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An apparent critical point in binary mixtures of nitrotoluene with alkanes: Experimental and simulation study

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Abstract. We report an experimental and simulation study of binary mixtures of o- and m-nitrotoluene with decane and hexadecane. Mixtures of o-nitrotoluene with alkanes form a classical critical mixtures, but m-nitrotoluene / n – alkane mixtures show an apparent critical point, which lies in a metastable, experimentally inaccessible state, below the 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 Nonlinear Dielectric Effect (NDE) measurements as an anomalous increase in the NDE values typical of critical concentrations. The phase diagram of this mixture shows evidence that the system freezes in the homogenous phase and its melting point is higher than its critical temperature [1–3]. For such a system, we performed Monte Carlo simulations aimed at analysing the kind of phase transitions observed, and the conditions of their occurrence in a nonpolar/dipolar mixture. We perform studies for classical critical systems of o-nitrotoluene with decane and hexadecane The enthalpy, configurational energy and radial distribution function have been estimated by the MC simulation method in the NPT system. Immiscibility conditions according to Schoen and Hoheisel [4] approach are also discussed.

Keywords: Metastable mixtures, MC simulations, near critical point, nonlinear dielectric effect

1. Introduction

The presence of the apparent critical point has now 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 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 behaviour of many physical quantities sensitive to the inhomogeneity of the medium. Critical fluctuations appearing in such a system at temperatures well above the critical are frozen *in statu nascendi* forming separate molecular

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structures 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:

$$\xi = \xi_0 \left(\frac{T - T_C}{T_C} \right)^{-\nu} \tag{1}$$

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 characterised by a correlation range of 10^2 nm, which tends to infinity at the critical point. At temperatures much higher than Tc, the value of ξ decreases according to Eq. (1). In mixtures exhibiting apparent critical point behavior, 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 at temperatures well above Tc, and are good detectors of pre-critical phenomena. One of such method is that based on the phenomenon of Nonlinear Dielectric Effect (NDE), defined as a change in the electric permittivity induced by a strong electric field E:

$$\frac{\Delta\varepsilon}{E^2} = \frac{\varepsilon^E - \varepsilon^0}{E^2} \tag{2}$$

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 NDE method has been applied in the 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 the NDE takes high positive values, increasing as the temperature approaches Tc. Later, using the droplet model of phase transitions [26,27], Goulon & Greffe [28,29] have shown that the fluctuation in NDE is described by the critical exponent Φ, according to:

$$\left(\frac{\Delta\varepsilon}{E^2} \right)_{fl} = \left(\frac{\Delta\varepsilon}{E^2} \right) - \left(\frac{\Delta\varepsilon}{E^2} \right)_b = A \left(\frac{T - T_C}{T_C} \right)^{-\phi} \tag{3}$$

where: $(\Delta\varepsilon/\mathrm{E}^2)$ – is the measured effect of NDE, and $(\Delta\varepsilon/\mathrm{E}^2)_b$ is the background effect, for the mixture in absence of critical fluctuations, A is the amplitude, T_C – the critical temperature and the critical exponent Φ is defined by the relation:

$$\Phi = \gamma - 2\beta = (2 - \eta)\,\nu - 2\beta \tag{4}$$

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 even at temperatures 20-50K above Tc [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 approaches its critical value. NDE investigations have proved that 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 characterised 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 exists two kinds of molecular clusters: one richer and the other poorer in the polar component [7]. These clusters, 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 analysis of the second virial coefficients [10], fell in the range of temperatures below their melting points, corresponding to a metastable, experimentally inaccessible state. The results of these studies have proved that 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 simulations performed for a simple model of mixtures of o- and m-nitrotoluene with n – decane and n – hexadecane, aimed at analysing 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 Schoen and Hoheisel [4] approach are also discussed.

2. Simulation method

A model of the mixtures of m- and o-nitrotoluene with decane and hexadecane [10] were 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 3 dimensions. The systems studied are a mixtures of dipolar and non-dipolar molecules. For such systems we can apply the potential:

$$u\left(r_{ij}\right) = 4\varepsilon_{\alpha}\left[\left(\frac{\sigma_{\alpha}}{r_{\alpha}}\right)^{12} - \left(\frac{\sigma_{\alpha}}{r_{\alpha}}\right)^{6}\right] - \frac{\alpha\mu^{2}}{r_{\alpha}^{6}} \tag{5}$$

This model has been successfully applied to a mixture nitrobenzene – cyclododecane, showing similar properties [31]. This potential takes into regard the dipolar moment of the dipolar molecule (μ) and polarizability (α). In the mixtures studied there are three possible types of interactions: nonpolar molecule – nonpolar molecule (u_{11}), dipolar molecule – dipolar molecule (u_{22}) and nonpolar molecule – dipolar molecule (u_{12}). For the first type interactions u_{11}: $\mu = 0$, and Eq. (5) takes the form of the L- J potential.

