⁴³⁵ (SM). These hydrocarbons were, respectively: n-hexane, n-octane, benzene ⁴³⁶ and toluene. In these tables, $AAX_{W,HC}$ and $AAX_{HC,W}$, which are the average ⁴³⁷ absolute deviations for the compositions in LLE, are defined by Eqs. (26)

Table 2: Parameters selected using the VLE-LLE Methodology for water, comparing to the parameters from literature (Kontogeorgis et al., 1999). The T_R range adopted was [0.42 - 0.95]. Note that the parameters in the Set 01 are close to the literature values. wconsists of the weight inserted on Eq. (21).

Parameter	Literature	Set 00	Set 01	Set 02	Set 03
1000w	-	0.000	8.770	0.149	1.150
$a_0 \; [\text{bar } \mathrm{L}^2 \; \mathrm{mol}^{-2}]$	1.2278	1.1534	1.2224	1.1191	1.0978
$b \; [\text{mol } \mathbf{L}^{-1}]$	0.0145	0.0147	0.0145	0.0146	0.0145
c_1	0.6736	1.2323	0.6650	1.1643	1.0120
$\varepsilon/R~[{ m K}]$	2003.25	1758.06	2008.84	1812.91	1897.87
1000eta	69.20	108.66	68.90	101.22	89.08
S_{pure}	3.45e-4	1.95e-4	3.44e-4	2.01e-4	2.28e-4
$AAP \ [\%]$	0.78	0.30	0.78	0.42	0.62
AAD~[%]	1.20	1.15	1.22	1.13	1.11

 $_{438}$ and (27), respectively.

$$AAX_{W,HC} = \frac{100\%}{n_e} \sum_{i=1}^{n_e} \frac{|x_{W,HC}^e - x_{W,HC}^*|}{x_{W,HC}^e}$$
(26)

$$AAX_{HC,W} = \frac{100\%}{n_e} \sum_{i=1}^{n_e} \frac{|x_{HC,W}^e - x_{HC,W}^*|}{x_{HC,W}^e}$$
(27)

The subscript 'HC, W' stands for the hydrocarbon content in the aqueous phase and vice-versa for 'W, HC'. Also, for the binary parameters, it is important to point out that all of these parameters were optimized in *Ther*mOpt, even for the literature set of parameters, in order to standardize the comparisons.

444 Hence, the following can be deduced from this results:

The Set 01 had not only the objective function terms close to the calculated values from the Literature Set (Kontogeorgis et al., 1999), but also their parameters were particularly similar. It is important to emphasize that Sets 00 to 03 were all obtained independently from the literature data, thus it was possible to reproduce the literature values with the VLE-LLE Methodology.

- All sets could satisfactorily predict the LLE data, with the exception
 of Set 00 in aqueous solutions with the alkanes, which was expected
 due to the fact that its pure parameters were not obtained from LLE
 data at all.
- As this consists of a Pareto analysis, there is no single 'optimal set' in
 it, but rather a region whose sets culminate in acceptable deviations
 both in VLE and LLE. For this reason it is necessary to determine
 specific criteria to select the proper parameters.
- Due to the better prediction of LLE with alkanes (i.e. lower values of 459 $AAX_{W,HC}$ and $AAX_{HC,W}$), in this work we considered the Set 03 as the 460 main parameter set to be evaluated and compared against published 461 binary parameters and experimental data. Its variable ε/R is closer 462 to the value reported by Koh et al. (1993) without losing accuracy in 463 the LLE predictions. Thus, if this tendency confirms in the natural 464 gas calculations, this set is a potentially adequate alternative to the 465 parameters published by Kontogeorgis et al. (1999). 466

Finally, it is essential to state that the goal of this analysis was to provide a systematic guide to facilitate a subsequent selection of the best parameter values. Eventually, the final decision should be taken by the user.

470 4.3. Binary Parameter Estimation Through Water Content

471 4.3.1. Analysis of the Binary Mixture $H_2O + CO_2$

As expressed in the beginning of this paper, the pre-salt reservoirs contain a CO₂ rich natural gas. Also, due to its particular characteristics, specially its capability to do cross association when mixed with water, the proper prediction of this binary mixture becomes crucial in the upstream processes. In order to perform this analysis, the following steps were taken:

- For the pure components, literature parameters (Kontogeorgis et al., 1999) and the Set 03 from the previous Section were used for water, and the parameters from Tsivintzelis et al. (2010) were used for CO₂.
 They are listed in Table 3.
- In this work, it is considered that there is a solvating effect between CO₂
 and water, even though the former does not self-associate (Kontogeorgis
 et al., 2006b).
- The binary parameters in the CERE Database (Tsivintzelis et al., 2012)
 were used as initial estimatives to re-estimate these parameters using
 water content calculation optimized by the Simplex method.

