Detailed calculation of complex fluid phase equilibrium sections for ternary systems

Gerardo O. Pisoni[a, b, c], Martín Cismondi[b], Marcelo S. Zabaloy[c, *], Lucio Cardozo-Filho[a]

[a] *Departamento de Engenharia Química/Universidade Estadual de Maringá, 87020-900 Maringá, PR, Brazil*
[b] *IDTQ- Grupo Vinculado PLAPIQUI—CONICET, Argentina*
[c] *Planta Piloto de Ingeniería Química (PLAPIQUI), Departamento de Ingeniería Química (DIQ), Universidad Nacional del Sur (UNS)-CONICET, Bahía Blanca, Argentina*

ABSTRACT

Phase equilibrium diagrams of fluid phases in ternary systems can have a high complexity. In this work, a strategy and calculation methods for the computation of complete sections of ternary fluid phase equilibrium surfaces is proposed. To illustrate the methodology, we present computed results for the fluid phase equilibrium of an isothermal section for the ternary highly non-ideal system $CO_2 + H_2O + $ 2-propanol(IPA), as described by a given model and given set of values of the model parameters. The calculation method is based on the prior identification of (univariant) key points (KPs) of the ternary isotherm. From such KPs, it is possible to build the different equilibrium lines that constitute the ternary isothermal diagram, with the help of a numerical continuation method. The results show a high level of complexity including a number of three-phase loci, critical loci, and ternary critical endpoints, together with a ternary four-phase equilibrium point.

1. Introduction

The rigorous calculation of phase equilibria presents general interest in the simulation and optimization of separation processes, and it is also a matter of scientific interest. In such sense, procedures and calculation tools with the capability of computing phase equilibrium diagrams, especially if non-ideal and highly complex behaviors occur, are required. Moreover, the ability of computing complex equilibrium diagrams improves the understanding of the equilibrium phenomenology for systems with a highly non-ideal behavior. Such behaviors could present, in narrow ranges of pressure and/or temperature, a rich variety of phase equilibria. Such complexity could lead the untrained eye to misinterpret the experimental data. On the other hand, commercial software may fail when generating binary, ternary or multicomponent phase equilibrium diagrams, if the system behavior is highly complex.

Phase diagrams of particular interest are those computed for binary or ternary mixtures. Binary data are typically used to fit interaction parameters of phase equilibrium models, and ternary data, when available, to test model predictions. In both cases, the availability of reliable algorithms for the generation of phase diagrams useful to make the comparison between model and experimental data is of significant importance. This work focuses on the efficient and reliable generation of ternary phase equilibrium diagrams involving fluid phases only (solids are not considered in this work).

A type of section of special interest is the phase equilibrium diagram at constant temperature (isothermal diagram), since temperature is an easy to control variable in equilibrium experiments. An isothermal diagram is one that includes all equilibrium lines and special equilibrium points (e.g., pure compound liquid-vapor points) that become defined once the temperature value is set.

Most of the points (or hyper-points) belonging to a ternary isothermal diagram (TI) are phase equilibrium objects having two degrees of freedom (DOFs) (divariant (DV) objects), i.e., (indeed) the temperature, and some other intensive variable (e.g.: Pressure). Special points of a TI have a number of DOFs less than two (univariant (UV) or invariant (=zero variance, (ZV) points). The prefix "hyper" means "existing in a multidimensional space". This space is in this work made of several dimensions such as pressure, phase densities, phase compositions and temperature, just to mention the variables that can be measured in a laboratory. Notice that the variable (or variables) involved in a given specification that spends a DOF should be of the intensive type.

To fix ideas, as an example, a two-phase ternary equilibrium point is considered in this work not to contribute to a TI because it requires, according to the phase rule, to specify the values for three variables (trivariant (TV) points). Thus, the thermodynamic objects that are commonly part of a TI are mainly ternary critical lines (T-CLs) and ternary three-phase lines (T-3PLs).

The following terms refer to ternary fluid phase equilibrium objects. They have been used in previous publications (e.g., Refs. [1,2]). Details

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on their meanings are provided in Appendix B. The list of terms follows:

[a] ternary three-phase point (T-3PP)

[b] ternary three-phase line (T-3PL)

[c] ternary critical point (T-CP)

[d] ternary critical line (T-CL)

[e] ternary critical endpoint (T-CEP)

[f] ternary critical end line (T-CEL)

[g] ternary four-phase (equilibrium) point (T-4PP)

[h] ternary four-phase (equilibrium) line (T-4PL)

[i] ternary critical endpoint of a four-phase (equilibrium) line (T-CEP-4PL)

[j] ternary tricritical endpoint (T-TCEP) [also named ternary tricritical point (T-TCP)]

Some of the ternary phase equilibrium objects in the list above, e.g., the T-CELs, are elements of the characteristic map (T-CM, see Appendix D) [1] of the fluid phase behavior of the ternary system. Ref. [1] deals with the computation of T-CMs and Ref. [2] with the calculation of T-CELs.

A point of a T-CL has two DOFs. The same is true for a point of a T-3PL. Eventually, the ternary isotherm may contain ternary critical end points (T-CEP, one degree of freedom (DOF)), ternary four-phase equilibrium points (T-4PP, one DOF), binary critical points (B-CP, one DOF), ternary tricritical points (T-TCP, zero DOFs), ternary critical end point of a four phase line (T-CEP-4PL, zero DOFs), etc. A one or zero DOFs object is present in a TI if the set TI temperature equals the object's temperature. In this work, only T-CEPs, T-4PPs and B-CPs are considered, in the calculation examples, among the ternary objects with a number of DOFs less than two.

Schneider and Scheidgen [3] analyzed the experimental behavior of fluid phases for CO_2 + 1-decanol + n-tetradecane system. Such system, is presented as an example with complex and rare phenomenological behavior. This system shows types of behaviors that are uncommon for systems with three components, and the authors named these phenomena "Holes", "Windows" and "Closed loops". Three-dimensional (3D) diagrams of critical surfaces for the above ternary system are shown in Ref. [3]. These critical surfaces are complex and may have "miscibility windows". These miscibility windows can be observed in a diagram at constant pressure, where a homogeneous closed region is completely surrounded by a two-phase region. (see Ref. [3] Fig. 4a and b).

Scheidgen and Schneider [4] studied ternary systems of the type CO_2 + 1-alkanol + n-alkane. These systems exhibit behaviors as the ones mentioned in Ref. [3]. In Ref. [4] a ternary diagram at constant temperature (375 K, isothermal diagram), similar in nature to the computed diagrams presented in Appendix A of this work, is shown. This is Fig. 15 in Ref. [4]: [a] the system is CO_2 + decanoic acid + 1-dodecanol, [b] the figure includes a T-CL associated to the equilibrium phenomenon named "island system", and [c] the behavior shown in the figure is, in relative terms, simple. The phenomenon named "island system" is observed when a ternary fluid phase equilibrium diagram at constant pressure and temperature presents a closed two-phase region completely surrounded by an homogeneous region (see in Ref. [4] Fig. 14 [a,b and c] and Fig. 15).

Adrian et al. [5] reported experimental data on three phase equilibrium, four phase equilibrium and critical points for the CO_2 + H_2O + 1-propanol system. The authors used 3D qualitative phase diagrams at constant temperature with the aim of describing the equilibrium behavior observed for the system. Qualitative isotherms, made of sub-diagrams at constant T and P, were shown to appreciate the evolution of the ternary three-phase equilibrium. This is the case of Fig. 3 in Ref. [5], which shows that changes in pressure at constant temperature may result in going from sub phase diagrams having a single three-phase region to sub phase diagrams with presence of two different three-phase regions. This is also discussed, in a very detailed way, in Ref. [2]. Such complex ternary phase behavior might lead to

confusion when experimental works are carried out, if the level of awareness, about the wide-ranging possibilities for the ternary phase equilibrium phenomenology, is not high enough. One way to understand it is to analyze the (experimental or computed) ternary three-phase equilibrium in a wide range of pressure. For example, if, at constant temperature, a T-4PP is present within the covered pressure range, it should be known that four different three-phase regions originate at such point, i.e., two three-phase regions above the T-4PP pressure, and two three-phase regions below the T-4PP pressure.

Refs. [3–5] do not describe a calculation method to compute ternary isothermal diagrams. On the other hand, several diagrams are qualitative in such works, being used as an aid in interpreting the experimental data obtained. Adrian et al. [6] did declare and solve the mathematical conditions for some types of phase equilibrium objects involved in ternary isothermal diagrams. However, Ref. [6] lacks the description of procedures for starting off the calculation of the different equilibrium lines, and for computing their endpoints. It is important to mention that in Ref. [6] the relationship between the ternary isothermal phase diagrams and the ternary fluid phase equilibrium characteristic maps (T-CMs) was discussed. A definition for T-CMs is given in Appendix D.

The computation of a complex ternary section, in particular of an isothermal phase diagram, requires a detailed procedure, involving especially a strategy for obtaining the initial guesses for all variables that characterize a given equilibrium point. Ref. [7] describes an approach for calculating binary phase equilibrium diagrams at constant pressure or temperature using, as a starting point, information from higher level phase equilibrium diagrams previously computed. These diagrams are maps of the, in a way "global", binary fluid phase equilibrium behavior (B-CMs = binary characteristic maps). They are computed after setting the values of all pure-compound and interaction parameters. B-CMs were defined and classified by Scott and van Konynenburg [8] (without using the name B-CM) and involve UV and ZV binary fluid phase equilibrium objects, i.e., B-CMs are made of pure compound critical points, binary critical endpoints, binary critical lines (B-CLs), binary three phase lines (B-3PLs), pure compound vapor-liquid equilibrium lines (P-VPLs), etc. From these lines, UV key points are obtained in Ref. [7] which are relevant for a specified isothermal or isobaric section. Such key points are endpoints of the equilibrium lines which constitute the isothermal phase diagram (or the isobaric one). The advantage of applying the approach of Ref. [7] is that the use of thermodynamic stability tests is minimized or avoided. In addition, the knowledge of key points for the binary isotherm or isobar makes possible to deduce beforehand the qualitative topology of the isothermal or isobaric diagram to be calculated, which facilitates the development of more efficient algorithms and calculation methods. The algorithms in Ref. [7] are limited to the most frequent binary phase behavior types. The name used in Ref. [7] for the B-CMs is "global phase equilibrium diagrams". We feel that such name could lead some readers to confusion. We thus prefer to use the name B-CM. The word "map" seems appropriate since what a B-CM provides is the essential features and not the details of the binary phase behavior. A relatively recent discussion on the classification of the binary phase behavior is available in Ref. [9].

The main goal in this work is to extend the approach of Ref. [7], which deals with binary isothermal or isobaric phase equilibrium sections, to the computation of equilibrium sections for ternary systems. The case study here is a particularly complex ternary phase equilibrium isotherm, which will be built in a wide range of pressure, using information from the previously computed T-CM (see Appendix D). The selected ternary system is highly non-ideal.

A brief description of the methodology of computation of ternary phase equilibrium sections is anticipated in Appendix C.

The computations performed in this work are limited to a model system for which only the fluid state is available, i.e., the appearance of solid phases is not covered by the thermodynamic model used here. Thus, under part of the ranges of conditions of the fluid phase equilib-

ria here computed, the real system could present one or more solid phases.

2. Ternary characteristic map (T-CM)

Appendix D provides details on what at T-CM is.

For illustration purposes, Fig. 1 shows qualitatively a portion of a T-CM of possible existence. Each pure vapor pressure line (P-VPL, only one is shown in Fig. 1) ends at the pure critical point (P-CP). From the P-CP in Fig. 1 a binary critical line (B-CL) begins, and ends at a binary critical end point (B-CEP). From the B-CEP, two equilibrium lines originate, a binary three phase line (B-3PL) and a first ternary critical end line [T-CEL(1)]. The T-CEL(1) extends up to a first ternary critical end point of a four phase line [T-CEP-4PL(1)], from which, a second T-CEL(2) begins, that ends at a ternary tricritical point (T-TCP). A third T-CEL(3) exists between the T-TCP and a second T-CEP-4PL(2). Between the two T-CEPs-4PL a T-4PL develops. Finally, from the T-CEP-4PL(2) the T-CEL(4) begins, which extends towards low pressures and temperatures.

It is important to mention that the level of complexity of a computed T-CM depends on the system studied and on the thermodynamic model (and its parameter values) used to describe the phase equilibria. In Ref. [1] several computed T-CMs were presented, showing from simple to very complex topologies. Ref. [1] also provides a flowchart describing the calculation algorithm for computing T-CMs.

