

Specific heat capacity singularity and related weak anomalies in the nitroethane-cyclohexane critical binary mixture

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An adiabatic scanning calorimeter has been used to measure the specific heat capacity $C_{p,x}$ of a critical nitroethane-cyclohexane binary liquid mixture in the one-phase and the two-phase region above and below the consolute point. The temperature dependence of the refractive index n has been measured with a grating interferometer. Also the change of the critical temperature with pressure has been measured. Combining these new results with existing results for the dielectric constant ϵ and the density ρ allowed a broad inspection of several relationships among these physical quantities. From our analysis it followed that the data are fully consistent with scaling predictions. The critical exponent α and the critical heat capacity amplitude ratio values agree very well with the theoretical values for the three-dimensional Ising universality class. Reasonable agreement was found between the critical amplitude from experimental density data and the value calculated from the specific heat capacity amplitude and the slope of the critical line. In contrast to the dielectric constant results, where a large intrinsic effect is present, a similar effect in the refractive index within the experimental uncertainties could not be detected. [S1063-651X(96)06706-2]

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I. INTRODUCTION

Intensive experimental and theoretical efforts during the last two to three decades have resulted in the concept of universality according to which the properties of a system near a critical point can be divided into a small number of universality classes. This concept of universality implies that the critical exponents describing critical behavior of macroscopic properties should only depend on the spatial dimension, the symmetry of the order parameter, and the symmetry and range of interactions, but not on the details (like form and magnitude) of the interactions [1,2]. Both one-component pure fluids near their liquid-gas critical point and binary liquid mixtures near their consolute point belong to the same universality class as the three-dimensional Ising model [3,4]. In this universality class the critical behavior is determined by two relevant scaling fields, a strong ordering field related to the order-parameter fluctuations and a weak temperaturelike field related to the energy fluctuations.

We are concerned here with binary liquid mixtures near a consolute point, in which case the order parameter may be identified with the concentration and the strong scaling field with the chemical potential difference [5,6]. One of the consequences of the energy fluctuations is the weak divergence in $C_{p,x}$, the specific heat capacity at constant pressure and critical concentration $x=x_c$ for binary liquid mixtures [6-8]. Since binary liquid mixtures can be investigated at different pressures, there is a line of second-order consolute points with the critical temperature T_c varying with pressure. The work described further was carried out at or near a pressure of 1 atm.

It can be shown [7] that, asymptotically close to the criti-

cal point, the singular part of $C_{p,x}$ and of the thermal expansion coefficient at constant pressure and composition $\alpha_{p,x} = \rho^{-1}(\partial\rho/\partial T)_{p,x}$ diverge with the same critical exponent α and are related to the change of the critical temperature with pressure dT_c/dp . Since the value for α is small ($\alpha_I = 0.110 \pm 0.002$) [9], the density will have a weak cusp near T_c , increasing or decreasing, depending on the sign of dT_c/dp . Besides the pressure field variable other fields, e.g., an electric field, will also give rise to lines of critical points. Exploring an argument originally proposed by Mistura [10], Sengers *et al.* [11] applied critical point universality to the thermodynamic behavior of fluids in the presence of an electric field, and predicted that in addition to an anomalous contribution arising from the density behavior, there should also be an intrinsic $(1-\alpha)$ anomaly in the dielectric constant ϵ and in the refractive index n related to the change of T_c with the square of the electric field dT_c/dE^2 .

In this paper we present for the binary liquid system nitroethane-cyclohexane (NE-CH) data for the specific heat capacity $C_{p,x}$ along the critical composition line $x=x_c$ in the homogeneous phase and in the two-phase region, for the refractive index n in the homogeneous phase at $x=x_c$, and for dT_c/dp . Together with previously obtained results for the dielectric constant [12] and the density [13], this results in a rather complete characterization of this binary system, allowing exploration of different relationships among the weak anomalies in a large set of physical parameters.

II. THEORETICAL BACKGROUND

The application of critical point universality to binary liquid mixtures by Sengers *et al.* [11] results in the homoge-

neous phase for the critical composition $x - x_c$ in the following functional forms for the energy U (per mole), the density, the dielectric constant, and the refractive index:

$$U = U_c(1 + U_1\tau^\theta + U_2\tau + U_3\tau^{\theta+\Delta_1} + \dots), \quad (1)$$

$$\rho^{-1} = \rho_c^{-1}(1 + R_1\tau^\theta + R_2\tau + R_3\tau^{\theta+\Delta_1} + \dots), \quad (2)$$

