

AUTOMATED GENERATION OF PHASE DIAGRAMS FOR SUPERCRITICAL FLUIDS FROM EQUATIONS OF STATE

Martín Cismondi^{1,*}, Michael L. Michelsen² and Marcelo S. Zabaloy³

¹ *Facultad de Ciencias Exactas Físicas y Naturales. Universidad Nacional de Córdoba. Av. Velez Sarsfield 1611, Ciudad Universitaria. X5016GCA Córdoba, ARGENTINA.*

² *IVC-SEP, Department of Chemical Engineering, Bygning 229, DTU, DK 2800 Lyngby, DENMARK.*

³ *Planta Piloto de Ingeniería Química, PLAPIQUI-UNS-CONICET. Camino La Carrindanga Km. 7. 8000 Bahía Blanca, ARGENTINA.*

*Corresponding author. e-mail: mcismondi@efn.uncor.edu ; mcismondi@plapiqui.edu.ar

Abstract

Phase behavior is of major importance in the analysis and development of applications of supercritical fluids. Different classes of phase diagrams of fluid mixtures are useful to understand mixing/demixing processes, to explore conditions at which such processes occur and to study the influence of temperature and pressure on solubility values.

Equations of state are an important type of thermodynamic models. They can be used to model properties of liquid, vapor or supercritical phases, with continuous transitions among such states. Unfortunately, phase equilibrium calculations are not simple. They require iterative procedures, which have no guarantee for convergence, rely on often crucial initial estimates and provide solutions that need to be tested for stability. Special attention has been given in the literature to the development of calculation procedures for two-phase and multiphase flashes, saturation points, phase envelopes, critical points, etc [1]. However, the development of calculation algorithms for phase equilibria has not reached yet a plateau. For instance, a general algorithm for automated construction of phase diagrams for binary mixtures covering all possible situations of fluid-fluid and solid-fluid equilibria for systems of varying asymmetry is, to our knowledge, not yet available.

In other words, we not only face the problem of finding a good model for the representation of the experimental reality, but also the problem of finding reliable calculation algorithms to faithfully unveil the reality within the universe of the chosen model. In our opinion, in the scientific community, the level of awareness towards the first of these problems is significantly higher than for the second.

During the last years we have focused on the goal of developing tools able to generate phase diagrams in a general and automated way. Such work led to algorithms that apply to a relatively wide variety of phase behavior situations while setting the user free from initializing the calculations. The first part of this presentation reviews such previous contribution, which produced the software GPEC (Global Phase Equilibrium Calculations) [2, 3]. The algorithms are so far restricted to binary systems [4, 5, 6]. They cover, without requiring advance user's knowledge of the system phase behavior type, the automated location of Critical End Points (CEP), the automated calculation of critical lines and liquid-liquid-vapor (LLV) lines, the integration of the previous items into global-phase equilibrium diagrams, and the automated generation of Pxy and Txy diagrams. The second part of this work discusses and illustrates a new algorithm for the automated generation of complete fluid phase envelopes at specified composition, for binary mixtures. The algorithm is based on the location of key points at the set system composition, before starting off the building of the phase envelope. Such key points include vapor-liquid critical points, liquid-liquid critical points and saturated phases at LLV points. Finally, we discuss our future work in the field of equation of state phase diagrams generation.

1 Introduction

The goal in this work is to complement previously developed tools for the analysis of the phase behavior of binary mixtures.

The program GPEC (Global Phase Equilibrium Calculations) is based on recent works by Cismondi and Michelsen [4, 5] and Cismondi et al. [6]. It allows the automated generation of a global phase equilibrium diagram, comprising critical, LLV, azeotropic and pure saturation lines, from a chosen model and parameters, covering phase behaviours from type I to V in the classification of Scott and van Konynenburg [7]. From the points intersected at a specified temperature or pressure in a global phase equilibrium diagram, GPEC generates the corresponding Pxy or Txy diagram in an automated way, i.e. without intervention of the user. The only as yet missing projection plane of the PTx tridimensional surface is therefore the PT phase envelope for constant composition or isopleth, which is treated in this work.

In the same way as for Pxy or Txy diagrams generation, we should be able to automatically identify all regions or segments of the isopleth that need to be calculated for each given composition. Moreover, since we know in advance the limits for each segment to be calculated, stability analysis should not be required.

The computational implementation of this integrated approach requires automating the following stages:

1. Reading and storing the vectors of critical and LLV lines, as well as pure compound critical points and critical end points (CEPs). Identification of the type of phase behaviour predicted.
2. Detection of composition local minima or maxima in critical lines, as well as in vapour or liquid branches of LLV lines.
3. Determination of the pressure-temperature-density coordinates at which the different lines intersect the plane of the specified composition.
4. Deduction, from the intersection points obtained, of the number and nature of the segments the isopleths will be constituted of.
5. Calculation of each segment of the isopleth.

