Impact of Pressure on Low-Molecular Weight Near-Critical Mixtures of Limited Miscibility

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ABSTRACT: Near-critical mixtures of limited miscibility are significant for chemical physics, soft matter physics, and a variety of challenging applications. Their basic properties can be tuned by compressing or a systematic change of one of the components. This report addresses these issues, based on experimental studies in nitro-compound (nitrobenzene, o-nitrotoluene, and 1-nitropropane) and n-alkane (from pentane to eicosane) critical mixtures. Studies reveal new patterns for the evolution of the critical consolute temperature \(T_C\) and concentration \(x_C\) (mole fraction) within the tested homologous series: \(T_C(n) \sim n^2\) and \(x_C(n) \sim n^{1/2}\). They also show two paths of the high-pressure impact: (i) \(dT_C(P)/dP > 0\) and overlapping of normalized\(\bar{T}_C(P)\) dependences and (ii) the crossover \(dT_C(P)/dP < 0\) \(\rightarrow\) \(d\bar{T}_C(P)/dP > 0\) with increasing \(n\)-alkane length. The consistent parameterization of all \(T_C(P)\) dependencies is introduced. Supplementary nonlinear dielectric effect studies indicate a possible molecular origin of the phenomenon. The coexistence curve under high pressure is in agreement with the isomorphism postulate for critical phenomena but with a surprisingly strong distortion from the Cailletet–Mathias law of the rectilinear diameter. The new and reliable method for estimating the critical concentration and temperature is proposed. It explores the analysis of relative volumes occupied by coexisting phases.

INTRODUCTION

Binary mixtures of limited miscibility constitute significant chapters of physical chemistry, \(^{1,2}\) phase transitions physics, \(^3\) and the soft matter physics. \(^4,5\) de Gennes “officially” introduced the latter during his Nobel Prize lecture, as systems with the dominance of collective and mesoscale structures and the extraordinary sensitivity to external perturbations. \(^6\) Near-critical mixtures of limited miscibility are a unique soft matter system for which “collectiveness” and the sensitivity to perturbations (“softness”) can infinitely increase on approaching the critical consolute point (CCP). \(^1,3\) They are essential for a variety of significant applications ranging from petrology, \(^7,8\) to modern material engineering. \(^9,10\) The knowledge of temperatures and concentrations controlling phase transitions from the homogeneous liquid to coexisting liquid phases is the base of liquid–liquid separation or liquid–liquid extraction technologies, relevant in the chemical, \(^9\) food, \(^11\) and pharmaceutical \(^12\) industries. In recent years, the significance of mixtures of limited miscibility in biology has risen as the phenomenon which underlies the formation of membrane compartments in cells. \(^13,14\) Near-critical phase equilibria have become significant for biotechnology \(^15,11\) or even medicine. The latter is associated with the evidence that the phase separation process can yield aberrant condensates, possibly associated with some forms of cancer or neurodegener-
where $T_C$ is the critical temperature, $\nu$ denotes the critical exponent of the correlation length, and $z$ is the dynamical exponent; $\xi_0$ and $\tau_0$ are critical amplitudes.

Critical exponents and ratios of critical amplitudes for different physical magnitudes are universal and depend solely on space ($d$) and order parameter ($n_{op}$) dimensionalities. Consequently, all systems in the near-critical state can be arranged into ($d$, $n_{op}$) universality classes. For critical mixtures of limited miscibility, one obtains: $\nu \approx 0.625$ and $z = 3$, what yields $z \nu \approx 1.875$. They belong to the $(3, 1)$ universality class, together with the GLCP, a simple magnetic system with the Curie point, and the Ising model system.\(^{3,9}\)

However, there is a notable difference between one-component fluids with the GLCP and binary mixtures with the CCP. In 1878, Gibbs\(^{20}\) introduced the phase rule for predicting the number of allowed coexisting phases: $F = C - P + 2$, where $F$ is the number of degrees of freedom, $C$ is the number of components, and $P$ is for the number of coexisting phases. Kohlrausch\(^{21}\) proposed its extension to include “near-critical states” for which $F = C - [P + (P - 1)] + 2 = C - 2P + 3$. The term $(P - 1)$ is for the maximal possible number of “critical phases,” linked originally to the number of disappearing meniscus separating coexisting phases. For a one-component system ($C = 1$), one obtains $F = 0$, and only a single GLCP can be expected. For binary mixtures ($C = 2$) of limited miscibility, $F = 1$ and a line of critical points, if changing pressure, appears. Compressing can also influence the critical consolute concentration, as well as such properties of critical mixtures as dielectric constant, diffusion, refractive index, electric conductivity, diffusion rates, or viscosity.\(^{3,26,22}\)

Regarding the impact of pressure on the critical consolute temperature, there is a set of heuristic, thermodynamic predictions,\(^{3,22,23}\) but the most important seems to be the phenomenological relation introduced by Myers, Smith, Katz, and Scott (MSKS)\(^{24}\):

$$\frac{dT_C}{dP} = \frac{V_E}{H_E}$$ \hspace{1cm} (2)

where $H_E$ is the mixing enthalpy excess, for critical mixtures with the UCCP\(^{10}\) $H_E > 0$; $V_E$ denotes the volume excess of the mixture.

The importance of $dT_C/dP$ coefficient for the temperature behavior under atmospheric pressure is briefly presented in Appendix 1. It also recalls extraordinary properties of critical mixture possible to arrange because of the selection of constituents.