3. Key points in ternary isotherms

The case considered in this work is the one of a complex ternary phase equilibrium isotherm (isothermal section), but the methodology is analogous for a section at constant pressure (isobar).

For the isothermal case, (generally UV) KPs are determined from a T-CM once the temperature of the isotherm has been specified. Such KPs are the intersection points between the plane at the set constant temperature (isothermal plane, a vertical line in Fig. 1), and the univariant lines of the T-CM. The KPs to be considered in this work are: Binary three phase points (B-3PPs); binary critical points (B-CPs); ternary critical end points (T-CEPs) and ternary four phase points (T-

4PPs). Note that a TI may contain one or more of the KPs mentioned above. The number and nature of the KPs of the TI depends on the complexity of the T-CM. Invariant (ZV) points with a temperature equal to the TI temperature will also be KPs of the TI, e.g., points of the types T-TCP, T-CEP-4PL, etc. Examples of computed TIs having invariant points are not provided in this paper. Besides, since azeotropy is not considered in this work, we do not deal here with azeotropic KPs.

A given, already known, ternary or binary KP is then used to produce a first converged point of a given ternary isothermal equilibrium line. In this work, and for a TI, such lines are ternary three phase lines (T-3PLs), and ternary critical lines (T-CLs). Note that the basic natures of the ternary lines of a given section (T-3PLs and T-CLs) are the same than those of the univariant binary lines (B-3PLs and B-CLs). The number and nature of the KPs determine the types of lines constituting the TI. In this sense, one or more T-3PLs will be present in the TI if B-3PPs, T-4PPs and/or T-CEPs are found among the KPs of the TI. Similarly, one or more T-CLs will be present in the TI if B-CPs and/or T-CEPs are located at the TI temperature. A given T-3PL or T-CL may be limited by two KPs, or it may have only one KP as its endpoint and extend indefinitely towards low or high pressures.

4. Ternary isotherms computation

This section describes in more detail the general procedures and calculation methods applied in this work to compute complete ternary phase equilibrium TIs. Once the KPs are determined, the thermodynamic objects to be calculated are T-3PLs and/or T-CLs.

4.1. Ternary three phase equilibrium: T-3PPs and T-3PLs

In a ternary three-phase point (T-3PP) three (non-critical) phases co-exist in equilibrium. To compute a T-3PP, the iso-fugacity condition for each component in the three phases present at equilibrium must be satisfied. Furthermore, all phases must have the same absolute pressure and the same absolute temperature. The equations that must be solved simultaneously to compute a T-3PP are described in Appendix A.1. Such system of equations (App. A.1) has twelve equations and fourteen
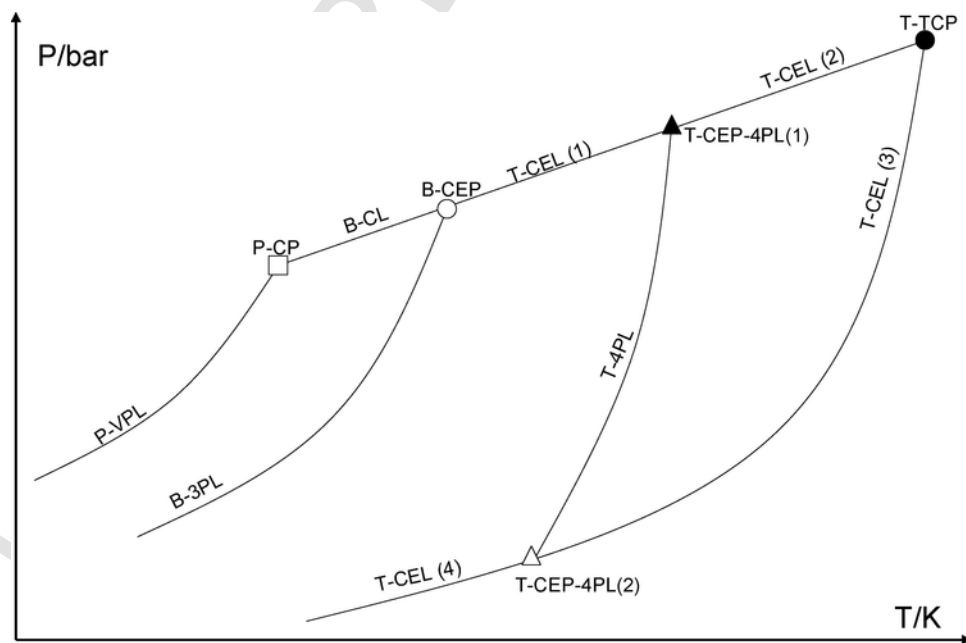

Fig. 1. Ternary phase behavior characteristic map (or a part of it). Qualitative diagram. P-VPL: Pure Compound Vapor Pressure Line. P-CP: Pure Compound Critical Point [□]. B-CL: Binary Critical line. B-CEP: Binary Critical End Point [B]. B-3PL: Binary three phase line. T-4PL: Ternary Four Phase Line. T-CEL: Ternary Critical End Line. T-CEP-4PL: Ternary Critical End Point of a Four Phase Line [T-CEP-4PL (1) for [:] and T-CEP-4PL (2) for [O]]. T-TCP: Ternary Tricritical Point [C].

variables (indeed before the DOFs are spent). The T-3PP variables are the following:

$$\Lambda^T = \begin{bmatrix} T & P & V^\alpha & V^\beta & V^\gamma & x_1^\alpha & x_2^\alpha & x_3^\alpha & x_1^\beta & x_2^\beta & x_3^\beta & x_1^\gamma & \cdots \end{bmatrix}$$

… where T is the absolute temperature, P is the absolute pressure, V^j is the molar volume of phase j. x_i^j is the mole fraction of component i in the phase j, where $i = 1$ to 3 and $j = \alpha, \beta$ or γ. Superscripts α, β and γ distinguish among the three phases in equilibrium. Since the number of equations (twelve equations) is less than the number of variables (fourteen variables), two variables must be specified to solve the system (or, more generally, two specifications have to be made). Note that, from the Gibbs phase rule, a T-3PP has two DOFs.

In Eq. (A.1.2) (Appendix A.1) it is assumed that all phases are represented by an EOS (φ–φ approach). If the γ–φ approach were used, then, only the vapor phase molar volume would be involved in the T-3PP system of equations (no liquid mixture molar volumes would appear), and the number of variables would be less than 14. However, the γ–φ approach cannot describe vapor-liquid critical points.

The information in each already known TI KP (KP of a type related to T-3PLs) can be used to initialize, at least in part, the vector Λ^T (Eq. (A.1.1)). Once Λ^T has been initialized, the T-3PP system of equations is solved to obtain the first converged point of the T-3PL to be computed.

All KPs (related to T-3PLs) have to be present in the final (full) set of calculated T-3PLs. This means that (in principle) all (known in advance) KPs must have been used in the process of computing the full set of T-3PLs of the TI.

To minimize the computation time, it is recommended to establish some order of priority for the KPs, in the context of their use in starting the calculations of the T-3PLs. According to the experience gained in the development of this work, the following order of priority seems to be appropriate:

1st: T-4PPs. If a KP is of the T-4PP type, then, four T-3PLs (of equal T for a TI) that originate at this point must be calculated (to understand why a T-4PP gives rise to four T-3PLs, see Section 4.1.1). To start the calculation of a T-3PL from a T-4PP has two important benefits. The first one being simplicity, as discussed in Section 4.1.1. Second, when the calculation of the four T-3PLs achieves completion, it is possible that some of the KPs not used to start the computation of such lines (e.g., a T-CEP) have been reached by the calculated T-3PLs, as their endpoints. These endpoints are immediately removed from the list of KPs not yet used to start the calculation of additional T-3PLs. Thus, duplication of computational effort is avoided. Notice that to start the computation of a T-3PL from a T-CEP is a task more complex (Section 4.1.3) than to start it from a T-4PP.

2nd: B-3PPs. Once all T-44Ps have been removed (during the T-3PLs calculation course) from the list of KPs not yet used to start the computation of additional T-3PLs, then, the KPs that are B-3PPs become the KPs of choice to begin the calculation of more T-3PLs. Starting the computation of a T-3PL from a B-3PP (Section 4.1.2) is slightly more complex than doing it from a T-4PP, but simpler than starting it from a T-CEP (Section 4.1.3).

3rd: T-CEPs. Finally, the calculation of T-3PLs starting from remaining isolated (not yet reached) T-CEPs (Section 4.1.3) has to be carried out. This is relatively more complex than doing it from a T-4PP or from a B-3PP.

In the following subsections, details are reported on how a converged T-3PP is obtained from a T-4PP, or from a B-3PP, or from a T-CEP.

4.1.1. Obtaining a converged T-3PP from a T-4PP key point

A converged T-44P is useful to obtain four T-3PPs each belonging to a different T-3PL. The system of equations valid at a T-4PP is analo-

gous to the one valid for a T-3PP shown in Appendix A.1. See paragraph about T-4PPs at the end of Appendix A.1.

At a T-4PP four non-critical phases coexit in equilibrium. The variables that characterize a T-4PP are the following: T, P, V^α, V^β, V^γ, V^δ, x_1^α, x_2^α, x_3^α, x_1^β, x_2^β, x_3^β, x_1^γ, x_2^γ, x_3^γ, x_1^δ, x_2^δ and x_3^δ. Where T is the absolute temperature, P is the absolute pressure, V^j is the molar volume of phase j, and x_i^j is the mole fraction of component i in the phase j, with i = 1 to 3 and j = α, β, γ, or δ. Superscripts α, β, γ, and δ distinguish among the four phases in equilibrium. Four different combinations of three phases at equilibrium are obtained from the set of four phases of a T-4PP: α-β-γ, β-γ-δ, α-β-δ and α-γ-δ. Each of these combinations is a mathematically converged T-3PP under the conditions of the already known T-4PP. Assume that the "α-β-γ" combination is chosen, then, the values of the variables of these three phases equal the values of the variables of a converged T-3PP (Eq. (A.1.1)), and from this converged T-3PP it is possible to start building the "α-β-γ" T-3PL. This procedure is repeated for each combination of three phases to complete the computation of the four T-3PLs that depart from an already calculated T-4PP.

4.1.2. Obtaining a converged T-3PP from a B-3PP key point

As previously stated, the variables that characterize a T-3PP are T, P, V^α, V^β, V^γ, x_1^α, x_2^α, x_3^α, x_1^β, x_2^β, x_3^β, x_1^γ, x_2^γ and x_3^γ. In a B-3PP the mole fraction variables x_3^α, x_3^β and x_3^γ (which imply the presence of the third component in each of the three phases) do not exist. A known converged B-3PP is useful to obtain a T-3PP where the third component is practically at infinity dilution while the other components have concentrations practically equal to those of the B-3PP.

More specifically, the procedure to initialize the variables of this T-3PP is to set T, P, V^α, V^β, V^γ, x_1^α, x_2^α, x_1^β, x_2^β, x_1^γ, x_2^γ equal to those of the known B-3PP, while x_3^α, x_3^β and x_3^γ are initialized to a value such that component 3 is highly diluted, for example at a mole fraction value equal to 1×10^{-6}. If convergence is not achieved, then, only one of the three mole fractions of the third component is set equal to a value in the order of 1×10^{-6}, e.g., $x_{3,\infty}^\alpha = 1 \times 10^{-6}$. The subscript "$\infty$" indicates "close to infinite dilution". Subsequently, the mole fractions of the component "3" in phase "β" and in phase "γ" are estimated using the following equations:

$$x_{3,\infty}^\beta = \frac{\overset{\wedge}{\varphi_3^\alpha}\left(T, V^\alpha, x_1^\alpha, x_2^\alpha, x_{3\to0}^\alpha\right)}{\overset{\wedge}{\varphi_3^\beta}\left(T, V^\beta, x_1^\beta, x_2^\beta, x_{3\to0}^\beta\right)} \cdot x_{3,\infty}^\alpha \tag{1}$$

$$x_{3,\infty}^\gamma = \frac{\overset{\wedge}{\varphi_3^\alpha}\left(T, V^\alpha, x_1^\alpha, x_2^\alpha, x_{3\to0}^\alpha\right)}{\overset{\wedge}{\varphi_3^\gamma}\left(T, V^\gamma, x_1^\gamma, x_2^\gamma, x_{3\to0}^\gamma\right)} \cdot x_{3,\infty}^\alpha \tag{2}$$

…where $x_{3,\infty}^\beta$ and $x_{3,\infty}^\gamma$ are the mole fractions of component "3" in the "β" and "γ" phases respectively, while $\hat{\phi}_3^\alpha$, $\hat{\phi}_3^\beta$ and $\hat{\phi}_3^\gamma$ are the fugacity coefficients of component 3 in the phases α, β and γ respectively. The fugacity coefficients are evaluated under the condition that the mole fraction of component 3 tends to zero in each of the phases. This is expressed as $x_{3\to0}^\alpha$, $x_{3\to0}^\beta$ and $x_{3\to0}^\gamma$; in this work $x_{3\to0}^j \cong 1 \times 10^{-30}$ is set. Note the difference between $x_{i,\infty}^j$ and $x_{i\to0}^j$. In this way an initial value has been assigned to all the variables of the first T-3PP. After convergence is achieved for the T-3PP, the calculation of the T-3PL is initiated with the help of a NCM. The initialization scheme based on Eqs. (1) and (2), is consistent with the values of the equilibrium ratios (or distribution coefficients) of component 3 when infinitely diluted in the binary three-phase system.

