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Temperature, concentration, and frequency dependence of the dielectric constant near the critical point of the binary liquid mixture nitrobenzene-tetradecane

Jan Leys,1,a Patricia Losada-Pérez,1 George Cordoyiannis,1 Claudio A. Cerdeiriña,2 Christ Glorieux,1 and Jan Thoen1,b
1Département Natuurkunde en Sterrenkunde, Laboratorium voor Akoestiek en Thermische Fysica, Katholieke Universiteit Leuven, Celestijnenlaan 200D–bus 2416, B-3001 Leuven, Belgium
2Departamento de Física Aplicada, Universidad de Vigo (Campus de Ourense), As Lagoas s/n, Ourense 32004, Spain

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Detailed results are reported for the dielectric constant $\varepsilon$ as a function of temperature, concentration, and frequency near the upper critical point of the binary liquid mixture nitrobenzene-tetradecane. The data have been analyzed in the context of the recently developed concept of complete scaling. It is shown that the amplitude of the low frequency critical Maxwell–Wagner relaxation (with a relaxation frequency around 10 kHz) along the critical isopleth is consistent with the predictions of a droplet model for the critical fluctuations. The temperature dependence of $\varepsilon$ in the homogeneous phase can be well described with a combination of a $(1 - \alpha)$ power law term (with $\alpha$ the heat capacity critical exponent) and a linear term in reduced temperature with the Ising value for $\alpha$. For the proper description of the temperature dependence of the difference $\Delta \varepsilon$ between the two coexisting phases below the critical temperature, it turned out that good fits with the Ising value for the order parameter exponent $\beta$ required the addition of a corrections-to-scaling contribution or a linear term in reduced temperature. Good fits to the dielectric diameter $d_4$ require a $(1 - \alpha)$ power law term, a $2\beta$ power law term (in the past considered as spurious), and a linear term in reduced temperature, consistent with complete scaling. © 2010 American Institute of Physics. [doi:10.1063/1.3332586]

I. INTRODUCTION

The anomalous behavior displayed by some thermodynamic properties in the vicinity of the critical point in liquid-liquid phase transitions has been the subject of both experimental and theoretical intensive researches. Particular interest has been devoted to the critical behavior of the dielectric constant, $\varepsilon$, for which the first experimental study dates to 1932 by Piekara.1 He observed for nitrobenzene-hexane that the dielectric constant increases but at a decreasing rate when approaching the critical temperature, $T_c$, in the one-phase region above $T_c$, while no such behavior was observed for the density $\rho$. Subsequent measurements in this region resulted in a rather confusing situation. It was found in many cases that the normal almost linear increase in the dielectric constant with decreasing temperature changes to much smaller $|d\varepsilon/dT|$ values close to $T_c$.1-7 In another group of investigations a sharp increase in $\varepsilon$ was observed when approaching $T_c$ along the same critical isopleth.8-11 In several cases conflicting results were obtained for the same system. It was not until 1980 that this confusing situation was solved when Thoen and co-workers12 shed light on this issue by invoking the Maxwell–Wagner (MW) effect, a low frequency dispersion phenomenon occurring in heterogeneous media because of the presence of ionic impurities in the mixture and the occurrence of large concentration fluctuations near $T_c$. Following this observation it became possible to investigate the singular behavior of $\varepsilon$ near $T_c$ in the homogeneous region by proper choice of the measuring frequency.

Many data showed that the observed singularity in the static dielectric constant in the homogeneous phase was consistent with including a $|t|^{1-\alpha}$ term [with $t = (T - T_c)/T_c$ and $\alpha$ the heat capacity critical exponent],12-17 in agreement with the predictions of a scaling formulation for fluids under an electric field.18 Moreover, the anomalous behavior of $\varepsilon$ in the one-phase region was experimentally confirmed to be an intrinsic effect,13,14,19,20 different from the critical behavior of the density $\rho$

Though less numerous, studies of $\varepsilon$ in the two-phase region were also carried out. In 1988, Kindt et al.21 reported accurate measurements observing a curvature in the diameter of the coexistence curve in the $\varepsilon-T$ plane, which could be described by a $|t|^{2\beta}$ critical contribution (with $\beta$ the order parameter critical exponent). Further measurements were carried out by Tveekrem et al.15 for polystyrene+diethyl malonate, by Paluch et al.22 for 1-nitropropane+hexadecane, and by Malik et al.23 for nitrobenzene+octadecane. The latter studies were done along isothermal as well as along isobaric paths, again encountering evidence for a $|t|^{2\beta}$ contribution to the singularity in the diameter. From a theoretical viewpoint, the conventional scaling formulation predicts leading

aPostdoctoral Researcher for Research Foundation–Flanders (FWO). Electronic mail: jan.leys@fys.kuleuven.be.
bElectronic mail: jan.thoen@fys.kuleuven.be.
|τ|^{1−α} singularity of the diameter without the possibility of a |τ|^{2β} singularity, which is often regarded as a spurious contribution arising from an improper choice of the order parameter. A recent theoretical study, which incorporates nonordering fields in the (actual case, an external electric field E) into the complete scaling formulation of liquid-liquid phase transitions, predicts the existence of a leading |τ|^{2β} contribution that seems to be consistent with the previous experimental results. New experiments that provide further insights into the new theoretical predictions are highly desirable.

In this work, we report on dielectric measurements in both the one- and two-phase regions of the binary mixture nitrobenzene-tetradecane, a member of a series of nitrobenzene-alkanes that have often been studied. We have chosen this system because its coexistence curve diameter. Accordingly, the manuscript is organized as follows. Section II gives theoretical background information, introducing the relevant theoretical equations and definitions of some experimental dependent quantities. Section III gives information on the samples and the experiments carried out. Section IV gives an overview of the experimental data. In Secs. V and VI the analyses of the data in the one-phase and the two-phase regions are presented, respectively. A summary and conclusions are given in Sec. VII.

