Calculation of Critical Curves for Carbon Dioxide+n-Alkane Systems

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Abstract: The critical curves of eight binary systems from carbon dioxide+methane to carbon dioxide+octane at temperatures from 200 to 570 K and pressures from 2.5 to 14.7 MPa have been calculated. The critical pressures, the critical temperatures, the critical mole fractions, the critical molar volumes and the critical densities are obtained by using an Equation of State (EOS), which consists of a hard body repulsion term and an additive perturbation term. The latter term accounts for the attractive molecular interactions and uses a square-well potential, so three adjustable parameters are required. Good agreement was obtained between the experimental data, the literature data and the calculated values.

Keywords: Carbon dioxide, equation of state, critical curves, hard body repulsion term, additive perturbation term

Introduction

High pressure vapor-liquid equilibria of carbon dioxide+hydrocarbon systems have been widely investigated. Since the mid-1980s, supercritical (SC) CO$_2$+lower molecular weight alkanes or alcohols systems have been of interest because of their importance of SC fluids and cosolvent pairs in the separation of biomaterials (Formani, 1990; Dohn, 1995; Christov and Dohn, 2002). The calculation of critical curves for binary mixtures is very important in the study of phase equilibria. Critical states of mixtures are of interest for a number of reasons. They delineate the homogeneous and heterogeneous regions. They are also used in numerous correlations for the properties of mixtures. They are intricately connected with retrograde phenomena. Measurements of critical points are very difficult. Therefore, they are often determined from thermodynamic models using phase equilibrium parameters. A robust method for this task is a powerful tool for the calculation of critical loci.

Early theoretical discussions by van der Waals on critical phenomena in pure and mixed fluids were instrumental in encouraging many researchers in the latter part of the last century to undertake experimental work in this field (Van der Waal, 1900). Scott and Van Koniynenburg (1970) have classified critical curves using the van der Waals equation for nonpolar components. Schneider (1978) and Rowlinson and Swinton (1978) have published a comprehensive discussion on the classification of critical curves for binary systems. Although there is a great deal of literature describing the measurements of critical points, the calculation of critical curves for SC CO$_2$+lower molecular n-alkanes has not been reported in detail. Especially, the data of critical molar volume and critical densities are absent. Nechtel and Franck (1996) have calculated the critical curves of several binary systems by means of the Heilig-Franck Equation of State (EOS). Tian et al. (2003) have calculated the critical curves for supercritical CO$_2$+1-alkanol systems. Many equations of state have been proposed and
applied in the past. In this study, the Heilig-Franck EOS is employed in which only three adjustable
parameters are required and the experimental data are not required.

Equation of State and Thermodynamic Relations

To predict the gas-liquid critical curves of binary mixtures under high temperatures and pressures,
an appropriate equation of state (Heilig-Franck EOS) was derived from a perturbation method by using
a square-well molecular interaction potential. Employing a hard body repulsion term and an additive
perturbation term, the pressure is given by

\[
p(T, V, x_1, \ldots, x_n) = p(\text{repulsion}) + p(\text{attraction})
\]

\[
= RT \frac{V_i^2}{V_n (V_i - \beta_i)^2} + RT \frac{B_i}{V_i^2 + V_n C_i / B_i}
\]

(1)

where the \(B_i\) and \(C_i\) parameters are the second and third virial coefficients of a square-well fluid and
\(\beta_i\) represents the molecular volume of the fluid. \(V_n\) is the molar volume of the mixture and \(x_i\) is the
molar fraction of component \(i\).

Each of the molecular terms can be given by

\[
\beta_i(T) = \sum x_i \beta_i(T)
\]

\[
\beta_i(T) = \frac{\pi}{6} \sigma_i^3 N_i
\]

\[
\beta_i(T) = \beta_i \left( \frac{T_i}{T} \right)^{3/m}
\]

(2)

where \(T_i\) is the critical temperature of component \(i\) and \(m\) is a temperature-dependent exponent. The
applicability of this relationship is limited to a region of relatively high temperatures. The value of the
characteristic exponent, \(m\), can be estimated from the general properties of molecular interaction or
from adjustments of experimental pVT-data (Christoforakos and Franck, 1986). For the calculations
in the present study \(m = 10\) has been chosen (Wu et al., 1990). \(\sigma\) is the sphere diameter and \(N_i\) is
Avogadro’s constant.