If a T-3PL tends to a B-3PP (this could be the case of a T-3PL whose calculation has been initiated at, e.g., a T-4PP), then, the mole fraction in each of the phases for the component that is not present in the B-3PP tends to zero. When this situation is detected (e.g.: when $\max[x_j^\alpha, x_j^\beta, x_j^\gamma] < 10^{-6}$, being j the component not present at the B-3PP), then, the calculation of the T-3PL is terminated.

4.1.3. Obtaining a converged T-3PP from a T-CEP key point

A known T-CEP is useful to obtain a T-3PP where two of the phases are quasi-critical (QC). This T-3PP can be named QC T-3PP.

In a T-CEP two phases coexist in equilibrium, a critical phase with a non-critical phase. The variables that characterize a T-CEP are: T, P, V^c, V^α, x_1^c, x_2^c, x_3^c, x_1^α, x_2^α, x_3^α, u_1, u_2, u_3 and λ. Where T is the absolute temperature, P is the absolute pressure, V^j is the molar volume of phase j, and x_i^j is the mole fraction of component i in the phase j, with $i = 1$ to 3 and $j = c$ or $j = \alpha$. The superscript "c" refers to the critical phase, and the superscript "α" refers to the non-critical phase. u_1, u_2 and u_3 are the three components of certain eigenvector related to the critical conditions to be satisfied by the ternary critical phase present in the T-CEP, and λ is the eigenvalue associated to such eigenvector. The conditions that must be satisfied to compute a ternary critical point and a T-CEP will not be treated in this work, for more details see Refs. [2,10].

Initializing variables to calculate a QC T-3PP using the information from a T-CEP is relatively more complex than the procedures presented in the sub-sections above. The values of temperature (T) and pressure (P) of the QC T-3PP are set equal to those of the known T-CEP. And the values of molar volume (V^α) and of mole fractions x_1^α, x_2^α and x_3^α of the (far from critical) phase "α" of the QC T-3PP are set equal to the corresponding values of the variables of the phase α (noncritical phase) present in the known T-CEP.

To produce a QC T-3PP, the critical phase of the T-CEP is taken to a condition where it splits into two quasi-critical phases (phases β and γ), having compositions close to that of the critical phase. To achieve this separation, it is necessary to know the direction (in the mole fractions space) along which it occurs. This would be somewhat complicated for the case of ternary mixtures, since the tie-line connecting the compositions of phases β and γ, could have, at first sight, any direction. However, a direction chosen at random will in most cases lead to a lack of convergence. To estimate the compositions of the quasi-critical phases, the following equations are used:

$$x_i^\beta = x_i^c + s u_i \sqrt{x_i^c} \quad i = 1..3 \tag{3}$$

$$x_i^\gamma = x_i^c - s u_i \sqrt{x_i^c} \quad i = 1..3 \tag{4}$$

… where x_i^β and x_i^γ are the unknown mole fractions of component i in phase β and phase γ of the QC T-3PP, respectively, and x_i^c is the known mole fraction of component i in the critical phase "c" of the T-CEP. u_i is a known component of the eigenvector mentioned above and "s" is a distance parameter that is set equal to a value of about 1×10^{-5}. Eigenvector $\vec{u}$ is the direction along which the split of the critical phase is to be carried out. Eqs. (3) and (4) are based on Eq. (5) of Appendix A of Ref. [2].

Once the values for the mole fractions of each component in the phase "β" and phase "γ" are obtained from Eqs. (3) and (4), V^β and V^γ are calculated at the temperature and pressure of the T-CEP using the chosen EOS (SRK-EOS [11] in this work). At this point all variables of the QC T-3PP have an initial value assigned. Next, the QC T-3PP point is converged. To do so, the specified variable is, in this work, the ratio of molar volumes V^α/V^β of the quasi-critical phases. This ratio is set equal to a value close to unity, e.g., 0.9995 (we remind that, at set temperature (or set pressure), a T-3PP has as single DOF left). This value makes possible to avoid the trivial solution during the process of

converging the QC T-3PP, since it forces the QC phases to be different, while keeping their properties very similar. With this QC T-3PP already converged and with the help of a NCM, the complete T-3PL is calculated.

A T-3PL could tend to a T-CEP. This may happen for T-3PLs having departure points of any kind (i.e, a T-4PP or a B-3PP or another T-CEP: in this last case the T-3PL has a T-CEP in each of its ends.). If a T-3PL tends to a T-CEP, two of the three phases in equilibrium become identical in composition and molar density (or molar volume), in other words, two of the three phases in equilibrium in the T-3PL become critical. The detection of this situation is used by the algorithm to terminate the calculation of the T-3PL. More specifically, when $\left| x_{1(i)}^\beta - x_{1(i)}^\alpha \right|$, $\left| x_{2(i)}^\beta - x_{2(i)}^\alpha \right|$, $\left| x_{3(i)}^\beta - x_{3(i)}^\alpha \right|$ and $\left| V_{(i)}^\beta - V_{(i)}^\alpha \right|$ are all simultaneously less than 1×10^{-6}, then, it is assumed that phases "α" and "β" have become critical for the "i^{th}" calculated point of the T-3PL: computations are then stopped. The use of the NCM makes possible to distinguish between the trivial solution and criticality when approaching a T-CEP, during the computation of a T-3PL.

4.2. Ternary critical equilibrium: t-CP and T-CL

A critical point (e.g., a T-CP or a B-CP) is a state where a stable fluid phase is at its limit of intrinsic stability. By "stable" we generally mean that the fluid is neither unstable nor metastable. A critical point belongs simultaneously to the phase coexistence surface and to the spinodal surface.

The vector of variables that are used in this work to describe a T-CP is the following:

$$\Lambda_{T-CP}^T = \begin{bmatrix} T & P & V & x_1^c & x_2^c & x_3^c & u_1 & u_2 & u_3 & \lambda \end{bmatrix} \tag{5}$$

T is the absolute temperature, P is the absolute pressure, V is the molar volume, and x_i^c is the mole fraction of component i in the critical phase "c", where $i = 1$ to 3 . u_1, u_2 and u_3 are the three components of certain eigenvector related to the critical conditions to be satisfied by the ternary critical fluid, and λ is the eigenvalue associated to such eigenvector.

The KPs from which the calculation of a T-CL can be initiated are: binary critical points (B-CPs) and ternary critical end points (T-CEPs). Starting a T-CL from a T-CEP is a relatively simple procedure, since the critical phase present in the T-CEP is already a converged critical point. The values of the variables of the critical phase in the known T-CEP equal the values of the variables of the first point of the T-CL. The application of a NCM is thus straightforward: there is no need to converge the first T-CP.

If during the computation progress of a T-CL such line tends to a T-CEP as its endpoint, then, the "critical phase" present in the T-CL will become "globally unstable" by the appearance of the "non-critical phase" present in the T-CEP.

A known B-CP is useful to obtain a converged T-CP where the third component is in practical terms infinitely diluted in the original critical binary system.

The variables by which a B-CP is described are in this work: T, P, V, x_1^c, x_2^c, u_1, u_2 and λ. The difference between a B-CP and a T-CP is that for a B-CP the variable x_3^c does not exist; and so is the case for u_3. Note that the eigenvector components in this case (B-CP) are two since it is a binary point. To obtain a converged T-CP, all variables of the T-CP which also exist in the B-CP are, for the T-CP, set equal to those of the known B-CP, except for λ and for the components of the eigenvector. Next, the value 1×10^{-6} is assigned to x_3^c. This value corresponds, practically, to the infinite dilution limit. The eigenvalue λ and the eigenvector of components u_1, u_2 and u_3 are associated to a 3×3 matrix whose elements are second derivatives with respect to composition

of the natural logarithms of the fugacities. These elements depend on temperature, critical volume and mole fractions, including x_3^c. After setting $x_3^c = 1 \times 10^{-6}$, the values of the elements of the matrix become defined. The eigenvalue and eigenvector calculation, which is straightforward, is then carried out. At this point all variables of the first T-CP of the T-CL have initial values assigned. The T-CP is then calculated, at the TI temperature, setting $x_3^c = 1 \times 10^{-6}$, thus spending the second DOF of the T-CP.

Priority is ascribed to T-CEPs over B-CPs (if both types of KPs are present in the set of KPs) for starting the computation of the T-CLs of the phase equilibrium section to be calculated.

For details on procedures and systems of equations to calculate multicomponent/ternary critical points or related objects see Refs. [2,10].

5. Results and discussion

To illustrate the results that can be obtained by using the computation strategy here proposed, for calculating phase equilibrium sections for ternary systems, a complete, quite complex, phase equilibrium ternary isotherm (TI) was computed for the $CO_2 + H_2O + 2$-propanol(IPA) system. The model used is the SRK-EOS [11] coupled to van der Waals mixing rules, which are quadratic with respect to mole fraction.

The choice of system $CO_2 + H_2O + 2$-propanol is motivated in its highly non-ideal behavior, which includes the existence of four-phase equilibria. The computations over wide ranges of conditions carried out for this system are stringent tests for the proposed computation strategy.

Table 1 shows the parameter values [12] used for the three pure components of this ternary system. These parameters are required to carry out the calculations using the SRK equation of state (EOS) [11]. Table 2 reports the values of binary interaction parameters [13] used here. Table 3 reports the predicted types of phase behavior (according to the classification of Scott and van Konynenburg [8]) of the three binary sub-systems of the ternary system, i.e., it reports the types of B-CMs. Such B-CMs (and the ternary behavior) are the result of the parameter values in Tables 1 and 2. The calculation algorithms used to obtain the B-CMs are described in Ref. [14].

To compute a TI, using the methodology proposed in this paper, the computed T-CM for the studied ternary system is required. Figs. 2 and 3 show part of the T-CM computed for the $CO_2 + H_2O + 2$-propanol system following the procedures of Ref. [1]. As it can be seen, the T-CM for this system is highly complex and it is composed of a variety of thermodynamic objects, including: T-CELs, T-4PLs, T-CEP-4PLs, T-TCPs, etc. T-CELs are identified with the labels "a", "b", "c", etc. Fig. 3

is a zoom of Fig. 2. This region has a large number of thermodynamic objects.

The temperature at which the phase equilibrium isotherm was calculated is T = 330 K (vertical line in Figs. 2 and 3). The choice of this temperature value implies a maximum number of intersection points between the constant temperature (330 K) hyper-plane and the system's univariant lines. A greater number of intersection points implies a greater complexity for the ternary phase equilibrium isotherm to be calculated. Figs. 2 and 3 show the plane at T = 330 K as well as its intersection points with the univariant lines of the T-CM. These points are the UV KPs to be used to calculate the ternary isotherm.

The KPs at 330 K are a total of six, and are identified as: T-CEP (e) (Fig. 2), and (Fig. 3) T-CEP (d), T-CEP (a), T-4PP, T-CEP (c) and B-CP. Note that the labels "a", "c", "d" and "e" that identify these KPs, are the same than those of the T-CELs to which they belong. Tables A.3.1–A.3.3 in Appendix A.3 report the calculated values of all variables that characterize each of these KPs.

5.1. Results shown in prism diagrams

Fig. 4 shows a three dimensional diagram (3D) with the complete TI calculated. This diagram is a 3D phase equilibrium prism. Its base is the well-known Gibbs triangle, regularly used to represent ternary phase compositions. A given side of the Gibbs triangle corresponds to one of the three binary sub-systems of the ternary system. Notice that the phase equilibria of the binary subsystems at 330 K is not shown in Fig. 4. If shown, they would be seen on the vertical prism faces. The only exception is the B-CEP indicated in Fig. 4, which is located in the CO2 + IPA prism face. In this work, the concentration scale in the prisms is the mole fraction.

