Systematic investigation of the phase behavior in binary fluid mixtures. II. Calculations based on the Carnahan-Starling-Redlich-Kwong equation of state

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(Received 10 July 1991; accepted 12 September 1991)

Phase diagrams of binary fluid mixtures have been calculated from the Carnahan-Starling-Redlich-Kwong equation of state in connection with standard quadratic mixing rules. The phase diagrams were classified according to the system of van Konynenburg and Scott and then used to construct global phase diagrams showing the extent of the various phase diagram classes in the space of the parameters of the equation of state. For molecules of equal size, the global phase diagram is rather similar to that of the Redlich-Kwong or the van der Waals equation. For molecules of different sizes, however, a new tricritical line appears. Such a behavior is observed for cubic equations of state only if nonadditive covolumes are assumed. Along this new tricritical line, some unusual phase diagrams involving four-phase states and high-density instabilities can be found. The influence of molecular size ratios on the global phase diagrams and the relationship of the equation of state of this work to the ternary symmetric lattice gas and the van der Waals lattice gas are discussed.

I. INTRODUCTION

During the previous years, the topology of fluid phase diagrams has received increasing scientific interest. While the work of van Konynenburg and Scott, as well as the work of Furman et al., certainly explained the experimentally observed phase equilibrium types and seemed to indicate that—at least for nonpolar binary mixtures—the set of possible fluid phase diagram classes was completely known, recent work has shown that apparently not all possibilities had been exhausted. The prediction of class VI behavior, (experimentally observed so far only in strongly polar mixtures) as well as the “discovery” of four-phase states in binary mixtures proved that the present understanding of fluid phase diagram classes was not complete. It must be noted, however, that most of the not too numerous systematic investigations of fluid phase diagram topology which had been carried out in the past were concerned mostly with cubic equations of state (e.g., the van der Waals equation and the Redlich-Kwong equation), or models that are analogous to cubic equations (e.g., the van der Waals lattice gas and the symmetric ternary lattice gas). A survey of the literature on fluid phase diagram classification has been given in a previous publication; most of the work on noncubic equations of state published until now is concerned with a rather narrow range of molecular parameters. In order to gain some insight into the behavior of noncubic equations of state in phase equilibrium calculations, we have extended our previous work towards the Carnahan-Starling-Redlich-Kwong equation. This equation is one of the simplest possible noncubic equations, but yet useful also for quantitative calculations.

II. EQUATION OF STATE AND MIXING RULES

The Carnahan-Starling-Redlich-Kwong equation (CSRK) is a combination of a hard sphere repulsion term and a Redlich-Kwong attraction term

\[ P = \frac{RT}{V_m} \left[ 1 + \frac{4\rho - 2\rho^2}{(1 - \rho)^3} \right] - \frac{a}{\sqrt{V_m} (V_m + b)}, \]

\[ \rho = \frac{b}{4V_m}, \quad a = 8RT^{1/2}b. \]

The reduced density \(\rho\) is calculated from the volume and the van der Waals covolume parameter \(b\). This covolume parameter as well as the attraction parameter of the equation of state are given by quadratic mixing rules

\[ a = x_1^3a_{11} + 2x_1x_2a_{12} + x_2^3a_{22}, \]

\[ b = x_1^3b_{11} + 2x_1x_2b_{12} + x_2^3b_{22}. \]

In order to reduce the number of degrees of freedom in our investigation, we define four dimensionless parameter ratios

\[ \xi = \frac{d_{12} - d_{11}}{d_{12} + d_{11}}, \]

\[ \lambda = \frac{d_{22} - 2d_{12} + d_{11}}{d_{22} + d_{11}}, \]

\[ \xi = \frac{b_{22} - b_{11}}{b_{22} + b_{11}}, \]

\[ \eta = \frac{b_{22} - 2b_{12} + b_{11}}{b_{22} + b_{11}}. \]

The \(d_{ik}\) are cohesive energy densities defined by

\[ d_{ik} = T_k^* (d_{ik}/d_{ik}). \]

For real molecules, the interaction parameters \(\xi, \lambda, \xi, \eta\) and \(\eta\) are not entirely independent of each other, but subject to certain restrictions (combining rules). The following combining rules for the binary interaction parameters (the so-called Berthelot-Lorentz rules) are relatively crude approximations and usually insufficient for the quantitative prediction of phase equilibria, but nevertheless large deviations from these rules are quite unlikely.
For equal-sized molecules, this condition depends on the mixing rule of the attraction parameter only; hence the result is the same as for the Redlich–Kwong equation or the van der Waals equation

\[ x_i^c = \frac{a_{22} - a_{12}}{a_{11} - 2a_{12} + a_{22}}. \]  

(18)

The limits of azotropy, which are specified by \( x_i^c \rightarrow 0 \) or \( x_i^c \rightarrow 1 \), hence correspond to \( \lambda = \pm \xi \).

