Automated calculation of complete Pxy and Txy diagrams for binary systems

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Abstract

An algorithm for the calculation of global phase equilibrium diagrams has been recently developed [M. Cismondi, M.L. Michelsen, Global phase equilibrium calculations: critical lines, critical end points and liquid–liquid–vapour equilibrium in binary mixtures, J. Supercrit. Fluids 39 (2007) 287–295]. It integrates the calculation of critical lines, liquid–liquid–vapour (LLV) lines and critical end points, and was implemented in the software program GPEC: global phase equilibrium calculations [M. Cismondi, D.N. Nuñez, M.S. Zabaloy, E.A. Brignole, M.L. Michelsen, J.M. Mollerup, GPEC: a program for global phase equilibrium calculations in binary systems, in: Proceedings of the CD-ROM EQUIFASE 2006, Morelia, Michoacán, Mexico, October 21–25, 2006; www.gpec.plapiqui.edu.ar]. In this work we present the methods and computational strategy for the automated calculation of complete Pxy and Txy diagrams in binary systems. Being constructed from the points given by the global phase diagram at a specified temperature or pressure, their calculation does not require the implementation of stability analysis.

We illustrate the application of the algorithm through a variety of Pxy and Txy diagrams generated using the RK-PR EOS.
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1. Introduction

There are different types of phase equilibrium calculations which require, for a point or a sequence of points, finding the compositions of two phases in equilibrium. Among them are the calculation of two-phase flashes and phase envelopes for constant composition or isopleths, for which robust methods are presented in the book by Michelsen and Mollerup [4], based on the works by Michelsen in the early eighties [5–8]. Pxy or Txy diagrams, which are phase envelopes for binary systems at constant temperature or pressure, respectively, can be constructed following a similar approach to the one proposed by Michelsen for phase envelopes or, more primitively, as a sequence of two-phase flashes. In any of these cases, certain limitations or difficulties prevent the automated

and generalized construction of Pxy and Txy diagrams if certain limiting points have not been located previously. First of all, stability analysis is required in order to identify a possible border between a liquid–vapour and a liquid–liquid region, which corresponds to a point of liquid–liquid–vapour equilibrium. Second, the construction of a Pxy diagram can usually be started from a pure component saturation point, which is easily calculable, but Txy diagrams for a pressure higher than the critical pressure of the more volatile component do not show such saturation point. Finally, even for Pxy diagrams, some regions start and/or end at a critical point, without connection to a pure component, being usually ignored in calculations.

In our computational implementation we aim to integrate the generation of Pxy and Txy diagrams as a stage following the construction of a global phase equilibrium diagram [1–3]. Therefore, we should be able to automatically identify all regions that need to be calculated for each given temperature or pressure. Moreover, since we know in advance the limits for each two-phase region to be calculated, stability analysis should not be required.

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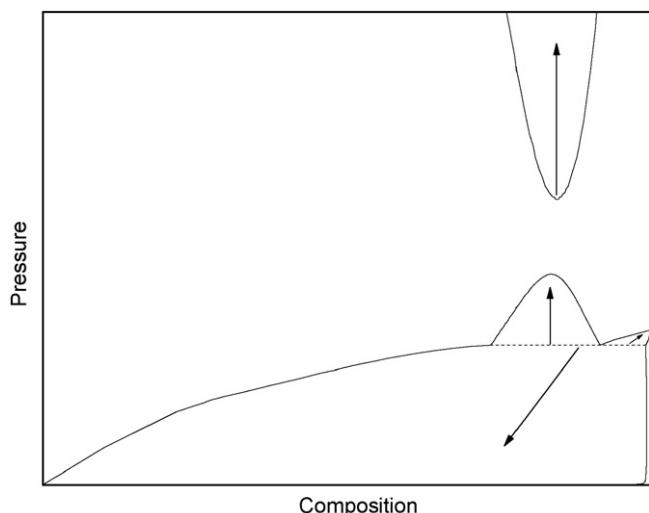
Fig. 1. Calculation of different two-phase regions in a Pxy diagram, from the points provided by a global phase equilibrium diagram. The arrows indicate the direction in which the calculation proceeds for each region (see text, Section 4).

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

- Reading and storing the vectors of pure component saturation lines, critical and LLV lines, as well as critical end points (CEP). Identification of the type of phase behaviour predicted.
- Detection of local temperature and pressure minima or maxima in critical lines.
- Determination of the pressures (or temperatures) at which the different lines intersect at the specified temperature (or pressure).
- Deduction, from the points obtained, of how many and which zones there will be.
- Calculation of each zone or two-phase region.