Parameter	Water (Literature)	Water (Set 03) ^{<i>a</i>}	CO_2
$a_0 $ [bar L ² mol ⁻²]	1.2278	1.0978	3.5081
$b \; [\text{mol } \mathbf{L}^{-1}]$	0.0145	0.0145	0.0272
c_1	0.6736	1.0120	0.7602
$\varepsilon/R~[{ m K}]$	2003.25	1897.87	-
1000β	69.20	89.08	_

Table 3: Pure component parameters used in this work. Literature values were taken from Kontogeorgis et al. (1999) for water and from Tsivintzelis et al. (2010) for CO_2 .

 a This work

Table S.8 (SM) summarizes the experimental data used, and Table S.9 (SM) presents the bounds of the estimated variables.

Finally, Table 4 displays the results of this procedure. S_y is the objective function calculated by Eq. (22), and the absolute average deviation for water content AAY is calculated according to Eq. (28).

$$AAY = \frac{100\%}{n_e} \sum_{i=1}^{n_e} \frac{|y_i^e - y_i^*|}{y_i^e}$$
(28)

From these results, it is possible to infer that the optimization based on water content executed properly, where the estimated parameters resulted in values close to the set reported by Tsivintzelis et al. (2012), but with greatly reduced deviations in the water content, specially in high pressures (P > 200 bar according to this Table). Figs. 2 and 3 illustrate these results with isotherms.

Analysing these charts, it is inferred that even though all sets of parameters have predicted the inversion effect of water content when the pressure

Table 4: Results for the mixture $H_2O + CO_2$. Estimation A: from pure water literature parameter values (Kontogeorgis et al., 1999). Estimation B: from Water (Set 03, this work). Literature data for the binary parameters were taken from Tsivintzelis et al. (2012). AAY_{200} is the absolute average deviation for water content considering only P > 200 bar.

Case	k_{ij}	β_{ij}^{cross}	S_y	$AAY \ [\%]$	AAY_{200} [%]
Literature Data	0.1145	0.1836	4.01e-2	16.1	23.7
Estimation A	0.1542	0.1765	2.15e-2	10.8	3.4
Estimation B	0.1701	0.2093	2.11e-2	10.7	3.3

increases, the potential results of this study have seemed to be superior than
the published parameters (Tsivintzelis et al., 2012).

In addition to that, the Set 03 obtained for water has succeeded to predict its content with slightly lower deviations than the optimization calculated from the literature set (Kontogeorgis et al., 1999).



Figure 2: Chart containing values of pressure versus water content in dew point for H₂O + CO₂ in isotherms at T = 298.15 K and T = 304.15 K. Experimental data: Wiebe and Gaddy (1941). Literature parameters: Tsivintzelis et al. (2012) ($k_{ij} = 0.1145$, $\beta_{ij}^{cross} = 0.1836$). Optimized parameters: this work (Set 03, $k_{ij} = 0.1701$, $\beta_{ij}^{cross} = 0.2093$).



Figure 3: Chart containing values of pressure versus water content in dew point for H₂O + CO₂ in isotherms at T = 323.15 K and T = 348.15 K. Experimental data: Wiebe and Gaddy (1941). Literature parameters: Tsivintzelis et al. (2012) ($k_{ij} = 0.1145$, $\beta_{ij}^{cross} = 0.1836$). Optimized parameters: this work (Set 03, $k_{ij} = 0.1701$, $\beta_{ij}^{cross} = 0.2093$).

505 4.3.2. Validation through Multicomponent Dew Point Calculations

In this stage, the results previously presented have been further validated, replicating the same analysis as $H_2O + CO_2$ for the following compounds: H_2S , methane, ethane, propane and n-butane. The goal is to properly predict the water content in dew point of multicomponent mixtures containing these substances. Even though all of these components are not self-associating, H_2S is considered to solvate i.e. cross-associate with H_2O , just as CO_2 (Santos ⁵¹² et al., 2015b).

Table 5 presents the results obtained with these mixtures, compared to their published values in the literature (Tsivintzelis et al., 2012).

Table 5: Estimation results for the aqueous binary mixtures studied in this work. For each mixture presented, the first line of interaction parameters were taken from the literature (Tsivintzelis et al., 2012) and the second line consists on the optimization performed from the Set 03 for water in this work. 'mCR-1' means that ε_{ij}^{cross} was calculated according to Eq. (8).

