

An apparent critical point in binary mixtures of *m*-nitrotoluene with *n*-alkanes; experimental and simulation study

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Abstract

We report a simulation study of the system *m*-nitrotoluene–*n*-decane, showing an apparent critical point, which lies in their metastable, experimentally inaccessible state, below their melting point, affecting physical and chemical properties of this systems in the stable liquid phase. The presence of the apparent critical point in this mixture has been experimentally observed by the non-linear dielectric effect (NDE) as an anomalous increase in the NDE values typical of critical concentrations. The phase diagrams of this mixture have evidenced that the system freezes in the homogenous phase and its melting point is higher than its critical temperature [M. Śliwińska-Bartkowiak, B. Szurkowski, T. Hilczer, Chem. Phys. Lett. 94 (1983) 609, M. Śliwińska-Bartkowiak, Ber. Bunsenges. Phys. Chem. 94 (1990) 64, M. Śliwińska-Bartkowiak, Phys. Lett. A 128 (1988) 84]. For such a system, we performed Monte Carlo simulations aimed at analyzing the kind of phase transition observed, and their conditions of their occurrence in a Lennard-Jones mixture. The enthalpy, configurational energy and radial distribution function have been estimated by the MC simulation method in the NPT system. Immiscibility conditions according to Hoheisel [M. Schoen, C. Hoheisel, Mol. Phys. 57 (1986) 65] approach have also been discussed.

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1. Introduction

In recent years the presence of the apparent critical point has been established for a large group of liquid mixtures having a positive mixing enthalpy [1,2,5–10]. The melting point of these mixtures is higher than their critical point. Their critical point falls in the range of metastable states, and direct experimental determination of the critical point in such a systems is usually impossible because of the problem with reaching the desired overcooled state. The presence of such a point affects the physico-chemical properties of the system in the stable liquid phase and is the reason for anomalous behavior of many physical quantities sensitive to the medium inhomogeneities. Critical fluctua-

tions appearing in such a system at temperatures much higher than the critical one are frozen in statu nascendi forming separate molecular structures also in the solid phase. In classical critical mixtures [11] in which the phase separation is observed, the density correlation range is described by the exponential law

$$\xi = \xi_0 \left(\frac{T - T_c}{T_c} \right)^{-\nu}, \quad (1)$$

where the mean range of molecular interactions correlation for the liquids of small molecules is $\xi_0 \sim 0.2$ nm. The critical range in which large density fluctuations lead to formation of two phases from the single homogeneous phase is characterized by a correlation range of 10^2 nm, which tends to infinity at the critical point. At temperatures much higher than T_c , the value of ξ , decreases according to Eq. (1). In mixtures exhibiting apparent critical point behavior,

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the increase in the correlation range ceases on freezing, and the value of ξ remains finite.

The methods allowing monitoring of the increase in the correlation range in critical systems are able to detect inhomogeneities in the structure of the mixture already at temperatures much higher than T_c , and are good detectors of the pre-critical phenomena. Such a method is that based on the phenomenon of non-linear dielectric effect (NDE), defined as a change in the electric permittivity induced by a strong electric field E :

$$\frac{\Delta\epsilon}{E^2} = \frac{\epsilon^E - \epsilon^0}{E^2}, \quad (2)$$

where ϵ^E is the permittivity in the field E , and ϵ^0 that in its absence. The sign and magnitude of NDE of a liquid depends on the kind of inter- and intramolecular interactions and their energies. The method based on NDE measurements has been applied in investigation of interdipolar interactions, intermolecular rotation, formation of hydrogen bonds and molecular associations [12–17]. Since NDE is sensitive to inhomogeneities of the medium, it has been applied to study mixtures with limited miscibility and a critical point [17–25]. The earliest investigation carried out by Piekara [18,19], proved that in the vicinity of the critical point NDE takes high positive values, increasing as the temperature approaches T_c . Later, using the drop model of phase transitions [26,27], Goulon and Greffe [28,29] have shown that the fluctuation in NDE is described by the critical exponent Φ , according to

