An apparent critical point in binary mixtures: Experimental and simulation study

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We report the experimental and simulation studies for the system of nitrobenzene-cyclododecane, showing an apparent critical point, which lies in their metastable, experimentally inaccessible state, below their melting point, affecting physical and chemical properties of this system in the stable liquid phase. The nonlinear dielectric effect (NDE) was measured in the mixture of nitrobenzene with cyclododecane. The mixture has been found to show an apparent critical point which lies below the melting point, manifested as anomalous NDE behavior in the vicinity of the critical concentrations in the stable liquid phase. The melting temperature of this system was estimated using the differential scanning calorimetry method. For such a system, we also performed Monte Carlo (MC) simulations that aimed to analyze the kinds of phase transitions observed and the conditions of their occurrence in Lennard-Jones mixture. The enthalpy, configurational energy, and radial distribution function have been estimated by the MC simulation method in the *N-P-T* system. Immiscibility conditions according to the approach by Schoen and Hoheisel [Mol. Phys. **57**, 65 (1986)] are also discussed. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2191052]

I. 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.[1–7,31] 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 physicochemical properties of the system in the stable liquid phase and is the reason for the anomalous behavior of many physical quantities sensitive to the medium inhomogeneities. Critical fluctuations appearing in such a system at temperatures much higher than the critical one are frozen *in statu nascendi* forming separate molecular structures in the solid phase as well. In classical critical mixtures[8] 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 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, 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 mixture structure already at temperatures much higher than T_C, and are good detectors of the precritical phenomena. Such a method is 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 depend 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.[9–14] Since NDE is sensitive to inhomogeneities of the medium, it has been applied to study mixtures with limited miscibility and a critical point.[14–22] The earliest investigation carried out by Piekara[15,16] 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,[23,24] Goulon and co-workers[25,26] have shown that the fluctuation in NDE is described by the critical exponent Φ according to

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

where $(\Delta \varepsilon / E^2)$ is the measured effect of NDE; $(\Delta \varepsilon / E^2)_b$ is the background effect, typical for the mixture in absence of

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critical fluctuations; A is the amplitude; T_C is the critical temperature; 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 at temperatures even $20-50$ K above T_C.[14,19,20] 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 a NDE typical of critical mixtures, but solidify in the homogeneous phase.[1–4,27]

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.[3,5] 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.[4] 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 the physical and chemical properties of these systems in the stable liquid phase.

In this paper we report NDE measurements for mixtures of nitrobenzene with cyclododecane. The mixture has been found to show an apparent critical point which lies below the melting point of this mixture and is manifested as anomalous NDE behavior in the vicinity of the critical concentrations in the stable liquid phase. For such a system, we also performed Monte Carlo simulation that aimed to analyze the kinds of phase transitions observed and the conditions of their occurrence in Lennard-Jones mixtures. The enthalpy, configura-

tional energy, and radial distribution functions have been estimated using the Monte Carlo (MC) simulation method in the *N-P-T* ensemble. Immiscibility conditions according to the approach by Schoen and Hoheisel[28] are also discussed.

II. EXPERIMENT

A. The method

NDE measurements were performed for the system of nitrobenzene-cyclododecane for various temperatures and molar fractions of nitrobenzene in the mixture, using the setup described in Ref. 29. Tests were conducted for the frequency of the weak measuring field $f_m=1.6$ MHz at the voltage of 1.5 V. The electric field was applied in the form of dc pulses of duration $\Delta t_D=1-8$ ms. The period between pulses was $1-3$ s, and the voltage was $190-1100$ V. The capacitor gap was $0.12-1.20$ mm, and the empty capacitor capacity was $C_0=23.15-2.31$ pF. The temperature was measured by means of a platinum resistor placed on one of the capacitor covers and by a Meratronik V543 Multimeter. The measurements were performed within the temperature range from 313 to 343 K, with the temperature stabilized within 0.02 K.