In this way, for example, if at a specified composition we find a critical point and a saturated liquid phase at a LLV point, and the phase behaviour is of type II, III or IV, the corresponding isopleth diagram will be of the type of the one shown in Figure 2. We then proceed, one by one, to the calculation of the three segments that conform the isopleth, with the limits given by the intersection points available, by the pre-specified minimum temperature for the low pressure dew point line and, in this case, also by the maximum pressure specified for the saturated liquid line.

Stages 1 and 2 are fairly trivial. The following sections are dedicated to the other three stages (3 to 5) listed above. Notice that, in the present approach, the LLV line is known from an independent calculation, before computing a given isopleth.

2 Determination of intersection points at specified composition

This is also quite easy/straightforward to implement. With respect to critical lines, we consider that the following recommendations might help in the development of a general and efficient algorithm:

- Consider each critical line independently, i.e. determine how many intersections there are for each line. We suggest adopting the classification of lines proposed in [4], namely A to E.

- The relative position of the specified composition value, with respect to the ending points of the line and to possible maxima and minima in composition, will tell us whether the number of intersections is 0, 1 or 2. The number of critical points in the diagram is the sum of the numbers of intersections for all critical lines.
- There is also the possibility of three intersections in the case of a line C [4] (phase behaviour of type III) when there are local maximum and minimum composition points and the specified composition falls in the intermediate range.
- Lines A and D may intersect only once the specified composition, since they do not present minimum or maximum points.

The same applies to LLV lines, i.e., each of the three branches should be considered independently. Two intersections with the same liquid branch are frequent in a phase behaviour of type III (Fig. 1).

3 Deduction of the number of segments and their type

Once we know the number of LLV and critical intersection points, their types and $TP\rho$ coordinates, we need to deduce from this information how many segments will make up the homogeneity boundary in our isoplethic diagram and what the limits will be for each segment. To that end, we performed a systematic study that led to the identification of 18 different types of isoplethic diagrams for non azeotropic binary systems showing phase behaviour of types I to V. Due to space limitations, we list in Table 1 only four of those cases, i.e., Table 1 describes four different types of isopleths, and the features of the involved constituent segments. The limits or ending points for each segment are indicated inside brackets. These limits can be a critical point (C) and/or a liquid (L) or vapour (V) phase in a LLV point. They can also be pre-specified limit values for temperature or pressure, i.e., the minimum temperature for a low-temperature dew point line or bubble point line (LTDP and LTBP, respectively) and the maximum pressure for a high pressure liquid point (HPLP). The “x” or “y” superscript, for each segment of an isopleth in Table 1, indicates whether the saturated phase of specified composition z will be the phase poorer or richer in component 1 respectively –which for VLE means liquid or vapour- along the segment. In other words, the incipient phase in segments with a “y” superscript will be heavier than the saturated phase, and the opposite applies to segments with an “x” superscript. Component 1 is the most volatile of the two. Notice that there is a column in Table 1 indicating which portions of the independently calculated LLV line need to be printed together with the isopleth segments generated, in order to complete the information on the number and type of phases predicted for the mixture of specified composition, at set pressure and temperature conditions (see figures in section 5).

To fix ideas, let us consider Figure 2 beforehand, which corresponds to case 7 in Table 1. In this case three different segments are calculated. Such segments constitute the solid line in Fig. 2. This line limits the homogeneity region. The steepest segment, located on the left side of Fig. 2, is the segment which we identify as $(L | HPLP)^{x,y}$. It meets a $(L | C)^x$ segment at an L point. In turn, the $(L | C)^x$ segment meets a $(C | LTDP)^y$ segment at the critical point. The dashed line in Fig. 2 is part of the LLV equilibrium line, whose calculation is completely independent from that of the solid lines. The details on the LLV calculations are available in Ref. [4].

Cases as case 11 in Table 1 require to make a distinction between two liquids of identical composition, both belonging to the same LLV line: L_1 denotes a liquid phase at the higher temperature LLV point, while L_2 refers to the lower temperature point (see Fig. 1).

