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A Note on the Critical Locus of Mixtures of Carbon Dioxide and Ethane

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Abstract This note presents an update of an evaluation of the critical parameters of mixtures of carbon dioxide and ethane, previously reported by Abbaci et al. (Int. J. Thermophys. **13**, 1043 (1993)).

Keywords Carbon dioxide · Critical azeotropy · Critical parameters · Ethane · Vapor–liquid equilibrium

1 Introduction

There exists considerable interest in the thermodynamic properties of supercritical fluid mixtures [1–4]. Furthermore, the theory of critical phenomena has progressed so that it has become possible to formulate scaled equations of state for the thermodynamic properties of mixtures in a broad region of thermodynamic states around the critical locus [5–11]. One interesting mixture is that of carbon dioxide and ethane, since this mixture exhibits critical azeotropy [5]. However, in formulating such scaled equations of state, one needs reliable information for the critical temperature T_c, the critical density ρ_c, and the critical pressure p_c, as a function of the concentration x. For this purpose, Abbaci et al. [12] made an evaluation of the available experimental data for the critical parameters of mixtures of carbon dioxide and ethane, and proposed recommended equations for the critical parameters as a function of concentration. These equations for the critical parameters were adopted by Jin et al. [7], in an attempt

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to formulate a scaled equation of state on the basis of an extensive set of experimental p-ρ-T-x data reported by Weber [13], for mixtures of carbon dioxide and ethane. However, there remained some lingering questions about the precise location of the critical locus of these mixtures that limited the accuracy obtained for the equation of state in the immediate vicinity of the critical line [7]. A part of the problem was that Weber had not been able to determine values for the critical density from his experimental data. In formulating an alternative scaled equation of state for the mixtures on the basis of the experimental data of Weber, Kiselev and Kulikov [14] adopted equations with as many as five adjustable coefficients for each of the critical parameters.

We therefore decided to revisit the issue of fitting a scaled equation of state to the experimental p-ρ-T-x data of Weber without imposing equations for the critical parameters a priori. To our surprise, such an analysis of Weber's data yielded values for the critical density ρ_c, that differ from the values previously reported by Khazanova et al. [15–17], upon which the equations recommended by Abbaci et al. [12] had been based. For this reason, we concluded that the equations for the critical parameters of mixtures of carbon dioxide and ethane had to be reconsidered.

2 Method of Analysis

According to the principle of isomorphism of critical phenomena, mixtures satisfy the same scaled equation of state as one-component fluids, provided that the mixtures are not studied at constant composition, but with a field variable ζ kept constant [18]. In practice, this "hidden" field variable ζ is related to the chemical potentials μ_1 and μ_2 of the two components, and defined in such a way that $0 \leq \zeta \leq 1$ [5,19]. In our approach, the hidden field ζ is defined as [7]

$$\zeta = \frac{1}{1 + e^{(\mu_1 - \mu_2)/RT}}, \tag{1}$$

where R is the universal molar gas constant. For each value of ζ, the mixture has a critical temperature $T_c(\zeta)$, a critical density $\rho_c(\zeta)$, and a critical pressure $p_c(\zeta)$. It is then possible to define a Helmholtz-energy density such that, near the critical line, this free-energy density has the same singular dependence on $\Delta T = T - T_c(\zeta)$ and $\Delta\rho = \rho - \rho_c(\zeta)$ as the Helmholtz free-energy density of the pure components ($\zeta = 0$ and $\zeta = 1$) near their critical points, but with system-dependent coefficients that depend parametrically on the variable ζ [7].

In order to apply a scaled Helmholtz-energy density to a mixture, one needs to relate the field variable ζ to the concentration x of the mixture. For this purpose the field variable has customarily been chosen so as to coincide with the concentration x on the critical locus [5,20]. However, one does not have the thermodynamic freedom to impose the condition that $\zeta \equiv x$ everywhere on the critical locus, unless one introduces in the transformation, Eq. 1, a temperature-dependent coefficient [5,21,22]. Even if one would introduce such a temperature-dependent coefficient, for an azeotropic mixture, like carbon dioxide and ethane, there is an additional complication that the critical temperature is not a monotonic function of concentration [5]. For this reason, we have re-analyzed the experimental p-ρ-T-x data of Weber in terms of a scaled crossover Helmholtz-energy density without imposing the a priori condition that ζ be equal to x everywhere on the critical line. Instead we have represented $T_c(\zeta)$, $\rho_c(\zeta)$, and $p_c(\zeta)$ by polynomial functions of ζ (not x) with adjustable coefficients [23]. For the critical parameters of the pure components, we have retained the values obtained by Abbaci et al. [12] from the experimental data of Moldover [24] for carbon dioxide, and of Douslin and Harrison [25] for ethane. They agree, within the uncertainty, with values of the critical parameters subsequently proposed by Wagner and coworkers [26,27]. Our procedure has yielded a representation of the p-ρ-T-x data of Weber significantly better than the one obtained previously [7]. To fully specify all coefficients in the Helmholtz energy, one needs not only p-ρ-T-x data but also some caloric property information for the mixture. For the latter purpose, specific-heat-capacity data reported by Shmakov [28] have been used. Comparisons of the improved Helmholtz energy density with experimental p-ρ-T-x data, vapor–liquid equilibrium data, heat-capacity data, and enthalpy data have been documented in a Ph.D. dissertation [23]. Here we focus our attention on the implications of our re-analysis of Weber's data for the location of the critical locus.

