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Leung–Griffiths Model for the Thermodynamic Properties of Mixtures of CO_2 and C_2H_6 Near the Gas-Liquid Critical Line

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Leung and Griffiths have proposed a fundamental thermodynamic equation for a binary mixture near the critical line and have successfully applied it to the mixture of He^3 and He^4 in which the critical line is a nearly linear function of composition. We have used a Leung–Griffiths type equation of state to describe the thermodynamic properties of the mixture of carbon dioxide and ethane. The critical line of this mixture is, unlike that of He^3 and He^4, a nonlinear function of composition, and the azeotropic line extends to the critical line. Comparison of the predictions of the equation to experimental data shows a good agreement for the mixture of CO_2 and C_2H_6.

KEY WORDS: carbon dioxide; critical point; equation of state; ethane; mixtures; thermodynamic properties.

1. INTRODUCTION

An equation of state is essential for the prediction of many thermodynamic properties of a fluid system, be it a pure fluid or a mixture. Near a critical point where a "classical" equation of state of the van der Waals type fails to describe correctly the singular behavior of a system, there is a need for a nonclassical equation of state which describes the thermodynamic properties more accurately. In the case of pure fluids, great success has been achieved by the use of nonclassical critical indices and a scaled equation of

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state for describing a system near the gas-liquid critical point [1]. In the case of fluid mixtures near a gas-liquid critical line, Leung and Griffiths postulate that the mixture properties can be obtained from an interpolation between the critical properties of the pure components when a suitable set of variables is used [2]. They propose that the variables should be "field" variables instead of "density" variables. "Field" variables are those which have the same value for coexisting phases, such as temperature and chemical potentials, whereas "density" variables are those which have different values for coexisting phases, such as density and composition. They applied the idea to the mixtures of He^3 and He^4 and succeeded in describing the critical properties of the mixtures of all compositions along the entire critical line.

The mixtures of He^3 and He^4 are fundamentally simple in the sense that the critical temperatures, pressures, and densities are nearly linear functions of composition. Although Leung and Griffiths demonstrated the success of their idea in a simple system, their basic idea should be applicable to mixtures with a more complex critical line than that of the mixtures of He^3 and He^4 as long as it is continuous between the gas-liquid critical points of the pure components. In fact, D'Arrigo et al. have successfully used an equation of the type of that of Leung and Griffiths to describe the mixtures of carbon dioxide and ethylene [3]. This system is significantly different from that of He^3 and He^4 in that the former exhibits azeotropy and the azeotropic line extends to the critical line. The point common to both lines is the critical azeotrope. Furthermore, the critical temperature is nearly a quadratic function of composition over the entire range with the minimum located very close to pure ethylene. Moldover et al. have also adapted the idea of Leung and Griffiths and formulated a thermodynamic potential for a number of binary mixtures [4, 5] including those of carbon dioxide and ethane [4]. Their formulation has been used, so far, successfully only in correlating the thermodynamic properties of the vapor-liquid equilibrium states near the critical locus of mixtures.

In this report we attempt to provide an equation of the type of that of Leung and Griffiths for the mixtures of carbon dioxide (CO_2) and ethane (C_2H_6). This system also exhibits critical azeotropy, and the minimum critical temperature is located at the composition of CO_2 equal to approximately 55% mole fraction. The motivations behind this work are many. For instance, in our earlier light scattering experiment on the mixtures near a critical point [6] there was a need to estimate the scattering amplitudes, gravity effects, and some other properties of the mixtures. Furthermore, on a different ground, we would like to know to what extent the idea of Leung and Griffiths may be extended beyond the simple mixture of He^3 and He^4, as D'Arrigo et al. have attempted to do. For our mixture of carbon dioxide and ethane, however, more and different experimental data are available than for that of carbon dioxide and ethylene. Finally, we want to show how one may systematically determine the free parameters in the Leung–Griffiths equation from experimental data in order to enable others to apply this type of equation of state to near-critical mixtures.

