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Critical behaviour in nitrobenzene–hexane mixture by approaching the liquid–liquid critical line

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Abstract

The pressure dependence of the critical consolute temperature in nitrobenzene–hexane mixture has been studied in the −28 to +110 MPa range. The negative pressure part of the locus was determined by the extrapolation of the pretransitional anomaly of nonlinear dielectric effect and analyzed by a modified Simon–Glatzel type equation, which makes the extension into the $P < 0$ domain possible. This equation is parameterised by invariant coefficients and exhibits a negative power exponent. Our results proved that fluctuations can be important even far away from the critical consolute point.

Keywords: Liquid–liquid locus; Negative pressure; Nitrobenzene; Hexane; Dielectric behaviour; Simon–Glatzel

1. Introduction

Although the extensibility of liquid–liquid locus into the range of negative pressures has been proposed more than a half decade ago [1], most experiments and calculations are terminated at $P = 0$ or at vapour pressure. The reason of this termination is partly the “exotic” nature of stretched liquid states [2–4], partly the small number of experimental results in this domain [5–10]. Due to the liquid–vapour metastability of stretched liquid states (i.e. they can boil at any time spontaneously), direct experimental observations – stretching the liquid, then determining the liquid–liquid phase transition points – are very difficult, tedious and usually they cannot be performed in very deep negative pressures.

As an alternative way, measurement of quantities with strong and well-established pretransitional anomalies can be utilized to estimate the location of the liquid locus. In this case one does not have to measure all the way to the phase transition, but can stop at some point (in this case the measurement should start at certain high pressure and terminate at the vapour pressure) and extrapolate the measured quantity. Having a binary solution with critical concentration, the pretransitional anomalies will turn into critical anomalies with well-known critical exponents.

A few years ago we published our first results about the determination of the critical liquid–liquid locus in nitrobenzene–hexane system [11], using the pretransitional anomaly of the dieletric permittivity, associated with the phase transition. Since then we are trying to extend the number of methods as well as the number of systems [12]. In this short paper we would like to describe how the nonlinear dielectric effect (the high-field counterpart of the dielectric permittivity) can be used to determine the liquid–liquid locus almost down to the liquid spinodal (the thermodynamical limit for liquid state and also a limit for any liquid–liquid locus [3,13]). It is also shown that an extended Simon–Glatzel relation can be used to parameterize the obtained data.

2. Methods

2.1. Determination of the liquid–liquid critical points

NDE is the “nonlinear” counterpart of the dielectric permittivity (ε) describing its changes due to the application of a strong

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electric field E [14]:

$$\varepsilon_{\mathrm{NDE}} = \frac{\Delta\varepsilon^{\mathrm{E}}}{E^2} = \frac{\varepsilon^{\mathrm{E}} - \varepsilon}{E^2} \qquad (1)$$

where ε^{E} and ε are dielectric permittivities under a strong and weak electric field, respectively.

It was shown before [14,15] that at constant pressure, changing the temperature, the strong pretransitional anomaly can be described by:

$$\varepsilon_{\mathrm{NDE}} - \varepsilon_{\mathrm{NDE}}(\mathrm{bckg.}) = \varepsilon_{\mathrm{NDE}}(\mathrm{crit.}) = \frac{A_{\mathrm{NDE}}}{(T - T_{\mathrm{C}})^{\psi}} \propto \langle \Delta M^2 \rangle_{\mathrm{V}} \chi \qquad (2)$$

as $T \to T_{\mathrm{C}}$, and at constant temperature, by changing the pressure:

$$\varepsilon_{\mathrm{NDE}}(\mathrm{crit.}) = \frac{A^{\mathrm{P}}_{\mathrm{NDE}}}{|P - P_{\mathrm{C}}|^{-\psi}} \propto \langle \Delta M^2 \rangle_{\mathrm{V}} \chi \qquad (3)$$