A Perkin-Elmer DSC7 differential scanning calorimeter was used to determine the melting temperature of the system by measuring the heat released in the melting of the mixture. The temperature scale of the differential scanning calorimetry (DSC) machine was calibrated using the melting temperature of pure nitrobenzene from the literature. The temperatures' scanning rates used from the melting runs varied from 0.2 to 0.5 K/min. The background of the raw DSC spectrum was calculated on the basis of a second order polynomial fit to the measured heat flow away from the signals of interest. The melting temperatures were determined from the position of the peaks of the heat flow signals.

Nitrobenzene was twice distilled under reduced pressure and dried over Al_2O_3. Its conductivity was of the order of 10^{-9} Ω^{-1} m^{-1}; for cyclododecane, after twice distillation, its electrical conductivity was of the order of 10^{-15} Ω^{-1} m^{-1}.

III. RESULTS

The mixtures of nitrobenzene with cycloalkanes, having $6-8$ carbon atoms in the molecule, form classical critical mixtures with phase separation at 277, 268.3, and 267 K, respectively.[30] The aim of the study reported was to establish the effect of a considerable increase in the melting point of a mixture of nitrobenzene-cycloalkane on the properties of the mixture in the stable liquid phase. The solvent was cyclododecane of the melting point $T_m=362$ K. The method used for monitoring the possible increase in the correlation range typical of the precritical effects was based on NDE.

NDE measurements were performed for the system of nitrobenzene-cyclododecane in the temperatures of 345 -315 K for the whole concentration range of nitrobenzene in the mixture. Figures 2(a)–2(d) present NDE versus temperature for four concentrations, expressed as a mole fractions of nitrobenzene in solution x_2. For the concentrations $x_2=0.249$ and $x_2=0.772$, NDE shows a negative value, decreasing with decreasing temperature, typical of the orientational
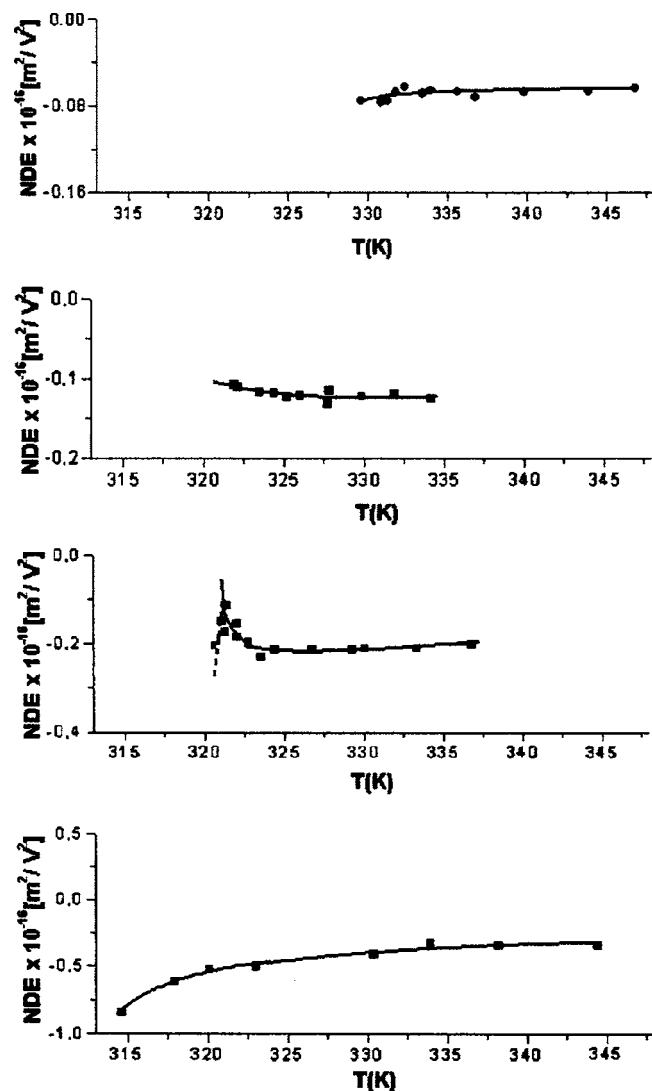
FIG. 1. NDE as a function of temperature in the system of nitrobenzene-cyclododecane for four concentrations: (a) $x_2=0.249$, (b) $x_2=0.481$, (c) x_2 =0.610, and (d) $x_2=0.772$, where x_2 is a mole fraction of nitrobenzene.

