

# PHASE TRANSITION PARAMETERS IN LIQUID MIXTURES WITH APPARENT CRITICAL POINT DETERMINED BY EXPERIMENTAL AND MOLECULAR SIMULATION METHODS

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## ABSTRACT

Nonlinear Dielectric Effect (NDE) was measured in the mixtures of nitrotoluene with alkanes and cycloalkanes [1], nitrotoluene with cycloalkanes [2,3] and 1,3-dimethoxybenzene with alkanes [4]. The mixtures were found to show apparent critical points below their melting points, which are manifested as anomalous NDE behaviour in the vicinity of the critical concentrations in the stable liquid phase. Recently, a similar phenomenon was found for the mixtures of nitrobenzene with cyclododecane. The MC simulation method was applied to a model mixture of m-nitrotoluene with n-decane. Analyses of the temperature dependencies of the configurational energies suggest the occurrence of two phase transitions in the system. In this system the apparent critical point was experimentally shown to be 8K below its melting point [3,5].

## INTRODUCTION

The Nonlinear Dielectric Effect (NDE) is defined as a change in the electric permittivity induced by a strong electric field E:

$$\frac{\Delta\varepsilon}{E^2} = \frac{\varepsilon^E - \varepsilon^0}{E^2} \quad (1)$$

where  $\varepsilon^E$  is the permittivity in the field E and  $\varepsilon^0$  – 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 [6]. Since NDE is sensitive to inhomogeneities of the medium, it has been applied to study mixtures with limited miscibility and a critical point.

The earliest investigation carried out by Piekara [7,8], proved that the vicinity of the critical point NDE takes high positive values, increasing as the temperature approaches  $T_c$ . An increase in NDE in the vicinity of critical concentrations has been observed at temperatures even 20-50K above  $T_c$  [1,9-13]. 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 characterised by an NDE typical of critical mixtures, but solidify in the homogeneous phase [1-5,14].

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]. On the other hand, analysis of the phase diagrams  $(T, x)_p$  showing the melting points  $T_m$  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 [15]. 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 [5] 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 o-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.

Recently, NDE was measured in the mixture of nitrobenzene with cyclododecane. The mixture have been found to show an apparent critical point which lies below the melting point of this mixture and is manifested as anomalous NDE behaviour in the vicinity of the critical concentrations in the stable liquid phase.

The configurational energy has been estimated by the MC simulation method for a system of m-nitrotoluene with n-decane in order to explain the possibility of a liquid-liquid phase transition and a phase transition related to the melting of the system in close temperatures.

## EXPERIMENTAL

The phase diagrams  $(T_m, x_2)_p$ , where  $T_m$  – melting point,  $x_2$  – molar fraction of nitrobenzene in the mixture, for the system of nitrobenzene – cyclododecane was determined on the basis of the temperatures of permittivity changes  $\epsilon$ , accompanying the systems' transitions from the liquid to solid state [16,17]. The measurements were performed using the impedance analyser Solatron 1260.

NDE measurements were performed using the setup described in Ref. [18]

Tests were conducted for the frequency of the weak measuring field  $f_m=1,6$  MHz, the voltage (peak-peak) of which was 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 1–3s and the voltage 190–1100 V. The capacitor gap was (0.12 –1.20) mm, for the empty capacitor conductivity  $C_0=(23,15 - 2,31)$  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 313K to 343K; with the temperature stabilised within 0.02K.

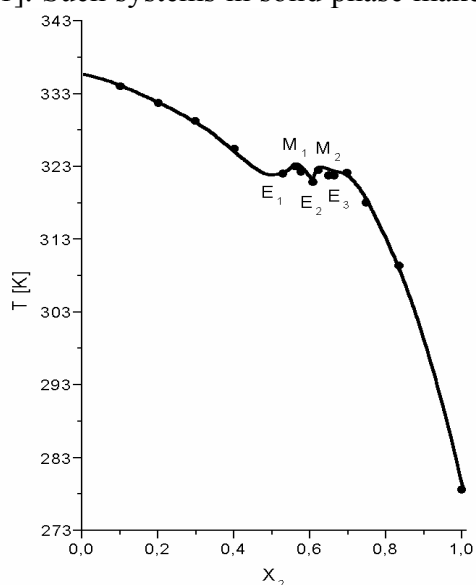
Nitrobenzene was twice distilled under reduced pressure and dried over  $Al_2O_3$ . Its conductivity was of the order  $10^{-9}\Omega^{-1}m^{-1}$ ; cyclododecane, after twice distillation its electrical conductivity was of the order of  $10^{-15}\Omega^{-1}m^{-1}$ .

