Critical behavior of n-alkanes + nitrobenzene systems

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Abstract

We report the experimental and simulation study of the *n*-alkanes + nitrobenzene systems which show the classical critical behavior with upper critical points. The Metropolis Monte Carlo simulation method for the *NPT* ensemble has been used. Density, enthalpy, radial distribution functions, critical parameters and melting character of these liquid mixtures have been estimated [1,2]. Immiscibility conditions according to the approach by Schoen and Hoheisel [3] have been also discussed.

The simulation results have been compared with experimental ones obtained by Differential Scanning Calorimetry measurements.

1. Introduction

The studied systems: *n*-decane+nitrobenzene and *n*-hexadecane+nitrobenzene form the critical binary mixtures. Above the critical temperature T_c with corresponding critical concentration x_c (x stands for molar fraction of nitrobenzene in the solution) they are homogeneous mixtures. Below T_c the phase separation occurs and we can observe two coexisting phases. For critical mixtures, as it is showed at Fig.1 [4] the concentration x' characterizes the saturated dissolvent and x'' characterizes the dissolved substance.

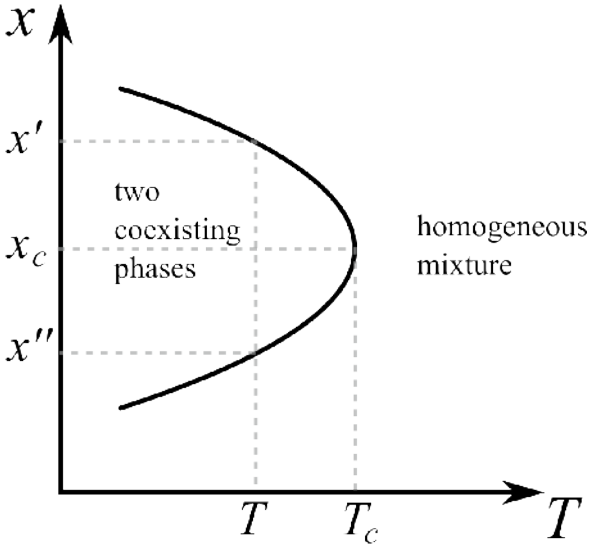

Fig. 1. Phase coexistence curve in (x, T) plane of a critical binary mixture [4]

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Below the critical point the melting behavior of the separated phases can be measured using Differential Scanning Calorimetry. The temperature at which we can observe the heat release due to the phase transition can give the information about the melting points of both phases.

The critical transition of studied mixtures is preceded by formation of two kinds of molecular clusters [1]: one reacher and one poorer in the polar component (nitrobenzene in our studies). It can be detected by Nonlinear Dielectric Effect (NDE) measurement which is sensitive to inhomogeneities of the system and is used to investigate the cluster formation of the mixtures with limited miscibility and critical point [5-13]. NDE is defined as a change in electrical permittivity induced by an electric field *E* of large value:

$$\frac{\Delta\epsilon}{E^2}=\frac{\epsilon^E-\epsilon^0}{E^2} \quad , \tag{1}$$

where ϵ^E is the permittivity in the field *E*, and ϵ^0 in its absence. NDE large positive peak is observed in a critical point vicinity but even 20-50K above T_c the pre-critical anomalies of NDE are observed [5,9-13] (for critical concentration) what indicates the formation of the molecular clusters.

Formation of molecular clusters can be investigated by simulation using *g* parameter [3]:

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

where $g_{ij}^{\max}$ corresponds to the first maximum of a radial distribution function $g_{ij}(r_{ij})$ of *I* and *j* species of molecule. As it was postulated by Schoen and Hoheisel [1] the value of the *g* parameter indicates the system phase separation tendency. If no clusters are formed in the system then $g = 1$ and when clusters formation occurs then $g > 1$. The value of *g* parameter is proportional to the formed clusters size and therefore it is a useful criterion of the phase separation behavior of the mixtures.

2. Experimental and simulation method

For the DSC measurement of the mixtures of *n*-decane+nitrobenzene system in concentration range from 0.23 to 0.91 a Perkin-Elmer DSC7 differential scanning calorimeter was used. The melting temperature of the system was determined 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 temperature scanning rates of 10 K/min were used in all cases.