In this way, for example, if at a specified temperature we find a LLV point, two pure component saturation points and two critical points, the corresponding Pxy diagram will be of the type of the one shown in Fig. 1. We then proceed, one by one, to the calculation of the four two-phase regions in the diagram, with the limits given by the points available and, in this case, of the maximum pressure specified.

The first two stages are fairly trivial. The following sections are dedicated to the other three stages listed above.

2. Determination of intersection points at specified temperature or pressure

This is also quite easy to implement. With respect to critical lines, we consider 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 [1], namely A to E.
- When a temperature is specified (i.e. a Pxy-diagram is to be calculated), the relative position of its value with respect to the ending points of the line and to possible maxima and minima in temperature 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 lines.
- The same applies when a pressure is specified (Txy diagram), adding the possibility of 3 intersections with a line C [1], in a system of type III, when there are maximum and minimum pressure points and the specified pressure falls in the intermediate range. Actually, we also found the possibility of three intersections with the same critical line in a Pxy diagram (see Fig. 5 in Section 5). This case, occurring only for quite unusual cases and in very limited ranges of

Table 1
Regions to be calculated for a Pxy diagram, depending on the intersections with the global phase equilibrium diagram

NLLV	NSAT	NCRI	Two-phase Regions	
0	0	1	(C $\mid$ O)	
		2	(C $\mid$ C)	
	1	0	(S2 $\mid$ O)	
		1	(S2 $\mid$ C)	
		2	(S2 $\mid$ C_{C1}) (C_{C2} $\mid$ O)	
		3	(S2 $\mid$ C_{C1}) (C_{C2} $\mid$ C_{C3})	
	2	0	(S1 $\mid$ S2)	
		1	(S1 $\mid$ S2) (C $\mid$ O)	when Type $\neq$ 3
			(S1 $\mid$ C) (S2 $\mid$ O)	when Type = 3
		2	(S1 $\mid$ C_{A2}) (S2 $\mid$ C_{A1})	
		3	(S1 $\mid$ C_{A2}) (S2 $\mid$ C_{A1}) (C_B $\mid$ O)	
1	1	1	(L_IV $\mid$ S2) (L_{II}V $\mid$ C) (LL $\mid$ O)	
		2	(L_IV $\mid$ S2) (L_{II}V $\mid$ C_D) (LL $\mid$ $C_{B/C}$)	
		3	(L_IV $\mid$ S2) (L_{II}V $\mid$ C_D) (LL $\mid$ C_{B1}) (C_{B2} $\mid$ O)	
			(L_IV $\mid$ S2) (L_{II}V $\mid$ C_D) (LL $\mid$ C_{C1}) (C_{C2} $\mid$ O)	
	2	0	(L_IV $\mid$ S2) (L_{II}V $\mid$ S1) (LL $\mid$ O)	
		1	(L_IV $\mid$ S2) (L_{II}V $\mid$ S1) (LL $\mid$ C)	
		2	(L_IV $\mid$ S2) (L_{II}V $\mid$ S1) (LL $\mid$ C_{C1}) (C_{C2} $\mid$ O)	
			(L_IV $\mid$ S2) (L_{II}V $\mid$ S1) (LL $\mid$ C_{B1}) (C_{B2} $\mid$ O)	

S1, S2: liquid–vapour saturation point of component 1 or 2; LL: liquid phases in the LLV point; L_IV: heavy liquid and vapour phases in the LLV point; L_{II}V: light liquid and vapour phases in the LLV point; C_X: critical point corresponding to the line of type X [1]; O: open, the limit is given by a pre-specified maximum pressure.

temperature, was nonetheless included in the classification exposed in the next section (Tables 1 and 2).

