

# Electric permittivity in the one- and two-phase region of 1-nitropropane–hexadecane near-critical solution

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Received 20 May 1996

## Abstract

Results of dielectric constant measurements in a one- and two-phase region of near-critical 1-nitropropane–hexadecane solution are presented. For the critical anomaly in the homogeneous region the critical exponent  $1 - \alpha = 0.87 \pm 0.03$  was found. The influence of the correction-to-scaling has been discussed. Below  $T_c$ , the analysis of the binodale gave  $1 - \alpha = 0.88 \pm 0.12$  for the diameter and  $\beta = 0.328 \pm 0.06$  for the order parameter, neglecting the influence of the correction-to-scaling in the tested temperature range  $T - T_c \approx 5$  K. All above values are in very good agreement with theoretical predictions. For the pretransitional anomaly in the homogeneous region the analysis of the low-frequency Maxwell–Wagner dispersion effect gave the critical exponent  $x = 0.41 \pm 0.02$ , a bit higher than the theoretically predicted value  $x \approx 0.3$ .

## 1. Introduction

Studies of anomalous behaviour of electric permittivity near the critical consolute point in binary solutions began in Poland more than sixty years ago [1,2]. Nevertheless, there have not been many publications dealing with such studies in the two-phase region [3,4]. For a long time the weakness of the pretransitional anomaly and its sensitivity to spurious effects caused severe experimental difficulties and often gave puzzling results [5].

In the seventies, from a few theoretical models the conclusion was reached that [6–8]:

$$\varepsilon = \varepsilon_c \left( 1 + A_1 t + A_2 t^{1-a} + A_3 t^{1-\alpha+A_1} + \dots \right),$$
$$T > T_c, \quad (1)$$

where  $t = |(T - T_c)/T_c|$  where  $T_c$  is the critical consolute temperature,  $\varepsilon_c$  denotes the value of the electric permittivity at the critical point,  $A_1$  is the amplitude associated with the behaviour remote from  $T_c$ ,  $A_2$  is the critical amplitude and  $A_3$  is the amplitude of the first correction-to-scaling term. The critical exponent  $\alpha \approx 0.110 \pm 0.0045$  [9] describes the singularity of the specific heat,  $\Delta_1 \approx 0.5$  is the first correction-to-scaling exponent [10].

Particularly promising was the application of critical point universality to the critical behaviour of a liquid in the presence of an electric field by Sengers et al. [8]. Apart from the above relation, the model gave the dependence of the critical amplitude from the rate of the shift of  $T_c$  induced by the electric field ( $dT_c/dE^2$ ) and by the hydrostatic pressure ( $dT_c/dp$ ). It also indicated that the influence of

possible critical anomaly of the density ( $\rho$ ) can be minimised introducing to the analysis  $\varepsilon/\rho$  instead  $\varepsilon$ .

Thoen et al. [5] showed that the confusing experimental situation could be partly associated with the presence of the low-frequency dispersion effect (Maxwell–Wagner (MW) effect). They ascertained that the “static” electric permittivity, required in Eq. (1), can be measured only for a sufficiently high frequency, where this dispersion is absent. Eq. (1), as well as the influence of the MW effect, have been successfully tested in recent experiments [11–16].

As for the critical behaviour of electric conductivity, there are still essential differences, both theoretical and experimental. A brief discussion of this matter is given elsewhere (see for instance Ref. [11]).

One could expect that the behaviour of  $\varepsilon$  in the two-phase region is associated with properties of the coexistence curve [10,17]. For the mean value of electric permittivity in coexisting phases the same behaviour as for the diameter of binodale [10] can be expected:

$$\frac{1}{2}(\varepsilon_L + \varepsilon_U) = A(1 + a_1 t + a_2 t^{1-\alpha} + a_3 t^{1-\alpha+\Delta_1} + \dots), \quad T < T_c \quad (2)$$

where L and U indices stand for the lower and upper phase respectively.

The difference of electric permittivities in coexisting phases should play the role of the order parameter [10,17]:

$$\varepsilon_L - \varepsilon_U = B(1 + b_1 t + b_2 t^\beta + b_3 t^{\beta+\Delta_1} + \dots), \quad T < T_c \quad (3)$$

where the critical exponent  $\beta \approx 0.325$  [10,17].

