

Dielectric constant and the electric conductivity near the consolute point of the critical binary liquid mixture nitroethane–3-methylpentane

J. Hamelin and T. K. Bose

Groupe de Recherche sur les Diélectriques, Département de Physique, Université du Québec à Trois-Rivières, Trois-Rivières, Québec, Canada G9A 5H7

J. Thoen

Laboratorium voor Akoestiek en Warmtegeleiding, Departement Natuurkunde, Katholieke Universiteit Leuven, Celestijnenlaan 200D, 3030 Leuven, Belgium

(Received 8 May 1990)

Experimental data are presented for the dielectric constant ϵ and the electric conductivity σ near the consolute point of a binary liquid mixture nitroethane–3-methylpentane. Fitting the data for ϵ and σ as a function of temperature, we find for both a $1-\alpha$ power-law singularity with an α value consistent with the Ising value $\alpha=0.11$. The temperature dependence of the amplitude of the observed low-frequency Maxwell-Wagner critical dispersion has been explained on the basis of a droplet model for the critical fluctuations.

I. INTRODUCTION

There have been number of studies made, both theoretically¹⁻⁴ and experimentally,^{5,10} to understand the anomalous behavior of the dielectric constant near the consolute point of binary liquid mixtures. The behavior of the dielectric constant of the liquid-liquid transition of critical mixtures follows the same power law as in the case of the gas-liquid transition.

Following an idea first proposed by Mistura¹ on the applicability of critical-point universality to the behavior of fluids in the presence of an electric field, Sengers *et al.*⁴ developed a complete theory of 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 due to the divergence of the thermal expansion coefficient proportional to the rate of change of the critical temperature T_c with pressure P and an explicit contribution proportional to the change of T_c with the electric-field square E^2 . Recent experimental results of the dielectric constant of binary liquid mixtures at the critical point seem to confirm theoretical predictions based on the thermodynamic model of Mistura¹ and Sengers *et al.*⁴ However, several experimental and theoretical aspects need further clarification. The temperature and frequency dependence of the dielectric constant of liquid-liquid critical mixtures are still not fully established and clearly understood. The purpose of the present article is to give precise experimental results on the dielectric constant and the electric conductivity at the critical point of a binary critical mixture composed of nitroethane and 3-methylpentane (NE-3M). The particular interest in this liquid mixture resides in the fact that its density behavior near the critical point has already been studied by Greer and Hocken¹¹ and can be used to determine the explicit contribution to the dielectric constant.

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, all of the recent theories predict for the static dielectric constant ϵ near the critical temperature T_c a leading behavior of the form

$$\epsilon \approx \epsilon_c + At^\theta, \quad (2.1)$$

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. Although various theories make the same predictions for the behavior of the dielectric constant at the critical point, they are quite different in their approaches.

Stell and Hoyer² developed a theory on the critical behavior of the dielectric constant of a simple nonpolar fluid. They expanded the Clausius-Mossotti function in powers of polarizability and showed that the lowest-order term in the expansion is closely related to the internal energy. If higher-order terms are neglected, the static dielectric constant should show the singularity of the internal energy.

Mistura¹ uses thermodynamic arguments and the smoothness postulate to relate also the singular part of the static dielectric constant to that of the internal energy. The singular part of the internal energy is characterized along the same critical path by the critical exponent $1-\alpha$.

Goulon, Greffe, and Oxtoby³ have made a phenomenological analysis of the dielectric constant of binary liquid mixtures. They combine the droplet model of Oxtoby and Metiu,¹² which provides a physical picture of the microscopic nature of systems in the critical region, with

the electrostatic models of Wagner¹³ and Onsager-Bötcher.¹⁴ For both electrostatic models, the same asymptotic behavior of ϵ identical to Eq. (2.1) is derived.

Sengers *et al.*⁴ obtained a functional form for the static dielectric constant near the critical point that includes correction to scaling terms. They applied the critical-point universality to the thermodynamic behavior of fluids and mixtures in the presence of an electric field. They found that for $X = X_c$ (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

$$\epsilon\rho^{-1} = \epsilon_c\rho_c^{-1}(1 + A_1t + A_2t^\theta + A_3t^{\theta+\Delta} + \dots). \quad (2.2)$$

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

$$\rho^{-1} = \rho_c^{-1}(1 + B_1t + B_2t^\theta + B_3t^{\theta+\Delta} + \dots). \quad (2.3)$$

The correction-to-scaling exponent Δ results from the Wegner¹⁵ expansion for higher-order critical contributions. Renormalization-group calculations¹⁶ give $\alpha = 0.110 \pm 0.003$ and $\Delta = 0.51 \pm 0.03$ 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 's and B_i 's are system-dependent nonuniversal parameters. From Eqs. (2.2) and (2.3) one deduces the dielectric constant ϵ itself:

$$\epsilon = \epsilon_c(1 + C_1t + C_2t^\theta + C_3t^{\theta+\Delta} + \dots), \quad (2.4)$$

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: (1) a contribution due to the divergence of the thermal expansion ($B_2 \neq 0$) and (2) 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 density must be included in the analysis in order to assess unambiguously the critical behavior of the dielectric constant.