$$\left(\frac{\Delta\epsilon}{E^2}\right)_f = \left(\frac{\Delta\epsilon}{E^2}\right) - \left(\frac{\Delta\epsilon}{E^2}\right)_b = A \left(\frac{T - T_c}{T_c}\right)^{-\Phi}, \quad (3)$$

where $(\Delta\epsilon/E^2)_f$ – is the measured effect of NDE, and $(\Delta\epsilon/E^2)_b$ – the background effect, typical for the mixture in absence of critical fluctuations, A – amplitude, T_c – critical temperature and the critical exponent Φ is defined by the relation

$$\Phi = \gamma - 2\beta = (2 - \eta)\nu - 2\beta, \quad (4)$$

where γ and β are the usual critical exponents for the isothermal compressibility and density difference between the two phases respectively, and η and ν are the critical exponents of the total correlation function $g(r)$ and the correlation length ξ .

An increase in NDE in the vicinity of critical concentrations has been observed at temperatures even 20–50 K above T_c [17,22,23]. The anomalous increase in NDE near the phase transition point has been attributed to the increasing intensity of molecular fluctuations in the region of critical concentrations when the temperature reaches its critical value.

NDE investigation has proved that the mixtures of *o*-nitrotoluene and *n*-alkanes are classical critical mixtures, whereas mixtures of *m*-nitrotoluene and *n*-alkanes and *o*- and *m*-nitrotoluene with cycloalkanes are characterized

by an NDE typical of critical mixtures, but solidify in the homogeneous phase [1,5–7,30].

An attempt has been made at interpreting the phenomena taking place in the two types of mixtures by assuming the same mechanism in both cases. The attempt was justified by the fact that for both types of mixtures, the temperature dependence of NDE related to critical fluctuations is described by a power law with the same values of the critical exponents [2,6]. On the other hand, analysis of the phase diagrams $(T, x)_p$ showing the melting points as functions of concentrations x of the *m*-nitrotoluene–alkane mixtures under atmospheric pressure, proved that in the concentration range in which NDE anomalies were observed, there exist two kinds of molecular compounds: one richer and the other poorer in the polar component [7]. These compounds, unstable in the liquid phase, remain distinct in the solid phase. Interpreted as molecular clusters characteristic of a precritical state, they point to the possibility of freezing of the critical fluctuations of the system. The hypothetical critical temperatures of these mixtures estimated from the analysis of the second virial coefficients fell in the range of temperatures below their melting points, corresponding to a metastable, experimentally inaccessible state. The results of the above discussed studies have proved that the mixtures of *m*-nitrotoluene with alkanes as well as *o*- and *m*-nitrotoluene with cycloalkanes and 1,3-dimethoxybenzene with alkanes in their metastable state below their melting point, show an apparent critical point affecting physical and chemical properties of these systems in the stable liquid phase.

In this paper we report the results of Monte Carlo simulation performed for the mixture *m*-nitrotoluene–*n*-decane, aimed at analyzing the kinds of phase transitions observed, and the conditions of their occurrence in Lennard-Jones mixtures. The enthalpy, configurational energy and radial distribution functions have been estimated using the MC simulation method in the NPT ensemble. Immiscibility conditions according to the Hoheisel [4] approach are also discussed.

2. Simulation method

A model of the mixture of metanitrotoluene–*n*-decane was studied by Monte Carlo simulations in the (N, P, T) ensemble (where the number of particles, N , is fixed, and both pressure, P , and temperature T , are constant). The molecules were contained in a cubic box with periodic boundary conditions in all three dimensions. The system studied is a mixture of dipolar and non-dipolar molecules. For such system we can apply the potential:

$$u(r_{ij}) = 4\epsilon_x \left[\left(\frac{\sigma_x}{r_x}\right)^{12} - \left(\frac{\sigma_x}{r_x}\right)^6 \right] - \frac{\alpha\mu^2}{r_x^6}. \quad (5)$$

