Intrinsic Dielectric Constant Anomaly in Critical Liquid Mixtures

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Experimental data are presented for the dielectric constant ε near the consolute point of the binary liquid mixture methanol-cyclohexane and that of pseudobinary liquid mixtures of methanol-cyclohexane–deuterated-cyclohexane. One of the methanol-cyclohexane–deuterated-cyclohexane mixtures is made isopycnic at the critical temperature. This has permitted us to investigate more directly the intrinsic critical contribution to ε near the critical point by reducing the contribution resulting from the mass density fluctuations.

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Following an idea first proposed by Mistura [1] on the applicability of critical point universality to the behavior of fluids in the presence of an electric field, Sengers *et al.* [2] developed a complete theory to explain the dielectric constant anomaly at the critical point. They showed that the divergent behavior of the temperature derivative of the dielectric constant at the critical concentration is governed by two distinct contributions: an implicit contribution because of 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 [3] to exist by combining precision measurement of the dielectric constant [3] and the mass density [4] on the same system. This way one can see that the anomalous behavior of the dielectric constant does not follow the same trend as that of the mass density. But, as far as we know, a direct attempt to measure the intrinsic contribution to the anomalous behavior of ε near T_c has never been made.

Since the contribution of the thermal expansion divergence is related to the mass density difference $\Delta\rho$ between the two phases, we have chosen a mixture in such a way that the mass density of each phase can be adjusted to become as close as possible to each other. In such a case one may expect to suppress the density-related implicit contribution to the critical behavior of the dielectric constant. Therefore we have decided to use the system methanol-cyclohexane since this system has been extensively studied by Houessou *et al.* [5] as a good contender for simulated microgravity measurements. The process of creating an isopycnic mixture is well known and has been well demonstrated by Houessou *et al.* [5] on the system methanol-cyclohexane and by Gopal *et al.* [6] on the system cyclohexane-acetonitrile. Addition of a specific amount of deuterated cyclohexane to the methanol-cyclohexane mixture makes the system isopycnic in the critical region while still retaining all the features of a critical binary liquid mixture.

The purpose of the present Letter is to report precise experimental data on the dielectric constant near the consolute point of three critical binary or pseudobinary mixtures: methanol + cyclohexane (ME-CH, run 1) and methanol + cyclohexane + deuterated cyclohexane (ME-CH-CH′) with a proportion of 4.5% of CH′ in the system CH-CH′ (run 2) and ME-CH-CH′ with a proportion of 9% of CH′ (run 3). The particular interest in these systems stems from the fact that, while both critical contributions are expected to be present in the first and the third systems, the contribution from the fluctuations in the mass density is expected to be absent or substantially reduced in the second isopycnic one, allowing a direct measurement of the explicit contribution to ε in the critical region. This last system is also a simulation on Earth for conditions encountered in a microgravity environment.

When the critical point of a binary liquid mixture at constant pressure is approached along the line of the critical concentration, all of the recent theories predict for the static dielectric constant ε near the critical temperature T_c, a leading behavior of the form

$$\varepsilon \approx \varepsilon_c + At^{\theta}, \tag{1}$$

where ε_c is the static dielectric constant at T_c, $t = (T - T_c)/T_c$ is the reduced temperature, and $\theta = 1 - \alpha$, with the critical exponent α describing the singularity of the specific heat at constant pressure and concentration. The most recent and successful theory to date is the one from Sengers *et al.* [2]. They obtained a functional form for ε near the critical point that includes corrections to scaling terms. They applied the critical point universality to the thermodynamic behavior of fluids and mixtures in the presence of an electric field, and deduced that for $X = X_c$

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(X being the mole fraction) the static dielectric constant in the one-phase region near a liquid-liquid critical point should have the functional form

$$\varepsilon\rho^{-1} = \varepsilon_c\rho_c^{-1}(1 + A_1 t + A_2 t^{\theta} + A_3 t^{\theta+\Delta_1} + \cdots). \quad (2)$$