Table 1: Types of isoplethic diagrams for binary non azeotropic systems illustrated in this work

NV	NL	NCRI	Phase Behav. Type	Segments of the isopleth homogeneity boundary	Portions of LLV line to print	Isopleth Case
0	0	1	III	$(C LTDP)^y (C HPLP)^x$	All	3
0	1	1	II/III/IV	$(C LTDP)^y (L C)^x (L HPLP)^{x/y}$	T_{\min} to L	7
0	2	0	III/IV	$(L_1 LTDP)^y (L_2 L_1)^x (L_2 HPLP)^y$	T_{\min} to L_2 L_1 to K	11
1	1	1	II/III	$(V LTDP)^y (C V)^y (L C)^x (L HPLP)^y$	T_{\min} to V	17

NL, NV	Number of liquid/vapour phases of specified composition, at LLV equilibrium.
NCRI	Number of critical points of specified composition
LTDP	Low-temperature dew point (at pre-specified minimum temperature)
HPLP	High-pressure liquid point (LLE, at pre-specified maximum pressure)
LTBP	Low-temperature bubble point (at pre-specified minimum temperature)
C	Critical phase of specified composition
L	Liquid phase of specified composition at LLV equilibrium
V	Vapour phase of specified composition at LLV equilibrium
L_1, L_2	Liquid phases of specified composition, at higher and lower temperature LLV points, respectively.
T_{\min}	Minimum temperature at which LLV calculation results are available
K	K-point: point where a LLV line meets a liquid-vapor critical line

4 Calculation of a segment of the isopleth

For the construction of each segment constituting the isopleth we implement a path-following method, analogous to the ones described in [1, 4, 5, 6] for calculation of multicomponent phase envelopes, critical lines, azeotropic lines or Pxy and Txy diagrams.

The calculation of a segment in the phase envelope for a binary mixture of constant composition (isopleth) can be performed using a system of equations quite similar to the system used for the calculation of a Pxy or Txy region [5]. Being the model an equation of state, the natural variables are temperature, composition of the incipient phase and volumes of both the saturated and the incipient phase. The corresponding basic set of equations would consider the equality of pressure for the two phases, the equality of fugacity for component 1 in both phases, the same for component 2, and a specification equation. Nevertheless, two different factors make clear the convenience of extending such a basic set of variables and equations. First, pressure will be the natural specification at liquid-liquid equilibrium conditions, and therefore it should be added as a variable¹. Second, the composition variable needs to be the logarithm of a molar fraction in the incipient phase, in order to properly follow the numerical behavior of phases that tend asymptotically to a pure compound. If this molar fraction is chosen to be of component 1, the calculation may fail when the incipient phase is richer in component 1 than the saturated phase, and the opposite applies when choosing the molar fraction of component 2. There are different possible ways of solving this problem, e.g.

¹ This is not strictly required, given that the specification of pressure can be based on the pressure as a function, without adding the pressure as a variable, as we did for the calculation of Pxy regions [5]. Nevertheless, for the sake of clearness and a better structured computational implementation, we prefer to add pressure as variable.

to establish alternative sets of equations and variables, depending on whether the incipient phase is richer or poorer in component 1 than the saturated phase, or use two composition variables in the same set. In order to have unique sets of equations and variables (and a unique subroutine in the computational implementation) and keep the same notation used for Pxy and Txy diagrams calculation, we use the same two composition variables defined in ref. [5], namely $\ln x_1$ and $\ln y_2$, and add an extra specification equation that tells us whether the specified composition z for the saturated phase will fix the composition of the compound 1 richer phase (y) or compound 2 richer phase (x). Our working sets of variables and equations are therefore the following:

$$X = \begin{bmatrix} \ln x_1 \\ \ln y_2 \\ \ln v_x \\ \ln v_y \\ \ln T \\ \ln P \end{bmatrix} \quad (1)$$

$$F = \begin{bmatrix} \ln P_x(x, T, v_x) - \ln P \\ \ln P_y(y, T, v_y) - \ln P \\ \ln \hat{f}_1^x(x, T, v_x) - \ln \hat{f}_1^y(y, T, v_y) \\ \ln \hat{f}_2^x(x, T, v_x) - \ln \hat{f}_2^y(y, T, v_y) \\ g_{phase}(X) - \ln z_i \\ g_{spec}(X) - S \end{bmatrix} = 0 \quad (2)$$

where x and y are the compositions in molar fraction of the phases richer in components 2 and 1 respectively, regardless of the LV or LL nature of the segment. They also indicate the phase for volumes and pressure functions, as a subscript, and for fugacities as a superscript.

The specification function $g_{spec}(X)$ can be set equal to any of the variables in Eq. (1), and also to one of two other conveniently defined functions. The first one, identified as NS=0, is the difference $y_1 - x_1$, already used in the calculation of Pxy and Txy regions [5], and specially useful for starting the calculation of a segment from a critical point. The other one (NS=7) is $X_4 - X_3 = \ln(v_y / v_x)$, already used for the calculation of azeotropic lines [6]. The $g_{phase}(X)$ function can be set equal to either X_1 or X_2 , i.e., $\ln x_1$ or $\ln y_2$. Accordingly, z_i will take the value of z_1 or z_2 in Eq. (2).

