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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.

Key words: 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) CO₂+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 (Fornari, 1990; Dohm, 1995; Christov and Dohm, 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 Konynenburg (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 literatures describing the measurements of critical points, the calculation of critical curves for SC CO₂+lower molecular n-alkanes has not been reported in detail. Especially, the data of critical molar volume and critical densities are absent. Neichel 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 CO₂+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

$$\begin{aligned}
 p(T, V_m, x_1, \dots, x_k) &= p(\text{repulsion}) + p(\text{attraction}) \\
 &= RT \frac{V_m^3 + V_m^2 \beta_x + V_m \beta_x^2 - \beta_x^3}{V_m (V_m - \beta_x)^3} + RT \frac{B_x}{V_m^2 + V_m C_x / B_x}
 \end{aligned}
 \tag{1}$$

where the B_x and C_x parameters are the second and third virial coefficients of a square-well fluid and β_x represents the molecular volume of the fluid. V_m 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

$$\begin{aligned}
 \beta_x(T) &= \sum \sum x_i x_j \beta_{ij}(T) \\
 \beta_{ij}(T) &= \frac{\pi}{6} \sigma_{ij}^3 N_0 \\
 \beta_{ii}(T) &= \beta_{ii} \left(\frac{T_{ci}}{T} \right)^{3/m}
 \end{aligned}
 \tag{2}$$

where T_{ci} 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). σ is the sphere diameter and N_0 is Avogadro's constant.

The virial attraction terms can be given by the following:

$$\begin{aligned}
 \beta_x(T) &= \sum \sum x_i x_j \beta_{ij}(T) \\
 \beta_{ij} &= 4 \beta_{ij} (\omega_{ij}^3 - 1) \Delta_{ij} \\
 \Delta_{ij} &= \exp(\epsilon_{ij} / kT) - 1
 \end{aligned}
 \tag{3}$$

Here k is Boltzmann's constant, ω is the relative width of the square-well in units of σ , ω is its depth and σ is its core diameter.

The selection of parameters for mixed interactions is a central problem. If identical relative square-well widths are $\omega_{ij} = \omega_i + \omega_j$ used for different particle combinations in the binary fluid mixtures, the usual Lorentz-Berthelot combination rules together with empirical parameters k_c and k_e can be applied:

$$\begin{aligned}\epsilon_{ij} &= k_\epsilon (\epsilon_{ii} \epsilon_{jj})^{1/2} \\ \sigma_{ij} &= k_\sigma (\sigma_{ii} + \sigma_{jj})/2\end{aligned}\tag{4}$$

k_ϵ and k_σ are binary mixing coefficients. The relative width of the potential well, ω , can be set at values between 1.5 and 2.5 or derived from vapor pressure curves. The ω -values decrease with the increase of the molecular polarity and can be correlated with an acentric factor (Christoforakos and Franck, 1986). These are adjustable parameters defined by combination rules. The factors k_ϵ and k_σ can be determined from experimental mixture data or can be predicted by analogy from existing values of related systems. It appears that k_ϵ and k_σ remain constant or vary only modestly and systematically within certain groups of systems. 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:

$$\begin{aligned}C_x &= \sum \sum \sum x_i x_j x_k C_{ijk} \\ C_{ijk} &= -\frac{1}{3} \left\{ \begin{aligned} &(I_{11}\Delta_{ij} + I_{12}\Delta_{ik} + I_{13}\Delta_{jk}) - \\ &(I_{21}\Delta_{ij}\Delta_{ik} + I_{22}\Delta_{ij}\Delta_{jk} + I_{23}\Delta_{ik}\Delta_{jk}) + (I_{33}\Delta_{33}\Delta_{ik}\Delta_{jk}) \end{aligned} \right\}\end{aligned}\tag{5}$$

The auxiliary functions of the virial coefficients I_{11} to I_{33} 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):

