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Critical properties in the vicinity of the critical consolute point for the 4-methoxybenzylidene-4′-butylaniline–isooctane solution

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Results are presented of measurements of the non-linear dielectric effect on approaching the critical consolute point in a solution composed of a liquid crystal (MBBA) and a non-mesogenic component (isooctane). The coordinates of the critical point are $T_C \approx 2°C$ and $x_C \approx 0{\cdot}77$ mole fraction of isooctane. The exponent ψ describing the critical effect of the non-linear dielectric effect is the same as that for a binary solution of ordinary liquids ($\psi \approx 0{\cdot}37$, i.e. it is non-classical). It should be stressed that it is the smallest critical effect which has been ever analysed by means of this method. For small concentrations of isooctane the exponent $\psi \approx 1$, i.e. the behaviour is classical. In the system studied the coexistence curve with the critical consolute point appears for concentrations of isooctane greater than 0·45. Its form is also characteristic of a solution of two ordinary, non-mesogenic, liquids (i.e. $\beta = 0{\cdot}34 \pm 0{\cdot}01$).

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1. Introduction

The non-linear dielectric effect [1] has hitherto been used to study pretransitional effects in binary solutions of limited miscibility of ordinary liquids [2–4] and in the isotropic phase of liquid crystals in the vicinity of the clearing temperature [5–7]. As a research method it is very complementary to the Kerr effect [8, 9] and, particularly in the case of liquid crystals, to the Cotton–Mouton effect as well as to light scattering [9, 10]. Similar to these effects the non-linear dielectric effect exhibits a strong critical anomaly [2–7, 9]

$$\left(\frac{\Delta\varepsilon}{E^2}\right)_C = \left(\frac{\Delta\varepsilon}{E^2}\right)_T - \left(\frac{\Delta\varepsilon}{E^2}\right)_B \approx At^{-\psi}, \quad T > T_c, \tag{1}$$

where $\Delta\varepsilon = \varepsilon_H - \varepsilon_L$, and the indices H and L denote high and low strength of the electric field E, respectively. The value of $\Delta\varepsilon/E^2$ is a measure of the effect. Indices T, C and B denote the total measured value of the non-linear dielectric effect, the critical effect and the non-critical background effect, respectively. T_c is the critical temperature, A and ψ are a critical amplitide and a critical exponent, respectively.

The experimental value of the exponent ψ determined from measurements made in a large number of binary, critical solutions of ordinary liquids [3, 4] was shown to be $\psi = 0{\cdot}37$–$0{\cdot}4$; the predicted theoretical value [11, 12] is 0·59. The reason for this discrepancy has yet to be elucidated. Agreement with the theory is, however, very good for liquid crystals [9]. Measurements were made in the isotropic liquid in the vicinity of the nematic [5], smectic [7] and blue phases [6]. In all these cases the classical value for ψ of 1 was obtained.

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The purpose of this paper was to study the behaviour of the non-linear dielectric effect near the critical consolute point in a solution for which one component has nematogenic properties and the second is a non-mesogenic liquid.

2. Measurements

The solution chosen for investigations was a mixture of 4-methoxybenzylidene-4′-butylaniline (MBBA) and 2,2,4-trimethylpentane (isooctane). Prior to each measurement MBBA (manufactured by the Riedel de Haen) was degassed. Isooctane (from Merck) was purified by means of standard methods [13]. The apparatus used for the non-linear dielectric effect measurements was developed on the basis of the Małecki method [14]. The frequency of the measurement field was a few MHz and the duration of the rectangular pulse of the strong electric field was about 1 ms. The value of the effect in the system studied was very small. To record it with an accuracy enabling analysis was possibly only due to the application of a system as cumulating the sample's responses [15]. Typically, about 50 accumulations were made. The samples studied were placed in a flat parallel capacitor with a gap of 0·2 mm; a voltage of 400–1000 V was applied to the plates of the capacitor. The temperature was stabilized with an accuracy to 0·01°C. All calculations were made by means of the least square method [16] and the errors are given as three standard deviations.