Models of the systems were studied by Monte Carlo simulations in the *NPT* ensemble. The molecules were contained in a cubic box with periodic boundary condition. The simulations were performed for *n*-decane+nitrobenzene and for *n*-hexadecane+nitrobenzene systems for $N = 500$ molecules at concentrations range from $x_2 = 0.2$ to $x_2 = 0.9$. The temperature range was from 200 K to 360 K. For the studied systems we apply the Lennard-Jones potential:

$$U(r_{ij})=4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12}-\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] \quad , \tag{3}$$

where *i,j* – indexes of molecule species, parameters σ_{12} and ϵ_{12} are [14]:

$$\sigma_{12} = \xi^{-1/6}\left(\frac{\sigma_{11}+\sigma_{22}}{2}\right) \;,\; \epsilon_{12} = \xi^{2}\sqrt{\epsilon_{11}\,\epsilon_{22}} \;,\; \text{where} \quad \xi = 1+\frac{\alpha_1 \mu_2^{*2}}{4\sigma_{11}^{3}}\sqrt{\frac{\epsilon_{22}}{\epsilon_{11}}} \;, \qquad (4)$$

μ_2 - dipole moment of the dipolar molecule, α_1 - polarizability of nondipolar molecule. Parameters σ_{11}, σ_{22}, ϵ_{11} and ϵ_{22} of investigated mixtures were found experimentally [14].

3. Results

As a result of the performed simulation we described the temperature dependences of enthalpy (thermodynamical potential of the NPT ensemble) and volume, radial distribution functions and consequently *g* paremeters (see equation (2)).

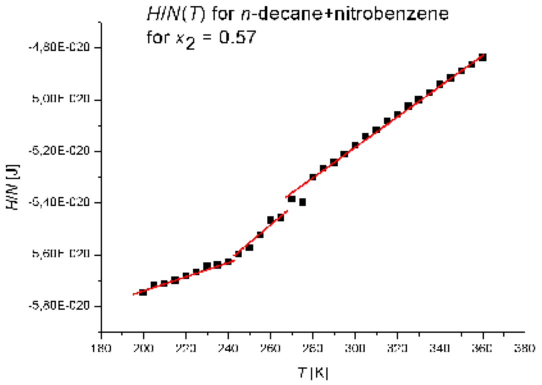

Fig. 2. Enthalpy per molecule against temperature for n-decane+nitrobenzene system of x_2 = 0.57 (from simulation)

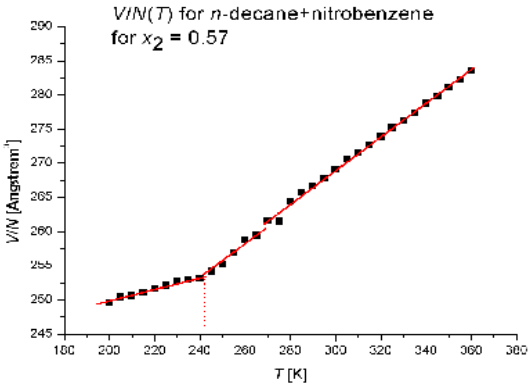

Fig. 3. Volume per molecule against temperature for n-decane+nitrobenzene system of x_2 = 0.57 (from simulation)

Figures 2 and 3 show the temperature dependences of enthalpy and volume per molecule respectively obtained by the simulation for the system of *n*-decane+nitrobenzene near the critical concentration (x_2 = 0.57). In the temperatures about 240K and 265K we can see enthalpy changes related with the melting transitions of the mixture ; at 240K melting of one separated phase of the system and at 265K of the other one are observed.