B. The electric conductivity

Anomalous contributions to the electric conductivity have been reported for several liquid-liquid critical points. The singular contribution to the electric conductivity in the homogeneous phase along $X = X_c$ for a liquid-liquid critical point can generally be analyzed by introducing a term in $t = (T - T_c)/T_c$ with a critical exponent θ . The detailed calculation taking into account correction to scaling gives¹⁷

$$\sigma = \sigma_c(1 + S_1t + S_2t^\theta + S_3t^{\theta+\Delta} + \dots). \quad (2.5)$$

The above equation has the same form as Eq. (2.4) and the exponents have the same meaning. The theoretical and experimental situations regarding the value of the exponent θ are not quite conclusive. It can probably be settled only with highly precise experimental values of σ near a liquid-liquid critical point. Stein and Allen¹⁸ suggested that the anomaly is mainly due to viscous drag on ion movements, resulting in a very small $\theta \approx 0.3$ value. Jasnow, Goldberg and Semura¹⁹ proposed $\theta = 1 - \alpha = 0.89$, on the basis of a proton hopping model.

Based on the percolation model, Shaw and Goldberg²⁰ obtained $\theta = 2\beta = 0.65$, where β is the order-parameter critical exponent. Ramakrishnan *et al.*²¹ proposed $\theta = 1 - \nu$, where ν is the correlation-length critical exponent. According to Fisher and Langer,²² the dominant anomaly is attributed to short-range fluctuations, and $(d\sigma/dT)$ should reflect the specific-heat anomaly and θ should be equal to $1 - \alpha$. Recently, the electric-conductivity results near T_c for both isobutyric acid-water¹⁸⁻²⁰ and phenol-water²⁰ systems have been carefully reanalyzed by Anderson and Greer,¹⁷ who found a $1 - \alpha$ exponent for both cases. Although the older, less precise values of σ near T_c sometimes gave values of the exponent ranging from 0.5 to 1, the more accurate recent results overwhelmingly favor a value of $\theta = 1 - \alpha$.

C. The Maxwell-Wagner effect

The experimental situation on the behavior of the static dielectric constant near the liquid-liquid critical point was until recently rather confusing. 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.¹⁰

III. EXPERIMENT

Although the experimental study of the critical behavior of the static dielectric constant of a binary mixture is difficult because of the weak $1 - \alpha$ expected singularity, the large dielectric constant of the binary liquid of interest, nitroethane-3-methylpentane, renders it possible to obtain precision dielectric constant values.

The present experiment consists in measuring both the dielectric constant and the electric conductivity of a critical nitroethane-3-methylpentane mixture as a function of temperature at several frequencies between 1 kHz and 1 MHz. Details of the apparatus and the experimental procedure are given below.

A. Apparatus used

The measuring cell (Fig. 1) is composed of an inner cylinder of 15.0 mm diameter and three circular plates, each having an inner diameter of 23.5 mm and an external diameter of 70.0 mm. The cylinder and the plates are

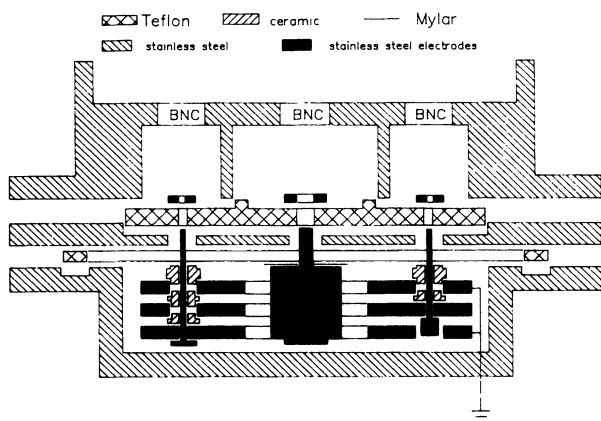


FIG. 1. Schematic diagram of the measuring cell.

made from 316 stainless steel. The plates are insulated from each other by means of ceramic of 3.0 mm thickness. The capacitance measurements are made with the inner cylinder and the central plate acting as two electrodes while the other plates are connected to the ground.

The arrangement of the capacitors covers a 15.0-mm region in the middle of the sample cell of 25.0 mm high and 80.0 mm in diameter. The capacitance and the electric conductance are measured with a Hewlett-Packard four-terminal impedance meter (Model No. HP4284A) with frequencies ranging from 20 Hz to 1 MHz and a General Radio three-terminal transformer bridge (Model No. GR1621) with frequencies ranging from 10 Hz to 100 kHz. For both the apparatuses used, the maximum resolutions that we could obtain for the capacitance and conductance measurements were, respectively, 0.001 pF and $0.001 \mu\Omega^{-1}$. The absolute precision for the capacity from the impedance meter at 1 MHz under the condition of measurement is ± 0.02 pF, but we have used instead the relative precision of ± 0.001 pF given by the statistical analysis of the experimental data.

The temperature of the sample cell is controlled to within 0.5 mK over a period of 4 h by means of a Tronac precision controller bath (Model No. 40). The temperature is measured with a Hewlett-Packard quartz thermometer (model No. HP2801A), which has a resolution of 0.1 mK and an absolute precision of ± 0.04 K.

B. Experimental procedure

3-methylpentane and nitroethane are both obtained from Aldrich Chemical Company. 3-methylpentane certified 99+% pure was used without further purification. Nitroethane, which is hygroscopic and corrosive, was only 96% pure. It was twice distilled under dry nitrogen at reduced pressure. Both 3-methylpentane and nitroethane were kept in a dessicator over silica gel to get out the last traces of water.

For the critical parameters Wims *et al.*²³ obtained $T_c = 26.456^\circ\text{C}$ and the critical mole fraction $X_c = 0.500$. Using an analytical balance under dry nitrogen atmosphere, we obtained a precision in terms of molar fraction for nitroethane of 0.500 ± 0.001 . The criticality of the mixture was then verified by checking visually in a

temperature-controlled glass bath ($\pm 0.05^\circ\text{C}$) the separation of the two liquids in the middle of a cylindrical vial. Once the critical composition was reached, the sample was transferred to the dielectric measuring cell in the homogeneous phase.