Mixture	k_{ij}	β_{ij}^{cross}	$\varepsilon_{ij}^{cross}/R$ [K]	S_y	AAY ~[%]
$\mathrm{H_2O} + \mathrm{H_2S^a}$	0.1913	0.0624	1308.32	2.20e-2	11.8
	0.4093	0.2550	mCR-1	1.39e-2	7.8
$\mathrm{H_2O} + \mathrm{C_1}^b$	0.0098	-	-	6.15e-3	5.6
	0.0449	-	-	5.40e-3	4.8
$\mathrm{H_2O} + \mathrm{C_2}^c$	0.1162	-	-	2.35e-2	10.2
	0.0721	-	-	1.39e-2	8.0
$\mathrm{H}_{2}\mathrm{O}+\mathrm{C}_{3}{}^{d}$	0.1135	-	-	2.96e-2	9.7
	0.0661	-	-	2.88e-2	10.1
$\mathrm{H_2O} + \mathrm{n-C_4}^e$	0.0875	-	-	1.98e-2	11.7
	0.4522	-	-	1.24e-3	2.0

^a Selleck et al. (1952)

 b Folas et al. (2007); Olds et al. (1942); Mohammadi et al. (2004)

 c Mohammadi et al. (2004); Reamer et al. (1943); Song and Kobayashi (1994);

Anthony and McKetta (1967)

 d Song and Kobayashi (1994); Kobayashi and Katz (1953)

 e Reamer et al. (1944)

These parameters have been then validated with various multicomponent systems studied in the literature. In this work four mixtures have been studied, with the following compositions on dry basis:

- Natural Gas (NG): 94% methane + 4% ethane + 2% n-butane (Chapoy et al., 2005).
- Natural Acid Gas 01 (NAG-1): 75% methane + 8% ethane + 4%
 propane + 13% CO₂ (Maddox et al., 1988).
- Natural Acid Gas 02 (NAG-2): methane + CO₂ + H₂S various compositions (GPSA, 1998; Huang et al., 1985).
- Natural Acid Gas 03 (NAG-3): methane + propane + CO_2 + H_2S various compositions (Ng et al., 2001).

Table 6 shows the deviations in the water content calculated using the literature and optimized parameters previously described in Table 5.

Table 6: Mean absolute deviations for water content (AAY [%]) calculated for each of the mixtures studied in this Section. Literature values were taken from Tsivintzelis et al. (2012).

Mintune	AAY ~[%]	$AAY \ [\%]$
Mixture	(Lit. Parameters)	(This Work)
NG	2.6	1.4
NAG-1	23.3	14.5
NAG-2	9.0	8.3
NAG-3	12.2	18.3

From these results, it can be inferred that the optimized parameters by 528 binary mixtures have a high potential of predicting the water content of 529 multicomponent mixtures. Also, it is important to emphasize that one of the 530 pairs, $H_2O + H_2S$, is calculated in the literature with three parameters (k_{ij}) 531 $\beta^{A_i B_j}$ and $\varepsilon^{A_i B_j}$), but in this work it was decided to use only the two former 532 variables to optimize, calculating the energy parameter from Eq. (8). That 533 is, it was made possible to improve most of the results by optimizing fewer 534 parameters. 535

The only exception was in the case of NAG-3, whose larger deviations may be due to the harsher conditions of the experiments (Ng et al., 2001), where the pressures could get as high as 690 bar. Simultaneously, for example, the conditions of the experimental data available for water + methane (Mohammadi et al., 2004; Folas et al., 2007; Olds et al., 1942) did not surpass 30 bar. Therefore, if experimental conditions in a broader range of pressures for the binary mixtures were available, it would be possible to improve these results.

However, if the user wishes to analyse specifically this mixture, it is pos-543 sible to re-estimate one or all water-containing binary parameters simulta-544 neously in *ThermOpt* for these conditions. For instance, if the $H_2O + H_2S$ 545 and water + methane parameters were to be re-estimated in NAG-3, keep-546 ing the remaining values equal to the ones found in this work, the Simplex 547 procedure of *ThermOpt* reaches the following values: $k_{H_2O-C_1} = 0.1470$, 548 $k_{H_2O-H_2S} = 0.5265$ and $\beta^{A_{H_2O}B_{H_2S}} = 0.2012$, with AAY = 11.6%, which 549 is lower than the 12.2% calculated using the parameters published by the 550 literature. This further corroborates the importance of a flexible optimizing 551 tool rather than overall optimized parameters. 552

553 4.4. Application to Natural Gas Compression

Having validated the parameter values obtained in the previous sections, 554 they have been directly tested in a natural gas compression process in its 555 transport stage to check whether the results follow the expected tendencies. 556 As it is a fictitious unit, there is no experimental data to validate the results. 557 Therefore, the calculations were performed inside the Petrobras' pro-558 cess simulation software Petrox[®] (Niederberger et al., 2009). This simulator 559 has already been extensively validated for such calculations (Santos et al., 560 2015a,b,c), and it was also possible to implement the parameter values ob-561 tained here in this simulator, so that the only difference between the results 562 of each simulation would be caused by these new values. Thus, this software 563 is a valid choice to perform this analysis. 564

The compression process studied here was simplified to only one stage, as the goal was to analyse its output conditions. The precipitation of liquid water in this stream must be avoided in all circumstances, which would cause



the hydrate formation. Fig. 4 presents the scheme of this simulation.