3 Results of Analysis

3.1 Critical Temperature

As explained in Sect. 2, our procedure yields values for the coefficients in polynomials for the critical parameters as a function of the field variable ζ. After the values of this field variable ζ are converted to values for the mole fraction x of ethane, the results obtained for $T_c(x)$ from a fit to Weber's p-ρ-T-x data appear to be still consistent with the equation earlier recommended by Abbaci et al. [12]. This equation has the form

$$T_c(x) = (1 - x)T_c(0) + xT_c(1) + (T_1x + T_2x^2 + T_3x^3 + T_4x^4)(1 - x), \qquad (2)$$

where $T_c(0) = 304.119\,\text{K}$ and $T_c(1) = 305.322\,\text{K}$ are the critical temperatures of pure carbon dioxide and pure ethane, respectively. The values of the coefficients in Eq. 2 as determined by Abbaci et al. [12] are included in Table 1, except that we have converted the temperature scale from IPTS-68 to ITS-90. As documented by Abbaci et al., this equation represents the critical temperatures within an estimated uncertainty of 0.3 K [12].

3.2 Critical Density

Unlike the critical temperatures, the critical densities deduced from a fit to Weber's p-ρ-T-x data are qualitatively different from those recommended by Abbaci et al. [12]. Instead, within the accuracy of the analysis, ρ_c^{-1} can be represented by a linear function of x:

$$\rho_c^{-1}(x) = (1 - x)\rho_c^{-1}(0) + x\rho_c^{-1}(1), \qquad (3)$$

Table 1 Coefficients in Eqs. 2–4 for the critical parameters of $(1-x)CO_2 + xC_2H_6$

Equation 2 for T_c(K)			
$T_c(0) = 304.119$	$T_c(1) = 305.322$		
$T_1 = -54.6413$	$T_2 = -52.6117$	$T_3 = +150.0669$	$T_4 = -88.0684$
Equation 3 for ρ_c ($\mathrm{mol \cdot L^{-1}}$)			
$\rho_c(0) = 10.630$	$\rho_c(1) = 6.870$		
Equation 4 for p_c (MPa)			
$p_c(0) = 7.3753$	$p_c(1) = 4.8718$		
$p_1 = -3.4961$	$p_2 = +4.0124$	$p_3 = -1.0637$	

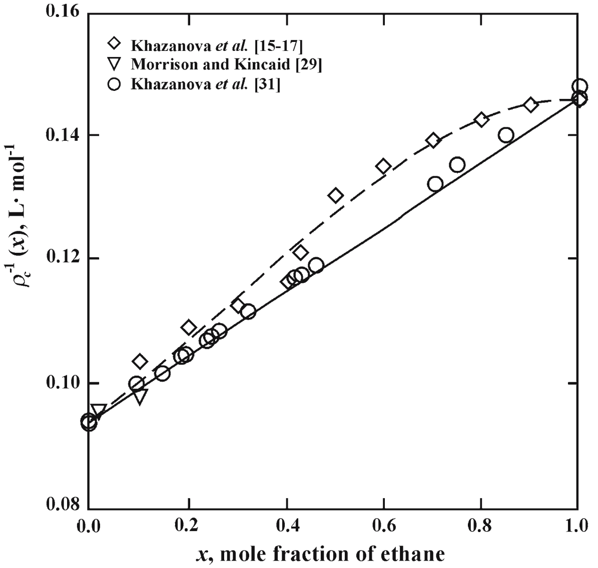

Fig. 1 Inverse critical density $\rho_c^{-1}(x)$ as a function of the mole fraction x of ethane. Dashed curve represents values previously recommended by Abbaci et al. [12], and solid line represents the linear Eq. 3 deduced from our analysis of Weber's p-ρ-T-x data [13]. Symbols indicate experimental data reported by (◇) Khazanova et al. [15–17], (▽) Morrison and Kincaid [29], and (○) Khazanova et al. [31]

where $\rho_c(0) = 10.630\,\mathrm{mol \cdot L^{-1}}$ and $\rho_c(1) = 6.870\,\mathrm{mol \cdot L^{-1}}$ are the critical densities of pure carbon dioxide and pure ethane, respectively. The available information for $\rho_c^{-1}(x)$, i.e., for the critical molar volume, as a function of the mole fraction x of ethane is shown in Fig. 1. The dashed curve represents the values previously recommended by Abbaci et al. on the basis of experimental values reported by Khazanova et al. [15–17] and Morrison and Kincaid [29]. The solid line represents the linear behavior deduced from our analysis of Weber's p-ρ-T-x data.