It is important to have standard specifications for starting the construction of each type of segment. Moreover, starting building the segment from one end can be in some cases clearly more convenient than starting from the other. Consider the Table 1. Writing for example (C | V) instead of (V | C) means that the calculation of the segment starts at the critical point C, from where NS=0 is always a proper specification for the first point and for imposing the direction of the line. On the other hand, if we had to start the segment construction at the LLV point V (with the vapour phase of composition z) there is not a default specification that will progress with the same direction and high sensitivity in all cases. Therefore, when the limiting points of a segment are of type C and V, the construction starts at the C point.

The situation is different when a segment starts at a LLV point L, i.e., with a liquid phase of composition z . In these cases, specification of pressure (NS=6) for the first point, with positive direction, is appropriate for segments ending either at the maximum specified pressure (HPLP) or at a critical point (C). The same applies to the specification of temperature (NS=5) for segments ending at a LTDP or at second LLV point. In this last case, we are assuming that the ending LLV point is the one with higher temperature, in order to use a default increasing temperature direction in all cases. Notice that this is the case for the (L | L) segment in Table 1.

5 Illustration of the algorithm

For illustration of the classification and methods proposed, we choose the phase behaviour of the system Ethane + Methanol, as calculated already in ref. [5] for illustration of different types of Pxy and Txy diagrams, i.e., using the RK-PR EOS [8], with interaction parameters $k_{ij} = 0.02$ and $l_{ij} = 0.20$. The system Ethane + Methanol was the first one for which phase behaviour of type III was experimentally measured, and offers the possibility of showing interesting isopleths, as well as Pxy or Txy diagrams, and in scales more convenient than for other systems. Fig. 1 shows the temperature-composition projection of the global phase equilibrium diagram (the corresponding P-T projection can be found in ref. [5], Fig. 2).