$$\epsilon\rho^{-1} = \epsilon_c\rho_c^{-1}(1 + E_1\tau^\theta + E_2\tau + E_3\tau^{\theta+\Delta_1} + \dots), \quad (3)$$

$$n\rho^{-1} = n_c\rho_c^{-1}(1 + N_1\tau^\theta + N_2\tau + N_3\tau^{\theta+\Delta_1} + \dots), \quad (4)$$

where $\theta = 1 - \alpha$ and the index c refers to the value at the critical point of the corresponding quantity. $\Delta_1 = 0.50$ is the first correction-to-scaling exponent [9,14] and $\tau \equiv (T - T_c)/T$ is only slightly different from the more commonly used reduced temperature difference $t = (T - T_c)/T_c$. From Eq. (1) one readily obtains for the specific heat capacity in the homogeneous phase ($T > T_c$)

$$C_{p,x} = C_0 + C_1\tau^{-\alpha} + C_2\tau + C_3\tau^{-\alpha+\Delta_1} + \dots \quad (5)$$

For the two-phase region ($T < T_c$) this corresponds to

$$C_{p,x} = C'_0 + C'_1|\tau|^{-\alpha} + C'_2|\tau| + C'_3|\tau|^{-\alpha+\Delta_1} + \dots \quad (6)$$

Since experimentally one does not measure $\epsilon\rho^{-1}$ or $n\rho^{-1}$ but ϵ or n as a function of temperature, one normally uses, e.g., for fitting purposes, the following types of expressions:

$$\epsilon = \epsilon_c(1 + D_1\tau^\theta + D_2\tau + D_3\tau^{\theta+\Delta_1} + \dots), \quad (7)$$

$$n = n_c(1 + F_1\tau^\theta + F_2\tau + F_3\tau^{\theta+\Delta_1} + \dots), \quad (8)$$

where now $D_1 = E_1 - R_1$, $F_1 = N_1 - R_1$, etc. One thus recognizes two possible contributions to the leading anomalous τ^θ behavior of the dielectric constant ϵ or the refractive index n : (1) a contribution due to the thermal expansion divergence ($R_1 \neq 0$), and (2) an intrinsic effect for the dielectric constant ($E_1 \neq 0$) or the refractive index ($N_1 \neq 0$). In experimental data analysis it is also common practice to fit instead of ρ^{-1} directly the density ρ with an expression of the form

$$\rho = \rho_c(1 + G_1\tau^\theta + G_2\tau + G_3\tau^{\theta+\Delta_1} + \dots). \quad (9)$$

As already pointed out in the Introduction, there is a relationship between the leading singular part of the specific heat capacity and thermal expansion coefficient in the limit $T \rightarrow T_c$. Indeed, using experimentally verified geometric analysis of phase diagrams of multicomponent systems and rigorous thermodynamic relations one arrives at the following relation between G_1 and C_1 in Eqs. (9) and (5) [7,15]:

$$G_1 = \frac{-\rho_c C_1}{1 - \alpha} \frac{dT_c}{dp}. \quad (10)$$

It should also be pointed out that the amplitudes of the singular terms in the equations for $C_{p,x}$ above and below T_c are not independent but related by a universal ratio C'_1/C_1 , identical for all members of a given universality class. The ratio of the amplitudes C'_3/C_3 of the correction-to-scaling terms (which are only important for large values of τ) is also considered to be a universal quantity.

III. EXPERIMENTAL METHODS

A. Specific heat capacity measurements

The $C_{p,x}$ measurements have been carried out by adiabatic scanning calorimetry previously also used to study binary and ternary liquid mixtures near consolute points [16] as well as several phase transitions in liquid crystal [17–19]. Full details on the construction of the calorimeters and possible modes of operation can be found elsewhere [20,21]. Here only a brief account of some basic aspect of the measuring procedure will be given as far as needed for proper understanding of the reported results.

In the adiabatic scanning calorimetric method a measured heating power is continuously applied to (or extracted from) the sample and the sample holder. In such a dynamic mode the total heat capacity C_t is given by

$$C_t = C_{p,x} + C_h = P_t/\dot{T} = (P_e + P_l)/\dot{T}. \quad (11)$$

In Eq. (11) the total heating power P_t has been divided into two parts: P_e , the power applied electrically to a heater incorporated in the sample holder, and P_l representing leaks with an (adiabatic) shield surrounding the sample holder. For cooling runs, P_l has to be given a controlled negative value. By keeping P_t or \dot{T} constant, combined with increasing or decreasing the sample temperature, four practical modes of operation are obtained [20,21]. These modes require different settings for the servosystems controlling the temperature and maintaining adiabatic conditions, or a constant heat transfer between sample holder and shieldings. The most interesting operating conditions are the ones with constant heating or cooling power (P_t constant). It is sufficient to consider here only the constant heating mode. In this case, $P_t = P_e$ and P_l is kept negligibly small. In order to obtain the heat capacity of the sample one has to measure P_e , \dot{T} , and C_h . P_e is easily obtained from a measurement of the current and the voltage drop across the heating resistor on the sample holder. The rate \dot{T} has to be obtained by numerical differentiation of the carefully measured time dependence of temperature with a sensor in close thermal contact with the sample. Values of $C_h(T)$ can be derived from calibration runs without the sample or with calibration fluids in the sample holder.