The model has been successfully applied to a mixture nitrobenzene–cyclododekane, showing similar properties [31]. This potential takes into regard the dipolar moment of the

dipolar molecule (μ) and polarizability (α). In the mixture studied there are three possible types of interactions: non-dipolar molecule–non-dipolar molecule (*n*-decane–*n*-decane) (u_{11}), dipolar molecule–dipolar molecule (*m*-nitrotoluene–*m*-nitrotoluene) (u_{22}) and non-dipolar molecule–dipolar molecule (*m*-nitrotoluene–*n*-decane) (u_{12}). For the first type interactions u_{11} : $\mu = 0$, and Eq. (5) takes the form of the Lennard-Jones potential:

$$u(r_{ij}) = 4\epsilon_{11} \left[\left(\frac{\sigma_{11}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{11}}{r_{ij}} \right)^6 \right]. \quad (6)$$

For the interactions u_{22} and u_{12} Eq. (5) can also be expressed in the form of the Lennard-Jones potential [10]:

$$u(r_{ij}) = 4\epsilon_x \left[\left(\frac{\sigma_x}{r_{ij}} \right)^{12} - \left(\frac{\sigma_x}{r_{ij}} \right)^6 \right]. \quad (7)$$

These two transformations require a conversion of the parameters ϵ and σ . For u_{22} ($\alpha = 22$) the values of ϵ and σ were taken after [10], while for u_{12} ($\alpha = 12$) we have

$$\sigma_{12} = \xi^{-\frac{1}{6}} \left(\frac{\sigma_{11} + \sigma_{22}}{2} \right), \quad (8)$$

$$\epsilon_{12} = \xi^2 \sqrt{\epsilon_{11}\epsilon_{22}}, \quad (9)$$

where

$$\xi = 1 + \frac{\alpha_1 \mu_2^2}{4\sigma_{11}^3} \sqrt{\frac{\epsilon_{22}}{\epsilon_{11}}} \quad (10)$$

For the mixture studied we have $\epsilon_{22}/k = 639.33$ K, $\sigma_{22} = 5.66$ Å, $\epsilon_{12}/k = 591.19$ K, $\sigma_{12} = 6.38$ Å, $\epsilon_{11}/k = 513.07$ K, $\sigma_{11} = 7.14$ Å.

The values of σ_{12} and ϵ_{12} correspond to: $\sigma_{12} = 1.00 * \sigma_{12LB}$, $\epsilon_{12} = 1.03 * \epsilon_{11LB}$, where ϵ_{12LB} and σ_{12LB} are the parameters ϵ_{12} and σ_{12} calculated from the Lorentz–Berthelot relations [32]:

$$\sigma_{12LB} = \frac{\sigma_{11} + \sigma_{22}}{2}, \quad (11)$$

$$\epsilon_{12LB} = \sqrt{\epsilon_{11}\epsilon_{22}}. \quad (12)$$

It is evidenced that the parameter ξ modifies the Lorentz–Berthelot relation for the parameter ϵ . The dipolar moment of *meta*-nitrotoluene enhances the u_{12} type interactions.

The simulations were performed for $N = 500$ molecules at the concentration for $x_2 = 0.20$ to $x_2 = 0.80$ ($x_2 = 0.54$ corresponds to the experimental pseudo-critical concentration of this mixture [10]). For each value of concentration the study was performed for 16 temperatures from $T^* = 0.3$ to $T^* = 0.6$ ($T^* = kT/\epsilon_{22}$), corresponding to 192–384 K. The pressure was assumed to be $p^* = 2.081 * 10^{-3}$ ($p^* = p\sigma_{22}^3/\epsilon_{22}$) which corresponds to 1 atm. We performed 10^5 Monte Carlo steps (MCSs) to equilibrate the system, followed by 10^5 MCSs to sample the data. However, at the selected temperature and Lennard-Jones interaction parameters we performed 10^7 MCSs to verify the quality of equilibration and sampling.

