

Global phase diagram for anisotropic binary fluid mixtures: reverse type IV behaviour

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(Received 10 December 2002; revised version accepted 21 April 2003)

Calculations of the critical properties of anisotropic binary mixtures are reported using the hard convex body–van der Waals equation of state in conjunction with conformal solution theory and the one-fluid model. The calculations are used to determine the global phase diagram for anisotropic binary mixtures of molecules of identical size. In the absence of other influences, mixtures with a moderate degree of anisotropy between the component molecules are only observed to exhibit type I, II or III behaviour. For highly anisotropic mixtures, a new type of behaviour is observed which we describe as ‘reverse type IV’.

1. Introduction

The fluid phase equilibria of many binary mixtures have been observed experimentally over a wide range of physical conditions including very high pressures [1]. Classification schemes [1–6] have been developed based on the critical equilibria behaviour of binary mixtures. The phase behaviour of the majority of commonly occurring binary mixtures can be broadly classified by their critical properties in terms of a few basic types [1, 2]. It has been demonstrated recently [5, 7] that almost all the known types of behaviour, including closed-loop immiscibility, can be calculated using the Carnahan–Starling–van der Waals (CSvdW) [8] or Guggenheim [9] equations of state. The success of these relatively simple equations of state to predict most aspects of binary mixture critical phenomena means that they can be used to generate a so-called global phase diagram [3–7].

A global phase diagram is a two-dimensional map, which identifies regions of different phase behaviour in accordance with the properties of the x and y coordinates. Critical transitions of different kinds generate boundary lines between different types of phase behaviour. Typically, the model used to construct the phase diagram assumes that the components of the binary mixture are isotropic, i.e. both components have a spherical geometry. Different phase types are identified on the global phase diagram by varying either the strength of unlike interaction between the spheres, the co-volume occupied by the spheres or the relative diameters of the spheres. Although these three factors are likely to be the main

contributors to the observed phase behaviour, real binary mixtures are seldom isotropic.

The aim of this work is to examine the effect of anisotropy on the phase behaviour of binary mixtures. To achieve this, we use calculations of the critical properties to develop a global phase diagram for a binary mixture containing spherical and non-spherical components.

2. Theory

The overall phase behaviour of binary mixtures can be conveniently classified in terms of variations in the critical properties of the binary mixtures. Details of the calculation of the critical properties of mixtures and the underlying theory are given extensively elsewhere [1, 7, 10] and only a brief outline of the main points is given here.

The critical properties of a binary fluid mixture were solved using the Hicks–Young algorithm [11] which is guaranteed to locate all critical points over the entire range of composition (x), temperature (T) and volume (V). The Helmholtz function was obtained from conformal solution theory [1, 12]. The configurational contribution to the Helmholtz function is determined by integrating a suitable equation of state. In this work, we used the hard convex body–van der Waals equation (HCBvdW) [13] obtained by combining Boublik’s [14] formula for hard convex bodies (HCBs) with the van der Waals representation of attractive interaction. The HCBvdW equation of state calculates the pressure (p) of the fluid from:

$$p = \frac{RT(1 + (3\alpha - 2)\eta + (3\alpha^2 - 3\alpha + 1)\eta^2 - \alpha^2\eta^3)}{V(1 - \eta)^3} - \frac{a}{V^2}, \quad (1)$$

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where R is the universal gas constant, η is the packing fraction ($\eta = v^*/V$; v^* is the volume occupied by one mole of HCBs), a is the van der Waals attractive term and α is the non-sphericity. A value of $\alpha > 1$ indicates departure from spherical geometry (anisotropy) of the HCB. When $\alpha = 1$, equation (1) becomes the CSvdW [8] equation of state for isotropic fluids. The role of equations of state in the calculation of high-pressure fluid phase equilibria has been reviewed recently [15].