Figure 4: Scheme of the simulation of a simple natural gas compression in Petrox[®] Process Simulator.

According to Fig. 4, the inlet stream 'HC01' contains a fixed composition 569 $(80\% \text{ methane} + 11\% \text{ ethane} + 5\% \text{ propane} + 4\% \text{ H}_2\text{S})$ in standard condi-570 tions (50 bar and 5°C). The streams 'CO2' and 'H2O' consist of pure CO_2 571 and pure water respectively. After mixing, the stream 'GAS0' is compressed 572 from the operation conditions to various pressures and then cooled to 40°C. 573 For each discharge pressure, the water content was calculated in order to 574 leave the outlet stream in dew point. That is, this is the highest safe value of 575 water content in the system in the specified conditions. The control module 576 'CCO2' manipulates the flow of the stream 'CO2' in order to fix the CO_2 577 content in the stream 'GAS0', from 10% to 80% in dry basis. The controller 578 'CDEW' modifies the flow of the stream 'H2O' to fix the temperature of 579 the dew point flash 'FDEW' to 40°C. Finally, the calculator module 'CALC' 580 explicitly calculates the water content in the outlet stream 'OUTL'. 581

It is expected that the presence of CO_2 induces the inversion effect of the water content in 'OUTL' when increasing the pressure of the system, as already stated the the previous results. That is, for each CO_2 content there is a pressure value (P_{min}) in which the water content is minimum (y_{min}) . Figs. 5 and 6 show the behaviour of these streams in all the studied region of pressures.



Figure 5: Chart containing values of pressure versus water content in dew point for the mixture Water + natural gas with 10% of CO_2 and 20% of CO_2 . The temperature was fixed at $T = 40^{\circ}$ C. Literature set: Tsivintzelis et al. (2012).



Figure 6: Chart containing values of pressure versus water content in dew point for the mixture Water + natural gas with 40% of CO₂, 60% of CO₂ and 80% CO₂. The temperature was fixed at $T = 40^{\circ}$ C. Literature set: Tsivintzelis et al. (2012).

The results are presented in the Table 7. It can be inferred that the parameter set selected for this work yielded less conservative values of water content than the literature sets. In most of the cases the water content values obtained with this work's parameters are higher than using the parameters presented in the literature, specially in lower CO_2 content streams. On the other side, in the 80% CO_2 case both sets resulted in practically the same curve.

⁵⁹⁵ However, the set selected in this work tend to foresee the inversion effect ⁵⁹⁶ in all of the streams, including the one with 10% of CO₂, differently from the

Table 7: Minimum water content (y_{min}) for each outlet stream composition simulated in this work and their respective pressures (P_{min}) . The maximum pressure evaluated in all cases was 555 bar. Literature Set: Tsivintzelis et al. (2012).

Case	Parameters	y_{min} [ppm]	P_{min} [bar]
1007 CO	Literature Set	898.5	-
10% CO ₂	This Work	959.8	260
2007 CO	Literature Set	1099	165
20% CO ₂	This Work	1138	155
$40\%~{\rm CO_2}$	Literature Set	1382	115
	This Work	1420	115
$60\%~{\rm CO_2}$	Literature Set	1629	95
	This Work	1668	95
$80\%~{\rm CO_2}$	Literature Set	1858	80
	This Work	1896	80

literature sets. The experimental data on the mixture water + CO_2 (Wiebe 597 and Gaddy, 1941) show the inversion of the water content curve versus pres-598 sure at $T \approx 40^{\circ}$ C, therefore this effect would be expected even with lower 599 contents of CO_2 . This result further validates the Set 03 obtained for wa-600 ter and, consequently, validating the methodology described in this paper. 601 Therefore, we consider that the VLE-LLE Methodology and the parameter 602 estimation procedure through the metric described in Eq. (22) are valid and 603 important contributions to the literature. 604

605 5. Conclusion

This work succeeded in proposing two new methodologies for systematically estimating parameters: one based on pure (VLE) and LLE properties at once and the other based on water content in dew point (Shiguematsu, 2014), with clear applications in the natural gas processing. Both of them were implemented in a friendly-user interface program called the *ThermOptmizer*.