B. Refractive index measurements

We have measured the variation of the refractive index with temperature by counting the fringe variation with a grating interferometer [22]. Figure 1 gives a schematic diagram of the optical setup. The advantage of this grating interferometer is that it performs a reversible counting and generates a dc compensated signal from the interference fringes.

A linearly polarized He-Ne laser light passes through the first grating (G_1), producing numerous diffraction orders. Two symmetrical beams of the first diffraction order are selected such that one of them acts as a reference beam and the other as a measuring beam. One of the beams passes through a $\lambda/2$ plate (P_1) such that the planes of polarization of the two beams are now perpendicular to each other. The two beams made parallel by the first objective (O_1) then enter the optical cell where one goes through the measuring section and the other through the reference section. This ensures

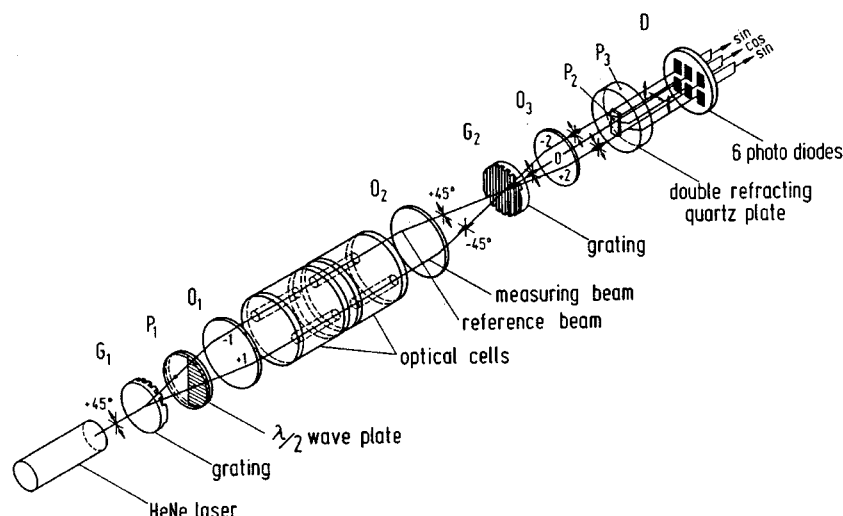


FIG. 1. Schematic diagram of the grating interferometer.

that to a great extent the variation in length due to change in pressure is compensated. The optical cell is embedded into a thermostat which controls the temperature to within ± 0.001 °C over a period of at least 24 h. A second objective (O_2) is used to focus the two beams on the second grating (G_2). The planes of polarization of the two beams are not affected by the two gratings. The beams focused on the second grating produce two diffraction patterns superimposed on one another. Among the resultant diffractions only three superimposed orders ($0, \pm 2$) have enough contrast so that they can be converted to electrical signals at a later stage.

C. Measurements of dT_c/dp

The experiment consists of measuring the change of the critical temperature as a function of pressure. The sample was contained in a cell made of Pyrex and the change in the critical temperature T_c was noted visually. The precision in the measurements of pressure and temperature was better than 1 kPa and 10 mK. The same experimental setup has previously been used to measure dT_c/dp for critical microemulsion systems, and full details can be found there [23,24].

D. Measurements of dielectric constant and density

For further analysis and discussion we will use our previously published results for the dielectric constant and the density for the critical binary nitroethane-cyclohexane mixture [12,13]. The dielectric constant data have been obtained with a measuring cell containing two vertically positioned cylindrical capacitors. Each capacitor was designed as a three-terminal system, i.e., both capacitor plates were isolated from the ground, which included the can surrounding the capacitors and containing the mixture. The two-capacitor setup allowed simultaneous measurements in the two-phase region below T_c . Above T_c it allowed us to verify the absence of composition gradients in the cell. Further details on the construction of the cell, the temperature control, and the measuring procedure can be found elsewhere [25]. The density data [26] were obtained with an A. PAAR, type DMA-02D, density meter, where density changes are derived from changes in the natural frequency of a hollow oscillating tube filled with the fluid.