effect of a dipolar liquid. For the concentration 0.481 and 0.610 the NDE increases with decreasing temperature, in contrast to the situation at the other concentrations studied. The factors determining the change in the sign of NDE are the specific intermolecular interactions, electrostriction phenomena, electrocalorific effect, and conductivity of the system.[10] The contribution of the two latter effects to NDE is negative, whereas that due to the specific intermolecular interactions and the electrostriction effect is positive. These two positive effects are particularly well pronounced near the phase transition point, so the observed increase in NDE [Figs. 1(c) and 1(d)] is related to structural changes in the system as a result of the appearing critical fluctuations. A relatively small increase in NDE observed at lower temperatures for this concentration, indicates that the hypothetical critical point lies in the temperatures much lower than 321 K. A decrease in NDE at about 320 K [Fig. 1(c)] is related to the freezing of the mixture, as when the molecules are immobilized the orientational polarizability of the system disappears. Figure 2 presents NDE as a function of the con-
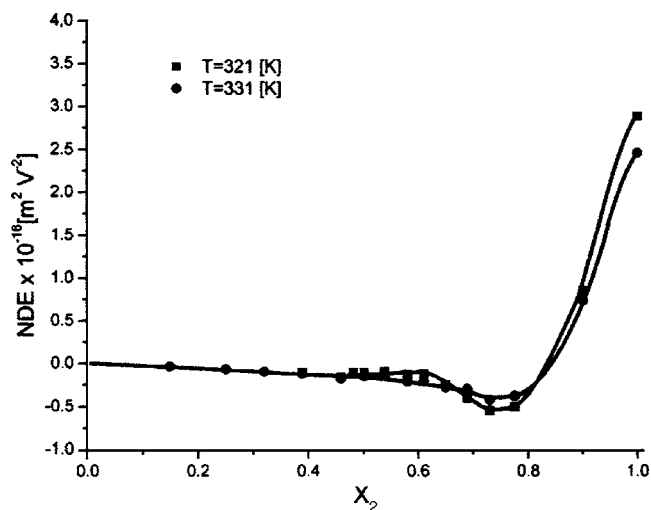

FIG. 2. NDE as a function of concentration in the system nitrobenzene-cyclododecane at various temperatures.

centration x_2 at two temperatures. At 331 K, a typical orientational negative NDE is observed for mixtures of concentrations up to $x_2=0.8$, at which the effect of pure nitrobenzene begins to dominate,[10] the positive value of NDE is observed. At 321 K, in the concentration range of 0.5–0.7, the NDE increases in a way typical of far precritical effects.[1–3] In this range of concentrations the far-range fluctuations appear, which is manifested as an increase in NDE with decreasing temperature. In the vicinity of the concentration $x_2=0.61$ the highest NDE increase occurs, suggesting that this concentration can correspond to the hypothetical critical concentration of the system.

The melting point of the mixture of the concentration $x_2=0.610$ was found from DSC measurements. Figure 3 presents the DSC scan for the nitrobenzene-cyclododecane mixture of $x_2=0.610$. The two peaks at 317 and 277 K, related to transition heat release, testify to the occurrence of two first type transitions taking place in the system. The temperature T_2 (solidus curve) corresponds to the melting point of the solution, while T_1 (liquids curve) corresponds to the melting point of cyclododecane—the component of a higher melting
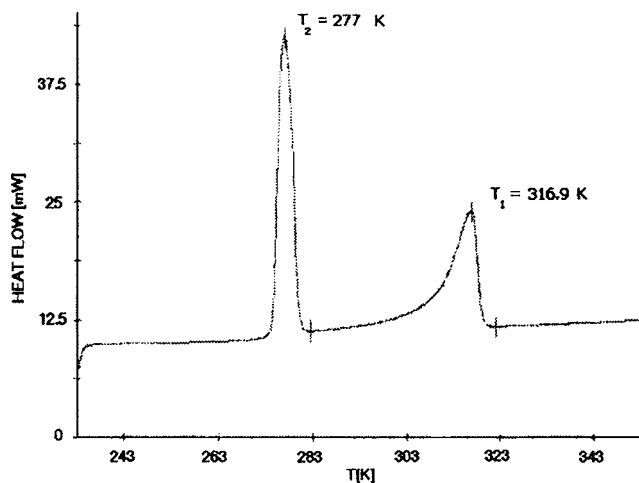

