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Calculation of Gas−Liquid Critical Curves for Carbon Dioxide−1-Alkanol Binary Systems

Yi-ling Tian,*[†,‡] Li Chen,[‡] Ming-wei Li,[‡] and Hua-feng Fu[‡]

Department of Chemistry, Tianjin University, and State Key Laboratory of C1 Chemical Technology, Tianjin University, Tianjin 300072, China

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The critical curves of the four binary systems from CO_2−methanol to CO_2−1-butanol at temperatures from 300 to 600 K and pressures from 4 to 18 MPa have been calculated. An equation of state that uses a perturbation type containing a repulsion term and a square-well potential attraction term for intermolecular interaction has been used. To use the pairwise combination rule for the square-well molecular interaction potential, three adjustable parameters are required. The experimental critical point data are compared with the values predicted from the equation of state. Good agreement is obtained between the experimental critical pressure−composition data and the calculated values.

Introduction

Supercritical CO_2 (SC CO_2) is a nontoxic, nonflammable, and inexpensive solvent. In separation processes, it generally leaves no solvent residues in the products. The high diffusivity, low viscosity, and low surface tension of SC CO_2 strongly depend on the system's pressure and temperature. Thus, the reaction mixtures or extracted materials can easily be precipitated from SC CO_2 by only using pressure reduction. These separations then become gas−liquid or gas−solid ones, and the fractionation of large amounts of dilute liquid solutions in the downstream phase usually can be avoided. Thus, it is possible that the product can be fractionated and purified directly from the mixture without the use of any other solvent. Furthermore, the heat needed to evaporate CO_2 is far less than that needed for organic solvents or water. From the mid-l980s, SC CO_2 and alcohol systems have received increased attention because of their importance as SC fluid/cosolvent pairs in the separation of biomaterials.[1,2] For example, low molecular weight alkanes and alkanols are the cosolvent best suited for the extraction of biomaterials and medicines. Therefore, it is necessary to define critical regions for the above systems.

The early theoretical work of van der Waals on critical phenomena in both pure and mixed fluids was instrumental in encouraging many talented research workers in the latter part of the last century to undertake experimental works in this field.[3] Scott and Van Konynenburg[4] have classified critical curves based on the van der Waals equation for nonpolar components. Schneider[5] and Rowlinson[6] have published comprehensive discussions of the classification of critical curves. Tian et al.[7] have measured phase equilibrium data from 353.5 to 453.2 K and from 2.0 to 14.0 MPa for the CO_2−ethanol system. Brunner[8] measured the critical curve of the CO_2−methanol system with a high-pressure view-cell. In addition, the literature contains several references describing phase behavior investigations of various CO_2−solvent binary mixtures. Gurdial et al.[9] discussed binary mixtures of CO_2−(C_1−C_6) 1-alkanols, CO_2−(C_5−C_{10}) alkenes, and CO_2−acetone. Jennings et al.[10] provided a detailed review for CO_2−1-alkanols systems, but none of these studies exceeded 333.15 K or solvent concentrations above 10 mol % in CO_2. Ziegler et al.[11] used supercritical fluid flow injection to estimate liquid−vapor critical loci of binary mixtures containing CO_2. Neichel and Franck[12] calculated the critical curves of binary systems from water−methane to water−hexane and water−dodecane by means of the Heilig−Franck equation of state (EOS). This EOS contains a hard-sphere repulsion term and a square-well attraction term. It has been successfully used at high pressures and temperatures and has even been used for component partners with high polarity differences.[13−15] Many EOSs have been proposed and applied in the past. In this work, we employ the Heilig−Franck EOS. It requires only three adjustable parameters.

Equation of State and Thermodynamic Relations

To predict the gas−liquid critical curves of binary mixtures under high temperatures and pressures, including those with highly polar partners, an appropriate equation of state (Heilig−Franck EOS) is derived from a perturbation method by using a square-well molecular interaction potential. Employing a repulsion term and an attraction term, the pressure is given by

$$p = RT\frac{V_m^3 + V_m^2\beta_x + V_m\beta_x^2 - \beta_x^3}{V_m(V_m - \beta_x)^3} + RT\frac{B_x}{V_m^2 + V_m C_x/B_x} \quad (1)$$

where V_m is the molar volume of the mixture, x_i is the molar fraction of component *i*, B_x and C_x are the second and third virial coefficients of the square-well fluid, and β_x represents the molecular volume of the mixture.