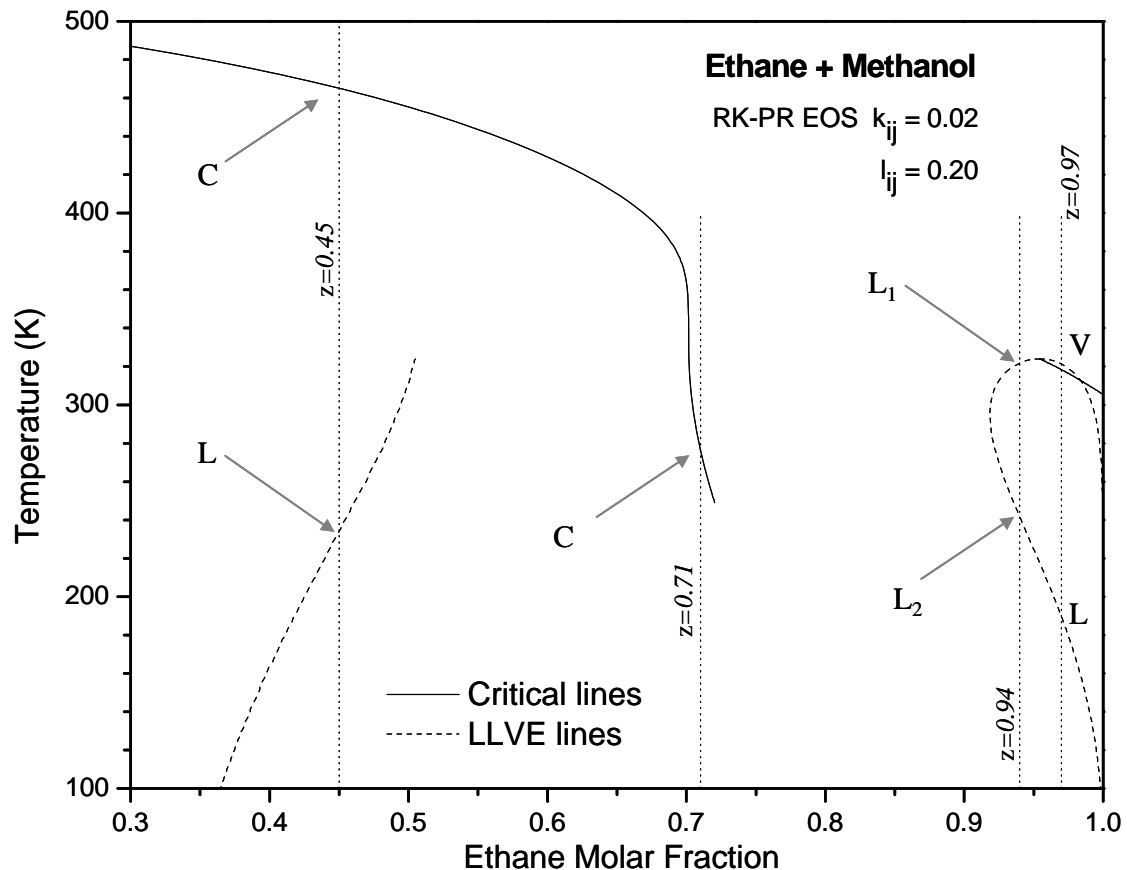


Figure 1. Temperature-composition projection of the calculated global phase equilibrium diagram for the system Ethane + Methanol. Model: RK-PR EOS, with $k_{ij} = 0.02$ and $l_{ij} = 0.20$. Vertical dotted lines indicate compositions for the isopleths shown in Figs. 2 to 5. Solid lines: critical loci. Dashed lines: phases at liquid-liquid-vapor equilibrium.

The vertical dotted lines indicate four different compositions, corresponding to Ethane molar fractions of 0.45, 0.71, 0.94 and 0.97. Figures 2 to 5 show the more important parts of the complete isopleths generated for those compositions, illustrating cases 7, 3, 11 and 17 respectively. Notice in these figures that the number of isopleth segments has a direct relation with the number of intersection points in Fig. 1. More precisely, the number of segments is always $NV+NL+NCRI+1$. Fig. 2 corresponds to 0.45 Ethane mole fraction. Fig. 1 tells us that the vertical line for this composition intersects a critical line at about 462 K (C point), and also the heavy liquid at liquid-liquid vapor equilibrium (L point) at about 233 K. Thus, the 0.45 isopleth must present a point at about 233 K where a LL segment $[(L | HPLP)^{x,y}]$ and a LV segment $[(L | C)^x]$ meet (Fig. 2), and also a LV critical point at about 462 K where two LV segments meet $[(L | C)^x$ and $(C | LTDP)^y]$. This is consistent with Fig. 2, which was generated using the described algorithm. In Fig. 2, part of the LLV equilibrium line (dashed line) is plotted together with the isoplethic diagram (solid line). Every shown LLV point, except for one of them, corresponds to a LLV equilibrium situation where none of the three phases has the isopleth composition. The inclusion in Fig. 2 of the independently calculated relevant portion of the LLV line is useful to visualize the nature of the present phases within the heterogeneity region, e.g., it is clear that at 200 K there is liquid-liquid equilibrium between the $(L | HPLP)^{x,y}$ segment and the LLVE line, while there is liquid-vapor equilibrium between the LLVE line and the $(C | LTDP)^y$ segment. At 0.71 Ethane mole fraction, Fig. 1 shows just an intersection point on a critical line (C point). This C point is of the liquid-liquid type. The isopleth will have only two segments. This is shown in Fig. 3, where we observe a $(C | HPLP)^x$ segment in the higher pressure range, and also a $(C | LTDP)^y$ segment. In this case, it is appropriate to over impose the full LLVE line, which has no common points with any of the segments of the isopleth. When going from LTDP to the C point within the $(C | LTDP)^y$ segment, there is a continuous transition from vapor-liquid equilibrium to equilibrium between two dense phases. The phase behavior at 300 K when lowering the pressure from, say, 300 bar to 0 bar will be the following: single dense phase up to the high pressure intersection (HPI) of the 300 K vertical line and segment $(C | LTDP)^y$, two dense phases between the HPI and the LLVE line, a dense phase in equilibrium with a vapor phase between the LLVE line and the low pressure intersection of the 300 K vertical line and segment $(C | LTDP)^y$, and finally, at very low pressure, a single vapor phase. Fig. 4 presents the 0.94 Ethane mole fraction isopleth, which reflects the presence of two intersection points in Fig. 1 between the vertical isopleth line and the LLV light liquid branch. In this case it is necessary to include in Fig. 4 two parts of the LLV line (see inset). Fig. 5 corresponds to the 0.97 Ethane mole fraction isopleth. For this case, Fig. 1 shows that the $z=0.97$ vertical line intersects the LLV light liquid branch at low temperature (L point) and the LLV vapor branch at higher temperature (V point) and, additionally, it also intersects a vapor-liquid critical line (C point). The inset shows the detailed isopleth geometry in the PT range containing the C and V points.

We stress that while the solid lines in Figs. 2 to 5 are boundaries between homogeneous and heterogeneous regions, the over imposed relevant segments of the LLVE lines are boundaries between pairs of heterogeneous regions, which are both enclosed within the phase envelope. In Figs. 2 to 4, the LLVE line separates a LLE region from a LVE region. In contrast, the high temperature segment of the LLVE line of Fig. 5 separates two LVE regions. Figs. 2 to 5 reflect the rich variety of phase envelopes that models of the equation of state type can describe. They correspond only to 4 out of the 18 cases that we have identified in this work for binary non azeotropic systems. We have not discussed here the remaining 14 cases, due to space limitations. They will be presented in an upcoming paper.