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

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

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

where A , 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_i , 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 μ_i^θ and pressure p^θ (McGlashan, 1979). From thermodynamics, A_m , which is a function of T , V_m and x_i , can be given by:

$$\begin{aligned}
 A_m(T, V_m, x_2, \dots, x_k) &= \sum x_i \mu_i^0 - RT + RT \sum x_i \ln x_i + RT \ln \left[\frac{RT}{(p^0 V_m)} \right] \\
 &\quad - \int_{\infty}^{V_m} \left[p(T, V_m, x_2, \dots, x_k) - \frac{RT}{V_m} \right] dV_m \\
 &= \sum x_i \mu_i^0 - RT + RT \sum x_i \ln x_i + RT \ln \left[\frac{RT}{(p^0 V_m)} \right] \\
 &\quad + RT \left\{ \frac{4\beta_x}{V_m - \beta_x} + \frac{\beta_x^2}{(V_m - \beta_x)^2} \right\} + RT \frac{B_x^2}{C_x} \ln \left\{ \frac{V_m}{V_m - (C_x/B_x)} \right\}
 \end{aligned} \tag{9}$$

Shmonov *et al.* 1993) and Deiters *et al.* (1993) have given more detailed descriptions.

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 (Konynenburg 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 Heilig-Franck EOS are shown (Fig. 1-8). A systematic classification of binary mixtures has been proposed by van Konynenburg and Scott (Konynenburg and Scott, 1980). In this classification different binary mixtures of carbon dioxide+n-alkanes belong to different types.

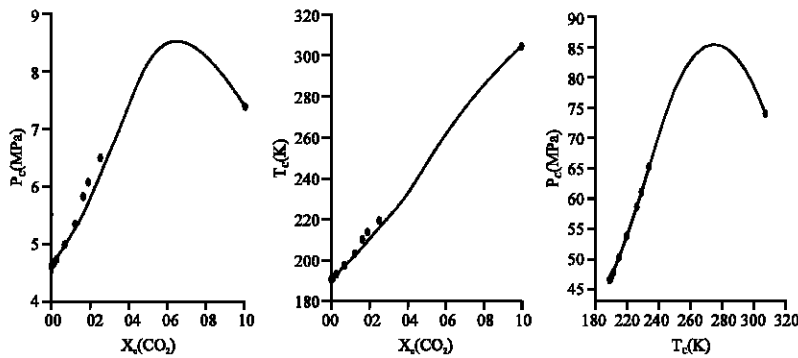


Fig. 1: T_c - x_c , p_c - x_c and p_c - T_c diagrams of the SC CO_2 + CH_4 system

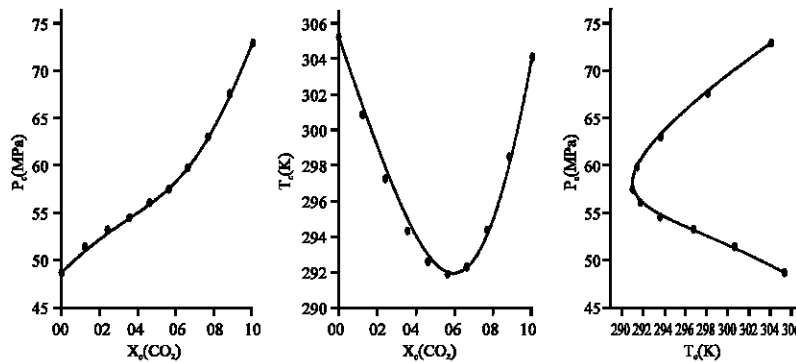


Fig. 2: T_c - x_c , p_c - x_c and p_c - T_c diagrams of the SC CO_2 + C_2H_6 system

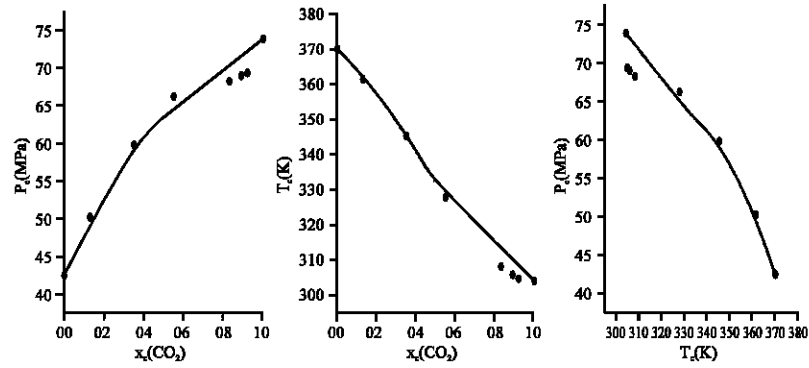


Fig. 3: T_c - x_c , p_c - x_c and p_c - T_c diagrams of the SC CO_2 + C_3H_8 system

