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CRITICAL CURVES IN MIXTURES OF CARBON DIOXIDE WITH ETHANE AND ETHYLENE BASED ON A GENERALIZED FLUCTUATION FORM OF THE VAN DER WAALS EQUATION OF STATE

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Critical curves of CO_2–C_2H_4 and CO_2–C_2H_4 mixtures are investigated using a new fluctuation equation of state. Particular attention is paid to the behavior of thermodynamic sensitives in the vicinity of the critical azeotropic points, at which the derivative of the molar volume with respect to the composition, which has no special features in the vicinity of the critical points of the pure components, becomes zero. Reliable agreement between the results of describing the critical curves of the mixtures and the known (including volumetric measurements) experiment is obtained. Possible intensification of supercritical extraction in using the CO_2–C_2H_6 mixture in the vicinity of the azeotropic point is predicted.

Data on the critical curve (CrC) and the behavior of mixtures in the critical region are urgently required when the prospects for employing a system as the working medium of thermal or refrigeration cycles are evaluated. Mixtures one of whose components is carbon dioxide (CO_2) as well as ethane (C_2H_6) and ethylene (C_2H_4) are of significant interest for the processes of extraction and supercritical fluid chromatography that are widely used in the modern food and pharmaceutical industries. The importance of data on the $P_{cr}(T)$-dependence of a CrC is that the latter divides a phase diagram into two parts: the part of total miscibility of the components with any compositions and the part of heterogeneous equilibria where division processes are realized. An advantage of the above substances is critical temperatures comparable with room temperature and relatively low (except for CO_2) critical pressures (see Table 1). We can consider the mixtures CO_2–C_2H_4 and CO_2–C_2H_6 investigated in this work interesting from the viewpoint of practical use since, in them, we observe a minimum on the $T_{cr}(x)$-dependence of the CrC and there are points of critical positive azeotropy (CPA) in accordance with [1, 2]. In the vicinity of them, not only does the mixture act as a pure substance but, according to the assumption of Rowlinson [1], it is also characterized simultaneously by mechanical and material instabilities of the states (a similar coincidence of mechanical and thermal instabilities is absent at the critical point of pure substances). In our opinion, this property can substantially improve the extraction efficiency when CO_2, C_2H_4, and C_2H_6 are replaced by their mixtures with the compositions $x \approx x_{CPA}$. The investigation performed in the work showed that we are to expect significant intensification of the process of supercritical extraction in the CO_2–C_2H_6 system in the vicinity of the parameters $x_{CPA}(CO_2) \approx 0.12$, $T \approx 297.2$ K, $P \approx 6.66$ MPa, and $v \approx 102 \cdot 10^{-6}$ m^3/mole.

It is known that classical semiempirical van der Waals equations of state (VDW-ESs) predict unrealistic values of the compressibility factor $z_{cr} = P_{cr}v_{cr}/RT_{cr}$ and the reduced slope (the Ridel parameter) of the $P_s(T)$-dependence: $A_{cr} = (T_{cr}/P_{cr})(dP/dT)_{cr}$ at the critical point of a pure substance. Similar ESs describe very approximately the liquid branch $\rho^{liq}(T)$ of the coexistence curve (CoexC) and reflect qualitatively incorrectly the behavior of thermodynamic derivatives in the critical region. In spite of the enumerated drawbacks, it is generally agreed that some most successful modifications (they include primarily the Redlich–Kwong (RK) ES and its numerous variants) are able to simultaneously provide realistic information on the coexistence surface

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TABLE 1. Critical Parameters and Coefficients Used in CrC Calculations

Substance	T_{cr}, K	P_{cr}, MPa	v_{cr}, cm^3/mole	c	b, cm^3/mole	a, N·m^4/mole	l	k
C_2H_4	282.34	5.0389	130.46	0.2532	43.487	0.2573	0.06	0.09
CO_2	304.17	7.3860	94.162	0.2667	31.387	0.1965		
C_2H_6	305.34	4.8713	145.35	0.2563	48.450	0.3087	−0.08	0