(5) Critical azotropic endpoints (coincidence of a critical endpoint and a critical azotrope)

\[ P^c_\lambda = P^c_\xi = P^c_\nu = 0, \quad \mu_i^c = \mu_i^*, \quad i = 1, 2. \]  

(19)

Phase diagrams containing these points form the boundary between the azotropic class III (III–A) and the heteroazotropic class III–H.

(10) In the publication on the phase behavior of the Redlich–Kwong equation, the equation of the azotropic composition (20) contains a wrong subscript [cf. Eq. (18)]. With the correct equation, the critical azotropic line of the Redlich–Kwong global phase diagram does not end on a tricritical line, but extends into the shield region as shown in Fig. 1.)

**IV. RESULTS FOR THE CSRK EQUATION**

For molecules of equal size, the global phase diagram of the CSRK equation (Fig. 1) is very similar to that of the van der Waals or Redlich–Kwong equation of state. Its prominent feature is a set of three tricritical lines, of which two are symmetrical. The third tricritical line coincides with the \( \lambda \) axis. The region around the apparent intersection point (intersection only in the \( \xi - \lambda \) projection), the so-called shield region, contains domains of rather complicated phase diagram classes that have been discussed elsewhere.  

Points where a boundary line terminates for physical reasons (e.g.,

**III. BOUNDARIES BETWEEN PHASE DIAGRAM CLASSES**

The various phase diagram classes and the \( P-T \) projections of typical phase diagrams have been described in the previous publication. For the reader's convenience, we list the mathematical conditions of the most important boundary classes between these classes, namely:

1. Tricritical states (a three-phase line shrinks to zero length)

\[ G_{2x} = G_{3x} = G_{4x} = G_{5x} = 0. \]  

(14)

\( G_{2x} \) is a shorthand notation for \( G_{xx} = (\partial^2 G_m/\partial x_i^2)_{P,T} \).

Phase diagrams with tricritical states form the boundaries between classes II and IV, I and V, or III and IV.*

2. Double critical endpoints (a critical line touches a three-phase line)

\[ G_{2x} = G_{3x} = 0, \quad \mu_i^c = \mu_i^*, \quad i = 1, 2. \]

\[ S_{2x}^c = S_{3x}^c = S_{4x}^c = - (x_1^c - x_2^c) S_{1x}^c. \]  

(15)

Here \( c \) denotes the critical phase and \( a \) the auxiliary noncritical phase. \( S_a \) and \( V_a \) are defined analog to \( G_a \). Phase diagrams containing double critical endpoints form the boundaries between classes III and IV, or II and IV.*

3. Zero-temperature endpoints

\[ G_{2x} = G_{3x} = 0 \quad \text{at} \quad P, T \rightarrow 0. \]  

(16)

Phase diagrams containing these points form the boundaries between classes I and II, or III and V. Equation (16) depends on the attractive part of the equation of state only; hence the results for the CSRK equation of state are the same as for the original Redlich–Kwong equation.*

4. Azotropes.

The condition of azotropy is

\[ \mu_i^c = \mu_i^*, \quad i = 1, 2, \quad x_i^c = x_i^f. \]  

(17)

* Points where a boundary line terminates for physical reasons (e.g.,

**FIG. 1.** A global phase diagram of the CSRK equation of state for molecules of equal size (\( \xi = 0, \eta = 0 \), tricritical line; \( \cdots \) its metastable part; \( \cdots \) critical point curve; \( \rightarrow \) azotropic boundary; \( \rightarrow \) combining rule (11); \( \rightarrow \) double or azotropic critical endpoint curve; \( O \) termination point. Note that the symmetric tricritical line coincides with the ordinate.)
pressure becoming zero) have been marked in the diagram.
The only topological difference to the global phase diagram of
the Redlich–Kwong equation is the behavior of the double
critical endpoint line. For cubic equations of state, this line
extends into the shield region and intersects the tricritical
line in a so-called van Laar point, whereas for the CSRK
equation, the double critical endpoint line becomes metaста-
able above \( \lambda \approx 0.04 \); hence no van Laar point and consequent-
ly no domain IV* exist in this diagram. Where the double
critical endpoint line is stable, it is so close to the tricritical
line that it is almost indistinguishable from it in the global
phase diagrams; the domains of class IV are very small.