FIG. 3. DSC scan for the $x_2=0.610$ concentration of the mixture nitrobenzene-cyclododecane.

point. The difference $T=T_1-T_2$ for the system studied is 40 K, and in this range the hypothetical critical point is expected to occur. Relatively small increase in NDE at the concentration $x_2=0.610$ indicates also that the hypothetical critical point lies in the temperatures much lower than 320 K, and estimation of the effective critical exponent Φ, defined for temperatures relatively close to T_C, would be too rough an approximation.

The earlier studies of the mixtures of nitrobenzene and cycloalkanes have shown that for the cycloalkanes with 6–8 carbon atoms in the molecule, the mixtures show a classical critical phenomena with phase separation. An increase in the number of carbon atoms in the molecule of the solvent leads to a significant increase in its melting point, becoming higher than the critical temperature of the system. The system of nitrobenzene-cyclododecane is an example of such a system.

IV. MOLECULAR SIMULATIONS

A. Simulation method

A model of the mixture of nitrobenzene-cyclododecane 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 interaction Lennard-Jones potential was used,

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

with the parameters of the mixture found experimentally[31] to be $\varepsilon_{22}/k=625.65$ K and $\sigma_{22}=5.408$ Å for nitrobenzene, and $\varepsilon_{11}/k=588.98$ K and $\sigma_{11}=7.214$ Å for cyclododecane. The distance parameter σ_{12} was found from the Lorentz-Berthelot rule[32] to be $\sigma_{12}=6.311$ Å, while ε_{12} was found from

$$\varepsilon_{12} = e\sqrt{\varepsilon_{11}\varepsilon_{22}},\qquad(6)$$

where e is a constant describing the degree of modification of the Lorentz-Berthelot rule for the parameter ε. This modification was necessary because a general condition of phase separation is the weakening of the ε_{12} interactions. Another reason for the introduction of the Lorentz-Berthelot rule is the possibility to monitor the behavior of the system after the introduction of a correction for the dipole moment to the potential of interactions. The nitrobenzene molecule is dipolar so the u_{22} potential (between the nitrobenzene molecules) changes. This fact is taken into regard in the parameter ε_{22}/k.[31] A similar situation happens when a dipolar molecule interacts with a nondipolar one (nitrobenzene-cyclododekane). Such interaction is described by the potential

$$U_{12} = 4\varepsilon_{12}\left[\left(\frac{\sigma_{12}}{r_{12}}\right)^{12} - \left(\frac{\sigma_{12}}{r_{12}}\right)^6\right]\frac{\alpha_1\mu_2^2}{r_{12}^6},\qquad(7)$$

where μ is the dipolar moment, and α is the polarizability.

This equation can be expressed as the Lennard-Jones potential, where the parameters σ_{12} and ε_{12} take the following values:

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

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

where

$$\xi = 1 + \frac{\alpha_1\mu_2^{*2}}{4\sigma_{11}^3}\sqrt{\frac{\varepsilon_{22}}{\varepsilon_{11}}}.\qquad(10)$$

For the system studied $\xi^{-1/6}\approx1.00$, so for the interaction U_{AB} the parameter σ_{AB} takes the value calculated from the Lorentz-Berthelot rule.[32] As $\xi^2=1.03$, the value of $\varepsilon_{AB}/k \approx 625$ K [Eq. (6)], so for $e=1.03$ the Lennard-Jones potential is modified by taking into account the dipolar moment of nitrobenzene.