Firstly, the VLE-LLE Methodology was validated for pure water, from 612 its parameter estimation with only saturation pressure and liquid density to 613 the gradual addition of the LLE term using weights. Eventually, a curve 614 with numerous possible parameter sets was generated in the form of Pareto 615 analyses. Employing a predetermined criterion, the Set of Parameters 03 for 616 water was selected in order to check if it is as efficient as the one published 617 in the literature (Kontogeorgis et al., 1999), but involving a more theoretical 618 background (Koh et al., 1993). 619

Thereon, the metric based on water content in dew point condition was 620 applied to binary aqueous mixtures with CO₂, H₂S and light hydrocarbons, as 621 well as multicomponent mixtures with these components, comparing to the 622 experimental data. There was a major improvement in the optimized results 623 compared to the literature data (Tsivintzelis et al., 2012), and the Set 03 624 produced similar or lower deviations than the literature set (Kontogeorgis 625 et al., 1999) in most of the cases. For instance, in the mixture $H_2O + CO_2$ 626 the deviations in the water content dropped from 23.7% to 3.3% in pressures 627 higher than 200 bar. 628

629

Finally, these results were applied to a simulation built in the Petrobras'

⁶³⁰ Process Simulator Petrox[®] (Niederberger et al., 2009). Although the Set 03 ⁶³¹ for water culminated in less conservatives (higher) values of water content ⁶³² in pressures from 100 bar and CO_2 content lower than 80%, it predicted the ⁶³³ expected inversion effect of the water content in all cases, unlike the literature ⁶³⁴ parameters in the case containing the stream with 10% of CO_2 in the natural ⁶³⁵ gas.

The results obtained in this work are examples of how these methodologies 636 can be applied. Hence, from the features of *ThermOptmizer* as a guide, and 637 with its further implementing, it is possible to perform even more complex 638 analyses. A suggestion for future studies is to improve the algorithm inserting 639 data on the respective liquid in equilibrium to the metric for light components 640 such as methane or CO_2 . Consequently, it would be possible to evaluate if the 641 parameters obtained here could predict properly liquid phase compositions 642 and, if necessary, generate new parameter values using the *ThermOptmizer*. 643

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647 Nomenclature

648 List of Abbreviations

CERE	center for energy resources engineering
CPA	cubic-plus-association
CR-1	combining rule defined by Eqs. (8) and (9)

EoS	equation of state
LLE	liquid-liquid equilibrium
NG	natural gas
NAG-1	natural acid gas 1
NAG-2	natural acid gas 2
NAG-3	natural acid gas 3
PR	Peng-Robinson equation of state
PSO	particle swarm optimization
SAFT	statistical associating fluid theory
SRK	Soave-Redlich-Kwong equation of state
VLE	vapour-liquid equilibrium

649 List of Symbols

- AAD average absolute density deviation calculated by Eq. (25) [%]
- AAP average absolute pressure deviation calculated by Eq. (24) [%]

 $AAX_{i,j}$ average absolute deviation for the composition of *i* in the phase rich in component *j*, calculated by Eqs. (26) and (27) [%]

AAY average absolute deviation for the water content in a gas [%]

 AAY_{200} average absolute deviation for the water content in a gas calculated only in the points with P > 200 bar [%]

 a_0 physical energy parameter of CPA EoS [bar L² mol⁻²]

- b co-volume parameter of CPA EoS [L mol⁻¹]
- c_1 parameter in the energy term of CPA EoS
- g radial distribution function (CPA EoS)

K_i	equilibrium constant $(\widehat{\phi}_{i(2)}/\widehat{\phi}_{i(1)})$
k_{ij}	binary interaction parameter from classical mixing rule
n_c	number of components
n_e	number of experimental points
n_v	number of calculated variables in the metric
P	pressure [bar]
P_c	critical pressure [bar]
P_{sat}	pure component saturation pressure [bar]
R	universal gas constant [$\approx 0.08314462~{\rm bar}~{\rm L}~{\rm mol}^{-1}~{\rm K}^{-1}]$
$S(\underline{X})$	objective function
S_{LLE}	objective function calculated by Eq. 19
S_{pure}	objective function calculated by Eq. 17
S_{otim}	optimized value of objective function $S(\underline{X})$
T	temperature [K]
T_c	critical temperature [K]
T_R	reduced temperature
V	volume [L]
w	acentric factor
X_{A_i}	fraction of type-A sites in molecule i not bonded at other sites
$x_{i(j)}$	composition of i in phase rich in component j
\underline{y}_{DG}	dry gas composition
y_{H_2O}	water content
Z	compressibility factor

650 Greek Letters

$\beta^{A_i B_j}$	association volume parameter between a type-A site in
	molecule i and a type-B site in molecule j
$\Delta^{A_i B_j}$	association strength between a type-A site in
	molecule i and a type-B site in molecule j
$\varepsilon^{A_i B_j}$	association energy between a type-A site in
	molecule i and a type-B site in molecule j [bar L mol ⁻¹]
ω	weight of the Eq. (21)
ϕ_L	liquid fugacity coefficient
ϕ_V	vapour fugacity coefficient
ρ, ρ_{liq}	liquid density
σ_k	variance of the variable k

651 Appendix A. Supplementary Material

⁶⁵² Supplementary data associated with this article can be found in the online⁶⁵³ version.