Four points in a prism, interconnected by straight lines (tie-lines), all having the same pressure and temperature (i.e., being all located within the same horizontal plane), represent the compositions of four ternary phases which are at equilibrium (T-4PP), at the set temperature and pressure (see the four empty squares in, e.g., Fig. 5). If the number of points is three instead of four, then, the three interconnected points correspond to a T-3PP. Clearly, a T-3PP corresponds to an horizontal triangle located inside the prism.

Since in a T-CP only a single phase is involved, a T-CP is represented by a single point (single composition) located inside the Gibbs triangle (e.g., full circles in Figs. A.2.2 and A.2.3). Figs. A.2.2 and A.2.3 in Appendix A.2, are examples of representations of ternary phase equilibria at set temperature and pressure in the Gibbs triangle. Clearly, if at constant temperature the pressure is variable, then, the equilibria are to be represented in a 3D prism like the ones in, e.g., Fig. 4 or Fig. A.2.1. In the prism, a continuous set of T-3PPs (T-3PL) will be seen as three continuous lines each showing the evolution of a given vertex of the three-phase equilibrium triangle, i.e., each showing the evolution of the composition of one of the three phases at three-phase equilibrium (e.g., solid lines in Fig. 8, i.e., T-3PL(4)). On the other hand, a continuous set of T-CPs is represented in the prism by a single line (e.g., T-CL(2) in Fig. 5).

Finally, in a prism at constant temperature, the ternary four-phase equilibrium is not seen as a set of four continuous lines, but as a single horizontal quadrilateral, i.e., the T-4PP exists only at a specific pres-

Table 1
Pure compound critical constants and acentric factor used in this work [12].

Compound	Critical Temperature (K)	Critical Pressure (bar)	Acentric Factor
2-propanol	508.3	47.64	0.6669
CO_2	304.21	73.83	0.2236
H_2O	647.13	220.55	0.3449

Table 2
Interaction parameters (SRK-EOS) [11].

Ternary System	Interaction Parameters [13]					
	Attractive			Repulsive		
	k_{12}	k_{13}	k_{23}	l_{12}	l_{13}	l_{23}
$CO_2(1) + H_2O(2) + 2$-propanol(3)	−0.053	0.017	−0.207	0	0	0

Table 3

Predicted type of phase behavior for the binary sub-systems (SRK-EOS. Parameters from Tables 1 and 2).

Ternary System	Type of phase behavior [8]		
	1–2	1–3	2–3
$CO_2(1) + H_2O(2) + 2$-$Propanol(3)$	III	II	II

sure once the temperature is fixed. This is because a T-4PP has only one DOF (e.g., squares in Fig. 6).

Figs. 4 and 5 show all the key points previously identified in Figs. 2 and 3. This figure also shows the computed T-3PLs and T-CLs, which begin or end at such KPs. In particular, there are four T-3PLs. All of them originate at the T-4PP.

Fig. 5 shows the isotherm in a pressure range from 101 to 108 bar. In order to distinguish between T-3PLs these are identified with the labels "1", "2", "3" and "4". T-3PL(1) and T-3PL(2) are located at pressures above the T-4PP pressure, while the T-3PL(3) (Fig. 5) and T-3PL(4) (Fig. 4) develop at pressures below the T-4PP pressure.

T-3PL(1) ends at the KP named T-CEP(d) (Fig. 5). Two of the three phases in equilibrium become critical (i.e., identical) at this point. T-3PL(2) starts at the T-4PP and ends at the KP named T-CEP(a) (Fig. 5). The pressure of the T-CEP(a) is less than the pressure of the T-CEP(d) (Fig. 5).

On the other hand, T-CL(1) stems from the critical phase of the T-CEP(a) (Fig. 5). The situation is the same for the T-CL(2) and the T-CEP(d) (Fig. 5). The T-CL(1) ends at the B-CP previously identified as a KP for the T = 330 K phase equilibrium isotherm (Fig. 5). The calculation of a converged T-CP using the information of this B-CP was not necessary because the T-CL (T-CL(1)) calculated using the information of the T-CEP(a) naturally tended to the B-CP in Fig. 5.

If the calculation departing from the B-CP were anyway done, then, the same T-CL(1) would be obtained, but it would grow, during the computation progress, in the opposite sense that in the default calculation procedure (such default procedure starts in this case at the location of the T-CEP(a)).

T-CL(2) stems from the critical phase of T-CEP(d) (as previously stated) and ends at T-CEP(c) (Fig. 5), i.e., both endpoints have the

same nature (both are T-CEPs). Notice that the pressure range of existence of the T-CL(2) includes the T-4PP pressure (this is more easily seen in Fig. 10).

Fig. 6 shows the 330 K isotherm in a narrower pressure range (102.6–104.4 bar). The T-3PL(1) and T-3PL(2) are shown to be located above the T-4PP. In addition, three-phase tie-lines are shown at three selected pressure values for both T-3PLs (six T-3PPs in total). This figure shows the existence for a given (properly set) constant pressure and given constant temperature (330 K) of two different three-phase regions. This happens within a pressure range located above the T-4PP pressure in Fig. 6. In other words, the continuous set of pairs of three-phase regions originate at the T-44P.

However, when the three-phase equilibrium of the T-3PL(2) reaches the T-CEP(a) (Fig. 6), the three-phase region associated to the T-3PL(2) comes to an end (Fig. 6). Then, at a given pressure greater than the T-CEP(a) pressure, there is only a single three-phase region (the one of the T-3PL(1), Fig. 5), which also comes to an end when the pressure of the T-CEP(d) (Fig. 5) is reached. Note in Fig. 6, that as the pressure increases, the length of one side of the three-phase triangle for the T-3PL(2) decreases, and this side of the triangle eventually collapses, resulting in a critical phase when the T-CEP(a) is reached (Fig. 6).

Fig. 7 shows the 330 K isotherm within the pressure range (101.4–103 bar) in which the two T-3PLs located below the pressure of the T-4PP are observed. The T-3PL(3) originates at the T-4PP and ends at the T-CEP(c). At this point the T-3PL(3) continuous set of three-phase regions (each region described by a pressure value and by three tie-lines) ends. As in the previous case of Fig. 6, but in a narrower pressure range (102.1–102.7 bar, Fig. 7), two different three-phase regions coexist at a given constant pressure and temperature (Fig. 7).

Fig. 8 shows, in the rotated prism, the T-3PL(4) which starts at the T-4PP and extends over a wide range of pressure, approximately from 102.7 bar down to 70 bar. The T-3PL(4) ends when the T-CEP(e) is reached. In this figure it can be clearly observed, e.g., how one side of the three-phase equilibrium triangle decreases in size as pressure decreases, collapsing into a point when the T-CEP(e) is reached. From the critical phase of T-CEP(e), the calculated T-CL (3) departs, extending indefinitely towards high pressures (Figs. 4 and 9) (in this case the calculation of T-CL(3) was stopped when the pressure reached 1000 bar). This implies that the model predicts that immiscibility will be observed up to indefinitely high pressures (the presence of a critical point at a
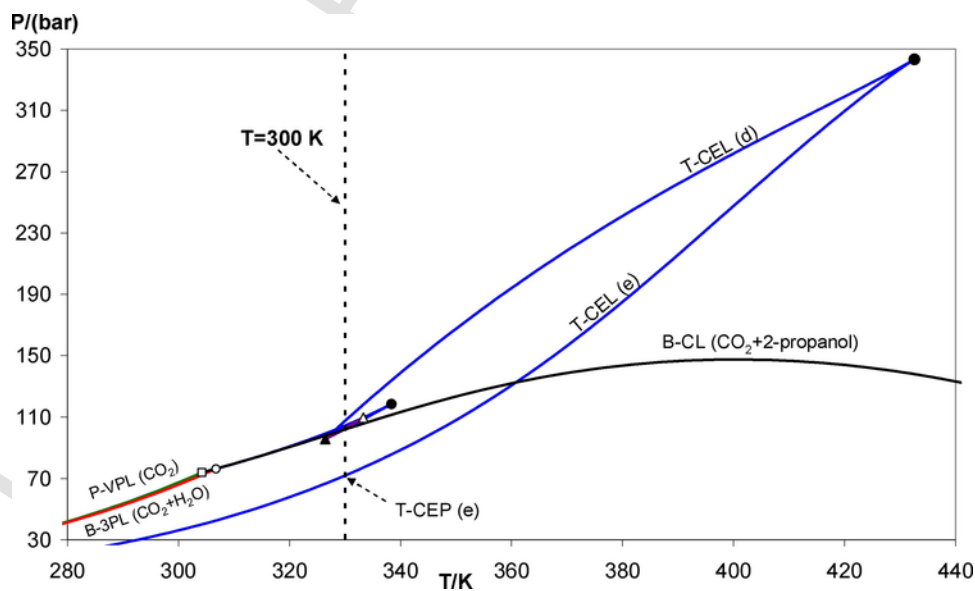

Fig. 2. Pressure-Temperature projection of part of the calculated ternary characteristic map (T-CM) for the CO_2 + H_2O + 2-Propanol system. Model: SRK-EOS [11]. Parameters in Tables 1 and 2. P-VPL: Pure Vapour Pressure Line. P-CP: Pure Critical Point [□]. B-3PL: Binary Three Phase Line. B-CL: Binary Critical Line. B-CEP: Binary Critical End Point [B]. T-CEP-4PL: Ternary Critical End Point of a Four Phase Line (T-CEP-4PL (1) [O] and T-CEP-4PL (2) [:]). T-CEL: Ternary Critical End Line [T-CEL (d and e)]. T-CEP: Ternary Critical End Point [T-CEP (e)]. T-TCP: Ternary Tricritical Point [C].
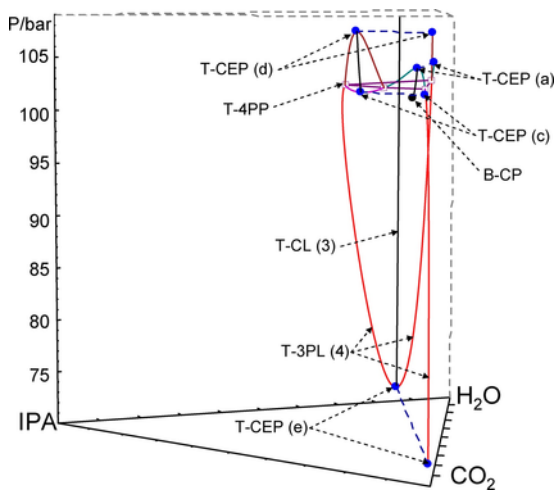
Fig. 4. Computed ternary phase equilibrium isotherm. Temperature: 330 K. System: CO_2 + H_2O + 2-Propanol(IPA). SRK-EoS [11]. Parameters in Tables 1 and 2. The light dashed auxiliary arrows are included to facilitate the identification of the phase equilibrium objects. T-CEP: Ternary Critical End Point (a, c, d and e). T-4PP: Ternary Four Phase Point. B-CP: Binary Critical Point. T-CL: Ternary Critical Line. T-3PL: Ternary Three Phase Line (4). Pairs of circles [◯] connected by a dashed tie-line indicate the T-CEP phase compositions and pressure. Empty squares [▢] indicate the T-4PP phase compositions and pressure. Concentration scale in the Gibbs triangle: mole fraction. Note: arrows are not to be confused with tie lines.
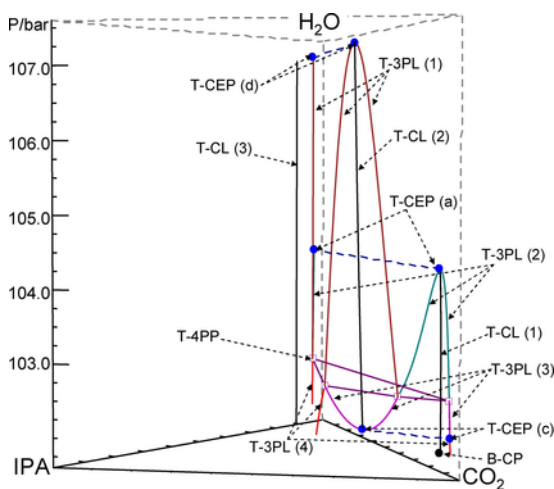
Fig. 5. Zoom of Fig. 4. Pressure range from B-CP pressure to T-CEP (d) pressure. Computed ternary phase equilibrium isotherm. Temperature: 330 K. System: CO_2 + H_2O + 2-Propanol(IPA). SRK-EoS [11]. Parameters in Tables 1 and 2. T-CEP: Ternary Critical End Point (a, c, d). T-4PP: Ternary Four Phase Point. B-CP: Binary Critical Point. T-CL: Ternary Critical Line (1, 2 and 3). T-3PL: Ternary Three Phase Line (1, 2, 3 and 4). Pairs of circles [◯] connected by a dashed tie-line indicate the T-CEP phase compositions and pressure. Empty squares [▢] indicate the T-4PP phase compositions and pressure. Concentration scale in the Gibbs triangle: mole fraction. Note: arrows are not to be confused with tie lines.

given temperature and given pressure implies the presence of an immiscibility region under such conditions of temperature and pressure).

