



Generation of characteristic maps of the fluid phase behavior of ternary systems



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ARTICLE INFO

Article history:

Received 15 July 2013

Received in revised form 2 October 2013

Accepted 4 October 2013

Available online 18 October 2013

Keywords:

Phase equilibrium

Equation of state models

Ternary characteristic maps

Ternary critical end lines

Ternary four-phase lines

ABSTRACT

The main features of the fluid phase behavior of a given binary system can be grasped at a glance by looking at its (binary) characteristic map (B-CM), which is made of unary and binary univariant lines, i.e., by geometrical objects having only one degree of freedom. Binary univariant lines are critical and azeotropic lines and liquid–liquid–vapor equilibrium lines. These lines are customary shown in the pressure–temperature plane together with the pure–compound vapor–liquid equilibrium lines (unary lines). Similarly, ternary systems also have characteristic maps for their phase equilibrium behavior. Such ternary characteristic maps (T-CMs) are made of unary, binary and ternary univariant lines. Possible ternary univariant lines are the following: ternary four-phase equilibrium lines (T-4PLs), ternary critical end lines (T-CEs) and ternary homogeneous azeotropy lines (T-ALs). T-CMs also present invariant points as the following: pure compound critical points, binary critical endpoints (B-CEPs), ternary critical endpoints of four-phase equilibrium lines (T-CEP-4PLs), ternary tricritical endpoints (T-TCEP), and all possible endpoints of binary and ternary homogeneous azeotropy lines. Analogously to B-CMs for binary systems, T-CMs make possible to quickly identify the main features of the phase behavior of a given ternary system. In other words, T-CMs provide key information on the fluid phase equilibria of ternary systems. When dealing with models for the fluid phase behavior of ternary systems, it would be useful to generate the T-CMs, in a way as automated as possible, once a ternary system and a model are chosen, and the model parameter values are set. This would make possible, among other outcomes, to quickly evaluate the main features of the model performance. B-CMs can be efficiently generated, when using a model of the equation of state (EOS) type, by applying available algorithms. In this work we show how the univariant lines of T-CMs can be efficiently computed for a given ternary system, given EOS and EOS parameter values. In general, a ternary univariant line (T-UVL) is generated in this work by using a numerical continuation method (NCM). NCMs are able to build, in their full extent, highly non linear T-UVLs, with minimum user intervention. In particular, we describe in this work how T-TCEPs and T-CEP-4PLs are detected and computed, and how the calculation of T-4PLs is started off. Finally, an algorithm for the generation of computed T-CMs is presented. The algorithm relies on previously computed critical endpoints of the binary subsystems of the ternary system under study. We have not considered yet the detection and computation of T-ALs and of closed loop T-CEs. We provide examples of T-CMs computed over wide ranges of conditions. The results of this work show that relatively simple models can generate highly complex topologies for the phase behavior of ternary systems.

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1. Introduction

The computation of the fluid phase equilibrium behavior of binary and ternary systems is of great importance to characterize

the performance of models and of their specified parameter values, as a necessary step to intend the reproduction of experimental information by the chosen model. Such characterization is best carried out when focusing on key equilibrium lines and points.

The key lines and points for the fluid phase equilibria of binary systems are those identified by Scott and Van Konynenburg in 1970 [1], i.e., critical, azeotropic and liquid–liquid–vapor lines, critical endpoints and a variety of endpoints for azeotropic lines, all typically shown in their pressure–temperature (PT) projection. Only

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Table 1
Acronyms used throughout this work.

Acronym	Meaning
B-3PL	Binary three-phase (equilibrium) line
B-CEP	Binary critical endpoint
B-CL	Binary critical line
B-CM	Binary characteristic map
B-QP	Binary quadruple point
B-UVL	Binary univariant line
I-T-3PE	Isothermal ternary three-phase equilibrium
LLV-BL	Liquid–liquid–vapour (equilibrium) binary line
LLL-V-TL	Liquid–liquid–liquid–vapour (equilibrium) ternary line
T-3PE	Ternary three-phase equilibrium
T-3PL	Ternary three-phase (equilibrium) line
T-3PP	Ternary three-phase (equilibrium) point
T-4PL	Ternary four phase (equilibrium) line
T-4PP	Ternary four-phase (equilibrium) point
T-AL	Ternary azeotropy line
T-AP	Ternary azeotropic point
T-CEL	Ternary critical end line
T-CEP	Ternary critical endpoint
T-CEP-4PL	Ternary critical endpoint of a four-phase (equilibrium) line
T-CM	Ternary characteristic map
T-TCEP or T-TCP	Ternary tricritical endpoint or ternary tricritical point
T-UVL	Ternary univariant line
VP	Pure compound vapour pressure

one degree of freedom is associated to the mentioned lines (i.e., the lines are univariant objects). The mentioned endpoints are invariant. Scott and Van Konynenburg [1] proposed a classification of the fluid phase behavior of binary systems based on their PT projections. Bolz et al. [2] presented an alternative system of names which is able to describe all known and yet unknown binary phase diagrams in a rational way. The meaning of the word “line” in the context of this work is made clear in Appendix B.

The univariant lines and invariant points that characterize the phase behavior of ternary systems are, e.g., the following: Ternary Critical End Lines (T-CEs), Ternary Four-phase Lines (T-4PLs), Ternary Azeotropic Lines (T-ALs), Ternary Critical Endpoints of a Four-Phase line (T-CEP-4PLs), Ternary Tricritical Points (T-TCPs), which we also name Ternary Tricritical Endpoints (T-TCEPs), and endpoints of ternary azeotropic lines. The PT projections of such lines and points, drawn all together, for a ternary system of interest, including also the unary (pure compound) and binary lines, will be named “characteristic map of the fluid phase behavior of the ternary system”. We will also name it, in a more compact way, “ternary characteristic map” (T-CM). Table 1 presents all acronyms used throughout this work.

Pisoni et al. [3] have computed T-CEs over a wide range of conditions and have listed their possible types. Other authors have studied T-CMs, but in all cases they have focused on relatively narrow regions of the T-CMs. Di Andreth [4] has shown, within limited ranges of conditions, a T-CM for the system $\text{CO}_2 + \text{H}_2\text{O} + \text{Isopropanol}$ containing, such T-CM, T-CEs, T-CEP-4PLs, T-4PLs, T-TCPs and phase equilibrium univariant lines of some of the binary subsystems. Di Andreth [4] did not provide details on the algorithms implemented for calculating the T-CEs, T-CEP-4PLs and T-4PLs. It seems that Di Andreth [4] developed algorithms for calculating three-phase and four-phase equilibria. Each point of a T-CEL would be identified [4], when calculating a continuous set of three-phase equilibria, when verifying the absence of convergence.

Gregorowicz and de Loos [5] have presented, within limited ranges of conditions, calculated T-CEs and T-TCPs for *methane + propane + n-eicosane* and *ethane + propane + n-eicosane*. Gregorowicz and de Loos [5] have proposed to use the information of calculated Binary Critical endpoints (B-CEPs) to initialize the calculation of ternary critical endpoints (T-CEPs) where the third component is at infinite dilution. In turn, such special T-CEPs were used [5] to start off the building of T-CEs. Gregorowicz and de Loos

[5] have not given details on how to initialize the concentration of the third component in either phase (critical and non-critical) of the mentioned special T-CEPs. In Ref. [5] it has been suggested to always set the value of the temperature as the independent variable for calculating a point of a T-CEL. In general terms, this could eventually lead to a lack of convergence, if the T-CEL being built had a highly non-linear behavior [3]. No details were given in Ref. [5] on the calculation of T-TCPs.

Adrian et al. [6] studied the ternary system $\text{CO}_2 + \text{H}_2\text{O} + 1\text{-propanol}$. They showed, within limited ranges of conditions, several qualitative PT projections containing T-CEs, T-CEP-4PLs, T-4PLs and T-TCPs. Later Adrian et al. [7] studied several $\text{CO}_2 + \text{H}_2\text{O} + \text{polar solvent}$ systems, which were modeled using the PR-EOS [8] coupled to a number of mixing rules. Ref. [7] shows both, qualitative and quantitative diagrams. In this last case, the diagrams consist of PT projections of T-CEs, T-CEP-4PLs, T-4PLs and T-TCPs, within limited ranges of conditions. The calculation algorithms have not been described with sufficient detail in Ref. [7].

In summary, in the previously quoted contributions, i.e., Refs. [4,6,7,9], which dealt with ternary systems, detailed descriptions of systematic procedures for computing each type of line of a T-CM are not available.

In this work, we describe a systematic method, of general applicability, for the construction of T-CMs. We apply such method to the computation of T-CMs for a variety of ternary systems, over ranges of conditions much wider than those that have been considered in previous works on ternary systems. The models are of the EOS type. The systems of equations to be solved are non-linear. For them, we use the multivariate Newton’s method. We include in this work details on how to detect and initialize the points where the building of ternary univariant lines is started off. In this work, every ternary univariant line is computed using a numerical continuation method (NCM). NCMs minimize the need for user intervention.

2. Calculation of ternary univariant lines and ternary non-variant points

A T-CM may have the invariant points and univariant lines mentioned in the previous section. We provide below a more detailed description of the phase equilibrium situation for each type of such thermodynamic objects, together with information on how such lines and points are calculated.

2.1. Ternary univariant lines

2.1.1. Ternary critical end lines (T-CEs)

A T-CEL (or hyper-line) is a continuous set of ternary critical endpoints (T-CEPs). At a T-CEP a critical fluid phase is at equilibrium with a non-critical fluid phase, being the system made of three components. A T-CEP generally is the termination of a ternary three-phase equilibrium line (T-3PL) (a discussion about this statement is provided in Appendix D). A T-3PL (or hyperline) may be, e.g., isothermal or isobaric. At a T-CEL, a three-phase hyper-surface and a critical hyper-surface meet. Appendix C gives details on the meaning of the word “hyper-surface” in the context of this work. It also explains that while an unrestricted continuous set of ternary three-phase equilibria is a hyper-surface, a continuous set of ternary three-phase equilibria satisfying a given single restriction, e.g., constant temperature, is a hyper-line. There are T-3PLs that have termination points of a nature different from the one of a T-CEP. A given T-CEP is reached by different T-3PLs, for instance by an isobaric T-3PL at the pressure of the given T-CEP, and by an isothermal T-3PL at the temperature of the given T-CEP. Actually, an infinite number of T-3PLs have a given T-CEP as their common endpoint.

The name given by Michelsen [10] to T-CELS is “critical three-phase lines” (see Fig. 5 in Ref. [10]). Michelsen calculated them by solving Eqs. (12)–(15) of Ref. [10]. The name T-CEL seems more expressive than the name “critical three-phase line” because, on one hand, only two phases are present at a point of a T-CEL (a critical phase, at equilibrium with a non-critical phase), and, on the other, a T-CEL sets the end of a ternary three-phase hyper-surface, in analogy to B-CEPs which generally set the end of binary three-phase lines.