(CoexS) and the critical curve of mixtures. This viewpoint is superfluously optimistic if it is remembered that the adoption of thermodynamic conditions in the indicated regions requires sets that are different for CoexS and CrC, respectively, and are matched to the data of a specific system of coefficients of "heterogeneous interactions." Furthermore, CrC parameters are required in constructing the scaling ES of mixtures that is proposed by Leung and Griffiths [3]. This approach is based on the hypothesis of isomorphism of the behavior of mixtures and pure components in the critical region. The scaling of the latter assumes individual critical parameters z_{cr} and A_{cr} to be insignificant in the context of the hypothesis of universality. If semiempirical ESs that do not describe the indicated parameters in a pure substance were able to reliably predict the CrC parameters of a mixture this would lead to the following paradox: a scaling description of the vicinity of the CrC would be based, in this case, on the classical ES, which fails to allow for fluctuations and is considered to be an antipode of the scaling ES.

We will show below that we are able to coordinate to some extent the classical and scaling approaches within the framework of the model of fluctuation thermodynamics (FT) [4, 5]. Its essence is in consistent allowance for the fluctuations of local (field and density) variables, which leads to the dependence of the coefficients of microscopic description on thermodynamic response functions (compressibilities, heat capacities). Use is made of the fact that the method of the FT model enables us to derive, under certain assumptions, a new fluctuation ES (FES) whose coefficients are directly related both to the average relative fluctuations of the density (Δ) of state and the average virial (ω) of the system. It is proposed that the indicated FES be mapped onto a modified VDW-form that contains the fluctuation coefficients a, b, and c. The third of them enables us to use experimental data on the critical volume v_{cr} (and hence z_{cr}) along with two characteristics of the critical point (P_{cr}, T_{cr}) commonly used in determining the coefficients a and b in VDW-ESs and RK-ESs. Finding the coefficients of an FES using the critical parameters corresponds to a quasiclassical form of the approach developed. CrC parameters for two mixtures of hydrocarbons with carbon dioxide are calculated.

Fluctuation Equation of State in a Quasiclassical Form. The proposed mapping of an FES [4, 5] onto a modified VDW-form appears as

$$P = n_0 k_B T - \frac{\omega(1+\Delta^2)}{6} n_0^2 = \frac{k_B T n (1-c)}{1-bn} - an^2 , \tag{1}$$

where n ($\le n_0 = N/V$) is the characteristic fluctuation density determined by the root-mean-square fluctuation

$$\Delta = \langle (1 - n/n_0)^2 \rangle^{1/2} = (\Delta^2)^{1/2} \ge 0 . \tag{2}$$

The first equality in (1) is an FES derived with the use of the virial theorem and the assumption, of the FT model, of the presence of stationary and homogeneous density fluctuations in each equilibrium state of a system of finite volume V. We note that, in classical ESs, the density n_0 itself is considered to be stationary and homogeneous (i.e., equilibrium), whereas in a system of finite volume the experimenter measures a value that is only close to n but, strictly speaking, not equal to the average value (n_0). The fundamental difference of FES (1) from other forms of ESs lies in an accurate fluctuation determination of each of the coefficients a, b, and c:

$$1 - c = (1-\Delta)/(1+\Delta^2)^{1/2} > 0 , \tag{3}$$

$$b = \Delta/n = \Delta/[n_0 (1 + \Delta^2)^{1/2}] = 1/n - (1 - c)/n_0 \geq 0 , \tag{4}$$

$$a = \omega/6 = (V/6)\,(1 + \Delta^2)^{-1/2} \left\langle \sum_{i,j} r_{ij}\, dU_{ij}/dr_{ij} \right\rangle \geq 0 , \tag{5}$$