IV. RESULTS

A. Specific heat capacity

Two different adiabatic scanning calorimetric runs have been carried out for a mixture of nitroethane-cyclohexane (NE-CH) with a critical mole fraction x_c (NE)= 0.453 ± 0.001 as determined from dielectric measurements in the homogeneous phase and in the two-phase region for mixtures with different composition [25]. The first run had a scanning rate $\dot{T} \leq 0.04$ K/h, and the second run had $\dot{T} \leq 0.01$ K/h. In both cases the sample was slowly stirred in the same way as described elsewhere [17,20]. Figure 2 gives an overview of the $C_{p,x}$ data of run 1, covering a temperature range between 19 °C and 28 °C. Run 2 only covered a temperature range of about 0.2 °C below and above T_c . Figure 3 gives $C_{p,x}$ results of run 2 in the immediate vicinity of T_c .

From simultaneous fits to the data of run 2 above and below T_c with Eqs. (5) and (6), under the restraints $C'_0 = C_0$, $C'_2 = C_2$, and $C'_3 = C_3 = 0$, the following values for relevant parameters have been obtained:

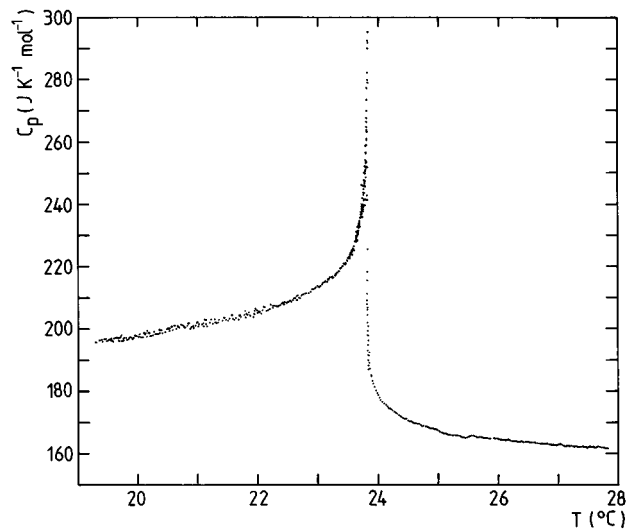


FIG. 2. The specific heat capacity results of run 1 for the critical binary liquid mixture of nitroethane-cyclohexane.

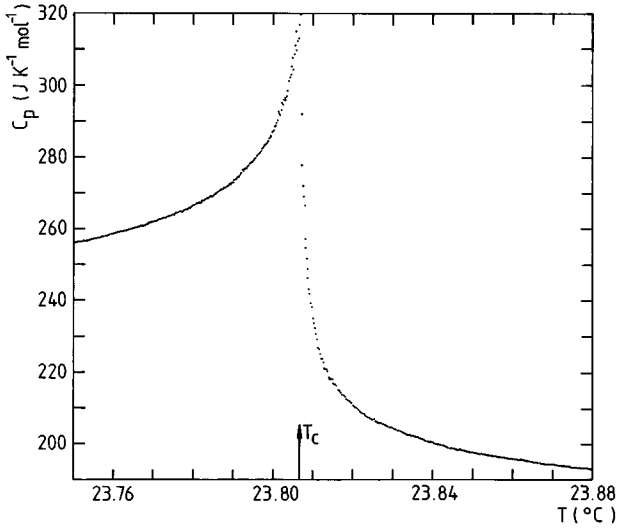


FIG. 3. The specific heat capacity results of run 2 for the critical binary liquid mixture of nitroethane-cyclohexane in a temperature range very close to the critical point.

$$\alpha = 0.11 \pm 0.02,$$

$$C_1 = 295(\pm 5) \text{ J K}^{-1} \text{ kg}^{-1}, \quad (12)$$

$$C'_1 = 567(\pm 8) \text{ J K}^{-1} \text{ kg}^{-1}.$$

Separate fits to the data above and below T_c gave, within the quoted uncertainties, the same parameter values. Fits to the data of run 1 resulted in parameter values with somewhat larger uncertainties but consistent with (12). Including correction-to-scaling terms ($C_3 \neq 0$, $C'_3 \neq 0$) in these fits did not significantly improve the quality of the fits.