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3. Results and discussion

Figure 1 shows the phase diagram for the MBBA–isooctane solution, which is similar to those obtained for other mixtures of this type [17]. The characteristic feature of this system is the appearance of the coexistence curve for concentrations of isooctane greater than 0·45 mol fraction. The enlarged binodal curve in the vicinity of the critical point is shown in the corner of figure 1; the behaviour of its diameter is also presented. The form of the coexistence curve obtained may be described by [18, 19] (see figure 2):

$$x_U - x_L \approx B t^{\beta}, \tag{2}$$

where x_U and x_L denote the mole fraction of isooctane in the upper and lower phase, respectively. $B = 1{\cdot}69 \pm 0{\cdot}1$ and $\beta = 0{\cdot}34 \pm 0{\cdot}01$ are the critical amplitude and exponent, respectively, and $t = (T - T_c)/T_c$ is the dimensionless temperature from the critical temperature T_c. The parameters of the critical consolute point are: $x_c = 0{\cdot}77$ and $T_c = 275{\cdot}16$ K (2°C). The value of the exponent β obtained is characteristic of the $d = 3$, $n = 1$ universality class, i.e. to within the limits of experimental error it is the same as for a binary mixture of limited miscibility of non-mesogenic liquids [17, 18]. It is of interest that the mixture studied is very easily supercooled. Virtually the whole coexistence curve was obtained in the supercooled state. Applying strong electric field pulses causes a non-continuous isotropic liquid–solid crystal (I–S) phase transition at higher temperatures. In figure 1 are shown several I–S transition points determined during our measurements. A characteristic minimum of the I–S transition temperature is observed for the critical concentration. Similar behaviour has been observed for solutions of *m*-nitrotoluene in alkanes [19]. For the critical concentration crystallization took place at 0·3°C above T_c.

The results of the non-linear dielectric effect measurement for this solution are shown in figure 3. Numerical analysis of these data confirm the validity of equation (1); values for ψ of $0{\cdot}37 \pm 0{\cdot}03$ and for A of $4{\cdot}7 \pm 0{\cdot}5 \times 10^{-20}\,\mathrm{m^2\,V^{-2}}$ were found. The value of the critical exponent is the same as in the case of critical binary solutions of non-mesogenic, liquids [3, 4]. It should be stressed it is the smallest critical effect which has