The v_m^* and a_m parameters for the mixture were obtained from the properties of the pure components by using the one-fluid prescriptions [1, 10]:

$$a_m = \sum_i \sum_j x_i x_j a_{ij}, \quad (2)$$

$$v_m^* = \sum_i \sum_j x_i x_j v_{ij}^*, \quad (3)$$

where the contribution from unlike interactions is given by the Lorentz–Berthelot [10, 12] combining rules.

$$a_{ij} = v_{ij}^* \left(\frac{a_{ii} a_{jj}}{v_{ii}^* v_{jj}^*} \right)^{1/2}, \quad (4)$$

$$v_{ij}^* = \frac{(v_{ii}^{*1/3} + v_{jj}^{*1/3})^3}{8}. \quad (5)$$

It should be noted that no external adjustable parameters have been introduced into either equation (4) or equation (5). The non-sphericity (anisotropy) parameter for the mixture (α_m) was obtained as a linear combination of the pure component values:

$$\alpha_m = \sum_i x_i \alpha_i. \quad (6)$$

3. Results and discussion

In general, the phase behaviour of binary mixtures can be classified [1, 2] into several basic types depending on the type of critical behaviour (figure 1). Here, we will focus our discussion on type I–IV behaviour. A detailed description of the other types of behaviour is available elsewhere [1, 2, 5, 7, 10].

Type I mixtures have a continuous vapour–liquid critical locus linking the critical points of the two components whereas type II–IV behaviour is associated with the addition of various types of liquid–liquid critical transitions. In type II behaviour, in addition to a vapour–liquid critical line, a locus of upper critical solution temperatures (UCSTs) commences at low temperatures from an upper critical end point (UCEP), which terminates a liquid–liquid–vapour (LLV) line.

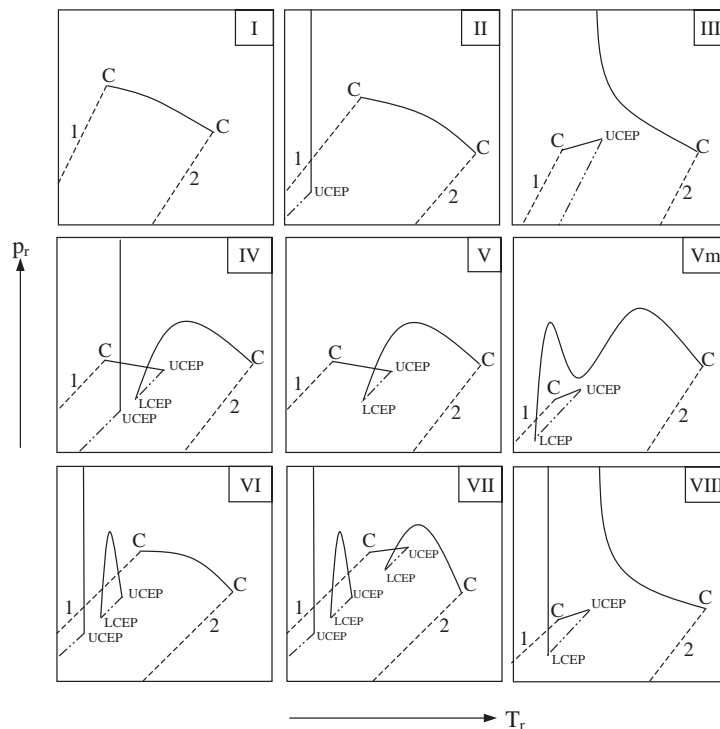


Figure 1. Phase behaviour classification scheme for binary mixtures. Type I, II, III, IV, V and VI behaviour are observed experimentally whereas behaviour of type Vm, VII and VIII have only been reported in the literature from calculations. Critical equilibria of the binary mixtures (—), the critical points of the pure components (C), the vapour pressure curves (---, 1, 2) and three-phase liquid–liquid–vapour (---) equilibria are illustrated.

In type III behaviour, the vapour–liquid critical line commencing from the critical point of the component with the highest critical temperature only extends partly to the critical point of the other component before veering abruptly to very high pressures. This high-pressure region represents liquid–liquid equilibria and the critical locus displays a continuous transition between vapour–liquid and liquid–liquid phenomena. The vapour–liquid locus commencing from the critical point of the component with the lowest critical temperature ends on an UCEP.

Type IV behaviour is characterized by three distinct critical lines. The vapour–liquid critical line from the component with the lowest critical temperature terminates at an UCEP whereas the other vapour–liquid critical line ends on a lower critical end point (LCEP). In addition, a line of UCSTs commences from another UCEP. It is apparent from figure 1 that the effect of these phenomena is to split the LLV line into two distinct parts.

