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Critical Parameters of Mixtures of Carbon Dioxide and Ethane

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This paper deals with an evaluation of the critical parameters reported for mixtures of carbon dioxide and ethane. Equations are presented for the critical parameters as a function of the concentration.

KEY WORDS: carbon dioxide; critical parameters; critical phenomena; ethane; plait point.

1. INTRODUCTION

During the past decades much progress has been made in the development of a theoretically based quantitative description of the behavior of the thermodynamic and transport properties of one-component fluids in the vicinity of the vapor–liquid critical point as reviewed elsewhere [1–3]. Moreover, in recent years the theory has been extended to deal with the nonasymptotic critical behavior of these properties including the crossover from singular behavior asymptotically close to the critical point to regular behavior far away from the critical point [4–9].

It is of considerable interest to extend the theory to fluid mixtures [6, 10–14]. In our opinion a suitable system to be considered for this purpose is the carbon dioxide + ethane system. A comprehensive set of experimental pressure data for this system has recently been obtained by Weber [15], specific-heat data have earlier been reported by Shmakov [16], and the thermal conductivity has been measured in our laboratory [13, 17, 18]. For a theoretical interpretation of these data we need the

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critical parameters as a function of the concentration. For this purpose we have made an assessment of the experimental information for the critical parameters of mixtures of carbon dioxide and ethane.

2. CRITICAL PARAMETERS FOR THE PURE FLUIDS

Values reported for the critical temperature T_c of carbon dioxide and of ethane are listed in Table I. The temperatures in this paper refer to the International Practical Temperature Scale of 1968 (IPTS-68). It can be seen that even for simple fluids like carbon dioxide and ethane, the literature values of T_c have a spread of 0.1 K. The early values given by Khazanova et al. [19, 20] seem to be too high, for both carbon dioxide and ethane. This cannot be explained by the presence of water as an impurity, since this would lead to an increase in T_c in carbon dioxide but a decrease in T_c in ethane as pointed out by Morrison [25]. Moreover, the temperature scale of these early measurements is not fully traceable. We have shifted these early values by -0.09 K to bring them in agreement with the value of T_c later found by Khazanova and Sominskaya for ethane [21, 22]. In addition, the values originally obtained by Morrison and Kincaid [25, 26] and by Chang et al. [27, 28] should be shifted by -0.06 K [28, 30]. With these corrections the spread in T_c values is reduced to 0.03 K as a measure of the accuracy with which these critical temperatures are currently known.

Values reported for the critical density ρ_c and the critical pressure P_c

Table I. Critical Temperatures (K) Reported for the Pure Fluids

		Carbon dioxide			Ethane		
First author	Year	Original	Shift	Final	Original	Shift	Final
Khazanova [19]	1966	304.19	−0.09	304.10	305.43	−0.09	305.34
Khazanova [20]	1967	304.21	−0.09	304.12	305.42	−0.09	305.33
Khazanova [21]	1968	304.20	−0.09	304.11	305.33	—	305.33
Khazanova [22]	1971	—	—	—	305.34	—	305.34
Shmakov [16]	1973	—	—	—	305.363	—	305.36
Douslin [23]	1973	—	—	—	305.33	—	305.33
Moldover [24]	1974	304.127	—	304.127	—	—	—
Morrison [25]	1981	304.202	−0.06	304.14	305.379	−0.06	305.32
Morrison [26]	1984	304.206	−0.06	304.15	305.393	−0.06	305.33
Chang [27, 28]	1986	304.178	−0.06	304.12	305.382	−0.06	305.32
Albright [29]	1987	304.107	—	304.11	—	—	—
Morrison [30]	1989	304.132	—	304.13	305.357	—	305.36

Table II. Values Reported for the Critical Densities (mol · L^{-1}) for the Pure Fluids

		Carbon dioxide			Ethane		
First author	Year	Original	Shift	Final	Original	Shift	Final
Khazanova [19]	1966	10.62	+0.01	10.63	6.757	+0.113	6.87
Khazanova [21]	1968	10.62	+0.01	10.63	6.766	+0.104	6.87
Khazanova [22]	1971	—	—	—	6.780	+0.090	6.87
Shmakov [16]	1973	—	—	—	6.817	—	6.817
Douslin [23]	1973	—	—	—	6.870	—	6.870
Moldover [24]	1974	10.63	—	10.63	—	—	—
Morrison [26]	1984	10.642	—	10.642	6.862	—	6.862
Allbright [29]	1987	10.627	—	10.627	—	—	—

of carbon dioxide and ethane are shown in Tables II and III. The values reported by Khazanova and co-workers [19, 21, 22] for ρ_c appear to be smaller, especially for ethane, than the values found later by other investigators [16, 23, 24, 26, 29]. We have adjusted the values of Khazanova et al. to confirm to the later determinations for reasons to be discussed in the subsequent section. The various values reported for P_c agree within 0.01 MPa.