IV. RESULTS AND DISCUSSION

We have measured the dielectric constant and the electric conductivity of the homogeneous critical binary liquid mixture nitroethane–3-methylpentane as a function of temperature ranging from 38.017°C to T_c (26.535°C) and as a function of frequency between 1 kHz and 1 MHz (Fig. 2).

The frequency dependence of the dielectric constant is given for a set of temperatures in Fig. 3. For high temperatures away from T_c , there is no frequency dependence present in the data. An increasing dielectric dispersion effect is clearly visible as the temperature approaches T_c . The amplitude of the dispersion effect

$$\Delta\epsilon_{\text{MW}} = \epsilon(1 \text{ kHz}) - \epsilon(1 \text{ MHz})$$

is plotted as a function of temperature in Fig. 4.

The dispersion effect in the electric conductivity σ is, however, less pronounced and more difficult to measure because it shows up at frequencies above f_{MW} in the region where conductance measurement is less precise. In Figs. 5 and 6 results for σ as a function of frequency for some temperatures and

$$\Delta\sigma_{\text{MW}} = \sigma(1 \text{ MHz}) - \sigma(1 \text{ kHz})$$

as a function of temperature are shown.

Although we have not looked specifically for the gravity effect by measuring ϵ as a function of height, we have shown in a previous publication⁷ 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 isooctane. Greer, Block, and Knobler²⁴ have studied extensively the gravity effect for NE-3M and found that the density change close to the center of the sample, near T_c , was insignificant. We can

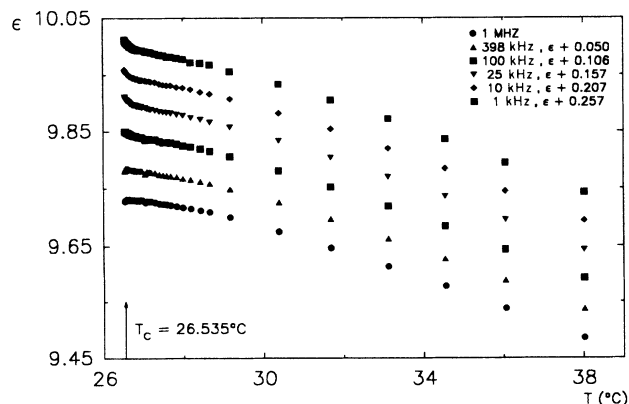


FIG. 2. Temperature dependence of the static dielectric constant in the homogeneous phase of the critical NE-3M mixture for several frequencies.

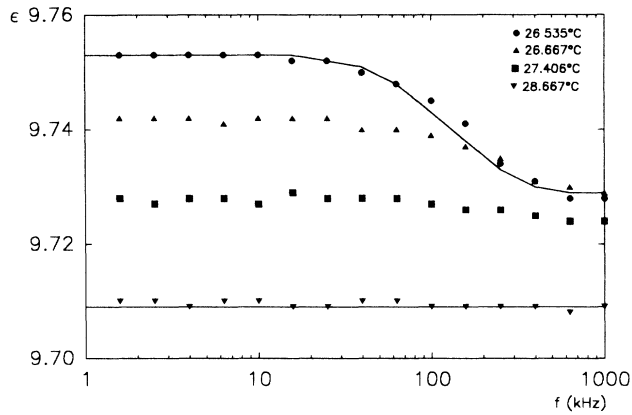


FIG. 3. Frequency dependence of the dielectric constant for several temperatures above T_c for the critical NE-3M mixture.

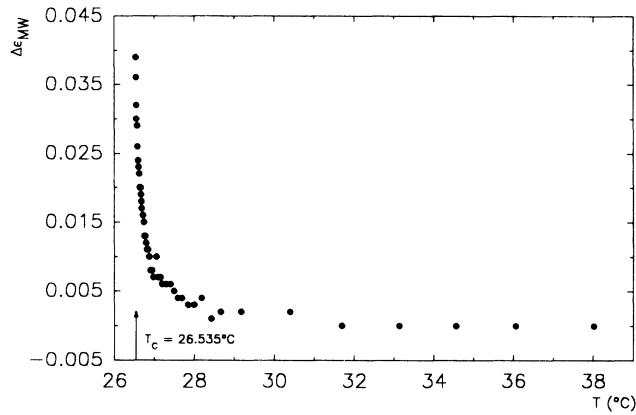


FIG. 4. Temperature dependence of the amplitude $\Delta\epsilon_{MW} = \epsilon_l - \epsilon_h$ of the Maxwell-Wagner effect for the critical NE-3M mixture.

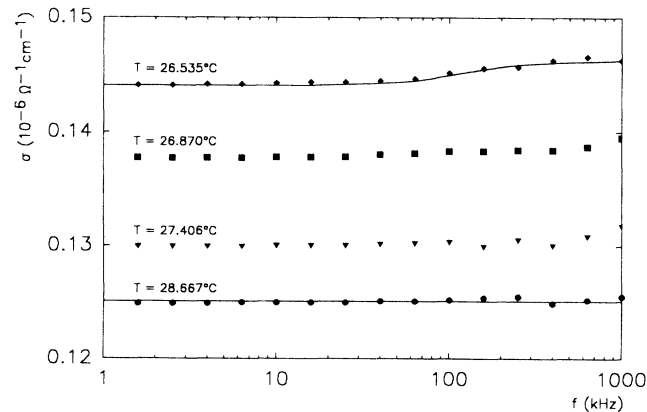


FIG. 5. Frequency dependence of the electric conductivity for several temperatures above T_c for the critical NE-3M mixture.