where the sum allows for all forms of pair interactions U_{ij} of the considered system. All determinations (1)-(5) pertain equally to pure substances and mixtures with any number of components. This agrees with the VDW concept, according to which a mixture of constant composition x is described by the same ES as the pure components. At the same time, there is a certain contradiction with the scaling ES, where, according to the proposition of Leung and Griffiths [3], x should be replaced by a certain combination of field variables (volatilities). In explicit form, the dependence on composition is found only in the coefficients of (3)-(5), where it is recognized as expedient to employ two standard corrections (k, l) to the combination rules proposed by Lorentz–Berthelot:

$$c = c_1 x_1^2 + 2c_{12} x_1 x_2 + c_2 x_2^2 , \quad c_{12} = (c_1 + c_2)/2 ; \tag{6}$$

$$b = b_1 x_1^2 + 2b_{12} x_1 x_2 + b_2 x_2^2 , \quad b_{12} = (1 - l)\,(b_1 + b_2)/2 ; \tag{7}$$

$$a = a_1 x_1^2 + 2a_{12} x_1 x_2 + a_2 x_2^2 , \quad a_{12} = (1 - k)\,(a_1 a_2)^{1/2} \tag{8}$$

and written here for a binary mixture. We note that the form of expression (6) for the coefficient c and the use of arithmetic-mean (expression (7)) and geometric-mean (expression (8)) combinations of the corresponding coefficients of the pure components are in complete agreement with the interrelationship of the FES coefficients that follows from (3)-(5).

A reliable calculation of the average values (Δ, ω) for specific systems is far from being a trivial problem, and therefore it is pertinent to evaluate the capabilities of FES (1), foremost in the critical region of pure substances. By adopting standard conditions of the critical point it is easy to express all the coefficients (a_i, b_i, c_i) in terms of the experimental values of the critical parameters $(T_{\mathrm{cr}}, v_{\mathrm{cr}}, P_{\mathrm{cr}})_i$

$$c_i = 1 - \frac{8}{3}\left(\frac{P_{\mathrm{cr}} v_{\mathrm{cr}}}{RT_{\mathrm{cr}}}\right)_i = 1 - \frac{8z_{\mathrm{cr}i}}{3} , \tag{9}$$

$$b_i = v_{\mathrm{cr}i}/3 , \tag{10}$$

$$a_i = 3\,(P_{\mathrm{cr}}\, v_{\mathrm{cr}}^2)_i , \tag{11}$$

where v_{cr} is the molar critical volume of the i-th component. Equations (10) and (11) correspond to an ordinary VDW-ES, and of greatest importance is the possibility of expressing, using (3) and (9), the maximum (critical) level of fluctuations $\Delta_{\mathrm{cr}i}$ in terms of the corresponding value of the compressibility factor $z_{\mathrm{cr}i}$.

Computational Procedure for the Critical Curve of Binary Mixtures. According to Gibbs, the critical point of a mixture is determined by the conditions

$$(\partial\mu/\partial x)_{P,T} = 0 , \tag{12}$$

$$(\partial^2\mu/\partial x^2)_{P,T} = 0 , \tag{13}$$

which can easily be rewritten (see, for example, [6]) in ES terms. A significant difference of this work from numerous variants of searching for the CrC using on classical semiempirical ESs (usually RK-ES) is the employment of a new FES (1) that is expressed in terms of the molar volume:

$$P = \frac{RT(1-c)}{v-b} - \frac{a}{v^2} \tag{14}$$

and that corresponds only formally to a certain three-constant modification of the VDW-ES. Unlike the latter, the coefficients a, b, and c are accurately defined functions (3)-(5) of the density fluctuations and the virial of the system of interacting particles, averaged over the volume. In principle, this leads to an effective dependence of the indicated coefficients on the parameters of equilibrium state that appears in them in terms of the mentioned average characteristics. In this work, use is made of a quasiclassical approximation for FES (9)-(11) that holds true in describing near-critical states of pure substances. The values of the coefficients presented in Table 1 are determined by the critical parameters of the components, and the values of the standard corrections k and l to the Lorentz–Berthelot combination rules in (7) and (8) for the usual single-liquid approximation are the only additional information required for calculating the CrC of a mixture.