We have determined the global phase diagram (figure 2) of anisotropic binary mixtures consisting of one spherical component ($\alpha_1 = 1$) and one non-spherical component ($\alpha_2 > 1$). Both spherical and non-spherical components were of equal volume. This means that different binary anisotropic mixtures are distinguished solely by the value of α_2 . Therefore, a global phase diagram can be constructed in terms of a $T_r - \alpha_2$

projection, where $T_r = T_2^c/T_1^c$ is the ratio of the vapour–liquid critical temperatures of the pure components.

Figure 2 represents the global phase diagram with a moderate degree of anisotropy ($\alpha_2 \leq 5$). Under these circumstances, the phase behaviour is limited to type I, II, III and III_m mixtures. Three different boundary states were identified. The transition between type I and type II occurs via a double critical end point (DCEP) at a temperature of zero Kelvin. This special case of DCEP phenomenon is usually called the zero Kelvin point (ZKP). The transition between type II and type III behaviour occurs via a conventional DCEP [16]. The transition between type III and type III_m occurs via a critical pressure set point (CPSP) [17].

The transition pathway between these phase types is illustrated in figure 3. In the global phase diagram [16], the transition between type I and II behaviour can occur via two different pathways. In some cases, the transition involves a DCEP followed by an intermediate type VI state whereas in other cases, it occurs directly after the ZKP. In this work, we observed the latter type of transition which does not involve an intermediate type VI stage (figure 3(a)). The transition between type II and type III_m behaviour (figure 2) occurred via a DCEP and this mechanism is illustrated in figure 3(b). In very rare cases [1, 7], the transition can also occur via a van Laar point formed when the DCEP line meets

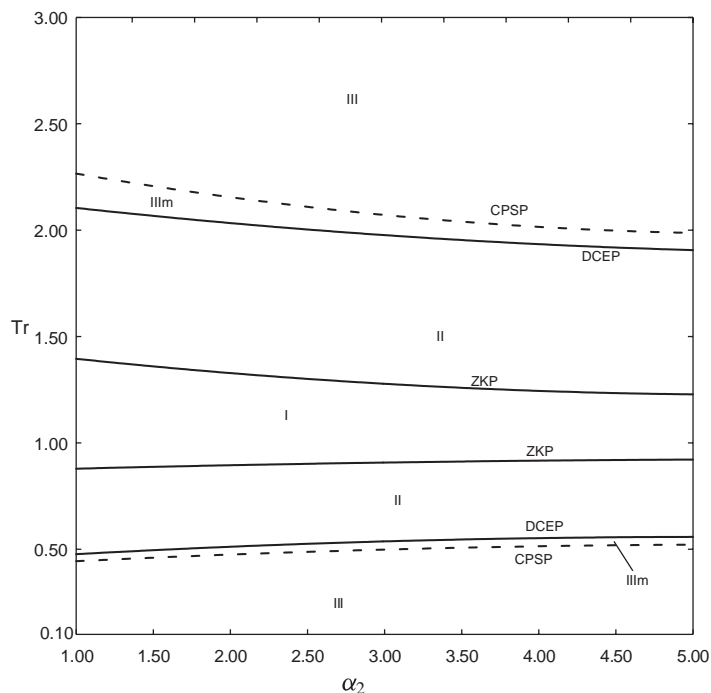


Figure 2. Global phase diagram of anisotropic binary mixtures predicted from the HCBvdW equation of state. Phase behaviour of type I, II, III and III_m is observed. The boundary lines involve double critical end points (DCEP), zero Kelvin points (ZKP) and critical pressure set points (CPSP).