B. Refractive index

We have performed three runs with the same critical sample (mole fraction $x_c = 0.453 \pm 0.001$) to verify also its chemical stability. For run 1 the critical temperature was between 23.844 °C (last point in the homogeneous phase) and 23.832 °C (the first point in the two-phase region). For run 2 T_c was between 23.868 °C and 23.852 °C and for run 3 between 23.874 °C and 23.869 °C. Between runs 1 and 3 there is a gradual increase of T_c by about 0.034 °C, which is acceptable. We started each run from about 30 °C, about 6 °C above the critical temperature, and measured the fringe variation Δk by gradually decreasing the temperature steps towards T_c . The refractive index variation $\Delta n = n - n(T_0)$ is calculated from Δk by

$$\Delta n = \Delta k \lambda / l, \quad (13)$$

where $n(T_0)$ is the refractive index value at the starting temperature of the run, $\lambda = 632.8$ nm the wavelength of the He-Ne laser, and l the sample thickness (9.15 mm). The Δn values for the three runs are displayed as a function of temperature in Fig. 4.

The data were fitted to the functional form

$$\Delta n = n_0 + n_1 t^\theta + n_2 t + n_3 t^{\theta + \Delta_1}. \quad (14)$$

The analysis of the data was carried out with a modified nonlinear least-squares computer program called MINUIT,

written originally by James and Roos [27]. In Table I, coefficients for the three different runs are given. Uncertainties on the parameters correspond to three standard deviations. We have limited T_c to the range between the last point in the one-phase region and the first point in the two-phase region. We varied T_c in the range given by these two data points and looked for a minimum in the reduced chi-square value χ^2_ν . For runs 1, 2, and 3 we obtained $T_c = 23.834$ °C, 23.854 °C, and 23.871 °C, respectively. The parameters obtained by leaving the exponents free in Eq. (14) compare very well with the ones obtained by fixing θ and $\theta + \Delta_1$ to the theoretical values [9] of 0.89 and 1.39, respectively. We also verified that replacing $t = (T - T_c)/T_c$ by $\tau = (T - T_c)/T$ in Eq. (14) did not significantly change parameter values.

C. Slope of the critical line

We have measured the change of the critical temperature with applied pressure for a critical mixture ($x_c = 0.453 \pm 0.001$) of nitroethane-cyclohexane in the way briefly described in Sec. III C. A graphical representation of the experimental values of the change in critical temperature $T_c(p) - T_c(p_0)$ for different values of $p - p_0$ with $p_0 = 1$ atm, are given in Fig. 5. These data have been fitted with a straight line. The slope of this straight line corresponds to the desired quantity

$$\frac{dT_c}{dp} = (1.484 \pm 0.004) \times 10^{-7} \text{ K Pa}^{-1}. \quad (15)$$

D. Dielectric constant and density

For this paper we did not carry out new measurements for the dielectric constant ϵ and the density ρ , because we have done this already in the past and reported them in previous papers [12,13]. For the purpose of the discussion in the next section we briefly repeat here the elements needed there.

The ϵ data in the homogeneous phase, measured at sufficiently high frequency to avoid the low-frequency Maxwell-Wagner relaxation phenomenon near the critical point [12,13], showed strongly nonlinear behavior as a function of temperature. Fitting these data with an expression of the form of Eq. (7) resulted in [12,29]

$$\begin{aligned} \theta &= 0.89 \pm 0.02, \\ D_1 &= 1.48 \pm 0.04. \end{aligned} \quad (16)$$

The density data [26] for a critical NE-CH mixture have been fitted [13] with Eq. (2). Good fits could be obtained for the range $\tau \leq 9 \times 10^{-3}$ with $\theta = 1 - \alpha_1 = 0.89$ and $R_3 = 0$ imposed. This resulted in

$$\begin{aligned} T_c &= 23.7811(\pm 0.0001) \text{ °C}, \\ \rho_c &= 864.845(\pm 0.002) \text{ kg m}^{-3}, \\ R_1 &= 0.034(\pm 0.002). \end{aligned} \quad (17)$$

V. DISCUSSION

The $\alpha = 0.11 \pm 0.02$ value given in (12), and obtained from the specific heat capacity data presented in Sec. IV A, fully