The accuracy of the description of the CoexS of phases and the CrC of a mixture depends strongly on the corrections k and l, which in turn are determined by the adopted ES model. Of course it is preferable to find k and l independently of experimental thermodynamic data using microscopic information on the parameters of the effective (and model) potential for heterogeneous interactions. However it should be taken into account that the always existing inadequacy of model (micro- and macro-) representations must lead to ambiguity of parameters k and l obtained by different procedures. In our opinion, this reduces somewhat the utility of numerous attempts, initiated by the well-known work of Scott and van Konynenburg [7], at representing a comprehensive diagram of the critical and phase behavior of mixtures in terms of one selected ES and as a function of some combinations of its coefficients. Indubitable is the ability of this diagram to render qualitatively correctly all the observed (and even to predict new) types of $P_{cr}(T)$-projections of the CrC but at the same time the possibilities of using it for a quantitative description seem very limited.

Here it should be noted that the majority of researchers (see, for example, [8, 9]) seek to describe only $P_{cr}(T)$-dependences and, accordingly, $P_{cr}(x)$- and $T_{cr}(x)$-projections and ignore the volumetric $v_{cr}(x)$-behavior of the system along the CrC and in its vicinity. This approach is forced in many respects when use is made of RK-type classical ESs that do not describe the actual values of v_{cr} (and z_{cr}). At the same time, it gives no way of investigating in full measure the effect of the correction l in (7) determined precisely by critical volumetry. This problem acquires special importance in the case of gas-liquid CrCs where infinitely dilute critical phases can exist [10]. In particular, it is of interest to investigate the abnormality of the partial molar volume of the solvent $\bar{v}_1$:

$$\bar{v}_1 = v - x\,(\partial v/\partial x)_{P,T}\,, \tag{15}$$

which does not tend to the critical molar volume v_{cr1} along the CrC but experiences a finite jump when $x \to 0$. The possibility of such behavior of this derivative was substantiated thermodynamically in [11, 12] and was verified experimentally in [13, 14]. In this case, the derivative $(\partial v/\partial x)_{P,T}$ must tend to infinity [10]. Rowlinson [1] predicted the divergence of this derivative at the CPA point, too. Fluctuation equation of state (1) used in the work ensures rather simple formulas that permit the study of basic derivatives for the CrC:

$$vK_{T,x} = -\left(\frac{\partial v}{\partial P}\right)_{T,x} = \frac{v^3(v-b)^2}{RT(1-c)\,v^3 - 2a\,(v-b)^2}\,, \tag{16}$$

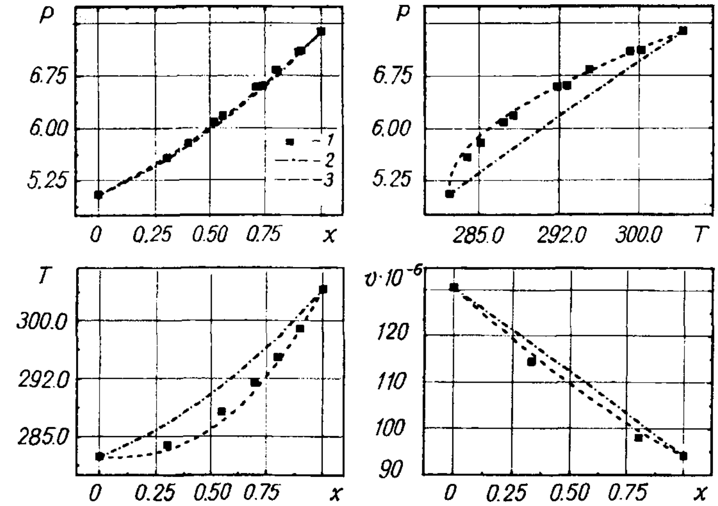

Fig. 1. Comparison of calculated and experimental data on the critical curve of a CO_2–C_2H_4 mixture: 1) experiment [15, 16]; 2) FES, $k = 0$, $l = 0$; 3) FES, $k = 0.08$, $l = 0.05$; the average relative error: $\langle \delta P \rangle = 0.32\%$ and $\langle \delta T \rangle = 0.16\%$; the maximum absolute deviation: $\Delta P_{\max} = 0.55$ MPa and $\Delta T_{\max} = 1.2$ K. P, MPa; T, K; x, mol. fraction of CO_2; v, m^3/mole.