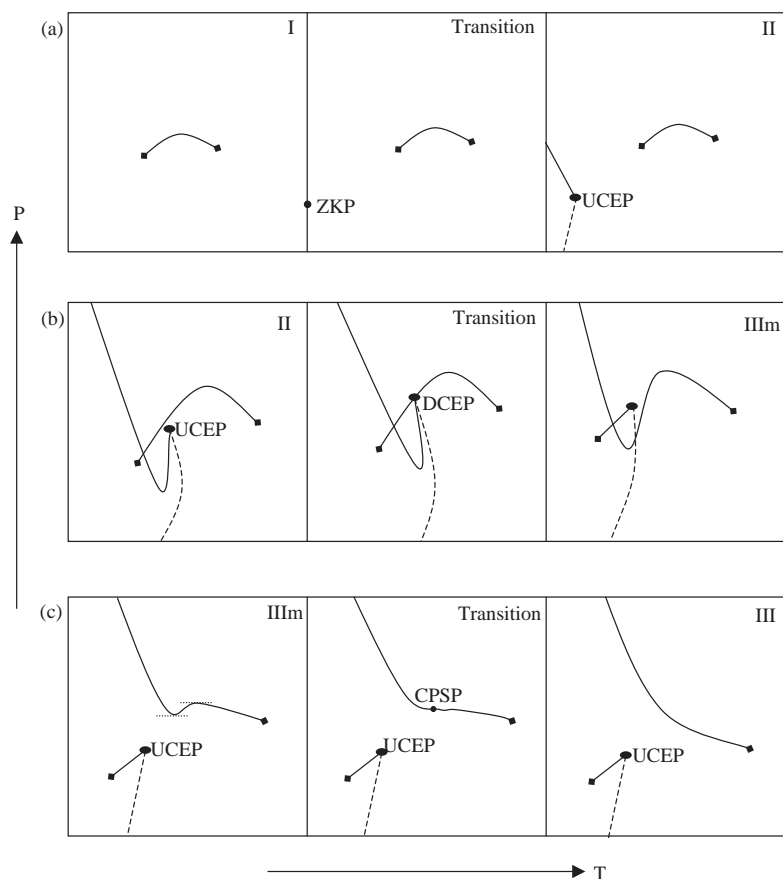


Figure 3. The transition path between (a) type I/II, (b) type II/III_m and (c) type III_m/III behaviour. The transition between type I and II behaviour is via a ZKP with the liquid–liquid critical curve appearing topologically below solidification at zero Kelvin.

a tricritical point line. This second possibility was not observed in our work. An extensive discussion of these and other boundary states is available elsewhere [4, 5, 7].

It is of interest to determine the effect of an extreme degree of anisotropy on the phase behaviour type. Figure 4 illustrates the pressure–temperature, pressure–mole fraction and pressure–packing fraction projections of critical lines in three different mixtures characterized by a second component with greatly different values of α . The calculations were performed at a constant value of T_r , which means that the difference in phase behaviour is solely a consequence of the value of α_2 . In addition to stable lines, metastable lines (extending to negative pressures) are also reported for completeness.

For low to moderately high values of α_2 (figure 4 (a)), conventional type II phenomena are observed with a continuous vapour–liquid critical line linking the pure component critical points. Increasing the value of α_2 beyond 10 results (figure 4 (b) and (c)) in a break in the vapour–liquid critical curve. Figure 5 shows this phenomenon in greater detail. It is apparent from figure 5 that this phenomenon can be described as ‘reverse’ type IV because, unlike normal type IV behaviour

(see figure 1), the vapour–liquid critical curve commencing from the component with the higher critical temperature ends on an UCEP whereas the critical curve from the other component ends on a LCEP. This is the reverse of normal type IV behaviour. We are unaware of any experimental evidence for such behaviour in type IV systems but we note that reverse type III behaviour has been experimentally observed [18] for water + eicosane. In common with our model systems, the combination of water and eicosane results in a highly anisotropic mixture.

Other variations of type IV phenomenon such as type IV* and IV₄ behaviour have been reported in the literature [16]. These should not be confused with the simple reverse type IV behaviour reported here. As shown in figure 6 (a), type IV* behaviour involves an UCST curve commencing from a high temperature critical end point. In both normal type IV (figure 3) and reverse type IV (figure 5) behaviour, the phenomena are associated with the low temperature critical end point. Type IV₄ behaviour (figure 6 (b)) is a hypothetical case involving a four-phase state. The phenomena exhibited in figures 5 and 6 (b) are clearly different.