For physical properties which are not proper order parameters, but which are analytic functions, an additional power term  $t^{2\beta}$  may appear in Eq. (3) [10,17].

Up to now experiments on the electric permittivity below  $T_c$  are very rare [3,4,18]. In this paper results of an experimental test on universal aspects of critical behaviour of electric permittivity on both sides of the critical consolute point in a near-critical 1-nitropropane–hexadecane solution are presented. The chosen solution enables measurements in a convenient range of temperature, with reasonable values of the electric permittivity and conductivity in coex-

isting phases. The recently determined dependence  $T_c(p)$  up to 200 MPa may be also of some importance for possible further studies in this solution [19].

## 2. Experimental

Experiments were conducted using a cylindrical capacitor constructed according to the proposition of Tveekrem et al. [18]. The internal cover was divided into two sectors, what created two separate measurement capacitors. It enabled simultaneous measurements of electric permittivity in coexisting phases below  $T_c$ . The total height of the capacitor was 63 mm, the diameter of the internal cover was 35 mm. The height of each measurement sector (capacitor) placed at the top and the bottom of the tested solution was 16 mm, what with the gap equal to 2.5 mm gave  $C_0 \approx 7$  pF for each measurement capacitor. The sample inside the capacitor was in contact only with stainless steel and Teflon. The capacitor with a tested sample was placed in a continuously mixed silicone oil bath, in a thermostatted vessel. The temperature of the vessel was stabilised by a double-stage system of water-circulating thermostats. Temperature was measured by a platinum resistor (A1 class, DIN 43 760) with resolution 0.002 K and precision 0.1 K, using a Keithley 195A multimeter. Additionally, two copper–constantan thermocouples monitored eventual temperature gradient along the capacitor. The electric permittivity was measured by means of a HP 4192A impedance analyser.

The critical parameters,  $T_c = 308.1$  K and  $x_c = 0.66$  mole fraction of 1-nitropropane, were determined using the visual method [19,20]. The temperature changes of the density in the homogeneous region of the tested solution were determined using a dilatometric method [17,20]:

$$\rho = (1.1047 \pm 0.0008) - (0.00086 \pm 0.000003)T, \quad T - T_c < 20 \text{ K}. \quad (4)$$

Here  $\rho$  is in  $\text{g cm}^{-3}$  and T in K. Within the limit of the experimental error the density did not exhibit a pretransitional anomaly.

1-Nitropropane (Fluka) and hexadecane (Reachim, Moscow) were three times distilled, the third time immediately prior to the measurement and dried over molecular sieves.

The data were analysed using the Origin 3.5 software (Microcal Inc.). All errors are given as three standard deviations.

### 3. Results and discussion

Results of measurements of electric permittivity for 4 selected frequencies are shown in Fig. 1. In the homogeneous solution ( $T > T_c$ ), values of permittivity increase systematically with the decrease of measured frequency. This effect, noted also before [11–16], is connected with the polarisation of capacitor plates for lower frequencies due to the presence of ionic impurities. However, in the tested solution this effect appears for a lower frequency than in earlier experiments. For  $f > 100$  kHz it is even negligible. Experimental data for  $f = 1$  MHz and  $f = 3$  MHz could be superimposed, with no visible discrepancy near  $T_c$ . Also the influence of the MW low-frequency dispersion seems to appear for lower frequencies than in earlier tested systems [11–16]. These features of the tested solution make it possible to consider 1 MHz as the frequency in which the MW effect is negligible and Eqs. (1) and (2) are satisfied. The conductivity (Fig. 2) of the solution is comparable with earlier tested solutions [11–16] and does not exhibit a pretransitional anomaly found often in these studies. The coexistence curve deter-