Pisoni et al. [3] have listed the types of T-CELS that can be found in a T-CM. A given type of T-CEL is defined by the nature of its endpoints. Besides, a T-CEL may follow a path lacking a definite endpoint. A given ternary system may have several T-CELS (Table 4) of varying types. For computing a T-CEP it is necessary to add, to the critical conditions, the isofugacity conditions between the critical and non-critical phases, together with the condition of uniformity of pressure and temperature throughout the heterogeneous system. In this work we have computed T-CELS by using the algorithms of Pisoni et al. [3].

2.1.2. Ternary four-phase equilibrium lines (T-4PLs)

A T-4PL (or hyper-line) is a continuous set of points, for a ternary system, where four fluid phases are at equilibrium. A T-4PL originates a T-CEP-4PL and may end at another T-CEP-4PL, or may otherwise have no definite endpoint. A ternary system may have zero, one or more T-4PLs (Table 4). Binary systems might eventually present quadruple points (B-QPs, four binary fluid phases at equilibrium) [2]. B-QPs are also points where a T-4PL originates. Ternary systems with binary subsystems having B-QPs have not been considered in this work.

For computing a four-phase equilibrium point the isofugacity condition is set for a given component in the four phases. This is done for all components. Other imposed conditions are the uniformity of temperature and pressure throughout the heterogeneous system. Also the summation of all mole fractions in a given phase is set equal to unity. The resulting (not shown) four-phase equilibrium system of equations has 17 equations and 18 variables. Indeed, the system has one degree of freedom. The system variables are the following:

$$[T, P, V^\alpha, V^\beta, V^\gamma, V^\varphi, x_1^\alpha, x_2^\alpha, x_3^\alpha, x_1^\beta, x_2^\beta, x_3^\beta, x_1^\gamma, x_2^\gamma, x_3^\gamma, x_1^\varphi, x_2^\varphi, x_3^\varphi] \quad (1)$$

where α, β, γ and φ are superscripts that identify the phases, T is the absolute temperature, P is the absolute pressure, V is the molar volume of a phase, and x_i is the mole fraction of component “ i ” in a phase. The system of equations is solved by using the Newton-Raphson method. A NCM is used to build the complete T-4PL. The first converged point of the T-4PL is obtained as described in Section 3.2.

2.1.3. Ternary azeotropic lines (T-ALs)

A T-AL is a continuous set of ternary azeotropic points (T-APs). At a T-AP a liquid phase and a vapor phase are at equilibrium, having both phases the same composition. The computation of T-ALs is beyond the scope of this work.

2.2. Ternary invariant points

2.2.1. Ternary critical endpoint of a four-phase equilibrium line (T-CEP-4PL)

In a T-CEP-4PL a ternary critical phase is at equilibrium with two ternary non-critical phases. A T-CEP-4PL sets the end of a ternary four-phase equilibrium line. At such end two of the four fluid phases become critical. Although the acronym T-CEP-4PL refers to an endpoint of a four-phase equilibrium line, a T-CEP-4PL is also an

endpoint of a T-CEL, i.e., a point where a system made of a critical phase and a non-critical phase becomes globally unstable (appearance of a third phase which is non-critical). Actually, two T-CELS meet at a T-CEP-4PL. This is because at a T-CEP-4PL two non-critical phases are at equilibrium with a critical phase. In other words, a T-CEP-4PL contains two T-CEPs. In conclusion, three univariant lines meet at a T-CEP-4PL, i.e., two T-CELS and a T-4PL.

For computing a T-CEP-4PL we add to the criticality system of equations proposed by Michelsen [11], i.e., to the critical conditions that one of the phases must meet, the isofugacity conditions between the critical phase and each of the two non-critical phases, together with the condition of uniformity of pressure and temperature throughout the heterogeneous system. Again the summation of all mole fractions in a given phase is set equal to unity. This results in a (not shown) system with 19 equations and 19 unknowns. Indeed the system has no degrees of freedom and it is thus invariant. The system variables are the following:

$$[T, P, V^c, v^0, V^\alpha, V^\beta, x_1^c, x_2^c, x_3^c, x_1^\alpha, x_2^\alpha, x_3^\alpha, x_1^\beta, x_2^\beta, x_3^\beta, u_1, u_2, u_3, \lambda] \quad (2)$$

where α and β , are superscripts that identify the non-critical phases, while superscript “ c ” identifies the critical phase. v^0 is the molar volume of the critical phase, and V^c is certain total volume involved in the implementation of the criticality conditions. Variables u_1, u_2 and u_3 are the components of certain eigenvector appearing in the critical conditions proposed by Michelsen [11]. λ is the eigenvalue associated to the mentioned eigenvector. The system of equations is solved by using the Newton-Raphson method. The initialization of the variables of the T-CEP-4PL system of equations is discussed in Section 3.1, test [C].

2.2.2. Ternary tricritical point (T-TCP)

Since a T-TCP is always an endpoint of a T-CEL, we also name it Ternary tricritical endpoint (T-TCEP). In a T-TCEP three phases at equilibrium become critical simultaneously. When a T-TCEP exists, an infinite number of paths within a ternary three-phase equilibrium hyper-surface, all leading to the T-TCEP, exist. However not every path within a ternary three-phase equilibrium hyper-surface contains a T-TCEP. Along a T-CEL (which as previously stated connects T-CEPs where a critical phase is at equilibrium with a non-critical phase), a T-TCEP is reached when the non-critical phase becomes critical with the critical phase. It should be clear that at a T-TCP the system is made of a single phase which is tricritical. Two T-CELS meet at a T-TCP.

For computing a T-TCP we used the tricriticality criterion of Ref. [12], which results, for a ternary mixture, in a system of 14 equations and 14 unknowns (see Appendix A). The system variables are the following:

$$[T, P, V, v^0, z_1, z_2, z_3, u_1, u_2, u_3, w_1, w_2, w_3, \lambda] \quad (3)$$

v^0 is the molar volume of the tricritical phase, and V is certain total volume involved in the implementation of the tricritical conditions [12]. Variables u_1, u_2 and u_3 are the components of certain eigenvector appearing in the tricritical conditions of Ref. [12] (see Appendix A). w_1, w_2 and w_3 are the components of a vector orthogonal to vector \mathbf{u} . λ is the eigenvalue associated to the mentioned eigenvector. z_1, z_2 and z_3 , are the mole fractions of the components in the tricritical phase. The system of equations for the ternary tricritical point calculation is presented in detail in Appendix A. The initialization of the tricritical system of equations is discussed in Section 3.1, test [B].

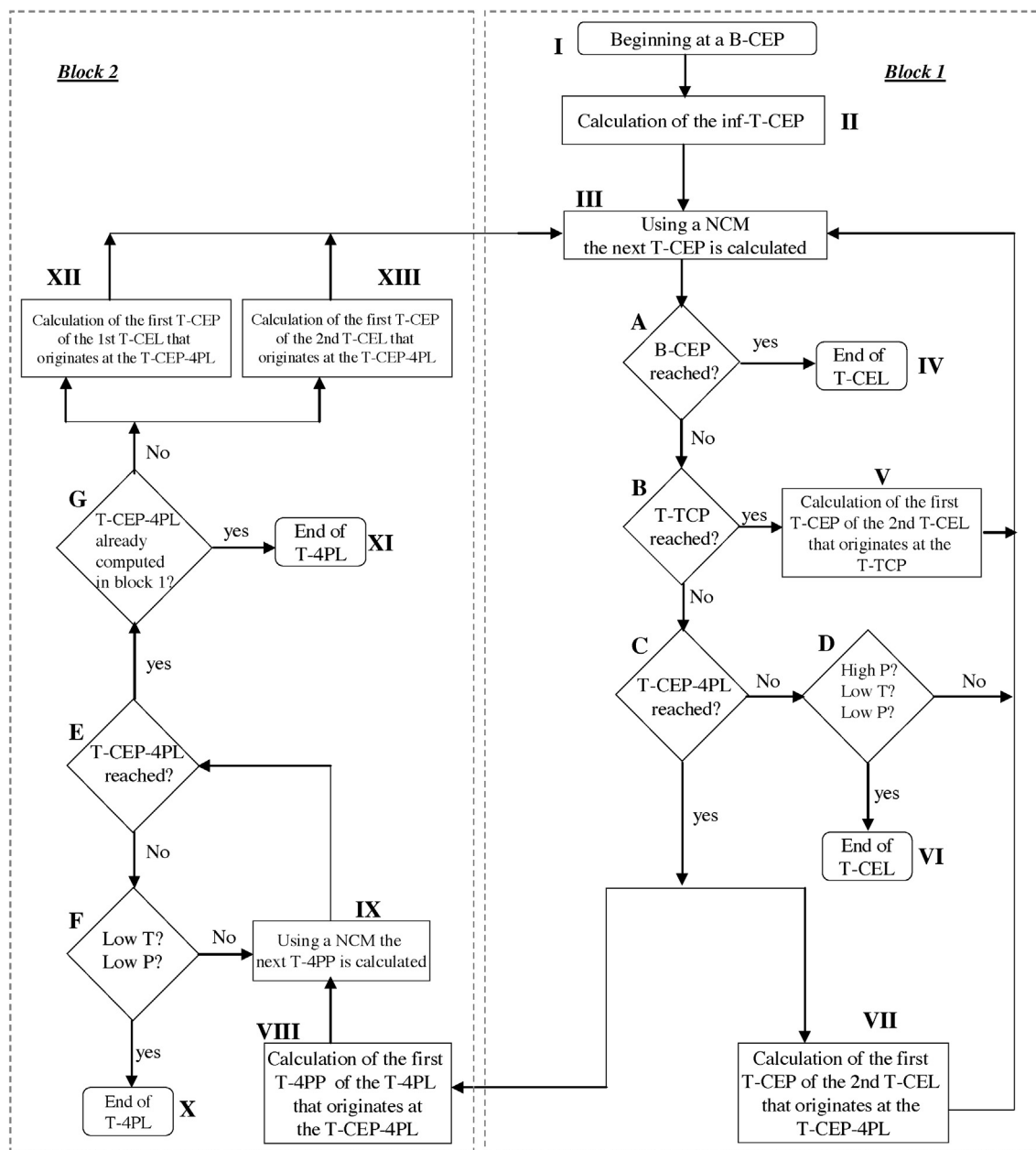


Fig. 1. Flow sheet of the algorithm for the computation of ternary phase equilibrium characteristic maps.

3. Strategy for the generation of complete characteristic maps of the fluid phase behavior of ternary systems

The generation of a T-CM, for a given ternary system, model, and model parameters values, requires the quantitative knowledge of the predicted phase behavior for the binary sub-systems. This has been done in this work (Table 4) by using the algorithms proposed for binary systems in Ref. [13]. Such algorithms lead to the knowledge of all B-CEPs. This is important because B-CEPs are endpoints of T-CEs. However, B-CEPs are not the only possible endpoints for T-CEs [3]. The endpoints, of all kinds, of the T-CEs, are the key in the definition of a procedure for generating T-CMs.