The simulations were performed for $N=500$ molecules at the concentration of $x_2=0.61$, which corresponds to the experimental pseudocritical concentration of this mixture. The simulations were carried out for 15 values of the parameter e (which was systematically varied from 0.89 to 1.03), corresponding to ε_{12}/k from 540.26 to 625.25 K, respectively. For each value of e the study was performed for 16 temperatures from $T^*=0.3$ to $T^*=0.6$ (where $T^*=kT/\varepsilon_{22}$), corresponding to 188–375 K. The pressure was assumed to be $p^*=1.855\times10^{-3}$ (where $p^*=p\sigma_{22}^3/\varepsilon_{22}$) 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 e, 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

$$Q_l = \sqrt{\frac{4\pi}{2l+1}\sum_{m=-l}^{l}|Q_{lm}^-|^2},\qquad(11)$$

where

$$Q_{lm}^- = \frac{1}{N_b}\sum Y_{lm}(\theta(r),\phi(r)).\qquad(12)$$

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}, and g_{22}) was recorded for each T and e values. The g parameter was found,

$$g = \frac{g_{11\,\text{max}} + g_{22\,\text{max}}}{2g_{12\,\text{max}}}.\qquad(13)$$

The parameters $g_{11\text{max}}$, $g_{22\text{max}}$, and $g_{12\text{max}}$ correspond to the first maxima of g_{11}, g_{22}, and g_{12}, respectively. According to the postulates of Schoen and Hoheisel[28] the value of the parameter g indicates if the system tends to phase separate. If
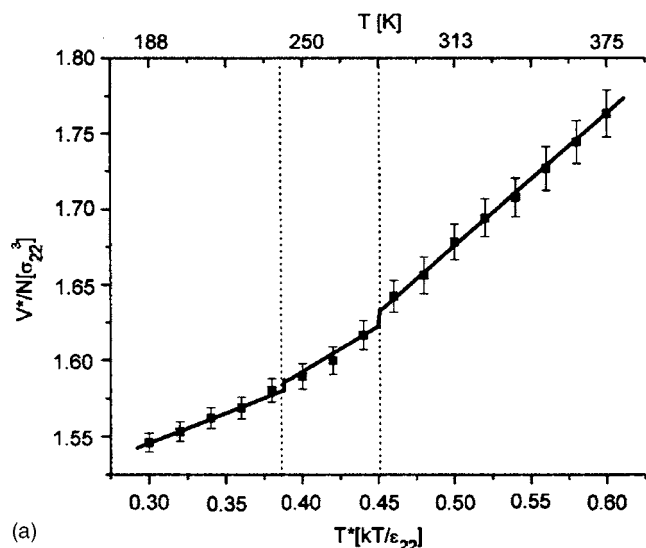
(a)
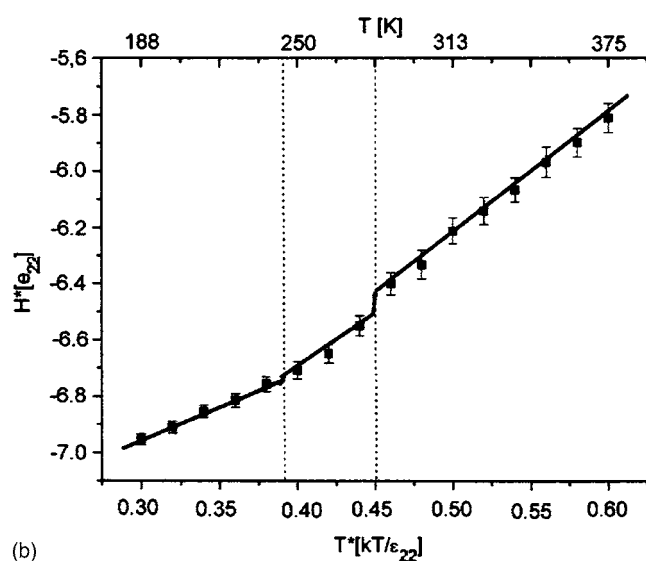
(b)

FIG. 4. (a) Temperature dependence of reduced volume for $e=0.93$ and (b) temperature dependence of reduced enthalpy for $e=0.93$. Jumpwise changes in these two parameters appear at $T_1^*=0.45$ and $T_2^*=0.39$. Similar behavior is observed for each e studied.