2. THERMODYNAMIC POTENTIAL OF THE LEUNG–GRIFFITHS TYPE

The thermodynamic potential, ω, is chosen to be the pressure, p, divided by RT, where R is the gas constant and T is the absolute temperature:

$$\omega = p/RT \tag{1}$$

The thermodynamic potential consists of a regular part, ω_r, and a singular part, ω_s, which incorporates the critical anomalies:

$$\omega = \omega_r + \omega_s \tag{2}$$

Although the fundamental independent variables are T and the chemical potentials per mole, μ_1 and μ_2 of the two components, more convenient variables are ζ, τ, and h, which are obtained through the following transformations:

$$\zeta = C_2 \exp(\mu_2/RT)/\Theta \tag{3}$$

$$\tau = B_c(\zeta) - 1/RT \tag{4}$$

$$h = \ln \Theta - H(\zeta, \tau) \tag{5}$$

where

$$\Theta = C_1 \exp(\mu_1/RT) + C_2 \exp(\mu_2/RT) \tag{6}$$

Here C_1 and C_2 are two positive constants, $B_c(\zeta)$ is the value of $1/RT$ along the critical line, and $H(\zeta, \tau)$ is the value of $\ln \Theta$ on the coexistence surface or its smooth extension into the one-phase region.

These three variables are a very natural choice in the following sense. In pure component 1, μ_2 tends to $-\infty$ and $\zeta = 0$, whereas in pure component 2, μ_1 tends to $-\infty$ and $\zeta = 1$. Thus ζ, which is bound between 0 and 1, is the variable that interpolates between two pure components. The quantity τ measures the distance from the critical line in the direction parallel to the coexistence surface while h measures the distance away from the coexistence surface.

One of the basic assumptions in the approach of Leung and Griffiths is that all functions other than ω_s can be expressed as a power series in ζ, τ, and h. The exact number of terms cannot be determined a priori. Instead, comparison with experimental data dictates the number of terms that are needed. Therefore, for the mixtures of CO_2 and C_2H_6 we have chosen the following interpolation equation with the designation that CO_2 is component 1:

$$B_c(\zeta) = a_0 + a_1\zeta + a_2\zeta(1-\zeta) + a_3\zeta^2(1-\zeta) \tag{7}$$

$$H(\zeta,\tau) = b(\zeta) + g(\zeta)\tau + s(\zeta)\tau^2 \tag{8}$$

$$\omega_r(\zeta,\tau,h) = c(\zeta) + d(\zeta)\tau + e(\zeta)\tau^2 + f(\zeta)h \tag{9}$$

where

$$b(\zeta) = b_1\zeta + b_2\zeta^2 \tag{10}$$

$$c(\zeta) = c_0 + c_1\zeta + c_2\zeta(1-\zeta) \tag{11}$$

$$d(\zeta) = d_0 + d_1\zeta \tag{12}$$

$$e(\zeta) = e_0 + e_1\zeta \tag{13}$$

$$f(\zeta) = f_0 + f_1\zeta + f_2\zeta(1-\zeta) \tag{14}$$

$$g(\zeta) = g_1\zeta \tag{15}$$

$$s(\zeta) = s_0 + s_1\zeta + s_2\zeta(1-\zeta) \tag{16}$$

The singular part takes on the form

$$\omega_s(\zeta,\tau,h) = q(\zeta)\pi(\bar{\tau},h) \tag{17}$$

with

$$\bar{\tau} = l(\zeta)\tau \tag{18}$$

where

$$q(\zeta) = 1 + q_1\zeta + q_2\zeta(1-\zeta) \tag{19}$$

$$l(\zeta) = 1 + l_1\zeta \tag{20}$$

Here $\pi(\bar{\tau},h)$ is the Schofield "linear model" [7], which is given by the parametric form

$$\pi(\bar{\tau},h) = r^{2-\alpha}\bar{p}(\theta) \tag{21}$$

with

$$h = \bar{a}r^{\Delta}\theta(1-\theta^2) \tag{22}$$

and

$$\bar{\tau} = r(1-\bar{b}^2\theta^2)/RT_{c1} \tag{23}$$

where T_{c1} is the critical temperature of the first component, and $\bar{b}^2 = (\delta - 3)/(\delta - 1)(1 - 2\beta)$. The critical indices α, β, δ, and $\Delta = \beta\delta$ are in their customary notations. The function $\bar{p}(\theta)$ is a polynomial quadratic in θ; it can be found in ref. [2]. The variable r is a measure of the distance of a state from criticality, and θ measures the distance along a contour of constant r. The singular behavior at a critical point is then determined by the behavior as $r \rightarrow 0$.