For each concentration, the temperature dependencies of the volume, enthalpy and configurational energy of the

system were analyzed. Moreover the angular functions [33] were recorded as expressed by

$$Q_l = \sqrt{\frac{4\pi}{2l+1} \sum_{m=-l}^l |\bar{Q}_{lm}|^2}, \quad (13)$$

where

$$\bar{Q}_{lm} = \frac{1}{N_b} \sum Y_{lm}(\theta(r), \phi(r)). \quad (14)$$

In the above formula N_b is the number of nearest neighbors and Y_{lm} is the spherical harmonic. The nearest neighbors were assumed to be the molecules at a distance shorter than 1.3σ . The angular functions were calculated for $l = 4$ and $l = 6$ (the functions Q_4 and Q_6). Analysis of these functions allows identification of the crystalline structure [33]. The shape of the radial distribution functions (g_{11} , g_{12} , g_{22}) were recorded and for each T and e values. The g parameter was found:

$$g = \frac{g_{11 \max} + g_{22 \max}}{2g_{12 \max}}. \quad (15)$$

The parameters $g_{11 \max}$, $g_{22 \max}$ and $g_{12 \max}$ correspond to the first maxima of g_{11} , g_{22} and g_{12} , respectively. According to the Hoheisel and Schoen postulates [4,31] the value of the parameter g indicates if the system tends to phase separate. If no clusters are formed in the system then $g = 1$, but when cluster formation starts $g > 1$. Moreover, the value of g is proportional to the size of the clusters formed.

3. Simulation results

The model of the system *m*-nitrotoluene–*n*-decane was studied by MC–N–P–T simulations for temperatures range 192–384 K and different values of x_2 .

Fig. 1 presents the calculated values of enthalpy and volume for $x_2 = 0.4$. In the vicinity of $T \approx 245$ K a jumpwise change in the functions $H^*(T^*)$ (enthalpy vs. temperature) and $V^*(T^*)$ (volume vs. temperature) was observed, indicating of the first order phase transitions [34]. For temperatures above 245 K the mixture is in the liquid phase. $T_S = 245$ K is the freezing point of the mixture. Interestingly, the angular functions Q_4 and Q_6 (Eq. (13)) calculated for $T < 245$ K do not indicate the presence of any of the structures: fcc, hcp, bcc, sc in the solid phase. The same result is obtained for each concentration x_2 .

Fig. 2 presents the temperature dependence of the parameter g (Eq. (15)) for the concentration $x_2 = 0.4$. The parameter g brings the information on the growth of clusters in the system studied. With decreasing temperature the value of g increases but the increase does not stop at the freezing point of $T = 245$ K. This observation suggests that the growth of clusters in the system has been stopped by the freezing but with not complete phase separation as for the phase separation $g \gg 1$. Therefore, the hypothetical critical point of this mixture is lower than $T_S = 245$ K. The same situation occurs for all concentrations x_2 : for a given

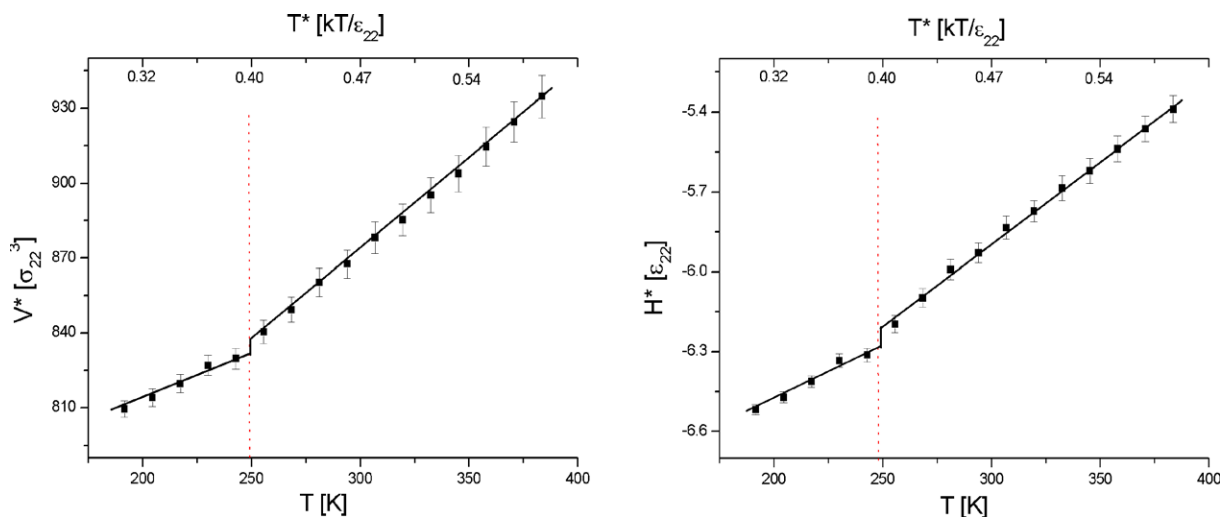


Fig. 1. Temperature dependence of reduced volume V^* and reduced enthalpy H^* for $x_2 = 0.4$. Jumpwise changes in these two parameters appear at $T = 245$ K.