The virial attraction terms can be given by the following:

\[
\beta_i(T) = \sum x_i \beta_i(T)
\]

\[
\beta_i = 4\beta_i (\alpha_i - 1) \Delta_i
\]

\[
\Delta_i = \exp(\varepsilon_i / kT) - 1
\]

(3)

Here \(k\) is Boltzmann’s constant, \(\omega\) is the relative width of the square-well in units of \(\sigma\), \(\omega\) is its depth
and \(\sigma\) is its core diameter.

The selection of parameters for mixed interactions is a central problem. If identical relative square-well widths are \(\alpha_i = \omega_i + \omega_i\) used for different particle combinations in the binary fluid mixtures,
the usual Lorentz-Berthelot combination rules together with empirical parameters \(k_1\) and \(k_2\) can
be applied:
\[ \varepsilon_0 = k_1 \left( \varepsilon_c \varepsilon_a \right)^{1/2} \]
\[ \sigma_1 = k_2 \left( \sigma_c + \sigma_a \right)/2 \]  

(4)

\[ \nu = k_3 \nu_c \]
\[ \gamma = k_4 \gamma_c \]

(5)

\( k_c \) and \( k_a \) are binary mixing coefficients. The relative width of the potential well, \( \omega_0 \), can be set at values between 1.5 and 2.5 or derived from vapor pressure curves. The \( \omega \)-values decrease with the increase of the molecular polarity and can be correlated with an acentric factor (Christoforakis and Franck, 1986). These are adjustable parameters defined by combination rules. The factors \( k_c \) and \( k_a \) can be determined from experimental mixture data or can be predicted by analogy from existing values of related systems. It appears that \( k_c \) and \( k_a \) remain constant or vary only modestly and systematically within certain groups of systems. The diameter \( \sigma \) and the depth, \( \varepsilon_0 \) of the square-well are derived from critical data of the pure partners.

The third virial coefficient is given by:

\[ C_2 = \sum \sum \sum x_i x_j x_k C_{ik} \]
\[ C_{ik} = \frac{1}{3} \left( \frac{1}{11} \lambda_{ik} + \lambda_{ik} + \lambda_{ik} \right) \]

(5)

The auxiliary functions of the virial coefficients \( l_{11} \) to \( l_{12} \) have been given by Hirschfelder et al. (1964). To determine the critical phenomena of binary systems, the stability criteria formulated with the Helmholtz energy \( A \) have to be observed.

The critical points of mixtures are obtained when all of the physical properties of two coexisting phases are identical. This is obtained when the following conditions are satisfied simultaneously (Sadus, 1992b):

\[ W = \begin{vmatrix}
\frac{\partial^2 A_m}{\partial \varepsilon_m^2} & -\frac{\partial^2 A_m}{\partial \varepsilon_m \partial V_m} \\
\frac{\partial^2 A_m}{\partial \varepsilon_m \partial V_m} & \left( \frac{\partial A_m}{\partial \varepsilon_m} \right)^2
\end{vmatrix}_T, V = 0 
\]

(6)

\[ X = \begin{vmatrix}
\frac{\partial W}{\partial m} & \frac{\partial W}{\partial x} \\
\frac{\partial^2 A_m}{\partial \varepsilon_m \partial V_m} & \left( \frac{\partial^2 A_m}{\partial \varepsilon_m^2} \right)^2
\end{vmatrix}_T, V = 0 
\]

(7)

\[ Y = \begin{vmatrix}
\left( \frac{\partial W}{\partial V_m} \right)_T & -\left( \frac{\partial X}{\partial x} \right)_T \\
\left( \frac{\partial^2 A_m}{\partial \varepsilon_m \partial V_m} \right)_T & \left( \frac{\partial^2 A_m}{\partial \varepsilon_m^2} \right)^2
\end{vmatrix}_T, V = 0 
\]

(8)

where \( A_m \), \( T \) and \( V \) denote the Helmholtz function, temperature and volume, respectively. The conditions \( W = 0 \) and \( X = 0 \) express the relationships between the temperature \( T \), the molar volume, \( V_m \) and the mole fraction, \( x_m \) of the critical point. The condition \( Y > 0 \) guarantees the thermodynamic stability of the calculated critical point. The analytical determination of the critical curve is possible only when relatively simple expressions for the molar Helmholtz function of the fluid mixture, \( A_m \), can be obtained. The equation contains a term for a residual free energy as well as terms for a reference state with chemical potentials \( \mu_i \) and pressure \( p_i \) (McGlashan, 1979). From thermodynamics, \( A_m \), which is a function of \( T \), \( V_m \) and \( x_m \), can be given by:

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Results and Discussion

The critical curve is of great importance for characterizing the real behavior of mixtures. Critical curves of binary mixtures are usually classified into six principal types (Konyinenburg and Scott, 1980). The shapes of critical curves are very sensitive to the molecular size and interactions of the components. In this section, the results for eight binary mixtures calculated by the Helig-Franck EOS are shown (Fig. 1-8). A systematic classification of binary mixtures has been proposed by van Konyinenburg and Scott (Konyinenburg and Scott, 1980). In this classification different binary mixtures of carbon dioxide+n-alkanes belong to different types.