3. Deduction of the number of regions and their type

Once we have the number of pure component saturation points, LLV and critical points, and their coordinates, we need to deduce from this information how many two-phase regions there will be in our Pxy or Txy diagram and what their limits will be. Table 1 shows the different types of Pxy diagrams, and the regions involved, that can be found for binary systems showing phase behaviour of types I to V. The limits or ending points for each region are indicated inside brackets. These limits can be pure component saturation points (S1 or S2 depending on the component, 1 being the more volatile), critical points (C), two of the three phases in a LLV point ($L_I V$, $L_{II} V$ or LL, I and II labelling the heavier and lighter liquid phase, respectively) or the maximum specified pressure when the region remains open up to that pressure (O). As an illustrative example, consider the line for NLLV = 1, NSAT = 2 and NCRI = 2, which corresponds to Pxy diagrams like the one in Fig. 1. When two or more critical points need to be distinguished in the specification of limits, the type of critical line is indicated as a subscript for each point. If more than one from a given line are present, they are numbered

according to their position in the line, starting at the critical point of component 2 for lines A, C and E, at the UCEP for B and at the critical point of component 1 for D.

Tables 1 and 2 show that there can be more than one possibility for a given specification (NLLV, NSAT, NCRI). Nevertheless, it must be pointed out that in cases like (1,1,3) those possibilities actually lead to the same type of Pxy or Txy diagram (the only difference being the type of global phase behaviour from which the intersections have been located) while in other cases like (0,2,1) they correspond to different types of diagrams. Accordingly, the two rows for (1,1,3) in Table 1 or 2 share the same cell in the column "Two-phase Regions".

There might still be some particular cases of Pxy or Txy diagrams not considered in Tables 1 and 2. Nevertheless, if we identify one of these cases, it can be treated in the same way as the others, extending the corresponding table and the algorithm.

4. Calculation of a two-phase region

Defining *x* and *y* as the compositions in molar fraction of the phases richer in components 2 and 1, respectively, regardless of the LV or LL nature of the region, we choose the following variables and equations for the calculation of each point in a Pxy region (constant temperature):

Table 2

Regions to be calculated for a Txy diagram, depending on the intersections with the global phase equilibrium diagram

NLLV	NSAT	NCRI	Two-phase Regions	
0	0	1	(C | O)	
		2	(C | C)	
		3	(C_{C1} | C_{C2}) (C_{C3} | O)	
			(C_{E1} | C_{E2}) (C_B | O)	
			(C_{A1} | C_{A2}) (C_B | O)	
	1	0	(S | O)	
		1	(S | C)	
		2	(S | $C_{A/E}$) (C_B | O)	when Type ≠ 3
		2	(S | C_D) (C_C | O)	when Type = 3
		4	(S | C_D) (C_{C1} | C_{C2}) (C_{C3} | O)	
			(S | C_D) (C_{E1} | C_{E2}) (C_B | O)	
	2	0	(S1 | S2)	
		1	(S1 | S2) (C | O)	when Type ≠ 3
			(S1 | C) (S2 | O)	when Type = 3
		2	(S1 | C_{A2}) (S2 | C_{A1})	
		3	(S1 | C_{A2}) (S2 | C_{A1}) (C_B | O)	when Type = 2
			(S1 | C_D) (S2 | C_{C1}) (C_{C2} | O)	when Type = 3
			(S1 | C_D) (S2 | C_E) (C_B | O)	when Type = 4
1	0	2	($L_I V$ | C_C) ($L_{II} V$ | C_D) (LL | O)	
		3	($L_I V$ | C_{E1}) ($L_{II} V$ | C_D) (LL | C_{E2})	
		4	($L_I V$ | C_{E1}) ($L_{II} V$ | C_D) (LL | C_{E2}) (C_B | O)	Type = 4
			($L_I V$ | C_{C1}) ($L_{II} V$ | C_D) (LL | C_{C2}) (C_{C3} | O)	Type = 3
	1	1	($L_I V$ | C_C) ($L_{II} V$ | S1) (LL | O)	
			($L_I V$ | S2) ($L_{II} V$ | C_D) (LL | O)	
		2	($L_I V$ | C_{E1}) ($L_{II} V$ | S1) (LL | C_{E2})	
			($L_I V$ | S2) ($L_{II} V$ | C_D) (LL | C_E)	
		3	($L_I V$ | C_{E1}) ($L_{II} V$ | S1) (LL | C_{E2}) (C_B | O)	Type = 4
			($L_I V$ | C_{C1}) ($L_{II} V$ | S1) (LL | C_{C2}) (C_{C3}| O)	Type = 3
			($L_I V$ | S2) ($L_{II} V$ | C_D) (LL | C_E) (C_B | O)	Type = 4
			($L_I V$ | S2) ($L_{II} V$ | C_D) (LL | C_{C1}) (C_{C2}| O)	Type = 3
	2	0	($L_I V$ | S2) ($L_{II} V$ | S1) (LL | O)	
		1	($L_I V$ | S2) ($L_{II} V$ | S1) (LL | C)	
		2	($L_I V$ | S2) ($L_{II} V$ | S1) (LL | C_E) (C_B | O)	Type = 4
			($L_I V$ | S2) ($L_{II} V$ | S1) (LL | C_{C1}) (C_{C2} | O)	Type = 3