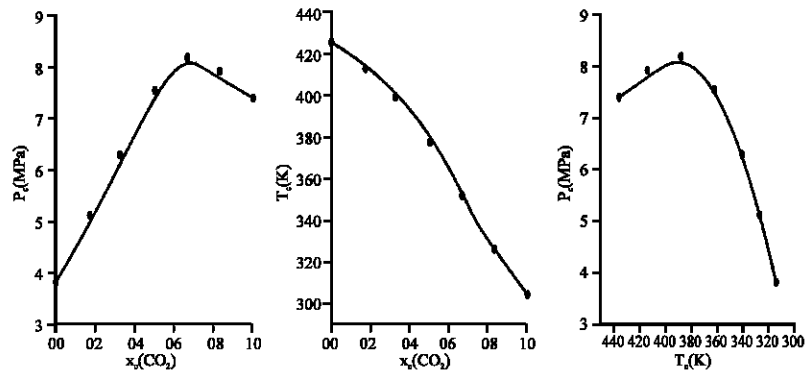


Fig. 4: T_c - x_c , p_c - x_c and p_c - T_c diagrams of the SC CO_2 + C_4H_{10} system

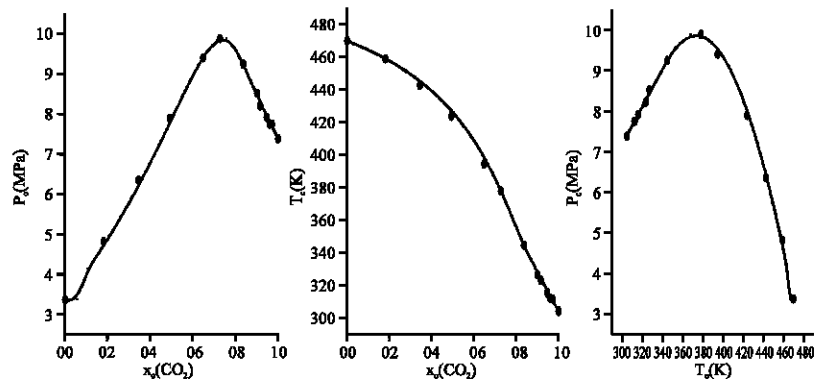


Fig. 5: T_c - x_c , p_c - x_c and p_c - T_c diagrams of the SC CO_2 + C_5H_{12} system

Type I 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 I 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

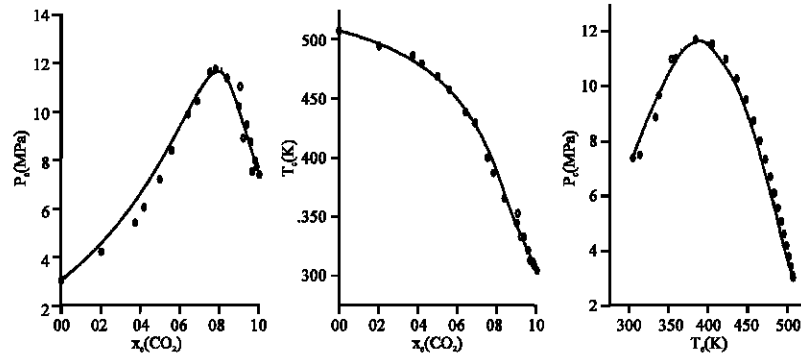


Fig. 6: T_c - x_c , p_c - x_c and p_c - T_c diagrams of the SC CO_2 + C_6H_{14} system