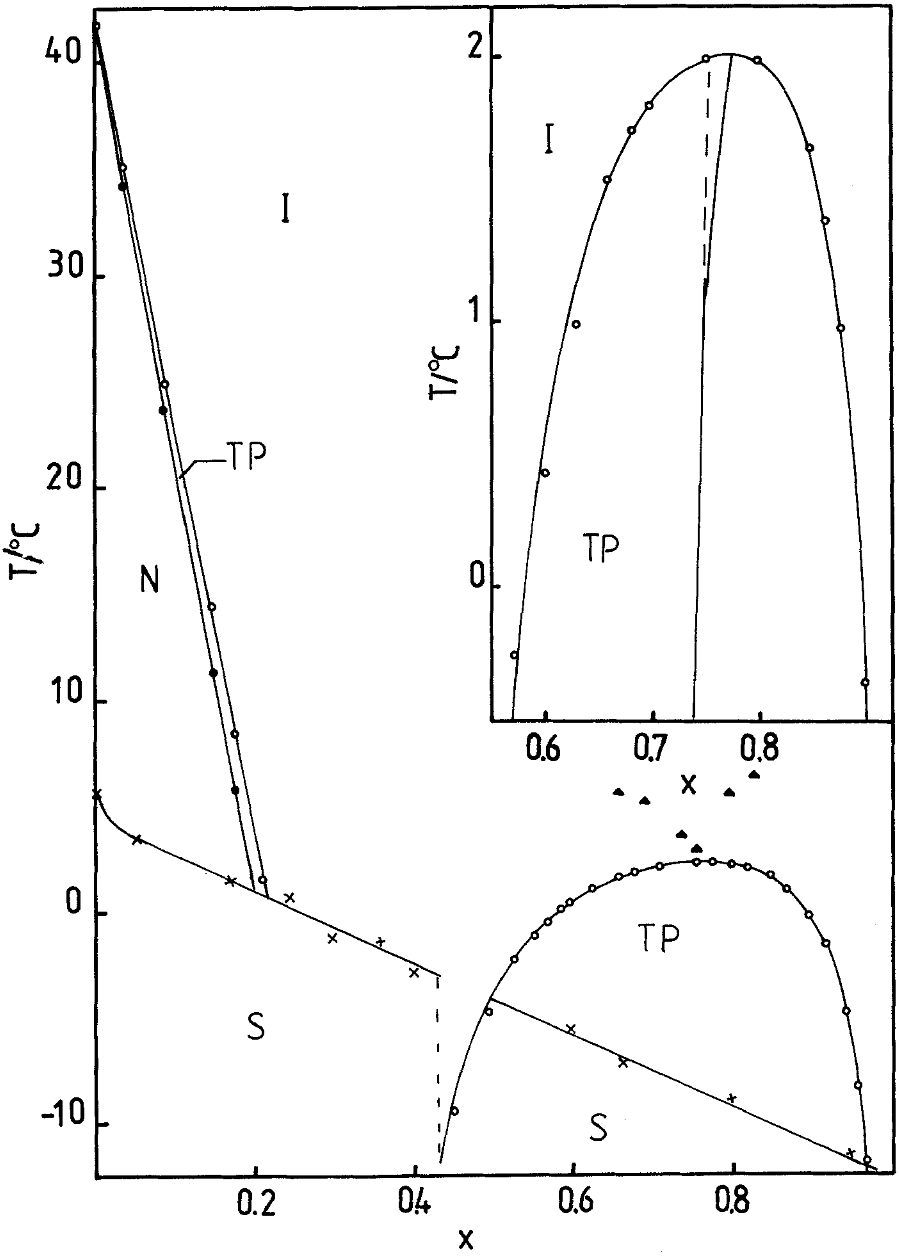

Figure 1. The phase diagram of the MBBA–isooctane solution. x is the mole fraction of isooctane. Open circles denote the transition from the isotropic to the two-phase region, full circles are for the transition to the nematic phase and crosses denote crystallization. Triangles denote crystallization caused by a strong electric field.

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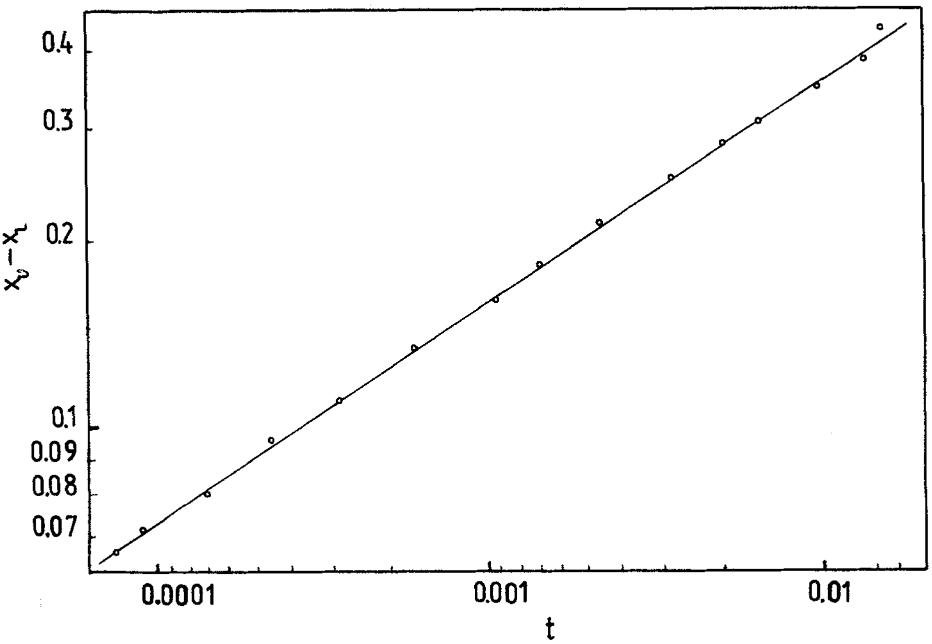

Figure 2. The log–log plot of the difference of isooctane concentration in coexisting phases (indices U and L are for the upper and lower phase, respectively) versus $t=(T-T_c)/T_c$. The slope of the straight line, i.e. the value of the critical exponent β describing the behaviour of the order parameter is 0·34 ± 0·01.

