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Computation and analysis of surfaces and lines of three-phase equilibrium in ternary systems: Application illustrated for a *$CO_2(1)+H_2O(2)+2$-propanol(3)*-like system

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ABSTRACT

In this work the rich phenomenology of the ternary three-phase equilibrium is studied for a *$CO_2(1)+H_2O(2)+2$-propanol(3)*-like system which presents a highly complex behavior. This is done through computations carried out over wide ranges of conditions using a model of the equation of state type. The developed computation and analysis strategies are applicable to any ternary system as described by any equation of state model, chosen for representing real systems having a high degree of complexity in their phase behavior. A systematic identification of phase equilibrium objects (or points) from which ternary three-phase lines (T-3PLs) originate is performed. Such points are used to start the computation of a variety of T-3PLs. Several computed T-3PLs are used to visualize a number of ternary three-phase surfaces (T-3PSs). Besides, the boundaries of the T-3PSs are established. A strategy to start the calculation of a T-3PL is proposed for each type of originating point. In addition, with the aim of avoiding convergence problems, a numerical continuation method is used to calculate complete T-3PLs. The visualization of 3D projections of T-3PSs in the temperature-pressure-fugacity space is proposed. This way of looking at the T-3PSs is of much help in the understanding on how they behave and interrelate. The results suggest, among other interesting conclusions, the possibility of continuous transitions from T-3PSs of a given type to T-3PSs of a different type.

1. Introduction

A type of fluid phase equilibrium of special interest is the three-phase equilibrium (3PE) (see, e.g., refs [1] and [2]). The accurate reproduction of experimental 3PE is a stringent test for thermodynamic models for multicomponent mixtures, mainly if the multicomponent system considered is highly non-ideal. If this test is passed by a given model, for the case of ternary systems, then, the user should be more confident about its performance for multicomponent systems. The calculation of the ternary 3PE (T-3PE) is also a stringent test for computation algorithms. This is because the behavior of continuous sets of three-phase equilibria may be of considerable complexity. Reliable algorithms are also needed in the process of fitting the model interaction parameters.

A ternary system can exhibit a wide variety of three-phase equilibria. Different 3PE points may belong to the same ternary three-phase surface (T-3PS) or to different T-3PSs. In turn, the topology of a T-3PS could be complex and difficult to interpret. In particular, to be aware of the variety of equilibrium phenomena of potential occurrence, when a continuous set of ternary three-phase equilibria comes to an end, is crucial to interpret properly T-3PE experimental results obtained in the laboratory, and even to study failures of computation algorithms.

Important fluid phase equilibrium diagrams are those that are made of univariant equilibrium lines and invariant equilibrium points. We name such diagrams phase equilibrium “characteristic maps”, more specifically, “Binary characteristic map” (B-CM) and “ternary characteristic map” (T-CM), for binary and ternary systems, respectively. A point of a univariant equilibrium line becomes defined when a single degree of freedom is specified. This means

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that it is ‘necessary’ to specify the value of a variable of the system to establish the equilibrium. Actually, and more generally, specifying a relationship between a sub-set of the variables of the system is also a way of spending the single degree of freedom available. On the other hand, an invariant equilibrium point is a point with zero degrees of freedom.

Scott and van Konynenburg [3] described a variety of B-CMs, and proposed a classification for their behavior. This classification is based on the observation, in the pressure-temperature plane, of the topology of computed univariant equilibrium lines. Such lines were calculated in Ref. [3] using the van der Waals equation of state (EoS). Cismondi and Michelsen [4] proposed a methodology for the calculation of B-CMs as those shown in Ref. [3].

The equilibrium behavior of the binary system is defined over the entire ranges of temperature, pressure and composition once all the parameters values of the EoS are set. The univariant lines that compose the B-CM are binary three-phase lines (B-3PLs), binary critical lines (B-CLs) and binary azeotropic lines; while the invariant points involved are binary critical end points (B-CEPs) and binary azeotropic end points. Tables 1 and 2 provide, respectively, the meaning of the acronyms used in this work, and the description of the physical situation for a variety of phase equilibrium objects. Not all binary behaviors have three-phase equilibrium. In addition, the (univariant) vapour-liquid equilibrium lines of the pure compounds and their respective (invariant) critical points are included in the B-CM.

