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Critical behavior of the dielectric constant in the triethylamine-water binary liquid mixture: Evidence of an intrinsic effect

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Experimental data are presented for the dielectric constant in the homogeneous phase near the consolute point of the binary critical liquid mixture composed of triethylamine and water. From a comparison with existing mass density measurements, it is concluded that the critical anomaly in the static dielectric constant clearly shows a strong intrinsic effect opposite in direction from the one in the mass density. Moreover, a complete picture of the critical behavior of the dielectric properties for this system is drawn by including previously published refractive index measurements.

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I. INTRODUCTION

The large fluctuations which develop near the consolute point of binary liquid mixtures affect many physical properties, such as mass density, dielectric constant, and refractive index. The mass density ρ exhibits an anomaly which can be related to the singularity in the heat capacity at constant pressure and concentration $C_{P,X}$, which has a power-law divergence with the critical exponent α. An anomaly is also expected for the static dielectric constant ε and the refractive index n on the basis of thermodynamic [1,4] as well as microscopic theories [2,3]. Following an idea first proposed by Mistura [4] on the applicability of critical point universality to the behavior of fluids in the presence of an electric field, Sengers *et al.* [5] developed a complete theory to explain the anomaly in ε and n at the critical point. They showed that the divergent behavior of the temperature derivative of ε at the critical concentration is governed by two distinct contributions: an implicit contribution due to the divergence of the thermal expansion coefficient related to the rate of change of the critical temperature T_c with pressure P, and an intrinsic contribution related to the change of T_c with the square of the electric field, E^2.

These two contributions have already been shown to exist by precision measurement of ε in the system nitroethane-3-methylpentane [6] and methanol-cyclohexane [7]. One can thus see that the anomalous behavior of the dielectric constant does not follow the same trend as the one of the mass density. The intrinsic anomaly for n has already been measured by Pépin, Bose, and Thoen [8] in the triethylamine-water binary liquid mixture, and, although its relative magnitude is smaller than the one in ε, it is nonetheless present and has the same sign.

The purpose of the present paper is to report precise experimental data on the dielectric constant as a function of temperature in the one-phase region near the lower critical solution point of the binary liquid mixture composed of triethylamine and water (TE-WT). The static dielectric constant measurements for conductive critical mixtures have to be carried out at high frequencies (radio frequency region) beyond the dispersion region of the Maxwell-Wagner absorption. This type of precision measurement is only possible now because of the availability of the impedance meter up to 30 MHz, with a precision of 0.1%.

II. THEORETICAL BACKGROUND

A. Static dielectric constant

When the critical point of a binary liquid mixture at constant pressure is approached along the line of the critical concentration (X_c), all of the recent theories of critical phenomena predict, for the mass density ρ, the refractive index n, and the dielectric constant ε near the critical temperature T_c a leading behavior of the form

$$\rho \approx \rho_c + R t^{\theta} , \tag{2.1}$$

$$n \approx n_c + N t^{\theta} , \tag{2.2}$$

$$\varepsilon \approx \varepsilon_c + D t^{\theta} , \tag{2.3}$$

where ρ_c, n_c, and ε_c are the values of the mass density, refractive index, and dielectric constant at the critical point, respectively, t is the reduced temperature $|T-T_c|/T_c$, and $\theta = 1-\alpha$ is the critical exponent. Note that α characterizes the divergence of the specific heat at constant pressure and concentration $C_{p,x}$. The most recent and successful theory to date is the one from Sengers *et al.* [5]. They obtained a functional form for the static dielectric constant (and the refractive index) near the critical point that includes correction to scaling terms. They applied critical-point universality to the thermodynamic behavior of fluids and mixtures in the presence of an electric field. They found that for $X=X_c$ the static dielectric constant in the one-phase region near a liquid-liquid critical point should have the functional form

$$\varepsilon\rho^{-1}=\varepsilon_c\rho_c^{-1}(1+A_1t+A_2t^{\theta}+A_3t^{0+\Delta_1}+\cdots)\ . \tag{2.4}$$

