



Critical end line topologies for ternary systems



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ABSTRACT

A ternary critical end line (T-CEL) is a line of Ternary critical end points (T-CEPs). T-CEs provide key information on the phase behavior of ternary systems, i.e., they are boundaries for the ternary three-phase equilibrium. A ternary system may have several T-CEs. It is desirable to have available a robust algorithm for computing complete ternary CELs, thus minimizing the need for user intervention. It is also important to reliably detect the key points where T-CEs originate or terminate. In this work, we propose to apply a numerical continuation method (NCM) for the fast and robust computation of T-CEs. We present calculated T-CEs for highly asymmetric systems showing the topologies that these lines define. We consider a model of the equation of state (EOS) type and use it over wide ranges of conditions. Such ranges are much wider than those previously considered in the literature. Our main conclusion is that models for the fluid phase equilibria of ternary systems may predict, for a given system, several T-CEs of varying types and topologies. Some of such topologies have been observed for the first time in this work.

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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 behavior of models and 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 end points and a variety of end points for azeotropic lines. The mentioned lines are actually non-linear and would therefore be named “curves” by a mathematician (ref [2], p. 114). In other words, critical, azeotropic and liquid–liquid–vapor lines are understood to be curves [2]. “Only tie lines are straight lines” [2].

In ternary systems, an important type of, in a way, key point, is the (ternary) critical end point (T-CEP). 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 is the termination of a

ternary three-phase equilibrium line. This line may be, e.g., isothermal or isobaric.

Appendix C presents a significant part of the phenomenology relevant to this work for the fluid phase behavior of ternary mixtures. Three and four-phase equilibria, critical lines and T-CEPs are represented together with other phase equilibrium objects in the familiar Gibbs triangles. Appendix C is mostly based on the comprehensive review by Adrian et al. [3]. Notice that after section 6, both, a list of acronyms and a list of symbols are provided.

For computing a T-CEP it is necessary to add, to the critical conditions, the isofugacity conditions between the critical and non-critical phases (Appendix A). The resulting system of equations (SE) has only one degree of freedom. Therefore, the T-CEP conditions define one or more continuous lines (or hyper-lines) of T-CEPs for a given ternary system, model, and parameter values. A proper name for a line of T-CEPs is “ternary critical end line” (T-CEL). Notice that a T-CEL is a T-CEP locus. A T-CEL (actually a hyper-line) is a characteristic univariant line of a ternary system. At a T-CEL, a three-phase hyper-surface and a critical hyper-surface meet. A T-CEL is indeed a key line whose computation makes possible to facilitate the systematic evaluation of a combination of a chosen model and a set of specified values for its parameters. A ternary system may have from none to several T-CEs. As it is the case for binary univariant lines, a ternary critical end line (or hyper-line) is understood to be a curve (or hyper-curve) despite the use of the word “line”.

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List of symbols

\hat{f}_i	fugacity of component i in the mixture
I	identity matrix
$J_{F^{(15)}}$	Jacobian matrix of vector function $F^{(15)}$
M'_{ij}	element of matrix \mathbf{M}'
n_i	number of moles of component i (i th element of vector \mathbf{n})
\mathbf{n}	number of moles vector
P	absolute pressure
P^*	logarithmically scaled P
R	universal gas constant
s	distance parameter
S_{spec}	value assigned to the specified variable
T	absolute temperature
T^*	logarithmically scaled T
tpd	tangent plane distance function
u_i	i th element of eigenvector \mathbf{u}
\mathbf{u}	eigenvector of matrix \mathbf{M}'
ν^0	molar volume of the critical phase
ν^{0*}	logarithmically scaled ν^0
V^*	logarithmically scaled V
V_x	molar volume of the non-critical phase
V_x^*	logarithmically scaled V_x
x_i	mole fraction of component i in the non-critical phase
x_i^*	logarithmically scaled x_i
\mathbf{x}	mole fraction vector, with elements x_i .
z_i	mole fraction of component i in the critical phase
z_i^*	logarithmically scaled z_i
\mathbf{z}	mole fraction vector, with elements z_i .
ΔS_{spec}	change in parameter S_{spec}
λ	eigenvalue associated to the eigenvector \mathbf{u}
Λ_s	specified variable
$\Lambda_{next\ point}^0$	initial estimate for the vector Λ of the next point of the T-CEL
$\Lambda_{conv.\ point}$	vector Λ of a converged point of a T-CEL

List of Acronyms

15D	having fifteen dimensions
2D	having two dimensions
3D	having three dimensions
4PE	four phase equilibrium
B-CEP	binary critical end point
EOS	equation of state
inf-T-CEP	T-CEP where one of the components is at infinite dilution
NCM	numerical continuation method
P-CP	pure (compound) critical point
PR-EOS	Peng-Robinson equation of state
SRK-EOS	Sove-Redlich-Kwong equation of state
T-4PL	ternary four phase (equilibrium) line
T-CEL	ternary critical end line
T-CEP	ternary critical end point
T-CEP-4PL	ternary critical end point of a four phase line
T-TCEP	ternary tricritical end point