II. THEORETICAL BACKGROUND

A. Complete scaling of binary mixtures under an electric field

In Ref. 27 Perez-Sanchez et al. proposed a scaling formulation for binary mixtures, starting from complete scaling for incompressible mixtures with the inclusion of pressure as a nonordering field. In this way, the isolated critical point is extended into a critical line without changing the universality class of the phase transition. By introducing the electric field (electrostatic work) into the fundamental equations of thermodynamics, the behavior of the dielectric permittivity ε of binary liquid mixtures is accessible. As a consequence, the Gibbs–Duhem relation of binary mixtures under an external electric field can be written as

\[ d(\mu_s) = sT dT + v d(p) + x_2 d\mu_2 + vE dT, \]  

where \( E \) = \( \varepsilon_0 E^2 / 2 \), with \( \varepsilon_0 \) the permittivity of vacuum, and where \( \mu_s, \mu_2, s, v, \) and \( x_2 \) denote the chemical potential of component 1, the chemical potential difference, the entropy per particle, the volume per particle, and the mole fraction of component 2, respectively. In complete scaling, three relevant scaling fields, i.e., an ordering field \( h_1 \), a thermal field \( h_2 \), and the singular part of the thermodynamic potential \( h_3 \) in analogy with the fields \( H, T \), and the singular part of the thermodynamic potential in the scaling description of a uniaxial magnet, are introduced:

\[ h_1 = \Delta \mu_{21} + a_1 \Delta \mu_1 + a_2 \Delta T + a_3 \Delta h + a_4 \Delta E, \]  

\[ h_2 = \Delta \mu_1 + b_1 \Delta \mu_1 + b_3 \Delta h + b_4 \Delta \mu_2 + b_5 \Delta E, \]  

\[ h_3 = -\Delta \mu_1 + c_1 \Delta h + c_2 \Delta \mu_1 - \varepsilon_2 \Delta E, \]

where \( \Delta \mu_i = (T - T_c) / T_c, \Delta \mu_1 = (\mu_1 - \mu_{1,c}) / \kappa T_c, \Delta \mu_{21} = (\mu_{21} - \mu_{21,c}) / \kappa T_c, \) and \( \Delta \mu_1 \) is the dimensionless critical deviations of the field variables, while \( a_1, b_1, c_1 \) stand for the nonuniversal mixing coefficients that characterize the way that physical fields enter into the scaling fields. (Please, note that \( \Delta \mu_i \) is identical to the previously defined \( T \).) The reader may consult Refs. 21 and 27 for a detailed account on the assumptions made when incorporating \( E \) and \( p \) into the scaling formulation, respectively. The fields \( \mu_1, \mu_{21}, \) and \( T \) are obviously relevant fields for the liquid-liquid phase transition to occur, while \( p \) and \( E \) are nonordering fields. For a weakly compressible binary mixture, the scaling fields \( h_1, h_2, \) and \( h_3 \) contain contributions from all physical fields (both ordering and nonordering physical fields). It can be shown that the mixing coefficients \( b_1, b_5, a_1, \) and \( a_3 \) account for the most important singularities ascribed to asymmetry in liquid-liquid criticality.

Since subsequent calculations fall beyond the scope of this article, here we will only include the results that describe the singular behavior of \( \varepsilon \) at criticality. A detailed review of such calculations can be found in Refs. 25 and 26. Along the critical isopleth in the one-phase region, \( \varepsilon \) reads

\[ \varepsilon^c(T) = \varepsilon_c + D^{c+}_{0,m} |\Delta \mu|^{1-\alpha} + D^{c+}_{0,m} |\Delta h| + \ldots. \]

This result is not new in the sense that it was obtained in the standard scaling formulation for fluids under an electric field. As regards the behavior of \( \varepsilon \) along coexistence, it can be expressed as

\[ \varepsilon^c(T) = \varepsilon_c \pm B^c_{0,m} |\Delta \mu|^\beta + D^c_{2,m} |\Delta \mu|^\beta + D^c_{1,m} |\Delta h|^{1-\alpha} + D^c_{0,m} |\Delta h| + \ldots, \]

with

\[ B^c_{0,m} = \begin{pmatrix} [a_5 + \varepsilon_3 a_3] Q U f_{-1} |T_m|^\beta, \end{pmatrix} \]

\[ D^c_{2,m} = \frac{a_3 (B^c_{0,m})^2}{a_5 + \varepsilon_3 a_3}, \]

\[ D^c_{1,m} = \left[ -b_1 b_3 + b_5 \frac{A_0}{1 - \alpha} |T_m|^{-1}, \right] \]

where + and − refer to the coexisting phases while \( A_0 \) is the leading critical amplitude of the dimensionless isobaric heat capacity at constant mole fraction in the two-phase region. \( Q \) and \( U \) are positive system-dependent constants, while \( f_{-1} \) is the first-order coefficient of the expansion for the universal scaling function along coexistence. The parameter \( T_m = (1 - b_1 a_2) + (b_2 - b_4 a_4) (e^c - a_2 c_4) \) is a mixing
factor. Equation (8) shows that a leading $|\Delta \hat{\zeta}|^{2\beta}$ singularity is the result of pressure mixing into the ordering field (note that $D_{2,m}^c$ is proportional to the pressure mixing coefficient $a_3$).