The previous figures illustrate how complex the phase behavior of a ternary system could be. Thus, relatively elementary algorithms for computing the ternary phase behavior should be expected to fail in cases as the one here considered.

5.2. Results shown in 2D diagrams

Fig. 9 shows the pressure (P) vs. $Ln\hat{f}_1$ projection of the computed T-CLs and T-3PLs, for the 330 K phase equilibrium isotherm of system
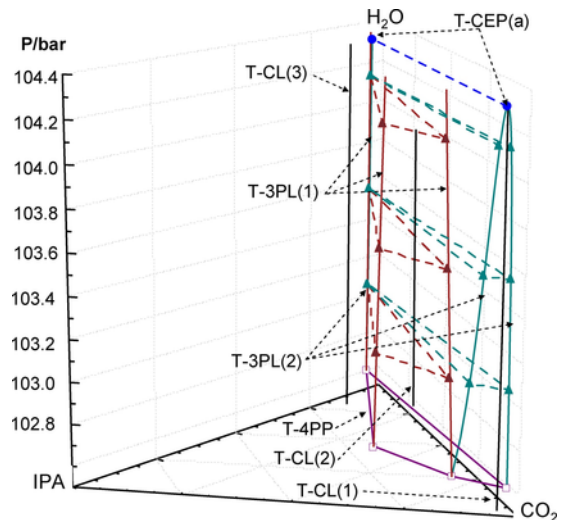

Fig. 6. Zoom of Fig. 4. Pressure range from the T-4PP pressure to the T-CEP (a) pressure. Computed ternary phase equilibrium isotherm with indication of six T-3PPs. Temperature: 330 K. System: CO_2 + H_2O + 2-Propanol(IPA). SRK-EoS [11]. Parameters in Tables 1 and 2. T-CEP: Ternary Critical End Point (a). T-4PP: Ternary Four Phase Point. T-CL: Ternary Critical Line (1, 2 and 3). T-3PL: Ternary Three Phase Line (1 and 2). T-3PP: Ternary three-phase point. Pairs of circles [◯] connected by a dashed tie-line indicate the T-CEP phase compositions and pressure. Empty squares [▢] indicate the T-4PP phase compositions and pressure. Triangle with dashed sides: T-3PP at set temperature and pressure. The dashed sides are the T-3PP tie-lines. The dashed sides connect full triangles [▲ and ▼] which indicate the phase compositions and the pressure of the T-3PP. Concentration scale in the Gibbs triangle: mole fraction. Note: arrows are not to be confused with tie lines.
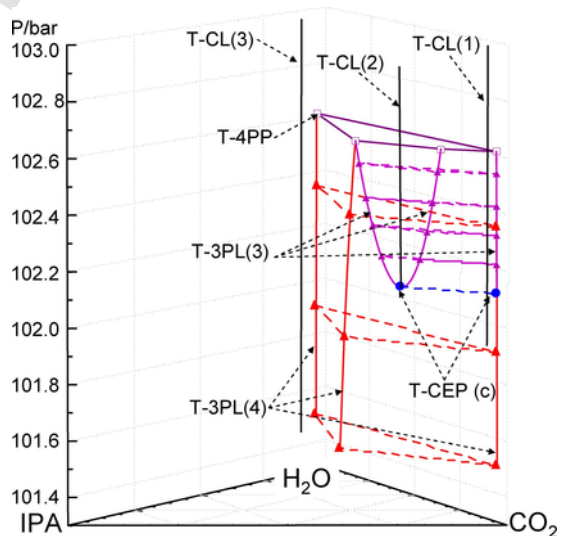

Fig. 7. Zoom of Fig. 4. Pressure range from slightly below the T-CEP (c) pressure to the T-4PP pressure. Computed ternary phase equilibrium isotherm with indication of several T-3PPs. Temperature: 330 K. System: CO_2 + H_2O + 2-Propanol(IPA). SRK-EoS [11]. Parameters in Tables 1 and 2. T-CEP: Ternary Critical End Point (c). T-4PP: Ternary Four Phase Point. T-CL: Ternary Critical Line (1, 2 and 3). T-3PL: Ternary Three Phase Line (3 and 4). T-3PP: Ternary three-phase point. Pairs of circles [◯] connected by a dashed tie-line indicate the T-CEP phase compositions and pressure. Empty squares [▢] indicate the T-4PP phase compositions and pressure. Triangle with dashed sides: T-3PP at set temperature and pressure. The dashed sides are the T-3PP tie-lines. The dashed sides connect full triangles [▲ and ▼] which indicate the phase compositions and the pressure of the T-3PP. Concentration scale in the Gibbs triangle: mole fraction. Note: arrows are not to be confused with tie lines.
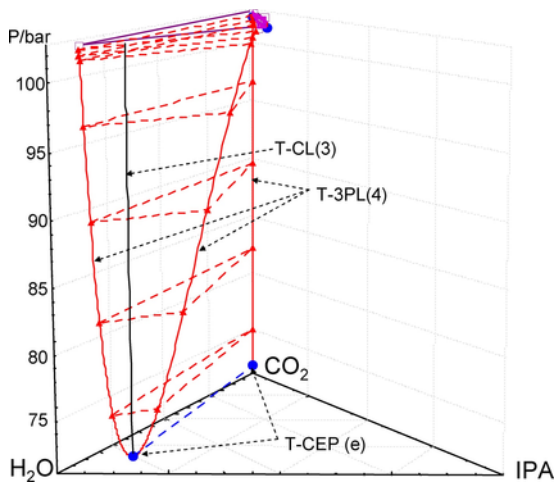
Fig. 8. Zoom of Fig. 4. Pressure range from the T-CEP (e) pressure to almost the T-4PP pressure. Computed ternary phase equilibrium isotherm with indication of several T-3PPs. Temperature: 330 K. System: CO_2 + H_2O + 2-Propanol(IPA). SRK-EoS [11]. Parameters in Tables 1 and 2. T-CEP: Ternary Critical End Point (e). T-4PP: Ternary Four Phase Point. T-CL: Ternary Critical Line (3). T-3PL: Ternary Three Phase Line (4). T-3PP: Ternary three-phase point. Pairs of circles [○] connected by a dashed tie-line indicate the T-CEP phase compositions and pressure. Empty squares [□] indicate the T-4PP phase compositions and pressure. Triangle with dashed sides: T-3PP at set temperature and pressure. The dashed sides are the T-3PP tie-lines. The dashed sides connect full triangles [▴] which indicate the phase compositions and the pressure of the T-3PP. Concentration scale in the Gibbs triangle: mole fraction. Note: arrows are not to be confused with tie lines.

$CO_2(1)$ + $H_2O(2)$ + 2-propanol(3). $\hat{f}_1$ is the fugacity of component 1 in the system.

Note that $\hat{f}_1$ is the same in all phases when these phases are at equilibrium (i.e., $\hat{f}_1$ is a "field" variable). The "field variable" nature of $\hat{f}_1$ makes interesting the study of equilibrium diagrams with $\hat{f}_1$ as one of its axes, when only one of the two measurable field variables T and P has been allowed to vary. In this case the "P vs. $Ln\hat{f}_1$" projection was selected, although the "P vs. $Ln\hat{f}_2$" or "P vs. $Ln\hat{f}_3$" projections would lead to graphics providing the same essential information. Fig. 9 shows

mainly how the T-3PL(4) reaches the T-CEP(e) at which the T-CL(3) begins.

The region in Fig. 9 with the highest concentration of equilibrium lines and KPs (region enclosed by a circle in Fig. 9) is best seen in Fig. 10, which is a zoom Fig. 9. In this figure it is observed that the four T-3PLs stem from the T-4PP. At pressures above the T-4PP pressure, the T-3PL(1) which ends at the T-CEP(d), and the T-3PL(2) which ends at the T-CEP(a), are visualized. Analogously, at pressures below the T-4PP pressure, the T-3PL(3) which ends at the T-CEP(c) and the T-3PL(4) which ends at the T-CEP(e) (Fig. 9) are seen.

Finally, the T-CLs departing from the critical phases of the corresponding T-CEPs are observed. T-CL(1) originates (Fig. 10) at the critical phase of the T-CEP(a) and ends at the B-CP (CO_2 + 2-propanol), while T-CL(2) begins (Fig. 10) in the critical phase of T-CEP(d) and ends at the critical phase of T-CEP(c).

Fig. 11 is a zoom of Fig. 10. It shows that T-3PL(3) and T-3PL(4) do not overlap (as it could have been concluded from looking at Fig. 10). In Fig. 11, it can be seen that the end point of the T-CL(2) does not match exactly (as it should) the T-CEP(c). This is ascribed to round-off errors of floating point operations.

Note the significant difference in complexity between this type of diagrams (P vs. $Ln\hat{f}_1$) and the 3D prisms of Figs. 4–8. In the diagrams "P vs. $Ln\hat{f}_1$" all the elements of the 330 K TI become reduced either to a single point, or to a single line in the 2D space. For example, in the 3D prisms the T-4PP was represented by four square markers (i.e., 4 points in the 3D space, e.g., Fig. 7) and their connecting tie-lines. In contrast, the same T-4PP in the "P vs. $Ln\hat{f}_1$" diagram becomes a single point in a 2D space (Fig. 10), since $\hat{f}_1$ is the same in all phases. The same applies to the T-3PLs: in the 3D prism three lines are required to represent the three-phase locus (e.g., T-3PL(4) in Fig. 4), whereas in a diagram "P vs. $Ln\hat{f}_1$" a T-3PL is represented by a single line, as shown in Figs. 9–11.

Diagrams such as those of Figs. 9–11 could be named "ternary isothermal phase equilibrium maps". They are, in a way, analogous to the T-CMs such as the one of Fig. 2. An important difference is that the axes in Fig. 2 correspond to measurable variables (T and P), while the abscissa $\left(Ln\hat{f}_1\right)$ in Figs. 9–11 is not a measurable quantity. In spite of this, Figs. 9–11 are useful to see, at a glance, the key features of the behavior of the model for a given phase equilibrium section (an isother-
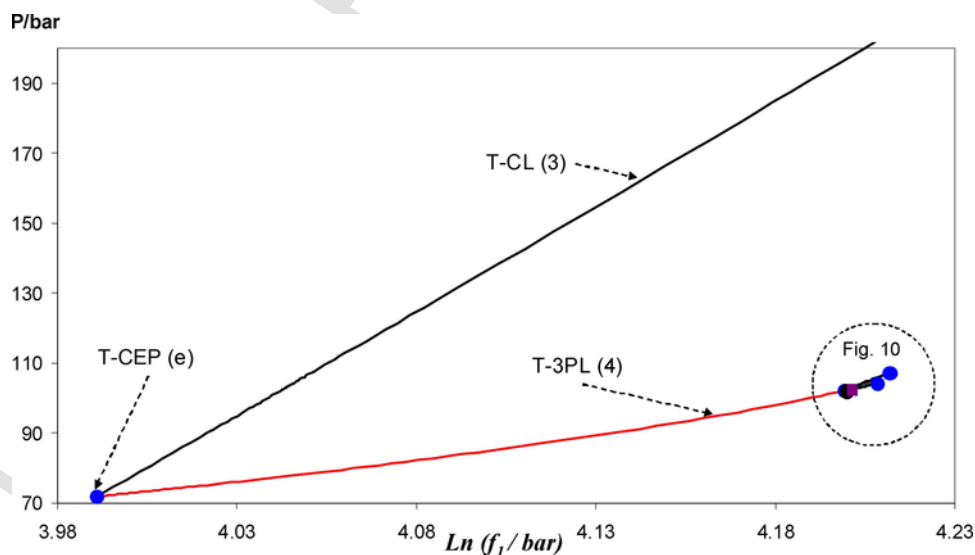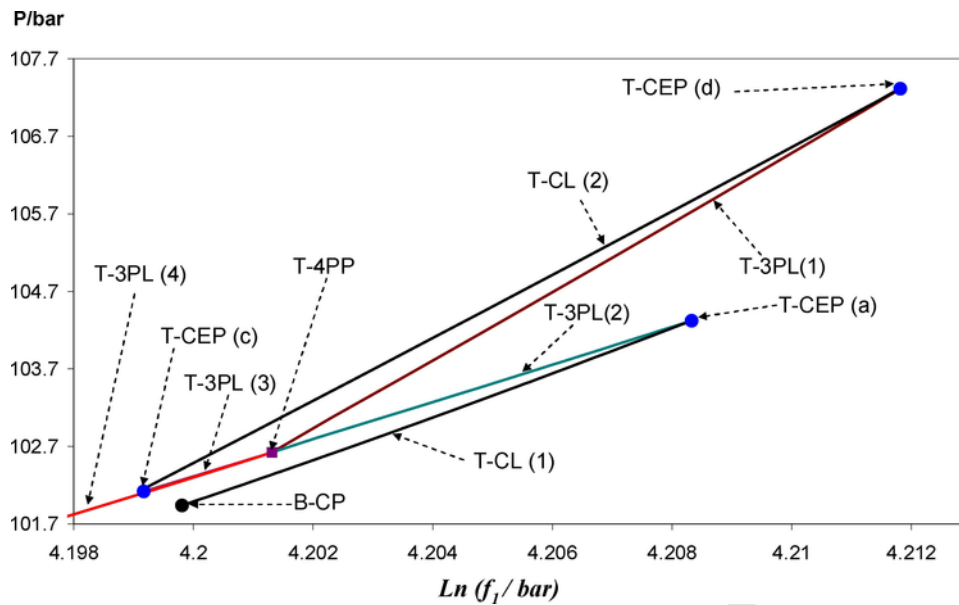