Pressure can be obtained directly from the potential by simply multiplying by RT, whereas density and composition are derived quantities and are obtained in a less straightforward way. The number density ρ, in units of number of moles per unit volume, and the composition, x which is the mole fraction of CO_2, are given by

$$\rho = \omega_h = f(\zeta) + q(\zeta)\,\bar{g}r^{\beta}\theta \tag{24}$$

and

$$x = (1-\zeta) - \zeta(1-\zeta)\,Q/\rho \tag{25}$$

where

$$Q = \omega_\zeta + B_\zeta\omega_\tau - \rho(H_\zeta + B_\zeta H_\tau) \tag{26}$$

The subscripts ζ, τ, and h for ω and H denote partial derivatives with respect to that variable, while the other two are held constant. B_ζ is the derivative of $B \equiv 1/RT$, which is also equal to that of $B_c(\zeta)$.

Other useful derived quantities are the internal energy, u, in units of energy per unit volume and the heat capacity at constant volume, C_{vx}, in units of energy per mole per degree, and they are given by

$$u = \omega_\zeta - \rho H_\tau \tag{27}$$

and

$$\rho C_{vx} = (\partial u/\partial T)_{\rho x}. \tag{28}$$

3. DETERMINATION OF PARAMETERS

3.1. Pure Components

The equations presented in Sec. 2 contain a total of 27 parameters to be determined in addition to the critical indices α, β, γ, and Δ. Of these 27, 16 are to be determined from the properties of the pure components. Since ζ is equal to 0 for CO_2 (component 1) and ζ is equal to 1 for C_2H_6 (component 2) critical temperatures, densities, and pressures of the pure components provide the following six parameters:

$$1/RT_{c1} = B_c(0) = a_0 \tag{29}$$

$$1/RT_{c2} = B_c(1) = a_0 + a_1 \tag{30}$$

$$\rho_{c1} = f(0) = f_0 \tag{31}$$

$$\rho_{c2} = f(1) = f_0 + f_1 \tag{32}$$

$$p_{c1} = RT_{c1}c(0) = RT_{c1}c_0 \tag{33}$$

$$p_{c2} = RT_{c2}c(1) = RT_{c2}(c_0 + c_1) \tag{34}$$

Further analysis of equation-of-state data of the pure components could provide values for other parameters. However, in our case, we choose to make use of the results of an extensive analysis of data by Sengers and Levelt Sengers [1]. Their analysis has determined the values for a and k for each of the two pure components, and these two parameters are defined by

$$(\rho - \rho_c)/\rho = r^{\beta}k\theta \tag{35}$$

and

$$[\mu(\rho, T) - \mu(\rho_c, T)]\rho_c/p_c = r^{\Delta}a\theta(1 - \theta^2) \tag{36}$$

Their parameters a and k for component 1, here redesignated as $\bar{a}_1$ and $\bar{g}_1$, respectively, and those for component 2, $\bar{a}_2$ and $\bar{g}_2$, can be shown to be related to our $\bar{a}$, $\bar{g}$, l_1, and q_1 in the following way:

$$\bar{g} = \rho_{c1}\bar{g}_1 \tag{37}$$

$$\bar{a} = p_{c1}\bar{a}_1/RT_{c1}\rho_{c1} \tag{38}$$

$$l_1 = (T_{c2}/T_{c1})A^{1/\Delta} - 1 \tag{39}$$

and

$$q_1 = (\rho_{c2}\bar{g}_2/\rho_{c1}\bar{g}_1)A^{-1/\delta} - 1 \tag{40}$$

where

$$A = \bar{a}_2 p_{c2} T_{c1}\rho_{c1}/\bar{a}_1 p_{c1} T_{c2}\rho_{c2} \tag{41}$$

and the subscripts 1 and 2 refer to components 1 and 2, respectively, as before.

The analysis of Sengers and Levelt Sengers [1] also provided us with the values for the critical indices α, β, γ, and Δ. Their values differ slightly from those of the universal Ising values. However, these "apparent" exponent values are adopted because, in simple fluids, the truly asymptotic scaled form of the equation of state with Ising exponents is valid only in a very small temperature range close to a critical point [8]. The use of the apparent values extends the temperature range in which the scaled equation of state is valid.