**B. The Maxwell–Wagner effect**

In a heterogeneous dielectric with nonzero electric conductance a low frequency dielectric dispersion can occur. This was already demonstrated in 1892 by Maxwell\(^\text{32}\) considering two different dielectric slabs (with different dielectric constants and different electric conductivities) between the plates of a parallel plate capacitor. The occurrence of a low frequency dielectric dispersion effect was demonstrated. This simple model was extended by Wagner in 1914 (Ref. 33) to dilute heterogeneous systems of droplets of a given phase D dispersed in another, phase B. Hence, the resulting low frequency dielectric dispersion effect is called the Maxwell–Wagner effect. Wagner considered spherical droplets with dielectric constant $\varepsilon_D$ and electric conductivity $\sigma_D$ dispersed in a medium with bulk properties $\varepsilon_B$ and $\sigma_B$. For $\varepsilon$ of the whole system, a low frequency dispersion effect with a single relaxation time, $\tau_{MW}$, between the limits $\varepsilon_1$ and $\varepsilon_0$ (with $\varepsilon_1 > \varepsilon_0$) was obtained. For the electric conductivity $\sigma$, a similar frequency dispersion with the same $\tau_{MW}$ was obtained within the limits $\sigma_1$ and $\sigma_0$ (with $\sigma_1 > \sigma_0$). Here we will only consider the dispersion in the dielectric constant. The results for $\varepsilon$, $\varepsilon_1 - \varepsilon_0$, and $\tau_{MW}$ are given in Eqs. (10)–(12) below and are expressed in terms of the properties of the droplets and the medium. $\phi$ is the volume fraction of the droplets in the mixture, and $\varepsilon_0$ is the permittivity of vacuum,

$$\varepsilon_0 = \frac{2\varepsilon_B + \varepsilon_D - 2\phi(\varepsilon_B - \varepsilon_D)}{2\varepsilon_B + \varepsilon_D + \phi(\varepsilon_B - \varepsilon_D)},$$

$$\varepsilon = \frac{\varepsilon_D - \varepsilon_B}{\varepsilon_D + \varepsilon_B + \phi(\varepsilon_B - \varepsilon_D)} + \frac{\varepsilon_B + \phi(\varepsilon_B - \varepsilon_D)}{1 + \phi(\varepsilon_B - \varepsilon_D)}$$

$$\tau_{MW} = \frac{1}{2\pi f_{MW}} = \varepsilon_0 \left( \frac{\varepsilon_B}{\sigma_B} - \frac{1}{1 - (1 - \phi)(\varepsilon_B - \varepsilon_D)/3\varepsilon_B}. \right)$$

Near a liquid-liquid critical point, one can observe large concentration fluctuations that can be considered as droplets.\(^\text{34}\) In many cases ionic impurities, when present, will prefer one of the components of the mixture (e.g., the polar one in polar-nonpolar systems). The fluctuations (droplets) will give rise to heterogeneity (with differences in $\varepsilon$ and $\sigma$), qualitatively similar to Wagner’s simple model. Thus, in systems with nonzero conductivity, there is a clear possibility for a MW-type dielectric dispersion near the critical point. Such a dispersion effect was clearly observed and reported in 1980 by Thoen et al.\(^\text{12}\) for the liquid-liquid critical point of benzonitrile-isooctane and subsequently confirmed for several other systems.\(^\text{13,14,16,19,35–37}\) By identifying the “size” of the droplets with the correlation length of the critical fluctuations $\xi$ and taking into account that (also in the homogeneous phase) the concentration difference in the fluctuations goes to zero with the same power law as the order parameter,\(^\text{38}\) Thoen et al.\(^\text{39}\) arrived at an expression for the temperature dependence of the MW-amplitude on approaching the critical point,

$$\Delta \varepsilon_{MW} = \varepsilon_1 - \varepsilon_0 \propto (T - T_c)^{-(\nu - \beta)}.$$  

(13)

In this equation $\nu$ is the critical exponent for the correlation length, and $\beta$ is the order parameter critical exponent. Liquid-liquid critical points belong to the Ising universality class, and on the basis of the theoretical values $\beta = 0.326$ and $\nu = 0.630$, one expects $\Delta \varepsilon_{MW}$ to diverge with an exponent $\nu - \beta = 0.304$.\(^\text{40}\)

**C. Power law expressions for some quantities derived from the dielectric constant**

In adiabatic scanning calorimetry (ASC), the primary result is the detailed behavior of the enthalpy, $H(T)$, as a function of temperature.\(^\text{41–43}\) For phase transitions the detailed knowledge of $H(T)$ allows one to discriminate between first order transitions (nonzero latent heat) and second-order transitions (no latent heat). The specific heat capacity (at constant pressure) is the slope $C^v(T)$ of $H(T)$ at a given temperature $T$ and can readily be obtained in ASC by numerical differentiation of the large amount of enthalpy data. However, for second-order phase transitions (as it is the case here), the enthalpy data allow to introduce a new quantity $C^v = [H(T) - H(T_c)]/[T - T_c]$. This quantity corresponds with the slope of the chord connecting $H(T)$ with $H(T_c)$ in an $H$ versus $T$ plot. It can easily be shown\(^\text{41–43}\) that both $C^v$ and $C^v$ exhibit a power law divergence at the critical point with the same critical exponent $\alpha$ but for the latter with an amplitude divided by $1 - \alpha$. For the Ising universality class, one has $\alpha = 0.109$.\(^\text{40}\) It turns out in practice that fitting $C^v$ has distinct advantages in arriving at the critical parameters.