In Ref. [5] they originally used $\tau=|T-T_c|/T$, but this has no bearing on the functional form. We have used T_c in the denominator of t to maintain the uniformity with the functional form used in the literature. For the mass density along the same $X=X_c$ line, a similar expression is obtained:

$$\rho^{-1}=\rho_c^{-1}(1+B_1t+B_2t^{\theta}+B_3t^{\theta+\Delta_1}+\cdots)\ . \tag{2.5}$$

The correction-to-scaling exponent Δ_1 results from the Wegner [9] expansion for higher-order critical contributions. Renormalization group calculations [10] give $\alpha=0.110\pm0.003$ and $\Delta_1=0.51\pm0.03$ for systems, like liquid mixtures, belonging to the three-dimensional Ising universality class. The critical parameters ε_c and ρ_c and the coefficients A_i's and B_i's are system-dependent nonuniversal parameters. From Eqs. (2.4) and (2.5) one deduces the dielectric constant ε itself:

$$\varepsilon=\varepsilon_c(1+C_1t+C_2t^{\theta}+C_3t^{\theta+\Delta_1}+\cdots)\ , \tag{2.6}$$

where now $C_2=A_2-B_2$, etc. There are thus two possible contributions to the critical t^{θ} behavior of the dielectric constant: (1) a contribution due to the divergence of the thermal expansion ($B_2\neq0$), and (2) an intrinsic effect ($A_2\neq0$) for the dielectric constant, which also implies $C_2\neq-B_2$. It is thus clear that the density must be included in the analysis in order to assess unambiguously the critical behavior of the dielectric constant.

B. Maxwell-Wagner effect

In the past the experimental situation on the behavior of the static dielectric constant near liquid-liquid critical points was rather confusing, until it was discovered [11] that this was mainly due to the presence of the Maxwell-Wagner effect in many systems. The Maxwell-Wagner (MW) effect is a low-frequency dielectric dispersion which can occur in heterogeneous systems. When two liquids A and B of conductivities σ_A and σ_B and dielectric constants ε_A and ε_B are mixed to form a single system, an additional contribution to the conductivity σ and the dielectric constant ε may result due to the accumulation of conducting charges at the interface in the boundary between two phases. This charge buildup has a frequency-dependent behavior. This is known as the Maxwell-Wagner dispersion effect. Binary liquid mixtures that might be completely homogeneous systems away from the critical point will show a certain degree of heterogeneity near T_c because of the occurrence of large-size concentration fluctuations. Thus the real static dielectric constant should only be considered at frequencies higher than the Maxwell-Wagner dispersion. The details of the MW effect have been discussed in a previous publication [12].

III. EXPERIMENT

The present experiment consists in measuring the static dielectric constant of a critical triethylamine-water mixture as a function of temperature at several frequencies between 100 kHz and 30 MHz. Extended frequency measurements in the range 200 MHz–20 GHz have also been carried out with a network analyzer in order to locate the relaxation frequency of triethylamine in water. Details of the apparatus and the experimental procedure are given below.

A. Apparatus used

A sectional view of the sample cell is shown in Fig. 1. The container block has two holes (D) drilled at its bottom surface to facilitate sample filling. On the top surface, a groove is machined to accommodate a Teflon O ring (G). This serves as the seal for the liquids. The bore of the block is chamfered at the top at an angle of 60° to the horizontal. This is to assure that the axial positioning of the electrode assembly within the bore is retained upon dismantling and subsequent reassembly. This is important as it has a bearing on the C_0 of the cell. In contrast to some designs in the literature, the container block here does not serve as the outer electrode; instead it is connected to the ground potential to be used as a shield against noise pickup. A neoprene O ring (C) acts as a seal along with a bakelite cylinder (not in figure) to prevent fouling of the electrical connections atop the assembled cell by the thermostatic fluid. The top lid (B) is also machined out of a 316 stainless steel rod. Six