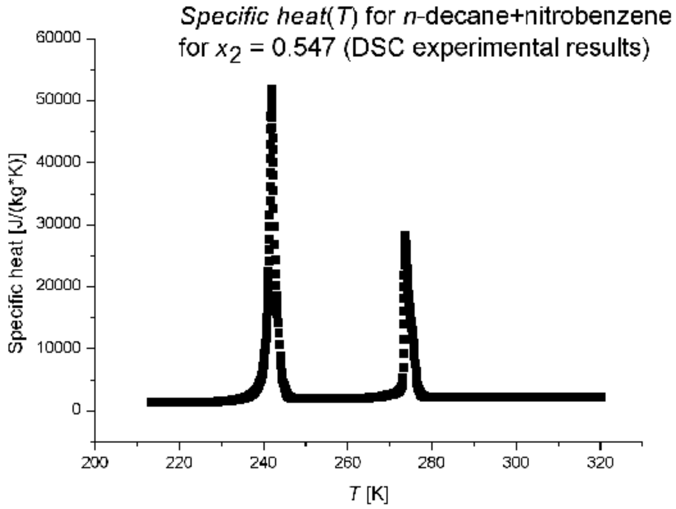

Fig. 4. Specific heat against temperature for n-decane+nitrobenzene system of x_2 = 0.547 (from DSC measurement)

DSC results presented in Fig. 4 show temperature dependence of specific heat for the n-decane+nitrobenzene system near the critical concentration ($x_2 = 0.547$). We can clearly see the two endothermic peaks of heat released at the two melting transition points: of one phase at 242.03 K and of the other one at 273.78 K.

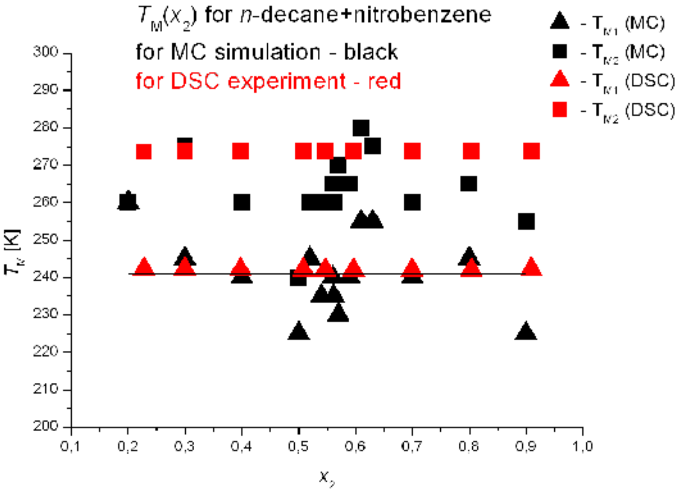

Fig. 5. Melting temperatures vs. concentration of the n-decane+nitrobenzene system for the simulation results (black points) and the DSC experimental ones (red points). The lines show average melting temperatures values for simulation.

Fig. 5 shows melting temperatures of the two separated phases of the system obtained from the DSC measurements (the red ones) of *n*-decane+nitrobenzene system *vs.* concentration and melting temperatures obtained by the simulation (the black ones) (see also Fig.3). We can see that the simulation results are in relatively good agreement with the experimental ones. The temperature shift of melting temperatures recorded by the experiment and the simulation is about 8 K.

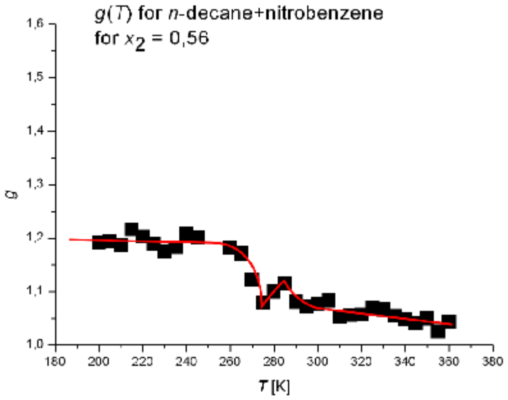

Fig. 6. Temperature dependence of g parameter for n-decane+nitrobenzene system for $x_2 = 0.56$

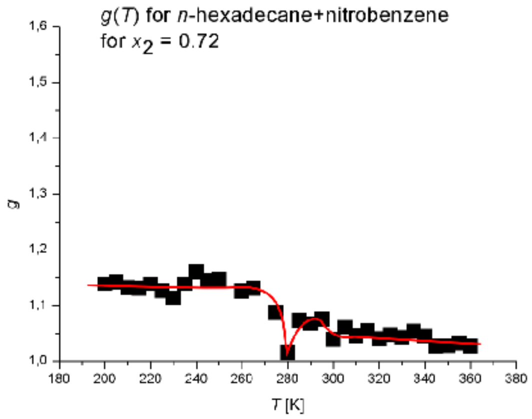

Fig. 7. Temperature dependence of g parameter for n-hexadecane+nitrobenzene system for $x_2 = 0.72$