The impact of pressure is also evidenced for the critical consolute concentration. To the best of the authors’ knowledge, this issue is addressed only in ref.\(^{25}\), where the following empirical dependence was introduced:

$$\frac{x_C(P) - x_C}{x_C} = \frac{T_C(P) - T_C}{T_C}$$ \hspace{1cm} (3)

where $x_C$ is given in mole fraction. Values $x_C$ and $T_C$ are related to atmospheric pressure.

Equation 3 is obtained because of the analysis of experimental data in the low-pressure regime, $P < 13$ MPa.\(^{25}\) Hence, the question of the impact of higher pressures ($x_C(P)$) remains.

The liquid–liquid coexistence curve (binodal) below the critical consolute temperature is portrayed by relations\(^{3,26}\):

$$\Delta x(T) = x_U - x_L = B(T_C - T)^\beta [1 + (T_C - T)^\Delta + ...]$$ \hspace{1cm} (4)

$$\Delta x(T) = \frac{x_U + x_L}{2} = x_C + aT + A(T_C - T)^{3-\gamma} [1 + (T_C - T)^{3b} + ...]$$ \hspace{1cm} (5)

where $\Delta x = x_U - x_L$ is the metric of the order parameter, $T < T_C$, and $x_L$ and $x_U$ are related to the concentration of the selected component of the binary mixture in the upper and lower coexisting phase, respectively, and $d(T)$ is for the diameter of the binodal. In square brackets, correction-to-scaling terms, necessarily remote from $T_C$,\(^{27}\) are given values of critical exponents for $(3, 1)$ universality class: $\alpha \approx 0.115$, $\beta \approx 0.325$, and $\Delta \approx 0.5$.\(^{3,26}\).

Linking eqs 4 and 5, two ‘branches’ of the binodal $x_C(T)$ and $x_L(T)$ can be described.\(^{26}\) Generally, eqs 4 and 5 can be expressed using concentrations in mole fraction $x(T)$, volume fraction $\phi(T)$, ... or by such physical properties as density ($\rho$), refractive index ($n$), and dielectric constant ($\epsilon$).\(^{26}\)

For decades, the diameter (eq 5) was described using the Cailletet–Mathias (CM) law of rectilinear diameter,\(^{1,3,26,30}\)

$$d(T) = x_C^\beta + aT, \quad d(T) = \rho_C^{\beta_\rho} + a\rho, \quad d(T) = \rho_C^{\beta_\rho} + a\rho$$

and served as the basic tool for determining the critical concentration or density ($x_{C0}, \rho_{C0}$, ...). Their determination is always puzzling because of the “flatness” of the top of the coexistence curve.\(^1,3,26,28,30\) Four decades ago, it became clear that the CM law of rectilinear diameter failed, and the precritical anomaly of the diameter is crucially important. However, its detection and portrayal were a challenge because of its weakness matched with the experimental error.\(^{26,29,30}\)

Notably, the simplified description of pretransitional/precritical effects via only a single power term is also possible but only in the immediate vicinity of $T_C$.\(^{3,9}\) In practice, the analysis of experimental data requires some temperature range $\Delta T_p$, which leads to effective critical exponents. For instance, for the order parameter\(^{18,19,26,31,33}\)

$$\Delta x(T) = x_U - x_L = B\Delta T^{\beta_\alpha}$$ \hspace{1cm} (6)

where the effective exponent: $\beta_\alpha = \beta + \sum \Delta h \Delta T^\gamma$ and then $\beta_\alpha \geq \beta$.

Regarding the impact of pressure, the postulate of the isomorphism of critical phenomena assumes the same universal description of the coexistence curve under arbitrary pressure.\(^3\)

The values of critical consolute temperatures and concentrations are system-dependent. Studies of their shifts by compressing or in homologous series of mixtures, with a systematically changed component, can be the way for searching new scaling patterns or links of $T_C$ and $x_C$ to molecular properties.\(^{10,21}\) The basic reference constitutes the mean-field theory by Flory et al.\(^{34}\) developed for polymer—low molecular weight solvent critical mixtures and resulted in following universal “scaling” patterns\(^{34,35}\):

$$T_C \approx \theta - \frac{20}{\sqrt{N}}$$ and $q_C = \frac{1}{1 + \sqrt{N}} \approx \frac{1}{\sqrt{N}}$ \hspace{1cm} (7)

where $N$ stands for the number of monounits in the polymer. Yelash et al.\(^{36}\) resumed the mentioned model and tested available experimental $q_C(N)$ values in various systems. They suggested the function:
\( q_c(N) = \sqrt{P + P_1 \ln(N)} / (P + \sqrt{N}) \) to explain the “general” empirical and experimental relation

\[ q_c \propto N^{-r} \] (8)

with exponents within the range 0.37 < N < 0.5.