Fig. 9. Pressure vs. natural logarithm of the fugacity of component '1' along computed isothermal critical and three-phase lines. System $CO_2(1)$ + $H_2O(2)$ + 2-propanol(3). T = 330 K. SRK-EoS [11]. Parameters in Tables 1 and 2. T-CEP: Ternary Critical End Point [T-CEP (e)]. T-CL: Ternary Critical Line [T-CL (3)]. T-3PL: Ternary Three Phase Line [T-3PL (4)]. Full blue circles [○] indicate the T-CEPs. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 10. Zoom of Fig. 9. Pressure vs. natural logarithm of the fugacity of component "1" along computed isothermal critical and three-phase lines. System $CO_2(1) + H_2O(2) +$ 2-propanol(3). T = 330 K. SRK-EoS [11]. Parameters in Tables 1 and 2. B-CP: Binary Critical point [C]. T-CEP: Ternary Critical End Point (a, c and d) [C]. T-CL: Ternary Critical Line (1 and 2). T-3PL: Ternary Three Phase Line (1, 2, 3 and 4). T-4PP: Ternary Four Phase Point [■].
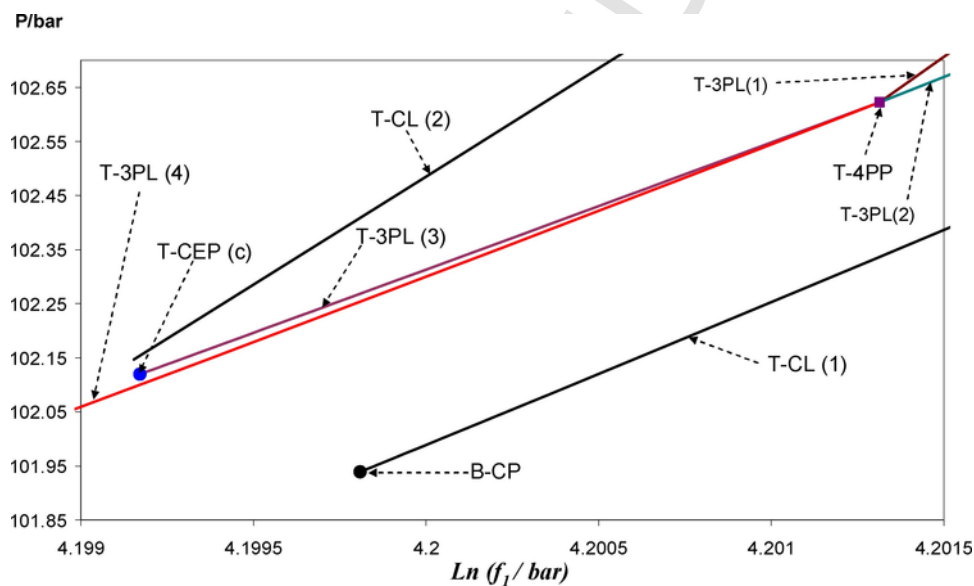

Fig. 11. Zoom of Fig. 10. Pressure vs. natural logarithm of the fugacity of component "1" along computed isothermal critical and three-phase lines. System $CO_2(1) + H_2O(2) +$ 2-propanol(3). T = 330 K. SRK-EoS [11]. Parameters in Tables 1 and 2. B-CP: Binary Critical point [C]. T-CEP: Ternary Critical End Point (c) [C]. T-CL: Ternary Critical Line (1 and 2). T-3PL: Ternary Three Phase Line (1, 2, 3 and 4). T-4PP: Ternary Four Phase Point [■].

mal section in this case). Figs. 9–11 convey less information than 3D diagrams such as Fig. 4, but provide, for the section of the equilibrium surfaces under study, a faster understanding on the connection among the involved T-3PLs, T-CLs and KPs.

6. Remarks and conclusions

In this work, a strategy for the computation of fluid phase equilibrium sections, for ternary systems, over wide ranges of conditions, using as starting point a previously computed ternary phase equilibrium characteristic map, was proposed. The computations were performed using a model of the equation of state type.

It has been shown, in view of the highly complex case study here considered, that the methodology of Ref. [7], proposed for binary mixtures, can be extended to the calculation of ternary phase equilibrium

sections of the phase equilibrium surfaces (isotherms or isobars). To illustrate the application of the proposed strategy, a complete complex ternary isothermal phase diagram (TI) was computed, by following the procedures described in Section 4. The chosen system was the ternary $CO_2 + H_2O +$ 2-propanol. This system presents four-phase equilibria, which is a highly non-ideal phase behavior.

Ternary three-phase lines (T-3PLs) and ternary critical lines (T-CLs) were calculated, in the context of the generation of a TI. For any given line to be computed, a key problem is to obtain its first converged point. Once this is done, a numerical continuation method (NCM) is applied to build the full line.

In this work, techniques to facilitate the variables initialization to converge a first point of a given line were proposed and tested satisfactorily. The NCM here used presented no problems, once the first point of the phase equilibrium line of interest was converged.

The computed ternary phase equilibrium isotherm made possible to carry out a detailed analysis of the (complex) phase equilibrium behavior given by the model, and an analysis of the different types of phase transitions that can occur in a ternary complex system over a wide range of pressure. For the isothermal section considered, a ternary four-phase point (T-4PP) was found. The presence of a T-4PP in a ternary isotherm (or isobar) results in four T-3PLs: two T-3PLs above the T-4PP pressure and two T-3PLs below this pressure. This type of phenomenon can lead to interpretation errors when experimental data are analyzed in the laboratory, since at fixed pressure and temperature there will be two different three-phase regions, if the conditions are close enough to that of the T-4PP (see, e.g., Figs. A.2.2 and A.2.3). In this sense, the tools here developed may be of use to the experimentalist.

Furthermore, a complete computed TI (or isobar) conveys key information about the equilibrium behaviors that can occur when, for the ternary system, another constraint is added, e.g., for a TI, constant pressure (on top of the constraint of constant temperature). Appendix A.2 shows diagrams at set T and P calculated using information obtained from a TI previously computed in this work. The figures shown in Appendix A.2 aim to show that the procedures used in this work are also helpful in the computation of equilibrium diagrams at constant pressure and temperature.

Although the model parameters were taken from the literature, no attempt was made in this work to compare the model predictions with the experimental data, i.e.,the focus of this work is the calculation strategy; not the evaluation of the quantitative performance of the model. Indeed the computation strategy here proposed is applicable to any model of the equation of state type, in the context of the 'φ–φ' approach.

Due to the complexity of the phase behavior of system CO_2 + H_2O + 2-Propanol, we reported in this work computation results only for a highly complex phase equilibrium isothermal section. However, the use of the present methodology for computing ternary phase equilibrium isobaric sections is fully analogous to that of the phase equilibrium isotherms.

Acknowledgements

Appendix A.1. Computation of a T-3PP

The system of equations and the vector of variables used in this work to compute a T-3PP are:

$$\Lambda^T = \begin{bmatrix} T & P & V^\alpha & V^\beta & V^\gamma & x_1^\alpha & x_2^\alpha & x_3^\alpha & x_1^\beta & x_2^\beta & x_3^\beta & x_1^\gamma & \cdots \end{bmatrix}$$

$$\mathbf{F} = \begin{bmatrix} F_1 \\ F_2 \\ F_3 \\ F_4 \\ F_5 \\ F_6 \\ F_7 \\ F_8 \\ F_9 \\ F_{10} \\ F_{11} \\ F_{12} \\ F_{13} \\ F_{14} \end{bmatrix}$$

$$= \begin{bmatrix} \ln \hat{f}_1(T, V^\alpha, \mathbf{x}^\alpha) - \ln \hat{f}_1(T, V^\beta, \mathbf{x}^\beta) \\ \ln \hat{f}_1(T, V^\beta, \mathbf{x}^\beta) - \ln \hat{f}_1(T, V^\gamma, \mathbf{x}^\gamma) \\ \ln \hat{f}_2(T, V^\alpha, \mathbf{x}^\alpha) - \ln \hat{f}_2(T, V^\beta, \mathbf{x}^\beta) \\ \ln \hat{f}_2(T, V^\beta, \mathbf{x}^\beta) - \ln \hat{f}_2(T, V^\gamma, \mathbf{x}^\gamma) \\ \ln \hat{f}_3(T, V^\alpha, \mathbf{x}^\alpha) - \ln \hat{f}_3(T, V^\beta, \mathbf{x}^\beta) \\ \ln \hat{f}_3(T, V^\beta, \mathbf{x}^\beta) - \ln \hat{f}_3(T, V^\gamma, \mathbf{x}^\gamma) \\ \psi(T, V^\alpha, \mathbf{x}^\alpha) - P \\ \psi(T, V^\beta, \mathbf{x}^\beta) - P \\ \psi(T, V^\gamma, \mathbf{x}^\gamma) - P \\ x_1^\alpha + x_2^\alpha + x_3^\alpha - 1 \\ x_1^\beta + x_2^\beta + x_3^\beta - 1 \\ x_1^\gamma + x_2^\gamma + x_3^\gamma - 1 \\ h_{cut}(\Lambda) - S_{cut} \\ g_{spec}(\Lambda) - S_{spec} \end{bmatrix} = 0$$

(A.1.2)

The vector Λ has 14 variables, where T is the absolute temperature, P is the absolute pressure, V^j is the molar volume of phase j. x_i^j is the mole fraction of component i in the phase j, where $i = 1$ to 3 and $j = \alpha$, β or γ. Superscripts α, β and γ distinguish the three phases at equilibrium. The vector $\mathbf{F}$ has 14 functions, where $F_1 = 0$, $F_2 = 0$, $F_3 = 0$, $F_4 = 0$, $F_5 = 0$ and $F_6 = 0$ impose the iso-fugacity condition for the three phases at equilibrium, with $\hat{f}_i$ representing the fugacity of component i in the mixture. $F_7 = 0$, $F_8 = 0$ and $F_9 = 0$ impose the equal pressure condition to the three-phases at equilibrium. Function ψ is the function that connects explicitly the temperature (T), the molar volume (V^j) and the mole fractions x_i^j with the pressure of phase j. The mathematical forms of ψ and $\hat{f}_i$ are imposed by the selected EOS (the SRK-EOS in this work). $F_{10} = 0$, $F_{11} = 0$ and $F_{12} = 0$ impose that the sum of the mole fractions of the three components must be equal to unity, for each of the three phases. The $F_{13} = 0$ and $F_{14} = 0$ equations are related to the two DOFs that must be specified to compute a ternary three-phase equilibrium point. The function $h_{cut}(\Lambda)$ in $F_{13} = 0$, equals in this work the variable (temperature or pressure) chosen to remain constant in the section of the three phase equilibrium surface (=T-3PL) to be computed. Clearly, $h_{cut}(\Lambda)$ defines

the nature of the plane at which the calculation of the complete T-3PL will be performed. The parameter S_{cut} is the value of the set constant temperature or constant pressure, depending on whether the section is isothermal or isobaric. For the case considered in this work, i.e., the calculation of an isotherm, we have $h_{cut}(\Lambda) = T$ and $S_{cut} = 330$ K. Thus, in such case, $F_{13} = 0$ becomes ($T - 330$ K $= 0$). This equation remains unchanged throughout the calculation of the T-3PL (which is a continuous set of T-3PPs). The $g_{spec}(\Lambda)$ function in equation $F_{14} = 0$ is related to the second DOF that must be specified, and this function is linked to the NCM implemented in this work [2].