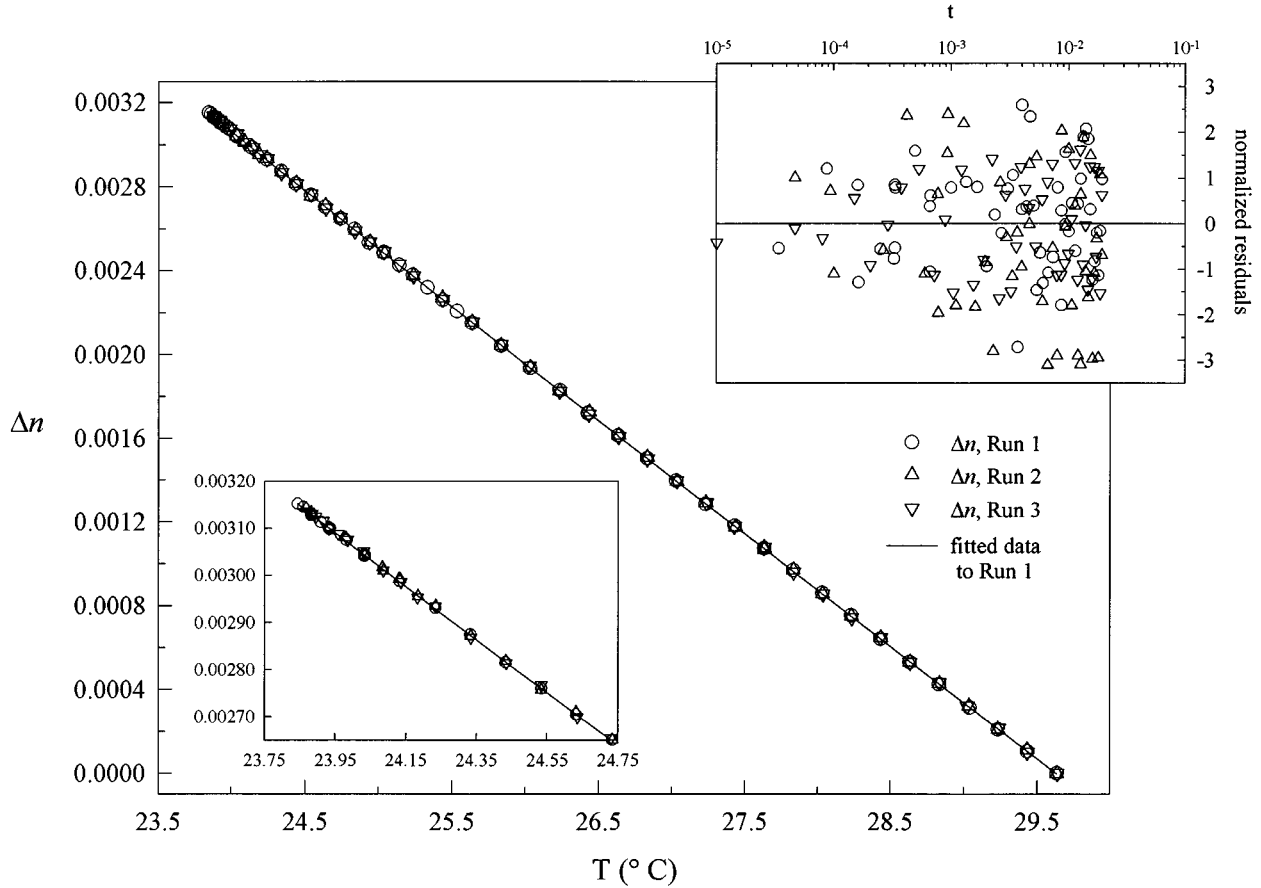


FIG. 4. Temperature dependence of the refractive index for the critical binary liquid mixture for runs 1–3. The solid curve results from a fit to the data of run 1 with Eq. (14). The inset at the upper right shows the random dispersion of the normalized residuals resulting from the fit with Eq. (14).

agrees with the theoretical [9] $\alpha_l = 0.110 \pm 0.002$. This result also confirms α results of previous high-resolution specific heat capacity measurements for critical mixtures of triethylamine–heavy water (TEA-D₂O) [16], 3-methylpentane–nitro-ethane (3MP-NE) [30], and 2,6 lutidine–water (2,5L-H₂O) [31]. The $\theta = 1 - \alpha$ values of (16) for the dielectric constant and of Table I for the refractive index confirm this conclusion.

Since other critical exponents are also in agreement with the theoretical values for the three-dimensional (3D) Ising model, it can be considered as a fact that consolute points of binary liquid mixtures belong to the 3D Ising universality class. Universality, however, not only predicts values for and

relationships among critical exponents, but also gives specific predictions for ratios of critical amplitudes above and below T_c for a given physical quantity as well as among amplitudes of different quantities. These relationships have been experimentally investigated in far less detail. Since in the case of NE-CH we have detailed results available on several different quantities, we will further concentrate on these aspects.

Universality predicts that the amplitude ratio C'_1/C_1 of the leading singular terms of the specific heat capacity above and below T_c in Eqs. (5) and (6) is a specific number for each universality class [32]. There are no exact theoretical values available for this ratio, and in the past numerical estimates

TABLE I. Results of least-squares fits with Eq. (14) to the experimental values of refractive index changes for the critical mixture of nitroethane–cyclohexane. The uncertainties quoted are three standard deviations. Parameter values between parentheses have been held constant in the fit.