Vapor pressure data of carbon dioxide [9–11] and ethane [10–12] can now be used, in conjunction with the 10 parameters already determined, to obtain d_0, d_1, e_0, and e_1 through the use of the vapor pressure equation:

$$p_\sigma(\zeta) = RT\left[c(\zeta) + d(\zeta) + e(\zeta)\tau^2 + q(\zeta)r^{2-\alpha}\bar{p}(1)\right] \tag{42}$$

where

$$r = RT_{c1}l(\zeta)\tau/(1 - \bar{b}^2) \tag{43}$$

Keep in mind that θ is equal to $+1$ or -1 along the coexistence curve and Eq. (42) is to be evaluated for $\zeta = 0$ for carbon dioxide and $\zeta = 1$ for ethane only. An excellent agreement between the data and Eq. (42) can be obtained, as shown in Fig. 1, by properly adjusting the values of the parameters.

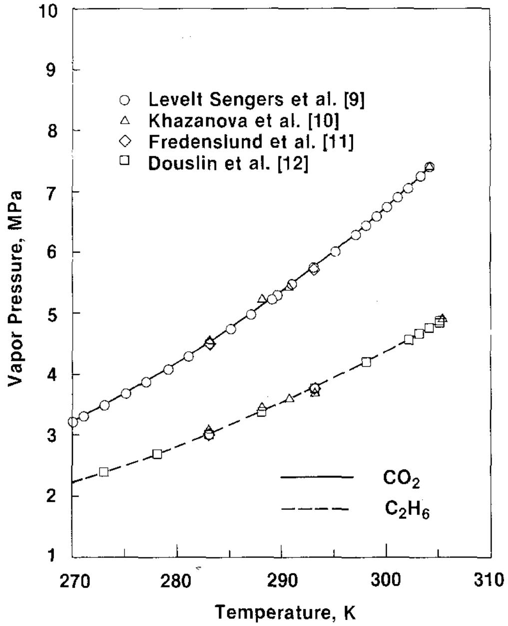

Fig. 1. Comparison between vapor pressure data of CO_2 and C_2H_6 and Eq. (42) evaluated for $\zeta = 0$ for CO_2 and $\zeta = 1$ for C_2H_6. The data are used to determine the values of d_0, d_1, e_0, and e_1.

Next, data for the heat capacities at constant volume of CO_2 [13] and C_2H_6 [14] along the critical isochore are used to determine s_0 and s_1. The equation for C_v along the critical isochore for pure fluids is

$$C_v = \left\{2\left[e(\zeta) - \rho s(\zeta)\right] + \left[\gamma(\gamma - 1)/2\alpha\bar{b}^2\right]\bar{a}\bar{g}(RT_{c1})^2 r^{-\alpha} q(\zeta) l(\zeta)^2\right\}/\rho R T^2 \tag{44}$$

where

$$r = l(\zeta)(T_{c1}/T)\left[T/T_c(\zeta) - 1\right] \tag{45}$$

Equation (44) is valid only for $\zeta = 0$ or 1, which is the case of pure fluids. The general expression for a mixtures contains additional terms with a prefactor of $\zeta(1 - \zeta)$, which vanishes when ζ is either 0 or 1. The value of s_0 is obtained by matching Eq. (44), evaluated at $\zeta = 0$ and $(T - T_c)/T_c = 5.6 \times 10^{-4}$, to the experimental data of CO_2 [13] at the same reduced temperature. Similarly, by matching Eq. (44), evaluated at $\zeta = 1$ and $(T - T_c)/T_c = 3.2 \times 10^{-4}$, to the experimental data of C_2H_6 [14], we obtain