For the mass density ρ along the same $X = X_c$ line, a similar expression is obtained as

$$\rho^{-1} = \rho_c^{-1}(1 + B_1 t + B_2 t^{\theta} + B_3 t^{\theta+\Delta_1} + \cdots). \quad (3)$$

The correction-to-scaling exponent Δ_1 results from the Wegner [7] expansion for higher-order critical contributions. Renormalization group calculations [8] give $\alpha = 0.110 \pm 0.003$ and $\Delta_1 = 0.51 \pm 0.03$ 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 and B_i are system-dependent nonuniversal parameters. From Eqs. (2) and (3) one deduces the dielectric constant ε itself:

$$\varepsilon = \varepsilon_c(1 + C_1 t + C_2 t^{\theta} + C_3 t^{\theta+\Delta_1} + \cdots), \quad (4)$$

where now $C_2 = A_2 - B_2$, etc. There are thus two possible contributions to the anomalous t^{θ} behavior of the dielectric constant: (a) a contribution because of the divergence of the thermal expansion ($B_2 \neq 0$) and (b) an intrinsic effect ($A_2 \neq 0$) for the dielectric constant, which also implies $C_2 \neq -B_2$. It is thus clear that the mass density must be included in the analysis or its contribution should be diminished in order to assess unambiguously the intrinsic critical behavior of the dielectric constant.

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 [9] that this was mainly because of the presence of the Maxwell-Wagner (MW) effect in many systems. The 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 because of the accumulation of conducting charges at the interfaces 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 may well be completely homogeneous 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 be considered only at frequencies higher than the MW dispersion range. The details of the MW effect have been discussed in a previous publication [10].

The measurements of the dielectric constant as a function of frequency and temperature for the different mixtures have been carried out using a sample cell containing two vertical cylindrical symmetric capacitors. Full details of the measuring cell, sample preparation, and measuring procedure will be given elsewhere [11].

The capacitance is measured with a Hewlett-Packard four terminal LF impedance analyzer (Model No. HP4192A) with frequency capability ranging from 5 Hz to 13 MHz. Experimental data have been obtained in the frequency range between 10 kHz and 13 MHz. The maximum resolution and reproducibility that we could obtain was 0.001 pF at 13 MHz. The temperature of the sample cell is controlled to within 0.5 mK over a period of at least 24 h and measured with a platinum resistance thermometer, which has a resolution of 1 mK and an absolute precision of ±0.05 K.

As pointed out above, the static dielectric constant data are obtained only at frequencies higher than the MW dispersion range. A completely different temperature dependence of the dielectric constant near the critical point can be obtained for measuring frequencies too close or below the MW relaxation frequency [9,10]. In all three critical mixtures the MW effect was present and measurements had to be extended into the MHz frequency range. This is clearly visible in Fig. 1 where for fixed measuring temperatures ε data are given as a function of temperature for all three critical mixtures. From a careful analysis of the frequency dependence and from fits with a single relaxation time expression [9,10] (solid curves in Fig. 1) it can be concluded that the differences between the ε (13 MHz) data and the extrapolated ε_{∞} values are smaller than the scatter of the data points displayed in Fig. 1. Moreover, it should be realized, as can be seen in Fig. 1, that the MW relaxation frequencies (inflection points in the fitted curves) are nearly the same (around 1.5 MHz) for all three mixtures, resulting in almost identical very small deviations [at equal $(T - T_c)$ values] from the static values. For the purpose of further analysis our 13 MHz data can be considered as static dielectric constant values for all three systems.