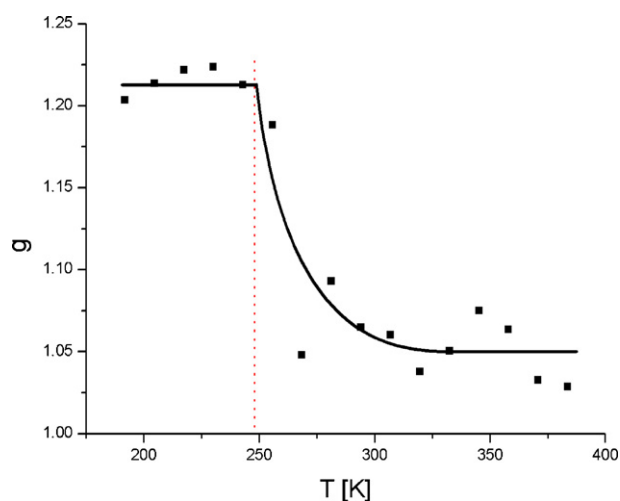


Fig. 2. Temperature dependence of g parameter for $x_2 = 0.4$. With decreasing temperature g increases and stops at $T = 245$ K – the freezing point of the mixture.

concentration x_2 below $T = 245$ K the parameter g is constant and does not depend on temperature. However, the value of g depends on the concentration x_2 for $T < 245$ K, as shown in Fig. 3. For $x_2 = 0.4$ the function shows a clear peak, which means that for this concentration the clusters grow to the largest size. Therefore, $x_2 = 0.4$ must be the critical concentration x_{C2} of this mixture. The experimentally determined critical concentration of this mixture is $x_{C2} = 0.54$ [10]. The difference between the experimental value and the result of the simulations is less than 20%.

Fig. 4 presents the parameter g as a function of concentration x_2 for four different temperatures T . For very high temperature ($T = 380$ K) $g(x_2)$ is constant, for all concentrations $g = 1$, which means no molecular clusters in the system. With decreasing temperature the peak at $x_2 = 0.4$ becomes more pronounced and for $T = 255$ K (only a bit

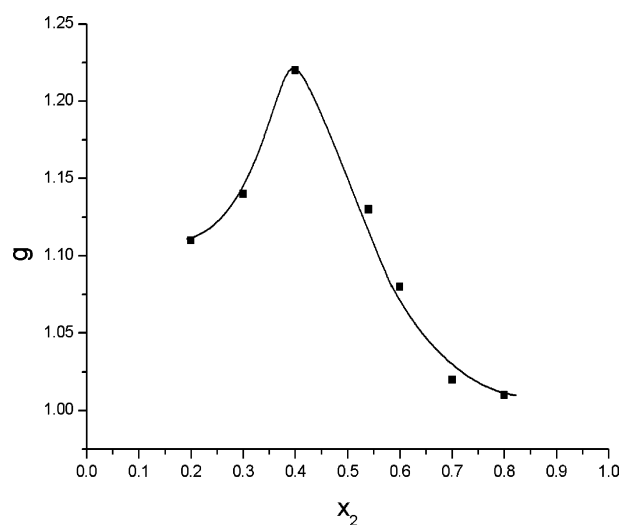


Fig. 3. Parameter g as a function of concentration x_2 for $T < 245$ K. A distinct peak appears at $x_2 = 0.4$.

higher than the freezing point $T = 245$ K) it is quite well developed. This result means that the largest clusters appear for $x_2 = 0.4$. For temperatures lower than $T_S = 245$ K the $g(x_2)$ is constant, which means that the freezing has stopped the growth of the clusters for all concentrations x_2 and the phase separation has not been complete.

