International Journal of Thermophysics, Vol. 9, No. 5, 1988

Dielectric Study of the Two-Phase Region of Binary Liquid Mixtures Near the Consolute Point[1]

R. Kindt,[2] J. Thoen,[2,3] and W. Van Dael[2]

We present new experimental results for the static dielectric constant as a function of temperature for the coexisting phases of the binary liquid mixtures benzonitrile–isooctane and nitroethane–cyclohexane near their consolute points. From the difference of the dielectric constants of the coexisting phases as well as from the temperature dependence of the dielectric constant in each phase, a critical exponent value $\beta = 0.325 \pm 0.005$ is obtained. The average of the dielectric constant shows curvature arising from a critical contribution with an exponent of 2β.

KEY WORDS: critical point; dielectric constant; mixtures (liquid); order parameter; phase transitions; two-phase region.

1. INTRODUCTION

The occurrence of large fluctuations in a fluid near the critical point also affects the behavior of the dielectric constant. Both phenomenological [1, 2] and microscopic [3, 4] approaches predict for the static dielectric constant ε an anomaly characterized by a critical exponent $1-\alpha$, where α is the exponent for the heat capacity divergence. Specifically for a lower liquid–liquid critical point Sengers et al. [2], for the critical concentration $x = x_c$ in the homogeneous phase, arrived at the following functional form:

$$\rho^{-1}\varepsilon = \rho_c^{-1}\varepsilon_c(1 + A_1\tau^{1-\alpha} + A_2\tau + A_3\tau^{1-\alpha+\Delta} + \cdots) \tag{1}$$

---

[1] Paper presented at the Tenth Symposium on Thermophysical Properties, June 20–23, 1988, Gaithersburg, Maryland, U.S.A.

[2] Laboratorium voor Molekuulfysika, Katholieke Universiteit Leuven, Celestijnenlaan 200 D, B-3030 Leuven, Belgium.

[3] Present address: Laboratorium voor Akoestiek en Warmtegeleiding, Katholieke Universiteit Leuven, Celestijnenlaan 200 D, B-3030 Leuven, Belgium.

The dielectric constant ε is divided by the mass density ρ, which also has a critical anomaly described by a functional form with the same τ dependence as in the right-hand side of Eq. (1). $\tau = (T - T_c)/T$ is only slightly different from the more commonly used reduced temperature $t = (T - T_c)/T_c$. The exponent Δ results from higher-order correction-to-scaling contributions in the Wegner expansion for the critical behavior [5]. Renormalization group calculations [6] give $\alpha = 0.11$ and $\Delta = 0.50$ for systems, like consolute points in liquid mixtures, belonging to the $d = 3$ Ising universality class. The critical parameters ρ_c and ε_c and the A_i's depend on the particular system.

In the two-phase region below T_c, the temperature dependence of the static dielectric constant of each of the coexisting phases will be determined largely by the temperature dependence of the order parameter, which is characterized by the critical exponent β (with an Ising value of 0.325). For the upper and the lower coexisting phase, respectively, one can write the following functional forms [2]:

$$\begin{aligned}\varepsilon_u = \varepsilon_c(1 &+ B_1\tau^{\beta} + B_2\tau^{\beta+\Delta} + B_3\tau^{1-\alpha} + B_4\tau^{\beta+2\Delta} \\ &+ B_5\tau^{\beta+1} + B_6\tau + B_7\tau^{1-\alpha+\Delta} + \cdots) \qquad (2)\end{aligned}$$

$$\begin{aligned}\varepsilon_l = \varepsilon_c(1 &+ C_1\tau^{\beta} + C_2\tau^{\beta+\Delta} + C_3\tau^{1-\alpha} + C_4\tau^{\beta+2\Delta} \\ &+ C_5\tau^{\beta+1} + C_6\tau + C_7\tau^{1-\alpha+\Delta} + \cdots) \qquad (3)\end{aligned}$$