$$v_x = \left(\frac{\partial v}{\partial x}\right)_{P,T} = \frac{RTc_x}{v-b} - \frac{RT(1-c)\,b_x}{(v-b)^2} + \frac{a_x}{v^2}, \qquad (17)$$

$$v_x/(vK_{T,x}) = (\partial P/\partial x)_{V,T}, \qquad (18)$$

where the subscript x denotes the derivative with respect to the composition; $K_{T,x} = \frac{1}{v}(\frac{\partial v}{\partial p})_{T,x}$.

Results for the Critical Curves in C_2H_4–CO_2 and CO_2–C_2H_6 Mixtures. In solving the system of equations (12) and (13), use was made of a variant of the "predictor–corrector" method developed by the authors that leads to rapid and rather reliable evaluation of corrections k and l (see Table 1) in Eqs. (7) and (8) matched to one experimental point of the CrC: P_{cr}, T_{cr}, and v_{cr} of the composition $x = 0.5$ or of a similar composition. It is obvious that the selection of the composition $x = 0.5$ is random and can be changed when this method (we hope to present it in detail in a following paper) is used. Rowlinson [1], for example, strongly recommended using data on the CPA point for evaluating the parameters of "heterogeneous interactions." Since in both mixtures the predicted compositions of the CPA point turned out to be somewhat larger than the compositions found earlier by $x(CO_2)$, preference was given to the composition $x = 0.5$. We note that in the C_2H_4–CO_2 mixture, using a rather approximate extrapolation evaluation of the experiment of Haselden et al. [15, 16], $x_{CPA}(CO_2) \approx 0.42$ was obtained [1, 17] and our result is $x_{CPA}(CO_2) \approx 0.62$; in the C_2H_6–CO_2 mixture, correspondingly, the CPA data [1, 18, 19] are $x_{CPA}(CO_2) \approx 0.71$ and our result is $x_{CPA}(CO_2) \approx 0.88$. All the critical parameters of the pure components and the mixtures shown in Table 1 and Figs. 1 and 2 are taken from [17-19]. Unfortunately, the available experimental data on the CrCs of the mixtures are scanty and not very accurate and rarely contain measurements of the volumetric behavior. With allowance for this fact, the accuracy of the description of CrC data in the work should be recognized as satisfactory. In particular, the parameters of the minima of $T_{cr}(x)$-projections are in complete agreement with the available experiment.

Of special interest are the dependences of derivatives (16) and (17) along the CrC given in Fig. 3. Whereas the behavior of the isothermal compressibility $K_{T,x}$ (16) in the vicinity of the CPA point and the critical points of the pure components indicates the divergence of this derivative in complete agreement with a