The results of molecular simulations relatively well describe the experimentally observed behavior of the mixture of *m*-nitrotoluene–decane [2]. The concentration dependence of NDE for different temperatures has revealed the greatest NDE increase at about $x_2 = 0.54$ (Fig. 5). The anomalous increase in NDE with decreasing temperature for the system of this concentration is related to the increase in the range of correlation of the density fluctuations typical of precritical systems.

Table 1 presents a comparison of the results of simulation with the experimental ones. The results differ by about

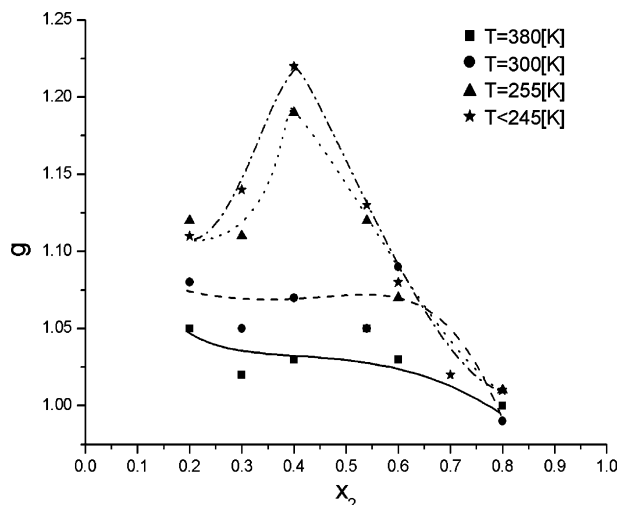


Fig. 4. Parameter g as a function of concentration x_2 for four temperatures: square and solid line – $T = 380$ K, circle and dash line – $T = 300$ K, triangle and dot line – $T = 255$ K, asterisk and dash-dot line – $T < 245$ K. With decreasing temperature the peak at $x_2 = 0.4$ becomes more pronounced. For $T < 245$ K the value of g is constant for all concentrations x_2 because the system freezes.

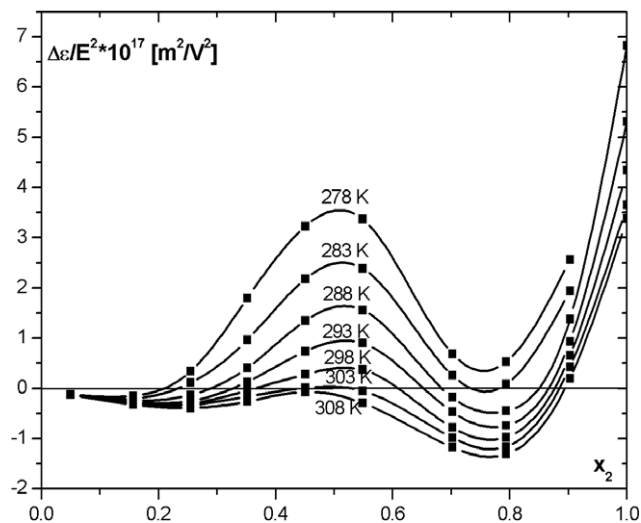


Fig. 5. NDE versus concentration for system *m*-nitrotoluene–*n*-decane at various temperatures.

Table 1

The critical concentrations, critical temperature and melting point obtained in the experiment and in the simulations

	Experiment	Simulation
Critical concentration x_{C2}	$x_{C2} = 0.54$	$x_{C2} = 0.4$
Critical temperature T_C	$T_C = 273$ K	$T_C < 245$ K
Melting temperature T_S	$T_S = 281$ K	$T_S = 245$ K

14% for the critical concentration and by about 13% for the melting point [3].

4. Conclusions

The results of the presented studies prove that the use of modified form of the Lennard-Jones potential, taking into account dipolar momentum, allows us to describe the thermodynamics of the studied systems relatively well and to observe the apparent critical point. Similar studies are planned for the a whole group of mixtures showing a similar precritical effect. The results will be compared with the experimental values.

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