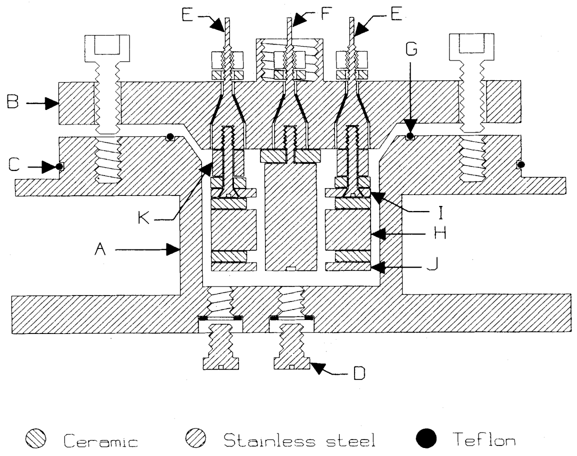

FIG. 1. Sectional view of the dielectric cell: I and J: upper and lower high electrodes, respectively; H: guard electrode; E: pair of feed-throughs for the upper high electrode; F: single feed-through for the low electrode; K: stand-offs (six of them); G: Teflon O-ring; D: two holes to fill the cell; A: cup; B: lid; C: neoprene O-ring for sealing off the electrode feedthroughs with another toplid (not shown). The two pairs of feedthroughs for J and H are not shown. A, B, and H are set to the ground. The cell is cylindrical.

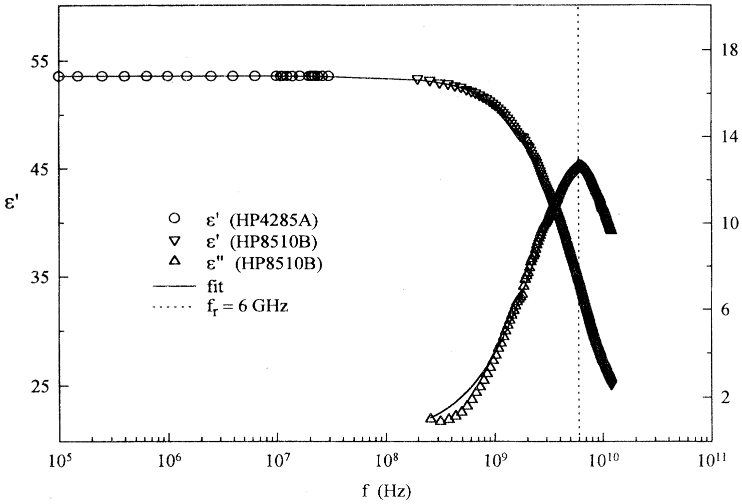

FIG. 2. Semilogarithmic plot of the frequency dependence of the dielectric constant for the critical TE-WT mixture at 10 °C.

feedthroughs (E) are mounted radially on the lid to facilitate both mechanical fixture of, and electrical connections for, the outer electrodes. Each of these electrodes H, I, and J contain a central bore and are mounted using two diametrically opposite feedthroughs. The inner electrode is in turn mounted onto the centrally placed feedthrough (F). Atop the conical section of each feedthrough, a thin Teflon conical sleeve is inserted for electrical isolation from the lid. The feedthroughs are tightened onto the lid uniformly with a torque of approximately 2.5 N m. This causes the Teflon to be compressed, and rigidly fixes the feedthroughs in addition to providing a liquid tight seal. The electrodes are separated by discs made of Macor machinable glass ceramic [13] with a quoted zero porosity value. After the assembly of the electrodes and the separating ceramic plates, the capacitor assumes very good mechanical rigidity. The feedthroughs are electrically terminated at *BNC* connectors.