However, three adjustable parameters in the Yelash et al. \(^36\) relation yield a significant problem for the analysis and validation. Worth recalling is also the equation by An et al., \(^37\) who focused on the ratio of critical concentrations of components in binary mixtures

\[ \frac{q_c}{1 - q_c} = A n^{-r_1} \] (9)

The analysis of ten homologous series of binary critical mixtures containing both polymers and low-molecular weight systems yielded exponents 0.31 < r < 0.74 and 0.16 < r < 0.43, respectively. \(^35–37\)

Results recalled above are for the UCCP. In refs.\(^{38,39}\) the opposite case was tested, namely: (i) high-molecular weight polystyrene–n-alkane mixtures \((S < n < 13)\), and (ii) for such mixture, the lower CCP (LCCP) exists. The authors proposed the numerical solution for the Born–Green–Yvon theory-based to test \( T_c(n) \) behavior; the fair agreement for \( 8 < n < 13 \) was obtained. Imre et al.\(^{40}\) tested the impact of pressure on polystyrene \((M_w = 1.24 \text{ kg/mol})\) and n-alkane (from octane to tetradecane) mixtures with the UCCP. They reported the shift \( dT_c/dP < 0 \rightarrow dT_c/dP > 0 \) with the increasing length of n-alkanes. The parallel rise of \( T_c(n) \) and critical concentrations (in weight fractions) is reported.

This brief resume indicates that despite decades of studies, essential aspects of the impact of pressure or molecular properties on near-critical binary mixtures of limited miscibility remain puzzling and poorly evidenced. It is particularly relevant for the most basic case of mixtures based on low-molecular weight liquids with the upper critical consolute temperature.

This report shows the experimental evidence aimed at filling the mentioned cognitive gaps. It is based on studies on nitro-compound (nitrobenzene, o-nitrotoluene, and 1-nitropropane) + n-alkane mixtures of limited miscibility. Studies revealed new patterns for \( T_c(n, P) \) and \( x_c(n) \) evolutions, particularly discussing the behavior related to: (i) \( dT_c(P)/dP > 0 \) and (ii) the crossover from \( dT_c(P)/dP < 0 \) to \( dT_c(P)/dP > 0 \). The explanation of observed phenomena based on volume excess and nonlinear dielectric effect (NDE) studies is proposed. In Appendix 2, the similar behavior in the oligostyrene–n-alkane critical mixtures\(^ {40}\) is discussed. Finally, the high-resolution detection of the coexistence curve under high pressures shows that the preservation of universal critical exponents, matched with the extreme violation of the CM law of rectilinear diameter,\(^ {28–30}\) was not observed under atmospheric pressure. The fiasco of the law of rectilinear diameter cancels the basic tool for determining the critical concentration, what constitutes some problem in the last decades. This report introduces the “new tool” for simple and reliable \((x_c, T_c)\) determination, based on the analysis of relative volumes occupied by coexisting phases (see the Experimental Section).

**RESULTS AND DISCUSSION**

**Critical Consolute Point.** Studies were carried out for three homologous series of critical mixtures composed of nitro-compounds and n-alkanes. Such systems are convenient for dielectric studies because of different dielectric constants of components, namely \( \varepsilon = 25–30 \) for nitro-compounds and \( \varepsilon \sim 2 \) for n-alkanes and relatively low electric conductivities. \(^{41}\) In these mixtures, dielectric constants for the homogeneous liquid as well as the upper and the lower coexisting phase are dramatically different, what facilitates precise estimations of the phase separation parameters (temperature, concentration, and pressure).

![Figure 1](https://dx.doi.org/10.1021/acsomega.0c01772)

**Figure 1.** Evolution of critical concentrations (in mole fraction) for nitro-compounds + n-alkane critical mixtures. The applied scale shows that for all tested homologous series \( x_c \sim n^{1/2} \). Values of parameters related to eq 10 are given in Table 1.

![Figure 2](https://dx.doi.org/10.1021/acsomega.0c01772)

**Figure 2.** Evolution of critical consolute temperatures in nitro-compound–n-alkanes critical mixtures. It is presented using the scale showing the prevalence of the description via the relation \( T_c \sim n^2 \). Values of parameters related to eq 11 are collected in Table 1.

Figures 1 and 2 reveal simple patterns that follow critical consolute temperatures and concentrations within the tested homologous series of critical mixtures:

\[ x_c(n)^2 = x_o + a_o \times n \rightarrow x_c(n) \propto n^{1/2} \] (10)

\[ T_c(n) = T_o + b_o \times n^2 \rightarrow T_c(n) \propto n^2 \] (11)

where \( x_c \) is given in mole fractions and \( T_c \) (K); \( n \) stands for the number of carbon atoms in the molecule, or it is the metric...
of the length of \( n \)-alkane molecules. The latter can also be noted as the sequence of units \( \text{H}−[\text{CH}_2]_n−\text{H} \).

Notably, the Flory-type models are based on the volume fraction (eqs 7–9)\(^{34–37} \) and directly do not yield the simple “scaling behavior”, as evidenced in Figures 1 and 2 and eqs 10 and 11. For a binary mixture with A and B components, the concentration in mole fraction (\( x \)) shows the comparison of the number of A-type and B-type molecules. The volume fraction (\( \phi \)) is related to the relative volume occupied by A-type molecules in the mixture. Consequently, eq 10 for the critical concentration seems to correlate with eq 9 and the “ideal” Flory model\(^{34,35} \) with the exponent \( r_2 = 1/2 \), although it was not “designed” for mixtures based on the low-molecular weight liquids. The authors did not find a model explaining the simple power dependence found for the critical consolute temperature (eq 11). The presented results also indicate that the focus on the mole fraction can be a promising path in searching for scaling patterns in critical binary mixtures.

Figures 3–5 presents pressure dependencies of critical consolute temperatures, for tested critical mixtures. The normalized scale shows that for nitrobenzene (Figure 3) and \( \alpha \)-nitrotoluene (Figure 4) + \( n \)-alkane mixtures, the crossover \( d \Delta T_c/dP < 0 \rightarrow d \Delta T_c/dP > 0 \) with the increasing length of \( n \)-alkanes takes place.