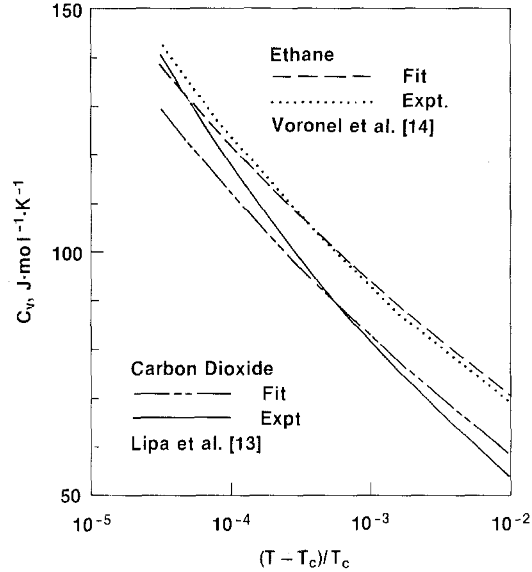

Fig. 2. Comparison between C_v data of CO_2 and C_2H_6 and Eq. (44) evaluated for $\zeta = 0$ for CO_2 and $\zeta = 1$ for C_2H_6. The data are used to determine the values of s_0 and s_1.

s_1. The comparison between the data and Eq. (44) so adjusted is shown in Fig. 2.

The last two parameters, C_1 and C_2, which may be determined from pure component properties, require critical entropy data or their equivalent. Being unaware of such data in the literature we must defer the determination of these two parameters. Fortunately, they are not needed in predicting many of the thermophysical properties of mixtures.

3.2. Mixtures

The remaining nine parameters must be determined from mixture data. The most useful are the critical line data which consist of critical temperatures, $T_c(x)$, critical pressures, $p_c(x)$, and critical densities, $\rho_c(x)$, as a function of composition, x which is the mole fraction of CO_2 in the mixture. Along the critical line we have $\tau = 0$, $h = 0$, and $r = 0$, and every quantity becomes a function of ζ only:

$$T_c(x) = 1/RB_c(\zeta) \tag{46}$$

$$p_c(x) = RT_c(x)c(\zeta) = c(\zeta)/B_c(\zeta) \tag{47}$$

$$\rho_c(x) = f(\zeta) \tag{48}$$

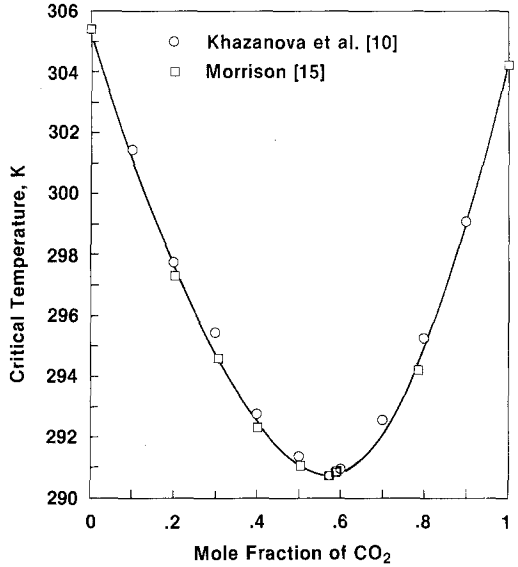

Fig. 3. Comparison between $T_c(x)$ data and Eqs. (46) and (49). The data, in conjunction with those for p_c and ρ_c, are used to determine the values of a_2, a_3, b_1, b_2, c_2, f_2, and g_1.

and

$$x = 1 - \zeta - \zeta(1 - \zeta)[Q_{c1}/f(\zeta) - Q_{c2}] \tag{49}$$

where

$$Q_{c1} = c_\zeta + B_\zeta d(\zeta) \tag{50}$$

and

$$Q_{c2} = b_\zeta + B_\zeta g(\zeta) \tag{51}$$

Through the use of Eqs. (46)–(51), and the experimental data of the critical line [10, 15], one determines simultaneously the seven parameters, a_2, a_3, b_2, c_2, f_2, and g_1. Although $T_c(x)$, $p_c(x)$, and $\rho_c(x)$ are affected by all of these seven parameters, their sensitivities to each of the parameters are different. For instance, the critical temperatures are sensitive to the values of a_2 and a_3, the critical pressures are sensitive to c_2, and the critical densities are sensitive to f_2. The conversion from ζ to x along the critical line involves all seven parameters, but the values of b_1, b_2, and g_1 affect mainly the small-x region. Therefore, by the method of successive iteration, one can arrive at a set of values for the seven parameters which yield a