3.1. Algorithm for generating T-CMs and initialization strategies

Fig. 1 represents the algorithm used in this work for generating the T-CMs. Using the information of an already computed B-CEP (Fig. 1, →I) [13], an infinite dilution T-CEP (inf-T-CEP) is calculated

(Fig. 1, →II). If the T-CEL originates at a B-CEP of, say, components 1 and 2, then, a T-CEP is calculated where component 3 is infinitely diluted (inf-T-CEP). All variables of the converged inf-T-CEP will have values identical to those of the B-CEP, except for the mole fractions of component 3 in both phases (z_3 and x_3), since z_3 and x_3 are variables that do not exist at the B-CEP. For converging the inf-T-CEP we set, as initial values, $z_3 = 10^{-4} \min(z_1, z_2)$ and $x_3 = 10^{-4} \min(x_1, x_2)$. After obtaining the converged inf-T-CEP, the T-CEL is built with the help of a NCM (Fig. 1, →III) similar in essence to the one used in Ref. [13]. For each calculated T-CEP (Fig. 1, →III), i.e., for each calculated point of the T-CEL, the following tests are performed:

[A] Is the calculated T-CEP close enough to a B-CEP different from the B-CEP at which the T-CEL originated (O-B-CEP)? (Fig. 1, →A). The answer is YES if the mole fraction of a component, which was present in the O-B-CEP, falls below certain (small enough) value, both, for the critical and non-critical phases.

[B] Is the calculated T-CEP close enough to a T-TCP (Fig. 1, →B)? The answer is YES if the differences in composition and density

fall below certain (small enough) tolerances, both, for the critical and non-critical phases. In such a case the last computed T-CEP is a quasi-tricritical T-CEP which provides excellent initial estimates for calculating the T-TCP considered in Section 2.2.2. Once the T-TCP is computed, we have available an already calculated (complete) T-CEL. A second T-CEL originates at the found T-TCP. The first point of the second T-CEL is calculated (Fig. 1, →V). Such first converged point of the second T-CEL could be probably obtained by using somehow the information contained in the known T-TCP. We have not yet developed such type of procedure. An alternative procedure is described in Section 3.3, and used in subblock V of Fig. 1. Having calculated the first point of the second T-CEL (Fig. 1, →V) the algorithm returns to subblock III.

[C] Is the calculated T-CEP close enough to a T-CEP-4PL? (Fig. 1, →C). To answer this question a stability test [14] is performed for the converged T-CEP. The stability test consists of searching for local minima of the tangent plane distance (tpd) function within the space of (ternary) composition of the trial phase. A negative tpd is indicative of a globally unstable T-CEP, i.e., of the appearance of a third (non-critical) phase. This indicates that the T-CEL has reached a T-CEP-4PL. The information of the unstable T-CEP, including the information corresponding to the new (third) phase, is used to initialize the calculation of the T-CEP-4PL considered in Section 2.2.1. The T-CEP-4PL has information on two solutions of the T-CEP system of equations. One of them corresponds to the equilibrium between the critical and non-critical phases of the T-CEL that was being built until the T-CEP-4PL was reached. The other solution corresponds to the same critical phase and the remaining non-critical phase. The information on this last phase, together with that of the critical phase, is used to converge the first point of the second T-CEL that originates at the detected T-CEP-4PL (Fig. 1, →VII). For bringing the computation of the second T-CEL to completion, the algorithm returns to subblock III.

[D] Do the calculated T-CEPs tend to high P, low P or low T? (Fig. 1, →D). The answer is “yes” if: (D1) the pressure P becomes greater than a preset, high enough, value, or, (D2) the pressure P becomes lower than a preset, low enough, value, or, (D3) the temperature T becomes lower than a preset, low enough, value. If the answer to subblock D of Fig. 1 is “yes”, then, the calculation of the T-CEL has been brought to completion. In such a case, the T-CEL has a path in the P vs T plane that extends indefinitely without finding an endpoint within the ranges of conditions considered (Fig. 1, →VI). If the answer to subblock D is “No”, then, the algorithm returns to subblock III (Fig. 1, →III).

The algorithm within Block 1 of Fig. 1 is applied, in principle, a number of times equal to the number of B-CEPs of the ternary system. Actually, it is not necessary to calculate T-CELS originating at B-CEPs that were previously detected as termination points of already calculated T-CELS (Fig. 1, →A, →IV).

In subblock C there is a bifurcation when the answer is “yes”. The reason is that a T-CEP-4PL is not only a point where a pair of T-CELS meet, but also an originating point of a T-4PL. Once the repeated execution of block 1 in Fig. 1 is finished, then, Block 2 is applied, i.e., the first point of the T-4PL associated to the previously found T-CEP-4PL is calculated (Fig. 1, →VIII). We identify the originating T-CEP-4PL as “O-T-CEP-4PL”. The information contained in the computed O-T-CEP-4PL is useful for calculating the first point of the T-4PL, as described in Section 3.2. Once the first ternary four-phase point (T-4PP) is converged, the next T-4PPs are obtained using a NCM (Fig. 1, →IX).

For each calculated T-4PP (Fig. 1, →IX), i.e., for each calculated point of the T-4PL, the following tests are performed:

[E] Is the calculated T-4PP close enough to a T-CEP-4PL different from the O-T-CEP-4PL? (Fig. 1, →E).

[F] Do the calculated T-4PPs tend to low pressure or low temperature? (Fig. 1, →F).

The following considerations are relevant with regard to test [E]. Along the T-4PL, close enough to the O-T-CEP-4PL, the critical phase of the O-T-CEP-4PL has splitted into two near-critical phases (Ph1 and Ph2) which are at equilibrium with two non-critical phases (Ph3 and Ph4). For every calculated point (located far enough from the O-T-CEP-4PL) of the T-4PL, it is tested whether two out of the four phases become critical (Fig. 1, →E). This is considered to be so if, for a couple of phases, the differences in composition and density fall below certain (small enough) values. To fix ideas, the T-4PL could reach, while being built, a point where a pair of phases, which in our experience should not be the pair [Ph1, Ph2], become critical. If this happens, then, a T-CEP-4PL different from the O-T-CEP-4PL has been found (Fig. 1, →E, →yes).

If the answer to test [F] is “YES”, then, the T-4PL that originated at a T-CEP-4PL has a path in the P vs T plane that extends indefinitely without finding an endpoint (Fig. 1, →X). If the answer is “NO”, then, the algorithm returns to subblock IX (Fig. 1, →IX). The termination corresponding to subblock X in Fig. 1 is done if the pressure (or the temperature) is lower than a preset low enough value.

When the answer to test [E] is “YES”, the following test is performed:

[G] Has the found (second) T-CEP-4PL already been computed (in subblock C of Block 1 of Fig. 1)? (Fig. 1, →G). If the answer is “YES”, then, the calculation is terminated (Fig. 1, →XI). If the answer is “NO”, then, two T-CELS are calculated (Fig. 1, →XII and Fig. 1, →XIII) and tested as prescribed in Block 1 of Fig. 1. This means that Block 1 has to be executed again, from subblock III on. This could lead to the finding of new T-CEP-4PLs.

Block 2 is executed a number of times equal to the number of “YES” answers to subblock C minus the number of “YES” answers to subblock G. Notice that the execution of subblocks XII and XIII could lead to additional “YES” answers to subblock C.

3.2. Generation of a first converged ternary four-phase equilibrium point

The NCM used to build a T-4PL requires the knowledge of a converged ternary four-phase equilibrium point (T-4PP). This first T-4PP (1st-T-4PP) is obtained by solving the system of equations mentioned in Section 2.1.2. In this work, the 1st-T-4PP is chosen to be very close to the T-CEP-4PL from which the T-4PL originates. In other words, two out of the four phases at equilibrium in the 1st-T-4PP are quasi-critical. The variables of the 1st-T-4PP are initialized as follows. The pressure and temperature, and compositions and densities of the two non-quasi-critical phases, are set equal to those of the T-CEP-4PL. For initializing the variables of the two quasi-critical phases, we take advantage of the information contained in the known eigenvector components (u_1 , u_2 and u_3) of the known T-CEP-4PL (see Section 2.2.1). To initialize the compositions of the two near-critical phases we proceed as follows. We use the following equation [11,15]

$$n_i = z_i \pm s \cdot u_i \cdot \sqrt{z_i} \quad (4)$$

where n_i is the number of moles of component “i” in the quasi-critical phases and z_i is the mole fraction of component “i” in the critical phase of the T-CEP-4PL, u_i is the i th component of the eigenvector of the T-CEP-4PL and “s” is a distance parameter. We set $s = 10^{-4}$ and calculate two sets of variables n_i . A set comes from using the plus sign in Eq. (4), and the other set from using the minus sign. The two n_i sets are easily transformed into a couple of mole fraction vectors. Each vector corresponds to one of the near-critical phases, and it is used as its initial composition estimate. Such composition is used together with the temperature and pressure of the T-CEP-4PL to calculate an initial density value of the considered near-critical phase. At this stage and excellent initialization of the 1st-T-4PP has been obtained. Next, the system of

Table 2
Interaction parameters used with the SRK-EOS [16].

System	Interaction parameters					
	k_{12}	k_{13}	k_{23}	l_{12}	l_{13}	l_{23}
Ethane(1)+Propane(2)+1-Propanol(3)	0	0	−0.1	0	−0.15	0
Ethanol(1)+n-Pentane(2)+n-Hexane(3)	0.17	0.24	0	0	0.108	0
CO ₂ (1)+n-Pentadecane(2)+n-Eicosane(3)	0.11	0.11	0	0	0	0
Ethane(1)+Propane(2)+n-Eicosane(3)	0.0616	0.0263	0.0114	0.092	0.019	0.009
CO ₂ (1)+H ₂ O(2)+Isopropanol(3) (System A)	0.19	0.1215	−0.1727	0	0	0
CO ₂ (1)+H ₂ O(2)+Isopropanol(3) (System B)	−0.053	0.017	−0.207	0	0	0

Table 3
Pure compound parameters [17].

Compound	Critical temperature (K)	Critical pressure (bar)	Acentric factor
Ethane	305.32	48.72	0.0995
Propane	369.83	42.48	0.1523
n-Pentane	469.7	33.7	0.2515
n-Hexane	507.6	30.25	0.3013
n-Pentadecane	708	14.8	0.6863
n-Eicosane	768	11.6	0.9069
Ethanol	514	61.37	0.6436
1-Propanol	536.8	51.69	0.6204
Isopropanol	508.3	47.64	0.6669
CO ₂	304.21	73.83	0.2236
H ₂ O	647.13	220.55	0.3449

equations mentioned in Section 2.1.2 is solved and the (converged) 1st-T-4PP is obtained (Fig. 1, →VIII). Next, within the context of the algorithm of Fig. 1, the T-4PL is built using a NCM (Fig. 1, →IX). From the phase rule, a ternary four-phase point has a single degree of freedom. When computing T-4PPs located close enough to the T-CEP-4PL, we avoid the trivial solution by specifying the value of the relative difference $[(V_x - V_y)/V_x]$ between the molar volumes of the two quasi-critical phases. Alternatively, a specification involving differences in mole fraction values could be set, but we have not considered such possibility in this work.