It is shown in Figure 3 that even the “design” of a quasi-critical mixture for which \( d \Delta T_c/dP \approx 0 \) in a broad range of pressures is possible. Such behavior obtained by the “fractional \( n \)-alkane” is defined as the mixtures of decane (\( x = 0.6 \) mole fraction) and undecane (\( x = 0.4 \) mole fraction). One can consider it as “fractional” \( n \)-alkane associated with \( n = 10.6 \).

For 1-nitropropane + \( n \)-alkanes, critical mixture (Figure 5) experimental data for the normalized temperature scale \( T_c(P) = T_c(P=0.1 \text{ MPa}) \) overlap for all tested critical mixtures, with monotonously decreasing value of \( d \Delta T_c/dP > 0 \) on compressing.

Pressure changes of \( T_c(P) \) dependencies for all tested critical mixtures can be well portrayed by the relation originally introduced for describing pressure changes of the glass temperature, which can be derived from the extended Clausius–Clapeyron equation\(^{33–45} \)

\[
T_c(P) = k \times R(P) \times D(P) = T_c^{\text{ref.}} \left(1 + \frac{\Delta P}{\Pi} \right)^{1/b} \times \exp\left(\frac{\Delta P}{\ell} \right) \tag{12}
\]

where \( \Delta T_c(P) = T_c(P) - T_c^{\text{ref.}} \), \( T_c(P = 0.1 \text{ MPa}) \), \( R(P) \), and \( D(P) \) are for the rising and damping terms, respectively; \( \Delta P = P - P_c^{\text{ref.}} \), \( \Pi = \pi + P_{\text{ref.}} \), and \( -\pi \) is the extrapolated, negative pressure asymptote for \( T_c(P \rightarrow -\pi) \rightarrow 0 \).

Optimal values of parameters, as shown in eq 12, can be determined using the following transformation of \( T_c(P) \) experimental data, resulted directly from eq 12, namely\(^{33–45} \).
Plots \(\frac{d\ln T_C(P)}{dP}^{-1}\) versus \(P\) yield a linear dependence if in eq 12, the damping term can be neglected: \(c \rightarrow \infty\), \(D(P) = 1\), and \(dT_C/dP \geq 0\). The presence of the damping term \(D(P)\) in eq 12 leads to eq 14 and a possible extremum of \(T_C(P)\) curves for higher pressures. If the atmospheric pressure is assumed as the reference, that is, \(\Delta P = P\), one obtains \(b = B\) and \(\Delta A = A/B\). Within the limit of experimental error, such condition can be approximated by the atmospheric pressure \(P_c^{15} \approx 0.1\) MPa (Figure 6).

\[
\left(\frac{d\ln T_C(P)}{dP}\right)^{-1} = b\pi + b \times \Delta P = A + BP
\]

**Figure 6.** Distortion-sensitive analysis of \(T_C(P)\) experimental data for 1-nitropropane—decane critical mixture. It is based on eq 13 and focuses on the domain of validity of eq 12, shown by the straight line. A hallmark of \(D(P)\) term (eq 14) emerges only for \(P > 220\) MPa. For some critical mixtures in nitrobenzene and \(o\)-nitrotoluene + \(n\)-alkane homologous series, the damping term cannot be neglected (Figures 3 and 4, Table 2).

**Table 1. Values of Parameters for Eqs 10 and 11, Describing Changes of the Critical Consolute Temperatures and Concentrations for Tested Homologous Series of Critical Mixtures**

| critical mixture                  | \(x_C\) | \(a_C\) | \(T_C(K)\) | \(b_C\) |
|-----------------------------------|---------|---------|------------|---------|
| nitrobenzene—\(n\)-alkanes, \(P = 0.1\) MPa | -0.0558 | 0.0328  | 289.4  | 0.0663  |
| nitrobenzene—\(n\)-alkanes, \(P = 50\) MPa  | 285.6   | 0.086   |         |         |
| \(o\)-nitrotoluene—\(n\)-alkanes, \(P = 0.1\) MPa | 0.0656 | 0.036   | 271.5  | 0.065   |
| 1-nitropropane—\(n\)-alkanes, \(P = 0.1\) MPa | 0.0632 | 0.0292  | 271.1  | 0.105   |

\[\Delta \varepsilon = -\frac{\varepsilon N_{\text{Debye}}^4}{54k_B T_S} \]  

where \(\varepsilon N_{\text{Debye}}\) is the local field factor, \(N_{\text{Debye}}\) denotes the number of permanent dipole moments in a unit volume, \(\mu\) means the permanent dipole moment and \(R_S\) stands for the dipole—dipole correlation factor.

Equation 15 illustrates the extreme sensitivity of NDE to basic molecular properties, including intermolecular interactions. Figure 8 presents experimental results coupled to eq 15, for mixtures of unlimited miscibility, in which the nondipolar solvent (carbon tetrachloride, CCl\(_4\)) occupies the same volume as hexane in the critical (dipolar) nitro-compound—hexane mixture of limited miscibility. For 1-nitropropane and CCl\(_4\) mixture, Piekara’s correlation factor \(R_S(x) \approx 1\), as shown in eq 15, and approximately linear changes of NDE toward negative values occur \(N_{\text{Debye}} \propto x\). The same pattern appears for diluted mixtures of nitrobenzene and \(o\)-nitrotoluene in a nondipolar solvent. For higher concentrations of these nitro-compounds, the dipole—dipole coupling emerges what yields the increasingly negative correlation factor \(R_S(x)\) and then for \(x \rightarrow 1\) the strongly positive NDE. The latter behavior results from the coupling of benzene rings leading to the antiparallel dipole moment arrangements. Notably, this is the confirmation for such coupling beyond NDE studies.