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

$$u\left(r_{ij}\right) = 4\,\varepsilon_{\alpha}\left[\left(\frac{\sigma_{\alpha}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{\alpha}}{r_{ij}}\right)^{6}\right] \tag{6}$$

Table 1
ε_{12}/k and σ_{12} values for studied mixtures

mixture	m-nitrotoluene – decane	m-nitrotoluene – hexadecane	o-nitrotoluene – decane	o-nitrotoluene – hexadecane
ε_{12}k	591,19[K]	580,82[K]	649,58[K]	
σ_{12}	6,383[A]	6,973[A]	6,387[A]	6,976[A]

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:

$$\sigma_{12} = \xi^{-\frac{1}{6}} \left(\frac{\sigma_{11} + \sigma_{22}}{2} \right) \tag{7}$$

$$\varepsilon_{12} = \xi^{2} \sqrt{\varepsilon_{11}\varepsilon_{22}} \tag{8}$$

where:

$$\xi = 1 + \frac{\alpha_1 \mu_2^2}{4\sigma_{11}^3} \sqrt{\frac{\varepsilon_{22}}{\varepsilon_{11}}} \tag{9}$$

The values of ε_{22}/k and σ_{22} for o- and m-nitrotoluene are: 625,41[K]; 5,660[A] and 639,33[K]; 5,660[A] respectively and for ndecane and nhexadecane: ε_{11}/k and σ_{11} are 513,07[K]; 7,140[A] and 645,32[K]; 7,140[A], ε_{12}/k and σ_{12} values for studied mixtures are presented in Table 1 [10].

The values of σ_{12} and ε_{12} in mixtures relative to the values calculated from the Lorentz – Berthelot relations:

$$\sigma_{12LB} = \frac{\sigma_{11} + \sigma_{22}}{2} \tag{10}$$

$$\varepsilon_{12LB} = \sqrt{\varepsilon_{11}\varepsilon_{22}} \tag{11}$$

are: $\sigma_{12} = 0.997{*}\sigma_{12LB}$, $\varepsilon_{12} = 1.032{*}\varepsilon_{11LB}$ (m-nitrotoluene – decane), $\sigma_{12} = 0.998{*}\sigma_{12LB}$, $\varepsilon_{12} = 1.029{*}\varepsilon_{11LB}$ (m-nitrotoluene – n-hexadecane) $\sigma_{12} = 0.998{*}\sigma_{12LB}$, $\varepsilon_{12} = 1.025{*}\varepsilon_{11LB}$ (o-nitrotoluene – n-decane), $\sigma_{12} = 0.998{*}\sigma_{12LB}$, $\varepsilon_{12} = 1.022{*}\varepsilon_{11LB}$ (o-nitrotoluene – n-hexadecane).

It is evident that the parameter ξ modifies the Lorentz–Berthelot relation mainly for the parameter ε^{eff}, the σ^{eff} parameter is practically the same as the LJ σ parameter. The dipolar moment of nitrotoluene enhances the u$_{12}$type interactions. The dipolar moment of m-nitrotoluene (13.6*10^{-30} Cm) is larger than dipolar moment of o-nitrotoluene (12.3*10^{-30} Cm), maling the $\varepsilon_{12}^{\text{eff}}$ parameter stronger for m-nitrotoluene mixtures than for o-nitrotoluene.

All simulations were performed for $N = 500$ molecules for concentrations in the range for x$_2 = 0.20$ to x$_2 = 0.80$. For each value of concentration the study was performed for 16 temperatures from T* $=$ 0.3 to T* $=$ 0.6 (where T* $=$ kT/ε_{22}), corresponding to 192 K–384 K for m-nitrotoluene- mixtures and 188 K–375 K for o-nitrotoluene- mixtures. The pressure was assumed to be $p{*} = 2{,}081{*}10^{-3}$ for m-nitrotoluene- mixtures and $p{*} = 2{,}127{*}10^{-3}$ for o-nitrotoluene- mixtures (where $p{*} = \mathrm{p}\sigma_{22}^3/\varepsilon_{22}$) which corresponds to 1 Atm. We performed 10^5 Monte Carlo Steps to equilibrate the system, followed by 10^5 steps to sample the data. However, at the selected temperature and Lennard-Jones interaction parameters we performed 10^7 steps 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 analysed. Moreover the angular functions [32] were recorded as expressed by:

$$Q_l = \sqrt{\frac{4\pi}{2l+1} \sum_{m=-l}^{l} \left| \bar{Q}_{lm} \right|^2} \tag{12}$$

where:

$$\bar{Q}_{lm} = \frac{1}{N_b} \sum Y_{lm} \left(\theta \left(r \right), \phi \left(r \right) \right) \tag{13}$$

In the above formula N_b is the number of nearest neighbours and Y_{lm} is the spherical harmonic. The nearest neighbours 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 [32]. The shape of the radial distribution functions (g_{11}, g_{12}, g_{22}) were recorded for each T values, and the g parameter was found:

$$g = \frac{g_{11\,\max} + g_{22\,\max}}{2g_{12\,\max}} \tag{14}$$

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 Schoen and Hoheisel postulates [4] 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 systems m- and o-nitrotoluene withn n- decane and n-hexadecane was studied by MPT-MC simulations for the temperature range $T^* = 0.3$ to $T^* = 0.6$ and different values of x_2.