Making the average and the difference of ε_u and ε_l results in the following expressions:

$$\Delta\varepsilon = \varepsilon_l - \varepsilon_u = \varepsilon_c(D_1\tau^{\beta} + D_2\tau^{\beta+\Delta} + D_4\tau^{\beta+2\Delta} + D_5\tau^{\beta+1} + \cdots) \qquad (4)$$

$$\varepsilon_d = \frac{\varepsilon_l + \varepsilon_u}{2} = \varepsilon_c(1 + d_1\tau^{1-\alpha} + d_2\tau + \cdots) \qquad (5)$$

In these expressions it is assumed that $|\varepsilon - \varepsilon_c|$ is proportional to the order parameter. If it is, however, more generally an analytical function of it, one expects [7, 8] the appearance of terms in $\tau^{2\beta}$, $\tau^{3\beta}$, $\tau^{2(\beta+\Delta)}$, etc.The $\tau^{2\beta}$ term may then be the dominant one for the diameter ε_d of the coexistence curve, and one has

$$\varepsilon_d = \varepsilon_c(1 + d_1'\tau^{2\beta} + d_2'\tau^{1-\alpha} + d_3'\tau + \cdots) \qquad (6)$$

We have carried out a detailed dielectric investigation of the binary liquid mixtures benzonitrile–isooctane and nitroethane–cyclohexane. For both systems results have been obtained in the homogeneous phase above T_c as well as for the coexisting phases below T_c. The frequency dependence in the range between 10 Hz and 2 MHz has also been investigated. Some of the results for the homogeneous phase of both mixtures have been discussed previously in two letters [9, 10].

In this paper we want to present dielectric constant results for NB–IO and NE–CH in the two-phase region below T_c. A double-capacitor arrangement in the measuring cell (see Section 2) allowed us to measure in the two coexisting phases simultaneously. From the results for ε_u, ε_1, and their difference $\Delta\varepsilon$, information on the oder parameter critical exponent β is derived using Eqs. (2)–(4). Also, the temperature dependence of the diameter ε_d is analyzed in search of the leading $\tau^{1-\alpha}$ or $\tau^{2\beta}$ singularity [Eqs. (5) and (6)].

Since the experimental data for ε in the frequency range between 10 Hz and 100 kHz have been obtained with ratio transformer bridges (see Section 2), balancing the bridge resulted not only in a capacitance but also in a conductance reading for the capacitors filled with these polar–nonpolar liquid mixtures. Thus for each value of the dielectric constant a corresponding value for the electric conductivity σ was obtained. The critical behavior of σ for the mixtures BN–IO and NE–CH and also for nitrobenzene–isooctane [11] will be discussed elsewhere [12]. There, also, a detailed analysis of the critical Maxwell–Wagner dispersion effect will be given.

2. EXPERIMENTAL

In Fig. 1 a vertical cross section of the dielectric cell for the measurements in NE–CH is shown. For BN–IO a very similar cell with a five times larger volume was used. The whole construction is made of stainless steel, Teflon, and glass. The measuring cell contains two vertically positioned cylindrical capacitors. Each capacitor is designd as a three-terminal capacitance system, i.e., both capacitor plates, L (low voltage) and H (high voltage), are isolated from the ground G, which includes the can surrounding the capacitors and containing the mixture. The electrodes are supported by glass beads (a) and connected to the supporting plates (b) with insulated screws (c). The supporting plates have many large holes, allowing free vertical movements of the fluid. The electric leads leave the cell through shielded connections (d) in the lid of the cell. The lid is hermetically sealed to the can with six screws and a Teflon ring (e). The lid also has a filling cap (not shown) and can be evacuated for the determination of the vacuum capacitance. The capacitance of each empty capacitor is about 7 pF. The two-capacitor setup allows simultaneous measurements in the two-phase region below T_c. Above T_c one can verify the absence of composition gradients in the cell.

For the data to be discussed here we used a General Ratio Model 1615 or 1616 bridge. The first one measures the unknown impedance as a capacitance in series with a conductance; the second one measures it as parallel elements. The results are, of course, interrelation. Depending on the frequency, there are different possible ranges for the conductance, and the choice between the two bridges was determined mainly by the electric conductivity of the samples [12].