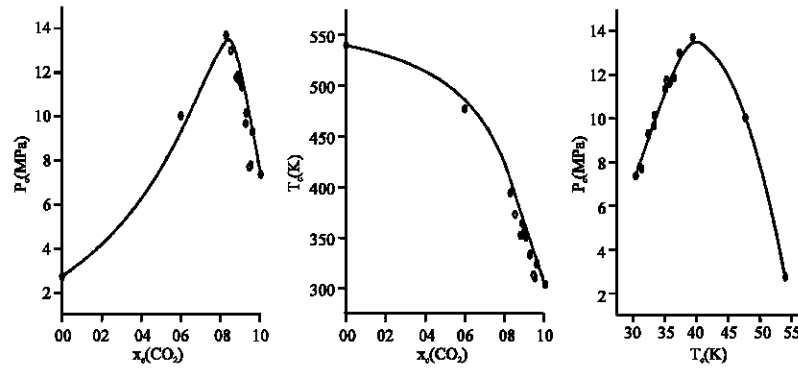


Fig. 7: T_c - x_c , p_c - x_c and p_c - T_c diagrams of the SC CO_2 + C_7H_{16} system

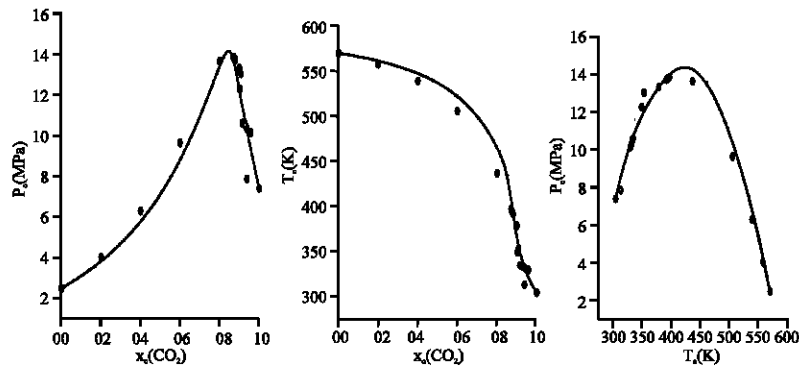


Fig. 8: T_c - x_c , p_c - x_c and p_c - T_c diagrams of the SC CO_2 + C_8H_{18} system

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 Konynenburg 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.

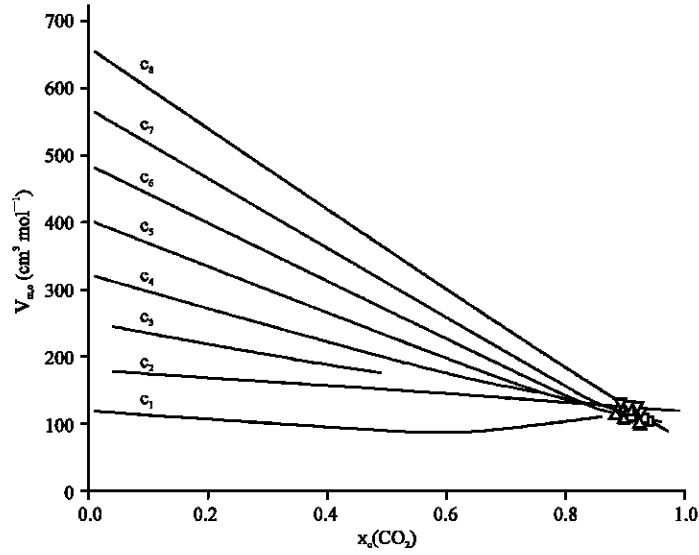


Fig. 9: $V_{m,c}$ - x diagram of the SC CO_2 +n-alkane systems. $\Delta \nabla \square$: experimental data