Each of the molecular terms can be given by

$$\beta_x(T) = \sum\sum x_i x_j \beta_{ij}(T)$$
$$\beta_{ij}(T) = \frac{\pi}{6}\sigma_{ij}^3 N_0 \quad (2)$$
$$\beta_{ii}(T) = \beta_{ii}\left(\frac{T_{c,i}}{T}\right)^{3/m}$$

where $T_{c,i}$ is the critical temperature of component *i* and *m* is a temperature-dependent exponent that equals 10 in this work.[16] σ is the sphere diameter and N_0 is Avogadro's constant.

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* Corresponding author. Telephone: +86-22-27403475. Fax: +86-22-27403475. E-mail: tianyiling@eyou.com.

[†] Department of Chemistry, Tianjin University.

[‡] State Key Laboratory of C1 Chemical Technology, Tianjin University.

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The virial attraction terms can be given by the following:

$$B_x(T) = \sum\sum x_i x_j B_{ij}(T)$$

$$B_{ij} = -4\beta_{ij}(\lambda_{ij}^3 - 1)\Delta_{ij} \tag{3}$$

$$\Delta_{ij} = \exp(\epsilon_{ij}/kT) - 1$$

Here k is Boltzmann's constant, λ is the relative width of the square well in units of σ, ϵ is its depth, and σ is its core diameter. The following combining rules are applied:

$$\lambda_{ij} = \lambda_{ii} = \lambda_{jj}$$

$$\epsilon_{ij} = \zeta(\epsilon_{ii}\epsilon_{jj})^{1/2} \tag{4}$$

$$\sigma_{ij} = \xi(\sigma_{ii} + \sigma_{jj})/2$$

ζ and ξ are binary mixing coefficients. The relative width of the potential well λ can be set at values between 1.5 and 2.5 or derived from vapor pressure curves. There is a relation to the Pitzer accentric factor. These are adjustable parameters defined by combination rules. It appears that within certain groups of systems ζ and ξ can remain constant or may vary only modestly and systematically. The diameter σ and the depth ϵ of the square well are derived from critical data of the pure partners.

The third virial coefficient is given by:

$$C_x = \sum\sum\sum x_i x_j x_k C_{ijk}$$

$$C_{ijk} = -\frac{1}{3}\{(I_{11}\Delta_{ij} + I_{12}\Delta_{ik} + I_{13}\Delta_{jk}) - (I_{21}\Delta_{ij}\Delta_{ik} + I_{22}\Delta_{ij}\Delta_{jk} + I_{23}\Delta_{ik}\Delta_{jk}) + (I_{33}\Delta_{ij}\Delta_{ik}\Delta_{jk})\} \tag{5}$$

The auxiliary functions of the virial coefficients I_{11} to I_{33} are given by Hirschfelder.[17] To determine the critical phenomena of binary systems, the stability criteria formulated with the Helmholtz function A have to be observed.

Every critical point of a binary mixture can be obtained when all of the physical properties of the two coexisting phases become identical. They also can be obtained when the following conditions are satisfied simultaneously:[18−20]

$$W = \begin{vmatrix} -(\partial^2 A_m/\partial V_m^2)_T & -(\partial^2 A_m/\partial x\,\partial V_m)_T \\ (\partial^2 A_m/\partial x\,\partial V_m)_T & (\partial^2 A_m/\partial x^2)_{T,V} \end{vmatrix} = 0 \tag{6}$$

$$X = \begin{vmatrix} (\partial W/\partial V_m)_T & (\partial W/\partial x)_{T,V} \\ (\partial^2 A_m/\partial x\,\partial V_m)_T & (\partial^2 A_m/\partial x^2)_{T,V} \end{vmatrix} = 0 \tag{7}$$

$$Y = \begin{vmatrix} (\partial X/\partial V_m)_T & (\partial X/\partial x)_{T,V} \\ (\partial^2 A_m/\partial x\,\partial V_m)_T & (\partial^2 A_m/\partial x^2)_{T,V} \end{vmatrix} > 0 \tag{8}$$

The conditions $W = 0$ and $X = 0$ express the relationships between the temperature T, the molar volume V_m, and the mole fraction x_i of the critical point. These conditions are required for the stability calculation of critical equilibria. The condition $Y > 0$ guarantees the thermodynamic stability of the calculated critical point. 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. A_m can be obtained by integration of a pressure-explicit equation of state that is based on a reference state with standard pressure $p°$ and standard chemical potential $\mu°$. From thermodynamics, A_m, which is a function of T, V_m, and x_i, can be given by

$$A_m(T,V_m,x_i) = \sum x_i\mu_i^\circ - RT + RT\sum x_i \ln x_i + RT \ln\left(\frac{RT}{p^\circ V_m}\right) + RT\left\{\frac{4\beta_x}{V_m - \beta_x} + \frac{\beta_x^2}{(V_m - \beta_x)^2}\right\} + RT\frac{B_x^2}{C_x}\ln\left\{\frac{V_m}{V_m - (C_x/B_x)}\right\} \tag{9}$$

Shmonov[21] and Deiters et al.[22] have given more detailed descriptions.