It is worth noting that we use the word “hyper-line” to identify a continuous set of points, each characterized by several coordinates, being defined, each point, by a single degree of freedom. A hyper-line has several projections, i.e., a hyper-line has an associated set of elementary curves that can be represented in a corresponding set of 2D diagrams. Besides, in this work we use the word “hyper-surface” to identify a continuous set of points, each characterized by several coordinates, being defined, each point, by two degrees

of freedom. A hyper-surface has an associated set of elementary surfaces: they are the projections of the hyper-surface and can be represented in a corresponding set of 3D diagrams. Notice that the prefix “hyper” means in this work “several (more than three) coordinates”. Levelt-Sengers ([2], p. 46) has referred to ternary “critical surfaces”, while Gauter et al. [4] have considered both, critical and three-phase ternary “surfaces”. In spite of the glossary of refs [2] and [4], we often prefer to add the prefix “hyper” to the word “surface” (or “line”) to bear in mind the multidimensionality of the thermodynamic objects of interest. For instance, on page 135 of ref [4], a ternary ($\text{CO}_2 + 1\text{-octanol} + \text{hexadecane}$) “critical surface” is represented in the 3D space of variables pressure, temperature and solvent-free mass fraction of a component (Fig. 7 of ref [4]). In such figure, the pressure is the dependent variable. However, an analogous plot would exist if the critical pressure were exchanged by, e.g., the density of the critical phase. Thus, several 3D ternary critical surfaces are all contained within a single critical hyper-surface. This justifies the use of the prefix “hyper”. Actually, Fig. 7 of ref [4] shows only one of the several possible 3D projections of a critical hyper-surface of system $\text{CO}_2 + 1\text{-octanol} + \text{hexadecane}$.

Di Andreth [5] studied the ternary system $\text{CO}_2 + \text{water} + 2\text{-propanol}$, and developed a couple of algorithms: one for computing ternary three-phase equilibria, and another one for calculating ternary four-phase equilibria. Di Andreth [5] showed T-CELS, computed with the Peng-Robinson EOS [PR-EOS, [6]], but did not provide detailed information on the calculation procedure for T-CEPs. According to the phase rule, a ternary three-phase equilibrium has two degrees of freedom (ref [2], p. 46). When one of them is spent, e.g., by setting a constant temperature, a three-phase equilibrium hyper-line, i.e., a continuous set of three-phase equilibria, becomes defined, e.g., an isothermal three-phase hyper-line. It seems that, in ref [5], each T-CEP of a given T-CEL would be identified while calculating a three-phase equilibrium hyper-line when verifying the absence of convergence. In other words, and in contrast with this work, Di Andreth [5] did not compute T-CEPs in a direct way.

Gregorowicz and de Loos [7] have presented calculated T-CELS for $\text{methane} + \text{propane} + n\text{-eicosane}$ and $\text{ethane} + \text{propane} + n\text{-eicosane}$. They have suggested to start off by computing the critical end points of the binary subsystems (B-CEPs), and next to use such information to initialize the computation of a number of T-CEPs equal to the number of B-CEPs. However, the authors have not provided details on how to initialize the T-CEP variables that do not exist in a B-CEP, which is located very close to the T-CEP to be computed. Such variables are the concentrations of the third component in the two equilibrium phases of the T-CEP. A T-CEP located very close to a B-CEP is an infinite dilution T-CEP, since the concentration of one of the three components, in either equilibrium phase, tends to zero. Besides, Gregorowicz and de Loos [7] have suggested to set the temperature as the independent variable in the computation of T-CEPs. Such choice might not be a convenient one if the T-CEL, to which the T-CEPs being computed belong, has a highly non-linear behavior. Specifying a value for temperature is not appropriate in parts of T-CELS where the temperature remains practically constant, or it changes slowly [e.g., T-CEL(d) in Fig. 5].

Adrian et al. [8] experimentally studied, at varying temperatures and pressures, three-phase and four-phase equilibria, and CEPs, for the ternary system $\text{CO}_2 + \text{H}_2\text{O} + 1\text{-propanol}$. They [8] presented several qualitative diagrams to explain the observed phase behavior. Besides, they [8] showed quantitative diagrams which present both, experimental data and modeling results. These phase diagrams include typical triangular diagrams at set temperature and pressure, and pressure versus mole fraction (or density) projections of three-phase equilibrium lines. Adrian et al. [8] did not describe the calculation algorithms that they used to generate their modeling results.

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