To obtain internally consistent critical parameters, we have decided for each fluid to select a set of values deduced from a single experiment. The experiment of Moldover was especially designed to determine the critical temperature and density directly. For carbon dioxide we have therefore adopted the critical parameters reported by Moldover [24]. For ethane we have adopted the set of critical parameters determined by Douslin and Harrison [23]. These values of the critical parameters $T_c^{(i)}$, $\rho_c^{(i)}$, and $P_c^{(i)}$, with $i = 1$ referring to carbon dioxide and $i = 2$ referring to ethane, are given in Table IV. They will form the pure-component reference values for the representation of the critical line of the mixtures.

Table III. Critical Pressures (MPa) Reported for the Pure Fluids

First author	Year	Carbon dioxide	Ethane
Khazanova [19]	1966	7.39	4.88
Khazanova [21]	1968	7.38	4.88
Khazanova [22]	1971	—	4.88
Douslin [23]	1973	—	4.8718
Moldover [24]	1974	7.3753	—
Morrison [26]	1984	7.384	4.878

Table IV. Critical-Line Parameters for $CO_2 + C_2H_6$

Equation (1) for T_c (K), $\sigma = 0.18$ K
$T_c^{(1)} = 304.127$, $T_c^{(2)} = 305.330$
$T_1 = -54.6413$, $T_2 = -52.6117$, $T_3 = +150.0669$, $T_4 = -88.0684$

Equation (2) for ρ_c(mol · L^{-1}), $\sigma = 1.8\%$
$\rho_c^{(1)} = 10.63$, $\rho_c^{(2)} = 6.870$, $\rho_1 = -2.5445$, $\rho_2 = -1.8498$

Equation (3) for P_c (MPa), $\sigma = 0.36\%$
$P_c^{(1)} = 7.3753$, $P_c^{(2)} = 4.8718$, $P_1 = -2.4904$, $P_2 = +1.4978$

Equation (4) for P_c/RT_c(MPa · mol · kJ^{-1}), $\sigma = 0.35\%$
$P_c^{(1)}/RT_c^{(1)} = 2.9167$, $P_c^{(2)}/RT_c^{(2)} = 1.9191$, $\hat{P}_1 = -0.39010$, $\hat{P}_2 = +0.23961$

3. CRITICAL PARAMETERS FOR THE MIXTURES

To represent the dependence of the critical parameters of the mixtures on the concentration x, we adopt analytic interpolation equations of the form

$$T_c(x) = T_c^{(1)}(1-x) + T_c^{(2)}x + (T_1 x + T_2 x^2 + T_3 x^3 + T_4 x^4)(1-x) \quad (1)$$

$$\rho_c(x) = \rho_c^{(1)}(1-x) + \rho_c^{(2)}x + (\rho_1 x + \rho_2 x^2)(1-x) \quad (2)$$

$$P_c(x) = P_c^{(1)}(1-x) + P_c^{(2)}x + (P_1 x + P_2 x^2)(1-x) \quad (3)$$

where x denotes the mole fraction of ethane. The coefficients T_j, ρ_j, and P_j have been determined by fitting Eqs. (1)–(3) to experimental data obtained by Khazanova et al. [19, 31] for T_c, ρ_c, and P_c, by Shmakov [16] for T_c and ρ_c, by Ohgaki and Katayama [32] for T_c and P_c, by Morrison and Kincaid [26] for T_c, ρ_c, and P_c, and by Chang et al. [27, 28] and Morrison [30] for T_c. For the reasons discussed in the preceding section the values obtained for T_c by Khazanova et al. [19, 31] were shifted by −0.09 K and the values obtained for T_c by Morrison and Kincaid [26] and Chang et al. [27, 28] were shifted by −0.06 K at all concentrations. We also wanted to retain the information for the critical densities of the mixture provided by the work of Khazanova et al. [19, 31] but faced the problem that they do not agree with the critical density values adopted for the pure fluids. We therefore increased these values by 0.13% at $x = 0$ (pure carbon dioxide) and by 1.68% at $x = 1$ (pure ethane), while for the intermediate values of x the percentage increase in the critical density was taken to be linear in x. The values obtained for the coefficients in Eqs. (1)–(3) are presented in Table IV, together with the standard deviations, σ, of the fits.