## RESULTS AND DISCUSSION

The phase diagram  $(T_m, x_2)$  obtained for a mixture of nitrobenzene–cyclododecane on the basis of the changes in permittivity at the melting point is shown in Fig.1.

The phase diagram is formally similar to the diagrams of liquid-solid equilibrium of binary systems whose components A and B make a congruently melting molecular compound [19-

21]. Such systems in solid phase make molecular compounds  $A_mB_n$  (where m and n stand for



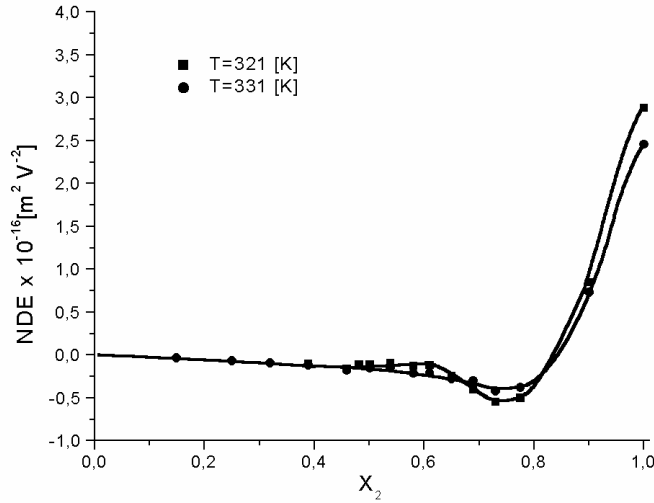
**Figure 1** : phase diagram  $(T_m, x_2)_p$  of the system nitrobenzene – cyclododecane.

the molar fraction of component A and B, respectively), formed reversibly of pure components. The compounds exist in solid phase, but their occurrence in liquid phase does not follow from the phase rule. If a compound type  $A_mB_n$  is stable up to the melting point, then the curve of the solid-liquid equilibrium reveals a maximum. If the components A and B make a few compounds, the phase diagram reveals a corresponding number of maxima. The stability of these compounds in the liquid phase is reflected by the shape of the equilibrium curve in the vicinity of the maxima. The flatter the curve the less stable the compound. For permanently stable systems the maximum becomes an arrow. Analysis of the phase diagram from Fig. 1 in this aspect shows the presence of two local maxima of the function  $T(x_2)$  that can be related to the two unstable systems type  $A_mB_n$ , whose melting points correspond to the temperatures of the maxima. The diagram can be analysed as corresponding to three eutectic systems, the eutectic point  $E_1$  corresponds to the equilibrium of the solid state solvent and solid state  $A_mB_n$  system,  $E_2$  – to the coexistence of two solid state species type  $A_mB_n$  and  $E_3$  - to the coexistence of a solid state  $A_mB_n$  and nitrobenzene. The molecular structures determined on the basis of the phase diagram from Fig. 1, with melting points at  $M_1$  and  $M_2$  are assigned to the systems  $A_mB_m$  and  $A_mB_{2m}$  containing greater and lower number of nitrobenzene molecules, respectively.

Similar diagrams have been obtained for the mixtures showing apparent critical point [15]. The unstable structure type  $A_mB_n$  were interpreted as two types of clusters: richer and poorer in the dipolar liquid, characteristic of the pre-critical state, which solidify in *statu nascendi* remaining separate in the solid state. Such a system in the liquid state is treated as an experimental equivalent of the drop model of phase transitions [22,23]. In this sense the occurrence of the above structures in the mixture studied can suggest that the system shows a far pre-critical effect, which however, does not lead to phase separation as the critical temperature is covered by the higher melting point. This suggestion has been supported by the results of the NDE study. In the vicinity of the phase transition, where far-range fluctuations appear, their influence on NDE is particularly pronounced. NDE increases with increasing range of the correlations of the critical fluctuations [24].

Fig. 2 presents NDE as a function of  $x_2$  concentration at two temperatures. At 321K the NDE

increases in the way typical of far pre-critical effects [1-4] in the range of concentrations in



**Figure 2** : NDE as a function of concentration  $x_2$  in the system nitrobenzene-cyclodecane at two temperatures

which two molecular species type  $A_m B_m$  and  $A_m B_{2m}$  exist, Fig.1. Near  $X_2=0.61$  ( $E_2$  in Fig.1) NDE takes a maximum value suggesting that this concentration can correspond to the hypothetical critical concentration of the system. The hitherto studies of the mixtures of nitrotoluene and cycloalkanes have shown that for the cycloalkanes of 6 to 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-cyclodecane is an example of such systems. The mixtures of nitrobenzene with lower cycloalkanes form classical critical systems. The apparent critical temperature of the mixture of nitrobenzene-cyclodecane will be approximated by the method of molecular simulations.

