Partial density and concentration of C_2H_6 in coexisting phases of the C_2H_6–CO_2 system, obtained from data on slow-neutron transmission

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A method for the study of the temperature dependence of the partial density and concentration of binary-solution components on the liquid-vapor coexistence curve is proposed and implemented. The shape of the C_2H_6–CO_2 solution coexistence curve is investigated at four medium concentrations of the components. The experimental data are compared with the predictions of the theory of isomorphism of critical phenomena.

1. INTRODUCTION

The introduction of the isomorphism hypothesis for critical phenomena[1,2] led recently to advances in the description of phase transitions in complex objects having a large number of independent variables, based on the scale-transformation theory developed for systems having an isolated critical point. According to the isomorphism hypothesis, the dependence of the thermodynamic potentials of such objects on suitably chosen isomorphous variables[4,5] should have the same functional form as for a certain "ideal" system.[1)] The isomorphism hypothesis for critical phenomena predicts also a difference between the anomalous behavior of thermodynamic potentials of a solution near the critical point from the character of the anomalies of the corresponding quantities for a single-component liquid in the case when the thermodynamic variables specified by the experimental conditions do not coincide with the isomorphous variables of the mixture. A check on the conclusions that follow from the isomorphism hypothesis calls for compatible experimental data on the heat capacity and compressibility, on the temperature and pressure dependences of the solution density, and also on the temperature dependence of the partial density and concentration of the mixture components on the liquid-vapor coexistence curve (CC) in the vicinity of the critical point. So far, however, the number of studies of the concentration of binary solutions on the liquid-vapor CC is negligible, and experimental data on the behavior of the spectral density of binary-solution components on this curve are practically nonexistent. The shortage of this experimental information is due to the difficulties involved in obtaining it by conventional methods for investigating critical phenomena, in view of the need of taking into account the gravitational effect and of producing an effective contrast to be able to observe the behavior of one component against the background of another.

Our aim was to study the singularities of the behavior of the partial density and concentration of the components in coexisting phases of a binary mixture near the liquid-vapor critical point. We propose to use for this purpose the method of slow-neutron transmission. In Sec. 2 we expound the theory of the proposed method. In Sec. 3 the investigated objects and the experimental procedure are described. The experimental results, their discussion, and comparison with the predictions of the isomorphism hypothesis for critical phenomena are given in Sec. 4.

2. THEORY OF METHOD

The anomalous increase of the compressibility of matter near the critical vapor-production point of binary solutions in a gravitational field give rise[8] to the appearance of considerable gradients in both the partial numerical density[2)] $N_1 = N_1(h, T)$, $N_2 = N_2(h, T)$, and the concentration $c_1 = c_1(h, T)$, $c_2 = c_2(h, T)$ of the binary-solution components (the gravitational effect). With allowance for the gravitational effect, the partial number density and the concentration on the CC can be obtained by investigating the functions $N_{1,2}(h)$, $c_{1,2}(h)$ at different temperatures $T \leqslant T^{cr}$, where T^{cr} is the mixture critical temperature.

In the slow-neutron transmission method, the height dependence of the partial number density of the binary-solution components can be obtained by solving a system of equations, each of which corresponds to a definite stage of the neutron experiment:

$$
\begin{gathered}
p_0=\exp\{-\Sigma l\}, \quad p_1=\exp\{-\bar{N}_1\sigma_1 x-\Sigma l\}, \\
p_2=\exp\{-\bar{N}_1\sigma_1 x-\bar{N}_2\sigma_2 x-\Sigma l\}, \\
p(h, T)=\exp\{-N_1(h, T)\sigma_1 x-N_2(h, T)\sigma_2 x-\Sigma l\}.
\end{gathered} \tag{1}
$$

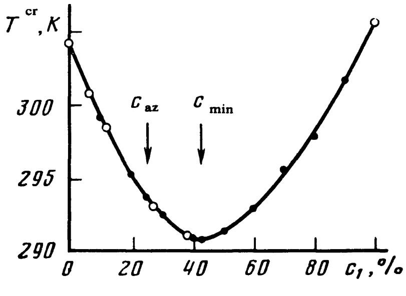

FIG. 1. Critical temperature vs composition of C_2H_6–CO_2 mixture. Open circles—our data, filled—data of Ref. 13. The arrows mark the mixture compositions corresponding to the critical azeotrope and to the minimum on the critical curve.