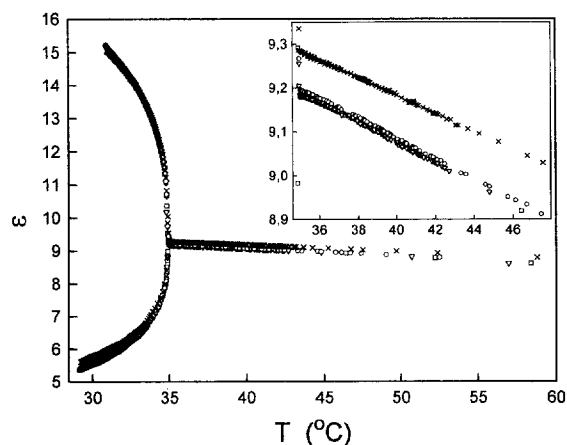


Fig. 1. The temperature dependence of electric permittivity in the homogeneous and two-phase regions of 1-nitropropane-hexadecane near-critical solution for frequencies of 1 MHz ( $\square$ ), 100 kHz ( $\circ$ ), 10 kHz ( $\nabla$ ), 1 kHz ( $\times$ ).

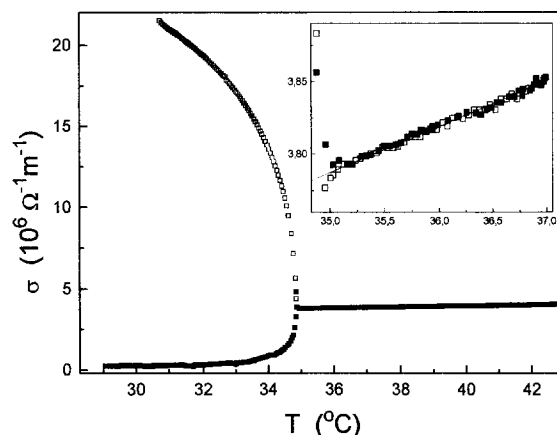


Fig. 2. The behaviour of the electric conductivity in the tested solution for  $f = 1$  MHz.

mined from conductivity studies is much more asymmetric than the one obtained from electric permittivity measurements.

The dependence of  $\varepsilon(T)$  for  $f = 1$  MHz (assumed “static regime”), determined from measurements in capacitors placed at the top and the bottom of the tested solution (i.e. in coexisting phases below  $T_c$ ) is presented in Fig. 3. The insert shows the critical deviation from the linear behaviour of  $\varepsilon(T)$  remote from  $T_c$ . Over the tested temperature range,  $T - T_c \approx$

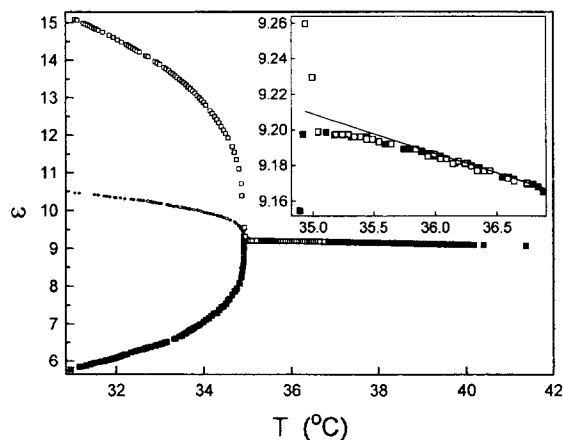


Fig. 3. The temperature dependence of electric permittivity for  $f = 1$  MHz in the homogeneous and two-phase region. The open and full squares are from measurements in capacitors placed at the top and the bottom of the 1-nitropropane-hexadecane solution. The insert shows the precritical anomaly. Below  $T_c$  the diameter of the binodal is also plotted.

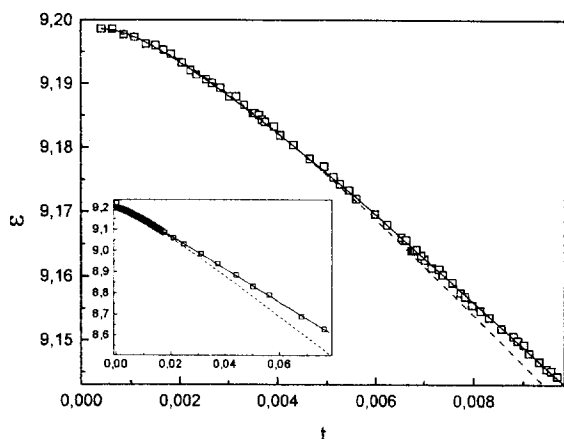


Fig. 4. The range of validity of the description of the electric permittivity in the tested solution with (dashed line) and without a correction-to-scaling term (solid line).