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 and therefore it is useful as a criterion of phase separation.

B. Simulation results

The model of the system nitrobenzene-cyclododecane was studied by MC–N-P-T simulations for temperatures range of 188−375 K and different values of e [Eq. (6)].

Figure 4 presents the calculated values of enthalpy and volume for $e=0.93$. In the vicinity of $T_1^*\approx0.45$ and $T_2^*\approx0.39$ a jumpwise change in the functions $H^*(T^*)$ (enthalpy versus temperature) and $V^*(T^*)$ (volume versus temperature) was observed, indicating a first order phase transitions.[34] With increasing value of e, the phase transition temperatures are somewhat changed but the temperature distance between them $(T_1^*-T_2^*)$ is the same and is equal to about 40 K as illustrated in Fig. 5 showing $T_1^*(e)$ and $T_2^*(e)$.
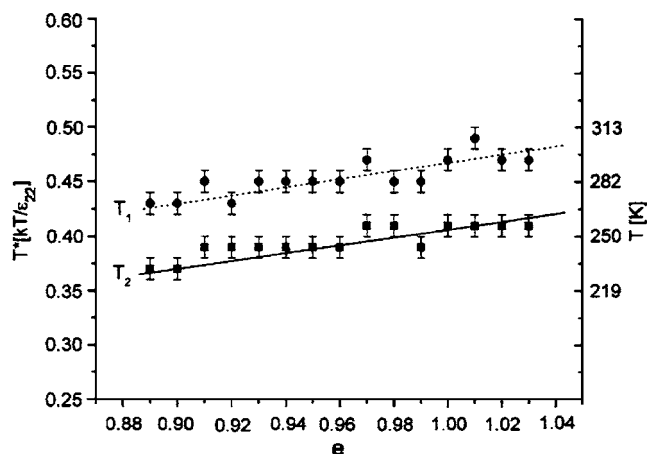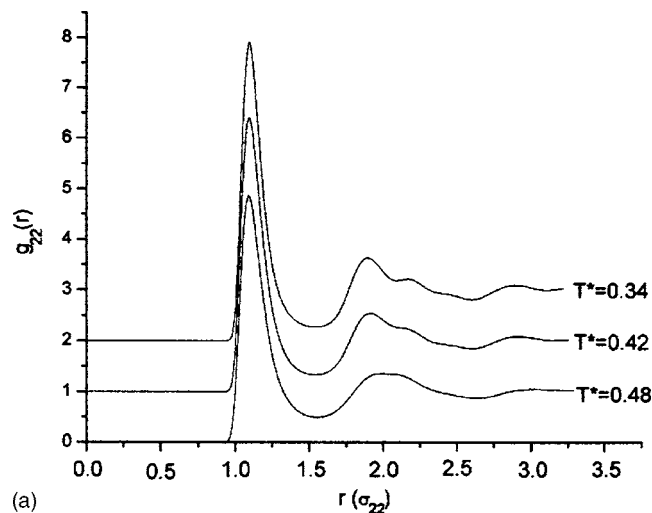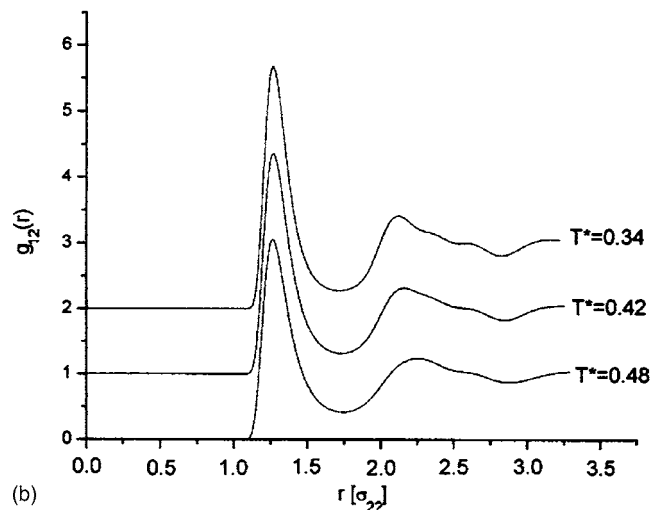

FIG. 5. Temperatures T_1 and T_2 as a function of e. For each e the difference T_1-T_2 is constant and equal ∼40 K.