The ε data taken in the one-phase region and at a frequency of 13 MHz for the three critical mixtures of

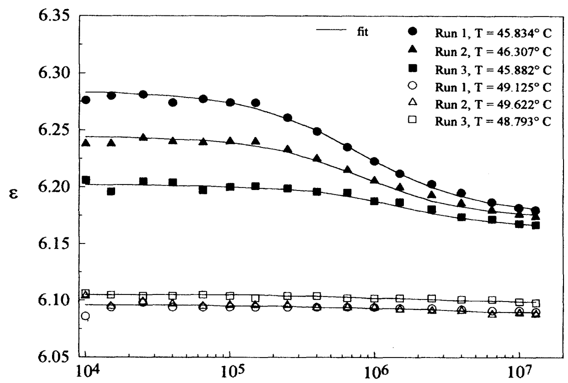

FIG. 1. Frequency dependence of the dielectric constant for several temperatures above T_c for the three different critical mixtures.

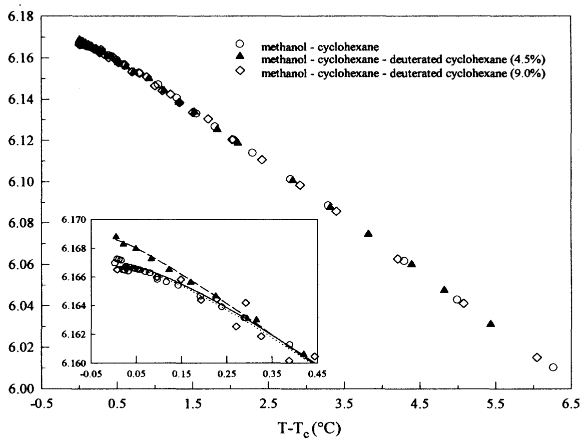

FIG. 2. Temperature dependence of the static dielectric constant (measured at 13 MHz) in the homogeneous phase of the critical mixtures investigated. The curves in the inset result from fits with the parameters given in Table I. Run 1 is the solid line, run 2 the dashed line, and run 3 the dotted line.

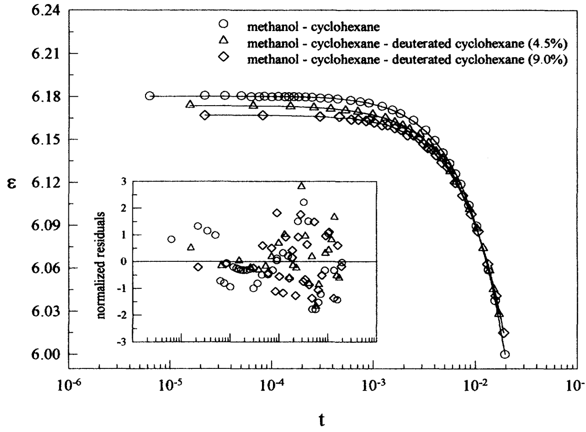

FIG. 3. Semilogarithmic plot of the temperature dependence of the static dielectric constant in the homogeneous phase of the three critical mixtures. Open symbols are the experimental data and the solid curves result from fits to Eq. (5) with the parameter values given in Table I.

ME-CH or ME-CH-CH′ are displayed in Fig. 2. The data were fitted to the following functional form:

$$\varepsilon = \varepsilon_c + D_1 t + D_2 t^{\theta} + D_3 t^{\theta+\Delta_1}, \tag{5}$$

which is identical to Eq. (4) 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 [12]. In Table I, coefficients for the different fits are given. Uncertainties on the parameters correspond to three standard deviations. For each run 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 χ^2 value χ_v^2. This permitted us to have a better resolution on the critical exponents since they are strongly correlated to the reduced temperatures. The parameters obtained by letting the exponents free in Eq. (5) compare very favorably with the ones obtained by fixing θ and $\theta + \Delta_1$ to the theoretical values [8] of 0.89 and 1.40, respectively. In Fig. 3 experimental data are compared with the fitting curves in a semilogarithmic plot.