A plot of the critical temperature as a function of x is presented in Fig. 1. The experimental data are shown with the adjustments discussed

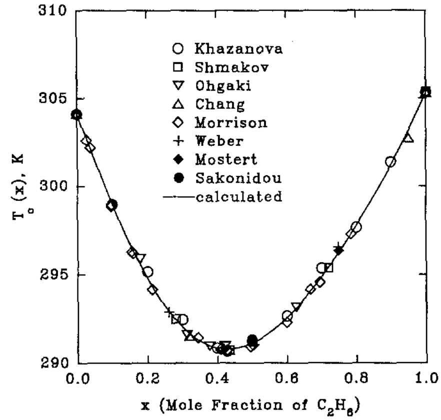

Fig. 1. The critical temperature as a function of the concentration. The curve represents the values calculated from Eq. (1).

above. We have also omitted a value $T_c = 292.04$ K at $x = 0.263$ [32]. The critical temperature goes through a minimum $T_{min} = 290.80$ K at $x = 0.43$ [19, 30, 31, 33–35]. In addition, the $CO_2 + C_2H_6$ system has a critical azeotrope at about $x = 0.28$ [34–38]. The differences between the measured and the calculated critical temperatures are shown in Fig. 2. It is seen that the critical temperatures reported by Khazanova et al. [19, 31] have a tendency to be larger than those found by most other investigators in spite of the applied shift of -0.09 K. Equation (1) represents the 48 measured values with a standard deviation of 0.18 K. If the term with coefficient T_4 in Eq. (1) is omitted, the standard deviation increases to 0.22 K.

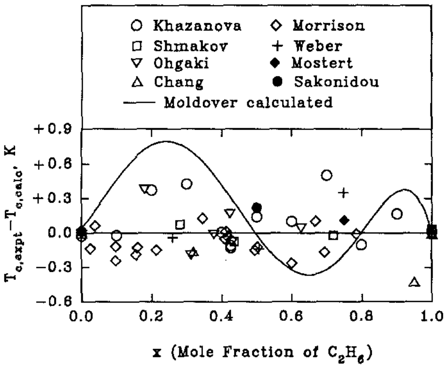

Fig. 2. A comparison between the measured and the calculated values for the critical temperature as a function of the concentration.

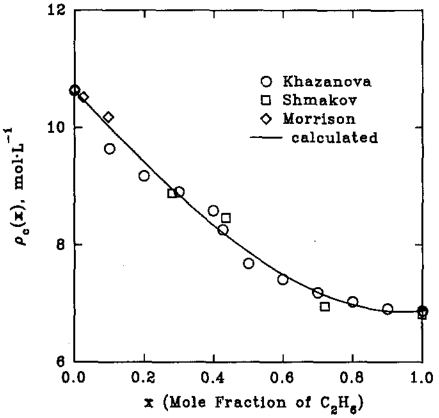

Fig. 3. The critical density as a function of the concentration. The curve represents the values calculated from Eq. (2).

Plots of the critical density and of the critical pressure as a function of x are presented in Figs. 3 and 4. Equation (2) represents the measured critical densities with a standard deviation of 1.8% and Eq. (3) represents the measured critical pressures with a standard deviation of 0.36%. Khazanova and Lesnevskaya [33] have suggested that the critical density exhibits a cusp-like behavior at $x = 0.43$, corresponding to the minimum critical temperature, causing the positive deviations from the smoothed curve in Fig. 3 at this concentration. A similar behavior has been observed by Hajjar et al.

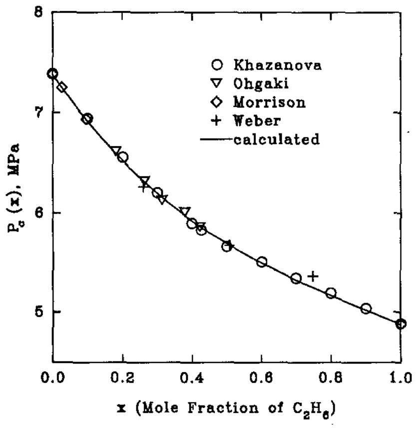

Fig. 4. The critical pressure as a function of the concentration. The curve represents the values calculated from Eq. (3).

[39] for the binary mixture of acetone and *n*-pentane. However, Genco and co-workers [40] have investigated several binary systems with a minimum temperature point on the critical locus and exhibiting azeotropy, but they did not observe any abnormal behavior. Following Moldover and Gallagher [35] we have not incorporated any anomalous behavior of ρ_c at $x = 0.43$ in our representative equation.