However, this approach cannot only be applied to the enthalpy (density) or entropy (density) but to every density variable (in the sense defined by Griffiths and Wheeler\(^\text{44}\)) or even to quantities (analytically) depending on such densities. In the past one of us introduced quantities similar to $C^v$ for the mass density, dielectric constant, and the refractive index in the one-phase region phase of mixtures near the liquid-liquid critical points.\(^\text{35,36,45,46}\) We introduce here also this type of quantities for the dielectric constant in the one-phase region (at the critical concentration) as well as for the $\varepsilon$ diameter, $\varepsilon_D = (\varepsilon^+ + \varepsilon^-)/2$, of the coexistence curve. From complete scaling, as explained above, we arrive at the following expressions for the dielectric constant $\varepsilon$ in the homogeneous phase and for the diameter $\varepsilon_D$:

$$\varepsilon = \varepsilon + A_\varepsilon |t|^{1-\alpha} + C_\varepsilon |t| + \ldots,$$

(14)
\[
e_d = \varepsilon_c + A_d|t|^{1-\alpha} + B_d|t|^{2\beta} + C_d|t| + \ldots
\]  

For simplicity of notation we replaced \(\Delta \tilde{T} = (T - T_c)/T_c\) used in Sec. II A by \(t\), already used in Sec. I. Also a simplified notation is introduced for the amplitudes in the different \(t\) dependent terms. On the basis of these equations, we can introduce the following new quantities:

\[
E_h' = \frac{d \varepsilon_h}{d|t|} = (1 - \alpha)A_h|t|^{\alpha} + C_h + \ldots,
\]

\[
E_d' = \frac{d \varepsilon_d}{d|t|} = (1 - \alpha)A_d|t|^{\alpha} + 2\beta B_d|t|^{2\beta-1} + C_d + \ldots,
\]

\[
E_h = \frac{\varepsilon_h - \varepsilon_c}{|t|} = A_h|t|^\alpha + C_h + \ldots,
\]

\[
E_d = \frac{\varepsilon_d - \varepsilon_c}{|t|} = A_d|t|^\alpha + B_d|t|^{2\beta-1} + C_d + \ldots.
\]

All these equations will be used in the data analysis in an effort to eliminate or at least reduce correlations between fitting coefficients often encountered in using the direct expressions of Eqs. (14) and (15).

III. EXPERIMENTS

The dielectric permittivity of the binary mixture nitrobenzene-tetradecane \([\text{NB-TD}], (\text{C}_6\text{H}_5\text{NO}_2-\text{C}_{14}\text{H}_{29})\] has been determined as a function of frequency and temperature for both the homogeneous phase and the two-phase region. We have used the same measurement cell as the one depicted in Fig. 1 in Ref. 21. This measurement cell has two capacitors at different heights in the sample, and it is entirely made of stainless steel, Teflon, and glass. Each of the capacitors is assembled in a three-terminal configuration, where the condensator plates are separated from the ground. This allows to cancel spurious contributions of stray capacitance. The empty capacitance of each of the capacitors is about 7 pF. The hand-balanced bridges used for the previous work \cite{21} have been replaced by a Hewlett-Packard HP4284A LCR meter. This instrument allows for an automatic determination of \(C\) (the capacitance of the sample, modeled as an ideal capacitor in parallel with an ideal resistor) and \(G\) (the conductance of the ideal resistor) in the frequency range from 20 Hz to 1 MHz. The dielectric permittivity was obtained by dividing the measured \(C\) by the measured value \(C_0\) of the empty cell. We have measured as a function of frequency, and the real part \(\varepsilon'\) of the complex dielectric permittivity \(\varepsilon'(f, T) = \varepsilon'(f, T) - i\varepsilon''(f, T)\) was obtained as a function of frequency. From this dispersion curve, the static dielectric permittivity \(\varepsilon\) was obtained by taking the value of \(\varepsilon'\) at such a frequency that neither the (high frequency) orientational rotation contributions nor the (low frequency) conductivity contributions play a role.

For the first series of measurements, the temperature control was provided by immersing the measurement cell directly in a water thermostat. The bath was also connected to a cooling unit. In this case, a temperature stability of 50 mK was reached. Later on, measurements with a higher accuracy temperature control were performed for NB-TD(b) mixtures by placing the measurement cell in a multistage setup. The measurement cell was immersed in an oil bath, equipped with a heater, a stirrer, and a Pt reference thermometer, of which the temperature could be controlled. This oil bath with Plexiglass walls was itself placed in the same temperature controlled water bath as before. In this case, the stability of the temperature proved to be better than 1 mK.

Two types of runs have been performed above as well as below \(T_c = 32.0 \, ^\circ\text{C} (305.2 \, \text{K})\). Both NB-TD(a) and NB-TD(b) runs have been performed with about 50–60 temperature points over the range from about 40 °C to about 26 °C. In these runs, full frequency spectra have been measured, taking 41 frequency points logarithmically spaced between 100 Hz and 1 MHz. These extensive spectra were used for a detailed analysis of electrode polarization effects and the critical MW effect. In addition for NB-TD(b) runs have also been performed with more than 500 closely spaced temperature points but with limited frequency values (100 Hz, 1 kHz, 10 kHz, 100 kHz, and 1 MHz). In this operation modus, the temperature steps near \(T_c\) were 2 mK.

Two different types of the NB-TD binary mixture systems have been measured. The first lower purity system, NB-TD(a), consisted of 99% pure NB and 99% pure TD. The second system, NB-TD(b), consisted of 99.5% pure NB and 99.5% pure TD. An overview of the measured mixtures is given in Table I.

<table>
<thead>
<tr>
<th>System</th>
<th>NB purity (%)</th>
<th>TD purity (%)</th>
<th>Molar concentration (x_{\text{NB}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>NB-TD(a)</td>
<td>99</td>
<td>99</td>
<td>0.655\textsuperscript{a}</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.661</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.673</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.678\textsuperscript{b}</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.684</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.684\textsuperscript{b}</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.699</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Initial concentration; other concentrations were prepared by adding NB to the previous one, starting from this concentration.

\textsuperscript{b}Critical concentration.

IV. RESULTS

In Fig. 1 the dielectric constant at 10 kHz for the five concentrations of NB-TD(a) is given. We will show later on...
in Sec. V B that the data in the homogeneous phase close to $T_c$ are at this frequency influenced by the critical MW relaxation and are therefore not the real static dielectric constant; however, the difference is small. Clearly visible is the critical temperature $T_c$ at about 305.2 K from the five concentrations. In the two-phase region, the curves are coinciding for all mixtures, whereas in the homogeneous phase, the dielectric constant is increasing with increasing concentration of NB. The asymmetry of the coexistence curve and the nonlinearity of the diameter of the coexistence curve are clearly visible.