$$X = \begin{bmatrix} \ln x_1 \\ \ln y_2 \\ \ln v_x \\ \ln v_y \end{bmatrix} ;$$

$$F = \begin{bmatrix} \ln P_x(x, T, v_x) - \ln P_y(y, T, v_y) \\ \ln \hat{f}_1^x(x, T, v_x) - \ln \hat{f}_1^y(y, T, v_y) \\ \ln \hat{f}_2^x(x, T, v_x) - \ln \hat{f}_2^y(y, T, v_y) \\ g(X) - S \end{bmatrix} = 0 \qquad (1)$$

where for volume, pressure and fugacity x or y indicates the phase.

The corresponding variables and equations for a Txy region (constant pressure) are the following:

$$X = \begin{bmatrix} \ln x_1 \\ \ln y_2 \\ \ln v_x \\ \ln v_y \\ \ln T \end{bmatrix} ;$$

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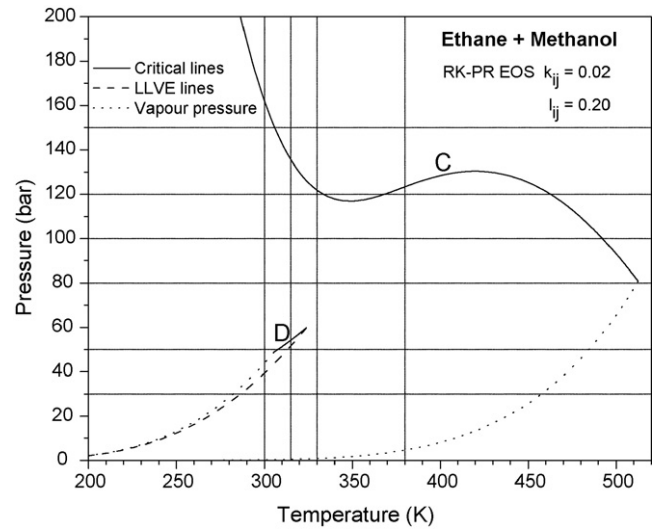

Fig. 2. P–T projection of the global phase equilibrium diagram for the binary mixture ethane + methanol, calculated with the RK-PR EOS. See the corresponding Pxy and Txy diagrams in Figs. 3 and 4.

For each system of equations we implement a multidimensional Newton method, analogous to the one described in [1,4,5] for calculation of phase envelopes or critical lines. When one of the limits of the region coincides with a LLV point, as it occurs in three of the four regions in Fig. 1, we choose to start from this point where we already have an approximate solution for the
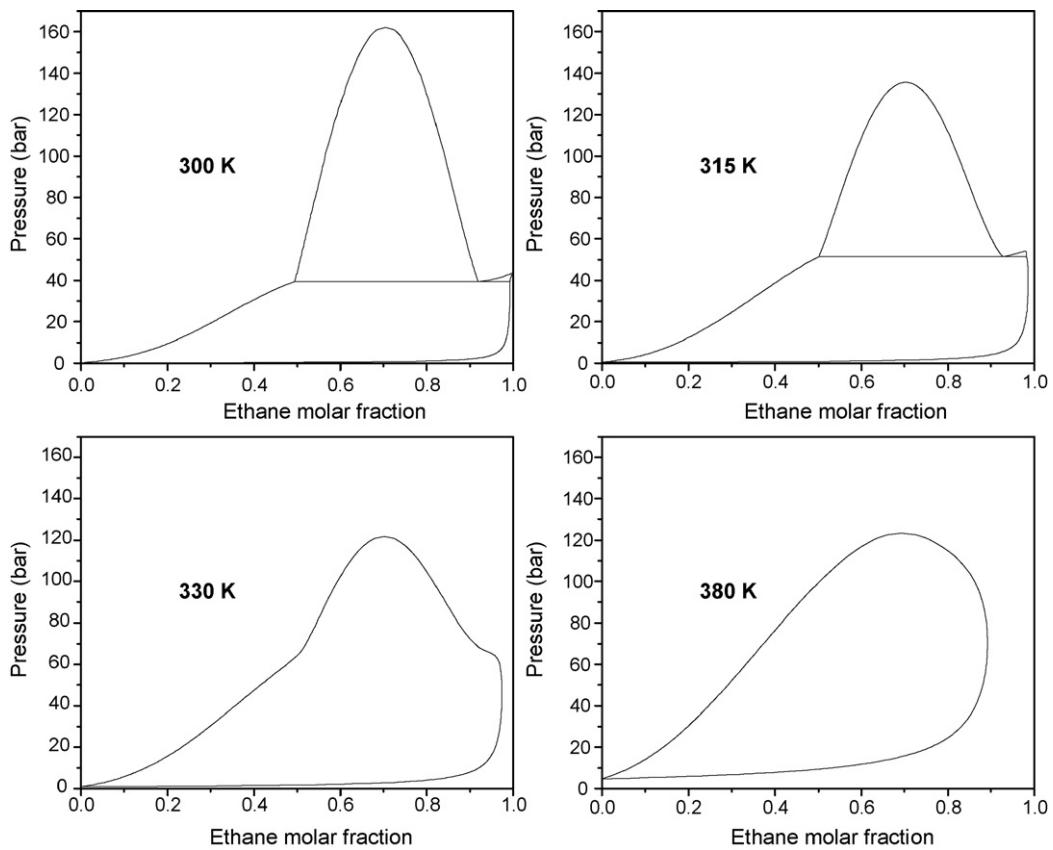