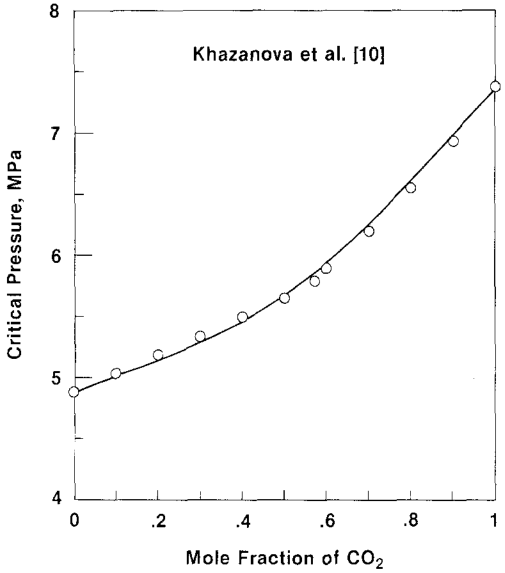

Fig. 4. Comparison between $p_c(x)$ data and Eqs. (47) and (49).

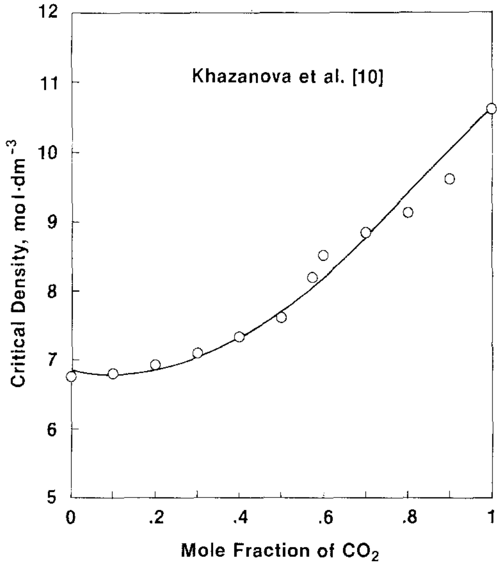

Fig. 5. Comparison between $\rho_c(x)$ data and Eqs. (48) and (49).

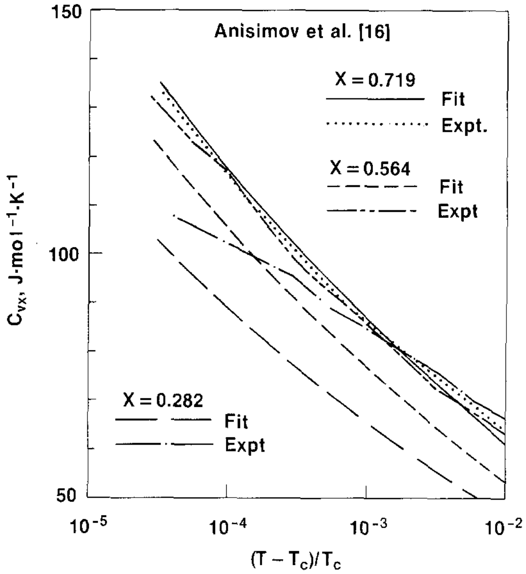

Fig. 6. Comparison between C_{vx} data of $x = 0.282$, 0.564, and 0.719 and the predictions. The predictions for C_{vx} are obtained from Eq. (2.27) of ref [2]. The data of $x = 0.719$ are used to determine the values of q_2 and s_2.

good agreement between the experimental data and Eqs. (46)–(48), as shown in Figs. 3, 4, and 5 for $T_c(x)$, $p_c(x)$, and $\rho_c(x)$, respectively. It should be mentioned that when data are fitted to the equations, the best fit is determined by visual inspection of the fit on a graphic display.

The remaining two parameters, q_2 and s_2, must be determined from some mixture data, and we have found that the heat capacities are most useful for this purpose. The equation for C_{vx} is rather complicated for mixtures, and we refer readers to ref. [2] for details. By adjusting q_2 and s_2 we can obtain a good agreement between the equation and the experimental data [16] for $x = 0.719$ as a function of $(T - T_c)/T_c$, and the comparison is shown in Fig. 6. The experimental data are represented by a dotted line whereas the predictions are represented by a solid line.