TABLE 1: Adjustable Parameters λ, ζ, and ξ for the Four CO_2−1-Alkanol Systems and the Critical Constants for CO_2 and the Four Alkanols

	CO_2−CH_3OH	CO_2−C_2H_5OH	CO_2−1-C_3H_7OH	CO_2−1-C_4H_9OH
λ	2.52	2.46	2.48	2.48
ζ	0.96	0.98	0.98	0.98
ξ	1.14	1.16	1.16	1.16

	CO_2	CH_3OH	C_2H_5OH	1-C_3H_7OH	1-C_4H_9OH
p_c/MPa	7.39	8.10	6.38	5.17	4.41
T_c/K	304.2	512.6	513.9	536.3	562.9

Results and Discussion

Critical curves of binary fluid mixtures are usually divided into six principal types.[23] Type I mixtures have continuous gas−liquid critical curves and complete miscibility of the liquid phases at all temperatures. Type I can be subdivided according to the shape of the continuous gas−liquid critical curve which connects the critical points of the two pure components. The first subdivision of type I critical curves is convex and usually exhibits a maximum pressure in the p−T and p−x planes. This occurs whenever there are moderately large differences between critical temperatures or between critical volumes of the pure components. Once the differences exceed some certain value, the critical curves become discontinuous.[24] These kinds of curves can be further subdivided by comparing the mixture's critical temperature with the pure component's critical temperature. When critical curves are concave everywhere and exhibit a pressure minima, they form the second subdivision of type I critical curves, which shows a large positive deviation from Raoult's law. Typical examples include some mixtures of aromatic hydrocarbons with aliphatic or alicyclic hydrocarbons.[25,26] Mixtures formed from substances with very similar critical properties, for example, $CO_2 + N_2O$ or benzene + toluene, present an almost linear critical locus. They belong to the third subdivision of type I critical curves. At higher temperatures, a type II mixture has a gas−liquid critical curve similar to that for type I, but at relatively low temperatures, it has liquid−liquid immiscibility and the loci of upper critical solution temperatures (UCSTs) remain distinct from the gas−liquid critical curve.

At the higher temperatures and pressures studied, the gas−liquid critical curves of the four binary systems CO_2−methanol to CO_2−1-butanol all belong to the first kind of curve (type I); however, both the CO_2−1-propanol and the CO_2−1-butanol systems exhibit type II behavior (liquid−liquid−vapor locus) at sufficiently low temperatures where CO_2 is not present as a solid.[27] The liquid−liquid−vapor loci for CO_2−1-propanol and CO_2−1-butanol terminate at upper critical end points of 15.29 bar, 245.89 K and 22.99 bar, 259.25 K, respectively. Our results are in excellent agreement with the work of Yeo et al.[28] Table 1 gives a compilation of the adjustable parameters

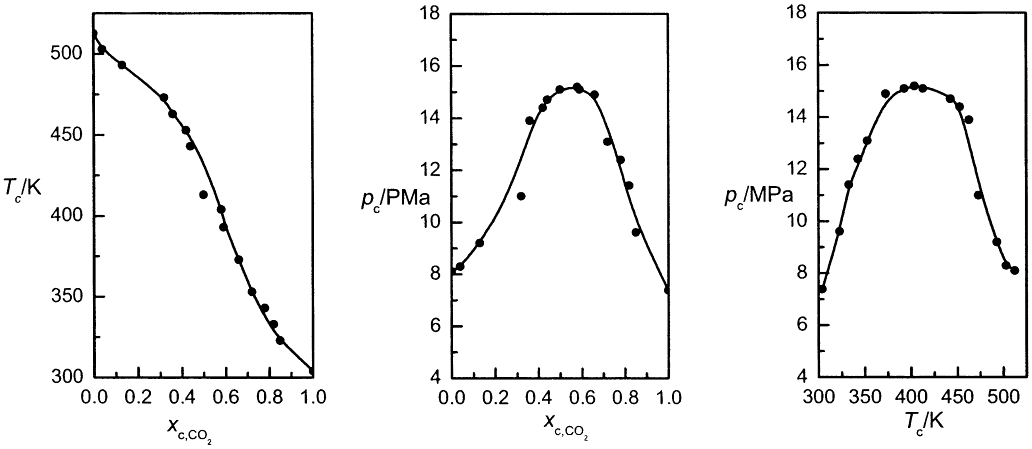

Figure 1. T_c−x_c, p_c−x_c, and p_c−T_c diagrams of the SC CO_2 + CH_3OH system.