Fig. 1: T-x, p-x, and p-T, diagrams of the SC CO2+CH4 system

Fig. 2: T-x, p-x, and p-T, diagrams of the SC CO2+C2H6 system
Type 1 binary p-T diagrams include CO$_2$+ethane (Fig. 2) and CO$_2$+n-butane (Fig. 4). This is the simplest case in which the p-T projection of the three dimensional pressure-temperature-composition (p-T-x) diagram consists of two vapor-pressure curves for the pure components and a critical line. Type 1 can be further divided into five subdivisions according to the shape of the continuous gas-liquid critical curve. The molecules of CO$_2$ and ethane have similar shapes and sizes. The quadrupole moment of carbon dioxide is much stronger than that of ethane. The binary p-T diagram of CO$_2$+ethane belongs
to the third subdivision of type I, in which the critical curve is convex and exhibits a minimum temperature in the p-T plane. The binary p-T diagram of CO$_2$-butane belongs to the second subdivision of type I, in which the critical curve is convex and exhibits a maximum pressure in the p-T plane. According to the classification of Konyenbourg and Scott (1980), the binary p-T diagrams of CO$_2$+methane (Fig. 1), CO$_2$+propane (Fig. 3), CO$_2$+pentane (Fig. 5) and CO$_2$+hexane (Fig. 6) should also belong to type I fluid phase behavior, although the binary mixture of CO$_2$+hexane may exhibit a metastable immiscibility at low temperature.
Type II binary p-T diagrams include, CO$_2$+n-heptane (Fig. 7) and CO$_2$+n-octane (Fig. 8). As the mutual solubility of the components decreases, the Upper Critical Solution Temperatures (UCSTs) versus pressure (UCSTs-p) line shows liquid-liquid immiscibility. This line starts at the liquid-liquid-gas triple phase line. There is a point on the UCSTs-p diagram, where the heavy component can be precipitated by a small temperature increase, a small pressure decrease, a large temperature decrease, or an extremely pronounced pressure increase. At higher temperatures, the gas-liquid critical curve of the type II mixture is similar to that of type I. However, at relatively low temperatures, it has liquid-liquid immiscibility and the loci of UCSTs remain distinct from the gas-liquid critical curve.

Figure 1-8 show the calculated critical curves for SC CO$_2$+n-alkanes (from methane to octane) in comparison with experimental curves from the literature (Mraw et al., 1978; Horstmann et al., 2000;
Table 1: The interaction parameters for the binary systems

<table>
<thead>
<tr>
<th>System</th>
<th>$w_i$</th>
<th>$k_i$</th>
<th>$k_j$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$+CH$_4$</td>
<td>2.5</td>
<td>1.0</td>
<td>0.90</td>
</tr>
<tr>
<td>CO$_2$+C$_2$H$_4$</td>
<td>2.3</td>
<td>1.0</td>
<td>0.90</td>
</tr>
<tr>
<td>CO$_2$+C$_3$H$_8$</td>
<td>2.3</td>
<td>1.0</td>
<td>0.82</td>
</tr>
<tr>
<td>CO$_2$+C$<em>5$H$</em>{12}$</td>
<td>2.3</td>
<td>1.0</td>
<td>0.78</td>
</tr>
<tr>
<td>CO$_2$+C$<em>7$H$</em>{16}$</td>
<td>2.3</td>
<td>1.0</td>
<td>0.75</td>
</tr>
<tr>
<td>CO$_2$+C$<em>9$H$</em>{20}$</td>
<td>2.3</td>
<td>1.0</td>
<td>0.75</td>
</tr>
<tr>
<td>CO$<em>2$+C$</em>{11}$H$_{24}$</td>
<td>2.3</td>
<td>1.0</td>
<td>0.80</td>
</tr>
</tbody>
</table>