The temperature of the sample cell was controlled by means of a two-stage temperature-regulating system. The sample cell was immersed in an oil bath with stirrer, heater, and temperature sensors. This oil bath (with

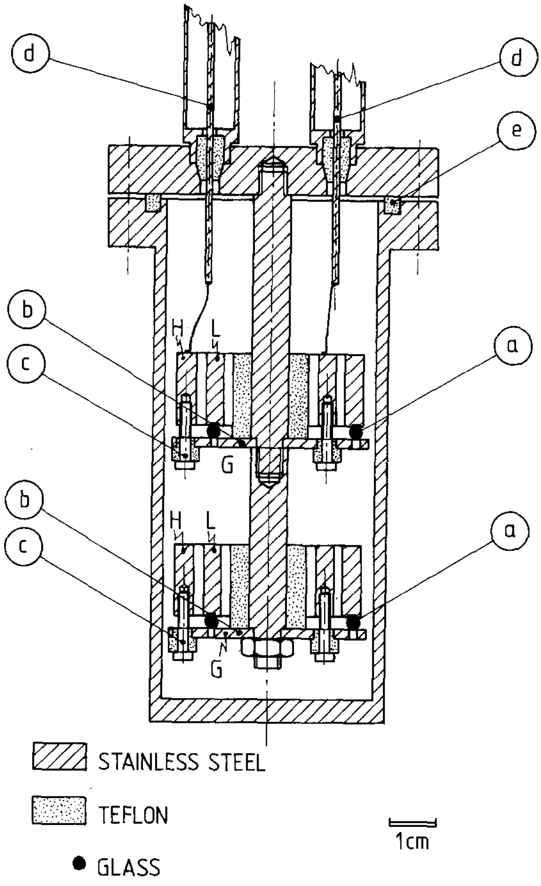

Fig. 1. Schematic diagram of the measuring cell. H, electrode at high potential; L, electrode at low potential; a, glass beads; b, supporting plate at ground potential G; c, isolated screws; d, lead connection; e, Teflon sealing ring.

plexiglass walls) was incorporated in a larger precision-controlled water thermostat. The temperature stability, which was 2 mK for the measurements in BN–IO, was improved to 0.5 mK for the NE–CH measurements. The temperature was measured with a quartz thermometer (Hewlett & Packard Model 2850), which was calibrated by means of a platinum thermometer with respect to the T-68 temperature scale.

For the mixtures BN–IO we used products with a purity better than 99% obtained from UCB (Union Chimique Belge). For the NE–CH system nitroethane from Aldrich–Europe was twice vacuum distilled, and a gas chromatographical analysis gave a purity of better than 99.8%. Cyclohexane with a purity of better than 99.7% was purchased from Riedel–de Haën. All products were dried with molecular sieves. The critical mole fractions $x_c(\mathrm{NB}) = 0.466 \pm 0.00$ for BNIO and $x_c(\mathrm{NE}) = 0.453 \pm 0.001$ for NE–CH were determined from dielectric measurements carried out for different compositions and from the results in the two-phase region.

3. RESULTS AND DISCUSSION

We have measured the dielectric constant of BN–IO for $x = x_c$ in the temperature range between 4 and 45°C and in the range between 22 and 37°C for NE–CH. Measurements were carried out for different frequencies in the range between 10 Hz and 2 MHz for BN–IO and 10 Hz and 100 kHz

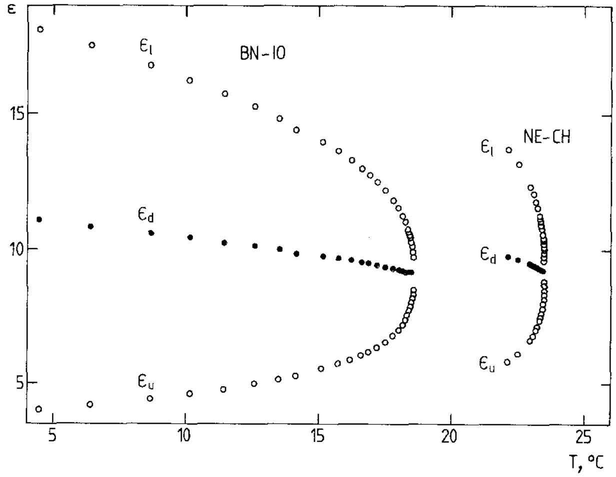

Fig. 2. The temperature dependence of the dielectric constant for the binary mixtures benzonitrile–isooctane and nitroethane–cyclohexane in the two-phase region below T_c. ε_l is the lower phase, ε_u is the phase, and $\varepsilon_d = (\varepsilon_l + \varepsilon_u)/2$ is the diameter of the coexistence curve.