Run	n_0	n_1	n_2	n_3	θ	$\theta + \Delta_1$	χ^2_ν
1	0.003 216 ± 0.000 004	−0.0162 ± 0.0002	−0.1382 ± 0.0003	0.006 ± 0.001	(0.89)	(1.39)	1.176
1	0.003 159 ± 0.000 002	−0.0162 ± 0.0002	−0.1381 ± 0.0003	0.006 ± 0.001	0.890 ± 0.002	1.36 ± 0.05	1.225
2	0.003 150 ± 0.000 005	−0.0162 ± 0.0002	−0.1381 ± 0.0004	0.006 ± 0.002	(0.89)	(1.39)	1.225
2	0.003 150 ± 0.000 007	−0.0161 ± 0.0007	−0.1378 ± 0.0009	0.004 ± 0.013	0.887 ± 0.007	1.3 ± 0.4	1.285
3	0.003 140 ± 0.000 007	−0.0163 ± 0.0003	−0.1381 ± 0.0005	0.007 ± 0.003	(0.89)	(1.39)	1.067
3	0.003 140 ± 0.000 005	−0.0164 ± 0.0003	−0.1382 ± 0.0005	0.008 ± 0.003	0.892 ± 0.004	1.45 ± 0.02	1.119

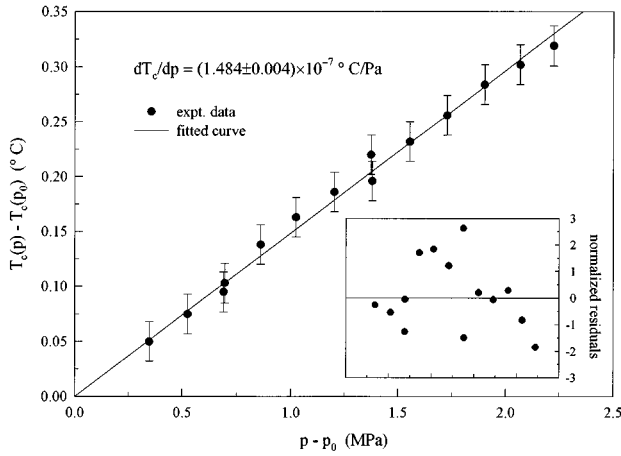


FIG. 5. Pressure dependence of the critical temperature of the critical binary liquid mixture of nitroethane-cyclohexane.

strongly depended on the calculation method. Recent results, reviewed by Privman, Hohenberg, and Aharony [32], seem to converge to a common value around 1.90. From ϵ -expansion calculations one finds $C'_1/C_1 = 1.91 \pm 0.04$, field theoretical calculations in 3D give 1.85 ± 0.05 , while $C'_1/C_1 = 1.91 \pm 0.04$ is now also obtained from series expansion and Monte Carlo calculations [32]. For NE-CH we obtain from (12) an experimental ratio $C'_1/C_1 = 1.92 \pm 0.05$, which is in very good agreement with the above theoretical values. Our value for NE-CH is somewhat larger than the previously reported value of 1.75 ± 0.03 for TEA-D₂O [16], 1.79 ± 0.06 for 3MP-NE [30], and 1.77 ± 0.9 for 2,6L-H₂O [31].

With Eq. (10) a value for G_1 , the amplitude of the leading singular term of the density in Eq. (9) can be calculated with the C_1 result in (12), the ρ_c value of (17), and dT_c/dp in (15). Further assuming $\alpha = \alpha_l = 0.110 \pm 0.002$, we obtain $G_1 = -0.042 \pm 0.002$. From the $R_1 = 0.034 \pm 0.002$ value (17) from the fit to the direct density data, we have $G_1 = -0.034 \pm 0.002$. The two values of G_1 can be considered in satisfactory agreement, also in view of the fact that results from three different experiments with different samples are involved in the calculations.

The existence of an intrinsic effect in the temperature dependence of the dielectric constant ϵ in the one-phase region on the critical concentration line of binary liquid mixtures is by now well documented since in 1980 [28] it was demonstrated that a low-frequency Maxwell-Wagner relaxation (caused by the presence of ionic impurities) was the reason for quite often conflicting results previously published. Subsequently in 1981, published results of Thoen, Kindt, and Van Dael [12] for NE-CH (briefly summarized in Sec. III D) showed a quite large intrinsic effect and fully confirmed the conclusions of Ref. [28]. In fact, in the case of NE-CH the intrinsic effect is much larger than and of opposite sign to the density related one (see Fig. 1 of Ref. [13]). This can also be verified by comparing the amplitudes $E_1 = D_1 + R_1 = 1.51 \pm 0.04$ and $R_1 = 0.034 \pm 0.002$, obtained from (16) and (17). The existence of an intrinsic, dT_c/dE^2 related, critical contribution to the temperature dependence of ϵ has also been observed for several other critical binary liquid mixtures [33–38].