Fig. 3. Pxy diagrams for the system ethane + methanol, calculated at the temperatures indicated in Fig. 2 by vertical dotted lines. Model: RK-PR EOS.

first point and for which we can calculate the sensitivity vector (dX/dS) and generate a good estimate for the second point.

The specification function $g(X)$ will be by default the pressure (in Pxy diagrams) or the temperature (Txy diagrams), except in the proximity of a pure component saturation point or – specially – a critical point, in which cases the separation $y_1 - x_1$ is more convenient.

Good starting values for the compositions in the first point of a region starting from a pure compound liquid–vapour saturation point can be estimated from the following relation, which holds for the component i at infinite dilution conditions:

$$y_i^\infty = x_i^\infty \frac{\phi_i^{L,\infty}}{\phi_i^{V,\infty}} \qquad (3)$$

For regions starting from a critical point, small symmetrical deviations from the critical compositions are used to generate starting values, as done in our previous work for starting the calculation of LLV lines from critical end points [1].

In both cases, i.e. regions starting from pure component saturation points or critical points, initial guesses for V_x and V_y are obtained by solving the pressure equation at the initial values of compositions.

Another simple improvement to the first order Newton method, that prevents divergence increasing the robustness of the algorithm, consists in correcting V_x using (dP_x/dV_x) when the relative value of P_x is too big or too small as compared to P_y (Pxy diagram) or P (Txy diagram).
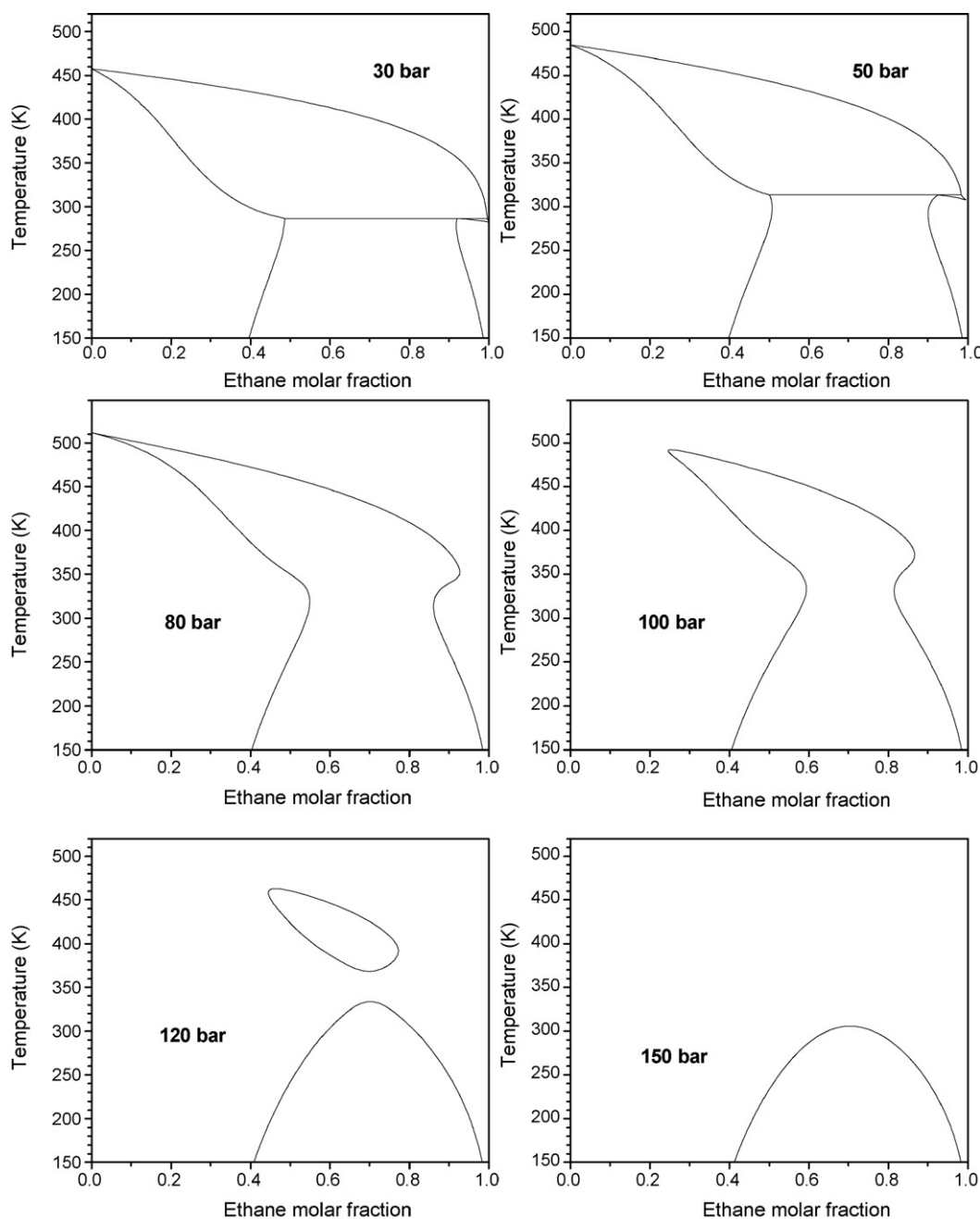

Fig. 4. Txy diagrams for the system ethane + methanol, calculated at the pressures indicated in Fig. 2 by horizontal dotted lines. Model: RK-PR EOS.

5. Illustration of the algorithm

Fig. 2 shows the pressure–temperature projection of the global phase equilibrium diagram of ethane + methanol, as calculated with the RK-PR EOS [9]. Although this diagram serves only illustrative purposes, interaction parameters were used in order to approximate the experimental critical line for this binary system, for which phase behaviour of type III was first observed a century