Table 2: The critical properties of the pure substances

<table>
<thead>
<tr>
<th>Substance</th>
<th>$P_c$ (MPa)</th>
<th>$T_c$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>7.38</td>
<td>304.2</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>4.61</td>
<td>190.6</td>
</tr>
<tr>
<td>C$_2$H$_6$</td>
<td>4.88</td>
<td>305.4</td>
</tr>
<tr>
<td>C$_3$H$_8$</td>
<td>4.25</td>
<td>369.9</td>
</tr>
<tr>
<td>C$<em>4$H$</em>{10}$</td>
<td>3.81</td>
<td>425.0</td>
</tr>
<tr>
<td>C$<em>5$H$</em>{12}$</td>
<td>3.36</td>
<td>469.6</td>
</tr>
<tr>
<td>C$<em>6$H$</em>{14}$</td>
<td>3.02</td>
<td>507.4</td>
</tr>
<tr>
<td>C$<em>7$H$</em>{16}$</td>
<td>2.74</td>
<td>540.0</td>
</tr>
<tr>
<td>C$<em>8$H$</em>{18}$</td>
<td>2.49</td>
<td>568.9</td>
</tr>
</tbody>
</table>

Roof and Baron, 1967; Freitas et al., 2004; Chen et al., 2003; Liu et al., 2003; Choi and Yeo, 1998; Kalra et al., 1978) and our experimental data. Our calculated results have excellent agreement with the experimental data. Table 1 gives a compilation of the adjustable parameters, $\omega$, $k_i$, and $k_j$, for the eight SC CO$_2$+n-alkane systems. Table 2 gives the critical constants for CO$_2$ and the eight alkanes. The values of $\omega$ and $k_i$ for each of the systems are 2.3 and 1, respectively. The value of $\omega$ is determined by the molecular polarity. Therefore, $\omega$ is constant for the nonpolar alkanes. The factor $k_i$ describes the deviations of $c_i$ from 1/2($c_i$+$c_j$) and the factor $k_j$ describes the deviations of $c_j$ from 1/2($c_i$+$c_j$). The value of $k_i$ decreases with the increase in alkane carbon number except for n-octane. Octane has a higher critical temperature and lower critical pressure and the binary p-T diagram of SC CO$_2$+n-octane belongs to type II. Therefore, it requires a higher $k_i$ value.

Figure 9 and 10 give the $V_n$, $\chi$, and $p_c$-$T_c$ curves. They show the similar rules that with the increase in alkane carbon number the curves give regular change, especially from C$_4$ to C$_7$.

The parameters in Table 1 provide a useful basis to estimate the homogeneous regions and the two-phase behavior of binary systems and can be applied to calculate the three-dimensional phase equilibrium surfaces. Using the parameter values in Table 2, the $T_c$-$x_n$, $p_c$-$x_n$, and $p_c$-$T_c$ diagrams have been plotted. The changes in the adjustable parameters $\omega$, $k_i$, and $k_j$ are very small for the different alkanes. If other cosolvents with different polarity and molecular size are used, then the values of $\omega$, $k_i$, and $k_j$ would be more dissimilar. The calculated data are compared with the experimental data in Fig. 1-8. They show a reasonable correlation. Therefore, the Helliig-Frank equation is suitable to predict bimodal curves and critical curves for the eight SC CO$_2$+n-alkane systems at higher temperatures and pressures.

**Conclusions**

- The critical curves of the eight binary systems from SC CO$_2$+methane to SC CO$_2$+n-hexane at higher temperatures and pressures all belong to type I and the critical curves of the binary systems for SC CO$_2$+n-heptane and SC CO$_2$+n-octane belong to type II.
- The critical molar volumes and densities are obtained with the equation of state by Helliig and Frank. The complete critical curves of carbon dioxide and low molecular alkanes afford more data to researching on the fundamental chemistry and chemical engineering.
The adjustable parameters, \( \omega, k_c \) and \( k_R \) for the eight SC CO\(_2\)+n-alkane systems have been given. The value of \( k_c \) decreases with the increase in alkane carbon number except for n-octane and the values of \( \omega \) and \( k_R \) are 2.3 and 1, respectively.

The adjustable parameters \( \omega, k_c \) and \( k_R \) for the eight SC CO\(_2\)+n-alkane systems and the critical constants for CO\(_2\) and the alkane partners may give a useful basis to estimate the homogeneous regions and two-phase behavior of binary systems and can be applied to calculate the three-dimensional phase equilibrium surface.

The calculated critical curves in these systems are in good agreement with experimental data. The greatest relative error for pressure is 5.69\% and for the mole fractions of CO\(_2\) it is 9.73\%. The Heilig-Franck equation of state has been found to have good prediction and correlation with binary vapor-liquid equilibrium data of the carbon dioxide+alkane systems.

References