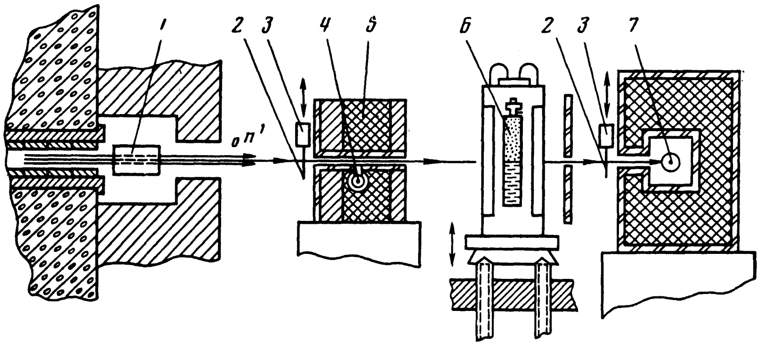

FIG. 2. Geometry of experiment (explained in text).

Here Σ is the macroscopic cross section[9] for neutron interaction with the walls of a sample of thickness l; σ_1 nad σ_2 are the total cross sections for neutron interaction with molecules of the first and second mixture components, respectively; x is the sample thickness; p_0 is the ratio of the neutron-beam intensities normalized to the monitor readings before and after passing through the container in the case of an empty sample (the transmission of an empty sample); p_1 is the transmission of a sample filled uniformly throughout its volume by the first component, with an average partial numerical density N_1; p_2 is the transmission of the sample with a binary mixture uniformly distributed throughout its volume at an average number density $\bar{N} = \bar{N}_1 + \bar{N}_2$ at $T > T^{\text{cr}}$; $p(h, T)$ is the transmission of the sample with the solution under investigation for a temperature T at a height h measured from the bottom of the sample. With allowance for the background and calibration measurements, the profile of the numerical density of the component with the larger neutron cross section can be obtained from an equation that is a solution of the system (1):

$$N_1(h, T) = \bar{N}_1 \frac{\ln[p(h,T)/p_0] + [N_2(h,T)/\bar{N}_2]\ln[p_1/p_2]}{\ln[p_1/p_2]}. \quad (2)$$

We note that for $\sigma_1/\sigma_2 \gg 1$ (strong contrast between the neutron cross sections of the solution components) we have $p_1 \approx p_2$, so that the temperature and height dependences of the second term in the numerator of (2) can be neglected. The method of slow-neutron transmission yields in this case information on the height dependence of the partial numerical density of the component with the larger neutron cross section.[10] This case can be realized for the C_2H_6–CO_2 mixture ($\sigma_1/\sigma_2 \approx 36$, Ref. 11). At $\sigma_1 \approx \sigma_2$ the slow-neutron transmission method yields correct information on the height distribution $N(h, T) = N_1(h, T) + N_2(h, T)$ of the numerical density of the entire mixture. The strong dependence of the total neutron cross section on the isotope composition of certain substances permits the pair of the binary-mixture components to be chosen so that $\sigma_1 \approx \sigma_2$, but with the isotope content changed to $\sigma_1 \gg \sigma_2$. This permits the use of the slow-neutron transmission method to investigate the temperature and field dependences of the concentrations of the solution components, particularly the concentration on the liquid-vapor CC.[12]