Nitrobenzene—hexane is the mixture where the limited miscibility takes place. The additional strong positive contribution from pretransitional fluctuations appears in the vicinity of the critical concentration, visible for nitrobenzene—hexane mixtures, as shown in Figure 8. Notably, that discussed above reference measurements in mixtures of unlimited miscibility constitute the necessary tool for determining the “critical” contribution on approaching the critical consolute temperature.

Figure 5 and Table 2 show that the damping term is absent for 1-nitropropane + \(n\)-alkane mixtures in the tested range of pressures: \(T_C(P) \propto R(P)\) and \(D(P) \approx 1\). The scaling behavior in Figure 5 indicates that in 1-nitropropane—\(n\)-alkanes homologous series, only the critical consolute temperature under atmospheric pressure changes.

To discuss molecular origins of the reported \(T_C(P)\) behavior, one can consider Figure 7, where for nitrobenzene—\(n\)-alkanes, critical mixture changes \(dT_C/dP\) are presented. The inset shows linear dependences of \(dT_C/dP\) versus \(V^\ast(n)\) (the volume excess), in agreement with MSKS, as shown eq 2. This figure also shows changes in \(dT_C/dP\) coefficient under pressure. Such behavior is in agreement with MSKS, as shown in eq 2.

The molecular explanation of presented \(T_C(P)\) dependences is possible when additionally taking into account the results of NDE studies in mixtures of tested nitro-compounds with a nondipolar solvent, as shown in Figure 8. NDE describes changes of dielectric constant because of the action of the strong electric field: \(\varepsilon(E) = \varepsilon(E \rightarrow 0) + \Delta \varepsilon E^2\) and then NDE is \(\Delta \varepsilon / E^2 = [\varepsilon(E) - \varepsilon(E \rightarrow 0)] / E^2\). In mixtures of unlimited miscibility, NDE is characterized by the Debye–Herweg–Piekara relation

\[
\frac{\Delta \varepsilon}{E^2} = -\frac{F_{\text{Debye}}^4}{54k_B T_S} \]  

where \(F_{\text{Debye}}\) is the local field factor, \(N_{\text{Debye}}\) denotes the number of permanent dipole moments in a unit volume, \(\mu\) means the permanent dipole moment and \(R_S\) stands for the dipole—dipole correlation factor.

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\[
\frac{\Delta \varepsilon}{E^2} = \left( \frac{\Delta \varepsilon}{E^2} \right)_B + \left( \frac{\Delta \varepsilon}{E^2} \right)_C + \left( \frac{\Delta \varepsilon}{E^2} \right)_b + \frac{\Delta N_{\text{Debye}}}{T - T_C^w}\]  

where \(x = x_C\), \(T > T_C\), the index “\(b\)” is for the noncritical background effect, “\(c\)” for the critical contribution, and the critical exponent \(\psi \approx 0.4\).

The isothermal (\(T \approx T_C\)) concentration-related changes of NDE, as visible in Figure 8, portray the relation

\[
\left( \frac{\Delta \varepsilon}{E^2} \right)_C = \frac{\Delta \varepsilon}{E^2} - \left( \frac{\Delta \varepsilon}{E^2} \right)_b \propto |x - x_C|^{\psi/p} \approx |x - x_C|^{-1.2}, \quad T \approx T_C
\]
The model explanation of NDE precritical effect is proposed in refs. 50, 52. It linked the anomalous increase to the appearance of critical fluctuations and their elongation under the strong electric field, which led to the relation:

\[ \chi \Delta \varepsilon \propto \langle \Delta \rangle \propto | - | = | - | \approx \psi \gamma \beta \]

where \( \langle \Delta \rangle \propto (T - T_{C}) \propto T \). Generally, the critical evolution of susceptibility (compressibility) is given by X \( \propto (T - T_{C})^{-\gamma} \approx (T - T_{C})^{-1.23} \). However, under the strong electric field, the classical = nonclassical crossover occurs and \( X \propto (T - T_{C})^{-1.02} \).

The comparison of results, as presented in Figures 7 and 8, shows the following behavior: \( dT_{C}/dP < 0, V^E < 0, \) and NDE < 0 (in eq 15: \( R_{S} \approx 1 \)) \implies \) increasing length of n-alkane and concentrations of nb and o-nt \( \implies \implies \) \( dT_{C}/dP > 0, V^E > 0, \) NDE > 0 \( (R_{S} < 0 \) in eq 15).

The correlation between the excess volume \( V^E \) and \( dT_{C}/dP \) agrees with the basic MSKS, as shown in eq 2. Results of NDE measurement can indicate that "better packing" of molecules in the mixture \( (V^E < 0) \) can be associated with the 2D molecular structure of nitrobenzene and o-nitrotoluene molecules, which may introduce some preferred local arrangements for...
surrounding them with rod-like \( n \)-alkanes. The coupling of nitrobenzene and \( o \)-nitrotoluene molecules for their higher concentrations leads to the appearance of 3D molecular structures, which cancels the mentioned mechanism, leading to \( V^* > 0 \). Such a concept agrees with the crossover \( dT_C/\Delta P < 0 \rightarrow dT_C/\Delta P > 0 \) also observed on compressing. The next confirmation of the proposed picture may be a similar behavior in oligostyrene--\( n \)-alkane mixtures (see Appendix 2 and ref 40). Notably, the mentioned mechanism has to be absent for 1-nitropropane--\( n \)-alkane mixtures, (see NDE behavior in Figure 8), in the agreement with the results, as shown in Figure 5.