After we had encountered this serious discrepancy with the critical densities earlier reported by Khazanova et al. [15–17] it was brought to our attention that a book of Anisimov [30] contains a plot also showing a linear dependence of the critical molar volumes of mixtures of carbon dioxide and ethane as a function of concentration, but the data source was unclear. Faced with this mystery, we contacted O.N. Sokolova at the State Institute for Nitrogen in Moscow through the courtesy of Anisimov. After a check of the records, we were informed that Khazanova et al. had published a revised set of critical parameters for mixtures of carbon dioxide and ethane at a much later date [31]. Since this information is not easily available, we have reproduced the revised critical parameters reported by Khazanova et al. [31] in Table 2, with the values of T_c converted to ITS-90. The critical temperatures in Table 2 agree with Eq. 2 within about ±0.2 K, but, as shown in Fig. 1, the revised inverse critical density $\rho_c^{-1}(x)$ appears indeed to vary linearly with x, a behavior which is qualitatively different from the behavior reported earlier [15–17]. The small difference in the linear behavior deduced by us from Weber's p-ρ-T-x data is related to the value $\rho_c^{-1}(1) = 0.1475\ \mathrm{L{\cdot}mol^{-1}}$ for pure ethane quoted by Khazanova et al. [31], which is slightly larger than the value $\rho_c^{-1}(1) = 0.1456\ \mathrm{L{\cdot}mol^{-1}}$ for pure ethane adopted by us. However, the latter value is clearly implied by the experimental data reported by Douslin and Harrison [25,32,33]. We conclude that $\rho_c^{-1}(x)$ of mixtures of carbon dioxide and ethane can indeed be approximated by a linear function of x. We note that an anomalous behavior of the critical density, suggested by Khazanova and Lesnevskaya [17] appears to be spurious, as was previously assumed by Moldover and Gallagher [20] and Abbaci et al. [12].

Table 2 Revised critical parameters of $(1-x)CO_2 + xC_2H_6$ reported by Khazanova et al. [31]

x	T_c (K)	p_c (MPa)	ρ_c^{-1} ($\mathrm{L{\cdot}mol^{-1}}$)
0.000	304.16	7.376	0.0940
0.094	298.99	6.890	0.1000
0.147	296.62		0.1020
0.187	295.02	6.525	0.1045
0.195	294.77	6.475	0.1050
0.236	293.51		0.1070
0.246	293.19	6.287	0.1078
0.255	292.95	6.257	0.1080
0.264	292.72	6.228	0.1085
0.321	291.59	6.059	0.1115
0.417	290.71		0.1170
0.431	290.70	5.816	0.1175
0.459	290.73		0.1190
0.604	292.45	5.451	0.1265
0.705	294.83		0.1320
0.750	296.28		0.1350
0.850		5.075	0.1400
1.000	305.33	4.884	0.1475

3.3 Critical Pressure

The critical pressure deduced from Weber's p-ρ-T-x data can be represented by an equation of the form,

$$p_c(x) = (1-x)p_c(0) + xp_c(1) + (p_1x + p_2x^2 + p_3x^3)(1-x), \tag{4}$$

where $p_c(0) = 7.3753\,\text{MPa}$ and $p_c(1) = 4.8718\,\text{MPa}$ are the critical pressures of pure carbon dioxide and pure ethane, respectively. The values of the coefficients in Eq. 4 are included in Table 1. Abbaci et al. [12] have noted a discrepancy between the critical pressures reported by Khazanova et al. [15–17] and Weber [13], of about 0.1 MPa, at the higher ethane concentration of about $x = 0.75$. Unfortunately, with the new values of Khazanova et al. for the critical pressure in Table 2, the discrepancy still persists. Equation 4 accommodates the (higher) critical pressure reported by Weber for $x = 0.75$, while the equation previously recommended by Abbaci et al. [12] agrees with the values of Khazanova et al. for $x = 0.75$. Subsequently, Goodwin and Moldover [34] have determined phase boundaries in the vicinity of the critical locus that appear to be consistent with Weber's p-ρ-T-x data within their combined experimental accuracy which give us some additional confidence in the critical pressures found by Weber [13]. However, additional experimental information to discriminate between Eq. 4 and the equation recommended by Abbaci et al. for $p_c(x)$ would be desirable.

4 Summary

Equation 2, previously recommended by Abbacci et al. [12] and here converted to ITS-90, still yields a satisfactory representation of the critical temperature within the spread of 0.2 K of the experimental data. The equation for the critical density previously recommended needs to be replaced by the linear relation, Eq. 3, for the molar volume. The equation previously recommended by Abbaci et al. [12] for the critical pressure continues to represent also the newer experimental data of Khazanova et al. [31], while Eq. 4 represents the experimental data of Weber [13] for the critical pressure.

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