3. MATERIALS INVESTIGATED AND EXPERIMENTAL PROCEDURE

The object investigated was chosen to be a C_2H_6–CO_2 solution. Study of this system is of interest from the viewpoint of checking the prediction of the isomorphism theory, since the plot of the critical temperature vs the solution composition has two singular points that are of interest from the standpoint of theoretical analysis [the point of the mixture minimum critical temperature and the point of intersection of the critical point with azeotrope line (Fig. 1)]. We investigated in the experiment solutions with the following compositions (the concentration is given here and elsewhere in molar %): (6.4% $C_2H_6 + CO_2$; 11.5% $C_2H_6 + CO_2$; 26.8% $C_2H_6 + CO_2$ (close to the critical azeotrope); 38.3% $C_2H_6 + CO_2$ (close to the temperature minimum of the critical curve). The samples were prepared from thoroughly dried CO_2 and C_2H_6 of purity better than 99.96%. Aluminum containers measuring 200×50×10 mm were filled with the sample solutions. The average partial number densities N_1 and N_2 are determined from the known values of the sample volume and of the masses m_1 and m_2 of the solution components, and are connected with the average mixture density $\bar{\rho}$ in the sample (the filling density) by the expression $\rho = (m_1 + m_2)/V = (\bar{N}_1 M_1 + N_2 M_2)/N_A$, where N_A is Avogadro's number, M_1 and M_2 are the molecular weights of the components. The filling density of each sample was chosen equal to the critical density of the mixture with given composition.

The experiments were performed with the VVR-M

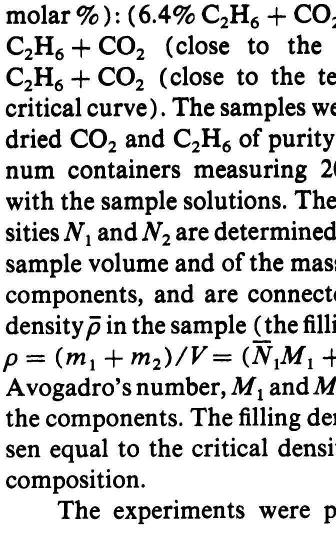

FIG. 3. Height dependence of the transmission of a 26.8% $C_2H_6 + CO_2$ solution at the following temperatures T (in °K): 1—287.38; 2—290.56; 3—292.860; 4 + 292.951

TABLE I. Critical parameters of investigated $C_2H_6 + CO_2$ solutions.

Average ethane concentration $\bar{c}_1$, %	T^{cr}, K	$N_1^{cr} \cdot 10^{-20}$, cm^{-3}	Average ethane concentration $\bar{c}_1$, %	T^{cr}, K	$N_1^{cr} \cdot 10^{-20}$, cm^{-3}
6,4	300,740±0,007	3,98±0,03	26,8	292,866±0,006	15,14±0,10
11,5	298,436±0,006	7,45±0,05	38,3	290,995±0,007	19,20±0,13

reactor of the Nuclear Research Institute of the Ukrainian Academy of Sciences. The geometry of the experiment is shown in Fig. 2. A neutron beam from the reactor was incident on monochromator 1 placed in a biological shield. The monochromator used was a Pb crystal that passed a stream of 1.5-Å neutrons. A collimator system 5 formed a vertically narrow 0.5-mm neutron beam incident on the sample 6 kept in a thermostatted container. The neutron beam that passed through the sample was recorded by detector 7. The intensity of the neutron flux incident on the sample was monitored with monitor 4. To determine the detector and monitor backgrounds, the direct neutron beams were blocked by cadmium shutters 2 driven by motors 3. The thermostatted container was placed on an elevating and laterally displacing stage that permitted the sample to be placed in the path of the neutron beam and to move it vertically in steps of 0.1 mm. The sample temperature was maintained constant by a two-stage thermostatting system accurate to ± 0.002 K over 24 hours. The sample temperature was measured with a platinum resistance thermometer and an R-363 potentiometer. The temperature gradient along the height 200 mm of the sample was recorded with a 16-junction copper-constantan thermopile and was less than 10^{-4} K/m. The intensity of the neutron beam passing through the sample was 10^6 min^{-1}, making possible the transmission to be determined with a statistical error $\sim 0.1\%$ in an exposure time of 5 min. The isotherms of the height dependence of the neutron transmission through the sample solutions were obtained in the course of the measurements for different relative temperatures $\tau = (T - T^{cr})/T^{cr}$ in the interval $2 \cdot 10^{-5} < |\tau| < 2.7 \cdot 10^{-2}$ (Fig. 3). The sample thermostatting time needed to obtain an equilibrium distribution of the density (and hence of the transmission) over the height ranged from 2 h at $T \ll T^{cr}$ to ~ 50 h at $T \approx T^{cr}$. It was assumed that the density distribution as a function of height reached equilibrium if the results of a repeated measurement of the transmission profile agreed within the random-error limits with the results of the preceding measurements. The critical temperatures of the solutions were those at which the jump of the neutron transmission of the interface of the corresponding phases vanished. The critical partial number density N_1^{cr} of C_2H_6 was determined by the inflection point of the critical isotherm of the height dependence $N_1 = N_1(h, T^{cr})$. The critical parameters T^{cr} and N_1^{cr} of the sample solutions are given in Table I.