Even at a relatively small size ratio \( \xi = 0.2 \), however,
departures from this topology are observed (Fig. 2). At the
left- and the right-hand sides of the kite-shaped figure con-
taining domains I and II, new tricritical lines appear. Similar
behavior is known for the Redlich–Kwong equation of state,
but only for larger \( \xi \) values, and only for negative \( \xi \) values;
the tricritical line at positive \( \xi \) values has not been observed
for cubic equations of state before.

In the phase diagrams of the classes I and IV, an addi-
tional critical line has been observed at extremely high
pressures. This line is a boundary of a high-pressure liquid–liquid
immiscibility which extends over a wide temperature range
(only beyond the critical temperatures of the less-volatile
component). Phase diagram classes with this high-pressure
immiscibility have been marked with a superscript "h.”

The curve with the label "P" on the left-hand side of the
global phase diagrams represents states which fulfill the cri-
terion for a double critical endpoint, but have a different
topology. Instead of merely touching a three-phase line, a
critical line intersects this line and the intersection point is an
infection point on the critical line. The P line is therefore not
a boundary line between different phase diagram classes, but
it marks a domain of phase diagrams where the liquid–liquid
critical lines have infection points. The curvature along
these critical lines is not large enough to create maxima and

minima, but it turns out that other noncubic equations of
state exist where such extrema are formed. This would give
rise to phase diagram classes VI and VII.4

In Fig. 2, the "old" tricritical line, which is also present
for equal-sized molecules, runs from the shield region down
towards negative \( \lambda \) values; the "new" tricritical line is sepa-
rate from this line. At still larger size ratios, however, the
new tricritical line runs towards the shield region, whereas
the low-\( \lambda \) branch of the old tricritical line is now separate
(Fig. 3). This change in topology is shown by Fig. 4 in
greater detail. On increasing the size ratio \( \xi \), the new tricriti-
ical line moves towards the old one, develops a cusp (the
section between cusp and endpoint is unstable), and finally
switches connections with the old tricritical line. The transition
state is a tricritical point and its thermodynamic condi-

tions are

\[
G_{x_k} = 0, \quad k = 2, \ldots , 7.
\]

The coordinates of the tricritical point are

\[
\xi = 0.2552, \quad \eta = 0.0, \quad \zeta = 0.06507, \quad \lambda = -0.03798, \quad \xi_1 = 0.8282.
\]

V. COMPARISON WITH LATTICE-GAS MODELS

A binary fluid mixture obeying the van der Waals
equation of state has a Helmholtz energy as follows:

\[
A_m^{\text{ad}} = x_1 A_1 + x_2 A_2 + \frac{RT}{x_1 \ln x_1 + x_2 \ln x_2 - \ln \frac{V_m - b}{V_m^*}} - \frac{a}{V_m}.
\]

As in Eq. (13), the superscript "+" denotes properties of
the thermodynamic reference state.

In lattice-gas theories of binary fluids, volume vari-
ations are modeled by introducing vacant sites ("holes") as a
third species. There are now three lattice site fractions

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**FIG. 2.** A global phase diagram of the CSKR equation of state for size ratios
\( \xi = 0.2, \eta = 0.0 \). For an explanation of symbols, see Fig. 1.