22 K, the pretransitional anomaly of electric permittivity in the isotropic phase can be described by means of Eq. (1):

$$\varepsilon = (9.19 \pm 0.02) [1 - (2.1 \pm 0.15)t + (0.79 \pm 0.1)t^{0.88 \pm 0.03} + (0.64 \pm 0.2)t^{0.5}] \quad (5)$$

(st.dev.  $\approx 1.5 \times 10^{-6}$  and  $\chi^2 \approx 1.2$ ).

In the immediate vicinity of the critical consolute point correction-to-scaling terms could be neglected:

$$\varepsilon = (9.19 \pm 0.02) [1 - (2 \pm 0.1)t + (0.8 \pm 0.13)t^{0.87 \pm 0.03}], \quad \text{for } T - T_c < 1 \text{ K} \quad (6)$$

(st. dev.  $\approx 6 \times 10^{-7}$  and  $\chi^2 \approx 1.2$ ).

Fig. 4 shows ranges of validity of Eqs. (4) and (5) and the quality of fits. The lack, within the limits of experimental error, of the anomaly of density causes that the analysis of  $\varepsilon/\rho$  only renormalizes amplitudes and does not change the value of the critical exponents.

Normalising data to remove the effect of polarisation of plates of the capacitor and taking data for the frequency of 1 MHz as the reference level, the Maxwell–Wagner effect may be estimated as (Fig. 5):

$$\Delta\varepsilon_{\text{MW}} = \varepsilon(10 \text{ kHz}) - \varepsilon(1 \text{ MHz}) = (2.86 \pm 0.3) \times 10^{-4} t^{0.41 \pm 0.02} \quad (7)$$

The value of the critical exponent is a bit greater than the theoretically predicted [5] one:

$$\Delta\varepsilon_{\text{MW}} \propto t^{\beta-\nu} \approx t^{0.302}, \quad (8)$$

where  $\nu \approx 0.63$  describes the correlation length [10]. The same value, within the limits of experimental error, was obtained experimentally in Ref. [11]. Taking into account the weakness of the pretransitional anomaly of  $\varepsilon(T)$  and of the MW effect the agreement with the theory seems to be reasonably.

The frequency dependence of the MW effect, for the three chosen isotherms, is presented in the insert in Fig. 5. For  $\Delta T$  closest to the critical consolute point, the strength of the MW effect is about 0.01. This value is much smaller than the typical value found in previous studies (for instance Ref. [11]). This weakness and the experimental error make any reliable analysis of this isothermal behaviour impossible.

In the two-phase region ( $T < T_c$ ) the difference in permittivity between the coexisting phases may be expressed throughout the tested temperature range ( $T - T_c < 6$  K) by a single, simple power relation (Fig. 6):

$$\varepsilon_1 - \varepsilon_2 = (39 \pm 1.2)t^{0.328 \pm 0.006}, \quad f = 1 \text{ MHz}. \quad (9)$$

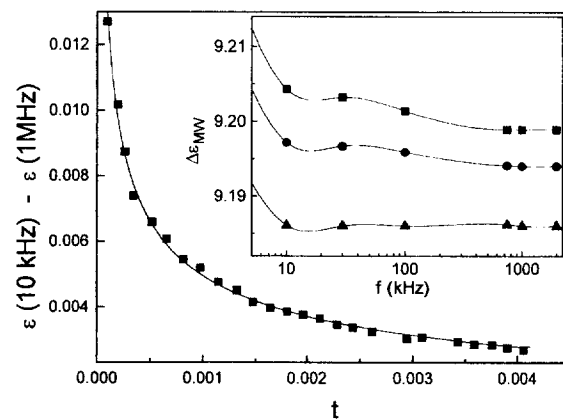


Fig. 5. The temperature dependence of the Maxwell–Wagner effect. The solid line presents the fit according to Eq. (1). The insert illustrates the dependence of the permittivity on frequency for following distances from the critical consolute point:  $\Delta T = 0.04$  K (■),  $\Delta T = 0.15$  K (●),  $\Delta T = 0.18$  K (▲).