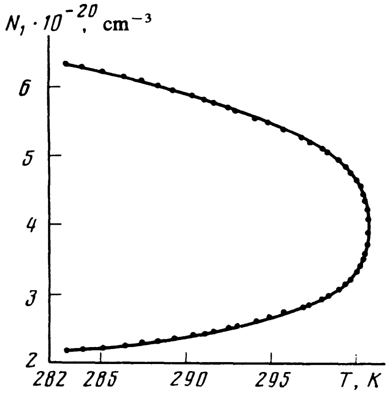

FIG. 4. Temperature dependence of the partial number density of C_2H_6 on the CC of a 6.4% $C_2H_6 + CO_2$ solution.

4. MEASUREMENT RESULTS AND DISCUSSIONS

1. Partial density of ethane on CC of C_2H_6–CO_2 solution

The liquid-vapor coexistence curve for the partial number density of C_2H_6 in a 6.4% $C_2H_6 + CO_2$ solution is shown in Fig. 4.

The experimental data on the temperature dependence of the C_2H_6 partial number density solution on the CC were reduced using the formula

$$[N_1^{\pm}(\tau) - N_1^{cr}]/N_1^{cr} = \pm B_0^* |\tau|^{\beta_0^*} + B_1 |\tau|^{\beta_1^*}, \tag{3}$$

where $N_1^{\pm}$ is the partial number density of the C_2H_6 in the liquid (+) and gas (−) phases of the solution. We emphasize that no expressions for the behavior of the partial density of the mixture components as functions of various thermodynamic quantities have been obtained in modern theory of critical phenomena. To describe the form of the CC near the liquid-vapor critical point we chose therefore the relation $N_1^{\pm} = N_1^{\pm}(\tau)$, whose form agrees with the CC equation predicted by scaling theory for the densities of individual substances. It is not known beforehand whether the critical exponents β_0^*, β_1^* agree with the corresponding exponents for the mixture density and composition on the CC of a binary solution.

The critical exponents and the coefficients of Eq. (3) were determined by least squares. To facilitate the regression analysis, Eq. (3) was divided into two, the first describing the symmetric part of the CC, and the second the behavior of its diameter:

$$[N_1^+(\tau) - N_1^-(\tau)]/2N_1^{cr} = B_0^* |\tau|^{\beta_0^*}, \tag{4}$$

$$[N_1^+(\tau) + N_1^-(\tau)]/2N_1^{cr} = 1 + B_1^* |\tau|^{\beta_1^*}. \tag{5}$$

TABLE II. Parameters of Eqs. (3) and (8) of the $C_2H_6 - CO_2$.