as $P \to P_{\mathrm{C}}$, where (T_{C}, P_{C}) denote the critical consolute temperature and pressure, respectively. $\varepsilon_{\mathrm{NDE}}$ is the measure of the experimental NDE values, $\varepsilon_{\mathrm{NDE}}(\mathrm{bckg})$ denotes the non-critical background-effect and $\varepsilon_{\mathrm{NDE}}(\mathrm{crit.})$ is the critical part of NDE. $\langle \Delta M^2 \rangle_{\mathrm{V}}$ is for the mean square fluctuation of the order parameter, the exponent $\psi = \gamma - 2\beta$, χ is the susceptibility related to the order parameter and described by the almost "classical" $\gamma \approx 1.02$ value, and finally $\beta \approx 0.325$ is the "non-classical" critical exponent for the order parameter. This yields $\psi \approx 0.37$ in the immediate vicinity of the critical consolute point and $\psi \approx 0.4$ when the influence of correction-to-scaling terms on moving away from T_{C} or P_{C} has to be taken into account [14,15]. The unique classical–non-classical critical behavior of NDE is associated with the anisotropic elongation of critical fluctuations due to the action of the strong electric field. The model explaining this phenomenon – characteristic both for NDE and the electrooptical Kerr effect – is given in refs. [14–16]. Relations (2) and (3) indicate that NDE is directly coupled to mesoscale fluctuations-heterogeneities appearing in the broad surrounding of the critical point [14–16]. The description of the dual-field, aperiodic and modulation domain based NDE spectrometer applied in this research is given elsewhere [14]. Generally, the NDE method is based on the application of few millisecond lasting pulse of a strong electric field inducing the shift of dielectric permittivity $\Delta\varepsilon^{E}$, registered via the weak radio-frequency measuring field. For results presented below $f_{\mathrm{weak}} = 12\,\mathrm{MHz}$, $U^{\mathrm{f}}_{\mathrm{weak}} = 1\,\mathrm{V}$ and $U^{\mathrm{DC}}_{\mathrm{strong}} = 500 - 1000\,\mathrm{V}$. The sample was placed in the capacitor made from Invar with $0.3\,\mathrm{cm}^3$ gap. The description of the pressure set-up is given elsewhere [14,17]. Studies were carried out for nitrobenzene–hexane solution of critical concentration $x_{\mathrm{c}} = 0.430$ mole fraction of nitrobenzene and $T_{\mathrm{C}}(0.1\,\mathrm{MPa}) = 19.5\,^{\circ}\mathrm{C}$ [18]. Tested components were purchased from Fluka. Nitrobenzene was distilled immediately prior to measurements. Generally, when analysing the behavior of any physical magnitude in the vicinity of the critical point the contribution from critical fluctuations and from non-critical molecular mechanisms should be separated. The latter can be determined from NDE measurements in the reference nitrobenzene–hexene (instead of hexane) solution of unlimited miscibility, assuming the same volume of nitrobenzene in the reference solution as in the critical nitrobenzene–hexane mixture [19]. These values are subtracted from the results of NDE measurements in the tested critical solutions to obtain the contribution linked solely to pretransitional fluctuations. Subsequently, the plot $\log[\varepsilon_{\mathrm{NDE}}(\mathrm{crit.})]$ versus $\log|P - P_{\mathrm{C}}|$ is analysed. For the optimal selection of P_{C} it should follow a linear dependence on the longest range of pressure, according to Eq. (3). The non-optimal selection of P_{C} strongly disturbs the evolution near $P = 0.1\,\mathrm{MPa}$. Consequently, the linear regression analysis can yield values of the critical exponent ψ and the amplitude A_{NDE}. The error of fitting increases when shifting above $T_{\mathrm{C}} = (P = 0.1\,\mathrm{MPa})$, i.e. by increasing the experimental "discontinuity" of the transition $\Delta P = -P_{\mathrm{S}}$. However, the procedure described above made it possible the reliable estimation of fitting errors of parameter as well as the domain of the description via Eq. (1). In the opinion of the authors the described way of analysis yields more reliable results than the direct nonlinear fitting via Eq. (3), where parasitic artifacts associated with the interplay of fitting parameters and the unequivocal range of validity of Eq. (3) may dominate. It is noteworthy that we obtain almost the same values of the critical amplitude and the critical exponent for each tested isotherm (within the limit of the experimental error), namely $\psi = 0.39 - 0.41$ and $A_{\mathrm{NDE}} = 5.5 - 5.7\,\mathrm{m}^2\,\mathrm{V}^{-2}\,\mathrm{MPa}$. These values strongly support the validity of analysis, including the estimation of $P_{\mathrm{S}}(T)$ loci. We would like to stress that in this paper NDE is used only as a method directly coupled to critical fluctuations and then yielding a strong pretransitional anomaly and portrayed by a single power dependence with a well defined critical exponent. In fact, one may expect that a similar analysis should be possible for the Kerr effect (KE), the light scattering or the neutron scattering (SANS) based studies [3,20–30]. However, in the opinion of the authors' for NDE the implementation of high-pressure technique is relatively simple. When discussing the application of mentioned methods for estimating the stability limit loci located in metastable and hardly accessible domains worth recalling is so-called pseudospinodal method introduced by Chu et al. [20]. They estimated the hypothetical position of the spinodal located below the binodal in isobutyric acid–water solution of limited miscibility using the light scattering measurements. This method was applied several times since then [3,20–23 and refs therein]. In ref. [22] its application based on NDE measurements in nitrobenzene–hexane was shown. The "pseudospinodal" extrapolation based on the light scattering NDE or KE studies is the fundamental method for estimating the discontinuity of the isotropoic–nematic phase transition [26,27 and refs. therein]. The analysis presented above may be considered as the extension of the "pseudospinodal method" [3,20–25] mentioned above. However, this method is linked to studies for binary mixtures of non-critical solution under atmospheric pressure, i.e. to inherently discontinuous transition.

Results presented in this paper are solely associated with the hypothetical continuous transition hidden in the metastable liquid domain (mainly in the region of negative pressures). In the opinion of the authors light scattering and neutrons scattering