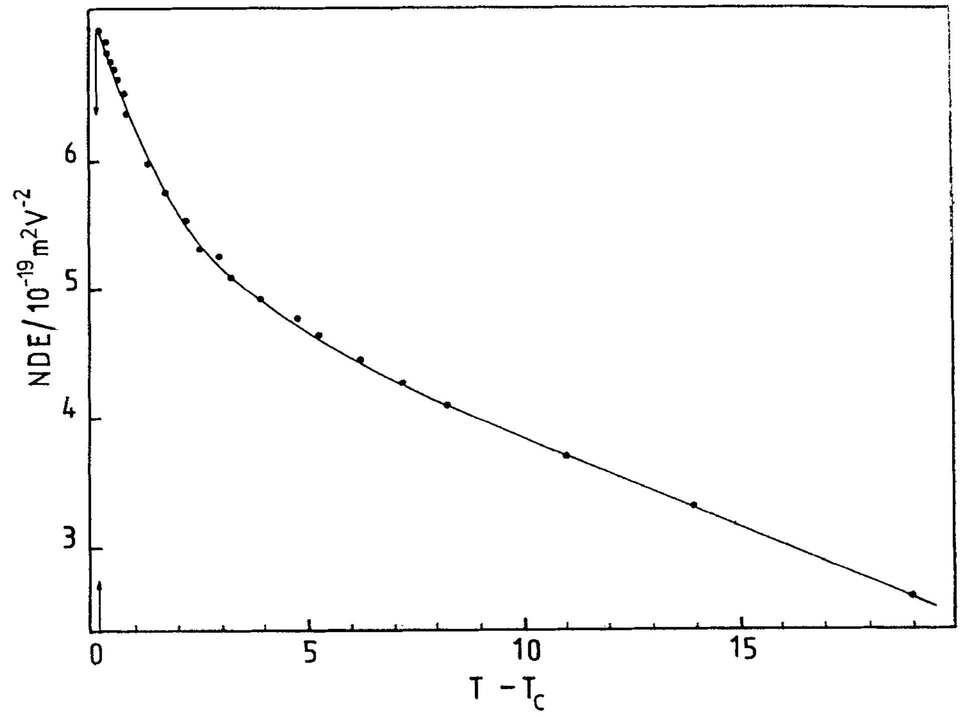

Figure 3. Results of the non-linear dielectric effect measurements in a critical MBBA–isooctane solution. Arrows denote the point of crystallization.

ever been analysed. Its value is of the same order as those originating from (very weak) non-critical statistical fluctuations [1].

As shown in our earlier studies [20], for small concentrations of the non-mesogenic component ($x < 0{\cdot}2$ in this case), where the biphasic region also appears but in a different way (see figure 1), the critical effect is classical: i.e. $\psi = 1$.

The characteristic feature of the system studied is that the critical increase as well as the total value of the measured effect is very small. The small value of the critical amplitude is caused by the relatively small difference between the electric permittivities of MBBA [21] ($\varepsilon \approx 6{\cdot}7$) and of isooctane [22] ($\varepsilon = 1{\cdot}940$). According to the droplet theory the dependence of the critical amplitude on the dielectric properties of the solution is given by [11, 23]

$$A \sim \frac{(\varepsilon_1 - \varepsilon_2)^4}{\varepsilon_c^2}, \qquad (3)$$

where the indices 1 and 2 denote the first and the second component of the solution, respectively. ε_c is the electric permittivity of the solution with the critical concentration. The validity of this relation may be checked by a comparison of the amplitudes for an MBBA–isooctane (MI) solution and for a nitrobenzene–heptane (NH) solution which exhibits a large critical effect [24] ($A = 0{\cdot}9 \pm 0{\cdot}06 \times 10^{-17}\,\mathrm{m}^2\,\mathrm{V}^{-2}$) and a large difference between the permittivities of constituents ($\varepsilon_1 - \varepsilon_2 \approx 32{\cdot}8$) [1, 22]

$$\frac{A_{\mathrm{NH}}}{A_{\mathrm{MI}}} \approx \frac{[(\varepsilon_1 - \varepsilon_2)^4/\varepsilon_c^2]_{\mathrm{NH}}}{[(\varepsilon_1 - \varepsilon_2)^4/\varepsilon_c^2]_{\mathrm{MI}}}. \qquad (4)$$

The right hand ratio is 138 while the ratio of the critical amplitudes is 189. Taking into account the approximate nature of this formula and also the experimental error the agreement may be taken to be good.

All of the results reported here indicate conclusively that in a solution composed of a nematogen and a non-mesogenic liquid, the properties near a critical consolute point appear to be very similar to those of a solution of limited miscibility of two ordinary liquids.

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