Figure 1 presents the calculated values of reduced volume (V^* in σ_{22}^3) for m-nitrotoluene – n-decane (a) and o-nitrotoluene – n-decane (c) and reduced enthalpy (H^* in kt/ε_{22}) for m-nitrotoluene – n-decane [33], (b) and o-nitrotoluene – n-decane (d), for their pre-critical and critical concentrations x_2 (for more details see Figs 5 and 7). For both mixtures in the vicinity of $T^* \approx 0.39$ a jumpwise change in the functions $H^*(T^*)$ (Fig. 1b and 1d) and $V^*(T^*)$ (Fig. 1a and 1c) was observed, indicating a first order phase transition [34]. For temperatures $T^* > 0.39$ the mixtures are in the liquid phase. $T^*_S = 0.39$ is the freezing point of the mixtures. Interestingly, the angular functions Q_4 and Q_6 Eq. (12) calculated for $T^* < 0.39$ 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 for these mixtures. The freezing temperatures in reduced units are the same for m- and o-nitrotoluene mixtures but m-nitrotoluene and o-nitrotoluene have different ε_{22} values, it being larger for m-nitrotoluene (Table 1). The relation between reduced temperature and absolute temperature is $T^* = kT/\varepsilon_{22}$ and $T^* = 0.39$ (solidification of m- or o-nitrotoluene – n-decane mixtures) corresponds to $T = 249$K for m-nitrotoluene – n-decane and to $T = 244$K for o-nitrotoluene – n-decane.

In Fig. 2. are presented the calculated values of reduced volume and enthalpy for m- and o-nitrotoluene with hexadecane. The results are similar to those for m- and o-nitrotoluene – decane mixtures (Fig. 1)