As follows from the radial distribution functions [$g_{11}(r)$, $g_{22}(r)$, and $g_{12}(r)$, Fig. 6], for $e=0.93$, at temperatures higher than T_1^*, the dependencies $g_{11}(r)$, $g_{22}(r)$, and $g_{12}(r)$ are typical of the liquid phase, that is, $g(r)$ oscillates about 1. In the range $T_2^*<T<T_1^*$ a significant change in the character of $g_{11}(r)$ is recorded. The split of the second maximum points to the appearance of the solid phase of the component 1, which suggests solidification in solution. The character of $g_{22}(r)$ does not change so the component 2 remains in the liquid phase. At temperatures below T_2^* the second maxima split for both functions. The results suggest that in the mixture at T_1^* the component 1 solidifies and the component 2 solidifies at T_2^*. Similar dependencies have been found for all values of e studied $(0.89<e<1.03)$. The temperature distance between the solidus and liquidus T_1-T_2 as determined experimentally (Fig. 3) is equal to $T_1^*-T_2^*$ as determined numerically (Fig. 5). Therefore phase transitions obtained from the simulations correspond to the experiment. The T_1^* and T_2^* values closest to the experimental values correspond to high values of e. The differences between the simulation (S) and experimental (E) results: $T_{1S}-T_{1E}$ and $T_{2S}-T_{2E}$ are ∼8% for $e=1.03$. The angular functions Q_4 and Q_6, calculated to establish possible types of crystalline phases (fcc, hcp, bcc, and sc),[33] did not show any of them.
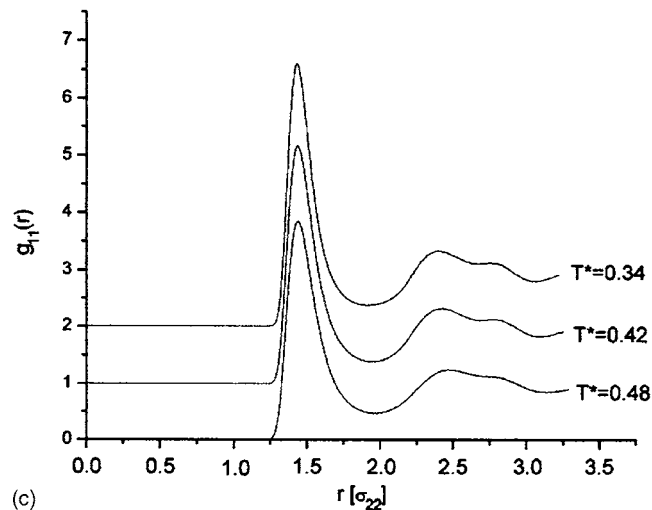
Anomalies in NDE observed near $x_2=0.610$ for nitrobenzene-cyclododecane suggest that the system realizes a far precritical state frozen at a temperature above the critical point. The value of g [Eq. (13)] was calculated to find out whether the system tends to phase separate (then $g>1$). Figure 7 presents g as a function of T^* for four values of e. For all these e values g is higher than 1, so the system has a tendency to critical cluster formation. For the lowest e the function $g(T)$ assumes values higher than 1 for all temperatures studied, which means that the system starts developing clusters already at relatively high temperatures. When $e=1.03$ the function $g(T)$ in the range of $T^*=0.50-T^*=0.60$ remains constant and approximately equal to 1, which indicates no tendency to cluster formation. Below $T^*=0.48$ the value of g increases to about 1.1 and below $T^*=0.46$ g remains constant. This behavior suggests the appearance of small size clusters, growing with decreasing temperature.