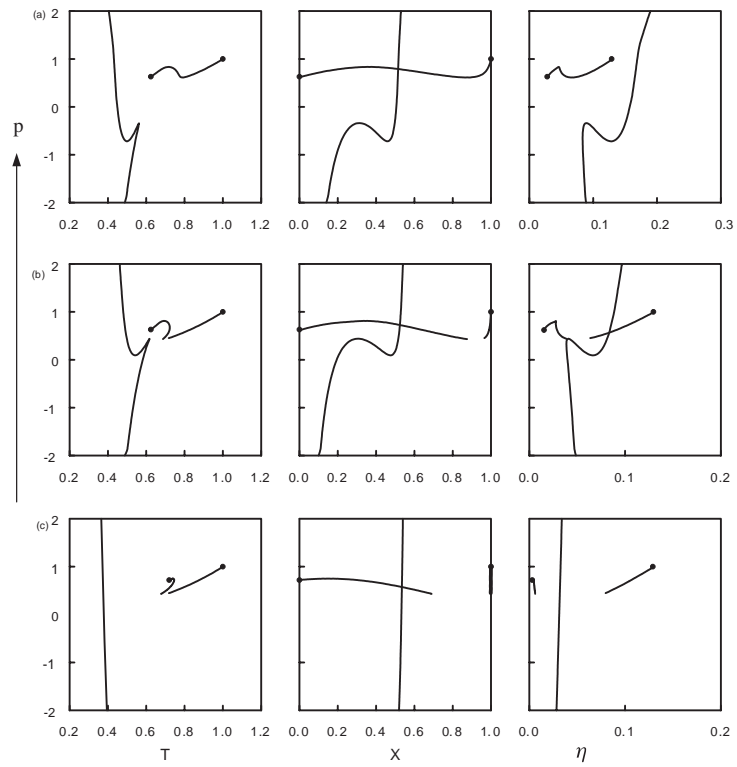


Figure 4. The calculated pressure–temperature, pressure–composition and pressure–packing fraction critical properties of highly anisotropic binary fluid mixtures when $T_r = 0.6$: (a) $\alpha_2 = 10$, (b) $\alpha_2 = 20$, (c) $\alpha_2 = 100$.

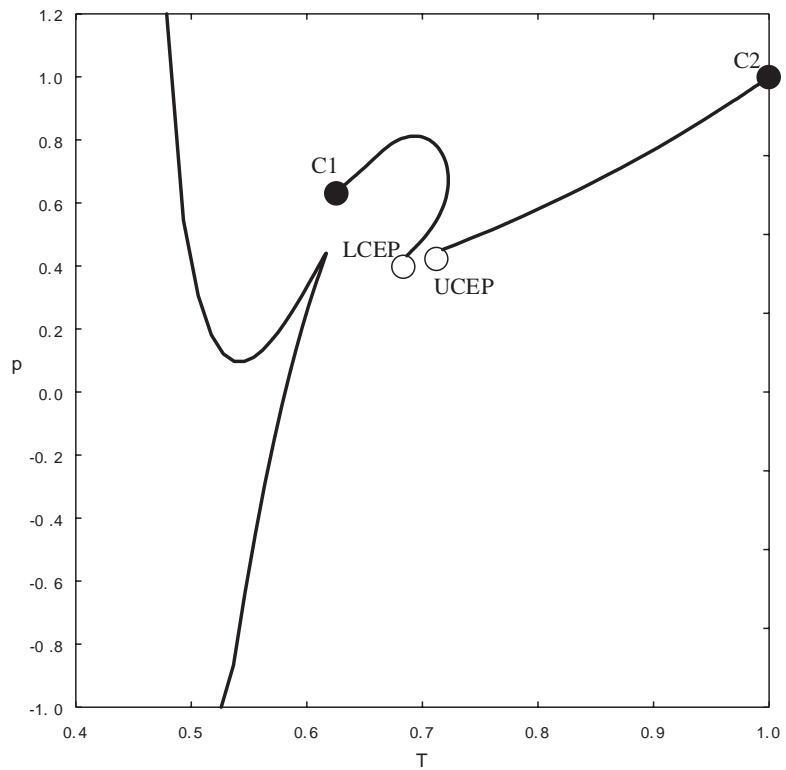


Figure 5. Enlargement of the ‘reverse type IV’ phase behaviour illustrated in figure 4 (b), showing the location of pure component critical points (C_1 and C_2), critical lines (–) and the position of the lower and upper critical end points.