To verify that we have measured the critical concentration, the value of the last point above $T_c$ was compared with the value of first point of the diameter below $T_c$: these should be the same in the limit of $T_c$. Figure 2 shows that the fourth concentration, 0.678, is the closest to meeting this criterion. However, the value in the homogeneous phase is somewhat above that of the diameter. However, one has to realize that the contribution of the critical MW is not yet subtracted, and after this operation is performed, the values are almost the same. Particularly remarkable is also the good concordance of the critical mole fraction obtained in this work, 0.678, with that obtained by Shen and co-workers, 0.676\textsuperscript{47}

In Fig. 3 the results for two selected runs on the NB-TD(b) system are presented. All the features already observed for NB-TD(a) can also be seen here. $T_c$ has not changed appreciably from the lower purity system and the concentration is the critical one within the experimental accuracy. The two runs displayed here are the runs for which the analysis of the critical behavior in the next sections has been performed. Run 1, used for the analysis of the homogeneous phase, started about 4 K above $T_c$ and ended about 0.5 K below $T_c$ such that $T_c$ could clearly be seen in the data. In the same way, run 2, used for the two-phase region, started about 0.4 K above $T_c$ and ended about 2 K below $T_c$.

We decided to measure the homogeneous phase and the two-phase region in two separate runs because of the long time required for these experiments, thus reducing the impact of potential problems that might occur during a run. Because of this, there are small differences in the critical parameters reported for run 1 and run 2; however, these differences fall within the limits of accuracy and reproducibility of this type of experiments and samples. Also, the analysis of the critical behavior is not influenced by this circumstance.

V. ANALYSIS OF THE DATA IN THE ONE-PHASE REGION

In the one-phase region, there are two phenomena to be studied: the critical MW relaxation and the critical behavior of the static dielectric permittivity. As discussed in Sec. II B, the MW relaxation is a critical phenomenon that leads to a low frequency dispersion in the dielectric permittivity. Depending on the measurement frequency, the outcome of the experiment may or may not reflect this extra contribution. Historically, the lack of knowledge of the critical MW has led to the observation of different types of critical behavior of the dielectric constant, as indicated in the introduction. Therefore, the analysis of the homogeneous phase should start with an analysis of the MW relaxation to obtain the
appropriate measurement frequency. Once this is done, one can analyze the critical behavior of the static dielectric constant itself.

This section is organized as follows. We have selected the most extensive run 1 of the runs on the NB-TD(b) system to analyze \( \epsilon \) in the homogeneous phase. First the choice of the critical parameters for this run is discussed. Then, the MW relaxation will be discussed in detail. The concentration dependence and the complete frequency behavior will be investigated based on a selection of runs both from the NB-TD(a) series and from the NB-TD(b) series. The critical behavior of the MW relaxation itself, in run 1 on the NB-TD(b) system, is presented, and finally the critical behavior of the static dielectric constant for the same run 1 is reported.

### A. Determination of the critical parameters

As already pointed out, for the investigation of the critical behavior in the homogeneous phase, the most complete run 1 on the NB-TD(b) system with the critical concentration of \( x_c = 0.677 \) was used. The run was started at 309.5 K, and the sample was cooled down below \( T_c \) with a decreasing temperature step, going down to 5 mK from about 1 K above \( T_c \). At each temperature point, the temperature was stabilized for several hours, and the measurement was performed at 100 Hz, 1 kHz, 10 kHz, 100 kHz, and 1 MHz.

Because of the high precision in both temperature and dielectric permittivity, values for \( T_c \) and \( \epsilon \) were obtained from the data directly. For \( T_c \), three possible values were selected. Because \( T_c \) should fall below the temperature of the last point of the homogeneous phase (at \( T = 305.1968 \) K) and above the first point of the two-phase region (at \( T = 305.1920 \) K), the value of \( T_c \) was chosen as the middle of this interval, leading to \( T_c = (305.1945 \pm 0.0025) \) K. An ex-

![FIG. 4. Dispersion curve for NB-TD(a) with \( x = x_c = 0.678 \) at about 305.29 K (last point before \( T_c \)), upper electrode data. The solid line is a fit to Eq. (20); the dashed line shows the contribution of the Maxwell–Wagner term.](image)

### Table II. Values of \( T_c \) and \( \epsilon \) as obtained from the data and used in the analysis.

<table>
<thead>
<tr>
<th>( T_c (K) )</th>
<th>( \epsilon )</th>
</tr>
</thead>
<tbody>
<tr>
<td>305.1945(^a)</td>
<td>12.958 14(^a)</td>
</tr>
<tr>
<td>305.1945</td>
<td>12.958 22</td>
</tr>
<tr>
<td>305.1945</td>
<td>12.958 02</td>
</tr>
<tr>
<td>305.1920</td>
<td>12.958 12</td>
</tr>
<tr>
<td>305.1968</td>
<td>12.958 17</td>
</tr>
</tbody>
</table>

\(^a\)Best choices.

![FIG. 5. Strength of the electrode polarization and the Maxwell–Wagner relaxation as a function of concentration. Calculated from the lower electrode data taken for NB-TD(a) of the five concentrations in Table I at \( T - T_c = 0.15 \) K.](image)

![FIG. 6. (a) Temperature dependence of the strength of the Maxwell–Wagner relaxation as obtained from the data of run 1 at \( x_c = 0.677 \) of NB-TB(b) in Table I. (b) Log-log plot for the Maxwell–Wagner relaxation strength vs reduced temperature as obtained from the data in the same run 1. Open circles: upper condensator; closed circles: lower condensator. The solid line has a slope of \(-0.304\).](image)
trapolation of the $\varepsilon$ data respecting the shape of the curve near $T_c$ led to an accompanying value of $\varepsilon_c = 12.95814 \pm 0.00010$. In order to verify the importance of the choice of $T_c$ and $\varepsilon_c$ within the bounds imposed by the quality of the experimental data and the careful extrapolation, four other couples ($T_c, \varepsilon_c$) have been used in the analysis. These couples were selected at the edges of the error bounds and thus provide the extreme cases. The values of the five selected ($T_c, \varepsilon_c$) couples are listed in Table II.

