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Direct detection of double retrograde behavior in binary systems for equation of state models

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ABSTRACT

In this work, a straightforward methodology is proposed to establish at a glance, for binary systems, whether a model of the equation of state type predicts the occurrence of double retrograde behavior (DRB), and to also establish what the ranges of conditions of DRB existence are. This is accomplished by computing three hyper-lines, which usually are highly non linear. One of them is the vapor–liquid critical line. The other two are loci of cricondenbar points and of cricondentherm points. Each line is efficiently calculated in a single computer run by resorting to a robust numerical continuation method.

1. Introduction

A well-known and common phenomenon in the high pressure phase behavior of mixtures is the retrograde behavior (RB). RB was predicted by Van der Waals and, according to ref [1], observed experimentally for the first time by Kuenen (1897). Binary mixtures which are asymmetric, with respect to molecular size and/or shape and/or attractive forces, may present a more complex and less common phenomenon, i.e., the so-called double retrograde behavior (DRB). DRB usually occurs within a narrow range of composition, close to that of the pure lightest component.

Available data on DRB seem to be scarce. Examples of binary systems for which DRB was experimentally observed are the following: methane + n-butane [2], methane + n-pentane [3], NaCl + H_2O [4], ethane + limonene [5,6], ethane + linalool [7,8] and ethane + orange Peel oil [9] (pseudo-binary system). According to Alfradique and Castier [10], the scarcity of experimental information may be due to the fact that DRB occurs in very narrow composition ranges.

Deiters [11] and Raeissi and Peters [12], analyzed the DRB from a theoretical point of view, using the Gibbs–Konowalow equation, which is an extension of the Clayperon equation for multicomponent mixtures. Raeissi and Peters [6] described the DRB in the context of either isothermal or isoplethic (constant composition) phase equilibrium diagrams, i.e., they considered the DRB at constant temperature and composition. Different equations of state (EoS) were used to study the DRB [10,13,14]. EoSs are important models for describing the properties of vapor, liquid and supercritical phases. Unlike other models, EoS offer a continuous description of these three different states, as experimentally observed.

Raeissi and Peters [6] have studied the ranges of conditions of existence of the DRB using an EoS, by computing a number of phase equilibrium diagrams, for binary systems.

This approach, which is typical in the literature, is not straightforward, since several vapor–liquid equilibrium diagrams are to be computed to find the ranges of conditions within which the EoS predicts DRB. The availability of an alternative, more direct, approach for establishing the occurrence or absence of DRB is desirable. The goal of the present work was to propose and test one such alternative straightforward approach. This is accomplished by computing a couple of, in a way special, binary phase equilibrium diagrams, which make possible the direct determination of the ranges of conditions where liquid–vapor DRB occurs, for a given binary system, according to the EoS model chosen to describe its

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phase behavior.

One of the diagrams is named CCB diagram, and the other is named CCT diagram. The diagrams cover the whole mole fraction range, or only part of it, depending on the user's interest. A given diagram, out of the two DRB diagrams, is made of a couple of lines, each one calculated in a single computer run. One of the lines is always the binary critical line. The second line is either the CCB line or the CCT line. Different projections of these lines can be visualized to study the DRB phenomenon.

The cricondenbar (CCB, e.g., point 1 in Fig. 8) is the maximum pressure at which a mixture of given composition (isopleth) can be heterogeneous. Analogously, the cricondentherm (CCT, e.g., point 1 in Fig. 1) is the maximum temperature at which a mixture of given composition can be heterogeneous. For the detection of the DRB we have found that it is convenient to use an extended definition of the CCB and of the CCT. Thus, in this work, a CCB point is a stationary point (derivative equal to zero) of the vapor liquid-equilibrium pressure, and a CCT point is a stationary point of the vapor liquid-equilibrium temperature. Local maxima, local minima and inflection points are all stationary points.

A continuous set of binary isopleths has associated continuous sets of CCBs and of CCTs. Such binary CCB and CCT sets are respectively the CCB line and the CCT line (or hyperlines). They can be computed using an EoS. The analysis of the computed CCB and CCT diagrams lead either to detect the DRB or to discard its occurrence.

Wichterle [15] and Barrufet and Eubank [16] have shown that a CCB point is also a Cricondencomp at constant pressure ($\mathrm{CCC_P}$).

A CCCp (e.g., point 1 in Fig. 9) is a phase equilibrium point, in a constant pressure diagram (Txy diagram), for which the mole fraction of one of the components (of the binary mixture) in one of the equilibrium phases is locally maximum. Notice that the (not shown) maximum temperature endpoint of the vapor–liquid region in Fig. 9 may be another critical point or a pure compound saturation point. This applies also to Figs. 12 and 14.

Similarly, a CCT point is also a Cricondencomp, but at constant temperature ($\mathrm{CCC_T}$). More specifically, a $\mathrm{CCC_T}$ point (e.g., point 1 in Fig. 2) is a phase equilibrium point in a constant temperature diagram (Pxy diagram) for which the mole fraction of one of the components (of the binary mixture) in one of the equilibrium phases is locally maximum.