The capacitance in the range 200 MHz–12 GHz is measured with a Hewlett-Packard network analyzer model HP8510B. The capacitance in the range 100 kHz–30 MHz is measured with a Hewlett-Packard four-terminal impedance meter model HP4285A. The HP4285A, which is an improvement over the original model [14] (HP4275A), uses a state-of-the-art electronic automatic bridge technique and a 90° phase reference generator. A microprocessor controls the analog section that includes the bridge section and manipulates the data taken from the analog section to obtain the desired parameters. The maximum resolution and reproducibility that we could obtain was 0.001 pF at all frequencies, and we measured on the full range of the apparatus which is 75 kHz–30 MHz. The absolute precision for the capacity is ±0.1% (about ±0.2 pF), but we have instead used the relative precision given from the statistical analysis of the experimental data (about ±0.004 pF, depending on the data set) due to our interest in the relative values of the physical parameters rather than their absolute values. The temperature of the sample cell is controlled to within 0.5 mK over a period of at least 24 h by means of a Tronac precision controller bath (model No. 41) filled with water. The temperature is measured with a Guildline platinum resistance thermometer (model No. 9540), which has a resolution of 1 mK and an absolute precision of ±0.05 K.

B. Experimental procedure

The critical composition of our sample was 32.1 wt. % triethylamine, and T_c was situated between 18.242 and 18.253 °C which are, respectively, the temperature of the last data point taken in the homogeneous phase and the temperature of the first one in the separated phase. This is the same composition as used by Pépin, Bose, and Thoen [8] for the refractive index, Thoen and co-workers [15] for the heat capacity, and Furrow and Greer [16] for the mass density.

IV. RESULTS AND DISCUSSION

We have measured the dielectric constant of the critical mixture TE-WT, in the homogeneous phase, as a

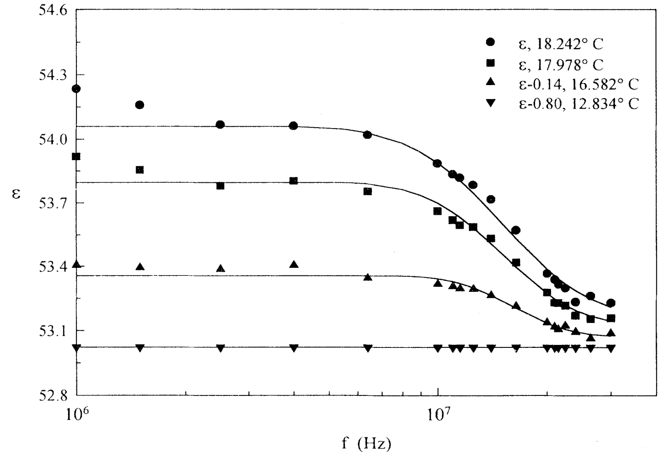

FIG. 3. Semilogarithmic plot of the frequency dependence of the dielectric constant for several temperatures above T_c for the critical TE-WT mixture.

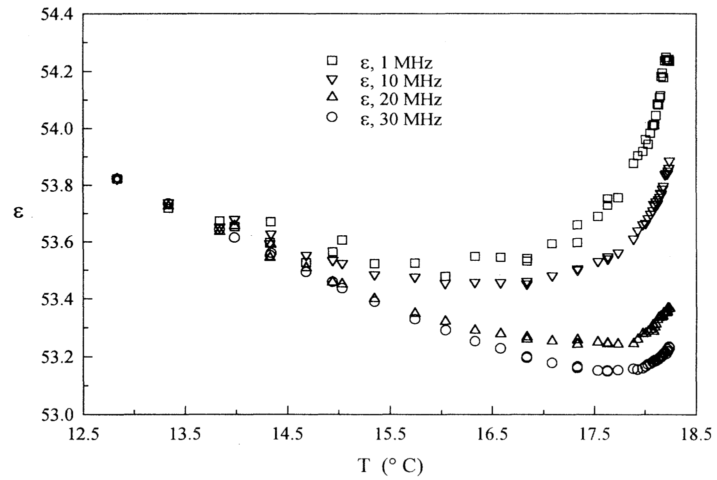

FIG. 4 Temperature dependence of the dielectric constant of the critical TE-WT mixture for four different measuring frequencies.

function of temperature in the range $0.0186 < t < 1.37 \times 10^{-5}$ and as a function of frequency between 100 kHz and 30 MHz. The critical temperature of demixing is situated between the last data point taken in the homogeneous phase (18.242 °C) and the first one in the separated phase (18.253 °C). We also verified that the dielectric constant was not affected by the normal relaxation of this system by measuring ε for a single temperature in the homogeneous phase in the frequency range 200 MHz–12 GHz.