c_1, %	B_0^*	β_0^*	B_1^*	β_1^*
6,4	1,39±0,008	0,345±0,007	0,90±0,10	0,90±0,10
11,5	1,55±0,07	0,344±0,006	0,96±0,08	0,86±0,07
26,8	1,92±0,06	0,343±0,005	0,94±0,07	0,89±0,06
38,3	2,08±0,06	0,344±0,005	0,96±0,05	0,92±0,06

c_1, %	B_0'	β_0'	B_1'	β_1'
6,4	−0,60±0,06	0,348±0,008	−0,28±0,09	0,70±0,05
11,5	−0,54±0,05	0,345±0,007	−0,30±0,10	0,68±0,04
26,8	~0	–	~0	–
38,3	+0,17±0,01	0,346±0,007	−0,40±0,15	0,74±0,03

It was assumed that the parameters $\beta_{0,1}^*$, $B_{0,1}^*$ are constant in the entire temperature range investigated. The data were repeatedly reduced for small changes of T^{cr} and N_1^{cr} within their error intervals given in Table I. For each set of experimental data, the values of $\beta_{0,1}^*$ $B_{0,1}^*$ were obtained at that critical temperature and that critical partial number density of C_2H_6 that minimized the mean squared deviation (minimum χ^2, Ref. 14). The parameters in question and their mean square deviations are given in Table II. Analysis of the residuals is pointed to absence of systematic deviations of the calculation from experiment.

2. Ethane concentration on the C_2H_6–CO_2 solution CC

The ethane concentration on the liquid-vapor CC is defined as

$$c_1^{\pm}(\tau)=N_1^{\pm}(\tau)/N^{\pm}(\tau), \tag{6}$$

where $c_1^{\pm}$ and $N^{\pm}$ are the respectively the density of the ethane and the numerical density of the coexisting phases of the sample solution. The values of $N^{\pm}$ (τ) were calculated from the equation

$$N^{\pm}(\tau)=N^{\text{cr}}(1\pm B_0{}^0|\tau|^{\beta_0{}^0}), \tag{7}$$

where N^{cr} is the critical number density of the C_2H_6–CO_2 solution with the specified composition. The parameters β_0^0, B_0^0 contained in (7) were determined by us beforehand by reducing the experimental data[13,16] on the temperature dependences of C_2H_6–CO_2 solution densities in a wide range of their component ratios. Analysis has shown that the critical exponent β_0^0 does not depend on the mixture composition ($\beta_0^0 = 0.34 \pm 0.01$), whereas the coefficient β_0^0 has a weak concentration dependence (dash-dot line in Fig. 5). Since the parameters β_0^0 and B_0^0, were determined from insufficiently accurate data,[13,16] the relative error of the C_2H_6 concentration on the CC greatly exceeded the error of the partial number density of ethane (0.4–0.5)% and reached several percent. The temperature dependence of the ethane concentration on the CC of the investigated solution are plotted in Fig. 6.

The experimental data on the concentration were reduced by means of the theory of scale transformations and of the isomorphism hypothesis, using the equation

$$[c_1{}^{\pm}(\tau)-c_1{}^{\text{cr}}]/c_1{}^{\text{cr}}=\pm B_0'|\tau|^{\beta_0'}+B_1'|\tau|^{\beta_1'}. \tag{8}$$

Here $c_1{}^{\text{cr}} = N_1{}^{\text{cr}}/N^{\text{cr}}$ is the critical C_2H_6 concentration in the mixture. The critical exponents and the coefficients in (8) were determined by least squares, using the procedure described, from the equations

$$[c_1{}^+(\tau)-c_1{}^-(\tau)]/2c_1{}^{\text{cr}}=B_0'|\tau|^{\beta_0'}, \tag{9}$$

$$[c_1{}^+(\tau)+c_1{}^-(\tau)]/2c_1{}^{\text{cr}}=1+B_1'|\tau|^{\beta_1'}. \tag{10}$$

The fit parameters obtained $\beta_{0,1}'$, $B_{0,1}'$ are listed in Table II.