**FIG. 3.** A global phase diagram of the CSKR equation of state for size ratios
\( \xi = 0.3, \eta = 0.0 \). For an explanation of symbols, see Fig. 1.
The corresponding equation for the ternary symmetric lattice gas is\(^2\)
\[
F^{sw} = y_1 \ln y_1 + y_2 \ln y_2 + y_0 \ln y_0
+ \sum_{i=0}^{2} \sum_{k \leq i} y_i y_k \omega_{ik}.
\] (26)

It is remarkable that the tricritical lines of the ternary symmetric lattice gas, which emerge from the shield region, pass through a tricritical point and bifurcate. In all the van der Waals models (van der Waals fluid, Redlich–Kwong fluid, and CSRK fluid), this tricritical point does not occur (for equal-sized molecules), and of the two parallel branches of the tricritical line, only the one running towards lower \(\lambda\) values is observed. This difference in behavior is attributed to the "loss of symmetry" caused by the transition from the entropy contribution \(y_0 \ln y_0\) in Eq. (26) to \((y_0 - 1) \ln y_0\) in Eq. (25).\(^{14}\)

In order to discuss the influence of size variations, it is advantageous to refer all reduced densities to a fixed co-volume parameter, e.g., \(b_{12}\),
\[
b = \sum_{i=1}^{2} \sum_{k=1}^{2} x_i x_k b_{ik} = b_{12} + (x_1 \Delta_1 + x_2 \Delta_2) - x_1 x_2 (\Delta_1 + \Delta_2)
\] (27)

With this notation, the reduced densities can be expressed in terms of concentration-independent co-volumes
\[
y_i = y_i^\sigma \left[ 1 + \frac{x_i^2 \Delta_1 + x_i^2 \Delta_2}{b_{12}} \right], \quad i = 1, 2
\] (28)
\[
y_0^\sigma = 1 - y_1^\sigma - y_2^\sigma
\]

It is now possible to discuss three different cases.

A. van der Waals fluid \(\xi \neq 0, \eta = 0\)

In this case, the co-volume differences are linked by \(\Delta_1 = -\Delta_2\), and the reduced densities can be expressed as
\[
y_i = y_i^\sigma \left[ 1 + \frac{\Delta_1 (x_1 - x_2)}{b_{12}} \right]
\] (29)

With the abbreviation
\[
\epsilon = \xi (x_1 - x_2)
\] (30)

Eq. (24) can be transformed into
\[
F^{sw} = \sum_{i=0}^{2} y_i \ln y_i + y_2 \ln y_2 + (y_0 - 1) \ln y_0
+ \frac{2}{1 + \epsilon} \sum_{i=0}^{2} \sum_{k \leq i} y_i y_k \omega_{ik}
\] (31)

This expression differs from Eq. (24) by the last term only, which can be expressed as
\[
(y_\beta^\alpha - 1) \ln \frac{y_\alpha}{y_\beta} = (y_\beta^\alpha - 1) \ln \frac{1 - (1 + \epsilon)(1 - y_\beta^\alpha)}{y_\beta} \\
= (y_\beta^\alpha - 1) \ln \left[ 1 + \epsilon (y_\beta^\alpha - 1) \right] \\
\approx (y_\beta^\alpha - 1)^2 \epsilon \approx \epsilon \ln^2 y_\beta. \quad (32)
\]

This additional contribution to \( F^{vdW} \) affects the entropic contribution of the hole species

\[
(y_\beta^\alpha - 1) \ln y_\alpha - (y_\beta^\alpha - 1 + \epsilon \ln y_\beta^\alpha) \ln y_\alpha - y_\beta \ln y_\beta.
\]

\( \text{vdW fluid, const. } b \) \( \text{vdW fluid, variable } b \) \( \text{symmetric} \) \( (33) \)

As \( \ln y_\beta^\alpha \) is always negative, the effect of this additional term depends on the sign of \( \epsilon \). The property is not a constant, but a function of composition, and as any new tetracritical point must lie on one of the tetracritical lines, it is possible to restrict the discussion to the range of mole fractions that occur along the tetracritical line. For positive values of \( \xi \) (species 2 larger than species 1) two cases must be distinguished:

- \( \xi > 0 \) — the tetracritical mode fraction in the vicinity of the \( \xi \) axis and below is above 0.8, hence \( \epsilon \) is positive. The additional term moves the van der Waals model away from the symmetric lattice gas model. Additional tetracritical lines are suppressed.
- \( \xi < 0 \) — the tetracritical mode fraction in the vicinity of the \( \xi \) axis and below is below 0.2, hence \( \epsilon \) is negative. The additional term moves the van der Waals model towards the symmetric lattice gas model. Additional tetracritical lines are made possible.

The argumentation is not quite rigorous, because the additional term depends on composition and therefore leads to further contributions to higher derivatives of the Gibbs energy. Nevertheless, it is made plausible why the additional tetracritical lines can appear and why this takes place for negative values of \( \xi \) only.