Preliminary determination of the configurational energy of the system as a function of temperature was performed for the mixture of m-nitrotoluene – n-decane whose hypothetical critical temperature has been already estimated by other methods [3,5]. The aim of the simulations was to check the possibility of appearance of two phase transitions of first and second order at relatively close temperatures, for the system whose melting point  $T_m=281K$  was higher than the critical point  $T_c=273K$ .

The model of mixture of m-nitrotoluene – n-decane was studied by the Monte Carlo method. The system's evolution was described by the Metropolis algorithm [25]. The mixture behaviour was simulated in the set of  $(N,V,T)$ . The simulated molecules were closed in a cubic box restricted with periodic boundary conditions. The Lennard-Jones potential of interactions was assumed:

$$u(r_{ij}) = 4\epsilon_{\alpha} \left[ \left( \frac{\sigma_{\alpha}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{\alpha}}{r_{ij}} \right)^6 \right] \quad (2)$$

where:

$\alpha=AA$  – for two m-nitrotoluene molecules interacting

$\alpha=BB$  – for two n-decane molecules interacting

$\alpha=AB$  – for the interaction of m-nitrotoluene and n-decane molecules

The Lennard-Jones potential parameters of the mixture were established experimentally [5]. The calculations were performed for the following values for m-nitrotoluene (A) and n-decane (B):

$$\epsilon_{AA}/k=639,33[\text{K}] \quad \epsilon_{BB}/k=513,07[\text{K}]$$

$$\sigma_{AA}=5,660[\text{\AA}] \quad \sigma_{BB}=7,140[\text{\AA}]$$

The parameters  $\epsilon_{AB}$  and  $\sigma_{AB}$  were calculated within the approximation:

$$\sigma_{AB} = \frac{\sigma_{AA} + \sigma_{BB}}{2} \quad (3)$$

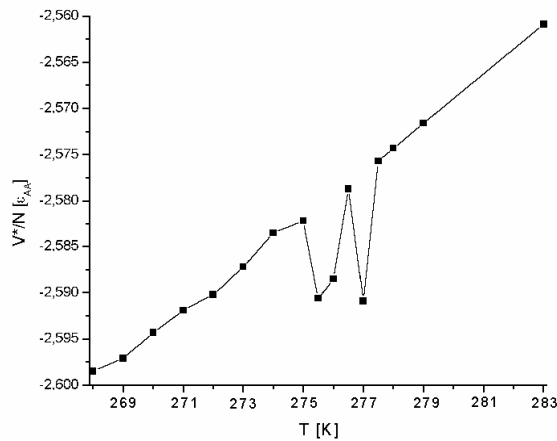
$$\epsilon_{AB} = \sqrt{\epsilon_{AA} \epsilon_{BB}} \quad (4)$$

All the simulations were performed for the molar fraction of m-nitrotoluene of  $x=0.535$  in the mixture, being a “critical” concentration of this mixture. The simulations were performed for  $N=500$  molecules.

The configuration energy of the system was determined [25]:

$$U = \sum_{i<j} u(r_{ij}) \quad (5)$$

Fig. 3 presents the temperature changes in the systems' configurational energy.



**Figure 3** : The temperature dependence of the system's energy

The changes in the system's energy at 275.5K and 277K suggest the occurrence of two phase transitions. The values of these temperatures are very close to the experimental results.

Results of the preliminary study of other quantities such as the radial distribution functions and the correlation radius of the system (to be published later) suggest that the energy change at 277K is related to the system's freezing, while that at 275.5K to the critical transition. Simulation studies of the system by other methods are underway.

## CONCLUSION

The aim of the study was to show that for some critical systems of nitrobenzene with cycloalkanes, an elevated melting point leads to the 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 pre-critical effect without a phase separation because the effect is inhibited by the system's freezing. As the increase in NDE is small relative to that in the typical critical

solutions, the system freezes at a temperature much higher than its apparent critical point. The model of the mixture of m-nitrotoluene – n-decane has been subjected to preliminary studies by the MC method. The temperature changes in the system's energy illustrated in Fig.3 suggest the occurrence of two phase transitions in close temperatures. The rdf and correlation range analyses, currently underway, suggest that the change in the system's energy at 277K is relate to the system's melting, while that at 275.5K to the critical transition. Similar study is planned for the model of the mixture nitrobenzene-cyclodecane in order to determine its hypothetical  $T_c$ .

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