for NE–CH. The investigations of the frequency dependence allowed us to avoid or correct for electrode polarisation and MW-dispersion effects [12, 13] in order to arrive at the temperature dependence of the static dielectric constant. In Fig. 2 the static dielectric constant values for the two coexisting phases of BN–IO and NE–CH are given as a function of temperature. In Fig. 3 a detailed plot is given for the NE–CH results, which were measured with a much better temperature resolution than the BN–IO data (see Section 2).

In the analyses of the data, we carried out several nonlinear least-squares fits [14] for Eqs. (2)–(6). To obtain the best parameter values, the reduced chi-square function

$$\chi_\nu^2 = (n-p)^{-1} \sum_{j=1}^{n} \frac{(y_{\text{exp}}^j - y_{\text{calc}}^j)^2}{\text{var}(y^j)} \tag{7}$$

---

[4] We used the CERN computer program MINUIT, CERN Computer Program Library No. 506.

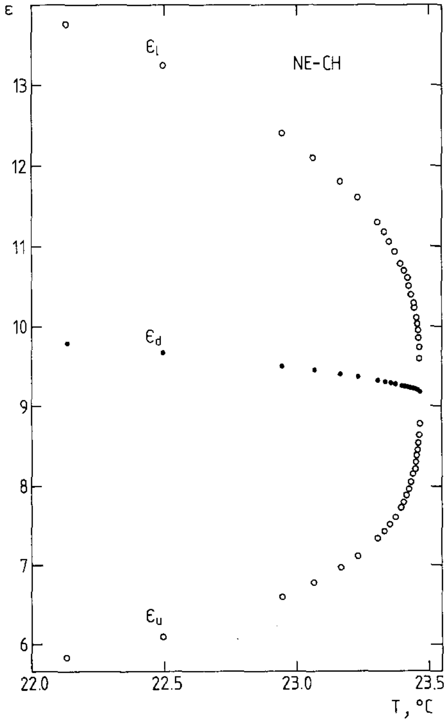

Fig. 3. Detailed results for the dielectric constant in the two-phase region near the critical point of nitroethane–cyclohexane. ε_l is the lower phase, ε_u is the upper phase, and $\varepsilon_d = (\varepsilon_l + \varepsilon_u)/2$.

was minimized for n data points and p adjustable parameters. For $y=\varepsilon_l-\varepsilon_u$, $y=\varepsilon_l-\varepsilon_c$, and $y=\varepsilon_c-\varepsilon_u$, the variance is given by

$$\mathrm{var}(y^j)=k\sigma_\varepsilon^2+\sigma_\mathrm{T}^2\left(\frac{\beta y^j}{T-T_\mathrm{c}}\right)^2\left(\frac{T_\mathrm{c}}{T}\right)^2 \tag{8}$$

The experimental uncertainties on ε and T are represented by σ_ε and σ_T. The parameter $k=2$ for $y=\varepsilon_l-\varepsilon_u$ and $k=1$ in the other cases. For $y=\varepsilon_\mathrm{d}$ the variance is

$$\mathrm{var}(\varepsilon_\mathrm{d}^j)=\frac{1}{2}\sigma_\varepsilon^2+\sigma_\mathrm{T}^2\left(\frac{\varepsilon_\mathrm{d}^j-\varepsilon_\mathrm{c}}{T-T_\mathrm{c}}\right)^2\left(\frac{T_\mathrm{c}}{T}\right)^2 \tag{9}$$

In the calculations of all variances approximate values for β, ε_c, and T_c have been used. For BN–IO we had $\sigma_\mathrm{T}=2$ mK and $\sigma_\varepsilon=0.015$. In the case of NE–CH this was $\sigma_\mathrm{T}=0.5$ mK and $\sigma_\varepsilon=0.005$.

