



Detailed calculation of complex fluid phase equilibrium sections for ternary systems



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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 $\text{CO}_2 + \text{H}_2\text{O} + 2\text{-propanol(IPA)}$, 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 multi-component 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

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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 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-CEs, 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-CEs.

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 CO₂ + 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 CO₂ + 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 CO₂ + 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 CO₂ + H₂O + 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 widening 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

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