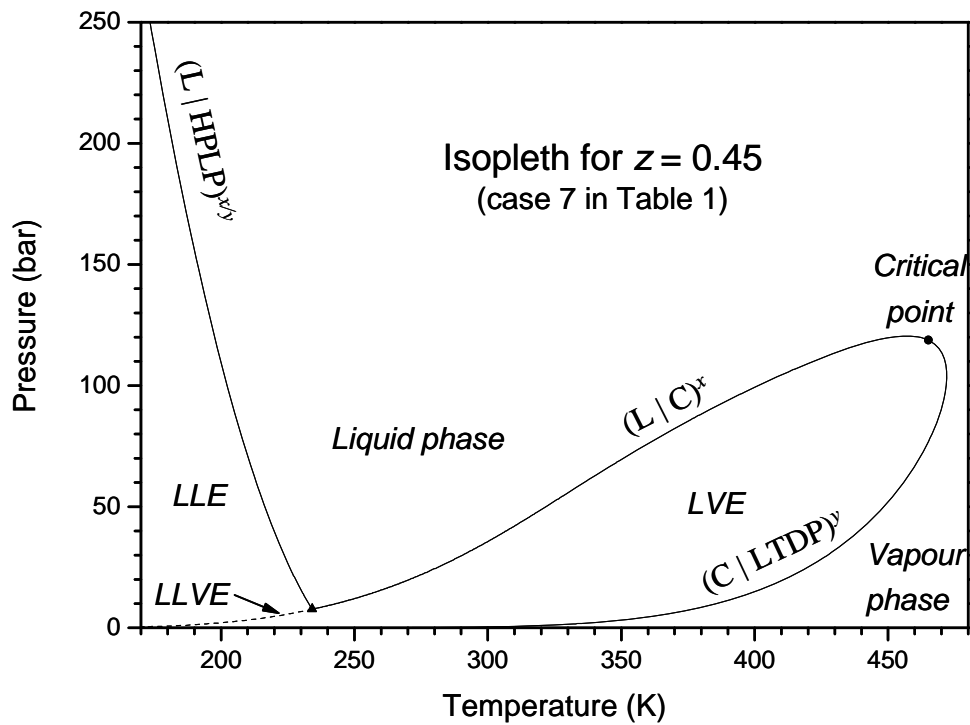


Figure 2. Isopleth for $z = 0.45$ (molar fraction of Ethane), generated in an automated way, according to the classification and methods described in this work, and starting from the points intersected in the global phase equilibrium diagram (Fig. 1). System: Ethane-Methanol. RK-PR EOS.