The function $g_{spec}(\Lambda)$ can be different for each T-3PP to be calculated, according to the criteria used by the implemented NCM. For example, for a given T-3PP the function $g_{spec}(\Lambda)$ could be defined as $g_{spec}(\Lambda) = V^{\alpha}$, and parameter S_{spec} could be imposed to be equal to 0.1 L/mol, i.e., $S_{spec} = 0.1$ L/mol. Then, $F_{14} = 0$ would take the form $V^{\alpha} - 0.1$ L/mol $= 0$. Clearly, in this case the NCM would have identified V^{α} as the most appropriate variable to be specified.

For the next T-3PP, the function $g_{spec}(\Lambda)$ could remain unchanged, or the NCM could identify a different variable as the most appropriate to be specified. For example, the NCM could decide to make the following definitions: $g_{spec}(\Lambda) = P$ and $S_{spec} = 101.1$ bar. In such a case, the new form for $F_{14} = 0$ would be $P - 101.1$ bar $= 0$. In other words, equation $F_{14} = 0$ would have been modified by the NCM after finishing the computation of a T-3PP, in order to perform the computation of the next one. The main reason for using a NCM is that specifications leading to a lack of solution of the system of Eqs. (A.1.2) are avoided during the computation of the T-3PL. Besides, the NCM always provides excellent initial guesses for the next T-3PP to be calculated. It does it based on information about the previous already converged T-3PP.

For more details on the NCM implemented in this work see Ref. [2]. Actually, in this work, for performing the computations, all positive variables, such as the mole fractions, were logarithmically scaled. This makes possible to easily deal with, e.g., very low values for mole fractions of highly diluted components. Some information on this scaling approach is also provided in Ref. [2].

A comment on T-4PPs

The system of equations valid at a T-4PP is as the one of Eq. (A.1.2) with the incorporation of three additional isofugacity conditions, one additional condition involving function ψ, one additional condition setting a summation of mole fractions equal to unity; and with the equation involving parameter S_{cut} removed. The equation involving parameter S_{spec} remains. Such equation is used to set the only degree of freedom of a T-4PP. The new variables (four in total) added to those in vector Λ are the molar volume and composition (three mole fractions) of the fourth phase.

Appendix A.2. Generation of ternary phase equilibrium diagrams at set pressure and temperature using information of a computed isotherm

In the same way that the T-CM is used to determine the (generally UV) KPs defined by a plane at constant temperature (plane that cuts the equilibrium surfaces), and then to build a complete TI using the information contained in such KPs, a calculated TI can be used to generate diagrams at constant temperature and pressure (Gibbs triangle).

Fig. A.2.1 is similar to Fig. 5. Fig. A.2.1 shows three dashed lines, located at P = 103,076 bar, connecting the three vertices of the Gibbs triangle. They define an horizontal constant pressure plane at P = 103,076 bar. This plane intercepts three T-CLs and two T-3PLs existing within the ranges of conditions of Fig. A.2.1. From this intersection points the following DV KPs are determined for the phase diagram at 330 K and 103,076 bar: T-CP(1), T-CP(2), T-CP(3), T-3PP(1) and T-3PP(2).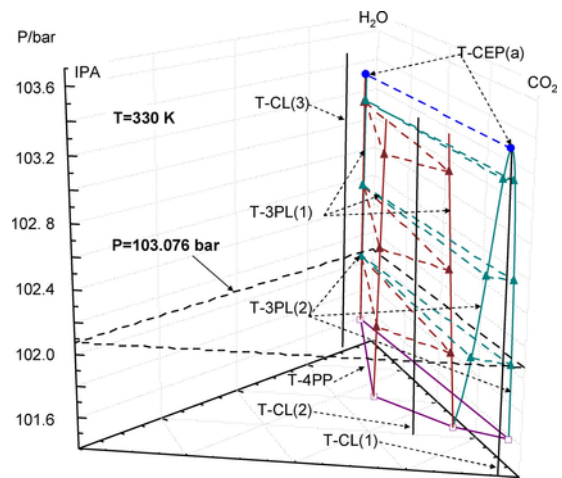 The presence of these KPs would be more easily seen by drawing an horizontal straight line located at 103,076 bar in Figs. 10 and

Fig. A.2.1. Computed ternary phase equilibrium isotherm with indication of six T-3PPs. Temperature: 330 K. System: CO_2 + H_2O + 2-Propanol(IPA). SRK-EoS [11]. Parameters in Tables 1 and 2. Pressure range: from the T-4PP pressure to the T-CEP(a) pressure at 330 K. The plane at a constant pressure P = 103.076 bar is indicated in the figure. T-CEP: Ternary Critical End Point (a). T-4PP: Ternary Four Phase Point. T-CL: Ternary Critical Line (1, 2 and 3). T-3PL: Ternary Three Phase Line (1 and 2). T-3PP: Ternary three-phase point. Pairs of circles [○] connected by a dashed tie-line indicate the T-CEP phase compositions and pressure. Empty squares [□] indicate the T-4PP phase compositions and pressure. Triangle with dashed sides: T-3PP at set temperature and pressure. The dashed sides are the T-3PP tie-lines. The dashed sides connect full triangles [▲ and ▼] which indicate the phase compositions and the pressure of the T-3PP. Concentration scale in the Gibbs triangle: mole fraction. Note: arrows are not to be confused with tie lines.

9. These equilibrium KPs are defined when two DOFs are specified (T = 330 K and P = 103,076 bar, DV KPs). Using the information in these points, and performing two-phase equilibrium calculations not described in this work, the phase diagram at constant *T* and *P* was built. The results are shown in Fig. A.2.2. In this figure the two three-phase regions are observed, these regions being characterized by the KPs T-3PP(1) and T-3PP(2) and their respective tie-lines.

A two-phase region originates at each side of each three-phase triangle. Each two-phase equilibrium line (T-2PL), in part delimiting a corresponding two-phase region, was calculated using, to start the computations, information contained in the T-3PP(1) and in the T-3PP(2). The symbols "α" and "β" were used to distinguish between the two phases in equilibrium in a given T-2PL. The T-2PL(1α) (Fig. A.2.2)

Fig. A.2.2. Calculated ternary fluid phase equilibrium at constant pressure (103.076 bar) and temperature (330 K) for the CO_2 + H_2O + 2-Propanol system. Phase diagram built from divariant key points obtained from Fig. A.2.1. T-CP: Ternary Critical Point (2 and 3) [○]. T-2PL: Ternary Two Phase Line. T-3PP: Ternary Three Phase Point (1 and 2) [▲ and ▼]. Concentration scale in the Gibbs triangle: mole fraction. Note: arrows are not to be confused with tie lines. Greek letters α and β identify two fluid phases at equilibrium.

and T-2PL(1β) (Fig. A.2.3) begin on one side of the T-3PP(2) triangle and end when the concentration of 2-propanol tends to zero, i.e., the lines end when the CO_2 + H_2O binary system is reached. These lines make the T-2PL(1) up and define a two-phase equilibrium region.

The T-2PL(2α) (Fig. A.2.2 insert) and T-2PL(2β) (Fig. A.2.2) delimit the two-phase region located in between the two three-phase regions T-3PP(1) and T-3PP(2). Note that the phase "α" in the T-2PL(2α) can be seen only by expanding the region where both three-phase regions are very close to each other (upper left corner of Fig. A.2.2).

Moreover in Fig. A.2.2, the two-phase region bounded by T-2PL(3α) and T-2PL(3β) is observed, starting at one side of the T-3PP(1) three-phase region, and ending when the T-CP(3) is reached.

In Fig. A.2.3, the two-phase regions that complete the diagram are shown. The T-2PL(4α) and T-2PL(4β) start at the T-3PP(1) and end at the T-CP(2) (shown in Figs. A.2.2 and A.2.3). The T-2PL(5) region, defined by the lines T-2PL(5α) and T-2PL(5β) (Fig. A.2.3), begins on one side of the of T-3PP(2) and ends at the T-CP(1). The calculation procedures applied to compute a T-2PL are analogous to those described for calculating a ternary isotherm.

It is noteworthy that, as in the case of TI, the labels identifying each DV KP of Figs. A.2.2 and A.2.3 are related to the equilibrium lines from which they come. For example, the KP labeled "T-3PP (1)" in Fig. A.2.2 comes from the T-3PL labeled "T-3PL (1)" in the TI of Fig. A.2.1. Similarly, the KP labeled T-CP(1) in Fig. A.2.3 comes from the T-CL(1) in the TI of Fig. A.2.1, etc. In addition, the colors of the equilibrium lines in the TI (Fig. A.2.1) and the colors of the corresponding key points in Figs. A.2.2 and A.2.3 are the same. For example, brown is the color of T-3PP(1) in Figs. A.2.2 and A.2.3, and brown is also the color of the line from which it comes [T-3PL(1)] in the TI of Fig. A.2.1. All T-CPs are shown in black in Figs. A.2.2 and A.2.3, as are the corresponding T-CLs in the isotherm of Fig. A.2.1.

Appendix A.3. Computed values of the coordinates that describe the key points of the 330 K phase equilibrium isotherm of system $CO_2(1)$ + $H_2O(2)$ + 2-propanol(3)*

Tables A.3.1–A.3.3

Appendix B. Meaning of terms that refer to ternary phase equilibrium objects:

[a] In a ternary three-phase point (T-3PP) three ternary non-critical phases are at equilibrium.
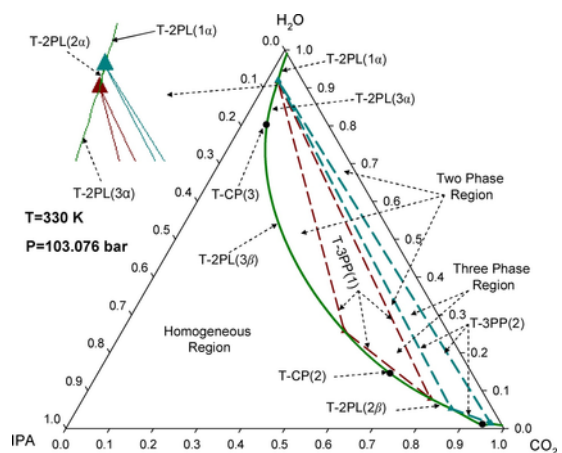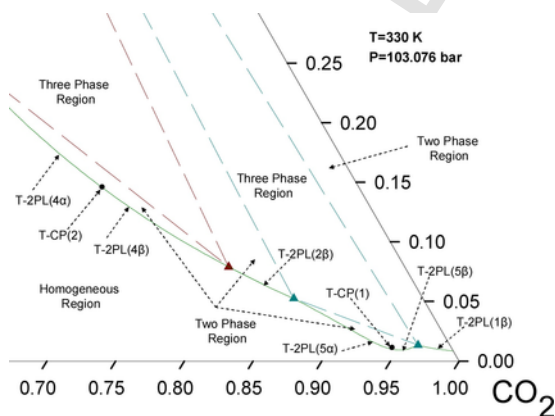

Fig. A.2.3. Zoom of Fig. A.2.2. Calculated ternary fluid phase equilibrium at constant pressure (103.076 bar) and temperature (330 K) for the CO_2 + H_2O + 2-Propanol system. Phase diagram built from divariant key points obtained from Fig. A.2.1. T-CP: Ternary Critical Point (1 and 2) [C]. T-2PL: Ternary Two Phase Line. T-3PP: Ternary Three Phase Point [▲ and ▲]. Concentration scale in the Gibbs triangle: mole fraction. Note: arrows are not to be confused with tie lines. Greek letters α and β identify two fluid phases at equilibrium.

[b] A ternary three-phase line (T-3PL) is a locus of T-3PPs.