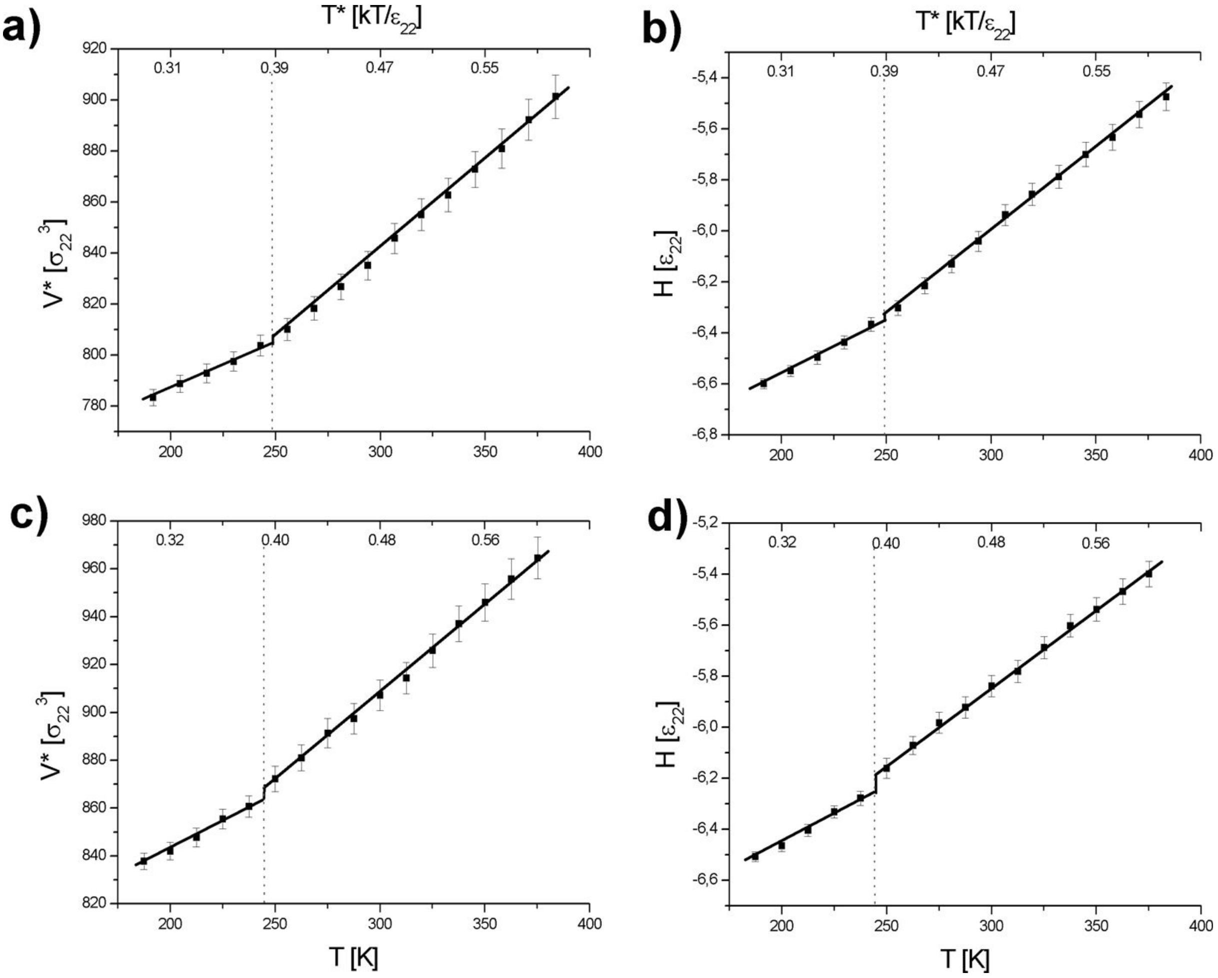

Fig. 1. Temperature dependence of reduced volume (V*) and reduced enthalpy (H*) for the systems: a) and b) m-nitrotoluene – decane, and c) and d) o-nitrotoluene – decane for their pre-critical and critical concentrations x_2. (for m-nitrotoluene – decane $x_2 = 0.49$, for o-nitrotoluene – decane $x_2 = 0.38$ – for more details see Figs 5 and 7).

but in this case the freezing temperature $T^*_S \approx 0.41$, which corresponds to $T_S = 263$ K for the m-nitrotoluene – n-hexadecane and $T_S = 256$ K to o-nitrotoluene – n-hexadecane systems. The freezing temperatures of these systems are higher than for the mixtures of these dipolar liquids with n-decane (Fig. 1). These results clearly show that the freezing temperature of the systems studied depends on the ε parameteters; ε_{11} for n-decane is lower than for n-hexadecane and freezing temperatures of the mixtures of dipolar liquids with n-decane are lower than with n-hexadecane. Also, regarding freezing temperature of the mixtures of o-and m-nitrotoluene with the same alkane, we observe that for higher ε_{22} value (m-nitrotoluene) the freezing temperature of the mixture is higher than for mixtures with lower value of ε_{22} (o-nitrotoluene).

Figure 3 presents the temperature dependence of the g parameter Eq. (14) for the pre-critical concentrations for m-nitrotoluene – n-decane and m-nitrotoluene – n-hexadecane. The g parameter can give information on the growth of clusters in the system studied. For both mixtures, with decreasing temperature the g value increases but the increase ceases at the freezing point ($T^* = 0.39$ for m-nitrotoluene –