4. DISCUSSION

We have determined the values of 27 parameters from data of the pure components and the mixtures. The values of the critical exponents in the equations were taken from the literature and are listed in Table I, along with the values of the parameters. With these parameters one can use the equation of state to predict quantitatively many thermophysical properties

Table I. Constants in the Equation of State for Mixtures of CO_2 and C_2H_6

Constant	Value	Constant	Value
a_0	$3.9547 \times 10^{-4}\ \text{mol} \cdot \text{J}^{-1}$	g_1	$4000\ \text{J} \cdot \text{mol}^{-1}$
a_1	$-1.5581 \times 10^{-6}\ \text{mol} \cdot \text{J}^{-1}$	l_1	-0.0183
a_2	$1.12 \times 10^{-4}\ \text{mol} \cdot \text{J}^{-1}$	q_1	-0.358
a_3	$-8.5 \times 10^{-5}\ \text{mol} \cdot \text{J}^{-1}$	q_2	-0.8
b_1	-0.3	s_0	$-2.977 \times 10^{7}\ \text{J}^2 \cdot \text{mol}^{-2}$
b_2	-0.15	s_1	$-6.428 \times 10^{6}\ \text{J}^2 \cdot \text{mol}^{-2}$
c_0	$2.9167 \times 10^{3}\ \text{mol} \cdot \text{m}^{-3}$	s_2	$-3.6 \times 10^{7}\ \text{J}^2 \cdot \text{mol}^{-2}$
c_1	$-9.976 \times 10^{2}\ \text{mol} \cdot \text{m}^{-3}$	$\bar{a}$	5.844
c_2	$-550\ \text{mol} \cdot \text{m}^{-3}$	$\bar{g}$	$15265\ \text{mol} \cdot \text{m}^{-3}$
d_0	$4.3 \times 10^{7}\ \text{J} \cdot \text{m}^{-3}$	α	0.1
d_1	$-1.7 \times 10^{7}\ \text{J} \cdot \text{m}^{-3}$	β	0.355
e_0	$-4.4 \times 10^{11}\ \text{J}^2 \cdot \text{mol}^{-1} \cdot \text{m}^{-3}$	γ	1.19
e_1	$1.55 \times 10^{11}\ \text{J}^2 \cdot \text{mol}^{-1} \cdot \text{m}^{-3}$	δ	4.352
f_0	$10630\ \text{mol} \cdot \text{m}^{-3}$	Δ	1.545
f_1	$-3763\ \text{mol} \cdot \text{m}^{-3}$	R	$8.31441\ \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
f_2	$-5200\ \text{mol} \cdot \text{m}^{-3}$	T_{c1}	$304.127\ \text{K}$

of the mixtures near the critical line. For instance, the composition of the mixture with the minimum T_c can be obtained by solving

$$B_\zeta(\zeta_m) = 0 \tag{52}$$

for ζ_m and then evaluating Eq. (25) for $h = 0$ and $\tau = 0$. The composition thus obtained is $x = 0.570$, which is close to the reported experimental value [16] of 0.564. The composition of the critical azeotrope is obtained by solving

$$\omega_\zeta(\zeta_a) - B_\zeta(\zeta_a)\omega_\tau(\zeta_a) = 0 \tag{53}$$

for ζ_a and then also evaluating Eq. (25) for $h = 0$ and $\tau = 0$. The composition thus obtained is $x = 0.709$, which is also very close to the reported experimental value [16] of 0.719.

Experimental data for C_{vx} are also available [16] for $x = 0.282$ and $x = 0.564$, and they are represented in Fig. 6 by a dash-dotted line and a long-short-short-dashed line, respectively. The predictions of the equation are represented in Fig. 6 by a long-dashed line and a short-dashed line, respectively, for $x = 0.282$ and $x = 0.564$. The lack of smoothness of the lines representing experimental data reflects the scatter of data points. From Fig. 6 one sees that the agreement between the data and the predictions is better for $x = 0.564$ than for $x = 0.282$, but the agreement for both cases improves at T gets closer to T_c.

Experimental data are also available for vapor pressure and density along the coexistence curve. The corresponding equations are given, respectively, by

$$p_\sigma = RT\left[c(\zeta) + d(\zeta)\tau + e(\zeta)\tau^2 + q(\zeta)\pi(\bar{\tau},0)\right] \tag{54}$$

and

$$\rho_\sigma = f(\zeta) + q(\zeta)\bar{g}r^\beta\theta \tag{55}$$

where $\theta = +1$ and -1, respectively, for liquid and vapor phases, and

$$r = l(\zeta)RT_{c1}\left[B_c(\zeta) - 1/RT\right]/(1 - \bar{b}^2) \tag{56}$$

The experimental data are given in terms of x, which should be evaluated from Eq. (25) accordingly for $h = 0$ and the appropriate value of θ. The comparisons between the data and the predictions are shown in Figs. 7 and 8.