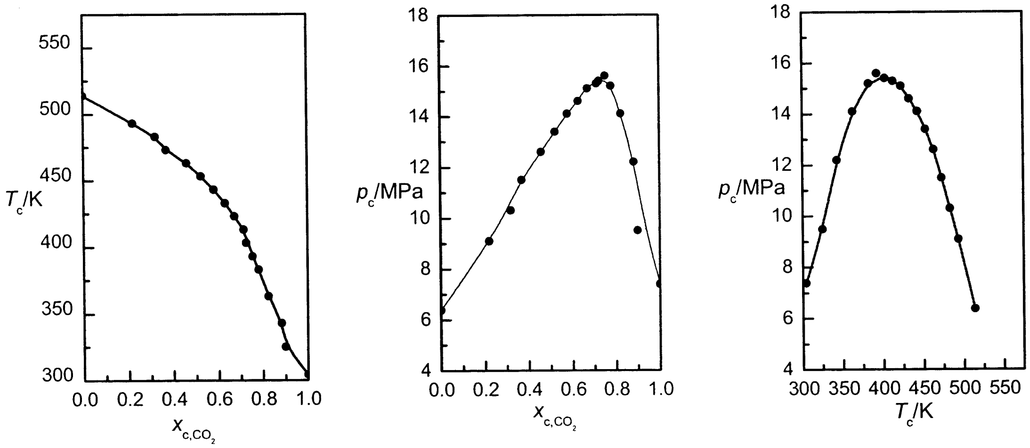

Figure 2. T_c−x_c, p_c−x_c, and p_c−T_c diagrams of the SC CO_2 + C_2H_5OH system.

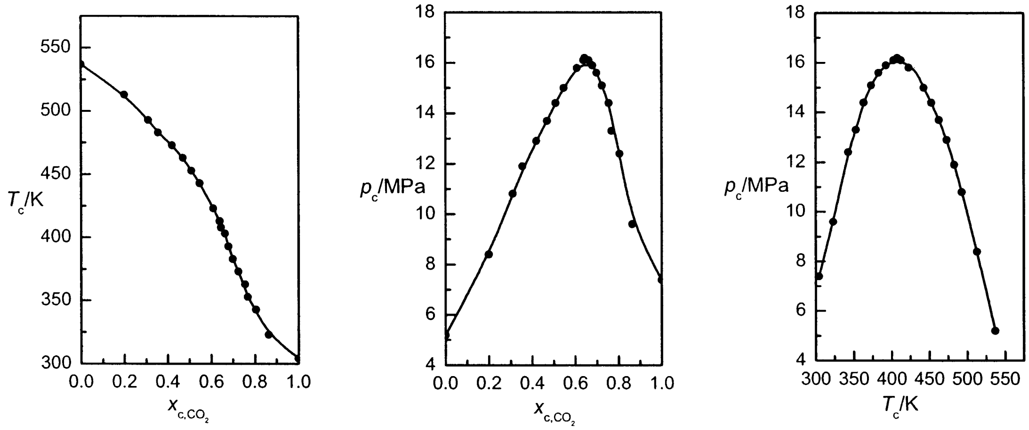

Figure 3. T_c−x_c, p_c−x_c, and p_c−T_c diagrams of the SC CO_2 + 1-C_3H_7OH system.

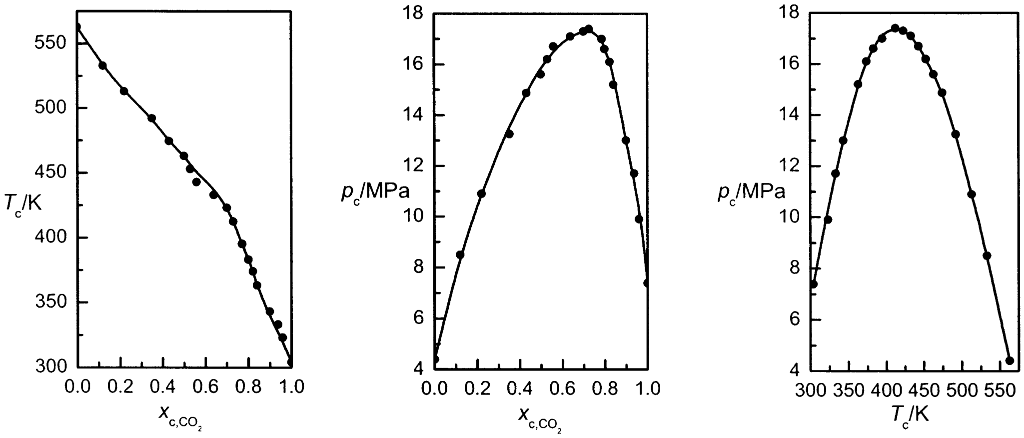

Figure 4. T_c−x_c, p_c−x_c, and p_c−T_c diagrams of the SC CO_2 + 1-C_4H_9OH system.