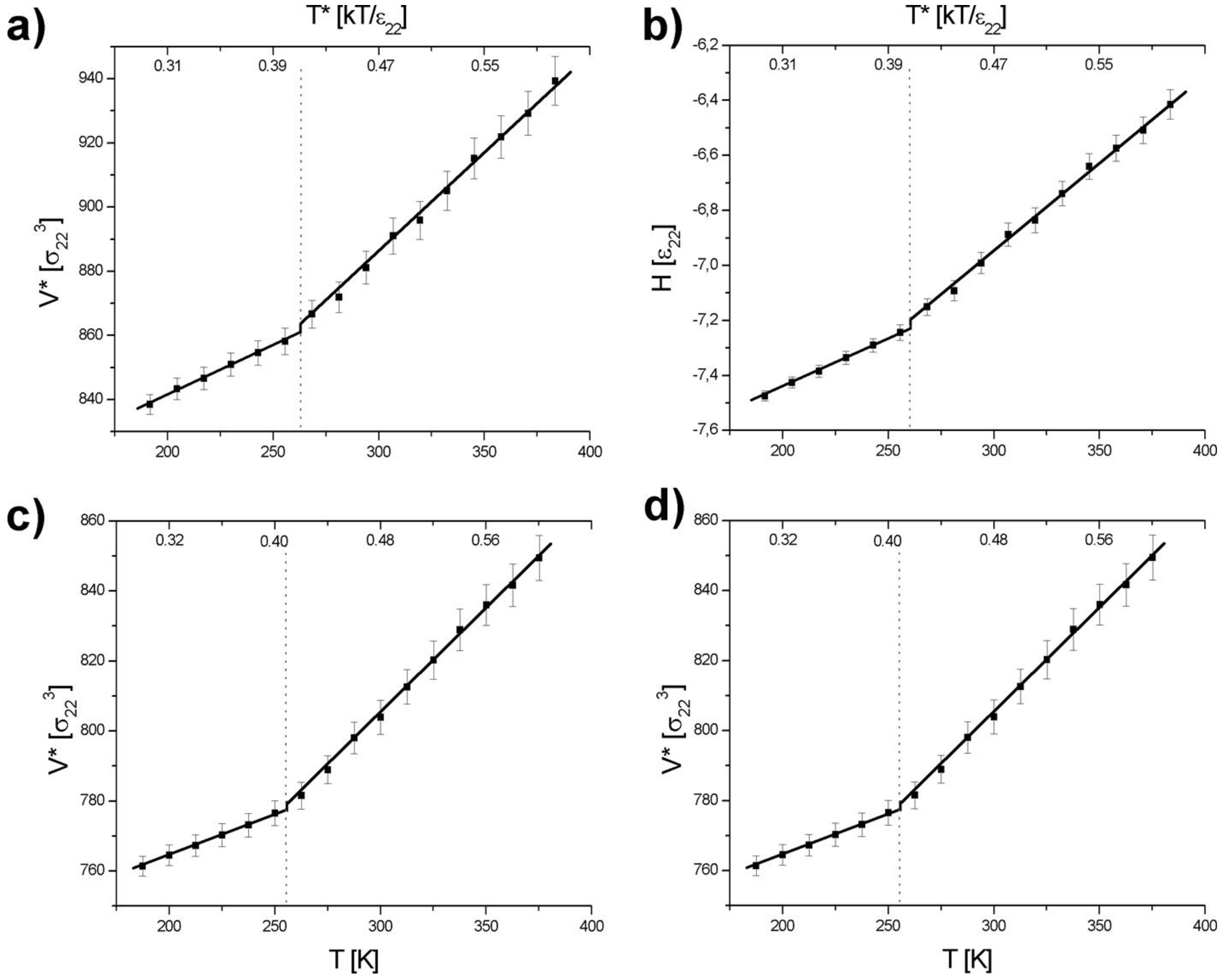

Fig. 2. Temperature dependence of of reduced volume (V*) and reduced enthalpy (H*) for the systems: a) and b) m-nitrotoluene – n-hexadecane,) and c) and d) o-nitrotoluene – n- hexadecane for their pre-critical and critical concentrations x_2. (for m-nitrotoluene – n-hexadecane $x_2 = 0.66$, for o-nitrotoluene – n-hexadecane $x_2 = 0.70$ – for more details see Figs 5 and 7).

n-decane and at $T^* = 0.41$ for m-nitrotoluene – n-hexadecane). This observation suggests that the growth of clusters in the system has been stopped by the freezing but with incomplete phase separation. Therefore, the hypothetical critical point of this mixture is lower than the freezing point.

Figure 4 presents the temperature dependence of the g parameter for the critical concentrations for o-nitrotoluene – n-decane (Fig. 4a) and o-nitrotoluene – n-hexadecane (Fig. 4b) mixtures. At the same temperature T* we observe the solidification of the systems, but the g values before solidification are much larger than for the mixtures of m-nitrotoluene with the same alkane. This shows that pre-critical clusters for the o-nitrotoluene mixtures are much larger than for m-nitrotoluene and the o-nitrotoluene systems are very close to their critical temperature. From experiment it is known that o-nitrotoluene-mixtures show a classical critical point at a temperature higher than their melting point, but those results clearly explain the stronger tendency for cluster formation for o-nitrotoluene mixtures than for m-nitrotoluene with alkanes.