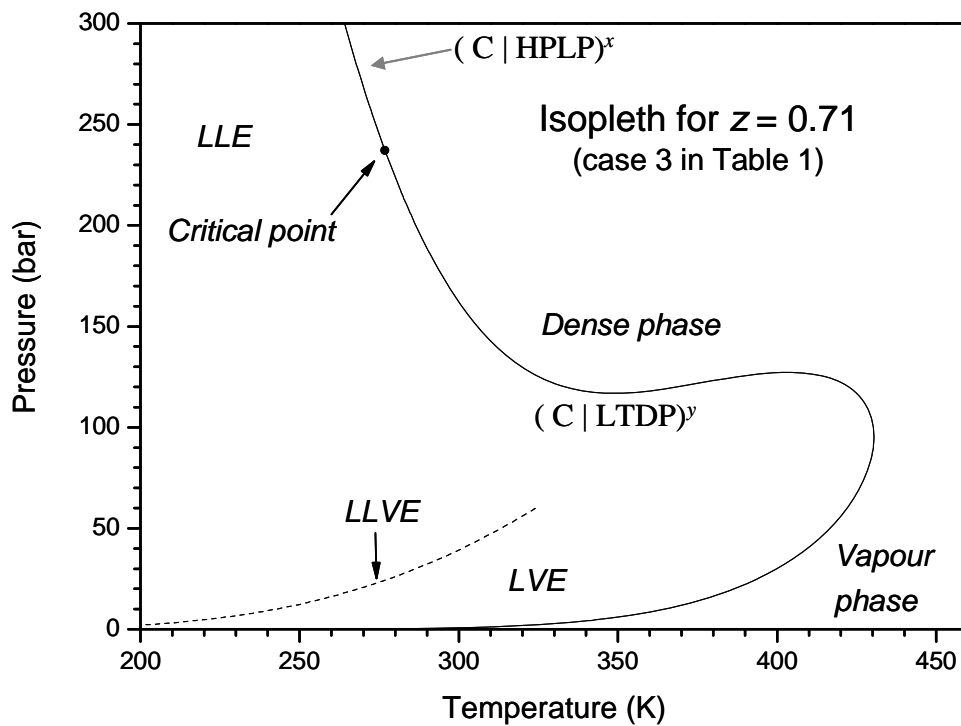


Figure 3. Isopleth for $z = 0.71$ (molar fraction of Ethane), generated in an automated way, according to the classification and methods described in this work, and starting from the points intersected in the global phase equilibrium diagram (Fig. 1). System: Ethane-Methanol. RK-PR EOS.

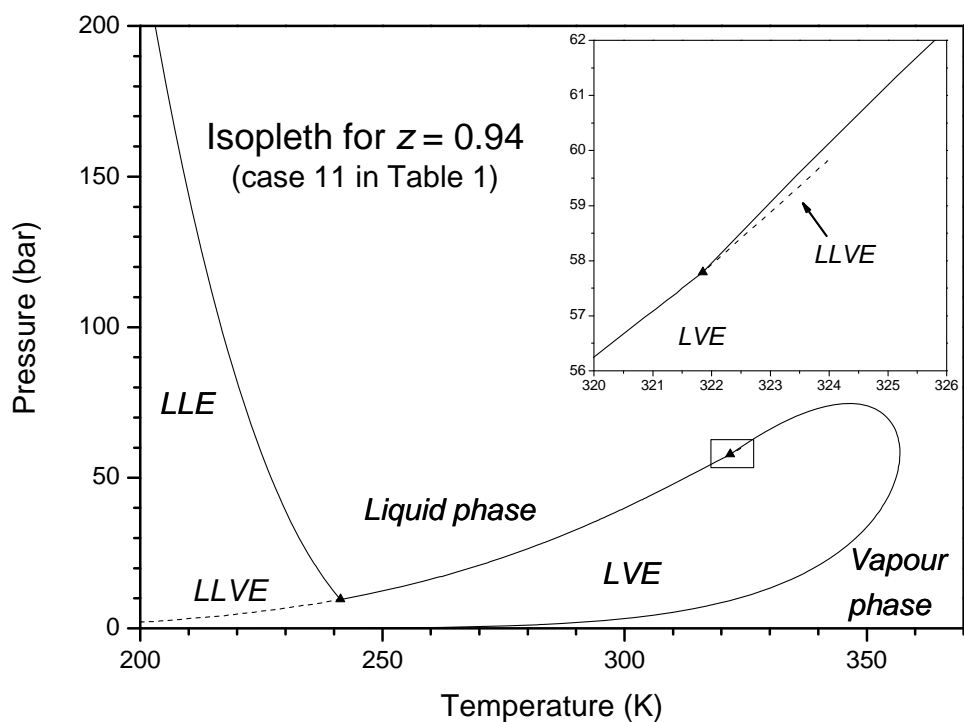


Figure 4. Isopleth for $z = 0.94$ (molar fraction of Ethane), generated in an automated way, according to the classification and methods described in this work, and starting from the points intersected in the global phase equilibrium diagram (Fig. 1). System: Ethane-Methanol. RK-PR EOS.