The procedure described above for initializing a quasi-critical T-4PP can be used also for initializing a quasi-critical three-phase equilibrium point of a ternary three-phase line originated at a T-CEP (i.e., at a point of a T-CEL).

3.3. Computation of a second T-CEL that originates at a T-TCP

For starting off the computation of a second (complete) T-CEL that originates at a T-TCP, we need to find at least one converged point of such T-CEL. For that, we calculate a ternary three-phase equilibrium line (T-3PL), either at constant pressure or at constant temperature. The variable kept constant is set equal to a convenient value. Such value is chosen assuming that the T-3PL will meet the T-CEL that we want to compute. This intersection happens when two of the phases of a point, of the T-3PL being computed, become identical (i.e., critical), i.e., when, for a couple of phases, the differences in composition and density fall below certain (small enough) tolerances. Such point of the T-3PL is very close to a converged point (actually a T-CEP) of the sought T-CEL. The values of the variables of the found quasi-critical ternary three-phase point (T-3PP) are used to initialize the variables of the system of equations mentioned in Section 2.1.1, which is solved to compute a T-CEP. This is a converged point of the T-CEL. Such point is used coupled to a NCM to compute the complete T-CEL according to Ref. [3].

4. Results

In this work we computed complete T-CMs for the six ternary systems listed in Table 2. We used the Soave–Redlich–Kwong equation of state (SRK-EOS) [16] coupled to quadratic mixing rules. We

obtained the pure compound critical temperatures and pressures, and acentric factors (Table 3), from the DIPPR database [17]. The values for the interaction parameters used in the calculations are given in Table 2. Table 4 shows the predicted type of phase behavior for the binary sub-systems according to the classification of Ref. [1]. We obtained this last information, i.e., the binary univariant lines and binary invariant points, using the algorithms proposed in Ref. [13]. Table 4 also lists the thermodynamic objects (mainly ternary univariant lines and ternary invariant points) computed in this work for each system. Such objects are shown in the computed T-CMs (see Fig. 2 and subsequent figures). Although the classification by Bolz et al. [2] is superior to the one of Ref. [1], our use of this last classification is adequate to the purposes of the present work.

Notice that the scope of this work is the phase equilibria that involves only fluid phases (interference by solid phases is not considered in this work).

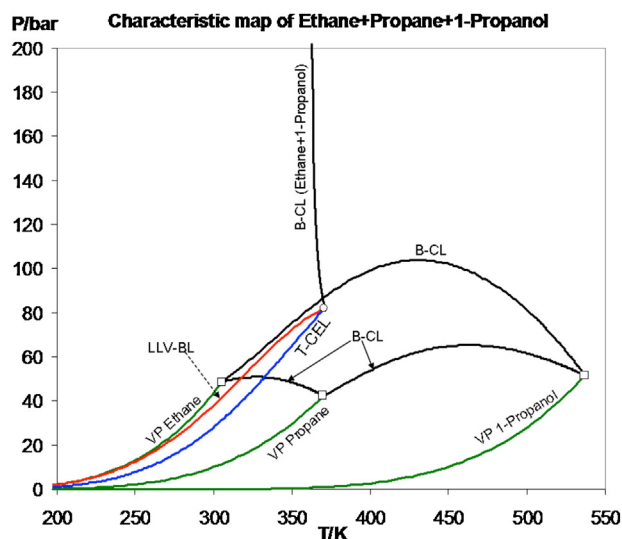


Fig. 2. Square: critical point of pure compound. Empty circle: binary critical endpoint. See Table 1.

Table 4
Computed^a type of phase behavior of the binary sub-systems, and computed^a binary and ternary thermodynamic objects.

Ternary system	Type of binary phase behavior			Thermodynamic objects (number of)				
	Binary sub-system			B-CEPs	T-CELS	T-CEP-4PLs	T-4PLs	T-TCPs
	1–2	1–3	2–3					
Ethane(1) + Propane(2) + 1-Propanol(3)	I	II	I	1	1	–	–	–
Ethanol(1) + n-Pentane(2) + n-Hexane(3)	II	II	I	2	1	–	–	–
CO ₂ (1) + n-Pentadecane(2) + n-Eicosane(3)	III	III	I	2	1	–	–	–
Ethane(1) + Propane(2) + n-Eicosane(3)	I	IV	II	4	3	–	–	1
CO ₂ (1) + H ₂ O(2) + Isopropanol(3) (System A)	III	III	II	3	4	1	1	1
CO ₂ (1) + H ₂ O(2) + Isopropanol(3) (System B)	III	II	I	2	11	6	3	2

^a Model: SRK-EOS [16] with parameters from Tables 2 and 3.

Fig. 2 shows the calculated T-CM for the system *Ethane + Propane + 1-Propanol*. The phase behavior is relatively simple. There is only one T-CEL. It originates at the only B-CEP of the system (Table 4). The B-CEP corresponds to the binary subsystem *Ethane + 1-Propanol*. The T-CEL extends indefinitely toward low pressures and temperatures (Fig. 1, →A, →B, →C, →D, →VI).

Fig. 3 shows the calculated T-CM for the system *Ethanol + n-Pentane + n-Hexane*. This system presents two B-CEPs (Table 4) corresponding to the binary sub-systems *Ethanol + n-Pentane* and *Ethanol + n-Hexane*. There is only one T-CEL which connects both B-CEPs (Fig. 1, →A, →IV). Notice that not every ternary three-phase line has T-CEPs. For instance, in Fig. 3, an isothermal T-3PL at 370 K would connect the two binary three-phase equilibrium points that exist at such temperature, without ever intersecting the T-CEL in Fig. 3. Hence, such isothermal T-3PL does not have a T-CEP.

Fig. 4 shows the calculated T-CM for the system *CO₂ + n-Pentadecane + n-Eicosane*. This system presents two B-CEPs (Table 4 and Fig. 5) corresponding to the binary sub-systems *CO₂ + n-Pentadecane* and *CO₂ + n-Eicosane*. Again there is only one T-CEL which connects both B-CEPs, as shown in Fig. 5 (again: Fig. 1, →A, →IV). Figs. 2–4 correspond to relatively simple ternary phase behaviors.

Fig. 6 shows the calculated T-CM for the system *Ethane + Propane + n-Eicosane*. This system presents a total of four B-CEPs (Table 4). Fig. 7 shows a zoom of part of Fig. 6 where the two high-pressure B-CEPs (HP-B-CEPs) can be better visualized. Fig. 8 is a zoom of Fig. 6 in the low temperature range. From the

two HP-B-CEPs two T-CELS originate (one from each B-CEP). Both T-CELS end at the same T-TCP (Fig. 7). The calculation of a T-CEL began at the B-CEP of highest pressure. This T-CEL reached a T-TCP (Fig. 1, →B, →V). From the found T-TCP, the second T-CEL was computed (Fig. 1, →B, →V, →III). This last T-CEL ends at a B-CEP (see Fig. 7) (Fig. 1, →A, →IV). Fig. 8 shows that the two low-pressure

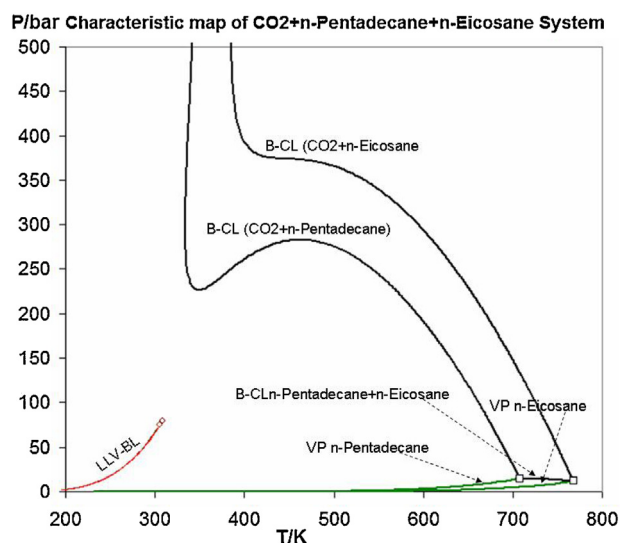


Fig. 4. Square: critical point of pure compound. Empty circle: binary critical endpoint. See Table 1.

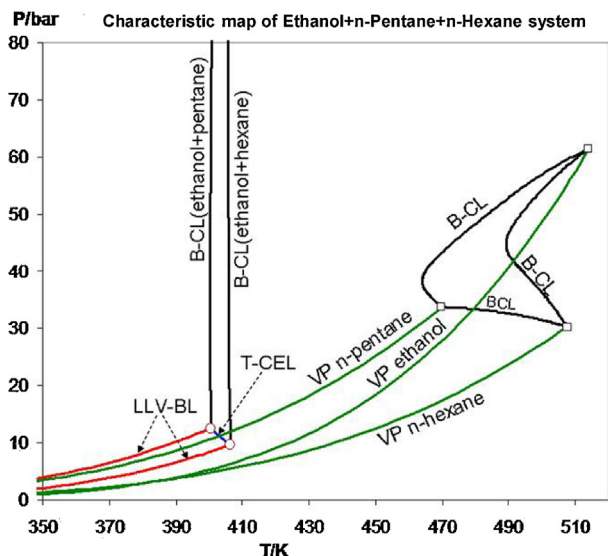


Fig. 3. Square: critical point of pure compound. Empty circle: binary critical endpoint. See Table 1.

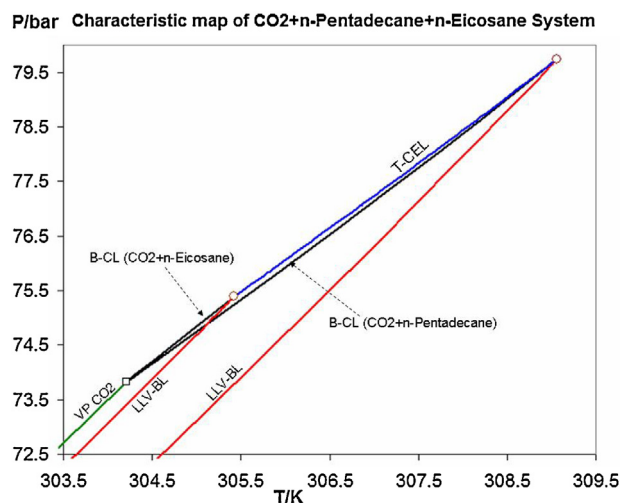


Fig. 5. Zoom of Fig. 4. Square: critical point of pure compound. Empty circle: binary critical endpoint. See Table 1.