Evidence for the presence of an intrinsic contribution to

the refractive index critical behavior has so far only been obtained for the binary system triethylamine-water. The existence of this intrinsic effect was pointed out by Furrow and Greer [39] by comparing their density data with the existing refractive index data of Beysens and Bourguo [40]. This was subsequently confirmed by Pépin, Bose, and Thoen [41] on the basis of refractive index data and the density data of Furrow and Greer. However, Beysens and Zalczer [42] carried out density and refractive index data and claimed that the critical behavior of the refractive index can be entirely accounted for by the density effect.

Although the critical contribution to both the density and the refractive index for NE-CH are an order of magnitude smaller than for TEA-H₂O (in accordance with two-scale-factor universality [43]), a comparison between our n results and the available ρ results is possible. From the exact relation

$$\left(\frac{\partial n}{\partial T}\right)_{p,x} = \left(\frac{\partial n}{\partial \rho}\right)_{p,x} \left(\frac{\partial \rho}{\partial T}\right)_{p,x}, \quad (18)$$

it follows that

$$\begin{aligned} \rho(T) - \rho(T_c) &= \int_{T_c}^T \left(\frac{\partial \rho}{\partial n}\right)_{p,x} \left(\frac{\partial n}{\partial T}\right)_{p,x} dT \\ &\approx \left(\frac{\partial \rho}{\partial n}\right)_{p,x}^{\text{reg}} [n(T) - n(T_c)]. \end{aligned} \quad (19)$$

In the last part of Eq. (19) the assumption of a regular temperature-independent $(\partial \rho / \partial n)_{p,x}$ is made. From a comparison of Eq. (19) with Eq. (14) one can define

$$Q_1 = \left(\frac{\partial \rho}{\partial n}\right)_{p,x}^{\text{reg}} n_1. \quad (20)$$

This quantity can be calculated from n_1 values of Table I provided a value for $(\partial \rho / \partial n)_{p,x}^{\text{reg}}$ is available. This quantity is usually estimated from the ρ and n results far away from T_c [41]. For NE-CH we obtain $(\partial \rho / \partial n)_{p,x} = (1.98 \pm 0.02) \times 10^3$ kg/m³ in this way. Further comparing Eqs. (14), (2), and (20) it follows that

$$R_1 = -Q_1 / \rho_c, \quad (21)$$

provided that the above assumptions are valid. An intrinsic contribution to n , which is large enough, would, however, result in an R_1 value from (21) different from R_1 obtained from direct density data analysis. A calculation of R_1 with Eqs. (21) and (20) gives $R_1 = 0.037 \pm 0.001$, which falls in between $R_1 = 0.034 \pm 0.002$ from the direct density results in (17) and $R_1 = 0.042 \pm 0.002$ from $R_1 = -G_1$ and Eq. (10). From this one has to conclude that a possible intrinsic contribution to the critical behavior falls within the experimental uncertainty limits.

VI. SUMMARY AND CONCLUSIONS

In this paper we have presented specific heat capacity $C_{p,x}$ and refractive index n data for the critical binary mixture of nitroethane-cyclohexane near the consolute point. Results for the slope of the critical line dT_c/dp have also been

reported. The specific heat capacity and refractive index data have been analyzed in terms of the appropriate theoretical expressions (given in Sec. II). The data are fully in agreement with the scaling predictions. The critical exponent α values (for the specific heat capacity and the refractive index) and the amplitude ratio C'_1/C_1 (for the specific heat capacity) agree very well with the theoretical values for the 3D Ising universality class.

The results of the analysis of these $C_{p,x}$, n , and $dT_c/d\rho$ data have been combined with our previously published results on the dielectric constant ϵ and density ρ , in an effort to investigate relations among several critical amplitudes of these physical quantities. Satisfactory agreement was found between the leading critical amplitude value calculated from the $C_{p,x}$ amplitude [with Eq. (10)] and the value obtained from the analysis of the direct ρ data. In contrast to the

situation for the dielectric constant ϵ , where a quite large intrinsic contribution (related to dT_c/dE^2) is present, the possible intrinsic contribution to the critical behavior of the refractive index n does not exceed the uncertainty on the amplitude of the indirect density contribution.

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