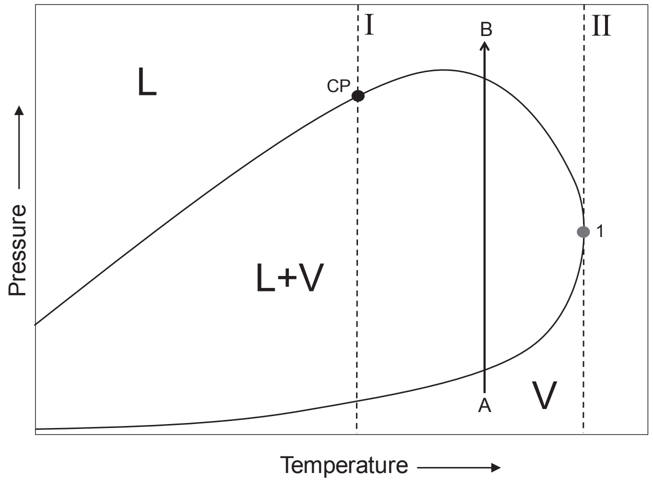

Fig. 1. Schematic Pressure–Temperature diagram for a vapor–liquid equilibrium isopleth showing RBxT in the I–II temperature range. CP: critical point. Point 1: CCT point.

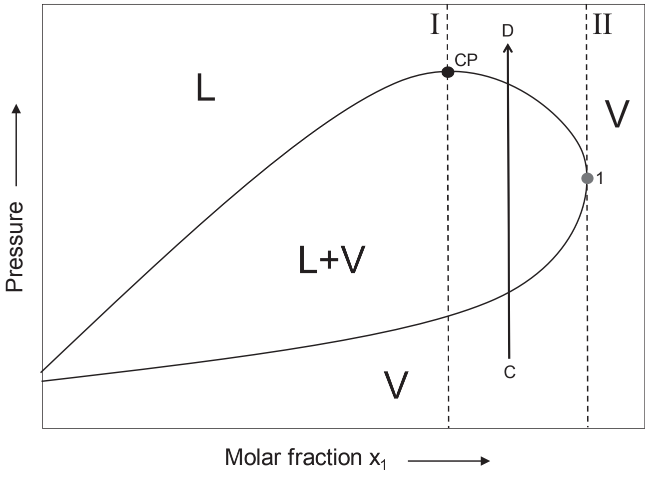

Fig. 2. Schematic Pressure-Molar fraction of component 1 diagram for a supercritical vapor–liquid equilibrium isotherm showing RBxT in the I–II composition range. CP: critical point. Point 1: $\mathrm{CCC_T}$ point.

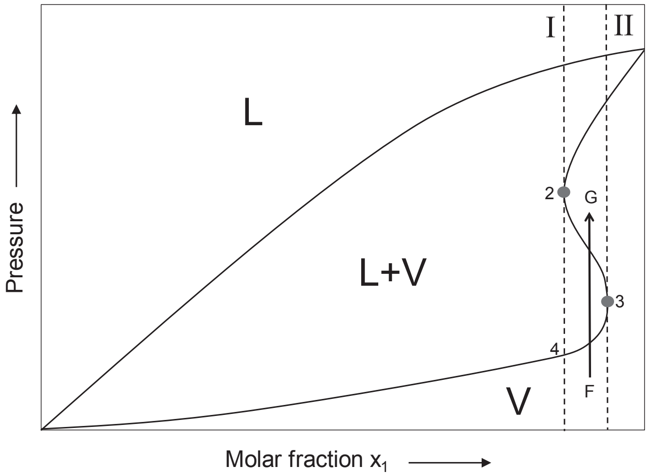

Fig. 3. Schematic Pressure-Molar fraction of component 1 diagram for a subcritical vapor–liquid equilibrium isotherm showing RBxT in the I–II composition range. Points 2 and 3: $\mathrm{CCC_T}$ points.

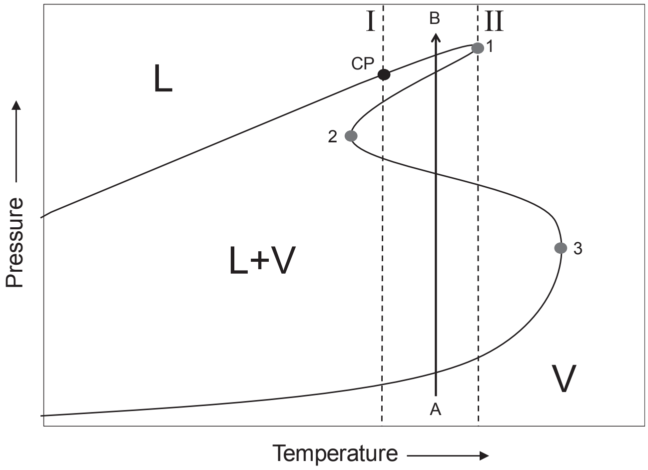

Fig. 4. Schematic Pressure–Temperature diagram for a vapor–liquid equilibrium isopleth showing DRBxT in the I–II temperature range. CP: critical point. Points 1, 2 and 3: CCT points.

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