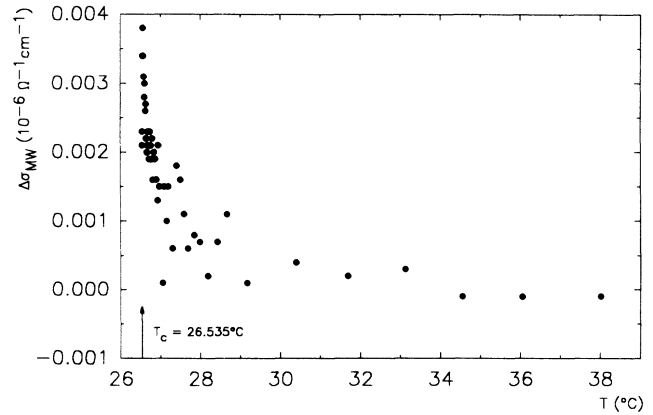


FIG. 6. Temperature dependence of the amplitude $\Delta\sigma_{MW} = \sigma_h - \sigma_l$ of the Maxwell-Wagner effect for the critical NE-3M mixture.

therefore assume that the present measurements, carried out near the center of the sample, should be unaffected by gravity.

As discussed in detail in a previous publication,¹⁰ Wagner's model seems to account for the dispersion effect of ϵ and σ near T_c rather well. One can see from Figs. 3 and 5 that the relaxation times of the dispersion are not dependent on the temperature, but are mainly determined by the overall conductivity.¹⁰

The ϵ data taken at a frequency of 1 MHz and covering the entire temperature range are compiled in Table I and displayed in Fig. 7. The complete data are fitted with a computer program similar to the FORTRAN computer routine CURFIT described by Bevington²⁵ and based on Marquardt's algorithm. The data are fitted with the following equation:

$$\epsilon = \epsilon_c + D_1 t + D_2 t^\theta + D_3 t^{\theta+\Delta}, \quad (4.1)$$

which is identical to Eq. (2.4) with $D_1 = \epsilon_c C_1$, $D_2 = \epsilon_c C_2$, $D_3 = \epsilon_c C_3$, and $\theta = 1 - \alpha$. In Table II coefficients for the different fits are given. Uncertainties on the parameters correspond to one standard deviation. The parameters obtained by the free fit of Eq. (4.1) compare very favor-

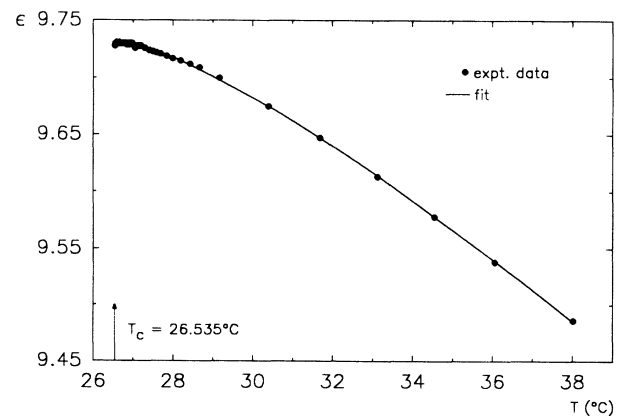


FIG. 7. Temperature dependence of the static dielectric constant in the homogeneous phase of the critical NE-3M mixture at 1 MHz.

ably with the ones obtained by fixing T_c , θ , and $\theta + \Delta$. Both cases give $\theta = 0.89 \pm 0.01$ and $\theta + \Delta = 1.3 \pm 0.1$ and agree well with the theoretical values¹⁶ obtained from renormalization-group calculations for θ (0.890 ± 0.003) and $\theta + \Delta$ (1.40 ± 0.03), the correction to scaling.

For comparison with the density data of Greer and Hocken¹¹ for NE-3M (Fig. 8), we fitted our experimental

TABLE I. Experimental values for the dielectric constant at 1 MHz and the electric conductivity at 1 kHz as a function of temperature in the homogeneous phase above T_c for the critical mixture of nitroethane-3-methylpentane.

No.	T (°C) (± 0.001)	ϵ (± 0.001)	σ ($\mu\Omega^{-1} \text{ cm}^{-1}$) (± 0.001)
1	38.017	9.486	0.117
2	36.052	9.538	0.121
3	34.547	9.578	0.123
4	33.123	9.613	0.123
5	31.689	9.647	0.124
6	30.389	9.675	0.125
7	29.171	9.700	0.124
8	28.667	9.709	0.125
9	28.430	9.712	0.126
10	28.189	9.715	0.126
11	27.993	9.717	0.128
12	27.838	9.719	0.128
13	27.689	9.721	0.129
14	27.591	9.722	0.129
15	27.499	9.723	0.130
16	27.406	9.724	0.130
17	27.300	9.726	0.134
18	27.197	9.728	0.134
19	27.150	9.728	0.135
20	27.094	9.728	0.135
21	27.048	9.726	0.136
22	26.972	8.730	0.136
23	26.944	9.730	0.137
24	26.922	9.730	0.138
25	26.900	9.729	0.137
26	26.870	9.730	0.138
27	26.838	9.729	0.138
28	26.812	9.730	0.138
29	26.797	9.730	0.138
30	26.778	9.730	0.138
31	26.756	9.730	0.138
32	26.738	9.730	0.138
33	26.717	9.730	0.138
34	26.687	9.730	0.140
35	26.677	9.730	0.140
36	26.667	9.730	0.140
37	26.657	9.730	0.140
38	26.646	9.731	0.140
39	26.635	9.731	0.140
40	26.626	9.731	0.141
41	26.610	9.731	0.142
42	26.596	9.731	0.142
43	26.582	9.731	0.142
44	26.567	9.730	0.142
45	26.559	9.730	0.142
46	26.553	9.730	0.143
47	26.543	9.728	0.143
48	26.535	8.728	0.144