The frequency dependence of the dielectric constant is given for a single temperature at 10 °C in Fig. 2. One can see that the relaxation mechanism of the triethylamine-water critical binary mixture has a relaxation frequency $f_r = 6$ GHz, and thus does not affect the value of ε in the frequency range 100 kHz–30 MHz. Figure 3 shows the frequency dependence of the dielectric constant for a set of temperatures in the homogeneous phase. An increasing dielectric dispersion, associated with the Maxwell-Wagner effect, is clearly visible as the temperature approaches T_c.

Although we have not looked specifically for the gravity effect by measuring ε as a function of height, we have shown in a previous publication [17] that no gravity effect could be detected within the experimental error, near T_c, in the one-phase region of a critical binary mixture composed of nitrobenzene and iso-octane. Greer, Block, and Knobler [18] studied the gravity effect for the system nitroethane-3-methylpentane extensively, and found that the density change close to the center of the sample, near T_c, was insignificant. We can therefore assume that the present measurements, carried out near the center of the sample, should be unaffected by gravity.

As pointed out above, the static dielectric constant data are only obtained at frequencies higher than the Maxwell-Wagner dispersion range. As already clearly demonstrated before [12], a completely different temperature dependence of the dielectric constant can be obtained for measuring frequencies too close to or below the MW relaxation frequency. This is clearly shown in Fig. 4, where we plotted our data for four fixed frequencies as a function of temperature. From Fig. 3 it can be seen

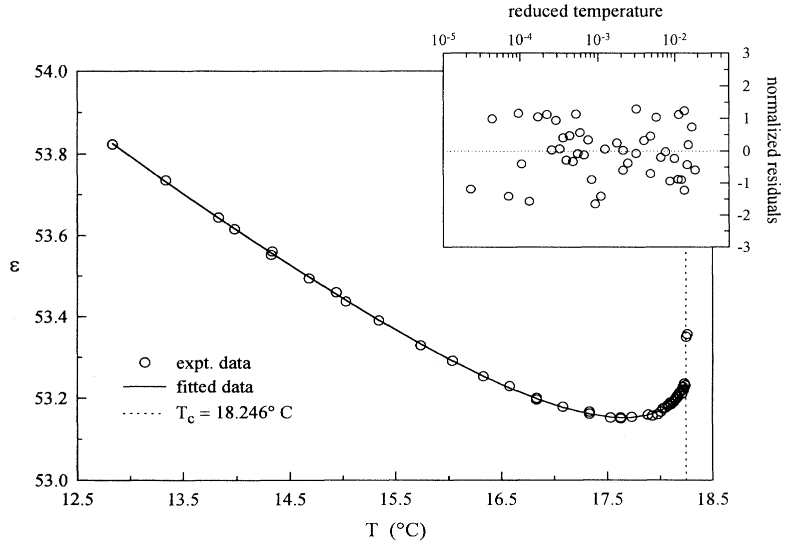

FIG. 5. Temperature dependence of the static dielectric constant (measured at 30 MHz) in the homogeneous phase of the critical TE-WT mixture. The inset shows the random dispersion of the normalized residuals resulting from the fit with Eq. (4.1).