**B. van der Waals fluid \( \xi = 0 \), \( \eta \neq 0 \)**

In this case, \( \Delta_\xi = + \Delta_1 \), hence the reduced densities can be written as

\[
y_\alpha = \eta^\alpha \left[ 1 + (\Delta_1/b_{12})(x_1^2 + x_2^2) \right]
\]

\[
y_\beta = \eta^\beta \left[ 1 + 2\eta(x_1^2 + x_2^2) \right]. \quad (34)
\]

Evidently, this case can be reduced to the previous case by redefining

\[
\epsilon = 2\eta(x_1^2 + x_2^2). \quad (35)
\]

As the term in parentheses is always positive, only the sign of \( \eta \) determines the possibility of additional tetracritical lines. The existence of tetracritical points and the branching of tetracritical lines is possible for negative values of \( \eta \) only, but if it occurs, it can be found for \( \xi > 0 \) as well as for \( \xi < 0 \).

**C. Carnahan–Starling–van der Waals fluid \( \xi \neq 0 \), \( \eta = 0 \)**

The repulsive term of the van der Waals equation of state is given by

\[
Z_{rep}^{vdW} = \frac{V_m}{V_m - b} = 1 + \frac{4\rho}{1 - 4\rho}.
\]

Where \( \rho \) is defined as in Eq. (1). This can be rewritten with reduced densities related to \( b_{12} \) by means of Eqs. (29) and (30)

\[
Z_{rep}^{vdW} = 1 + \frac{4(1 + \epsilon)\rho^*}{1 - 4(1 + \epsilon)\rho^*}.
\]

On the other hand, it is possible to expand the Carnahan–Starling hard-sphere equation around the van der Waals repulsion function

\[
Z^{CS} = 1 + \frac{4\rho - 2\rho^2}{(1 - \rho)^3}
\]

\[
\approx 1 + \frac{4}{4\rho} \left[ 1 - \frac{3}{2} \rho - \frac{11}{2} \rho^2 - 11\rho^3 \cdots \right]. \quad (38)
\]

Setting \( \rho = (1 + \epsilon)\rho^* \) in this equation and equating \( Z^{CS} = Z_{rep}^{vdW} \) leads to

\[
1 + \epsilon = \frac{(1 + \epsilon')^2}{1 - 6\rho^2(1 + \epsilon')^2 - 22\rho^3(1 + \epsilon')^2 - \cdots} \quad (39)
\]

The evaluation of this expression to first order yields

\[
\epsilon \approx -\rho^*(1 + \epsilon')^2 + \cdots. \quad (40)
\]

The leading additional term in this equation is always negative, regardless of the sign of \( \epsilon' \). Switching from the van der Waals to the Carnahan–Starling repulsion function is therefore equivalent to using more negative \( \epsilon \) in the perturbed van der Waals lattice-gas model [Eq. (31)] and this again implies a shift towards the symmetric lattice-gas model [Eq. (26)]. This explains the appearing of new tetracritical lines on both sides of the global phase diagram.

Equation (40) can also be written as

\[
\epsilon \approx -\rho^*(1 + \epsilon')^2 + \cdots \quad (41)
\]

Comparison with Eq. (35) shows that the Carnahan–Starling hard-sphere equation with \( \eta = 0 \) behaves approximately like the van der Waals repulsion function with \( \eta = -3\rho^*(1 + \epsilon')^2 \), i.e., with binary covolume \( b_{12} \), which is larger than the arithmetic mean of the pure component covolumes.

The above considerations refer to the van der Waals equation of state, or to related equations containing the van der Waals attraction term, but it is possible to generalize the results to the CSRK equation. The conditions of tetracritical states [Eq. (14)] do not contain derivatives of the Gibbs energy with respect to temperature, hence the pattern of tetracritical lines is not affected by the temperature dependence of the attraction term.15 Furthermore, the substitution of \( V_m \), the denominator of the van der Waals attraction term, by \( V_m (V_m + b) \) does not lead to large deviations in the density range considered; the global phase diagram of the Redlich–Kwong equation of state is merely a distorted version of the global phase diagram of the van der Waals equation.
VI. SYSTEMS WITH NONADDITIVE COVOLUMES

In the previous section, a new tricritical line has been predicted for van der Waals type equations of state with nonadditive covolumes, which should occur for positive \( \xi \) values. This has caused us to calculate the global phase diagram for a symmetric Redlich–Kwong mixture with \( \xi = 0, \eta = -0.05 \).