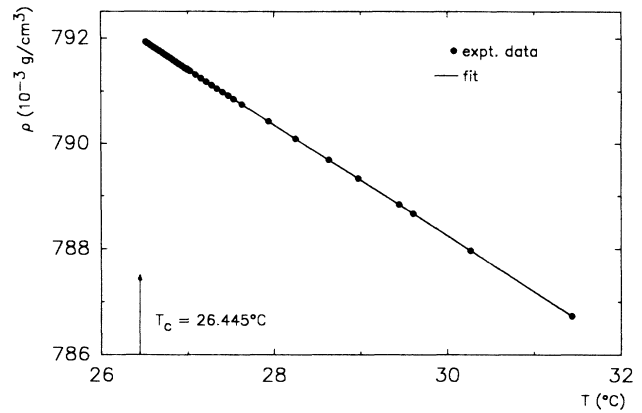


FIG. 8. Temperature dependence of the mass density in the homogeneous phase of the critical NE-3M mixture.

values of the dielectric constant from Table I to $t^* = T - T_c$ instead of $t = (T - T_c)/T_c$. We obtained

$$B_2 = 0.00032 \pm 0.00002,$$

$$A_2 = 0.0051 \pm 0.0004,$$

and

$$D_2/\epsilon_c = 0.0048 \pm 0.0001.$$

Then, we can easily verify that

$$C_2 = A_2 - B_2 = 0.0048 \pm 0.0004$$

corresponds exactly to D_2/ϵ_c . As discussed in a previous paper,²⁶ the critical behavior of the dielectric constant as compared with the density can be clearly elucidated if one plots $D_\epsilon = (\epsilon - \epsilon_c)/t$ and $D_\rho = (\rho - \rho_c)/t$ as a function of $t = (T - T_c)/T_c$ (Fig. 9). The comparison of the two curves near the critical point clearly shows that the behavior of the dielectric constant is opposite to that of the density. Moreover, a comparison between A_2 and B_2 shows that the intrinsic effect in ϵ due to dT_c/dE^2 is almost 16 times larger than the density effect related to dT_c/dP .

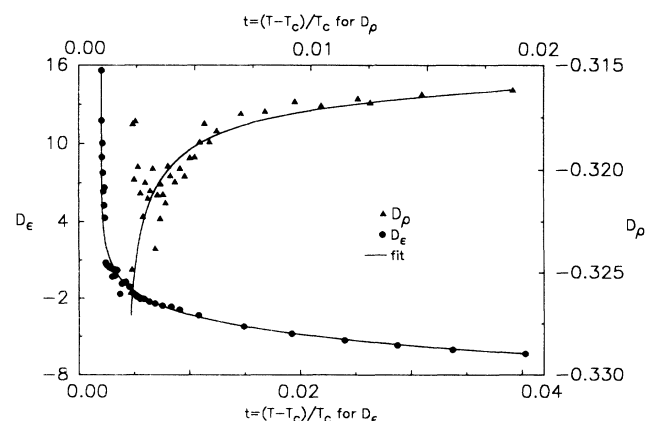


FIG. 9. Temperature dependence of the quantity D_ϵ and D_ρ for the critical NE-3M mixture.

TABLE II. Results of least-squares fits of Eq. (4.1) to the experimental values of the dielectric constant from Table I. Values shown in parentheses are held fixed during the fit and the uncertainties quoted are one standard deviation.

T_c (°C)	ϵ_c	D_1	D_2	D_3	θ	$\theta + \Delta$	χ^2_ν
(26.535)	9.7284 ± 0.0002	-22.6 ± 0.3	11.4 ± 0.2		(0.89)		1.0404
(26.535)	9.7284 ± 0.0003	-23.5 ± 0.9	12.2 ± 0.8		0.895 ± 0.005		1.0447
(26.535)	9.7292 ± 0.0003	-15 ± 2	8 ± 1	-8 ± 2	(0.89)	(1.39)	0.7504
26.5348	9.7293 ± 0.0003	-14 ± 1	7.5 ± 0.9	-8 ± 2	0.89 ± 0.01	1.3 ± 0.1	0.7857

From Fig. 3, where the frequency dependence of ϵ is given for a set of temperatures, it is clear that there is no frequency dependence present in the data away from the critical temperature (large T values). One sees, however, an increasing dielectric dispersion effect with decreasing temperature on approaching the critical point. The rapid increase of the amplitude of the dispersion effect $\Delta\epsilon_{MW}$, on approaching T_c , is more clearly visible in Fig. 4. The amplitude of the dispersion effect on the electric conductivity $\Delta\sigma_{MW}$ is less pronounced, but nevertheless observable, in Fig. 6 for the results very close to T_c . On the basis of the analogy with the dielectric behavior of water-in-oil (W-O) and oil-in-water (O-W) microemulsions, Thoen *et al.*¹⁰ formulated a droplet model for the temperature dependence of $\Delta\epsilon_{MW}$ in critical binary mixtures sufficiently close to T_c . The following result was obtained:

$$\Delta\epsilon_{MW} \approx (T - T_c)^{-(\nu - \beta)}. \quad (4.2)$$

Since for the universality class of the three-dimensional Ising model one has $\beta = 0.326 \pm 0.002$ and $\nu = 0.630 \pm 0.001$,¹⁶ $\Delta\epsilon_{MW}$ is expected to diverge with an exponent $\nu - \beta = 0.305$. In Fig. 10, $\Delta\epsilon_{MW}$ data have been plotted as a function of the reduced temperature $t = (T - T_c)/T_c$, on a double logarithmic scale. The slope of our data closest to T_c seems to be in agreement with the value $\nu - \beta = 0.30$ expected on the basis of Eq. (4.2).