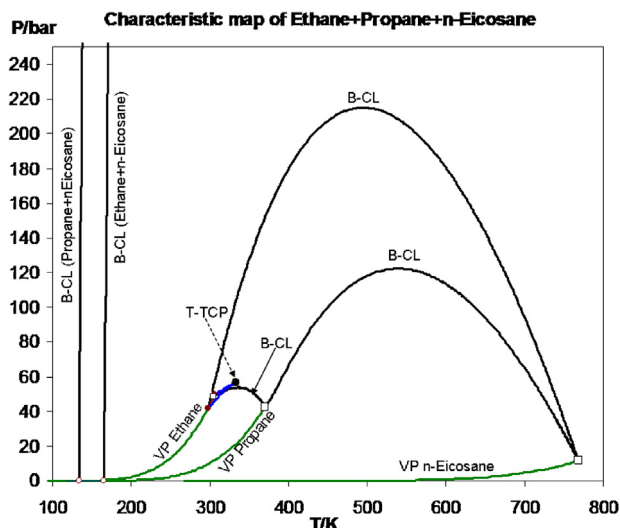


Fig. 6. Square: critical point of pure compound. Empty circle: binary critical endpoint. See Table 1.

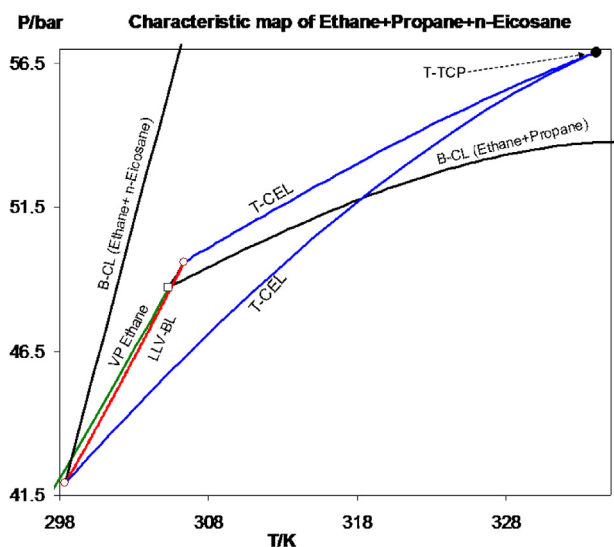


Fig. 7. Zoom of Fig. 6. Square: critical point of pure compound. Empty circle: binary critical endpoint. See Table 1.

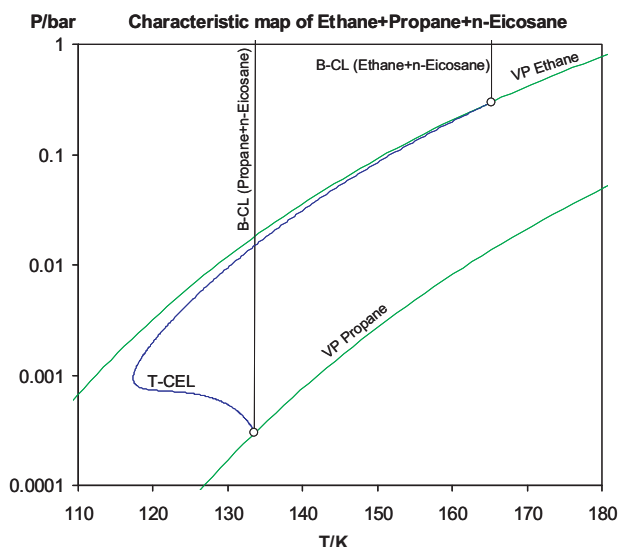


Fig. 8. Zoom of Fig. 6. Empty circle: binary critical endpoint. See Table 1.

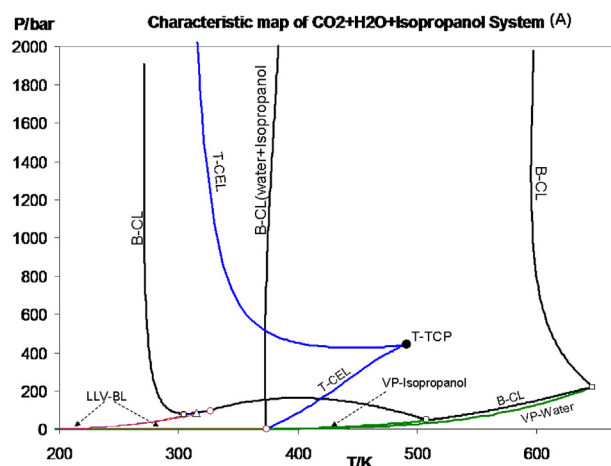


Fig. 9. Square: critical point of pure compound. Empty circle: binary critical endpoint. See Table 1.

B-CEPs are connected by a T-CEL with a highly non-linear behavior (Fig. 1, $\rightarrow A, \rightarrow IV$).

Fig. 9 shows the calculated T-CM for the system $CO_2 + H_2O + Isopropanol$ (system A, Table 4). Figs. 10 and 11 are zooms of Fig. 9. This system has three B-CEPs (Table 4). The phase behavior is quite complex.

Fig. 10 shows a T-CEL that originates at the B-CEP of highest pressure. The calculation of this T-CEL is executed until a T-CEP-4PL is found (Fig. 1, $\rightarrow A, \rightarrow B, \rightarrow C, \rightarrow yes$). At this point the calculation of the 2nd T-CEL begins (Fig. 1, $\rightarrow VII$). This line ends at the B-CEP of lowest pressure (Figs. 10 and 1, $\rightarrow A, \rightarrow IV$). The found T-CEP-4PL implies that block 2 of Fig. 1 will be executed (Fig. 1, $\rightarrow VIII$).

Starting at the low-pressure B-CEP shown in Fig. 11 the calculation of a T-CEL is carried out until a T-TCP is reached, as shown in Fig. 9 (Fig. 1, $\rightarrow B, \rightarrow yes$). From such T-TCP a second T-CEL is calculated (Fig. 9) which extends indefinitely toward high pressures (Fig. 1, $\rightarrow D, \rightarrow VI$). So far, the three B-CEPs have been considered. Next, sub-block VIII of Fig. 1 is executed for calculating a T-4PL (sub-block IX). In this case the T-4PL extends indefinitely toward low pressures and low temperatures as Fig. 10 partially shows (Fig. 1, $\rightarrow F, \rightarrow X$). Here the calculation of the T-CM ends, since there are no more B-CEPs and T-CEP-4PLs left.

Fig. 12 shows the calculated T-CM for the system $CO_2 + H_2O + Isopropanol$ (system B, Table 4). Figs. 13 and 14 are zooms of Fig. 12. This system has two B-CEPs (Table 4).

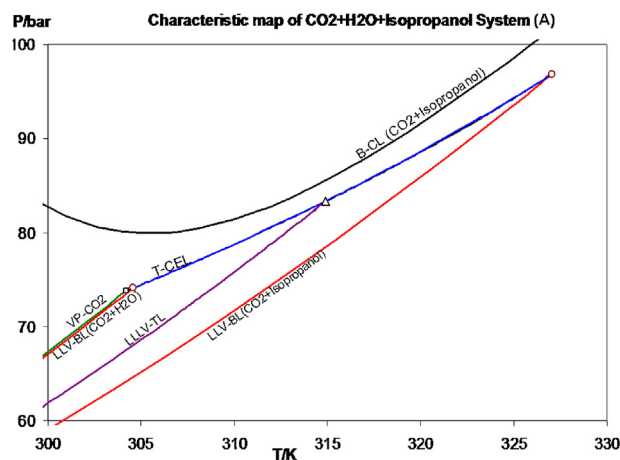


Fig. 10. Zoom of Fig. 9. Square: critical point of pure compound. Empty circle: binary critical endpoint. Triangle: ternary critical endpoint of four phase line. See Table 1.

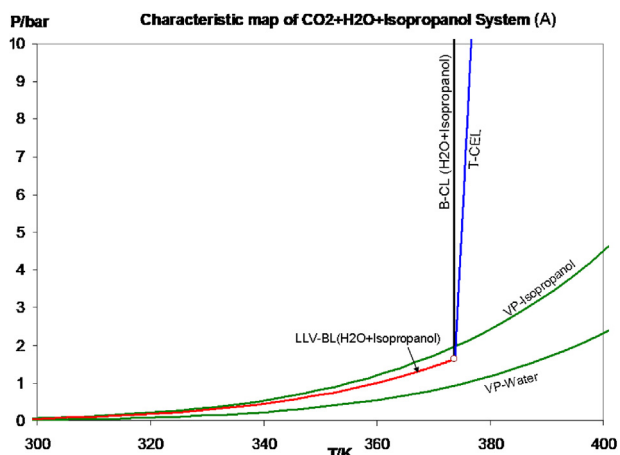


Fig. 11. Zoom of Fig. 9. Empty circle: binary critical endpoint. See Table 1.

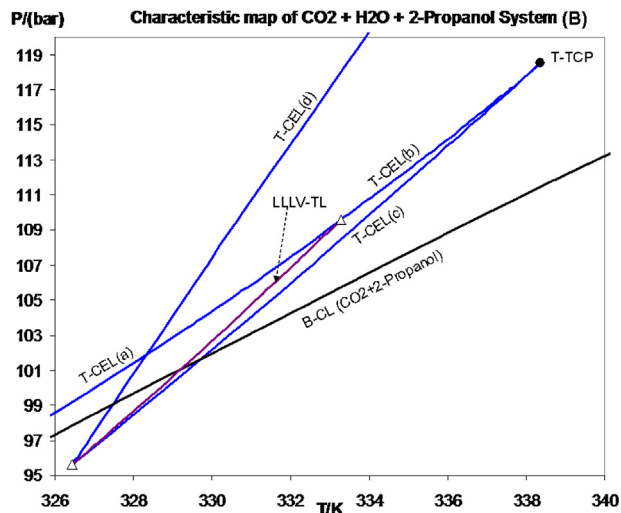


Fig. 14. Zoom of Fig. 12. Triangle: ternary critical endpoint of four phase line. Full circle: Ternary Tri-Critical Point. See Table 1.

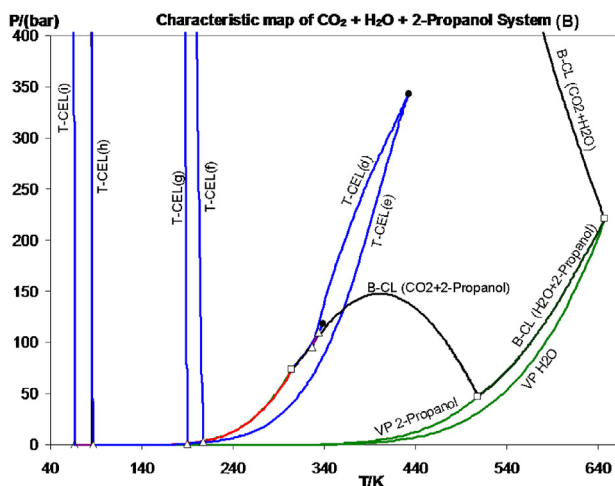


Fig. 12. Square: critical point of pure compound. Empty circle: binary critical endpoint. Triangle: ternary critical endpoint of four phase line. Full circle: Ternary Tri-Critical Point. See Table 1.