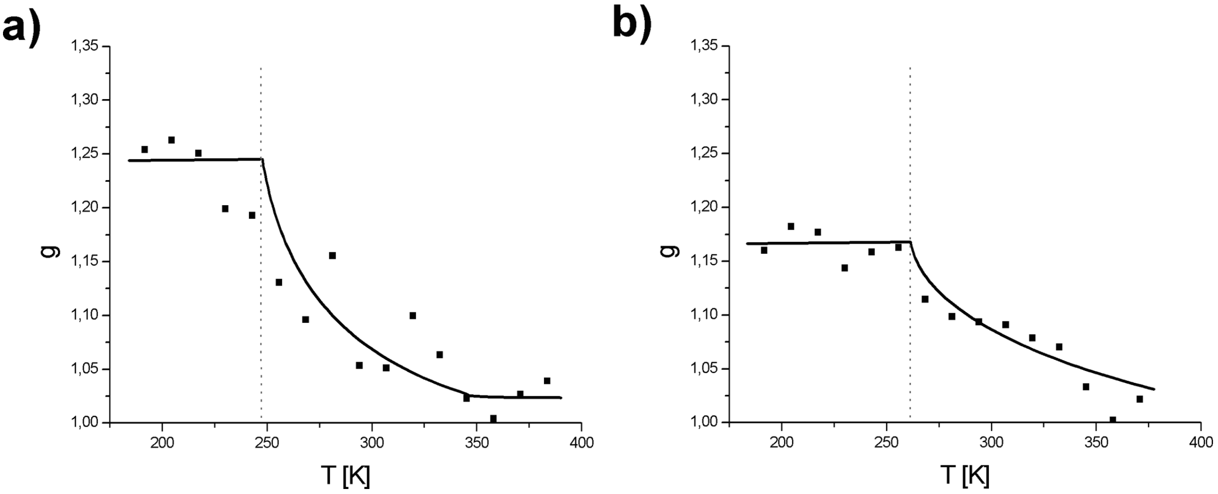

Fig. 3. Temperature dependence of g parameter for a) m-nitrotoluene – n-decane for $x_2 = 0.49$ and b) m-nitrotoluene – n-hexadecane for $x_2 = 0.66$. With decreasing temperature g increases until the freezing point of the mixture is reached.

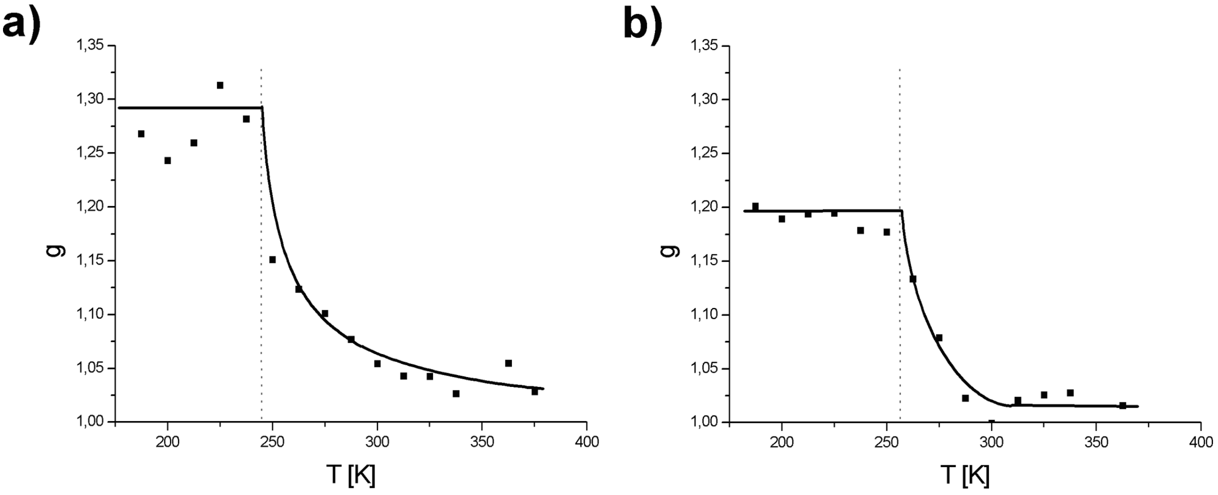

Fig. 4. Temperature dependence of g parameter for a) o-nitrotoluene – n-decane for $x_2 = 0.38$ and b) o-nitrotoluene – n-hexadecane for $x_2 = 0.70$.

In Fig. 5 we present the concentration dependence of the g parameters at a temperature just below T_s, for the systems m-nitrotoluene with n-decane and n-hexadecane. Near the concentrations: $x_2 = 0.49$ (m-nitrotoluene – n-decane) and $x_2 = 0.66$ (m-nitrotoluene – n-hexadecane) the $g(x_2)$ functions show a clear peak, showing that for this concentrations the clusters grow to their largest size. Therefore these values of x_2 must be pre-critical concentrations of these mixtures. Such results of molecular simulations describe the experimentally observed behaviour of the mixture of m-nitrotoluene with n-decane and n-hexadecane relatively well.

Figure 6 presents the NDE (x_2) functions for these systems at various temperatures [1]. The concentration dependence of NDE for different temperatures has revealed the greatest NDE increase at about $x_2 = 0.54$ and $x_2 = 0.68$ for mixtures of m-nitrotoluene with n-decane and n-hexadecane respectively. The anomalous increase in NDE with decreasing temperature for this systems of these concentrations