When going from binary to ternary systems, a ternary fluid phase equilibrium characteristic map arises (T-CM), and the behavior of the 3PE becomes considerably more complex. Clearly, the binary 3PE has a single degree of freedom which implies that a continuous set of binary 3PE points is a line (or hyper-line). In contrast, the 3PE in a ternary system has two degrees of freedom. This implies that an unrestricted continuous set of ternary 3PE points is a surface (or hyper-surface) and not a line, as it is in binary systems. Consequently, the ternary 3PE is not a thermodynamic object that contributes to the ternary characteristic map (T-CM).

Table 1
Acronyms used in this work and in Ref. [10–12].

Acronym	Meaning	# of phases	# of crit. phases
P-VPL	Pure (compound) vapour-pressure line	2	
B-3PP	Binary three-phase point	3	
B-3PL	Binary three-phase line (locus of B-3PPs)	3	
T-3PP	Ternary three-phase point	3	
T-3PL	Ternary three-phase line (locus of T-3PPs)	3	
T-3PS	Ternary three-phase surface	3	
T-4PP	Ternary four-phase point	4	
T-4PL	Ternary four-phase line (locus of T-4PPs)	4	
P-CP	Pure critical point	1	1
B-CP	Binary-critical point	1	1
B-CL	Binary-critical line (locus of B-CPs)	1	1
B-CEP	Binary-critical end point	2	1
T-CEP	Ternary-critical end point	2	1
T-CEL	Ternary-critical end line (locus of T-CEPs)	2	1
T-CEP-4PL	Ternary-critical end point of a four phase line	3	1
T-TCP	Ternary-tricritical point (this is a synonym of T-TCEP)	1	
T-TCEP	Ternary-tricritical end point (this is a synonym of T-TCP)	1	
T-CM	Ternary characteristic map (characteristic map of the fluid phase behavior of a ternary system)		
B-CM	Binary characteristic map (characteristic map of the fluid phase behavior of a binary system)		
NCM	Numerical Continuation Method		
3PE	Three-phase equilibrium	3	
T-3PE	Ternary Three-Phase Equilibrium	3	

Table 2
Thermodynamic objects present in a ternary characteristic map (T-CM).

	Type of thermodynamic object	No. of components	Phase condition
Univariant lines	Pure vapour pressure line (P-VPL)	1	L + V
	Binary three-phase line (B-3PL)	2	L + L + V
	Binary critical line (B-CL)	2	Critical phase (L1 = L2 or L = V)
	Binary Azeotropic Line	2	L + V (phases with same composition)
	Ternary critical end Line (T-CEL)	3	Critical phase + non-critical phase ((L1 = L2)+V or L1+(L2 = V))
	Ternary four phase Line (T-4PL)	3	L + L + L + V
	Ternary Azeotropic Line	3	L + V (phases with same composition)
Invariant Points	Pure Critical Point (P-CP)	1	Critical phase (L = V)
	Binary Critical End Point (B-CEP)	2	Critical phase + non critical phase ((L1 = L2)+V or L1+(L2 = V))
	Binary Azeotropic end Point	2	Two phases with same composition may become critical (L = V), or can be infinitely diluted in a component, or may become unstable by the appearance of a third phase at equilibrium with the azeotropic phases (L + L + V) [13]
	Ternary Critical End Point of a Four Phase Line (T-CEP-4PL)	3	A T-CEP-4PL is an endpoint of a T-4PL, where two of the four phases become critical. (e.g., L1+L2+(L3 = V), or, e.g., L1+(L2 = L3)+V, etc.)
	Ternary Tricritical Point (T-TCP) or Ternary Tricritical End Point (T-TCEP)	3	In a T-TCP three non-critical phases at equilibrium become critical simultaneously. (L1 = L2 = V)
	Ternary Azetropic end Point (T-AEP)	3	Not considered in this work.

L = Liquid; V=Vapour.