### B. Concentration and frequency dependence of the Maxwell–Wagner relaxation

The presence of fluctuations and impurities gives rise to a low frequency dispersion in binary mixtures, as discussed in Sec. II B. As an illustration, the dispersion curve at about $T-T_c=0.02$ K for $x=x_c=0.678$ was analyzed in detail. The data are presented in Fig. 4. The fast rise below 1 kHz is the contribution of electrode polarization: at low frequencies of the applied field, free ions in the system gather at the electrode interface and introduce a macroscopic polarization over the sample, resulting in a steep rise in the permittivity. The MW relaxation is the step situated between 1 kHz and 100 kHz. The static plateau, from which the dielectric constant $\varepsilon$ should be obtained, is reached at the higher frequencies above this region. The fitting line in Fig. 4 was obtained from a fit with

$$\varepsilon'(f) = A f^n + \text{Re} \left[ \frac{\Delta \varepsilon_{MW}}{1 + i 2 \pi f \tau_{MW}} \right] + \varepsilon. \quad (20)$$

$A$ and $n$ are parameters describing the electrode polarization, and a Debye relaxation term with strength $\Delta \varepsilon_{MW}$ and relax-
nearly constant in the five cases, while of these last two quantities are given in Fig. 5. The frequency dependencies of the data in Fig. 5 for NB-TD buildup at the droplets interfaces. Thus, as is clearly seen in the amount of free ions that can contribute to the charge concentration. The strength of the MW relaxation is not only one would a priori expect the maximum at the critical concentration. The strength of the MW relaxation is not only influenced by the importance of the fluctuations but also by the amount of free ions that can contribute to the charge buildup at the droplets interfaces. Thus, as is clearly seen in the data in Fig. 5 for NB-TD(a) system, the maximum for the MW strength apparently falls at a concentration close to the critical one but somewhat away from it to the side of increasing concentration of the polar compound because it is this compound that introduces the bulk of the free ions that are responsible for the interface polarization. The same conclusion could be drawn from the measurements on the NB-TD(b) system, where also concentrations above the critical one have been measured.

C. The critical behavior of the Maxwell–Wagner relaxation

From the preliminary analysis of the critical MW effect in the NB-TD(a) system and in the first run of the NB-TD(b) system (with extended frequency spectrum), it was clear that the relaxation is centered around 10 kHz. This means that one can get an excellent approximation for the strength of the MW by subtracting the data at 100 kHz from those at 1 kHz. However, because the low frequency end of the MW and the electrode polarization effect flow over into each other, it turns out that there is a small correction necessary to compensate for the electrode polarization, which is acting as a background on the MW strength. This leads to the calculation

$$
\Delta \epsilon_{MW}(T) = \epsilon(1 \text{ kHz}, T) - \epsilon(100 \text{ kHz}, T) - \Delta \epsilon_{EP}(T)
$$

(21)

for the dielectric strength of the MW relaxation. Here $\Delta \epsilon_{EP}(T)$ is the correction for the electrode polarization. Because the MW relaxation is a critical phenomenon, it does not show up at temperatures sufficiently high above $T_c$. In that case, the difference $\epsilon(1 \text{ kHz}) - \epsilon(100 \text{ kHz})$ can be attributed to the influence of the electrode polarization. For the run 1 that is considered here, this region reaches from 306.45 K to the highest temperatures. From the data in this region the linear background $\Delta \epsilon_{EP}(T)$ is obtained.

Since there is a small difference in the MW behavior as measured by the lower and the upper capacitors, the data are analyzed separately. Only $T_c = 305.1945$ K is used for the critical temperature because the difference in the obtained results is small.

The MW strength, as obtained from the calculation in Eq. (21), is plotted in Fig. 6. On the basis of Eq. (13), which

![Figure 7. Static dielectric constant $\epsilon$ in the homogeneous phase above $T_c$ as a function of temperature. The solid line results from fit 1 in Table III.](image-url)
states that the strength of the MW scales with a power law in $T-\bar{T}_c$, the data are presented in a log$_{10}|\Delta \varepsilon_{\text{MW}}|$ versus log$_{10}(t)$ plot. In this double-logarithmic representation, the expected power law should show as a straight line with the exponent as its slope. It is clear from Fig. 6 that this is only the case for the points approaching $\bar{T}_c$.

D. The critical behavior of the static dielectric constant

After our analysis of the MW relaxation, we can conclude for the static $\varepsilon$ that the appropriate measuring frequency is 100 kHz. We did not use the data at 1 MHz because the calibration of the empty cell was less reliable at this frequency (the upper edge of the instrument’s frequency range). Because there was no difference between the data at 100 kHz as measured with the lower or the upper condenser, the data were averaged, and this averaged data set was used for the final analysis.

As stated above in Sec. II A, both the classical scaling theory and the complete scaling theory for liquid-liquid mixtures in an electrical field predict for the homogeneous phase a critical behavior following Eq. (14). In order to verify this for the NB-TD system, we performed an analysis of the type proposed in Sec. II C. The values of the critical parameters, as given in Table II, are kept fixed during the fitting procedure. Also the value of $\alpha$ was fixed to the theoretically expected Ising value $\alpha=0.109$. This means that in fits with Eqs. (14), (16), and (18), only two free parameters are left, namely, the amplitudes of the $1-\alpha$ term and of the linear term, $A_h$ and $C_h$, respectively.