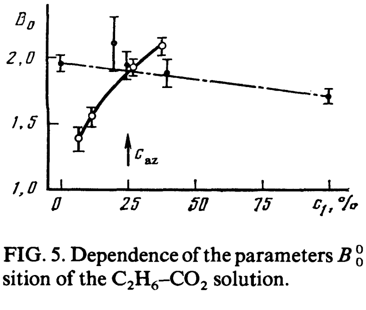

FIG. 5. Dependence of the parameters B_0^0 (●) and B_0^* (○) on the composition of the C_2H_6–CO_2 solution.

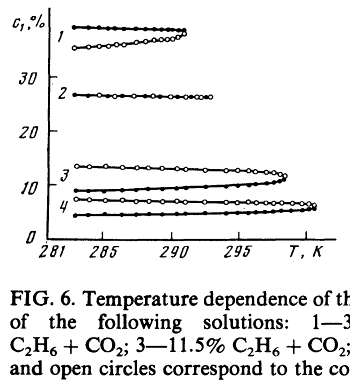

FIG. 6. Temperature dependence of the ethane concentration on the CC of the following solutions: 1—38.3% $C_2H_6 + CO_2$; 2—26.8% $C_2H_6 + CO_2$; 3—11.5% $C_2H_6 + CO_2$; 4—6.4% $C_2H_6 + CO_2$. The filled and open circles correspond to the concentrations in the liquid and gas phases.

3. Discussion of results

The partial numerical densities and concentrations of ethane on the liquid-vapor CC of the C_2H_6–CO_2 system were obtained from experiments performed at constant average density and constant concentration of the components. According to the isomorphism hypothesis, the thermodynamic profiles of the solution are not isomorphous to the thermodynamic profiles of a single-component liquid, and a rescaling of the critical exponents, $\beta \to \beta/(1-\alpha)$, $\gamma = \gamma/(1-\alpha)$, $\alpha \to \alpha/(1-\alpha)$, is possible in the immediate vicinity of the critical point. According to Ref. 2, the end point of the temperature interval $0 < |\tau| < \tau_n$, in which rescaling of the critical exponents is possible can be determined from the following relations:

For dilute solutions

$$\tau_n{}^\alpha \approx \frac{A}{R} c \left(\frac{1}{T^{cr}} \frac{dT^{cr}}{dc} \right)^2, \tag{11}$$

For concentrated solutions

$$\tau_n{}^\alpha \approx \frac{A}{(1-\alpha)(1-\omega)} \frac{dc}{d\mu} \left(\frac{dT^{cr}}{dc} \right)^2. \tag{12}$$

Here A is the coefficient in the relation $C_{v,\tilde{\mu}} \sim A\tau^{-\alpha}$; R is the universal gas constant; c is the molar fraction of the dissolved substance (C_2H_6);

$$\omega = \left(\frac{\partial \mu_1}{\partial T} \right)_{\rho^{cr}} \left(\frac{d\rho^{cr}}{dc} \right) \left(\frac{dT^{cr}}{d\tilde{\mu}} \right) - c_1 \left(\frac{dT^{cr}}{dc} \right);$$

c_1 is the regular part of the quantity $(dc/dT)_{v,\tilde{\mu}}$; $\tilde{\mu} = \mu_1 - \mu_2, \mu_1, \mu_2$, where μ_1 and μ_2 are the chemical potentials of the solution components. At small C_2H_2 concentrations $(0 < \bar{c}_1 < 12\%)$. Eq. (11) ($A/R \approx 5$, $\alpha \approx 0.11$, Ref. 2) yields the estimate $\tau_n \approx 10^{-11}$. The value $\tau_n \approx 5 \cdot 10^{-3}$ was obtained in Ref. 17 from Eq. (12) for the composition of a solution close to the critical azeotrope, and $\tau_n = 0(dT^{cr}/dc = 0)$ was obtained for a mixture with an average C_2H_6 concentration close to the minimum of the critical curve. The temperature range $2 \cdot 10^{-5} < |\tau| < 2.7 \cdot 10^{-2}$ in which our measurements were made does not overlap the range $0 < |\tau| < \tau_n = 10^{-11}$, so that no rescaling of the critical exponent β should be observed for the dilute solutions 6.4% $C_2H_6 + CO_2$ and 11.5% $C_2H_6 + CO_2$ or for the solution 38.3%$C_2H_6 + CO_2$ whose composition is close to the minimum on the critical curve. On the contrary, for a mixture with composition close to the critical azeotrope, the indicated temperature regions overlap and one can therefore expect to have $\beta \to \beta/(1-\alpha)$ and $|\tau| \to 0$.