Fig. 6 and 7 show the temperature dependence of *g* parameter for *n*-decane+nitrobenzene and *n-hexa*decane+nitrobenzene systems for near critical concentrations $x_2 = 0.56$ and $x_2 = 0.72$ respectively (see also Fig. 8 and 9). The increase of *g* parameter with the temperature decrease can be clearly see here; it indicates growing of the clusters. Below about 250 K *g* parameter stabilizes and become temperature independent as the clusters size stabilize below the melting point. The first significant peaks of *g* occur at about 285 K for *n*-decane+nitrobenzene and at 295 K for *n*-hexadecane+nitrobenzene mixture while the experimental critical temperatures T_c for these systems were 296.25 K and 309.59 K respectively [14]. Thus the temperature shift is about 10-17 K between these values. Similar peaks can be observed for other concentrations of both studied systems and we plotted their values *vs.* concentration x_2 obtaining Fig. 8 and 9.

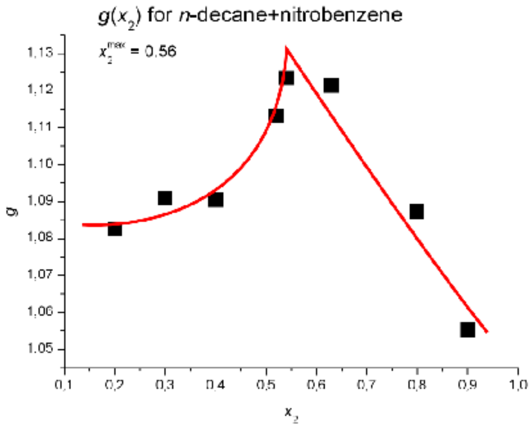

Fig. 8. Concentration dependence of g parameter first significant peaks for n-decane+nitrobenzene system. The highest value of g corresponds to $x_2 = 0.56$.

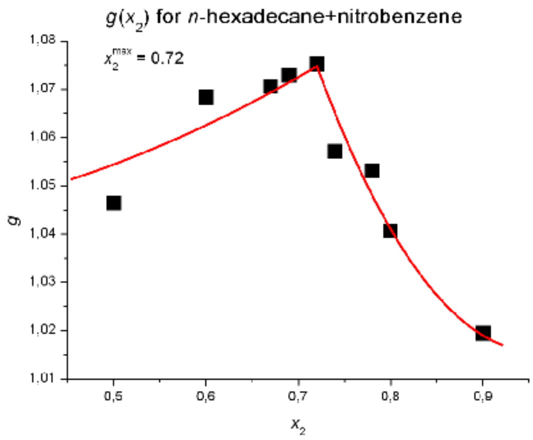

Fig. 9. Concentration dependence of g parameter first significant peaks for n-hexadecane+nitrobenzene system. The highest value of g corresponds to $x_2 = 0.72$.

As follows from Fig.8 for *n*-decane+nitrobenzene system *g* parameter first significant peak obtains the highest value for $x_2 = 0.56$ and for *n*-hexadecane+nitrobenzene (Fig.9) $x_2 = 0.72$.

These values of concentration are very close to the experimentally obtained critical concentration ones for these systems [14] which are $x_2 = 0.561$ and $x_2 = 0.718$ respectively. The difference between the experimental values and the results of simulation is less than 5%. The results obtained confirm the suggestions that of *g* parameter first significant peak indicates the critical point.

4. Conclusions

Analysis of the g parameters *vs.* temperature for the studied critical mixtures allows us to observe the forming of large molecular clusters, which leads to the phase separation. The good accordance of the presented simulation results with the experiment proves that the modified form of the Lennard–Jones potential allows us to describe the critical and melting behavior of the studied systems relatively well. Similar studies are planned for other critical mixtures. We are also planning to use molecular dynamics simulations to investigate dynamics of critical transitions of such systems.

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