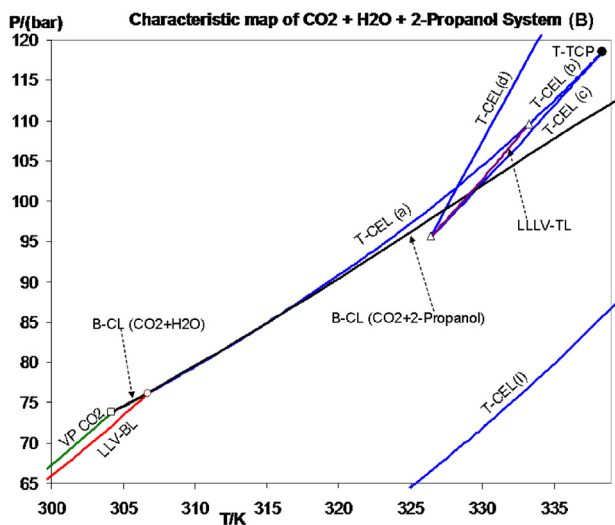


Fig. 13. Zoom of Fig. 12. Square: critical point of pure compound. Empty circle: binary critical endpoint. Triangle: ternary critical endpoint of four phase line. Full circle: Ternary Tri-Critical Point. See Table 1.

Figs. 12–14 show that the phase behavior is highly complex. For illustration purposes we will focus on the phenomena shown in Figs. 13 and 14. Fig. 13 shows the B-CEP of highest pressure. At such point the T-CEL(a) originates. Such line ends (Fig. 14) at a T-CEP-4PL (Fig. 1, $\rightarrow A, \rightarrow B, \rightarrow C, \rightarrow \text{yes}$), where T-CEL(b) originates (Fig. 14). T-CEL(b) ends at a T-TCP (Fig. 1, $\rightarrow A, \rightarrow B, \rightarrow \text{yes}$) from which T-CEL(c) stems (Fig. 1, $\rightarrow V$). This line extends up to a new T-CEP-4PL where T-CEL(d) originates, whose full extent can be seen in Fig. 12.

Notice in Fig. 14 that the two T-CEP-4PLs are connected by a T-4PL. Block 1 of Fig. 1 is executed again for the second B-CEP. A total of six T-CEP-4PLs are found (Table 4). Next, block 2 of Fig. 1 is executed as many times as required, always starting at sub-block VIII, being the overall result the complete diagram of Fig. 12.

5. Conclusions

Characteristic maps of the fluid phase behavior of ternary systems (T-CMs) were computed in this work by using the algorithm of Fig. 1 which relies, among other resources, on the use of numerical continuation methods for calculating the univariant phase equilibrium lines of which T-CMs are made of. Complete T-CMs were obtained, i.e., the ranges of conditions considered were the very wide ranges for which phase equilibrium calculations can be carried out using models, for the fluid state, of the equation of state (EOS) type. The solid state was not considered in this work, since the goal was to develop a strategy to completely characterize the behavior of a fluid-state model, once the values for its parameters are specified. Therefore, part of the T-CMs obtained here are metastable with respect to the formation of solid phases.

Although the EOS used is a relatively simple model, it can generate highly complex ternary phase behavior topologies, which seem not to have been previously documented in the literature. The found ternary phase behavior ranges from a relatively simple one, as in Fig. 2, to a highly complex behavior, as in Fig. 12.

The results of this work show that the features of a T-CM are not univocally established by the number of B-CEPs, as it is clear from Figs. 3 and 12: in both cases the number of B-CEPs equals two (see Table 4). This, together with other results presented in this work, suggests that the variety for the ternary fluid phase behavior is wide. A classification for the ternary fluid phase behavior should, on one hand, account for the mentioned wide variety, and, on the other, be based on the number, type and behavior of the ternary univariant lines, just as the classification for the binary phase behavior

of Refs. [1] and [2] are based on the univariant binary lines. Bolz et al. [2] have estimated that the total number of binary phase diagram classes is about 210, with the warning that “yet to be discovered restrictions on phase diagram topology” might decrease such number to some extent. In our view, the classification of the binary fluid phase behavior by Bolz et al. [2] is more a naming system than a classification. The strength of such naming system is that it is able to cover all known and yet unknown binary behaviors. 210 classes of binary phase behavior give an extremely large number of combinations of binary classes taken 3 at a time. If each class, among the 210 classes, were designated using a Greek letter, then, examples of ternary combinations would be $\{\alpha, \beta, \lambda\}$, $\{\beta, \lambda, \lambda\}$ and $\{\varepsilon, \varepsilon, \varepsilon\}$. From the large number of the mentioned combinations, we should expect a huge variety for the qualitative behavior of ternary systems, and just considering the univariant level alone (T-CMs). Such huge variety, together with the experience gained in this work, makes, in our opinion, the search for a classification of the ternary fluid phase behavior become an endeavor with no hope of success. Rather, the efforts should be focused on the search for a naming system, for the ternary fluid phase behavior, having the features of the one that Bolz et al. [2] proposed for binary systems.

We have verified that the strategies used in this work for obtaining the first converged point of a ternary univariant line were robust. This was also the case for the NCMs applied subsequently.

An important part of this work was the definition and evaluation of a methodology for computing a T-4PL, having, as the only known information, the one contained in the computed T-CEP-4PL at which the T-4PL originates. The basic idea of such methodology is also used for computing (as an auxiliary calculation) ternary three-phase equilibrium lines stemming from known T-CEPs. So far, we have not developed a method for starting off the computation of a T-CEL from a known (computed) T-TCP. This is the matter of future work, as it is the full automation of the algorithm for generating calculated T-CMs. We also foresee the inclusion of computed ternary azeotropic lines and of closed loop T-CEs. Such lines are neither connected to B-CEPs nor to T-CEP-4PLs.

Acknowledgements

We are grateful, for their financial support, to the following institutions: Consejo Nacional de Investigaciones Científicas y Técnicas de la República Argentina (CONICET), Universidad Nacional del Sur (U.N.S., Arg.), Agencia Nacional de Promoción Científica y Tecnológica (ANPCyT, Arg.), Universidad Nacional de Córdoba (UNC, Arg.), Capes/Brasil, Fundação Araucária (Brasil), FAPESP (Brasil) and CNPq (Brasil). M. S. Z. was a CAPES/Brasil Grantee at State University of Maringá during part of year 2013.

Appendix A. System of equations for the ternary tricritical point calculation

The system of equations to be solved for computing a ternary tricritical point (T-TCP) is the following:

$$F = \begin{bmatrix} F_1 \\ F_2 \\ F_3 \\ F_4 \\ F_5 \\ F_6 \\ F_7 \\ F_8 \\ F_9 \\ F_{10} \\ F_{11} \\ F_{12} \\ F_{13} \\ F_{14} \end{bmatrix} = \begin{bmatrix} \det(\mathbf{M}^* - \lambda I) \\ (M_{11}^* - \lambda)u_1 + M_{12}^*u_2 + M_{13}^*u_3 \\ M_{21}^*u_1 + (M_{22}^* - \lambda)u_2 + M_{23}^*u_3 \\ u_1^2 + u_2^2 + u_3^2 - 1 \\ \left(\frac{\partial^2 tpd^*}{\partial s^2}\right)_{s=0} \\ \left(\frac{\partial^3 tpd^*}{\partial s^3}\right)_{s=0} \\ V - v^0 \\ \left(\frac{\partial^4 tpd^{**}}{\partial s^4}\right)_{s=0} \\ \left(\frac{\partial^5 tpd^{**}}{\partial s^5}\right)_{s=0} \\ M_{11}^*w_1 + M_{12}^*w_2 + M_{13}^*w_3 - 1/2(cu_1 - r_1) \\ M_{21}^*w_1 + M_{22}^*w_2 + M_{23}^*w_3 - 1/2(cu_2 - r_2) \\ u_1w_1 + u_2w_2 + u_3w_3 \\ P - \psi(T, v^0, z_1, z_2, z_3) \\ z_1 + z_2 + z_3 - 1 \end{bmatrix} = 0 \quad (\text{A.1})$$

In system (A.1), the first equation, i.e., the equation $F_1 = 0$, is the equation for calculating the eigenvalues of the 3×3 matrix \mathbf{M}^* . I is the identity matrix and λ is the eigenvalue of matrix \mathbf{M}^* of minimum absolute value. The elements of matrix \mathbf{M}^* are defined as follows:

$$M_{ij}^* = \sqrt{z_i z_j} \left[\left(\frac{\partial \ln \hat{f}_i}{\partial n_j} \right)_{T, V, n_m} \right]_{T, V, z} \quad \text{with } m = 1 - 3 \text{ subject to } m \neq j \quad (\text{A.2})$$

In Eq. (A.2) \hat{f}_i is the function of the absolute temperature (T), total volume (V), and numbers of moles of the components in the multicomponent mixture (n_i , i = from 1 to number of components) that explicitly connects such variables with the fugacity of component “ i ” in the mixture. The chosen equation of state (SRK-EOS in this work [16]) imposes the form of function \hat{f}_i .

In the expression resulting from the differentiation process in Eq. (A.2), vector \mathbf{n} (whose elements are the numbers of moles of the components) has to be replaced by vector \mathbf{z} (whose elements, z_1 , z_2 and z_3 , are the mole fractions of the components in the tricritical phase). It is thus clear that matrix \mathbf{M}^* is a function of T , V , and \mathbf{z} ; and that F_1 depends on T , V , \mathbf{z} and λ .

In equations $F_2 = 0$, $F_3 = 0$, and $F_4 = 0$, in system (A.1), u_1 , u_2 and u_3 are the components of the (normalized) eigenvector of matrix \mathbf{M}^* , associated to eigenvalue λ . $F_2 = 0$ and $F_3 = 0$ correspond to the standard equations for computing the eigenvectors. $F_4 = 0$ is a normalization equation that imposes a unity module for eigenvector \mathbf{u} . tpd^* , which appears in equations $F_5 = 0$ and $F_6 = 0$, is defined as follows:

$$tpd^* = [tpd(T, V, \mathbf{n})]_{T, V, n_i = n_i^*} \quad (\text{A.3})$$

where tpd is the tangent plane distance function, defined as follows:

$$tpd(T, V, \mathbf{n}) = \sum_i n_i [\ln \hat{f}_i(T, V, \mathbf{n}) - \ln \hat{f}_i(T, v^0, \mathbf{z})] - \frac{V}{RT} (\psi(T, V, \mathbf{n}) - \psi(T, v^0, \mathbf{z})) \quad (\text{A.4})$$

R is the universal gas constant. Function ψ connects the total volume (V), the vector \mathbf{n} , and the absolute temperature (T) to the absolute pressure. Function ψ corresponds in this work to the pressure-explicit SRK-EOS coupled to quadratic mixing rules [16]. In Eq. (A.4), v^0 is the molar volume of the tricritical phase. The elements of vector \mathbf{n}^* [which appears in Eq. (A.3)] are defined as follows:

$$n_i^* = z_i + s u_i \sqrt{z_i} \quad (\text{A.5})$$

where variable “ s ” is a distance parameter.