We compare now the available experimental data with the theoretical predictions. For all the mixtures investigated, the asymptotic critical exponents of the CC equation for the partial numerical density and concentration of C_2H_6 (Table II) agree to within the limits of experimental error with the critical exponents of the CC equation for pure C_2H_6 (0.339 ± 0.005, Ref. 18), pure CO_2 (0.347 ± 0.004, Ref. 19),[3] and also with the critical exponent of the CC equation for the density of the entire C_2H_6–CO_2 solution ($\beta_0^0 = 0.34 \pm 0.01$). The results favor the hypothesis that the critical phenomena are isomorphous. We point out, however, that the theoretically predicted rescaling of the parameter β_0 does not exist for the 26.8% $C_2H_6 + CO_2$ solution.[4] The values of β_1^* given in Table II show that the rectilinear diameter law does not for the investigated system. Model calculations[20–22] predict that the behavior of the diameter should be described by a temperature dependence $|\tau|^{1-\alpha}$, where $\alpha \approx 1/8$. Our results are close to the predictions of the theory, but for a reliable determination of the asymptotic behavior of the CC diameter it is necessary to increase substantially the accuracy with which the partial numerical density and the concentration of the solution components are determined.

It can be seen from Fig. 6 that in C_2H_6–CO_2 solutions with $\bar{c}_1 < c_{az} \approx 24.9\%$ C_2H_6 (Ref. 13) the concentration of the C_2H_6 is higher in the gas phase of the solution than in the liquid phase. At a mixture composition close to the critical azeotrope the CC degenerates, within the limits of experimental error, into a straight line (the composition of the corresponding phase is the same in the entire investigated temperature interval). With further rise of the average concentration of the ethane in the solution, the CC branches diverge again, but then the C_2H_6 concentration becomes larger in the liquid phase than in the gas phase of the mixture. Thus, a change in the solution composition is accompanied by a reversal of the sign of the parameter B_0' that determines the qualitative form of the CC at different concentrations of the binary-mixture components: $B_0' < 0$ for $\bar{c}_1 < c_{az}$; $B_0' \approx 0$ for $\bar{c}_1 \approx c_{az}$; $B_0' > 0$ for $\bar{c}_1 > c_{az}$ (see Table II). Interest attaches, in our opinion, also to the equality of the coefficients B_0^0 and B_0^* when the mixture composition is close to the critical azeotrope.

Let us show that the experimental results cited above can be explained within the framework of the theory of scale transformation, supplemented by the isomorphism hypothesis. From (6) and (9) we have

$$\frac{c_1{}^+(\tau) - c_1{}^-(\tau)}{2c_1{}^{cr}} = \frac{N_1{}^+(\tau)/N^+(\tau) - N_1{}^-(\tau)/N^-(\tau)}{2N_1{}^{cr}/N^{cr}}. \tag{13}$$

Substituting (7) in (13) and recognizing that $(B_0^0|\tau|^{\beta_0^0})^2 \ll 1$, at small τ, we get

$$\frac{c_1{}^+(\tau) - c_1{}^-(\tau)}{2c_1{}^{cr}} = \frac{N_1{}^+(\tau) - N_1{}^-(\tau)}{2N_1{}^{cr}} - \frac{N_1{}^+(\tau) + N_1{}^-(\tau)}{2N_1{}^{cr}} B_0{}^0 |\tau|^{\beta_0{}^0}. \tag{14}$$