654 References

Abunahman, S. S., 2018. A computational tool for eos parameter estimation:
Evaluation of new methodologies and application in a natural gas processing simulation. Tese de M.Sc., COPPE/UFRJ, Rio de Janeiro, Brasil.

Anthony, R. G., McKetta, J. J., 1967. Phase equilibrium in the ethyleneethane-water system. Journal of Chemical and Engineering Data 12 (1),
21–28.

- Beltrao, R. L. C., Sombra, C. L., Lage, A. C. V. M., Netto, J. R. F., Henriques, C. C., 2009. Challenges and new technologies for the development
 of the pre-salt cluster, santos basin, brazil. In: Offshore Technology Conference. Houston, Texas, USA.
- Chapman, W. G., Gubbins, K. E., Jackson, G., 1988. Phase equilibria of
 associating fluids: chain molecules with multiple bonding sites. Molecular
 Physics 65 (5), 1057–1079.
- Chapoy, A., Mohammadi, A. H., Tohidi, B., 2005. Estimation of water content for methane + water and methane + ethane + n-butane + water
 systems using a new sampling device. J. Chem. Eng. Data 50, 1157–1161.
- ⁶⁷¹ Das, S., Koduru, P., Gui, M., Cochran, M., Wareing, A., Welch, S. M., Babin,
 ⁶⁷² B. R., Jul. 2006. Adding local search to particle swarm optimization. In:
 ⁶⁷³ IEEE Congress on Evolutionary Computation. Canada.
- Derawi, S. O., Michelsen, M. L., Kontogeorgis, G. M., Stenby, E. H., 2003.
 Application of the cpa equation of state to glycol/hydrocarbons liquidliquid equilibria. Fluid Phase Equilibria 209, 163–184.
- Folas, G. K., Froyna, E. W., Lovland, J., Kontogeorgis, G. M., Solbraa,
 E., 2007. Data and prediction of water content of high pressure nitrogen,
 methane and natural gas. Fluid Phase Equilibria 252, 162–174.
- Folas, G. K., Kontogeorgis, G. M., Michelsen, M. L., Stenby, E. H., 2006.
 Application of the cubic-plus-association (cpa) equation of state to complex
 mixtures with aromatic hydrocarbons. Ind. Eng. Chem. Res. 45, 1527–
 1538.

- GPSA, 1998. GPSA Engineering Databook, 11th Edition. GPSA Press, SI,
 Oklahoma, USA.
- Haghighi, H., Chapoy, A., Burgess, R., Tohidi, B., 2009. Experimental and
 thermodynamic modelling of systems containing water and ethylene glycol:
 Application to flow assurance and gas processing. Fluid Phase Equilibria
 276, 24–30.
- Huang, S. H., Radosz, M., 1990. Equation of state for small, large, polydis perse and associating molecules. Ind. Eng. Chem. Res. 29, 2284.
- Huang, S. S. S., Leu, A. D., Ng, H. J., Robinson, D. B., 1985. The phase
 behavior of two mixtures of methane, carbon dioxide, hydrogen sulfide,
 and water. Fluid Phase Equilibria 19, 21–32.
- Kennedy, J., Eberhart, R., 1995. Particle swarm optimization. In: Proceed ings of IEEE International Conference on Neural Networks. Perth, Aus tralia, pp. 1942–1948.
- Kobayashi, R., Katz, D. L., 1953. Vapor-liquid equilibria for binary
 hydrocarbon-water systems. Ind. Eng. Chem. 45 (2), 441–446.
- Koh, C. A., Tanaka, H., Walsh, J. M., Cubbins, K. E., Zollweg, J. A., 1993.
 Thermodynamic and structural properties of methanol-water mixtures: experiment, theory and molecular simulation. Fluid Phase Equilibria 83, 51.
- Kontogeorgis, G. M., Folas, G., 2010. Thermodynamic Models for Industrial
 Applications From Classical and Advanced Mixing Rules to Association
 Theories. Wiley, Amsterdam.