From Eqs. (A.3) and (A.4), it should be clear that tpd^* is a function of T , V , \mathbf{z} , \mathbf{u} , v^0 and s . The dependence of tpd^* on variable “ s ” implies the existence of the partial derivatives of tpd^* with respect to “ s ”, which are required by equations $F_5 = 0$ and $F_6 = 0$ in system (A.1). Such equations prescribe that the partial derivatives have to be evaluated at $s = 0$. For this reason, functions F_5 and F_6 do not depend on “ s ”. We used analytical (not numerical) expressions for the derivatives $\partial^2 tpd^* / \partial s^2$ and $\partial^3 tpd^* / \partial s^3$, within equations $F_5 = 0$ and $F_6 = 0$ of system (A.1).

Equation $F_7 = 0$ in system (A.1) imposes the equality between variables V and v^0 .

Variable c , which appears in equations $F_{10} = 0$ and $F_{11} = 0$ of system (A.1), is defined as follows:

$$c = u_1 r_1 + u_2 r_2 + u_3 r_3 \quad (\text{A.6})$$

Notice that c is a scalar number. r_1 , r_2 and r_3 are the components of vector \mathbf{r} . Such components appear in equations $F_{10} = 0$ and $F_{11} = 0$ of system (A.1). Vector \mathbf{r} is defined with reference to vector \mathbf{g}^* , which in turn is related to vector \mathbf{g} . The components of vector \mathbf{g} are the following:

$$g_i(T, V, \mathbf{n}) = z_i^{1/2} [\ln \hat{f}_i(T, V, \mathbf{n}) - \ln \hat{f}_i(T, v^0, \mathbf{z})] \quad i = 1 \dots 3 \quad (\text{A.7})$$

while vector \mathbf{g}^* is given by:

$$\mathbf{g}^* = [\mathbf{g}(T, V, \mathbf{n})]_{T, V, n_i = n_i^*} \quad (\text{A.8})$$

where vector \mathbf{n}^* has its components defined by Eq. (A.5). Vector \mathbf{g}^* depends on variables T , V , \mathbf{z} , \mathbf{u} , v^0 and s . Vector \mathbf{r} is defined with reference to vector \mathbf{g}^* as follows:

$$\mathbf{r} = \left(\frac{\partial^2 \mathbf{g}^*}{\partial s^2} \right)_{s=0} \quad (\text{A.9})$$

Vector \mathbf{r} depends on T , V , \mathbf{z} , \mathbf{u} and v^0 and it does not depend on s .

Equations $F_{10} = 0$, $F_{11} = 0$ and $F_{12} = 0$ of system (A.1) define vector \mathbf{w} , whose components are w_1 , w_2 , w_3 . From equation $F_{12} = 0$, it should be clear that vectors \mathbf{w} and \mathbf{u} are orthogonal ($\mathbf{u}^T \mathbf{w} = 0$).

In equations $F_8 = 0$ and $F_9 = 0$, tpd^{**} is defined as follows:

$$tpd^{**} = [tpd(T, V, \mathbf{n})]_{T, V, n_i = n_i^{**}} \quad (\text{A.10})$$

The elements of vector \mathbf{n}^{**} [which appears in Eq. (A.10)] are defined as follows:

$$n_i^{**} = z_i + (s u_i + s^2 w_i) \sqrt{z_i} \quad (\text{A.11})$$

tpd^{**} is a function of T , V , \mathbf{z} , \mathbf{u} , \mathbf{w} , v^0 and s . The analytical expression of the fourth partial derivative, with respect to “ s ”, of tpd^{**} ($\partial^4 tpd^{**} / \partial s^4$) is used in equation $F_8 = 0$ of system (A.1). Notice that ($\partial^4 tpd^{**} / \partial s^4$) _{$s=0$} , i.e., F_8 , depends on T , V , \mathbf{z} , \mathbf{u} , \mathbf{w} and v^0 but it does not depend on “ s ”.

The expression of the fifth partial derivative, with respect to “ s ”, of tpd^{**} ($\partial^5 tpd^{**} / \partial s^5$) used in equation $F_9 = 0$ of system (A.1), corresponds to a numerical differentiation recipe written in terms of the analytical fourth partial derivative $\partial^4 tpd^{**} / \partial s^4$, evaluated at two different values of “ s ” (centered finite-divided difference formula). Notice that ($\partial^5 tpd^{**} / \partial s^5$) _{$s=0$} , i.e., F_9 , depends on T , V , \mathbf{z} , \mathbf{u} , \mathbf{w} and v^0 but not on “ s ”.

Equation $F_{13} = 0$ in system (A.1) is the relationship between the absolute pressure (P), the absolute temperature (T), the molar volume (v^0) and the composition (\mathbf{z}) of the tricritical phase. We stress that function ψ corresponds in this work to the pressure-explicit SRK-EOS coupled to quadratic mixing rules. F_{13} depends on P , T , v^0 and \mathbf{z} .

Finally, equation $F_{14} = 0$ imposes that the mole fractions, in the tricritical phase, must add up to unity. Thus, F_{14} depends only on \mathbf{z} .

The T-TCP system of equations [system (A.1)] has 14 equations and 14 variables. The list of variables is the following:

$$T, P, V, v^0, z_1, z_2, z_3, u_1, u_2, u_3, w_1, w_2, w_3 \text{ and } \lambda$$

Since the number of variables equals the number of equations, system (A.1) has zero degrees of freedom. Thus, system (A.1) defines a hyper-point in a 14D hyper-space. It should be clear that, for a ternary system, a tricritical point is invariant.

Function tpd in Eq. (A.4), is a difference, i.e., the Helmholtz energy at (T, V, \mathbf{n}) minus the linear approximation to the Helmholtz energy at (T, v^0, \mathbf{z}) , evaluated, such approximation, also at (T, V, \mathbf{n}) . In other words, the tangent plane distance function is the difference between the Helmholtz energy surface and the plane that is tangent to the surface at (T, v^0, \mathbf{z}) , being, such difference, a function of (T, V, \mathbf{n}) .

In Eq. (A.4) the phase at (T, v^0, \mathbf{z}) is the tested phase and the phase at (T, V, \mathbf{n}) is the trial phase. A negative tpd value implies that the tested phase is not stable.

In system (A.1), equations $F_1 = 0$ to $F_{14} = 0$ are the tricriticality conditions. They are essentially the same than those proposed in Refs. [12] and [18]. The number (fourteen) of tricriticality conditions in system (A.1) comes from the fact that the variables involved are all considered explicitly. In this work, the tricritical equations are solved simultaneously.

The actual calculations were performed in this work using logarithmically scaled variables (this scaling approach is applicable for positive variables only).

Appendix B. Meaning of the word “line” in the context of this work

Each point of a binary critical line is defined by several coordinates, i.e., temperature, pressure, mole fractions of the components, and molar density. The count is 5 coordinates. However, it is possible to add even more coordinates to a critical point, e.g., the fugacities of the components in the critical phase, the molar enthalpy, entropy, Gibbs energy, etcetera. Thus, a binary critical point is actually a hyper-point (because of its several coordinates) and a binary critical line is actually a hyper-line. In this work, we often use the word “line” to actually mean “hyper-line”. Notice that the prefix “hyper” is considered, in this work, to have the following meaning: “existing in more than three dimensions”.

The situation of a binary critical line is analogous to that of, e.g., a binary liquid–liquid–vapor (LLV) line. Here the basic coordinates are temperature, pressure, both component mole fractions in the three phases, and the molar densities of the three phases. Clearly, a binary LLV line has more coordinates associated to it than a binary critical line. Due to the great number of coordinates the word “hyperline” is also applicable to binary LLV lines. Evidently, a binary LLV line exists in a space with more dimensions than the space associated to a binary critical line.

Binary critical and LLV hyperlines are real vector valued functions on R , where R is the set of real numbers. “Vector functions” is a topic considered in textbooks on multivariable calculus, e.g., Ref. [19]. In general real vector valued functions on R^n are functions $F: R^n \rightarrow R^m$, which means that F has domain $D \subseteq R^n$ and range $R \subseteq R^m$. Function F assigns a (dependent) m -dimensional vector to an (independent) n -dimensional vector. All components of either vector are real numbers. A binary critical hyperline could be considered to be a function $F: R \rightarrow R^{m_{crit}}$. A binary critical point has a single degree of freedom, which could be considered to be, e.g., the temperature $T (D_{crit} \subseteq R)$. Its dependent variables could be considered to be the following: pressure (P), mole fractions of the components ($x_{1,crit}$ and $x_{2,crit}$), and molar density (ρ). In such a case $m_{crit} = 4$ and the range R_{crit} of the binary critical line is such that $R_{crit} \subseteq R^4$. Notice that a binary critical line is a set of four 2-dimensional (2D) lines: P vs T , $x_{1,crit}$ vs T , $x_{2,crit}$ vs T , and ρ vs T . It is also a set of 3D lines, one of which is, e.g., the one in the space of the variables P , T and $x_{1,crit}$. Besides, it is a set of 4D lines, e.g., the one with variables P , T , $x_{2,crit}$ and ρ . Finally, a binary critical line is a single 5D line (or hyper-line).

Perhaps the reader does not feel at ease with the fact that in, e.g., the analysis of the previous paragraph, we have considered, in the count of variables of a binary critical point, both, $x_{1,crit}$ and $x_{2,crit}$. This might seem, at first sight, not to make sense, since $x_{1,crit}$ and $x_{2,crit}$ satisfy the equation $[x_{1,crit} + x_{2,crit} - 1 = 0]$. The argument would be that the relationship between $x_{1,crit}$ and $x_{2,crit}$ implies that both variables are not mutually independent and therefore it would have been enough to consider, among the variables of the problem, only $x_{1,crit}$, or only $x_{2,crit}$, but not both. Such choice is in principle acceptable. However, in the context of calculation algorithms, it may be convenient to make explicitly appear in the system of equations of interest the mole fractions of all components. Actually, and with reference to the previous paragraph, once the temperature T is set, then, the values of all dependent variables become defined, i.e., the set made by the union of independent and dependent variables is a set of variables which are not mutually independent, as it is the case of the subset that contains only the variables $x_{1,crit}$ and $x_{2,crit}$.