With allowance for (4) and (5), expression (14) is transformed in the limit as $|\tau| \to 0$ into

$$[c_1{}^+(\tau) - c_1{}^-(\tau)]/2c_1{}^{cr} = B_0{}^* |\tau|^{\beta_0{}^*} - B_0{}^0 |\tau|^{\beta_0{}^0}. \tag{15}$$

As noted above, the sample C_2H_6–CO_2 solutions have within the limits of experimental error $\beta_0^0 = \beta_0^* = \beta_0'$. Using this result we obtain from Eqs. (9) and (15)

$$[c_1{}^+(\tau) - c_1{}^-(\tau)]/2c_1{}^{cr} = B_0{}' |\tau|^{\beta_0{}'} = (B_0{}^* - B_0{}^0) |\tau|^{\beta_0{}'}. \tag{16}$$

It follows from (16) that the sign of the coefficient B_0' may change: $B_0' > 0$, if $B_0^* > B_0^0$, and, conversely, $B_0' < 0$ if $B_0^* < B_0^0$. For a mixture composition close to the critical azeotrope, it was found that $c_1^+ \approx c_1^-$ ($B_0' \approx 0$) in the entire temperature range investigated. In this case we should have $B_0^* = B_0^0$, according to (16), in full agreement with our results (see Fig. 5).

5. CONCLUSION

The method of slow-neutron transmission was found to be an effective tool for the investigation of liquid-vapor critical phenomena in binary solutions. Our main experimental results comprise the determination of the asymptotic values of the critical exponents and of the coefficients of the equation for liquid-vapor coexistence curve for the partial number density and concentration of C_2H_6 in a C_2H_6–CO_2 solution in a wide range of component concentrations. The experimental investigations of the CC of the C_2H_6–CO_2 solution show that the behavior of the partial number density and concentration can be described within the framework of the theory of scale transformations, supplemented by the hypothesis that the critical phenomena are isomorphous. The critical exponents of the asymptotic terms of the CC equation of the investigated system are close to the corresponding critical exponents for the individual substances. It must be noted that the cause of a certain discrepancy between the theoretical and experimental values of the parameter β_0^* for a solution with composition close to the critical azeotrope is still unclear. The coefficients of the equations that describe the temperature dependence of the partial numerical density and of the concentration of the components are concentration-dependent in the coexisting phases. For a mixture with composition close to the critical azeotrope we have $B_0^* = B_0^0$. This result allows us to conclude that a critical azeotrope can be realized in solutions in which the coefficients of the leading terms of the CC equations for the density of the entire mixture and of its components have a definite concentratiobn dependence, viz., the plots of $B_0^0 = B_0^0(c)$ and $B_0^* = B_0^*(c)$ should intersect. It seems to us that the method of slow-neutron transmission wil be found to be effective also in investigations of critical phenomena in a liquid-liquid system, particularly in the study of polymer solutions.

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1) As an "ideal" system for the description of the behavior of solutions in the critical region one can choose a single-component liquid isomorphous to the lattice-gas model (the liquid-gas critical point) and the incompressible binary alloy model (liquid-liquid critical point).[6] Recent investigations have shown that a number of models with several interacting order parameters can also serve as "model" systems.[7]

2) By partial number density of a binary-mixture component we mean the number of particles of this component per unit volume of the system.

3) The value of β determined in Ref. 19 for CO_2 is somewhat higher than the theoretical value obtained by a renormalization-group approach with the aid of ε-expansions ($\beta = 0.34$); this is apparently due to failure to take into account the nonasymptotic terms of the CC equation when the experimental data on CO_2 were reduced.

4) It is noted in Ref. 17 that there is no rescaling of the critical exponent α of the isochoric heat capacity for C_2H_6–CO_2 solutions, which are close in composition to the critical azeotrope and to the temperature minimum of the critical curve. This is in qualitative agreement with our results.

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