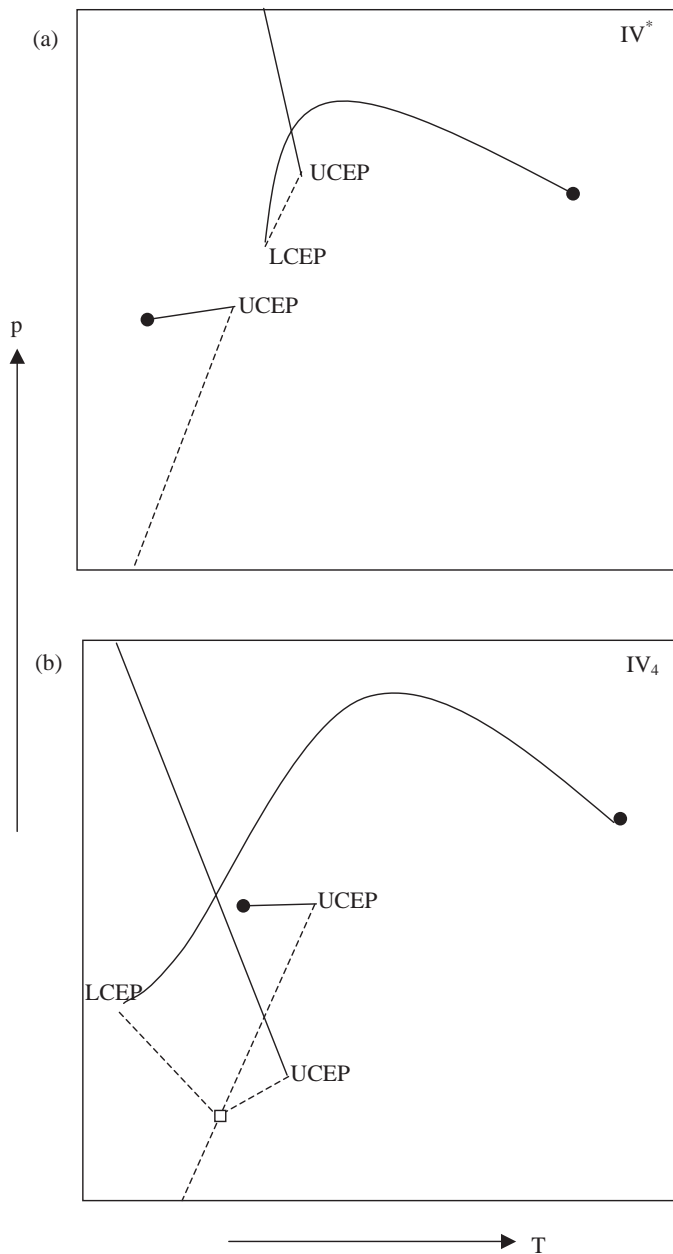


Figure 6. Other variations of type IV behaviour reported in the literature [16]. The critical lines (—), vapour–liquid–liquid lines (---), the critical points of the pure components (●) and the position of the lower and upper critical end points are illustrated. A feature of type IV₄ behaviour is a hypothetical four-phase point (□). These phenomena are different from reverse type-IV behaviour (figure 5) reported in this work.

Although our results are for model fluids, one can identify certain real types of mixtures for which the phenomena might occur. The requirement of equivalence in molecular volume effectively rules out this phenomenon for mixtures of relatively small molecules because it is unlikely that a small molecule could display the necessary deviation from spherical geometry. Mixtures composed of either a dendrimer or micelle together with either a long chain hydrocarbon or

polymer are possible candidate mixtures. The dendrimer/micelle component has a large degree of spherical geometry and the large volume that it occupies could be easily matched by a long chain hydrocarbon/polymer component of highly non-spherical geometry. Some aspects of the phase diagram of binary mixtures containing chain-like molecules and monomer/dimer mixtures have recently been investigated elsewhere [19, 20].

4. Conclusions

A global phase diagram has been developed for binary anisotropic fluid mixtures which enables us to identify the role of anisotropy on phase equilibria. Generally, the phase behaviour of anisotropic mixtures is limited to type I, II or III behaviour. However, reverse type IV behaviour is predicted for highly anisotropic fluids.

J-LW thanks the Australian Government for an Australian Postgraduate Award. The Australian Partnership for Advanced Computing provided a generous allocation of computing time.

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