Even with this small departure from covolume additivity, the global phase diagram (Fig. 5) already shows a pattern of tricritical lines similar to Fig. 3, thus confirming the prediction.

Because of the new tricritical line, the boundary between classes III and V can no longer be a line of 0 K endpoints. In order to determine the true nature of the transition from class III to V, we have calculated a series of phase diagrams in the vicinity of this tricritical line. The results are shown in Fig. 6 not only as \( P-T \) projections, but also—following a recommendation of Meijer et al.\(^{14,10}\)—as \( y_1 - y_2 \) density plots. The latter representation helps to understand the connectivity of the critical lines. For this purpose, the metastable and unstable portions of the critical lines are also shown.

In all \( P-T \) diagrams in Fig. 6, the critical line originating at the critical point of component 1 covers a very small temperature range, before it becomes metastable and—passing through a cusp—unstable. In the projection, the critical end-point on this critical line almost coincides with the pure fluid critical point and its three-phase line is practically indistinguishable from the vapor pressure line. In the Meijer diagrams, this critical line runs from the pure fluid critical point towards the lower right corner and practically coincides with the diagram abscissa.

The new tricritical curve marks the transition from class III to IV*. For a phase diagram on this boundary, the high-pressure three-phase line has zero length and its endpoints coincide, thus forming a tricritical point.

It must be noted that the connectivity of the critical lines changes within class IV*. The transition state, where the two cusps of the critical lines meet, is a mathematical double point and as such is unstable. This changeover of critical line branches would not be accessible to experiments.

The Meijer diagrams of the class IV* reveal that the whole phase diagram contains three different critical lines. This is unusual, because until now all common phase diagram classes of binary fluid mixtures could be represented by two different critical lines. (To the experimentalist, class IV has three critical lines, but the calculation always shows that two of them are joined by metastable or unstable sections and hence must be counted as one line only.)

The phase diagrams of the symmetric ternary lattice gas contain six unique critical points:

- three stable critical points (corresponding to the pure fluid critical points and the "jamming point" \( C_n \) at high pressure). These points are found on the sides of the Meijer triangle;
- three unstable critical points (corresponding to \( T = 0, P = 0 \) or similar "impossible" limiting states). These points are represented by the corners of the Meijer diagram.

As there are six points to choose from, it is possible to construct up to three critical lines between them. The appearance of a third critical line for the binary fluid mixtures studied in this work is further proof of our view that fluid mixtures with \( \xi > 0 \) or \( \eta < 0 \) are intermediates between the van der Waals ternary lattice gas and the symmetric ternary lattice gas. We note, however, that in the Meijer diagrams for the CSRK equation, more than one critical line can end in a corner, while another corner has no critical line.

If \( \lambda \) is decreased further, the critical endpoints of the liquid–liquid critical lines approach the liquid–liquid–gas three-phase line. For a small range of \( \lambda \) values, this leads to the formation of four-phase states (class IV*). The transition from class IV* to IV, is characterized by phase diagrams containing a critical phase coexisting with two non-critical ones (\( BA_n \), in the Griffiths nomenclature\(^\text{3} \)). For still lower \( \lambda \) values, class IV occurs. In contrast to the "usual" class IV, however, the high-pressure critical line is not an extension of the critical line originating at the critical point of component 2. Furthermore, it does not run towards the jamming point any more, but seems to form a loop in the Meijer diagram. It is possible for this distorted class IV to have the three-phase lines share the same temperature range.

A typical \( T-x_1 \) phase diagram for this case is shown schematically in Fig. 7. This diagram also applies to phase diagrams of class IV* slightly above the four-phase state, if the lower critical endpoint (on the critical line originating at the critical point of the less volatile compound) has a lower pressure than the four-phase state. Otherwise, three three-phase lines run from the four-phase point upwards and the resulting isobaric phase diagram is represented schematically by Fig. 8. A remarkable feature of this phase diagram is a homogeneous domain (labeled \( "_2^2" \)) in the midst of the two-phase regions.

Finally, the phase behavior looks like class V. However, the liquid–liquid immiscibility at extremely high pressures (> 5 GPa) persists. This is a natural consequence of having
FIG. 6. Phase diagrams of Redlich-Kwong mixtures with $\delta = 0.3$, $\gamma = 0.6$ for various $\lambda$ values. ---, critical line; —, vapor pressure line; ---., three-phase line; O, pure component critical point; A, endpoint.