**Coexistence Curve.** The coexistence curve (binodal) determines the border between the homogeneous region of unlimited miscibility and the two-phase domain, with the peak defining \( (x_C, T_C) \). However, the impact of pressure on the shape of the binodal is still poorly evidenced.\(^{22-24} \) It is undoubtedly because of difficulties associated with high-pressure studies. Relevant is the measuring module placed inside the high-pressure chamber, which must ensure the complete isolation from the pressure-transmitting medium matched with high reliability of results.\(^{50} \) Figure 9 shows the coexistence curve for nitrobenzene--decane mixture under \( P = 105 \) MPa. The straight dashed line is for the law of rectilinear diameter.\(^{28-30} \)

**Figure 9.** Coexistence curve for nitrobenzene--decane mixture of limited miscibility under \( P = 105 \) MPa. The straight dashed line is for the law of rectilinear diameter.\(^{28-30} \)

...dashed (red) line is for the CM law of rectilinear diameter.\(^{28-30} \)

The diameter-focused plot is presented in Figure 10. It exhibits the fairly well portrayal via eq 3, also remote from the critical point. Such evolution also can be expressed in the form\(^{3,26,29,30} \)

\[
d(T) = \frac{x_U + x_l}{2} = x_C + a_d t + A_d t^{1-\alpha}[1 + \Delta_d t^{\Delta_d} + ...] \tag{18}
\]

where the dimension-less distance from the critical temperature \( t = |T - T_C|/T_C \)

The analysis based on eq 18 offers an excellent portrayal of the strong \( d(T) \) pretransitional anomaly in the immediate vicinity of \( T_C \) as well as the almost linear behavior remote from \( T_C \) as presented in Figure 11. The red line in this figure shows that the CM rectilinear behavior\(^ {8-30} \) strongly failing close to \( T_C \).

**Figure 10.** Diameter of the coexistence curve in nitrobenzene--decane mixture under \( P = 105 \) MPa. The dashed brown line is for the CM law of rectilinear diameter.\(^ {28-30} \) The real critical concentration and the biased estimation via the CM law are indicated. The blue curve is related to eq 18 with \( x_C = 0.608, a_d = 0.09, A_d = 0.1, \Delta_d = 0.006, \) and exponents \( \alpha = 0.115 \) and \( \Delta_1 = 0.5 \). The red line shows the CM law.

**Figure 11.** Order parameter analysis of the shape of the coexistence curve for the nitrobenzene--decane system under \( P = 105 \) MPa. \( \Delta x \) denotes the difference between nitrobenzene concentrations in coexisting phases. The applied log--log scale reveals the linearity, as resulted from eqs 4 and 6. The single-exponent term portrayal is possible ca. for \( |T - T_C| < 1 \) K.

It is noteworthy that \( x_C^{CM} + a_d^{CM} t \neq x_C + a_d t \), that is, the linear term, as shown in eq 18, does follow experimental data remote from \( T_C \) as shown in Figures 9 and 10. This shows that all terms, as shown in eq 18, contribute to the critical effect of \( d(T) \), at any distance from \( T_C \).

The order parameter-focused analysis of the binodal, based on eqs 4 and 6, as shown in Figure 11. It yields the exponent \( \beta \approx 0.335 \pm 0.01 \) for \( T - T_C < 1 \) K, the value is within the limit of the experimental error in agreement with the \( (3, 1) \) universality class model value \( (\beta \approx 0.325) \) for \( T \to T_C \).\(^ {25} \) Notably, critical mixtures are strongly susceptible to contaminations, which influence values of both critical exponent and \( T_C \).\(^ {33,24} \) The analysis of the shape of the binodal showed a minimal shift of the critical concentration \( \Delta x < 0.01 \) mole fraction of nitrobenzene, in fair agreement with Jacobs’ eq 3.\(^ {23} \)

**CONCLUSIONS**

Results presented above show the evidence regarding the impact of pressure on the critical consolute temperature in...
three homologous series of mixtures of limited miscibility composed of dipolar nitro-compounds and the nondipolar solvent (n-alkanes). For nitrobenzene−n-alkanes and o-nitrotoluene−n-alkane critical mixtures, the transformation \( dT_c/dP < 0 \leftrightarrow dT_c/dP > 0 \) is observed. The correlation of this phenomenon with the shift of the volume excess \( V_E < 0 \leftrightarrow V_E > 0 \) and the appearance of dimer intermolecular coupling for the dipolar component (NDE studies) is evidenced. Notably, similar \( dT_c/dP \) changes appear for critical mixtures of oligostyrene−n-alkanes (see Appendix 2) and 1-alkanol−water, where the strong intermolecular coupling can also be expected. For 1-nitropropane and n-alkane critical mixtures, where the coupling is negligible, the same pattern of \( T_c(P) \) evolution and \( dT_c/dP > 0 \) is shown. In agreement with general expectations of the Physics of Critical Phenomena, even high compressing has no impact on universal critical exponents characterizing the coexistence curve. However, this report shows that the high compression causes a notable “amplification” of the pretransitional anomaly of the diameter (Figures 9 and 10), usually very weak under atmospheric pressure. Finally, worth stressing is the new evidence regarding changes of \( T_c(n) \) and \( x_c(n) \) (eqs 9 and 10) within homologous series of tested critical mixtures.