In Fig. 11 the temperature dependences of the electric conductivity σ for three different runs in the homogeneous phase above T_c of a single mixture are given. It is

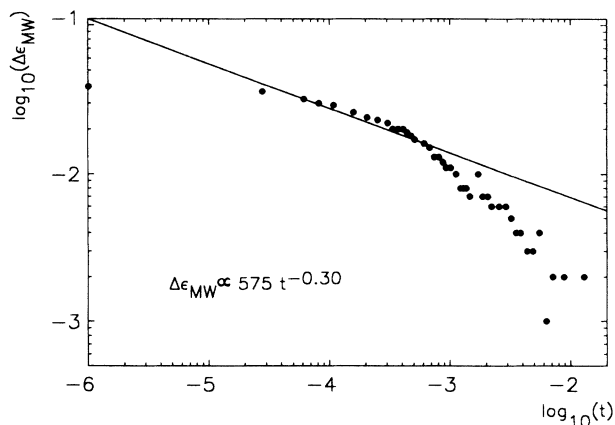


FIG. 10. Double logarithmic plot of $\Delta\epsilon_{MW}$ as a function of the temperature for the critical NE-3M mixture.

clear that there are qualitative as well as quantitative differences among the data of the three runs. The first run has the lowest overall σ and the third run the highest one. Even though the measuring cell was not opened between the runs, an increase in the number of ionic impurities occurred. Although a very slow increase of σ with time during the runs cannot be excluded, the main increase in σ occurred during the homogenizing process (by shaking the sample cell at $T > T_c$) after the sample had phase separated at the end of the previous run. Similar results were obtained for other binary mixtures.¹⁰ In spite of the fact that there were small changes of T_c of about 860 mK between run 1 and run 2 and 110 mK between run 2 and run 3, this had no discernible effect on the values of the static dielectric constant. As pointed out by Thoen *et al.*,¹⁰ the increase of the electric conductivity near T_c between run 1 and run 2 seems to be a typical behavior for poorly conductive samples, which becomes unobservable for large overall values of the conductivity σ .

Thoen *et al.*¹⁰ also pointed out that the theoretical expected $t^{1-\alpha}$ behavior should be observed for sufficiently large σ values. Although the change of σ is quite large near T_c for runs 1–4, it does not diverge at the critical point. This is clearly visible in Fig. 12, where we have plotted similar results for run 4 (which was the first run for a different sample and where the ϵ data are the ones used for this article) on a semilogarithmic plot as a function of $t = (T - T_c)/T_c$. Close to T_c there is clearly a sat-

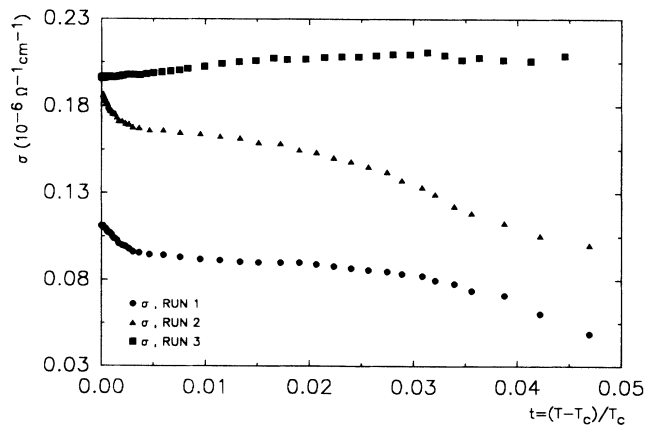


FIG. 11. Temperature dependence of the electric conductivity for three different runs with the same sample in the homogeneous phase of the critical NE-3M mixture.

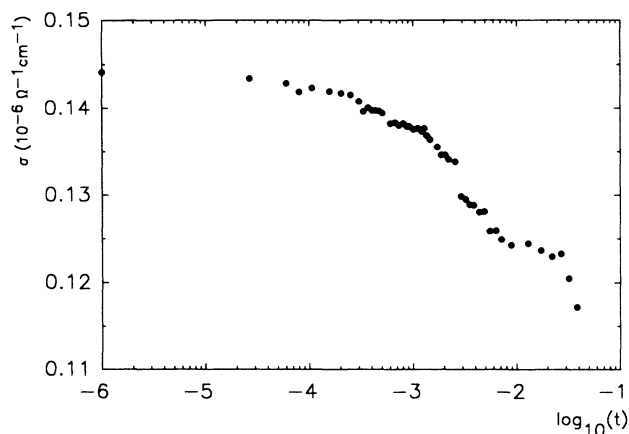


FIG. 12. Semilogarithmic plot of the temperature dependence of the electric conductivity for run 4 in the homogeneous phase of the critical NE-3M mixture.

uration effect for the critical increase of σ . This effect for very poorly conducting critical mixtures could also be explained on the basis of the droplet picture for critical fluctuations.¹⁰

TABLE III. Experimental values for the electric conductivity at 1 kHz as a function of temperature in the homogeneous phase above T_c for the critical mixture of nitroethane-3-methylpentane-Bu₄NHSO₄.