From the results shown in Table I, we can estimate the value of the critical parameter B_2 in Eq. (3). From run 2 we have $C_2 = D_2/\varepsilon_c = 0.74 \pm 0.01$. From run 1 and run 3, respectively, we obtain $C_2 = 1.96 \pm 0.08$ and $C_2 = 1.76 \pm 0.01$. If we now assume that in the case of run 2, where we have an isopycnic mixture, the contribution from the density anomaly is absent we obtain that $C_2 = A_2$ and only because of the intrinsic critical effect in ε. If we now assume further that in the mixtures of run 1 and run 3 the intrinsic contribution is nearly identical to the one of run 2 we can estimate the coefficients B_2 in Eq. (3) for the nonisopycnic critical mixtures. For run 1 we obtain $B_2 = A_2 - C_2 \approx -1.22 \pm 0.09$ and for run 3 we obtain $B_2 = A_2 - C_2 \approx -1.02 \pm 0.02$.

As discussed in previous papers [3,10], the critical behavior of the dielectric constant as compared with the density can be clearly elucidated if one plots $D_\varepsilon \equiv (\varepsilon - \varepsilon_c)/t$ and $D_\rho \equiv (\rho - \rho_c)/t$ as a function of $t = (T - T_c)/T_c$. To the best of our knowledge, mass density data do not exist for these systems; thus we can compare only D_ε for the three different runs 1, 2, and 3 as shown in Fig. 4. The position of the lower curve for the ME-CH-CH′ with 4.5% CH′ in the system CH-CH′ (run 2) as compared with run 1 and run 3 is again a clear indication of the absence or substantial reduction of the critical anomaly in the mass density.

In this Letter we have presented the results of an investigation of the dielectric constant near critical consolute points of the binary liquid mixture methanol-

TABLE I. Results of least-squares fits with Eq. (5) to the experimental values of the dielectric constant from runs 1 through 3 at 13 MHz. The uncertainties quoted are three standard deviations.

Runs	% CH′	ε_c	D_1	D_2	D_3	θ	$\theta + \Delta_1$	χ_v^2
1	0	6.1801 ± 0.0007	−30.90 ± 0.08	12.14 ± 0.08	20.2 ± 1.7	0.897 ± 0.003	1.44 ± 0.07	1.008
2	4.5	6.174 ± 0.001	−16.46 ± 0.07	4.56 ± 0.07	4.1 ± 2.2	0.89 ± 0.01	1.41 ± 0.03	1.072
3	9	6.167 ± 0.001	−29.2 ± 0.1	10.83 ± 0.07	17.8 ± 0.6	0.887 ± 0.003	1.36 ± 0.02	1.089

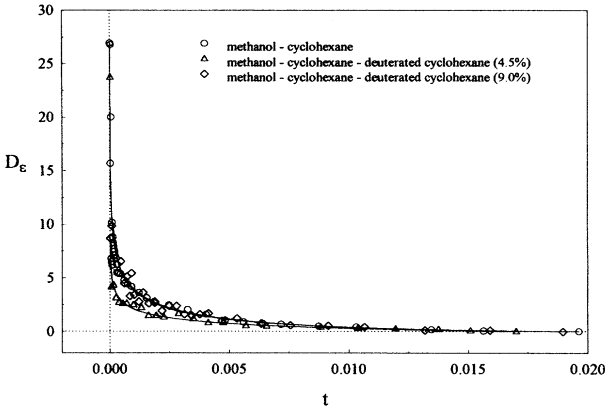

FIG. 4. Plots of the quantity $D_\varepsilon \equiv (\varepsilon - \varepsilon_c)/t$ as a function of the reduced temperature $t = (T - T_c)/T_c$ for the three critical systems investigated.

cyclohexane and of pseudobinary liquid mixtures of methanol–cyclohexane–deuterated-cyclohexane. One of the critical pseudobinary systems (run 2) was made isopycnic. This permitted us to investigate more directly the intrinsic contribution to the static dielectric constant by reducing the critical contribution from the mass density. A substantially smaller critical anomaly in ε was indeed observed in the isopycnic case.

It would also be interesting to carry out careful density measurements in these three systems. Finally, it would also be important, but substantially more difficult, to see if the intrinsic contribution for the refractive index [13] could be isolated in the same manner.

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