ago (see the review by Levelt Sengers [10] for an interesting historical perspective). In this figure, four temperatures and six pressures are indicated by vertical and horizontal dotted lines, respectively. The corresponding Pxy and Txy diagrams, calculated with the algorithm described in previous sections, are shown in Figs. 3 and 4.

Note that two Pxy diagrams that look very similar may correspond to different types with respect to their ending points. This is the case for the two first diagrams in Fig. 3. At 300 K the ending point of the smaller two-phase region is the saturation point for pure ethane, while at 315 K the same region ends at a mixture critical point. Accordingly, these diagrams can be identified with the lines (1,2,1) and (1,1,2) in Table 1. On the other hand, for 330 and 380 K we can see how a given type of Pxy diagram (0,1,1) can take different shapes depending on its relative position in the global phase equilibrium diagram and, for example, the proximity to a critical end point, like in the case for 330 K. Similar observations can be made for Txy diagrams. Those shown in Fig. 4, for pressures ranging from 30 to 150 bar, correspond to the types (1,2,0), (1,1,1), (0,1,0), (0,0,1), (0,0,3) and (0,0,1) in Table 2.

We should also point out here, with these examples, the limitations or difficulties referred to in Section 1. Note for example that the Txy diagram at 30 or 50 bar could not be automatically calculated without knowing the temperature and compositions of the liquid–liquid–vapour equilibrium point at the specified pressure. Eventually, an alternative approach would require localizing that point through stability analysis as the calculation progresses from one of the three two-phase regions, and then identifying the other two somehow. We find that the integration with global phase equilibrium diagrams, as proposed in this work, offers a more complete and efficient approach. Consider also the closed loop at 120 bar. If the critical line were not known in advance, the calculation might progress from low temperature until the critical point is reached, and it could be mistakenly concluded that from that temperature on the miscibility is complete between the two components.