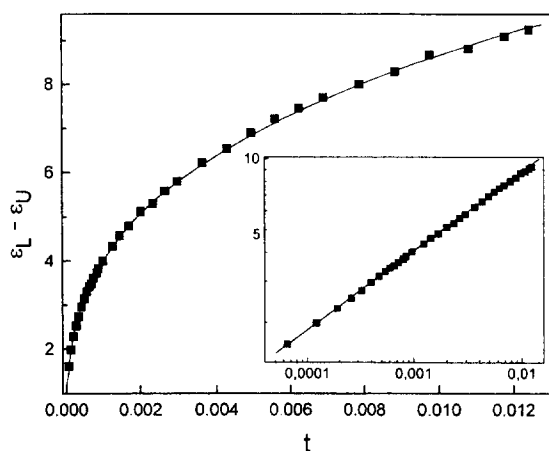


Fig. 6. The difference of electric permittivities in coexisting phases below  $T_c$  on a log–log scale in the tested 1-nitropropane–hexadecane solution (Eq. (9)).

The value of the critical exponent very close to  $\beta \approx 0.325$  indicates the very slight influence of correction-to-scaling terms in Eq. (3). The diameter of the coexistence curve exhibits a clear departure from the law of rectilinear diameter (Fig. 7). The best fit can be found for two power terms in Eq. (4):

$$\frac{1}{2}(\varepsilon_1 + \varepsilon_2) = (9.03 \pm 0.06) \left[ 1 + (176 \pm 10)t + (24.5 \pm 1)t^{0.65 \pm 0.1} + (162 \pm 7)t^{0.88 \pm 0.12} \right]. \quad (10)$$

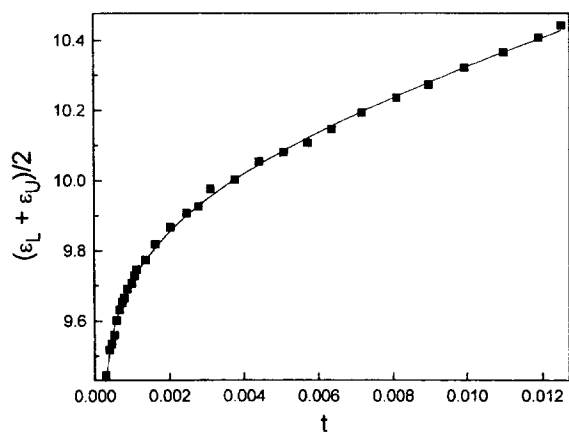


Fig. 7. The experimental (squares) and fitted (line, Eq. (10)) critical effect of the diameter of the electric permittivity in coexisting phases for the 1-nitropropane–hexadecane solution.

Fig. 7 illustrates the quality of the fit. The obtained values of critical exponents in the two-phase region are in very good agreement with theoretical prediction for the coexistence curve.

#### 4. Conclusions

Results obtained allowed for the discussion of universal critical properties of electric permittivity in a binary solution, both in the homogeneous region and along the coexistence curve. In all cases very good agreement with theoretical prediction was found. The validity of this result emphasises the possibility of neglecting correction-to-scaling terms in the two-phase region and above  $T_c$  for  $T - T_c < 1$ , what minimises the number of fitted parameters. Worth stressing is the lack of the critical anomaly of the electric conductivity within the limits of experimental error.

Concluding, the tested 1-nitropropane–hexadecane solution exhibits almost model agreement with theoretical prediction for the electric permittivity on the both sides of the critical consolute point. The specific property of the solution tested in this paper is a large difference between the sizes of the dipole component (1-nitropropane) and the non-dipole solvent (hexadecane). This, on the other hand, may induce other features for e.g. the weakness of the MW effect.

#### Acknowledgement

The authors are grateful J. Ziolo for support and fruitful discussions. The research was financially supported by the Committee for Scientific Research (KBN, Poland), project 2 P302 081 06.

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