In order to assess the quality of the fits, a $\chi^2$ was calculated for all the fits. The $\chi^2$ values have been calculated using the definition

$$\chi^2 = \frac{1}{N - p - 1} \sum (y(i) - f(i))^2.$$

where $N$ is the number of data points, $p$ is the number of fit parameters, $y(i)$ is the $i$th measurement value, and $f(i)$ is the corresponding fit value. The denominator corresponds to the variance on the data. Following this definition for $\chi^2$, an ideal fit should have $\chi^2 = 1$, and larger values indicate a lower quality fit. For the uncertainty in the dielectric permittivity data, repeated measurements on a reference liquid were made. Careful analysis of the noise in this test measurement leads to a value of $\sigma(i)=7 \times 10^{-5}$, thus an error of the order of 0.01% on the data point. For the chord and the derivative, the variance was obtained from the scatter in the data points.

The results of these fits are summarized in Table III. As a first remark, it is immediately clear from the data that both the linear background term and a critical $1-\alpha$ contribution are necessary to get a good fit of the data. Therefore, no fits with either $A_h=0$ or $C_h=0$ are included. This is also quite natural, considering that the $1/T$ temperature dependence of the dielectric constant (for this polar system), in the absence of critical behavior, should still be present. Locally, it can be approximated well by a linear function. On the other hand, the critical behavior is quite apparent in the increased curvature near $\bar{T}_c$. In Fig. 7 the data are displayed together with a fitting curve for the best choices of $\bar{T}_c$ and $\varepsilon_c$.

Combining these $\chi^2$ values, the residues of the fit and also visually assessing the quality of the fit, the data are well described by the proposed equations. Thus, the analysis confirms that Eqs. (5) and (14) with $\alpha=0.109$ are good fits to the data. Moreover, one can observe from Table III that the consistency relations between the quantities $\varepsilon_{\text{h}}$, $C^\sigma_h$, and $C^\varphi_h$, given in Sec. II C are confirmed.

VI. ANALYSIS OF THE DATA IN THE TWO-PHASE REGION

A. Determination of the critical parameters

For the investigation of the two-phase region, a high-resolution run with closely spaced temperatures near $\bar{T}_c$ was carried out for the high purity critical mixture ($\chi_{\text{NB}}=0.677$) of NB-TD(b): run 2. Near the critical point, temperature steps were as small as 2 mK. The temperature range of this run started about 0.4 K above $\bar{T}_c$ in the homogeneous phase and ended at about 2 K below $\bar{T}_c$ in the two-phase region.

FIG. 8. Temperature dependence of the difference $\Delta \varepsilon$ of the two coexisting phases below $\bar{T}_c$ as obtained from the data of run 2 at $\chi=0.677$ of NB-TD(b) in Table I. The solid curve results from fit 2, and the dotted line results from fit 4 in Table IV.

FIG. 9. Experimental data for the dielectric diameter $\varepsilon_{\text{d}}=(\varepsilon^+ + \varepsilon^-)/2$ compared with a fit with Eq. (24) with $\varepsilon_c$ fixed at 305.1999 and 12.951, respectively. The inset gives $\chi^2$ values for a set of different fixed $\theta$ values.
Because of the small temperature steps, a value $T_c = 305.1999 \pm 0.0004$ K was derived from the temperatures of the lowest point in the homogeneous phase and the highest point in the two-phase region. An extrapolation (over a few millikelvin) of the diameter in the two-phase region resulted in the corresponding $\epsilon_c = 12.951 \pm 0.004$ for this run.

### B. Analysis of the difference in $\epsilon$ of the two coexisting phases

From Eq. (6) it can be seen that the difference $\Delta \epsilon$ between $\epsilon^-$ (here the NB-rich phase) and $\epsilon^+$ (here the TD-rich phase) goes to zero at $T_c$ as a power law with the critical exponent $\beta$. Fits have been carried out on the difference $\Delta \epsilon = \epsilon^+ - \epsilon^-$ with the following power law expression:

$$\Delta \epsilon = B_\Delta |t|^{\beta(1 + C_\Delta |t|^{\delta})} + D_\Delta |t|^\delta.$$  \hspace{1cm} (23)

In addition to the leading power law term with the exponent $\beta$, also the first corrections-to-scaling term with the exponent $\Delta$ (fixed to a value of 0.50) was included. Also the possible contribution of a linear term was considered. This term might account for the higher order term 25,26 with exponent $3\beta = 0.978$, to be included in Eq. (6), or represent for the small $t$-range considered, the $1/T$ behavior of $\epsilon$ in this polar system. In the fits with Eq. (23), the $\chi^2$ in Eq. (22) was minimized with a value $\sigma(t) = 0.04$ for all data points. This value was estimated on the basis of the scatter in the experimental $\Delta \epsilon$ values.

In Table IV an overview of the results for the parameters in different fitting approaches is given. Fits 1–4 are different combinations for the best choice of the critical temperature. From a comparison of the fits 1 and 4, it can be observed that a simple power law fit with $\beta$ fixed to the theoretical value of 0.326 results in a substantially poorer fit than with $\beta$ also a free parameter. The obtained effective value for $\beta$ is $0.341 \pm 0.006$. However, including the corrections-to-scaling contribution (fit 2) or the linear term (fit 3) in Eq. (23), results in fits of the same quality as fit 4. Including both the corrections-to-scaling and the linear term did not significantly improve the fits. Fixing $T_c$ to values at the edges of the experimentally allowed $T$-range (fits 5–12) did not change the picture obtained from fits 1–4. In Fig. 8 the experimental data are compared with the curves obtained with the parameters of fits 2 and 4.