In the theory of critical phenomena in fluid mixtures, one often prefers to use as the independent thermodynamic field $\hat{P} = P/RT$, where $R = 8.3144\ \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$ is the molar gas constant, rather than the pressure P itself [12, 41–43]. We therefore also present an equation for $\hat{P}_c = P_c/RT_c$ of the form

$$\frac{P_c(x)}{RT_c(x)} = \frac{P_c^{(2)}}{RT_c^{(2)}}\,x + \left[\frac{P_c^{(1)}}{RT_c^{(1)}} + \hat{P}_1 x + \hat{P}_2 x^2\right](1-x) \qquad (4)$$

with coefficients $\hat{P}_1$ and $\hat{P}_2$ included in Table IV. The critical compressibility factor $Z_c = P_c/\rho_c RT_c$ as a function of x is shown in Fig. 5. The curve represents the values calculated from Eqs. (1)–(3). In this figure we show also the data points from the two authors [19, 26] who give simultaneously values for all three critical parameters.

From Fig. 2 we conclude that there still exists a considerable uncertainty in the values of the critical temperatures for the mixtures. For this reason an attempt has been made to determine the critical temperature of two such mixtures in our laboratory. The critical temperature was identified as the temperature at which by visual observation the continuous interference lines produced by a Twyman–Green interferometer would break up and a meniscus would appear at the center of the pattern [44]. The value $T_c = 296.36$ K thus found by Mostert [17] at $x = 0.75$ is 0.11 K higher than the T_c calculated from Eq. (1). The value $T_c = 291.34$ K thus

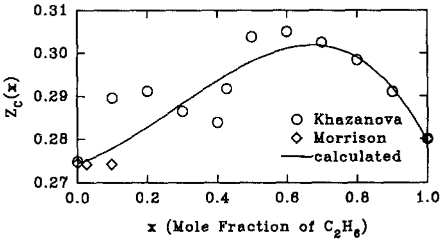

Fig. 5. The critical compressibility factor $Z_c = P_c/\rho_c RT_c$ as a function of the concentration. The curve represents the values calculated from Eqs. (1)–(3).

found by two of us [45] at $x = 0.50$ is 0.22 K higher than the T_c calculated from Eq. (1).

From his experimental $P-\rho-T-x$ data, Weber has deduced very recently values for T_c and P_c at $x = 0.260$, $x = 0.508$, and $x = 0.748$ [15]. For $x = 0.260$ and $x = 0.508$ his results are in agreement with the values implied by our correlating equations, Eqs. (1) and (3), but for $x = 0.748$ he deduces $T_c = 296.55$ K, which exceeds the value implied by Eq. (1) even by 0.35 K, albeit that Weber does not claim an accuracy better than 0.2 K. A related problem is that the value $P_c = 5.357$ MPa found by Weber at this concentration is substantially higher than the critical pressure reported by Khazanova et al. [19, 31]. These additional critical-temperature and pressure values are included in Figs. 1, 2, and 4. We must conclude that the critical temperatures of the mixtures are not known with an absolute accuracy much better than 0.3 K and additional experimental information for the critical parameters is desirable.

Equations for the critical parameters of some binary mixtures including carbon dioxide and ethane have been presented earlier by Moldover and Gallagher [35]. The differences between the values of T_c calculated from their equation (after correcting the sign of the coefficient T_2 [46]) and the values implied by our equation are represented by the solid curve in Fig. 2; the deviations up to +0.8 K appear to be outside the accuracy of the experimental critical temperatures. It should be noted that Moldover and Gallagher did not obtain their equations for $T_c(x)$ and $\rho_c(x)$ from a direct fit to experimental critical-parameter values, but deduced the critical locus from a fit of a theoretical model, based on the principle of critical-point universality, to $\rho-T-x$ data in the coexisting vapor and liquid phases. The theory predicts that the thermodynamic behavior of a mixture near the vapor–liquid critical line should be isomorphic with that of a one-component fluid near the critical point, if a field variable ζ, related to the chemical potentials of the two components, is kept constant [47–49]. In the practical implementation of this principle, one often tries to choose the field variable ζ in such a way that it reduces to the concentration x on the critical line [10–12, 35, 49, 50]. However, this is an approximation, since one does not have the thermodynamic freedom to impose such a critical-line condition [51, 52]. As a consequence, this approximation may cause a distortion of the critical line as suggested by the deviations shown in Fig. 2. The critical densities deduced by Moldover and Gallagher [35] deviate from our equation from −1.5 to +3.5% and the critical pressures from −0.15 to +0.2%; these deviations are compatible with the standard deviations of our fits.

The critical temperatures calculated from Eq. (1) refer to IPTS-68. If one wants to convert these temperatures to the new International

Temperature Scale of 1990 (ITS-90), one needs to apply a correction of -0.008 K at the critical temperatures of the pure fluids up to a correction of -0.004 K at the minimum critical temperature $T_c = 290.8$ K [53, 54]. These corrections are well within the accuracy with which the critical temperatures are known.

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