Since for NE–CH the accuracy of the data was higher and T_c was approached more closely than in the case of BN–IO, one can expect to arrive at more reliable information on the asymptotic critical behavior in the former case. We thus discuss only the fitting results for NE–CH in detail here and then given a brief comparison with the results of the BN–IO analysis.

In the first series of fits with Eqs. (2)–(4) we used the asymptotic forms including only the τ^β term and leaving only β and B_1, C_1, or D_1 as adjustable parameters. This is appropriate in the range where correction terms are unimportant. This can be verified by the procedure of range shrinking, which we have applied to our data. From the direct experimental results we obtained $T_\mathrm{c}=23.4708\pm0.0003$°C and $\varepsilon_\mathrm{c}=9.174\pm0.001$. The fits have been carried out with fixed values of T_c and ε_c but the effect of the experimental uncertainties in these parameters on the fits was also tested. In Fig. 4 the evolution of β is given as a function of τ_m; the maximum value of $\tau=(T_\mathrm{c}-T)/T$ for the data included in the fits. If one looks at the results for $\Delta\varepsilon=\varepsilon_l-\varepsilon_u$, an almost-constant β value is noticed for the most probable $T_\mathrm{c}=23.4708$°C value. Changing T_c within the experimental limits did have a small effect only close to T_c. The almost-constant value of β over the entire range indicates that correction terms are not very important for $\Delta\varepsilon$. These β results are consistent with a limiting $\beta=0.325\pm0.005$ value. In the case of a separate analysis of the two branches ε_l and ε_u, quite different and strongly range-dependent effective β values are obtained. On range shrinking, however, one clearly sees convergence to the β values for $\Delta\varepsilon$. The T_c uncertainty is indicated here by the length of the vertical bars through the symbols in Fig. 4. The effect of the ε_c uncertainty is neglegible compared that of to the T_c uncertainty.

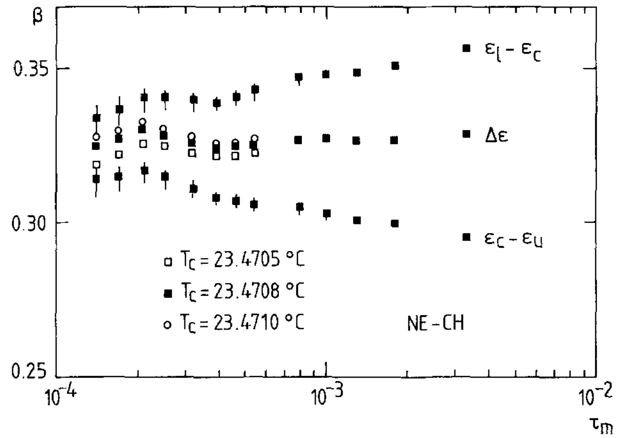

Fig. 4. The effect of range shrinking on the values of the critical exponent β from fits with simple power-law expressions derived from Eqs. (2)–(4) (see text).

Table I. Fitting Results for ε_l, ε_u, and $\Delta\varepsilon$ of the Mixture NE–CH[a]