- Kontogeorgis, G. M., Michelsen, M. L., Folas, G. K., Derawi, S. O., von
 Solms, N., Stenby, E. H., 2006a. Ten years with the cpa (cubic-plusassociation) equation of state. part 1. pure compounds and self-associating
 systems. Ind. Eng. Chem. Res. 45 (14), 4855–4868.
- Kontogeorgis, G. M., Michelsen, M. L., Folas, G. K., Derawi, S. O., von
 Solms, N., Stenby, E. H., 2006b. Ten years with the cpa (cubic-plusassociation) equation of state. part 2. cross-associating and multicomponent systems. Ind. Eng. Chem. Res. 45 (14), 4869–4878.
- Kontogeorgis, G. M., Voutsas, E. C., Yakoumis, I. V., Tassios, D. P., 1996.
 An equation of state for associating fluids. Ind. Eng. Chem. Res. 35, 4310–
 4318.
- Kontogeorgis, G. M., Yakoumis, I. V., Heijer, H., Hendriks, E., Moorwood, T., 1999. Multicomponent phase equilibrium calculations for watermethanol-alkane mixtures. Fluid Phase Equilibria 201, 158–160.
- Li, Z., Firoozabadi, A., 2009. Cubic-plus-association equation of state for
 water-containing mixtures: Is cross association necessary? AIChE J.
 55 (7), 1803–1813.
- Lundstrøm, C., 2005. Modeling of phase equilibria for petroleum reservoir
 fluids containing water and hydrate inhibitors. M.Sc. dissertation, Center
 for Phase Equilibria and Separation Processes (IVCSEP), Department of
 Chemical Engineering, Technical University of Denmark, Denmark.
- 727 Maddox, R. N., Lilly, L. L., Moshfeghian, M., Elizondo, E., Mar. 1988. Esti-

mating water content of sour natural gas mixtures. In: Laurence Reid GasConditioning Conference. Norman, OK, USA.

- Maribo-Mogensen, B., Kontogeorgis, G. M., Thomsen, K., 2014. Development of an electrolyte cpa equation of state for applications in the
 petroleum and chemical industries. D.Sc. dissertation, Center for Energy
 Resources Engineering, Technical University of Denmark, Denmark.
- Michelsen, M. L., 2006. Robust and efficient solution procedures for association models. Ind. Eng. Chem. Res. 45, 8449–8453.
- Mohammadi, A. H., Chapoy, A., Richon, D., Tohidi, B., 2004. Experimental
 measurement and thermodynamic modeling of water content in methane
 and ethane systems. Ind. Eng. Chem. Res. 43, 7148–7162.
- Moraes, A. O. S., Mitre, J. F., Lage, P. L. C., Secchi, A. R., 2015. A robust
 parallel algorithm of the particle swarm optimization method for large
 dimensional engineering problems. Applied Mathematical Modelling 39,
 4223–4241.
- Nelder, J. A., Mead, R. A., 1965. Simplex method for function minimization.
 The Computer Journal 7, 308–312.
- Ng, H. J., Chen, C. J., Schroeder, H., 2001. Water content of natural gas
 systems containing acid gas. GPA Research Report RR-174.
- Niederberger, J., Gama, M. S., Santos, L. C., da Silva, J. A., Vargas, C. E.,
 Ahón, V. R. R., Silva, E. P., Souza, D. F. S., Aquino, C. A. S., Aires, J.
 S. S., 2009. Petrox petrobras technology in process simulation. Comput.Aided Chem. Eng. 27, 675–680.

- Olds, R. H., Sage, B. H., Lacey, W. N., 1942. Phase equilibria in hydrocarbon
 systems. composition of the dew-point gas of the methane-water system.
 Ind. Eng. Chem. 34 (10), 1223–1227.
- Oliveira, M. B., Coutinho, J. A. P., Queimada, A. J., 2007. Mutual solubilities of hydrocarbons and water with the cpa eos. Fluid Phase Equilibria
 258, 58–66.
- Peng, D. Y., Robinson, D. B., 1976. A new two-constant equation of state.
 Ind. Eng. Chem. Fundam. 15, 59–64.
- Prausnitz, J. M., Lichtenthaler, R. N., de Azevedo, E. G., 1998. Molecular
 Thermodynamics of Fluid-Phase Equilibria. Prentice Hall PTR, Upper
 Saddle River, New Jersey, USA.
- Reamer, H. H., Olds, R. H., Sage, B. H., Lacey, W. N., 1943. Phase equilibria
 in hydrocarbon systems. composition of dew-point gas in ethane-water
 system. Ind. Eng. Chem. 35 (7), 790–793.
- Reamer, H. H., Olds, R. H., Sage, B. H., Lacey, W. N., 1944. Phase equilibria
 in hydrocarbon systems. compositions of the coexisting phases of n-butanewater system in the three-phase region. Ind. Eng. Chem. 36 (4), 381–383.
- Santos, L. C., 2015. Desenvolvimento de um modelo de associação para
 cálculo de equilíbrio de fases de misturas complexas com ênfase em sistemas de interesse no processamento de gás natural. Tese de D.Sc.,
 COPPE/UFRJ, Rio de Janeiro, Brasil.