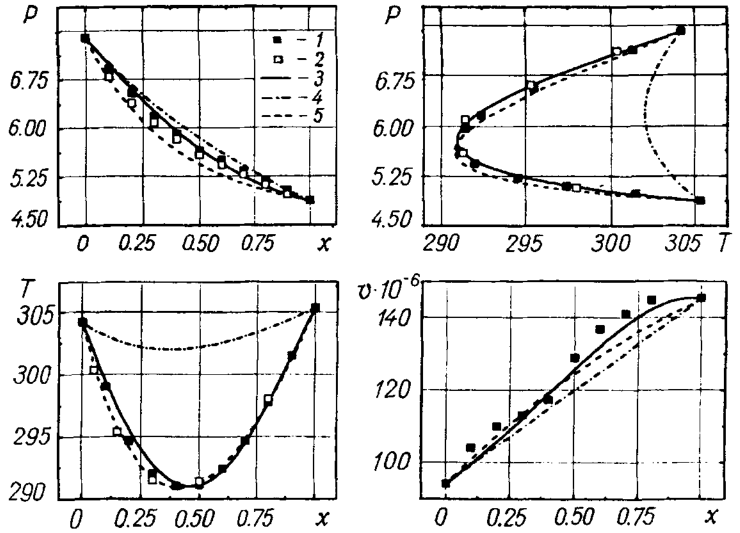

Fig. 2. Comparison of calculated and experimental data on the critical curve of a CO_2–C_2H_6 mixture: 1) experiment [20]; 2) same [21]; 3) approximation [18, 19]; 4) FES; $k = 0$, $l = 0$; 5) FES; $k = 0$, $l = -0.05$; the average relative error: $\langle \delta P \rangle = 2.3\%$, $\langle \delta T \rangle = 0.1\%$, and $\langle \delta v \rangle = 2.8\%$; the maximum absolute deviation: $\Delta P_{\max} = 0.25$ MPa, $\Delta T_{\max} = 0.97$ K, and $\Delta v_{\max} = 7.5 \cdot 10^{-6}$ m^3/mole.

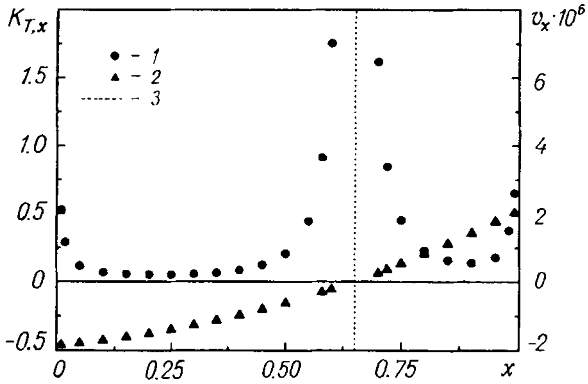

Fig. 3. Derivatives $K_{T,x}$ and v_x along the critical curve of a C_2H_4–CO_2 mixture: 1) $K_{T,x}$; 2) $(\partial v/\partial x)_{P,T}$; 3) $x_{CPA} = 0.65$. $K_{T,x}$ GPa^{-1}; $(\partial v/\partial x)_{P,T}$, m^3/mole.

thermodynamic analysis [1], data on v_x (17) confirm the available experiment [1] rather than the Rowlinson analysis [1]. We found that, at the CPA point, this derivative passes through zero (and does not diverge) and, furthermore, within the framework of FESs (1) and (11), it remains finite as the critical points of the components are approached (at least for the compositions $x = 0.05$ and 0.95). The scaling description [17-19] is based on the assumption of a weak (renormalized) divergence of the derivative $K_{T,x}$ along the CrC. This property (which is hard to check experimentally) can also be detected using FESs (1) and (14). We found that the regions of stable (binodal curve) and unstable behavior are extremely similar (within an average accuracy of ~2% for the experiment on the critical volume). We note that these facts can prove to be very useful if the parameters k and l are predicted from data on the effective potential rather than matched (as in this work) to an experiment on the critical point.

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NOTATION

$n_0 = N/V$, bulk (homogeneous) density of the number of particles N confined in volume V; n, fluctuation density of the number of particles; z_{cr}, critical compressibility factor; P_{cr}, critical pressure; T_{cr}, critical temperature; v_{cr}, critical molar volume; A_{cr}, Ridel parameter; ρ^{liq}, density of the liquid mass on the coexistence curve; k_B, Boltzmann constant; Δ, average fluctuation of the density n; ω, average virial of the system of particles; a, b, and c, fluctuation coefficients of the equation of state; $U_{ij}(r_{ij})$, effective potential of pair interactions; x, x_1, and x_2, compositions of the components of the mixture; k and l, correction factors for "heterogeneous interactions"; μ, chemical potential; $v = V/N$, molar volume of the mixture; $\bar{v}_1$, partial molar volume of the first component; $K_{T,x}$, isothermal compressibility of a mixture of constant composition; v_x, derivative of the molar volume with respect to the composition at constant P and T; P_s, pressure of the saturated vapor of a pure component.

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