No.	T (°C) (±0.005)	σ ($\mu\Omega^{-1} \text{ cm}^{-1}$) (±0.02)
1	36.521	57.16
2	36.032	57.00
3	35.539	56.84
4	35.044	56.64
5	34.559	56.46
6	34.063	56.26
7	33.516	56.00
8	33.084	55.81
9	32.592	55.58
10	32.094	55.34
11	31.609	55.11
12	31.116	54.77
13	30.633	54.47
14	30.084	54.07
15	29.886	53.96
16	29.642	53.81
17	29.409	53.68
18	29.149	53.47
19	28.964	53.32
20	28.764	53.19
21	28.569	53.04
22	28.369	52.85
23	28.274	52.75
24	28.171	52.65
25	28.125	52.61
26	28.074	52.49
27	28.041	52.47
28	28.003	52.44
29	27.984	52.42
30	27.972	52.40
31	27.952	52.35

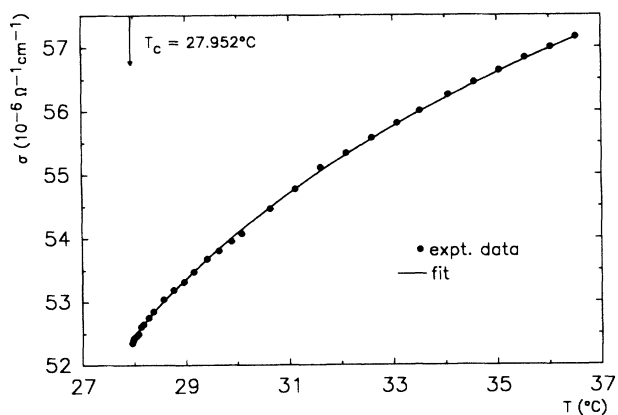


FIG. 13. Temperature dependence of the electric conductivity in the homogeneous phase of the critical NE-3M-Bu₄NHSO₄ mixture at 1 kHz.

Finally, we have made an additional run with the binary liquid mixture nitroethane-3-methylpentane with added salt tetra-*n*-butylammonium hydrogen sulfate (Bu₄NHSO₄) to study the critical behavior for the conductivity at the consolute point. It has been shown by Thoen *et al.*¹⁰ that the theoretically expected $t^{1-\alpha}$ behavior could only be observed for sufficiently large σ values. The NE-3M critical mixture with approximately 5 g per liter of Bu₄NHSO₄ shows a conductivity almost 500 times greater than the previous samples. The experimental data are listed in Table III and the results of the fitting by Eq. (2.5) are reported in Table IV. The ϵ values are not listed because the Maxwell-Wagner dispersion effect was still very high at 1 MHz. The critical behavior of σ as a function of temperature is shown in Fig. 13 and it clearly follows a t^θ behavior with $\theta=0.889\pm 0.006$ as expected.

We could not measure ϵ and σ simultaneously with a good precision both for the NE-3M mixture as well as the same mixture with added salt (Bu₄NHSO₄). This was mainly due to the fact that in the case of the pure mixture, the low conductivity values were affected by the fluctuations at the critical point which mask the ionic mobility and as such $1-\alpha$ critical behavior of σ could

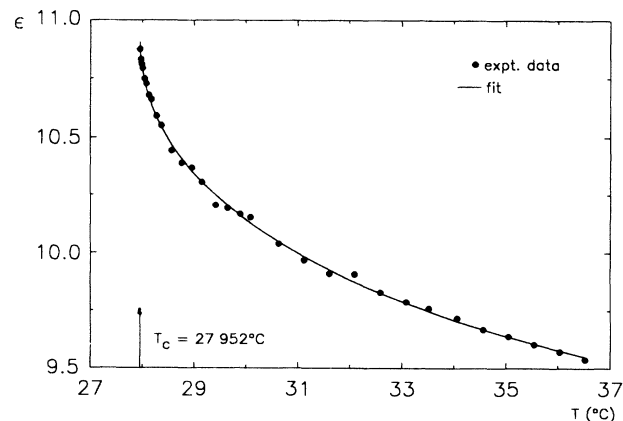


FIG. 14. Temperature dependence of the static dielectric constant in the homogeneous phase of the critical NE-3M-Bu₄NHSO₄ mixture at 1 MHz.

TABLE IV. Results of least-squares fits of Eq. (2.5) to the experimental values of the electric conductivity from Table III. Values shown in parentheses are held fixed during the fit and the uncertainties quoted are one standard deviation.

T_c (°C)	σ_c	$\sigma_c S_1$ ($10^{-6} \Omega^{-1} \text{ cm}^{-1}$)	$\sigma_c S_2$	$\sigma_c S_3$	θ	$\theta + \Delta$	χ^2_ν
(27.952)	52.258±0.09	33±3	41.3±0.7		(0.65)		7.9900
(27.952)	52.326±0.008	-342±9	348±6		(0.89)		3.5439
(27.952)	52.325±0.008	-286±15	297±14		0.878±0.004		3.8360
(27.952)	52.38±0.01	149±67	102±34	-526±71	(0.89)	(1.39)	1.6518
(27.952)	52.378±0.006	145±8	102±5	-522±23	0.889±0.006	1.39±0.05	1.7810

not be followed. On increasing the overall conductivity of the NE-3M mixture by adding Bu_4NHSO_4 , we were able to observe the $1-\alpha$ critical behavior of σ . But since the Maxwell-Wagner dispersion effect for the dielectric constant is proportional to σ , the relaxation frequency of the mixture NE-3M- Bu_4NHSO_4 shifted to higher values and as such we could not determine ϵ outside the dispersive region. We could, however, still observe a sharp increase of ϵ near T_c at 1 MHz (Fig. 14).