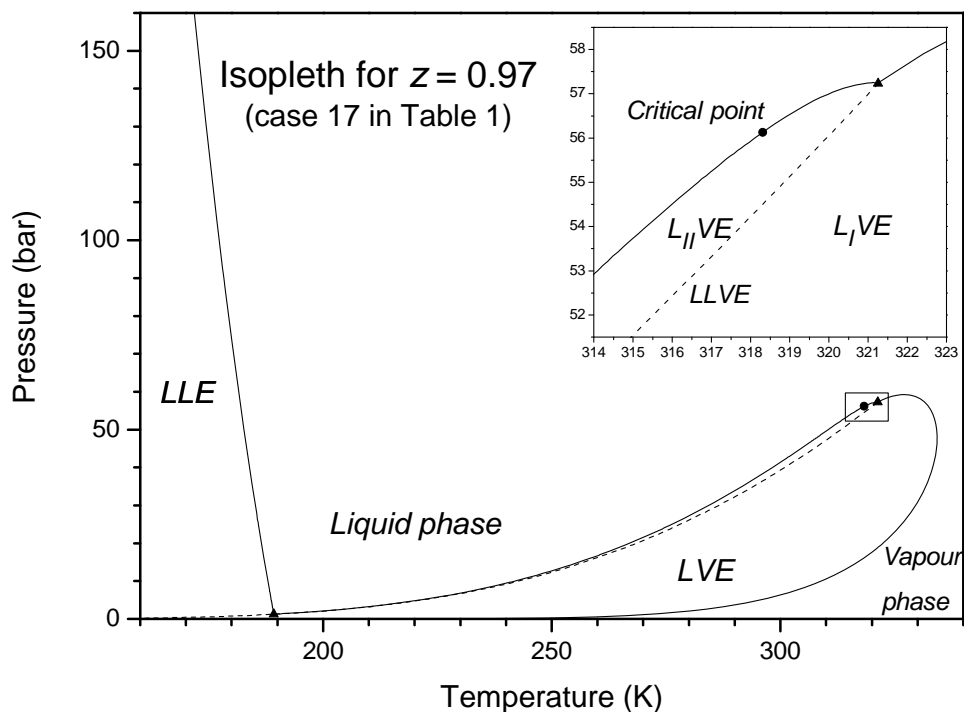


Figure 5. Isopleth for $z = 0.97$ (molar fraction of Ethane), generated in an automated way, according to the classification and methods described in this work, and starting from the points intersected in the global phase equilibrium diagram (Fig. 1). System: Ethane-Methanol. RK-PR EOS.

6. Remarks and Conclusions

In this work, we have proposed an algorithm for the automated generation of fluid phase equilibrium isopleths for binary systems described by models of the Equation of State type. The algorithm uses a systematic classification of phase envelopes. Such classification is based on the number of critical points of composition equal to the isopleth composition and also on the number and nature of liquid-liquid-vapor equilibrium points for which one of the phases has also the composition of the isopleth. Table 1 lists only 4 out of the 18 cases we identified in this work. In Table 1, each isopleth is characterized by a number of segments. In turn, a pair of limiting points describes the nature of each segment. The classification also considers the relevant segments of the independently calculated liquid-liquid-vapor equilibrium line that should be plotted, together with the phase envelope, so that the nature of the phases at equilibrium can be easily established, at arbitrary values of temperature and pressure, for the set overall system composition. We build an individual phase envelope segment by using a numerical continuation method able to track highly curved isopleths. The method differs with respect to the general method developed for multicomponent mixtures by Michelsen (see ref. [1]) essentially in two aspects. First, the equations are not set in terms of K factors, but directly in terms of molar fractions, which is simpler and efficient for the case of binary mixtures. Second, the system of equations and variables is volume based, i.e., the volumes of both the saturated and the incipient phase are independent variables, and therefore no pressure equation needs to be solved separately, except for obtaining initial estimates for the starting up of a segment construction in some cases. The distinguishing feature of the present algorithm is that all key points of a given phase envelope are known before starting the construction of the isopleth. Such key points are critical and LLV points. This makes unnecessary conducting stability tests as the building of the phase envelope progresses. The present algorithm requires as user input only the system components, the model choice and the values for the interaction parameters. The algorithm is able to produce complex phase envelopes, in single run, without missing any of its segments.

References

-
- [1] Michelsen, M.L., Mollerup J. Thermodynamic Models: Fundamentals & Computational Aspects, **2004** Tie-Line Publications.
 - [2] Cismondi, M., Nuñez, D. N., Zabaloy, M. S., Brignole, E. A., Michelsen, M. L., Mollerup, J. M. GPEC: A Program for Global Phase Equilibrium Calculations in Binary Systems. EQUIFASE 2006: VII Iberoamerican Conference on Phase Equilibria and Fluid Properties for Process Design. Morelia, Michoacán, Mexico. October 21-25, 2006.
 - [3] www.gpec.plapiqui.edu.ar
 - [4] Cismondi, M., Michelsen, M. L. Global Phase Equilibrium Calculations: Critical Lines, Critical End Points and Liquid-Liquid-Vapour Equilibrium in Binary Mixtures. *The Journal of Supercritical Fluids*, **2007**, 39, 287-295.
 - [5] Cismondi, M., Michelsen, M. L. Automated Calculation of Complete Pxy and Txy Diagrams for Binary Systems. *Fluid Phase Equilibria*, **2007**, 259, 228-234.
 - [6] Cismondi, M., Michelsen, M. L., Zabaloy, M. S. Automated calculation of azeotropic lines as part of global phase equilibrium diagrams for binary mixtures. 2007 (to be submitted for publication).
 - [7] van Konynenburg, P.H., Scott, R.L. Critical Lines and Phase Equilibria in Binary Van Der Waals Mixtures, *Philos. Trans. R. Soc. London*, 298 (1980) 495-540..
 - [8] Cismondi, M., Mollerup, J. Development and application of a three-parameter RK-PR equation of state, *Fluid Phase Equilibria*, 232 (2005) 74-89.