Eq. No.	β	P_1	P_2	P_4	P_6	χ_ν^2
(2)	0.2956 ± 0.0007	-1.827 ± 0.009	—	—	—	3.84
(2)	0.307 ± 0.002	-2.01 ± 0.03	—	23 ± 3	—	0.84
(2)	0.316 ± 0.003	-2.21 ± 0.05	3.0 ± 0.4	—	—	0.63
(2)	0.3237 ± 0.0001	-2.400 ± 0.002	6.16 ± 0.04	-25.6 ± 0.9	—	0.59
(2)	0.3299 ± 0.0001	-2.467 ± 0.004	—	—	12.6 ± 0.3	4.95
(2)	0.3203 ± 0.0001	-2.32 ± 0.01	6 ± 1	—	-7 ± 3	0.61
(10)	0.325 ± 0.003	-2.47 ± 0.08	2.1 ± 0.3	—	—	0.58
(10)	0.3299 ± 0.0001	-2.63 ± 0.02	3.2 ± 0.3	—	-3 ± 2	0.58
(3)	0.3566 ± 0.0006	3.38 ± 0.02	—	—	—	6.78
(3)	0.342 ± 0.002	2.99 ± 0.04	—	43 ± 4	—	1.11
(3)	0.329 ± 0.003	2.62 ± 0.07	5.1 ± 0.4	—	—	1.03
(3)	0.330 ± 0.008	2.642 ± 0.009	4.8 ± 0.6	3 ± 8	—	1.08
(3)	0.3300 ± 0.0001	2.678 ± 0.004	—	—	11.7 ± 0.3	1.45
(3)	0.328 ± 0.002	2.57 ± 0.05	6 ± 2	—	-2 ± 4	1.09
(11)	0.312 ± 0.005	2.1 ± 0.1	3.2 ± 0.2	—	—	1.09
(11)	0.3261 ± 0.0006	2.50 ± 0.03	1.6 ± 0.4	—	5 ± 2	1.08
(4)	0.3286 ± 0.0005	5.09 ± 0.02	—	—	—	1.39
(4)	0.3234 ± 0.0001	4.845 ± 0.007	1.7 ± 0.2	—	—	0.99
(4)	0.325 ± 0.001	4.93 ± 0.05	—	17 ± 5	—	0.93

[a] The parameters P_i have to be replaced by the coefficients with the same index in the equation indicated in the first column. $T_c = 23.4708$°C, $\varepsilon_c = 9.174$, and $\Delta = 0.5$ are held constant and the other adjustable parameters in relevant equations are set equal to zero.

In the second series of fits we have included higher-order terms in the fits for Eqs. (2)–(4). For these fits we used all the data ($\tau_m = 3.3 \times 10^{-3}$) and fixed T_c and ε_c to their best value. We also imposed $\Delta = 0.5$. This reduces the number of different correction terms in the equations because then $1 + \beta = \beta + 2\Delta$ and $\beta + \Delta \simeq 1 - \alpha$. In Table I a summary is given of the fitting results with different types of correction terms. In order to investigate how sensitive the leading exponent is to the choice of higher-order terms, we also used as fitting equations

$$\varepsilon_u = \varepsilon_c(1 + B'_1\tau^{\beta} + B'_2\tau^{2\beta} + B'_6\tau) \tag{10}$$

$$\varepsilon_l = \varepsilon_c(1 + C'_1\tau^{\beta} + C'_2\tau^{2\beta} + C'_6\tau) \tag{11}$$

From the results in Table I for ε_u and ε_l, one concludes that adding correction terms can result in good fits with nearly the same β values as obtained from the $\Delta\varepsilon$ analysis. It is, however, also clear that the type of correction terms is not very well resolved, because good fits are obtained for different combinations. Adding correction terms in the fit equation for $\Delta\varepsilon$ improved χ_ν^2 but did not affect the β value.

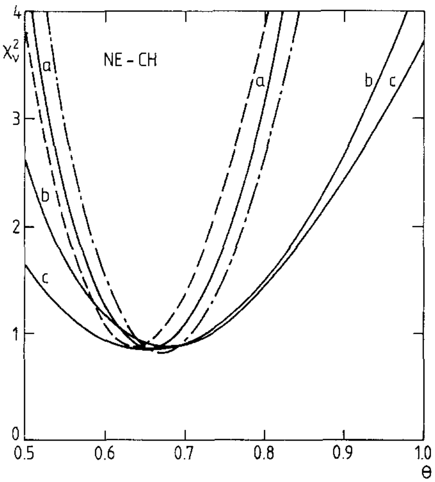

Fig. 5. Reduced chi-square values as a function of the parameter θ replacing $(1-\alpha)$ as the exponent in Eq. (5). For each imposed value of θ the parameters d_1 and d_2 in Eq. (5) were free to adjust. T_c was 23.4708°C and different fitting ranges, τ_m, and ε_c values have been chosen as follows: (a) $\tau_m = 3.3 \times 10^{-3}$ with $\varepsilon_c = 9.174$ (solid curve), $\varepsilon_c = 9.173$ (dashed curve), and $\varepsilon_c = 9.175$ (dashed–dotted curve); (b) $\tau_m = 1.8 \times 10^{-3}$; and (c) $\tau_m = 1.3 \times 10^{-3}$.