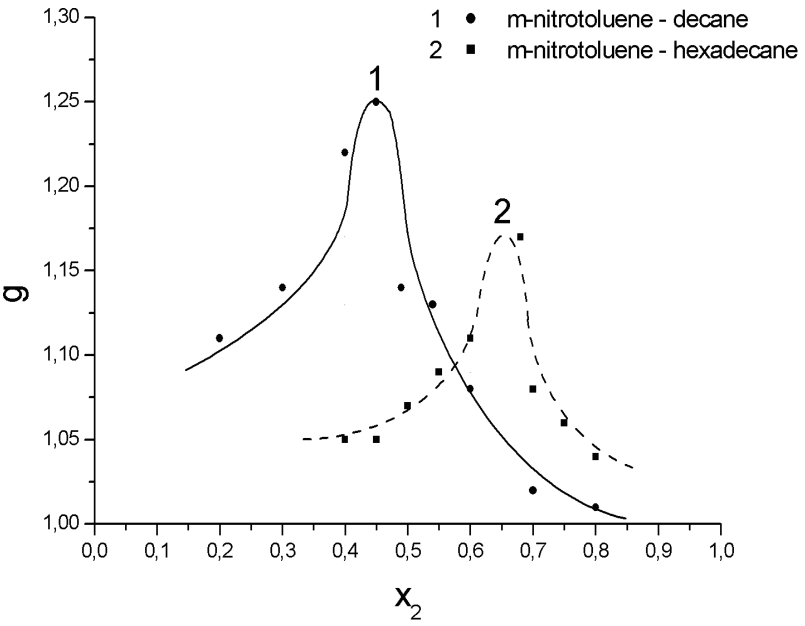

Fig. 5. Parameter g as a function of concentration x_2 for $T < T_S$ for 1: m-nitrotoluene – n-decane, 2: m-nitrotoluene – n-hexadecane. A distinct peak appears at $x_2 = 0.49$ and $x_2 = 0.66$ respectively.

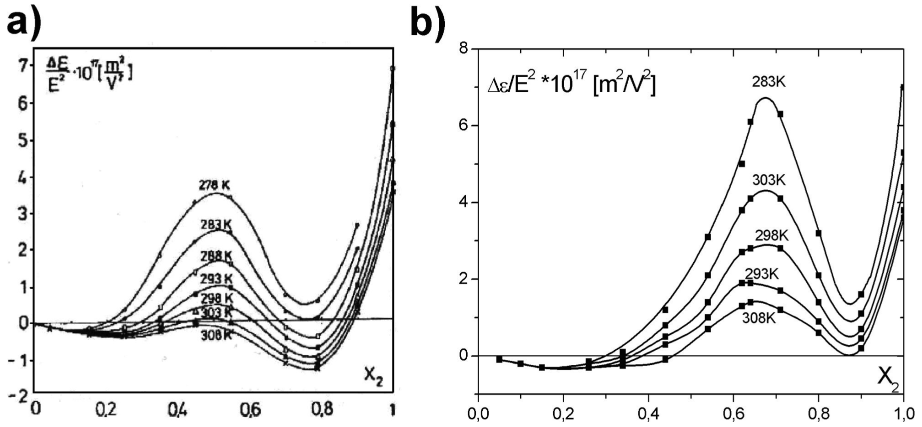

Fig. 6. The NDE vs. x_2 for a) m-nitrotoluene – decane and b) m-nitrotoluene – hexadecane at various temperatures.

is related to the increase in the range of correlation of the density fluctuations typical of pre-critical systems.

In Fig. 7 we present the concentration dependences of the g parameter at a temperature below T_s, for the systems o-nitrotoluene with n-decane and n-hexadecane. Near the concentrations: $x_2 = 0.38$ (o-nitrotoluene – n-decane) and $x_2 = 0.70$ (o-nitrotoluene – n-hexadecane) the $g(x_2)$ function has a peaks, showing that for this concentrations the clusters grow to the largest size. For these systems these are critical concentrations, as is experimentally confirmed by the results of NDE.

Figure 8 presents typical NDE vs. concentration results for critical o-nitrotoluene with n-decane [1] and n-hexadecane [35] systems at various temperatures. An anomalous increase of NDE near the critical

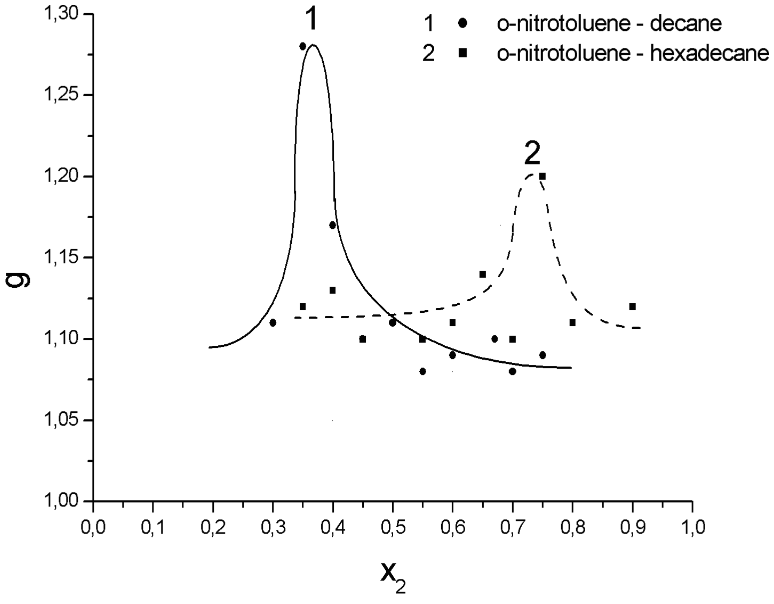

Fig. 7. Parameter g as a function of concentration x_2 for $T < T_S$ for 1: o-nitrotoluene – n-decane, 2: o-nitrotoluene – n-hexadecane. A distinct peak appears at $x_2 = 0.38$ and $x_2 = 0.70$ respectively.