TABLE 2: Maximum Critical Values of the Mixtures

	CO_2 + CH_3OH	CO_2 + C_2H_5OH	CO_2 + 1-C_3H_7OH	CO_2 + 1-C_4H_9OH
$p_{c,max}$/MPa	15.2	15.6	16.2	17.4
$T_{c,max}$/K	404	393	408	413
$x_{c,max}$	0.580	0.754	0.646	0.760

λ, ζ, and ξ for the four CO_2−1-alkanol systems and also gives the critical constants for CO_2 and the four alkanols. The values of the λ parameters for each of the systems are very close, except methanol needs a slightly higher value. The factor ξ describes the deviations of σ_{ij} from $^1/_2(\sigma_{ii} + \sigma_{jj})$, and the factor ζ describes the deviations of ϵ_{ij} from $(\epsilon_{ii} + \epsilon_{jj})^{1/2}$. The values for both ζ and ξ are constant with the exception of those for methanol. Methanol has the lowest critical temperature and highest critical pressure and therefore probably requires lower ζ and ξ values than the other alkanols. This may be related to the structural differences between methanol and the other alkanols and the fact that methanol with a low molecular weight has a rather large dipole moment of 1.70 D. Similar behavior is found in other analogous systems. The parameters in Table 1 provide 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 surfaces.

Using the parameter values in Table 1, the p_c−T_c, p_c−x_c, and T_c−x_c diagrams have been plotted. The calculated critical curves are compared with experimental data in Figures 1−4. They show a reasonable correlation. With the exception of the CO_2−methanol system, the curves in Figures 2−4 show similar shapes. The curves for the p_c−T_c and p_c−x_c diagrams of the CO_2−methanol system show a slower change near the maximum critical values than the others. This may be due to the large dipole moment of methanol. The maximum critical values for the mixtures of the four systems composed of CO_2 and the four alkanols are given in Table 2. The maximum critical pressures of the mixtures increase slightly with the increase of the carbon number of the alkanol, and the maximum critical temperatures have the same tendency, again with the exception of methanol. It is assumed that the Heilig−Franck equation is suitable to predict bimodal curves and critical equilibria for the four CO_2−1-alkanol systems at higher temperature and pressure.

From Table 1, the changes in the adjustable parameters λ, ζ, and ξ are very little for different alkanols combined with CO_2. If the properties of polarity and molecular size were more different from those of alkanols, then the values of λ, ζ, and ξ would be more dissimilar. We have calculated the critical curves of $CO_2 + H_2O$ systems,[29] with the above three parameters equal to 2.50, 0.78, and 1.00, respectively. The agreement between calculated and measured values is very good too.[30]

Conclusions

1. The critical curves of the four binary systems from CO_2−methanol to CO_2−butanol at higher temperature and pressure all belong to type I. The critical curves of the latter two both exhibit type II behavior at sufficiently low temperatures. The Heilig−Franck EOS is suitable for systems with high-polarity components at high temperatures.

2. The adjustable parameters λ, ζ, and ξ for the four CO_2−1-alkanol systems have been given. It is found that the values of λ are very close and that, with the exception of methanol, the values of ζ and ξ are equal to 0.98 and 1.16, respectively. The lower values for methanol may be related to the structural differences between methanol and the other alkanols.

3. The adjustable parameters λ, ζ, and ξ for the four CO_2−1-alkanol systems and the critical constants for CO_2 and the alkanol 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 surfaces.

4. The calculated critical curves in these systems are in good agreement with experimental data. The greatest relative error for pressure is 1.20% and 1.31% for mole fractions of CO_2.

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Symbols

p = pressure
p_c = critical pressure
T = temperature
T_c = critical temperature
V_m = molar volume
x = molar fraction
B and C = the second and the third virial coefficients
β = molecular volume
λ, ϵ = relative width and depth of the square well
σ = core diameter
k = Boltzmann constant
ζ, ξ = binary mixing coefficients
A_m = mole Helmholtz function

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