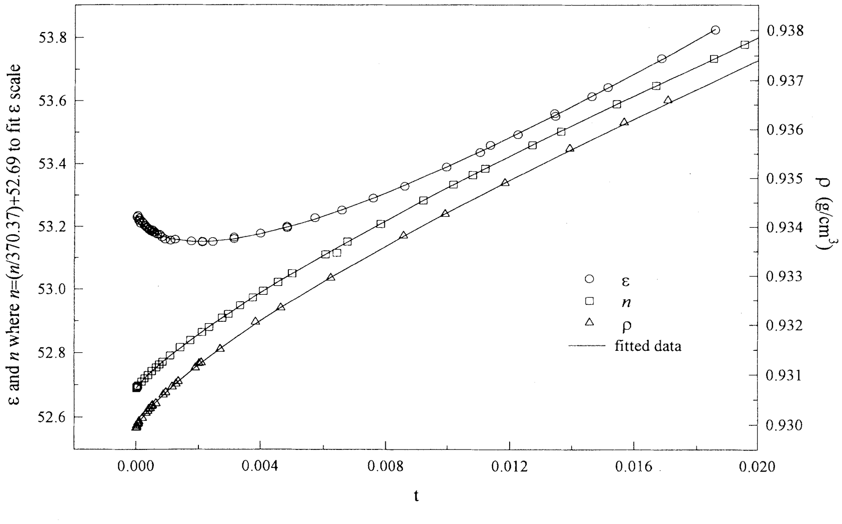

FIG. 6. Temperature dependence of the static dielectric constant (at 30 MHz), refractive index, and mass density in the homogeneous phase of the critical TE-WT mixture.

that the relaxation frequency is situated at about 15 MHz. It has been observed by numerical analysis that a possible contribution of the MW dispersion to our 30-MHz data was smaller than the experimental resolution. These 30-MHz data can then be considered as static dielectric constant values.

The ε data taken in the one phase region and at a frequency of 30 MHz are displayed in Fig. 5. The data were fitted to the following functional form:

$$\varepsilon=\varepsilon_c+D_1 t+D_2 t^{\theta}+D_3 t^{\theta+\Delta_1} , \qquad (4.1)$$

which is identical to Eq. (2.6) with $D_1=\varepsilon_c C_1$, $D_2=\varepsilon_c C_2$, $D_3=\varepsilon_c C_3$, and $\theta=1-\alpha$. The analysis of the data was carried out with a modified computer program for nonlinear equations called MINUIT, written originally by James and Roos [19]. In Table I, coefficients for the different fits are given. Uncertainties on the parameters correspond to three standard deviations. We have fixed $T_c$between the last point in the one-phase region and the first point in the two-phase region. We then varied T_c in the range given by these two data points, and looked for a minimum in the reduced chi square value χ_ν^2. This permitted us to have a better resolution on the critical exponents since the are strongly correlated to the critical temperature. The parameters obtained by letting the exponents free in Eq. (4.1) compare very well with the ones obtained by fixing θ and $\theta+\Delta_1$ to the theoretical values[11] of 0.89 and 1.39, respectively.

Now, from the results shown in Table I and the parameters obtained by Furrow and Greer [16] for the mass density, we can calculate the value of A_2 in Eq. (2.4):

$$A_2=C_2+B_2=-4.44\pm0.02+0.74\pm0.04$$
$$=-3.70\pm0.06 ,$$

which is five times larger than B_2 and opposite in sign. In their paper, Pépin, Bose, and Thoen [8] have also shown that the refractive index, for the same system, demonstrates an intrinsic $t^{1-\alpha}$ anomalous contribution which is also opposite in sign to the density contribution. By gathering all the data for ρ, ε, and n, we plot in Fig. 6 a complete picture of the different contributions at the critical point for the critical triethylamine-water binary liquid mixture. The refractive index data are from Pépin,

TABLE I. Results of least-squares fits with Eq. (4.1) to the experimental values of the dielectric constant at 30 MHz. The uncertainties quoted are three standard deviations. The values inside the parentheses are held constant for the fit.