A binary LLV hyperline can be considered to be a vector valued function $F: R \rightarrow R^{10}$ [independent variable: e.g., T ; dependent variables: pressure (count=1), component mole fractions in the three phases (count=6), phase densities (count=3); total count of

independent variables = 10]. Often the pressure at LLV is plotted as a function of the temperature. This process considers only one of the components of the dependent 10-dimensional vector, i.e., the pressure. The same can be done with, e.g., x_{1,l_1} [i.e., the mole fraction of component 1 in one of the phases at LLV equilibrium (phase l_1)] plotted as a function of temperature. It is clear that three lines can be plotted involving the mole fraction x_1 , i.e., x_{1,l_1} , x_{1,l_2} and $x_{1,v}$ as functions of temperature. Since the nature of the mole fraction concentration scale is unique, all three lines can be plotted together, as customary done, in the Temperature vs x_1 plane. Notice that the pressure is a “field” variable while x_{1,l_1} , x_{1,l_2} and $x_{1,v}$ are “density” variables [2].

Appendix C. Meaning of the word “hyper-surface” in the context of this work

The variables of a ternary three-phase equilibrium (T-3PE) can be considered to be temperature (T , count=1), pressure (P , count=1), mol fractions of the components in the phases at equilibrium (count=9), and the phase densities (count=3) [total count=14 variables, including both, independent and dependent variables]. According to the phase rule, a T-3PE has two degrees of freedom. Thus, we have 2 independent variables and 12 dependent variables. Therefore, an unrestricted continuous set of ternary three-phase equilibria can be seen as a real vector valued function $F: R^2 \rightarrow R^{12}$. Let's assume that the independent variables are T and P . One of the components of the 12D dependent vector will then be the density of the lightest phase at T-3PE ($\rho_{light,T-3PE}$). If $\rho_{light,T-3PE}$ is plotted as a function of T and P we obtain a surface in the 3D “ $P, T, \rho_{light,T-3PE}$ ” space. Such surface, when projected on the P - T plane, defines a region in such plane. If we change the variable $\rho_{light,T-3PE}$ by any other variable of the 12D dependent vector we obtain a new surface. Thus, several surfaces in different 3D spaces are associated to an unrestricted continuous set of ternary three-phase equilibria. This is the reason for the use of the word hyper-surface associated to ternary three-phase equilibria.

If we wrote the system of equations for ternary three-phase equilibrium (T-3PE), and added to that system the additional equation, e.g., “T-300K=0”, then, we would be writing a system of equations valid for the isothermal ternary three-phase equilibria (I-T-3PE) at 300K. Thus, the I-T-3PE has one degree of freedom less than the unrestricted T-3PE. Consequently, while the unrestricted T-3PE corresponds to a hyper-surface (or to a number of hyper-surfaces), the I-T-3PE corresponds to a hyper line (or to a number of hyper-lines). It should be clear that $D_{T-3PE} \subseteq R^2$ and that $D_{I-T-3PE} \subseteq R$. When we impose, e.g., a constant temperature on the ternary three phase equilibria we cut the previously mentioned surface in the 3D “ $P, T, \rho_{light,T-3PE}$ ” space with a plane at constant temperature. This results in a line in the 2D “ $P, \rho_{light,T-3PE}$ ” space.

To fix ideas, Fig. 2 in page 189 of Ref. [6] shows a sequence of three-phase equilibrium triangles at a constant temperature equal to 333 K, for the system carbon dioxide–water–(1-propanol). The information that such triangles provide is contained in the I-T-3PE hyperline at 333 K for the mentioned system. In Figs. 6 and 7 of page 26 of Ref. [10], Michelsen has presented a couple of calculated ternary three-phase equilibrium hyper-lines. They do not correspond to constraints that impose a constant value on a variable (e.g., constant temperature or constant pressure). Otherwise, they were obtained imposing an equidistance constraint that involves the mole fractions of component 1 in the three equilibrium phases $[\ln(y_1/x_1) - \ln(x_1/w_1) = 0]$. Such constraint is convenient when searching for an excellent approximation to a ternary tricritical point, through a conceptually simple method.

As it is the case for a ternary three-phase equilibrium, a ternary critical point also has two degrees of freedom and several coordinates that describe it. Therefore, an unrestricted continuous set of

ternary critical points is a critical hyper-surface. As declared in the main text of this paper, at a T-CEL a three-phase hyper-surface and a critical hyper-surface meet. Because a T-CEP has a single degree of freedom, a T-CEL is a hyper-line, i.e., a vector function with domain $D_{T-CEL} \subseteq R$.

Notice that if an equilibrium object (e.g., a ternary three-phase equilibrium or a T-CEP) has a single degree of freedom, then, it belongs to a hyper-line (e.g., a T-CEP is a hyper-point of a T-CEL). If an equilibrium object has two degrees of freedom, then, it belongs to a hyper-surface (e.g., a ternary three-phase equilibrium is a hyper-point of a three-phase hyper-surface).

Probably, the words hyper-point, hyper-line and hyper-surface have been used, in the literature, associated to meanings different from those considered in this work. Therefore these words should be handled with care.

Appendix D. Situations where a T-CEP is not a termination point of a T-3PL

An isopleth is an equilibrium diagram at constant overall composition, typically shown in its pressure–temperature (P – T) projection. The isopleth has a line, named phase envelope, which is the boundary between the homogeneous and the heterogeneous regions. Since the phase envelope is in most of its points a boundary between the homogeneous region and the two-phase region, it could also be named 2-phase envelope. Eventually the phase envelope may have, e.g., a three-phase equilibrium point (see, e.g., Fig. 9 of Ref. [10]).

Since a ternary three-phase equilibrium hyper-surface is projected as a region in the P – T plane, a ternary isopleth of given overall composition may have, within the heterogeneous region, a sub-region where three-phase equilibrium occurs. The boundary that separates the isopleth three-phase sub-region from the isopleth two-phase sub-region can be named 3-phase envelope (since such boundary “envelops” the three-phase region). Actually, a ternary 3-phase envelope may eventually also enclose a T-4PL or a part of it. A point of a 3-phase envelope can be computed through a special three-phase flash calculation [10]. The flash computation is performed at an overall composition equal to that of the isopleth, at set P (or T), and setting the phase mole fraction of one of the three phases equal to zero [10]. In other words, a point that belongs to a ternary 3-phase envelope satisfies simultaneously the condition of ternary three phase equilibrium and the condition of incipency for one of the equilibrium phases. That is to say that a point on a ternary 3-phase envelope is represented, in the Gibbs (composition) triangle, as a three-phase equilibrium triangle such that the overall (isopleth) composition falls on one side of the three-phase triangle. Eventually, two of the three phases may merge into a critical phase at some location along the 3-phase envelope, as shown, e.g., for the system methane + CO₂ + H₂S in Fig. 6 of page 308 of Ref. [15] (point labeled “CP” in the mentioned figure). Since at such point a critical phase is at equilibrium with a non-critical phase, such point is a T-CEP, according to our glossary.

Michelsen and Mollerup [15] have shown, in Fig. 7 of page 309 of Ref. [15], a dashed line which corresponds to the lower pressure part of a 3-phase envelope of a 5-component mixture. A point, labeled “CP”, is indicated on such dashed line [15]. Such “CP” point is a critical endpoint, because two of the three equilibrium phases are critical at the “CP” point. It can be seen in Ref. [15] that the “CP” point has temperature and pressure values intermediate with respect to the temperature and pressure ranges of existence of the 3-phase envelope. Clearly, the “CP” point is not a termination point of the 3-phase envelope for the 5-component mixture. This behavior should also be expected for ternary 3-phase envelopes, i.e., T-CEPs which are not termination points of ternary

3-phase envelopes. This would seem to be in contradiction with the statement: “A T-CEP is the termination of a ternary three-phase equilibrium line”.

For binary systems it is accepted that a critical endpoint is a termination point of a three-phase equilibrium line, as established, e.g., in page 2237 of Ref. [2]: “A three-phase curve in a binary system involving two or three fluid phases can be terminated in a (P , T) projection by a so-called critical endpoint in case of coalescence of two fluid phases ($F=1$) in the presence of the third phase.” However, for binary systems it has been shown (see, e.g., Fig. 5a of Ref. [2]) that when a critical line meets a three-phase line tangentially (“osculation point” [2]), then, a B-CEP becomes some intermediate point of the 3-phase line, and receives the name “double critical endpoint” (DCEP) [2]. In conclusion, for binary systems, B-CEPs are generally considered termination points, but it is known that there might be situations where the “termination” nature of the B-CEP is absent. When changing continuously a parameter of a chosen model, a binary DCEP is obtained when “two critical endpoints of the same nature and on different three-phase curves coincide, such that the three-phase curves are joined” [2].

The T-CEL in Fig. 8 of the main text of this work has a temperature minimum (T_{\min}). If the system temperature T is in between T_{\min} and the temperature of the B-CEP of propane + n-Eicosane ($T_{B-CEP,C3-C20}$), i.e., if $T_{\min} < T < T_{B-CEP,C3-C20}$, then, the ternary system presents two T-CEPs at T . At such temperature, two different T-3PLs exist, each one ending at one of the two T-CEPs. When T approaches T_{\min} , such that $T > T_{\min}$, the two T-CEPs become increasingly closer until they coincide so that the two associated T-3PLs are joined. In other words, at $T = T_{\min}$ there is an osculation point where the isothermal ternary 3-PL meets tangentially the T-CEL, and the T-CEP at $T = T_{\min}$ will lie on some intermediate point of the isothermal T-3PL at $T = T_{\min}$, thus losing its termination nature. Clearly, the situation for the ternary system at $T = T_{\min}$ is analogous to the one described in the previous paragraph for the DCEP of a binary system. Therefore, it is acceptable to state in general that a T-CEP is the termination of a ternary three-phase equilibrium line, but bearing in mind that T-3PLs may present osculation points where T-CEPs do not really set the termination of the T-3PL. For the sake of completeness, we observe that a T-3PL at a temperature T such that $T < T_{\min}$ will not have T-CEPs, i.e., it will connect continuously the two binary LLV points existing at such temperature.

Notice that while for an isothermal T-3PL at T_{\min} the corresponding T-CEP in Fig. 8 loses its termination nature, the same T-CEP does have such nature for an isobaric T-3PL at a pressure equal to the pressure of the T-CEL at T_{\min} . In conclusion, whether a T-CEP has a termination nature depends on how a T-3PL is specified, e.g., isothermal T-3PL versus isobaric T-3PL, i.e., the presence or absence of a T-CEP termination nature depends on how the T-CEP is approached by the T-3PL. Perhaps, in view of the behavior of ternary systems, it would be more appropriate to state that a T-CEP is the termination of a ternary three-phase equilibrium line as long as such line does not meet tangentially the T-CEL to which the T-CEP belongs; or, more concisely, as long as the T-3PL and the T-CEL do not have an osculation point.

With regard to the previously mentioned expectation of a non-termination nature for T-CEPs present in “ternary 3-phase envelopes”, our conjecture is that, at such T-CEPs, the 3-phase envelope should meet the corresponding T-CEL tangentially.

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