[c] A ternary critical point (T-CP) is a stable ternary phase at its limit of intrinsic stability. Slight changes in conditions, performed in a proper direction, lead to the formation of a pair of quasi-critical phases.

[d] A ternary critical line (T-CL) is a locus of T-CPs.

[e] In a ternary critical endpoint (T-CEP), a ternary critical phase is at equilibrium with a ternary non-critical phase.

[f] A ternary critical end line (T-CEL) is a locus of T-CEPs. A T-CEL is an intersection line between a ternary three-phase equilibrium surface and a ternary critical surface.

[g] At a ternary four-phase (equilibrium) point (T-4PP), four ternary non-critical phases are at equilibrium.

[h] A ternary four-phase (equilibrium) line (T-4PL) is a locus of T-4PPs.

[i] A T-4PL may end at a ternary critical endpoint of a four-phase (equilibrium) line (T-CEP-4PL) where a ternary critical phase is at equilibrium with two ternary non-critical phases.

[j] If, along a T-3PL, three phases become critical simultaneously, then, a ternary tricritical endpoint (T-TCEP) [also named ternary tricritical point (T-TCP)] has been reached.

See Refs. [1,2] for more details. Some of the ternary phase equilibrium objects in the list above are elements of the characteristic map (T-CM, see Appendix D) [1] of the fluid phase behavior of the ternary system. Table B1 lists the acronyms used in this work and their expansions.

Appendix C. Brief description of the methodology of computation of ternary phase equilibrium sections

The problem begins by computing, as an initial step, thermodynamic objects of relatively abstract nature. These thermodynamic objects are those that constitute the phase equilibrium "characteristic map of a ternary system" (T-CM) [1]. Ref. [1] presents a methodology to compute T-CMs. The T-CM provides key information for subsequent calculations. Details on the different types of thermodynamic objects that constitute a T-CM are discussed in Appendix D. Simple equation of state (EOS) models can lead to very complex T-CMs [1].

Next, a set of (generally UV) key points (KPs) for the specified temperature (or pressure) are obtained from the already computed T-CM. Then, the appropriate isothermal (or isobaric) ternary equilibrium lines are calculated, using the information provided by such key points to find the first converged point of a given line.

The calculation of the ternary equilibrium lines is carried out by solving, for each of its points, a nonlinear system of equations using the full Newton-Raphson method. This is done in a range of conditions. Such system of equations imposes the conditions that must be satisfied at each equilibrium point. The system of equations depends on the type of ternary equilibrium of interest, either a ternary three-phase equilibrium or a ternary critical point. In addition, the algorithm for solving the system of equations of interest is coupled to a numerical continuation method (NCM) [2,15] that makes possible the computation of full equilibrium lines with minimal user intervention. The NCM begins to build a given line after a first equilibrium converged point is obtained. The necessary information that allows converging the first point is provided by the (generally UV) KPs. Initialization strategies are discussed in Section 4 of the main text. The basic features of the NCM implemented in this work is described in Refs. [2,15].

Appendix D. Ternary Characteristic Maps

A T-CM is a fluid phase equilibrium diagram composed of ternary, binary and pure compound "univariant equilibrium lines" and "invariant points". The pure components are the three components of which the ternary system is made of; and the binary systems are all three bi-

Table A.3.1
T-4PP Key Point at 330 K*. System $CO_2(1) + H_2O(2) + 2\text{-}propanol(3)$. See Tables 1–3 of main text.

$T(K)$	$P(bar)$	$V^\alpha(L/mol)$	$V^\beta(L/mol)$	$V^\gamma(L/mol)$	$V^\delta(L/mol)$	x_1^α	x_2^α	x_3^α	x_1^β	x_2^β	x_3^β	x_1^γ	x_2^γ	x_3^γ	x_1^δ	x_2^δ
329.96	102.62	0.0285	0.0605	0.1061	0.0521	0.025	0.917	0.057	0.805	0.073	0.121	0.966	0.012	0.021	0.499	0.26

Table A.3.2
T-CEP Key Points at 330 K*. System $CO_2(1) + H_2O(2) + 2\text{-}propanol(3)$. See Tables 1–3 of main text.

Label	$T(K)$	$P(bar)$	$V^c(L/mol)$	$V^\alpha(L/mol)$	x_1^c	x_2^c	x_3^c	x_1^α	x_2^α	x_3^α	u_1	u_2	u_3	λ	Figure
T-CEP(d)	329.96	107.31	0.0547	0.0284	0.636	0.166	0.196	0.025	0.918	0.056	−0.427	0.783	0.451	3.05E-10	3
T-CEP(a)	329.96	104.32	0.0818	0.0280	0.937	0.021	0.040	0.023	0.926	0.050	0.640	0.435	0.632	9.91E-11	3
T-CEP(c)	329.96	102.11	0.0558	0.1098	0.676	0.139	0.183	0.968	0.011	0.019	−0.377	0.774	0.508	-2.23E-09	3
T-CEP(e)	329.96	71.80	0.0347	0.2611	0.058	0.800	0.141	0.988	0.005	0.005	−0.429	0.815	−0.388	-5.40E-13	2

Table A.3.3

B-CP Key Point at 330 K*. System: $CO_2(1) +$ *2-propanol(3) (IPA)*. See Tables 1–3, and Fig. 3, of main text.

329.96^a	101.93	0.0927	0.953	0.0466	0.731	0.681	3.10E-12
$T(K)$	$P(bar)$	$V^c(L/mol)$	x_1^c	x_3^c	u_1	u_3	λ

[a] Note that the exact temperature value used for the calculations was actually 329.96 K.

Table B1

Acronyms used in this work [1,2].

Acronym	Meaning	# of phases	# of crit. phases
P-VPL	Pure (compound) vapour-pressure line	2	
B-2PP	Binary two-phase point	2	
B-2PL	Binary two-phase line	2	
T-2PP	Ternary two-phase point	2	
T-2PL	Ternary two-phase line	2	
B-3PP	Binary three-phase point	3	
B-3PL	Binary three-phase line	3	
T-3PP	Ternary three-phase point	3	
T-3PL	Ternary three-phase line	3	
T-4PP	Ternary four-phase point	4	
T-4PL	Ternary four-phase line	4	
P-CP	Pure critical point	1	1
B-CP	Binary-critical point	1	1
B-CL	Binary-critical line	1	1
T-CP	Ternary-critical point	1	1
T-CL	Ternary-critical line	1	1
B-CEP	Binary-critical end point	2	1
T-CEP	Ternary-critical end point	2	1
T-CEL	Ternary-critical end line	2	1
T-CEP-4PL	Ternary-critical end point of a four phase line	3	1
T-TCP	Ternary-tricritical point	1	
TI	Ternary Isothermal Diagram		
KP	Key Point		
DOFs	Degrees of freedom		
T-CM	Ternary characteristic map (characteristic map of the fluid phase behavior of a ternary system)		
B-CMs	Binary characteristic map (characteristic map of the fluid phase behavior of a binary system)		

nary sub-systems of the ternary system. A univariant equilibrium line is a line where each point on such equilibrium line is determined when a DOF is specified. This means that it is necessary to specify the value of only a single variable of the system to establish equilibrium. In mathematical terms, a univariant object is the one for which a single specification makes the system of equations become a system for which the number of unknowns equals to the number of equations. A univariant equilibrium line of a pure component, in the fluid region, is the vapor pressure line (P-VPL, vapor-liquid equilibrium).

Univariant equilibrium lines examples in a binary system are:

[a] "Binary three phase lines" (B-3PLs). At a point of a B-3PL three binary non-critical phases coexist at equilibrium.

[b] "Binary critical lines" (B-CLs). A point of a B-CL is a binary critical point.

[c] "Binary Azeotropic Lines" (B-ALs). At a point of a B-AL two binary non-critical phases of equal composition and different density coexist at equilibrium.

Univariant lines in a ternary system are: T-CELs (loci of T-CEPs), T-4PLs (loci of T-4PPs), and, finally, "Ternary Azeotropic Lines" (T-ALs). At a point of a T-AL two ternary non-critical phases having identical composition and different density coexist at equilibrium.

The only invariant point of a pure compound in the fluid region is its critical point ("Pure Critical Point" (P-CP)). The invariant points of a binary system in the fluid region are: the "Binary Critical End Points" (B-CEPs), where a binary critical phase coexists at equilibrium with a binary non-critical phase; and a variety of "Binary Azeotropic end Points" (B −AEPs), which are endpoints of the B-ALs. In a B-AEP the two azeotropic phases present in the B-AL may become critical, or can become unstable by the appearance of a third (liquid) phase in equilibrium with the azeotropic phases [16]. There are even more possibilities for B-AEPs [16].

Note that the basic nature of the equilibrium in a B-CEP is the same than the one in a T-CEP. Furthermore, a B-CEP could be an endpoint of a T-CEL (Fig. 1).

Finally, the invariant points in a ternary system are of the types: "Ternary Critical end Point of a Four Phase Line" (T-CEP-4PL); "Ternary Tricritical Point" (T-TCP), and "Ternary Azeotropic end Points " (T-AEP).

A T-CEP-4PL is an endpoint of a T-4PL, where two of the four phases are critical (i.e., identical). Therefore, in a T-CEP-4PL a critical phase coexists in equilibrium with two non-critical phases. A T-AEP is an endpoint of a T-AL. We have not yet studied this kind of endpoints. Azeotropy is not covered in this work. We plan to address the incorporation of ternary azeotropy into T-CMs in the near future.

Scott and van Konynenburg [8] used pure compound and binary univariant lines and invariant points, to build binary phase behavior characteristic maps, to describe and characterize the equilibrium behavior of fluid phases for binary systems. Pisoni et al. [1] added ternary univariant and invariant objects (ternary univariant lines and ternary invariant points) to characterize the fluid phase behavior of ternary systems (T-CMs), i.e., the T-CMs of Ref. [1] are made of unary, binary and ternary invariant points and univariant lines.
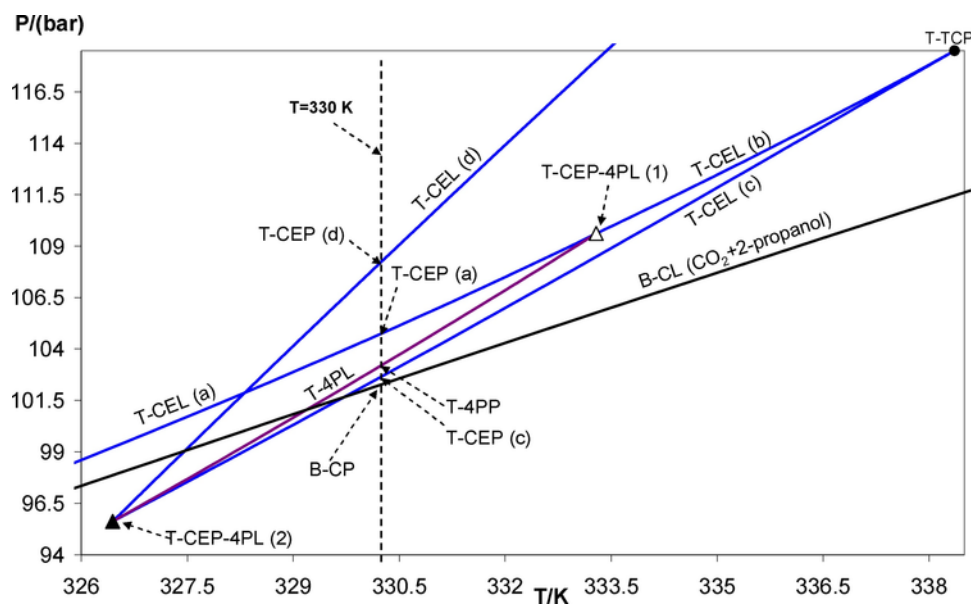
Fig. 3. Zoom of Fig. 2. Pressure-Temperature projection of part of the calculated ternary characteristic map (T-CM) for the CO_2 + H_2O + 2-Propanol system. Model: SRK-EOS [11]. Parameters in Tables 1 and 2. B-CL: Binary Critical line. B-CP: Binary Critical Point. T-4PL: Ternary Four Phase Line. T-4PP: Ternary Four Phase point. T-CEL: Ternary Critical End Line (a, c and d). T-CEP: Ternary Critical End Point (a, c and d). T-CEP-4PL: Ternary Critical End Point of a Four Phase Line [T-CEP-4PL (1) [O] and T-CEP-4PL (2) [:]]. T-TCP: Ternary Tricritical Point [C].

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