In this comparison, we must mention two aspects or conditions of the Schofield model. First, the model begins to lose its accuracy when the distance parameter $r \simeq 0.1$ or greater. When translated into temperature

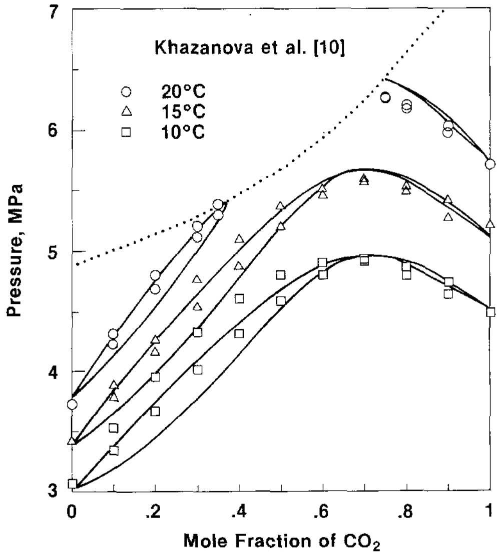

Fig. 7. Comparison between p_σ data and Eq. (54). The dotted line is the critical line.

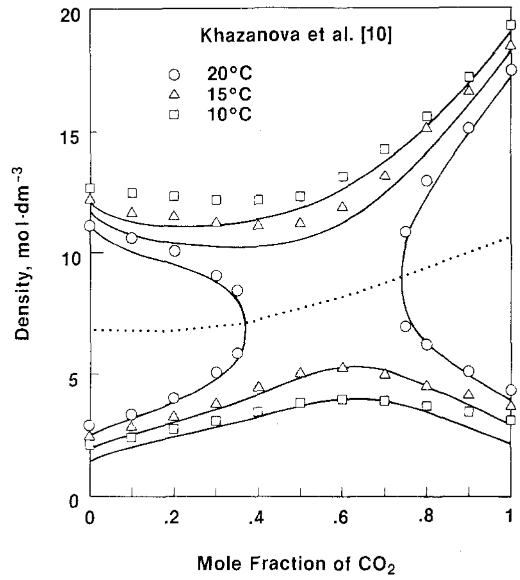

Fig. 8. Comparison between ρ_σ data and Eq. (55). The dotted line is the critical line.

range along the coexistence curve, it is equivalent to $T_c - T \simeq 10$ K and greater. Second, the model assumes that the coexisting densities are symmetric with respect to the critical density for the pure components. Whereas the first condition restricts the range of temperature in which the equation is applicable, the second is believed to be the major cause of discrepancy between the data and the predictions because CO_2 and C_2H_6 do not have a symmetric coexistence curve. Examination of Figs. 7 and 8 reveals that the agreement between the data and the predictions is indeed better for the data at 20°C than at other temperatures, but the agreement at 10°C is still very good with only about 10% discrepancy.

One of the major differences between the equation proposed by Moldover et al. [4, 5] and ours is that a skewness of the coexistence curves is incorporated in their equation. But the introduction of the skewness is expected to make their equation less suitable than ours to describe the one-phase region.

5. CONCLUSIONS

A total of 27 parameters in the equations have been determined. Of these 27, sixteen are determined from experimental data of pure components, and nine are from those of mixtures. The procedure to determine the values of the parameters from pure component data is straightforward, whereas the procedure to determine those pertaining to the mixture properties is not. In the latter case simultaneous determination of several parameters is required, and some of the parameters are strongly correlated, which can lead to a rather ambiguous determination of their values, especially when the precision of the experimental data is poor. Although the available data for the mixture are in general limited and are not of high accuracy, they are sufficient for the purpose of providing a useful equation of state of the mixture. For instance, the equation of state has been used to calculate density and concentration gradients [17] induced by gravity in the mixtures near a gas-liquid critical point.

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