### C. Analysis of the dielectric diameter of the coexisting phases

Information on the singular terms in the critical behavior of the diameter $\epsilon_d = (\epsilon^+ + \epsilon^-)/2$ can be obtained by fitting the direct $\epsilon_d$ data with Eq. (15) or by fitting the derived quantities $E'_d$ or $E''_d$ with Eq. (17) or Eq. (19), respectively. In all fits considered the theoretical Ising values $\alpha = 0.109$ and $\beta = 0.326$ have been imposed. For the fits also the experimental limits for the critical temperature $T_c$ and for the critical value $\epsilon_c$ of the dielectric constant, discussed in Sec. VI A, are implemented.

As an initial test to see whether one of the terms of Eq. (15) was dominant, we did fits with a simplified power law of the form

$$\epsilon_d - \epsilon_c = \Gamma |t|^\theta.$$  \hspace{1cm} (24)

A fit with $T_c = 305.1999$ K and $\epsilon_c = 12.951$ fixed resulted in a value $\theta = 0.827 \pm 0.05$. This value is smaller than $1 - \alpha = 0.891$ but substantially larger than $2\beta = 0.652$. In the log-log plot in Fig. 9, the straight line with slope $\theta = 0.827$ represents this best fit. In the inset of that figure the $\chi^2$ values for fixed $\theta$ values are also given. Apparently, no good fits can be obtained with the simplified Eq. (24), all terms of Eq. (15) or Eqs. (17) and (19) have to be considered.

In Table V an overview of the fit parameters of different kinds of fits with Eq. (15) or Eq. (19) is given. Fits 1–8 are fits with Eq. (19) of the quantity $E'_d$. For the calculation of $\chi^2$ [Eq. (22)] in these fits $\sigma(t) = 0.025$ was used. From fits 1–3 it follows that good fits can be obtained with the three amplitude parameters in Eq. (19) adjustable and that changing $T_c$
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FIG. 10. Experimental data for the quantity $E_d$ in Eq. (19) compared with different fitting results in Table V. Solid: line fit 1; dotted line: fit 7; dash-dotted line: fit 6; and dashed line: fit 8.

FIG. 11. Temperature dependence of the dielectric diameter of $e$ in the two-phase region obtained from the data of run 2 at $x_c = 0.677$ of NB-TD(b) in Table I. The solid curve results from fit 9 in Table V.

FIG. 12. Temperature dependence of the quantity $E_d'$ in Eq. (17). The solid line results from a direct fit with Eq. (17). The dotted curve results from using the parameters of fit 1 in Table V for the quantity $E_d'$ and the dashed line by using the parameters of fit 9 for the direct $E_d'$. These data can then be fitted with the expression of Eq. (17), the advantage being that a value of $e_c$ is not needed. It turned out, however, that because of the substantial scatter in the data near $T_c$ (see Fig. 12), the minimum in $\chi^2_e$ was very wide, and a broad range of parameters gave reasonable fits to the $E_d'$ data. The solid line in Fig. 12 represents one of the best direct fits. It is however also possible to test the consistency of the $E_d'$ data with good quality fit parameters, $A_d$, $B_d$, and $C_d$ as obtained by fitting $E_d'$ and $E_d''$ with Eqs. (15) and (19), respectively. The two other curves in Fig. 12 clearly show excellent consistency.

Lacking additional information on other physical parameters in this system, it is presently not possible to use the information on $B_d$ [of Eq. (15)] in Table V, to obtain reliable values of the different mixing coefficients of Eqs. (6)–(9). Moreover, it was pointed out by one of the referees that because of the nonlinear relationship between the dielectric constant and the density as a result of the Clausius–Mossotti (CM) relation, an additional $|d|^{10}$ term should be expected even in the absence of critical fluctuations. It should be remarked that in the present polar mixture of a polar and a nonpolar liquid, the CM relation is not applicable. Relevant relations should rather be of the Debye, Onsager, or Kirkwood type, taking the dipole moments of the polar molecules into account. However, these equations also exhibit nonlinearity between $e$ and the density (and concentration) and thus might also give rise to a contribution similar to the CM one suggested by the referee. Estimates of such a contribution from our experimental data are currently not possible.

VII. SUMMARY AND CONCLUSION

Experimental data have been presented for the dielectric constant $e$ for the binary liquid mixture nitrobenzene-tetradecane in the homogeneous phase above the critical temperature $T_c$ as well as in the two-phase region below $T_c$. Measurements have been carried out as a function of temperature for several (near critical) mole fractions $x$. The frequency range was between 100 Hz and 1 MHz. The data have been analyzed in the context of the recently developed...
concept of complete scaling. From the analysis of the frequency dependence a low frequency (below about 1 kHz) electrode polarization effect was observed for the whole temperature range investigated. In the homogeneous phase near the critical temperature also a low frequency critical Maxwell–Wagner relaxation effect (with a relaxation frequency around 10 kHz) was clearly visible for the critical mole fraction as well as for near critical mole fractions. It was shown that the temperature dependence along the critical isopleth of the amplitude of this critical MW effect is consistent with predictions of a droplet model for the critical concentration fluctuations.\(^{39}\) It was also shown that data measured at 100 kHz (well above the electrode polarization and MW frequency range) can be considered as static values. Fitting these static values in the homogeneous phase as a function of temperature results in a contribution of a linear term in \(t\) \([\text{with } t = (T - T_c)/T_c]\) and of a power law singularity of the form \(|t|^{\alpha - 2}\), with \(\alpha\) consistent with the Ising value \(\alpha = 0.109\). Fitting the temperature dependence of the difference \(\Delta \varepsilon\) of the dielectric constants in each of the coexisting phases with a simple power law of the form \(|t|^{\beta}\) resulted in a critical exponent value \(\beta = 0.341\), somewhat higher than the Ising value \(\beta = 0.326\). Good fits with the Ising value were only obtained by including a corrections-to-scaling or a linear term in \(|t|\). Fits without one of the terms resulted in poor fitting. Thus the data confirm the theoretical expectation of a contribution from \((1 - \alpha)\) and \(2\beta\) terms.

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