In Fig. 5 we show a particular behaviour that may be found for certain asymmetric systems, in this case obtained for carbon dioxide + n-docosane with the RK-PR EOS. It is characterized by a local minimum temperature and local maximum temperature in the portion of the critical line close to the heavy component critical point. The evolution of the Pxy diagrams in that region, including closed loops, is shown in Fig. 6. These diagrams correspond to the types (0,1,3) and (0,1,1) in our classification in Table 1.

Diagrams showed in Figs. 2–6 for illustration were generated using the RK-PR equation of state. Nevertheless, and since the computational implementation is modular based, the methods
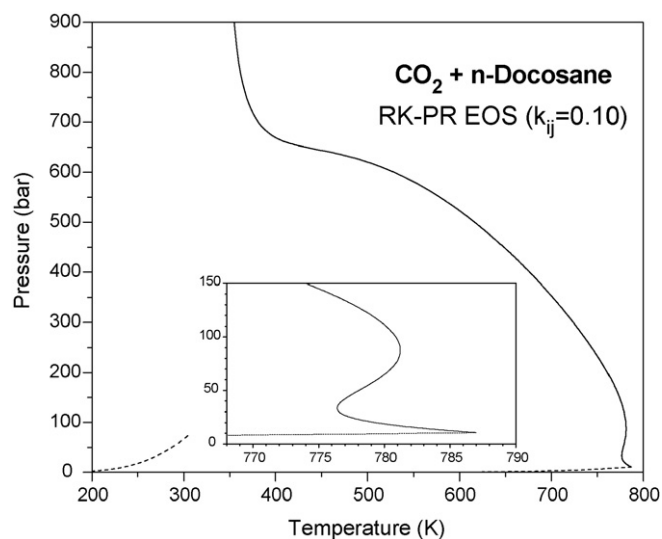

Fig. 5. P–T projection of the global phase equilibrium diagram calculated with the RK-PR EOS for the binary mixture carbon dioxide + n-docosane.
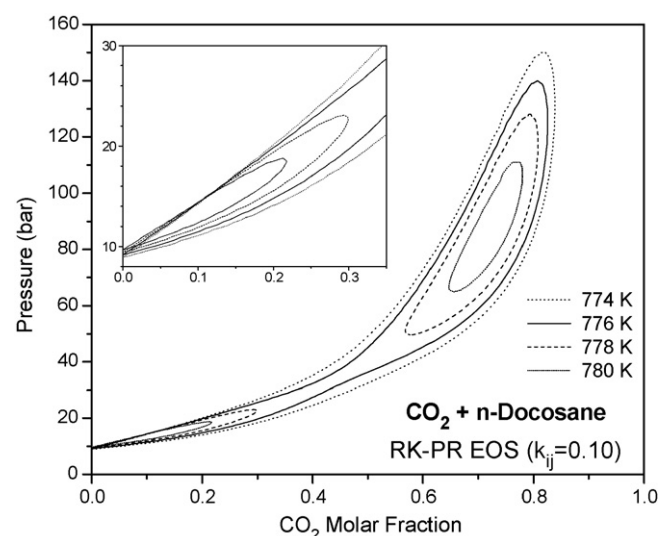

Fig. 6. Evolution of Pxy diagrams in the augmented P–T region of the global phase equilibrium diagram in Fig. 5.

proposed in this work and in [1] are completely independent of the model chosen to describe a system. Besides the RK-PR EOS, we have so far coupled these methods with the SRK, PR, SPHCT, PC-SAFT and GC-EOS with equally good results.

6. Conclusions

In this work we have presented a method for the calculation of two-phase regions in binary systems at constant temperature or constant pressure. We also presented the basis for an algorithm that integrates this method with the information given by a calculated global phase equilibrium diagram, in order to construct different types of complete Pxy and Txy diagrams. The wide variety of situations that our algorithm can handle was illus-

trated though different diagrams obtained for systems showing complex phase behaviour.

The generation of diagrams showing azeotropy, which requires knowing the azeotropic locus as part of the global phase equilibrium diagram, will be considered in a separate future publication.

Acknowledgements

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