<table>
<thead>
<tr>
<th>$\lambda$</th>
<th>I</th>
<th>II</th>
<th>III</th>
</tr>
</thead>
<tbody>
<tr>
<td>$-0.125$</td>
<td>$-0.145$</td>
<td>$-0.200$</td>
<td></td>
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</tbody>
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a negative $\eta$. The mixture covolume is larger than the arithmetic mean of the pure component covolumes and therefore a sufficiently high pressure will always enforce demixing. Since the CSRK equation shows similar phase behavior as the Redlich–Kwong equation with negative $\eta$, this explains the high-pressure immiscibility mentioned in Fig. 2.

For still more negative $\eta$ values, the high pressure immiscibility would extend to lower pressures and perhaps interact with the usual liquid–gas phase equilibria, thus creating new phase diagram classes. It is possible that this is the reason for some unusual phase diagrams obtained with the simplified perturbed hard chain theory (SPHCT) equation, which contains a modified Carnahan–Starling function.3

VII. DISCUSSION

In the previous sections, the interaction parameters $\xi$, $\lambda$, $\xi$, and $\gamma$ have been treated as independent variables. Since with real molecules, deviations from the combining rules (9) and (10) of more than 20% would be rather exceptional, it has been concluded17 that it will not be possible to find a real system with a sufficiently high $\lambda$ value to belong to the shield region. It must be noted, however, that the parameter range into which the shield region falls depends on the equation of state. For equal-sized molecules, the $\lambda$ parameter for the center of the shield region is approximately 0.44 for the van der Waals equation of state, 0.34 for the Redlich–Kwong equation, and 0.29 for the CSRK equation. One might conclude that the more realistic the equation of state is, the lower the shield region will be. Therefore, the task of finding an experimental binary system belonging to the shield region classes II*, III*, or III** might not be hopeless after all.

Another interesting, but rather speculative feature of this work is the prediction of phase diagram classes with four-phase states. Such states are predicted for mixtures having either negative $\eta$ parameters or large size ratios $\xi$. While the global phase diagrams for the CSRK equation contain two domains of phase diagram class IV*, the cubic equations (with $\eta = 0$) have only one. This region occurs at very negative $\xi$ values and at values of the binary interaction parameter $\lambda$, which are close to the abscissa. Such $\lambda$ values would be far below the values calculated from the combining rules (9) and (10), and hence might be considered unrealistic.

There is, however, a case in which the Berthelot–Lorentz combining rules would be inappropriate. In a microscopically heterogeneous fluid, the quadratic mixing rules (2) and (3) would have to be replaced by linear ones. For the energy parameter, this would be equivalent to replacing the geometric mean in the combining rule by the arithmetic mean and this would indeed lead to $\lambda \approx 0$. Therefore, an appropriate binary system to show class IV* behavior should meet the following requirements:

(1) its first component should have a high critical pressure and a small molecular volume (e.g., water);
(2) its other component should have a low critical pressure and a large molecular volume and either interact extremely favorably with the other component (e.g., a long-chain polymer); or
(3) the mixture should form micelles.

An interesting candidate for class IV* behavior might be the system (water + 3,6,9,12-tetraoxadodecanol). Its second component is a nonionic surfactant ("C_{10}E_{12}"). In this binary system, a three-phase state has been observed experimentally, where three liquid phases coexist.18 The experiments had been carried out at ambient or slightly elevated pressure; lowering the pressure towards the vapor pressure of water would certainly have brought about a four-phase state (three liquid + one vapor phase). Until now, only a small part of the phase diagram of this binary mixture is known and it is not entirely clear to which phase diagram class it belongs, but at least the practical existence of fluid four-phase states is made certain. Furthermore, these results indi-
cate that equations of state can at least describe qualitatively the phase behavior of oil–surfactant–water mixtures.

ACKNOWLEDGMENTS

The authors wish to thank Paul H. E. Meijer (Catholic University of America, Washington, D.C.) for fruitful discussions. Financial support by the Deutsche Forschungsgemeinschaft and by the Fonds der Chemischen Industrie e. V. is gratefully acknowledged. One of us (U. K. D.) has received a stipend from the Karl-Winnacker-Stiftung.

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