Four decades ago, the CM law of rectilinear diameter ceased to be the omnipotent tool for estimating the critical concentration in critical binary mixtures. No alternative concept of its precise and easy determination has appeared since then. This report presents the new and reliable experimental tool for the fast estimation of the critical concentration and temperature (see the Experimental Section).

In conclusion, this report presents a set of new dependencies, which can portray changes of the critical consolute temperature and concentration, as the function of pressure and within homologous series of low-molecular liquids composed of a nitro compound and n-alkanes. It is shown that it is even possible to prepare a critical mixture for which \( dT_c/dP \approx 0 \) in a broad range of pressures. All these can be significant for fundamental modeling and practical implementations exploring unique near-critical features.

**Experimental Section**

Studies were carried out in mixtures of nitrobenzene, o-nitrotoluene, and 1-nitropropane with n-alkanes. Nitro compounds were distilled twice under vacuum. Solvents (n-alkanes) were purchased from Sigma-Aldrich and used without additional purification. Coordinates of critical points were determined using the new implementation of the visual method (see below) for which the coexistence curve is determined via observations of the fractional meniscus heights in a set of ampoules with mixtures of different concentrations. They were placed in a transparent thermostatted system (50 L volume). Observations started in the homogeneous liquid phase, and on cooling, the temperature of the phase separation associated with the binodal was registered. Figure 12 shows ampoules with noncritical \((x < x_c)\) and critical \((x = x_c)\) concentrations, just after the separation of coexisting phases.

On further cooling, the position of the meniscus for noncritical samples shifts toward the middle of the ampoule. The analysis of the volume occupied by coexisting phases, and on cooling, the temperature of the phase separation associated with the binodal was registered. Figure 12 shows ampoules with noncritical \((x < x_c)\) and critical \((x = x_c)\) concentrations, just after the separation of coexisting phases.

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Phase separation temperatures under pressure were determined using dielectric constant measurements ($f = 10$ kHz, Alpha Novocontrol Impedance Analyzer) via the detection of sharp changes of its value when passing the coexistence curve border on cooling or compressing. It was associated with the fact that the gap of the capacitor was in the lower coexisting phase, in which dielectric constant was notably higher than in the homogeneous liquid phase, in the case of nitro-compound + n-alkane mixtures. The vast majority of tests was carried out as the function of pressure because of the appearance of the precritical effect in the homogeneous liquid phase, more robust than for the temperature path. Such behavior was estimated using the visual method described below. Notably, the innovative analysis of resonant method for NDE measurement was used. The capacitive, namely $\varepsilon$, was used for supporting the homogenization of the tested mixture. After detecting the phase transition, the sample returned to the homogeneous liquid phase via heating and/or decompressing. Additionally, the sequence of high-voltage pulses from the apparatus used for the NDE studies was used for the homogenization of the tested mixture. After reaching the homogeneous liquid state, subsequent temperatures and pressures associated with the coexistence curve could be detected. NDE describes changes of dielectric constant because of the action of the strong electric field $E$: $\Delta \varepsilon / E^2 = (\varepsilon(E) - \varepsilon(E_0))^1$. NDE measurements are associated with detecting minimal changes of dielectric capacitance, namely $\Delta C(E)/C \sim 10^{-6}$. For measuring such subtle differences in the electric capacitance, the dual-field resonant method for NDE measurement was used. The detection was carried out by the weak measuring field ($f_{\text{meas.}} = 1$ MHz and $U_{\text{meas.}} = 1$ V), and the strong electric field was applied in the form of DC pulses, lasting $\Delta t = 2$ ms, $U = 500–1200$ V, and 100 ms distance between subsequent strong electric field pulses.

Reference values of critical concentrations and temperatures were also taken from earlier studies of the authors and estimated using the visual method described below. Notably, the innovative analysis offers a new and fast method for determining $\phi(x, T_C)$: see below.

For the visual method for determining phase equilibria and critical parameters, a set of mixtures with different concentrations is prepared and placed in cylindrical ampoules (Figure 12). Initially, the mixture is homogeneous, but on cooling samples, it entered the two-phase region. Considering the entire volume of the sample ($V$) and volume of the lower ($V^L$) and upper phase ($V^U$) coexisting phases, separated by the meniscus, one obtains the equation

$$V = V^L + V^U$$

and $h^L = \frac{V^L}{V}$ assuming $h^U = \frac{V^U}{V}$

(19)

In the two-phase domain, for $T = \text{const}$, mixtures (A and B components) with an arbitrary total concentration of the mixture $\phi = \phi_A = \frac{V_A}{V}$ are characterized by the same concentration in coexisting phases $\phi^L$, $\phi^U$, but volumes $V^L$, $V^U$ and then different $h^L$, $h^U$ are different. Considering two samples with different total concentration $\phi$, one obtains a couple of equations

$$\phi_i = \phi^L h_i^L + \phi^U (1 - h_i^L)$$

$$\phi_j = \phi^L h_j^L + \phi^U (1 - h_j^L)$$

where the temperature $T = \text{const}$ and $\phi_i \neq \phi_j$

Values $\phi_i$, $\phi_j$ are known after the preparation of samples, and fractional meniscus heights can be determined for subsequently tested temperatures. Their evolution is shown in Figure 13. The solution of the system of relations (eq 20) yields values $\phi^L$ and $\phi^U$, for subsequently tested temperatures. These values define the coexistence curve (binodal). One can increase the accuracy when testing $k$ mixtures with different concentrations leading to $\frac{1}{2} \left( \frac{k}{2} \right)$ pairs of equations, like eq 20, and a similar set of $\phi^L$ and $\phi^U$. They can be statistically analyzed, for each tested temperature.