Experimentally, it turns out to be very difficult to obtain simultaneously high-precision data for the static behavior of the dielectric constant ϵ as well as for the electric conductivity σ . In order to arrive at high-precision static ϵ data in the experimentally favorable frequency range (≤ 1 MHz), the Maxwell-Wagner relaxation frequency, and thus also the conductivity σ , have to be rather low. This then results unavoidably in less accurate results for σ . Moreover, in the poor conductivity regime one has to consider also the critical effect in $\Delta\epsilon_{\text{WM}}$, as reported by Thoen *et al.*¹⁰ In the high σ regime, it is possible to have a much better precision for σ , but then the MW relaxation is above the upper frequency limit for

precise measurements, and the ϵ values become less precise and do not give the static behavior near T_c . Our results show that the static ϵ behavior, showing the $\theta=1-\alpha$ anomaly, should be measured for very small σ values, while the $\theta=1-\alpha$ behavior for σ can only be observed for substantially larger conductivity values. We thus feel that it would be very difficult to find a binary system where simultaneous critical measurements of ϵ and σ are possible. Gunasekharan *et al.*²⁷ claim to have made such measurements, but unfortunately they did not present the results of their measurements in a way that renders a possible comparison with our data.

ACKNOWLEDGMENTS

This work was supported by the Natural Sciences and Engineering Research Council (NSERC) of Canada and by the government of Québec through its Formation de Chercheurs et l'Aide à la Recherche (FCAR) funds. We would like to thank the governments of Québec and Flanders for financial support of an exchange program between our two laboratories.

¹L. Mistura, *J. Chem. Phys.* **59**, 4563 (1973).

²G. Stell and J. S. Hoyer, *Phys. Rev. Lett.* **33**, 1268 (1974).

³J. Goulon, J. L. Greffe, and D. W. Oxtoby, *J. Chem. Phys.* **70**, 4742 (1979).

⁴J. V. Sengers, D. Bedeaux, P. Mazur, and S. C. Greer, *Physica A* **104**, 573 (1980).

⁵J. Thoen, R. Kindt, and W. Van Dael, *Phys. Lett.* **76A**, 445 (1980); **87**, 73 (1981).

⁶D. T. Jacobs and S. C. Greer, *Phys. Rev. A* **24**, 2075 (1981).

⁷M. Merabet and T. K. Bose, *Phys. Rev. A* **25**, 2281 (1982).

⁸B. C. Miller, E. A. Clerke, and S. C. Greer, *J. Phys. Chem.* **87**, 1063 (1983).

⁹J. L. Tveekrem, S. C. Greer, and D. T. Jacobs, *Macromolecules* **21**, 147 (1988).

¹⁰J. Thoen, R. Kindt, W. Van Dael, M. Merabet, and T. K. Bose, *Physica A* **156**, 92 (1989), and reference therein.

¹¹S. C. Greer and R. Hocken, *J. Chem. Phys.* **63**, 5067 (1975).

¹²D. W. Oxtoby and H. Metiu, *Phys. Rev. Lett.* **36**, 1092 (1976).

¹³K. W. Wagner, *Arch. Elektrotech. (Berlin)* **2**, 371 (1914).

¹⁴C. J. F. Böttcher, *Rec. Trav. Chim. Pays-Bas* **64**, 47 (1945).

¹⁵F. Wegner, *Phys. Rev. B* **5**, 4529 (1973).

¹⁶J. V. Sengers and J. M. H. Levelt Sengers, *Ann. Rev. Phys.*

Chem. **37**, 189 (1986), and reference therein.

¹⁷E. M. Anderson and S. C. Greer, *Phys. Rev. A* **30**, 3129 (1984).

¹⁸A. Stein and F. G. Allen, *J. Chem. Phys.* **59**, 6079 (1973).

¹⁹D. Jasnow, W. I. Goldburg, and J. S. Semura, *Phys. Rev. A* **9**, 355 (1974).

²⁰C. H. Shaw and W. I. Goldburg, *J. Chem. Phys.* **65**, 4906 (1976).

²¹J. Ramakrishnan, N. Nagarajan, A. Kumar, E. S. R. Gopal, and G. Ananthakrishna, *J. Chem. Phys.* **68**, 4098 (1978).

²²M. E. Fisher and J. S. Langer, *Phys. Rev. Lett.* **20**, 665 (1968).

²³A. M. Wims, D. McIntyre, and F. Hynne, *J. Chem. Phys.* **50**, 616 (1969).

²⁴S. C. Greer, T. E. Block, and C. M. Knobler, *Phys. Rev. Lett.* **34**, 250 (1975).

²⁵P. R. Bevington, *Data Reduction And Error Analysis For The Physical Sciences* (McGraw-Hill, New York, 1969).

²⁶C. Pépin, T. K. Bose, and J. Thoen, *Phys. Rev. Lett.* **60**, 2507 (1988).

²⁷M. K. Gunasekharan, S. Guha, V. Vani, and E. S. R. Gopal, *Ber. Bunsenges. Phys. Chem.* **89**, 1278 (1985).