- Santos, L. C., Abunahman, S. S., Tavares, F. W., Ahón, V. R. R., Kontogeorgis, G. M., 2015a. Cubic plus association equation of state for flow
 assurance projects. Ind. Eng. Chem. Res. 54 (26), 6812–6824.
- Santos, L. C., Abunahman, S. S., Tavares, F. W., Ahón, V. R. R., Kontogeorgis, G. M., 2015b. Modeling water saturation points in natural gas
 streams containing co₂ and h₂s comparisons with different equations of
 state. Ind. Eng. Chem. Res. 54 (2), 743–757.
- Santos, L. C., Tavares, F. W., Ahón, V. R. R., Kontogeorgis, G. M., 2015c.
 Modeling mea with the cpa equation of state: A parameter estimation
 study adding local search to pso algorithm. Fluid Phase Equilibria 400,
 76–86.
- Schwaab, M., Jr., E. C. B., Monteiro, J. L., Pinto, J. C., 2008. Nonlinear
 parameter estimation through particle swarm optimization. Chemical Engineering Science 63, 1542–1552.
- Schwaab, M., Pinto, J. C., 2007. Análise de Dados Experimentais I: Fundamentos de Estatística e Estima ção de Parâmetros. e-papers, Rio de
 Janeiro, Brasil.
- Selleck, F., Carmichael, L., Sage, B., 1952. Phase equilibrium in the hydrogen
 sulfide-water system. Ind. Eng. Chem. 44, 2219–2226.
- Shi, Y., Eberhart, R., 1998. A modified particle swarm optimizer. In: Proceedings of the IEEE International Conference on Evolutionary Computation. Anchorage, Alaska.

- Shiguematsu, F. M., 2014. Cálculo de saturação de água em gás natural
 contendo gases ácidos. M.Sc. dissertation, Universidade Federal do Rio de
 Janeiro, Rio de Janeiro, Brasil.
- Smith, J. M., van Ness, H. C., Abbott, M. M., 2005. Introduction to Chemical
 Engineering Thermodynamics, 7th Edition. McGraw-Hill, New York.
- Soave, G., 1972. Equilibrium constants from a modified redlich-kwong equation of state. Chemical Engineering Science 27 (6), 1197–1203.
- Song, K. Y., Kobayashi, R., 1994. The water content of ethane, propane and
 their mixtures in equilibrium with liquid water or hydrates. Fluid Phase
 Equilibria 95, 281–298.
- Tsivintzelis, I., Kontogeorgis, G. M., Michelsen, M. L., Stenby, E. H., 2010.
 Modeling phase equilibria for acid gas mixtures using the cpa equation of
 state. part 1. mixtures with h₂s. AIChE Journal 56, 2965–2982.
- Tsivintzelis, I., Maribo-Mogensen, B., Frost, M., Folas, G. K., Muro-Sune,
 N., Leon, F. R., Breil, M. P., von Solms, N., Michelsen, M. L., Kontogeorgis, G. M., 2012. The cubic-plus-association eos parameters for pure
 compounds and interaction parameters. In: Report, CERE, Center for
 Energy Resources DTU, Copenhagen, Denmark.
- Tsonopoulos, C., Wilson, G. M., 1983. High-temperature mutual solubilities
 of hydrocarbons and water. part i: Benzene, cyclohexane and n-hexane.
 AIChE Journal 29 (6), 990–999.
- Wei, Y. S., Sadus, R. J., 2000. Equations of state for the calculation of fluidphase equilibria. AIChE Journal 46 (1), 169–196.

- Wertheim, M. S., 1984a. Fluids with highly directional attractive forces: I.
 statistical thermodynamics. J. Stat. Phys. 35 (1–2), 19–34.
- Wertheim, M. S., 1984b. Fluids with highly directional attractive forces: Ii.
 thermodynamic perturbation theory and integral equations. J. Stat. Phys.
 35 (1-2), 35-47.
- Wertheim, M. S., 1986a. Fluids with highly directional attractive forces: Iii.
 multiple attraction sites. J. Stat. Phys. 42 (3–4), 459–476.
- Wertheim, M. S., 1986b. Fluids with highly directional attractive forces: Iv.
 equilibrium polymerization. J. Stat. Phys. 42 (3–4), 477–492.
- Wiebe, R., Gaddy, V. L., 1941. Vapor phase composition of carbon dioxidewater mixtures at various temperatures and at pressures to 700 atmospheres. J. Am. Chem. Soc. 63, 475–477.
- Yakoumis, I. V., Kontogeorgis, G. M., Voutsas, E. C., Tassios, D. P., 1997.
 Vapor-liquid equilibria for alcohol/hydrocarbon systems using the cpa
 equation of state. Fluid Phase Equilibria 130, 31–47.
- Zirrahi, M., Azin, R., Hassanzadeh, H., Moshfeghian, M., 2010. Prediction
 of water content of sour and acid gases. Fluid Phase Equilibria 299 (2),
 171–179.