T_c (°C)	ε_c	D_1	D_2	D_3	θ	$\theta+\Delta_1$	χ^2	χ_ν^2
(18.248)	52.230 ± 0.006	279.8 ± 0.7	−159.3 ± 0.4		(0.89)		113.2	2.632
(18.246)	53.241 ± 0.006	442.6 ± 0.6	−236.5 ± 0.4	−211 ± 4	(0.89)	(1.39)	30.87	0.735
18.249 ± 0.025	53.242 ± 0.008	442.5 ± 0.7	−236.7 ± 0.4	−209 ± 4	(0.89)	(1.39)	30.50	0.744
(18.249)	52.243 ± 0.008	443.6 ± 0.7	−236.3 ± 0.8	−220 ± 15	0.889 ± 0.002	1.400 ± 0.008	30.28	0.757

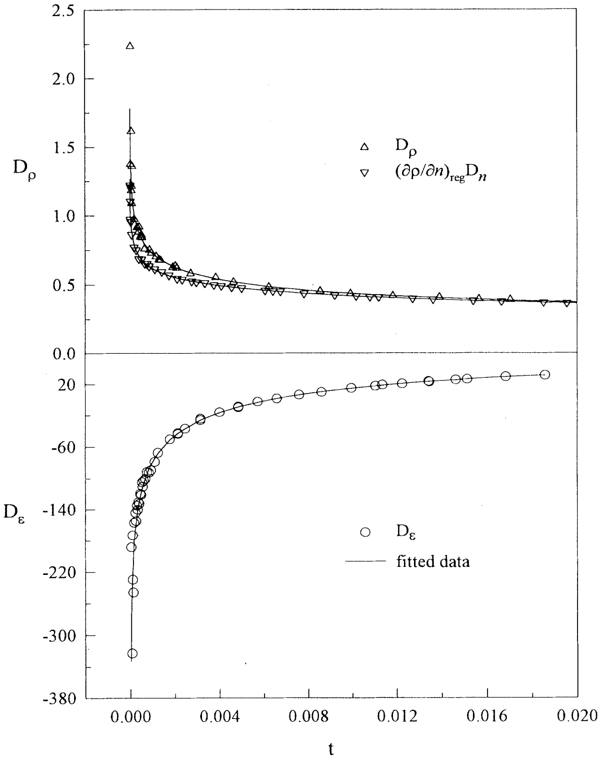

FIG. 7. Plot of the quantity $D_\varepsilon=(\varepsilon-\varepsilon_c)/t$, $(\partial\rho/\partial n)^{\rm reg}_{p,x}D_n\equiv(\partial\rho/\partial n)^{\rm reg}_{p,x}(n-n_c)/t$, and $D_\rho\equiv(\rho-\rho_c)/t$ as a function of $t=(T_c-T)/T_c$ for the critical TE-WT mixture.

Bose, and Thoen [8], while the mass density data are taken from Furrow and Greer [16].

As discussed in previous papers [6–8,12], the comparison of the critical behavior of the dielectric constant and the refractive index with the mass density can be clearly elucidated if one plots $D_\varepsilon\equiv(\varepsilon-\varepsilon_c)/t,(\partial\rho/\partial n)^{\rm reg}_{p,x}D_n\equiv(\partial\rho/\partial n)^{\rm reg}_{p,x}(n-n_c)/t$, and $D_\rho\equiv(\rho-\rho_c)/t$ as a function of $t=(T_c-T)/T_c$ (Fig. 7). The comparison of the three curves near the critical point clearly shows that the behavior of the dielectric constant is opposite to that of the mass density, while that of the refractive index is in the same direction as that of the density but smaller in magnitude, thus suggesting an intrinsic critical contribution also opposite in sign from the density contribution.

V. SUMMARY AND CONCLUSION

In this paper we have presented the results of an investigation of the dielectric constant near the critical consolute point of the triethylamine-water binary liquid mixture. From a comparison with available mass density [16] measurements, we have established that the static dielectric constant possesses an intrinsic contribution to its critical behavior which is five times larger and opposite in sign than the extrinsic contribution coming from the mass density. This investigation, along with the refractive index results from Pépin, Bose, and Theon [8] and the mass density results from Furrow and Greer [16] constitutes the only comprehensive dielectric study of the critical behavior of a binary liquid mixture so far, to our knowledge.

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