FIG. 6. Radial distribution functions: (a) $g_{22}(r)$, (b) $g_{12}(r)$, and (c) $g_{11}(r)$ for $T^*=0.34$, $T^*=0.42$, and $T^*=0.48$.

FIG. 7. Parameter g as a function of T^* for four different e. Only for $e=1.03$ the value of g in high temperatures is 1, while in low temperatures it is higher than 1.

formation as observed in the experiment. Moreover, the value of ε_{12} corresponds to the situation when the correction for the dipole moment of nitrobenzene is taken into account in this parameter. Therefore, for the mixture studied, and assuming the Lennard-Jones model, the value $e=1.03$ seems to be the best fit. For $e=1.03$ both phenomena, cluster formation and freezing, exhibit the same qualitative behavior which is revealed in the simulation and experimental studies.

V. CONCLUSIONS

The aim of the study was to show that for some critical systems of nitrobenzene with cycloalkanes, an elevated melting point leads to an apparent critical point in the metastable phase of the system, below its melting point. The NDE study and analysis of the phase diagrams obtained for the mixture of nitrobenzene-cyclododecane have indicated that the system shows a far precritical effect without phase separation, because the effect is inhibited by the system's freezing. As the increase in NDE is small relative to that in typical critical solutions, the system freezes at a temperature much higher than its apparent critical point.

The influence of the ε_{12}/k parameter varied from 540 to 625 K on phase separation in binary liquid is studied with $\sigma_{12}=6.311$ A. The best agreement between the experimental and numerical results was obtained using the Lorentz-Berthelot model modifications in which the effect of the dipolar moment of nitrobenzene was taken into account. For this value of the ε_{12}/k parameter ($\varepsilon_{12}/k=625$ K), we obtained two first order phase transitions from the temperature dependence of enthalpy, whose temperatures corresponded to those observed experimentally. We calculated the binary correlation functions, $g_{11}(r)$, $g_{22}(r)$, and $g_{12}(r)$, which allowed the immiscibility criterion of Schoen and Hoheisel, according to Eq. (9). For $\varepsilon_{12}/k=625$ K the above criterion is fulfilled and the system exhibits a tendency to clusterization arrested by the solidification of the system. The analysis of Q_4 and Q_6 angular functions did not indicate the existence

The cessation of cluster growth (g remains constant, see Fig. 7) takes place at about T_1^*. A relatively small increase in NDE near the critical concentration, see Fig. 2, confirms this suggestion. When $e=1.03$ the Lennard-Jones parameters are approximately equal $\varepsilon_{12}\approx\varepsilon_{22}$, which can lead to small but higher than 1 value of g, corresponding to restricted cluster
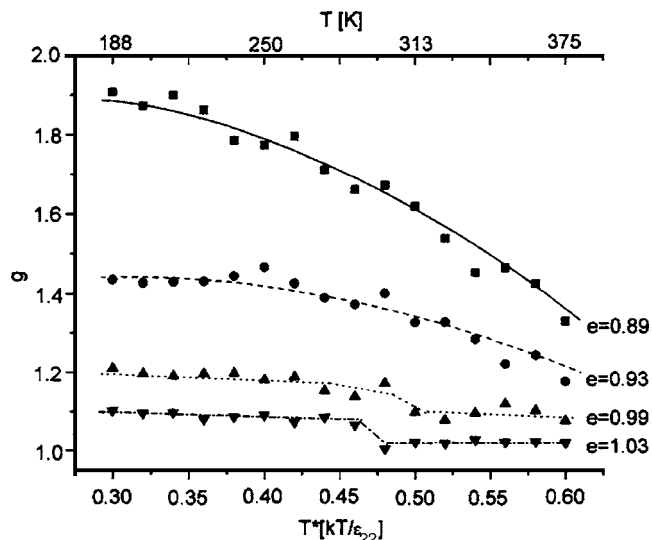
any of the phases: fcc, hcp, bcc, and sc. However, the preliminary neutron diffraction results show the signatures of the crystalline phases.[30]

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