Tests can be simplified and speed-up if focusing solely on values of the critical concentration and temperature. The latter is easy relatively determined experimentally because the peak of the binodal curve is “flat”, that is, in the broad surrounding of the critical concentration, $\phi_C \pm \Delta \phi$ the detected phase transition temperature is “the same”, within the experimental error: in this report $T_C \pm 0.02$ K. This favorite feature for $T_C$ estimated creates fundamental problems for the critical concentration. For decades, the CM law was broadly used as a convenient tool for the determination of critical concentration, density, and so on. However, its usage requires at least rough knowledge of the binodal curve, which can constitute some problems. It also leads to the substantial error because of the precritical anomaly of the diameter.

However, based on eq 19 and eq 20, one can propose the new way of the simple, fast, and accurate determining of the critical concentration. Equation 20 directly yields the dependence for the fractional meniscus height

$$h(\phi, T = \text{const}) = \frac{\phi - \phi^L}{\phi^U - \phi^L} = \frac{\phi}{\phi^L - \phi^U} - \frac{\phi^L}{\phi^U - \phi^L} = A \phi + a$$

(21)

For $T = \text{const}$ in coexisting $\phi^L = \text{const}$ and $\phi^U = \text{const}$, for the arbitrary total concentration, $\phi = \phi$, the mixture, and then one can define coefficients: $a = \phi^U/(\phi^U - \phi^L) = \text{const}$ and $A = 1/(\phi^U - \phi^L) = \text{const}$, $a = \phi^L/(\phi^L - \phi^U) = A \phi^U = \text{const}$. The linear isothermal behavior resulted from eq 21 is validated by experimental data, as shown in Figure 14. For different temperatures, one obtains a set of lines that intersects for $\phi = \phi_C$. Hence, the critical concentration can be estimated.
The knowledge of the impact of pressure on the critical consolute temperature is essential for explaining properties observed in temperature tests under atmospheric pressure. For instance, the value of \( (dT_C/dP) \) is contained in critical amplitudes \(^{59-62}\):

\[
E^* \propto \left( \frac{2}{\ell_0} \frac{dT_C}{dP} + \frac{dT_C}{dP} \right) \tag{A1a}
\]

\[
C^* = \frac{\rho_C}{\alpha(\alpha-1)} \frac{dT_C}{dP} \tag{A1b}
\]

\[
R_\xi = \xi^o \left( \frac{\alpha A^* \rho_C}{(dT_C/dP)\ell_0} \right) \approx \left( \frac{\rho_C}{4\pi} \right)^{1/d} \approx 0.271 \tag{A1c}
\]

where parameters are related to the behavior for dielectric constant, specific heat \( c(T) = c_C + c_T + C \Gamma^{\alpha} + \ldots \), the thermal expansion coefficient \( \alpha(T) = \alpha_C + \alpha_T + A^\alpha \Gamma^{\alpha} + \ldots \), and density \( \rho(T) = \rho_C + \rho_T + \Theta \Gamma^{\alpha} + \ldots \), and the correlation length \( \xi(T) = \xi^o \Gamma^{\alpha} \). They describe changes above the critical consolute temperature \( T > T_c \) (\( P = \text{const} \)), as the function of \( t = (T - T_c)/T_c \). \( R_\xi \) is the universal “critical” coefficient; note that it is determined solely by values of dimensionalities \( d \) and \( n_{\text{top}} \), what is the actual prediction for universal properties within the Physics of Critical Phenomena.\(^3\)

Worth recalling are unique features of critical mixtures that can appear because of the selection of components. For instance, in methanol--cyclohexane mixtures, matching of densities causes that phenomena generally expected in the Space Lab appear.\(^62\) For nitroethane--isooctane critical mixture, matching of refractive indexes makes the critical opalescence almost absent.\(^60\) One can also tune dielectric constant or viscosity.\(^63\)

### APPENDIX 2

In ref 40, the pressure evolution of the critical consolute temperature in \( n \)-alkane--oligostyrene mixtures of limited miscibility was tested.

Based on these experimental data, Figure A1 was prepared, assuming critical consolute temperatures under atmospheric pressure as the reference. It shows explicit the change of the sign of \( dT_c/dP \) occurring on increasing the length of \( n \)-alkane and also on compressing. Solid curves show that the possibility of portraying \( T_c(P) \) experimental data via eq 12.
Figure A1. Pressure changes of critical temperatures for oligostyrene—n-alkane critical mixtures. As a reference, values of $T_C$ under atmospheric pressure are assumed. The structures of styrene and polystyrene units are shown. Solid curves are related to eq 12. The authors are grateful to Imre for experimental data, first published in ref 40, but without the normalized scale and the functional portrayal.

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A.D.-R. and S.J.R. are responsible for critical concepts of the report, the analysis, and paper writing. They also carried out the majority of experimental results. J.K. is accountable for the majority of experimental results and the preparation of photos.

**Notes**

The authors declare no competing financial interest.

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