For the fits for the diameter of the coexistence curve we used the following equations, similar to Eqs. (5) and (6):

$$\varepsilon_d = \varepsilon_c(1 + d_1''\tau^{\theta} + d_2''\tau) \tag{12}$$

One expects $\theta = 0.89$ if the $\tau^{1-\alpha}$ term in Eq. (6) is dominant and $\theta = 0.65$ if the $\tau^{2\beta}$ term dominates. In Fig. 5 χ_ν^2 values are plotted as a function of θ. Different values for τ_m and the effect of the experimental uncertainty on ε_c have been tested also. All curves show a minimum value consistent with $\theta = 0.65 \pm 0.05$. This clearly indicates that the curvature of the diameter of the coexistence curve is dominated by the $\tau^{2\beta}$ term.

For the results of BN–IO, which were less detailed near T_c but extended over a larger T range ($\tau_m = 6 \times 10^{-2}$), an analogous analysis was carried out [13]. Here, also, strongly range-dependent β values were obtained from simple power-law fits to ε_l and ε_u. For $\tau_m > 10^{-2}$, also, some range dependence was noticed for fits to $\Delta\varepsilon$. Because fewer data were measured close to T_c than for NE–CH, range shrinking could not go beyond $\tau_m \simeq 2 \times 10^{-3}$. The β values for that range are, however, nearly the same as the corresponding values for NE–CH and are consistent with a limiting β value between 0.32 and 0.33. The results for the diameter of the coexistence curve are very similar to those of NE–CH, and for large τ_m values even sharper minima centered around $\theta = 0.65$ are obtained.

4. SUMMARY AND CONCLUSIONS

In this paper we have presented new experimental data for the static dielectric constant ε as a function of temperature for the coexisting phases of the binary liquid mixtures benzonitrile–isooctane and nitroethane–cyclohexane near their liquid–liquid critical points. For the first system ε values in the temperature range $T_c - T \simeq 15°\text{C}$ were obtained. For the second one a detailed study with high temperature resolution was carried out for the range $T_c - T = 1.5°\text{C}$. From a nonlinear least-squares analysis of the temperature dependence of ε_l (lower phase) and ε_u (upper phase) and of their difference $\Delta\varepsilon = \varepsilon_l - \varepsilon_u$, a value of 0.325 ± 0.005 was obtained for the critical exponent β. This is in very good agreement with the theoretically [6] calculated value $\beta_I = 0.325 \pm 0.002$ for the $d = 3$ Ising model. The diameter of the dielectric coexistence curve shows a curvature that can be ascribed to a contribution with an exponent of 2β.

REFERENCES

1. L. Mistura, *J. Chem. Phys.* **59**:4563 (1973).
2. J. V. Sengers, D. Bedeaux, P. Mazur, and S. C. Greer, *Physica A* **104**:573 (1980).

3. G. Stell and J. S. Høye, *Phys. Rev. Lett.* **33**:1268 (1974).
4. J. Goulon, J. L. Greffe, and D. W. Oxtoby, *J. Chem. Phys.* **70**:4742 (1979).
5. F. Wegner, *Phys. Rev. B* **5**:4529 (1973).
6. J. C. Le Guillou and J. Zinn-Justin, *J. Phys. Lett.* **46**:L137 (1985).
7. M. J. Buckingham, in *Phase Transitions and Critical Phenomena, Vol. 2,* C. Domb and M. S. Green, eds. (Academic, London, 1972), p. 18.
8. S. C. Greer and M. R. Moldover, *Annu. Rev. Phys. Chem.* **32**:233 (1981).
9. J. Thoen, R. Kindt, and W. Van Dael, *Phys. Lett. A* **76**:445 (1980).
10. J. Thoen, R. Kindt, and W. Van Dael, *Phys. Lett. A* **87**:73 (1981).
11. M. Marabet and T. K. Bose, *Phys. Rev. A* **25**:2281 (1982).
12. J. Thoen, R. Kindt, W. Van Dael, M. Merabet, and T. K. Bose, *Physica A* (in press) (1989).
13. R. Kindt, Ph.D. thesis (Leuven, 1982) (unpublished).