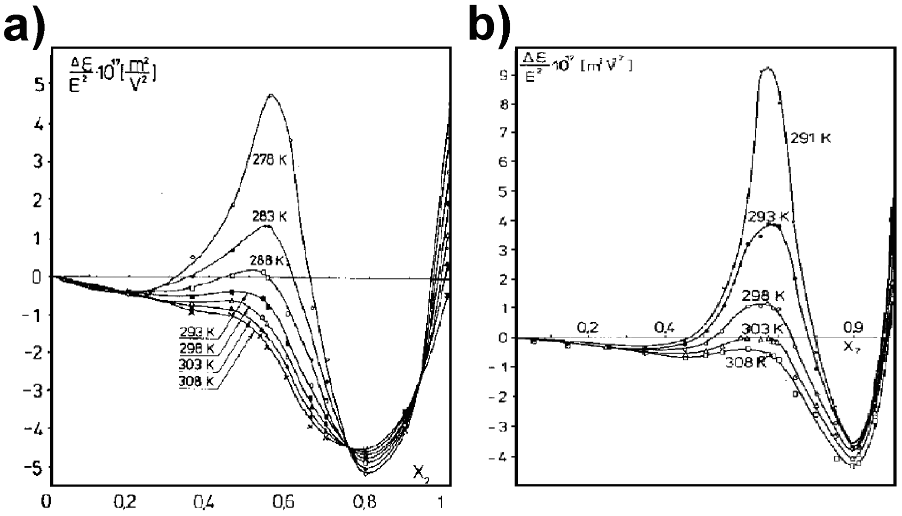

Fig. 8. The NDE vs. x_2 for a) o-nitrotoluene – n-decane and b) o-nitrotoluene – n-hexadecane systems at various temperatures [2].

concentration is observed. The critical concentrations shown in Fig. 8 are very close to the concentrations of the maxima of the $g(x_2)$ functions (Fig. 7).

Figure 9 presents experimental values of critical (for the mixtures of o-nitrotoluene with n-alkanes) and pre-critical (for the mixtures of m-nitrotoluene with n-alkanes) concentrations x_C, vs. number of carbon atoms n in alkanes [10]. The value of critical concentration increases with the number of C atoms and so with increasing molecular volume of n-alkanes. The same values of x_c and precritical values of x'_c for the same alkane are related with the similar molecular volume of o- and m-nitrotoluene [10].

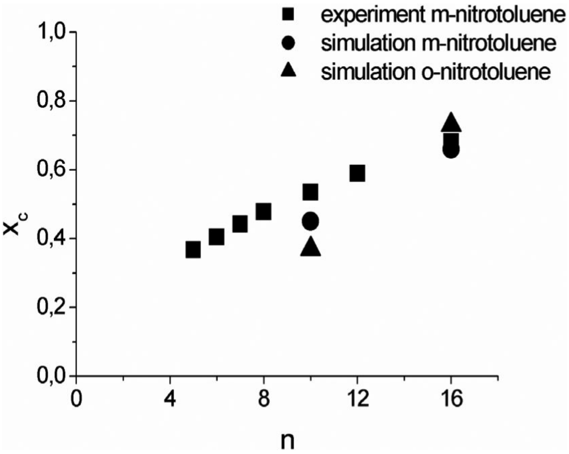

Fig. 9. Experimental and simulation results of critical concentration x_C vs. number of carbon atoms n in n-alkane. For large alkanes the critical concentration is larger than for small alkanes.

The values obtained from the simulations are very close to the experimental results. For longer alkanes the critical concentrations are larger relative to the shorter alkanes, and is related to the increase of σ_{11} parameter of alkanes.

4. Conclusions

The aim of the study was to show that for some critical mixtures of m- nitrotoluene with alkanes, a elevated melting point leads to an apparent critical point in the metastable phase of the system, below its melting point. NDE studies for these mixtures have indicated that the systems show a far pre-critical effect without phase separation, because the effect is inhibited by the system's freezing. The results of the simulations presented show that the use of an effective potential of Lennard – Jones form, taking into account dipolar forces, allows us to describe the thermodynamics of the systems studied relatively well, and to observe the apparent critical point. A comparison of the behavior of m-nitrotoluene – n-alkane systems with classical critical systems (o-nitrotoluene with n-alkanes) shows the influence of the ε_{22} parameter on the freezing temperature of these mixtures and clearly show the tendency to phase separate in both types of mixture. Similar studies are planned for a group of a mixture showing a similar pre-critical effect.

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