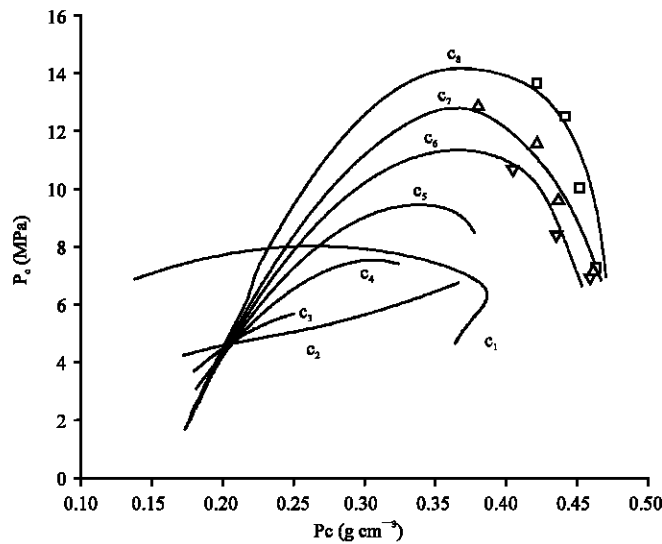


Fig. 10: p_c - p_c diagram of the SC CO_2 +n-alkane systems. $\Delta \nabla \square$: experimental data

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

System	W_{ij}	k_c	k_σ
CO ₂ +CH ₄	2.3	1.0	0.90
CO ₂ +C ₂ H ₆	2.3	1.0	0.90
CO ₂ +C ₃ H ₈	2.3	1.0	0.82
CO ₂ +C ₄ H ₁₀	2.3	1.0	0.78
CO ₂ +C ₅ H ₁₂	2.3	1.0	0.76
CO ₂ +C ₆ H ₁₄	2.3	1.0	0.75
CO ₂ +C ₇ H ₁₆	2.3	1.0	0.75
CO ₂ +C ₈ H ₁₈	2.3	1.0	0.80

Table 2: The critical properties of the pure substances

substance	P_c (MPa)	T_c (K)
CO ₂	7.38	304.2
CH ₄	4.61	190.6
C ₂ H ₆	4.88	305.4
C ₃ H ₈	4.25	369.9
C ₄ H ₁₀	3.81	425.0
C ₅ H ₁₂	3.36	469.6
C ₆ H ₁₄	3.02	507.4
C ₇ H ₁₆	2.74	540.0
C ₈ H ₁₈	2.49	568.9

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, ω , k_c and k_σ , for the eight SC CO₂+n-alkane systems. Table 2 gives the critical constants for CO₂ and the eight alkanes. The values of ω and k_c for each of the systems are 2.3 and 1, respectively. The value of ω is determined by the molecular polarity. Therefore, ω is constant for the nonpolar alkanes. The factor k_c describes the deviations of σ_{ij} from $1/2(\sigma_{ii}+\sigma_{jj})$ and the factor k_σ describes the deviations of ϵ_{ij} from $1/2(\epsilon_{ii}+\epsilon_{jj})$. The value of k_c 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 CO₂+n-octane belongs to type II. Therefore, it requires a higher k_c value.

Figure 9 and 10 give the $V_{m,c}-x_c$ and p_c-P_c curves. They show the similar rules that with the increase in alkane carbon number the curves give regular change, especially from C₄ to C₈.

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_c , p_c-x_c and p_c-T_c diagrams have been plotted. The changes in the adjustable parameters ω , k_c and k_σ are very small for the different alkanes. If other cosolvents with different polarity and molecular size are used, then the values of ω , k_c and k_σ would be more dissimilar. The calculated data are compared with the experimental data in Fig. 1-8. They show a reasonable correlation. Therefore, the Heilig-Franck equation is suitable to predict bimodal curves and critical curves for the eight SC CO₂+n-alkane systems at higher temperatures and pressures.

Conclusions

- The critical curves of the eight binary systems from SC CO₂+methane to SC CO₂+n-hexane at higher temperatures and pressures all belong to type I and the critical curves of the binary systems for SC CO₂+n-heptane and SC CO₂+n-octane belong to type II.
- The critical molar volumes and densities are obtained with the equation of state by Heilig and Franck. 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, ω , k_c and k_{cs} , for the eight SC CO₂+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 ω and k_{cs} are 2.3 and 1, respectively.
- The adjustable parameters ω , k_c and k_{cs} , for the eight SC CO₂+n-alkane systems and the critical constants for CO₂ 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 CO₂ 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.

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